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Corrosion of an Iron Rotating Disk

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Abstract:

The corrosion rate of iron rotating disks is studied by calculating the current and potential distribution on the surface of the disk. The results show that the surface towards the center of the disk is corroded with a maximum rate, while the edge of the disk remains almost unattacked. The effect of different parameters on the corrosion behavior of the rotating disk is studied.
Introduction:

LaQue has conducted some corrosion 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 disks, the greatest attack occurs on the surfaces towards the center that move more slowly. The system should be amenable to analysis because the hydrodynamic flow is well known near a rotating disk, and one can calculate the current and potential distribution on the disk. Levich has found the limiting rate of mass transfer to a rotating disk, and Newman has given the current distribution on the surface of the rotating disk below the limiting current.

In practice, usually the anodic and cathodic reactions occur on different parts of the same surface (or on two different surfaces which are in contact) and causes localized corrosion. The rotating disk seems to be an ideal case for studying localized corrosion, because it is the simplest model that can be used to study this complicated situation.

It should be noted that velocity has not a direct effect on the rate of corrosion; its only role is that it usually (but not always) increases the rate of transfer of corrosive species to the metal, and consequently it may increase the corrosion rate. In the case of a rotating disk in the laminar region, the limiting rate of mass transfer to the disk is not a function of linear velocity. Consequently the disk is corroded uniformly in spite of the fact that there is a velocity gradient on its surface.
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 the turbulent region) and the amount of oxygen that reaches them is higher. Consequently the corrosion rate would be higher too. For the iron disks, the results can be explained when it is noted that iron is an active-passive metal, and a high oxygen concentration tends to produce a protective oxide coating on such metals. The surfaces towards the periphery of the disk are passivated because of the greater amount of oxygen that reaches them.

In the case of an iron rotating disk, the outer region of the disk, which is exposed to a higher oxygen concentration, acts as a cathode to the central portion. The reaction taking place on these cathodic areas would be the reduction of oxygen:

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

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

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

These local anodes and cathodes form a corrosion cell, and a current will pass through the solution. As there is no external current to the rotating disk, the total net current on the disk should be zero, i.e.:

$$I_{net} = I_{Fe} + I_{O_2} = 0 \quad (1)$$
Development of the Model

The current and potential distribution on the surface of a rotating disk are:

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

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

where \( \Phi_0 \) is the ohmic potential, \( R \) is the gas constant, \( T \) is absolute temperature, \( F \) is Faraday's number, \( B_n \) is a constant, \( P_{2n}(\eta) \) is the Legendre polynomial of order \( 2n \), \( i(\eta) \) is the current density, \( \kappa_\infty \) is the conductivity of the solution, \( \eta \) is the rotational elliptic coordinate, and \( M_{2n}(0) \) is a known constant (see ref. 5).

In the case of corrosion of the rotating disk, the current density \( i(\eta) \) in equation (2) would be the net current density which is the sum of anodic and cathodic current densities at each point on the disk, i.e.:

\[ i(\eta) = i_{Fe}(\eta) + i_{O_2}(\eta) \quad . \]

If the relations between the iron and oxygen current densities and the potential are known, one is in a position to solve equations (1) to (4) to determine the current and potential distribution on the disk, and consequently find the corrosion behavior of the disk. The
polarization curve of iron, which gives the relation between iron current density and potential, has been found by many investigators in different solutions.\textsuperscript{7,8} The following equation is used to describe the iron kinetics:

\[ i_{Fe} = 1.5 \times 10^{-3} \exp[-5 \times 10^{3}(V - \Phi_0 + 0.2)^2] + 10^{-7} \quad (5) \]

for \( V - \Phi_0 > -0.25 \),

where \( V - \Phi_0 \) is the potential of the electrode relative to a hydrogen electrode close to its surface. (It should be noted that the concentration overpotential of iron has been neglected.)

In the case of oxygen, one should consider both the concentration and surface overpotentials, because both are important. The limiting rate of mass transfer to a rotating disk in laminar flow was calculated by Levich\textsuperscript{4}, and is given by the following equation:

\[ \text{Nu}_{\text{lam}} = c_1 \text{Re}_{\text{loc}}^{1/2} \text{Sc}^{1/3} \quad (6) \]

where \( \text{Nu}_{\text{lam}} \) is the local Nusselt number, \( \text{Re}_{\text{loc}} \) is the local Reynolds number, \( \text{Sc} \) is the Schmidt number, and \( c_1 \) is a function of Schmidt number,\textsuperscript{9} approaching 0.6205 for large Schmidt numbers.

For the turbulent region, there are some experimental correlations in the literature. Ellison\textsuperscript{10,11} has given the following expression for the rate of mass transfer to a rotating disk in the turbulent region, for Reynolds numbers between \( 8.9 \times 10^5 \) and \( 1.18 \times 10^7 \) and for Schmidt numbers between 35 and 1350:
\[
\overline{\text{Nu}}_t = 1.17 \times 10^{-2} \text{Re}^{0.896} \text{Sc}^{0.249},
\]  \hspace{1cm} (7)

where \(\overline{\text{Nu}}_t\) is the average Nusselt number and \(\text{Re}\) is the overall Reynolds number. Equation (7) can be used to find the local rate of mass transfer to the disk in the turbulent region. By definition:

\[
\overline{N_1 \pi r^2} = \int_0^\infty 2\pi r N_1 \text{dr},
\]  \hspace{1cm} (8)

where \(\overline{N_1}\) is the average rate of mass transfer to the disk. Differentiation of this equation with respect to \(r\) and substitution of \(\text{Re}_{loc}, \overline{\text{Nu}}_t\), and \(\text{Nu}_t\) (from their definitions) yield:

\[
\frac{d}{d\text{Re}_{loc}^{1/2}} \left( \overline{\text{Nu}}_t \text{Re}_{loc}^{1/2} \right) = 2\text{Nu}_t.
\]  \hspace{1cm} (9)

From Ellison's correlation one can then get:

\[
\text{Nu}_t = 1.6332 \times 10^{-2} \text{Re}_{loc}^{0.896} \text{Sc}^{0.249},
\]  \hspace{1cm} (10)

where \(\text{Nu}_t\) is the local Nusselt number in the turbulent region.

Equations (6) and (10) yield the following expressions for the limiting current density on the surface of the rotating disk:

\[
i_{lim} = nFdC_1 \sqrt{\frac{\Omega}{\nu}} \text{Sc}^{1/3} \text{ for laminar region},
\]  \hspace{1cm} (11)

\[
i_{lim} = nFdC_2 \left( \frac{\Omega^2}{\nu} \right)^{0.316} \text{Sc}^{0.249} \text{ for turbulent region},
\]  \hspace{1cm} (12)
where $\Omega$ is the rotation speed (rad/sec), $\nu$ is the kinematic viscosity, and $C_2 = 1.6332 \times 10^{-2}$.

The kinetics of the oxygen reaction will be described by the following equation:

$$i_{O_2} = i_0(c_o) \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( -\frac{\alpha_c F}{RT} \eta_s \right) \right], \quad (13)$$

where $\eta_s$ is the surface overpotential, $\alpha_a$ and $\alpha_c$ are the transfer coefficients, and $i_0(c_o)$ is the exchange current density. For the reduction of oxygen, the first term in eqn. (13) can be neglected (this is a good approximation for the potentials far removed from the equilibrium potential of oxygen). The concentration overpotential can be written as

$$\eta_c = - \frac{RT}{nF} \ln \frac{c_o}{c_{\infty}}, \quad (14)$$

and the total potential is:

$$V = \eta_s + \eta_c + \phi_o + U, \quad (15)$$

where $U$ is the equilibrium potential of oxygen relative to a normal hydrogen electrode (about 1.229 volts).

The exchange current density depends on the concentration of reactants and products on the surface of the electrode. If the concentration variations of $\text{OH}^-$ and $\text{H}_2\text{O}$ are neglected, one can write the following equation for the oxygen exchange current density:
where \( i_o(c_\infty) \) is the oxygen exchange current density evaluated at the bulk concentration \( c_\infty \). And the ratio of oxygen concentration on the surface to that in the bulk solution can be expressed as:

\[
\frac{c_o}{c_\infty} = 1 - \frac{i_{o2}}{i_{lim}} \tag{17}
\]

Substitution of equations 14, 15, 16 and 17 into equation 13 yields:

\[
i_{O2} = -i_o(c_\infty) \left(1 - \frac{i_{o2}}{i_{lim}}\right) \exp \left[-\frac{\alpha F}{RT} (V - \phi_0 - U)\right] \tag{18}
\]

where \( i_o(c_\infty) \) can be found from the polarization curve of oxygen reduction on iron, which has been given by some investigators. The values used here are:

\[
i_o(c_\infty) \exp(-\frac{\alpha F}{RT} U) = 7.4 \times 10^{-4} \text{ A/cm}^2 \text{ for } c_\infty = 10^{-7} \text{ mole/cm}^3
\]

\[
= 16.0 \times 10^{-4} \text{ A/cm}^2 \text{ for } c_\infty = 5 \times 10^{-7} \text{ mole/cm}^3
\]

Equations (5) and (18) give the desired relations that can be used in parallel with equations (1) to (4) to find the current and potential distribution on the disk. It should be noted that there are six equations with six unknowns, namely \( i_{Fe}, i_{O2}, i(\eta), \phi_0, B_n \) and \( V \).
These simultaneous equations are highly nonlinear and should be solved by numerical methods. The following iterative procedure is used to solve the equations:

1- A net current distribution is assumed for the disk.
2- Equation (3) is used to find the coefficients $B_n$.
3- The ohmic potential $\Phi_o$ is calculated from equation (2).
4- A value is assumed for the potential $V$ of the disk.
5- Iron and oxygen current densities are calculated from equations (5) and (18), respectively.
6- The current densities found in step 5 should satisfy equation (1); if they do not, another value is assumed for $V$, and the 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 a multi dimensional Newton-Raphson method, another value is found for the net current, and the calculations enumerated in steps 2 through 6 are repeated until no significant changes occurred in the net current.

Limitation of the Model

The iron current density is a function of $Fe^{++}$ concentration, chloride ion concentration, and pH of the solution, as well as potential. In general one can write:

$$i_{Fe} = i_{Fe}(V - \Phi_o, c_{Fe^{++}}, c_{Cl^{-}}, pH)$$
In the case of corrosion of the rotating disk, the outer portion of the disk acts as the aerated cathode where oxygen is being reduced to water and/or hydrogen peroxide with an increase of pH, while the central portion of the disk, which is active, is the less well aerated anode where the metal undergoes corrosion and hydrolysis with decrease of pH. Thus, the pH does not remain uniform on the surface of the disk.

The concentration of iron ion and chloride ion are likewise not uniform on the surface of the disk. Fe$^{++}$ is higher at the center and decreases towards the periphery. Migration may increase the concentration of the chloride ion on the central portion of the disk.

It should be noted that the variations of $c_{Fe^{++}}$, $c_{Cl^-}$, and pH are not large, and they are neglected in this work. They may, however, be crucial to the stability of a situation where part of the disk is active and part is passive.

Results and Discussion

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. 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:

$$A = \left| \frac{i_{O_2}}{i_{Fe} \max i_{Fe}} \right|_{\Omega \to \infty}$$  \hspace{1cm} (19)
would be the last variable. This quantity is indicated in the graphical representation of the results.

Figure 1 shows the iron current density (which is proportional to the rate of corrosion), oxygen current density, and the ohmic potential on the surface of the rotating disk. The iron current density curve shows that the corrosion rate is high at the center, increases slowly with radial position, passes through a weak maximum, and then drops rapidly to a very low value at the periphery. This is in agreement with the experimental results. The curve for the oxygen current density has a flat part, which is related to the laminar region of the disk, and a sharp increase of the current, that shows the transition from laminar to turbulent region. The ohmic potential is high and positive at the center and decreases to negative values at the periphery. The net current would also be positive at the center and negative at the edge of the disk. 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 on the corrosion rate of the rotating disk is shown in Figs. 2 and 3. As it was mentioned earlier, the only effect of velocity is to increase the rate of transfer of oxygen to the disk (in the turbulent region). Thus, increasing the rotation speed has much the same effect on the corrosion as increasing the oxygen concentration. One should of course note that changing the oxygen concentration, will change $i_0(c_\infty)$. As the rotation speed is increased, the point of maximum corrosion on the disk moves towards the
Fig. 1. Iron and oxygen current densities and ohmic potential distribution on the surface of iron rotating disk.
periphery, and the total corrosion of the disk increases. 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 \((A > 1)\), there will be a sudden change in the shape of the corrosion distribution, and the whole disk is passivated.

Figure 4 shows the corrosion behavior of the rotating disk when the conductivity of the bulk solution is a parameter. As the conductivity increases, the corrosion rate becomes more uniform. For the solutions with low conductivity, the nonuniformity in the corrosion rate increases, and the central region of the disk will have the maximum rate of corrosion, while passivation occurs at the edge. As the conductivity decreases, a larger area of the disk is passivated, and for very low conductivities, the whole disk would be in the passive region. As it can be understood from Fig. 4, for large values of conductivities one can also get total passivity provided the rotation speed is high enough and there will be no limitation for the electrode kinetics of oxygen.

The effect of the size of the rotating disk on the corrosion rate is given in Fig. 5. It 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. For small disks, the whole area of the disk would be in the laminar region, and, consequently, the corrosion rate would be uniform, as it is shown in Fig. 5. It should be noted that the size of the disk is an important factor in the corrosion rate, because it is not only a variable as far
Fig. 2. The effect of rotation speed on the corrosion rate of iron rotating disk.
Fig. 3. The effect of rotation speed on the corrosion rate of iron rotating disk.
Fig. 4. The effect of conductivity of the solution on the corrosion rate of iron rotating disk.
Fig. 5. The effect of the size of the disk on the corrosion rate of iron rotating disk.
as the ohmic potential is concerned but also a factor that determines the limiting rate of oxygen transfer to the disk.

**Conclusions**

The development followed in the preceding sections shows that the main reason for the peculiar corrosion behavior of an iron rotating disk is the passivation that occurs at the edge of the disk. Besides that, in order to have such a nonuniform corrosion rate on the surface of the rotating disk, the outer region of the disk has to be in the turbulent region. That is, if the size of the disk is small and/or the rotation speed is low so that the whole disk is in laminar region, one would get a uniform corrosion rate. The results also show that by changing the different parameters of the system, one can get total passivity. It should be noted that in a system where the rate of transfer of corrosive species to the metal is high, the relation between the anodic and cathodic reaction rates is very important, because it is usually the electrode kinetics that limits the corrosion rate.

Because of the peculiar shape of iron polarization curve, for a given condition of the system, it is possible to get three different schemes for the corrosion behavior of the rotating disk from the model developed above. Thus one would wonder which one of these solutions is physically meaningful. It should be noted that in the corrosion experiments of active-passive metals such as iron, one usually expects to obtain a hysteresis. That is, the corrosion rate of the metal at a given condition depends on the way
the system approaches that specific condition. Thus in the case of iron rotating disk, one would also expect to get a hysteresis by increasing and decreasing the rotation speed, and the actual corrosion scheme of the disk would be one of the three solutions obtained from the calculations depending upon the way we approach a given condition.

Acknowledgment

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Nomenclature

A see equation 19

B

n coefficients in series for potential

c

o concentration at electrode surface, mole/cm

3

c

∞ bulk concentration, mole/cm

3

D diffusion coefficient of oxygen, cm

2/sec

F Faraday's constant, Coulomb/equiv

i net current density at electrode surface, amp/cm

2

i

Fe iron current density, amp/cm

2

i

lim limiting current density, amp/cm

2

i

0 oxygen current density, amp/cm

2

i

o exchange current density, amp/cm

2

I total net current on the disk, amp

I

Fe total iron current on the disk, amp

I

02 total oxygen current on the disk, amp

M

2n a Legendre function

n number of electrons produced when one oxygen molecule reacts (-4)

N

i

i flux of species i, mole/cm

2/sec

N

u

Nu

N

1

i

r/D(c

∞-c

o), local Nusselt number

Nu

N

1

i

0 r/D(c

∞-c

o), average Nusselt number

P

n Legendre polynomial of order n

r radial coordinate, cm

r

0 radius of disk, cm

R universal gas constant

Re = r

2 n/ν, overall Reynolds number
Re_{loc} = r^2 \Omega / \nu, \text{ local Reynolds number}

Sc = \nu / D, \text{ Schmidt number}

T = \text{ absolute temperature, } °K

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

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

\alpha_d, \alpha_c = \text{ transfer coefficients}

\eta = \text{ elliptic coordinate}

\eta_c = \text{ concentration overpotential, volt}

\eta_s = \text{ surface overpotential, volt}

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

\Phi_0 = \text{ external potential extrapolated to electrode surface, volt}

\Omega = \text{ rotation speed, radians/sec}
References

1. F. L. LaQue, Corrosion, 13, 303t (1957).
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