

INTRODUCTION TO CORROSION AND CORROSION MONITORING

Corrosion may be defined as the deterioration of a substance (usually a metal) because of a reaction with its environment.

Some countries such as U.K., U.S.A. and west Germany have attempted to quantify their corrosion losses in terms of monetary value. But though such systematic efforts have not been taken in our country, we are definite that a substantial portion of our national wealth is being lost by way of corrosion. It will not be an exaggeration if we put that we can build a new fertilizer plant or a power plant every year by way of resultant savings by corrosion control.

The "Corrosion damage", is a composite term which incorporates the factors- the loss of appearance, maintenance and operating cost, cost of plant shut down, the effects of contamination of product, the loss of valuable products and the effects of safety and reliability.

WHY METAL CORRODE

The driving force that makes metals corrode is a natural consequence of their temporary existence in the metallic form. They reach this metallic state from their occurrence in nature in the form of various chemical compounds, called ores, it is necessary for them to absorb and store up for later return by corrosion, the energy required to release the metals from their original compounds. The amount of energy required and stored up varies from metal to metal. It is relatively high for such metals as magnesium, aluminium, and iron and relatively low for such metals as copper and silver.

A typical cycle is illustrated by iron. The most common iron one, hematite, is

an oxide of iron (Fe_2O_3). The most common product of corrosion of iron, rust has the same chemical composition. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the same compound. Only the rate of energy change is different.

The energy difference between metals and their ores can be expressed in electrical terms which are related to heats of formation of the compounds.

The relative difficulty of extracting metals from their ores in terms of the energy required and the consequent relative tendency to release this energy by corrosion is reflected by the positions of pure metals in a list where the energy involved determines its position. This has been discussed earlier as the "electromotive series".

ELECTROCHEMICAL NATURE OF CORROSION :

While corrosion can take one or other of the several forms the mechanism of attack in aqueous solutions will involve some aspect of electrochemistry. There will be a flow of electricity from certain areas of a metal surface to other areas through a solution capable of conducting electricity, such as sea water or hard water.

The term "anode" is used to describe that portion of the metal surface that is corroded and from which current leaves the metal to enter the solution.

The term "cathode" is used to describe the metal surface from which current leaves the solution and returns to the metal.

The circuit is completed outside the solution through the metal or through a conductor joining two pieces of metal.

A solution capable of conducting electricity is called an "electrolyte". Its

ability to conduct electricity is due to the presence of water are called "ions". there are positively or negatively charged atoms or groups of atoms in solution.

The electrolyte forming a corrosive environment may be any solution, rain or even moisture condensed from the air. It can range from fresh water or salt water to the strongest alkali or the strongest acid.

In any corrosive environment, regardless of its nature, the basic mechanism of corrosion is in principle the same as the electrochemical action in an electric dry cell. Here we have an anode, the zinc container and a graphite cathode. When the external circuit is closed, the current generated by corrosion of the zinc, flows through the cell to the graphite cathode and from the graphite (+) to the zinc (-) in the external circuit, which often consists of a light bulb.

For facility of discussion, the anodes and cathodes involved in a corrosion reaction, like the zinc & graphite in a dry cell, are called electrodes. The electrodes may consist of two different kinds of metal or they may be different areas on the same piece of metal. The negative electrode, anode, is where corrosion occurs.

ANODIC PROCESSES :

Let us consider what takes place at the anode when corrosion occurs. Positively charged atoms of metal leave the solid surface and enter into solution as ions. They leave their corresponding negative charges in the form of electrons which are able to flow through the metal or any external electronic conductor. The ionized atoms can bear one or more positive charges. In the Corrosion of iron, atom becomes an iron ion carrying two positive charges and generated two electrons. This is shown diagrammatically in Figure 2-1. These electrons travel through the metal or an external electronic conductor to complete the circuit at the cathode, where a corresponding reaction consumes these electrons.

CATHODIC PROCESSES :

What has been taking place at the cathode in parallel with that has been going on at the anode ?

The electrons generated by the formation of metallic ions at the anode have passed through the metal to the surface of the cathode area immersed in the electrolyte. Here, they restore the electrical balance of the system by reacting with and neutralizing positive ions such as hydrogen ions in the electrolyte. Hydrogen ions can be reduced to atoms, and these often combine to form hydrogen gas by such reaction with electrons at a cathode surface. This reduction of hydrogen ions at the cathode surfaces will disturb the balance between the acidic hydrogen H^+ ions and the alkaline hydroxyl $(OH)^-$ ions and make the solution less acid or more alkaline in this region. This is shown diagrammatically in Figure 2-2.

Briefly then, for corrosion to occur, there must be a formation of ions and release of electrons at an anodic surface, where oxidation and deterioration of the metal occurs. There must be a simultaneous acceptance at the cathodic surface of the electrons can take the form of neutralization of positive hydrogen ions, or the formation of negative ions. The anodic and cathodic reactions must go on at the same time and at equivalent rates. But corrosion occurs at the areas that serve as anodes.

If we place a piece of mild steel in a solution of hydrochloric acid, we observe a vigorous formation of hydrogen bubbles. Under such conditions, the metal corrodes very quickly. The dissolution of the metal is occurring only at anodic surfaces. The hydrogen bubbles are forming only at the cathodic surfaces even though it may appear that they are coming from the entire surface of the metal rather than at well-defined cathodic area. The anodic and cathodic areas may shift from time to time so as to give the appearance of uniform corrosion.

If we could see this action through a suitable microscope, we would see many tiny anode and cathode areas shifting around on the surface of the metal. These areas are often so small as to be invisible and so numerous as to be almost inseparable.

COMBINED ANODIC AND CATHODIC PROCESSES :

If we could see just one anode and one cathode in a magnified view of a piece of iron in an acid solution, we would see electrons generated by the formation of ferrous ions flowing through the metal from an anodic area to a cathodic area. This is illustrated in Figure 2-3. At the cathode surface, the electrons would meet hydrogen ions from the solution. One hydrogen ion would accept one electron and be converted into a hydrogen atom which could enter the metal and lead to hydrogen embrittlement, or, as in most cases, it could combine with another hydrogen atom and become molecular hydrogen gas which would either cling to or be released as a bubble from the cathodic surface. As this process continues, oxidation (corrosion) of the iron occurs at the anodic surface and reduction of hydrogen ions occurs at the cathodes.

PATES OF CATHODIC REACTIONS

This formation of hydrogen from hydrogen ions and its release as atoms or hydrogen gas are the principal reactions in corrosion by acids. But in neutral solutions such as sodium chloride, the evolution of hydrogen gas and its accumulation

on the cathodic surfaces can slow down the cathodic reaction. This also slows the corrosive anodic process which cannot proceed at a higher rate than electrons can be consumed at the cathodic surfaces.

Such slowing down of cathodic reactions is called "cathodic polarization". Similarly, anything that directly slows down the anodic reaction is called "anodic polarization"

FORMATION OF CORROSION PRODUCTS :

The products of the anodic and cathodic processes frequently migrate through the solution and meet to enter into further reactions that yield many of our common visible corrosion products. For example with iron in water, the hydroxyl ions from the cathodic reaction, in their migration through the electrolyte towards the anodic surfaces, encounter ferrous ions moving in the opposite direction. These ions combine to form ferrous hydroxide which subsequently reacts further with oxygen in solution to form ferric hydroxide.

TYPE OF CELLS

There are three main types of cells that take part of corrosion reactions.

1. Dissimilar Electrode Cells

These are illustrated by the dry cell, discussed earlier. A metal containing electrically conducting impurities on the surface as a separate phase, a copper pipe connected to an iron pipe, and a bronze propeller in contact with the steel hull of a ship are examples of this type of corrosion cell. These cells also include cold-worked metal in contact with the same metal annealed, grain-boundary metal in contact with grains, and a single metal crystal of definite orientation in contact with another crystal of differing orientation.

2. Concentration Cells

These are cells having two identical electrodes each in contact with a solution of differing composition, and there are two kinds. The first is called a salt concentration cell. For example, if one copper electrode is exposed to a concentrated copper sulfate solution, and another to a dilute copper sulfate solution, on shortcircuiting such a cell, copper dissolves from the electrodes in contact with the dilute solution (anode) and plates out on the other electrode (cathode). Both reactions tend to bring the solutions to the same concentration.

The second kind of concentration cell, which in practice is the more important, is called a differential aeration cell. This may include two iron electrodes in dilute sodium chloride solution, the electrolyte around one electrode being thoroughly aerated (cathode), and the other de-aerated (anode), brought about, for example, by bubbling through nitrogen. The difference in oxygen concentration produces a potential difference and causes current to flow.

3. Differential Temperature Cells

Components of these cells are electrodes of the same metal, each of which is at a different temperature, immersed in an electrolyte of the same initial composition. Less is known about the practical importance and fundamental theory of differential temperature cells than for the cells previously described. They are found in heat exchangers, boilers, immersion heaters, and similar equipment. In practice, cells responsible for corrosion may be a combination of these three types.

CORROSION RATE EXPRESSION

Corrosion rates have been expressed in a variety of ways in the literatures, as listed in Table 2-1. Weight loss in grams or milligrams and percent weight change of

materials after exposure to the corrosion environment are poor ways of expressing corrosion resistance.

It is obvious that both of these expressions will be influenced by the duration of the exposure. Further, the shape of the exposed article will also exert an influence on the results obtained. For example, consider a sphere and a thin sheet, both having the same weight when exposed to a corrosion medium. If the corrosion tests are performed with these samples, both weight loss and percent weight change will be larger for the sheet specimen, since a greater surface area per unit volume is exposed to the corrosive. Thus, because of vagueness and the possibility of mis-interpretation, both of these expressions should be avoided when describing corrosion rates.

The next group of expressions are merely variations of the generalized expression of weight loss per unit area per unit time. Milligrams per square decimeter per day (mdd) is commonly used in English and American corrosion literature. Unlike the first two expressions, these expressions include the effect of the exposed area and the duration of exposure. However, they all have a serious disadvantage - they do not express corrosion resistance in terms of penetration. From an engineering view point, the rate of penetration, or the thickness of a structural piece, can be directly used to predict the life of a given component. The next four expressions, which include inches penetration per year, inches penetration per month, millimeters penetration per year, and mils penetration per year (mpy), express corrosion resistance directly in terms of penetration. From the standpoint of convenience, mils per year is preferred, since the corrosion rate of practically useful materials varies between approximately 1 and 200 mpy. Thus, using this expression, it is possible to present corrosion data using small whole numbers and avoiding decimals. It is obvious that the expressions inches per year and inches per month will involve decimal points and numerous naughts which frequently lead to errors when transcribing data.

For the reasons noted above, the expression mils per year is considered to be

the most desirable way of expressing corrosion rates. This expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the formula given below :

$$\text{mpy} = \frac{534 W}{\text{DAT}}$$

Where

- W = Weight loss, mg.
- D = Density of specimen, g/cm³
- A = Area of specimen, sq. in
- T = Exposure time, hr.

TABLE 2-1

**COMPARISON OF CORROSION RATE EXPRESSIONS
FOR ENGINEERING APPLICATIONS**

EXPRESSIONS Weight loss, g. or mg. percent weight change	COMMENT Poor-sample shape and exposure time influence results.
Milligrams per square decimeter per day (mdd)	
Grams per square decimeter per day	Good-but expressions
Grams per square centimeter per hour	Do not give penetration rates.
Grams per square meter per hour	
Grams per square inch per hour	
Moles per square centimeters per hour	
Inches per year	
Inches per month	
Millimeters per day	Better - expressions give penetration rates.
Mils per year (mpy)	Best - expresses penetration without decimals or large numbers.

QUIZ NO. 2

1. How do you describe a portion of a metal surface from which current leaves to enter the solution ?
2. The ability of electrolytes to conduct electricity is due to the presence of what are called
3. The process that directly slow down the anodic reaction is known as
4. Name the Three types of corrosion cells :
5. please match the following :

1. Cold worked metal in contact with the same metal annealed	:	(a)	Dissimilar metal electrode
2. Two iron electrodes in dilute NaCl solution, the electrolyte around one electrode aerated and the other deaerated.	:	(b)	Differential aeration aeration cell
3. One electrode exposed to a concentrated copper sulphate solution, & another to a dilute copper sulphate solution.	:	(c)	Salt concentration cell.
6. The best possible expression for Corrosion rate is :

(a) gm or mg	<input type="checkbox"/>
(b) mpy	<input type="checkbox"/>
(c) mdd	<input type="checkbox"/>

MATERIALS FOR CORROSIVE ENVIRONMENTS

A large variety of materials, ranging from platinum to concrete, is used by the engineer to construct bridges, automobiles, process plant equipment, pipelines, power plants, etc. The corrosion engineer is primarily interested in the chemical properties

(corrosion resistance) of materials, but he must have knowledge of mechanical, physical, and other properties to assure desired performance. The properties of engineering materials depend upon their physical structure and basic chemical composition.

MECHANICAL PROPERTIES :

These properties are related to behavior under load or stress in tension, compression, or shear. Properties are determined by engineering tests under appropriate conditions. Commonly determined mechanical properties are tensile strength, yield point, elastic limit, creep strength, stress rupture, fatigue, elongation (ductility), impact strength (toughness and brittleness), hardness and modulus of elasticity (ratio of stress to elastic strain rigidity). Strain may be elastic (present only during stressing) or plastic (permanent) deformation. These properties are helpful in determining whether or not a part can be produced in the desired shape and also resist the mechanical forces anticipated.

OTHER PROPERTIES :

The corrosion engineer is often required to consider one or more properties in addition to corrosion resistance and strength when selecting a material. These include density or specific gravity (needed to calculate corrosion rates); fluidity or castability; formability; thermal, electrical, optical, acoustical, magnetic properties; and resistance to atomic radiation. For example, a particular part must be castable into an intricate shape, possess good heat-transfer characteristics, and not be degraded by atomic radiation. In another case, the equipment must be a good insulator, reflect heat and have low unit weight. Incidentally, radiation sometimes enhances properties of a material, e.g., the strength of polyethylene can be increased by controlled radiation.

Cost is not a property of a material, but it may be the overriding factor in selection of a material for engineering use, based on economic consideration and therefore should always be kept in mind.

METALS AND ALLOYS

CAST IRON :

Cast iron is a generic terms that applies to high carbon iron alloys containing silicon. The common ones are designated as gray cast iron, white cast iron, malleable cast iron and ductile or nodular cast iron.

GRAY CAST IRON :

Ordinary gray iron contain about 2 to 4 percent carbon and 1 to 5 percent silicon. These are the least expensive of the engineering metals. The dull or grayish fracture is due to the free graphite flakes in the microstructure. Gray cast irons can be readily cast into intricate shapes because of their excellent fluidity and relatively low melting points. They can be alloyed for improvement of corrosion resistance and strength.

These materials are brittle and exhibit practically no ductility. They do not show a clearly defined yield point, but the yield strength is about 85 percent of the tensile strength.

WHITE CAST IRONS :

White cast irons have practically all of their carbon in the form of iron carbide. These are extremely hard and brittle. Silicon content is low because this element promoted graphitization.

MALLEABLE CAST IRONS :

These are produced by high-temperature heat treatment of white irons of suitable composition. The graphite forms as rosettes or clusters instead of flakes and the material shows good ductility (hence the name malleable).

DUCTILE CAST IRONS :

These materials also known as nodular cast iron, exhibit ductility in the as-cast form. The graphite is present as nodules or spheroids as a result of a special ladle additions to the molten metal. The mechanical properties of ductile cast irons can be altered by heat treatment similar to that used for ordinary steels.

HIGH SILICON CAST IRONS :

When the silicon content of gray cast iron is increased to over 14 per cent, it becomes extremely corrosion resistant to many environments. The notable exception is hydrofluoric acid. In fact, these high-silicon irons are the most universally resistant of the commercial (nonprecious) metals and alloys. Their inherent hardness makes them resistant to erosion corrosion. A straight high-silicon iron, such as Duriron,⁽¹⁾ contains about 14.5 percent silicon and 0.95 percent carbon.

These alloys are available only in cast form for drain lines, pumps, valves and other process equipment. They have found extensive use as anodes for impressed current cathodic protection.

The excellent corrosion resistance of high - silicon irons is due to the formation of an inert S_iO_2 surface layer which forms during exposure to the environment.

OTHER ALLOY CAST IRON

In addition to silicon and molybdenum, nickel, chromium and copper are added to cast irons for improved corrosion and abrasion resistance, heat resistance and also mechanical properties. Copper additions impart better resistance to sulfuric acid and atmospheric corrosion.

1) Trade names belonging to the Duriron Co., Dayton, Ohio

The high nickel-chromium cast irons with and without copper (upto 7 per cent) are the most widely used of this group. These austenitic alloys, known as Ni-Resist, ⁽²⁾ are the toughest of the gray cast irons.

Ni-Hard ⁽²⁾ is a white cast iron containing about 4 percent nickel and percent chromium. It is very hard, with a Brinell hardness of 550 to 725. Ni-hard has found wide application where erosion-corrosion resistance is needed in near neutral and alkaline solutions or slurries.

CARBON STEELS AND IRONS

Hardness and strength of steels depend largely upon their carbon content and heat treatment.

Commercial pure irons are ingot iron and Armco ⁽³⁾ iron. These are relatively weak and not used where strength is a major requirement.

Wrought iron is a very low carbon iron with a high slag content. Many claims of better corrosion resistance are made for this material, but each proposed application should be carefully studied and corrosion tested to be sure the extra cost over ordinary steel is justified.

(2) Trade names of the International Nickel Co., Inc., New York, N.Y.

(3) Armco Steel Corp., Middletown, Ohio.

LOW-ALLOY STEELS:

Carbon steel is alloyed, singly or in combination, with chromium, nickel,

copper, molybdenum, phosphorus and vanadium in the range of a few percent or less to produce low-alloy steels. The higher alloy additions are usually for better mechanical properties and hardenability. The lower range of about 2 percent total maximum is of greater interest from the corrosion standpoint. Strengths are appreciably higher than those of plain carbon steel but the most important attribute is much better resistance to atmospheric corrosion. Appreciable advantage is sometimes obtained in aqueous solutions.

STAINLESS STEELS:

The main reason for the existence of the stainless steels is their resistance to corrosion. Chromium is the main alloying element and the steel should contain at least 11 percent. Chromium is a reactive element but it and its alloys passivate and exhibit excellent resistance to many environments. A large number of stainless steels are available. Their corrosion resistance, mechanical properties and costs vary over a broad range. For this reason, it is important to specify the exact stainless steel desired for a given application.

Group I materials are termed martensitic stainless steels because they can be hardened by heat treatment like ordinary carbon steel. Strength increases and ductility decreases with increasing hardness. Corrosion resistance is usually less than in Groups II and III. Martensitic steels can be heat-treated to obtain high tensile strengths. Corrosion resistance is generally better in the hardened condition than in the annealed or soft condition. They are used in applications requiring moderate corrosion resistance plus high strength or hardness. These steels are not often made into process equipment such as tanks and pipelines.

Type 416 is easier to cut and is used for valve stems, nuts, bolts and other parts to reduce machining cost.

Group II ferritic nonhardenable steels are so designated because they do not undergo a high temperature phase transformation; and therefore cannot be hardened by heat treatment.

Type 430 can be formed readily and has good corrosion resistance to the atmosphere. It is used in ammonia oxidation plants for making nitric acid and for tank cars and tanks for storage of nitric acid. The first chemical plant application of stainless steel was a Type 430 tank car for shipping nitric acid. However, in these chemical applications, it has been largely displaced by 18-8 because of ease of welding and better ductility - plus better corrosion resistance if properly heat-treated.

Types 442 and 446 find application where heat resistance is required such as in furnace parts and heat-treating equipment. They possess good resistance to high-temperature oxidation and sulfur gas attack because of their high chromium content. These materials do not possess very good structural stability or high-temperature strength and should be selected with care.

One of the most interesting aspects of the Group II steels is their resistance to stress corrosion. They do quite well in many cases where the 18-8 types fail, particularly in chloride-containing waters.

Group III austenitic stainless steels are essentially non magnetic and cannot be hardened by heat treatment. Like the ferritic steels, they are hardenable only by cold-working. Most of these steels contain nickel as the principal austenite former but the relatively new ones like Types 201 and 202 contain less nickel and substantial amounts of manganese to compensate.

The austenitic steels possess better corrosion resistance than the straight chromium (Groups I and II) steels and generally the best resistance of any of the four groups except for CD-4MCu. For this reason austenitic steels are widely specified for the more severe corrosion conditions such as those encountered in the process industries. They are rust resistant in the atmosphere and find wide use for architectural purposes, in the kitchen, in food manufacture and dispensing and for applications where contamination (rust) is undesirable.

Types 201 and 202 steels show about the same corrosion resistance as the Type 302 grade. The 'workhorses' for the process industries are Types 304, 304L, 316 and 347. The molybdenum bearing steel, Type 316 is considerably better in many applications than Type 304. Type 316 exhibits much better resistance to

pitting, sulfuric acid and hot organic acids. Corrosion resistance and heat resistance generally increase with nickel and chromium contents. For instance, Type 310, also called 25-20 is one of the better heat-resistant alloys.

Alloy 20 has been listed in Group III because of its extensive use in corrosion applications. This alloy is best known in wrought forms as Carpenter 20(4) and in the cast form as Durimet 20(1). It possesses the best overall corrosion resistance. It is made with and without columbium additions.

Group IV consists of the age-hardened or precipitation-hardened steels. They are hardened and strengthened by solution-quenching followed by heating for substantial times at temperatures in the approximate range of 800 to 1000 F (427 - 538 C). Corrosion resistance to severe environments is generally less than that of 18-8 except for CD-4MCu. CD-4MCu is also superior to the 18 Cr-8Ni steels.

ALUMINIUM AND ITS ALLOYS:

Aluminium is a reactive metal but it develops an aluminum oxide coating or film that protects it from corrosion in many environments. This film is quite stable in neutral and many acid solutions but it can be artificially produced by passage of electric current. This process is called anodizing. The high-copper alloys are utilized mainly for structural purposes. The copper-free or low-copper alloys are used in the process industries or where better corrosion resistance is required.

In addition to corrosion resistance, other properties contributing to its widespread application are colorless and nontoxic corrosion products, appearance, electrical and thermal conductivity, reflectivity and lightness or good strength-weight ratio.

Pure aluminum is soft and weak, but it can be alloyed and heat-treated to a broad range of mechanical properties. Strengthening usually decreases

(4) Carpenter Steel Co., Reading, Pa.

corrosion resistance, particularly resistance to stress corrosion and for this reason the structural alloys are Alclad(5) or covered with a thin skin or pure aluminum.

Aluminum alloys lose strength rapidly when exposed to temperatures of 350 F (177 C) and higher. Aluminum shows excellent mechanical properties at sub-zero temperatures.

MAGNESIUM AND ITS ALLOYS:

Magnesium is one of the lightest commercial metals, specific gravity 1.74. It is utilized in trucks, automobile engines, ladders, portable saws, luggage, aircraft and missiles because of its light weight and also its good strength when alloyed. However, it is one of the least corrosion resistant and is accordingly used as sacrificial anodes for cathodic protection and dry-cell batteries. It is generally anodic to most other metals and alloys and must be insulated from them.

Magnesium exhibits good resistance to ordinary atmospheres due to the formation of a protective oxide film. This protection tends to break down (pit) in air contaminated with salt, so protective measures are required. These include coatings and 'chrome' pickling, which also provides a good base for a coating. Corrosion resistance generally decreases with impurities and alloying. Alloys are quite susceptible to stress corrosion and must be protected. Presence of dissolved oxygen in water has no significant effect on corrosion.

(5) A trade name belonging to Aluminum Co. of America, Pittsburgh, Pg.

The metal is susceptible to erosion-corrosion. Magnesium is much more resistant than aluminum to alkalies. It is attacked by most acids except chromic and hydrofluoric. The corrosion product in HF acts as a protective film.

LEAD AND ITS ALLOYS:

Lead forms protective films consisting of corrosion products such as sulphates,

oxides and phosphates. Most of the lead produced goes into corrosion applications; a large portion involves sulfuric acid. Lead and its alloys are used as piping, sheet linings, solders (Pb-Sn), type metals, storage batteries, radiation shields, cable sheath, terneplate (steel coated with Pb-Sn alloy), bearings, roofing and ammunition. Lead is soft, easily formed and has a low melting point. Lead-lined steel is often made by 'burning on' the lead. It is subject to erosion-corrosion because of its softness.

When protection against corrosion is required for process equipment, chemical lead containing about 0.06 percent copper is specified, particularly for sulfuric acid. This lead is resistant to sulfuric, chromic, hydrofluoric and phosphoric acids in certain strengths; neutral solutions; sea water and soils. It is rapidly attacked by acetic acid and generally is not used in nitric, hydrochloric or organic acids.

Chemical lead exhibits a tensile strength of about 2300 psi at room temperature. Hard leads, containing 3 to 18 percent antimony double this strength. However, the strength of both materials drops rapidly as temperature increases and they show about the same strength around 230 F (110 C). Design strength at appreciably higher temperatures drops to zero.

COPPER AND ITS ALLOYS:

Copper is different from other metals in that it combines corrosion resistance with high electrical and heat conductivity, formability, machinability and strength to urban, marine and industrial atmospheres and waters. Copper is a relatively noble metal and hydrogen evolution is not usually part of the corrosion process. For this reason it is not corroded by acids unless oxygen or other oxidizing agents (e.g., HNO₃) are present. For example, reaction between copper and sulfuric acid is not thermodynamically possible; but corrosion proceeds in the presence of oxygen and the products are copper sulphate and water. Reduction of oxygen to form hydroxide ions is the predominant cathodic reaction for copper and its alloys. Copperbase alloys are resistant to neutral and slightly alkaline solutions with the exception of those containing ammonia, which cause stress corrosion and sometimes rapid general attack. In strongly reducing conditions at 575 to 750 F (300 to 400 C), copper alloys are often superior to stainless steels and stainless alloys.

The most common alloys are brasses (Cu-Zn), bronzes (Sn, Al or Si additions to Cu) and cupronickels (Cu-Ni).

Copper and brasses are subject to erosion-corrosion or impingement attack. The bronzes and aluminum brass are much better in this respect. The bronzes are stronger and harder. The cupronickels with small iron additions are also superior in erosion-corrosion resistance.

Copper and copper alloys are available as duplex tubing (one metal inside, another outside) in combination with steel, aluminum and stainless steels. This construction solves many heat-exchanger materials problems. For example, tubing with ammonia on one side (steel) and brackish water on the outside (Admiralty metal).

copper and its alloys find extensive application as water piping, valves, heat-exchanger tubes and tube sheets, hardware, wire, screens, shafts, roofing, bearing, stills, tanks and other vessels.

NICKEL AND ITS ALLOYS:

An important group of materials for corrosion applications is based on nickel. Nickel is resistant to many corrosives and is a natural for alkaline solutions. Most tough corrosion problems involving caustic and caustic solutions are handled with nickel. In fact, the corrosion resistance of alloys to sodium hydroxide is roughly proportional to their nickel content. For example, 2 percent Ni cast iron is much superior to unalloyed cast iron. Another important attribute is the large and rapid increase in stress corrosion resistance as the nickel content of stainless alloys exceeds 10 per cent. For example, Inconel(2) shows excellent stress corrosion resistance and many tons of it are used for this reason. Nickel generally shows good resistance to neutral and slightly acid solutions. It is widely used in the food industry. It is not resistant to strongly oxidizing solutions, e.g. nitric acid and ammonia. Nickel forms are good base for alloys requiring strength at high temperatures. However, nickel and

its alloys are attacked and embrittled by sulphur-bearing gases at elevated temperatures.

Monel is a natural for hydrofluoric acid. Chlorimet 3(1) and Hastelloy C(6) are two of the most generally corrosion-resistant alloys commercially available. Chlorimet 2 and Hastelloy B are very good in many cases where oxidizing conditions do not exist. Hastelloy D is brittle like the high-silicon irons. Nichrome(2) is used for electrical resistors-heating elements. Nickel, high-nickel alloys and alloys containing substantial amounts of nickel (8 percent) are the most common materials used for most of the more severe corrosion problems.

ZINC AND ITS ALLOYS:

Zinc is not a corrosion-resistant metal, but it is utilized as a sacrificial metal for cathodic protection of steel. Its chief use is in galvanized (zinc-coated) steel for piping, fencing, nails, etc. It is also utilized in the form of bars or slabs as sacrificial anodes to protect ship hulls, pipelines and other structures.

TIN:

Tin shows excellent resistance to relatively pure water. It shows good resistance to atmospheric corrosion, dilute mineral acids in the absence of air and many organic acids but is corroded by strong mineral acids. It is generally not used for handling alkalies.

(6) A trade name of Materials Systems Div., Union Carbide Corp., Kokoma, Ind.

TITANIUM AND ITS ALLOYS:

Titanium is a relative newcomer in that it was first used as a structural metal in 1952. It is now utilized in the space and chemical process industries. It is reactive metal and depends on a protective film (TiO₂) for corrosion resistance. Melting and

welding must be done in inert environments or the metal becomes brittle due to absorbed gases. For this reason, it is not a high-temperature material and is rarely used above 1000 F (538 C).

Titanium has three outstanding characteristics which account for many of its applications in corrosive services. These are resistance to (1) sea water and other chloride salt solutions, (2) hypochlorites and wet chlorine, (3) nitric acid including fuming acids. Salts such as FeCl_3 and CuCl_2 , which tend to pit most other metals and alloys, actually inhibit corrosion of titanium. It is not resistant to relatively pure sulphuric and hydrochloric acids but does a good job in many of these acids when they are heavily contaminated with heavy metal ions such as ferric and cupric. Titanium shows surprisingly low galvanic effects because it readily passivates.

REFRACTORY METALS:

These metals are characterized by very high melting points as compared with iron and steel. Melting points of these metals are shown in Table 6 - 1. Unfortunately they show poor resistance to high-temperature oxidation, and protective coatings are needed.

TABLE 6-1 - MELTING POINTS OF REFRACTORY METALS

Columbium exhibits good corrosion resistance to organic and inorganic acids except hydrofluoric and hot concentrated sulphuric and hydrochloric acids. Apparently the formation of a Cb_2O_5 film results in protection. Columbium is poor in alkaline solutions.

Molybdenum shows good resistance to hydrofluoric, hydrochloric and sulphuric acids, but oxidizing agents such as nitric acid cause rapid attack. It is good in aqueous alkaline solutions. This metal forms a volatile oxide (MoO_3) in air at temperatures above about 1300 F.

Tantalum has been used for many years because of its superior resistance to most environments. A few exceptions include alkalis, hydrofluoric and hot concentrated sulphuric acid. It is used in handling chemically pure solutions of such corrosives as hydrochloric acid. Because of tantalum's wide spectrum of corrosion resistance it is utilized in repair of glass-lined equipment. Any evolution of hydrogen (corrosion reaction or otherwise) near tantalum will result in absorption and embrittlement of this metal. Desorption of hydrogen to restore ductility is not practical because of the high temperature and high vacuum required. Tantalum sheet is strong, so cost is reduced through the use of thin sections. Tantalum is used for surgical implants.

Zirconium has found increased use following the advent of nuclear energy primarily because it has a very low thermal neutron cross section and resists high-temperature water and steam. Its excellent corrosion resistance is due to a protective oxide film. This metal exhibits good corrosion resistance to alkalis and acids (including hydroiodic and hydrobromic acids), except for hydrofluoric acid and hot concentrated hydrochloric and sulphuric acids. Cupric and ferric chlorides cause pitting. Zirconium has found some application in hydrochloric acid service. Its corrosion resistance is affected by impurities such as nitrogen, aluminum, iron and carbon.

Zirconium alloyed with small amounts of tin, iron, chromium and nickel (zircalloys) shows improved resistance to high-temperature water. Zirconium and its alloys in high temperature water show first a decreasing corrosion rate that may be followed by a rapid linear rate of attack (termed 'breakaway'). They also tend to pick up hydrogen from the corrosion reaction and become brittle.

NOBLE METALS:

These materials are characterized by highly positive potentials relative to the hydrogen electrode, excellent corrosion resistance and high cost. They are being used for lining, cladding and coatings with inexpensive substrates, thus providing strength.

GOLD:

Gold is very good in dilute nitric acid and hot strong sulphuric acid. It is attacked by aquaregia, concentrated nitric acid, chlorine and bromine, mercury and alkaline cyanides.

PLATINUM:

Platinum is used because it is resistant to many oxidizing environments and particularly to air at high temperatures.

Platinum is attacked by aqua regia, hydroiodic and hydrobromic acids, ferric chloride and chlorine and bromine.

SILVER:

Silver loses its 'nobility' in contact with sulphur compounds - tarnishing is well known. It serves as electrical contacts, electrical bus bars (even at red heat), brazes, solders and dental alloys with mercury. Silver is widely used in the chemical industry as solid silver and also as loose, clad, or brazed linings. Applications include stills, heating coils, and condensers for pure hydrofluoric acid, evaporating pans for production of chemically pure anhydrous sodium hydroxide, autoclaves for production of urea and all kinds of equipment for production of foods and drugs where purity of product is paramount. It is highly resistant to organic acids.

Silver is attacked by nitric acid, hot hydrochloric acid, hydroiodic and hydrobromic acids, mercury and alkaline cyanides and may be corroded by reducing acids if oxidizing agents are present.

NON-METALLICS

NATURAL AND SYNTHETIC RUBBERS:

The outstanding characteristic of rubber and other elastomers is resilience, or low modulus of elasticity. Flexibility accounts for most applications such as tubing, belting and automobile tires. However, chemical and abrasion resistance and good insulating qualities result in many corrosion applications. Rubber and hydrochloric acid form a natural combination in that rubber-lined steel pipes and tanks have been 'standard' for this service for many years.

Generally speaking the natural rubbers have better mechanical properties (resiliency and resistance to cuts and their propagation) than the synthetic or artificial rubbers, but the synthetics have better corrosion resistance.

NATURAL RUBBER

Corrosion resistance usually increases with hardness. In the case of lining pipes and tanks the rubber is usually applied soft and then cured in place (for large items) or in autoclaves.

SYNTHETIC RUBBERS:

A wide variety of synthetic rubbers is available, including combinations with plastics. Plasticizer fillers and hardeners are compounded to obtain a large range of properties - elasticity, temperature and corrosion resistance. Table 6-2 illustrates these points. Note the varieties obtainable in hardness, elongation, tensile strength, elasticity, temperature resistance, tear and corrosion resistance. Neoprene and nitrile rubber possess resistance to oils and gasoline. One of the first extensive applications of neoprene was, and is, gasoline hoses. An outstanding characteristic of butyl rubber is impermeability to gases. This accounts for its use as inner tubes and process equipment such as a seal for floating-top storage tanks. Butyl rubber exhibits better resistance to oxidizing environments such as air and dilute nitric acid. The temperature resistance shown in Table 6-2 is for air. Note 580 F (304 C) for silicone

rubber. Temperatures listed are considerable reduced in some corrosives - to room temperature for natural rubber in 70 percent sulfuric acid, for example. Neoprene and nitrile-rubber -lined vessels handle pure and strong sodium hydroxide.

One of the newer elastomers is a chloro-sulfonated polyethylene (Hypalon) (7) which possesses superior resistance to oxidizing environments such as 90 percent nitric acid at room temperature.

Soft rubbers are best for abrasion resistance. A common mistake, because of metals-oriented thinking is to use hard rubber for erosion-corrosion conditions. Linings also may consist of hard and soft layers.

(7) Trade names of E.I. Du pont de Nemours and Co., Inc., Wilmington, Del.

PLASTICS:

Plastics are readily divided into two classes, thermo-plastics and thermosetters. The former soften with increasing temperature and return to their original hardness when cooled. Most are meltable; for example, nylon is extruded into fibers of filaments from the molten state. The thermosetters harden when heated and retain hardness when cooled. They 'set' into permanent shape when heated under pressure. Generally they cannot be reworked as scrap.

Table 6-3 lists some properties and corrosion resistance of several well known plastics. A wide range of properties are available. These properties can be changed considerable through plasticizers, fillers and hardeners.

Plastics do not generally dissolve like metals. They are 'degraded' or corroded because of swelling, loss in mechanical properties, softening, hardening, spalling or discoloration.

THERMOPLASTICS

FLUOROCARBONS:

Teflon (7), and Kel-F (8) and other fluorocarbons are the 'noble metals' of the plastics in that they are corrosion resistant to practically all environments up to 550 F (228 C). They consist of carbon and fluorine. The first polytetra-fluoroethylene was produced by Du Pont and designated Teflon (TFE). Similar materials, with the composition modified, or copolymers, are Kel-F and Viton.

(8) A trade name of 3M Company, St. Paul, Minn.

(7) The uses are seals and gaskets, wire insulation, expansion joints, linings for pipe, tubing, valve diaphragms, coatings and even heat exchangers (thin-walled tubing).

POLYPROPYLENES:

Polystyrene exhibits better heat and corrosion resistance and is stiffer than polyethylene.

POLYSTYRENE:

Polystyrene possesses good chemical resistance but is too brittle for many structural applications. Polystyrene shows good resistance to hydrofluoric acid.

RIGID POLYVINYL CHLORIDE:

This material is basically rigid but can be softened by additions of polyvinyl acetate and plasticizers to vary mechanical properties. PVC is used for pipe and fittings, ducts, fans sheet, containers and linings.

THERMOSETTERS

EPOXIES:

Epoxies represent perhaps the best combination of corrosion resistance and mechanical properties. Epoxies are available as castings, extrusions, sheets, adhesives and coatings. They are used as sinks, bench tops, pipe, valves, pumps, small tanks, potting compounds, adhesives, linings, protective coatings, dies for forming metal, printed circuits, insulation and containers.

PHENOLICS:

Phenolic materials are among the earliest and best known plastics. They are mostly based on phenol formaldehyde. Applications include radio cabinets, telephones, electrical sockets and plugs, pumps, valves, trays, auto distributors, rollers and coatings.

SILICONES:

Silicones (Dow Corning) offer outstanding heat resistance. Mechanical properties change little with variations in temperature. These plastics differ from most plastics in that an important ingredient is inorganic silicon. Silicones are used for molding compounds, laminating resins and insulation for electric motors and electronic equipment. Resistance to attack by chemicals is not outstanding.

UREAS :

Ureas were the second important class, after the phenolics, of the thermosetting resins to be developed. They are based on urea and formaldehyde. Corrosion resistance is not good.

LAMINATES AND REINFORCED PLASTICS:

These materials usually consist of thermosetting resins 'filled' or laminated with cloth, mats, paper, chopped fabrics, or fibers such as fiber glass, which is commonly used. The main advantage is that tensile strength can be increased to as high as around 50,000 psi. This results in a high strength-weight ratio for these light materials. Availability and uses include tanks, pipe ducts, sheets, rod, car bodies (Corvette), boats, and missile and satellite parts.

OTHER NON-METALLICS CERAMICS:

Ceramic materials consist of compounds of metallic and nonmetallic elements. A simple example is MgO or magnesia. Other ceramics include alumina (Al_2O_3), thoria (ThO_2) glass, brick, stone, fused silica, stone-ware, clay tile, porcelain, concrete, abrasives, mortars and high-temperature refractories.

In general, compared with metals, ceramics resist higher temperatures, have better corrosion and abrasion resistance, including erosion-corrosion resistance and are better insulators; but they are brittle, weaker in tension and subject to thermal shock. Most ceramic materials exhibit good resistance to chemicals, with the main exceptions of hydrofluoric acid and caustic. Parts are formed by pressing, extrusion or slip casting.

ACID BRICK:

This material is made from fire clay with a silica content about 10 percent greater than ordinary firebrick. A common application is lining of tanks and other vessels to resist corrosion by hot acids or erosion-corrosion. A bricklined steel tank usually contains an intermediate lining of lead, rubber or a plastic. Acid-resistant cements and mortars join the brick. Floors subject to acid spillage are made of acid brick.

STONEWARE AND PORCELAIN:

Both of these find many applications because of their good corrosion resistance. Porcelain parts are usually smaller in size than stoneware and the porcelain is less porous. Stoneware sinks, crocks and other vessels, absorption towers, pipes, valves and pumps are available. Porcelain can be made into similar equipment (e.g acid nozzles).

GLASS:

Glass is an amorphous inorganic oxide, mostly silica, cooled to a rigid condition without crystallization. Glass laboratory ware, such as Pyrex (9), and containers are well known. Piping and pumps are available. Transparency is utilised for equipment such as flowmeters. Glass fibers are widely used for air filters, insulation and reinforced plastics. Hydrofluoric acid and caustic attack glass and it shows slight attack in hot water.

VITREOUS SILICA:

This material, also called fused quartz (almost pure silica), has better thermal properties than most ceramics and excellent corrosion resistance at high temperatures. It is used for furnace muffles, burners, reaction chambers, absorbers, piping , etc. particularly where contamination of product is undesirable.

CARBON AND GRAPHITE :

These are unique nonmetallics in that they are good conductors of heat and electricity. High thermal conductivity results in excellent thermal shock resistance. They are used for heat exchangers, columns, pumps and impressed current anodes. Carbon and graphite are inert to many corrosive environments. They are weak and brittle compared to metals. Tensile strength varies between about 500 and 3000 psi and impact resistance is nil. Abrasion is poor. High-temperature stability is good and they can be used at temperatures up to 5000°F (2760 C) is protected from oxidation.

(9) A trade name belonging to Corning Glass Works, Corning, N.Y. (Burning). Silicon base coatings (silicides or silicon carbide) and iridium coatings are claimed to give protection up to around 2900 F (1593 C) in air.

Carbon exhibits good resistance to alkalis and most acids, but oxidizing acids such as nitric, concentrated sulfuric and chromic acid attack it. Fluorine, iodine, bromine, chlorine and chlorine dioxide are likely to attack carbon. In the chemical process industries. Graphite in nuclear reactors is quite well known.

Phrolytic graphite, which is a dense, anisotropic material, has better strength and oxidation resistance than the more common types of carbon.

WOOD:

Cypress, pine, oak and redwood are the main woods used for corrosion applications. Filter-press frames, structural members of buildings, barrels and tanks are often made of wood. Containers must be kept wet or the staves will shrink, warp and leak. Generally speaking, wood is limited to water and dilute chemicals. Strong acids and dilute alkalis attack woods. They are also subject to biological attack. Impregnation with waxes and plastic resins helps reduce chemical and biological attack.

QUIZ NO.6

1. High Silicon cast iron is NOT suitable for
 - (a) Hydro-chloric acid of concentration >37 percent.
 - (b) Bleaches
 - (c) Hydrofluoric acid

2. In stainless steel, what is the minimum chromium content that should be

3. Please choose the right statement,
 - (a) Martensitic S.S cannot be hardened by heat treatment.
 - (b) Ferritic steels cannot be hardened by heat treatment.
 - (c) Austenitic S.S can be hardened by heat treatment.

4. What material you would suggest for shipping nitric acid.

5. Which one of the following does well in chloride containing waters.
 - (a) Martensitic S.S
 - (b) Ferritic S.S
 - (c) Austenitic S.S

6. Among the three groups (i.e., Martensitic, ferritic and austenitic) of S.S generally which one is most resistant for severe corrosion conditions.

7. What type of S.S known as 'Work horses' in process industries.

8. For HF Acid, which one of the following, you will choose.
 - (a) Aluminium
 - (b) Magnesium
 - (c) Copper

9. What is chemical lead.
10. The corrosion resistance of Titanium temperatures of _____
11. Silicon rubber can withstand a maximum temperature of _____ C in air.
12. What are the two classification of plastics.
13. What is the chemical name for Teflon.
14. Mention atleast 3 thermoplastics.
15. Mention at least 3 thermosetters.
16. The environments given below attack some materials. Match them properly.

Environment	Metal
1. Acetic acid	(a) Nickel
2. Aerated acids	(b) Chemical Lead
3. Oxidizing solutions such as HNO ₃ , NH ₃ .	(c) Copper
4. Alkalies	(d) Tin

17. The Metals given below are resistant to some environments. Match them properly.

Metal	Environment
1. Austenitic S.S	(a) hot organic acids
2. Type 316 S.S	(b) atmosphere corrosion
3. Nickel	(c) Pure water.

4. Tin (d) Caustic solutions.

18. Which one of the following is 'true'

- (a) Titanium is not resistant to sea water.
- (b) Titanium is resistant to wet chlorine
- (c) Titanium is resistant to pure HCL acid.

19. Which one of the following is 'False'

- (a) Columbium is not suitable for hot concentrated H_2SO_4 acids
- (b) Molybdenum is not suitable for oxidising acids such as HNO_3
- (c) Tantalum is not resistant to alkalies HF, and hot concentrated H_2SO_4 .
- (d) Carbon is not attacked by HNO_3 , conc. H_2SO_4 and chromic acid.

20. Relate the following:

- | | |
|--------------|------------------------|
| 1. Aluminium | (a) Sacrificial anode |
| 2. Magnesium | (b) Fuming nitric acid |
| 3. Titanium | (c) Anodizing. |

PROTECTIVE COATINGS

In general, protective coatings can be classified as low temperature coatings, high temperature coatings, metallized coatings and non-metallic coatings.

USE OF SURFACES COATINGS:

By surface coatings we mean protective films provided by corrosion inhibitive paints when applied as a system i.e. Primer and subsequent coats. The paint film is generally permeable to Oxygen and moisture and in order to protect the base metal it is necessary to choose a proper vehicle or a binder and incorporate selective pigments. Before selecting a proper coating one has not only to understand the service conditions to which this coating would be subjected, but also the mechanism which is responsible for providing the that paint films retard corrosion by presenting a barrier resistance to the flow of the current, responsible for corrosion. Hence, coatings having high electrical resistance would inhibit corrosion more effectively and if this resistance is lowered by deterioration, water absorption or other causes, the degree of protection would be reduced. This property of high electrical resistance is provided by the medium i.e. the resinous film which by itself is not corrosion inhibitive.

In order to reinforce the corrosion resisting property of the paint film it is necessary that an adequate mechanical barrier between the corrodible substance and the corrosive environment is also provided. The determining properties of such a barrier are related to 'continuity' which is a measure of the ability of the resinous film to form a holiday free film (gap free) at low coating weights and to 'permeability' which is a measure of the diffusion rates of water vapour and other gases diffusing through the 'continuous' film. The third and equally important factor is 'adhesion' and 'cohesion' which are measures of the tenacity with which the resin molecules bend to the substrate and to each other. The barrier should also be chemically inert to prevent degradations by hydrolytic, oxidation and thermal action.

Permeability characteristics of a resinous vehicle can be improved

considerably by addition of suitable pigments. Adhesion of the paint film would largely depend on the degree of the cleanliness of the metal surface.

SURFACE PREPARATION

The performance of any paint depends primarily on proper surface preparation which contributes more than any other single factor to the success of protective systems. There are several methods of surface preparation as listed below and the choice between them is influenced by the nature of the structure, the condition of the steel surfaces and the corrosiveness of the environment. It may be noted that badly corroded steel needs special attention and it is likely that more than one method would have to be employed.

1. Pickling
2. Manual or hand tool cleaning
3. Mechanical or power tool cleaning
4. Flame cleaning
5. Blast cleaning

1. PICKLING:

This method is suitable in production line when the surface areas are not large and the articles can be easily handled. It is not feasible in the case of large fabricated members of large sections beams or equipment as the cost of providing the required facilities would be very high.

2. HAND TOOL CLEANING

This method is employed only when loose rust, scale and old coatings (not firmly adhering) are to be removed. Thorough chipping and scrapping should be carried out prior to use of vigorous wire brushing, followed by emery paper cleaning. This method is largely ineffective as residual rust and scale is always left behind. However, hand tool cleaning may be adopted in the absence of better facilities like power tool cleaning or blast cleaning. This is an acceptable method for spot cleaning

during maintenance painting or when the surface is exposed to internal and normal atmospheric condition.

3. POWER TOOL CLEANING :

This includes use of electrical or pneumatic tools such as rotating wire brushes, sanding machines and discs, abrasive grinders, chipping hammers, needle guns and rotary descalers. All traces of oil and grease are first removed by degreasing with an aromatic solvent and heavy layers of scale and rust should also be removed preferably by hand tools.

4. FLAME CLEANING

This method is used for cleaning new steel as well as old painted steel. Steel and mill scales have different coefficients of expansion and on heating, stresses are produced in the scale which cause it to crack and flake. Experience has shown that flame cleaning will not effectively remove tightly adherent mill scale but is quite effective and will remove loose scale, old paint, etc. Flame cleaning is used on location or in the shops when blast cleaning is not possible and this is definitely a better method.