FUNDAMENTALS OF CORROSION & ITS PREVENTION

Indranil Chattoraj
*National Metallurgical Laboratory, Jamshedpur 831007*
Email : ichatt_62@yahoo.com

INTRODUCTION

Most metals other than the noble metals, do not exist in their native states but exist as compounds of the metals (oxides, sulphides, etc.) indicating that such states are energetically more favourable. It is no wonder therefore that most metals tend to revert back to their more stable compound state through corrosion. Corrosion is thus inevitable for metals and alloys. Corrosion is the most predominant cause of metal failures today, surpassing other failure modes like fatigue, creep, impact, and others. The cost of corrosion is not only the cost of replacement but additional costs as well such as:

➢ Loss of production due to shutdown or failure
➢ High maintenance costs
➢ Compliance with environmental and consumer regulations
➢ Loss of product quality due to contamination from corrosion of the materials
➢ High fuel and energy costs as a result of leakage from corroded pipes
➢ Extra working capital and larger stocks

Corrosion is differentiated from chemical attack in that it normally involves two or more electrochemical reactions. Thus while an insulating material can react with a strong chemical, such a degradation would not be considered corrosion as there are no electrochemical reaction involved. Any degradation suffered by a chemical or component resulting from electrochemical reactions involving species of the constituent material is corrosion. Corrosion may involve substantial material loss, but that is not universally true. Corrosion when manifested as pitting can cause very small total loss of material while destroying the component integrity. Similarly, hydrogen embrittlement can occur with no material loss, when hydrogen produced in an electrochemical fashion, enters the material leading to its loss of material properties. The study of corrosion therefore is also a study of material-environment interaction through a set of electrochemical reactions. It naturally requires detailed understanding of the metallurgy of the material including time dependent changes in the metallurgy, stresses present in the component, operational parameters, environment chemistry and reaction thermodynamics and kinetics.

A point of view proposed by Professor Staehle, a well known corrosion expert, is that all engineering materials are reactive chemically and that the strength of materials depends totally upon the extent to which environments influence the reactivity and subsequent degradation of these materials. In order to define the strength of an engineering material for a corrosion based design it is essential to define the nature of the environments affecting the material over time. The corrosion event is a culmination of the conjoint action of various factors. The factors affecting the corrosive degradation of materials are shown schematically in the Fig.
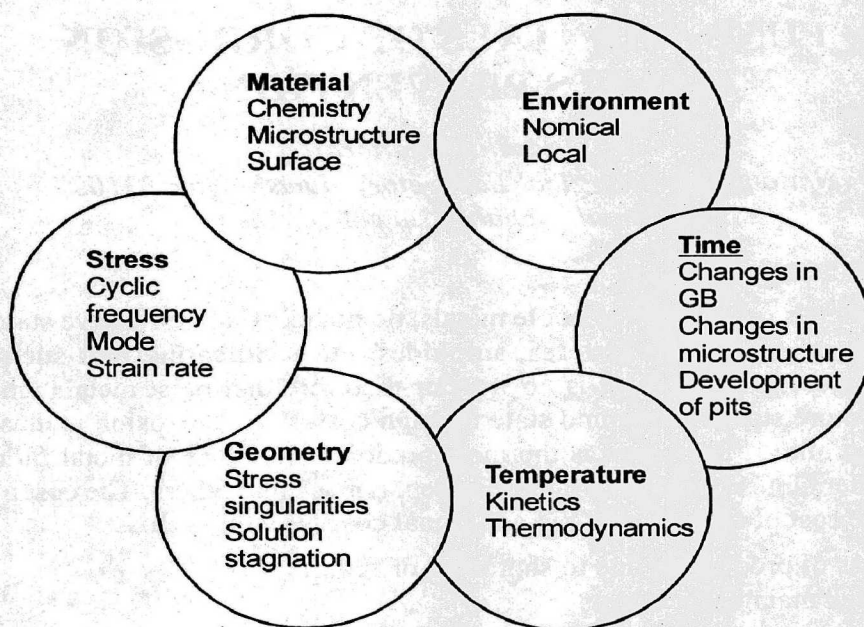
**Fig. 1** : *Factors influencing corrosive degradation of materials*

BASIC ELECTROCHEMISTRY

Electrochemistry is the study of the relationship between chemical change and electrical work. It is examined via the use of electrochemical cells which are systems that incorporate a redox reaction to produce or utilize electrical energy. Whether an electrochemical process releases or absorbs free energy it always involves the movement of electrons from one chemical species to another in an oxidation/reduction or redox reaction. In any redox process oxidation involves the loss of electrons and reduction involves the gain of electrons. An oxidising agent is the species that performs the oxidation, taking electrons from the species being oxidised. A reducing agent is the species that performs the reduction, giving electrons to the substance being reduced. After the reaction the oxidized substance has a higher (more positive, less negative) oxidation number, and the reduced substance has a lower (less positive, more negative) one. Oxidation (electron loss) always accompanies reduction (electron gain). The oxidizing agent is reduced and the reducing agent is oxidized.

In a Galvanic cell (like a common torch battery) a spontaneous cell reaction produces electricity. The spontaneous reaction occurs as a result of the different abilities of materials (such as metals) to give up their electrons and the ability of the electrons to flow through the circuit. Galvanic cells form the basis of energy storage and energy conversion devices (battery systems and fuel cells). Electrons leave a Galvanic cell at the anode (negative electrode), travel through the external circuit, and re-enter the cell at the cathode (positive electrode). The circuit is completed inside the cell by the electro-migration of ions through the salt bridge. A corroding system is essentially a galvanic cell with the difference that in this case the anode and cathode are electrically shorted.

Electrode Potential & Electromotive Series

The difference in electrical potential between the anode and cathode is called: cell voltage, electromotive force (emf) or cell potential. To measure the reducibility or the oxidizibility of the individual components in a redox couple, e.g. an electrochemical cell, the electrode potential for the individual component needs to be defined. The electrode potentials can be defined by first considering the individual reduction or oxidation reaction which are also called half cell reactions as they involve only half of an electrochemical cell. Thus for a Cu-Zn couple, and following the convention that electrode potentials are written as reductions, the half cell reaction for the anode (Zn) is written as

$$Zn_{2+} + 2_{e-} = Zn(s)$$
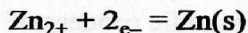
A half cell cannot exist by itself and therefore the determination of the electrode potential requires a reference electrode so that the circuit can be completed and the redox reaction can proceed. A hydrogen reference electrode with specified extrinsic and intrinsic conditions (temperature, pressure, concentration) is the most common reference electrode used. In this way the half cell potential or electrode potential for metals can be measured. Using the convention used above, all metals which have a negative electrode potential would tend to be oxidized when coupled with a standard hydrogen reference electrode, and vice versa. In this fashion by noting down the electrode potentials of all metals under standard conditions of temperature and activity, a list of the electrode potentials in a decreasing order may be compiled. This is the electromotive series for metals as shown below in Table 1. The series provides a relative measure of the ease with which metals tend to oxidize or corrode (the metals lower down in the series). However, in reality, such standard conditions are rare in practice and the best way to gauge the corroding (oxidizing) tendency of a metal in a given system is to measure its electrode potential insitu.

Table I : Electromotive series showing common metals

Au	$= Au^{3+} + 3e^-$	+ 1.498
Pt	$= Pt^{2+} + 2e^-$	+ 1.2
Ag	$= Ag^+ + e^-$	+0.799
Cu	$= Cu^{2+} + 2e^-$	+ 0.337
H2	$= 2H^+ + 2e^-$	0.00
Pb	$= Pb^{2+} + 2e^-$	-0.126
Sn	$= Sn^{2+} + 2e^-$	-0.136
Ni	$= Ni^{2+} + 2e^-$	-0.250
Co	$= Co^{2+} + 2e^-$	-0.277
Fe	$= Fe^{2+} + 2e^-$	-0.440
Cr	$= Cr^{3+} + 3e^-$	-0.744
Zn	$= Zn^{2+} + 2e^-$	-0.763
Al	$= Al^{3+} + 3e^-$	-1.662
Mg	$= Mg^{2+} + 2e^-$	-2.363

SOME IMPORTANT ISSUES IN CORROSION

The mixed electrode

It is well known that in corrosion and other electrodic processes, oxidation and reduction processes occur simultaneously. The oxidation process occurs at the anode and the reduction process at the cathode in a corrosion cell. This often creates the impression that physically separate entities function as cathode and anode in a corroding system. What is not realised is that most often both the cathodic and anodic reactions occur on the same material. For example, when a piece of Zn is dropped into dilute HCl, the anodic or oxidation process of Zn dissolution (ionisation to Zn2+) as well up the cathodic process of Hydrogen reduction ($2H+ + 2e- = H2$) occur on the same piece of Zn! Bubbles of hydrogen can be seen coming out of the Zn metal as proof of this. For an initiate into corrosion science it is important to appreciate and realise this concept of "mixed electrodes". If physically separate anode and cathode were required for corrosion, the problem of corrosion would be much less threatening. Corrosion mitigation would simply have involved physical (electrical) separation of the anode and the cathode. Such is not the case because on the surfaces of metals, alloys and conducting ceramics, different sites behave as microelectrodes, some of which act as cathode and others as anode.
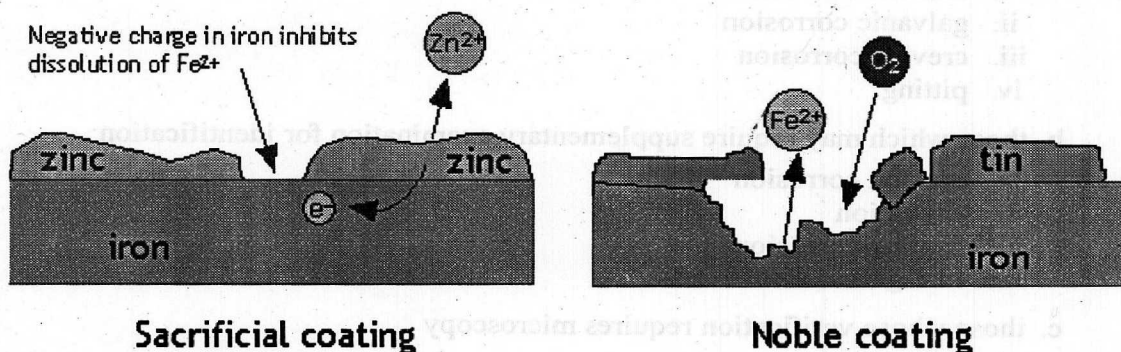
The area effect

It is also readily appreciated that charge conservation must be followed in corrosive reactions just as in any other reaction. A corroding system which comprises of two or more chemically different and physically separate entities (a steel bolt in a copper plate for instance) set up what is known as a galvanic couple. This is a case where the anode and cathode are physically separate. This is not a contradiction of the earlier paragraph on mixed electrodes; we are talking on a macro scale now. And since charge has to be conserved, the specific areas of cathode and anode become important. The significance of this is that a small cathode and a large anode will mean low anodic dissolution, that is low corrosion rate (N.B. it is the anode that always corrodes). On the other hand, a small anode and a large cathode is a recipe for disaster. The anode with its much smaller area has to supply the equal current as that of the large cathode, albeit opposite in sign, so that the corrosion current density or anodic current density is very high. A classic comparison is that of a steel bolt in a copper plate versus a copper bolt in a steel plate. The steel bolt corrodes very fast while the copper bolt and the steel plate remain unaffected when exposed to a corroding environment. The same applies for a sacrificial coating as opposed to a noble coating on a metal as shown in Fig.2 below. Small holidays in the sacrificial coatings do not lead to further corrosion of the underlying substrate nor of the overlying Zn. On the other hand the small anode underneath the noble coating corrodes very rapidly when there is a holiday.

Passivation

Passivation is the process of making a material "passive" in relation to the environment. A typical passivation process of cleaning stainless steel tanks involves cleaning with NaOH and citric acid followed by nitric acid (up to 20% at 120F) and a complete

water rinse. In the context of corrosion, passivation is the spontaneous formation of a hard non-reactive surface film that inhibits further corrosion. This layer is usually an oxide, oxyhydroxide or nitride that is a few atoms thick. Under normal conditions of pH and oxygen concentration, passivation is observed in aluminium, iron, zinc, magnesium, copper, stainless steel, titanium, and silicon. Ordinary steel can form a passivating layer in alkali environments, as rebar does in concrete. The conditions (pH and electrode potential) necessary for passivation are governed by the thermodynamic stability of the passive film in the environment as illustrated in the pertinent Pourbaix diagrams for the material-environment combination.

Fig. 2 : *Demonstration of the area effect for coatings*

In the industry, the term passivation while maintaining the connotation of "protection" is used somewhat loosely. Here, passivation is the removal of exogenous iron or iron compounds from the surface of stainless steel by means of a chemical dissolution, most typically by a treatment with an acid solution that will remove the surface contamination, but will not significantly affect the substrate material itself. In lay terms, the passivation process removes "free iron" contamination left behind on the surface of the stainless steel from machining and fabricating. Additionally, passivation facilitates the formation of a thin, transparent oxide film that protects the stainless steel from corrosion. Passivation does not usually result in a marked change in appearance of the steel surface.

CORROSION CLASSIFICATION

Eight Forms of corrosion

The industry views corrosion with a restricted perspective, which arises from an industry personnel's concern with only the types of corrosion that affect his plant or factory. Thus industrial nomenclatures for corrosion is often environment or material based. For instance one hears of acid corrosion, sulphide attack, brass cracking, ammonia attack and so on. The corrosion engineers classification is more general. The most popular is the appearance based classification proposed by Mars G. Fontana, one of the most eminent

corrosion scientists. This suggests that there are eight forms of corrosion. It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Fontana's classification has stood the test of time although newer materials, environments and corrodents have evolved since it was proposed some decades ago. An alternate classification which is possibly more relevant for corrosive failure analysis is based on ease of identification and gives us the following forms of corrosion

a. those that are visually identifiable

    i.   uniform corrosion
   ii.   galvanic corrosion
  iii.   crevice corrosion
  iv.   pitting

b. those which may require supplementary examination for identification

    i.   erosion corrosion
   ii.   cavitation
  iii.   fretting corrosion
  iv.   Intergranular corrosion

c. those whose verification requires microscopy

    i.   exfoliation
   ii.   dealloying
  iii.   corrosion fatigue
  iv.   stress corrosion cracking

In this article we use the more conventional eight -form classification.

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are: (1) uniform, or general attack, (2) galvanic, or two-metal corrosion, (3) crevice corrosion, (4) pitting, (5) intergranular corrosion, (6) selective leaching, or parting, (7) erosion corrosion, and (8) stress corrosion. This listing is arbitrary but covers practically all corrosion failures and problems. The forms are not listed in any particular order of importance.

Other Corrosion Nomenclatures

The eight forms of corrosion are discussed in detail in another article and will not be included here. However there are a few other manifestations of these forms which require separate mention and are often included or listed as separate entities due to their industrial importance. Hydrogen damage, although not a form of corrosion, often occurs indirectly as a result of corrosive attack, and is known to plague a number of industrial components especially those related to petrochemicals, power plants and oil and gas sectors. Similarly cavitation corrosion which can be thought of as a subset of erosion corrosion, can be disastrous for components experiencing high pressure and pressure changes like turbines, pumps, impalers, etc. The presence of microbes and other organisms can severely compromise the integrity of components by catalysing and intensifying corrosion. Although

phenomenologically these can be pitting, crevice, general or even erosion corrosion, Microbiologically induced corrosion (MIC) is often spoken of as a different class of corrosion. In this article we discuss these three classes of corrosion in some detail.

Cavitation Corrosion

Characteristics & Occurrence

Cavitation-corrosion is a particular form of erosion caused by the "implosion" of gas bubbles on a metal surface (Fig. 3). Cavitation corrosion occurs in areas with high flow rates and rapid pressure changes. Cavitation occurs when a fluid's operational pressure drops below it's vapor pressure causing gas pockets and bubbles to form and collapse. This gives a high force on the metal surface which can remove oxide and reveal an active surface. This can occur in a rather explosive and dramatic fashion. In fact, this can actually produce steam at the suction of a pump in a matter of minutes. When a process fluid is supposed to be water in the 20-35°C range, this is entirely unacceptable. Additionally, this condition can form an airlock, which prevents any incoming fluid from offering cooling effects, further exacerbating the problem. This form of corrosion will eat out the volutes and impellers of centrifugal pumps with ultrapure water as the fluid. It will eat valve seats. It will contribute to other forms of erosion corrosion, such as those found in elbows and tees.

Treatment

Cavitation should be designed out by reducing hydrodynamic pressure gradients and designing to avoid pressure drops below the vapor pressure of the liquid and designing to avoid air ingress. A regular hydraulic regime in the fluid is extremely important. A good surface condition decreases the number of potential sites for the formation of vapour bubbles. An increase in fluid pressure is often sufficient to maintain a single phase fluid, thus avoiding the formation of vapour bubbles. Plastic or rubber coatings have often proved to be effective, although the problems of adherence between the coating and the metal are frequently an obstacle. The use of resilient coatings and cathodic protection can also be considered as supplementary control methods. A listing of some possible protection means is provided below:

- Select a higher-grade and more corrosion-resistant material
- Alter equipment design (shape, geometry, etc.)
- Avoid abrupt changes in diameter
- Use adequately dimensioned sealing rings
- Reduce surface roughness
- Alter environment (reduce flow velocity, change temperature, avoid boiling, etc.)
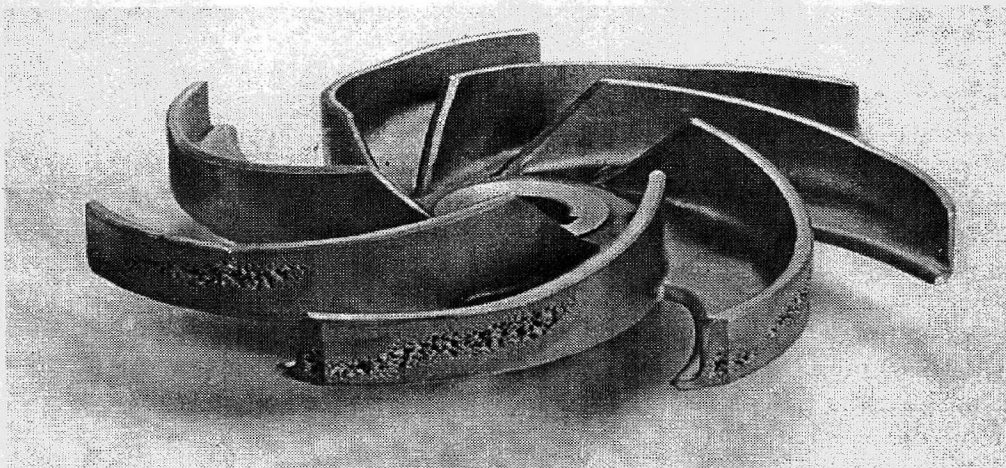- Apply coatings
- Use cathodic protection

Test Methods

ASTM D 2809: Standard Test Method for Cavitation Corrosion and Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants.

ASTM G 32 - Test Method for Cavitation Erosion Using Vibratory Apparatus.

ASTM G 134 - Test Method for Erosion of Solid Materials by a Cavitating Liquid Jet

***Fig. 3.*** *: Cavitation corrosion in a stainless steel pump impeller*

Microbiologically Influenced Corrosion (MIC)

Characteristics & Occurrence

Microorganisms are abundant in many environments and readily enter industrial systems wherever conditions are right. They flourish in a wide range of habitats and show a surprising ability to colonize water rich surfaces wherever nutrients and physical conditions allow. Microbial growth occurs over the whole range of temperatures commonly found in water systems, pressure is rarely a deterrent and limited access to nitrogen and phosphorus is offset by a the ability to sequester, concentrate and retain even trace levels of these essential nutrients. Many engineers continue to be surprised that such small organisms can lead to spectacular failures of large engineering systems. The microorganisms of interest in Microbiologically Influenced Corrosion (MIC) are mostly bacteria, fungi, algae and protozans.

In many systems which should be only minimally corrosive, severe corrosion is observed which results from MIC. Examples of such systems include pipelines, process piping, vessels and water handling equipment. Though most often found at carbon steel and in open condenser water systems, MIC has also been shown to cause severe deterioration to copper and galvanized steel domestic water pipe. Typically, biological action can increase the severity of corrosion experienced in both steel and stainless alloys as a result of:

1. Biological deposits on the material surface.
2. Production of corrosive chemical species
   (e.g.. H2S from sulfate reducing bacteria - SRB's).
3. Disruption of normal electrochemical reactions and film formation.

8
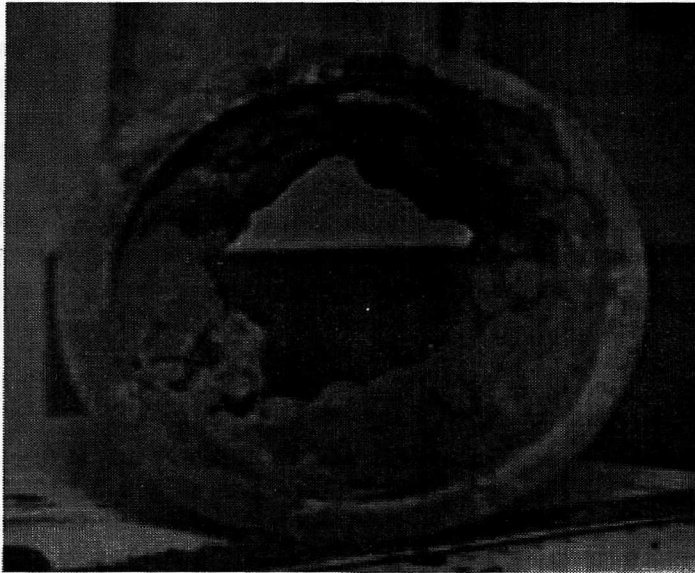
Fig. 4 : MIC inside a domestic water supply pipe

Microbes and microorganisms cause corrosion and/or the enhancement of corrosion through any of the following actions:

- **Chemical attack of metals, concrete and other materials by the by-products of microbial life, namely acids (e.g. sulphuric, carbonic or other organic acids), hydrogen sulfide or ammonia.**
- **Microbial attack of organic materials (e.g. organic paint coatings, plastic fittings and linings), conversion of some natural inorganic materials (e.g. sulphur) or degradation of inhibitors.**
- **Depassivation of metal surfaces and induction of corrosion cells.**
- **Depolarization of cathodic reaction (hydrogen reaction).**
- **Attack of metal by a process in which microbes and the metal cooperate to sustain the corrosion reaction.**
- **Attack due to a combination of bacteria.**

Evidence that MIC is occurring can be:

- **High Steel Corrosion Rates Exceeding 10 Mils Per Year (MPY)**
- **Extremely Premature Pipe Failure**
- **Tubercular Deposits**
- **High Microbiological Plate Counts**
- **Pinhole Leaks**
- **Growths In The Cooling Tower Basin, Or Pans**
- **Microbiological Growths Or Slimes**

Treatment

It is important in these cases to evaluate the system components and media and chemical treatments which can prevent such problems without interfering with the baseline materials performance (i.e. pitting of stainless steels from chlorine injection) or with other chemical treatments for corrosion inhibition. Metallurgical testing often offers the first evidence of an MIC problem by exposing the distinctive profile of the corroded pit area caused by specific microbiological organisms. A follow-up chemical analysis of the pit for the metabolic by-products of such microorganisms will provide further evidence that MIC exists. The presence of sulfuric acid or sulfur based compounds, for example, would strongly suggest an MIC condition since it is a common by-product of MIC related sulfur reducing bacteria.

Degradation of metals or alloys by hydrogen

The interactions of hydrogen with metals or alloys result in diverse harmful effects on their mechanical and physical properties. The extent of degradation due to hydrogen is dependent on the type of alloys, alloy microstructure, amount of discontinuities in metal or alloys, method of heat treatment, stress state, environment, time of exposure, temperature and pressure etc. The most popular way to classify hydrogen degradation is based on the temperature and stress requirements for the degradation phenomenon. Following this classification philosophy, there are three broad classes of hydrogen degradations possible, namely:

(a) Hydrogen attack (HA)

(b) Hydrogen induced cracking (HIC)

(c) Hydrogen Embrittlement (HE)

While HA is a high temperature phenomenon, HIC and HE occur at low temperatures. HIC occurs in high fugacity hydrogen environments while HE generally occurs at relatively lower fugacities; HIC does not require the presence of stresses while HE always occurs in stressed bodies, although such stresses may be residual stresses too. The three types of degradations are discussed below:

Hydrogen Attack (HA)

The primary reaction is probably the reaction of hydrogen with the carbon in the steel to form methane. It occurs in plain carbon and low alloy steels that are exposed to high pressure, high temperature hydrogen for long times. The reaction may occur at the surface, resulting in decarburization with loss in strength, or it may occur internally, resulting in both decarburization and the formation of fissures and cracks, which result in loss in both strength and ductility. Hydrogen attack can be prevented or minimized by using alloy steels with strong carbide formers.

Prevention or Remedial Action

- selection of material (for steels, use of low and high alloy Cr-Mo steels; selected Cu alloys; non-ferrous alloys).
- limit temperature and partial pressure of H2.

Hydrogen induced cracking (HIC)

HIC occurs in high fugacity environments in the absence of stresses. It is prevalent in components exposed to sour gas environments found in gas and oil exploration and their transportation, where it is also known as Step-wise cracking (SWC) owing to the peculiar appearance of the cracks (Fig. 5) . Several other high hydrogen fugacity degradation phenomena like blistering and shatter cracking, flaking and fisheye formation may also be included in this classification. Blistering occurs when atomic hydrogen enters steel from some suitable source and then deposits as molecular hydrogen at a microstructural defect, such as nonmetallic inclusions. High pressures of molecular hydrogen can build up at that site as atomic hydrogen continues to enter the steel, ultimately forming a blister. As the blister grows, the metal membrane enclosing the blister can be deformed plastically until it ruptures. Shatter cracks, flakes and fisheyes are defects observed primarily in heavy forgings. They are generally thought to be the result of hydrogen picked up during the melting operation, and they occur primarily as the result of hydrogen segregation to, and precipitation in, voids and discontinuities, such as micro-shrinkage cavities or gas holes, during cooling of the solidified steel.

Prevention or Remedial Action

- use of steel with low levels of impurities (i.e. sulfur and phosphorus).

- modifying environment to reduce hydrogen charging.

- use of surface coatings and effective inhibitors.

Test Methods:

NACE TM0177 - laboratory testing of metals for resistance to sulfide stress cracking in H2S environments.

NACE TM0284 - evaluation of pipeline and plate steels for resistance to stepwise cracking.
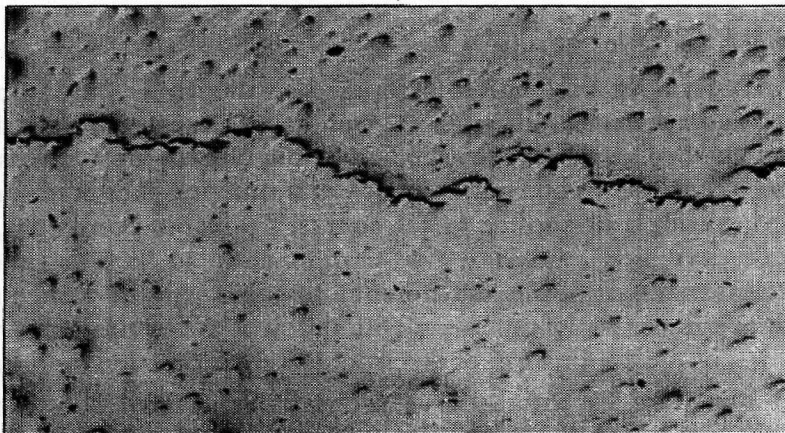
Fig. 5 : Stepwise cracking in a linepipe steel

Hydrogen embrittlement (HE)

HE is the degradation in mechanical properties when components are strained in contact with a hydrogen source. All steels, ferritic, martensitic, and austenitic, when exposed to hydrogen exhibit loss in tensile ductility. The percentage loss in ductility is a measure of the extent of HE. Similar effects have been found in a number of other metals and alloys (nickel based alloy, aluminum alloys, and titanium alloys). Embrittlement in Ta, Nb, Zr, Zr alloys, Ti alloys, and others has been associated with the formation of the respective hydride phases of these metals as a precipitate.

Prevention or Remedial Action

- use of lower strength (hardness) or high resistance alloys.
- careful selection of materials of construction and plating systems.
- heat treatment to remove absorbed hydrogen.

Test Methods :

ASTM G129 - slow strain rate test for determination of environmentally assisted cracking.

ASTM G142 - tension tests in hydrogen environments.

ASTM G146 - hydrogen induced disbonding of stainless clad steel plate in refinery hydrogen service.

ASTM F-326 - method for electronic hydrogen embrittlement test for cadmium electroplating processes.

ASTM F-519 - method for mechanical hydrogen embrittlement testing of plating processess and aircraft maintenance chemicals.

ASTM A-143 - practice of safeguarding against embrittlement of hot dip galvanized structural steel products and detecting embrittlement.

ASTM B-577 - hydrogen embrittlement of deoxidized and oxygen free copper.

CORROSION PREVENTION

The various corrosion prevention techniques available are based on two working principles: alter the component or alter the environment. The alteration of the component can be through design changes which are especially effective where the corrosion is affected by fluid flow characteristics (erosion corrosion, cavitation), presence or absence of gaseous phases (cavitation, pitting), dissimilar metal contact (galvanic corrosion), and solution stagnation (crevice corrosion). Alteration of component also includes alteration of the material of construction, i.e. choosing a different alloy grade for the same component, and the application of coatings. On the other hand alteration of the environment would include the use of inhibitors, or the application of electrochemical protection (anodic or cathodic).

Therefore there are essentially five broad categories of corrosion prevention methodologies available which may be used separately or in conjunction depending on the operational ease of application of each method, cost effectiveness and system compatability:

1. Coatings
2. Alloying
3. Inhibition
4. Electrochemical means
5. Component design alterations

Of these, component design alterations are often in the realm of the industrial/ mechanical engineer than the corrosion engineer and are not dealt with here. Inhibitors are dealt with in some detail in a separate article in this compendium and are also not discussed. The other three methodologies are discussed below.

Coatings

There are many ways of classifying coatings, here we use the coating material type as our basis and accordingly there are three different types of coatings (metallic, inorganic and organic):

Metallic coatings

Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. Application can be by dipping, flame spraying or electroplating or advanced processes such as plasma arc spraying, plasma implantation, laser alloying, etc.

The most widely used metallic coating method for corrosion protection is galvanizing, which involves the application of metallic zinc to carbon steel for corrosion control purposes. Hot-dip galvanizing is the most common process, and as the name implies, it consists of dipping the steel member into a bath of molten zinc resulting in a metallurgically bonded coat. Galvannealing is a modification of galvanizing in which through heat treatment immediately after galvanizing, a Fe-Zn intermetallic is formed. Galvannealled surfaces have a dull matte appearance compared with the shiny bright surface of hot-dip galvanized surface. This matte surface is excellent for painting and is harder and therefore more resistant to scratches during handling.

Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions with the metal object to be plated made the cathode. The process is controlled through a number of parameters, like the applied voltage and current, temperature of bath, residence times, and the purity of bath solutions.

Inorganic coatings

Inorganic coatings can be produced by chemical or electrochemical means. The treatments change the immediate surface layer of metal into a film of metallic oxide or compound which has better corrosion resistance than the natural oxide film and provides an effective substrate for supplementary protection. Some of the more important inorganic coating techniques are as follows:

Anodizing

Anodizing is the electrolytic oxidation of a metal surface resulting in a tightly adherent oxide scale which is thicker than the naturally occurring film. In anodizing aluminum is used as the anode. The electric current passing through an electrolyte converts the metal surface to a durable aluminum oxide. As opposed to plating, in anodizing the oxide coating is an integral part of the substrate. Such surfaces are hard and abrasion resistant, and provides some degree of corrosion resistance. The Al2O3 coating produced by anodizing is typically 2 mm to 25 mm thick, and consists of a thin non?porous barrier layer next to the metal with a porous outer layer that can be sealed by hydrothermal treatment in steam or hot water for several minutes. However anodizing cannot be relied upon to provide corrosion resistance to corrosion prone alloys, and further protection by painting is usually required. Anodizing treatments are also available for magnesium and titanium alloys.

Chromate filming

This usually involves short time immersion in strongly acid chromate solutions, but spraying or application by brushing or swabbing can also be used. The resulting films are usually about 5 mm thick, and are colored depending on the base alloy, being golden yellow on aluminum, dull gold on cadmium and zinc, and brown or black on magnesium. The films contain soluble chromates which act as corrosion inhibitors, and they provide a modest improvement in corrosion resistance of the base metal. However their main purpose is to provide a suitable surface for sealing resins or paints. Epoxy primer, for example, which does not adhere well to bare aluminum, adheres very well to chemical conversion coatings.

Phophatizing

This involves application by brushing, spraying or prolonged immersion in an acid orthophosphate solution containing iron, zinc or manganese. The coatings consist of a thick porous layer of fine phosphate crystals, tightly bonded to the steel. When forming steel sheet, the parts are often phosphatized in order to improve the surface properties of the sheet. The coatings do not provide significant corrosion resistance when used alone, but they provide an excellent base for oils, waxes or paints, and they help to prevent the spreading of rust under layers of paint.

Organic Coatings

Diverse types of paints, and high performance organic coatings have been developed as a need to protect equipment from environmental damage. The building blocks for epoxies and modern polyurethane coatings are other derivatives produced by refining petroleum products.

Alloying

Alloying with the aim to specifically improve corrosion resistance has been an activity which has received much attention. Stainless steel is a very good example of an alloy which owes its popularity largely due to its excellent corrosion resistance. Improvement in corrosion resistance through alloying is adopted provided the mechanical properties, other physical

properties (like thermal conductivity, joining ability, machinability, etc.) and ensuing cost escalation can be tolerated. The basic philosophy is either addition of an element which increases the electrode potential towards nobler directions or enhances the possibility of a protective film. Stainless steel (SS) which has significant chromium in it, exploits the latter, through the ability of Cr to provide an impervious oxide film. Certain alloying elements in very small quantities significantly improve specific corrosion resistance. For example, addition of Mo improves the pitting resistance of stainless steels, addition of tin to brass improves its resistance to dealloying, addition of rare earth elements to linepipe grade steels can improve resistance to HIC by scavenging S present in the steel, and addition of B to Ni-aluminides is essential to reduce hydrogen embrittlement. Weathering steels, a special class of steels especially resistant to alternate wetting and drying, acquires it high corrosion resistance on account of Cu, Si and P present in small amounts.

In a contrary fashion, removal or reduction of certain harmful elements can also substantially improve the corrosion performance. Reducing C in SS as is done for the 304L and 316L grades significantly improves sensitization resistance. This is obvious because the governing event in sensitization is carbide precipitation, so that lower the available C, less the chance of carbides. Similarly reducing S in linepipe grade steels would improve the HIC resistance, not only which, even a change in the shape and angularity of the sulphide inclusions would be beneficial. The development of alloy grades for high temperature applications is a good demonstration of how through alloying manipulations better and better corrosion resistance has been achieved.

Electrochemical means

The electrochemical methodologies resort to the application of voltage or current to the component to be protected. The philosophy of electrochemical potential is based on the fact that there are regimes of potential in which the material of construction does not corrode. This is done by either rendering it passive (anodic protection) or it is forced to the cathodic regimes where the oxidation reaction (corrosion) is suppressed (cathodic protection).

Anodic protection

In strongly alkaline or acidic environments, anodic protection is a useful corrosion control technique. The method involves applying a potential to the component thereby taking it to its anodic regime where it passivates. Therefore, anodic protection is applicable only for material-environment combinations which show passivation. Specifically, in metal-environment conditions where active-passive behaviour is demonstrated, anodic protection is usually effective. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements. Anodic protection has been most extensively applied to protect equipment used to store and handle sulfuric acid. Historically, anodic protection has the widest application in the process industries and in particular on mild or stainless steel equipment use for concentrated sulphuric acid storage. Equipment, such as pulp and paper mill digesters and recausticizing (white, green & black) liquor clarifiers and storage tanks have also been effectively protected.

15

Cathodic protection

The basic principle of CP is the reduction of metal dissolution through the application of a cathodic current. Cathodic protection is often applied to coated structures, with the coating providing the primary corrosion protection and thereby reducing the current requirements for cathodic protection. Cathodic protection is the most widely used method for corrosion of metallic structures. Cathodic protection can be brought about by essentially two means:

Using Sacrificial Anodes

This exploits the fact that certain metals/ alloys are more reactive electrochemically than others. When two metals are electrically connected to each other in a electrolyte, electrons flow from the more active metal to the other causing the more reactive metal/ alloy to corrode while the less reactive metal/alloy is protected. The more reactive metal which sacrifices itself is called the sacrificial anode. It is obvious that the most reactive metal in the galvanic series would act as the best sacrificial anode. Therefore magnesium heads the list as the most suitable anodic metal while zinc and aluminum are two other candidates. In fact galvanizing is nothing but the operation of zinc sacrificial anode on steel or iron surface. Sacrificial anodes are inherently safer system than impressed cathodic protection systems because the normal potentials generated are insufficient to damage coatings present on the surface to be protected.

Impressed Current Cathodic Protection

Cathodic protection can be also applied by connecting the metal to be protected to the negative terminal of a direct current (DC) source while an auxiliary anode is connected to the positive terminal. In such an arrangement there is no need for the anode to be more active than the structure to be protected. There are basically three types of anode: Inert or non consumable anodes, Semi-consumable anodes and Consumable anodes. The metal is effectively polarized to high negative potentials thereby rendering it immune to corrosion.

Summary

Corrosion is an energitacally favourable phenomenon for reactive metals and alloys. The propensity for corrosion of a metal or alloy can be gauged through its electrode potential in a given electrochemical media. A listing of the electrode potential, also known as the electrochemical series, helps in this diagnosis and also indicates the relative resistance of two metals to corrosion. Corrosion is however a kinetic phenomena and requires an understanding of the various kinetic issues related to it. Corrosion occurs through the operation of electrochemical cells with oxidation (release of electron/s) occurring at the anode and reduction (acceptance of electron/s) occurring at the cathode. Thus the anode corrodes by metal dissolution. In metallic corrosion, the anodic and cathodic reactions may and often occurs on the same metal surface. This "mixed electrode" behavior is what is responsible for corrosion of single metals, not in contact with any other metal, in solution. Any electrochemical reaction mandates charge conservation, that is, the total number of electrons produced at the anode must be equal to the total number of electrons absorbed at the cathode. This gives rise to the "area effect" in corrosion, which forecasts a high corrosion for a low anode/cathode ratio and vice versa. It is also observed that certain metals and

their alloys (aluminum for example) in spite of being quite active thermodynamically, do not corrode substantially under normal corroding conditions. This is due to their ability to "passivate" or the ability to form a protective oxide film, best exemplified in stainless steels.

Phenomenologically and on the basis of appearance, eight forms of corrosion is the most popular form of classification. A few subsets of these forms, demand special mention due to either their widespread presence, or certain peculiarities in their causative agents. Hydrogen assisted degradation for instance can be found in a host of components experiencing from very low to very high hydrogen concentrations (or fugacities). Microbiologically Induced Corrosion (MIC) phenomenologically fall in one or the other of the more conventional forms of corrosion (pitting, crevice or general) and yet deserves separate mention as the causative agents are microorganisms which directly or indirectly enhance corrosion. Cavitation is a special case of erosion corrosion caused by pressure differentials in fluids.

Corrosion prevention methodologies can be categorized roughly into five. These methods have their own inherent advantages and disadvantages. The suitability and applicability of each method depends on the component-environment combination, safety perceptions and economics.

REFERENCES :

1) *The Corrosion Handbook; MPI Group, (Inst. of Materials, Inst. Of Corrosion) 1999.*

2) *Cathodic Protection; 2nd Edition; J.H. Morgan, National Association of Corrosion Engineers (NACE) 1987.*

3) *Peabody's Control of Pipeline Corrosion; 2nd edition, Ed by R Bianchetti, NACE, 2000.*

4) *Corrosion and corrosion control; H H Uhlig, Wiley, New York, 1985 (3rd edition).*

5) *Corrosion; L L Shreir, Newnes-Butterworth, 3rd edition.*

6) *Cathodic Protection Criteria - A Literature Survey; National Association of Corrosion Engineers (NACE) 1989.*

7) *Handbook of Cathodic Corrosion Protection; 3rd edition; W.V. Baeckmann, Gulf Pub., 1997.*

8) *Corrosion Resistant Materials Handbook; D. J. De Renzo & Ibert Mellan; William Andrews, 1985.*

9) *Corrosion Basics: An Introduction, 2nd Edition, by P. R. Roberge, NACE Press Book, 2006.*

10) *Corrosion Inspection and Monitoring; P. R. Roberge, John Wiley & Sons; 2007.*

11) *Handbook of Corrosion Engineering; by P. R. Roberge, McGraw-Hill; 2000.*

12) *ASM Handbook Volume 13A: Corrosion: Fundamentals, Testing, and Protection; Edited by Stephen D. Cramer and Bernard S. Covino, Jr.*

13) *An Introduction to Metallic Corrosion; U.R. Evans; Edward Arnold, 1948.*

14) *Corrosion Engineering; M.G. Fontana .& N.D. Greene; McGraw-Hill, 1967.*

15) *Corrosion for Students of Science and Engineering; K.R. Trethewey & J.Chamberlain; Longman Scientific & Technical, 1988.*

16) *The Causes and Prevention of Corrosion; A.A. Pollitt; Ernest Benn, 1923.*

17) *Fundamentals of Electrochemical Corrosion; E. E. Stansbury & R. A. Buchanan, ASM International, 2000.*

18) *Principles and Prevention of Corrosion, 2nd Edition; Denny A. Jones; Prentice Hall, 1995*

19) *Corrosion Science and Technology; David E.J. Talbot & James D.R. Talbot; CRC, 1997.*

20) *A Practical Manual on Microbiologically Influenced Corrosion, Volume 2; John G. Stoecker (Editor); NACE International,2001.*

21) *Atmospheric Corrosion, 1st edition; C. Leygraf & T. Graedel; Wiley-Interscience, 2000*