

CHAPTER - II

EXPERIMENTAL METHODS :

ELECTROCHEMICAL STUDY

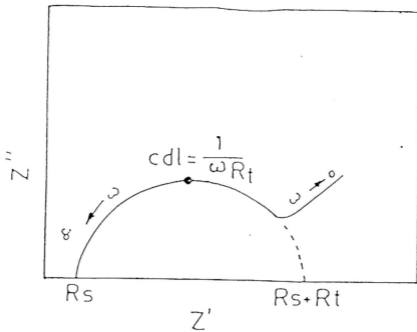
Several experimental techniques are used to study corrosion products and understand the process of corrosion. In the present study, we have used AC impedance analysis and Scanning Electronic Microscope with EDAX attachment. The basic principle of these techniques will be briefly discussed below.

A. C. Impedance method :

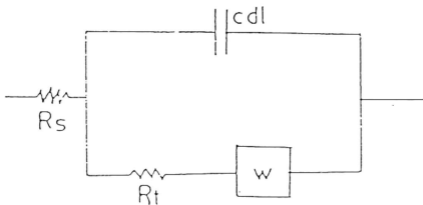
The Impedance method has been widely used in recent years to measure the corrosion rate of the metals, resistance and capacitance behavior of the coated metal substrates. The advantage of this is that it completely eliminates the solution resistance. The equivalent of a corroding system which has both Anodic and Cathodic activation controlled reaction may be represented as shown in the figure.

Solution resistance is represented by R_s , Charge transfer resistance is given by R_t and the double layer capacitance is shown by C_{dl} . Using Stern and Geary equation, (11) I_{corr} is obtained from R_t , since

$$I_{corr} = \frac{b_a \times b_c}{2.303 (b_a + b_c)} \times 1/R_t \rightarrow 2.1$$



where, Z' Real part
 Z'' Imaginary part



R_s = Solution resistance
 R_t = Charge transfer resistance
 cdl = Double layer capacitance
 w = Warburg Impedance

Figure 9 : Schematic representation of impedance plot and its equivalent circuit

The impedance of the above circuit for the given ω . ($\omega = 2\pi F$) is,

$$\begin{aligned} Z &= R_s + 1 / (j\omega C_{dl} + 1/R_t) \quad \rightarrow \quad 2.2 \\ &= R_s + \frac{R_t / (i + \omega^2 C_{dl}^2 R_t^2)}{j\omega C_{dl} R_t^2 / (i + \omega^2 C_{dl}^2 R_t^2)} \\ &= \quad \quad \quad Z' \quad \quad \quad - \quad \quad \quad jZ'' \end{aligned}$$

Thus the cell impedance Z consists of real (Z') and imaginary (Z'') parts. A plot of Z' Vs Z'' for various frequencies is a semi circle. At high frequency, Z corresponds to R_s and at low frequency, Z corresponds to $R_s + R_t$ and the difference between the two values gives R_t .

The double layer capacitance value is determined from break point frequencies of the $\log Z$ Vs $\log F$ (bode plots) or from the frequency at which Z'' is maximum.

$$F_{bl} = 1 / 2\pi (R_s + R_t) C_{dl} \quad \rightarrow \quad 2.3$$

$$F_{bh} = 1 / 2\pi R_s C_{dl}$$

$$F_{(max)} = 1 / 2\pi C_{dl} R_t .$$

EIS for coating evaluation :

Electrochemical Impedance Spectroscopy (EIS) measurements (12 – 20), were made using a system based on **Hioki** 3520 LCR bridge interfaced with a computer for data acquisition.

The electro-chemical cell consists of two electrodes, the painted metal under test, and a large area platinum wire gauze as the auxiliary electrode, both immersed in the test solution, usually 3% NaCl solution as the corrosive electrolyte under ambient aeration. Impedance data were collected at frequencies ranging from 40 Hz to 100 kHz. The electrochemical cell comprised of a cylinder made of glass tube attached to a coated steel surface using M-seal adhesive. The exposed sample area of the coated steel was 1 cm^2 in all cases.

The coating system resistance generally degrades with time. A lower limit of about 10^6 ohms/cm^2 is noticed, below which corrosion occurs beneath the coating. This generality was found with both AC and DC resistance measurement techniques. The degradation was associated with ion and water penetration into the coating, transport of ions through the coating, and the subsequent electrochemical reactions (corrosion) at the coating-metal interface.

Capacitance measurements were used to estimate water uptake rates by coatings. The rates were correlated with coating performance and were useful in calculating minimum protective coating thickness. A schematic instrumentation diagram is shown in figure in page 36.

CHEMICAL AND CORROSION RESISTANCE :

1. SALT SPRAY TEST:

This test was done according to the method ASTM B-117. The coated specimens were coated with wax along the edges and corners and placed in a closed transparent chamber where a solution of 3 % sodium chloride was sprayed continuously. The specimens were inspected periodically to find out the start of visible corrosion. The time for which it had withstood the accelerated test was observed and reported.

2. HUMIDITY TEST :

This test was carried out by exposing the painted and waxed panels in a 100 % humidity chamber at room temperature, as per ASTM D 6097. By periodic inspection, the time for which it had withstood the condition is reported.

3. IMMERSION TEST :

2" x 3" coated and waxed (in edges) specimens were immersed in different chemicals and periodically observed for any attack for a period of 1500 hours and the observations are reported . The following chemicals are used:

- 1] 5% Hydrochloric acid
- 2] 5% Sulfuric acid
- 3] 5% Sodium chloride
- 4] 5% Sodium hydroxide
- 5] buanol
- 6] xylene
- 7] Methyleneisobutylketone

pH MEASUREMENTS:

pH is simply the negative logarithm of the hydrogen ion concentration. For example, a pH of 7 indicates that there are 10^{-7} grams atoms of hydrogen ion per litre of solution. A pH of 7 indicates a neutral solution while a pH of 0 represents a very acidic media, and pH of 14 or above denotes a highly alkaline solution.

Effect of pH

The effect of pH on the corrosion of iron in aerated water is shown in figure. Since iron dissolves in strong acid even without electro-mechanical action, it is not surprising that corrosion is most rapid at low pH. Corrosion rate is nearly independent of pH between about 4 and 10. In this pH region, the initial corrosion causes a layer of ferrous hydroxide to precipitate near the anode. Subsequently, the rate is controlled by the rate of oxygen diffusion through the layer. Underneath, the surface of the iron is in contact with an alkaline solution whose pH is about 9.5. At pH above 10, corrosion rate is slow, due to formation of the passive ferric oxide film in the presence of dissolved oxygen. At pH above about 14 without dissolved oxygen, corrosion rate may increase when the soluble ferrite ion, HFeO_2^- , forms.

Corrosion rate also depends on temperature. The reactions proceed more rapidly at higher temperatures, as indicated by the increase in corrosion rate in a closed system. However, the solubility of oxygen in water decreases as temperature increase so that in an open system, where the oxygen can escape, the rate of corrosion goes through a maximum at some intermediate temperature. The temperature at which corrosion rate maximizes is quite system dependent.

pH measurements were made using a system based on **JENWAY 3020** pH meter. The model 3020 is microprocessor based, laboratory pH meter, measuring pH, absolute and relative mV and temperature. In addition to normal pH measurement, the units can be used for Redox and Ion selective analysis.

SCANNING ELECTRON MICROSCOPE :

An instrument that is related to the electron microprobe is the scanning electron microscope (SEM). A beam of electrons is focused on the surface of a sample as with EXPMA. An image of the surface of a sample can be obtained from the intensity of back scattered electrons. A scanning transmission electron microscope (STEM) obtains an image of the sample from the electrons that are transmitted through the sample. With either the SEM or the STEM, fixed-energy electron beam is scanned across the surface of the sample.

The results are similar to those obtained from an optical microscope except that the magnification is considerably greater. STEMs have been developed which have been diameters as small as 2 nm. They can be used for studies of corrosion products and the cracks developed on the coated metal surface. In addition to providing a visual image of the sample, scanning electron microscope is used in conjunction with x-ray spectrometers to obtain the elemental composition of the sample. The process is similar to that used with the electron microscope. The elemental composition can be obtained across the surface of the sample during a scan or at various steps at a single location. Scanning electron microscopes generally use energy-dispersive x-ray spectrometers. Scanning electron microscope consists of 4 main parts, they are the electron source /gun, a deflection system and a vacuum system as shown in figure. Electron gun produces a source of electrons and accelerates these electrons to an energy in the range 1 - 40 keV. Electron lenses are used to reduce the diameter of this source of electrons (spot size, less than 10 nm) and to place a small, focused electron beam on the specimen.

A deflection system consist of two pairs of electromagnetic deflection coils (scan coils) are used to control the raster of beam in order to produce contrast in an image. The interaction of the electron beam with the specimen

causes the generation of many signals and the two most often used to produce images are secondary electrons (SE) and back-scattered electrons (BSE). These electrons are collected detectors and converted into an electrical signal. The electron beam traverse the sample surface point-by along a line and the back-scattered electron signal is collected and generated into an image.

X-rays emitted from a specimen bombarded with the finely focused electron beam of the SEM can be used to identify which elements are present in the sample. This technique is known as energy dispersive X-ray analysis. It allows quantitative analysis of chemical composition with an accuracy and precision approaching 1%. Elemental constituents can be determined to concentrations ranging as low as .01% (100ppm) which corresponds to limits of detection in terms of mass 10^{-16} to 10^{-15} g. Its limitations are that it cannot distinguish between ionic, non-ionic and isotopic species and EDAX in particular cannot detect the low atomic number elements. EDAX fitted with Beryllium window detectors can detect elements with $Z < 11$ while EDAX windowless detectors can detect elements with $z > 5$. EDAX is a surface analytical technique and because of the vacuum requirements of the SEM, it is not suitable for hydrated samples.

The thermal degradation of the coating has been studied using a scanning electron microscope [PHILIPS 515] equipped with an energy dispersion chemical analysis [EDAX]. Before SEM, EDAX analysis, all the heat treated panels are coated with carbon using a Bio - Rad high - vacuum sputter coating unit model E5100 Series II.

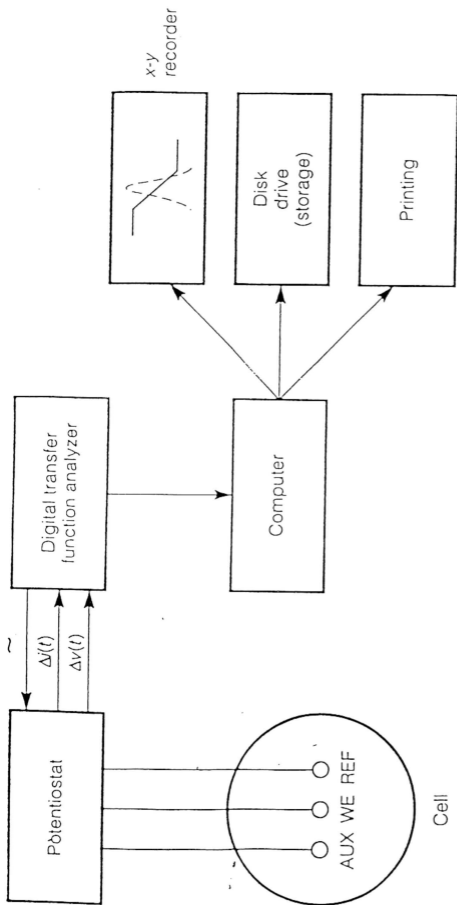


Figure 10 : Schematic instrumentation for conducting electrochemical impedance spectroscopy

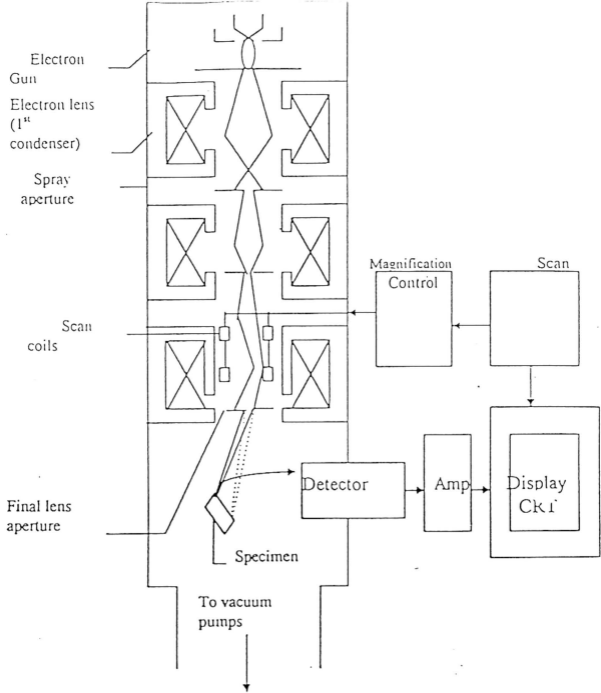


Figure 11 : Schematic drawing showing the electron column, the deflection system and the electron detectors