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## FUNDAMENTALS OF CORROSION

*Аннотация:* в данной статье говорится о том, что общим определением коррозии является деградация материала через взаимодействия с окружающей средой. Авторы работы разделяют основы коррозии на дисциплины термодинамики и кинетики.

*Ключевые слова:* окружающая среда, потенциал, коррозия, окисление, электрод, анод, гальваническая серия, термодинамика, восстановление, свободная энергия, катод, кинетика.

*Abstract:* one general definition of corrosion is the degradation of a material through environmental interaction. The fundamentals of corrosion can be divided into the disciplines of thermodynamics and kinetics.

*Keywords:* environment, corrosion, anode, galvanic series, potential, thermodynamics, electrode, oxidation, reduction, free energy, cathode, kinetics.

### *Introduction*

The fundamentals of corrosion can be divided into the disciplines of thermodynamics and kinetics. Thermodynamics is used to indicate whether a specific corrosion process is possible and kinetics is used to understand and predict actual rates of corrosion. Both topics are discussed in greater detail in this chapter.

### *Thermodynamics*

A significant amount of energy is put into a metal when it is extracted from its ores, placing it in a high-energy state. These ores are typically oxides of the metal such as hematite ( $\text{Fe}_2\text{O}_3$ ), for steel or bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ), for aluminum. One principle of thermodynamics is that a material always seeks the lowest energy state. In other words, most metals are thermodynamically unstable and will tend to react with something in their environment (e.g., oxygen or water) in order to reach a lower, more stable energy state such as an oxide.

### *Electrode Potentials*

The corrosion of most common engineering materials at temperatures near ambient usually involves water and is electrochemical in nature. The corrosion process occurs with the removal of electrons (oxidation) of the metal and the consumption of those electrons by some other reduction reaction, such as oxygen. Since the oxidation and reduction reactions are different, the corrosion process is not reversible and is not at equilibrium. A system has attained a state of equilibrium when it shows no further tendency to change its properties with time. A corroding metal changes its state with time and is, by definition, not at equilibrium. The individual oxidation and reduction reactions are referred to as half-cell reactions and can occur locally at the same site on the metal or can be spatially separated.

The free energy of each pair of half-cell reactions is related to a reversible electromotive force ( $E$ ) through the equation

$$\Delta G = -|z|F E$$

in which  $z$  is the valence change associated with the reaction and  $F$  is Faraday's constant.

The potential of any two half-cell reactions can be calculated as shown in the following equation, where the EMF series is written as reduction reactions

$$E = E_{(reduction)}^0 - E_{(oxidation)}^0$$

For example, for the reactions;  $\text{Au}^{3+} + 3e^- = \text{Au}$  and  $\text{Al} = \text{Al}^{3+} + 3e^-$ , the potential is  $E^0 = 1.498 - (-1.662) = 3.160 \text{ V}$ .

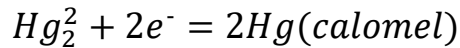
## Reference Electrodes

One definition of a reference electrode is «a reversible electrode used for measuring the potentials of other electrodes». As described in the previous section, a reversible electrode must be at equilibrium, which means that there is no net change in the electrode over time. Desirable properties of a good reference electrode include the following:

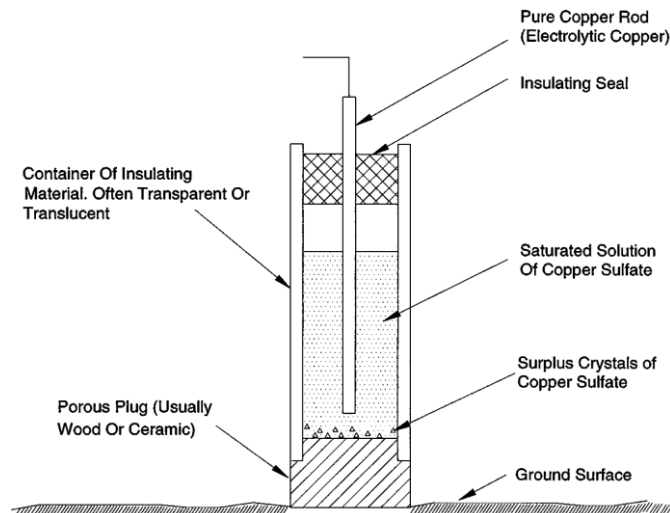
1. Easy to use and maintain.
2. Stable potential over time.
3. Potential varies little with current flow (does not polarize readily).
4. Not easily contaminated.
5. Does not contaminate what is being measured.

Common reference electrodes include silver-silver, chloride, calomel, and copper-copper sulfate.

Each reference electrode potential is based on the equilibrium reaction for the respective metal



The copper-copper sulfate reference electrode (CSE) is the most common reference electrode used for underground corrosion. It is frequently referred to as a half-cell based on the copper half-cell reaction. A schematic of the CSE is given in Figure 1.1



*Figure 1.1. Schematic of copper-copper sulfate reference electrode*

The electrochemical series is derived from thermodynamic data and represents equilibrium conditions. One rarely encounters such conditions in the real world except for the case of reference electrodes. A galvanic series is similar in appearance to an electrochemical series but represents actual potential. The series was generated by measuring the stable potential between the metal and a CSE in a neutral soil. This potential is referred to as corrosion potential, an open circuit potential, or a native potential. Note that the potentials measured may vary considerably, depending on the temperature, the type of soil, the moisture content of the soil, and the amount of time the metal is in contact with the soil before the measurement.

As described in the previous section, the oxidation and reduction reactions on a corroding metal are polarized from their equilibrium values. A definition of polarization is «the deviation (change) in potential of an electrode as a result of the passage of current.» The potential deviation (polarization) can be measured from the equilibrium potential or from the corrosion potential. The amount of polarization is referred to as the overvoltage or over potential and is assigned the term  $\eta$  ( ).

One type of polarization commonly observed in corroding metal systems is activation polarization. In the case of activation polarization, the rate of the corrosion reaction is limited by the electron transfer reaction at the metal surface. This electron transfer process has an associated activation energy and the rate of this process is exponentially related to the free energy change. Since the free energy is directly related to the potential, and the rate is directly related to the electrical current, the relationship becomes the following

$$\Delta I \propto e^{\eta/RT}$$

in which  $I$  is the corrosion current,  $R$  is the gas constant, and  $T$  is the absolute temperature.

*Kinetics*

The corrosion potential for a metal in an environment is established at a potential where the net sum of the reduction reactions is equal to the net sum of the oxidation

reactions. This is because there can be no net accumulation of charge; all of the electrons liberated by the oxidation of the metal must be consumed by the reduction reactions. The differential aeration cell is probably the most common corrosion cell found on pipelines or other underground structures. The upper parts of the structure are exposed to higher concentrations of oxygen and become the cathodes in the cell while the lower parts of the structure are oxygen deficient and become the anodes. Books on CP commonly state that the following four conditions are required for a corrosion cell to function:

1. There must be an anode.
2. There must be a cathode.
3. There must be a metallic path electrically connecting the anode and cathode.

(Normally, this will be the pipeline itself.)

4. The anode and cathode must be immersed in an electrically conductive electrolyte (normally, moist soil).

#### *Other Differential Corrosion Cells*

##### *Galvanic Corrosion*

The differential aeration cell is one example of a differential corrosion cell. Galvanic corrosion is another example. In the case of galvanic corrosion, the potential difference is created by the presence of different metals. Referring to the galvanic series described in the thermodynamics section, each material has a different corrosion potential in a given environment. When these metals are electrically coupled, the metal with the most positive corrosion potential is cathodically polarized, reducing its corrosion rate, while the more negative member of the couple is anemically polarized, increasing its corrosion rate.

##### *New and Old Pipe*

A condition closely related to dissimilar metal corrosion occurs when new steel pipe, is intermixed with old steel pipe. This has often been found in older distribution piping systems where a section of pipe has been replaced because of corrosion damage.

##### *Dissimilar Soils*

A steel pipeline passing through dissimilar soils can establish corrosion cells in much the same manner that corrosion cells can be established with dissimilar metals. This is illustrated by Figure 1.2, which shows a pipeline passing through two dissimilar soils. The potential of the pipeline in soil A is slightly different from the potential in soil B. As indicated in the section of the book on the galvanic series, the corrosion, or native potential of a metal can vary with differences in the environment. This causes the potential difference illustrated and satisfies the conditions necessary to establish a differential corrosion cell. In the figure, the pipe in soil A is anodic to that in soil B and is corroding as indicated by the current discharge.

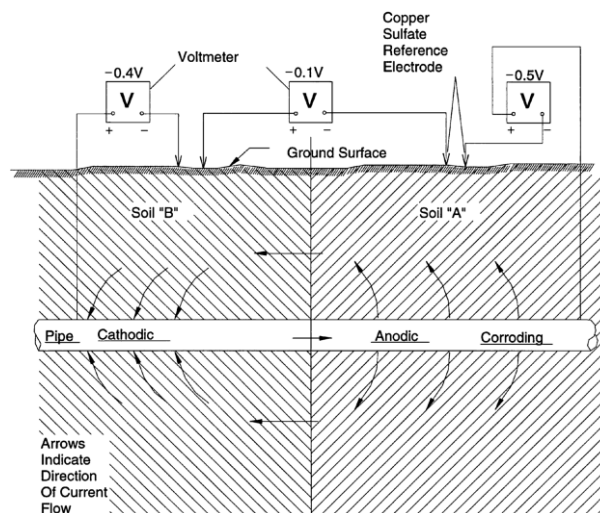


Figure 1.2. Schematic showing differential corrosion cell created by dissimilar soils

In some instances, different soil types are layered so that the backfill contacting the pipe will be a mixture of soil types when a pipeline trench is excavated and the pipe is laid and backfilled. This produces many small corrosion cells at the pipe surface that are not necessarily detectable by potential measurements taken at the surface of the ground.

### *Список литературы*

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