CHAPTER III

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A number of corrosion tests are carried out in various laboratories everyday. The value and reliability of the results obtained depend upon the proper planning of the experiments. A number of methods for corrosion testing are available in literature (348-350). Many workers have given an account of major methods for measuring corrosion rates (351-354). A brief description of the methods outlining the fields of its usefulness and the major advantages and limitations are given below.

Methods of studying corrosion

Visual observation is simple and valuable. It provides the general nature of corrosion. However, it is qualitative in character and within human errors. Most widely adopted, useful and simple procedure is the weight loss method. It is quantitative and direct but errors can occur due to incomplete removal of corrosion products from the specimens and multiple specimens are required. Gain in weight method is useful and applicable where corrosion products adhere to the surface, for example in indoor atmospheric corrosion. This method has limited applicability and requires knowledge of the composition and nature of the corrosion products.
Several methods are used to report pitting, maximum pit depth, number of pits per unit area, average depth and also a complete statistical analysis. Out of these, maximum pit depth is important. Interpretation of pitting data requires careful consideration of edge effect. Size of the exposed specimens and exposure time must be as large as possible (355). Multiple specimens are required to determine time-penetration curves. Microscopic methods are useful for the determination of the depth of pits and constituents of the metal.

Electrical resistance methods depend upon the increase in resistance of a thin strip specimen. This method is advantageous, as specimens need not be removed for weighing; measurements can be made externally and can be continuously recorded with suitable instruments (356). However, this method is an indirect one, requiring previous calibration which is subject to surface to volume errors and does not distinguish the types of attack.

Hydrogen effusion method is applied when hydrogen resulting from the corrosion reaction diffuses through metal and is collected in a vacuum system. The rate of hydrogen evolved is a direct measure of the corrosion rate. Oxygen absorption method also gives the rate of corrosion.

Change of physical properties, such as tensile strength, ductility, resistance and hardness of materials
can be used to evaluate their deterioration. However, it is not possible to distinguish the type of attack separately.

The electrochemical methods are measurements of single electrode potential, shorted cell current measurement, potential difference between unlike metals, anode and cathode polarization and film resistance.

The linear polarization technique provides a means of remotely measuring corrosion rates (357). Corrosion rates can be calculated by measuring the electrochemical characteristics of the corroding specimens by applying a small current. Though this method is useful for rapid determination of corrosion rates and is applicable even to cases where specimen removal is difficult, the accuracy achieved is not always sufficient.

Materials and specifications

Before carrying out corrosion testing, it is very important to have complete information regarding the materials, such as its chemical composition, fabrication history and metallurgical treatment. It is therefore essential to procure sufficient material of information in a single lot to ensure complete reliability of the results.

Use of rolled materials for corrosion testing has been recommended because of ease of handling and surface preparation. Rolled sheets are available in a variety of
thickness and specimens of different shapes and sizes can be cut from the metal. A large ratio of rolled area to edge area is desirable in corrosion testing because in equipment made from rolled sheet, the rolled surface is exposed to corrosion. The shape and dimensions of specimens should be such as to permit weighing on an accurate balance and to facilitate accurate measurement and calibration of the area of each specimen (358). According to Champion (359) and Knapp (360) it is desirable to adopt a standard size as far as possible to obtain comparable results. Further, it is advantageous to adopt a size and shape of specimen giving a low edge area to surface area ratio and a reasonably large area.

Surface preparation

Fontana and Green (358) report that in corrosion testing the specimen should be identical with the surface of the actual equipment to be used in the plant. However, this is usually impossible because the surface of commercial metals and alloys vary as produced and fabricated. The nature and extent of surface contamination, degree of scaling or oxide film vary, from surface to surface. To ascertain the corrosion characteristics of a given surface in different environments, it is desirable and also necessary to have a standard surface conditions.
A widely used surface finish is produced by polishing with No. 120 abrasive cloth or paper or its equivalent. During cleaning, there should be no contamination or much rising of temperature of the surface. Soft metals cannot be cleaned by the above mentioned method. Scrubbing with pumice powder is used for aluminium, magnesium (361) and rubbing with a hard eraser for lead is recommended (362). Several articles on cleaning of aluminium surface have been published (363-365).

It has been reported that (350, 366-368) thin, invisible film of grease which interferes with corrosion testing, can be removed by proper organic and inorganic solvents.

Exposure conditions

For proper interpretation of the results of corrosion testing, it is most essential that a proper ratio of the volume of the corroding solution to the total area of the metal surface exposed should exist (369). Several workers have suggested various values of the ratios which vary from 6.7 ml (350) to 50.0 ml (370) per square centimeter. In selecting the above ratio it is important that the volume of the corroding solution should be large enough to avoid any appreciable change in its corrosivity through exhaustion of the corrosive agents or accumulation of corrosion products over the surface that may alter the further corrosion rate.
The technique adopted for the tests should be such that the corrosion should have easy access to the specimen. Support and container for the specimen should be immune to corrosion. Specimens should be adequately insulated to avoid galvanic effect and specimens should be properly positioned to get active results of partial immersion and complete immersion tests. If possible each specimen may be tested in a separate container (350).

**Duration**

Corrosion rate may increase, decrease or remain constant with time. Duration is an important consideration in corrosion testing. The alternation in the corrosion rates is due to factors like accumulation of corrosion products at the surface, nature of the corrosion products, destruction of a scale already existing over the metal surface, change in the concentration of the corrosive agent, formation of corrosion inhibition agents, etc. Thus, results of short time or too long time may be misleading (371).

A very rough yardstick for checking results with respect to minimum test time is the formula (372) 2000/mils per year = hours (duration of test). This formula is based on the general rule that the lower the corrosion rate is, the longer the test should run. If a specimen is
completely dissolved in 2 hours, a reliable result is obtained even though it is a negative one.

Under the circumstances, it is desirable that the duration of the test should be decided by the length of the time required to produce a reasonable amount of corrosion. In fact, the duration of the corrosion testing may be determined by its nature and purpose.

Temperature

Perhaps the most important single factor in corrosion is the effect of temperature. Pronounced change may be brought about by variation in temperature. Laboratory tests are often made in controlled temperature water baths. Temperature should be controlled to ±2°C or better (373). Champion (374) recommends a limit of ±0.5°C.

Cleaning specimens after exposure

If the assessment of corrosion is to be carried out by the weight loss method, it is necessary to make the surface free from the corrosion products without loss of any base metal after exposure.

One common cleaning procedure consists of holding the specimen under a stream of tap water and vigorously scrubbing the surface with a rubber bung. This method is not always satisfactory, particularly when appreciable quantities of corrosion product adhere to the specimen.
Champion (375) has discussed the general methods of cleaning. Cleaning methods may be classified as (i) mechanical, such as sand blasting, and the rubber-stopper method, (ii) chemical, such as the use of chemicals and solvents and (iii) electrolytic, which involves making the specimen a cathode under an impressed current in the presence of a variety of chemical reagents with or without inhibitors. The duration of immersion should be kept minimum to prevent the attack by the acid on specimen. Specimen should be lightly scrubbed in a stream of water with a rubber stopper. Alternate dipping and scrubbing is recommended to hasten the cleaning. It is essential to carry out blank determination to ascertain the amount of metal removed by the cleaning method itself (376).

Even if all necessary precautions are taken for corrosion testing and even if the testing is carried in identical conditions, it is known that, some variations in corrosion rates are always observed. These variations involve some random errors. Representative results can be obtained only if the number of observations are increased manifold. According to Humes, Passeno and Hayes (366) error of average decreases with increase in number of repetitions of specimens. Evans (377) suggests that all experiments should be carried out at least in duplicate. It becomes obvious that
when large variations in results are obtained the number of sets in the experiments should be invariably increased.

Materials

In the present investigation, corrosion of aluminium and its inhibition has been studied in a totally immersed condition. Aluminium alloy used was 36, 1⁄2 hard (22 SWG) in the form of sheets manufactured by Hindustan Aluminium Corporation, Mirzapur (U.P.). These sheets were purchased in a single lot and were of uniform composition and thickness. They were free from stains and scratches. The composition of the aluminium alloy as supplied by the manufacturer, was as under:

- Al - 97% (minimum)
- Mn - 1.0 - 1.5 (maximum)
- Fe - 0.75 (maximum)
- Cu - 0.15 (maximum)
- Si - 0.60 (maximum)
- Zn - 0.10 (maximum)

No further information could be obtained regarding the presence of other impurities by qualitative tests in the laboratory.

Specification on corrosion tests, in general, recommends that the dimensions of specimens should not be
less than $5 \times 2 \text{ cm}$ (373). Specimens of size $6 \times 3 \text{ cm}$ (thickness 22 SWG) with a small hole about 2 mm diameter, just near to the one end (3 cm side) of the specimen for suspension have been used.

Specimens were first rubbed with pumice powder and the final polishing was done using Jewller's rouge, 'Monak' the polishing materials (361). They were then degreased with sulphur free, double distilled carbon tetrachloride (379) dried, weighed, and kept in a desiccator. The specimens were suspended in a corning beaker by corning glass hooks and rods. Each specimen was suspended to the same depth of 1.5 cm below the surface of the liquid (380). The volume of the liquid for all the experiments was 250 ml. Only one specimen was suspended in each beaker. The beakers were placed in a double-walled, asbestos cupboard. The cupboard was insulated within and maintained at $32\pm2^\circ\text{C}$. Experiments were performed in triplicate. The level of the corrosive liquid in beakers was maintained by periodic addition of distilled water. For satisfactory assessment of corrosion it is necessary to remove the products of the corrosion from the surface of the specimen. At the same time, it is desirable to avoid, as far as possible, further attack on the metal during the cleaning of specimen by any method such
as (i) chemicals, (ii) electrochemical treatment or (iii) mechanical treatment. Friend (331) pointed out that mechanical removal of rust or any kind of film formed during corrosion test is the best method since it gives minimum error. It has, however, one drawback that it cannot remove completely the corrosion products from pits. It was found that use of concentrated nitric acid (A.R.) containing 5% chromic acid (E.M.) gave satisfactory results (382). The corroded specimens were dipped in the acid mixture for five minutes and, if needed, rubbed with a rubber bung attached to a glass rod. It was subsequently washed with distilled water followed by acetone and dried between filter papers and weighed.

Following systems have been employed for the studies:

In the present investigation the following systems have been studied:

1. Hydrochloric acid solutions (0.5, 1.2, 2 M) for two durations each (for 0.5 M HCl one and two days; for 1.2 M HCl 60 and 90 minutes; for 2.0 M HCl 15 and 30 minutes). The object of the two durations was to evaluate the efficiencies at comparatively longer duration; the object of using different concentration of HCl was to evaluate the efficiencies in different strength of the acid. While fixing the duration for a given acid, the main object was to get reasonably high corrosion losses at a given duration which may help in
evaluating the inhibitor efficiencies. In short, it was thought apt to have high corrosion rate and high inhibition efficiencies, if possible.

2. Sodium Hydroxide (0.1 and 0.5 M).

The durations of exposures for this solution were 2 and 6 hours.

3. Sodium Chloride

3% sodium chloride solution for 45 and 90 days durations.

4. Sodium Chloride and Sodium Bicarbonate Solutions

(1.5% NaCl + 1.5% NaHCO₃) for 45 days and 90 days. The main reason for selecting this particular composition was that this mixture has got a high tendency to develop pits for aluminium and a reasonably high corrosion rate.

5. Water (A typical natural water)

The natural water selected in this system is the hard water available in the campus of Gujarat University where the author is working. Its major components are sodium chloride, calcium bicarbonate, magnesium bicarbonate and sodium bicarbonate. Such hard water leads to very high corrosion rates for aluminium in slowly moving condition. It was at the instance of these studies that studies of system(4) were carried out separately.
Inhibitors

Following types of inhibitors have been studied in most of the systems mentioned above.

1. Proteins
2. Carbohydrates
3. Amino acids
4. Miscellaneous

Names of the inhibitors selected for the studies are given at the end of this chapter (pp. 75 ).

The main object of the present work was to study the colloids as inhibitors. As the composition of some of the colloids was available in literature, an attempt was made to study the effect of some of the components of the colloids individually. The selection of the component was mainly based on either the prices or availability from known and reliable sources. In some cases however, it was observed that these components were not forming apparently colloidal solutions in the concentration range in which they have been studied.

Regarding the concentration of inhibitors in the solutions, it was thought fit to maintain a uniform concentration of the compound, depending upon the nature of the studies as far as possible. In the case of slowly moving water it was not possible however, to have a definite percentage of the inhibitor in the solution as the inhibitor was gradually added to the flowing water in the form of a suspension from a burette.
In this case the concentration of the inhibitor was calculated on the basis of the total amount of the substances added to the total quantity of the water that was flown.

The following concentrations of the inhibitors were selected for general purpose:

(a) Hydrochloric acid and sodium hydroxide systems:
   0.1, 0.2, 0.5, 1.0 and 2.0%
(b) Sodium chloride and water:
   10, 20, 50, 100, 250 ppm
(c) NaCl + NaHCO₃ mixture:
   10, 50, 100, 150, 200 ppm.

In the case of hydrochloric acid and sodium hydroxide the object of the study was to find out the extent of inhibition. In the case of NaCl and NaHCO₃ and in tap water the object was to retard corrosion as well as to prevent the pitting of the specimens. The suspensions or 'solutions' of the inhibitors for study in the stagnant condition were prepared as follows. A definite quantity of the compound "inhibitor" was weighed on a watch glass and the compound was transferred to a beaker containing the corrosive medium and stirred. The specimens were dipped in the solutions so prepared. In some cases colloidal character was maintained throughout the course of the experiment. While in other
cases a part of the compound was found to have either settled at the bottom or floating at the surface of the solution.

**EXPERIMENTAL CONDITIONS**

The experimental conditions employed were as follows:

A. **Stagnant condition**

In stagnant condition, specimens were subjected to corrosive media with and without inhibitor, in 250 ml corning beakers maintained at a specific temperature. Specimens (3x6 cm) and (4x6 cm) were dipped into beakers for the desired duration. They were taken out, cleaned, dried and weighed.

B. **Slowly Moving Water**

In this system specimens were subjected to slowly moving water, the inhibitor solution being added continuously from a burette. Here, specimens were kept steady and the media was allowed to flow slowly. Specimens (4x8 cm) were completely immersed in a polyethylene tub (24x15x12 cm) using corning glass hooks. The water from the main tap was collected in a polyethylene container (capacity 500 litres) which acted as a reservoir of a constant level for eight similar systems. Water from the reservoir was allowed to
enter into one such system consisting of two polyethylene
tubs. Those two tubs (called A and B) were connected to
each other by a small glass tube. The water first entered
the tub A and left A at its top on the opposite side and
entered the bottom of second tub B through a glass tube.
Finally the water left tub B through a glass tube kept at the
top on the side opposite to the entry. It was then allowed
to drain away. In tub A blank coupons were kept, while in
tub B the coupons were exposed to water containing an
inhibitor. The inhibitor was added to water in tub B by the
following arrangement.

A 'solution' of known concentration of each
inhibitor was prepared in water. This solution of inhibitor
was transferred to a burette (100 ml). The solution was
prepared fresh every day. The solution was gradually added
to the water in tub, dropwise. The adjustment was such that
the solution entered directly the bottom of the tub. The
rate of flow of the solution was controlled so that a
definite quantity of the solution was regularly added to
the system in a definite interval. Photograph of the system
(side view) is shown in diagram \( \gamma \) on page 362A. The
polyethylene reservoir was able to feed eight such systems
simultaneously. Though the rate of flow of the water varied
somewhat from one system to another, yet it was almost
constant for a given system. The rate of flow of water was
measured every day and average rate was considered. Knowing the concentration of inhibitors in the solution (filled in burette) and its rate of flow and knowing the volume of water flowing in a system during definite interval, it was possible to calculate the concentration of inhibitor in a bulk of water in terms of ppm. The specimens were removed from the tubs after definite interval (i.e. 15, 30 and 45 days). The percentage of efficiency of inhibitors and wdd values, were calculated after cleaning and weighing the specimens.

6. Specimen moving system

Specimens were moved in the corrosive media with or without inhibitors. The modus operandi was as follows: (Diagram on page 406A)

Four aluminium rods (diameter 0.5 cm) were attached vertically downwards to a circular iron plate (diameter 16 cm and thickness 0.2 cm) with bolt through four holes in the plate drilled at equal distance from each other near the edge. These rods were covered with a polyethylene tube and sealed with glass rods at the open end to avoid direct contact with the solution. Four aluminium specimens were vertically fastened between the above rods. Each specimen was attached to two adjacent aluminium rods using thin nylon threads through small circular holes (diameter 2 mm)
drilled at the four corners of the specimen. The specimens were diagonally opposite and their faces were facing each other. The circular iron plate was rotated by a \( \frac{3}{8} \) h.p., electrically driven motor through an arrangement of pulleys and belts, the specimens being moved in the medium cutting the solution through edges. The specimens were completely immersed in six litres of test solutions kept in a polythene tub (capacity 10 litres), the total height of the solution above the upper edge of the specimen being approximately ten centimeters.

In one assembly, four circular iron discs (arranged in series) were rotated by the motor simultaneously so that the number of specimens that could be worked at a time was sixteen. No attempt was made to regulate the temperature. Two separate systems were assembled with 120 and 240 RPM. As the average distance of the plate from the centre was 5.5 cm, they gave a speed of 2490 m/hour in 120 RPM and 4980 m/hour in 240 RPM.

The concentration of the inhibitors was 0.1% for proteins, carbohydrates etc. and 10 ppm for amino acids, keeping in view the availability and economy of the inhibitors.

D. Exposure to moist - HCl vapours

In order to study the behaviour of the film, if formed, over the surface of the aluminium specimens in the
stagnant condition towards a corrosive vapour medium, the following experiment was carried out.

The plates were first immersed in water in 250 ml corning beakers containing 0.2 % inhibitor for a duration of one day. The plates were then removed from the beakers, air dried and placed in 250 ml empty beakers and these beakers were finally kept in a closed glass cup board.

Two beakers, one containing 250 ml hydrochloric acid (10 M) and the other containing 250 ml distilled water, were placed in all the four corners of the cup board. The relative humidity outside the cup board was 60-70%. An attempt was made to make the cup board air tight. The plates were removed from the cup board after one day and were cleaned, dried and weighed.

An experiment was also carried out in air tight desiccators. Immediately after the pretreatment, as mentioned above, plates were hung by means of a glass stand placed in the desiccator, containing 10 M HCl (100 ml) for the fixed duration. The plates were removed, cleaned by rubbing with rubber cork, dried and weighed.

GALVANOSTATIC STUDIES

Studies in polarization of cathode and anode is of great assistance in understanding the mechanism of corrosion and inhibition. It may give information regarding polarization characteristics of the corroding metals. The
steady state potential of the specimen is measured against a saturated calomel electrode, this being a potential of the corroding metal in the absence of an external source of emf. The potential of the corroding metal is made up of the potential of its cathodic and anodic areas. The passage of the current may lead to polarization which is due to slowing down of the processes at the cathode and/or the anode. The shift of the potential towards more cathodic value may indicate anodic polarization, while shift towards more anodic value may indicate cathodic polarization. However, interpretation of the results are rather difficult and it is more useful to measure the current density when the corroding metal is made, the anode or the cathode, when external emf., is applied. Fig. given on page 92A represents the system for measuring the potential of the corroding metal and Fig. given on page 92A represents the system to measure the shift in the potential when the corroding metal is made the: anode will be of similar type. The aluminium coupon used in the present studies had an effective area of 4 sq. cm (size 2 x 2 cm), the length of the handle being 4 cm. The handle as well as the back of the coupons was coated with purpex and wax. Polarization studies were made with aluminium coupon cathode or anode, the other electrode being of platinum of the same dimensions back
FIG. ARRANGEMENT OF APPARATUS FOR CATHODE POLARISATION MEASUREMENT.
and handle of this electrode was also coated with purpex and wax.

The galvanostatic studies of corrosion of aluminium were made with and without the inhibitor in 100 ml Corning beaker containing corrosive medium. The external current was supplied from a storage battery (90 V. Eveready Battery No. 701) and the change in potential was noted by making aluminium coupon either anode or cathode on a D.C. microvolt meter (Philips India GM 6021) against a saturated calomel electrode. Attempts were made to minimize liquid junction potential by keeping the tip of the salt bridge very near to the metal surface.

Remarks

Most of the chemicals used in the investigation were of A.R. quality. The organic compounds were of C.P. grade. Some of the chemicals including amino acids were supplied by Delhi University (India). The concentration of the inhibitor expressed in the text indicates gram of the substance added per 100 ml of the corrosive solution. Most of the inhibitors used were colloidal in nature, so it was difficult to prepare a clear solution. The chemicals were added to the solutions by weighing for individual compounds. Distilled water was used for the preparation of the solutions.

The weights were taken on a metler one pan balance, M5 type. Corrosion loss is expressed as (i) loss in milligrams
(mg), (ii) loss in milligrams per decimeter square (mg/dm²),
(iii) loss in milligrams per decimeter square per day (mdd)
The reproducibility of percentage inhibition is ±2%

**Scope of the present work**

Extensive data is available in literature on the inhibition of corrosion of ferrous metals, more particularly of mild steels. The inhibition studies of non-ferrous materials are comparatively much less. The inhibitors employed are mostly organic compounds having a polar group containing nitrogen (e.g., amines) or sulphur (e.g. thiourea derivatives) as key atom. Among the non-ferrous materials, copper and its alloys (usually brasses) have occupied a prominent position in such studies.

Aluminium is one of the most widely employed material in most of the industries now a days because of its numerous favourable properties and is fast replacing the older equipments in some of the industries. In the domestic field, in India, aluminium has substantially replaced brass and copper vessels and is the most popular metal with middle income and poor income groups of people. It is extensively used for storing water and for cooking food. Due to variety of its uses, an attempt has been made in the present investigation to study the corrosion characteristics of the commercially available aluminium alloy (35 Al ½ hard, 22 S.W.G.) in the commonly employed media viz. hydrochloric
acid solutions and natural water (hard water available in the campus of the Gujarat University where the author is working). The inhibitors studied are those which have been seldom selected for inhibition purposes. Most of them are colloids in character. Majority of them are safe to handle, easily available, least or nearly non-toxic and, some of them, are quite cheap.

Following inhibitors have been studied in most of the systems, already mentioned:

1. **Proteins**:- Gelatine, Casein, Haemoglobin, Egg Albumin, Yeast, and Liver Extract.

2. **Carbohydrates**:- Agar Agar, Dextrin, Maltose, Dextrose agar, Malt agar, Cellulose, Carboxymethylcellulose, (C.M.C.), Plantago ovata Forsk (Isabagul), Gum tragacanth, Gum acacia, Dextrose (D-glucose), Starch.


4. **Miscellaneous**:- Calcium lignosulfonate, Ferrochromligno-
sulphonic acid, Tannic acid, Kaolin, Urotropin and Sodium thioglycollate.