Chapter-III
3.1 Introduction

It is well known that most of the corrosion reactions are electrochemical in nature. A corroding metal is usually characterized by the following pair of reactions occurring at the interphase

$$M \rightarrow M^{n+} + n\, e^- \quad (1)$$

$$O + n\, e^- \rightarrow R \quad (2)$$

Generally in corroding systems, the reverse reactions (1) and (2) are negligible. In such a case, a steady state is altered when the net rate of one of the reactions becomes equal to the net reactions of the other. For instance, in acid solution this happens when the net rate of metal dissolution equals the net rate of discharge of hydrogen ions. The potential of the corroding metal is the mixed potential of anodic and cathodic reactions (1) and (2) and the net current is zero. This potential is known as “corrosion potential”. According to the homogeneous theory of corrosion put forth by Wagner and Traud the entire surface of the metal acts both as a cathode as well as an anode. In other words, cathodic and anodic areas are not spatially separated on the metal surface. Both the conjugate reactions (1) and (2) take place over the entire surface and hence corrosion is assumed to be uniform.

A study of kinetics of corrosion processes is quite useful in the evaluation of corrosion resistance of materials and methods of protection against corrosion. Hence corrosion monitoring may be defined as the “systematic measurements of corrosion rate
of plant materials with the objective of diagnosis and controlling corrosion. Recent development of *insitu* corrosion monitoring meters has helped to:

i. Obtain information of the state of operational equipment. This avoids unplanned shut-downs and foreseen deterioration of the plant.

ii. Obtain information on the inter-relation between corrosion processes and operating variables and

iii. Control operating conditions so that deterioration may be maintained at an acceptable rate/or the plant run closer to its limits of safety.

Different monitoring methods can be grouped into the following three categories:

i. Non-electrochemical methods

ii. Electrochemical and special methods

iii. Non-destructive testing (NDT) methods

3.2 Non electrochemical methods

3.2.1 Coupon method

Weighed specimens are exposed to the environment for a specified period and the loss of metal is measured. From the weight loss, corrosion rate is determined by the relationship,

\[
\text{Corrosion rate (mm per year)} = \frac{\text{Weight loss (mg) } \times 87.6}{\text{Area (cm}^2\text{)} \times \text{time (hrs)} \times \text{density}}
\]

The coupons can be in the form of discs, rods, plates or any convenient shape, but the edges should be machined and polished to avoid preferential attack due to residues from the cropping operation. Comprehensive guidance for preparation of specimens is given in ASTM-G4-68. The specimens are mounted on the racks and exposed. After
exposure, the coupons are either cleaned mechanically or pickled in inhibited acids in order to remove the corrosion products.

This technique is still widely used since many different materials can be exposed at one site and unambiguous data on the form of corrosion on the specimen can be obtained. This method yields average corrosion rate but is inherently inaccurate when it involves measuring small differences in weight. Besides, continuous monitoring of corrosion rate is not possible.

3.2.2 Electrical resistance method

This method involves the measurement of the change in resistance of a metal element as it corrodes. The electrical resistance of the metal is given by:

\[ R = \frac{P \times L}{A} \]

Where, \( P \) is the specific resistance, \( L \) is the length of specimen and \( A \) is the area.

On exposing the metal to the corrosive environment the reduction in cross-section of the metal causes an increase in the electrical resistance. Hence, measurement of change in electrical resistance is proportional to the increase in corrosion. The measuring instrument is normally based on Kelvin or Wheatstone resistancebridge which measures the ratio of the resistance exposed element to the protected element (Fig. 1). The resistance ratio is calibrated in terms of the variation of thickness of the element.
This technique gives the integrated corrosion rate. The major advantage is its ability to measure corrosion rate in liquid and vapour phase. The disadvantages are that interpretation of the results is not easy unless cross ion is uniform. So, this method is not suitable where pitting or stress corrosion attacks are likely. Moreover, errors are introduced in the measurement due to the metallurgical condition of the probe element and due to temperature changes.

3.3 Electrochemical and special methods

3.3.1 Polarisation resistance method

The polarization resistance or linear polarization technique is based on the measurement of apparent ‘resistance’ of a test cell when it is polarized by a small voltage of the order of 5 to 20 mV. Stern and Geary have shown that the polarization resistance.

\[
\left( \frac{dn}{di} \right) \bigg|_{n \to 0} = \frac{b_a \times b_c}{2.3 (b_a + b_c) I_{corr}}
\]

\[
R_p = \frac{K}{I_{corr}}
\]

Where, \(b_a\) and \(b_c\) are Tafel constants, and \(I_{corr}\) is the corrosion current (amp/m²).
The value of $I_{corr}$ is readily converted to the more practical units of metal loss (mm/year) using Faraday’s Law. In most cases $k$ is found to be in the order of 0.012 to 0.03 V.

In this method, 10 to 20 V is applied to a pair of electrodes (in the case of two electrode probe) and the resultant current is measured. The measured current is calibrated in terms of ipy or mmpy.

This method gives the instantaneous corrosion rate while the electrical resistance gives the average corrosion rate. Hence, this method is more sensitive to small variations in the corrosion rate. The main disadvantage of this technique is that the media must have sufficient conductivity. In low conducting media and in the presence of surface films, the IR drop is more predominant than $R_p$. This technique is normally limited to situations where uniform corrosion is expected and it is rarely suitable where pitting or other forms of localized corrosion is likely.

3.3.2 Methods based on polarization curves

By determining the polarization curve (pilot between polarization current and potential of the test electrode – Fig. 2). Information like corrosion rate, corrosion mechanism, susceptibility towards localized corrosion, etc., can be evaluated. These curves can be determined galvanostatically. A potentiostat along with a sweep generator, is used for potentiodynamic measurements whereas constant current power supply can be used for galvanostatic measurements. From the polarization curve, the corrosion current density, $I_{corr}$ of the test electrode can be estimated. The corrosion current or exchange current can be converted into the corrosion rate using the Faraday’s law. Fig.3 shows the shape of a polarization curve for an active-passive region below the transpassive
potentials at which such increase in current takes place is used to compare localized corrosion susceptibilities of different materials or media. Such polarization curves can be obtained through commercially designed three electrode probes inserted into the process stream. High temperature or pressure sometimes makes it impossible to place a reference electrode near the test electrode. In such cases, an external reference electrode with an extended fibrous arm, whose tip is placed closed to the test electrode internally, can be used.

Fig.2 Anodic and cathodic polarization curves

![Anodic and cathodic polarization curves](image)

Fig.3 Anodic polarization curve for active-passive metal

![Anodic polarization curve for active-passive metal](image)
3.3.3 Corrosion potential measurement method

This is a simple method for understanding the corrosion processes taking place on the materials. The method is particularly useful for the materials showing active/passive behaviour or when the material is susceptible to localized corrosion and hydrogen embrittlement. The information on the corrosion potential can indicate whether the material is above the critical potential for pitting/crevice corrosion or it is in the range of passivation, stress corrosion cracking, cathodic protection or hydrogen embrittlement regions. The method involves measurement of potential of the component material or test specimens with respect to a reference electrode. The measurements can be done intermittently or continuously.

3.3.4 Hydrogen detection methods

Atomic hydrogen produced at the cathode during corrosion reaction can diffuse through many alloys, when it does not combine to form hydrogen molecules. In presence of sulphides in the process stream such as in sour service and some refinery streams, the atomic hydrogen produced by corrosion reaction diffuses fast through materials like ferritic steels. This diffusion through the component material thickness could be indicative of a corrosion reaction. In such cases, the hydrogen can be detected by hydrogen probe based on pressure measurement technique or by a hydrogen monitoring system based on electrochemical technique. The hydrogen detection is important when the material is susceptible to hydrogen blistering and embrittlement.

In the pressure measurement type probe, hydrogen is made to diffuse through thin wall of tube of the probe inserted into the system. The hydrogen is collected in a small free volume built in the probe and the increase in the pressure indicative of hydrogen
diffusion from the component material is detected through a pressure gauge or a transducer.

In the electrochemical measurement types of probe, hydrogen which diffuses through the material wall is detected electrochemically by mounting a probe on the surface of the wall. In this type of probe (Fig. 4), a palladium foil placed on the wall material is used as working electrode and maintained at a constant anodic potential with the help of an auxiliary and reference electrode in sulphuric acid electrolyte. At a fixed anodic potential (by using potentiostat) of the palladium foil, the hydrogen which diffuses out from the foil gets oxidized and the oxidizing current measured is indicative of the hydrogen penetration rate. This rate could be indirectly related to the corrosion reaction taking place inside the process medium.

![Fig.4 Electrochemical hydrogen probe](image)

**3.3.5 Impedance method**

In recent years, the impedance technique has been widely used for the measurement of corrosion rate. The equivalent circuit of a corroding metal is represented as:
\[ I_{\text{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)R_t} = \frac{K}{R_t} \]

in which \( R_s \) = solution resistance, 
\( C_{\text{dl}} \) = double layer capacitance, and 
\( R_t \) = charge transfer resistance

The charge transfer resistance \( R_t \) is a measure of the corrosion rate.

The essential difference between \( R_t \) and \( R_p \) is that the latter will also include the iR drop. Hence, measurement of \( R \) is the measure of the true corrosion rate.

\( R_t \) is measured by the impedance method. In this method, an alternating voltage of 10-20 mV is applied to the cell and the resulting current and phase angle is measured for various frequencies. The impedance \( |Z| \) is the ratio of AC voltage / AC current. The cell impedance is resolved into two parts, i.e., real part \( Z' = |Z| \cos \) and imaginary part \( Z'' = |Z| \sin \). Plot of \( Z' \) vs \( Z'' \) is a semicircle which cuts the \( Z' \) axis at high frequency corresponding to \( R_s + R_t \) (Fig. 5) Subtraction of impedance at high frequency from low frequency gives \( R_t \). This principle is used in the AC corrosion monitor. Here, the AC voltage of 10-20 mV at frequencies 0.01 Hz and 10 kHz is simultaneously applied between a period of electrode and the AC current is measured. The circuit is designed to get the difference in values of impedance at low and high frequency which is calibrated in terms of corrosion rate, as shown in Fig.5.
This method also gives the instantaneous corrosion rate. The main advantage of this technique is that this method is useful even for low conducting media since the solution resistance is completely eliminated.

3.4 Non-destructive testing (NDT) methods

NDT methods are widely used for detecting the defects and damages taking place on the components during the service as well as after or before the service. Some important methods are described below:

3.4.1 Visual examination method

Examination of the internal or external surface of a component with naked eye or magnifying glass gives an indication of corrosion damage (general or localized) and extent of surface damage could be assessed. In addition to magnifying glass, an instrument called endoscope or boroscope can be used in the visual examination. These instruments are used to allow visual examination of the interior of hollow components which are otherwise inaccessible to the eye. The image of the investigating spot is
transferred from objective to eye piece by a lens system in the endoscope and a source of
light is also provided along with, for illuminating the spot. For the inspection of curved
hollow components a flexible endoscope is used. The flexible endoscope employs glass
fiber optics for transmitting the light and image. A measuring system can also be attached
to the endoscope to assess the depth of the corroded region.

3.4.2 Dye penetrant method

Dye-penetrant tests are used to detect cracks and pores which originate in the
surface or, are closely associated with it. In these tests, liquids of low surface tension are
used to penetrate the defects and later they are sucked out with an absorbent developer
applied to the surface resulting in the colouring of the area. Very fine cracks and pores
can be detected by this technique. Components made from materials which are not
attacked or coloured by the testing chemicals can be examined by this method. The
surface of the components which have a porous structure such as sintered metal or
sprayed metal coatings can not be examined by this method.

3.4.3 Magnetic stray flux method

This technique is particularly suited for the detection of defects in or immediately
below the surface of ferromagnetic materials. Due to different magnetic permeability of
ferromagnetic materials compared with air or nonmagnetic inclusions at boundaries in the
materials magnetic stray, flux is produced on magnetization. If the cross section through
which the magnetic lines of force are flowing changes, suddenly, then a part of the
magnetic lines of force comes out of the material, including stray fluxes. If the cracks lie
below the surface, the action of the stray flux is smaller. If the cracks lie parallel to the
lines of force, no stray flux arises. The method consists of first magnetization of the
material and then detection of the stray flux by applying magnetic powder above the surface. Magnetic probes are also used to detect the stray fluxes above the crack.

### 3.4.4 Potential drop method

This method is utilized for the measurement of depth of the crack which has been detected by visual methods. If an electric current is passed through a work piece, a constant potential (voltage) drop is measurable between two probes on the surface at a constant distance apart, provided that the electrical resistance of the work piece remains constant and there is no crack in the region between the two probes. If however, there is a crack between the two probes, the current has to travel a longer path, depending on the crack, which leads to a greater voltage drop compared with the crack-free case. The potential difference compared with the crack-free state is a direct measure of the crack depth. Alternating current (ac) or direct current (dc) can be used for detection and measurement of defects.

### 3.4.5 Eddy current method

When an alternating magnetic field produced by a test coil acts on a work piece with a certain electrical conductivity and magnetic permeability, eddy currents are induced in the work piece. Those eddy currents cause an alternating magnetic field, which by Lenz's law, is in the opposite direction to the original field. Local changes in the material influence the secondary magnetic field induced by the eddy currents. This effect is used in eddy current method to discover defects in the material resulting from cracks or by localized corrosion attack. Eddy current testing is particularly suitable for indicating in homogeneities or corrosion damage in heat exchanger tubes. Examination using eddy current is carried out by using a suitable travelling probe. In regular moni-
toring and maintenance procedures, the results of such testing are stored in a data file so that, on subsequent testing, critical changes in the components can be quickly recognized.

3.4.6 Ultrasonic method

In the ultrasonic method mechanical vibrations having frequency of above 20 kHz (which is the upper limit for detection by human ear) are used for detecting the defects in the material. The usual working frequency for material testing lies in the region of 100 kHz to 20 MHz. Piezoelectric effect is used in the test heads of the probe to produce and receive ultrasonic waves. A coupling medium (which is usually oil) has to be used to transmit the ultrasonic waves to the test piece. The velocity of propagation of the waves is a material constant. When the waves encounter a boundary between two materials or different transmission velocities they are reflected and refracted. Flaws such as cracks, shrinkage cavities, or other inhomogeneities are detected since the ultrasonic waves are reflected at these flaws as well as at boundaries of the work piece. For optimal application of ultrasonic testing, perpendicular sounding technique is used in which the defect is at right angle to the incident waves. For most applications, the oblique method in which incident waves, waves at 35° to 80° are generally used. Ultrasonic testing can also be used for measurements of wall thickness of components. Structural components which are subjected to corrosion or wear can be regularly examined for changes in wall thickness with ultrasonic. Portable instruments for measuring wall thickness are commercially available.

3.4.7 Radiographic methods

In these methods, x-rays or gamma-rays are used to view the interior of the material and to detect the hidden defects. The method can be used to detect corrosion
cracks/ defects in components while in service. This is also used for the detection of blockages and deposits and monitoring components exposed to corrosion or abrasive wear for reduction in wall thickness. Due to the very short wave length of $10^7$ and $10^{10}$ cm, x-rays, gamma-rays can penetrate the solid materials. The radiation is attenuated in passing through the material. This is a function of the density and thickness of the irradiated object. Less radiation absorption occurs at areas of defects or regions of smaller wall thickness. The photographic film placed behind the irradiated object receives different amounts of radiation owing to the different radiation absorption at inhomogeneities or varying wall thicknesses. Depending upon the nature of the problem and also on the accessibility of the components, either x-rays or gamma-rays can be selected.

A specific type of a particulate radiation called neutrons can also be used to form a radiographic image of a test piece. This form of NDT method is known as neutron radiography. In neutron radiography, interaction of neutron with the nuclei of the atoms in specimens is used rather than interaction with orbital electrons as in the case of conventional radiography. Neutron radiography is advantageous in imaging low atomic number materials present in high atomic number matrices. For example, it is possible to detect certain isotopes of hydrogen radiographically. The high attenuation of hydrogen offers many possibilities of application including inspection of component assemblies for detection of adhesion, explosives, lubricants, water, hydrides, corrosion plastics or numbers. Corrosion of zirconium alloy components in water in nuclear reactor core can be easily detected by this technique as the corrosion is associated with hydride formation.
3.4.8 Acoustic emission detection method

Acoustic emission is a high frequency stress wave generated by rapid release of strain energy that occurs within a material during crack growth, oxide scale cracking, plastic deformation, phase transformation, etc. This energy may originate from a stored elastic energy as in crack propagation or from stored chemical free energy as in the case of phase transformation. Acoustic emission inspection detects and analyzes minute acoustic emission signal generated by discontinuities material under stress. Proper analysis of these signals can provide information concerning initiation and location of defects and cracks. Basically there are two types of acoustic emissions: continuous and burst. The wave form of continuous type emission is similar to Gaussian random noise, but the amplitude varies with acoustic emission activity. In metals, the form of emission is associated with the dislocation movement in the grains. Burst type emission is of short duration pulse (10 μs to a few ms in length) and are associated with discrete release of strain twining, micro yielding and development of micro and macro cracks. Burst typo emission has greater amplitude than the continuous type. Detection of acoustic emission from components can be used for: continuous surveillance of pressure vessels for location and detection of active flaws; detection of incipient fatigue fracture; determination of onset of localized corrosion (particularly stress corrosion cracking and hydrogen embrittlement).

3.4.9 Photo electrochemical laser imaging method

This is a recent technique in which the principles of photo-electrochemistry have been utilized for characterization of surface films. The technique is sensitive to change in thickness, composition and structure of passive film. In this technique, a laser beam of
size about 10 μm is scanned over the surface and response of photo current is measured at each point. Since the photo current is highly dependent on surface properties, a 3-dimensional image (photo electrochemical) can be constructed. This technique is considered to be useful in the *insitu* studies of corroding and non-corroding surfaces.

3.4.10 **Infrared imaging method (thermography)**

This is also a new technique and is based on the measurement of heat distribution across the surface of the object. This is essentially mapping of a temperature distribution on the surface of the object in a non-contact manner. Thermography makes use of infrared (IR) spectral band. The system basically consists of an IR scanner, monitor and control unit. This technique can be used for detection of corrosion on the inner surface of tubes. By suitably monitoring the thermal distribution, it is possible to identify the corroded areas. This detection depends on parameters like emissivity variation on the surface of the tube, presence of adjacent heat sources, temperature differential inside and outside the tube and material wall thickness and curvatures.
3.5 REFERENCES


