Mathematical modeling for corrosion analysis

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1 Introduction

Corrosion is all around us and can affect our lives in many ways, because metals are so widely used in our world. Corrosion-related failures in the industries often result in catastrophic failures. Corrosion is not only dangerous, but costly. The cost of corrosion is estimated to be huge and protecting or reducing corrosion is one of the most important problems in engineering. Many attempts have been made to predict analytically corrosion behaviors [1].

In this chapter, firstly, we will explain basics of corrosion as electro-chemical process. The principle of Voltaic cells is explained, in order to help the understanding about basics of corrosion phenomena at the point of view of electro chemistry. We also refer to the principles of Voltaic cells Galvanic corrosion and cathodic protection.

After we have a basic understanding of the electro-chemical nature of corrosion and behavior of metals in corrosive fluids, we will explain quantitative treatments of corrosion rate. Finally, a mathematical modeling for corrosion rate analysis is constructed.

Purely mathematical treatments would have to be limited to simplified geometric electro-chemical sources. However, thanks to the recent progress of numerical analysis method such as finite element method and boundary element method, corrosion rate analysis of practical structure can be performed by using proposed model [2–4].

2 Basics of corrosion

2.1 Corrosion as an electro-chemical process

Corrosion is an electro-chemical process in which metal atoms are oxidized from positive ions while other chemical species are reduced [6]. This results in a flow
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of electrons from one site on the metal surface to another. A piece of bare iron left outside where it is exposed to moisture will rust quickly. If the moisture is salt water, it will rust even more quickly. The corrosion is accelerated by an electro-chemical in process oxidizing the iron. A water drop forms a voltaic cell in contact with the metal in this process.

Let’s consider a water oxidizing iron supplies electrons at the edge of the water drop to reduce oxygen from the air as shown in fig. 1. At the iron surface inside the water drop oxidation process occurs. This involves a loss of electrons. A Site where oxidation occurs is defined as Anode.

\[
\text{Fe(s)} \rightarrow +\text{Fe}^{2+} (\text{aq}) + 2e^- \tag{1}
\]

For this reaction to occur, simultaneous reduction process, which is a gain of electrons, should occur as the following.

\[
\text{O}_2 (\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4e^- \rightarrow 4\text{OH}^- (\text{aq}) \tag{2}
\]

The site where reduction takes place is defined as cathode. Cathode action reduces oxygen from air, forming hydroxide. The hydroxide ions can move into the water drop to react with the iron(II) ions moving from the oxidation region. Iron(II) hydroxide forms and precipitates.

\[
\text{Fe}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Fe(OH)}_2 (\text{s}) \tag{3}
\]

Producing rust by the oxidation of the precipitate is expressed with the following process:

\[
4\text{Fe(OH)}_2 (\text{s}) + \text{O}_2 (\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \tag{4}
\]

The rusting of bare iron in the presence of air and water cannot be avoided because it is driven by an electro-chemical process. However, other electro-chemical processes are applicable to protection against corrosion.

![Figure 1: Electro-chemical process of iron corrosion.](image-url)
2.2 Galvanic corrosion

Galvanic corrosion refers to corrosion damage induced when two different materials are coupled in a corrosive electrolyte [7]. This is also called ‘different metal corrosion’ or wrongly ‘electrolysis’. It occurs when two (or more) different metals are brought into electrical contact under solution such as sea water. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would by itself. On the other hand, one of the metals becomes the cathode and corrodes slower than it would alone. Both metals in the couple may or may not corrode by themselves in sea water. When contact with a different metal is made, however, the self corrosion rates of both anode and cathode will change into accelerated and decelerated/stopped, respectively.

Galvanic corrosion can be one of the most common forms of corrosion as well as one of the most destructive. The driving force for corrosion is a potential difference between the different materials. Figure 2 shows the concept for help in understanding of driving force of corrosion. In order to analyse the corrosion rate, it is important to quantify this potential difference. In section 3, we will explain the electro chemical treatment which handles this driving force (potential gap) quantitatively.

2.3 Voltaic cells

Consider zinc and copper metals connected with a lead wire and placed in solutions such as $\text{H}_2\text{SO}_4$ as shown in fig. 3. This is one of the simplest ways to generate a sustained electrical current. An electro-chemical cell which causes external electric current flow can be created using any two different metals since metals differ in their tendency to lose electrons. Zinc more readily loses electrons than copper, so placing zinc and copper metals in solutions of their salts can cause electrons to flow through an external wire which leads from the zinc to the copper.

![Figure 2: Conceptual diagram for imaging driving force of corrosion.](image-url)
As a zinc atom provides the electrons, it becomes a positive ion and goes into aqueous solution, decreasing the mass of the zinc electrode.

On the copper side, the two electrons received allow it to convert oxygen from solution into hydroxide. The two reactions are typically written

\[ \text{Zn} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2e^- \]  
\[ \text{H}_2 + 2e^- \rightarrow \text{H}_2 (g) \]

Energy is required to force the electrons to move from the zinc to the copper electrode, and the amount of energy per unit charge available from the voltaic cell is called the electro-motive force (emf) of the cell. Energy per unit charge is expressed in volts (1 volt = 1 joule/coulomb).

Clearly, to get energy from the cell, you must get more energy released from the oxidation of the zinc than it takes to reduce the hydrogen. The cell can yield a finite amount of energy from this process, the process being limited by the amount of material available either in the electrolyte or in the metal electrodes. For example, if there were one mole of the sulfate ions \( \text{SO}_4^{2-} \), then the process is limited to transferring two moles of electrons through the external circuit. The amount of electric charge contained in a mole of electrons is called the Faraday constant, and is equal to Avogadro’s number times the electron charge:

\[
\text{Faraday constant} = F = N_A e = 6.022 \times 10^{23} \times 1.602 \times 10^{-19} \\
= 96,485 \text{ Coulombs/mole}
\]
The energy yield from a voltaic cell is given by the cell voltage times the number of moles of electrons transferred times the Faraday constant.

\[
\text{Electrical energy output} = nF E_{\text{cell}} \quad (8)
\]

The energy yield from the standard electrode potentials for both the reactions. For the zinc/hydrogen cell under the standard conditions, the calculated cell potential is 0.76 volts.

### 2.4 Cathodic protection against corrosion

Cathodic protection operates according to the same principle as voltaic cell [8]. This principle was also engineered into the protection of metallic structures. The sacrificial corrosion of one metal such as zinc, magnesium or aluminum is a well-known method of cathodically protecting metallic structures. In a bimetallic couple, the less noble material will become the anode of this corrosion cell and tend to corrode at an accelerated rate, compared with the uncoupled condition. The more noble material will act as the cathode in the corrosion cell. The flow of cathodic protection current causes the zinc anode to corrode (oxidation), while the steel pipe is protected from corrosion (reduction).

Underground steel pipes offer the strength to transport fluids at high pressures, but they are vulnerable to corrosion driven by electro-chemical processes. A measure of protection can be offered by driving a zinc rod into the ground near the pipe and providing an electrical connection to the pipe. Since the zinc has a standard potential of $-0.76$ volts compared to $-0.41$ volts for iron, it can act as an anode of a voltaic cell with the steel pipe acting as the cathode. With soil serving as the electrolyte, a small current can flow in the wire connected to the pipe. The zinc rod will be eventually consumed by the reaction

\[
\text{Zn(s)} \rightarrow +\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \quad (9)
\]

while the steel pipe as the cathode will be protected by the reaction

\[
\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq}). \quad (10)
\]

Cathodic protection is also commonly employed by impressed current systems. The electrical circuit is similar to that of a sacrificial anode system except for the fact that a DC power supply is used.

### 3 Corrosion modeling for corrosion rate analysis

#### 3.1 Standard electrode potentials

In an electro-chemical cell, an electric potential is created between two different metals [9]. This potential is a measure of the energy per unit charge which is available from the oxidation/reduction reactions to drive the reaction.
The driving force for the above reaction can be measured by placing a voltage measuring device in the circuit. We may consider this force as being the sum of two potentials called half cell potentials or single electrode potentials, one of these is associated with the half cell reaction occurring at the anode and the other is associated with the half cell reaction taking place at the cathode.

It is customary to visualize the cell reaction in terms of two half-reactions, an oxidation half-reaction and a reduction half-reaction.

\[
\text{Reduced species} \rightarrow \text{oxidized species} + ne^{-} \quad \text{Oxidation at anode} \quad (11)
\]

\[
\text{Oxidized species} + ne^{-} \rightarrow \text{reduced species} \quad \text{Reduction at cathode} \quad (12)
\]

The cell potential has a contribution from the anode which is a measure of its ability to lose electrons ‘it will be called its oxidation potential’. The cathode has a contribution based on its ability to gain electrons, its ‘reduction potential’. The cell potential can then be written

\[
E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential} \quad (13)
\]

If we could tabulate the oxidation and reduction potentials of all available electrodes, then we could predict the cell potentials of voltaic cells created from any pair of electrodes. Actually, tabulating one or the other is enough, since the oxidation potential of a half-reaction is the negative of the reduction potential for the reverse of that reaction.

To obtain consistent relative half cell potential data, it is necessary to compare all electrodes against a common reference. The reference electrode should be easy to construct, exhibit reversible behavior, and give constant and reproducible potentials for a given set of experimental conditions. The standard hydrogen electrode (SHE) meets these requirements and is commonly used as the ultimate reference electrode. Thus, two main difficulties must be overcome to establish such a tabulation. (1) We cannot measure absolute potentials for half cell reactions but the relative half cell
Table 1: List of standard electrode potentials for common metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Standard Electrode Potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active End</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>K↔ K⁺ +e⁻ − 2.92</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg↔ Mg²⁺ +2e⁻ − 2.38</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al↔ Al³⁺ +3e⁻ − 1.66</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn↔ Zn²⁺ +2e⁻ − 0.76</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr↔ Cr³⁺ +3e⁻ − 0.71</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe↔ Fe²⁺ +2e⁻ − 0.44</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni↔ Ni²⁺ +2e⁻ − 0.23</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2H⁺ +2e⁻ ↔ H₂ 0.00</td>
</tr>
<tr>
<td>Noble or Passive End</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cu↔ Cu⁺² +2e⁻ +0.34</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag↔ Ag⁺ +e⁻ +0.80</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt↔ Pt⁺² +2e⁻ +1.20</td>
</tr>
<tr>
<td>Gold</td>
<td>Au↔ Au⁺³ +3e⁻ +1.42</td>
</tr>
</tbody>
</table>

In practice, the first of these difficulties is overcome by measuring the potentials with respect to a standard hydrogen electrode. The electrode basically consists of a platinum wire immersed in a solution containing hydrogen ions, and hydrogen gas is bubbled across the surface of the platinum. This type of electrode is called a gas electrode because the platinum takes no part in the electro-chemical reaction. The half cell reaction of the cell is given as

$$H_2(g) \rightarrow 2H^+ + 2e^-$$  \hspace{1cm} (14)

It is the nature of electric potential that the zero of potential is arbitrary; it is the difference in potential which has a practical consequence. Tabulating all electrode potentials with respect to the same standard electrode provides a practical working framework for a wide range of calculations and predictions. The standard hydrogen electrode is assigned a potential of zero volts. The standard electrode potential of commonly encountered metal is shown in table 1.
3.2 Polarization

When one measures the normal electrode potential, it is noted that each half-cell reaction of oxidation and reduction is at equilibrium in a solution of its own ions compared to the potential of the reference electrode. To be equilibrium means that an equal number of ions are always being produced and reduced.

In case this equilibrium is not balanced, the electrode potential starts to drop for cathodic reaction and increase for anodic reaction. This potential shift is called polarization. The equilibrium can be braked by impressing external current to the metal electrode. Polarization is defined as the change in the potential of an electrode from the open circuit potential to the potential resulting from a current flow.

The relationship between the potential change and the net current density is also called a polarization curve which is usually a non-linear function.

A simple experimental setting for measuring a polarization is shown in fig. 5. The variable resistance is used to change the externally impressed current. Platinum is often used for counter electrode, because it will not polarize excessively, in order not to contaminate the solution. The reference electrode is frequently Ag/Ag chloride or Hg/calomel in KCl solution. Experimental setting often employs a Luggin capillary placed very close to the specimen, which enables measuring the potential at a specific place on a specimen surface.

Since the potential is changing refer to the current density through the surface of material, it is important to model this polarization effect for corrosion rate analysis. The conceptual diagram for understanding driving force of corrosion as shown in fig. 2 can be updated as in fig. 6, when the polarization characteristics are modeled.

3.3 Corrosion rate

The current which flows through the surface of metal per unit area is called corrosion current density $i_{corr}$. Referring to fig. 1, one iron ion is released into the electrolyte

![Figure 5: Simple experimental setting for measuring polarization curve.](image-url)
for each 2 electrons which flow into the metal surface. Because $i_{corr}$ is a measure of electron flow per unit time and unit area, it is obviously proportional to amount of metal loss per unit time. $i_{corr}$ is a good measure of corrosion rate.

Corrosion current [$\text{mA/cm}^2$], mass loss [$\text{g/m}^2 \text{ day}$] and penetration rates [$\text{mm/y}$ or mpy] are often used for express corrosion rates. The following equation provides a simple way to convert data from corrosion current $i_{corr} [\text{mA/cm}^2]$ to penetration rates $d [\text{mm/yr}]$.

$$d [\text{mm/yr}] = 3.28 i_{corr} M/n \rho [\text{mA/cm}^2]$$  \hspace{1cm} (15)

where, [mpy] is milli-inch per year, $n$ is number of electrons freed by the corrosion reaction, $M [\text{g}]$ is atomic mass and $\rho [\text{g/cm}^3]$ is density. Since we are able to know the relationship between current density and potential by measuring the polarization curve, once one could obtain the potential value on the metal surface, the current density (corrosion rate) can be estimated.

4 Mathematical modeling for corrosion rate analysis

In case of assuming the electro-chemical reaction on the metal surface is not interfered by solution velocity, the current density in the electrolyte domain $\Omega$ can be expressed with the following electro migration diffusion equation [5, 10–12]:

$$i = F \sum_j z_j D_j \text{grad}c_j - F^2 \sum_j z_j^2 c_j u_j \text{grad} \phi$$  \hspace{1cm} (16)

where $i$ is the current density vector, $F$ is Faraday’s constant, $z_j$, $c_j$, $u_j$ and $D_j$ are the charge, concentration, mechanical mobility and diffusion coefficient, respectively, for species $j$. $N$ is the number of species and $\phi$ is the electro-chemical potential. Let’s define the conductivity of the electrolyte as the following:
\[ \kappa \equiv F^2 \sum_j z_j^2 u_j \]  

(17)

The conductivity \( \kappa \) has the dimension \([\Omega^{-1} \text{m}^{-1}]\) or \([\text{Sm}^{-1}]\). Substituting the above definition to (16), the equation reduces to:

\[ i = F \sum_j z_j D_j \text{grad} c_j - \kappa \text{grad} \phi \]  

(18)

The first term of (18) corresponds to the current density sustained by concentration gradients. This term can be neglected in large-scale simulations, because concentration gradients exist only in the diffusion layer which is very thin compared to the size of simulation domain. These concentration effects are taken into account as polarization curves, and applied as boundary conditions. Finally, the current density in the electrolyte domain \( \Omega \) is expressed by the following:

\[ i = -\kappa \text{grad} \phi \]  

(19)

Assuming that there is no accumulation or loss of ions in the bulk of electrolyte, the following conservation equation should be required:

\[ \text{div} i = -\text{div} (\kappa \text{grad} \phi) = 0. \]  

(20)

In case of the conductivity of the electrolyte, such as considering sea water, the conductivity \( \kappa \) is constant. Thus (20) reduces to a simple Laplace equation:

\[ \kappa \nabla^2 \phi = 0. \]  

(21)

It is noted that the potential \( \phi \) is defined with referring to the metal and has the inverse sign of the employed usually in the corrosion science in which the potential \( E \) is defined to a reference electrode such as saturated calomel electrode (SCE) or (SHE).

The current density \( i \) on boundary of the electrolyte domain \( \Omega \) is defined by the following equation:

\[ i \equiv i \cdot (-n) = \kappa \frac{\partial \phi}{\partial n} \]  

(22)

where \( n \) is outward normal vector, \( \partial / \partial n \) is the outward normal derivative. It is noted that \( i \) is positive when the current flows into the electrolyte from the boundary.

Let \( \Gamma \) be the whole surface of the electrolyte domain \( \Omega \) as shown in fig. 7. The boundary \( \Gamma \) consists of the following three types of boundaries:

- The Neumann-type boundary \( \Gamma_n \) on which the current density \( i \) is prescribed.
- The Dirichlet-type boundary \( \Gamma_d \) on which the potential value \( \phi \) is prescribed.
- The metal surface \( \Gamma_m \) on which the relationship between the potential value \( \phi \) and the current density \( i \) is prescribed with the polarization curve.
In case of considering the surface of sea water or electrically insulated material such as plastic resin wall, the current density \( i \) is 0 for these boundaries, so that they can be modeled with the Neumann-type boundary \( \Gamma_n \). The mathematical form of the above three types of boundaries can be expressed as the following:

\[
\begin{align*}
  i &= i_0 \quad \text{on} \quad \Gamma_n \\
  \phi &= \phi_0 \quad \text{on} \quad \Gamma_d \\
  -\phi(\equiv E) &= f_A(i) \quad \text{on} \quad \Gamma_A \\
  -\phi(\equiv E) &= f_C(i) \quad \text{on} \quad \Gamma_C
\end{align*}
\]

where, \( i_0 \) and \( \phi_0 \) are the prescribed value, respectively. \( f_A(i) \) and \( f_C(i) \) are the non-linear functions representing the experimentally determined polarization curves for anode and cathode, respectively. Therefore, the corrosion rate analysis reduced to solving the boundary potential problem of which (21) is the governing equation and (23)–(26) is the boundary condition.

References


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