Lawrence Berkeley National Laboratory
Recent Work

Title
CORROSION OF IRON ROTATING DISK

Permalink
https://escholarship.org/uc/item/5cs0v00w

Author
Vahdat, Nader.

Publication Date
1972-06-01
CORROSION OF IRON ROTATING DISK

Nader Vahdat
(M.S. Thesis)

June 1972

AEC Contract No. W-7405-eng-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>v</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>The Effect of Different Parameters on the Rate of Corrosion of Iron</td>
<td>3</td>
</tr>
<tr>
<td>Oxygen Concentration Cell.</td>
<td>9</td>
</tr>
<tr>
<td>Corrosion Rate of Rotating Disk</td>
<td>10</td>
</tr>
<tr>
<td>The Passivity of Iron</td>
<td>12</td>
</tr>
<tr>
<td>The Rate of Oxygen Transfer to a Rotating Disk</td>
<td>15</td>
</tr>
<tr>
<td>Oxygen Electrode</td>
<td>20</td>
</tr>
<tr>
<td>Current and Potential Distribution on the Surface of Rotating Disk</td>
<td>25</td>
</tr>
<tr>
<td>Development of the Model</td>
<td>28</td>
</tr>
<tr>
<td>Limitation of the Model</td>
<td>33</td>
</tr>
<tr>
<td>Results</td>
<td>35</td>
</tr>
<tr>
<td>Discussion of the Results</td>
<td>37</td>
</tr>
<tr>
<td>Figures</td>
<td>43</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>54</td>
</tr>
<tr>
<td>References</td>
<td>56</td>
</tr>
<tr>
<td>Computer Program</td>
<td>60</td>
</tr>
</tbody>
</table>
CORROSION OF IRON ROTATING DISK

Nader Vahdat

Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

June 1972

Abstract

The corrosion rate of iron rotating disks was studied by calculating the current and potential distribution on the surface of the disk. The results show that the surface toward the center of the disk is corroded with a maximum rate, while the edge of the disk remains almost unattacked. This is in agreement with the experimental results. The effect of different parameters (rotation speed, oxygen concentration, conductivity of the solution, and radius of the disk) on the corrosion behavior of the rotating disk was studied.
INTRODUCTION

For a metal to be corroded, it should be in a suitable environment. In acidic solutions, it is the hydrogen ion that is responsible for the corrosion of the metals, and in neutral solutions, oxygen causes the corrosion. As long as there is a continuous supply of these corrosive species, the metallic corrosion continues. It is obvious that the rate of transfer of these species is an important factor in the corrosion. Stirring usually increases the rate of mass transfer to the metal; consequently, in the experiments for studying the corrosion rate of metals, velocity is used as a parameter to vary the rate of transfer of corrosive species to the metal.

The effect of velocity on the corrosion rate can be studied by different methods. One way is to pass the corrosive liquid through or over a stationary specimen. Another way is to use rotating specimens such as disks, cylinders, etc.

The rotating disk is an ideal case for studying localized corrosion, because the hydrodynamic flow is well known near a rotating disk, and one can calculate the current and potential distribution on the surface of the disk.

The motion of a fluid due to an infinite rotating disk has been considered first by Karman. He transformed the Navier-Stokes equations into coupled ordinary differential equations, and then he solved these with an approximate method. Later on, Cochran solved these equations by a method of numerical integration and thereby obtained more accurate results. Levich used these results to solve the convective diffusion
equation and has shown that the current distribution on the surface of the disk is uniform at the limiting current (for laminar flow). There are also some experimental correlations in the literature for the rate of mass transfer to the rotating disk in the turbulent region. Newman has calculated the current distribution on the surface of the disk below the limiting current and has shown that it is not uniform.

LaQue has conducted some experiments with copper and iron disks rotating in sea water. His results show that the copper disks are corroded at the periphery and remain almost unattacked at the center, but in the case of iron disk, the greatest attack occurs on the surfaces towards the center that move more slowly.

The results for the copper disks can be explained by the fact that the surfaces towards the periphery of the disk move with a higher velocity (being in turbulent flow) and the amount of oxygen that reaches them is higher, so the rate of corrosion would be higher too. LaQue has explained these by a different mechanism: as the effect of erosion and metal-ion cell.

The explanation of the results for the iron disks does not seem to be obvious a priori. But when it is noticed that iron is an active-passive metal and a high oxygen concentration tends to produce a protective oxide coating on such metals, the results can be explained. The surfaces towards the periphery of the disk are passivated because of the greater amount of oxygen that reaches them.

The purpose of this work is to study the corrosion of iron rotating disks by calculating the current and potential distribution on the surface of the disk.
THE EFFECT OF DIFFERENT PARAMETERS ON
THE RATE OF CORROSION OF IRON

The corrosion rate of iron in aqueous solutions depends on oxygen concentration, pH, composition of the solution, flow rate, temperature, surface roughness, and the metal composition. Besides these factors, the corrosion rate depends also on the local variation of potential on the surface of the metal. This last factor is of special importance in the localized corrosion.

The effects of these parameters on the corrosion rate of iron are described here.

a. Oxygen Concentration

Oxygen concentration is the most important factor in the corrosion of metals in neutral solutions. A small amount of oxygen increases the corrosion rate of iron, but a high concentration of oxygen tends to produce a protective film on the metal, and the corrosion rate drops to almost zero. Tomashov\(^9\) has studied the effect of oxygen concentration on the corrosion of iron in neutral solutions. His results show that upon increasing the oxygen concentration in distilled water, corrosion initially increases, and after passing through a maximum, it drops sharply.

Frese\(^10\) has studied the corrosion rate of steel under different oxygen pressures in distilled water and neutral sodium chloride solutions. His results show that the oxygen pressure corresponding to the maximum corrosion rate is below one atmosphere (in both of these media), and at higher pressures the corrosion rate will be decreased. On the other
hand Riggs, Sudbury and Hutchinson\textsuperscript{11} have found the corrosion to increase with oxygen pressure at least up to 515 psia in a 5\% sodium chloride solution. Lee\textsuperscript{12} has shown that up to about 20 atmosphere pressure of oxygen the rate of corrosion of steel in N/10 KCl increases with pressure. In these experiments chloride ion is responsible for the prevention of passivity even with high oxygen pressures. (Frese's results in chloride solution are contradictory in this respect.)

b. Hydrogen ion Concentration (pH)

Hydrogen ion is the main corrosive species in the acidic solutions. The corrosion rate of metals usually increases with increasing the hydrogen ion concentration in such a solution. Riggs, Sudbury and Hutchinson\textsuperscript{11} have studied the effect of pH on the corrosion rate of mild steel in a 5\% sodium chloride solution. (The solution was adjusted to the desired pH by use of dilute HCl or NaOH.) They have shown that the corrosion rate is very high at low pH, constant over the neutral zone (pH 4-9) and decreased to very low values at high pH. Tomashov\textsuperscript{13} has found the same results for the corrosion of steel in water. In acidic solutions, the corrosion rate is governed by the rate of hydrogen ion diffusion, so increasing pH will decrease the corrosion rate. In the neutral zone, the corrosion rate is controlled by the oxygen diffusion which is independent of the hydrogen concentration; consequently in this region pH has no effect on the corrosion rate. Tomashov\textsuperscript{13} has explained the decrease of the corrosion rate in alkaline solution to be due to a decrease in the solubility of the corrosion products.

It should be noticed that there are some acidic solutions that actually prevent the corrosion. For example in the concentrated nitric
acid, the iron is passivated, although its corrosion rate is high in dilute nitric acid.

Pourbaix\textsuperscript{14,15} has studied extensively the potential-pH equilibrium diagrams for iron as well as other metals. These diagrams (known as Pourbaix diagrams) show the effect of pH on the equilibrium potential of the various possible electrochemical reactions of iron (or other metals). From these diagrams one can find the conditions of corrosion, immunity and iron passivation in the solutions.

Rosenfeld\textsuperscript{16} has studied the effect of pH on the potential of iron. His results show that increasing pH will decrease the potential linearly, at a pH between 4 and 5 the potential increases rapidly, and in the neutral zone it is independent of pH.

c. Composition of the Solution

The composition of the corrosive solution has an important role in the corrosion of the metals. There are some oxidizing agents that act as inhibitors by passivating the metal. Stern\textsuperscript{17} has studied the effect of many inhibitors on the corrosion rate of stainless steel and has shown that many oxidizing agents are capable of shifting the metal to the passive region. The concentration of these oxidizing agents should be higher than a specific value to act as an inhibitor; if it is lower than this critical value, it may increase the corrosion rate. The best example of this group of inhibitors is probably oxygen.
There are also some chemicals that promote the corrosion rate of metals. One of the most important promoters of iron corrosion is chloride ion. It is very difficult to passivate iron in a solution containing large amounts of chloride ion. Some data obtained by Copson \(^1\) in sea water show that, passivation does not occur even with a velocity of 25 ft/sec. McBee and Kruger \(^2\) have studied the effect of chloride ion on the passive film of iron. They have proposed that the main reason for chloride entry in the passive film is anion vacancies.

Pourbaix \(^3\), \(^4\), \(^5\) has found that the chloride ion distroys the passive film at a specific potential known as rupture (breakdown) potential. Above this potential, localized corrosion occurs. If the metal is then repassivated by decreasing the potential, a hysteresis loop is observed, and the metal is passivated at a potential below the rupture potential. This potential is called protective potential. Below the protective potential, pitting will not occur. In the range between the rupture and protective potential, the metal will be corroded if its surface is damaged. He has also shown that protective potential does not change with \(pH\), but the rupture potential increases with increasing the \(pH\) of the solution.

Pourbaix et al. \(^2\) have shown that the break down and protective potentials depend on the chloride ion concentration. According to their results, for each steel alloy composition and heat treatment, there exists a certain critical value of the chloride concentration, below which the polarization curve shows no rupture of the passivity film. And the addition of oxidizing agents usually increases this critical value of the solution.
d. **Velocity**

Velocity has no direct effect on the rate of corrosion of metals. For example, in a deaerated solution the corrosion rate of iron is almost independent of velocity. But stirring has some indirect effects; it will increase the rate of diffusion of the corrosive species to the metal and also the rate of diffusion of corrosion products away from the metal. In an aerated solution, the corrosion rate of iron increases with velocity passes through a maximum and then drops sharply. This behavior is equivalent to the effect of oxygen concentration on the corrosion rate.

The velocity corresponding to the maximum corrosion is not constant and depends on the composition of the solution and the surface roughness of the metal. A review of the literature dealing with the effect of velocity on the corrosion of iron is given by Mahato, Voora and Shemilt.

At very high velocities one should worry about the erosion. The high velocity tends to wash the protective film away, and the corrosion rate increases again.

e. **Temperature**

Temperature is a factor that increases the corrosion rate by promoting the rate of electrochemical reaction on the surface of the metal. But as the temperature increases, the solubility of the corrosive species (e.g., oxygen) in the solution decreases. The net result is that the corrosion rate increases with temperature, passes through a maximum and then decreases. Copson has shown that the temperature corresponding to the maximum corrosion of steel in water is about 80°C.
f. Surface Roughness

Surface roughness is another variable that changes the corrosion rate of the metals. Usually the corrosion rate of a rough surface is higher than that of a polished one. Russell, Choppell and White\(^{23}\) have conducted some experiments for finding the effect of velocity on the corrosion rate of steel specimens with smooth and rough surfaces. Their results show that at each velocity, the corrosion rate of a rough surface is higher than that of a smooth one. Furthermore, they have found that it is very difficult to passivate a metal with a rusted surface. Forrest, Roetheli, and Brown\(^{26}\) have explained this by the fact that accumulation of corrosion products prevents oxygen from reaching the surface.
OXYGEN CONCENTRATION CELL

In neutral water solutions, the oxygen concentration is of major importance in determining the corrosion rate of most metals. Local variations in oxygen content may set up an oxygen concentration cell. The surfaces exposed to relatively high oxygen concentration tend to become cathodic. A high oxygen concentration also tends to produce protective oxide coatings which make the potential more anodic. The result is that the part of the metal less exposed to oxygen is corroded, and a current passes through the solution from anode to cathode. A review of the literature dealing with such oxygen concentration cells is given by Wilson Lynes.27

Copson18 has shown that in sea water, as the velocity increased from 0 to 14 ft/sec, the steel becomes 130 mV more positive. Cohen28 has got a potential difference of 700 mV by increasing the velocity from zero to 12 ft/sec in tap water. These correlations may be misleading because the factor that is responsible for shifting the potential of the metal to more positive values is the increase in the oxygen concentration on the surface of the metal, and stirring is only a means by which one can usually (but not always) increase the rate of oxygen transfer to the metal. So it would be more proper to correlate the potential of the metal with oxygen concentration.

As shown experimentally by Evans,29 the effect of restricting access of oxygen to a part of surface of metal is not to increase the total corrosion, but to concentrate on the nonaerated area the corrosion which would otherwise be distributed over the surface. Evans also demonstrated that, at such places that are anodic owing to the absence of oxygen, the product of the corrosion is usually a soluble salt.
CORROSION OF ROTATING DISK

As it was mentioned in the last section, local variations of oxygen content will set up an oxygen concentration cell. In the case of an iron disk rotating in aerated solutions, because of the nonuniform rate of oxygen transfer to the surface of the disk, a differential aeration cell is formed. The surfaces towards the periphery of the disk which move with a higher velocity (and consequently are in a turbulent region) are exposed to a higher oxygen concentration and act as cathode to the central portion of the disk. The reaction taking place on the cathodic areas would be the reduction of oxygen:

$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$$

and the anodic reaction (taking place on the central portion of the disk) would be the dissolution of iron:

$$Fe \rightarrow Fe^{++} + 2 e^-$$

These local anodes and cathodes form a corrosion cell, and a current will pass through the solution from the anode to the cathode. The magnitude of this current at each point is equal to the sum of the oxygen and iron current densities at that point. When a metal is exposed to a uniform oxygen concentration, these local oxygen and iron current densities would be equal at each point, and will cancel each
other, and no current passes through the solution (uniform corrosion). In the case of the rotating disk, the local current densities are not equal (if there is turbulent flow at the edge of the disk) and a net current will pass through the solution. As no external current is applied to the disk, the total net current on the disk should be zero, i.e.,

\[ I_{\text{net}} = I_{\text{Fe}} + I_{O_2} = 0 \]
THE PASSIVITY OF IRON

For an ordinary active metal, the rate of corrosion increases with increasing its potential, and the polarization curve of such a metal shows a linear relationship between the current and potential on a semi-log plot. But there are some metals, including iron, that behave differently. Figure 1 schematically illustrates the typical behavior of this category of metals. As the potential is shifted to the more noble direction, the metal follows typical Tafel behavior, and the dissolution rate increases exponentially. This is called the active region. At more positive potentials, the rate of corrosion decreases rapidly to a very small value, and further increase of the potential has no effect on the dissolution rate of the metal. This is called the passive region. At very noble potentials, the corrosion rate again increases with potential. This is called the transpassive region.

There are many theories about the passivity of iron in the literature. Pryor and Cohen have shown that the oxygen dissolved in the solution is mainly responsible for the passivity by virtue of its heterogeneous reaction with surface iron atoms to form a thin film of γ-Fe₂O₃ (approximately 20 A thick). On the other hand, Uhlig and King have suggested that the passive film is essentially chemisorbed oxygen, according to the following equation:

$$3 \text{H}_2\text{O} + \text{Fe}_\text{surface} \rightarrow 0.02 \text{(adsorbed on Fe)} + 6 \text{H}^+ + 6 \text{e}^-$$

The structure $0.02$ is a complete monolayer of chemisorbed oxygen atoms.
Fig. 1 Typical polarization curve of an active-passive metal.
through gaps of which a further layer of \( \text{O}_2 \) molecules is chemisorbed.

Although there are different theories for the passivity of iron, all of these have one thing in common, and that is the fact that the oxygen has an important role for the passivity to occur.

Anodic polarization curves of iron have been obtained in different solutions by many investigators. Steigerwald and Greene\(^{32}\) have found the iron polarization curve in normal sulfuric acid. Pourbaix\(^{14}\) has given a set of polarization curves for the whole range of pH (from 0 to 14). Hisamatsu, Yoshii and Matsumura\(^{33}\) have found the effect of chloride iron on the polarization curve of stainless in normal sulfuric acid. Their results show that the chloride ion increases the height of the peak of the polarization curve (\( i_{\text{Fe max}} \)) and shifts it to more positive potential. But in the solutions containing the chloride ion more than \( 3\text{N} \), the curves coincide, and the peak potential is \(-0.15 \text{ V (SCE)}^* \).

From these polarization curves one can get a relation between the current density and the potential of the iron, in the following form:

\[
i_{\text{Fe}} = f(V - \Phi_{0})
\]

where \( V \) is the potential (relative to a reference electrode at infinity) and \( \Phi_{0} \) is the ohmic potential. (Thus, \( V - \Phi_{0} \) signifies the potential of the iron relative to a reference electrode close to the surface.) The following equation is used to describe the iron kinetics:

\[
i_{\text{Fe}} = 1.5 \times 10^{-3} \exp[-5 \times 10^{3}(V-\Phi_{0}+0.2)^2] + 10^{-7} \text{ for } V-\Phi_{0} > -0.25 \tag{1}
\]

where \( V - \Phi_{0} \) is the potential relative to hydrogen electrode, and \( i_{\text{Fe}} \) is the current density (A/cm\(^2\)).

---

* Relative to the saturated calomel electrode.
RATE OF OXYGEN TRANSFER TO A
ROTATING DISK

If a disk is rotating with a high enough angular velocity, the outer portion of the disk would be in the turbulent region, but the central portion will be always in laminar flow. As the angular velocity is increased, the area of the laminar region will decrease but never disappear. The flow is laminar up to a diameter which corresponds to a local Reynolds number \((r^2 \Omega / \nu)\) between \(1.9 \times 10^5\) and \(3 \times 10^5\)."
\[
\frac{i(1-t)}{nF(c_\infty - c_0) \sqrt{\nu \Delta}} = 0.6205 \, Sc^{-2/3}
\]  
(4)

where \(Sc = \nu/D\). Equation 4 gives a value which is about 3\% higher than equation 2 for a Schmidt number of 1000.\textsuperscript{34}

Newman\textsuperscript{34} has expanded the exponential in equation 2 for large Schmidt numbers and integrated analytically, and has found the following equation:

\[
\frac{i(1-t)}{nF(c_\infty - c_0) \sqrt{\nu \Delta}} = \frac{0.62048 \, Sc^{-2/3}}{1 + 0.2980 \, Sc^{-1/3} + 0.14514 \, Sc^{-2/3}}
\]

This equation gives a value which is in good agreement with equation 2, which a maximum error less than 0.1\% for Schmidt numbers greater than 100.\textsuperscript{34}

For a neutral molecule \(t = 0\) so:

\[
\frac{i}{nF(c_\infty - c_0) \sqrt{\nu \Delta}} = \frac{0.62048 \, Sc^{-2/3}}{1 + 0.2980 \, Sc^{-1/3} + 0.14514 \, Sc^{-2/3}}
\]

or

\[
\frac{i}{nF(c_\infty - c_0) \sqrt{\nu \Delta}} \, Sc^{2/3} = C_1
\]

(5)

where \(C_1\) is just a function of Schmidt number and can be found from the following equation:

\[
C_1 = \frac{0.62048}{1 + 0.2980 \, Sc^{-1/3} + 0.14514 \, Sc^{-2/3}}
\]

(6)
From the definition of the Reynolds and Nusselt numbers:

\[ \text{Re} = \frac{r^2 \Omega}{\nu} \]  

(7)

\[ \text{Nu} = \frac{k r}{D} = \frac{m_1 r}{D (c_\infty - c_0)} = \frac{ir}{nFD (c_\infty - c_0)} \]  

(8)

Where \( \text{Re} \) is local Reynolds number, \( \text{Nu} \) is local Nusselt number, \( k \) is mass transfer coefficient, and \( m_1 \) is the rate of mass transfer.

If equations 5 and 7 are substituted into equation 8, one can get the following expression:

\[ \text{Nu}_{lam} = C_1 \text{Re}_{loc}^{1/2} \text{Sc}^{1/3} \]  

(9)

where \( C_1 \) can be found from equation 6.

Mass transfer to a rotating disk in the turbulent region cannot be found analytically, but there are some experimental correlations in the literature. Almost all of these correlations are in the following form:

\[ \overline{\text{Nu}}_t = C_2 \text{Re}^m \text{Sc}^n \]  

(10)

where \( \overline{\text{Nu}}_t \) is the average Nusselt number and \( \text{Re} \) is the overall Reynolds number, \( C_2, m, \) and \( n \) are constants and are different from one correlation to the other. Recently Ellison has found the following expression for the Reynolds numbers between \( 8.9 \times 10^5 \) and \( 1.18 \times 10^7 \) and for Schmidt numbers between 35 and 1350.
The local mass transfer rate to the disk in the turbulent region can be found from the following equation.

\[
\bar{\bar{m}}_i \pi r^2 = \int_0^r 2\pi r m_i dr
\]

where \( \bar{m}_i \) is the average mass transfer to the disk. If this equation is differentiated with respect to \( r \):

\[
\frac{d}{dr} (\bar{m}_i r^2) = 2rm_i
\]

Equations 7 and 12 yield:

\[
\frac{d}{dr} (\bar{\bar{N}}_t r) = 2 \bar{\bar{N}}_t \tag{13}
\]

where \( \bar{\bar{N}}_t \) is the local Nusselt number. Equation 13 can be rewritten as

\[
\frac{d}{d\text{Re}^{1/2}} (\bar{\bar{N}}_t \text{Re}^{1/2}) = 2 \bar{\bar{N}}_t
\]

or

\[
\bar{\bar{N}}_t = \frac{1}{2} \frac{d}{d\text{Re}^{1/2}} (C_2 \text{Re}^m \text{Sc}^n \text{Re}^{1/2})
\]

If this equation is differentiated with respect to \( \text{Re} \):
From Ellison's correlation:

\[ \text{Nu}_t = \frac{C_2(2m + 1)}{2} \text{Re}^m \text{Sc}^n \]  

\[ (14) \]

Let \( C_3 = \frac{C_2(2m + 1)}{2} \) so

\[ \text{Nu}_t = C_3 \text{Re}^m \text{Sc}^n \]  

\[ (15) \]

From Ellison's correlation:

\[ C_2 = 1.17 \times 10^{-2}, \quad m = 0.896, \quad n = 0.249 \]

and

\[ C_3 = 1.63332 \times 10^{-2} \]

\[ \text{Nu}_t = 1.63332 \times 10^{-2} \text{Re}^{0.896} \text{Sc}^{0.249} \]  

\[ (16) \]

Equations 8, 9, and 16 yield the following expressions for the limiting current density \((c_0 = 0)\) on the surface of the rotating disk:

\[ i_{lim} = nFDc_\infty C_1 \sqrt{\frac{\Omega}{\nu}} \text{Sc}^{1/3} \quad \text{For laminar region} \]  

\[ (17a) \]

\[ i_{lim} = nFDc_\infty \frac{C_3}{r} \left(\frac{r\Omega}{\nu}\right)^{0.896} \text{Sc}^{0.249} \quad \text{For turbulent region} \]  

\[ (17b) \]

where the flow is considered to be laminar up to a radius which corresponds to a local Reynolds number of \(3 \times 10^5\).
**OXYGEN ELECTRODE**

The cathodic reduction of oxygen on the electrodes is generally very rapid, and the limiting step is the rate of diffusion of oxygen to the electrode. But in some conditions, especially when the solution is being stirred, the rate of oxygen supply to the electrode is so high that the oxygen reaction cannot catch up. In such a case the electrode kinetics of the oxygen reaction should be considered too.

The oxygen electrode does not behave in a thermodynamically reversible manner. Hoar\(^\text{35}\) has found that oxygen electrodes: (a) tend to be irreproducible, (b) do not obey the thermodynamic relation between electrode potential and partial pressure of oxygen and (c) are readily polarized even by minute currents. There are some explanations for the behavior of the oxygen electrode. One is the formation of hydrogen peroxide., i.e.,

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O
\]

The other explanation\(^\text{35}\) is the formation of oxide on the surface of the electrode. Delahay\(^\text{36}\) has shown that for the reduction of oxygen on an iron electrode, hydrogen peroxide is produced at potentials from -0.2 to -0.6 volts (NHE\(^\text{*}\)).

\*Relative to a normal hydrogen electrode.
In general, a polarization curve for the cathodic reaction of oxygen consists of three parts. At very low current densities (when the potential is close to the equilibrium potential of oxygen) a linear potential-current curve is obtained. At higher current densities, the curve becomes exponential, i.e., on a semi-log plot, it has a constant slope, which is called the Tafel slope. At very high current densities a limiting current is reached, and hydrogen begins to be evolved.

The Tafel slopes of the oxygen reduction on different metals are almost the same. Vetter has shown that, for many metals, the Tafel slope is 0.1 to 0.12 volt/decade in acid solutions, and 0.036 to 0.045 in alkaline solutions. Hoare has found the Tafel slope to be about 0.05 in alkaline and about 0.1 for acid and neutral solutions.

The dependence of oxygen current density on the surface overpotential can be shown by the following expression:

$$i_{O_2} = i_0(c_0) \left[ \exp \left( \frac{\alpha_a F \eta_s}{RT} \right) - \exp \left( \frac{\alpha_c F \eta_s}{RT} \right) \right]$$

(18)

where $F$ is Faraday's constant, $R$ is the gas constant, $T$ is temperature, $i_0(c_0)$ is the exchange current density evaluated at the surface concentration, $\alpha_a$ and $\alpha_c$ are kinetic parameters, and $\eta_s$ is the surface overpotential (the potential of the electrode relative to a reference electrode of the same kind close to the electrode).

When a concentration gradient of oxygen exists near the electrode, there will be a concentration overpotential. If the concentration of (OH)$^-$ ion is assumed to be uniform, one can write:
\[ \eta_c = \frac{RT}{nF} \ln \frac{c_0}{c_\infty} \]  \hspace{1cm} (19)

when \( \eta_c \) is the concentration overpotential and \( n \) is the number of electrons.

The total overpotential is

\[ \eta = \eta_s + \eta_c \]  \hspace{1cm} (20)

where \( \eta \) is the total overpotential. Equations 19 and 20 can be used to eliminate \( \eta_s \) in equation 18. The result is:

\[ i_{O_2} = i_0(c_0) \left[ \exp \left( \frac{\alpha_a F \eta}{RT} \right) \left( \frac{c_0}{c_\infty} \right)^{-\alpha_a/n} \exp \left( -\frac{\alpha_c F \eta}{RT} \right) \left( \frac{c_0}{c_\infty} \right)^{-\alpha_c/n} \right] \]  \hspace{1cm} (21)

The exchange current density depends on the concentration of reactant and product on the surface of the electrode. One can write the following equation for the exchange current density:

\[ i_0 = nF k_c k_a \alpha_i c^{q_i} + \alpha_c s_i \]  \hspace{1cm} (22)

where \( k_c \) and \( k_a \) are rate constants, \( q_i \) is the reaction order of species \( i \), \( s_i \) is the stoichiometric coefficient of species \( i \), \( \alpha_a \) and \( \alpha_c \) are kinetic parameters. Substitution of this equation for oxygen reaction into equation 21 (and neglecting the concentration variations of \((\text{OH})^-\) and \(\text{H}_2\text{O}\)) yields:

\[ i_{O_2} = i_0(c_\infty) \left[ \exp \left( -\frac{\alpha_a F \eta}{RT} \right) - \left( \frac{c_0}{c_\infty} \right) \exp \left( -\frac{\alpha_c F \eta}{RT} \right) \right] \]  \hspace{1cm} (23)
where \( i_0(c_\infty) \) is a constant.

In equation 23, the first exponential represents the rate of the anodic process (oxygen evolution), and the second term represents the rate of the cathodic process (oxygen reduction). When the potential is far removed from the equilibrium potential of oxygen (1.229 V NHE) the first exponential is negligible so:

\[
i_{O_2} = i_0(c_\infty) \frac{c_0}{c_\infty} \exp \left( \frac{-\alpha_F \eta}{RT} \right)
\]  

(24)

If this equation is rewritten as:

\[
\eta = - \left( 2.303 \frac{RT}{\alpha_F} \right) \log(-i_{O_2}) + \left( 2.303 \frac{RT}{\alpha_F} \right) \log \left( i_0(c_\infty) \frac{c_0}{c_\infty} \right)
\]

then \( S = 2.303 \frac{RT}{\alpha_F} \) is the Tafel slope for the cathodic reaction of oxygen and can be found from the polarization curve of oxygen.

The total potential of the electrode can be written as:

\[
V = \eta + \phi_0 + U
\]

(25)

where \( \phi_0 \) is the ohmic potential and \( U \) is the equilibrium potential of oxygen relative to hydrogen electrode. Substitution of equation 25 into 24 yields:

\[
i_{O_2} = -i_0(c_\infty) \frac{c_0}{c_\infty} \exp \left[ \frac{-\alpha_F n}{RT} \left( V - \phi_0 - U \right) \right]
\]

(26)
The rate of oxygen diffusion to the electrode is:

\[
\frac{i_{O_2}}{nF} = \frac{D(c_\infty - c_0)}{\delta}
\]  \hspace{1cm} (27)

where \(\delta\) is the thickness of the diffusion layer. In this equation, as \(c_0 \rightarrow 0, i_{O_2} \rightarrow i_{lim}\), thus:

\[
\frac{i_{lim}}{nF} = D \frac{c_\infty}{\delta}
\]  \hspace{1cm} (28)

If the both sides of equation 27 are divided by equation 28,

\[
\frac{i_{O_2}}{i_{lim}} = 1 - \frac{c_0}{c_\infty}
\]  \hspace{1cm} (29)

This equation can be used to eliminate \(c_0/c_\infty\) in the equation 26 the result is:

\[
i_{O_2} = -i_0(c_\infty) \left(1 - \frac{i_{O_2}}{i_{lim}}\right) \exp \left[-\frac{\alpha c F}{RT} (V - \phi - U)\right]
\]  \hspace{1cm} (30)

where \(i_{lim}\) can be found from equations 17. The value of oxygen exchange current density used here is:

\[
i_0(c_\infty) \exp \left(-\frac{\alpha c F}{RT} U\right) = 7.4 \times 10^{-4} \text{ A/cm}^2
\]
Newman has found the current distribution on a rotating disk electrode of finite size embedded in an infinite insulating plane. The mathematical development is repeated here.

Outside the diffusion layer, where there is no concentration gradient, the potential satisfies Laplace's equation:

\[ \nabla^2 \phi = 0 \]  \hspace{1cm} (31)

If this equation is transformed to rotational elliptic coordinates, it reads

\[ \frac{\partial}{\partial \xi} \left[ (1+\xi^2) \frac{\partial \phi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1-\eta^2) \frac{\partial \phi}{\partial \eta} \right] = 0 \]  \hspace{1cm} (32)

\( \xi \) and \( \eta \) are related to the cylindrical coordinates \( r \) and \( y \) by:

\[ y = r_0 \xi \eta \]

\[ r = r_0 \sqrt{(1+\xi^2)(1-\eta^2)} \]

where \( r_0 \) is the radius of the disk. The boundary conditions for equation 32 are:
\[ \frac{\partial \phi}{\partial \eta} = 0 \] at \( \eta = 0 \)

\[ \phi = 0 \] at \( \xi = \infty \)

\( \phi \) well behaved at \( \eta = 1 \) (on the axis of the disk)

The solution of equation 32 with these boundary conditions is:

\[ \phi = \frac{RT}{2F} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi) \quad (33) \]

where \( P_{2n}(\eta) \) is the Legendre polynomial of order \( 2n \), \( B_n \) is a constant, and \( M_{2n}(\xi) \) is a Legendre function of imaginary argument satisfying the differential equation:

\[ \frac{d}{d\xi} \left[ (1 + \xi^2) \frac{dM_{2n}}{d\xi} \right] = 2n(2n + 1) M_{2n} \]

and the boundary conditions:

\[ M_{2n} = 1 \text{ at } \xi = 0 \text{ and } M_{2n} = 0 \text{ at } \xi = \infty \]

At \( \xi = 0 \) equation 33 gives:

\[ \phi_0 = \frac{RT}{2F} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \quad (34) \]

This is the potential just outside the diffusion layer.
The current density on the surface of the disk can be found from the following equation:

\[ i = -\kappa_\infty \frac{\partial \phi}{\partial y} \bigg|_{y=0} = -\frac{\kappa_\infty}{r_0 n} \frac{\partial \phi}{\partial \xi} \bigg|_{\xi=0} \]

or

\[ i = -\frac{\kappa_\infty}{r_0 n} \frac{RT}{2F} \sum_{n=0}^{\infty} B_n P_{2n}(n) M^i_{2n}(0) \tag{35} \]

where \( \kappa_\infty \) is conductivity of the bulk solution and

\[ M^i_{2n}(0) = -\frac{2}{\pi} \left( \frac{1}{P_{2n}(0)^2} \right) = -\frac{2}{\pi} \frac{(2^n n!)^4}{((2n)!)^2} \tag{36} \]

Equations 34 and 35 can be used to find the current and potential distribution on the rotating disk.
DEVELOPMENT OF THE MODEL

In order to find the corrosion distribution on the surface of the rotating disk, the following equations are used:

1. Polarization curve of iron (Fig. 1)

\[ i_{Fe} = 1.5 \times 10^{-3} \exp\left[-5 \times 10^{-3} (V - \Phi_0 + 0.2)^2\right] + 10^{-7} \text{ for } V - \Phi_0 > -0.25 \]  

2. Oxygen polarization curve

\[ i_{O_2} = -i_0(c_\infty) \left(1 - \frac{i_{O_2}}{i_{lim}}\right) \exp\left(-\frac{\alpha_c F(V - \Phi_0 - U)}{RT}\right) \]  

3. Current distribution on the rotating disk.

\[ i(\eta) = -\frac{K}{r_0^{\eta}} \frac{RT}{2F} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(0) \]  

4. The ohmic potential distribution on the disk.

\[ \Phi_0 = \frac{RT}{2F} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \]  

5. The net current at each point on the disk is the sum of anodic and cathodic current densities.

\[ i = i_{Fe} + i_{O_2} \]  

6. The total net current on the rotating disk should be zero.
\[ I = r_0^2 \int_0^1 2\pi \text{ind} \eta = 0 \]

or

\[ \int_0^1 \text{ind} \eta = 0 \] (38)

So there are 6 equations with 6 unknowns \( i_F, i_{O_2}, i, \phi, B_n \) and \( V \). These equations should be solved simultaneously to find the unknowns. Obviously this cannot be done by a direct method, because we have a set of implicit equations.

If both sides of equation 35 are multiplied by \( \eta P_{2m}(\eta) \), integrated with respect to \( \eta \) and simplified with the orthogonality relation:

\[ \int_0^1 P_{2n}(\eta) P_{2m}(\eta) d\eta = \begin{cases} 1/(4n + 1) & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases} \]

one can get the following equation for the coefficient \( B_n \):

\[ \frac{RT}{2F} B_n = -\frac{(4n + 1)r_0}{\kappa M_{2n}(0)} \int_0^1 i(\eta) P_{2n}(\eta) \eta d\eta \] (39)

Equation 39 can be used instead of equation 35 in the set of simultaneous equations. The following iterative procedure is used to solve these equations.

1. A net current distribution is assumed for the disk.
2. Equation 39 is used to find the coefficients \( B_n \).
3. The ohmic potential $\phi_0$ is calculated from equation 34.

4. A value is assumed for the potential $V$ of the disk.

5. Iron and oxygen current densities are calculated from equations 1 and 30 respectively.

6. The current densities found in step 5 should satisfy equation 38, if they do not, another value is assumed for $V$, and step 5 is repeated.

7. The sum of iron and oxygen current densities should be equal to the net current assumed in step 1 at each point on the disk; if it is not, using the new net current ($i_{\text{net}} = i_F + i_O$), the calculations enumerated in steps 2 through 6 are repeated until no significant changes occurred in the net current.

A computer program based on this procedure was developed to solve the equations. The flow chart of this program is shown in Figure 2. As it is understood from the procedure discussed above, the problem consists of two loops, the inner loop for iterating on the potential $V$ of the disk, and the outer loop for iterating on the net current distribution. There are three different solutions for $V$ as it can be predicted from Fig. 1, and it is very difficult to separate these solutions and converge to the right one, especially at the higher rotation speeds. To overcome this difficulty, linear interpolation and Newton-Raphson methods were used as convergence procedure. That is, for the first few iterations, the new value of $V$ was calculated from linear interpolation, and when the value of $V$ was close enough to the solution, Newton-Raphson was used as convergence procedure.

For the outer loop (which is an iteration on $i_{\text{net}}$), direct substitution was first used as a convergence method. Although it worked well
READ THE FIRST ASSUMPTION FOR $i_{\text{net}}$

COMPUTE $B_0$ and $\Phi_0$ FROM EQUATIONS 39 and 34

ASSUME A VALUE FOR $V$

COMPUTE $i_{Fe}$ and $i_{O2}$ FROM EQUATIONS 1 and 30

$\int_0^1 (i_{Fe} + i_{O2}) \eta d\eta = 0$

ASSUME ANOTHER VALUE FOR $V$

ASSUME ANOTHER NET CURRENT DISTRIBUTION

$\neq$

STOP

Fig. 2 Computation scheme.
for low rotation speeds (when the three solutions are far away from each other), for higher rotation speeds, the problem of multi solutions made it jump from one solution to another for successive iterations, and it never converged. To overcome this difficulty, the following method was used. After a few iterations with direct substitution, a multi dimensional Newton-Raphson method was used to converge to the solution. This procedure worked well and enabled us to find the whole three solutions for different rotation speeds. The computer program used for solving the equations is given at the end of this report.
LIMITATION OF THE MODEL

The iron polarization is a function of different parameters such as potential, \( \text{Fe}^{++} \) concentration, chloride ion concentration, and pH of the solution. In general one can write:

\[
i_{\text{Fe}} = i_{\text{Fe}}(V - \phi_0, c_{\text{Fe}^{++}}, c_{\text{Cl}^-}, \text{pH})
\]  

Thus, a polarization curve gives a relation between \( i_{\text{Fe}} \) and \( V - \phi_0 \) for a fixed value of \( c_{\text{Fe}^{++}}, c_{\text{Cl}^-}, \) and pH. If these last three parameters are not constant in a system, one should consider the effect of these factors on the polarization curve.

In the case of the corrosion of a rotating disk, the outer portion of the disk which is exposed to a higher concentration of oxygen acts as the aerated cathode where oxygen is being reduced to water and/or hydrogen peroxide with increase of pH according to the reaction:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]

The surfaces towards the center of the disk which are active are acting as nonaerated anodes, where the metal undergoes corrosion and hydrolysis with decrease of pH according to the reaction:

\[
\text{Fe} \rightarrow \text{Fe}^{++} + 2e^- \\
3 \text{Fe}^{++} + 4H_2O \rightarrow \text{Fe}_3\text{O}_4 + 8H^+ + 2e^-
\]
This shows that the pH does not remain uniform on the surface of the disk; it is low at the center and increases towards the periphery.

The concentrations of iron ion (Fe\(^{++}\)) and chloride ion are likewise not uniform on the surface of the disk. The Fe\(^{++}\) concentration is higher at the center and decreases towards the periphery of the disk. Migration may increase the concentration of the chloride ion on the central portion of the disk (the anodic part). Consequently, there will also be a chloride ion concentration gradient on the disk.

The foregoing discussion would suggest that one should use different iron polarization curves for calculating the corrosion rate at different points on the rotating disk, and that the four parameters in equation 40 vary on the disk.

It should be noted that the variations of \(c_{Fe^{++}}\), \(c_{Cl^-}\), and pH are not large, and they are neglected here. But if one wants to find a more accurate solution for the corrosion distribution on the rotating disk, he should take these variations into account.
RESULTS

The method that was discussed in the last section was used to calculate the potential distribution, net current, oxygen current density, and iron current density (which is proportional to the corrosion rate of iron) on the rotating disk. The results are shown in Figures 3 to 14.

The corrosion rate of the rotating disk depends principally on oxygen concentration, rotation speed, conductivity of the solution, radius of the disk, and a factor that takes into account the relation between the rates of oxygen and iron reactions on the surface of the disk. (It is also a function of $c_{\text{Fe}^{2+}}$, $c_{\text{Cl}^-}$, and pH of the solution.) For the last variable one can use the ratio of oxygen and iron current densities at a potential corresponding to the maximum of the iron polarization curve and for a high rate of oxygen transfer to the disk ($\Omega \to \infty$). That is

$$A = \left| \begin{array}{c} 1 \\ (\frac{0.2}{i_{\text{Fe}}}) \end{array} \right| \max i_{\text{Fe}} \Omega \to \infty$$

would be the last variable (the effect of this variable on the corrosion rate of the rotating disk will be described later).

Figure 3 shows typical curves for ohmic potential, iron current and oxygen current distributions on the surface of the rotating disk. Figure 4 shows the effect of rotation speed on the corrosion rate, for a low value of oxygen concentration and high oxygen exchange current density. Figures 5 and 7 give the results for a higher oxygen concentration. The effect of rotation speed on the potential of the disk is shown in
Fig. 6. The corrosion behavior of the rotating disk when the cathodic reaction of oxygen is a limiting step ($A < 1$) is given in Figures 8 and 9. Figures 10 and 11 show the effect of the conductivity of the solution on the corrosion rate. The results for a case in which the size of the disk is a parameter are illustrated in Figures 12 and 13.
DISCUSSION OF THE RESULTS

Figure 1 shows that the polarization curves of iron and oxygen can intersect each other at three points, one in the active region, one on the descending part of the iron curve, and the last one in the passive region. Consequently, one would expect to get three different solutions for the corrosion of rotating disk.

Figure 3 shows that for the rotating disk, the corrosion rate is high at the center, increases slowly with radial distance, passes through a weak maximum and then drops rapidly to a very low value at the periphery. This result is in agreement with the experimental result of LaQue. However in a diagram given by LaQue for the corrosion rate versus linear velocity, he has extrapolated the curves for the corrosion rate to zero at the center. The development here shows that the corrosion rate at the center is high and pretty close to the maximum corrosion of the disk.

The oxygen current distribution on the disk is also given in Fig. 3. This curve shows that $i_{O_2}$ is almost uniform for the central portion of the disk, increases sharply at a specific value of radial distance, and finally decreases near the periphery of the disk. The first part of the curve is related to the laminar region of the disk. The limiting rate of oxygen transfer to the disk is uniform in this region, consequently $i_{O_2}$ is almost uniform. The sharp increase in the oxygen current density gives the transition zone from the laminar to turbulent region. In the turbulent region, the limiting rate of oxygen transfer increases with the radial position, and the second part of the oxygen curve is related to this part. Near the periphery of the disk, the concentration of
oxygen is high; consequently both the rate of diffusion and the rate of oxygen reaction are important factors in the corrosion rate of the metal. The result is that the oxygen current density may decrease at the periphery (as it is shown in Fig. 3).

The ohmic potential is high and positive at the center and decreases with radial distance to negative values at the periphery (Fig. 3). The net current is also positive at the center and negative at the outer region. This shows that in the central portion of the disk, anodic current has the larger contribution to the net current, and the cathodic reaction dominates on the outer portion.

The Effect of Rotation Speed and Oxygen Concentration

As was mentioned earlier, velocity has no direct effect on the corrosion rate, but it increases the rate of transfer of corrosive species to the metal. This would suggest that increasing the velocity or the bulk concentration of the corrosive species should have a similar effect on the corrosion rate. (Note that in the laminar region of a rotating disk, the limiting rate of mass transfer is independent of linear velocity). Figures 4 to 9 show this point clearly.

As the rotation speed and/or oxygen concentration increases, the point of maximum corrosion on the disk moves towards the periphery, that is, the anodic part of the disk (where the corrosion rate of the metal is high) increases and consequently, the total corrosion of the disk increases too. But if the rotation speed is increased to higher values, provided there is no limitation as far as the electrode
kinetics of oxygen is concerned (A > 1; Figs. 4 and 5), there will be a sudden change in the shape of the corrosion distribution, and the whole disk is passivated.

According to the polarization curves (Fig. 1), these results suggest that increasing the rotation speed and/or oxygen concentration moves the solution more towards the maximum of the iron curve, and then shifts it to the passive region. In other words, the potential of the disk first becomes more negative with increasing rotation speed, and then it is suddenly shifted to much more positive values, as it is shown in Fig. 6. For example, the potential of the disk decreases from -0.1943 to -0.2004 V (NHE) when rotation speed increases from 100 to 400 rad/sec, and then it increases to 0.2203 V for a rotation speed of 600 rad/sec. And at the same time, the total corrosion of the disk increases from 1.16185 to 1.70476 A and then decreases to 0.000125 A.

As it was mentioned earlier, there should also be a solution in the active region of the iron polarization curve (where the whole disk will be corroding). This solution (Fig. 7) gives a corrosion rate which is almost uniform on the disk, and the effect of rotation speed is to shift the potential to more positive values (and consequently increases the total corrosion). For the higher values of rotation speed and/or oxygen concentration, the disk is shifted to the passive region.

From Figures 5 and 7 it can be understood that, the two solutions for this problem move towards each other by increasing the rotation speed and/or oxygen concentration, join and then disappear. Figure 6 shows this with special clarity.
If the oxygen exchange current density is small, the rate of the cathodic reaction would be an important factor in the corrosion rate of the disk, and an increase in the rotation speed may have little effect on the corrosion. Figures 8 and 9 show this point clearly. For large values of rotation speed, the corrosion rate would be almost independent of these factors. Thus, for this case \((A < 1)\) one cannot get total passivity by increasing the rotation speed. As rotation speed tends to infinity, one should expect to get a uniform corrosion rate on the disk.

As the oxygen concentration in the bulk solution is increased, the limiting rate of oxygen transfer to the disk, as well as the rate of oxygen reaction on the disk, increases (the exchange current density of oxygen in the bulk solution \(i_0(c_\infty)\) is an increasing function of oxygen concentration). Thus, one can get total passivity by increasing the oxygen concentration.

### The Effect of the Conductivity of the Solution

Figures 10 and 11 show that as the conductivity of the solution increases, the corrosion rate becomes more uniform on the surface of the disk. This is what we should expect to get, because increasing the conductivity will decrease the ohmic potential (equations 34 and 37), and the potential distribution becomes more uniform. Consequently, the corrosion rate should be uniform too. For the solutions with low conductivity, where the nonuniformity in the corrosion rate increases, the central portion of the disk will have the maximum rate of corrosion,
while passivation occurs at the edge of the disk, and as the conductivity decreases, a larger area of the disk is passivated. For very low conductivities, the whole disk is passivated.

As it can be understood from Fig. 11, total passivity can also occur for very high conductivities, provided $A > 1$ and the rotation speed is high enough.

**The Effect of the Size of the Disk**

The size of the disk is an important factor in the corrosion rate. Figure 12 shows that increasing the radius of the disk has a tendency to increase the nonuniformity of corrosion rate, and for very large disks the whole disk is passivated. If this result is compared with the one obtained for the case in which conductivity of the solution is a variable (Figures 10 and 11), one may conclude that increasing the size of the disk has much the same effect on the corrosion rate as decreasing the conductivity of the solution. But it should be noticed that these two parameters have not exactly the same effect on the corrosion. The conductivity of the solution is a variable that changes only the ohmic potential. The radius of the disk is not only an important factor as far as the ohmic potential is concerned (equations 34 and 39), but it is also a variable that determines the limiting rate of oxygen transfer to the disk (equation 17). Figure 13 shows this point clearly. This Fig., which gives the results for a case of higher concentration and exchange current density of oxygen, is no longer similar to the results in which conductivity is a variable.
For small disks, the whole area of the disk would be in the laminar region, and, consequently, the corrosion rate will be uniform as it is shown in Figures 12 and 13.

The Multiple Solutions

The results given above, show that in general, for a given condition (rotation speed, oxygen concentration, conductivity of the solution, and the radius of the disk) one can get three different schemes for the corrosion behavior of the rotating disk. Thus, the next task is to see which one of these solutions is physically meaningful.

In the experiments dealing with the corrosion of active-passive metals, one is usually faced with a phenomenon called "hysteresis." That is the corrosion rate of the metal for a specific concentration of the oxidizer, depends on the way we attain that concentration. If in an experiment, the oxidizer concentration is increased from a low value to the desired value, or if the concentration is decreased from a high value to that specific concentration, one may get different results.

Thus, in the case of the rotating disk, one would expect to get the hysteresis event by increasing or decreasing the rotation speed and/or oxygen concentration. And for a given condition, the actual solution would be one of the three solutions depending upon the way the system approaches that state.

This work was done under the auspices of the U. S. Atomic Energy Commission.
\( c_\infty = 10^{-7} \text{ mole/cm}^3 \)
\( \Omega = 800 \text{ rad/sec} \)
\( r_0 = 20 \text{ cm} \)
\( \kappa = 0.1 \text{ mho/cm} \)
\( A = 0.5 \)

**Fig. 3** Iron and oxygen current densities and ohmic potential distribution on the surface of iron rotating disk.
Fig. 4 The effect of rotation speed on the corrosion rate of iron rotating disk.

<table>
<thead>
<tr>
<th>$\Omega$, rad/sec</th>
<th>$I_{Fe}$, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.39284</td>
</tr>
<tr>
<td>200</td>
<td>0.62038</td>
</tr>
<tr>
<td>400</td>
<td>0.95760</td>
</tr>
<tr>
<td>800</td>
<td>1.31401</td>
</tr>
</tbody>
</table>

$c_{\infty} = 10^{-7}$ mole/cm$^3$
$r_0 = 20$ cm
$\kappa = 0.1$ mho/cm
$A = 1.07$
The effect of rotation speed on the corrosion rate of iron rotating disk (high oxygen concentration).

\[ \begin{array}{c|c|c}
\hline
\Omega, \text{rad/sec} & I_{Fe,A} & \\
\hline
50 & 0.78477 & \\
100 & 1.16185 & \\
200 & 1.48364 & \\
400 & 1.70464 & \\
600 & 0.000125 & \\
\hline
\end{array} \]

\[ c_\infty = 5 \times 10^{-7} \text{ mole/cm}^3 \]
\[ r_0 = 20 \text{ cm} \]
\[ \kappa = 0.1 \text{ mho/cm} \]
\[ A = 1.07 \]
Fig. 6 The effect of rotation speed on the potential of iron rotating disk.
Fig. 7 The effect of rotation speed on the corrosion rate of iron rotating disk (active solution).
Fig. 8 The effect of rotation speed on the corrosion rate of iron rotating disk (small oxygen exchange current density).

- $c_\infty = 10^{-7}$ mole/cm$^3$
- $r_0 = 20$ cm
- $\kappa = 0.1$ mho/cm
- $A = 0.5$

<table>
<thead>
<tr>
<th>$\Omega$, rad/sec</th>
<th>$I_{Fe}$, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.27215</td>
</tr>
<tr>
<td>400</td>
<td>0.40685</td>
</tr>
<tr>
<td>800</td>
<td>0.48670</td>
</tr>
</tbody>
</table>
Fig. 9 The effect of rotation speed on the corrosion rate of iron rotating disk (small oxygen exchange current density, high oxygen concentration).
Fig. 10 The effect of the conductivity of the solution on the corrosion rate of iron rotating disk.
Fig. 11 The effect of the conductivity of the solution on the corrosion rate of iron rotating disk (large oxygen exchange current density).
Fig. 12 The effect of the size of the disk on the corrosion rate of iron rotating disk.
Fig. 13 The effect of the size of the disk on the corrosion rate of iron rotating disk (large oxygen exchange current density).
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>see eqn. 41</td>
</tr>
<tr>
<td>$B_n$</td>
<td>coefficients in series for potential</td>
</tr>
<tr>
<td>$c_0$</td>
<td>concentration at electrode surface, mole/cm$^3$</td>
</tr>
<tr>
<td>$c_\infty$</td>
<td>bulk concentration, mole/cm$^3$</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient, cm$^2$/sec</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant, coulomb/equiv</td>
</tr>
<tr>
<td>$i$</td>
<td>net current density at electrode surface, amp/cm$^2$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>exchange current density, amp/cm$^2$</td>
</tr>
<tr>
<td>$i_{Fe}$</td>
<td>iron current density, amp/cm$^2$</td>
</tr>
<tr>
<td>$i_{lim}$</td>
<td>limiting current density, amp/cm$^2$</td>
</tr>
<tr>
<td>$i_{O_2}$</td>
<td>oxygen current density, amp/cm$^2$</td>
</tr>
<tr>
<td>$I$</td>
<td>total net current on the disk, amp</td>
</tr>
<tr>
<td>$I_{Fe}$</td>
<td>total iron current on the disk, amp</td>
</tr>
<tr>
<td>$I_{O_2}$</td>
<td>total oxygen current on the disk, amp</td>
</tr>
<tr>
<td>$k$</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>$k_{a}, k_{c}$</td>
<td>rate constants</td>
</tr>
<tr>
<td>$m_i$</td>
<td>rate of mass transfer of species $i$ to the disk, mole/cm$^2$ sec</td>
</tr>
<tr>
<td>$\bar{m}_i$</td>
<td>average rate of mass transfer of species $i$ to the disk, mole/cm$^2$ sec</td>
</tr>
<tr>
<td>$M_{2n}$</td>
<td>a Legendre function</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons produced when one reactant ion or molecule reacts</td>
</tr>
<tr>
<td>$Nu$</td>
<td>local Nusselt's number</td>
</tr>
<tr>
<td>$\overline{Nu}$</td>
<td>average Nusselt's number</td>
</tr>
<tr>
<td>$P_n$</td>
<td>Legendre polynomial of order $n$</td>
</tr>
<tr>
<td>$q_i$</td>
<td>reaction order of species $i$</td>
</tr>
</tbody>
</table>
r \quad \text{radial coordinate, cm}

r_o \quad \text{radius of disk, cm}

R \quad \text{universal gas constant}

\frac{r^2}{V} {\dot{\Omega}} \quad \text{overall Reynolds number}

\frac{r^2}{V} {\dot{\Omega}} \quad \text{local Reynolds number}

s_i \quad \text{stoichiometric coefficient of species i}

Sc \quad \text{v/D, Schmidt number}

t \quad \text{transference number of reactant}

T \quad \text{absolute temperature, } ^\circ \text{k}

U \quad \text{equilibrium potential of oxygen, volt (1.229 NHE)}

v_y \quad \text{velocity component in } y \text{ direction, cm/sec}

V \quad \text{potential of metal disk electrode, volt}

y \quad \text{normal distance from disk, cm}

\alpha_a, \alpha_c \quad \text{parameters in kinetic expression}

\delta \quad \text{thickness of diffusion layer, cm}

\eta \quad \text{elliptic coordinate}

\eta \quad \text{total overpotential, volt}

\eta_c \quad \text{concentration overpotential, volt}

\eta_s \quad \text{surface overpotential, volt}

\kappa_\infty \quad \text{conductivity of bulk solution, ohm}^{-1} \text{ cm}^{-1}

v \quad \text{kinematic viscosity, cm}^2/\text{sec}

\xi \quad \text{elliptic coordinate}

\phi \quad \text{electrostatic potential, volt}

\phi_0 \quad \text{external potential extrapolated to electrode surface, volt}

\Omega \quad \text{rotation speed, radians/sec}
REFERENCES


7. F. L. LaQue, "Theoretical studies and laboratory techniques in sea water corrosion testing evaluation" Corrosion, 13, 303t (1957).


12. A. R. Lee, "The effect of oxygen pressure on the corrosion of steel"
13. N. D. Tomashov, Theory and protection of metals. The science of
14. Marcel Pourbaix, "Some application of electrochemical thermodynamics"
Corrosion, 6, 395 (1950).
15. Marcel Pourbaix, "Recent applications of electrode potential measure-
ments in the thermodynamics and kinetics of corrosion of metals"
16. I. L. Rosenfeld, "Review: Crevice corrosion" Presented before National
Association of Corrosion Engineers, December 1971, Williamsburg,
Virginia.
17. Miltan Stern, "The mechanism of passivating-type inhibitors"
19. C. L. McBee and J. Kruger, "Events leading to the initiation of the
pitting of iron" presented before National Association of Corrosion
20. Marcel Pourbiax, "The electrochemical basis for localized corrosion"
Presented before National Association of Corrosion Engineers, December,
1971, Williamsburg, Virginia.
21. Marcel Pourbiax, "Application of electrochemistry to corrosion studies"
Corrosion A Symposium, held at the University of Melbourne, December,
1955.
22. M. Pourbaix, L. Kimzack-Mathieiu, Ch. Mertens, J. Meunier, Cl. Vanlevyen-
Haghe, L. De Munck, J. Laureys, L. Neelemans and M. Warzee,


33. Yoshihiro Hisamatsu, Tuguyasu Yoshii and Yoshikazu Matsumura, Electrochemical and Microscopical study of pitting corrosion of Austenitic stainless steel" Presented before National Association of Corrosion
34. John Newman, "Schmidt number correction for the rotating disk"
   142A, 628 (1933).
36. Paul Delahay, "A polarographic method for the indirect determination
   of polarization curves for oxygen reduction on various metals"
37. James P. Hoare, "Oxygen overvoltage measurements on bright platinum
38. Allen D. Garrison and Johnny Fay Lilly, "The relation between oxygen
   1967, p. 634.
   Prentice-Hall, Inc., to be published, section 56.
PROGRAM Disk (InPut,Output)
DIMENSION W(R),WU(40),B(40),VO(40),PM(40),PG(40,R)
DIMENSION CURFE(R),WU(40),XG(40),OXLIM(40)
DIMENSION A(40,40),R(40),DW(0,0)
COMMON A*R,XG,WU,OXLIM,CURFE,CUROX,W
101 FORMAT(12X,F12.7)
102 FORMAT(12X,F10.7)
103 FORMAT(F10.6,2F17.10)
104 FORMAT(H15//2X*RO* SPEED* F6.1*5X,*OP CONC* F17.10*5X,*RO*F7.2* 
15X*COND* F6.3//)
105 FORMAT(12X,A12)
106 FORMAT(2F21.21)
107 FORMAT(7X*R/RO* 7X*FE CURRENT* 4X*OP CURRENT* 4X*NET CURRENT* 
16X*Ohmic POTENTIAL*)
108 FORMAT(7X*F12.7*7X*F12.7*7X*F12.10)
109 FORMAT(7X*NO. OF ITERATIONS=* I1)
110 FORMAT(F17.10)
111 FORMAT(5X*NO CONVERGENCE*)
112 FORMAT(5X*V = F10.6//)
113 FORMAT(5X*CURRNT* AX,*OR* CURRENT* AX'*NET (CURRENT* 
16X*Ohmic POTENTIAL*)
114 FORMAT(7X*F12.7)
115 FORMAT(2X*F12.7*5X*F12.10)
116 FORMAT(3F10.6)
READ 101,NN,TOL
READ 102,RO,RS,COND,VIS
READ 103,XCOI,DO,CO
READ 117,V1,V2,DV
READ 105,HH,NA
IHPI=IH+1
READ 106, (XG(J),WU(J), J=IHPI,NA)
DO 2 J=1,NA
IF(J>GH) GO TO 1
IR=NA-J+1
XG(J)=5-5*XG(IR)
WU(J)=5*WU(IR)
GO TO 2
1 XG(J)=5+5*XG(J)
WU(J)=5*WU(J)
2 CONTINUE
DO 3 N=1,NN
3 PM(N)=-6366198/P(7*N-7,0,0)***
DO 4 J=1,NA
XX=SORT(1.-XG(J))***
DO 4 N=1,NN
4 PG(N,J)=P(7*N-2,XX)
Rc=SORT(R5*VIS/RS)/RO
CALL OXY (1.,VIS,RS,RO,DO,CO,NA,VS,TOL,DIOX,AIO,XCO1,J)
DO 5 J=1,NA
5 READ 110,WU(J)
JA=0
6 JA=JA+1
DO 8 N=1,NN
SS=0.
DO 7 J=1,NA
7 SS=SS-RO*WU(J)*XG(J)*PM(N,J)*WU(J)/COND
8 B(N)=SS*(4*N-3)/PM(N)
DO 9 J=1,NA
VO(J)=0.
DO 9 N=1,NN
9 VO(J)=VO(J)+8(N)*DG(N,J)
DO 11 J=1,NA
11 WW(J)=W(J)
12 K=0
V=V1
13 FUN=0.
DO 15 J=1,NA
VS=V-VO(J)
CALL FE (VS,CURFE(J),DIFE)
CALL OXY (.7*VIS*RS*RO*DO*CO*NA*VS*TOL*DIOX*CUROX(J)*XCO1,J)
15 FUN=FUN+(CURFE(J)+CUROX(J))*XG(J)*WG(J)
K=K+1
16 IF(K.EQ.1) 16,16,17.
17 FUN1=FUN
V=V2
GO TO 14
18 FUN2=FUN
IF(FUN1) 21,21,22
21 IF(FUN2) 22,22,24
22 IF(FUN2) 25,25,12
23 IF(ABS(FUN1)-ABS(FUN2)) 25,25,12
24 IF(ABS(FUN1)-ABS(FUN2)) 24,24,26
25 KK=2
GO TO 18
26 K=1
18 L=0
IF(JA.EQ.1) V=V1
IF(JA.GT.1) V=VF
20 DFUN=0.
L=L+1
FUN=0.
PRINT 115,V
IF(L.GT.40) GO TO 52
DO 26 J=1,NA
VS=V-VO(J)
CALL FE (VS,CURFE(J),DIFE)
CALL OXY (.7*VIS*RS*RO*DO*CO*NA*VS*TOL*DIOX*CUROX(J)*XCO1,J)
W(J)=CURFF(J)+CUROX(J)
DW(J)=DIOX+DIFE
DFUN=DFUN+DW(J)*WG(J)*XG(J)
26 FUN=FUN+W(J)*XG(J)*WG(J)
PRINT 113,FUN
IF(ABS(FUN)-TOL) 42,42,27
27 IF(ABS(FUN)+.00001) 31,.91,28
28 IF(FUN) 29,42,30
29 IF(KK.EQ.1) V=V+DV
IF(KK.EQ.2) V=V-DV
GO TO 20
30 IF(KK.EQ.1) V=V-DV
IF(KK.EQ.2) V=V+DV
GO TO 20
31 V=V-FUN/DFUN
GO TO 20
32 JA=JA+1
DO 33 J=1,NA
33 WW(J)=W(J)
DO 34 35 N=1,NN
34 R(N)=0.
35 R(N)=R(N)+W(J)*PG(N,J)*WG(J)*XG(J)
DO 37 N=1,NN
36 R(N)=R(N) NWG(N,J)*WG(J)*DW(J)
DO 38 N=2,NN
37 R(N)=R(N)+A(N,L)*R(L)
38 A(N,L)=A(N,L)-PM(N)*COND/RO/(4*N-1)
CALL MATINV (NN,(DETERM)
V=R(1)
39 PRINT 115,V
B(1)=0.
40 N=2,NN
41 B(N)=R(N)
42 PRINT 107
VF=V
43 PRINT 104,RS,CO,RO,COND
44 PRINT 112,V
45 PRINT 107
46 PRINT 108,R,XG(J),CURF(E(J),CUROX(J),W(J),VO(J)
47 IF(JA+GT+30) GO TO 52
48 IF(ABS(W(J)-WW(J))/W(J) .GT. 0.001) 45,45,51
CONTINUE
PRINT 104,RS,CO,RO,COND
PRINT 112,V
PRINT 107
49 PRINT 108,R,XG(J),CURF(E(J),CUROX(J),W(J),VO(J)
50 IF(JA-7) 51,51,51
51 VF=V
52 STOP
END
SUBROUTINE OXY (LEE, VIS, RS, RO, DO, CO, NA, VS, TOL, DIOX, AI0, XCO; J)
DIMENSION XG(8U), WG(RU), OXLIM(RU), CURFE(R0), CURROX(R0), W(R0)
DIMENSION A(40, 40), R40)
COMMON A, R, XG, WG, OXLIM, CURFE, CURROX, W
IF (LEE .GT. 1) GO TO 4
SC = VIS/DO
RC = SQRT((2.0E5 * VIS / RS) / RO)
SC1 = SC**1.67
C1 = 6.2048/(1.0*290/SC1 + 14514/SC1**3)
AK3 = 0.16922*3.0E6/SC1**3.06/SC1**7.06/C1
Q = 3.86E5 * CO * DO * C1 * SC1 * SQRT(RS / VIS)
DO 3 J = 1, NA
IF (XG(J) - RC) 1, 1,
1 OXLIM(J) = -Q
GO TO 3
2 OXLIM(J) = -Q * AK3 * (XG(J) / RC) ** 0.7
3 CONTINUE
RETURN
4 A10 = OXLIM(J) / 3.
IF (VS .LE. -0.1) S10 = 0.75
IF (VS .GT. -20) S10 = 10.
5 ALPH = 0.591686 * S10
BE = 0.937 * S10
EX = EXP(-BE * (VS + 2))
AI0 = -XCO1 * EXP/(1.0 - XCO1 * EXP/OXLIM(J))
Y = BE * XCO1 * EXP/(1.0 - XCO1 * EXP/OXLIM(J)) + BE * XCO1 ** 2 * EXP ** 2 * OXLIM(J)
Z = 1.0 - XCO1 * EXP/OXLIM(J) ** 2
DIOX = Y / Z
RETURN
END
FUNCTION P(N,X)
    P1=1.0
    P2=X
    IF(N=1) 1,2=3
1 P=P1
   RETURN
2 P=P2
   RETURN
3 NM1=N-1
   DO 4 NU=1,NM1
      P=(X*FLOAT(2*NU+1)*P2-FLOAT(NU)*P1)/FLOAT(NU+1)
      P1=P2
4 P2=P
   RETURN
END
SUBROUTINE FE (VS, AIFE, DIFE)
S = -5.0E-3
A = 1.5E-3
EX = EXP(S*(VS+2)**2)
AIFE = A*EX + 1.0E-7
DIFE = 2.0*5*(VS+0.2)*EX
RETURN
END
SUBROUTINE MATINV (N*DFTERM)
DIMENSION ID(40),R(40*40),D(40)
COMMON R
DTERM=1.
DO 1 I=1,N
1 ID(I)=0.*0
DO 18 NN=1,N
BMAX=0.*0.
DO 6 I=1,N
2 DO 5 J=1,N
3 IF(ABS(B(I,J))>BMAX) 4,4,4
4 BMAX=ABS(B(I,J))
5 IROW=I
JCOL=J
6 CONTINUE
7 DTERM=0.*0.
RETURN
8 ID(JCOL) =1.
9 DO 10 J=1,N
10 B(JCOL,J)=SAVE
SAVE=D(IROW)
D(IROW)=D(JCOL)
D(JCOL)=SAVE
12 F=1./B(JCOL,JCOL)
DO 13 J=1,N
13 B(JCOL,J)=B(JCOL,J)*F
D(JCOL)=D(JCOL)*F
DO 18 I=1,N
18 CONTINUE
RETURN
END
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.