4.3 Electrochemical series& Determination of corrosion rate by weight loss method.

(Galvanic series or (EMF series)

Definition;

Electrochemical series is the series of elements arranged in the increasing order of the standard reduction potential.

Electrode	E^o (volt)
Li+/ Li	-3.04
Zn^{2+}/ Zn	-0.76
$2H^+$ / H_2	0
Cu^{2+} / cu	+0.34
Ag+ / Ag	+0.80

Significance

i) The tendancy of metal to go into solution can be noted using electrochemical series.
(eg) Metals on the top of the series easily go into solution.

ii) Metals with negative standard from potential displace hydrogen from acid solution.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$

$$E^oZn = -0.76 \text{ v}$$

But Ag will not displace hydrogen because it has positive electrode potential

$$Ag + H_2SO_4 \longrightarrow \text{No reaction}$$

$$E^o \text{ Ag} = + 0.80\text{v}$$

iii) The metals with negative electrode potential are more subjected to corrosion than the metals with positive electrode potential.

iv) Metals with higher positive electrode potential can liberate ions of metal lower in the series.

v) Spontaneity of redox reaction can be predicted from EMF value
If EMF is +ve –spontaneous
If EMF is –ve – Non- spontaneous

Factors influencing Corrosion

Corrosion depends on

i) Nature of metal

ii) Nature of the Environment.

Nature of the Metal

a) *Position in the emf series*

Metals above hydrogen in the emf series (negative reduction potential) get corroded easily.

b) Relative area of anode & cathode

The rate of corrosion will be more if anode area is smaller and cathodic area is larger.

c) Purity of metal

Impurities in a metal cause heterogeneity and form minute/ tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded. The cent percent pure metal will not undergo any type of corrosion. For example, the rate of corrosion of aluminium in hydrochloric acid with increase in the percentage impurity is noted.

% purity of aluminium	99.99	99.97	99.2
Relative rate of corrosion	1	1000	30000

(d) Over voltage:

The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v when zinc metal is placed in 1 M sulphuric acid and the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal.

(e)Nature of surface film

If the volume of oxide layer is less than volume of metal corrosion rate is more and if the volume of oxide layer is greater than volume of metal corrosion rate is low.

(f)Nature of corrosion product

If the corrosion product is soluble or volatile, corrosion rate will be more.

i) Nature of the Environment

a. Temperature: The rate of corrosion is directly proportional to temperature ie., rise in temperature increases the rate of corrosion. This is because the rate of diffusionof ions increases with rise in temperature.

b. Humidity of air: The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce theelectrolyte which is required for setting up a corrosion cell.

c. Presence of impurities in atmosphere: Atmosphere in industrial areas contains corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl, H_2SO_4 etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

d. Presence of suspended particles in atmosphere: In case of atmospheric corrosion:
(i) if the suspended particles are chemically active in nature (like NaCl, Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.
(ii) if the suspended particles are chemically inactive in nature (eg., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.

Determination of corrosion rate by weight loss method.

The weight loss method is a commonly used technique for determining the corrosion rate of materials, especially metals. This method involves measuring the amount of material that has been lost due to corrosion over a specified period. Here’s a step-by-step guide to the weight loss method for determining corrosion rate:

Steps for Weight Loss Method:

1. Sample Preparation:

- **Select and Prepare Specimens:** Choose the metal samples to be tested. Clean the samples to remove any existing rust, scale, or contaminants. This is typically done using abrasive materials or chemical cleaners, followed by rinsing with distilled water and drying.
- **Weigh the Samples:** Accurately weigh each sample using a precision balance to determine the initial weight. Record this weight as Wi.

2. Exposure to Corrosive Environment:

- **Prepare the Corrosive Environment:** Place the cleaned samples in a controlled corrosive environment. This could be a solution (such as acid, saltwater, or base) or an environment where the metal will be exposed to corrosive gases.

- **Exposure Period:** Leave the samples in the corrosive environment for a specified period, which could range from hours to several months depending on the type of corrosion being studied.

3. Removal and Cleaning:

- **Remove Samples:** After the exposure period, carefully remove the samples from the corrosive environment.
- **Clean Samples:** Clean the samples again to remove any corrosion products, like rust or scale. This step is crucial as it ensures that only the corroded material is being weighed. Cleaning methods might include washing with water, using a weak acid or abrasive cleaning.

4. Weigh the Corroded Samples:

- **Dry and Weigh:** After cleaning, dry the samples thoroughly and weigh them again using the precision balance. Record this weight as $W_{f..}$

5. Calculate Weight Loss:

- **Determine Weight Loss:** Calculate the weight loss of each sample by subtracting the final weight from the initial weight

  Weight $\text{Loss}=Wi-W_f$

6. Calculate Corrosion Rate:

- **Determine Corrosion Rate:** The corrosion rate can be expressed in various units, such as millimeters per year (mm/year) or grams per square meter per day (g/m^2/day). To calculate the corrosion rate, use the following formula:

  $$\textbf{Corrosion Rate} = \frac{\textit{Weight loss X K}}{\textit{Area X Exposure Time}}$$

  where K is a constant that converts the units into desired form. For example, in mm/year, K is typically 8.76×10^{-4}.

- **Area and Exposure Time:** Ensure to accurately measure the area of the sample exposed to the corrosive environment and the exposure time. The formula can be adjusted based on the units used for area and time.

Example Calculation:

1. **Initial Weight (Wi):** 50.000 grams
2. **Final Weight (Wf):** 49.800 grams
3. **Weight Loss:** 50.000 - 49.800 = 0.200 grams
4. **Sample Area:** 10 cm² (0.001 m²)
5. **Exposure Time:** 30 days

   Convert to the appropriate units and apply the corrosion rate formula. For example, if you want the corrosion rate in g/m²/day:

   $$\text{Corrosion Rate} = \frac{0.200 gram}{0.001 m^2 X\ 30\ days} = 6.67 g/m^2/day$$

Advantages:

- Simple and straight forward.
- Provides direct measurements of corrosion through weight loss.
- Useful for assessing general corrosion rates.

Limitations:

- Requires careful sample preparation and cleaning to avoid errors.
- Not suitable for studying localized corrosion (like pitting).
- Weight loss method can be affected by the accuracy of measurements and environmental conditions.