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SCHOOL OF BIO & CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Corrosion Engineering – SCH1614

INTRODUCTION

Corrosion is a natural process, which converts a refined metal to a more stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and stopping corrosion. Corrosion can be defined as the degradation of a material dueto a reaction with its environment.

Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure.

Materials can be metals, polymers (plastics, rubbers, etc.), ceramics (concrete, brick, etc.) or composites-mechanical mixtures of two or more materials with different properties. Because metals are the most used type of structural materials most of this web site will be devoted to the corrosion of metals.

Corrosion Engineering is the specialist discipline of applying scientific knowledge, natural laws and physical resources in order to design and implement materials, structures, devices, systems and procedures to manage the natural phenomenon known as corrosion. Generally related to Metallurgy, Corrosion Engineering also relates to non-metallics including ceramics. Corrosion Engineers often manage other not-strictly-corrosion processes including (but not restricted to) cracking, brittle fracture, crazing, fretting, erosion and more.

THE CONSEQUENCES OF CORROSION / CORROSION DAMAGE

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarised as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a cracklike structure, very considerable weakening may result from quite a small amount of metal loss.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

CORROSION RATE EXPRESSION

Corrosion rates have been expressed in a variety of ways such as percent weightloss, milligrams per square centimeter per day and grams per square inch per hour.These do not express corrosion resistance interms of penetration. From an engineering point of view, the rate of penetration or the thinning of a structural piece can be used to predict the life of a given component.

The expression mils per year (mpy) is the most desirable way of expressingcorrosion rates.

Mpy = 534 W / DAT

Where

W is the weight loss in mg

D is the density of the Specimen in g/cm^{3}A is

the area of the specimen in Sq.In

T is the exposure time in Hr

CLASSIFICATION OF CORROSION

Corrosion can be classified in different ways, such as

- Chemical and electrochemical
- High temperature and low temperature
- Wet corrosion and dry corrosion.

Dry corrosion occurs in the absence of aqueous environment, usually in thepresence of gases and vapours, mainly at high temperatures.

There are different forms of corrosion such as

1. Galvanic corrosion
2. Crevice corrosion
3. Pitting
4. Intergranular corrosion
5. Erosion corrosion
6. Stress corrosion

ELECTROCHEMICAL CORROSION REACTION

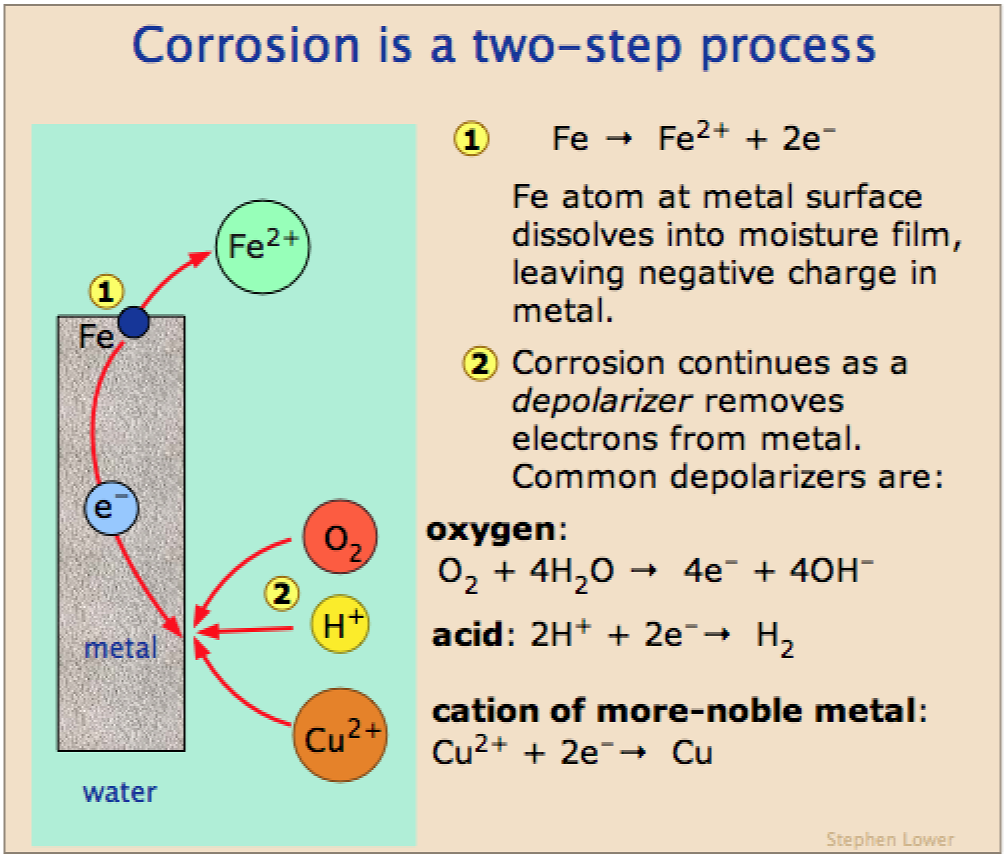
Electrochemical nature of corrosion can be understood by examining zincdissolution in dilute hydrochloric acid.

$Zn + 2HCl = ZnCl2 + H2$

Anodic reaction is $Zn = Zn^{++} + 2e$

with the reduction of $2H^+ + 2e = H2$ at cathodic areas on the surface of zinc metal.There are two half reactions constituting the net cell reaction.

Environmental effects such as those of presence of oxygen and other oxidizers,changes in flow rates (velocity), temperature, reactant concentrations and pH would influence rates of anodic and cathodic reactions.



Corrosion is a two-step process

① $Fe \rightarrow Fe^{2+} + 2e^-$

Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

② Corrosion continues as a *depolarizer* removes electrons from metal. Common depolarizers are:

oxygen:
$O_2 + 4H_2O \rightarrow 4e^- + 4OH^-$

acid: $2H^+ + 2e^- \rightarrow H_2$

cation of more-noble metal:
$Cu^{2+} + 2e^- \rightarrow Cu$

Stephen Lower

Rusting of iron consists of the formation of hydrated oxide, $Fe(OH)_3$, $FeO(OH)$, oreven $Fe_2O_3.H_2O$. It is an electrochemical process which requires the presence of water, oxygen and an electrolyte. In the absence of any one of these rusting doesnot occur to any significant extent. In air, a relative humidity of over 50% providesthe necessary amount of water and at 80% or above corrosion of bare steel is worse.

When a droplet of water containing a little dissolved oxygen falls on an steel pipe,the solid iron or Fe(s) under the droplet oxidizes:

$Fe(s) \text{ --> } Fe^{2+}(aq) + 2e^-$

The electrons are quickly consumed by hydrogen ions from water (H_2O) and dissolved oxygen or $O_2(aq)$ at the edge of the droplet to produce water:

$4e^- + 4H^+(aq) + O_2(aq) \rightarrow 2H_2O(l)$

More acidic water increases corrosion. If the pH is very low the hydrogen ions willconsume the electrons anyway, making hydrogen gas instead of water:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

Polarization

Mechanism in which the electrochemical reaction tends to be carried outActivation

Polarization

Activation polarization occurs when the electrochemical reaction proceeds throughseveral successive steps. The speed of the overall reaction is determined by the slowest step (known as the rate-determining step) of the process. For example, in ahydrogen reduction reaction, the reaction may proceed as follows:

1. Hydrogen ions are absorbed from the solution onto the anode surface.
2. Electron transfer occurs from the anode to the hydrogen ions to formhydrogen.
3. The hydrogen atoms form hydrogen gas molecules.
4. Hydrogen gas bubbles are formed.

Concentration Polarization

Concentration polarization of an electrode is the result of formation of a diffusion layer adjacent to the surface of the electrode where there is a gradient of ion concentration. Diffusion of the ions through the layers controls the electrochemicalreaction and is important for processes such as electroplating and corrosion.

Concentration polarization may be reduced by increasing agitation or raising thetemperature of the electrolyte.

Passivity

Passivity occurs when an oxide layer forms a continuous film on a metal surfacethat prevents further oxidation (corrosion). Metals that are normally subject to corrosion will sometimes exhibit passivity.

Passivity is caused by the buildup of a layer of metal oxide on the surface of a metal. In order to provide passivity, this oxide layer must be both stable and tenacious. It is formed by corrosion when the products of corrosion are insoluble inthe particular environment to which the metal is exposed. The metal oxide acts as abarrier by separating the metal surface from its environment and prevents corrosionuntil the reactants diffuse through the oxide film. This diffusion can take a very long time, or may never occur at all.

Metals such as zirconium, chromium, aluminum and stainless steel form oxide films when exposed to the atmosphere or to water. In some cases, the film is sothin that it's invisible to the naked eye. Nevertheless, it is still very effective in giving these metals passivity.

Passivation refers to a material becoming "passive," that is, less affected or corroded by the environment of future use. Passivation involves creation of an outer layer of shield material that is applied as a microcoating, created by chemicalreaction with the base material, or allowed to build from spontaneous oxidation in the air. As a technique, passivation is the use of a light coat of a protectivematerial, such as metal oxide, to create a shell against corrosion. Passivation can occur only in certain conditions, and is used in microelectronics to enhance silicon.

Environmental effects

1. Effect of oxygen and oxidizers
2. Effect of velocity
3. Effect of temperature
4. Effect of corrosive concentration
5. Effect of galvanic coupling

Effect of oxygen and oxidizers

For metals that exhibit active-passive transition, passivity is achieved only if a sufficient quantity of oxidizer is added to the medium. Increasing corrosion ratewith increasing oxidizer concentrations is characteristic of monel and copper inacid solutions containing oxygen. Both of these materials do not passivate.

An increase in corrosion rate, followed by a rapid decrease and then a corrosion rate that is independent of oxidizer concentration is characteristic of such active- passive metals and alloys. By knowing the basic characteristics of a metal or alloyand the environment to which it is exposed it is possible to predict the effect of oxidizer additions.

Effects of Velocity

The effect of velocity on corrosion rate depends on the characteristics of the metaland the environment to which it is exposed. For corrosion processes that are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate. If the corrosion process is under cathodic diffusion control, the agitation increases the corrosion rate.

Effect of Temperature

Temperature increases the rate of almost all chemical reactions.A very rapid or exponential increase in corrosion rate occurs with increasing temperature.

Effects of corrosive concentration

Many materials that exhibit passivity effects are only negligibly affected by wide changes in corrosive concentration.

Effect of galvanic coupling

In many practical applications, the contact of dissimilar materials is unavoidable. In complex process streams and piping arrangements, different metals and alloys are frequently in contact with each other and the corrosive medium. Consider a piece of zinc in a hydrochloric acid solution and contacted to a noble metal such as platinum. Since platinum is inert in this medium, it tends to increase the surface at which hydrogen evolution can occur. Further, hydrogen evolution occurs much more readily on the surface of platinum than on zinc.

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TYPES OF CORROSION

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode whenexposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the rusting of steel. Corrosion processes are usually electrochemical in nature, having the essential features of a battery.

When metal atoms are exposed to an environment containing water molecules theycan give up electrons, becoming themselves positively charged ions, provided an electrical circuit can be completed. This effect can be concentrated locally to forma pit or, *sometimes a crack*, or it can extend across a wide area to produce general wastage. *Localized corrosion* that leads to pitting may provide sites for fatigue initiation and, additionally, corrosive agents like seawater may lead to greatly enhanced growth of the fatigue crack. *Pitting corrosion* also occurs much faster in areas where *microstructural changes* have occurred due to welding operations.

The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons, as shown in the simple model on the left, that are consumed by a secondary process (cathodic reaction). These two processes have to balance their charges. The sites hosting these two processes can be *located close to each othe*ron the metal's surface, *or far apart depending on the circumstances*. This simple observation has a major impact in many aspects of corrosion prevention andcontrol, for designing new corrosion *monitoring techniques* to avoiding the most insidious or *localized forms of corrosion*.

Factors influencing corrosion

1. Based on the nature of the metal

Position in galvanic series
Overvoltage
Relative areas of the anodic and cathodic partsPurity
of the metal
Physical state of the metal Nature of
the surface film Passive character of
the metal Solubility of corrosion
productsVolatility of corrosion
products

2. Nature of the corroding environment

Temperature
Humidity of air
Presence of impurities in atmosphereInfluence of
Ph
Nature of ions present
Conductance of the corroding medium Formation
of oxygen concentration cellFlow velocity of
process stream Polarization of electrodes

General Attack Corrosion

Also known as uniform attack corrosion, general attack corrosion is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately,the metal deteriorates to the point of failure.

General attack corrosion accounts for the greatest amount of metal destruction by corrosion, but is considered as a safe form of corrosion, due to the fact that it is predictable, manageable and often preventable.

Localized Corrosion

Unlike general attack corrosion, localized corrosion specifically targets one area ofthe metal structure. Localized corrosion is classified as one of three types:

- Pitting: Pitting results when a small hole, or cavity, forms in the metal, usually as aresult of de-passivation of a small area. This area becomes anodic, while part of theremaining metal becomes cathodic, producing a localized galvanic reaction. The deterioration of this small area penetrates the metal and can lead to failure. This form of corrosion is often difficult to detect due to the fact that it is usually relatively small and may be covered and hidden by corrosion-produced compounds.Pitting Corrosion occurs under certain conditions, which leads to accelerated corrosion in certain areas rather than uniform corrosion throughout the piece. Such conditions include low concentrations of oxygen or high concentrations of chlorides (anions) that interfere with the alloy’s ability to reform a passivating film. In the worst cases, most of the surface remains protected, but tiny fluctuations degrade the film in a few critical areas. Corrosion at these points is amplified and can cause pits.

- Crevice corrosion: Similar to pitting, crevice corrosion occurs at a specific location. This type of corrosion is often associated with a stagnant micro- environment, like those found under gaskets and washers and clamps. Acidicconditions, or a depletion of oxygen in a crevice can lead to crevice corrosion.
- Filiform corrosion: Occurring under painted or plated surfaces when water breaches the coating, filiform corrosion begins at small defects in the coatingand spreads to cause structural weakness.

Galvanic Corrosion

Galvanic corrosion, or dissimiliar metal corrosion, occurs when two different metals are located together in a corrosive electrolyte. A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly than it would otherwise.

Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact, and
- The metals must be exposed to an electrolyte

Here is a brief overview of some common types of corrosion:

Galvanic corrosion is the most common and impactful form of corrosion. It occurswhen two dissimilar (different) metals are in contact in the presence of an electrolyte. In a galvanic cell (bimetallic couple), the more active metal (anode) corrodes and the more noble metal (cathode) is protected. There are a number of factors that affect the galvanic corrosion including types of metals, relative size of anode, and environment (temperature, humidity, salinity, etc.)

Galvanic corrosion is extraordinarily common, and occurs when two metals with different electrochemical charges are linked via a conductive path. Corrosion occurs when metal ions move from the anodized metal to the cathodic metal. Inthis case, a corrosion resistant coating would be applied to prevent either the transfer of ions or the condition that causes it. Galvanic corrosion can also occur when one impure metal is present. If a metal contains a combination of alloys that possess different charges, one of the metals can become corroded. The anodized metal is the weaker, less resistant one, and loses ions to the stronger, positively charged cathodic metal. Without exposure to an electrical current, the metal corrodes uniformly; this is then known as general corrosion.

Environmental Cracking

Environmental cracking is a corrosion process that can result from a combination of environmental conditions affecting the metal. Chemical, temperature and stress- related conditions can result in the following types of environmental corrosion:

- Stress Corrosion Cracking (SCC)
- Corrosion fatigue
- Hydrogen-induced cracking
- Liquid metal embrittlement

- Microbial corrosion, commonly referred to as microbiologically influenced corrosion (MIC) is caused by microorganisms. It applies to both metallic andnon-metallic materials with or without oxygen. When oxygen is absent,sulfate-reducing bacteria are active and produce hydrogen sulfide causing sulfide stress cracking. When oxygen is present, some bacteria may directly oxidize iron to iron oxides and hydroxides. Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

- Stress-corrosion cracking (SCC) can seriously damage a component beyond the point of repair. When subjected to extreme tensile stress, a metal component can experience SCC along the grain boundary—cracks form, which are then targets for further corrosion. There are multiple causes of SCC, including stress caused by cold work, welding, and thermal treatment. These factors, combined with exposure to an environment that often increases and intensifies stress-cracking, can mean a part goes from suffering minor stress-corrosion to experiencing failure or irreparable damage.

Crevice Corrosion

Crevice corrosion is a localized attack on a metal adjacent to the crevice between two joining surfaces (two metals or metal-nonmetal crevices). The corrosion is generally confined to one localized area to one metal. This type of corrosion can beinitiated by concentration gradients (due to ions or oxygen). Accumulation ofchlorides inside crevice will aggravate damage. Various factors influence crevice corrosion, such as. Materials: alloy composition, metallographic structure.Environmental conditions such as pH, oxygen concentration, halide concentrations, temperature. Geometrical features of crevices, surface roughness. Metal to metal ormetal to nonmetal type. Filiform corrosion is a special type of crevice corrosion

Erosion Corrosion

Erosion corrosion is the deterioration of metals and alloys due to relative movement between surfaces and corrosive fluids. Depending on the rate of this movement, abrasion takes place. This type of corrosion is characterized by groovesand surface patterns having directionality. Typical examples are Stainless alloy pump impeller, Condenser tube walls. All equipment types exposed to moving fluids are prone to erosion corrosion. Many failures can be attributed to impingement (impingement attack). Erosion corrosion due to high velocity impingement occurs in steam condenser tubes, slide valves in petroleum refinery athigh temperature, inlet pipes, cyclones and steam turbine blades. Cavitation damage can be classified as a special form of erosion corrosion. This is usually caused by formation and collapse of vapour bubbles in liquids closer to a metal surface. Typical examples include ship‟s propellers, pump impellers and hydraulic turbines. Surface damage similar to that of pitting can occur and both corrosionand mechanical factors are involved. Corrosion occurring at contact regions between materials under load subjected to slip and vibration can be termed Fretting. Such friction oxidation can occur in engine and automotive parts. Frettingis known to occur at bolted tie plates on rails.

Waterline Corrosion

When water is stored in a steel tank, it is generally found that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus. The area above the waterline acts as cathodic and is completely unaffected by corrosion.

Hydrogen Damage

It is a general term which refers to the mechanical damage of a metal caused by thepresence of or interaction with hydrogen. Hydrogen damage may be classified into four distinct types

1. Hydrogen blistering
2. Hydrogen embrittlement
3. Decarburization
4. Hydrogen attack

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UNIT – III – Corrosion Engineering – SCH1616

CORROSION PROTECTION MEASURES

3.0 Causes of Corrosion

All materials or products, plants, constructions, and buildings made of such materials are subject tophysical wear during use.

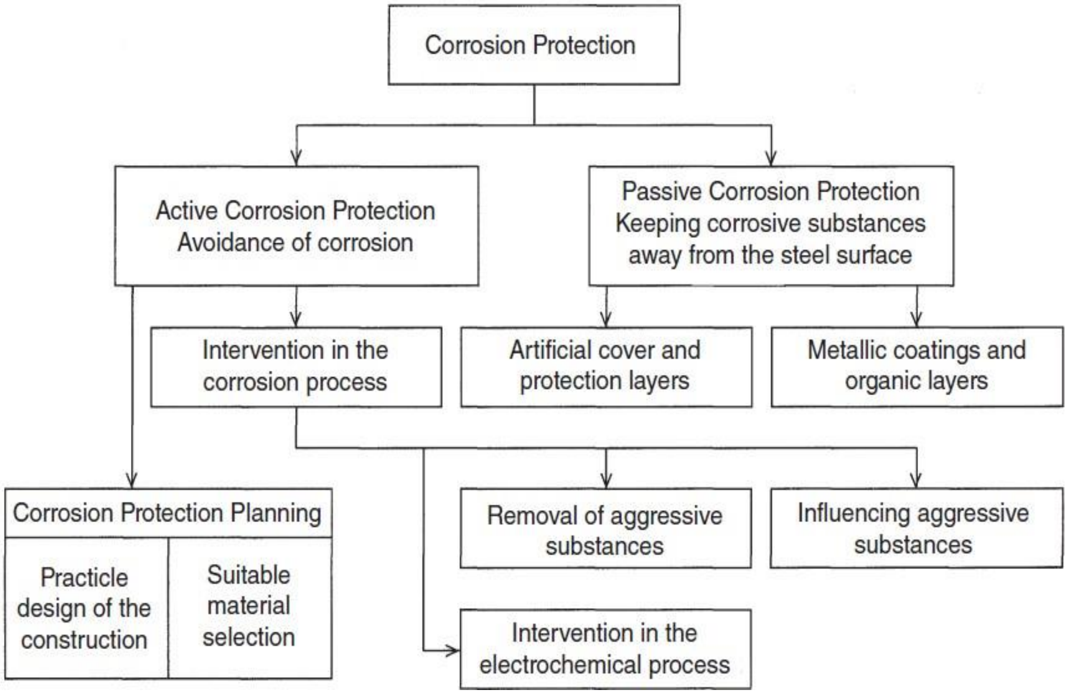
The technical and economic mastering of physical wear is difficult, since several causes are intertwinedand mutually influence each other. The interaction with certain media of the environment results in undesired reactions of the materials that trigger corrosion, weathering, decaying, embrittlement, and fouling.

While mechanical reactions lead to wear, chemical and electrochemical reactions cause corrosion. Suchprocesses emanate from the materials’ surfaces and lead to modifications of the material properties or totheir destruction. According to DIN EN ISO 8044, corrosion is defined as:

“ Physical interaction between a metal and its environment which results in changes of the metal ’ s properties and which may lead to significant functional impairment of the metal, the environment or thetechnical system of which they form a part. ”

3.1 Corrosion Protection

All methods, measures, and procedures aimed at the avoidance of corrosion damages are called corrosionprotection. Modifications of a corrosion system in so far as corrosion damages are minimized.



Methods, measures, and procedures of corrosion protection

3.1.1 Active Procedures

Active corrosion protection helps reduce or avoid corrosion by means of manipulation of the corrosion process, corrosion protection - related material selection, project engineering, design and manufacturing. But it is also a significant precondition for the effectiveness of passive corrosion - protection procedures. The following aspects are surveyed in this respect:

Design - Engineering Requirements The basic design - engineering requirements of the corrosion - protection - related design of steel structures are defined in the DIN

EN ISO 12944 - 3:

- corrosion protection of steel structures by protective paint systems;
- basic rules for protective coating;
- EN ISO 14713;
- protection of iron and steel structures against corrosion – zinc and aluminum coatings. In the figurative sense, they also apply to other products, unless these contain precise requirements determined in the respective DIN. In his engineering work, the design engineer has to consider the corrosive stress triggered by the corrosion types and phenomena. He has to depict a design engineering solution that is expected to provide an efficient protection period with optimal quality.

Here, essential aspects are:

- **Materials used**

Knowledge of their properties and corrosion behavior are required.

- **Surface design**

Preference to components with small corrosion - prone surfaces.

- **Profiles used**

Preference to profiles forming the smallest number of edges. The angle profile ranks before the U - profile,the U - profile before the I - profile.

Component arrangement

Components and structures have to be arranged in a way to prevent or minimize the impact of aggressivemedia and to ensure an unimpeded circulation of air.

- **Component joining**

The joining of components preferably requires smooth, closed surfaces. Fasteners require the samecorrosion protection as the constructions, or an equivalent one with regard to the protection period.

- **Manufacturing requirements**

The application of a passive corrosion - protection procedure entails the consideration of manufacturingcriteria already in the design phase.

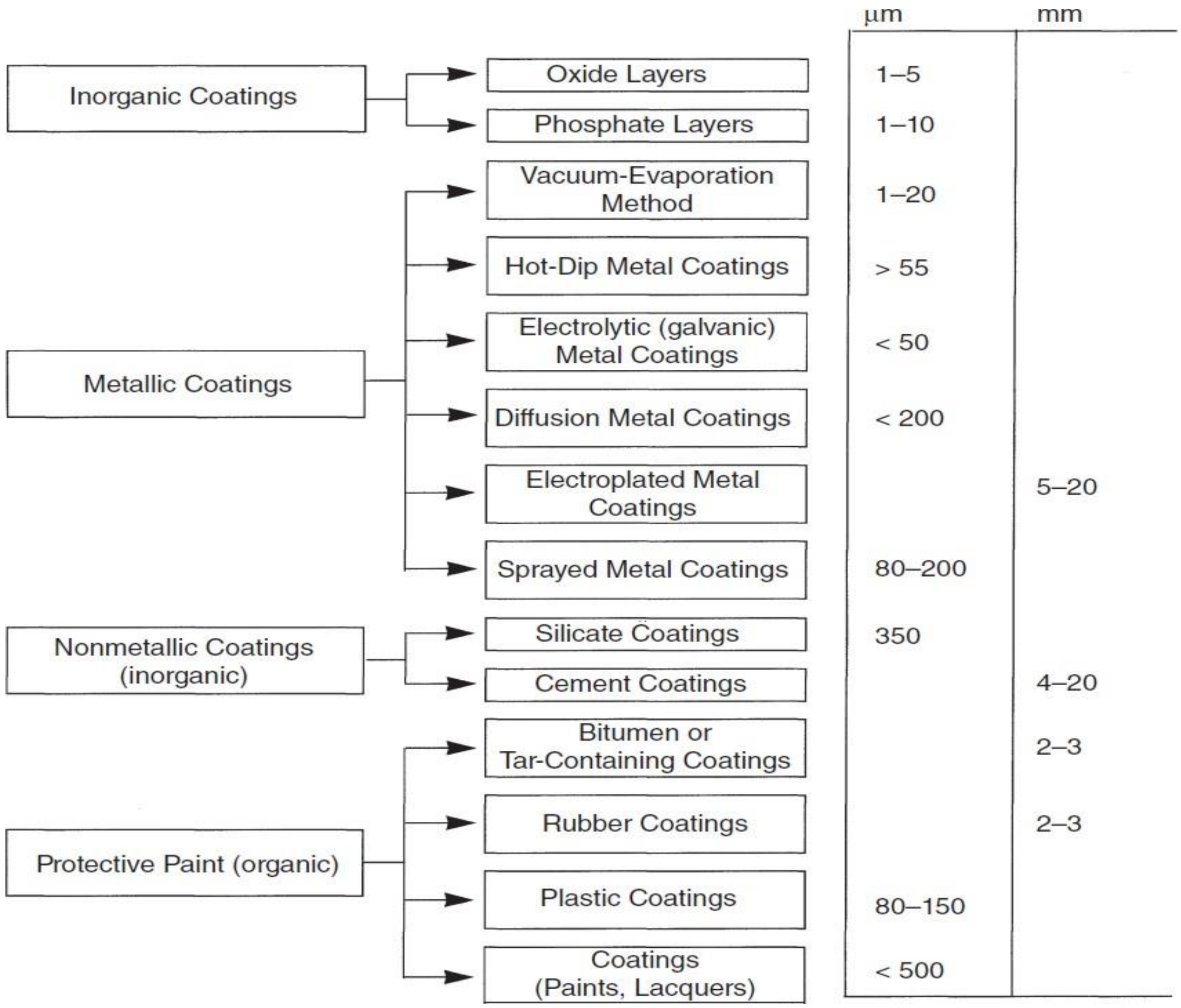
The determination of a corrosion - protection procedure results, *inter alia* , in the demand for a designcompatible with coating, hot - dip galvanizing, sputtering, enameling and galvanizing.

- **Maintenance - related requirements** The corrosion protection design has to allow for the possibility of efficient maintenance measures. Since the service life of components, constructions, products, plants and buildings differs from the protection period of the corrosion protection, repeated protection measures are usually required.

3.1.2 Passive Procedures

In passive corrosion protection, corrosion is prevented or at least decelerated through the isolation of themetal material from the corrosive agent by the applied protective layers. The technical preconditions of acorrosion layer are:

- the protective layer has to be pore - free;
- it must adhere firmly to the base material;
- it must be resistant to external mechanical stress;
- it must possess a certain ductility; and
- it must be corrosion resistant.



Overview of passive corrosion - protection procedures

3.2 Anodisation

Anodising is a process for producing decorative and protective films on articles made of aluminium and its alloys. The article is made the anode of an electolytic cell with aqueous sulfuric acid as electrolyte where the following overall oxidation reaction occurs.

$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$

A dense even layer of oxide about 0.08 μm thick is formed rapidly, followed much more slowly with a more porous layer up to 25μm thick.

Before anodising the surface of the article must be horoughly cleaned, normally using a detergent based process, and etched with a solution of sodium hydroxide.

After anodising the surface may be coloured with a dye or by an electrolytic method using appropriate metal cations, and then sealed by placing in boiling water, the pores in the oxide layer being closed off.

Anodizing successfully combines science with nature to create one of the world's best metal finishes. It is an electrochemical process that thickens and toughens the naturally occurring protective oxide. The resulting finish, depending on the process, is the second hardest substance known to man, second only to the diamond. The anodic coating is part of the metal, but has a porous structure which allows secondary infusions, (i.e. organic and inorganic coloring, lubricity aids, etc.)

Anodizing Definitions and Methods

While the chemical anodizing process remains the same for all applications, the mechanical methods varyaccording to the two physical types and shapes of metals used:

- **Batch Anodizing** - Involves racking parts and immersing them in a series of treatment tanks. Extrusions, sheets or bent metal parts, castings, cookware, cosmetic cases, flashlight bodies, and machined aluminum parts are just a few of the items that are batch anodized.
- **Continuous Coil Anodizing** - Involves continuous unwinding of pre-rolled coils through a series ofanodizing, etching and cleaning tanks, and then rewinding for shipment and fabrication. This method is used for high volume sheet, foil and less severely formed products such as lighting fixtures, reflectors, louvers, spacer bars for insulated glass, and continuous roofing systems.

Appearance options and quality are improved through the use of dyes and special pretreatment procedures. This makes the aluminum look like pewter, stainless steel, copper, brushed bronze or polished brass and can also be colored with brilliant blues, greens, reds, and many varieties of metallic gold and silver.

The unique dielectric properties of an anodized finish offer many opportunities for electrical applications.

On the Theory of Corrosion

In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen.

Electrolytic Theory of Corrosion of Iron

From the standpoint of the electrolytic theory, the explanation of the corrosion of iron is not complicated, and so far has been found in accordance with all the facts. Briefly stated, the explanation is as follows: Iron has a certain solution tension, even when the iron is chemically pure and the solvent pure water. The solution tension is modified by impurities or additional substances contained in the metal and in the solvent. The effect of the slightest segregation in the metal, or even unequal stresses and strains in the surface, will throw the surface out of equilibrium, and the solution tension will be greater at some points than at others.

The driving force that causes metals to corrode is a natural consequence of their temporary existence in metallic form. In order to produce metals starting from naturally occurring minerals and ores, it is necessary to provide a certain amount of energy. It is therefore only natural that when these metals are exposed to their environments they would revert back to the original state in which they were found. A typical cycle is illustrated by iron. The primary corrosion product of iron, for example, is $Fe(OH)2$ (or more likely $FeO·nH2 O$), but the action of oxygen and water can yield other products having different colors: • $Fe2 O3 ·H2 O$ or hydrous ferrous oxide, sometimes written as $Fe(OH)3$, is the principal component of red-brown rust. It can form a mineral called hematite, the most common iron ore. • $Fe3 O4 ·H2 O$ or hydrated magnetite, also called ferrous ferrite ($Fe2 O3 ·FeO$), is most often green but can be deep blue in the presence of organic complexants. • $Fe3 O4$ or magnetite is black. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the original compound. Table 2.1 describes the results of x-ray diffraction of products found on specimens exposed to real environments where it can be seen that the metals often revert to naturally occurring mineral forms during the corrosion process [1]. The amount of energy required and stored in a metal or that is freed by its corrosion varies from metal to metal. It is relatively high for metals such as magnesium, aluminum, and iron, and relatively low for metals such as copper, silver, and gold. Table 2.2 lists a few metals in order of diminishing amounts of energy required to convert them from their oxides to metal

The surface of the aluminum itself is toughened and hardened to a degree unmatched by any other process or material. The coating is 30 percent thicker than the metal it replaces, since the volume of oxide produced is greater than that of the metal replaced.

The resulting anodic coating is porous, allowing relatively easy coloring and sealing.

Hard Anodizing is a term used to describe the production of anodic coatings with film hardness or abrasion as their primary characteristic. They are usually thick by normal anodizing standards (greater than 25 microns) and they are produced using special anodizing conditions (very low temperature, high current density, special electrolytes). They find application in the engineering industry for components which require a very wear resistant surface such as piston, cylinders and hydraulic gear. They are often left unsealed, but may be impregnated with materials such as waxes or silicone fluids to give particular surface properties.

Batch and Coil Anodizing

Batch and coil anodizing are accomplished in five carefully controlled, calibrated, quality-tested stages:

- **Cleaning.** Alkaline and/or acid cleaners remove grease, and surface dirt.

- **Pre-Treatment**

Etching. An appealing matte surface finish is created with hot solutions of sodium hydroxide to remove minor surface imperfections. A thin layer of aluminum is removed to create a matte or dull finish.

Brightening. A near mirror finish is created with a concentrated mixture of phosphoric and nitric acids which chemically smooths the aluminum's surface.

- **Anodizing.** The anodic film is built and combined with the metal by passing an electrical current through an acid electrolyte bath in which the aluminum is immersed. The coating thickness and surface characteristics are tightly controlled to meet end product specifications.
- **Coloring.** Coloring is achieved in one of four ways:

Electrolytic Coloring (The two-step method) - After anodizing, the metal is immersed in a bath Anodizing Line containing an inorganic metal salt. Current is applied which deposits the metal salt in the base of the pores. The resulting color is dependent on the metal used and the processing conditions (the range of colors can be expanded by over dyeing the organic dyes). Electrolytic colors can be specified from any AAC member. Commonly used metals include tin, cobalt, nickel, and copper. This process offers color versatility and the most technically advanced coloring quality.

Integral Coloring - This so-called one-step process combines anodizing and coloring to simultaneously form and color the oxide cell wall in bronze and black shades while more abrasive resistant than conventional anodizing. It is the most expensive process since it requires corrosion prevention.

there are a variety of measures you can take to minimize corrosion. Here we'll highlight four of these methods based on cost and effectiveness.

BARRIER COATINGS

One of the easiest and cheapest ways to prevent corrosion is to use barrier coatings like paint, plastic, or powder. Powders, including epoxy, nylon, and urethane, are heated to the metal surface to create a thin film. Plastic and waxes are often sprayed onto metal surfaces. Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds. Today's paint systems are actually a combination of different paint layers that serve different functions. The primer coat acts as an inhibitor, the intermediate coat adds to the paint's overall thickness, and the finish coat provides resistance to environmental factors.

The biggest drawback with coatings is that they often need to be stripped and reapplied. Coatings that aren't applied properly can quickly fail and lead to increased levels of corrosion. Coatings may also contain volatile organic compounds, which can make them vulnerable to corrosion.

HOT-DIP GALVANIZATION

This corrosion prevention method involves dipping steel into molten zinc. The iron in the steel reacts with the zinc to create a tightly bonded alloy coating which serves as protection. The process has been around for more than 250 years and has been used for corrosion protection of things like artistic sculptures and playground equipment. Compared to other corrosion prevention methods, galvanization is known for lower initial costs, sustainability, and versatility.

Unfortunately, galvanization can't be done on-site, meaning companies have to pull equipment out of work to be treated. Some equipment may simply be too large for the process, forcing companies to abandon the idea altogether. In addition, if the process isn't done properly, the zinc can chip or peel. And high exposure to environmental elements can speed up the process of zinc wear, leading to increased maintenance check-ups. Lastly, the zinc fumes that release from the galvanizing process are toxic.

ALLOYED STEEL (STAINLESS)

Alloyed steel is one of the most effective corrosion prevention methods around, combining the properties of various metals to provide added strength and resistance to the resulting product. Corrosion-resistant nickel, for example, combined with oxidation-resistant chromium results in an alloy that can be used in oxidized and reduced chemical environments. Different alloys provide resistance to different conditions, giving companies greater flexibility.

Despite its effectiveness, alloyed steel is very expensive. Companies with limited financial resources will likely have to turn to other methods. Monitoring surface conditions are critical, as cracks or scratches can result in an increase in corrosion. Companies also need to make sure the agents used in maintenance don't include corrosion properties.

CATHODIC PROTECTION

Cathodic protection protects against galvanic corrosion, which occurs when two different metals are put together and exposed to a corrosive electrolyte. To prevent this, the active sites on the metal surface need to be converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

While cathodic protection is highly effective, anodes need to be checked often which can drive up costs of maintenance. They also increase the weight on the attached structure and aren't always effective in high-resistivity environments. Finally, anodes lead to increased water flow on ships and other underwater equipment.

EONCOAT

Choosing the right corrosion prevention for your equipment isn't easy. Each of the above methods has its pros and cons, which is where EonCoat comes in. Compared to the cost-effective, maintenance-free, and on-site ability of EonCoat, other methods can't compete. EonCoat uses no toxic chemicals and is environmentally friendly. Our 30-year warranty ensures your equipment stays protected for longer. We've made it a point to provide the best corrosion protection method available to help companies like yours moving along with as little hassle as possible. There's no reason not to take advantage of EonCoat's power today.

There are several cost effective ways to prevent corrosion including:

- Use non-corrosive metals, such as stainless steel or aluminium
- Make sure the metal surface stays clean and dry
- Use drying agents
- Use a coating or barrier product such as grease, oil, paint or carbon fibre coating
- Lay a layer of backfill, for example limestone, with underground piping
- Use a sacrificial anode to provide a cathodic protection system

Organic Dyeing - The organic dyeing process produces a wide variety of colors. These dyes offer vibrant colors with intensities that cannot be matched by any other paint system in the market. They can also provide excellent weather-fastness and light-fastness. Many structures built with these finishes have lasted more than 20 years. The color range can be broadened by over-dyeing the electrolytic colors with the organic dyes for a wider variety of colors and shades. This method is relatively inexpensive and involves the least amount of initial capital of any other coloring process.

Interference Coloring - An additional coloring procedure, recently in production, involves modification of the pore structure produced in sulfuric acid. Pore enlargement occurs at the base of the pore. Metal deposition at this location produces light-fast colors ranging from blue, green and yellow to red. The colors are caused by optical-interference effects, rather than by light scattering as with the basic electrolytic coloring process.

- **Sealing**. This process closes the pores in the anodic film, giving a surface resistant to staining, abrasion, crazing and color degradation.

Quality control. Throughout the entire anodizing process, AAC members monitor the process and quality of the product. The application of electrical power and color is preprogrammed and verified on all batches and coils.

This quality control ensures uniformity to end product specifications for film thickness, density, abrasion resistance, corrosion resistance, color uniformity, fade resistance, reflectivity, image clarity, insulative properties, adhesion and sealing.

In many cases, AAC members use Statistical Process Control (SPC) methods to meet rigorous quality assurance standards.

3.3 Enameling

Vitreous enamel is glass bonded by fusion to a metal surface. The most common glass is a fusion of silica, soda, lime, and a small amount of borax. Though normally transparent, various amounts of opacity can be produced by adding or growing crystals within the glass structure. A wide range of colors are produced by incorporating certain elements, mostly transition metals. The physical properties of glass can be controlled to permit bonding to most metals, for example: gold, platinum, silver, copper, steel, cast iron, aluminum and titanium. The word "Enamel" refers to the glass material, as well as to the finished product.

Enamel (glass) is crushed to a powder somewhat finer than granulated sugar and somewhat coarser than flour. This powder is applied, by one of several methods, to the metal surface. Next, the article is heated to 1000-1600°F, either in a preheated furnace, or with a hand-held torch. After few minutes, the article is removed and allowed to cool to room temperature. Subsequent coats, normally different colors, are applied. Sometimes 10-20 firings are required to bring about the desired results.

3.4 What is Rubber Lining?

Rubber lining is the skilled application of unvulcanised rubber sheet to prepared metal surfaces. The lined items are then vulcanised in a steam autoclave, fully bonding the rubber to the metal surface creating a durable and resilient protective rubber coating.

The rubber coating can be from 2mm to 50mm thick depending on the application, and can be bonded to mild steel, stainless steel, cast iron and aluminum.

Benefits

The principal benefits of rubber lining are its excellent resistance to corrosive and abrasive chemicals and materials, e.g. acids, alkalis, salt water, slurries, sand, shotblast media, crushed rock etc. In addition rubber linings provide other benefits including noise and vibration reduction, electrical and thermal insulation and product protection.

In general, a surface which requires protective coating from wear, corrosion and rust, a coat of rubber lining is applied. The lining of rubber is mostly applied to inner surfaces of the container. The surface to be rubber lined has to be cleaned by sandblasting to white metal. When the old lining to be replaced, surface decontamination may be required prior to sandblasting. Then the surface will be coated with adhesive with the help of a brush or roller. The adhesive. coating consists generally of two to three coats of different adhesives. Then rubber is applied by cutting the rubber sheet to fit to the shape of the surface to be lined and adhering it to the surface. Care is taken to remove any air trapped between surface and the rubber sheet. A special care to be taken for this. For pipe linings, a specialized methods are followed. Then the rubber along with the surface to be cured or in other words vulcanized in autoclave or under cover of steamor hot air. The final inspection consists of spark testing the lined surface by a high voltage which detects any pin holes in the lining and if it is found they has to be repaired and retested before putting the surface inrequired service.

3.4 Glass Lining

Glass Lining Properties Glass-lined steel equipment features unique characteristics that make it mandatory for use in processes when service conditions are particularly difficult. This is the case for applications involving products that exceed the resistance limitations for corrosion, abrasion, mechanical and thermal shocks. Chemical and pharmaceutical companies are continually extending the limits of their processes in order to increase productivity or succeed in new developments, calling for higher temperatures, lower temperatures, higher pressures, and higher concentrations. The capability to extend standard limitations is possible only if the equipment in use can withstand these progressive operating requirements.

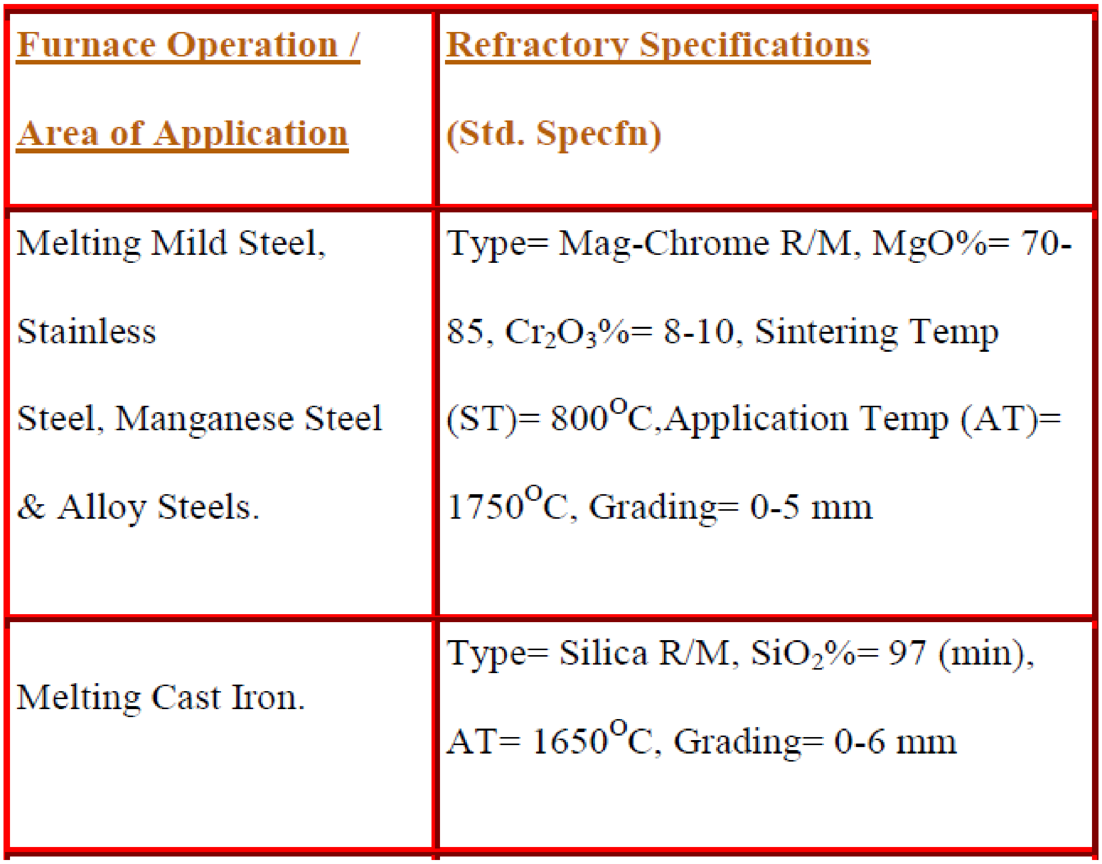
GLASS-LINED STEEL BENEFITS Glass-lined steel's composite metal/glass material of construction provides the best of both worlds of each of the primary components. The external steel construction.

Earlier was known, it would be possible to convert this current to an equivalent mass loss or corrosion penetration rate with a very useful relation discovered by Michael Faraday, a nineteenth century pioneer in electrochemistry. Faraday's empirical laws of electrolysis relate the current of an electrochemical reaction to the number of moles of the element being reacted and the number of moles of electrons involved. Supposing that the charge required for such reaction was one electron per molecule, as is the case for the plating or the corrosion attack of silver described respectively.
Ag e Ag(s) + − + → Ag(s) Ag e → + − + According to Faraday's law, the reaction with 1 mol of silver would require 1 mol of electrons, or 1 Avogadro's number of electrons (6.022 × 1023). The charge carried by 1 mol of electrons is known as 1 faraday (F).

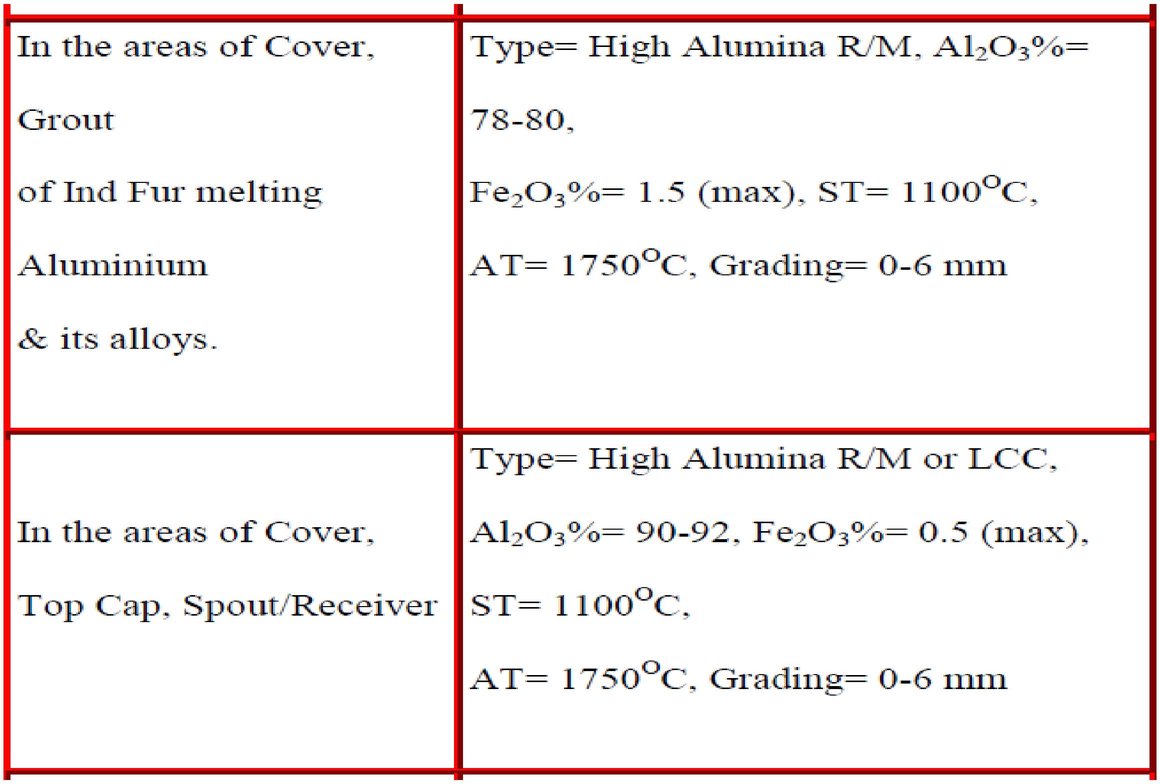
The faraday is related to other electrical units through the electronic charge; the electronic charge is 1.6 × 10−19 coulomb (C). Multiplying the electronic charge by the Avogadro number means that 1 F equals 96,485 C/(mol of electrons). Combining Faraday's principles with specific electrochemical reactions of known stoichiometry leads that relates the charge Q to chemical descriptors N and where N is the number of moles and ΔN the change in that amount n is the number of electrons per molecule of the species being reacted The charge Q can be defined in terms of electric current where I is the total current in amperes (A) t is the duration of the electrochemical process in seconds (s) provides strength while the internal glass lining gives nearly universal corrosion protection and a smooth non-contaminating surface. Additionally, companies choose to use glass-lined equipment for the various other benefits it offers, including: • Anti-Stick - Many substances will not stick to glass, but will stick to metal. • Purity - Glass has high quality standards for food and drug applications. • Flexibility – Glass can handle a diverse range of chemical conditions. Drastic changes in process involve no added investment for new equipment. • Ease of Cleaning – Fire polish lends itself to quick, easy cleaning and sterilization. • Absence of Catalytic Effect – Eliminates the possibility of catalytic effect. • Economy – Glass-lined steel equipment is the most corrosive resistant material. The cost is comparable to stainless and most alloys.

3.5 Refractory lining

The refractory lining is a protective layer installed inside the kiln or furnace to insulate the furnace steel structure from high temperatures. It also protects it from thermal shocks and chemical attack, and abrasion wears. It may consist of refractory bricks or monolithic refractories such as castable, gunning mixes. The refractory selection depends upon the temperature inside the unit and the chemical nature of the material being processed. The thickness of the lining is generally in the range 80 to 300mm. The shell must be maintained at low temperature to avoid deformation and also to save energy and protect the plant



Furnace Operation / Area of Application	**Refractory Specifications** **(Std. Specfn)**
Melting Mild Steel, Stainless Steel, Manganese Steel & Alloy Steels.	Type= Mag-Chrome R/M, MgO%= 70-85, Cr_2O_3%= 8-10, Sintering Temp (ST)= 800^{O}C,Application Temp (AT)= 1750^{O}C, Grading= 0-5 mm
Melting Cast Iron.	Type= Silica R/M, SiO_2%= 97 (min), AT= 1650^{O}C, Grading= 0-6 mm



In the areas of Cover, Grout of Ind Fur melting Aluminium & its alloys.	Type= High Alumina R/M, Al_2O_3%= 78-80, Fe_2O_3%= 1.5 (max), ST= 1100°C, AT= 1750°C, Grading= 0-6 mm
In the areas of Cover, Top Cap, Spout/Receiver	Type= High Alumina R/M or LCC, Al_2O_3%= 90-92, Fe_2O_3%= 0.5 (max), ST= 1100°C, AT= 1750°C, Grading= 0-6 mm

3.6 Factors Affecting Corrosion

1. Nature of the Metal 2. Nature of the environment.

3.6.1 Nature of Metal

(i) Position in Galvanic Series:

If two metals are present in electrolyte, the metal with less reduction potential undergoescorrosion.

- Greater the difference faster the corrosion.

(ii) Over Voltage:

Due to high evolution of hydrogen, the rate is slow.

(iii) Area and Distance:

When anodic metal area is smaller than cathodic area, rate of corrosionat anode is higher because of demand of electron by cathodic area.

(iv) Physical and Mechanical properties of Metal:

- Pure metals are more corrosion resistant.
- Smaller grain size metal have high solubility and corrosion.
- Uniform distribution of stress on metal reduces rate of corrosion.

- Passive metals shows higher corrosion resistance because of formation of protective oxide film ontheir surface.
- Polycrystalline forms are more sensitive.

3.6.2 Nature of Environment

- **Temperature:** directly proportional
- **Humidity:** faster in humid conditions
- **pH :** If less than 7 rate is high. Al, Zn, Sn, Pb, and Fe are affected by both acid and bases.
- **Impurities and Suspended Particles:** When these will get dissolved in moisture, provideselectrolyte for conductivity and hence corrosion increases.

3.7 Corrosion Control:

3.7.1 Selection of metal and alloy:

- Using pure and noble metals
- Practically not possible because of low strength of pure metal
- Use of metal alloys which are homogeneous

3.7.2 Proper design of metal:

- Minimal contact with medium
- Prevention from moisture
- Adequate ventilation and drainage
- Welding
- Avoid cervices b/w adjacent parts
- Bend should be smooth
- Bimetallic contacts should be avoided
- Paint cathodic portion
- Prevent uneven stress

➢ **Cathodic Protection:**

Force the metal to be protected to behave like cathode.

➢ **Sacrificial anodic protection**:

- Metal to be protected from corrosion connected to more anodic metal
- Commonly used metals Mg, Zn, Al and their alloys

➢ **Impressed current method:**

- Direct current is applied in opposite direction to nullify the corrosion current Converts the corrodingmetal from anode to cathode.

Modifying Environment

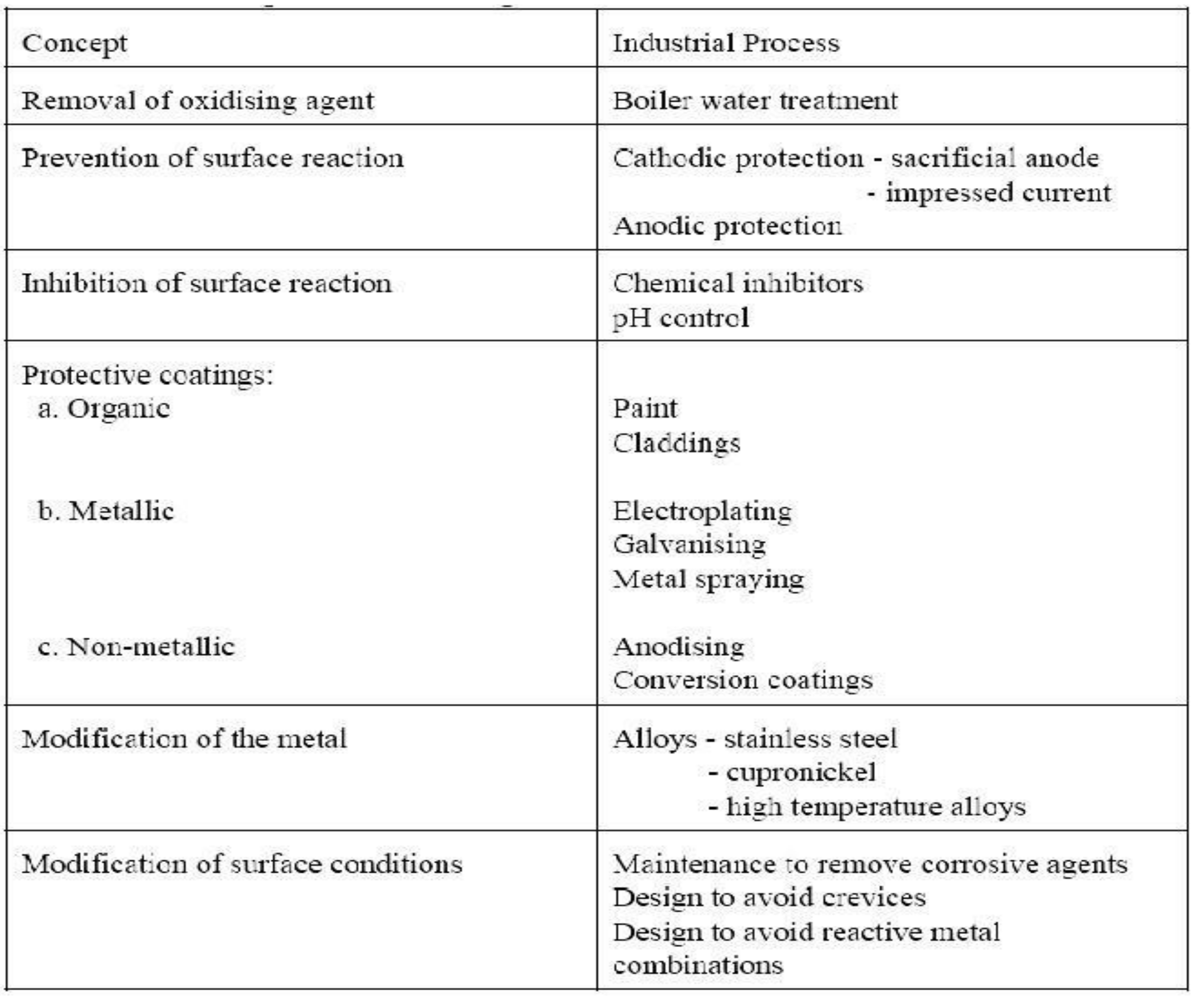
➢ **Eliminating dissolved oxygen**:

- De-aeration

- By using chemical substances like sodium sulphite and hydrazine. Also called **Deactivation.**
  - **Reducing Moisture:**
- Dehumidification by using silica gels
  - **Reducing Acidity**:
- Neutralizing the acidic environment by adding lime, NaOH, Ammonia
- Commonly used in refineries

  - **Protective coating:**
- Application of coating
- Coating material should be chemically inert under particular temp and pressure.

  - **Use of corrosion Inhibitor**
  1. **Anodic Inhibitor:**
- These are oxygen and oxidizing agent.
- They combine the anodic metal forming an oxide film which reduce corrosion
  2. **Cathodic Protection:**
- Organic inhibitors like amines, mercaptans, urea and thiourea reduces the H ion diffusion byadsorption
- Mercury, arsenic and antimony deposits films at cathodic area which raise the hydrogen overvolume.
- Eliminating Oxygen from the medium by adding sodium sulphate and hydrazine.



Concept	Industrial Process
Removal of oxidising agent	Boiler water treatment
Prevention of surface reaction	Cathodic protection - sacrificial anode - impressed current Anodic protection
Inhibition of surface reaction	Chemical inhibitors pH control
Protective coatings:	
a. Organic	Paint Claddings
b. Metallic	Electroplating Galvanising Metal spraying
c. Non-metallic	Anodising Conversion coatings
Modification of the metal	Alloys - stainless steel - cupronickel - high temperature alloys
Modification of surface conditions	Maintenance to remove corrosive agents Design to avoid crevices Design to avoid reactive metal combinations

3.8 Protective Coating

Surface preparation for Coating:

1. **Cleaning:**
- To prepare for suitable condition
- Removing contaminants to prevent detrimental reaction product
- E.g. de-greasing, sand blasting, vapour degreasing, pickling and alkaline cleaning.

2. **Solvent Cleaning:**
- Must be non-inflammable and nontoxic
- Trichloro trifluoroethane which has low toxicity are costlier
- Vapour de-greasing is economical and advantageous because of continuous cleaning with smallquantities of solvent.

3. **Electrolyte Pickling:**
- Provides better and rapid cleaning by increasing hydrogen evolution resulting in agitation andblasting action
- Sand blasting is mechanical cleaning.

4. **Alkaline Cleaning:**

- Cheaper and less hazardous
- Used in conjunction with surface active (wetting) agent
- Ability depends on pH, rapidly decreases below 8.5
- Other abilities are rinsability, detergent properties, sequestering, wetting etc.

5. **Acid Cleaning**

- Acid such as HCl, H_2SO_4, H_3PO_4 is very effective.
- 5-10% H_2SO_4 and HCl used to remove inorganic contaminants.
- Pickling are performed at high temp. (60 ℃)
- Is effective for removal of grease, oil , dirt and rust.

3.9 Methods of Application of Metallic Coating

1. **Hot Dipping:**

- Metal is kept in molten state and base metal is dipped into it.
- Used for producing a coating of low M.P
- E.G. Tinning (Tin coating on Iron)
- Process is followed by cooling the coating through a palm oil to prevent oxidation of tin plate to itsoxide.
- Palm oil layer is removed by alkaline cleansing agent.

2. **Metal Cladding:**

- The surface to be protected is sandwiched between two layers of the coating metals and pressedbetween rollers.
- E.g. Alclad Sheeting– Plate of duralumin is sandwiched between 99.5%pure aluminum

3. **Electro Plating**:

- Pure metal is made as cathode and base metal as anode.
- Electrochemically coat metal is deposited on base metal.
- This metal gives smooth, fine and uniform coating
- It depends on

  (i) Temperature (ii) Current density (iii) Electrolyte Concentration
  (iv) Nature of base metal (v) Time

4. **Electroless Plating:**

- Nobel metal is deposited catalytically on less noble metal by using reducing agent without usingelectrical energy.
- Advantage over Electro plating
  - More economical since no electricity required
  - Irregular shape can be plated uniformly
  - Plating on plastics can also be done

5. **Metal Spraying:**

- Coating is applied by means of spraying device
- E.g. Aluminum is plated in this way on Aircrafts.

6. Chemical Conversion Coating

- These are formed on metal surface by chemical reaction b/w metal surface and inorganic saltsolution
- Coating base metal is converted into one of the resultant protective film.
- These films are insoluble, adherent, crystalline or amorphous in nature.
- Can be done in 3 ways

1. Phosphate coating
2. Chromate coating
3. Anodized coating

1. Phosphate Coating

- Produced by chemical reaction b/w base metal and aq. H3PO4, Zn or Fe or Mn Phosphate
- Phosphate coating are applied Iron, Steel, and Zinc
- Film formed on base metal after coating consist of Zn-Fe, Mn-Fe Phosphates.

2. Chromate Coating

- Produced by dipping the base metal in Potassium chromate (acidic) followed by immersion inneutral chromate bath.
- Resulting film consist of trivalent and hexavalent chromium.
- Used as base for paints, lacquers and enamels.

3. Anodized Coating

- Formed by anodic oxidation process
- This is produced on non-ferrous metals like Al, Zn, Mg
- In this method base metal is made as anode
- Process is carried out by passing moderate direct current through a bath in which the metal issuspended as anode.
- Coating are formed as a result of Progressive oxidation starting at surface of base metal.

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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV-CORROSION ENGINEERING-SCH1614

4.0 APPLICATION OF CORROSION ENGINEERING

The mechanisms and methods of corrosion protection for stainless steel differ from that of carbon steels in filtration systems. The majority of carbon steel vessels have been manufactured with bare internal metal surfaces. In these cases, corrosion protection is provided by the formation of the natural barrier oxide coating (rust) that separates the metal from the surrounding environment. The degree of protection provided by the oxide film is a function of the thickness and physical characteristics of the oxide. Once the oxide forms and thickens over time without disruption, corrosion protection is good unless the film is mechanically removed. In addition, if water chemistry conditions are right, calcareous (calcium-rich) deposits from the water can provide a "self-healing" protective film on the surface of the metal or oxide. In some cases with carbon steel, mechanically adherent and tough organic coatings, such as epoxies, have been used as the primary corrosion protection system. In these cases the dielectric coating acts as the barrier between the metal and the environment. The use of dielectric coatings alone for corrosion protection does not guarantee corrosion protection since coating imperfections or "holidays" can allow contact with the environment. The corrosion protection of the organic coating can be supplemented by the use of a sacrificial anode. The combination of the epoxy coating with a sacrificial anode is a proven engineering solution to corrosion control in water systems. Stainless steels exhibit good general corrosion resistance in aerated water environments. Corrosion protection is provided by the formation of a relatively thin passive film that forms on the surface of the stainless steel if water and physical conditions are right. Passivation refers to the naturally formed "coating" on the surface of stainless steel. In general, if the water environment is aerated and the oxygenated water can reach the surface of the stainless steel, then the passive film forms, remains intact and provides excellent corrosion resistance. A corollary to their good general corrosion resistance is the fact that stainless steels are susceptible to localized forms of corrosion, such as pitting, crevice, stress cracking, etc. Localized corrosion problems arise when conditions within the tank construction or the water prevent formation of the passive film on some part of the stainless steel surface. In these situations, one portion of the stainless steel corrodes (the anode) to "protect" another portion of the metal (the cathode). For example, when pitting occurs, the bottom of the pit corrodes as the anode to protect the cathodic area (metal) adjacent to the opening of the pit. Eventually, the bottom of the pit can perforate the metal with a pinhole, while the vast majority of the stainless steel exhibits little or no corrosion. One possible explanation for the difference in service life performance between stainless and mild steel may be as simple as the thickness of the material used for construction and the difference in the mode of corrosion damage between the two materials. Typically, mild steel systems use a minimum of 3/16" (0.1875") thick plate for fabrication and general (uniform) corrosion is the primary mode of corrosion damage. Stainless steels in filtration systems range from 10 gage (0.135") to 14 gage (0.075") thickness and localized corrosion (crevice, pitting or microbiological corrosion) is the mode of corrosion damage. Since localized corrosion rates tend to be much greater than uniform corrosion rates, thinner members subjected to localized corrosion could fail in significantly shorter periods of time as

Crevice Corrosion: Crevice corrosion is a form of localized corrosion that is similar to pitting . Crevice corrosion occurs when any physical situation restricts access of oxygen to the surface of the material. By contrast, pitting usually initiates at metallurgical features present in the microstructure of the material. Crevice corrosion occurs at features inherent to the structure due to design, fabrication or operation (gaskets, lap welds, filtration media/metal interface, pockets of debris, etc.). The resistance of a stainless steel alloy to crevice corrosion is related to the composition and product form of the stainless steel, the severity of the crevice and the environment. Two of the most common grades of a stainless steel are type 304 and 316. The figures below show that, although some improvement in crevice performance is gained by changing the alloy from type 304 to type 316 stainless steel, crevice corrosion can persist. Further, increases in crevice corrosion resistance can be made with additional changes (increases) in alloy composition, but these improvements in corrosion resistance generally involve higher material cost and, possibly, changes in fabrication processes.

4.1 PUMPING: There are few industrial processes that exist today that do not depend on the humble centrifugal pump for efficient, reliable fluid transport. Some centrifugal pumps operate at extremes of temperature and pressure while others work just as hard maintaining a reliable supply of clean potable water. Irrespective of application, the reliability of modern centrifugal pumps is a testament to the pump manufacturer‟s knowledge of application, material properties and engineering design. Such is the reliability of modern centrifugal pumps that in all but the most challenging or critical of applications, reliability is often taken for granted. Only when a centrifugal pump falls short of service life expectations or fails unexpectedly does the technical complexity of moving fluids become apparent. By nature of operating principle, the components contained within a centrifugal pump are subjected to damaging mechanisms that challenge the design and materials used in pump construction. These damaging mechanisms apply equally to small and large centrifugal pumps alike. Fractional horsepower pumps such as those used domestically are affected by the same damaging mechanisms that affect some of the world‟s largest centrifugal dewatering pumps. In order to appreciate these damaging forces at work within an operating centrifugal pump, the basic components and principle of operation of a centrifugal pump needs first to be considered.

PUMP FAILURE The maintenance clearance tolerances between moving and stationary wetted components inside a centrifugal pump are critical for the efficient conversion of rotational energy into fluid flow or a pressure increase. The importance of tolerance increases with the pressure rating of the pump. Low pressure/high flow pumps are provided generous clearances and hydrodynamic inter-stage sealing to reduce fluid friction and enable the pumps to handle suspended solids. Conversely, medium/high pressure pumps have small clearances and are equipped physical sealing devices (such a wear rings) to provide inter-stage sealing . Medium/high pressure pumps typically also have closed face impellers with stationary diffuser vanes surrounding the impeller vane outlets. The geometry of the diffuser and impeller vanes are critical design features required for the desired hydrodynamic flow patterns within the pump. A change to the geometry of these components can produce profound reductions to both pump performance and efficiency. Medium/high pressure pumps do not tolerate solid particles contained in the fluid well because of these necessary features. High pressure, multiple stage pumps tolerate solids even less and special precautions are required to ensure that the service life of such pumps is not comprised by suspended solids.

CHEMICAL CORROSION The number of specific chemical corrosion processes documented to date is matched only by the variety of materials and material-environment systems affected. Although it is not possible to discuss all such systems, it is possible to examine those commonly encountered when working with centrifugal pumps constructed from standard engineering materials and operating in an aqueous service environment. Materials and especially metals contain much potential chemical energy as illustrated by the energy intensive methods required to prepare them from their ores. Steel for example, is made by purifying and alloying iron that comes from the reduction of iron ores (usually hematite) in a blast furnace. Much energy in the form of coal (as coke) is consumed in the process. Similarly, aluminum is made by first purifying ore (bauxite) to an aluminum oxide and then using electricity to produce the metal from a bath of molten oxide. The amount of electricity required to produce 1kg of metal is so large that aluminum is sometimes referred to as „solid electricity‟. Therefore, it is not surprising these and similar reactive metals lay dormant inside equipment waiting patiently for exposure to a suitable environment with which they can chemically react enabling them to release at least some of their stored potential chemical energy.

GALVANIC CORROSION Galvanic corrosion is a very common electrochemical corrosion phenomenon that can occur within centrifugal pumps. Galvanic corrosion occurs when two dissimilar metals are coupled together and exposed to a common corrosive water environment. The result is induced current flow between the metals, the flow of ions in the water and corrosion of the more active metal. Galvanic corrosion produces macroscopic metal loss and can be visually identified by careful examination. Galvanic corrosion is an important corrosion mechanism within centrifugal pumps because of the variety of different metals used in construction of a single pump unit. These metals are generally all coupled together inside a pump and most are exposed to the corrosive water environment as wetted pump surfaces.

PITTING CORROSION Pits are defined as cavity or hole where the surface diameter is equal to or less than the depth. The mechanism that causes pitting corrosion is an electrochemical process that occurs when a protective passive film is allowed to break-down on a susceptible metallic surface. Therefore the phenomenon is most common on metals that rely on a protective oxide for corrosion resistance such as stainless steels. Pitting corrosion is caused by the breakdown of a passive film on the surface of the metal forming small anodic regions while the majority of the metallic surface remains a large cathodic site. As a result of the „area effect‟ covered in the previous topic of galvanic corrosion, corrosion is greatly concentrated at small anodic sites producing deep localized metal loss. The focused intensity of the electrochemical process at anodic sites also results in the pitting corrosion process progressing rapidly. Pitting corrosion is a localized corrosion process but can be easily detected upon visual inspection because of the large number of pits formed and the wide general distribution of pits across a surface.Pitting corrosion can develop very quickly and is much more destructive that general corrosion for that reason. Also, once a pit has been initiated, it tends to remain an anodic site and continues to grow through an autocatalytic process. The environmental variables that effect the pitting corrosion of a susceptible metal are also those that tend to adversely affect the formation of passive/protective oxide films. These include the concentration of corrosive ions, the pH, dissolved O2 concentration as well as temperature of the water.

DEALLOYING CORROSION De-alloying corrosion (also known as selective leaching) is a corrosion process where a single metal is selectively removed from the metallic microstructure of an alloy. The removal of zinc from brass is the most common example of dealloying and is referred to as de-zincification. The electrochemical process that causes de-zincification is mechanistically similar to that of galvanic corrosion, but on a microscopic scale. The process involves the corrosion of metallic crystal grains rather than large metallic surfaces. The most commonly affected centrifugal pump components are brass impellers, bushings and bearing surfaces. Similar to graphitic corrosion, dezincification often does not result in dimensional change of a component but significantly effects the components wear properties and mechanical strength. When de-zincification presents over the entire wetted surface of the zinc containing copper alloy it is referred to a „layer‟ de-zincification. Occasionally, the mechanism may be concentrated under deposits or follow the variations in the metallic crystalline structure of a component such as casting artifacts. Although relatively uncommon in centrifugal pumps, this form of highly localized de-zincification known as „plug type dezincification‟ and can occur in brass accessories. The component containing water develops porosity at a small region usually at a low point and commences to slowly leak. The identification of layer type de-zincification is relatively straightforward on large surfaces such as impellers as these affected components exhibit a characteristic red discoloration due to remaining elemental copper. Identification on bushings and bearings is more complex and requires destructive metallurgical analysis for confirmation.

STRESS CRACKING CORROSION Stress cracking corrosion (SCC) results from the combination of a tensile stress with a corrosion mechanism. SCC is characterized by brittle fractures of thick walled materials that appear as intergranular cracks when examined using metallurgical microscopic techniques. For susceptible metals, a specific corrosive agent can usually be attributed to causing SCC in the presence of sufficient mechanical stress. For example, water containing ammonia is known to cause SCC of many copper containing alloys. AISI 304 and 316 stainless steels are also susceptible to SCC with the corrosive agent being the chloride ion. For SCC to occur, there exists a minimum applied stress and minimum concentration of corrosive agent needed. Prevention of SCC can therefore be affected by controlling the tensile stress to which a component is subjected as well as selecting materials based on the maximum concentration of corrosive agent that will be encountered in-service. Unless a complete fracture of a component occurs, SCC is difficult to detect with the naked eye and as a result often goes undiagnosed during inspection. Perhaps the best known example of SCC is that caused by the chloride ion on Austenitic stainless steels. The potential for SCC to occur increases not only with the tensile stress applied across the metallic surface, but also with the concentration and temperature of the chloride containing water to which the metals are exposed. Factors that affect the onset of SCC also include stagnation with SCC of 300 series stainless steels occurring at lower concentrations of chloride when dissolved oxygen is diminished. Concentrating mechanisms like evaporation can increase the localized concentration of a corrosive agent beyond that typically expected in the water being pumped. An example of this occurs when pumps using gland packing have water evaporate from the packing leaving behind elevated concentrations of salts. The heat generated by friction between the shaft and packing can result in SCC being initiated under the stress of rotational torque. The net result is inevitable shaft failure. The most effective method of preventing such shaft failures is by using a supply of fresh clean cold water to cool the packing or utilizing non-contact shaft sealing methods such as labyrinth seals.

MICROBOILOGICALLY INFLUENCED CORROISON Microbiologically influenced corrosion (MIC) is defined as the direct chemical interaction of organisms with materials to produce new corrosion chemistries and/or a marked acceleration of pre-existing corrosion processes. There are two forms of MIC classified a passive attack and active attack. Passive attack occurs when the growth of organisms on a metallic surface produces a deposit (called a biofilm). The biofilm consists of biological material secreted by organisms and acts as a binding material for suspended solids circulating in the water. As with under-deposit corrosion, the biofilm occludes the metallic surface from oxygen contained in the bulk water causing oxygen concentration cell to form. As with underdeposit corrosion, the nature of the corrosion is determined by the characteristics of the metallic surface and is most pronounced on metals relying on a protective oxide film. Active attack occurs when the organisms growing on a metallic surface produce metabolic by-products that are inherently corrosive to the metallic substrate. The three most common classes of organisms responsible for active attack are the sulfate reducers, acid producers and metal depositors. Sulfate reducers grow in anaerobic conditions and prefer to colonize low oxygen environments such as those created by deposits or general biofilms. These bacteria derive their metabolic energy from the reduction of sulfate present in water and hydrogen present at cathodic metallic surface regions to sulfides. In so doing, they produce regions of extreme metal loss with metallic sulfides as well as oxides produced as corrosion products. Equipment used to transfer waters within the oil and gas industries are particularly susceptible to attack by sulfate reducing bacteria due to the occlusion of oxygen created by oily films on metallic surfaces and a presence of high concentrations of organic/inorganic sulfur compounds present in such waters. Acid producers are another class of organism that can produce either inorganic or organic acids as a result of metabolic growth. These bacteria are also anaerobic and prefer to grow under biofilms and deposits usually in conjunction with sulfate reducing bacteria. These bacteria can cause deep metal loss in metallic surfaces susceptible to acidic corrosion such as steels, AISI 304 and AISI 316. Metal depositing bacteria derive their metabolic energy from the oxidation of metals. Gallionella is a filamentous bacterium that converts the ferrous to ferric ion. In the process, they produce large quantities of insoluble iron hydroxide and deep localized metal loss. Some bacteria like Gallionella are also capable of oxidizing manganese and causing precipitation onto metallic surfaces to the detriment of metals susceptible to severe under-deposit corrosion caused by manganese deposits such as brasses and cupronickels. Equipment used to draw bore waters are particularly susceptible to attack by metal depositing bacteria due to the relatively high concentrations of ferrous ion present in such waters.

UNDERDEPOSIT CORROSION Underdeposit corrosion is a corrosion form that occurs on the wetted surfaces of metals beneath a deposit. Underdeposit corrosion is form of corrosion frequently observed on pump casing surfaces especially those outside the main path of fluid flow and those behind impellers in the proximity of shaft seals. The deposit can form as a result of the accumulation of suspended particles, the precipitation of minerals contained in water or in-situ by another corrosion process. Underdeposit corrosion is relatively easy to identify visually during inspection when it occurs under a large mound of accumulated material. More subtle are those deposits visible only as small layered accumulations just proud of metal surface. Careful removal of the deposit reveals wastage of the metal underneath in an area confined to the original shape of the deposit. Underdeposit corrosion can cause metal wastage either directly or indirectly. The direct mechanism occurs when a deposit is inherently aggressive and corrosive to the metal surface. The corrosion of brass and 90:10 cupronickels by manganese containing deposits is an example. Indirect underdeposit corrosion is corrosion that occurs when a deposit or sediment covers the surface of a susceptible metal and excludes the supply of oxygen to the corroding surface beneath. The corrosion process under the deposit continues in the absence of oxygen and generates a localized low pH causing deep etch corrosion. The mechanism is similar to crevice corrosion, with the accumulation of positive metal ions under the deposit and displacement of the cathodic oxygen reduction reaction to a region of the metallic surface not covered by the deposit. The deposit acts like a filter allowing only the smallest most highly charged negative ions such as chloride to penetrate and concentrate under the deposit. The result is not only a high concentration of aggressive ions such as chloride but also pH depression. The magnitude and form of metal wastage caused by underdeposit corrosion is dependent on not only the nature of the deposit but also the type of metal affected. On metals that do not rely on protective oxides for corrosion resistance such as steels, underdeposit corrosion produces general metal loss beneath the deposit in the form of a broad shallow depression. On metals that rely on a protective oxide for corrosion resistance such as AISI 304, AISI 316 and titanium, deep pitting beneath the deposit is often observed.

Centrifugal pumps constitute some of the hardest working and most critical plant components within industry. There are many physical and chemical mechanisms activity working to damage pump components. Many of the damaging mechanisms are occurring simultaneously and have the potential to accelerate each other. As the direct result of existing damaging producing chemical and hydrodynamic by- products, new damaging mechanisms can be initiated. Although significant corrosion mechanisms have been discussed through the discourse of this paper, there are many others too specific to review within the scope. A significant conclusion drawn from the many damaging mechanisms discussed is that knowledge of the service water chemistry plays (and how it may change) is paramount for selecting the most durable pump materials package. It therefore stands to reason that to achieve the best possible leverage of OEM pump supplier knowledge and experience, spending resources to quantify water chemistries and potential changes to these chemistries is a wise investment.

4.2 FILTRATION

Backwash method :A variety of filtration methods can be used for solid/liquid separations due to the differing concentration of solids in liquid streams. For high solids loading, a backwash system may be the optimum filtration solution, while disposable filters would be used for lower solids loading applications. In some cases, removal of solids may require a combination of backwash technology followed by a disposable filter for polishing. Regardless of the amount of solids present in the liquid, Pall can provide a product or combination of products to achieve optimum performance and economy. Pall originally developed backwash technology in the 1960‟s in response to the needs of hydrogenated chemical producers. This technology was introduced to refiners and started to gain acceptance in the late 1980‟s when refiners needed to upgrade the value of slurry oil in Fluid Catalytic Cracking (FCC) units by removing catalyst fines. Today Pall‟s advanced backwash technology is used in other refining processes for the purpose of extending the life of fixed bed catalyst reactors and improving conversion in hydrotreaters and hydrocrackers. Pall‟s backwash systems offer significant benefits over conventional wedgewire systems that can be used to protect fixed bed catalyst reactors.

Backwash Systems A backwash system is designed to remove and/or collect suspended solids from a liquid process stream while periodically regenerating itself. A porous filter medium with suitable pore size will efficiently collect solids on its surface, where they form a permeable cake. During backwash, a reverse flow will be initiated at a predetermined filter pressure drop and/or time interval, discharging the collected solids to recovery. The filter will then be returned to full forward flow. Its pressure drop just after backwash will remain essentially constant through backwash cycles.

Gas Assist Backwash Method The gas assist backwash method is used when process flow rates are high or continuous, and uninterrupted flow is required. For backwash, one vessel is isolated and the downstream side of the vessel is pressurized with a controlled quantity of filtered air or other suitable gas. The vessel drain port is rapidly opened, resulting in a hydraulic pulse that “bumps” the collected solids from the filter surface. Forward flow is restored to the vessel and the remaining filter vessels are backwashed sequentially. During gas assist backwash, the expanding gas bubble forces the liquid through the elements in the reverse direction (inside-out) at a velocity as high as seven times the normal forward flow velocity. This effectively dislodges the accumulated cake from the elements, while significantly reducing the volume of liquid required. Thus, the concentration of the solids discharge is high.

Disposible Filters • Gradient of pore sizes for full utilization of the filter • Strength and durability to withstand changing process conditions • Chemical and thermal compatibility with process conditions to ensure long life

Corrosion Control for Stainless and Mild Steel: The mechanisms and methods of corrosion protection for stainless steel differ from that of carbon steels in filtration systems. The majority of carbon steel vessels have been manufactured with bare internal metal surfaces. In these cases, corrosion protection is provided by the formation of the natural barrier oxide coating (rust) that separates the metal from the surrounding environment. The degree of protection provided by the oxide film is a function of the thickness and physical characteristics of the oxide. Once the oxide forms and thickens over time without disruption, corrosion protection is good unless the film is mechanically removed [4]. In addition, if water chemistry conditions are right, calcareous (calcium-rich) deposits from the water can provide a "self-healing" protective film on the surface of the metal or oxide. In some cases with carbon steel, mechanically adherent and tough organic coatings, such as epoxies, have been used as the primary corrosion protection system. In these cases the dielectric coating acts as the barrier between the metal and the environment. The use of dielectric coatings alone for corrosion protection does not guarantee corrosion protection since coating imperfections or "holidays" can allow contact with the environment. The corrosion protection of the organic coating can be supplemented by the use of a sacrificial anode. The combination of the epoxy coating with a sacrificial anode is a proven engineering solution to corrosion control in water systems [5]. Stainless steels exhibit good general corrosion resistance in aerated water environments. Corrosion protection is provided by the formation of a relatively thin passive film that forms on the surface of the stainless steel if water and physical conditions are right. Passivation refers to the naturally formed "coating" on the surface of stainless steel. In general, if the water environment is aerated and the oxygenated water can reach the surface of the stainless steel, then the passive film forms, remains intact and provides excellent corrosion resistance. A corollary to their good general corrosion resistance is the fact that stainless steels are susceptible to localized forms of corrosion, such as pitting, crevice, stress cracking, etc. Localized corrosion problems arise when conditions within the tank construction or the water prevent formation of the passive film on some part of the stainless steel surface. In these situations, one portion of the stainless steel corrodes (the anode) to "protect" another portion of the metal (the cathode). For example, when pitting occurs, the bottom of the pit corrodes as the anode to protect the cathodic area (metal) adjacent to the opening of the pit. Eventually, the bottom of the pit can perforate the metal with a pinhole, while the vast majority of the stainless steel exhibits little or no corrosion. One possible explanation for the difference in service life performance between stainless and mild steel may be as simple as the thickness of the material used for construction and the difference in the mode of corrosion damage between the two materials. Typically, mild steel systems use a minimum of 3/16" (0.1875") thick plate for fabrication and general (uniform) corrosion is the primary mode of corrosion damage. Stainless steels in filtration systems range from 10 gage (0.135") to 14 gage (0.075") thickness and localized corrosion (crevice, pitting or microbiological corrosion) is the mode of corrosion damage. Since localized corrosion rates tend to be much greater than uniform corrosion rates, thinner members subjected to localized corrosion could fail in significantly shorter periods of time as compares with thicker members subject to uniform corrosion.

Crevice Corrosion: Crevice corrosion is a form of localized corrosion that is similar to pitting . Crevice corrosion occurs when any physical situation restricts access of oxygen to the surface of the material. By contrast, pitting usually initiates at metallurgical features present in the microstructure of the material. Crevice corrosion occurs at features inherent to the structure due to design, fabrication or operation (gaskets, lap welds, filtration media/metal interface, pockets of debris, etc.). The resistance of a stainless steel alloy to crevice corrosion is related to the composition and product form of the stainless steel, the severity of the crevice and the environment. Two of the most common grades of a stainless steel are type 304 and 316. The figures below show that, although some improvement in crevice performance is gained by changing the alloy from type 304 to type 316 stainless steel, crevice corrosion can persist. Further, increases in crevice corrosion resistance can be made with additional changes (increases) in alloy composition, but these improvements in corrosion resistance generally involve higher material cost and, possibly, changes in fabrication processes.

Microbiological Corrosion: Microbiological corrosion (MIC) refers to corrosion and ensuing loss of metal caused by biological organisms [7]. MIC can occur in any aqueous environments, and because of the omnipresent nature of microbes in agricultural and groundwater systems, MIC is a common phenomenon. MIC is a common problem in industrial and agricultural processes due to the presence of microbes, adequate nutrients and their corrosive byproducts. As mentioned above, the corrosion on stainless steels is determined by the rate at which oxygen in solution is be delivered to the metal surface. Biological organisms present in the aqueous medium often tend to increase or decrease oxygen transport to the surface; consequently, these organisms have a role in increasing or decreasing corrosion. Most MIC shows up as localized corrosion because most organisms do not form a large continuous film on the metal surface. Microscopic organisms tend to settle on metal surfaces in the form of discrete, spotty colonies, rather than continuous films. Biological organisms that cause corrosion on metals fall into two groups based on the conditions under which they occur: Anaerobic and aerobic conditions. Sulfate reducing bacteria (SRB) are a typical example of anaerobic MIC and occur when conditions in the environment are oxygen free. Aerobic sulfur-oxidizing bacteria that can occur with oxygen present can create an environment of up to 10 percent sulfuric acid, thereby encouraging rapid localized corrosion.

Corrosion Control Strategies: For stainless steels, improving alloy composition or use of coatings and sacrificial anodes can, in some instances, be used to solve both crevice corrosion and MIC. Increasing alloy composition can change material and fabrication costs. In addition, application of coatings to stainless steels can be difficult and expensive. Sacrificial anode performance should be similar for either stainless or mild steel, if both interiors are coated. For mild steel, the performance of uncoated steel has been historically good. If additional corrosion protection is desired, high quality dielectric coatings, such as polyamide epoxies, as the primary corrosion protection with and without sacrificial anodes have been an effective corrosion control strategy. Because of the differences in mechanisms of corrosion protection, mild steel can be less susceptible to crevice corrosion and MIC as compared to stainless steel. Again, the improved performance may be due in part to the fact that mild steel filtration vessels are, in general, thicker than stainless steels used for filtration systems. Mild steel systems do suffer from a maintenance issue in that if the exterior coatings are not maintained, rust will form and spoil the appearance of the system. In general, unpainted stainless steel exposed to atmospheric conditions will require little or no maintenance to preserve its aesthetics. Unfortunately, localized corrosion on the internal stainless steel surf

4.3 BOILER CORROSION

Corrosion is one of the main causes of reduced reliability in steam generating systems. It is estimated that problems due to boiler system corrosion cost industry billions of dollars per year.

Many corrosion problems occur in the hottest areas of the boiler-the water wall, screen, and superheater tubes. Other common problem areas include deaerators, feedwater heaters, and economizers.

Methods of corrosion control vary depending upon the type of corrosion encountered. The most common causes of corrosion are dissolved gases (primarily oxygen and carbon dioxide), under-deposit attack, low pH, and attack of areas weakened by mechanical stress, leading to stress and fatigue cracking.

These conditions may be controlled through the following procedures:

- maintenance of proper pH and alkalinity levels
- control of oxygen and boiler feed water contamination
- reduction of mechanical stresses
- operation within design specifications, especially for temperature and pressure
- proper precautions during start-up and shutdown
- effective monitoring and control

CORROSION TENDENCIES OF BOILER SYSTEM COMPONENTS

Most industrial boiler and feedwater systems are constructed of carbon steel. Many have copper alloy and/or stainless steel feedwater heaters and condensers. Some have stainless steel superheater elements.

Proper treatment of boiler feedwater effectively protects against corrosion of feedwater heaters, economizers, and deaerators. The ASME Consensus for Industrial Boilers specifies maximum levels of contaminants for corrosion and deposition control in boiler systems.

The consensus is that feedwater oxygen, iron, and copper content should be very low (e.g., less than 7 ppb oxygen, 20 ppb iron, and 15 ppb copper for a 900 psig boiler) and that pH should be maintained between

8.5 and 9.5 for system corrosion protection.

boiler water blowdown and turbine extraction or excess exhaust steam. Feedwater heaters are generally classified as low-pressure (ahead of the deaerator), high-pressure (after the deaerator), or deaerating heaters.

Regardless of feedwater heater design, the major problems are similar for all types. The primary problems are corrosion, due to oxygen and improper pH, and erosion from the tube side or the shell side. Due to the temperature increase across the heater, incoming metal oxides are deposited in the heater and then released during changes in steam load and chemical balances. Stress cracking of welded components can also be a problem. Erosion is common in the shell side, due to high-velocity steam impingement on tubes and baffles.

Corrosion can be minimized through proper design (to minimize erosion), periodic cleaning, control of oxygen, proper pH control, and the use of high-quality feedwater (to promote passivation of metal surfaces).

Deaerators

Deaerators are used to heat feedwater and reduce oxygen and other dissolved gases to acceptable levels. Corrosion fatigue at or near welds is a major problem in deaerators. Most corrosion fatigue cracking has been reported to be the result of mechanical factors, such as manufacturing procedures, poor welds, and lack of stress-relieved welds. Operational problems such as water/steam hammer can also be a factor.

Effective corrosion control requires the following practices:

- regular monitoring of operation
- minimization of stresses during start-up
- maintenance of stable temperature and pressure levels
- control of dissolved oxygen and pH in the feedwater
- regular out-of-service inspection using established nondestructive techniques

Other forms of corrosive attack in deaerators include stress corrosion cracking of the stainless steel tray chamber, inlet spray valve spring cracking, corrosion of vent condensers due to oxygen pitting, and erosion of the impingement baffles near the steam inlet connection.

Economizers

Economizer corrosion control involves procedures similar to those employed for protecting feedwater heaters.

Economizers help to improve boiler efficiency by extracting heat from flue gases discharged from the fireside of a boiler. Economizers can be classified as nonsteaming or steaming. In a steaming economizer, 5-20% of the incoming feedwater becomes steam. Steaming economizers are particularly sensitive to deposition from feedwater contaminants and resultant under-deposit corrosion. Erosion at tube bends is also a problem in steaming economizers.

Oxygen pitting, caused by the presence of oxygen and temperature increase, is a major problem in economizers; therefore, it is necessary to maintain essentially oxygen-free water in these units. The inlet is subject to severe pitting, because it is often the first area after the deaerator to be exposed to increased heat. Whenever possible, tubes in this area should be inspected closely for evidence of corrosion.

Economizer heat transfer surfaces are subject to corrosion product buildup and deposition of incoming metal oxides. These deposits can slough off during operational load and chemical changes.

Corrosion can also occur on the gas side of the economizer due to contaminants in the flue gas, forming low-pH compounds. Generally, economizers are arranged for downward flow of gas and upward flow of water. Tubes that form the heating surface may be smooth or provided with extended surfaces.

Superheaters

Superheater corrosion problems are caused by a number of mechanical and chemical conditions. One major problem is the oxidation of superheater metal due to high gas temperatures, usually occurring during transition periods, such as start-up and shutdown. Deposits due to carryover can contribute to the problem. Resulting failures usually occur in the bottom loops-the hottest areas of the superheater tubes.

Oxygen pitting, particularly in the pendant loop area, is another major corrosion problem in superheaters. It is caused when water is exposed to oxygen during downtime. Close temperature control helps to minimize this problem. In addition, a nitrogen blanket and chemical oxygen scavenger can be used to maintain oxygen-free conditions during downtime.

Low-Pressure Steam and Hot Water Heating Systems

Hot water boilers heat and circulate water at approximately 200°F. Steam heating boilers are used to generate steam at low pressures, such as 15 psig. Generally, these two basic heating systems are treated as closed systems, because makeup requirements are usually very low.

High-temperature hot water boilers operate at pressures of up to 500 psig, although the usual range is 35- 350 psig. System pressure must be maintained above the saturation pressure of the heated water to maintain a liquid state. The most common way to do this is to pressurize the system with nitrogen.

Normally, the makeup is of good quality (e.g., deionized or sodium zeolite softened water). Chemical treatment consists of sodium sulfite (to scavenge the oxygen), pH adjustment, and a synthetic polymer dispersant to control possible iron deposition.

The major problem in low-pressure heating systems is corrosion caused by dissolved oxygen and low pH. These systems are usually treated with an inhibitor (such as molybdate or nitrite) or with an oxygen scavenger (such as sodium sulfite), along with a synthetic polymer for deposit control. Sufficient treatment must be fed to water added to make up for system losses, which usually occur as a result of circulating pump leakage. Generally, 200-400 ppm P-alkalinity is maintained in the water for effective control of pH. Inhibitor requirements vary depending on the system.

Electric boilers are also used for heating. There are two basic types of electric boilers: resistance and electrode. Resistance boilers generate heat by means of a coiled heating element. High-quality makeup water is necessary, and sodium sulfite is usually added to remove all traces of dissolved oxygen. Synthetic polymers have been used for deposit control. Due to the high heat transfer rate at the resistance coil, a treatment that precipitates hardness should not be used.

Electrode boilers operate at high or low voltage and may employ submerged or water-jet electrodes. High- purity makeup water is required. Depending on the type of system, sodium sulfite is normally used for oxygen control and pH adjustment. Some systems are designed with copper alloys, so chemical addition must be of the correct type, and pH control must be in the range suitable for copper protection.

TYPES OF CORROSION

Corrosion control techniques vary according to the type of corrosion encountered. Major methods of corrosion control include maintenance of the proper pH, control of oxygen, control of deposits, and reduction of stresses through design and operational practices.

Galvanic Corrosion

Galvanic corrosion occurs when a metal or alloy is electrically coupled to a different metal or alloy.

The most common type of galvanic corrosion in a boiler system is caused by the contact of dissimilar metals, such as iron and copper. These differential cells can also be formed when deposits are present. Galvanic corrosion can occur at welds due to stresses in heat-affected zones or the use of different alloys in the welds. Anything that results in a difference in electrical potential at discrete surface locations can cause a galvanic reaction. Causes include:

- scratches in a metal surface

- differential stresses in a metal
- differences in temperature
- conductive deposits

Caustic Corrosion

Concentration of caustic (NaOH) can occur either as a result of steam blanketing (which allows salts to concentrate on boiler metal surfaces) or by localized boiling beneath porous deposits on tube surfaces.

Caustic corrosion (gouging) occurs when caustic is concentrated and dissolves the protective magnetite ($Fe3O4$) layer. Iron, in contact with the boiler water, forms magnetite and the protective layer is continuously restored. However, as long as a high caustic concentration exists, the magnetite is constantly dissolved, causing a loss of base metal and eventual failure.

Steam blanketing is a condition that occurs when a steam layer forms between the boiler water and the tube wall. Under this condition, insufficient water reaches the tube surface for efficient heat transfer. The water that does reach the overheated boiler wall is rapidly vaporized, leaving behind a concentrated caustic solution, which is corrosive.

Porous metal oxide deposits also permit the development of high boiler water concentrations. Water flows into the deposit and heat applied to the tube causes the water to evaporate, leaving a very concentrated solution. Again, corrosion may occur.

Caustic attack creates irregular patterns, often referred to as gouges. Deposition may or may not be found in the affected area.

Boiler feedwater systems using demineralized or evaporated makeup or pure condensate may be protected from caustic attack through coordinated phosphate/pH control. Phosphate buffers the boiler water, reducing the chance of large pH changes due to the development of high caustic concentrations. Excess caustic combines with disodium phosphate and forms trisodium phosphate.

Sufficient disodium phosphate must be available to combine with all of the free caustic in order to form trisodium phosphate.

Disodium phosphate neutralizes caustic by the following reactions

Acidic Corrosion

Low makeup or feedwater pH can cause serious acid attack on metal surfaces in the preboiler and boiler system. Even if the original makeup or feedwater pH is not low, feedwater can become acidic from contamination of the system. Common causes include the following:

- improper operation or control of demineralizer cation units
- process contamination of condensate (e.g., sugar contamination in food processing plants)
- cooling water contamination from condensers

Acid corrosion can also be caused by chemical cleaning operations. Overheating of the cleaning solution can cause breakdown of the inhibitor used, excessive exposure of metal to cleaning agent, and high cleaning agent concentration. Failure to neutralize acid solvents completely before start-up has also caused problems.

In a boiler and feedwater system, acidic attack can take the form of general thinning, or it can be localized at areas of high stress such as drum baffles, "U" bolts, acorn nuts, and tube ends.

Hydrogen Embrittlement

Hydrogen embrittlement is rarely encountered in industrial plants. The problem usually occurs only in units operating at or above 1,500 psi.Hydrogen embrittlement of mild steel boiler tubing occurs in high-pressure boilers when atomic hydrogen forms at the boiler tube surface as a result of corrosion. Hydrogen permeates the tube metal, where it can react with iron carbides to form methane gas, or with other hydrogen atoms to form hydrogen gas. These gases evolve predominantly along grain boundaries of the metal. The resulting increase in pressure leads to metal failure.The initial surface corrosion that produces hydrogen usually occurs beneath a hard, dense scale. Acidic contamination or localized low-pH excursions are normally required to generate atomic hydrogen. In high- purity systems, raw water in-leakage (e.g., condenser leakage) lowers boiler water pH when magnesium hydroxide precipitates, resulting in corrosion, formation of atomic hydrogen, and initiation of hydrogen attack.

Coordinated phosphate/pH control can be used to minimize the decrease in boiler water pH that results from condenser leakage. Maintenance of clean surfaces and the use of proper procedures for acid cleaning

also reduce the potential for hydrogen attack.

Oxygen Attack

Without proper mechanical and chemical deaeration, oxygen in the feedwater will enter the boiler. Much is flashed off with the steam; the remainder can attack boiler metal. The point of attack varies with boiler design and feedwater distribution. Pitting is frequently visible in the feedwater distribution holes, at the steam drum waterline, and in downcomer tubes.

Oxygen is highly corrosive when present in hot water. Even small concentrations can cause serious problems. Because pits can penetrate deep into the metal, oxygen corrosion can result in rapid failure of feedwater lines, economizers, boiler tubes, and condensate lines. Additionally, iron oxide generated by the corrosion can produce iron deposits in the boiler.

Oxygen corrosion may be highly localized or may cover an extensive area. It is identified by well defined pits or a very pockmarked surface. The pits vary in shape, but are characterized by sharp edges at the surface. Active oxygen pits are distinguished by a reddish brown oxide cap (tubercle). Removal of this cap exposes black iron oxide within the pit Oxygen attack is an electrochemical process that can be described by the following reactions:

The influence of temperature is particularly important in feedwater heaters and economizers. A temperature rise provides enough additional energy to accelerate reactions at the metal surfaces, resulting in rapid and severe corrosion.

At 60°F and atmospheric pressure, the solubility of oxygen in water is approximately 8 ppm. Efficient mechanical deaeration reduces dissolved oxygen to 7 ppb or less. For complete protection from oxygen corrosion, a chemical scavenger is required following mechanical deaeration.

Major sources of oxygen in an operating system include poor deaerator operation, in-leakage of air on the suction side of pumps, the breathing action of receiving tanks, and leakage of undeaerated water used for pump seals.

The acceptable dissolved oxygen level for any system depends on many factors, such as feedwater temperature, pH, flow rate, dissolved solids content, and the metallurgy and physical condition of the system. Based on experience in thousands of systems, 3-10 ppb of feedwater oxygen is not significantly damaging to economizers. This is reflected in industry guidelines.

the ASME consensus is less than 7 ppb (ASME recommends chemical scavenging to "essentially zero" ppb)

TAPPI engineering guidelines are less than 7 ppb

EPRI fossil plant guidelines are less than 5 ppb dissolved oxygen

METALLIC OXIDES IN BOILER SYSTEMS

Iron and copper surfaces are subject to corrosion, resulting in the formation of metal oxides. This condition can be controlled through careful selection of metals and maintenance of proper operating conditions.

Iron Oxide Formation

Iron oxides present in operating boilers can be classified into two major types. The first and most important is the 0.0002-0.0007 in. (0.2-0.7 mil) thick magnetite formed by the reaction of iron and water in an oxygen- free environment. This magnetite forms a protective barrier against further corrosion.

Magnetite forms on boiler system metal surfaces from the following overall reaction:

3Fe	+	4H2O	→	Fe3O4	+	4H2
iron		water		magnetite		hydrogen

The magnetite, which provides a protective barrier against further corrosion, consists of two layers. The inner layer is relatively thick, compact, and continuous. The outer layer is thinner, porous, and loose in structure. Both of these layers continue to grow due to water diffusion (through the porous outer layer) and lattice diffusion (through the inner layer). As long as the magnetite layers are left undisturbed, their growth

Many factors influence the corrosion rate of copper alloys:

- temperature
- pH
- oxygen concentration
- amine concentration
- ammonia concentration

rate rapidly diminishes.

The second type of iron oxide in a boiler is the corrosion products, which may enter the boiler system with the feedwater. These are frequently termed "migratory" oxides, because they are not usually generated in the boiler. The oxides form an outer layer over the metal surface. This layer is very porous and easily penetrated by water and ionic species.

Iron can enter the boiler as soluble ferrous ions and insoluble ferrous and ferric hydroxides or oxides. Oxygen-free, alkaline boiler water converts iron to magnetite, Fe_3O_4. Migratory magnetite deposits on the protective layer and is normally gray to black in color.

Copper Oxide Formation

A truly passive oxide film does not form on copper or its alloys. In water, the predominant copper corrosion product is cuprous oxide (Cu_2O). A typical corrosion reaction follows:

$8Cu$	+	O_2	+	$2H_2O$	→	$4Cu_2O$	+	$2H_2$
copper		oxygen		water		cuprous oxide		hydrogen

the oxide that develops on the copper surfaces is comprised of two layers. The inner layer is very thin, adherent, nonporous, and comprised mostly of cupric oxide (CuO). The outer layer is thick, adherent, porous and comprised mainly of cuprous oxide (Cu_2O). The outer layer is formed by breakup of the inner layer. At a certain thickness of the outer layer, an equilibrium exists at which the oxide continually forms and is released into the water.

Maintenance of the proper pH, elimination of oxygen, and application of metal-conditioning agents can minimize the amount of copper alloy corrosion.

Metal Passivation

The reaction of hydrazine and hydroquinone, which leads to the passivation of iron-based metals, proceeds according to the following reactions:

N_2H_4	+	$6Fe_2O_3$	→	$4Fe_3O_4$	+	$2H_2O$	+	N_2
hydrazine		hematite		magnetite		water		nitrogen

$C_6H_4(OH)_2$	+	$3Fe_2O_3$	→	$2Fe_3O_4$	+	$C_6H_4O_2$	+	H_2O
hydroquinone		hematite		magnetite		benzoquinone		water

Magnetite and cuprous oxide form protective films on the metal surface. Because these oxides are formed under reducing conditions, removal of the dissolved oxygen from boiler feedwater and condensate promotes their formation. The effective application of oxygen scavengers indirectly leads to passivated metal surfaces and less metal oxide transport to the boiler whether or not the scavenger reacts directly with the metal surface.

CORROSION CONTROL FACTORS

Steel and Steel Alloys

Protection of steel in a boiler system depends on temperature, pH, and oxygen content. Generally, higher temperatures, high or low pH levels, and higher oxygen concentrations increase steel corrosion rates.

Mechanical and operational factors, such as velocities, metal stresses, and severity of service can strongly influence corrosion rates. Systems vary in corrosion tendencies and should be evaluated individually.

Copper and Copper Alloys

The impact of each of these factors varies depending on characteristics of each system. Temperature dependence results from faster reaction times and greater solubility of copper oxides at elevated temperatures. Maximum temperatures specified for various alloys range from 200 to 300°F.

Methods of minimizing copper and copper alloy corrosion include:

- replacement with a more resistant metal
- elimination of oxygen
- maintenance of high-purity water conditions
- operation at the proper pH level
- reduction of water velocities
- application of materials which passivate the metal surfaces

pH Control

Maintenance of proper pH throughout the boiler feedwater, boiler, and condensate systems is essential for corrosion control. Most low-pressure boiler system operators monitor boiler water alkalinity because it correlates very closely with pH, while most feedwater, condensate, and high-pressure boiler water requires direct monitoring of pH. Control of pH is important for the following reasons:

- corrosion rates of metals used in boiler systems are sensitive to variations in pH
- low pH or insufficient alkalinity can result in corrosive acidic attack
- high pH or excess alkalinity can result in caustic gouging/cracking and foaming, with resultant carryover

- speed of oxygen scavenging reactions is highly dependent on pH levels

The pH or alkalinity level maintained in a boiler system depends on many factors, such as sys-tem pressure, system metals, feedwater quality, and type of chemical treatment applied.

The corrosion rate of carbon steel at feedwater temperatures approaches a minimum value in the pH range of 9.2-9.6 . It is important to monitor the feedwater system for corrosion by means of iron and copper testing. For systems with sodium zeolite or hot lime softened makeup, pH adjustment may not be necessary. In systems that use deionized water makeup, small amounts of caustic soda or neutralizing amines, such as morpholine and cyclohexylamine, can be used.

In the boiler, either high or low pH increases the corrosion rates of mild steel .The pH or alkalinity that is maintained depends on the pressure, makeup water characteristics, chemical treatment, and other factors specific to the system.

The best pH for protection of copper alloys is somewhat lower than the optimum level for carbon steel. For systems that contain both metals, the condensate and feedwater pH is often maintained between 8.8 and

9.2 for corrosion protection of both metals. The optimum pH varies from system to system and depends on many factors, including the alloy used .

To elevate pH, neutralizing amines should be used instead of ammonia, which (especially in the presence of oxygen) accelerates copper alloy corrosion rates. Also, amines form protective films on copper oxide surfaces that inhibit corrosion.

Oxygen Control

Chemical Oxygen Scavengers. The oxygen scavengers most commonly used in boiler systems are sodium sulfite, sodium bisulfite, hydrazine, catalyzed versions of the sulfites and hydrazine, and organic oxygen scavengers, such as hydroquinone and ascorbate.

It is of critical importance to select and properly use the best chemical oxygen scavenger for a given system. Major factors that determine the best oxygen scavenger for a particular application include reaction speed, residence time in the system, operating temperature and pressure, and feedwater pH. Interferences with the scavenger/oxygen reaction, decomposition products, and reactions with metals in the system are also important factors. Other contributing factors include the use of feedwater for attemperation, the presence of economizers in the system, and the end use of the steam. Chemical oxygen scavengers should be fed to allow ample time for the scavenger/oxygen reaction to occur. The deaerator storage system and the feedwater storage tank are commonly used feed points.

MONITORING AND TESTING

Effective corrosion control monitoring is essential to ensure boiler reliability. A well planned monitoring program should include the following:

- proper sampling and monitoring at critical points in the system
- completely representative sampling
- use of correct test procedures
- checking of test results against established limits
- a plan of action to be carried out promptly when test results are not within established limits
- a contingency plan for major upset conditions
- a quality improvement system and assessment of results based on testing and inspections

Monitoring Techniques

Appropriate monitoring techniques vary with different systems. Testing should be performed at least once per shift. Testing frequency may have to be increased for some systems where control is difficult, or during periods of more variable operating conditions. All monitoring data, whether spot sampling or continuous, should be recorded.

Boiler feedwater hardness, iron, copper, oxygen, and pH should be measured. Both iron and copper, as well as oxygen, can be measured on a daily basis. It is recommended that, when possible, a continuous oxygen meter be installed in the feedwater system to detect oxygen intrusions. Iron and copper, in particular, should be measured with care due to possible problems of sample contamination.

If a continuous oxygen meter is not installed, periodic testing with spot sampling ampoules should be used to evaluate deaerator performance and potential for oxygen contamination from pump seal water and other sources.

For the boiler water, the following tests should be performed:

- phosphate (if used)
- P-alkalinity or pH
- sulfite (if used)
- conductivity

Sampling

It is critical to obtain representative samples in order to monitor conditions in the boiler feedwater system properly. Sample lines, continuously flowing at the proper velocity and volume, are required. Generally, a velocity of 5-6 ft/sec and a flow of 800-1000 mL/min are satisfactory. The use of long sample lines should be avoided. Iron and copper sampling should be approached with extreme care because of the difficulty of obtaining representative samples and properly interpreting results.

Trends, rather than individual samples, should be used to assess results. Copper sampling requires special precautions, such as acidification of the stream. Composite sampling, rather than spot sampling, can also be a valuable tool to determine average concentrations in a system.

Results and Action Required

All inspections of equipment should be thorough and well documented.

Conditions noted must be compared to data from previous inspections. Analytical results and procedures must be evaluated to ensure that quality standards are maintained and that steps are taken for continual improvement. Cause-and-effect diagrams can be used either to verify that all potential causes of problems are reviewed, or to troubleshoot a particular corrosion-related problem.

4.4 BEST PRACTICES FOR CONDENSATE SYSTEM PIPING

The best method for improving steam system energy efficiency, reducing chemical costs, and reducing make-up water costs is to return the maximum quantity of condensate to the boiler plant. There are several factors that impact the reliability, performance, longevity, and maintenance requirements for the condensate piping system. Some of these factors are listed below:

- Condensate line sizing that factors condensate liquid, and flash steam quantities.
- Location of the condensate line with respect to the process equipment.
- Locations of the condensate branch line connection into the main condensate headers.
- Insulation techniques

An important factor to increase overall steam system efficiency is to maximize the temperature of the returning condensate. This permits high thermal cycle efficiency for the overall steam system.

Energy

Condensate contains a relatively large percentage (16 percent in some cases, depending on pressure) of the energy used to produce the steam. With today‟s rising energy costs, facilities must return all possible condensate back to the boiler plant. The condensate should be maintained in a high-energy state or simply as hot as possible. A typical reason for condensate loss in the system is due to condensate component failure.

Maintenance

A reasonable specification for condensate system design is to provide a reliable and long operational life span of more than 20 years without a primary condensate system failure. Plant personnel must assume that the condensate system designs shall include reasonable maintenance and plant services. Forgoing a proactive maintenance plan will reduce the anticipated lifespan of the condensate system.

Materials

Because condensate pipelines are potentially subjected to carbonic acid, a damaging corrosive element, material selection is important. The recommended material to use for a condensate system is stainless steel. Stainless steel greatly enhances the pipes‟ ability to withstand the corrosive attack for a longer, more reliable operational life. However, understanding the cost limitations to an all stainless steel condensate system, other alternatives are available. If carbon steel piping is used for economical consideration, schedule 80 pipe is used because of the heavier wall thickness, which prolongs the life of the pipe in a corrosive environment.

Connection Types

Welding the condensate pipe or using tubing with tube connectors will minimize leaks. Condensate pipe will expand and contract during normal thermal cycling of a steam system operation. Unfortunately; steam component manufacturers still provide a large number of components with threaded (NPT) connections. These threaded connections are inherently a weak point in the steam/condensate system and will be the first item attacked by the corrosive carbonic acid, particularly the threads near the bottom of the pipe. Also, the threaded connections do not have the ability to withstand the expansion and contraction of the steam/condensate system, therefore leaks will occur. The most common condensate piping connections are listed below in order of preference:

- Welded joints
- Tube material with tube connectors
- Flanges
- Threaded pipe only when necessary

Pipe vs. Tubing

is time consuming and expensive. Using tubing material reduces the number of welds needed in an installation.

Maintainability

Most mechanical systems operate at peak performance levels following a new installation. However, system maintainability really determines the resiliency and reliability of the system. The system‟s components, including piping, tubing, steam traps, condensate pumps, etc., must be designed and installed with maintenance functions in mind. Frankly, if the devices are not accessible by plant personnel, there will be little or no maintenance performed and the overall system integrity will deteriorate.

Condensate Pipe/Tubing Sizing

Sizing of condensate lines is calculated differently from sizing other fluids transferred in pipes. Although condensate is hot water, sizing a condensate line as if it were hot water would result in an undersized line. Undersized condensate lines will create excessive backpressure in the system, as well as maintenance and process problems throughout the system. The key item to remember is that there are two major differences between condensate and hot water. Condensate lines will contain two phases, condensate (liquid) and flash steam (gas.) Therefore, the correct size of a condensate line is somewhere between a hot water line and a steam line. With proper knowledge, a condensate line may be sized for the following:

- Condensate liquid load
- Flash steam load
- Neglect factor

This is defined as steam loss resulting from faulty steam traps or open bypass valves. This is more common in systems than typically acknowledged. Blow-by steam will add steam flow to the return line and must be included in the calculations. Condensate that is free of flash steam may be pumped and sized as liquid only (single phase flow). Condensate pipe velocities (liquid and flash steam) must be lower than 4500 feet per minute to prevent system waterhammer and other damaging effects. Condensate piping velocities (liquid only) must be lower than 7 feet per second.

Correct Identification of Condensate Type

Gravity

This describes all process equipment with a modulating inlet steam valve and a very low steam pressure application where the condensate return line must be at or close to atmospheric conditions. Therefore, the condensate drains by gravity to a vented (atmospheric) condensate collection tank.

- Low pressure return
    - Condensate return that is less than 15 psi.
- Medium pressure
    - Condensate return that is between 15 and 100 psi.
- High pressure return
    - Condensate return piping system pressures of 100 psi or higher

Most of the condensate system problems are from the location of the condensate lines in relationship to the heat transfer equipment, steam trap, and other drainage type devices.

Connecting into the Condensate Header

It is imperative that all condensate branch lines are connected into the top dead center of the main condensate header on a horizontal plane. This cannot be overstated and there is no exception to this rule. Improper condensate connections are listed below:

- Connection to the bottom of a condensate header.
- Connection to the side of a condensate header.
- Connection to a vertical condensate header.

The condensate connections listed above will cause system problems, primarily water hammer. Flash steam introduced to the main condensate header due to an improper connection location will interact with cooler condensate causing water hammer. Water hammer is the leading cause of premature component failures in a steam/condensate system.

Pressure Gauges

Finally, a note regarding pressure gauges. These devices, when properly installed in the condensate return system, are a great advantage to assisting in identifying the process and steam system malfunctions. If pressure gauges are not installed, always put the necessary taps in the system for a pressure gauge. This will allow maintenance personnel to install a gauge during troubleshooting procedures. It is necessary to include a siphon pipe (pigtail) and isolation valve with each pressure gauge. The isolation valve must be rated for the pressure and temperature of the operating system. Additionally, a liquid filled pressure gauge will be more resilient to system vibrations.

Many factors influence the corrosion rate of copper alloys:

- temperature
- pH
- oxygen concentration
- amine concentration
- ammonia concentration

and flowrate.

Conclusion

Condensate contains a high percentage of the energy (typically 16 percent) used to produce steam. Recovery and return of all possible condensate back to the boiler plant is the best method for cost containment and improved energy efficiency. Remember these tips: Recover and return all possible condensate back to the boiler plant as hot as possible. Accept no component failure within three years of operation. Install components with maintenance in mind. Size condensate lines understanding the medium will be two phase flow. Utilize connections that minimize leaks. Understand the various pressures of condensate returns available in order to design the piping system with proper flow. Remember to allow for pressure gauge installations throughout the system. These inexpensive devices are a key aid in troubleshooting the steam and condensate system. Following these rules will help to ensure a reliable and long life span of the condensate system.

4.5 RIVETS:

- A Rivet is a permanent mechanical fastener. It is a short metal pin or bolt for holding together two plates of metal, its headless end being beaten out or pressed down when in place.
- To slow or prevent corrosion, rivet bodies and mandrels are often made from identical materials, including low-carbon and stainless steels and nickel-copper and aluminum alloys.
- When joining dissimilar materials, engineers specify protective coatings and sleeves to prevent corrosion or when rivets do not share the same physical and mechanical properties as the parent materials.
- **Stainless steel break stems** offer the best corrosion protection in environments such as swimming pool ladders and city bus exposed to salt.
- An aircraft, even though made of the best materials and strongest parts, several methods are used to hold metal parts together, they riveting and welding.
- **Aluminum**and its alloys are difficult to solder. Riveting is satisfactory from the standpoint of strength and neatness and is much easier to do than welding.
- Types:
  - Solid rivets (ex. Hanger strips, window blinds, wind guards, even doors & windows)
  - Brake rivets (ex. Application of truck, Lorries etc.)

- Self-piercing rivets (ex. Sunroof manufacturing)
- Shoulder rivet (ex. Roll clinches, spun, flared or press clinched)

V.Copper

- Henrob Company also has direct experience in designing and building bonnet manufacturing, vehicle manufacturing etc.

4.6 WELDING:

- Steels are in an environment which causes active corrosion it is often found that weldments are more severely affected than parent materials. This is known as preferential weld corrosion.
- The weld metal and base metal can generate a potential difference in certain environments, thus setting up a galvanic cell, lead to corrosion.
- Even if the weld metal is close in chemical composition to the base material, difference in as welded microstructure could make the weld metal sufficiently different from and even less corrosion resistant than the base metal.
- Preferential corrosion of welds usually occurs when the environment in contact with the material has a high electrical conductivity, such as seawater, but can also occur in low conductivity co2 containing environments.
- It is used to high strength steel pipes used in drilling and completion of oil and gas wells.
- Austenite is highly soluble to prevent cold cracking.
- Corrosion of weldments
    - Weldments design
    - Fabrication technique
    - Welding sequence
    - Moisture contamination
    - Organic or inorganic chemical species
    - Porosity
    - Cracks
- Welding practice to minimize corrosion
    - Material and welding consumable selection
    - Surface coating
    - Post weld and interpass temperature
    - Avoidance of forming cracking
    - Removing source of hydrogen

- Passivation treatment

- It also used as reactor. Also used welding transformer – step down transformer.
- Also used to welding equipment, materials prousing, automotive, transportation & ships.

4.7 BOILING & HIGH TEMERATURE ENVIRONMENTS:

- The corrosion of mild steel in boiling solutions of the chlorides and sulfates of sodium, magnesium and calcium has been examined.

- Application of corrosion in metal

I.Steel II.Stainless steel III.Aluminum IV.Brass

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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Corrosion Engineering – SCH1614

CORROSION TESTING AND MEASUREMENTS

Many corrosion tests are made to select materials of construction for equipment inprocess industries. It is very important for the tests to duplicate the actual plant service conditions as closely as possible. The greater the deviation from plant conditions the less reliable the test will be.

Purpose of Corrosion testing

1. Evaluation and selection of materials for a specific environment or a givendefinite application.
2. Evaluation of new or old metals or alloys to determine the environments inwhich they are suitable.
3. Control of corrosion resistance of the material or corrosiveness of the environment.

Classification

Corrosion testing is divided into four classifications

1. Laboratory tests including acceptance or qualifying tests
2. Pilot plant or semiworks tests
3. Plant or actual service tests
4. Field tests

Materials and specimens

This is the first step in corrosion testing. Chemical composition , fabrication history, metallurgical history, and positive identification of specimen are required.In order to avoid confusion and to increase the reliability of the tests,many laboratories maintain stocks of material for corrosion testing only.

Surface preparation

The surface of the test specimen should be identical with the surface of the actualequipment to be used in the plant. A common surface finish is produced by polishing with an abrasive cloth or paper. Prior treatments such as machining, grinding or polishing may be necessary if the specimen surface is very rough.
Clean polishing papers should be used to avoid contamination of the metalsurface.

Measuring and weighing

After surface preparation the specimens should be carefully measured to permitcalculation of the surface area. After measuring, the specimen is degreased by washing in a suitable solvent such as acetone, dried. The specimen should be stored in a dessicator.

Laboratory and accelerated corrosion testing methods

Salt spray test

The **salt spray test** is a standardized test method used to check corrosion resistanceof coated samples. Coatings provide corrosion resistance to metallic parts madeof steel or brass. Since coatings can provide a high corrosion resistance through the intended life of the part in use, it is necessary to check corrosion resistance byother means.

Salt spray test is an accelerated corrosion test that produces a corrosive attack to the coated samples in order to predict its suitability in use as a protective finish.The appearance of corrosion products (oxides) is evaluated after a period of time. Test duration depends on the corrosion resistance of the coating; the more corrosion resistant the coating is, the longer the period in testing without showing signs of corrosion.

Salt spray testing is popular because it is cheap, quick, well standardized, and reasonably repeatable. There is however only a weak correlation between theduration in salt spray test and the expected life of a coating (especially on hot dip galvanized steel where drying cycles are important for durability), since corrosion is a very complicated process and can be influenced by many external factors. Nevertheless, salt spray test is widely used in the industrial sector for the evaluation of corrosion resistance of finished surfaces or parts.

Corrosion Immersion Tests

In immersion testing, acceleration is achieved principally by:

- Lengthening the exposure to the critical conditions that are suspected to cause corrosion damage. For example, if a vessel is to be batch-processed with a chemical for 24 h, then laboratory corrosion exposure of 240 h shouldbe considered
- Intensifying the conditions in order to increase corrosion rates, i.e. increasing solution acidity, salt concentration, temperature or pressure etc.

Once the environmental conditions have been determined, and the test designed, then it should be repeated a sufficient number of times to determine whether it meets the desired standard for reproducibility. Immersion tests can be divided into two categories:

Simple immersion tests

basically small sections of the candidate material are exposed to the test medium and the loss of weight of the material is measured for a period of time. Immersion testing remains the best method of screening and eliminating from further consideration those materials that should not be considered for specific applications. But while these tests are the quickest and most economical means for providing a preliminary selection of best suited materials, there is no simple way to extrapolate the results obtained from these simple tests to the prediction of system lifetime.

Alternate immersion tests

another variation of the immersion test is the cyclic test procedure where a test specimen is immersed for a period of time in a test environment, then removed anddried before being re-immersed to continue the cycle. Normally hundreds of these cycles are completed during the course of a test program.

High Temperature Corrosion Testing

Autoclave corrosion tests are a convenient means for laboratory simulation of many service environments. The reason for such tests is to recreate the hightemperatures (HT) and high pressures (HP) commonly occurring in commercial or industrial processes. Factors affecting corrosion behavior are often intimately linked to the conditions of total system pressure, partial pressures of variousssoluble gaseous constituents and temperature. There are many HT/HP environments of commercial interest, which include those in industries such as petroleum, nuclear, chemicals, aerospace and transportation where reliability, serviceability and concerns for corrosion are paramount.

Corrosion coupons can be placed in the aqueous phase, vapor space, or at phase interfaces depending on the specific interest involved. Additionally, it is also possible to conduct electrochemical tests in HT/HP vessels. If multiple liquidphases are present it can be necessary to stir or agitate the media or test vessel to produce mixing and conditions whereby the corrosion test specimens are contactedby all of the phases present. Special magnetic and mechanical stirrers are available that can be used to produce movement of the fluid to produce a mixing of the phases. In some cases where contact of the specimens with both liquid and gaseousphases is important in the corrosion process, it may be necessary to slowly rotate orrock the test vessel to produce the intended results. HT/HP corrosion tests have special requirements not common to conventional corrosion experiments conducted in laboratory glassware.

Four variations of common HT/HP test methods that have been found to be useful in materials evaluation involving corrosion phenomena will be briefly described. However, these types of evaluations can be accomplished through careful planning and test vessel design. These include:

Windowed test vessels

special transparent windows and other fixtures such as fiber optics have been used to make visual measurements or observations within the confines of test vessels.

Besides being able to withstand the pressures, temperatures, and corrosion environments, these windows may have to perform other functions related to the introduction of light or other radiation if these are part of the test variables.

Electrochemical measurements

most conventional electrochemical techniques have been used for experiments conducted inside HT/HP vessels. The most critical electrochemical component in these experiments always has been the reference electrode. The design and construction of the reference electrode is particularly important, as it must providea stable and standard reference potential. In many applications, test vessels have been modified to accommodate an external reference electrode to minimize the effects of temperature, pressure, or contamination, or a combination thereof.

Hydrogen permeation

hydrogen charging is often a problem that affects materials submitted to HT/HP test conditions. In such cases, it may be necessary to measure hydrogen permeationrates and diffusion constants in order to estimate the potential hazard of hydrogen attack. For hydrogen permeation measurements at high temperatures, it may be imperative to use solid state devices.

Mechanical property testing

HT/HP vessels have been designed to conduct a variety of mechanical tests such as slow strain rate (SSR), fracture or fatigue testing. The main problem is always one of selecting the fixtures that could withstand the corrosive environments generated in HT/HP tests.

Potentiodynamic polarization methods

Polarization methods such as potentiodynamic polarization, potentiostaircase, and cyclic voltammetry are often used for laboratory corrosion testing. These techniques can provide significant usefulinformation regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential.

- Anodic polarization: the potential is changed in the anodic (or more positive direction) causing the working electrode to become the anode and causing electrons to be withdrawn from it.
- Cathodic polarization: the working electrode becomes more negative andelectrons are added to the surface, in some cases causing electrodeposition.
- Cyclic polarization: both anodic and cathodic polarization are performed in a cyclic manner.

Several methods may be used in polarization of specimens for corrosion testing. Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. It is probably the most commonly used polarization testing method for measuring corrosion resistance and is used for a wide variety of functions: (reference)

- **Cyclic polarization tests:** These tests are often used toevaluate pitting susceptibility. The potential is swept in a single cycle (or slightly less than one cycle), and the size of the hysteresis is examined along with the differences between the values of the starting open circuit corrosion potential and the return passivation potential. The existence of the hysteresis is usually indicative of pitting, while the size of the loop is often related to the amount of pitting.

- **Cyclic voltammetry:** Cyclic voltammetry involves sweeping the potentialin a positive direction until a predetermined value of current or potential is reached, then the scan is immediately reversed toward more negative values until the original value of potential is reached. In some cases, this scan is done repeatedly to determine changes in the current-potential curve produced with scanning.
- **Potentiostaircase method:** This technique polarizes an electrode in a series of potential steps where the time spent at each potential is constant, whilethe current is often allowed to stabilize prior to changing the potential to the next step. The step increase may be small, in which case, the technique resembles a potentiodynamic curve, or it may be large.
- **Electrochemical potentiodynamic reactivation (EPR):** This technique allows measuring the degree of sensitization of stainless steels such as S30400 and S30403 steels. This method uses a potentiodynamic sweep over a range of potentials from passive to active (called reactivation).
- **Linear polarization resistance (LPR):** A widely used technique, the polarization resistance of a material is defined as the slope of the potential- current density curve at the free corrosion potential, yielding the polarizationresistance, as described in the next section.

Corrosion testing-monitoring-inspection methodsVisual

Inspection

It is the simplest and cheapest of all techniques. In this method the weld isinspected visually by an authorized personal to detect flaws, cracks appearing on the surface on the weld. Sometimes special equipment is used to guide the inspector. The disadvantages of this method are: micro sized cracks cannot be detected by humans, sub-surface defects remain undetected, and there are always chances of human error.

Liquid Penetrant based Inspection

In this process a liquid with high surface wetting characteristics is applied to the surface of the part and allowed time to seep into surface breaking defects. After removing the excess liquid, a developer (powder) is applied to pull the trapped penetrant out the defect and spread it on the surface where it can be seen. The penetrant used contains fluorescent material and starts glowing when exposed to UV light. The principle is shown schematically in *Figure*. This procedure is sometimes called as die penetration test when the liquid penetrant used is a die. In this case upon application of developer, the die comes out from the crack and becomes visible to eye. This method can detect micro sized cracks that are not visible to naked eye but cannot detect sub surface defects.

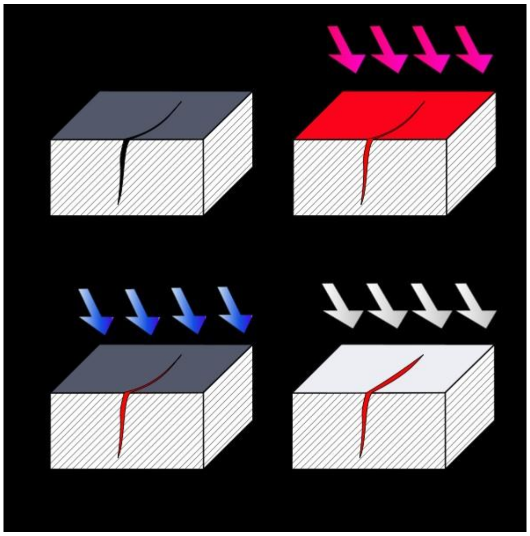


Figure (1) Crack, (2) Penetrant applied, (3) Developer applied, (4) Crack Visible

Magnetic Particle inspection

This method is based on the principle that magnetic lines change their pathswhenever discontinuity is encountered in the path. The first step in a magnetic particle inspection is to magnetize the component that is to be inspected. After the component has been magnetized, iron particles, either in a dry or wet suspended form, are applied to the surface of the magnetized part. The particles will be attracted and cluster at the flux leakage fields, thus forming a visible indication thatthe inspector can detect. It is a very simple procedure but applicable only for Ferromagnetic materials. Often the material has to be demagnetised after performing the test.

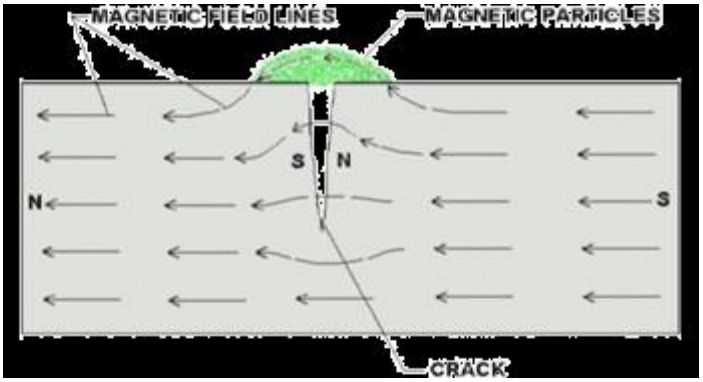
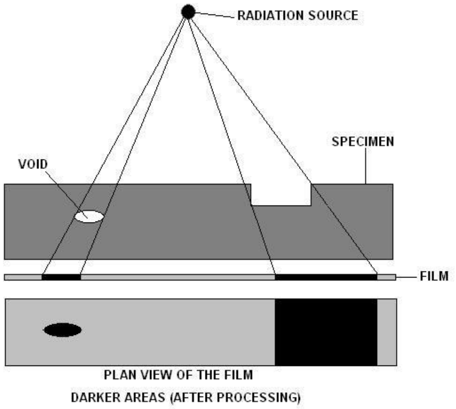


Figure - Principle of Magnetic particles Inspection

Radiographic Testing

Radiographic Testing is a non-destructive testing method of inspecting materialsfor hidden flaws by using the ability of short wavelength electromagnetic radiation (high energy photons) to penetrate various materials. In this method the part is placed between the radiation source and a piece of film. A pattern will be generated on the film depending on the thickness of the inspected part. Where ever there is a defect, the amount of radiation absorbed will be different and corresponding pattern will be generated. Detection of subsurface defects is the major advantage of this test but proper safety measures have to be taken to prevent exposure to these radiations. The figure schematically shows a typical radiographictesting set-up.

Ultrasonic Inspection



Ultrasonic testing uses the basic physical property that sound waves travel atknown constant velocities through any medium. By measuring the time for a soundwave to travel through a material it can be determined how far that wave has travelled. In this way sound waves can be used to measure distances. So, in an ultrasonic inspection, a high frequency sound wave is passes through the materialto be inspected. Presence and position of any defects can be detected by analysing the sound wave reflected by the flaw. *Figure* - schematically shows a set-up for ultrasonic testing of defects.

Various advantages of ultrasonic testing include – (a) high penetrating powerleading to the detection of flaws deep in the part, (b) high sensitivity, (c) greater accuracy than other non-destructive methods in particular in determining the depth of internal flaws, (d) capability of estimating the size, orientation, shape and natureof defects, (e) non-hazardous to operations or to nearby personnel.

Besides these advantages it has few disadvantages too such as – (1) manual operation and hence, requires careful attention, (2) experienced personnel are required, (3) surface must be prepared by cleaning and removing loose scale, paint,etc.

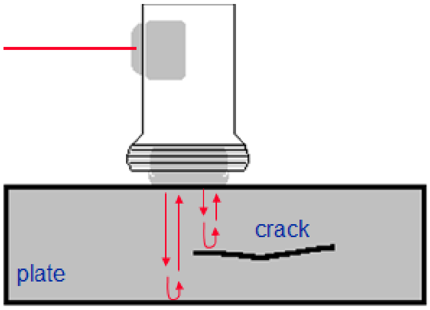


Figure - Principle of Ultrasonic Testing

Huey Test for stainless steels

This test consists of exposure to boiling 65% nitric acid for five 48 hr periods. Sensitized material exhibits high corrosion rates. Maleic acid, lactic acid, coppersulfate-sulfuric acid, and ferric sulfate- sulphuric acid are also used to determinesusceptibility to intergranular corrosion of stainless steels.

Streicher test for stainless steels

The Huey test is time consuming and expensive. The test consists of polishing a small specimen through no 000 emery paper etching in 10% oxalic acid for 1.5minunder an applied current density of 1 A/cm2 , and then examining the surface at 2580 to 500 magnification. The specimen is the anode and a stainless steel beaker is the cathode.

Warren Test

Type 316L stainless steel poses a special problem in connection with the use of Huey test. When sensitized for 1hr at 1250 deg F, type 316 L may form a sigma phase. Sigma containing material shows high corrosion rates and fails Huey test.Warren proposes the use of 10% nitric acid – 3% hydrofluoric acid mixture at 70or 80 degree C to evaluate 316L type.

- The rate and type of attack are found to be dependent on the type of salt, its concentration and the period of test.
- The type of attack varies from predominantly pitting in pure water to even etching in strong magnesium and calcium salt solutions.
- Applications of high temperature environments is boiling heat transfer equipment, separation & extraction equipment, ionic liquids equip, high boiling equip, boiler ,heat exchanger, evaporator, reactor etc..
- Application of boiling also similar to application of high temperature environment.
- This is the application of corrosion.