ANALYSIS OF GALVANIC CORROSION UNDER MASS TRANSFER CONTROLLED CONDITIONS

Qasim, J.M Slaiman  Basim O. Hasan  Baker M. Al-Zaidy
Chemical Eng. Dept.- Nahrain University-Baghdad -Iraq

ABSTRACT
Because of practical importance of protecting industrial equipments from galvanic corrosion, the need arises to analyze the effects of variables, such as temperature, velocity, and area fraction of metals on galvanic corrosion in systems under mass transfer control as in seawater (pH=7). For these reasons the galvanic corrosion of Fe-Zn is analyzed to study the influence of Reynolds number, temperature, and area fraction on the galvanic corrosion rates and galvanic corrosion potential under mass transfer control.

It is found that galvanic corrosion rate of more active metal (Zn) is increased with Reynolds number while the corrosion rate of more noble metal (Fe) is slightly increased with Re depending on the galvanic potential that depends on the area fraction. Increasing Reynolds number shifts the galvanic potential to more positive values. Also increasing temperature leads to shift the corrosion potential to more negative values and to change the corrosion rate of more active metal (Zn) depending on two parameters oxygen solubility and oxygen diffusivity. As area fraction of more active metal (Zn) increased the galvanic potential is shifted to the negative anodic direction while the corrosion rate for more noble metal is decreased.

KEY WORDS: Galvanic corrosion, mass transfer control, Fe-Zn couple, temperature, area fraction

INTRODUCTION
Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is some times also applied to the degradation of plastics, concrete, and wood but generally refers to metals. The consequences of corrosion are many and varied and the effect of these on the safe, reliable, and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of
corrosion are [Shreir 2000]: reduction of metal thickness, hazards or injuries to people arising from structural failure, loss of time, reduced value of goods, contamination of fluids in vessels and pipes, perforation of vessels and pipes, loss of technically important surface properties of a metallic component, and mechanical damage to valves, pumps, etc. Galvanic corrosion, often misnamed "electrolysis," is one common form of corrosion in marine environments. It occurs when two (or more) dissimilar metals are brought into electrical contact under corrosive environment. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. Either (or both) metal in the couple may or may not corrode by itself (themselves) in seawater. When contact with a dissimilar metal is made, however, the self-corrosion rates will cause the corrosion of the anode to accelerate and corrosion of the cathode to decelerate or even stop. If any two metals are coupled together, the one closer to the anodic (or active) end of the series, will be the anode and thus will corrode faster, while the one toward the cathodic (or noble) end will corrode slower. The two major factors affecting the severity of galvanic corrosion are, (i) the voltage difference between the two metals on the galvanic series, (ii) the size of the exposed area of cathodic metal relative to that of the anodic metal.

Corrosion of the anodic metal is more rapid and more damaging as the voltage difference increases. It is well known that the rate-controlling step in most aerated water corrosion processes is the cathodic half reaction. The most important cathodic process in aerated waters is oxygen reduction. The rate of this half reaction is generally limited by the speed at which oxygen can reach the surface of the metal. This oxygen is transported from the bulk water to the surface across the boundary layer by diffusion [Smith et. al. 1989, Cheng and Steward 2004].

Many investigations were carried out to study the galvanic corrosion. Copson [1945] studied the galvanic action between steel coupled to nickel in tap water with 3 to 1 area ratio of Ni/Fe and found that the galvanic corrosion of steel was appreciable. Pryor [1946] investigated the galvanic corrosion of Al/steel couple in chloride containing solution and found that aluminum completely protects steel cathodically within the pH range 0-14, and the galvanic current and the corrosion rate of aluminum are at a minimum in the nearly neutral pH range. Wranglen et al. [1969] studied the difference between the galvanic corrosion rates of high and low carbon steel in acid solutions and concluded that the engineers should not depend only on the galvanic series in the selection of their materials of construction. Mansfled et al [1971, 1973a, 1973b, 1973c, 1973d] investigated experimentally many factors that affect the galvanic interaction of various metals and alloys (as Al and Ti) in 3.5% NaCl solution and in HCl and gave a detailed explanations. Tsujino et al.[1982] studied the galvanic corrosion of steel coupled to noble metals (Pt, Cu, 304 stainless steel) in sodium chloride solution and found that the local currents on the steel depend on the area ratio of the steel to the cathodic metal and these currents are not related to the concentration of sodium chloride in neutral solutions. Bardal et al.[1984] predicted galvanic corrosion rates by means of numerical calculation and experimental models based on boundary element method. Glass and Ashworth [1985] perform experimental study to determine the corrosion rates of zinc- mild steel couple at 65 °C in pH of 8. They determined and discussed the variation of corrosion potential and corrosion rate with time. Fangteng et al.[1988] presented a theoretical approach for galvanic corrosion allowing for cathode dissolution, and found that the cathode of the couple is also corroded at the galvanic corrosion potential where the corrosion is controlled by the rate of oxygen diffusion to the electrode surfaces and the cathode dissolution in a galvanic system leads to a decrease in the galvanic current and it has been shown that the current density through the anode is independent of the area ratio of the electrodes. Jones and Paul [1988] stated that many semi conducting minerals have sufficient conductivity to permit electrochemical reactions on their surfaces and consequently, galvanic interactions will occur when such minerals are coupled to metals or other conducting minerals. Morris and Smyrl [1989] calculated galvanic currents and potentials on heterogeneous electrode surfaces comprised of random configurations of coplanar anodes and cathodes, for the purpose of investigating system behavior on different electrode geometries. Symniotis [1990] investigated the active dissolution of a duplex stainless steel in two
different acidic solutions together with a comparison of the active dissolution of the corresponding γ and α phases and found that the galvanic action takes place between the two phases. Also he studied the influence of dependence of anodic currents on time, surface morphology, and surface area. Chang et al [1997] studied the galvanic corrosion behavior of tungsten coupled with several selected metals/alloys. They stated that from an environmental perspective, tungsten is a more desirable material than depleted uranium (DU) for penetration applications. Lee et al [2000] investigated the corrosion behavior of an as-cast magnesium alloy focusing on the galvanic corrosion between a precipitate and Mg-rich matrix. Al-Hadithi [2002] investigated experimentally the effects of temperature, pH, and area fraction on the galvanic corrosion rate of binary galvanic system by coupling carbon steel, zinc, copper, and brass under activation control conditions. He studied the coupling of each pair of these metals individually. Song et al [2004] investigated experimentally the galvanic corrosion of magnesium alloy AZ91D in contact with zinc, aluminum, and steel alloys. AL-Maypof [2006] studied the galvanic coupling between magnetite and iron in acidic solution.

The present study aims to analyze the galvanic corrosion behavior of binary metals (Fe-Zn) under mass transfer control to investigate the influence of temperature, Reynolds number, and area fraction, on the free corrosion rate and galvanic corrosion rate for binary galvanic system under mass transfer (diffusion) control.

ANALYSIS

When two different metals are in a corrosive environment, they corrode at different rates according to their specific corrosion resistances to that environment, however, if the two metals are in contact, the more corrosion prone (metal 1) corrodes faster and the less corrosion prone (metal 2 the more noble one) corrodes slower than originally, i.e. when no contact existed. The accelerated damage to the less resistant metal is called galvanic corrosion, and is heavily dependent on the relative surface areas of the metals.

To determine the potential of a system in which the reduced and oxidized species are not at unit activity, the familiar Nernest equation can be employed:

\[
E = E^o + \frac{RT}{nF} \ln \frac{a_{\text{red}}}{a_{\text{oxid}}} 
\]  

(1)

The relationship between reaction rate and overvoltage for activation polarization is

\[
\eta^A = \pm \beta \log \frac{i}{i^o} 
\]  

(4)

The reaction rate is given by the reaction current or current density [David and James 1998]:

\[
i^a = i^o e^{(E^a - E^a^o)/\beta_a}
\]  

(5)

and

\[
i^c = i^o e^{(E^c - E^c^o)/\beta_c}
\]  

(6)

The effect of temperature is to change the value of exchange current density \(i^o\) as follows [Nesic et al 1996]:
The anodic current is given by [West 1965]

\[ I_a = i_{an}A \exp \left[ \frac{\alpha_a n_a F}{RT} (E_a - E_{a\alpha}) \right] \]  

or

\[ i_a = i_{an}f_a \exp \left[ \frac{\alpha_a n_a F}{RT} (E_a - E_{a\alpha}) \right] \]  

and cathodic one

\[ I_c = i_{cn}A \exp \left[ -\frac{\alpha_a n_a F}{RT} (E_c - E_{c\alpha}) \right] \]  

\[ i_c = i_{cn}f_c \exp \left[ -\frac{\alpha_a n_a F}{RT} (E_c - E_{c\alpha}) \right] \]  

For diffusion (mass transfer) controlled corrosion systems the reaction current is given by Fick's law [Shreir 2000]

\[ \frac{I}{z_c FA} = D \frac{dC}{dx} = k(C_b - C_v) \]  

The limiting current, i.e., the maximum current under diffusion control is obtained when \( C_v = 0 \), so

\[ I_L = z_c FAkC_b \]  

Where the mass transfer coefficient, \( k \), is defined by, \( k = \frac{D}{\delta} \). The corrosion current is then

\[ I_{corr} = I_L = z_c FAkC_b \]  

or

\[ i_L = z_c FkC_b \]  

\( z_c \) is used because in the corrosion processes the cathodic reaction is the one likely to be controlled by diffusion. The bulk concentration of oxygen in the solution changes with temperature as shown in Table 1.

The mass transfer coefficient (k) varies with flow or relative speed between metal and environment, the geometry of system, and the physical properties of the liquid. To calculate k in dynamic environment, the dimensionless groups are often used. Over the years there were many correlations proposed for predicting k for systems under mass transfer control. The well known correlation is that of Poulson and Robinson [1986] under turbulent flow conditions:

\[ Sh = 0.026 Re^{0.82} Sc^{0.35} \]  

Hence the expression of k is

\[ k = (D/d) \ 0.026 Re^{0.82} Sc^{0.35} \]
The effect of temperature and pressure on the diffusion coefficient is given by [Brodkey and Hershey 1989]

\[
D_{p,T} = D_o \frac{P_p}{P_o} \left( \frac{T}{T_o} \right)^n
\]  

(17)

where the exponent \( n \) varies from 1.75 to 2.

For galvanic corrosion under mass transfer or activation control at galvanic potential (\( E_g \)):

\[
I_{corr} = I_a = [I_c]
\]

and

\[
\Sigma I_a = \Sigma I_c
\]

(19)

For two metal galvanic corrosion

\[
i_{a,1}A_1+i_{a,2}A_2 = i_{c,1}A_1+i_{c,2}A_2
\]

(20)

or

\[
i_{a,1}f_1+i_{a,2}f_2 = i_{c,1}f_1+i_{c,2}f_2
\]

(21)

Where \( f_1 \) and \( f_2 \) are the area fractions (individual metal area/total metals area) of metals 1 and 2 respectively. At galvanic corrosion potential, \( E_a = E_c = E_g \), hence at \( E_g \)

\[
i_{o1} = i_{o,a1} \exp\left[ \frac{\alpha_{n_a} F}{RT} (E_g - E_{c,o1}) \right]
\]

(22)

\[
i_{o2} = i_{o,a2} \exp\left[ \frac{\alpha_{n_a} F}{RT} (E_g - E_{c,o2}) \right]
\]

(23)

\[
i_{c1} = i_{c,1} \exp\left[ \frac{\alpha_{n_c} F}{RT} (E_g - E_{c,c1}) \right]
\]

(24)

\[
i_{c2} = i_{c,2} \exp\left[ \frac{\alpha_{n_c} F}{RT} (E_g - E_{c,c2}) \right]
\]

(25)

For mass transfer control the summation of cathodic currents equal the oxygen limiting diffusion currents on both metals since the hydrogen evolution currents are negligible (pH=7). Hence

\[
\Sigma I_a = \Sigma I_L
\]

\[
i_{a,1}f_1+i_{a,2}f_2 = i_L f_1+i_L f_2
\]

(27)

since \( f_1+f_2=1 \), hence

\[
i_{a,1}f_1+i_{a,2}f_2 = i_L
\]

(28)

Insertion of Eqs. (22) and (23) in Eq.(28) with \( i_L \) from Eqs. (14) and (16), \( E_g \) can be obtained by iteration method.

Simplifications leading to analytic solutions of the above equations are so complex, so numerical solutions must be attempted. As an example, a numerical method implemented on a microcomputer. The sweeping method is as follows:

a. Estimate equilibrium potentials for metals using equation (1) at a particular temperature for pH of 7. The calculations are performed for the activity of oxidized species (\( \text{F}^{2+} \) and \( \text{Zn}^{2+} \)) of \( 10^{-6} \) molar.
b. Tafel slopes for anodic and cathodic reactions are established from equations (2) and (3) with $\alpha_a = \alpha_c = 0.5$.

c. The exchange current density is calculated from equation (7) for three values of temperatures 25, 40 and 60 °C with $E_{act}$ from Table 2. Table 3 gives values of $i_a$ at 25 °C.

d. Bulk concentration of oxygen in water at any temperature is from Table (1).

e. The value of oxygen diffusivity is estimated from Eq. (17) at different temperatures 25, 40 and 60 °C with oxygen diffusivity at 25 °C ($D_o$) of $2.04 \times 10^{-9}$ m$^2$/s [Perry and Green 1997].

f. The mass transfer coefficient $k$ is calculated by using Eq. (16) with $d=5$ cm.

g. The limiting current is estimated from Eqs. (14) and (16) at a particular Re at each temperature. To calculate Schmidt number ($Sc=\nu/D$) the physical properties of water are taken from Perry and Green [1997].

h. $E_g$ is assumed to start the iteration. It is necessary to realize that the galvanic corrosion potentials ($E_g$) of the reactions involved are chosen between the more negative equilibrium potential and the less negative one.

i. The values of $E_a$, $i_a$, and $E_g$ are substituted in Eqs.(22) and (23) to determine anodic currents.

j. The summations of the anodic and limiting currents (cathodic currents) are compared to determine the absolute value of their difference.

k. A new value of $E_g$ is assumed as in h until the difference between the summation of the anodic and cathodic (limiting) currents becomes very small to obtain the galvanic corrosion potential.

RESULTS AND DISCUSSION

Free Corrosion

Fig. 1 shows the variation of free corrosion potential with Re for the two metals Fe and Zn at 25 °C. The Fig. indicates that increasing Re shifts the corrosion potential to more positive direction for both metals. Fig. 2 shows the variation of Fe free corrosion potential with Re at different temperatures. The Fig. reveals that increasing Re shifts the free corrosion potential to more positive values. This can be ascribed to the increased oxygen transport to the metal surface. Also the Fig. indicates that increasing temperature shifts the free corrosion potential to more negative due to the decreased oxygen solubility. Fig. 3 shows the variation of oxygen limiting current density with Re at various temperatures. The oxygen limiting diffusion current equals the total cathodic currents since the hydrogen evolution current is negligible in systems of PH=7. Increasing Re increases the limiting current density via increasing oxygen supply to the metal surface by eddy diffusion [Fontana and Green 1984, Poulson and Robinson 1986]. Also the figure reveals that the higher the temperature is the lower the $i_L$ because the O$_2$ solubility in the bulk of the solution decreases with temperature.

Galvanic Corrosion

Fig. 4 shows the variation of galvanic corrosion potential with Re at various area fraction values. The Fig. shows that increasing Re leads to increase the galvanic potential to more positive direction for the whole range of area fractions. This is ascribed to the fact that increasing Re leads to increase the supply of cathodic species (oxygen) and hence increase the oxygen limiting diffusion current density shifting the corrosion potential to more positive. Also at a particular Re the higher the area fraction of Fe is the more positive value of galvanic corrosion potential. This trend holds for the whole range of temperature. Fig. 5 for area fraction of Fe of 0.1 and Zn of 0.9 shows the variation of current density with Re. It is evident that the Zn corrosion current density is equal to the oxygen limiting current density while the Fe corrosion current density is very low or negligible indicating that at coupling Fe with Zn, the Fe is totally protected because the equilibrium potential of Fe is higher than the galvanic potential of Fe= Zn couple. Also the galvanic corrosion current density of Zn increases appreciably with Re while that of Fe is not affected with Re since it is galvanically protected with Zn because coupling Zn with Fe shifts the galvanic potential below the equilibrium potential of Fe stopping its corrosion. Mansfeld [1971] stated that the corrosion rate of more active metal in
aerated neutral solutions is controlled by the diffusion rate of the oxidizer (oxygen) to the metal surface. Fig. 6 for area fraction of Fe and Zn of 0.5 exhibits the same trend. Fig. 7 shows that decreasing area fraction of Fe (or increasing area fraction of Zn) leads to decrease the Fe galvanic corrosion current density indicating that increasing the area fraction of more active metal leads to decrease the corrosion rate of more noble metal. Also at high Fe area fraction, increasing Re increases the corrosion current density of Fe. Fig. 8 indicates that the Zn corrosion current density increases with Re and slightly affected with the area fraction.

Figs. 9 and 10 for Re=10000 and 60000 respectively show the variation of galvanic corrosion potential with temperature at various area fractions. The figures reveal that increasing the temperature shifts the corrosion potential to more negative values. This behavior is attributed to certain solubility considerations. Many gases such as oxygen have lower solubility in open systems at higher temperatures. As temperature increases, the resulting decrease in solubility of gas causes corrosion potential and corrosion rate to go down [Nesic et al. 1996, Shreir 2000]. The effect of Re on the Fe galvanic corrosion current density in galvanic coupling with Zn at various temperatures is shown in Figs. 11 and 12 for different area fractions. The figures reveal also that the Fe galvanic current density varies with temperature where the highest corrosion current occurs at 40 °C and the lowest at 60 °C depending on two parameters, oxygen solubility and oxygen diffusivity.

Practically Zn in certain environmental conditions may exhibits a passivity or polarity reversal when coupled with Fe as noticed by Glass and Ashworth [1985] in 0.01 M NaHCO₃ at 65 °C.

CONCLUSIONS
1- At coupling two metals in systems under mass transfer control, the galvanic corrosion rate of more active metal increases with increasing Re. The galvanic corrosion rate of more noble metal is slightly affected by Re. The effect of Re on both metal is depending on area fraction of both metals.
2- Increasing temperature shifts the galvanic corrosion potential to more negative while the effect of temperature on the corrosion rate is unstable.
3- Increasing area fraction of more active metal has negligible effect on the corrosion rate of this metal and decreases the corrosion rate for more noble metal via shifting the corrosion potential to more negative.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Solubility of oxygen mg/l</th>
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<tbody>
<tr>
<td>25</td>
<td>7.8</td>
</tr>
<tr>
<td>40</td>
<td>6.0</td>
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<tr>
<td>60</td>
<td>3.1</td>
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<table>
<thead>
<tr>
<th>Metal</th>
<th>Activation Energy (J/mol)</th>
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<tbody>
<tr>
<td>Fe</td>
<td>2625</td>
</tr>
<tr>
<td>Zn</td>
<td>13609</td>
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<table>
<thead>
<tr>
<th>Metal</th>
<th>Eₒ, V</th>
<th>iₒ, A/cm²²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-0.44</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.76</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>
Fig. 1: Variation of Free Corrosion Potential with Re.

Fig. 2: Variation of Free Corrosion Potential of Fe with Re.
Fig. 3: Variation of Limiting Current Density with Re.

Fig. 4: Variation of Galvanic Potential with Re for Fe-Zn Couple at T=25 C.
Fig. 5: Variation of Current Density with Re for Fe-Zn Couple at T=25 °C.

Fig. 6: Variation of Current Density with Re for Fe-Zn Couple at T=25 °C.

Fig. 7: Variation of Current Density of Fe with Re at Various Area Fractions at T=25 °C.
Fig. 8: Variation of Current Density of Fe with Re for Various Area Fractions at T=25 °C.

Fig. 9: Variation of Galvanic Corrosion Potential with Temperature at Re=10000.
Fig.10: Variation of Galvanic Corrosion Potential with Temperature at $Re=6000$.

Fig. 11: Variation of Fe Corrosion Current with $Re$ at Various Temperatures for Fe Area Fraction of 0.1.

Fig. 12: Variation of Fe Corrosion Current with $Re$ at Various Temperatures for Fe Area Fraction of 0.9.
NOMENCLATURE

A  Surface area of specimen  \(m^2\)

a  Activities (concentration) of reduced and oxidized species  Mol/liter

C  Bulk concentration  mole/m^3

D  Diffusion coefficient of reacting ion  \(m^2/s\)

d  Diameter  m

E  Electrode potential  V

F  Faradays constant  96487 Coulomb/g.equivalent

i  Current density  \(\mu A/cm^2\)

I  Total corrosion  \(\mu A\)

i_o  Exchange current density at concentration  \(\mu A/cm^2\)

k  Mass Transfer Coefficient  m/s

L  Distance between the pressure taps  m

n  Number of electrons transfer

R  Gas constant  8.314 J/mol.K

Re  Reynolds number

Sc  Schmidt number.

T  Temperature  \(^\circ C\) or K

u  Velocity  m/s

z  Number of electrons Transferred

Greek Letters

α  Symmetry factor

β  Tafel slope  V

δ  Thickness of diffusion layer  m

η  overpotential  V

μ  Viscosity  Kg/m.sec^2

ν  Kinematic viscosity  \(m^2/s\)

ρ  Density  Kg/m^3

Subscripts

a  anode

b  bulk

c  cathode

e  equilibrium

g  galvanic

L  limiting

s  surface

Abbreviations

corr  corrosion

oxid  oxidation

red  reduction
REFERENCE


