CHAPTER II

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Corrosion consists of reactions between a metal and its environment, and thus corrosion depends both on the metal and environment to which it is exposed. It is, therefore, necessary to consider and control factors associated with both the phases for the establishment of satisfactory exposure conditions during a corrosion test. It is, thus, obvious that there is no universal standard test procedure.

The following literature provides a review of the generally accepted corrosion testing procedures and is presented to provide a basis for the methods employed in this investigation.

Jelinek(1) and Bärgmann(2) summarized the major methods for measuring the amount and intensity of corrosion as well as certain qualitative aids in determining the amount of corrosion. Both of them point out that the use of two or more methods will remove many of the criticisms given for the individual methods. A brief description of individual methods outlining the fields of usefulness and the major advantages and limitations follows:
Visual observation may be useful to detect the occurrence of attack and for identifying its general nature. This method is simple and valuable in conjunction with other methods. It is subject, however, to human error and is qualitative.

Loss in weight is useful to determine the extent and rate of uniform corrosion. It is simple, quantitative and direct. The method is subject to error of incomplete removal of corrosion products and loss of uncorroded metal. Special types of attacks are not measured and multiple specimens are necessary.

Gain in weight is useful to determine the extent and rate of uniform corrosion, where no loss of corrosion products occurs. The method is applicable to indoor atmosphere corrosion and high temperature corrosion studies. In this method, error due to improper removal of corrosion products is eliminated. An analysis of corrosion products is, however, essential to determine the loss of metal. Moisture in corrosion products may vary and, thus, influence the results. Special types of attack are not measured by this method.

Electrical resistance change can be used in gaseous or poorly conducting environments or in other environments if the specimen is removed for measurement. In addition to its usefulness in evaluating environment
corrosivity, it can be used to follow certain property and composition changes, and the method is non-destructive and adaptable to continuous measurement. However, the method is indirect, requires calibration, does not distinguish between types of attack, is subject to surface-to-volume errors, and if small wires are employed, the attack may be different in amount from that on a more massive specimen.

Hydrogen evolution may be followed for tests in which corrosion takes place solely with hydrogen evolution. The method is adaptable to rate measurement, but does not determine the distribution of attack.

Measurement of oxygen absorption is useful in tests where corrosion takes place mainly with the absorption of oxygen. The method is adaptable to rate measurement, but does not determine the distribution of attack, and an analysis of corrosion products is required for metals capable of existing in more than one ionic states.

Depth of pitting measurements (other than microscopic) are useful for tests made to determine the service ability of metals as containers of fluids. This method is used in conjunction with methods of determining total attack, and it gives a correct measure of penetration of a metal by corrosion except when the
corrosion is intergranular. Multiple specimens are required to determine time-penetration curves.

Microscopic methods are useful to determine the kind of attack, to measure the depth of pits, and to determine the constituents of the metal that are specially capable of initial attack. This method is excellent to supplement other measures, but is not generally useful in making quantitative measurements.

Changes in physical properties, such as tensile strength, ductility, resistance and hardness of metals can be used to evaluate their deterioration. It is not possible, however, to evaluate the damage resulting from each type of attack separately by this method.

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.

Single electrode potential methods are useful to study film formation and breakdown at a metal surface. The method distinguishes between anodic and cathodic control, and measures the electrochemical driving force however, it does not measure the extent or rate of attack.
Shorted cell current measurement is useful to measure the extent or corrosion relative to a standard noble metal. An arbitrary choice of a cathode metal may distort the normal influence of such areas on the metal under study. The anode and cathode are separated by a much greater distance than usual, hence resistance of solution and unnatural formation of corrosion products are the sources of error.

Anode and cathode polarization methods are useful to study galvanic and concentration cell corrosion and to determine the total polarization current. The method does not measure the distribution of attack.

Film resistance may be used to determine the penetrability of surface films by various anions.

The electrometric method is useful to measure the thickness of surface films. This method is only useful on adherent, thin, surface films of some metals.

Optical methods are useful to study the growth of tarnish and other surface films.

It was decided from the above information that the weight loss, visual observation, electrode potential, and polarization methods would be used for the present investigation. The weight loss method facilitates a simple, direct, quantitative measure of the extent and
rate of corrosion. The visual observation method is simple and of value in conjunction with other methods, is useful to detect the occurrence of attack and identify its general nature. The principal limitations of weight loss method are that multiple specimens are required and caution need be exercised in development of a treatment to remove corrosion products.

Evens(3) points out that in wet corrosion, the measure of attack is often the loss of weight after exposure. Fontana(4) also states that change in weight of the specimens is most often used as a measure of corrosion. Champion(5) also points out that the gravi-metric method is normally used for determining the metal remaining after corrosion.

Champion(5), Börgmann(2) and Speller(6) present a comprehensive discussion of general corrosion testing procedures. They discuss the general procedures to be followed in total immersion corrosion tests. The American Society for Testing Materials(7) ("ASTM") presents specific detailed test procedures for use to evaluate a number of corrosion problems.

A review of factors pertaining to the metal, corrosive media, exposure conditions and assessment of effects on the metal and media important in corrosion studies follows:
FACTORS PERTAINING TO METAL

Factors pertaining to the metal are - selection of the specimens, size and shape of specimens, replication and number of immersion periods, preparation of specimens, and cleaning of the specimens after corrosion. Champion(8) points out that test specimens should be representative of the material under test. He further states that rolled products are widely used because they provide the following advantages:

(a) They are most extensively used in service.
(b) A wide range of thicknesses can be obtained.
(c) Major variations in corrosion resistance over the surface of a rolled sheet are unusual.
(d) Sheets of large surface area can be obtained, thus, permitting the preparation of a large number of replicate specimens.
(e) Relatively simple methods of preparation of the specimens from the sheet can be employed.

The 'ASTM', in discussing test specimens and their preparation, states that the shape and size of specimens will vary with the purpose of the test, the nature of the materials to be tested, and the testing apparatus to be used. The size may also be limited by the necessity of preserving a proper ratio between the area of the specimen and the volume of the testing solution.
when the latter must be limited. In general, an effort should be made to have the ratio of surface to mass large and that of edge area to total area small. The shape and dimensions of the specimens shall be such as to permit weighing on an accurate balance and to facilitate accurate measurement and calculation of the area of each specimen.

Champion(9) and Knapp(10) point out that the size and area chosen are often determined by experimental convenience, but, that it is desirable to adopt a standard size as far as possible to insure that comparable results will be obtained. According to them, it is advantageous to adopt a size and shape of specimen giving a low edge to surface area ratio and a reasonably large area. Champion(9) states that thickness of 0.036 in. is convenient for many purposes. He also states that the German specification on corrosion tests, in general, recommends that the dimensions should not be less than 5 x 2 cm.

Fontana(4) states that the original area is used to calculate the corrosion rate throughout the test. If the dimensions of the specimen change appreciably during the test, the error introduced is not important because the material is, probably, corroding at too fast a rate for its practical use.
Borgmann (2) points out that it is not to be expected that absolute reproducibility will be achieved because there are factors beyond the control of the experimenter. However, statistical control is often achieved. The absolute error of measurement can be reduced only by increasing the number of specimens tested. The reproducibility of the results depend upon the type of attack. The reproducibility will be much greater if the attack is uniform than when it is localised.

Evans (11) points out that, in general, it is well to perform all experiments in duplicate or triplicate. He says that in the case of localised attack, this will not be adequate for good reproducibility.

Champion (12) recommends a minimum of three replicates. He also points out that when it is known that the corrosion rate is constant from the beginning of exposure, a single replicate set of specimens will be adequate. With non-linear corrosion time curves, further replicates are necessary, and when the shape of the corrosion time curve is not known, it is suggested that at least three replicate sets should be exposed for withdrawal after increasing periods of time. The degree of replication to be adopted, however, depends on the accuracy required in the mean result and the scatter which is to be expected in the individual results.
An 'ASTM'(7) method, which describes procedures for carrying out total immersion corrosion tests, discusses the problem of determining the number of specimens to be used from a statistical approach. They state that, observations on some typical metals immersed under controlled conditions in typical corrosive media have indicated that the coefficient of variation may reasonably be expected to be less than 7%. They refer to the work of Humes, Passano, and Hayes(13) when presenting their statistical procedures. They state that, E. error of average in $\% = \frac{2V'}{N}$ where, $Z = 1.96$ for a statistical probability, P, of 0.95; $V'$ = Universe coefficient of variation of 7%, and N the number of repetitions of specimens. Thus, the expected errors of the average of different number of the specimens would be $N = 8$, $E = \pm 4.8\%$ and $N = 4$, $E = \pm 6\%$ $N = 2$, $E = \pm 9.7\%$. It was stated that, running total immersion tests in quadruplicate would make it highly probable that the average would be within 7% of the true average and this should be satisfactory for most corrosion research programmes.

Care must be taken to properly clean and prepare specimens for corrosion tests. The surface preparation will vary with the type of test. Surface preparation usually consists of a pre-cleaning or degreasing operation to remove surface contamination. A pickling process may be required to remove scale.
There is a strong opinion, in certain groups of workers, that the surface of the test specimen should be identical with the surface of the actual equipment to be used in the plant. This is, however, an impossible condition, because the surface of commercial metals and alloys vary as produced and as fabricated. The degree of scaling on the equipment varies and also the condition of other surface contaminants. Moreover, the determination of the corrosion resistance of the metal or alloy itself is of prime importance. In most cases, a clean metal surface is generally used. A standard surface condition is also desirable in order to facilitate comparison with results of others.

Champion (13) states that extremely thin, invisible films of grease can interfere with the corrosion process. Evans (14), Jelinek (1), 'ASTM' (7), Knapp (10) and Mayer (15) also note the importance of removal of grease and other surface contaminants.

Champion and Meyer (15) discuss, in considerable detail, the general methods for metal pre-cleaning and degreasing. The solvent and vapour cleaning methods are: simple solvent cleaning, emulsifiable solvent cleaning and vapour degreasing.

Evans (10), Jelinek (1), Champion (17) and Speller (18) point out that in tests where corrosion is
assessed by weight loss, it is necessary to remove the corrosion products from the specimen after exposure. It is necessary that the specimens be thoroughly cleaned of all corrosion products without loss of any base metal. In the literature, there are many satisfactory methods of cleaning specimens, but, whatever be the method, its effect in removing base metal should be determined for the metal under investigation. Drastic methods are unsuited where there are indications of only a small weight loss resulting from corrosion.

Champion (17) discusses, in detail, the general methods for corrosion products removal from metal specimens. The various methods are: mechanical treatment such as wet scrubbing with a bristle brush, abrasive and detergent. Chemical treatments using various chemical reagents are often employed, but are generally specific for certain materials. Cathodic cleaning has been found useful with a large number of metals and alloys, but there is a possibility of deposition of metal from dissolved corrosion products or contaminants in the solution may occur.

Champion (19) observes that sulphuric acid is an appropriate solvent for the corrosion products of copper and its alloys and attacks the metal less than the other mineral acids. Concentrations of 5.0% and 10.0% are recommended.
The corrosion medium is another important factor in corrosion. Champion (20) presents a general discussion of corrosion media based on the literature. The 'ASTM'(7) points out that test solution be made up accurately, with the composition controlled to the fullest extent possible and the composition of the test solution should be checked by analysis.

FACTORS PERTAINING TO EXPOSURE CONDITIONS

Wesley (21) states that, perhaps the most common danger of mistaken interpretation of laboratory immersion test results from exhaustion of ingredients in the original solution which control the rate or type of attack, or from accumulation of products, which are corrosion inhibitors or accelerators. This emphasizes the importance of volume of solution per area of specimen and adequate replenishment of solutions. Included in the following table are some of the recommended ratios for volume of solution per square centimeter of metal surface:

<table>
<thead>
<tr>
<th>Source</th>
<th>Volume per square centimeter</th>
<th>Surface area per 500 millimeter</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Corrosion&quot;(22)</td>
<td>50.0 ml</td>
<td>10.0 cm²</td>
</tr>
<tr>
<td>Wesley(23)</td>
<td>40.0 ml</td>
<td>12.5 cm²</td>
</tr>
<tr>
<td>Champion(24)</td>
<td>33.3 ml</td>
<td>15.0 cm²</td>
</tr>
<tr>
<td>Calcott et al(25)</td>
<td>8.3 ml</td>
<td>60.0 cm²</td>
</tr>
<tr>
<td>'ASTM'(7)</td>
<td>6.7 ml</td>
<td>75.0 cm²</td>
</tr>
</tbody>
</table>
Champion pointed out that the volume of solution recommended per square centimeter of metal surface varied from 6 ml to 40 ml. The important point to be noted is that the volume of the testing solution should be large enough to avoid any appreciable change in its corrosiveness through the exhaustion of corrosive constituents or the accumulation of corrosion products that might affect further corrosion.

Wesley(23) and 'ASTM'(7) suggest that each specimen should be tested in a separate container because it has been found that the practice of testing several specimens of the same material in a single container gives results which do not measure the true variability of the test as determined by repeated separate tests. In addition, containers and specimen supports should be used which do not affect the corrosion process.

Temperature control of the corrosive media is another important factor to be considered. Champion(26) suggests that temperature control to ± 0.5°C is often regarded as adequate for many corrosion tests. Wesley(23) and 'ASTM'(7) point out that thermostatic control at the desired temperature, ± 1°C is usually considered satisfactory.

An important consideration in any corrosion test is its duration and the number and length of exposure period to be employed.
Speller(27) remarks that, in general, the initial rate of corrosion is much greater than after the action has proceeded for sometime. He states that, as for example, the initial corrosion rate of iron in alkaline solutions is several times greater than the rate after a few hours. He mentions, further, that the initial rate of corrosion is dependent to a large extent upon the character of the corrosion product deposited on the metallic surface and that this should be determined for a specific case. Thus, it is likely that the results of short-time tests may be misleading. It is advisable in all cases that the length of test should be determined by the length of time required to produce a reasonable amount of corrosion.

Wesley(23) states that a constant rate of corrosion is encountered frequently in total immersion tests. He states, further, that if the test is too short, some materials which build-up protective corrosion product films slowly may be ruled out as unsatisfactory, and if the test is too long, the effects of exhaustion of ingredients or accumulation of corrosion products may be pronounced.

According to 'ASTM', the duration of the corrosion test will be determined by its nature and purpose. According to them, it is desirable to expose a number of specimens so that certain of them can be removed after
definite intervals so as to provide a measure of change of corrosion rate with time. When removal of solid corrosion products is essential, the same specimens will not measure accurately normal changes of corrosion with time because the effect of corrosion products on subsequent corrosion is not evaluated. They also suggest that higher the rate of corrosion, the shorter may be the testing period.

The next important phase is assessment of corrosion. Champion has reviewed and discussed the assessment of corrosion effects on metal and media. He includes considerable information on quantitative and qualitative assessment by gravimetric and microscopic methods respectively. Champion points out that the analytical balance available in most laboratories provide adequate accuracy for many corrosion tests and that this general availability of suitable apparatus is, no doubt, largely responsible for the extensive use of gravimetric methods for the quantitative assessment of corrosion. He mentions that determinations of loss of weight can be used over a much wider range of conditions that gain in weight; although, the accuracy may be lower when cleaning of the specimen after exposure is necessary.

Fontana(4) points out that in many cases, visual observation of the specimens on removal from the test
solution provides valuable information concerning the mechanism of the corrosion involved.

Champion (28) points out that in microscopic examination, it is often useful to examine the corroded metal in two stages: first with the corrosion products still adhering to the metal, and again after removal of the corrosion products.

METHODS OF STUDYING THE ACTION OF INHIBITORS

In order to measure the effect of inhibitors, the weight loss of a metal specimen should be measured. It is essential to know the action of the inhibitor for very short and long durations. Electrochemical method is suitable theoretically but sometimes, the data is not concurrent with those obtained by long immersion tests.

The knowledge of relation between corrosion potential and time is essential in ascertaining the effect of inhibitors. The shift of potential towards noble potential with time generally signifies the adsorption of the inhibitor, or the formation of the protective film. As the measurements can be made without disturbing the natural state of corrosion, this method is very important. However, in the case of unknown polarization characteristics, results should be treated carefully. The relation between the electrode potential and current is
useful for evaluating the unknown corrosion system and to calculate the efficiency of the inhibitor.

In galvanostatic method, the stationary potential is measured under a constant current between the specimen and auxiliary electrode. This method can be used as the best method for evaluating the efficiency of the inhibitor. However, the violent change which occurs in the transition from active state to passive state due to the circuit characteristic cannot be followed by this method(31). In galvanostatic method, the potential is measured as the sum of polarization resistance of overvoltage and inner resistance derived from bath and apparatus. In the case of high reaction rate, it is not possible to measure absolutely the change of overvoltage, which is a weak point of galvanostatic method(31).

In the potentiostatic method, the inner resistance in the circuit is reduced and exact polarization curves can be measured. Even by a small potential change, a strong current change is observed and the potential is devised to keep at a certain value. This method is very useful in investigating the films made by inhibitors(32).

In pulsepolarizer(33), the potential change of metal with time under very high current density is measured oscillographically.
In the null-bridge process (34), polarization values of each electrode under a constant current and film resistance of each electrode can be measured. The resistance change of each electrode can be measured independently by this method.

The efficiency of inhibitors can also be measured by A.C. impedance (35). However, natural corrosion cannot be studied by this method as direct current is not used.

Cell current-time curve method (36) is very simple but as both the electrodes change by the corrosion conditions, and the reaction velocity of polarization is not constant, the results obtained by such a short time test should be carefully treated.

**EXPERIMENTAL PROCEDURES**

Rectangular specimens of area 6 cm x 3 cm (thickness 28 S.W.G.) with a small hole of about 2 mm diameter just near the one end (3 cm side end) of the specimen for suspension have been used.

A specimen of the metal was first washed with distilled water several times and dried. It was then polished using successively '0' to '0000' oakley emery papers. The final polishing was done using jeweller rouge which gave a mirror like finish. The specimen
was finally degreased by immersion in A.R. Carbon-tetrachloride (sulphur free). A small piece of the polished specimen was utilised for the determination of copper and zinc in the alloy by standard methods (37, 38). The specimens were suspended by Pyrex glass hooks. Each specimen was suspended to the same depth of 1.5 cm below the surface of the liquid (29). The volume of the liquid for all the experiments was 230 ml. Only one specimen was suspended in each container which was a Pyrex beaker of 250 ml capacity. Triplicate experiments were performed. In long duration tests, the level of the corrosive liquid was maintained by periodic addition of distilled water. Experiments were conducted at 35 ± 0.1°C. For the satisfactory assessment of corrosion, it is necessary to remove corrosion products from the specimen; at the same time, it is essential to avoid further attack on metal during cleaning process. It was observed that for this purpose 5% sulphuric acid was satisfactory. Rajagopalan (30) et al. have suggested the use of citric acid - sulfamic acid mixture in presence of thiourea and saponin for removal of corrosion products from metal surfaces.

DETERMINATION OF COPPER AND ZINC

Copper was determined iodometrically (37) and zinc was determined volumetrically using 8-quinolinol (38).
Potential and Polarization Measurement

For potential and polarization studies, the metal coupon was of a circular design, diameter 2.902 cm, with a handle 3 cm long and 0.5 cm wide. The handle, as well as, the back of the coupon were covered with perspex leaving only a circular portion of apparent surface area $6.156 \text{ cm}^2$ exposed. The other electrode was platinum of the same dimension. For these measurements, H-type Pyrex glass cell with porous partition to separate the two compartments was used. It also contained a built-in capillary to make connection to the reference saturated calomel electrode. In each compartment the volume of the corrosive medium was 80 ml.

All the chemicals used in the investigation were of A.R. quality. Distilled water was used throughout the work. All the volumetric apparatus like the burette, the pipette etc., were of standard quality and calibrated before use. The weights were taken on a Metler balance, M5 type.

Scope of the Work

Studies on metallic corrosion and its inhibition have been concentrated more on ferrous metals as compared to non-ferrous metals. Further, detailed studies of an academic character which are essential in order to obtain
the necessary background information are lacking in literature for many systems. Apart from the practical importance of the corrosion inhibition data in the field of corrosion prevention, they are also useful in the interpretation of the mechanism of the corrosion inhibition.

Detailed investigations on the inhibition of the corrosion of brass in nitric acid, sodium hydroxide, and potassium persulphate solutions were undertaken with a view to study the effect of variables on corrosion rates, inhibitor efficiencies and cathode as well as anode polarizations as well as to observe whether any correlation occurs between the molecular structure of inhibitors and their protective action. The optimum conditions for satisfactory retardation of corrosion have been established.
FIG. NO. 21 ARRANGEMENT OF APPARATUS FOR CATHODE POLARISATION MEASUREMENT.
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