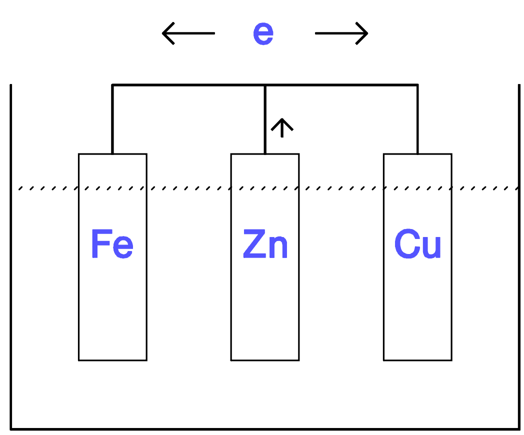
CHAPTER 6

CORROSION PROTECTION AND MONITORING

As inferred during the previous discussion of the Pourbaix diagram, corrosion may be prevented by introducing electrical currents from external sources to counteract the normal electrochemical reaction. There are two basic types of so-called cathodic protection systems, namely, sacrificial anodes and impressed current. Sacrificial anodes consist of expendable electrodes, usually zinc, aluminum or magnesium, or their alloys, whose natural potentials provide adequate protective current to a structure. Impressed current systems are those that employ a direct current (DC) power source to provide the necessary current.

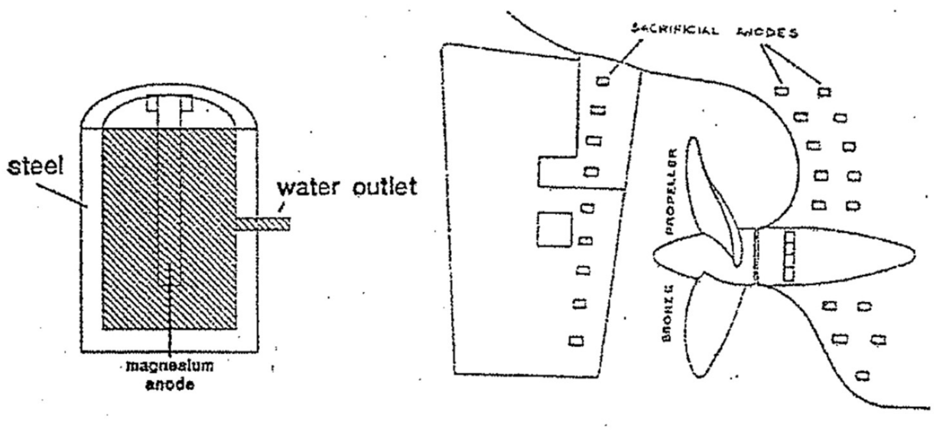
6.1 Cathodic Protection: Sacrificial Anodes

When iron and copper are attached in a galvanic cell, we have seen that the result is the corrosion of the iron, with electrons flowing out of the iron (the anode) and into the copper (the cathode). Suppose that we now place a zinc bar in the cell as illustrated below:



Sacrificial Zinc Anode

In this case, we now find, that because of the potentials involved, that electrons flow out of the zinc and into both the iron and copper. Thus the zinc corrodes and the iron and copper, which now both function as cathodes, do not. This is the basis for sacrifical anode protection, namely, the use of an expendable anode to protect another metal from corrosion. Two examples of this type of corrosion protection are shown in Figure 28. The first is the protection of an ordinary hot-water heater with a magnesium anode and the second is the protection of a ship's hull in the vicinity of the bronze propeller by zinc anodes. Without the protection, the steel hull of the ship is, of course, subject to galvanic corrosion because of the presence of the bronze material used for the propeller.



Hot Water Heater | Ship Hull & Rudder

Example Sacrificial Anodes

To determine the amount of material needed for sacrificial anode protection of a structure, we use Faraday's Law together with an estimate of the current density needed for protection (typically in the range of 10-15 ma/ft^2).

<u>Example</u>: *If an aluminum alloy is 100% efficient as a sacrificial anode (i.e. it follows Faraday's Law exactly) determine the number of pounds of aluminum needed to protect a steel structure with 80 ft^2 of surface area in seawater for 18 months. Assume a current density of 10 ma/ft^2 is needed for current protection.*

<u>Solution</u>

$$W=\_CI$$

From Faraday' Law we have

$$C=\frac{\frac{27}{3}}{96,500}=9.33 \times 10^{-5} \text{ grams/amp\_sec}$$

where

$$w = -7.45 \times 10^{-5} \text{ grams/sec}$$

Hence

$$w=(7.35 \times 10^{-5})(2.205)(10^{-3})(3600)(24)(365)=5.19 \text{lb/year}$$

in lbs/yr

For total consumption in 18 months, we must have (for 100% efficiency)

$$w = (5.19)(1.5) = 7.7 \text{ lbs}$$

<u>Example</u>: A chemical company advertises aluminum-alloy sacrificial anodes with an average current output of 1176 amp-hours/lb. Calculate the efficiency.

<u>Solution</u>: From Faraday's Law we have the consumption given as

$$C = \frac{\frac{27}{3}}{96{,}500} = 9.33 \times 10^{-5} \text{ grams/amp-sec}$$

hence, the current output is

$$C^{-1} = 1.07 \times 10^{4} \text{ amp-sec/gm}$$

or

$$C^{-1} = 1350 \text{ amp-hours/lb}$$

The efficiency of the advertised anodes is therefore 1176/1350 = 0.87 or 87%.

<u>Example</u>: An offshore structure has 10,000 ft^2 of submerged area to be protected for 20 years with aluminum-alloy anodes (85% efficient) weighing 150 lbs each. Determine the number of anodes required if 15/ma ft^2 is needed for protection.
<u>Solution</u>:

Again, from Faraday's Law we have

$$C = \frac{\frac{27}{3}}{96{,}500} = 9.33 \times 10^{-5} \text{ grams/amp\_sec}$$

and

$$I = 150 \text{ amp}$$

so that

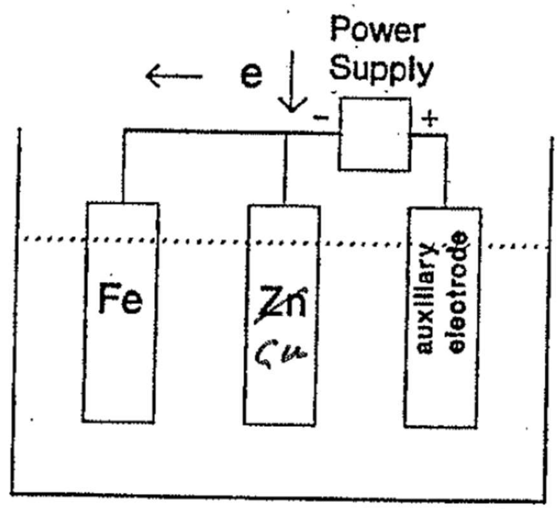
$$w = -0.014 \text{ gm/sec} = 973 \text{ lbs/year}$$

Hence, w = 973 x 20 = 19463 lbs if the anodes were 100% efficient. Since they are only 85% efficient, 19463/.85 = 22,900 lbs are required and 22,900/150 = 152.6 or 153 anodes.

6.2 Cathodic Protection: Impressed Current

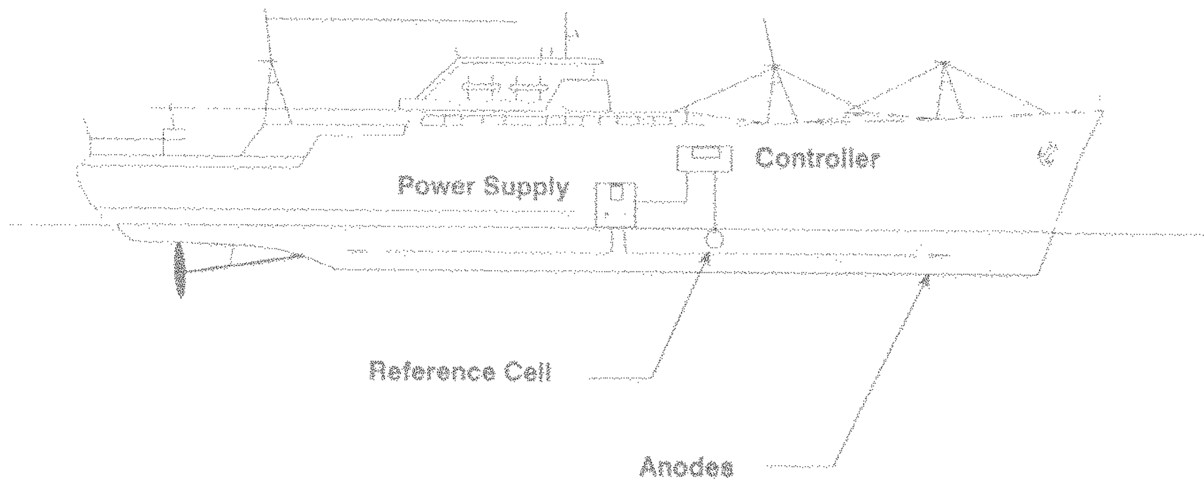
In an impressed current system of cathodic protection, the current can be supplied from such sources as storage batteries, rectifiers, or generators depending on convenience and the amount of current required. The anodes used in an impressed current systems can be expendable, being made of ordinary steel. Such steel anodes would require periodic replacement, since they are destroyed at a rate of about 20 pounds/ampere-year by the passage of the protective current. It is common to use permanent impressed current anodes which are not destroyed or are destroyed very slowly by the passage of the protective current. These anodes are platinum; platinum sheathed titanium, tantalum, or niobium. Steel structures exposed to seawater are normally protected if they are polarized to a potential of -0.85 volts versus a silver/silver-chloride or a copper/copper-sulfate reference electrode.

A description of such a system follows. Consider again the case of iron and copper attached together in a galvanic cell, with the iron corroding and the copper protected. Instead of using a sacrifical anode to supply electrons to the steel and protect it, we use a DC power supply. In this case, we have the cell described in the figure below.



Impressed Current Cathodic System

By proper choice of the power supply voltage, we can over-ride the potential difference between the iron and copper and make each act as a cathode (receive electrons) and be protected. In selecting the proper potential, it must be the same as the open-circuit potential of the local anode. This means that the voltage is chosen such that current is neither entering or leaving the iron, nor is it flowing between the local anode and cathode regions on the iron. By use of a standard half-cell, as in Figure 29, a polarization diagram can also be produced. The open circuit potential and applied current can be determined in this manner. Thus, the rule for selecting the proper voltage setting of the power supply is to <u>adjust the power supply until the potential of the iron (and copper) relative to a standard half-cell is equal to the open circuit potential of the local anode regions, which was determined experimentally</u>. Some examples of impressed current protection are shown below .



<u>Example</u>: Use the Nernst equation to establish the potential of steel (iron) relative to the copper/copper-sulfate half-cell needed for protection from corrosion.

<u>Solution</u>: We assume a concentration of 10^{-3} ions/liter in the electrolyte adjacent to the steel to indicate essentially negligible corrosion activity. From the Nernst equation, we then have relative to the hydrogen half-cell,

$$E = -0.44 + (0.0592/2)Log_{10}10^{-3}$$

or

$$E = -0.53 \text{ v}$$

The potential of the copper/copper-sulfate half-cell relative to the hydrogen is +0.32V. Hence

$$E = V_{Fe} - V_{H2} = V_{Fe} - V_{Cu} + V_{Cu} - V_{H2}$$

or

$$-0.53 = V_{Fe} - V_{Cu} + 0.32$$

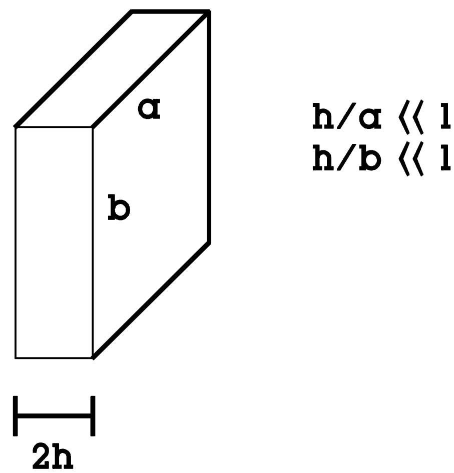
or

$$V_{Fe} - V_{Cu} = -0.85 \text{ v}$$

6.3 Measures of Corrosion Rate

The Galvanic Series gives us information on which metals will corrode when connected with others in seawater, but it does not tell us anything about the rate of corrosion. Polarization experiments can give us information on the rate of corrosion of metals connected together or freely corroding. When time permits, field tests can provide the simplest and most reliable way to obtain corrosion-rate data.

Weight-Loss Tests. These experiments are conveniently made using flat plates, as shown in the figure below.



Sample for Weight Loss Test

The weight of the plate is given in terms of geometry of the figure above and the specific weight γ of the material as

$$2\gamma abh = W$$

and the rate of weight loss is given by differentiation as

$$2\gamma(abh + abh + abh) = W$$

or with

$$h = \frac{a}{2} = \frac{b}{2}$$

denoting the corrosion rate, as

$$2\gamma abh(\frac{2h}{a} + \frac{2h}{b} + 1) = W$$

For thin plates, this expression yields

$$h = \frac{W}{2\gamma ab}$$

Writing A = 2ab = total surface area of plate and $\overset{o}{W} = \Delta w/\Delta t$, where Δw denotes weight loss in time Δt, we have

$$h = \frac{\Delta w}{\gamma A \Delta t}$$

The corrosion rate may vary with time under various circumstances, but for purposes of calculation we may generally assume it to be constant. In examining test data, it is usual to replace Δw and Δt by w and T where w denotes the total weight loss in time T, so that the equation becomes

$$h = \frac{W}{\gamma AT}$$

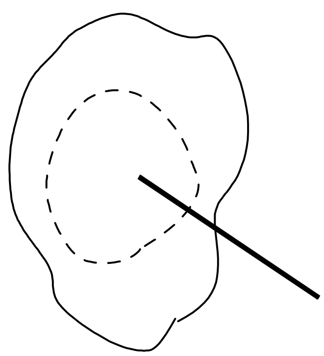
These two equations are of course equivalent only if the rate of weight loss is constant.

Example. A steel plate of dimensions 3 x 6 x (1/8) inches is known to suffer a weight loss of 0.025 lb when exposed in seawater for 6 months. Determine the corrosion rate.

Solution: We have $A = 2(3 \times 6) = 36\ in^2$, $\gamma = 0.28\ lb/in^3$, $T = 0.5$ *years and* $W = 0.025$ *lbs. Hence the equation gives*

$$h = \frac{0.025}{(0.28)(36)(0.5)} = 0.005\ \text{inches/year} = 5\ \text{MPY}$$

If, in place of the thin plate, we have a specimen of arbitrary shape, we may construct a weight-loss formula similar to that for the flat plate. Consider, in particular, the effect of corrosion on the cross section shown in the figure below.



During a time Δt, the surface of the solid will move inward an amount $\dot{h}\Delta t$. If S denotes the lateral surface area of the solid, the volume loss will be $\dot{h}\Delta tS$ and the weight loss $\Delta w = \gamma\dot{h}\Delta tS$, where γ denotes the specific weight. Hence, solving for $\dot{h}$ we have

$$h = \frac{\Delta w}{\gamma S \Delta t}$$

If we take S to be the initial lateral surface area of the solid and write $W = \Delta w$, $T = \Delta t$, we have

$$h = \frac{W}{\gamma ST}$$

Because the lateral surface area changes with time, this equation will be only valid only as long as the lateral area change is small.

<u>Example</u>. A cylindrical steel test rod of 0.50 inches in diameter and 2 inches in length is exposed in seawater for 3 years. The measured weight loss is 0.0165 lbs. Find the corrosion rate.

<u>Solution</u>:

We have $\gamma = 0.28\ lb/in^3$, $T = 3$ years

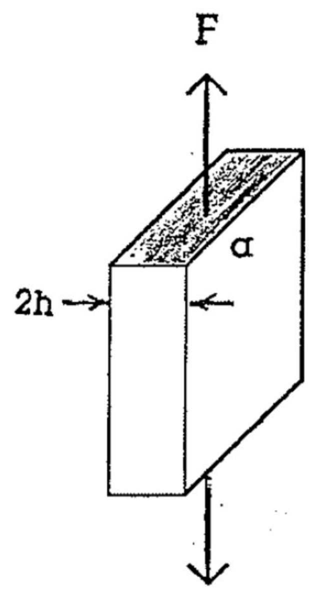
and

$S = (\pi \times .5 \times 2) + (2 \times \pi \times 0.25^2) = 3.53\ in^2$

$$h = \frac{0.0165}{(0.28)(3.53)(3)} = 0.0055 \text{ inches/year} = 5.5 \text{ MPY}$$

Note: This is not a particularly good example of our assumption of the total area, S, staying constant. If one recalls that corrosion occurs through the wetted surface area, it can be shown that since 12% of the area is at the ends of the cylinder, 12% of the corrosion must have occured there. The remaining 88% of the corrosion occured through the cylinder walls.

<u>Strength Reduction Test</u>. Instead of using the weight loss test to determine the corrosion rate, we may use a strength- reduction test. Suppose we have a thin plate with a failure (breaking) force F applied over area 2ha, as shown in the figure below:



We assume the failure stress Y is the same, regardless of the amount of corrosion so that

$$\frac{Y}{Y_o} = \frac{\frac{F}{A}}{\frac{F_o}{A_o}} = 1$$

where the subscript o denotes initial value. Solving for A/A_o, we have

$$\frac{A}{A_o} = \frac{F}{F_o}$$

now the area A is given by A = 2ah where (neglecting corrosion of the edges as is permissible for thin plates)

$$h = h_o - ht$$

hence we have

$$\frac{A}{A_o} = \frac{2ah}{2ah_o} = 1 - \frac{h}{h_o}t$$

so that h may be determined as

$$h = \frac{(1-\frac{F}{F_o})h_o}{T} = \frac{\Delta F h_o}{F_o T}$$

where T denotes the duration of exposure.

Example: A thin-plate of 1/8 inch thickness is exposed for 6 months in seawater. The initial yield strength of the plate was 28,000 lbs. After exposure the strength is 25,000 lbs. Determine the corrosion rate h.

$$h = \frac{\Delta F h_o}{F_o T}$$

$$hdot = \frac{(3000)\ (0.0625 inches)}{(28000)\ \ (0.5 years)} = 0.0134 inches/year = 13.4\ MPY$$

Solution:
Suppose that a standard cylindrical tensile specimen is used in place of the flat-plate specimens in the above scheme. In this case, we have as before

$$\frac{A}{A_o} = \frac{F}{F_o}$$

But now,

$$\frac{A}{A_o} = (\frac{R}{R_o})^2 = (1 - \frac{hdot_t}{R_o})^2$$

so that

$$h = (\frac{1 - \sqrt{\frac{F}{F_o}}}{T})R_o$$

<u>Example</u>: A standard 0.5 inch diameter tensile specimen is found to suffer a 15% loss in strength when exposed in seawater for 2 years. Determine the rate of corrosion.

$$\Delta\frac{F}{F_o} = \frac{F_o - F}{F_o} = 1 - \frac{F}{F_o} = 0.15$$

$$\frac{F}{F_o} = 0.85$$

$$h = (1 - \sqrt{.85})(\frac{0.25}{2})$$

$$h = 0.0099 inches/year = 9.9 MPY$$

6.4 Corrosion Allowance Calculations

The following examples illustrate engineering calculations associated with corrosion allowances.

<u>Example:</u> A submerged pipeline is corroding on the outside with a corrosion rate of 15 MPY and on the inside with a rate of 5 MPY. Find the design wall thickness of the pipe if the design life is 30 years.

<u>Solution</u>: The inside radius is denoted by r_1, and its initial value by r_{1o}. If the corrosion rate is $\overset{o}{h}_1$, then

$$r_1 = r_{1o} + h_1 T$$

where T = life of the pipe. Similarly, with r_2 denoting the outside radius and r_{2o} its initial value. If the corrosion rate is $\underline{h}_2$, then

$$r_2 = r_{2o} - h_2 T$$

From a corrosion standpoint we require that $r_1 = r_2$ at T = 30 years. Hence the initial wall thickness required is

$$r_{2o} - r_{1o} = (h_1 + h_2)T$$

$$r_{2o} - r_{1o} = (.20)(30) = 0.6 inches$$

From a true design standpoint, we would also need to account for the fact that this pipeline is going be carrying a fluid at a design flow rate and that it is going to be exposed to both internal and external pressures. At T = 30 years there will some required wall thickness to withstand this pressure, p = absolute value of ($p_{external} - p_{internal}$) and at T = 0, there will be a minimum r_1 to allow for the rated flow at the design pumping pressure. Since we know which material is going to be used, we also know its shear strength τ. We can now solve for the required wall thickness and subsequently the outside radius.

$$r_2 - r_1 = \frac{pr_1}{\sigma} + (h_1 + h_2)T$$

Example: *A steel cable is to be used as an underwater guide wire in an off shore structure. In the absence of corrosion, a section area of 1 in^2 is recommended. If tests show the rate of corrosion at the site and for this material to be 25 MPY, what initial area of cable should be used for a design life of 20 years.*

Solution: *With R_o denoting the initial cable radius and R its radius after T years, we have*

$$R = R_0 - \dot{h}T$$

where $\underline{h}$ is the corrosion rate. Now $\pi R^2 = 1$ and $R_o = 0.564$ inches.

$$0.564 = R_o - (0.025)(20)$$

or

$$R_o = 1.06 \text{ inches, and the required initial area is } 3.53 \text{ in}^2.$$