CORROSION EVALUATION AND MONITORING PRACTICES

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Corrosion tests are aimed at to evaluate and select suitable materials for process, evaluation of corrosivity of environment, and to check the effectiveness of the applied corrosion control measures. These tests may be performed in laboratory, in actual process plant, or in the field such as atmosphere tests. The laboratory tests are generally carried out using small specimens, small volume of solution (simulated synthetic or from actual process). These are useful and economic to screen out the most useful or useless materials for the process or to test further in plant environment. The actual in-plant test needs plant availability for the desired test and may take certain time and cost. There are several methods being used for evaluating corrosion. Laboratory test methods may be categorized as an electrochemical, which are based on the measurements of current evolves from electrochemical reactions, while non-electrochemical techniques are based on the overall weight lost by the specimen or surface features due to corrosion such as pit, crevice, crack or microstructural changes appeared after the test. However, for choosing appropriate method one needs to know about the type of corrosion against which resistance of materials is being sought. For instances, to determine the thinning rate of a steel pipe, methodologies for general/uniform corrosion such as weight loss, polarization resistance etc. will be more useful than the others. The knowledge of a parameter of concern that defines the resistance of materials against specific form of corrosion is also important. For example, pitting and protection potentials (obtained in electrochemical experiments) are characteristic features (parameters of concern) to illustrate the pitting susceptibility of any passivating alloy in a corrosive environment. Several methods being practiced to evaluate different types of corrosion are discussed in forthcoming sections.

GENERAL/ UNIFORM CORROSION

A most common form of corrosion is uniform or general corrosion. The electrochemical reactions occur uniformly over the large surface exposed to corrosive environment and results in thinning of the component. For instance, steel or zinc exposed to the dilute sulfuric acid. This form of corrosion can be accurately predictable by laboratory or in-plants tests. Various methods (standard or routine) can be used to evaluate general corrosion; a few such techniques are briefly discussed below:

Weight Loss Test

The weight-loss tests provide data on the resistance of materials against uniform corrosion and should not be used for predicting localized attack. One need to choose the corrosion test method judiciously, for instance, this method may be an unsuitable choice if

selected to asses the resistance localized corrosion. The latter results into the formation of minute pinholes on the surface that often lead to failure (perforation and leakage) while showing insignificant weight loss. The data from uniform corrosion may be converted to express the corrosion rate in units of mils per year (mpy) or as millimetres per year (mm/y), etc. in metric units. The test includes specimen preparation [1] (polishing, cleaning, and degreasing) followed by the dimensional measurements, weighing, and identification of each specimen (by marking or tagging the specimen) before exposure for the test. The surface finish of coupons should be nearly the equipment or component in service.

The size of test coupons should be large enough to give significant mass loss but should be able to fit into the test chamber. The volume of test solution shall be measured based on the area of coupon and should also be able to immerse the entire specimen surface. The exposure time of the coupons shall be planned in a way that the resolvable weight loss is obtained. The material having high corrosion resistance should be exposed for significantly long time for obtaining measurable mass loss. Several materials corrode rapidly in the early stages of exposure to an environment (prior passive film formed) and thereafter corrode at a much lower rate. The extrapolation of corrosion rate, based on the results obtained in short durational test, for longer time will be very conservative and should be avoided. It is always good to design the test for different time periods.

After completion of the test period, corrosion products on the specimen surface is cleaned mechanically such as by abrasive blasting, brushing, or by chemically (preferably added with inhibitor), or electrolytic methods. Any corrosion product left on the surface may cause errors in the final results. The cleaning method itself may produce material loss of the base substrate. Such errors in mass loss may be overcome by subjecting the fresh coupon for cleaning in a number of cycles. After completion of the test, the corrosion rate may be calculated from the mass loss as follows:

$$\text{Corrosion Rate} = (K \times W) / (A \times T \times D)$$

Where

K = Constant

T = time of exposure, h,

A = area, cm^2

W = mass loss, g, and

D = density, g/ cm^3 (D for steels and stainless steels ~7.9 g/cm^3,

for copper 8.9 g/cm^3 for aluminum ~2.7g/cm^3).

K = 3.45 x 10^6 for a corrosion rate in mpy.

Other constants include K= 8.76 x 10^4 for a corrosion rate in mm/y.

Refer to ASTM G1 for a complete listing of constants.

Salt (fog) Spray

Salt spray test is an accelerated corrosion test methodology in a controlled environment. This is most often used to evaluate the effectiveness of coatings or paints or to rank the various alloys developed for specific corrosive environment. This requires a fog chamber, a reservoir, air supply system, spray nozzles and specimen support. The salt solution may be prepared from 5% sodium chloride solution with pH in the range 6.5-7.2

and the exposure chamber should be maintained at 35°C. The time device may be attached to the cabinet for intermittent spraying of the solution. The exposure period is generally agreed between the customer and vendor and is advised in multiples of 24 hours. The detailed methodology is given in the ASTM B117-03.[2] The environmental conditions may be varied according to the requirements. In a modified salt spray test methods given in ASTM G85-02 [3], several environments and test parameters have been suggested. These includes acetic acid salt spray test which is sodium chloride solution pH: 3.1 – 3.3 added with glacial acetic acid. The salt fog is sprayed continuously for 16-240 hours. The similar solution, in a different test procedure, may be sprayed in various cycles with intermittent drying and humidifying rather than continuous spraying (3/4h spray, 2h dry air purging, and 3-1/4h soak at high humidity). The temperature of cabinet should be around 49±1.1°C. The synthetic sea salt solution (42 g / litre) is used with periodic sulphur dioxide (SO_2) gas (at flow rate $1 cm^3/min.ft^3$) in another test method. The specimens during and after completion of the tests are observed and compared for the time at which rust begins to appear, surface coverage by the rust, pits/ crevice, weight loss etc.

Atmospheric Corrosion

Corrosion resistance of newly developed alloy, paints and coatings can be evaluated worldwide by conducting the atmospheric corrosion test. For atmospheric corrosion, selection of exposure sites are important which may be defined as rural, marine, and industrial. Corrosion in atmosphere mainly depends upon the temperature, humidity, rainfall, wind speed and direction, chemical species, and solid contents in the air. Rural atmospheres are least corrosive among all; industrial atmosphere contains various pollutants and corrosive gases such as sulfur containing gases/ compounds, CO_2, NO_x, H_2S, and condensate with low pH that increase the corrosion rate. The marine atmosphere is generally the most severe one. It contains chloride ions and high humidity. The corrosion rate further depends upon the distance from the sea.

The test includes test coupons and test panels to fix the specimens on the exposure site. The coupon size should be sufficiently large to result into significant weight loss. Commonly used specimen size may be 4 x 6 inch or mutually agreed between vendor and customer. The identification of specimens needs to be carefully maintained to avoid any error in the test findings. The concentration and presence of corrosives such as sulfur compounds, Cl-, humidity, rainfall, temperature etc. record at definite time interval will be useful to correlate and describe the corrosion rate variations. Cleaning of the specimens after exposure can be performed as per the ASTM G1 and corrosion rate may be determined as discussed earlier under weight loss section. The detailed test method may be seen from the ASTM G 50 & 104 [4,5].

LOCALIZED CORROSION

Most often premature and catastrophic failure of engineering components occurs due to localised corrosion such as pitting, crevice, intergranular and intergranular stress corrosion cracking (IGSCC), SCC, hydrogen assisted damage etc. During localised corrosion, the large surface of materials remained unattacked, however, only specific locations are attacked at a

relatively higher rate. The test method must be selected depending upon the type of localised corrosion anticipated from the specific material-environment combination.

Pitting and Crevice Corrosion

Pitting corrosion generally appears in the form of small pinholes, sometimes deep across the thickness of coupon. The area of pits is extremely small as compared to the surface of the specimen. Once the pit formation initiates, the solution chemistry inside it alters to be extremely corrosive as compared to the bulk solution. Presence of certain anions such as chloride, thiosulphate etc. are responsible for this form of corrosion. The crevice corrosion generally occurs under the shielded/ occluded regions such as bolted assembly, under the deposits, gaskets etc. The pits or crevices often become the preferable site for several other types such as SCC, corrosion fatigue, fretting fatigue etc. These forms of corrosion can be evaluated by electrochemical as well as by non-electrochemical techniques described in following sections.

Pitting Tests [6,7]

To rank various stainless steels against pitting corrosion in oxidizing chloride media can be simulated by ferric chloride test. This test method is primarily intended to generate the environment close to that observed inside the pits. This method includes the exposure of polished (followed by weighing) coupons of the size 25 x 50 mm in ferric chloride solution (volume roughly around 5 ml /cm^2) at an ambient or 50°C temperature. For coupons larger than the prescribed size, 5 ml/cm^2 of ferric chloride solution should be added. Experimental solution is prepared by dissolving 100g reagent grade $FeCl_3.6H_2O$ in 900 ml reagent water (10% $FeCl_3$ solution). After exposure for about 24–72 hours, clean (by including ultrasonic cleaner) the specimens for pitting details such as maximum pit depth, pit density, and average pit depth. Coupons should be weighed to obtain the mass-loss for corrosion rate analysis. Recommended temperatures for evaluation are 22 ± 2°C and 50 ± 2°C.

Crevice Tests

Crevice corrosion test needs crevice block assembly with 'O' rings. The two TFE-fluorocarbon blocks are fastened on the two sides of test specimen with O-rings or rubber bands. Finger or hand contact to surfaces during handling should be avoided. The specimen fastened with crevice block may be placed in the solution as described for pitting in earlier section. After reasonable test period (24-72 h), specimens may be inspected for the crevice attack under the contact point O-ring or rubber bands and under both TFE-fluorocarbon blocks. After the test is over, the specimen may be cleaned for weight loss and pit analysis under creviced or occluded locations.

Critical Pitting Temperature (CPT)

Tests can be carried out for obtaining the minimum temperature at which pitting will be initiated. The solution for this test is more acidic and prepared by adding about 1% HCl to 6-7 wt% ferric chloride in reagent water. The apparatus need to have condenser to test at

increasing temperature. This will prevent the decrease in solution level by evaporating. The start temperature may be obtained from the following formula

$$CPT \ (°C) = (2.5 \times \% \ Cr) + (7.6 \times \% \ Mo) - (31.9 \times \% \ N) - 41.0$$

Maintaining temperatures within ± 1°C, and test temperature may be increased at intervals of 5°C. The suggested temperature range for the test is between 0 to 85°C and test period is 24 hours. After the completion of experiment, check for the pit depth; if pit depth is 0.025 mm or higher then pitting corrosion is established. If pit depth is below this, the experiment should be repeated at a temperature higher by 5°C. If pitting depth greater than 0.025 mm is present, the experiment may be repeated at a temperature lower than the earlier.

Critical Crevice Temperature (CCT)

The critical crevice temperature (CCT) may be determined in similar solution and test conditions as for CPT. The multiple crevice assemblies (MCA) with a fastener of Alloy 276 is used for crevice formation. The starting temperature may be obtained by using following formula

$$CCT \ (°C) = (3.2 \ x \ \% \ Cr) + (7.6 \ x \ \% Mo) + (10.5 \ \% Nb) - 81.0$$

The analysis of pit rating can be made in terms of pit depth, density and size as per the standard chart given in ASTM G 46 - 94. The pitting can also be represented as 'Pitting Factor' which is the ratio of deepest pit to the average pit depth on the open surface or under crevice surface. Pitting factor of one indicates general corrosion.

Intergranular Corrosion (IGC) [8]

Corrosion propagate along the grain boundary in preference to the grain matrix in several environment-material combination and is called intergranular corrosion. This weakens the grain boundaries and reduces the overall strength of materials. The IGC is prevalent in sensitized stainless steels structures. Sensitization process, which results from the exposure of stainless steels to the temperature range of 500-750°C, is precipitation of carbides and depletion of the chromium from nearby grain boundaries. This reduces the corrosion resistance of grain boundary in several corrosive environments. Various test methods are available to detect the susceptibility of the stainless steels and nickel-based alloys to intergranular corrosion (IGC) and are described below [8]

Oxalic Acid Etch

The oxalic acid etching is a rapid test method used to screen out specimens which are free from intergranular corrosion susceptibility. This test method also serves as a basis for specimens to go for other test as prescribed in this standard, however, rejection of materials cannot be made based on this test. Solution is prepared by adding 10% oxalic acid (AR grade $H_2C_2O_4.2H_2O$) chemical in distilled water (dissolve 100 g oxalic acid in 900 ml distilled water). A carefully polished (from coarse 80 or 120 grit to 4/0 emery paper or finer) and degreased specimen preferably 1 cm² area is exposed to the solution. The

specimen should be etched at a current density of $1A/cm^2$ for 90s. The current may be accurately applied by using a battery or rectifier that can deliver desired current density. The temperature of solution increases with etching cycles that should be restricted below 50°C. Fresh solution is preferred for every etching cycle. Post etch structures are categorized as step, dual, and ditch as shown in Fig 1. These correspond to no grain boundary attack (only steps are visible); slight or discontinuous grain boundary attack and continuous ditching of grain boundaries. The material showing step structure is acceptable or free from IGC for service and does not require testing by other methods. Stainless steels which contain low carbon or stabilized types are tested after sensitization at 675°C) for about 1 hour.

Ferric Sulfate-50% Sulfuric Acid Test (Streicher Test)

The specimens which show non-acceptable etch structure (from oxalic acid etching) are subjected to this test. This test is a quantitative measure of the relative performance of the material based on mass-loss determinations. The 50% sulphuric acid solution may be prepared by slowly adding ~236 ml H_2SO_4 (98% by wt.) to 400 ml distilled water. 25 g of $Fe_2(SO_4)_3$ is added to the sulphuric acid solution and dissolved by heating. The test specimen may be prepared by polishing on coarse grit emery papers (such as 80 or 120) followed by degreasing. Overheating during polishing or grinding should be avoided. The sharp edges should be removed before subjecting them for tests. Specimen area and weight should be measured prior to putting them for the test. The solution is boiled in an Erlenmeyer flask with proper condensing (of vapours) arrangement. Test coupon may be placed in the solution after boiling starts. The boiling may be continued for 24 to 120h as desired by the customer. After the completion of the test, remove the specimen from the flask and rinse in water, dry and clean with acetone. Weigh the specimen and note down the final weight; calculate the difference between the initial and final weight. The corrosion rates may be determined in millimetres of penetration per month, as follows:

Corrosion rate (millimeter per month) = $(7290 \times W)/(A \times t \times d)$

Where: t = time of exposure, h, A = area, cm^2
W = weight loss, g, and d= density, g/cm^3
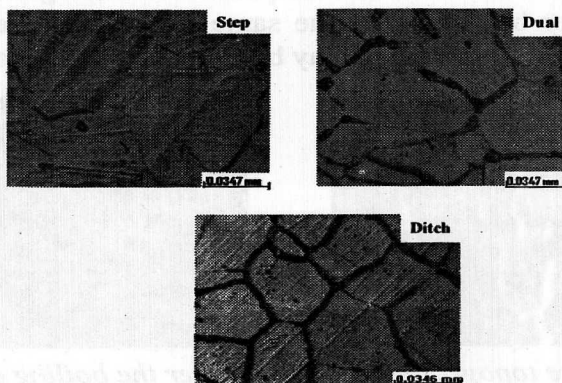(For steels, d = 7.9 g/cm^3, for chromium-nickel-molybdenum steels, d = 8.00 g/cm^3)

Fig. 1: Microstructures after electrolytic oxalic acid

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Nitric Acid Test (Huey Test)

Boiling nitric acid is a strongly oxidizing environment to detect the chromium depleted regions as well as intermetallic precipitations, like sigma phase in the stainless steels. The state of the specimens should possibly be close to the one being used in service. It may be polished up to 80 or 120 grit emery paper. The edges evolved during cutting should be repolished. The overheating of specimen during preparation needs to be prevented. The degreased and polished specimens are boiled in a 1L Erlenmeyer flask containing 65% nitric acid with condenser. Volume of the solution for the test should be at least 20ml/cm². Specimen shall be placed after boiling starts. After completion of each period, specimens are cleaned and weighed after drying. The corrosion rate during each boiling period is calculated from the difference of weight of the specimens before and after the test and by using a formula described earlier. This test also may be able to indicate the right heat treatment and sensitisation state of the specimens. Customer can decide and draw a line for accepting the materials depending on corrosion rate.

Copper-Copper Sulphate 16% Sulphuric Acid Test (Strauss Test)

This procedure is conducted to determine the susceptibility of austenitic stainless steel to intergranular attack associated with the precipitation of chromium-rich carbides. The test solution i.e. copper sulfate-16% sulphuric acid solution may be prepared by dissolving 100g copper sulphate in distilled water in a 1000 ml flask. Add 100 ml of sulphuric acid to it and then dilute further with distilled water to 1000 ml. Place the solution in Erlenmeyer flask containing Allhin condenser. Sufficient quantity of electrolytic grade copper shots or grindings should be used along with the solution (8 ml/cm²). The galvanic coupling between the copper shots and test specimen must be assured. The specimen size may be specified by the customers. Also the possible dimensions of rod, plate or tube are described in ASTM A262-Practice E. After surface finishing followed by boiling in the Erlenmeyer flask containing above solution for 24 – 72 h, samples need to be rinsed and cleaned if copper is deposited on the specimen surface. The specimen is then subjected to bending through 180° over a mandrel. In case of weld materials, the HAZ shall lies in the centre of the bend. The bent location shall be examined under low magnification (5-20X) where the appearance of fissures or cracks indicates the presence of intergranular corrosion attack as illustrated in Fig 2. For better clarity the same region may be viewed under higher magnifications. Crack length and depth may be evaluated and recorded.
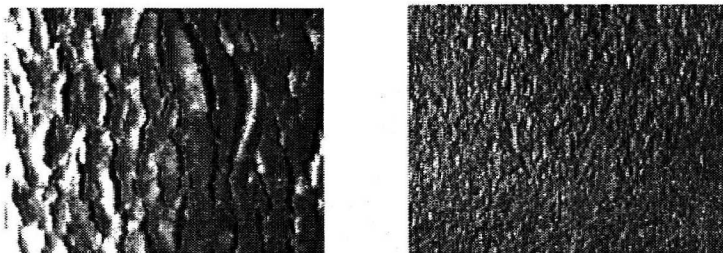
Fig. 2 : Surface topographical features after the boiling and bend tests
(A) appearance of IGC fissures (B) sample passed during the test

## Copper–Copper Sulphate 50% Sulphuric Acid Test (Modified Strauss test)

This procedure is based on the relative weight loss of specimen subjected to boiling in copper-copper sulfate-50% sulphuric acid test. The solution may be prepared by adding 236 ml sulphuric acid slowly to 400 ml distilled water and then 72 g of copper sulphate in the Erlenmeyer flask. Place the copper shots/ chips in the flask. Clean and weigh the specimen before putting them in boiling copper sulfate-50% sulphuric acid solution. After 24-72 hours of boiling, the specimens are removed and cleaned for any oxide or copper deposition on specimens followed by weighing. Determining the weight-loss and corrosion rate can be calculated by using formula mentioned above.

Stress Corrosion Cracking (SCC)

SCC is cracking of materials in the presence of tensile stresses (residual or operational) in cracking prone environment. The SCC prone environments including hydrogen can cause material to fail at stresses much below the yield or design stress. Crack may propagate along the grain boundary, (intergranular stress corrosion cracking) or across the boundary (transgranular cracking). Significant numbers of test method have been developed to evaluate the stress corrosion cracking resistance of engineering materials. The test methods are broadly categorized as constant strain, static loading, and dynamic loading. Specimens may be smooth, notched or pre-cracked, based on fracture mechanics principles. Constant-deformation (strain) tests are conducted by using widely known geometries of the specimen such as C-ring, O-ring, bent-beam and U-bend.[9-13] In all the bent specimens, state of stress is much more complex than in tensile specimen where it is almost uniform throughout the cross section. The maximum tensile stress zone in the bent specimen is at convex surface and reduces to zero at neutral axis. This becomes compressive and maximum at the concave surface and therefore 50% of surface is under tension and rest under compression. The crack initiation time and propagation rates are observed under various environmental and metallurgical conditions.

C-Ring Test [10]

The C-ring specimens may be machined from thick tubes, bars, plates in various sizes, but minimum outer diameter should be above 16 mm due to difficulties in machining. Tensile stresses are generated at the exterior (on the circumference) of the ring by tightening of bolt. A few C ring geometries are shown in Fig 3.

Constant strain   Constant load
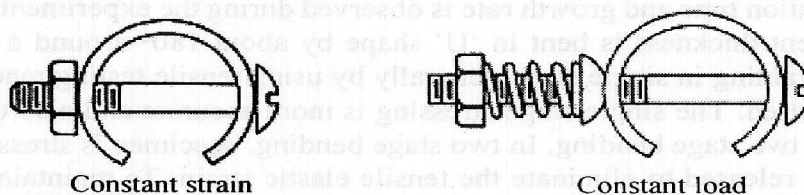
Fig. 3 : *C-Ring geometries for SCC test*

Tensile stresses on the surface applied by the deformation loading are controlled by restricting the strain with in the elastic range. The stresses on circumferential and transverse sections can be accurately calculated and controlled using following formula

$$\sigma_C = E / (1 - \mu^2) . (\varepsilon_C + \mu\varepsilon_T) \quad \text{and}$$
$$\sigma_T = E / (1 - \mu^2) . (\varepsilon_T + \mu\varepsilon_C)$$

where E = Young modulus of elasticity, μ= Poisson's ratio, ε_C = circumferential strain and ε_T = transverse strain. The circumferential and transverse strain can be measured by strain gages or micrometers.

The final diameter or deflection in the C-ring also can be obtained by the formula given below

$$OD_F = OD - \Delta$$

Where $\Delta = f\pi D^2/4EtZ$

ODF = final outside diameter (mm), OD= outside diameter before stressing (mm), f= desired stress (MPa) within the proportion limit (elastic range), Δ = changes in the OD to give desired stresses, t = wall thickness (mm) mean diameter D = OD-t, E = elastic modulus (MPa), Z = a correction factor for curved beams.

The C-ring typically is under constant-strain till the crack initiate, however, by placing a calibrated spring on the bolt, a constant load can be applied to it. Details for fabricating C ring is given in ASTM G 38.

Similar to the C-ring, bent beams are another kind of geometry in several configurations such as two points, three point and four point bent beam. Tensile stress on the convex side is below the elastic limit and may be calculated precisely. [11]

U –bend Test in Boiling Magnesium Chloride Solution [12, 13]

Relative resistance of alloys to stress corrosion cracking is frequently assessed by exposing 'U' bend specimens in boiling magnesium chloride solution. This method is specifically useful for all alloys (sufficiently ductile) susceptible to chloride related stress corrosion cracking and not for chloride-free SCC. The bent area contains large amount of plastic and elastic stresses, though the stress conditions are not precisely known. This method may not be suitable when the effect of small stresses on SCC is the main objective but is rather useful to see the SCC resistance of one alloy in different metallurgical conditions. The crack initiation time and growth rate is observed during the experiment. A rectangular strip of sufficient thickness is bent in 'U' shape by about 180° around a predetermined radius. Slow straining in single stage generally by using tensile testing machine or in two stages may be used. The single stage stressing is more accurate and also useful for thick sections unlike two stage bending. In two stage bending, specimen is stressed to almost U shape and then released to eliminate the tensile elastic strain. To maintain the stress, the parallel legs of the U bend are suitably bolted. The details about the U-bend fabrication are given elsewhere in ASTM G30, a few are illustrated in the Fig 4.

The test environment i.e. magnesium chloride ($MgCl_2.6H_2O$) solution is prepared such that it boils at ~155.0 ±1.0°C (311.0 ± 1.8°F). To prepare about 400 ml of the test solution, weigh 600 g of reagent grade $MgCl_2.6H_2O$ and add this to Erlenmeyer flask containing a thermometer along with 15 ml of reagent water. After the solution boils slowly add water at the top of the condenser to reduce the temperature to 155°C (311°F). A solution of 25 weight percent magnesium chloride is required for the trap if the test duration exceeds seven days without a solution change. Stressed specimens may also be tested for stress corrosion cracking in alternate immersion method.[14]

Welded bend
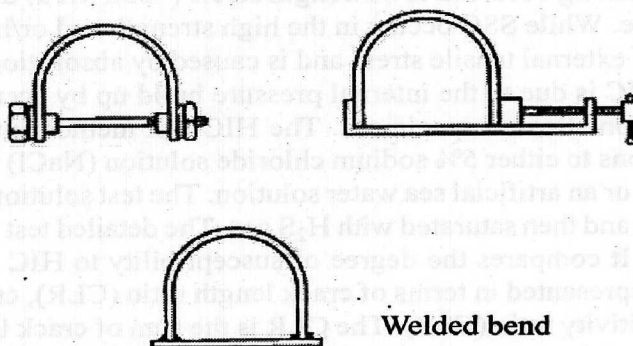
Fig. 4 : Various U-bend geometries

Slow Strain Rate test [15]

The constant strain by an external means is applied on the gage section of the tensile or precracked specimen. The low extension rate is such that it allows time to corrosion processes to occur on the surface and fast enough to produce cracking in reasonably short time. The slow extension rate produces the strain rate in gage section in the range of 10^{-4} to 10^{-7}/s. However, the selection of suitable strain rate depends upon the type of alloy and environment. Too high a strain rate will result in ductile fracture and too low rate may prevent corrosion by passive film repair and SCC may not occur. This method requires tensile testing machine with calibrated load cell, gripping devices for smooth transfer of applied load to the specimen and fixtures, displacement gages, environment cell or autoclave for high temperature test. The test specimen preparation shall be in accordance with the ASTM E8. The dimensional measurement such as gage length and cross section are made prior to the test. The data from SSR test can be analyzed for time-to-failure ratio, plastic elongation ratio, % reduction in area. Each of these parameters shall be normalized with respect to the controlled environment.

Polythionic Acid Cracking

Polythionic acid is found in petroleum refineries and strongly influences the IGSCC susceptibility of stainless steels. Stainless steels that have undergone sensitization treatments are frequently tested in the polythionic acid solution, in laboratory, for determining their susceptibility to IGSCC. Sensitized stainless steels are fabricated in a U-bend as described

earlier and immersed in the polythionic acid. The initiation of cracking and crack growth rate can be monitored with time of exposure. The polythionic acid is prepared by bubbling H_2S gas through the sulfurous acid (H_3SO_3). The latter may be produced by bubbling SO_2 gas in distilled water, in accordance with the ASTM specification.[16]

Hydrogen Induced Cracking (HIC) and Sulfide Stress Cracking (SSC) [17]

Hydrogen damage is common failure mode in the pressure vessels and pipe line steels exposed to wet sour environments such as in petroleum and natural gas industries. Hydrogen induced cracking occurs in low strength steels (<550 MPa) during wet hydrogen sulfide (H_2S) exposure. While SSC occurs in the high strength and or/high hardness steels under the influence of external tensile stress and is caused by absorption of hydrogen from wet H_2S corrosion. HIC is due to the internal pressure build up by accumulated hydrogen (molecular) even in non-stressed specimens. The HIC test method involves exposure of unstressed steel coupons to either 5% sodium chloride solution (NaCl) + 0.5 % acetic acid solution (CH_3COOH) or an artificial sea water solution. The test solution shall be deaerated with argon or nitrogen and then saturated with H_2S gas. The detailed test method is available in NACE TM-02-84. It compares the degree of susceptibility to HIC in each section for different steels. It is represented in terms of crack length ratio (CLR), crack thickness ratio (CTR) and crack sensitivity ratio (CSR). The CLR is the sum of crack length of each array divided by the width of the section and multiplied by 100%. The CTR is the sum of the crack thickness of each crack array divided by the thickness of the section and multiplied by 100%. The CSR is the sum of the effective cracked area of each crack array divided by the area of the section and multiplied by 100%. The standard does not specify pass or fail values. However, some companies used maximum CLR ~15% to qualify the steels for wet sour line pipe applications.

Concrete Corrosion

Corrosion of concrete rebar is primarily influenced by the various admixtures used and chloride ingress from the environment or concrete constituents. Concrete rebar can be tested for corrosion in laboratory as well as in the atmosphere.[18, 19] For this, two rebar of certain sizes are placed in the mould which then is filled with concrete and admixtures which are being tested for corrosive effects. A control concrete rebar shall also be prepared from the concrete not containing the admixtures. Concrete beam are prepared as per the standard ASTM C192/192M. After curing and drying the specimen in a moist room, an artificial pond is created with one surface of the concrete as the pond base. This ensures that one of the rebar is wet while the other is relatively dry. This pond is maintained for two weeks in 3% NaCl solution at 23+/-3ºC; the solution volume should be around 400 ml and depth 40 mm. The solution is then sucked off and the voltage across the 100-ohm resistor between the rebar is measured. By cyclically ponding with 3% sodium chloride, the chloride permeates through the concrete and the upper bar begins to corrode, with the bottom bars acting as cathodes. The current can be measured as I = V/100.

Also measure the corrosion potential of bars against reference electrode and monitor the current every week for some time. Visual observations of the bars on test completion will reveal percentage of corroded area and may be recorded.

ELECTROCHEMICAL METHODOLOGIES

Electrochemical tests methods need a device for measuring and applying accurate current and potentials (a Potentiostat/ Galvanostat), an electrochemical cell containing reference electrode (e.g. saturated calomel, silver-silver chloride), a counter electrode (such as platinum or graphite) and working electrode (a test specimen) along with experimental solution. Reference electrode measures the potential of the specimen-solution interface and the counter electrode facilitate electrochemical current flow. Electrochemical tests for corrosion resistance evaluation are preferred due to short experimental time, and can provide real time (time-corrosion) data on a single specimen. With the advent of advanced instrumentation, these methods became even easier and attractive. Electrochemical methods are specifically useful for studying the mechanism of corrosion in the different current-potential region corresponding to various environmental situations. Various electrochemical techniques are available to evaluate the different forms of corrosion such as general, pitting, crevice, IGC, galvanic etc. Regardless of the technique, each relies on the same basic principles; in each test, a metallic coupon in an electrolyte is subjected to the application of current or potential from an external source (Potentiostat/ Galvanostat). This current/potential stimulates the surface corrosion reactions. The voltage or current response of the corroding coupon is recorded and correlated with the current or potential applied. In either case, the resultant current is representative of the rate determining mass transfer or charge transfer rate.

Corrosion Rate Determination

For general corrosion where corrosion rate is of concern, polarization resistance, Tafel extrapolation, and electrochemical impedance methods are employed.[20-23]

Tafel Extrapolation

A relationship is obtained between log current density and applied potential. A perturbation of ± 250mV is applied with respect to open circuit potential (E_{corr}) in cathodic as well as anodic direction and the resulting current is recorded by potentiostat. However, such a large over potential may be damaging to the surface particularly during anodic polarization in which a metal surface gets changed due to corrosion/ passivation processes. The cathodic polarization is therefore more realistic and surface damage is relatively small. Corrosion current (i_{corr}) may be determined by extrapolating the straight linear region from either cathodic or anodic curve to the open circuit potential as shown in the Fig 5. For better accuracy the linear region must be minimum an order of magnitude of current.

Linear Polarization Resistance (LPR) [20, 21]

The Tafel extrapolation method is dependent on activation controlled electrochemical reactions. For concentration controlled reactions, however there may be deviations from linearity for large overpotentials. The LPR technique exploits the linearity that appears within 5 to 10 mV of the corrosion potential as described by the Stern and Geary, shown schematically in Fig 6. The potential is scanned at a constant rate (0.6V/h) with a short potential range. The slope of the resultant current versus potential plot gives the polarization resistance (inverse of corrosion current density).

$$i_{corr} = \beta_a \beta_c / 2.3 R_p (\beta_a + \beta_c)$$

where i_{corr} is current density, β_a and β_c are anodic and cathodic slope, R_p is polarization resistance. After obtaining the corrosion current density or the polarization resistance values, a corrosion rate can be calculated by formula given in ASTM G 102.

Corrosion rate = $(K \times i_{corr} \times EW)/(D)$

Where

Corrosion rate = mm/y

i_{corr} = corrosion current density, $\mu A/cm^2$

K = 3.27×10^{-3}, mm g/mA cm yr,

EW = equivalent weight (atomic weight of the base alloying element/number of electrons involved in the oxidation process),
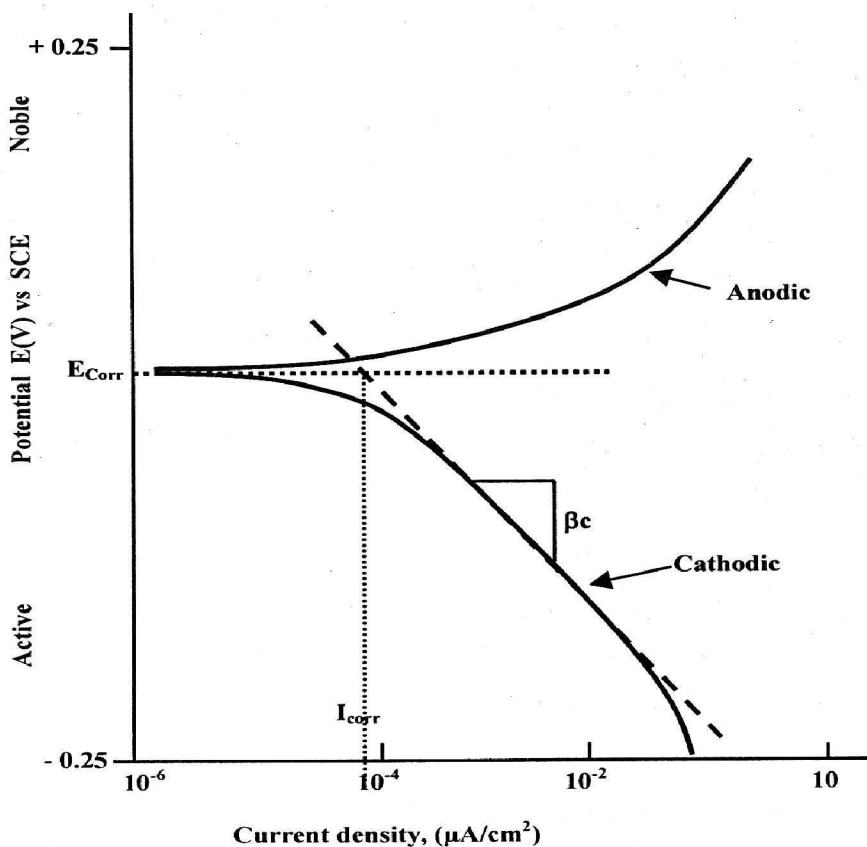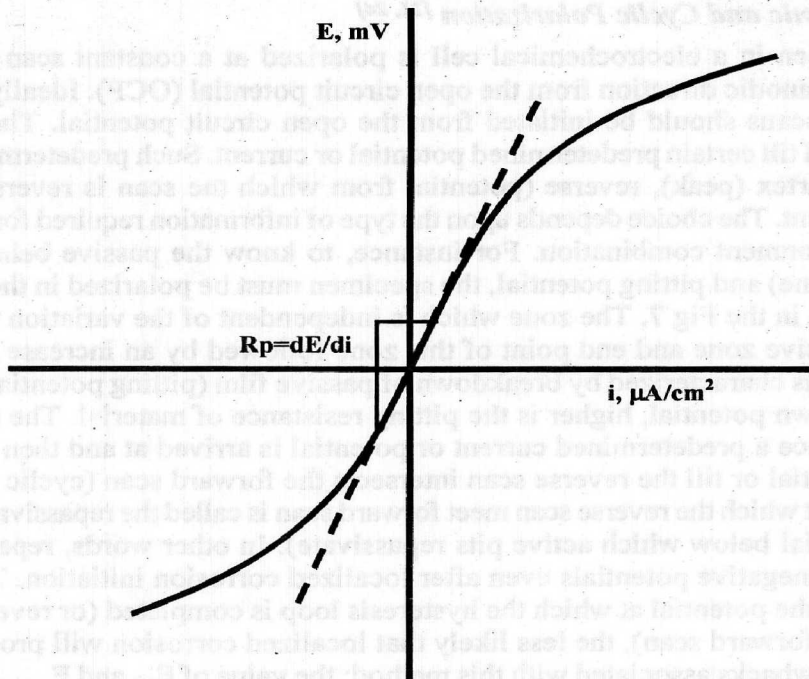
D= Material density, g/ cm^3

Fig. 5 : *Tafel extrapolation*

Fig. 6 : Linear polarization curve

## Electrochemical Impedance Spectroscopy (EIS) [22]

This is another method for determining the corrosion rate and widely used as a research tool to understand the various corrosion mechanisms. It is also known as AC impedance method. A small amplitude sinusoidal (AC) potential or current is applied to the working electrode at various frequencies. The resultant waveform will show a sinusoidal response which is out of phase with the applied potential or current by certain amount and with current amplitude that is inversely proportional to the impedance of the interphase. A corroding system is modeled as an equivalent AC circuit containing elements such as solution resistance, capacitance, inductance and polarization resistance. The values of various circuitry elements are obtained by curve fitting procedure using commercial computer software. By doing so and obtaining the polarization resistance value, corrosion rate can be calculated using formula given above. The detailed procedures are available in ASTM G109. [22]

Localized Corrosion Resistance Evaluation

Electrochemical methods are widely used for evaluating localized corrosion resistance such as pitting and crevice corrosion susceptibility, galvanic corrosion resistance, passivity, sensitisation and IGC resistance etc. Potentiodynamic, cyclic polarization, potentiostatic & galvanostatic, and scratch repassivation tests are useful for pitting corrosion resistance and to know the passivation/ repassivation state of materials. A few of these are discussed below

Potentiodynamic and Cyclic Polarization [21, 24]

Specimen in a electrochemical cell is polarized at a constant scan rate (0.6V/h) towards more anodic direction from the open circuit potential (OCP). Ideally, both anodic and cathodic scans should be initiated from the open circuit potential. The specimen is often polarized till certain predetermined potential or current. Such predetermined potential may be the vertex (peak), reverse (potential from which the scan is reversed) and final potential /current. The choice depends upon the type of information required for the particular material-environment combination. For instance, to know the passive behavior (current and passive zone) and pitting potential, the specimen must be polarized in the transpassive zone as shown in the Fig 7. The zone which is independent of the variation in potential is called the passive zone and end point of this zone followed by an increase in the current with potential is characterized by breakdown of passive film (pitting potential E_{pit}). Higher is the breakdown potential, higher is the pitting resistance of material. The scanning may be reversed once a predetermined current or potential is arrived at and then continued till the final potential or till the reverse scan intersects the forward scan (cyclic polarization). The potential at which the reverse scan meet forward scan is called the repassivation potential, $E_{protect}$ (potential below which active pits repassivate). In other words, repassivation will occur at more negative potentials even after localized corrosion initiation. Therefore, the more positive the potential at which the hysteresis loop is completed (or reverse/backward scan intersect forward scan), the less likely that localized corrosion will propagate. There are certain drawbacks associated with this method; the value of E_{pit} and $E_{protect}$ are sensitive to potential scan rate and the value of $E_{protect}$ vary with the polarizing (vertex) potential in the transpassive zone. Higher vertex (potential from which scan is reversed) may result into lower $E_{protect}$. The details about conducting this test is given in ASTM G 61.[21, 24]
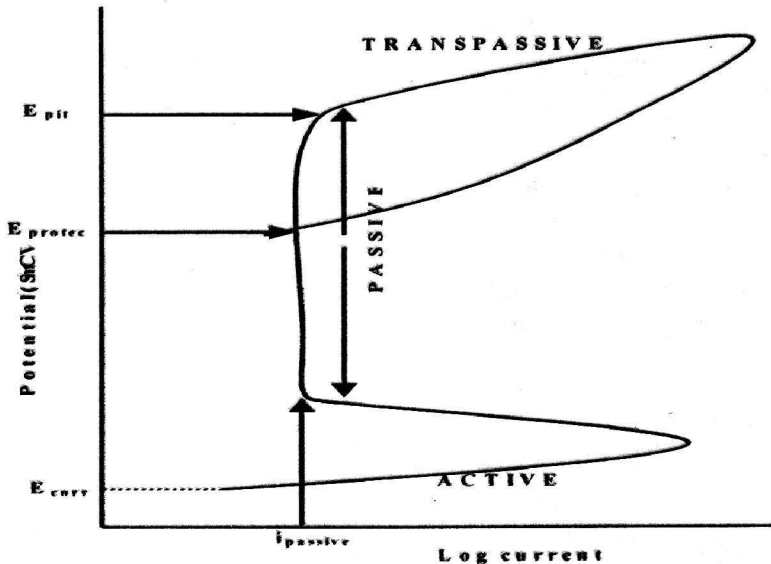
Fig. 7 : *Schematic cyclic anodic polarization curve*

Potentiostatic and Galvanostatic Methods

The sensitivity of scan rate in evaluating the localized corrosion resistance (using cyclic potentiodynamic) may be overcome by potentiostatic methods. The E_{pit} can be obtained by polarizing specimen at potentials above and below the values of E_{prot} and E_{pit} determined from the potentiostatic polarization. The initiation of pitting is indicated by the increase in current with time. By conducting a series of current versus time curves at an increment of 50 mV, the E_{pit} is identified as lying between two potentials at which current-potential curve shows deviation from decreasing or constant trend. For E_{prot} the pits are intentionally initiated at a potential higher than the E_{pit} and then quickly shifted to below the $E_{protect}$ for current versus-time curve. The repassivation of pits will be indicated by decrease in current with time (see ASTM F746 and ASTM G 100 for details).[25, 26]

Evaluation of Sensitization

Electrochemical techniques such as single and double loop electrochemical potentiokinetic reactivation (SL-EPR and DL-EPR, respectively) are only available methods to quantify the sensitization in stainless steels and nickel based alloys. The SL-EPR and DL-EPR are based on potentiodynamic and cyclic polarization respectively and quantify sensitization in terms of degree of sensitization (DOS).[27] Both tests are conducted in 0.5 M H_2SO_4 + 0.01 M KSCN solution at room temperature at a scan rate of 6V/h. In single loop technique, sample is allowed to stabilize in the solution at an open circuit potential typically around -400 mV with respect to SCE. After the sample is stabilized, a potential of +200 mV (w.r.t. SCE) is applied in order to passivate the steel for about 120 seconds. The potential is then scanned from +200 mV down to the open circuit potential as shown in Fig 8.
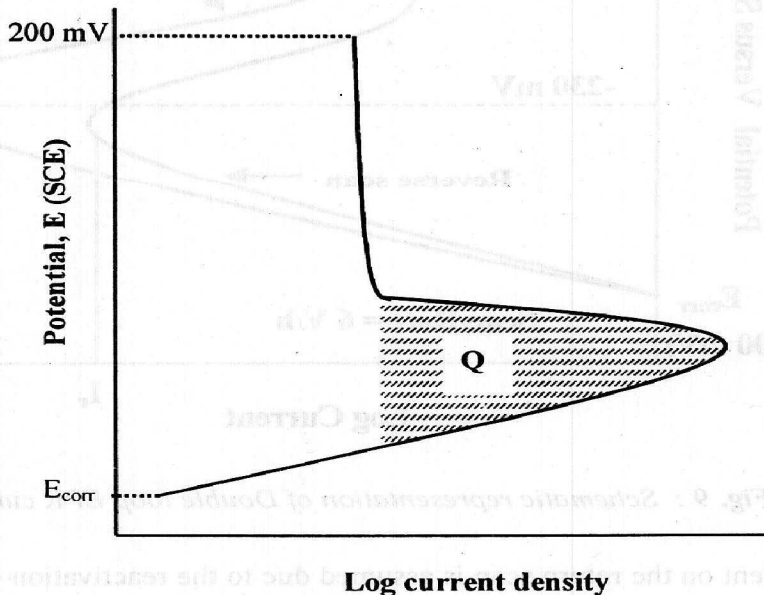

Fig. 8 : *Schematic of single loop EPR polarization curve*

With decrease in potential, the sensitized grain boundaries will preferentially activate while the grain matrix remains passivated. The total anodic current or charge (Q) passed, during decreasing potential (reverse scan), is proportional to the grain boundary area activated. This is indicative of the degree of sensitization. The normalized charge (P_a) in units of coulombs/cm^2 is calculated using following equation:

$P_a = Q/X$

where

Q = charge measured on current integration measuring instrument (coulombs).

Q is normalized for both specimen size and grain,

$X = A_s [5.1 \times 10^{-3} e^{0.35G}]$

A_s = specimen area (cm^2), and

G = Grain Size at 100X (in accordance with test method ASTM E 112).

In a double loop EPR, the specimen is allowed to stabilize at an open circuit potential. The specimen is then anodically polarized from the OCP (typically ~-400 mV SCE) up to the +300 mV (w. r. t. SCE) and scanned back down to the OCP, schematically shown in Fig 9. The peak current during anodic loop (I_a) is compared with the peak current during backward scan (I_r).
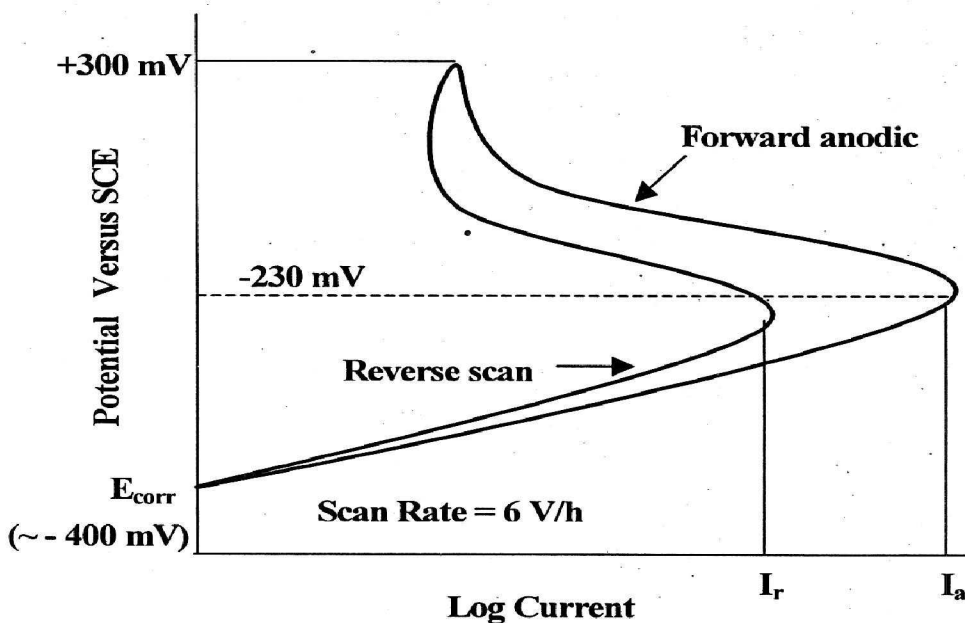

Fig. 9 : Schematic representation of Double loop EPR curv

The current on the return scan is assumed due to the reactivation of the chromium depleted grain boundaries. The ratio of (I_r/I_a) x 100 is known as the percentage degree of sensitization (% DOS).

Galvanic Corrosion

Galvanic corrosion needs a couple consisting two metals or alloys of interest. The couple should be in electrical contact of each other and connectivity may be checked before exposing them to desired environment. Electrical contact of the dissimilar metals should be checked periodically. The connectivity between the dissimilar metals/ alloys can be made by pressure contact, soldering or brazing, spot welding, bolting etc. The corrosion at the joint locations would however be inevitable which, in turn, may affect the electrical contact between the two candidates of the couple. To prevent the corrosion at such joints, coating may be a useful solution. The couple should not be in electrical contact with the test chamber or container. The corrosion or corrosion rate of the couple may be evaluated which would indicate the corrosion of the anodic component of the couple. The cathodic member, however, will be protected cathodically. The exposure time for galvanic corrosion test should be of sufficient length so that the corrosion processes have reached steady state and intermediate variations in corrosion reaction would not underestimate or overestimate the corrosion rate. More detail on galvanic corrosion testing in electrolytes is given in ASTM G 71[28]

Hydrogen Transport, Diffusion, and Permeation

Among the different form of degradations, hydrogen damage such as hydrogen embrittlement, hydrogen induced cracking, blistering are quite common to cause premature failures of industrial components. Hydrogen entry into the material can occur during melting, electroplating, and in service due to corrosion. The degradation due to hydrogen may vary with composition, microstructure, and stress levels of the material in service. The concentration of hydrogen traps in the material determines the level or degree to which the material can suffer. The concentration is a function of diffusion coefficient, which can be determined experimentally by different methods such as: electrochemical method, sub-surface micro hardness profiling, nuclear reaction analysis and nanoindentation measurements. The method that has greater acceptance in determining the diffusion in materials is the hydrogen permeation technique. This method can help to recognize how alloy contents and crystal defects affect the diffusion process. In solid solution, hydrogen at low concentration in the material does not change the mechanical properties, except during the application of load. As a consequence of loading, dislocations are generated with the possibility of becoming hydrogen traps (as these tend to migrate towards areas of high strain field). The transported hydrogen can eventually cause high local pressure thereby reducing the stress intensity factor and culminating in brittle fracture. For hydrogen permeation experiments, a two-cell system based on the Devanathan and Stachurski technique with some modifications is used.

The hydrogen charging of the sample on the left side (cathodic) cell is controlled potentiostatically or galvanostatically by a DC power source. Electrolyte used in the charging cell may be 0.1M H_2SO_4 (for steel). Poison such as $Na_2HAsO_4.7H_2O$ may be used to increase the hydrogen entry rate and subsequent permeation. The exit side (anodic cell) is controlled by potentiostat in different modes such as potentiostatic, galvanostatic, potentiodynamic etc. The environment in the exit or anodic side, should be such that high anodic or background current may be minimized (for example 0.1M NaOH for steels).

Calculations for such as steady state permeation current, diffusion coefficient etc may be performed as per the ASTM G148 and ISO: 17081. [29, 30]

ONLINE CORROSION MONITORING

A few corrosion test methods have been automated to portable corrosion probes such as LPR (linear polarization resistance), ER (electrical resistance probes which can be used to monitor the corrosion rates in-situ as described in ASTM G96.[31] Such probes are widely used in the petrochemical industries, cooling water system, refineries etc. The developments have been made to provide online real-time monitoring techniques and progress on corrosion damage can now be seen in a very short interval (within minutes). These developments could reduce the time and efforts to obtain corrosion data. The LPR probes are based on the linear polarization resistance as also mentioned in the earlier sections. The electrical resistance probes are based on the principle that the decreasing cross section thickness will increase the electrical resistance represented as

$R = \rho l/A$, where r is resistivity, l is length of conductor, and A is area of cross section.

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3. *ASTM G85 :Practice or Modified salt spray (fog) test*

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5. *ASTM G104: test method for assessing galvanic corrosion caused by the atmosphere.*

6. *ASTM: G 48 - 03 Standard test methods for pitting and crevice corrosion resistance of stainless Steels and related alloys by use of ferric chloride Solution.*

7. *ASTM G 46 - 94 Examination and evaluation of pitting corrosion*

8. *ASTM 262 A-F: Standard practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels*

9. *ASTM E8: Test method or tension testing of the metallic materials*

10. *ASTM G38: Making and using C-ring stress corrosion test specimens*

11. *ASTM G39: Practice for preparation and use of bent beam stress corrosion test specimen*

12. *ASTM G30: Making the U bend stress corrosion test specimen*

13. *ASTMG36: Practice for performing stress corrosion cracking test in a boiling magnesium chloride solution*

14. *ASTM G44: Practice for evaluating stress corrosion cracking resistance of metals and alloys by alternate immersion in 3.5 % NaCl solution*

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30. *ASTM 148-97: Evaluation of hydrogen uptake, permeation and transport in metals by an electrochemical technique.*

31. *ASTM G96 Practice of online monitoring of corrosion in pant equipment (electrochemical and electrical resistance methods)*