الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الرابعة

هندسة التاكل

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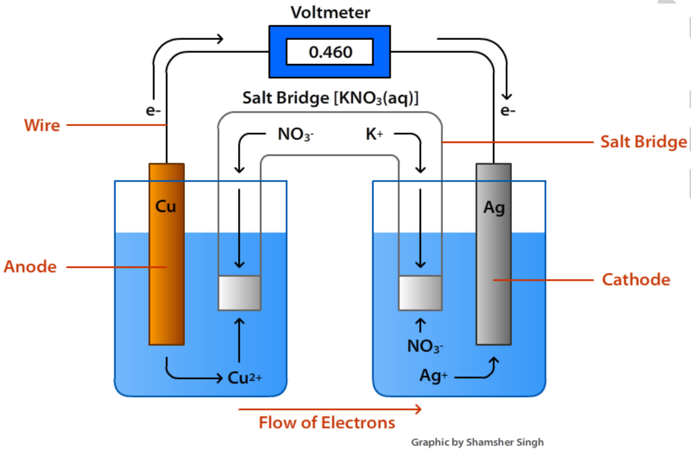
TYPES OF CORROSION CELLS

There are several types of corrosion cells

(1) Galvanic cells
(2) Concentration cells
(3) Electrolytic cell
(4) Differential temperature cells.

1- <u>Galvanic cell:</u>

The galvanic cell may have an anode or cathode of dissimilar metals in an electrolyte for example, steel and copper electrodes immersed in an electrolyte, represents a galvanic cell. The more noble metals copper acts as cathodic and the more active iron acts as an anode. Current flows from iron (anode) to copper (cathode) in the electrolyte.



Graphic by Shamsher Singh

2- <u>Concentration Cell:</u>

This is similar to galvanic cell except with an anode and cathode of the same metal in a heterogeneous electrolyte. Concentration cells may be set up by:

a- Variation in the amount of oxygen in soils.
b- Difference in moisture content of soils.
c- Difference in composition of the soils.

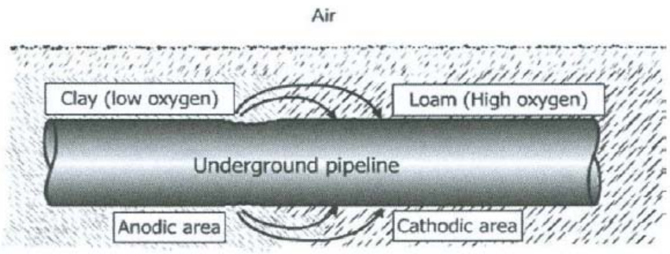
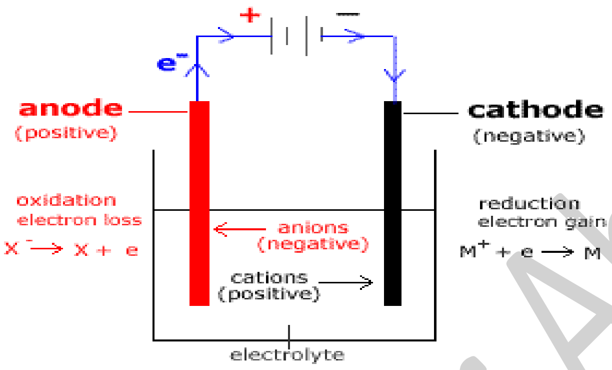


Figure 2.6 Concentration cell formation in an underground pipeline

3- Electrolytic cell

This type of cell is formed when an external current is introduced into the system. It may consist of all the basic components of galvanic cell and concentration cell plus an external source of electrical energy.

Notice that anode has a (+) polarity and cathode has (-) polarity in an electrolyte cell, where external current is applied. This is the type of cell set up for electrically protecting the structures by cathodic protection. The polarity of an electrolytic cell is opposite to that in galvanic cell.



4- Differential temperature cells

In electrolytic cells of the differential-temperature type, the anode and cathod consist of the same metal and differ only in temperature. If the anode and cathode are areas on a single piece of metal immerse in the same electrolyte, corrosion proceeds as in any short-circuited galvanic cell.

For copper in aqueous salt solutions, the area of the metal at the higher temperature is the cathode and the area at the lower temperature the anode. In the preferential attack on the anode, copper dissolves from the cold area and deposits on the warmer area. Lead acts similarly, but for silver the polarity is reversed, with the warmer area being attacked preferentially.

CORROSION KINETICS

FARADAY'S LAWS OF ELECTROLYSIS AND ITS APPLICATION IN DETERMINING THE CORROSION RATE

The classical electrochemical work conducted by Michael Faraday in the nineteenth century produced two laws published in 1833 and 1834 named after him. The two laws can be summarized below.

The First Law:
The mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed. Thus:

$$m \propto It \text{ or } m = ZIt \qquad (1)$$

where
I= current in amperes
t = time in seconds
m = mass of the primary product in grams
Z = constant of proportionality (electrochemical equivalent). It is the mass of a substance liberated by 1 ampere-second of a current (1 coulomb).

The Second Law:
The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction:

$$m_1 \propto \frac{M_1}{n_1} \propto Z_1 \qquad .....2$$

$$m_2 \propto \frac{M_2}{n_2} \propto Z_2 \qquad ......3$$

where
m1,m2 = masses of primary product in grams
M_1, M_2 = molar masses ($g.mol^{-1}$)
n_1, n_2 = number of electrons
Z_1, Z_2 = electrochemical equivalent.

Combining the first law and the second law, as in equation:

$$m = Zit$$

Substituting for Z, from equation 2 in 1

$$m = k\frac{M}{n}It \qquad ....4$$

or

$$m = \frac{1}{F} \cdot \frac{M}{n}It \qquad ....5$$

where F = Faraday's constant. It is the quantity of electricity required to deposit the ratio of mass to the valency of any substance and expressed in coulombs per mole (C (g equiv.)-1). It has a value of 96 485 coulombs per gram equivalent. This is sometimes written as 96 485 coulombs per mole of electrons.

Applications of Faraday's Laws in Determination of Corrosion Rates of Metals & Alloys

Corrosion rate has dimensions of mass x reciprocal of time:

$$(g \cdot y^{-1} \text{ or kg} \cdot s^{-1})$$

In terms of loss of weight of a metal with time, from equation (5), we get:

$$\frac{dw}{dt} = \frac{MI}{nF} \quad (I = \text{current}) \qquad ....6$$

The rate of corrosion is proportional to the current passed and to the molar mass. Dividing equation (5) by the exposed area of the metal in the alloy, we get

$$\frac{w}{At} = \frac{MI}{nFA} \qquad .... 7$$

But, $\frac{I}{A}$ = current density (i). Then:

$$\frac{w}{At} = \frac{Mi}{nF} \quad (i = \text{current density}) \qquad .... 8$$

The above equation has been successfully used to determine the rates of corrosion.
A very useful practical unit for representing the corrosion rate is milligrams per decimeter square per day ($mg.dm^{-2}.day^{-1}$) or mdd. Other practical units are millimeter per year ($mm\ y^{-1}$) and mils per year (mpy).

Below are some examples showing how Faraday's laws are used to determine the corrosion rate.

Example 1

Steel corrodes in an aqueous solution, the corrosion current is measured as 0.1 mA • cm^{-2} . Calculate the rate of weight loss per unit area in units of mdd.

Sol.:

For Fe —> $Fe^{+2} + 2e$

$$\frac{w}{At} = \frac{Mi}{nF}$$

Where:

M= 55.9 $g.mol^{-1}$
i = 0.1 $mA.cm^{-2}$
n = 2

$$\frac{w}{At} = 2.897 \times 10^{-8}\ g\,cm^{-2}s^{-1}$$

Now converting g to mg (x 10^3), we get $\frac{w}{At}$ = 2.897 x 10^{-5} mg cm^{-2} s^{-1}

$$2.897\text{x } 10^{-5}\ \frac{mg}{cm^2 s} * \frac{100\,Cm^2}{dm^2} * \frac{3600\ S}{h} * \frac{24\ h}{day} = 250.3 \text{ mdd}$$

Example 2

Iron is corroding in seawater at a current density of 1.69 x 10^{-4} A/cm^2. Determine the corrosion rate in

(a) mdd (milligrams per decimeter^2 day)
(b) ipy (inches per year)

Sol.:

(a) Apply Faraday's law

$$\overset{\text{mdd}}{\boxed{\frac{w}{At}}} = \frac{Mi}{nF}$$

= 422.8 mg dm^{-2} day^{-1}

(b) ipy = mdd x 0.00144/ρ, ρ = density

$$= 422.8 \times \frac{0.00144}{7.86} = 0.077 \text{ ipy}$$

or 77 mpy , because 1 mil= 0.001 inch , mpy=mdd x 1.144/ ρ

Example 3

A sample of zinc anode corrodes uniformly with a current density of 4.27×10^{-7} A/cm^2 in an aqueous solution. What is the corrosion rate of zinc in mdd? **Ans.: 1.25 mdd**

Penetration unit time can be obtained by dividing equation (8) by density of the alloy. The following equation can be used conveniently:

$$\text{Corrosion rate, } r = C \cdot \frac{Mi}{n\rho} \qquad \text{........ 9}$$

where
ρ = density (g/cm3)
i = current density (A/cm2)
M = atomic weight (g • mol-1)
n = number of electrons involved
C = constant which includes F and any other conversion factor for units (depending on units)
= 0.129 in mpy
= 3.27 in mm/y

For instant, the above relationship can be used to establish the equivalent of corrosion current of 1 μA/cm^2 with the rate of corrosion for iron in mpy as shown below

$$1\ \mu\text{A/cm}^2 = 0.129\left[\frac{(55.8)(1)}{(2)(7.86)}\right] = 0.46\ \text{mpy}$$

Example 4

Determine the corrosion rate of AISI 316 steel corresponding to 1 μA/cm^2 of current. Following is the composition of alloys:
Cr = 18%
Ni = 10%
Mo = 3%
Mn = 2%
Fe = balance, 67%

Sol.:

$$1\ \mu\text{A/cm}^2 = 0.128\left[\frac{52.3}{(1)(7.19)}\right]0.18 + 0.128\left[\frac{54.94}{(2)(7.45)}\right]0.02 + 0.128\left[\frac{95.95}{(2)(10.1)}\right]0.03 + 0.128\left[\frac{55.65}{(2)(7.86)}\right]0.07\ \text{mpy}$$

n=1 (Ag, Cr, Mo)
n=2 (Zn, Fe, Cu, Ni)
n=3 (Al)

mpy = $\frac{534\,W}{\rho\ A\ T}$

where:

W= weight loss, mg

ρ = Density of specimen , g/cm^3

A= area of specimen, in^2

T = Exposure time, hr

Example 5

A sample of zinc corrodes uniformly with a current density of 4.2×10^{-6} A/cm^2 in an aqueous solution.

(a) What is the corrosion rate of zinc in mg/dm^2/day?

(b) What is the corrosion rate of zinc in mm/year?

(a) Given current density, i = 4.2×10^{-6} A/cm^2 , zinc atomic weight, M = 65.38 g/mol, density, ρ = 7.1 g/cm3, n = 2, F = 96 500 coulombs/mole.

From the formula:

$$\frac{w}{At} = \frac{Mi}{nF}$$

(b) We can also use the relationship given below to determine the rate of corrosion in mm/year or other units by changing the constants. The constant for mm/year is 0.00327.

$$\text{Corrosion rate, } r = C \cdot \frac{Mi}{n\rho}$$

Where ρ is the density in g/cm^3, *i* is the current density in $\mu A/cm^2$, and C is the constant = 0.00327 for mm/year.

$$\text{Corrosion rate} = \frac{0.00327 \times 65.38\,\text{g/mol} \times 4.2}{2 \times 7.13}$$

Corrosion rate = 0.0629 mm/year

Example 7

AISI 316 steel has the following nominal composition:

Cr = 18%	n = 1	ρ = 7.1 g/cm^2	At. wt. = 52.01 g/mol
Ni = 8%	n = 2	ρ = 8.9 g/cm^2	At. wt. = 58.68 g/mol
Mo = 3%	n = 1	ρ = 10.2 g/cm^2	At. wt. = 95.95 g/mol
Fe = 70%	n = 2	ρ = 7.86 g/cm^2	At. wt. = 55.85 g/mol

Find the equivalence between the current density of 1 $\mu A/cm^2$ and the corrosion rate (mpy).

Solution:

$$\text{Corrosion rate} = C \cdot \frac{Mi}{n\rho}$$

Where C is the constant for conversion depending on unit.

$$\text{C.R} = 0.129\left\{\left(\frac{52.01}{1\times 7.1}\right)0.18+\left(\frac{58.68}{2\times 8.9}\right)0.08+\left(\frac{95.95}{1\times 10.2}\right)0.03+\left(\frac{55.85}{2\times 7.86}\right)0.70\right\}$$

$$= 0.129\,[1.318 + 0.263 + 0.282 + 2.48]$$

$$= 0.55 \text{ mpy (mils/year)}$$

Example 8

Calculate the corrosion rate in mpy of Al specimen (5 cm^2) immersion in aqueous solution for 2 days, given that ($\rho = 2.71$ g/cm^3)

Example 9

A copper surface area , A=100 cm^2, is exposed to an acid solution. After 24 hour, the loss of copper due to corrosion (Oxidation) is $15*10^{-3}$ gram. Calculate:

(a) The current density in $\mu A/cm^2$.
(b) The corrosion rate in mm/y
Given that: molar mass for copper = 63.54 g/mole, $\rho = 8.96$ g/cm^3