Corrosion theory

Monitoring and control in oil and gas fields

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DOKTORSKI RAD

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Advanced Corrosion Management in Oil and Gas Industry

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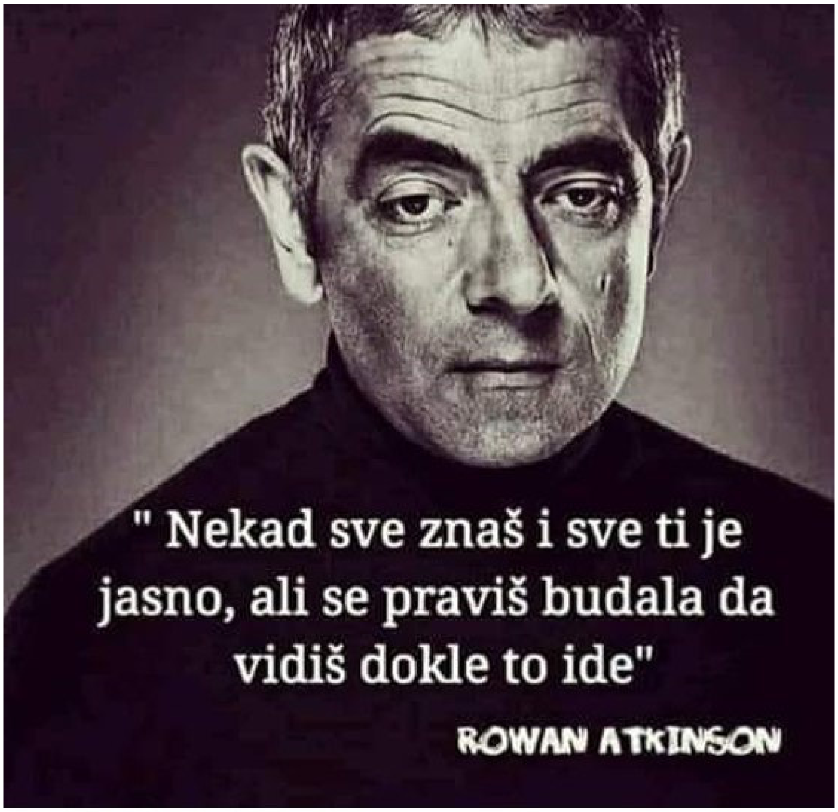


" Nekad sve znaš i sve ti je jasno, ali se praviš budala da vidiš dokle to ide"

ROWAN ATKINSON

Sometimes you know everything and everything is clear to you, but you pretend to be curious to see how far it goes.

Biti dobar ne znači da si idiot.
Biti **dobar** je vrlina koju **idioti** ne razumiju.

Advanced Corrosion Management in Oil and Gas Industry.

Corrosion theory, forms, Monitoring, and
control in oil and gas fields.

Contents

Chapter 1

Corrosion Definition and cost

1.1 Definition of Corrosion

Several definitions of corrosion have been given such as:
(A) Corrosion is the surface wastage that occurs when metals are exposed to reactive environments.
(B) Corrosion is the result of interaction between a metal and environments, which results in its gradual destruction.
(C) Corrosion is an aspect of the decay of materials by chemical or biological agents.
(D) Corrosion is an extractive metallurgy in reverse. For instance, iron is made from hematite by heating with carbon. Iron corrodes and reverts to rust, thus completing its life cycle. The hematite and rust have the same composition (Fig. 1.1).
(E) Corrosion is the deterioration of materials because of reaction with its environment
(Fontana - NACE).
(F) Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with the environment (Uhlig).
Deterioration of a metal by physical causes is not called corrosion, but is described as erosion, galling, or wear. In some instances, chemical attack accompanies physical deterioration, as described by the following terms: corrosion – erosion, corrosive wear, or fretting corrosion. Nonmetals are not included in this definition of corrosion. Plastics may swell or crack, wood may split or decay, granite may erode, and Portland cement may leach away, but the term corrosion, in this book, is restricted to chemical attack of metals.“ Rusting” applies to the corrosion of iron or iron - base alloys with formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metals, therefore, corrode, but do not rust.

1.1.1 Corrosion Science and Corrosion Engineering

Since corrosion involves chemical change, the student must be familiar with principles of chemistry in order to understand corrosion reactions. Because corrosion processes are mostly electrochemical, an understanding of electrochemistry is also important. Furthermore, since structure and composition of a metal often determine corrosion behavior, the student should be familiar with the fundamentals of physical metallurgy as well.
The corrosion scientist studies corrosion mechanisms to improve (a) the understanding of the causes of corrosion and (b) the ways to prevent or at least minimize damage caused by corrosion. The corrosion engineer, on the other hand, applies scientific knowledge to control corrosion. For example, the corrosion engineer uses cathodic protection on a large scale to prevent corrosion of buried pipelines, tests and develops new and better paints, prescribes proper dosage of corrosion inhibitors, or recommends the correct coating. The corrosion scientist, in turn, develops better criteria of cathodic protection, outlines the molecular structure of chemical compounds that behave best as inhibitors, synthesizes corrosion - resistant alloys, and recommends heat treatment and compositional variations of alloys that will improve their performance. Both the scientific and engineering viewpoints supplement each other in the diagnosis of corrosion damage and in the prescription of remedies.

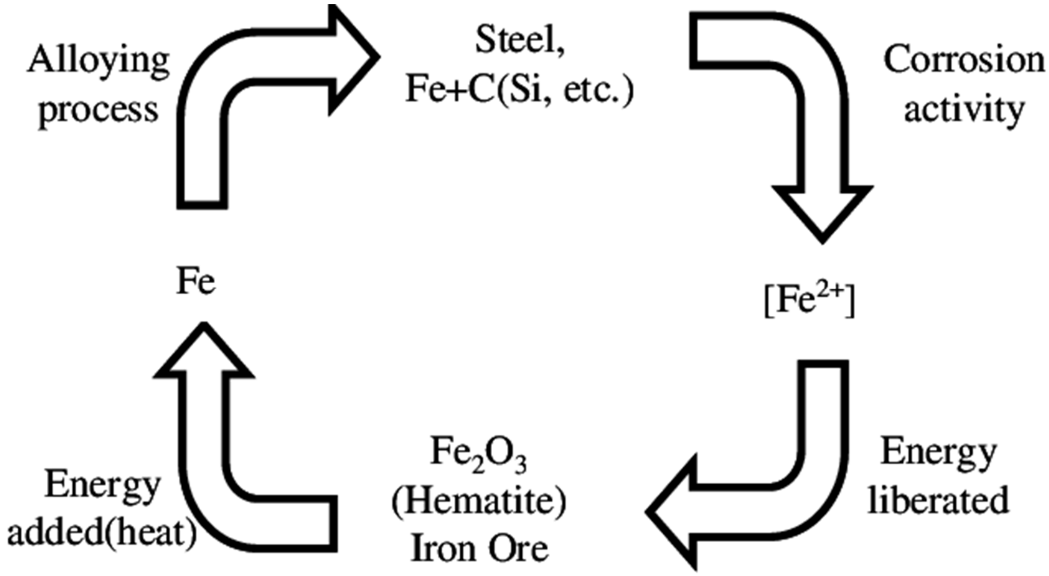


Fig.1-1. Corrosion cycle of Iron

1.1.2 Corrosive Environment

Corrosion cannot be defined without a reference to environment. All environments are corrosive to some degree. Following is the list of typical corrosive environments:
(1) Air and humidity.
(2) Fresh, distilled, salt and marine water.
(3) Natural, urban, marine and industrial atmospheres.
(4) Steam and gases, like chlorine.
(5) Ammonia.
(6) Hydrogen sulfide.
(7) Sulfur dioxide and oxides of nitrogen.
(8) Fuel gases.
(9) Acids.
(10) Alkalis.
(11) Soils.

Therefore, it may be observed that corrosion is a potent force, which destroys economy, depletes resources and causes costly and untimely failures of plants, equipment and components.

1.2 Importance of Corrosion

The three main reasons for the importance of corrosion are economics, safety, and conservation. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on. Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences) of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources — metal, energy, water, and human.

Economic losses are divided into (1) direct losses and (2) indirect losses.

Direct losses include the costs of replacing corroded structures and machinery or their components, such as condenser tubes, mufflers, pipelines, and metal roofing, including necessary labor. Other examples are (a) repainting structures where prevention of rusting is the prime objective and (b) the capital costs plus maintenance of cathodic protection systems for underground pipelines. Sizable direct losses are illustrated by the necessity to replace several million domestic hot - water tanks each year because of failure by corrosion and the need for replacement of millions of corroded automobile mufflers. Direct losses include the extra cost of using corrosion - resistant metals and alloys instead of carbon steel where the latter has adequate mechanical properties but not sufficient corrosion resistance; there are also the costs of galvanizing or nickel-plating of steel, of adding corrosion inhibitors to water, and of dehumidifying storage rooms for metal equipment.

The economic factor is a very important motivation for much of the current research in corrosion. Losses sustained by industry and by governments' amount to many billions of dollars annually, approximately $ 276 billion in the United States, or 3.1% of the Gross Domestic Product (GDP), according to a study in 2002. It has been estimated that about 25 – 30% of this total could be avoided if currently available corrosion technology were effectively applied.

Studies of the cost of corrosion to Australia, Great Britain, Japan, and other countries have also been carried out. In each country studied, the cost of corrosion is approximately 3 – 4 % of the Gross National Product according to a study in 2006.

Indirect losses are more difficult to assess, but a brief survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined. Examples of indirect losses are as follows:

1. *Shutdown.* The replacement of a corroded tube in an oil refinery may cost a few hundred dollars, but shutdown of the unit while repairs are underway may cost $ 50,000 or more per hour in lost production. Similarly, replacement of corroded boiler or condenser tubes in a large power plant may require $ 1,000,000 or more per day for power purchased from interconnected electric systems to supply customers while the boiler is down. Losses of this kind cost the electrical utilities in the United States tens of millions of dollars annually.
2. *Loss of Product.* Losses of oil, gas, or water occur through a corroded -pipe system until repairs are made. Antifreeze may be lost through a corroded auto radiator; or gas leaking from a corroded pipe may enter the basement of a building, causing an explosion.
3. *Loss of Efficiency.* Loss of efficiency may occur because of diminished heat transfer through accumulated corrosion products, or because of the clogging of pipes with rust necessitating increased pumping capacity. It has been estimated that, in the United States, increased pumping capacity, made necessary by partial clogging of water mains with rust, costs many millions of dollars per year. A further example is provided by internal - combustion engines of automobiles where piston rings and cylinder walls are continuously corroded by combustion gases and condensates. Loss of critical dimensions leading to excess gasoline and oil consumption can be caused by corrosion to an extent equal to or greater than that caused by wear. Corrosion processes can impose limits on the efficiencies of energy conversion systems, representing losses that may amount to billions of dollars.
4. *Contamination of Product.* A small amount of copper picked up by slight corrosion of copper piping or of brass equipment may damage an entire batch of soap. Copper salts accelerate rancidity of soaps and shorten the time that they can be stored before use. Traces of metals may similarly alter the color of dyes. Lead equipment, otherwise durable, is not permitted in the preparation of foods and beverages because of the toxic properties imparted by very small quantities of lead salts. The U.S. Bureau of Food and Drugs, for example, permits not more than 1 ppb of lead in bottled drinking water. Similarly, soft waters that pass through lead piping are not safe for drinking purposes. The poisonous effects of small amounts of lead have been known for a long time. Another form of contamination is spoilage of food in corroded metal containers. A cannery of fruits and vegetables once lost more than $ 1 million in one year before the metallurgical factors causing localized corrosion were analyzed and remedied. Another company, using metal caps on glass food jars, lost $ 0.5 million in one year because the caps perforated by a pitting type of corrosion, thereby allowing bacterial contamination of the contents.
5. *Overdesign.* Overdesign is common in the design of reaction vessels, boilers, condenser tubes, oil - well sucker rods, pipelines transporting oil and gas at high pressure, water tanks, and marine structures. Equipment is often designed many times heavier than normal operating pressures or applied stresses would require in order to ensure reasonable life. With adequate knowledge of corrosion, more reliable estimates of equipment life can be made, and design can be simplified in terms of materials and labor. For example, oil - well sucker rods are normally overdesigned to increase service life before failure occurs by corrosion fatigue. If the corrosion factor were eliminated,

losses would be cut at least in half. There would be further savings because less power would be required to operate a lightweight rod, and the expense of recovering a lightweight rod after breakage would be lower.

Indirect losses are a substantial part of the economic tax imposed by corrosion, although it is difficult to arrive at a reasonable estimate of total losses.

In the event of loss of health or life through explosion, unpredictable failure of chemical equipment, or wreckage of airplanes, trains, or automobiles through sudden failure by corrosion of critical parts, the indirect losses are still more difficult to assess and are beyond interpretation in terms of dollars.

Chapter 2

Fundamentals of Electricity and Electrochemistry

2.1 Atomic Structure

The basic structure of all materials that are seen, or used every day conforms with a set pattern known as the atomic structure of matter. When a building is under construction, there are definite steps that are followed by the builders from its beginning to its completion. The materials used in the construction (steel girders, bricks, cement, etc.), when placed in their proper order and number, form a building. This concept of definite parts in a proper order can be related to the basic structure of all matter.

Matter

Matter is anything that has mass and occupies space. Matter may take many forms. It may be a liquid, such as water; a gas, such as oxygen; or a solid, such as stone. Matter, as we know it, normally has weight because anything that has mass and is on or near the earth is influenced (pulled) by the force of the earth's gravity. Matter may be made up of a single element, or it may be a combination of two or more elements.

Element

An element is a substance that cannot be broken down through chemical reaction or changed by chemical means. Elements are the basics of building blocks of all matter. There are 92 naturally occurring elements, ranging from the lightest hydrogen, to the heaviest, uranium. Iron, oxygen, and gold are also elements.

Compound

A compound is a combination of two or more elements. A compound is a pure substance and has a fixed composition.
Examples of chemical compounds are:

- Carbon Dioxide – CO_2
- Salt – NaCl
- Water- H_2O
- Ferric Oxide- Fe_2O_3

Mixture

A mixture is a combination of elements, compounds, or both held together by physical rather than chemical forces. A mixture does not have physical composition. Air, for example, is roughly 20% oxygen and 78% nitrogen, but it also contains other substances, such as argon (1%) and varying amount of carbon dioxide and water vapor. Soil is a mixture of minerals formed from elements and compounds.

Atom

The smallest particle to which an element can be reduced and still retain its original characteristics is the atom.

The simplest atom is hydrogen, which is shown in fig 2.2. This atom consists of a central body with one small body revolving around the center in an orbit. The central body is called the nucleus, and the revolving or planetary body is called an electron. The nucleus contains a positive unit particle known as a proton. The electron is a negative unit particle and the proton is a positive unit particle. We can replace the term "unit particle" with "charge".

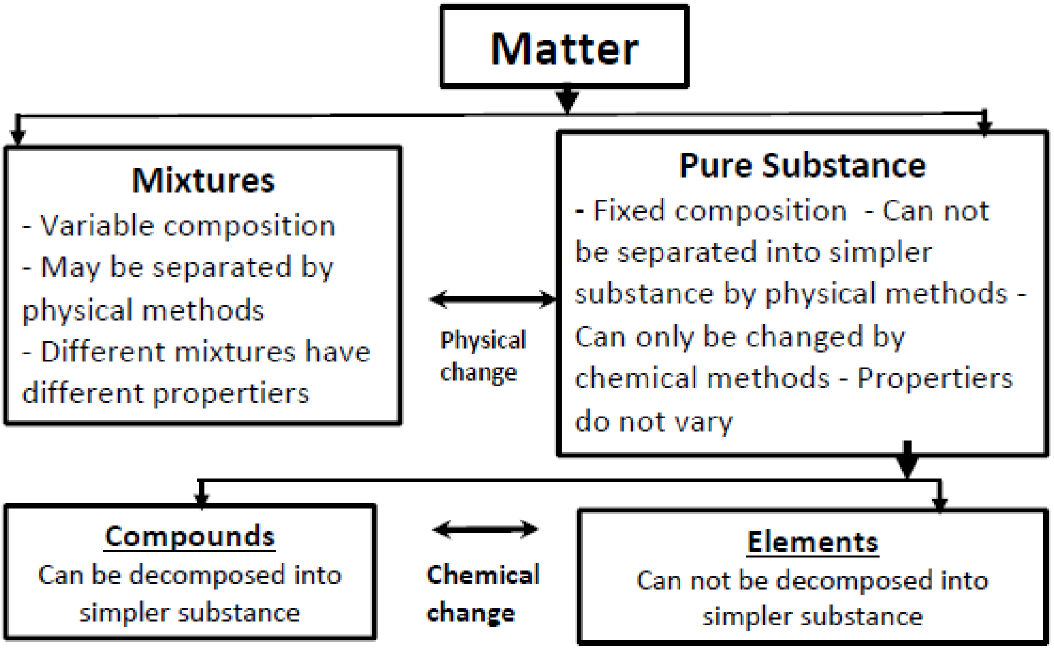


Figure 2.1.Matter configuration.

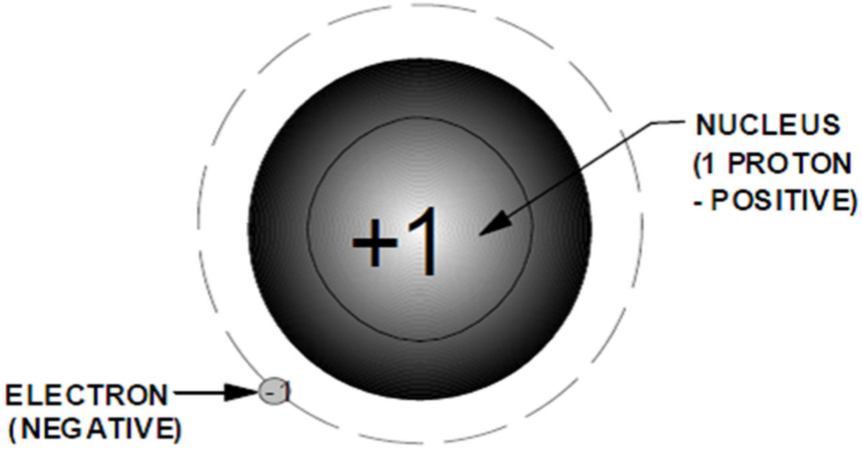


Fig. 2.2. Hydrogen atom

When a particular atom such as copper is neutral, or balanced, the negative charges balance the positive charges, and the net charge on the atom is zero.

Electron Charge + Proton Charge = Atom Charge
(-29) (+29) = 0

If, through some outside force, an electron is broken away from the outer orbit, the atom is no longer neutral. Assume that one electron is removed from a copper atom. When this action takes place, the copper atom becomes a positive body with a net charge to +1 due to the absence of one electron which would make it neutral.

Electron Charge + Proton Charge = Atom Charge
(-28) (+29) +1

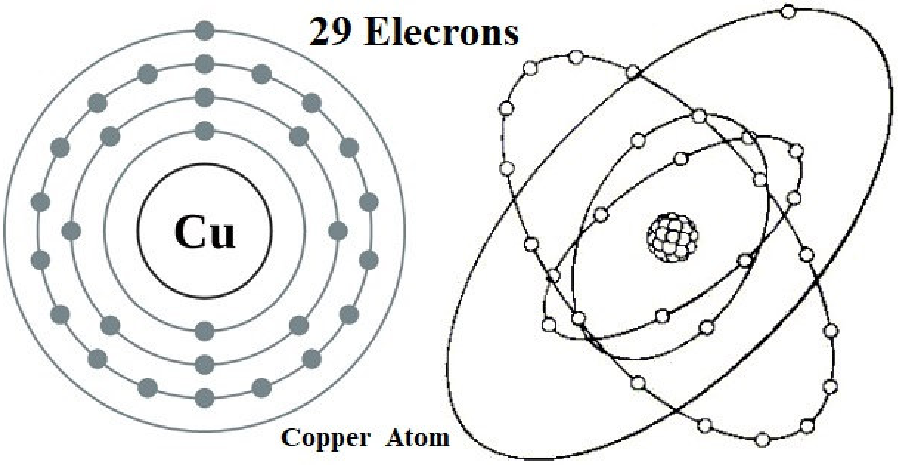


Fig. 2.3. Copper atom

Conversely, if through some outside force, an additional electron is forced into the outer orbit of a copper atom, the atom becomes a negative body with a charge of -1.

Electron Charge + Proton Charge = Atom Charge
(-30) (+29) -1

In making the copper atom a positive body, the question arises: What happened to the electron? Whenever an electron is removed from its orbit through the action of some outside force, it becomes a free electron. Free electrons are electrons which have been removed from their orbits and are free to move about among the atoms of the material.

Molecules

The smallest particle of the element (H_2, Cl_2, O_2) or compound (H_2O, HCl, CH4) that retains all the chemical properties of that compound or element.

Ions: An ion is a charged atom or molecule. An ion may be an atom or molecule with either extra electrons or missing electrons.

Cations: If an atom or molecule loses one or more electrons, the ion will has a positive charge.

Anions: If an atom or molecule gains an electron it is negatively charged and called an anion.

Anion	Cation
Negative ion	Positive ion
Net negative charge	Net Positive charge
Formed by addition of electrons	Formed by loss of electrons
Attracted to anode	Attracted to cathode

Table. 2-1. Characteristics of ions.

Anion	Cation
Sulfate ion (SO_4)	Ferrous ion (Fe^{++})
Chloride ion (Cl^-)	Ferric ion (Fe^{+++})
Hydroxyl ion (OH^-)	Hydrogen ion (H^+)

Table. 2-2. Examples of ions.

Electrolytes

are chemical compounds such as **liquids** or gels that **contain ions** and can conduct electricity through the flow of ions. Anions flow towards the anode and cation flow towards the cathode. An electrolyte contains equal amounts of charge on the ions contained in it. The electrolyte may be highly conductive because of the high content of ions (seawater) or only mildly conductive because of its very low content of ions (pure water).

2.2 Chemical and Elecrochemical Chemical Reaction

The chemical reaction is the process that goes on during the conversion of reactants into products and does not include electron transfer.

Example: $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

The electrochemical reaction is a chemical reaction involves electron transfer, so it is a process in which electrons flow between a solid electrode and substance, such as an electrolyte.

Most corrosion reactions are electrochemical reactions, called oxidation/reduction reactions.

Oxidation/reduction reaction occur through an exchange of electrons. In corrosion reactions, these exchanges occur at specific sites called cathode and anode. Oxidation occurs at sites called anode and reduction occurs at sites called cathode.

The electron given off at the anodes travel through the metal to the cathode, where they are consumed in reduction reaction. Corrosion reaction occur in electrolyte that supply the reactants for these reactions. (Refer to figures 2-4 and 2-5).

Oxidation – Anodic reaction	**Reduction – Cathodic reaction**
Loss of electrons	Gain of electrons
Increase positive charge Or decrease negative charge	Increase negative charge Or decrease positive charge
Electrons remain in metal and transfer to cathodic area.	Electrons are consumed in the cathodic reaction at the metal/environment interface.

Table. 2-3. Characteristics of oxidation/reduction reaction.

Oxidation– Anodic reaction	**Reduction– Cathodic reaction**
$Fe^0 \rightarrow Fe^{++} + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
$Fe^0 \rightarrow Fe^{+++} + 3e^-$	$2H_2O + O_2 + 4e^- \rightarrow 4(OH^-)$
$Fe^{++} \rightarrow Fe^{+++} + e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Table. 2-4. Examples of oxidation and reduction.

2.3 Corrosion as an Electrochemical Process

Except for high-temperature corrosion, all corrosion reactions are electrochemical reactions occurring in an electrolyte. Refer to tables 2-3 and 2-4, and figures 2-4 to 2-8.

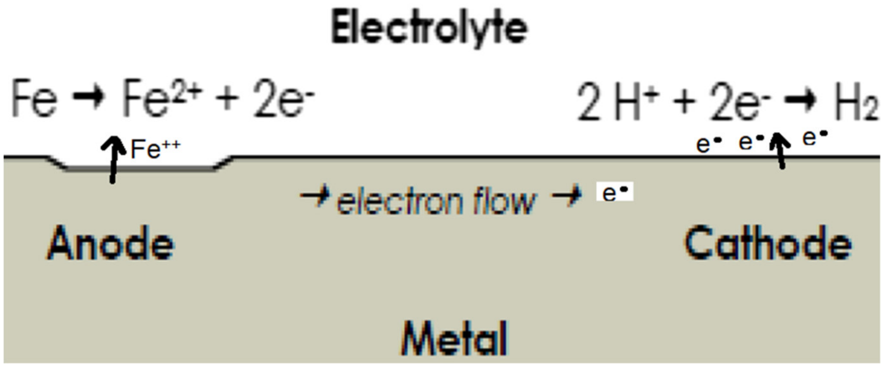


Fig. 2-4. Corrosion cell.

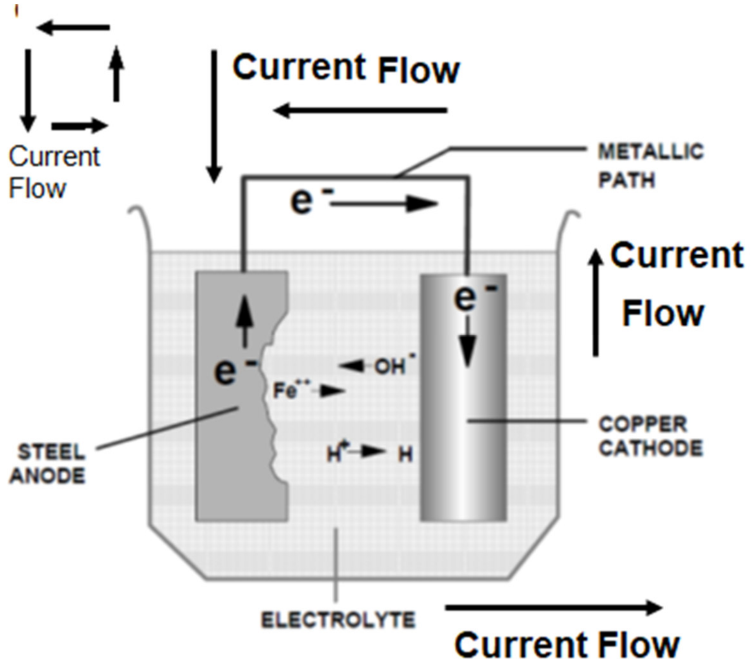


Fig. 2-5 .Corrosion cell and current flow direction.

2.4 Corrosion Cell (The Complete Corrosion Circuit)

When an anodic reaction occurs, the electrons remain in the metal, and unless consumed in reaction at the cathode, will build up and tend to stifle the corrosion reaction. The reaction at the anode that results in the loss of metal can only proceed as fast as electrons are consumed at the cathode. The rate of any chemical reaction is slowed by the buildup of the reaction products. In this case, the reaction products of the oxidation reaction are electrons that remain in the metal and metal ions that enter the solution. Generically, this type of reaction is written:

$$M^0 \rightarrow M^{n+} + ne^-$$

A buildup of either the metal ions in the electrolyte or of the reaction in the metal will tend to reduce the reaction rate. In many corrosion reactions, the metal ions are consumed by reacting with other molecules or compounds in the electrolyte. These reactions reduce the dissolved metal ion content and allow the electrochemical oxidation reaction to proceed rapidly. The metal ions produced by oxidation at the anode combine with other substances in the electrolyte to form corrosion products. The formation of corrosion products is a side reaction that can affect the rate of corrosion, but is not directly involved in the present electrochemical oxidation/reduction reactions.

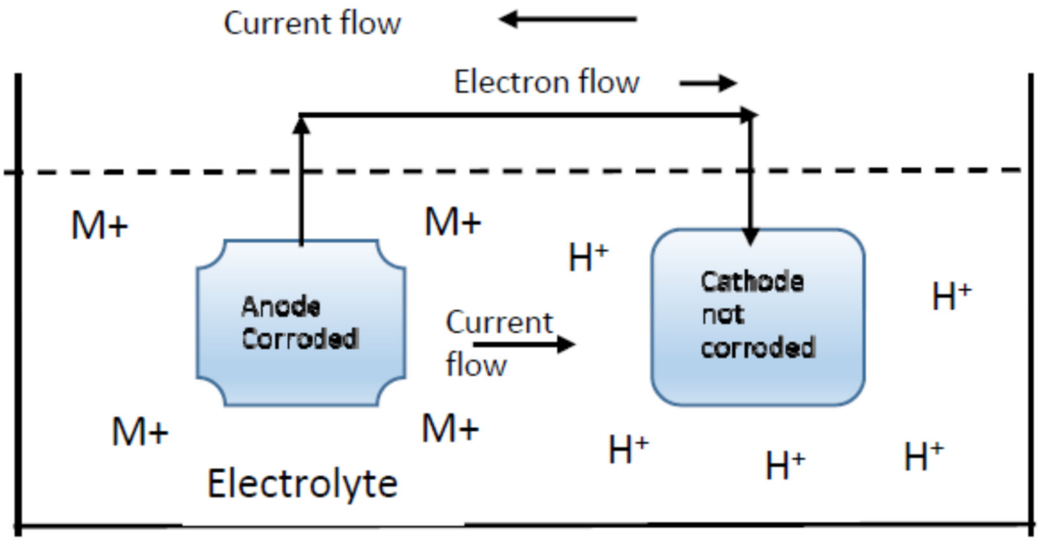
Cathodic reaction consumes electrons. Three of the most common cathodic reactions that consume electrons are given in Table 2-4. Many other reactions are possible, depending on the chemical composition of the electrolyte and other conditions.

Metals are generally good conductors of electricity. Unlike electrolytes, which conduct electricity through the flow of ions, metals conduct electricity through the flow of electrons. Electron flow in metals from areas with more negative charge (excess electrons) to areas with more positive charge (less negative charge – fewer electrons).

One point of confusion is the difference between current flow and electron flow.

The Conventional current flow in an electrical circuit is described as the opposite of electron flow (Electron flow is from more negative to positive or less negative).

Therefore the current flow is from the more positive area in the circuit to the less positive (or less negative to more negative) areas. Transfer of positive ions is considered a current flow since it is transfer from more positive to less positive.



Current flow from cathode to Anode through the metalic connection, and from anode to to cathode through electrolyte (protection current)

Fig. 2-6 .Corrosion cell and conventional current opposite to electrons flow.

In a corrosion cell, electrons flow through the metal from sites where anodic reactions are occurring to sites where they allow cathodic reactions to occur.

Electrical current also flows through the electrolyte to balance the flow of electrons in the metal. In this case, the carriers of the electrical current are ions in the electrolyte.

Anions (negatively charged ions) flow toward the anode and cations (positively charged ions) flow toward the cathode.

The complete corrosion reaction recuires all these components (four components) to be present and active. Therefore, for the corrosion to take place, the formation of a *corrosion cell* is essential. A corrosion cell is essentially comprised of the following four components (Figures. 2-4 to 2-8).

1- Anode

The anode is the site where metal is lost and electrons are produced.

Anodic reaction (Oxidation) **$M^0 \rightarrow M^{n+} + ne^-$**

Anodic reaction is an oxidation reaction results in generation of electrons and increase of the positive charge of a metal. As seen in table 2-4.

Example: $Fe^0 \rightarrow Fe^{++} + 2e^-$

2- Cathode

The cathode is the site where the electron produces at the anode are consumed.

Cathodic reaction (Reduction) is any reaction consumes electrons as in table 2-4.

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

3- Metallic path.

The metallic pass conducts electrons from the anodic sites to the cathodic sites.

4- Electrolyte

The electrolyte provides reactants for the cathodic reactions and allow the flow of ions.

A very important point is that if any of these processes can be slowed or stoped, corrosion can be slowed or eliminated.

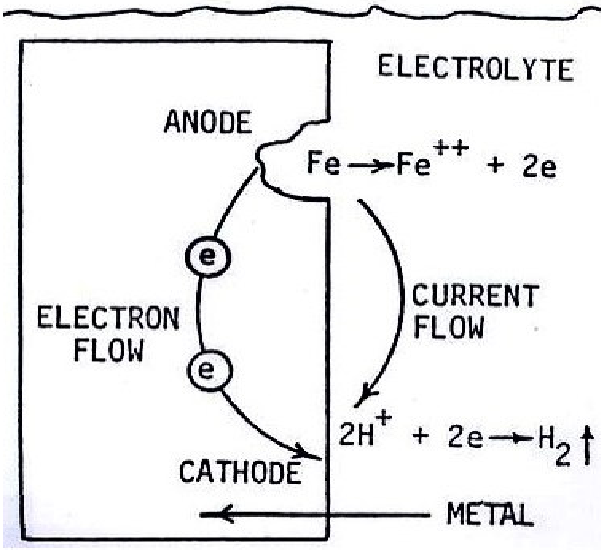


Fig. 2-7. Corrosion cell.

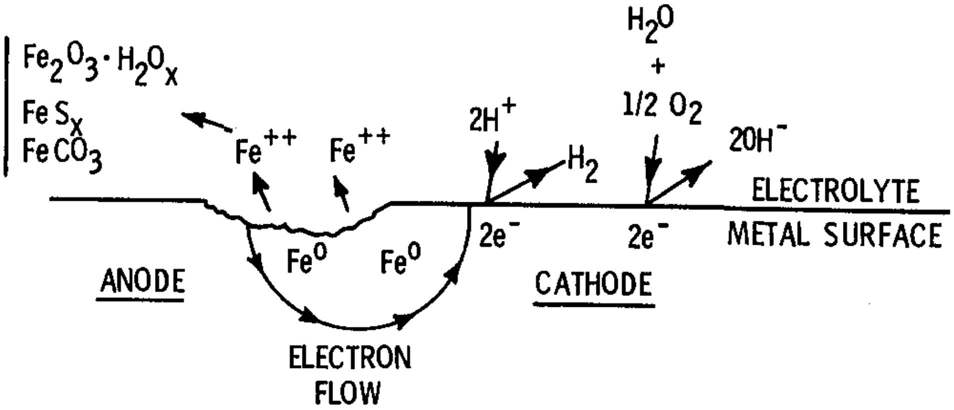


Fig. 2-8. Corrosion cell.

2.5 Basics Electricity

2.5.1 Current

An electric current is a flow of electrons, through some material, from a point of negative potential to a point of positive potential. The rate of flow of electrons is expressed in terms of the ampere.

A current flow of one ampere is said to flow at a point when one Coulomb (6.24 billion billion electrons = 6.24 x 10^{18} electrons) passes through a given point in one second. Expressed in a formula:

$$I=Q/T$$

where:

I = Current in amperes

Q = Quantity of electrical charge in Coulombs

T = Time in seconds

2.5.2 Electromotive Force (EMF)

Electromotive force is the force that pushes the electrons along a conductor that causes current flow. The strength of this electromotive force is measured with a voltmeter.

2.5.3 Resistance

Resistance to electric current flow is a fundamental characteristic of any material. The resistance of any conductor is directly proportional to the conductor’s length and is inversely proportional to its cross-sectional area.

2.5.4 Units of Electric Current - Ampere

An instrument known as an ammeter is used to measure electrical current density in Amperes. The Ammeter must be included in the current circuit to measure the current. The current can also be measured by a clamp ampere, which measure the current from the external of the wire without interrupting the circuit.

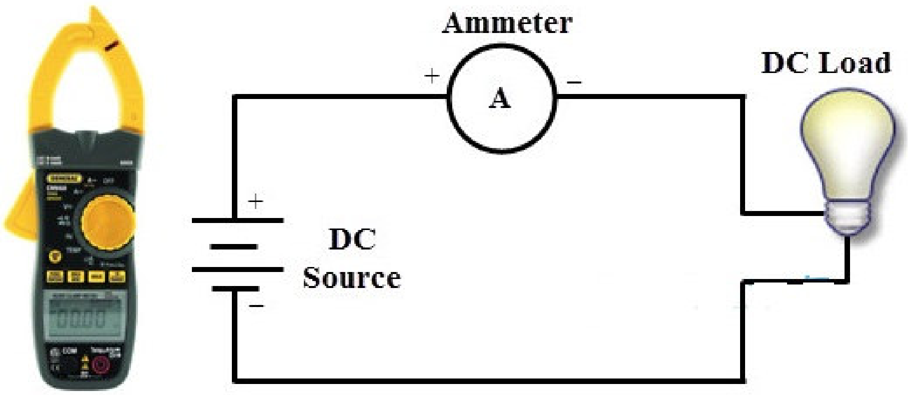


Fig. 2-9 Current measurements

2.5.5 Unit of Electromotive Force - Volt

The electromotive force or difference of potential needed to establish a flow of current in a conductor is measured in volts. The ordinary dry cell, when new, has an electromotive force of 1.5 (one and one-half) volts. The unit of electromotive force is responsible for the term voltage being used to express electromotive force and difference of potential. The instrument generally used to measure electromotive force, or voltage, is the voltmeter.

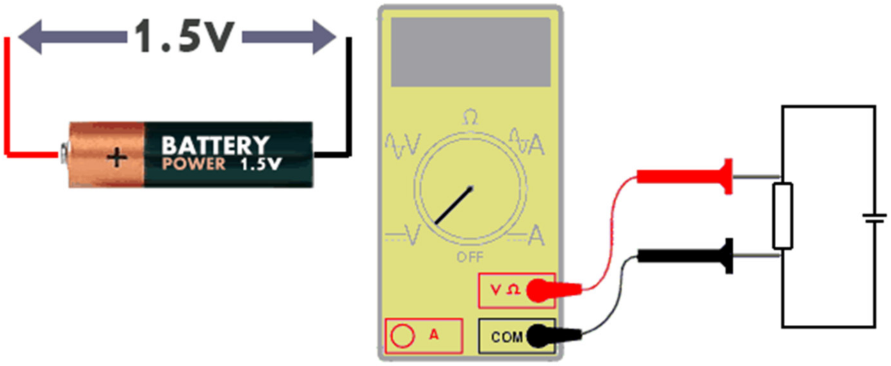


Fig.2-10. Potential difference (voltage) measurements

2.5.6 Unit of Resistance - Ohm

Any substance, the atoms of which have a number of free electrons, is a conductor of electricity. Copper is a good conductor. Iron, aluminum, silver, gold, and many other metals, are all conductors of electricity. Wire made of these metals, of the same diameter and length as the copper wire, will conduct electricity, but the amount of current measured with an ammeter will be different for every metal used, other conditions, such as the voltage of the battery and the dimensions of the wire, remaining the same. That quality of a conductor, which limits or opposes the flow of electrons, or current, is called resistance. Resistance is expressed in ohms.

The resistance of a conductor is 1 ohm when an EMF of 1 volt causes a current flow of 1 ampere to occur. In practice, the resistance of a conductor or of a circuit may be calculated when the values of the applied voltage and the resultant current are known. It may also be measured with an instrument know as an ohmmeter.

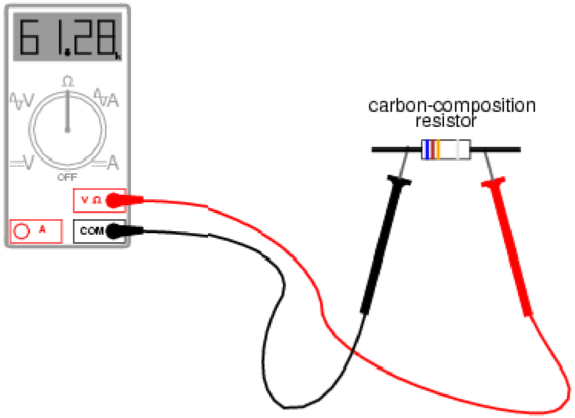


Fig.2-11. Resistance measurements

2.5.7 Ohms Law

There is a definite relation between the voltage, the current, and the resistance of a circuit. This relation is given by Ohms Law which may be expressed in the form of rules or equations. The rules are as follows:

Rule 1: The current, in amperes, is equal to the applied voltage, in volts, divided by the resistance, in ohms.

Amperes = Volts / Ohms

I = V/R

Rule 2: The resistance, in ohms, is equal to the voltage, in volts, divided by the current, in amperes.

Ohms = Volts / Amperes

R = V/I

Rule 3: The voltage, in volts, is equal to the current, in amperes, multiplied by the resistance, in ohms.

Volts = Amperes x Ohms

V = I x R

Ohms law is often expressed in the forms above, but with the generally adopted symbols: I for current, or amperes; E for voltage, or volts; and R for resistance, or ohms. When expressed in this manner, Ohms Law becomes:

I = E/R or R = E/I or E = IxR

An easy way to remember Ohms Law is with a triangle relation. By covering the parameter you are looking for, the remaining characters tell you what to do. Thus, if you want to know the voltage, place your thumb over the E and that leaves you with I x R. Another example would be current. Cover the I with your thumb and that leaves you E/R.

The foregoing rules and equations show that in a direct current circuit three different quantities are involved, namely, volts, amperes, and ohms. When any two of these quantities are known, the third may be determined by Ohms Law.

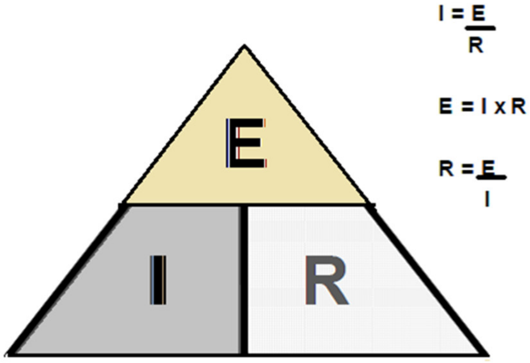


Figure 2-12. Ohms law.

2.5.8 The Two General Types of Electricity

There are two general types of electric current flow, which will be involved with corrosion and corrosion control work. These are alternating current (AC) and direct current (DC).

2.5.8.1 What is Alternating Current?

Alternating current (AC) electricity is that which flows first in one direction and then in the opposite direction in accord with an established pattern. As an example, the usual alternating current power sources in domestic use have a frequency of 50 or 60 cycles per second. This is referred to as 50 or 60 Hertz (50 or 60 Hz).

As can be seen from figure 2-13, the current flow at the beginning of the cycle (left side of the illustration) is zero. The current builds up to a peak in the forward direction and then drops back to zero at the end of the first half cycle. It then reverses its direction of flow and builds up to a maximum in the reverse direction. Following this, it again drops back to zero at the end of the second half cycle (which is the end of one full cycle). At this point, it again reverses direction to start the next cycle.

From this, it can be seen that there are, in effect, two net current reversals for one full cycle. This means that for a normal 60 Hz alternating current power source, the current flow changes direction 120 times per second.(For 50 Hz, the current flow changes 100 times per second). The shape of the normal current flow plot from the usual alternating current commercial power source is known as a sine wave.

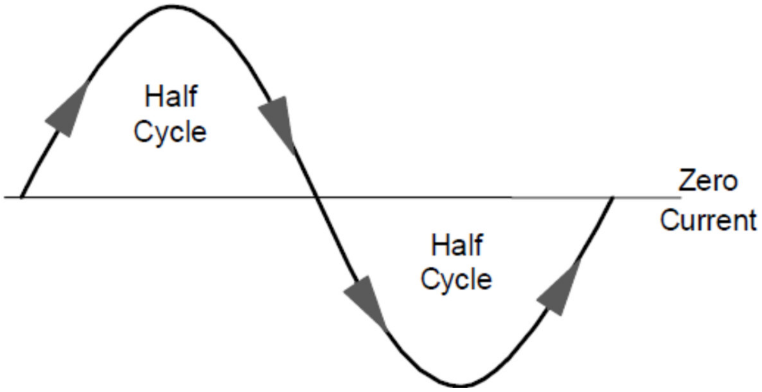


Fig. 2-13. Alternating current.

Significance of Alternating Current

Alternating current electricity is a relatively insignificant factor as a cause of corrosion except in very special cases.

2.5.8.2 What is Direct Current?

Direct current (DC) electricity is that which normally flows in one direction only rather than changing direction in accord with an established pattern as was discussed for alternating current.

An example of direct current is that from a battery powering a common flashlight. Figure 2-14.

Significance of Direct Current

DC electricity is of prime importance in the consideration of the corrosion process. It is directly involved in various types of corrosion cells. It is also directly involved in corrosion control by the use of various types of cathodic protection.

2.5.9 Unit of Resistivity

It was found that the resistance of a conductor is proportional to the length and that the resistance is inversely proportional to the cross-sectional area.

To mathematically relate these for any conductor, we must introduce proportionality constant, called resistivity whose symbol is the Greek letter ρ (rho). We can express the resistance of any conductor by, $R = \rho L/A$ or $\rho = RA/L$

Since R is in ohms, and if A is in square centimeters (cm^2), and L is in centimeters (cm), then:

$\rho = ohms \times cm^2/cm = ohm\text{-}cm$

Thus, ρ, that is, resistivity has the dimension ohm-centimeter. Resistivity then is equal to the resistance of a conductor which is 1 centimeter long with a constant cross-sectional area of 1 square centimeter.

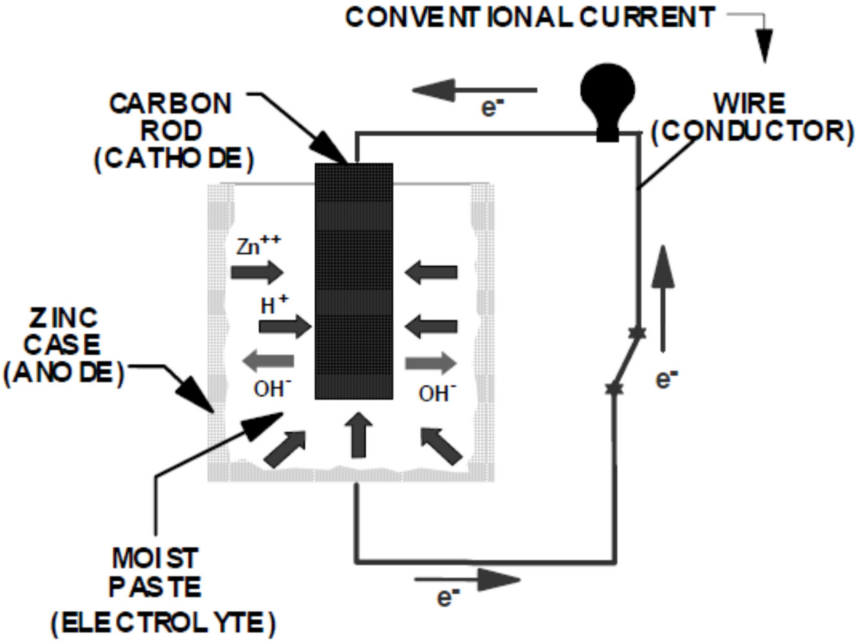


Fig. 2-14. Dry cell battery.

2.6 Thermodynamics

Thermodynamics is the science of the flow of energy. In some chemical reactions, such as in the burning of wood or oil, the energy is in the form of heat; thus, the term is derived from “thermo” (heat) + “dynamics” (movement). In corrosion, the chemical reactions usually produce heat at such a slow rate that it is difficult to detect; however, energy flows in corrosions, usually in the form of electrical energy.

The flow of energy determines the direction of all chemical reaction, including corrosion reactions. The energy content of metals is higher than the energy content of the corrosion products that result from corrosion reactions. Natural processes always tend to reduce the total energy content of a system. In this case the system is the metal and its environment. In nature, metallic elements are usually found in the form of chemical compounds, called ores. In refining these compounds into pure metals, energy is required either in the form of heat or electricity. The more reactive metals require more energy input to produce pure metals from their ores. From an energy standpoint, corrosion is simply the natural process of returning these high-energy form of the metallic elements as pure metals, or as mixtures of metals called alloys, into a lower energy state, where they are combined with other elements to form chemical compound. In fact, corrosion products are often the same compounds as ores. For instance, iron ore is primarily ferric oxide (Fe_2O_3), which is a common form of rust produced by the corrosion of iron and steel. Another interesting point is that the metals requiring little energy to produce pure metals from their ores are more corrosion resistant. In some ores, copper is found as a pure metal, and in some (but not all) environments, copper is stable and essentially free of corrosion.

This energy difference is given off as heat (usually immeasurable) and electrical flow (easily measurable in many cases).

2.7 Potential

Measurement of electrical potential is one way of measuring energy differences. In corrosion, the anode (negative electrode) is of higher energy state than the cathode (positive electrode). The electron flow from a high-energy area to one of lower energy.

The electron flow is dependent on the energy difference existing between the anode and the cathode. This amount of energy can be measured as a difference in potential between the anode and the cathode, providing that a voltmeter can be inserted between the anode and the cathode in the electrical circuit. This energy (potential) difference is normally on the order of a few volts or less.

Measuring the potential difference between galvanized steel and copper in water is an example such a potential measurement. The potential of the electrode connected to the common test lead is more negative than the potential of the electrode connected to the positive lead when the potential reading is positive. (Figure 2-15).

The potential of the galvanized steel is more negative than that of the copper by 0.851 V. The potential of each metal in this case was not measured; all that was measured was the potential difference between them. As in the case of measuring the heights of various points on the earth, it is necessary to establish a reference height in order to speak of the potential of individual electrodes (anodes or cathodes). In the case of the measurement of heights of the earth's surface, a reference height of sea level is given an arbitrary value of zero. A given point can be given in terms of a foot above or below sea level. The height difference between two points can be determined by subtracting the height of the higher point (as measured from sea level) from the height of the lower point (also as measure from sea level). Sea level is useful as a reference height because it is approximately the same all over the earth.

In the measurements of potentials, a reference electrode is frequently used. A reference electrode is constructed so that the potential will be reproducible. Many reference electrodes can be constructed, and each is particularly suited for its intended use. In laboratory use, the hydrogen reference electrode has been assigned the zero value for potential. Other reference electrodes that can be more conveniently used in the laboratory and in the field can be compared to the arbitrary zero potential of the hydrogen reference electrode. When potentials are measured with respect to these other reference electrodes that have non zero potential, it is necessary to indicate which reference electrode was used.

2.8 Reference Electrodes

Calomel, silver, and copper reference electrodes are frequently used under laboratory or field conditions. To make a reference electrode with a reproducible potential, a metal is immersed in an electrolyte with a reproducible chemical composition, in particular, a specific content of ions.

2.8.1 Calomel Reference Electrode

This reference electrode is primarily used under laboratory conditions. It consists of mercury as the metal and a solution of potassium chloride as the electrolyte with mercury chloride (calomel) as an intermediate compound. The potential off the calomel electrode is dependent on the concentration of potassium chloride used; saturated, normal, and one-tenth normal potassium chloride are commonly used.

The electrolyte in the reference electrode and the electrolyte with which the electrode to be measured is immersed are brought into contact through a porous glass disk or a capillary tube. The electrode is usually constructed from glass and is not durable enough for field measurements.Figure 2-16.

Fig. 2-15.Potential difference measurements.

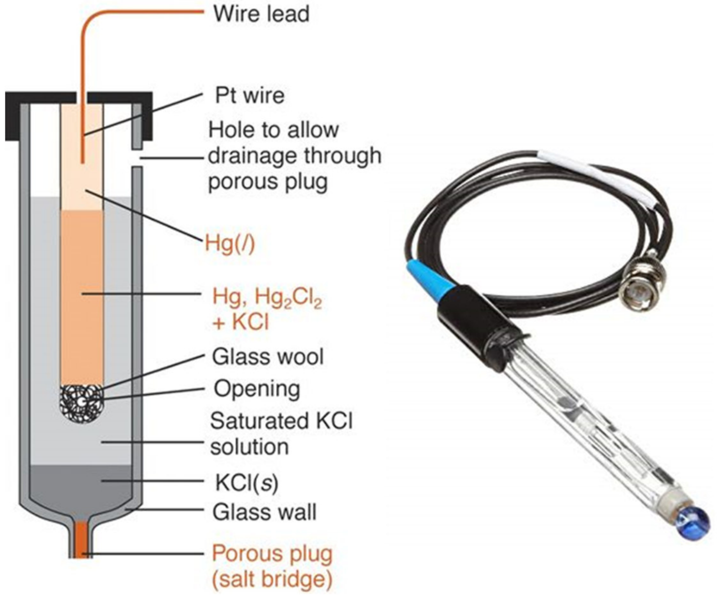


Fig. 2-16.Calomel reference electrode.

2.8.2 Silver-silver chloridereference electrode

This reference electrode is used under both laboratory and field conditions. Silver is the metal; the silver is coated with silver chloride. In the “wet type” of silver chloride, a solution of potassium chloride is used as the electrolyte and the potential of the reference electrode is dependent on the concentration of potassium chloride. Either a normal or saturated solution is commonly used. The electrolyte in the reference electrode and the electrolyte within which the electrode to be immersed are brought into contact through a porous glass disk or a capillary tube.Figure 2-17.

In the “dry type” of silver-silver chloride reference electrode, the silver chloride-coated silver is directly immersed in the electrolyte contains the electrode to be measured. This type of reference electrode is most commonly used in seawater, where the concentration of chloride (the important ion with regard to the potential difference of the electrode) is reasonably constant. The dry type of silver chloride reference electrode is particulary rugged and is widely used to measure the potentials of metals in sea water.

2.8.3 Copper-copper sulfate reference electrode

The copper-copper sulfate reference electrode is very widely used as a reference electrode for measuring potentials in soils and fresh water. It consists of a copper metal wire or rod immersed in a saturated solution if copper sulfate. Contact between the copper sulfate electrolyte and the external electrolyte is made through a porous plug, usually made of ceramic or wood. The copper-copper sulfate reference electrode is particularly rugged and inexpensive.

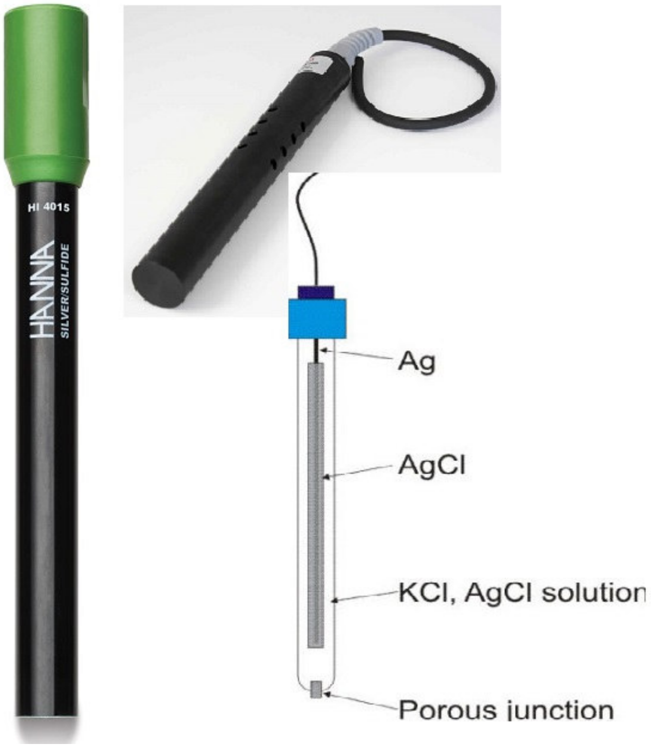


Fig. 2-17.Silver-silver chloride reference electrode.

When measuring the potential it is important to know and record the type of reference electrode that is used. In the slide (fig. 2-15), the potential of zinc is being measured using a copper-copper sulfate reference electrode. In this case, the zinc is connected to the common (negative) terminal. The positive reading on the voltammeter indicates that the potential of zinc is more negative than that of the copper-copper sulfate electrode by 1.029 V.

The potential should be reported as (-1.029 V) with respect to copper-copper sulfate reference. This is usually recorded as -1.029 V vs Cu/$CuSO_4$.

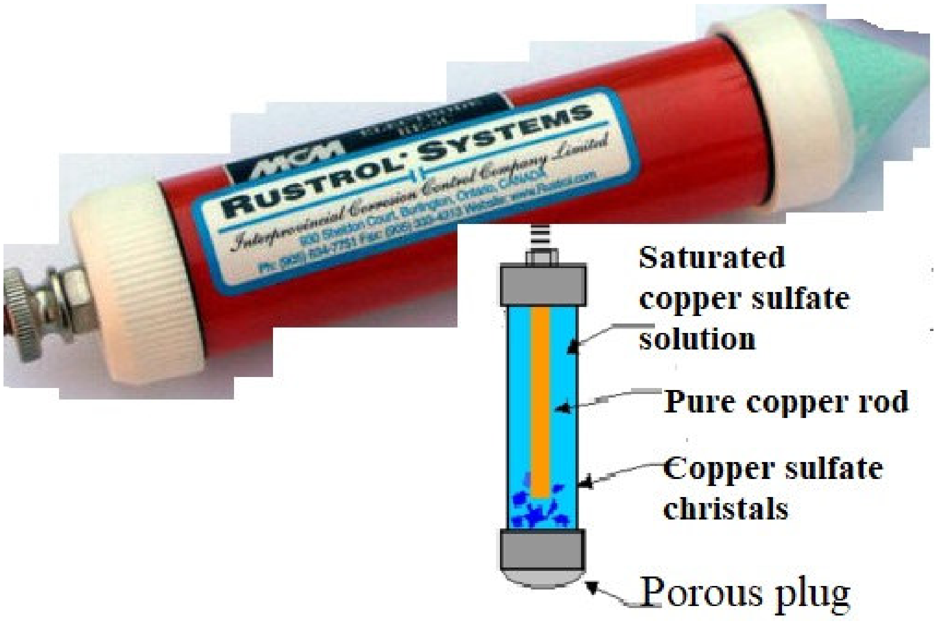


Fig. 2-18.Copper-copper sulfate reference electrode.

2.8.4 Comparison of Reference Electrode's Potentials.

The potential of the following reference electrodes are measures with respect to the hydrogen reference electrode under laboratory conditions. The potentials are as follows:

Reference Electrode	Potential (Volts)
Calomel (0.1) Molar	+0.3337
Calomel (1.0) Molar	+0.2800
Copper-Copper sulfate	+0.3160
Silver-Silver Chloride (dry in seawater)	+0.25
Calomel (Saturated)	+0.2415
Silver-Silver Chloride (Saturated)	+0.2250
Silver-Silver Chloride (Molar)	+0.2222
Hydrogen	0.0000

Table.2-5. Comparison of potential measured using different reference electrodes.

To compare reference electrodes to each other, simply subtract the potential of one reference electrode from that of the other to obtain the difference between them. For example, the potential difference between a dry-type silver-silver chloride reference electrode in seawater and a copper-copper sulfate reference electrode will be:

0.3160 V - 0.2500 V = 0.0660 V

The copper-copper sulfate reference electrode is more positive than the dry-type silver-silver chloride electrode in seawater by 0.066 V.

For example the potential of an electrode (metal pipe) immersed in an electrolyte (moist earth) measured using one reference electrode can be related to the potential of that same combination measured using any other electrode.

In this case, the potential of the metal would be -0.850 V if measured using a copper-copper sulfate reference electrode and, all would be – 0.784 V if measured using a saturated calomel reference electrode.

2.9 The Galvanic Series

The galvanic series is a listing of metals in order of their potentials in one specific environment. Other definition is "the galvanic series lists metals in the order of their nobility". (Noble metals are those that are resistant to corrosion and oxidation). The galvanic series is similar to, but significantly different from, the electromotive potential series, as we shall see later in this chapter. The galvanic series may be different for different environments. The most commonly seen galvanic series is for metals in seawater. A short galvanic series of metals in seawater is given in figure 2-19.

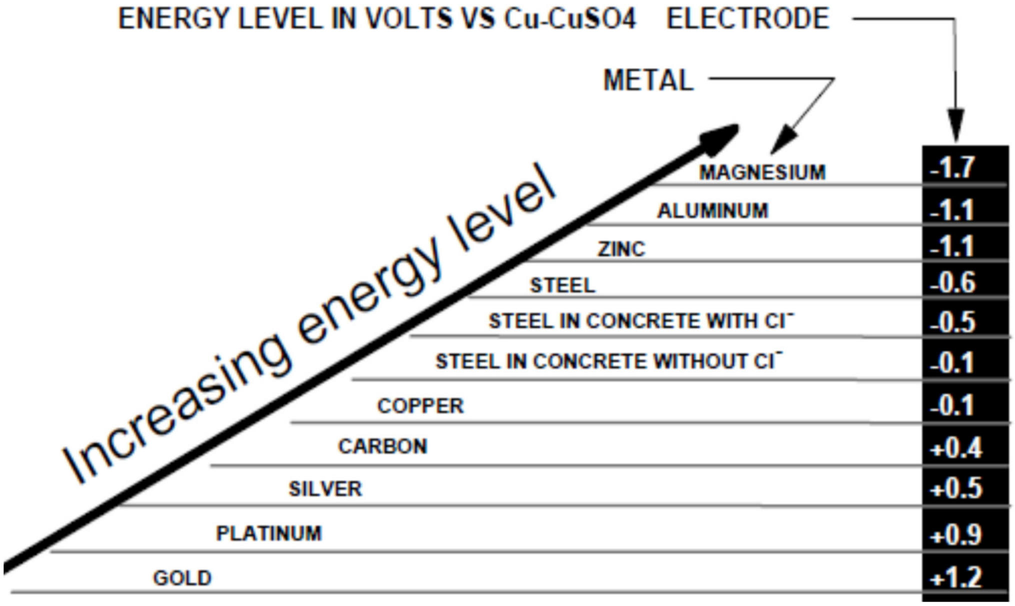


Fig. 2-19. Galvanic series of some metals.

The galvanic series is very useful for determining the interaction between metals when they are coupled together. More information about the galvanic series will be given later in this book.
There is a general tendency for the active metals to corrode more rapidly than the metals that are less active, but this is only general trend and there are many exceptions. The galvanic series only considers corrosion potential. Many other factors affect actual corrosion rate.

2.10 Nernst Equation

The Nernst equation is an electrochemical equation that relates the potential of pure metals in solutions containing various concentration of ions. The Nernst equation is:

$$E = E^{\circ} - \frac{RT}{nF} \times \ln \left(\frac{(\text{reaction products})}{(\text{reactants})} \right)$$

Eqn. 2-1

Where
E = actual reaction potential
E^0 = potential under standard conditions (all activities =1)
R = Gas constant
T = Temperature (Kelvin)
n = number of electron transferred in the reaction
F = Faraday’s constant (96,500 coul/mol)
In = natural logarithm
Activity = 1 for metals in their metallic state, and 1 for ions in M concentration (I mol w/L) roughly equal to the concentration of ions (in terms of molar concentration) in dilute solutions.

Using a temperature 72^0 F; using the actual values of constants R, T, and F; and converting from natural logarithms to normal base 10 logarithms, the Nernst equation becomes:

$$E = E^{\circ} - \frac{0.059}{n} \times \log \left(\frac{(\text{reaction products})}{(\text{reactants})} \right)$$

Eqn. 2-2

The Nernst equation applies to many corrosion reactions and to the potentials of reference electrodes. For example, if the potential of the reaction $Fe^0 \rightarrow Fe^{++} + 2e^-$ is reported in volts (versus a hydrogen electrode) when the activity of Fe^{++} ion is 1 (1 mol/L = 55.85 g/L) [this is an activity of 1 for the Fe^{++} ion], then E^0 is -0.44 V. The concentration of Fe^{++} is then changed and the resulted potential can be calculated. Say that the new concentration of Fe^{++} is reduced to 0.1 M (activity of 0.1); the new potential (E) is:

$$E = -0.44\text{ V} - (0.059/2)\ \text{Log}\ (0.1/1) = -0.410\text{ V}$$

The Nernst equation explains the difference between the potentials of the calomel reference electrodes with different concentrations of potassium chloride. The calomel reference electrode with a potassium chloride concentration of 1 M cell has the standard potential E^0. When the concentration of potassium chloride is changed, the potential of the reference electrode changes. For example, when a calomel reference electrode has a potassium chloride concentration of 0.1 M, the Nernst equation can be used to compare the potential of this reference electrode to the standard one, potassium chloride concentration of 1 M. Note that in the reaction in the calomel reference electrode, only one electron is transferred.

$$E = +0.2800\text{ V} - (0.059/1)\ \text{Log}\ (0.1/1) = +0.3390\text{ V}$$

The small difference (0.0053 V) in the calculated potential (0.3390 V) and the potential previously given in table for the 0.1 N calomel reference electrode (0.3337 V) is due to the use of the concentration of potassium chloride rather than its activity.

2.10.1 EMF Series

The electromotive force series (emf) is similar to the galvanic series in that it lists metal oxidation potentials in order of their potential. However, the galvanic series lists the metals in the order of their potentials in a single environment. The emf series lists the metals in order of their potentials in solutions of standard (1 M) ions concentrations. The emf series is also called the standard oxidation-reduction (redox) series. These are the E^0 potentials for pure metals in solutions of their ions with an activity of 1.The emf series can be used to determine whether, or not a metal will corrode in a given environment. A metal with a more negative emf will tend to be oxidized and a metal with a more positive emf will tend to be reduced. In the case of zinc in water (water reacts at the hydrogen potential), the zinc has a more negative potential than the hydrogen and will tend to corrode. In the case of copper in water, the copper has a more positive emf than hydrogen and will tend to be stable.

It is important to remember that the emf series is for pure metals in solutions of standard activity; reactions of impure materials in other solutions will be different.

2.12 Pourbaix diagrams

Pourbaix diagrams are used to predict the stability of metals and corrosion products in environments of varying pH. pH is the relative acidity or alkalinity of solution. A pH of 7 is neutral, a pH lower than 7 is acidic, and a pH greater than 7 is alkaline. pH will be discussed in more details later in this book.

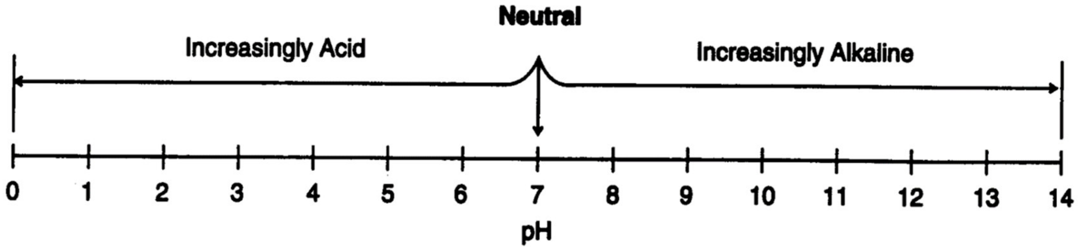


Fig. 2-20. pH scale.

A Pourbaix diagram for iron is given in figure 2-21. Areas where the metal (Fe in this case) is shown indicates stability of iron under this conditions of pH and potential. Where area in which ions are stable (Fe^{+2} and Fe^{+3}, in this case), iron may be expected to corrode readily.

Under conditions where corrosion products form (in this case $Fe(OH)_2$, $Fe(OH)_3$, and $H(FeO_2)^-$ reactions to form these compounds or ions are possible, but in some cases, the corrosion products can completely cover the metal cases and inhibit further corrosion.

Pourbaix diagrams are very useful for predicting whether, or not corrosion can occur under certain conditions of pH and potential, for estimating the corrosion product composition, and for predicting what changes in pH and potential can increase, reduce, or eliminate corrosion.

2.13 Kinetics

Kinetics is the study of speed. Applies to corrosion, Kinetics determines the rates of the chemical processes responsible for corrosion. As current (actually, electron) flow is fairly easy to measure, we normally measure the rate of the electrochemical reactions responsible for corrosion by measuring the rate of current flow. The amount of current flowing is can be used to determine the corrosion rate; the total amount of current flowing over a period of time can be used to calculate the amount of material lost.

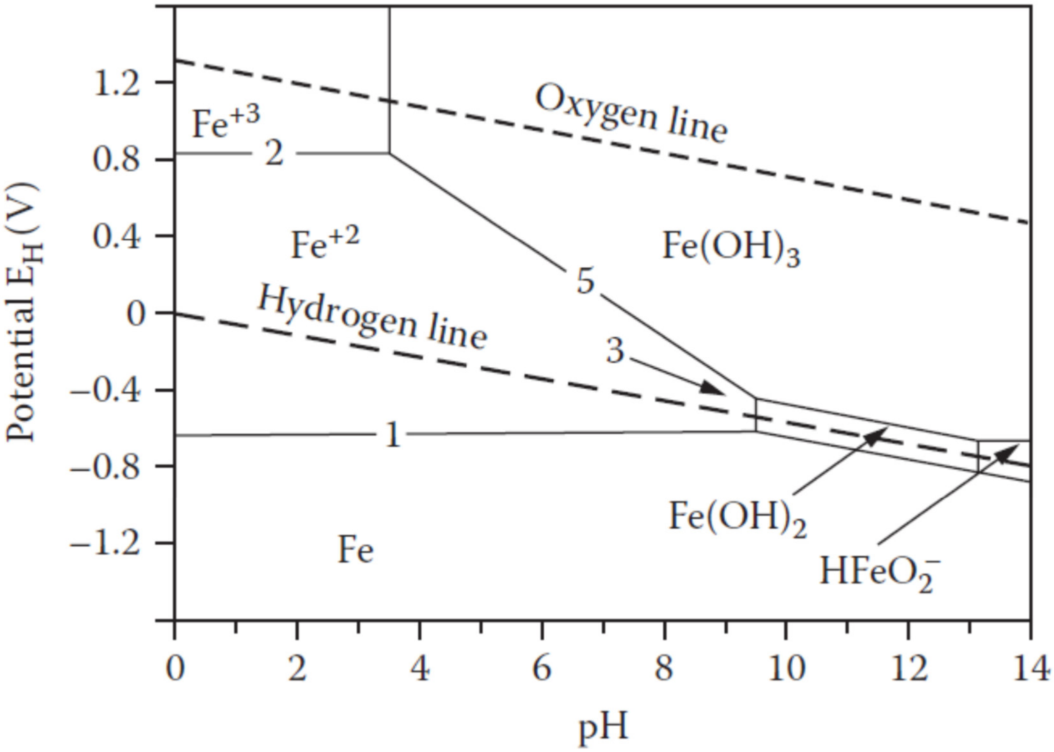


Fig. 2-21. Pourbaix diagram for iron

2.13.1 Faraday's Law

Faraday's law gives the relationship between the flow of current and the amount of material corroded.

$$W = MtI/nF \qquad \text{Eqn. 2-3}$$

Where

W = weight of material reacted, gm.

M = atomic weight of material reacted

t = time in seconds

I = current flow in amperes

n = number of electrons exchanged

F = Faraday's constant = 96,500 coulombs (Ampere. Second).

For example, say that a current flow of 1A flows in a corrosion cell for a period of one year. If the anode in the cell is iron and is reacting to form Fe^{++}, what is the weight loss of iron reacted?

Solution:

W = MtI/nF

W = (55.58 x 60x60x24x365x1) / (2x96500) = 9.1 Kg

2.13.2 E Log I Curves (Evans Diagrams)

Evans diagram are useful for showing how electrochemical cells function. In an Evans diagram, the potential is typically plotted on the vertical axis and the logarithm of the current flow is plotted on the horizontal axis. The Evans diagram shows the effect of polarization on corrosion behavior.

Polarization is the change in potential on a metal surface due to current flow. Both anode and cathode in a corrosion cell are subjected to polarization of varying degrees. The polarization behaviors of anodes and cathodes in a corrosion cell greatly affect the corrosion rate at anode. In an Evans diagram, points on the vertical axes, as shown in figure 2-22 represent the open-circuit (uncoupled) potentials of the anode and the cathode.

As current is allowed to flow from the anode, the potential of the anode changes with increased current, as shown in figure 2-23.

Note that the potential of the anode becomes less negative with current flow.

Since current also flows from the cathode, the cathode also polarizes with increasing current, as shown in figure 2-24.

When both the anodic and cathodic polarization are shown on the same Evans diagram, the corrosion current flowing in the cell can be determined as shown in figure 2-25.

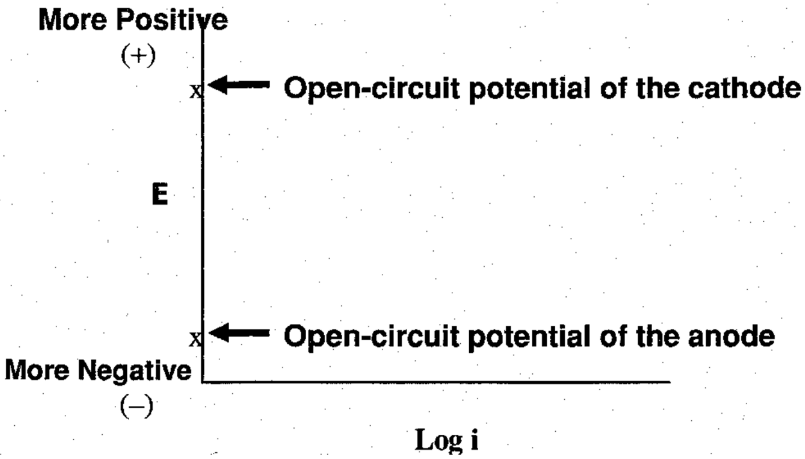


Fig. 2-22. Open circuit potential (Evans diagram)

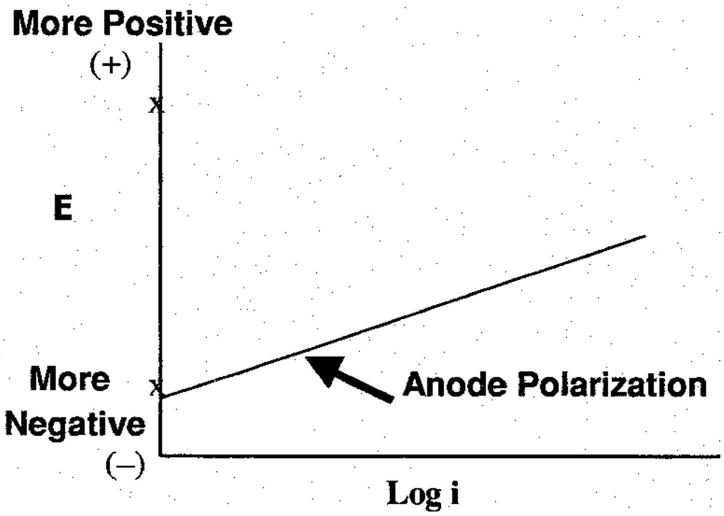


Fig. 2-23. Anode polarization

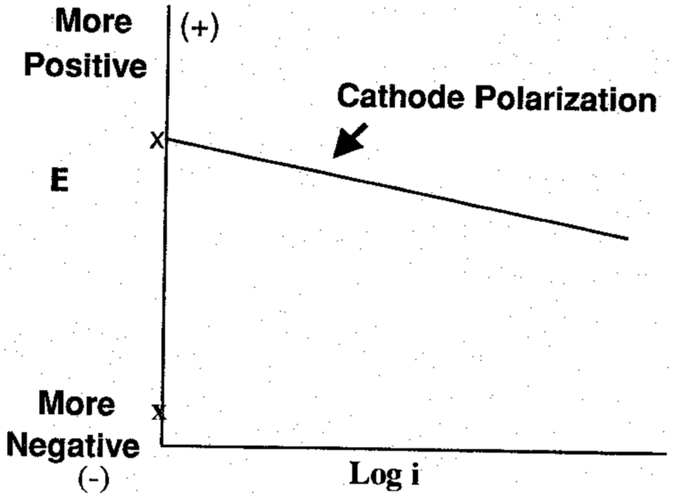


Fig. 2-24. Cathode polarization

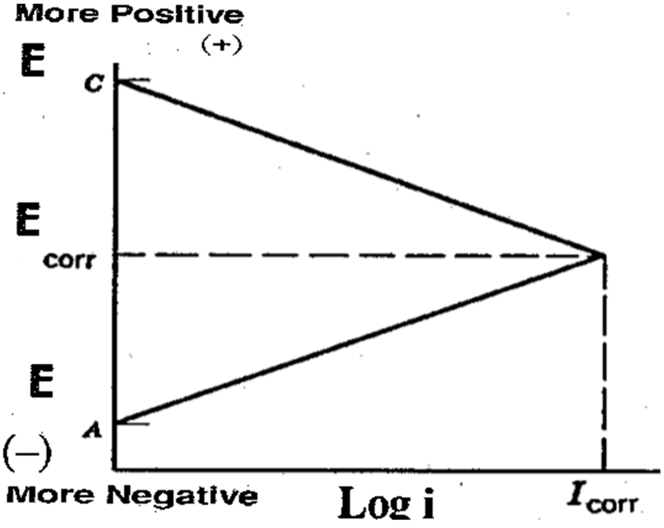


Fig. 2-25. Anodic and cathodic polarization

Evans diagram is used to show the effects of changes in the characteristics of the anode and cathode polarization on corrosion current.

2.13.3 Area Effects

In corrosion reactions, the current density, measured in units of current per unit area, such as milliamps per square centimeter, are used because current density rather than total current determines the intensity of an electrochemical reaction on surface. For the same total amount of current the effect of an electrochemical reaction will have less intense effect on large electrode than on a small one. The total amount of reaction will be the same in both cases, but in case of the small electrode, the effect is concentrated over a smaller area. The effect of current density can be shown using an Evans diagram. In figure 2-25, polarization of a cell with equal anodic and cathodic area is shown.

If the area of the cathode is reduced, the current will be more intense in the surface of the cathode and its polarization will increase as shown in figure 2-26.

In this example, the increased polarization of the cathode significantly decreases the corrosion current. As the area of the anode remains unchanged, the corrosion current is spread over the same anode area. The total amount of metal reacted and the corrosion at any point are reduced.

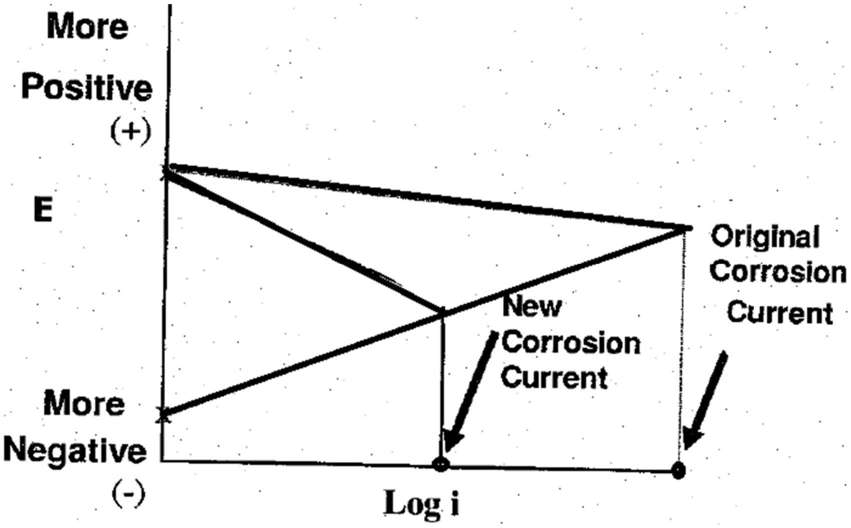


Fig. 2-26. Reduction of cathodic area (cathodic control)

If, however, the area of the anode is reduced while the area of the cathode remains the same, a different effect is found. As shown in figure 2-27, the total current flow is reduced but the current is now concentrated on a smaller anode. Even though less total material is lost, the loss is concentrated on a smaller anode and the intensity of corrosion can actually increase.

The effect of area ratio will be covered in more detail in the section of Galvanic Corrosion and other portions of this book.

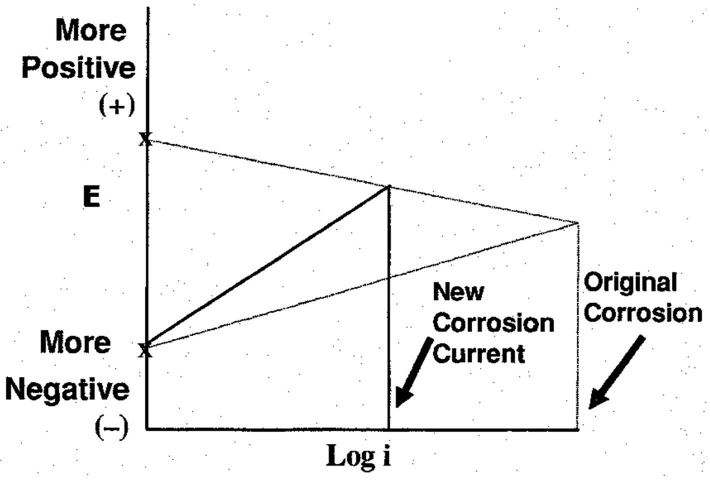


Fig. 2-27. Reduction of anodic area (anodic control)

2.14 Electrochemical Cells

When there is a difference in potential between two electrodes in an electrochemical cell, and the electrodes are electrically connected and exposed to an electrolyte, corrosion can occur.

2.14.1 Galvanic Corrosion

When the potential difference is created by a difference in the chemical compositions of the electrodes, the resulting corrosion is called galvanic corrosion.

2.14.2 Concentration Cell Corrosion

When the potential difference is created by a difference in environment between different areas on the same metal, the resulting corrosion is called concentration cell corrosion, Crevices, either metal-to-metal or metal-to-nonmetal, that allow the electrolyte to enter the crevice but impede the circulation of the electrolyte can cause the difference in concentration responsible for concentration cell corrosion. The details of concentration cell corrosion will be covered later in this book.

2.14.3 Active/Passive Cells

When a portion of the surface of a metal is covered with a film of corrosion products that inhibits corrosion, the potential difference between the portion of the metal covered with the film and the portion of the metal that is not covered can create a corrosion cell. In most cases, the area covered by the corrosion products is cathodic with respect to the uncovered areas. The active position represents the uncovered material and the passive position is that of the covered material. In this case, the potential difference is larg and the concentration cell may be very active. This large potential can cause very rapid localized attack if the anode to cathode area area ratio is small (small anode/large cathode). This will be discussed in more details in pitting corrosion.

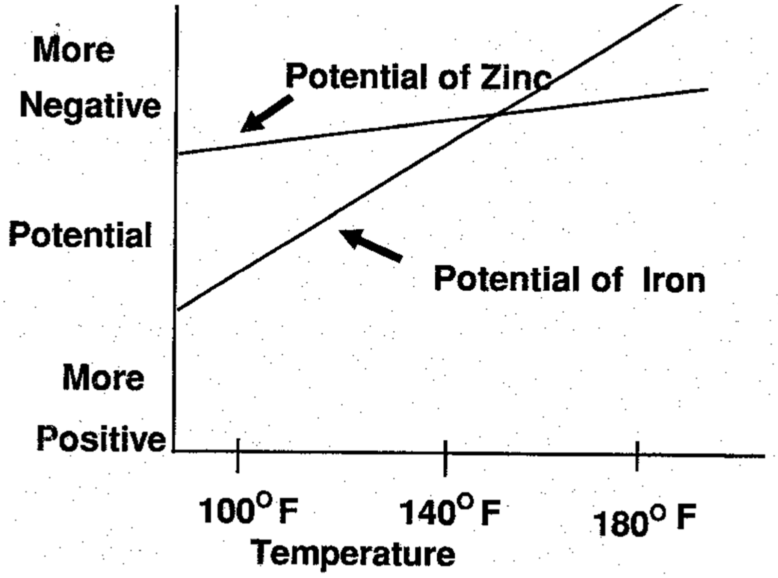


Fig. 2-28. Change of metal potential with temperature

2.14.4 Thermogalvanic Corrosion

Temperature can affect the corrosion potentials of metals. In most cases, a metal exposed to a higher temperature will have more active (negative) potential than the same metal at lower temperature. Thus, the metal at a higher temperature will become the anode if it is electrically connected to the same metal at lower temperature. One result of this effect is the thermogalvanic corrosion between hot and cold domestic copper water pipes when both are buried in the soil under a house, or buried in the concrete slab foundation. In this case, the external surfaces of the hot-water pipes can corrode because of the difference in potential.
Different metals show different degrees of change of potential with temperature. In some potable waters, the potential of the iron becomes more negative than the potential of the zinc, and galvanized (zinc-coated) steel hot-water tank do not perform well. This is shown in figure 2-28.
Where at lower temperature, the iron is the cathode and the zinc corrodes preferentially, as intended. In hotter waters, the situation reverses and the iron corrodes preferentially, causing rust contaminated "red" water and rapid corrosion of the tank wall.

2.15 Passivity

Passivity is the reduction of chemical reactivity of a metal or alloy under certain circumstances. In some cases, film formation occurs naturally in air and can provide a very substantial reduction in the corrosion of these materials. Aluminum, whith its very active position in the galvanic and emf series, is expected to corrode rapidly. Because of the presence of a thin, tightly adherent film of aluminum oxide That forms on the aluminum upon exposure to air, aluminum alloys have good resistance to corrosion in many environments where the oxide film responsible for their passivity is stable. In some cases such as in stainless steels, active metals, such as chromium are added to iron . The active chromium helps to form the tightly adherent film responsible for the corrosion resistance of stainless steels in many environments. The addition of other elements , such as nickel and molybdenum, to the chromium-iron alloys further improves the stability of this passive film and improves corrosion resistance in a wide variety of environments.

An increase in the oxidizing strength of the environment can also improve the stability of the passive films on some materials. This may occur when a strong oxidizing agent, such as nitric acid, is present in moderate quantities. The effect of oxidizing agent increases the stability of the passive film and reduces the corrosion rates substantially. When the oxidizing strength of the electrolyte is increased too much in some alloys, the passive film is no longer stable and the corrosion rate increases. This phenomena is called transpassive behaviour. The behaviour of a passive metal with respect to the increasing oxidizing power of the electrolyte is shown in figure 2-29.

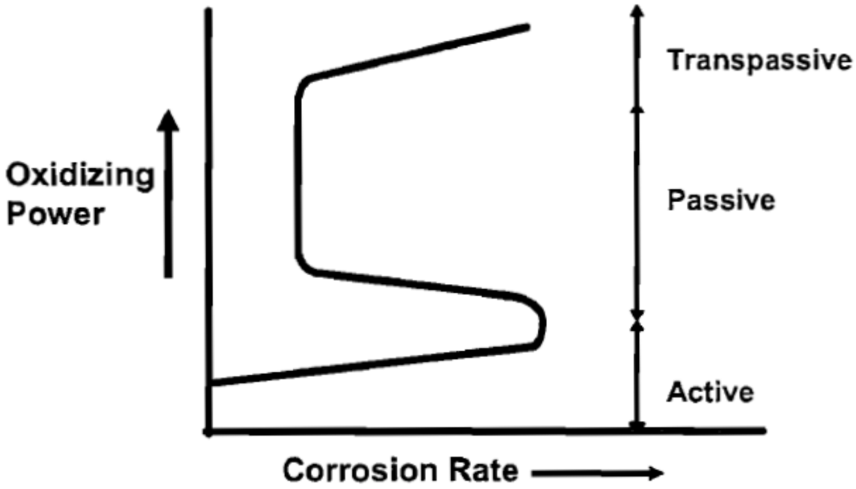


Fig. 2-29. Passivity

A similar effect can be produced for some metals in certain environments if a current is applied to a metal surface to make it more negative. This has the same effect as increasing the oxidizing power of the electrolyte. If the potential is maintained so that the metal remains in the passive range, corrosion can be reduced to very low levels. This is the basic principles of anodic protection, which will be discussed later.

Chapter 3

Environments

3.1 Introduction

Corrosion is the interaction between a material and the environment to which it is exposed. Understanding the environment and the factors that affect corrosion are important in understanding corrosion. Understanding the environment helps us determine what factors contribute to corrosion activity and often leads to the identification of appropriate methods for corrosion control.

Corrosion environments typically are classified into four major types:

- Atmospheric
- Underground
- Liquid
- High temperature

The means of classification is arbitrary but has been developed by corrosion engineers over the years. Each environment has characteristics that can vary considerably with time and can affect the corrosion of material in many different ways.

In some cases, the materials of interest may be exposed to more than one type of environment. For example, the part of a small boat that are below the water line must be resistance to both atmospheric and immersion environments if the boat is to be brought ashore for transportation or storage.

3.2 Atmospheric

Natural atmospheric exposures are classified into four type for purposes of understanding their effect on corrosion. It is assumed that all these atmospheres are primarily composed of a mixture of oxygen (about 20%) and nitrogen (about 78%). While the oxygen present in natural atmospheres is important in atmospheric corrosion, it remains fairly constant as far as corrosion reactions go. It is the other materials in the atmosphere that vary considerably and that must be identified properly to understand atmospheric corrosion.

These materials include solids, liquids, and gases.

Solids

An example of solids that affect atmospheric corrosion is the salt present in most marine environments. It can be carried far inland, creating a marine-type environment several miles from the sea.

Liquid

The best example of a liquid that affects corrosion is water. As we shalll see, corrosion occurs at a much higher rate when surfaces are moist than when they are free of liquid water. Not only is the amount of rainfall, but its distribution with time and the time required for drying are also important. Moistures may also be benificial by removing corrosive contaminants from surfaces. While rain is fairly effective in this cleaning, fog or dew are less effective, because they increase the time of witness. Moisture from either rain or dew can accumulate in crevices or other areas that trap and hold water. This creates wet conditions for very long periods, perhaps even continuously. The effects of fog and dew are controlled by the relative humidity of the environment. Relative humidity is a measure of the actual moisture content of the atmosphere compared to the maximum amount of water vapor that can be held at a specific temperature. Temperature changes relative to time are also important in evaluating the effects of fog and dew. A heated surface may remain dry even though the temperature of the ambient air falls below that of the dew point. Moistures will begin to collect on surfaces at or below the dew point of ambient air. If the temperature of the surface is below that of the ambient air, as in case of building during early morning, the surfaces may remain below the dew point and continue to collect and hold moisture for long periods even after the ambient air is above the dew point. With steel, the effects of relative humidity usually predominate over the effects of temperature in atmospheric environments.

Gases

Gasses that can affect corrosion include nitrogen and sulfur oxides, which are present in the corrosive acid rain that has become part of our industrialized society. These gases can also dissolve in dew and fog to create more aggressive conditions than the acid rain, as they tend to remain on surfaces and concentrate rather than become more dilute through rinsing action.

Temperature

Temperature affects corrosion in the atmosphere. Although corrosion rates normally increase with increasing temperature, higher temperature can have a benificial effect in promoting surface drying, thus decreasing the time of wetness . In the case of steel corrosion, the benificial effects of elevated temperatures in reducing time of wetness usually prevail over the potentially adverse effects of increased temperature.

3.3 Types of atmosphere

3.3.1 Industrial Atmospheres

Industrial atmospheres are characterized by high levels of such corrosive gases as sulfur dioxide, oxides of nitrogen, and carbon monoxide, which can create a severely corrosive environment. Many of these gases are soluble of water and when combined with water in natural environment cause the water to become acidic. Soot and other solids are also prevalent in industerial atmospheres. These solids may be corrosive by themselves, or may simply coat surfaces with a layer of material that can hold water and keep the surfaces wet for longer periods than would otherwise be the case.

3.3.2 Marine Atmospheres

Marine atmospheres are characterizer by high levels of chlorides and other salts from the sea. These salts are dissolved in sea spry and may be carried many miles inland by winds. While ordinary table salt (sodium chloride) is the primary constituent of sea salt by weight, other salts have important corrosive effects. Some of the compounds in sea salts, such as magnesium chloride, are hygroscopic. Hygroscopic materials tend to absorb water vapor and tend to release the water only during conditions of very low relative humidity. Surface contaminated with sea slats will remain wet much longer than uncontaminated surfaces.

The chloride in sea salt are particularly aggressive towards many materials. Some aluminum alloys and stainless steels, usually corrosion resistant in most atmospheres, are often attacked by the high chloride content in marine atmospheres. These chlorides are also particularly aggressive because metal chlorides tend to be soluble. Chloride-containing corrosion products do not form the protective films of insoluble corrosion products.

Many industrial areas are located near the sea; the aggressiveness of the combination of industrial and marine environments is usually higher than either would be alone.

3.3.3 Rural Atmospheres

Rural atmospheres do not contain the strong chemicals found in industrial atmospheres or the sea salt that characterize marine atmospheres. They can, however, contain aggressive dusts and gases. The dusts may be either organic or inorganic.

A wide variety of inorganic chemicals are used in farming activities. These include fertilizers, soil amendments, herbicides, insecticides, and fungicides.

Many of these chemicals are corrosive and some are hygroscopic.

Organic materials include manure and crop residue. Manure is usually acidic. Coating of any of these dusts will increase the time of wetness of surfaces. Amonia, either from manure or from fertilizers, can also be aggressive. Copper alloys are particularly susceptible to corrosion by amonia compounds.

Arid atmospheres can also be rural. In arid environments, there is little rainfall, but in some locations the relative humidity can be high and condensation can occur. High ambient temperature, intense sunlight, and wind-driven sand are common in arid atmospheres and can be significant factors in the corrosion of materials.

3.3.4 Tropical Atmospheres

Tropical atmospheres are characterized by high relative humidity and intense sunlight. There are long periods during the night when condensation occurs. In sheltered area, these condensation may persist for long periods, even continuously. In addition, living organisms such as fungi and lichens can grow on surfaces and these organisms, in addition to prolonging time of wetness, can excrete corrosive materials.

3.3.5 Indoor Atmospheres

Indoor atmospheres are unique in that they can be controlled. Aggressive solids can be removed by filteration. Aggressive gases can be removed by entrainment in water sprays. Temperature and relative humidity can be controlled. Indoor environments are usually not aggressive and this may be an important factor in design of equipment intended for indoor use. Consideration, however, must be given to the aggressiveness of the environments that will be encountered during shipment and storage before the controlled indoor environment is achieved. Thus, cossosiveness encountered during shipment and storage often mandates the corrosion control equipment.

3.4 Underground

The corrosiveness of underground environments has a very wide range. The underground environment will be described in terms of soil characteristics. In this book, soil will be considered any solid material covering a structure and may consists of sand, silt, clay, loam, rocks, or a mixture of these components.

The corrisveness depends upon the chemical characteristics of the soil, its moisture content, its electrical resistivity, the amount of aeration, and the presence (or absence) of bacteria.

An important factor in soil corrosivity is that the environment can vary greatly over both larg and small distances. Underground environments can also vary with time. In some locations, seasonal variations can be significant. Year-round soil conditions must be considered during the design of underground structures.

Where an underground structure contacts a rock, the local area between the rock and the structure has significantly different characteristics from the surrounding surface in contact with finer-grained material. Most buried structures are buried in distributed soil and the control, or lack of control of the backfilling can have a great effect on the corrosiveness of the underground environment. As we have learned, corrosion thrives on differences. The more uniform environment, the less aggressive it will be.

3.4.1 Physical Soil Characteristics

The physical characteristics of soils affecting corrosion are primarily related to grain size and distribution, and moisture retention and aeration. In a soil that contains an uneven distribution of particle sizes or larg rocks, differential environment corrosion cells can be created. Soils with otherwise benign characteristics can become very corrosive.

3.4.2 Chemical Soil Characteristics

Soils have a wide variety of chemical characteristics. Important chemical characteristics include pH (acidity or alkalinity) and the presence of water-soluble salts. pH has a great effect on corrosion of many material; however, the effect is not uniform. Moderate alkalinity (high pH, 8- 10) is not aggressive toward steel but may be very aggressive toward aluminum.

Salts, in the presence of moisture, have two effects. One is to provide corrosive ions that can directly enter into corrosion reactions or affect the formation of protective films on the surface of the buried structure. The second is to increase the electrical conductivity of the soil. Chlorides and sulfates are particularly harmful through their direct chemical interactions. Any dissolved salt will increase the electrical conductivity of the soil, this effect on the corrosiveness of the soil will be discussed later in this chapter.

3.4.3 Moisture Content

The moisture content of soils can vary from 1% to 2% (or less in arid environments) to saturated conditios in swamps, or locations below the water table. Moistures provides the electrolyte necessary fo corrosion, and affects soil conductivity. In arid locations, the soil environment can be essentially atmospheric in that there is insufficient moisture to provide wetness of the buried surface. In most soils; however, there is sufficient moisture to provide surface wetness most of time.

3.4.4 Electrical Resistivity

Electrical resistivity generally correlates with the aggressiveness of soils. Electrical resistivity is different from electrical resistance: resistivity is a material property, whereas resistance depends on the electrical resistivity of the material along with the length and cross-sectional area of the material that is carrying current. Electrical resistivity is also an indirect measurements of two other important soil characteristics which are moisture content and disolved salt levels. The lower the resistivity, the higher the conductivity.
Resistivity is commonly measures in ohm-centimeters (Ω-cm) and is represented by the Greek leter rho (ρ).
Conductivity is a reciprocal of resistivity and is usually represented by the Greek letter kappa (k)

$$K = 1 / \rho \qquad \text{Eqn. 3-1}$$

The units of conductivity are most commonly given as micromhos (mho is ohm backwards!) per centimeter. Most corrosion engineers use resistivity (Ω-cm) when describing the electrical properties of environments. Soil resistivity is affected by other factors, such as compaction and soil type. Soil resistivity, like soil moisture content, can vary considerably with time. Seasonal variations in soil resistivity must be taken into account in the design of underground structures.
Lower soil resistivity allows a high corrosion current, with attendant high corrosion rates. Soil resistivity is also an important factor to be considered in the application of cathodic protection to control underground corrosion.

3.4.5 Aeration

The amount of oxygen available in soil affects the corrosion rate of many materials. Most commonly, more aeration increases corrosion rate of steels. However, low aeration can cause accelerated attack of some materials, such as stainless steels. When there is no free oxygen (anaerobic conditions), soils can become very aggressive through the action of anaerobic bacteria. This aspect is discussed below.

3.4.6 Bacteria

Bacteria are present in most soils. Most bacteris that live under aerobic conditions (good aeration) do not cause accelerated corrosion. However, bacteria that live under anaerobic conditions can produce chemical by-products that greatly affect corrosion, and some can even act as cathodic depolarizers, directly entering corrosion process. One particularly aggressive type of soil bacteria is the sulfate-reducing bacteria (SRB), which produce sulfides as waste products. When there are active, the sulfides they produce can cause very rapid corrosion to steel.

3-5 Liquids

Immersion in liquids presents a wide variety of corrosive environments. The liquids can either be naturally occuring waters, treated waters, or harsh chemical process fluids. Water is considered to be common constituent in some corrosive envronmentts. Such liquids are designated aqueous fluids. Nonaqueous liquids, such as alcohols, ketones, ets., can cause deterioration of other materials, such as plastics or elastomers.
The external surface of a system can be exposed to immersion in natural liquid environments. The submerged hulls of ships and submarines are examples of such exposures. The liquid in this case is sea water, fresh water, or a combination of the two, which is called brackish water. Sea water, with its high content of corrosive salts and low resistivity, can be particularly corrosive. Biological activity in seawater, both large fouling organisms that accumulate on surfaces exposed for extended periods and microscopic organisms that quickly form a thin layer of slim on surface immersed in sea water, affect the corrosion.
Process liquids can vary from relatively noncorrosive demineralized water to strongly aggressive chemical mixtures in a chemical plant. In closed systems, some process liquids can be deareated to control corrosion. Further control of corrosion in process liquids is possible through careful control of the liquid composition and temperature. In addition the intentional addition of chemicals (inhibitors) can be used to control corrosion.

3.5.1 pH

One factor in corrosivity of liquid is pH. Pure water is very slightly ionized by the breakdown of a few of the water molecules to form hydrogen ions (H^+) and hydroxyl ions (OH^-) through the reaction.

$$H2O \rightarrow H^+ + OH^-$$

Very little of the water breaks down in this manner. In fact, only 1 in 10,000,000 water molecule are broken down. Scientists use the notation 10^{-7} to represent this small number. Since there are equal number of H^+ and OH^- ions in pure water, each has a concentration of 10^{-7} .

pH is the negative of the concentration of H^+ expressed as a power of 10. Thus, pure water with a hydrogen ion concentration of 10^{-7} has a pH of 7.0 . This is considered neutral. Another important fact about pH is that the total concentration of H^+ and OH^- ions in a water based solution is alwayes 10^{-14}, Acid solutions contain a greater concentration of hydrogen ions (H^+) than neutral solutions and alkaline solutions contain a greater concentration of hydroxyl ions (OH^-) than neutral solutions.

In acid solution with a concentration of hydrogen ions of 10^{-4} (note that the smaller negative number for the power of 10 represents a larger number of hydrogen ions), the pH will be 4.0. For an alkaline solution with a concentration of hydroxel ions of 10^{-4}, the total concentration of hydrogen and hydrogen ions will still be 10^{-14}, so the concentration of hydrogen would be 10^{-10}. The pH of this solution will be 10.

It is important to remember that a change of one pH unit, changes the concentration of both hydrogen ions and hydroxyl ions by a factor of 10. Seemingly small changes in pH can have very significant effect on corrosion.

As a rule of thump, Corrosion rate of steel increases at lower pH. (Acidic solutions, pH 6 and lower). Strong alkaline solutions prevent corrosion (pH 10 and higher)

While Zinc and Aluminium, have low corrosion rate at close to neutral solutions, and high corrosion rate in both acidic and alkaline solutions. Figure 3-1.

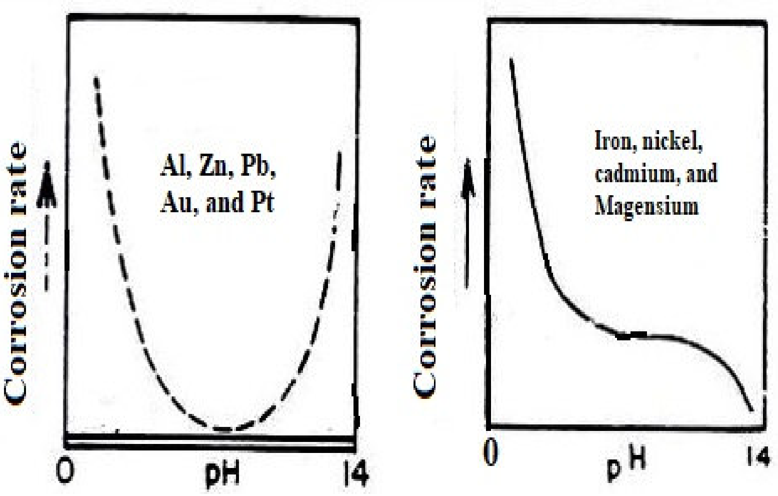


Fig. 3-1. Effect of pH on corrosion rate.

Other factors that have significant effects on the internal surfaces of systems carrying or storing liquids are the physical configuration of the system, the chemical makeup of the liquids, the flow rate of the liquid, the presence of solids in the system, the temperature of the liquid, the pressure of the liquid, and the presence of biological organisms.

3.5.2 Physical Configuration of The System

The physical configuration of the system can affect many corrosion-related factors. Surfaces may be exposed to both liquids and vapors. Tanks and vessels may or may not be designed to drain completely. The flow in the system may be either smooth or turbulent. We will discuss many of these factors relative to the interaction of corrosion and design later in this book.

3.5.3 Chemical Makeup of The Liquid

the chemical makeup of the liquid depends on the application. Dissolved substances can include dissolved gases, such as oxygen and carbon dioxide.

3.5.4 Flow Rate

As we shall discuss later in this book, flow rate can affect corrosion in two ways. Increased the availability of reactants in the corrosion process, particularly the availability of such cathodic depolarizer as oxygen. High flow rates also carry away the more soluble anodic reaction products that would otherwise build up and slow the corrosion reaction. The second way high flow rates can affect corrosion is by removing the corrosion product films necessary for the corrosion resistance of many metals in liquid environments. The corrosion of copper heat exchanger tubes at high fluid velocity is an example of the removal of protective corrosion product films. Fig. 3-2.

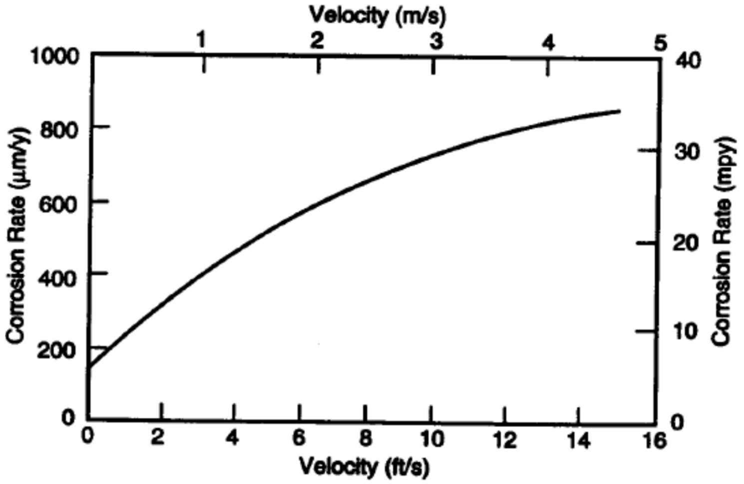


Fig.3-2. Effect of seawater velocity on the corr. rate of mild steel at ambient temp. (38 days exposed)

3.5.5 Temperature

The effect of temperature on corrosion in liquids is complex. In the largest number of cases, increasing temperature causes higher corrosion rates by increasing diffusion rates that affect the ions in the liquid as they pass through surface films. In other cases, the reduced solubility of gases with increasing temperature can reduce corrosion rates at higher temperatures. Other temperature effects can include scaling from deposition of soluble compounds that have reduced solubility at higher temperatures,or the elimination of scales that have a higher solubility at higher temperature.

In open system, increasing temperature will let CO_2 and O_2 gases to go out of solution, consequently the pH will increase, corrosion will be reduced, and scale tendency will increase. While in closed system, increasing temperature is usually wil cause increasing corrosion rate. Figure 3-3.

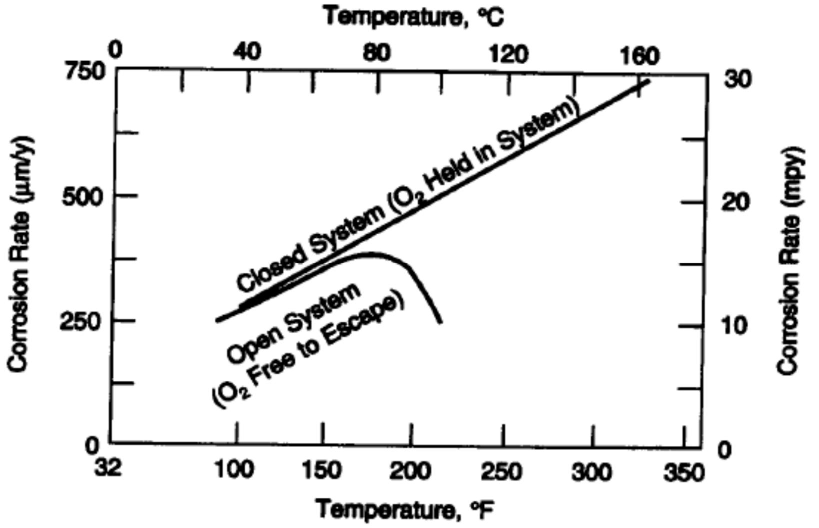


Fig. 3-3. Effect of temperature on the corrosion rate of mild steel.

3.5.6 Pressure

Pressure by itself has little direct effect on corrosion. However, pressure can increase the solubility of gases in liquids. If free gas is present in the system, more of it will go into solution at higher pressure.

The solubility of CO_2 in water, like all gases, is a function of the partial pressure of CO_2 .

Since CO_2 forms carbonic acid in water, the greater the %mole of CO_2 and line pressure, the lower pH will be, and greater corrosion rate.

Partial pressure of CO_2 = total system pressure x mole fraction of CO_2 in gas. If CO_2 Partial pressure is above 7 psi, this indicates the need for corrosion control.

For example, in a well with a bottom hole pressure of 3500 psi and a gas containing 2% mole CO_2 .

Partial pressure= total pressure x mole fraction of CO_2 in gas

= 3500 x 0.02 = 70 psi

Another example, if CO_2 = 2.4 % mole, and line pressure= 900 psi

Partial pressure= 900 x 0.024 = 21.6 psi.

Is the system considered corrosive? ….Refer to figure 3-4.

3.6 High Temperature

In this book, we will consider high temperatures to be conditions above 650 ^{0}C (1200 ^{0}F). At these temperatures, liquid water is no longer required for oxidation/reduction corrosion-type reactions to occur.

3.6.1 High-Temperature Oxidation

As in other forms of oxidation, high-temperature oxidation involves the following:

- Electrons are lost
- The charge becomes more positive
- Oxygen is not necessarily involved

In oxidizing atmospheres, the formation of stable oxide film on the metal surfaces is usually required for good resistance to high temperature corrosion.

Exposure to temperatures above the stability temperatures of these oxide films can cause very rapid corrosion.

For good high-temperature service performance, materials should have oxide films with the following characteristics:

- Physical stability (they do not melt)
- Low volatility (they do not boil)
- Maintenance of good mechanical integrity (they do not crack)
- Adherence to the substrate (they do not fall off)
- Slow groth kinitecs (they do not allow rapid corrosion)

Sulfur, like oxygen, can cause oxidation at elevated temperatures. Reaction with sulfur called sulfidation, can be more destructive than oxidation by oxygen. Sulfur tends to form scales that do not have the desirable properties just listed. Sulfide films tend to crack and spall more readily than oxide scales and tend to have higher groth rate.

Some materials, such as vanadium oxide and sodium sulfate, melt at elevated temperature, and the melted material can cause rapid attack of such metals as steel. Molten salts, particularly chlorides, can interfere with the formation of scales with desirable properties and can cause rapid attack at elevated temperatures.

3.6.2 High-Temperature Reduction

Damage can also occur in reducing atmospheres, where reducing gases such as hydrogen (H_2), carbon monoxide(CO), carbon dioxide (CO_2), or hydrogen sulfide (H_2S) are present. The presence of sulfur can increase the amount of corrosion under reducing conditions.

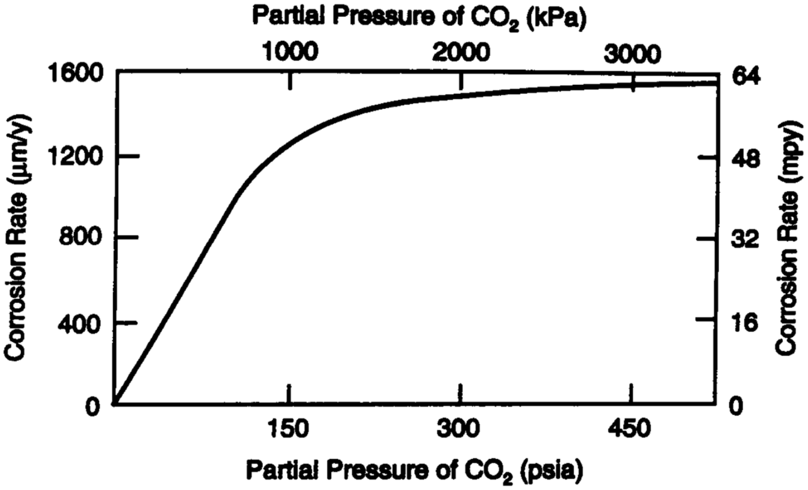


Fig. 3-4. Effect of CO_2 partial pressure on the corrosion rate of mild steel.

Chapter 4

Engineering Materials

4.1 Introduction

To fully understand many of the mechanisms of corrosion as they occur on engineering materials, it is necessary to understand the fundamentals of the structure and the properties of the materials. Engineering materials are usually separated into two groups, metals, and nonmetals.

4.2 Metals

Metals are very widely used because of their combination of strength, ductility, toughness, formability, and (if properly matched to their environment) resistance to corrosion. A metal is distinguished from a nonmetal by its luster, malleability, good electrical conductivity, good thermal conductivity, and unfortunately, its ability to give up electrons (oxidize).

4.3 Metallurgy Concepts

Most of the metals used in engineering are alloys, and almost all are aggregates of numerous small crystals. Alloys are mixtures of two or more elements. The basic characteristics of an alloy come from the elements that are used. By manipulating the distribution of the elements within the crystals and the size and shape of the crystals, alloys with a wide variety of properties can be produced. The distribution of the elements within the alloy and the crystalline structure mau be manipulated through both thermal and mechanical treatments.

4.3.1 Crystal Structure of Metals

The crystaline structure of a metal is not obvious in most cases. In most metals the crystals, sometimes called grains, are very small and conform to the surface of the metal. In a typical metal, these grains range from 0.25 mm to 0.025 mm (0.01 in. to 0.001 in.) in size. Figures 4-1 and 4-2.

The atoms in the metal grains are arranged in a regular three-dimensional pattern. This pattern, or crystal structure, is mad up of repeating patterns of attoms called unit cells. In most metals, these unit cells are of three types: The body-Centered cubic, the face-centered cubic, and the hexagonal close-packed. Figure 4-3. Within each grain, the crystal structure is fairly uniform. The grains are initially formed as the metal solidifies from the molten state. Each crystal starts to grow from an initial point called nucleation site. Figure 4-4.

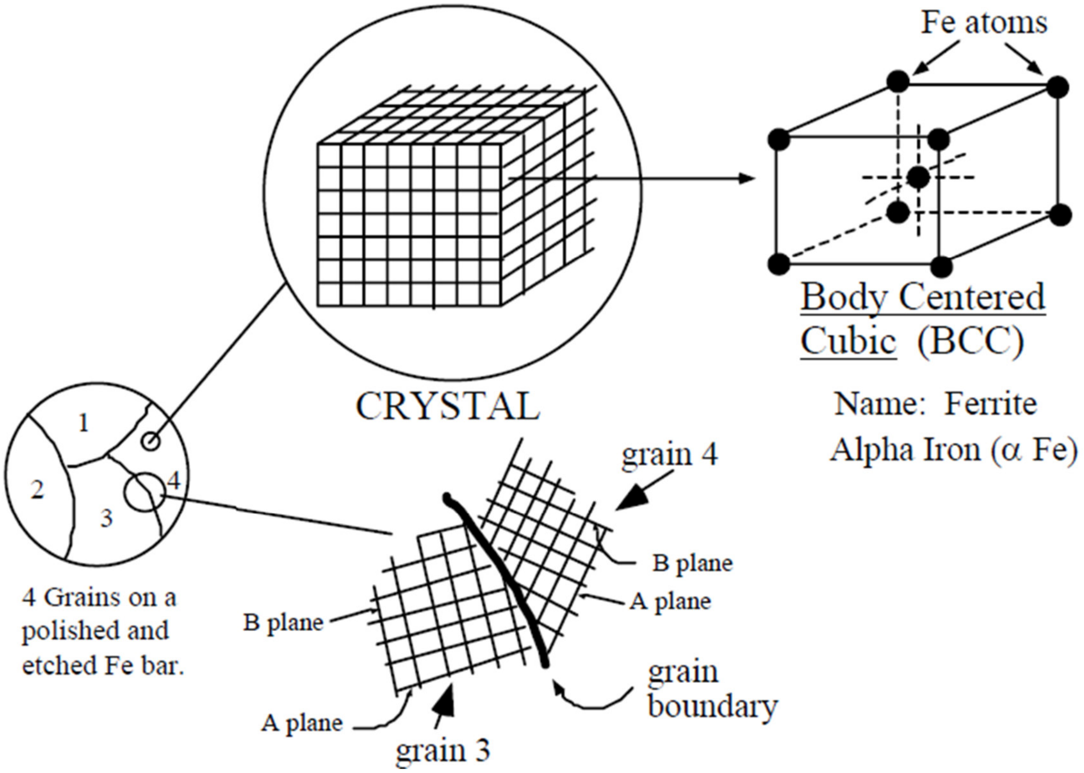


Fig. 4-1. Atoms - crystals and graina of metals.

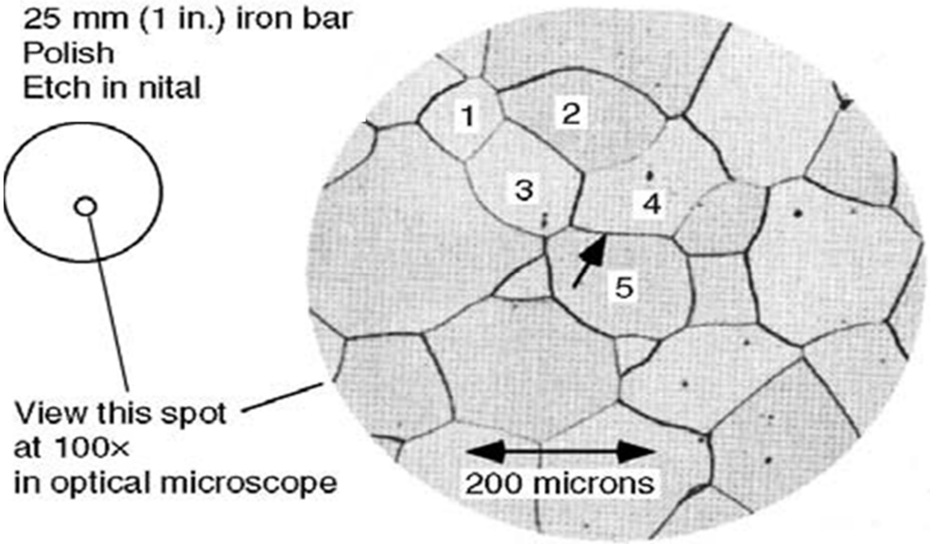


Fig. 4-2. Grain and grain boundaries of metals.

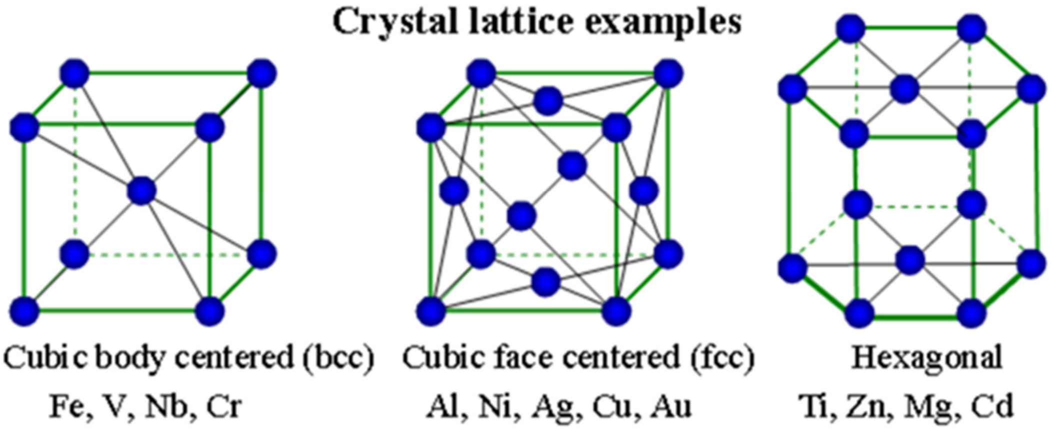


Fig. 4-3. Crystal Lattice examples of metals

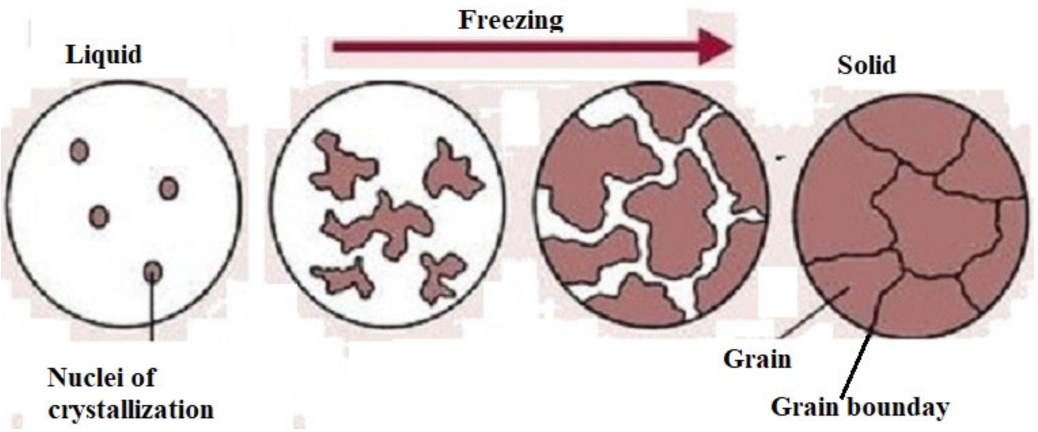


Fig. 4-4. Solidification of metals (*nucleation of crystals, crystal growth, irregular grains form as crystals grow together, grain boundaries as seen in a microscope)*.

The crystals grow from the molten metal in a uniform pattern untill they finally meet the metal totally solidifies. Having started from many sites, the crystal structure of the grains are not aligned with each other. They meet areas of disorder called grain boundaries. These grain boundaries also tend to be less pure than the crystal grains themselves, as impurities are rejected as the metal atoms form their regular crystal structure.

The crystal structure within the metal grains is not perfect. Imperfections can arise from the presence of atoms of different sizes in the crystall structure or from atom missing from unit cells. Atoms of different sizes may either be impurities or intentionally added alloying elements. Imperifications can also arise simply from misalignment of atoms within the crystal or from extra atoms are trapped between atoms in unit cells.

4.3.2 Alloying

By mixing different metals together, and sometimes by adding nonmetals such as carbon, engineering metals with a wide variety of mechanical and corrosion resistance properties can be manufactured. In many cases, alloys have been developed to have properties that are best suited for specific application. Alloys are usually made during the melting process.

Alloys are of two basic types, solid solution and multiphase.

Solid-Solution alloys: Such as brass, are made by mixing two or more metals, dissolved in each other in a molten state. As they solidify, the atoms occupy random locations in the crystal structure and the resulting structure is uniform and homogeneous. The properties of these solid-solution alloys are usually somewhere between the properties of the metals that are used to make the alloys.

Multiphase alloys: In other cases, the metals dissolve in one another at high temperatures but, as they cool, separate into discrete crystals with different chemical compositions and crystal structures. These crystals, each with its own composition and structure, are called phases and can have very different properties from each other. These phases commonly form at temperatures below the melting point of the alloy through solid-phase reaction.

The properties of the multiphase alloys are dependent on the amount, size, shape, and distribution of these phases. These properties can be manipulated by heat treatment, mechanical working, or both. Manipulation of these phases can give a variety of mechanical and corrosion resistance in a metal with a single composition. Formation and stability of the phases are described using phase diagrams. Phase diagrams are also useful for developing and understanding the effects of heat treatment or the changes in the properties that may occur during long term services at elevated temperature. Annex A, includes basic metallurgy information recquired for corrosion engineers.

4.3.3 Welding

One factor in the use of metals that relies heavily on an understanding of metallurgy is welding. Welding has many benefits, including low cost, high strength, and high corrosion resistance. During welding, melting, solidification, and the formation of crystals and phases occur in a few seconds, with much less control than can be achieved during refining and heat treatment during metal manufacture. Through the effects of localized heating during welding, thermal stresses can also be induced that remain in the structure after welding, unless intentionally relieved. Welding processes, material, and procedures must be developes and used carefully to ensure that the resulting weldment has the mechanical and corrosion resistance properties required for the application.

The basic metallurgical structure of metals and alloys not only affect their mechanical and physical properties, but also can affect their resistance to corrosion. The effects of metallurgical structure on corrosion will be discussed later in this book when forms and mechanism of corrosion are described.

4.3.4 Carbon and Low-alloy Steels

Carbon and low-alloy steels are, by weight, the most commonly used engineering metals. They are relatively in expensive, readily available in large number of shapes and sizes, and have a wide range of mechanical properties. They can be heat-treated to give the best combination of strength and ductility for specific applications. They are readily weldable both in the shop and in the field. The most commonly used steels are the carbon steel that are essentially iron-carbon alloys.

The most common carbon steels contain about 0.2% carbon, although the carbon content of carbon steel can vary widely. The tensile strength of this material can range from about 40,000 to 200,000 psi (275 to 1400 Mpa).

"Stress is the amount of effort attempting to fracture an item, the ability to resist that stress is known as Strength. If the stress on a part exceeds its strength, the part will break."

Stress = force per square unit area resisting that force.

Tensile stress: Tensile stress is that type of stress in which the two sections of material on either side of a stress plane tend to pull apart or elongate as illustrated in Figure 4-5. Figure 4-6, illustrates types of stresses may apply on a metal.

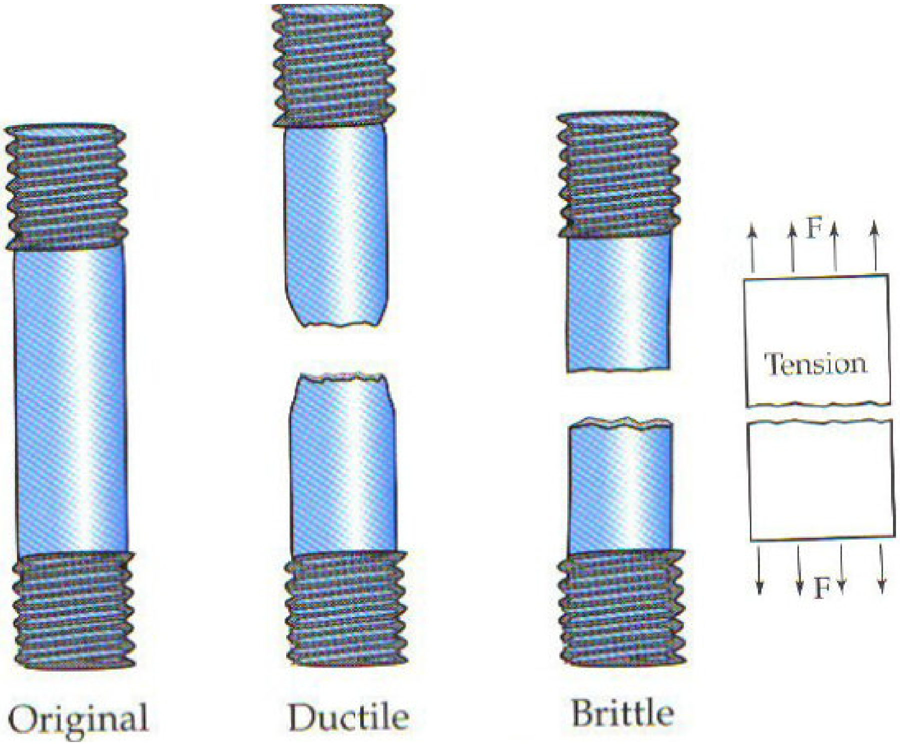


Fig. 4-5. Tension stress, ductile and brittle materials.

The corrosion resistance of all carbon steels is about the same in most environments, but may vary slightly with some carbon content is some chemical environments, such as strong sulfuric acid.

Low-alloy steels are carbon steels with varying small amounts of such elements as chromium, nickel, copper, molybdenum , phosphorous, and vanadium-added. The toral alloy addition content can be up to a few percent. These alloy additions primarily enhance the steel's mechanical properties, but some of the low-alloy steels have substantially better corrosion resistance in atmospheric environments than ordinary carbon steel or other low-alloy steels. Figure 4-7.

In General: Steel is a material composed primarily of iron. Most steels are more than 90% iron. All types of steel contain a second element (Carbon), and may contain other alloying material. Carbon content usually ranges from just > 0 % to 2 %.

Steel with less carbon is more flexible (ductile) than high carbon steel , but is also weaker. Carbon increases strength , hardness and brittleness.

4.3.5 Cast Iron

Cast irons contain much larger amounts of carbon than carbon steel or carbon low-alloy steels, usually in the range from 2 to 6%. Cast iron is low cost and can be formed into a wide variety of shapes ready or nearly ready for final use. Most cast iron contains free carbon in the form of graphite. The shape and amount of of the graphite phase has a great effect on the mechanical properties of the cast iron, particularly with respect to their ductility.

Gray cast irons: Contain carbon in the form of flakes and are relatively brittle.

Malleable cast irons: Contain graphite in the form of rosettes or clusters and are much more ductile than gray irons.

White cast irons: Are hard and brittle and have much of their carbon in the form of iron carbide instead of graphite.

Ductile cast irons: Have their graphite in the form nodules or spheroids.

High-silicon cast irons (over 14% silicon): Are brittle, but highly corrosion resistant in many environments. Some of the high-silicon cast irons also have addition of chromium that further increase their corrosion resistance. The high-silicon cast irons are widely used for corrosion-resistance castings and for anodes used in cathodic protection.

Alloy cast irons: Have also been developed for improved resistance to corrosion at elevated temperature service. Addition of copper improve resistance to sulfuric acid and resistance under atmospheric exposures.

Highly alloyed cast iron containing nickel and chromium are also highly corrosion resistant in many environments. “Ni-Resist” cast iron are very ductile and are widely used in corrosion resistance casting, such as in pumps and turbines. “Ni-Hard” cast iron are white cast irons with high alloy content and have good resistance to corrosion in some environments.

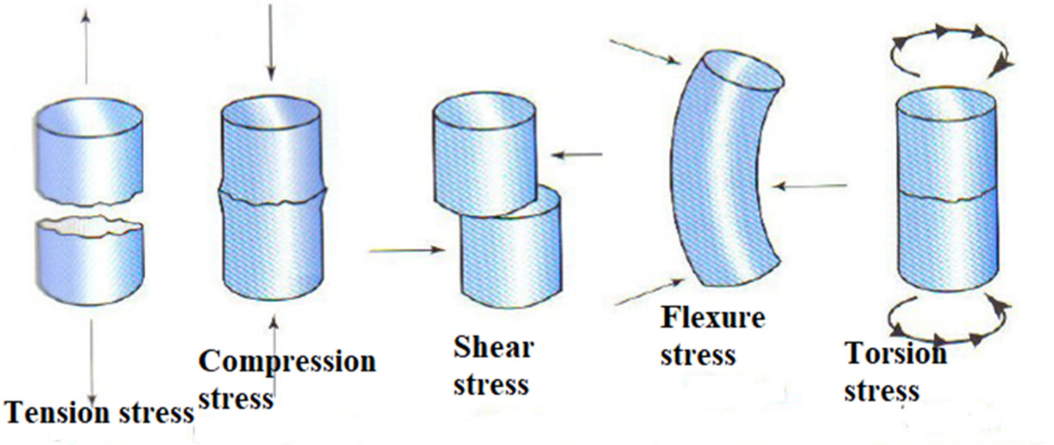


Fig. 4-6. Types of stress may apply on a metal.

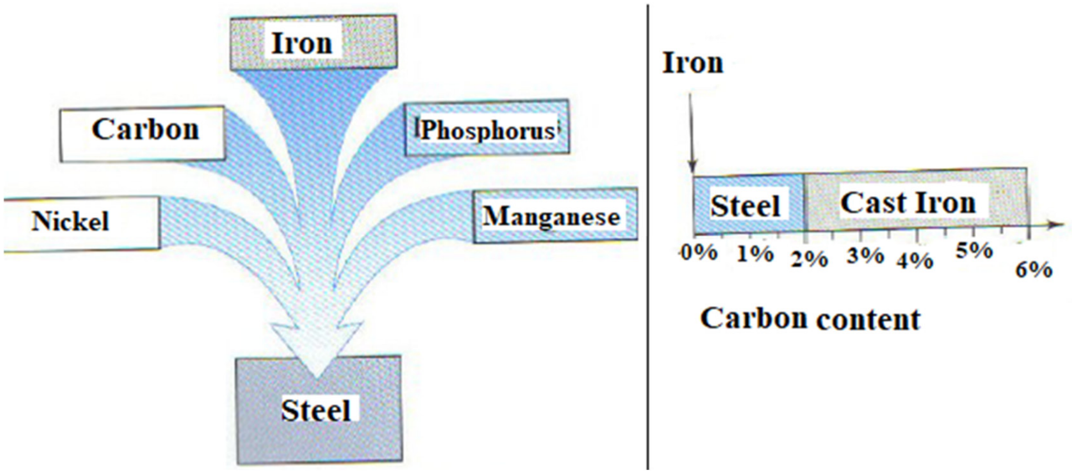


Fig. 4-7. Steel and iron

4.3.6 Copper Alloy

Copper alloys combine corrosion resistance with high heat and electrical conductivity. The are very easy to form and fabricate. There are a large number of copper alloys with a wide ranges of mechanical properties and corrosion resistance.

Strictly speaking, brasses are copper-zinc alloys and bronzes are copper-tin alloys.

Most cooper-alloys are used for their corrosion resistance rather than for their strength. On the other hand, such alloys as beryllium cooper can be heat treated to strengths of up to 200,000 psi (1350 MPa)

4.3.6.1 Characteristics of Copper Alloys

1. The corrosion resistance of copper alloys is primarily due to the noble position of copper in the emf series. Because it is below hydrogen in the emf series, copper tends to be stable in aqueous environments
2. The presence of oxidizers, such as nitric acid or oxygen, can cause copper to corrode in aqueous solutions.

3. In some aqueous solutions, a passive oxide film is formed on copper alloys. If stable, this film can reduce corrosion. The film can be removed by high velocity flow; thus, copper alloys are generally subjected to erosion-corrosion in high-velocity flow conditions.
4. Copper alloys can also be attached in aqueous solutions by carbon dioxide, acids, chlorides, or sulfides.
5. In mild atmospheric environments, many copper alloys become coated with a thin protective layer of corrosion products called a patina. This patina can reduce corrosion rate of the alloy to very low levels and has a pleasing appearance. Sulfur compound in industrial atmospheres and chlorides in marine atmospheres tend to inhibit formation of the patina.
6. Copper alloys are not, in general, resistant to atmospheric environments containing ammonia.
7. Copper alloys are widely used for water piping, pumps, valves, heat-exchanger tubes and tube sheets, hardware, wire, screens, shafts, roofing, tanks, and vessels.

4.3.7 Stainless Steel

Stainless steels are widely used for their corrosion resistance in many natural and chemical environments.

In the other hand, not all stainless steels are resistant to corrosion in all environments, and some environments are corrosive to all stainless steels.

Great care must be gives to the selection of the proper stainless steels for a given application.

All stainless steels contain chromium. Although chromium is an active element (see its position in emf series), ferrous alloys containing chromium passivate readily after exposure to air and this thin passive film is stable in many environments. The corrosion resistance of stainless steel is dependent on the stability of this passive film. The stability of this passive film on stainless steels is enhanced by alloying the straight chromium stainless steel with other elements, particularly nickel and molybdenum.

Stainless steel are commonly grouped into families with common characteristics. These groups and a short description of the characteristics of the alloys in each group are given below.

4.3.7.1 Martensitic Stainless steels

- AISI 400 series.
- Essentially straight chromium stainless steels with 12% to 17% chromium and minor additions of other elements.
- Can be hardened by heat treatment.
- Magnetic.
- Moderate corrosion resistance in mild environments.
- Relatively high strength.
- Used for valve parts and bearings, surgical instruments, and cutlery.

4.3.7.2 Ferritic Stainless Steel

- AISI 400 series.
- Essentially straight chromium stainless steels with 12% to 30% chromium.
- Cannot be hardened by heat treatment.
- Magnetic.
- Difficult to wild.
- Have moderate-to- good corrosion resistance depending on chromium content and environment.
- Some alloys have good resistance to high-temperature oxidation.
- Resistant to chloride ion stress corrosion cracking.
- Used for automotive trim and exhaust system, furnace parts, heat-treating equipment, and for service in nitric acid.

4.3.7.3 Austenitic Stainless steels

- AISI 200 and 300 series.
- The 300 series is based on alloys with about 18% chromium and 8% nickel, thus the term 18-8 stainless steel.
- Typically alloys contain 17% to 25% chromium and 9% to 10% nickel.
- The 200 series uses manganese as a substitute for the portion of the nickel in the 300 series-type alloys.
- Cannot be hardened by heat treatment

- Nonmagnetic
- Easy to weld
- Welding procedure are important to corrosion resistance of weldments.
- Better corrosion resistance than straight chromium stainless steels because of stabilizing influence of nickel on the passive films.
- Highly resistant to neutral and oxidizing aqueous environments as well as the atmospheric environments.
- Alloys 304, 304L, 316, and 316L (L indicates low carbon content) are the most commonly used alloys in this group.
- Molybdenum addition improve resistance to corrosion in chloride-containing environments, such as seawater.
- Susceptible to chloride ion stress-corrosion cracking at elevated ambient temperatures.
- High nickel content reduce susceptibility to chloride ion stress-corrosion cracking.

4.3.7.4 Precipitation-Hardening Stainless Steels

- AISI 600 series.
- Can be heat treated to high strength.
- Tensile strength of up to 200,000 psi (1350 MPa) can be achieved.
- Magnetic
- Corrosion resistance generally less than austenitic grades but generally more than martensitic and ferritic grades
- Widely used where high strength and moderate corrosion resistance in mild environments is required.
- Widely used in aerospace applications
- Susceptible to chloride ion stress corrosion cracking at high strength level.

4.3.7.5 Duplex Stainless Steels

- A relatively recent development
- Metallurgical structure consists of a mixture of ferrite and austenite.
- About twice as strong as the commonly used austenitic stainless steels.
- Have good ductility
- Can be welded
- Are not harden able by heat treatment.
- Magnetic
- Corrosion resistance of these alloys is generally equal to or slightly better than that of austenitic stainless steels in many environments.
- Resistant to chloride ion stress corrosion cracking.
- Used for tanks, vessels, and piping.
- Higher strength gives weight advantage for tank trucks and marine tanker application.
- Used in oil and gas production and chemical process industry for heat exchangers and process piping.

4.3.7.6 Super-Austenitic Stainless Steels

- Highly alloyed cousins of austenitic stainless grades.
- Contain highest amounts of chromium and nickel
- Contains 4% to 6% molybdenum.
- Many alloys contain less than 50% iron.
- Corrosion resistant, especially to pitting and crevice corrosion in chloride-containing environments, more than the ordinary austenitic stainless steel.
- More resistant to chloride ion stress corrosion cracking than austenitic stainless steel.
- About 50% stronger than austenitic stainless steel.
- Used for tanks, pumps, heat exchangers, piping, and valves. Particularly in chloride containing environments, such as seawater.

4.3.8 Nickel Based Alloys

There is a wide range of nickel alloys available; they are widely used for their resistance to corrosion and to elevated temperatures. Many severe corrosion problems can be solved using nickel-based alloys; however, they are not universally corrosion resistant. The proper alloy for a specific application must be carefully selected.

Nickel and nickel-based alloys are very resistant to corrosion in alkaline environments. They are also resistant to corrosion in neutral chemical and many neutral environments. Many nickel-based alloys show excellent resistance to pitting, crevice corrosion, and stress corrosion cracking in chloride-containing environments.

4.3.9 Aluminum and Aluminum Based Alloys

Aluminum and aluminum-based alloys are very widely used where weight is a significant factor. Aluminum is a reactive metal, but is passive in many mildly corrosive environments. Because of the formation of a thin film of aluminum oxide. In more corrosive environments, this film can break down and corrosion can occur. The film is generally stable in neutral and oxidizing acidic environments. The film is generally unstable in reducing acids, alkaline environments, and environments containing chlorides. The oxide film on aluminum alloys can be artificially thickened through a chemical treatment called anodizing.

Aluminum alloys are grouped into series much like stainless steels. The series of aluminum alloys is based on the primary alloying elements used. A list in table 4-1.

Series	**Primary alloying element**	**Heat treatable ?**	**Relative corrosion resistance to atmosphere**
1000	None	No	Excelent
2000	Cu	Yes	Fair
3000	Si/Mn/Cu/Mg	Most yes	Good
4000	Si	No	Good-fair
5000	Mg	No	Excelent-good
6000	Mg + Si	Yes	Good
7000	Zn	Yes	Fair

Table. 4-2. Aluminum alloys.

Aluminum alloys are very easy to form and fabricate and can be welded. They are widely used where a high strength-to-weight ratio, good electrical and thermal conductivity, and moderate corrosion resistance are required. One factor in the use of aluminum alloys is that their corrosion products are nontoxic and are colorless or white, therefore, the appearance of corroded aluminum is less objectionable than the appearance of corroded steel.

4.3.10 Titanium

Titanium and titanium alloys are reactive, and their corrosion resistance, like that of aluminum alloys and stainless steels, is dependent on a thin oxide film. In titanium and titanium alloys, however, this film is extremely stable in a wide range of environments. It is highly resistant to seawater and other chloride environments; it is also resistant to chlorine, and hypochlorite. Titanium and titanium alloys do, however, corrode in some environments, such as pure hydrochloric and sulfuric acids.

Titanium alloys are relatively high in strength. The low density of titanium leads to high strength-to-weight ratios.

Titanium alloys are relatively difficult to form and fabricate. Titanium and titanium alloys can be welded in an inert environment.

4.4 Nonmetals

Nonmetals are also widely used as structural materials or where their properties, such as flexibility, high strength-weight-ration, stiffness, or other property, is required. Although nonmetallic materials donot corrode through the action of electrochemical cell, they are subjected environmental deterioration, and this deterioration can also be called corrosion.

4.4.1 Concrete

Concrete is the most widely used artificial material in terms of tonnage. Concrete is durable in many application, but it is subjected to deterioration. This deterioration is usually slow in most natural environments, but it can be very rapid if the combination of concrete quality and the environment are not properly matched. In Many cases,concrete is reinforced, usually using steel, to improve its structural strength and reduce cracking. While concrrete is strong in compression, it is weak in tension. Reinforcing with steel allows tensile stresses to be transferred from the steel, which has a relatively high tensile strength.

Concrete is made with naturally-occuring aggregates. Much of th concrete used is mixed, poured, and cured under field conditions. For these reasons, there are a large number of variables involved in the production of concrete. The variables must be carefully controled to obtain a concrete with the required mechanical properties and resistance to deterioration.

4.4.1.1 Components of Concrete

Concrete is composed of three basic components: Cement, aggregate, and water.

Cement

Cement is the material that bonds the aggregate particles together. Most cement used today is Portland cement made by heating naturally-occuring materials containg the required minerals for making cement. Portland cement is called hydraulic cements because they react with water to form compounds capable of bending aggregate particles together. The reaction of the cement with water is called hydration. Hydraulic cements donot bend aggregates together by drying process, but They chemically react with water and can do so even under water. In most cases, it is undesirable to allow freshly poured concrete to dry before completion of the hydration reactions that form the binding compounds.

Aggregates

Aggregates used to make Portland cement concretes are usually naturally-occuring rocks, gravel, and sand.

Water

Clean water is a very important part of Portland cement concrete. The water should be free of sediment and debris. It should also be free of chemical contaminations, particularly chlorides and organic compounds.

To obtain a high-quality concrete that is dense and strong with low permeability, the proper amount of water must be added. Sufficient water must be added for hydration of the cement and to give the mix enough fluidity. Excess water will significanty decrease the density and strength of Portland cement concretes and increase their permeability. Water cement ratio of 0.4 by weight are commonly specified for the maximum strength and durability required.

4.4.1.2 Effects of Environment on Concrete

Concrete can degrade through either mechanical or chemical processes, or ay combination of the two. Damage by stress, vibration, and abrasion is very possible.

Freezing and Thawing

Concrete because it contains water, is also subjected to damage by repeated freeze-thaw cycles. Both the aggregate and the hydrated cement may be damaged by freeze-thaw.

Agrressive Chemical Exposure

Exposure to aggressive chemicals can cause rapid deterioration of concrete. Exposure to environments containing sulfate, such as sea water or soils containing sulfate, can cause rapid deterioration of concrete and commonly result in the expansion of cement paste and disruption of the concrete because of the resultant tensile stresses. The use of type V-sulfate-resisting cements is recommended wherever sulfate exposure is possible.

Exposure to acidic environments results in a reaction between the acid and the alkaline concrete constituents. The cement paste is always alkaline; the aggregate may or may not be reactive in acids. In many cases acids are not compatible with concrete. Acid attack can also cause corrosion of reinforcing steel, causing cracking and spalling.

Abrasion

Although concrete is relatively resistant to abrasion, abrasion from production operations, vehicles or foot traffic, and wind or water brone particles can cause concrete deterioration, particulary when combined with chemical attack.

Corrosion of Embedded Steel

The corrosion of embedded steel is perhaps the most significant form of concrete deterioration. The corrosion of embedded steel is electrochemical process. In good concrete, the alkalinity of the concrete, combined with its low permeability to such corrdents as water and oxygen, allows the steel to become passive. If this passivity is destroyed, the steel can corrode with catastrophic results. The primary problem with corrosion of embedded steel is that the products of corrosion of steel occupy a larger volume than the steel that produces them. The resulting expansion and tensile stresses cause cracking and spalling of the concrete. This results in easier penetration of the corrodents to the steel, with damage occuring at an increasing rate.

Chlorides existing in the initial concrete mix, or that enter the concrete from the environments, are very effective is destroying the alkalinity of the concrete and the passivity of the embedded steel. Corrosion of steel in highways and bridges due to the application of road salts has contributed significantly to the $300 billion loss from corrosion in the United States. Corrosion of embedded steel in some structures, such as parking garages, from de-icing salts has resulted in structure collapse. Any factor that reducing the alkalinity of concrete, such as reaction with acids or atmospheric carbon dioxide, can also allow the embedded steel to corrode. Any factor that causes cracking of the concrete can also allow corrosive agents to reach the embedded steel more quickly and destroy its passivity.

Corrosion of embedded steel can be corntoled through cathodic protection in many cases.

Stray Electrical Currents

Stray electrical currents can also cause corrosion of reinforcing steel in concrete. This is most commonly encountered in buried structures, such as reinforced concrete pipes, tanks, and building foundations.

Corrosion Cells within Concrete

Whenever conditions within the concrete adjacent to the reinforcing steel are not uniform, the difference can lead to local corrosion. The most severe form of this attack occurs when the environment allows local depassivation of the steel. The resulting active/passive corrosion cells can cause rapid corrosion of the normally unfavorable anode/cathode area ratio. The large potential difference between the active and passive states of embedded steel (> 0.5 V) can result in a very high corrosion rates. The high electrical resistivity of good concrete reduced the intensity of this attack, but the electrical resistivity of concrete is reduced by many of the same factors that allow corrosion of the embedded steel.

Chemical Reactions of Aggregate

The alkalinity inherent in Portland cement concrete can cause chemical attack of some aggregates, particularly those high in silica. The reaction commonly causes the expansion of aggregate, with resultant cracking and spalling of the concrete.

Repair of Concrete

Damage to concrete structures can be repaired in many ways.

- The damaged concrete must be removed and the exposed concrete surfaces must be properly prepared to accept repair.
- Bonding agents to improve adhesion of the new concrete to the old concrete are often used.
- Corroded reinforcing steel must be replaced, by splicing new bars to sound (the good) stubs of the reinforcement in the structure.
- New concrete may be added using several methods:
  - Forms may be erected and new concrete is placed in a manner similar to new construction.
  - Shotcrete, where cement and fine aggregate are sprayed using compressed air and a special gun, is widely used where the thickness of the repair is not great.
  - Topping of fine aggregate and cement are also commonly used to repair surface damage due to abrasion or limited chemical attack.

One factor in repair of reinforced concrete that is frequently overlooked is that the steel exposed to the fresh sound concrete in the repaired area is usually very passive. Electrical contact between the reinforcement in the repaired area and the less passive reinforcement in the original structure can result in a corrosion cell. The zone at the interface between the original structure and the repair is particularly vulnerable. This effect can be counteracted by coating the reinforcement in the area to be repaired, thus effectively reducing the exposed cathodic area.

Use of Coating to Enhance Concrete Durability

Coating may be used on concrete to increase its resistance to deterioration. Most coatings are intended to reduce the intrusion of water into concrete. This can improve freeze-thaw performance, protect the substrate from aggressive environments, and reduce the corrosion of the embedded steel.

Corrosion of Concrete in Aqueous Environments

Soft waters tend to leach calcium from the cement paste and can rapidly attack Portland cement concrete. This is frequently occur in tanks, dams, and intake structure where water is soft. Acidic water can also attack the cement pastes, aggregates, and reinforcing steel as described above. Sulfates,particularly in seawater, can attack concrete unless type V Portland cement is used.

Corrosion of Concrete in Underground Environments

Concrete is frequently used in contact with soil. It may be placed on the surface or buried on such structures as footings, tanks, and pipes. Soil environments may be aggressive if the pH is less than 6; if the pH is neutral but hydrogen ions are available; if there is a high sulfate, sulfide, or chloride content; or if there is a high content of magnesia (MgO). Type V cements should be used where sulfate attack is possible.

Chapter 5

Forms of Corrosion

5.1 Introduction

In this book, the various forms of corrosion will be described. Among with describing each type of corrosion, we will discuss specific mechanisms that result in these types, the rates of attacke and ways of measuring and predicting each form of attack, examples of typical metal-environment combinations resulting in each form, and methods thatt can be used to control each type.

5.2 Forms of Corrosion

The following forms of corrosion will be covered

- General (uniform) attack corrosion
- Localized corrosion
- Pitting corrosion
- Crevice corrosion
- Filiform corrosion
- Galvanic corrosion
- Environmental corrosion cracking
  - Stress corrosion cracking
  - Hydrogen-induced cracking and sulfid stress cracking
  - Liquid metal embrittlement
- Corrosion fatigue
- Velocity effect corrosion
  - Erosion corrosion
  - Impingement corrosion
  - Cavitation corrosion
- Intergranular corrosion
- Dealloying
- Fretting corrosion
- High-temperature corrosion

In most cases, the combination of the metals used in structures and equipments, coupled with a wide range of environments encountered, will result in more than one form of corrosion within a system. Even a single alloy, exposed to different environments at different points within the system, can undergo more than one type of attack.

5.2.1 General (uniform) attack corrosion

5.2.1.1 Definition and Description

General attack is a corrosion that proceeds more or less uniformly over the exposed surface without appreciable localization of the attack.

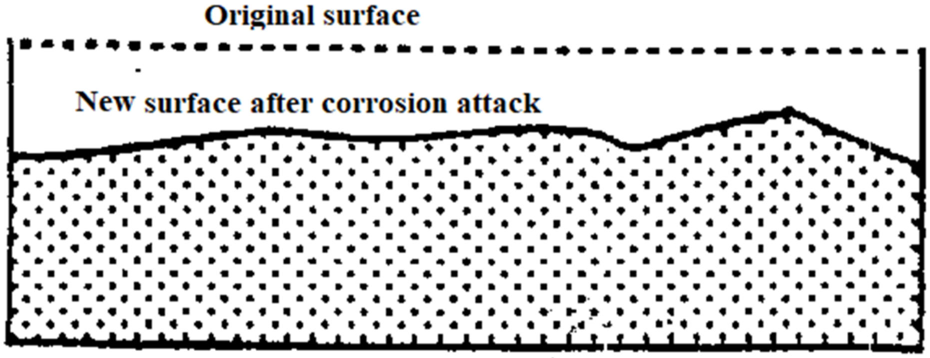


Fig. 5-1. General attack corrosion

General attack corrosion is also called general corrosion, or uniform corrosion. For sheet or plate materials, this leads to relatively uniform thinning. For round bar or wires, corrosion proceeds radially inward at essentially a uniform rate around the entire circumference. The result is the production of a bar or wire of progressively smaller diameter. Pipe and tubing that suffer general corrosion are thinned from one side or the other (or both), depending on the nature of exposure to the corrosive environment. Misapplying materias in corrosive environments often results in severe general corrosion.

5.2.1.2 Recognition

General attack corrosion can be recognized by roughening of the surface and by the presence of corrosion products. In some cases, however, the corrosion products may not be present, as they can be soluble or can be removed by the action of wind, rain or other forces.

5.2.1.3 Mechanism

The mechanism of General attack is typically an electrochemical process taking place on the surface of the material. The anodes and cathodes are caused by minor difference in composition or orientation between small area on the metal surface. These site change their potential with respect to the surrounding areas, and the corrosion proceeds more or less uniformly over the surface. Of the many forms of corrosion, general attack is perhaps the least insidious, since the life of a part that is subject only to truly general attack may be readily predictable.

5.2.1.4 Corrosion rate

Depending on the specific material and environment, the rate of general corrosion may be:

- Linear
- Decreasing with time
- Increasing with time

5.2.1.5 Predictability and Measurement

When corrosion rates are linear or decrease with time, long-term projections of corrosion damage are possible. When corrosion rates increase with time, it is much more difficult to predict long-term corrosion damage.

General attack corrosion is usually measures in terms of penetration rate per unit time in millimeter per year (mm/yr) or mils per year (mpy). Experimental measurement of general attack corrosion is usually made by measuring weight loss and calculating the equivalent loss of metal thickness. Both in experimental measurements and in the field, loss of thickness can be measured directly usin a micropmeter caliper or ultrasonic thickness measurement instrument.

Relative corrosion Resistance	mpy	Mm/yr	um/yr
Outsttanding	<1	<0.02	<25
Excelent	1-5	0.02 – 0.1	25-100
Good	5-20	0.1-0.5	100-500
Fair	20-50	0.5-1	500 – 1000
Poor	50-200	1-5	1000-5000
Unacceptable	200+	5+	5000+

Table 5-1. Corrosion rate classification.

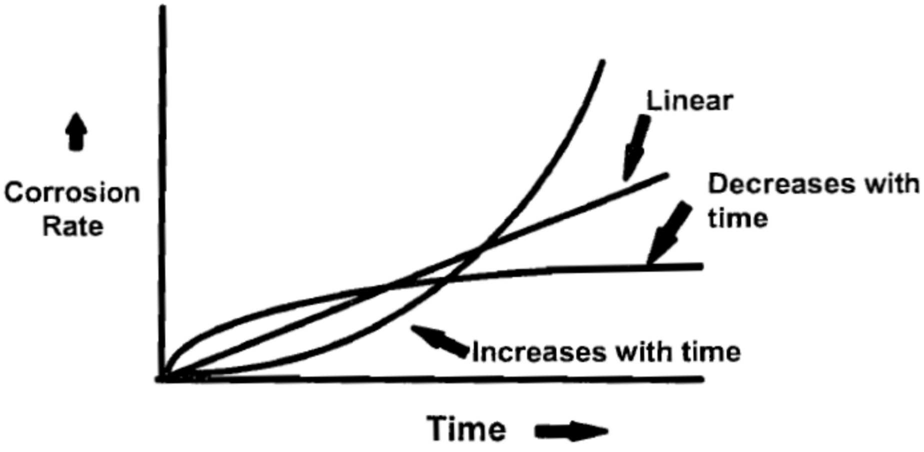


Fig. 5-2. Corrosion rate of general attack corrosion.

5.2.1.6 General attack corrosion- Performance of Metals and Alloys

Carbon and low alloy steels perform well in a wide variety of environments, including atmospheric exposure, immersion in natural waters and many chemicals, and underground.

Copper and copper alloys also perform well in a wide variety of environments.

Aluminum and aluminum alloys may be used where localized corrosion do not occur. Rates of uniform corrosion of aluminum can be very high in alkaline environments.

5.2.1.7 Control of General Attack Corrosion

When corrosion rates are low and are either linear or decrease with time, uniform corrosion can be tolerated without the need to control it. The effect of the corrosion loss is relatively easy to asses, and allowances can be made in the initial design for anticipated loss in thickness. If rate of attack is unacceptable (when it cannot be reasonably be handled by a corrosion allowance, or where metal contamination cannot be tolerated), it may be necessary to modify the original design, either at the initial design stage, or through modification after construction. In some cases a more corrosion resistant material can be used. The design can be changed to eliminate the corrosive conditions. This may involve every thing from simple reorientation of surfaces to avoid features that trap and hold water to significant changes in operation conditions.

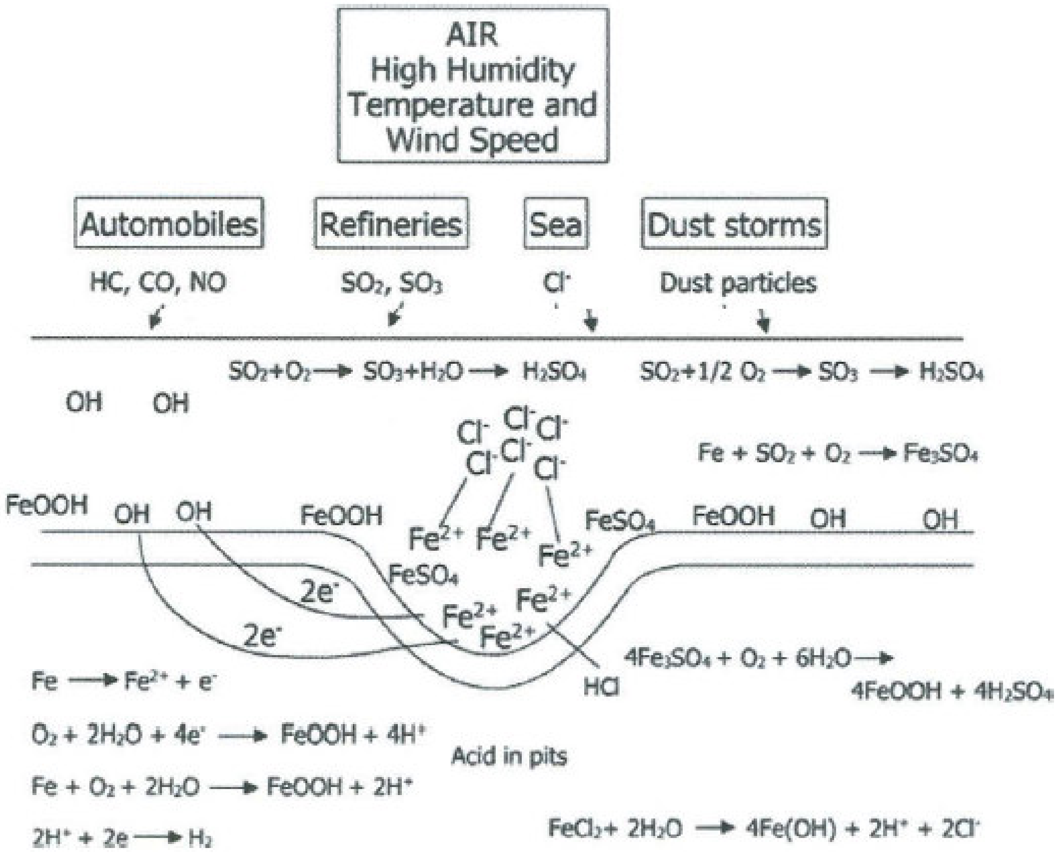


Fig. 5-3. General corrosion of iron in marine atmosphere.

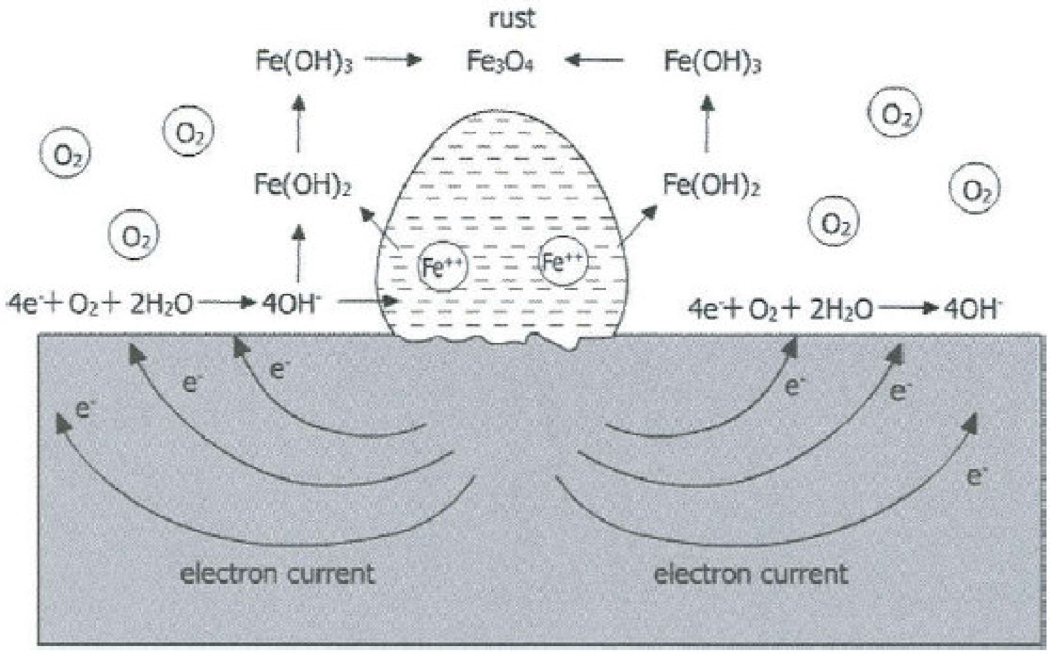


Fig. 5-4. General aqueous corrosion of iron .

If the environment can be controlled, such as by dehumidification of interior spaces or the addition of corrosion inhibitors to liquid environments, corrosion may be reduces to accepted levels.

Protective coatings are particularly effective in controlling uniform corrosion. When the coating is defective, or fails due to environmental exposure, only relatively slow uniform attack occurs. Recoating or local coating repair can stop the attack before it progresses far enough to cause a significant loss of material.

Cathodic protection, a method which interferes with the flow of the current in the electrochemical cell, can be used in underground or immersion situations. We will cover cathodic protection in more detail later in this book.

Some low-allot steels have been formulated specifically to form tightly adherent, denese corrosion products that inhibit corrosion in some atmospheric environments. In environments where these protective corrosion products form, these “weathiring steel” show low rate of corrosion, usually at a rate that decreases with time. These alloys are useful for many structural and architectural applications. In some environments, the corrosion products are not protective, and there is a little or no reduction in corrosion over that of the ordinary carbon and low-alloy steels.

5.2.2 Localized Corrosion

5.2.2.1 Introduction

Localized corrosion, unlike general attack corrosion, occurs at discrete sites on metal surface. While corrosion activity at these sites may start and stop with changes in the environments and new sites may start corroding, corrosion is concentrated at these sites. The area surrounding the sites where localized corrosion occur are corroded to lesses extent, or may be essentially unattacked.

5.2.2.2 Types

Four forms of localized attack will be described in this section:

- Pitting corrosion
- Crevice Corrosion
- Filiform corrosion
- Pack Rust Corrosion

5.2.2.3 Pitting Corrosion

Defination

Pitting is a deep, narrow corrosive attack which often cause rapid penetration of the substrate thickness. Pitting corrosion is characterized by corrosive attack in a localized region surrounded by noncorroded surfaces, or surfaces that are attacked with a much lesser extent. Pitting corrosion can initiate in some statistical manner on an open, freely-exposed surface, or at random imperfections where protective surface films or coatings have broken down.

Mechannism

Very often, a local cell is setup between interior of the pit and the external surface. The interior contains acidic, hydrolyzed salts that are quite corrosive compared to the bulk solution. An anode is established within the pit, and the surrounding area acts as cathodes. This is particulary the case for alloys that rely on a resistant, passive film for protection (such as stainless steel, titanium, and aluminum). It also may occur on iron, steel, lead, and other metals. Pits develop at weak spot in the surface film and at sites where the film is damaged mechanically under conditions where self-repair will not occur. Figures 5-5 to 5-8B Pitting corrosion.

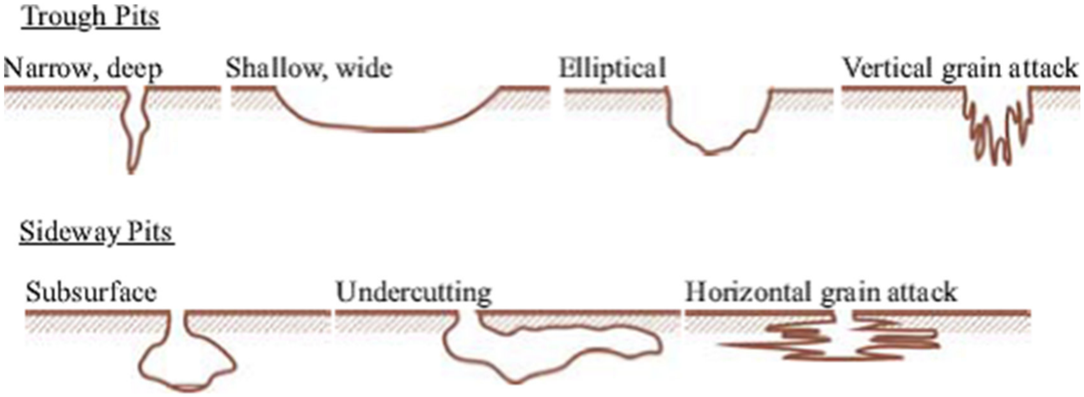


Figure 5-5 Pitting corrosion.

Figure 5-6 Pitting corrosion in water well tubing.

Figure 5-7. External pitting corrosion in undergotound pipe

Fig.5-8A. Internal pitting corrosion in steel pipe.

Fig.5-8B. Pitting corrosion in stainless steel sheet.

Pitting Rates

The practical importance of pitting depends on the thickness of the metal and on the penetration rate. The rate usually decreases with time . Thus, on thin sections pitting may be serious, while in thick section it may be less important. In general, the rate of penetration decreases if the number of pits increases. This is because adjacent pits have to share the available adjacent cathodic area, which controls the corrosion current that can flow. Movement of the solution over a metal surface often reduces and even may prevent pitting that otherwise would occur if the liquid were stagnant (such as with some austenitic stainless steels in sea water). Pitting corrosion usually occur in steps

- Initiation
- Propagation
- Termination
- Reinitiation

Initiation: Pits initiate at defects or imperfection in a protective or passive film. The deffect may either be randomly distributed, or caused by mechanical damage to the films. In some alloys, it may take a considerable amount of time for the passive films to break down. Pitting may not initiate for long periods, but once it initiates, the pitting can propogate rapidly.

Propagation: In the propagation stage, corrosion is driven by the potential difference between the anodic area inside the pit and the surrounding cathodic area. In addition, the environment within the pit can become more aggressive and further accelerate corrosion within it.

Termination: A pit may terminate because of increased internal resistance of the local cell (caused by filling with corrosion products, filming of the cathode area, etc.) If a pitted surface is dried out, of course, the pit will terminate.

Reinitiation: When re-wetted, some of the pits may initiate. This may be due to the re-establishment of the conditions, or to the differential aeration between the solution in the main pit cavity and solutions in some of the cracks that emanate from it deeper into the metal.

In structural members where strength alone is the concern, pitting may not be as important as in a service of a containing fluid.

Pitting Resistance Equivalent (PRE)

The pitting resistance equivalent (PRE) is a “rule of thumb” guide to the pitting resistance of a metal. The alloying element that increase the resistance to pitting and crevice corrosion are chromium and molybdenum which is expressed as pitting resistance equivalent (PRE). PRE = %Cr + 3.3 x %Mo

A good resistance to pitting corrosion is indicated if PRE is equal to or greater than 40.

Alloy name (UNS)	PRE
304L(S30403)	19
316L(S31603)	26
2507(S32750)	35
2304(S32304)	43

Table 5-2. PRE for some stainless stells.

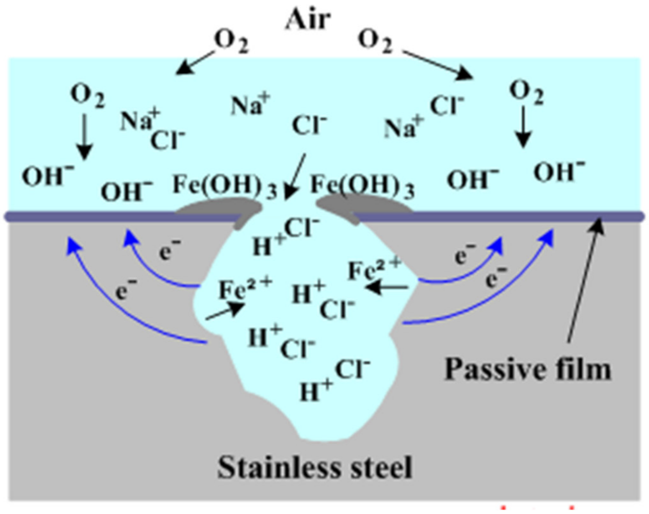


Fig.5-9. Pitting corrosion in stainless steel

Predictabiliy/Measurements

Pitting corrosion is measured by measuring the depth of the pits below the surrounding surface. This may be accomblished by using such instruments and methods as:

- Calibrated microscopy
- Dial gauge with needle probe
- Metallographic sectioning
- Routing

In measuring pits with a calibrated microscope, the microscope is first focused on the surface surrounding the pit, then on the bottom of the pit. The difference in focusing distance read from a scale on the microscope represents the depth of the pit.

When using a dial gauge with with a needle probe, the gauge is zeroed on a flat surface, then the needle is inserted into the pit and the pit depth is read directly from the dial indicator. It is important that the needle reach the deepest part of the pit.

Metallographic measurement of pits requires sectioning the sample at pit sites. It is also deffecult to ensure that the section is at the deepest point of pit.

Routing removes material from the surface untill no further pits are evident. This method is the most accurate because, even in metallographic sectioning, it is difficult to find the location of the deepest penetration.

In most cases, the deepest pit and the average depth of a number of pits (commonly the 10 deepest pits) are reported. Another measurement of pitting is the pitting frequency, which is the number of pits per unit area (usually pits per square centimeter).

The effect of pitting corrosion is more difficult to apply than the effect of uniform corrosion, because the exact location of the pits cannot be predicted. In addition, the depth of the pitting is statistically distributed. It is not possible, based on limited corrosion testing, to be sure the deepest pit measured on a small area in a test will predict or portray the deepest pit that actually occurs over a larg area in a service exposure.

Pitting corrosion- Performance of Metals and Alloys.

- Aluminum alloys
- Stainless steels and nickel-based alloys
- Copper alloys
- Lead

Aluminum alloys

The introduction of small amounts of ions of metals such as copper, lead, or mercury may cause sever corrosion of aluminum equipments. For example, corrosion of upstream copper alloy equipment can cause

contamination of cooling water. Under these circumstances, copper can plate out on down stream equipment and pipe, setting up local galvanic cells that can result in severe pitting and perhaps perforation.
Mercury also causes severe pitting and stress cracking of aluminum. Common sources of mercury contamination include blown manometers, broken thermometers and seals, the mercury-containing biocides. Aluminum alloys may also pit in seawater or other environments containing chlorides or other halide salts, such as bromides or iodides.

Stainless Steels and Nickel-Based Alloys
The resistance of stainless steels and nickel-based alloys depends on the specific alloy used and the environment. Pitting should always be a concern when selecting stainless steels and nickel alloys. Stainless steels are usually susceptible to chloride pitting. Surface films of either organic or inorganic origin may occlude and concentrate chlorides to cause widespread pitting over a surface area. Except for localized attack under marine deposits in seawater, pitting of pure nickel is rare. The nickel-copper alloy, Monel, is also subjected pitting corrosion in seawater; however, the occurance of such pitting is rare.

Copper Alloys
Copper alloys are used extensively in various water handling system because of their good corrosion behavior and resistance to pitting. Copper alloys are attacked by ammonia, which can cause both pitting and stress corrosion cracking. Hot oxygenated water can also cause pitting of many copper alloys.
Very soft fresh water can promote some pitting of copper, particularly if CO_2 levels are high. Steam with sufficiently high quantities of CO_2, O_2, and NH_3 can be corrosive and lead to pitting of some coppper alloys.
Deposits of iron oxide resulting from upstream iron corrosion or other sources can also cause pitting corrosion of copper alloys.
Sulfides in water, including sea water, lead to severe pitting of most coppper alloys.
Copper alloys are not recommended for handling oxidizing acids or acids with oxidizing agents (such as oxygen or ferric ions) since high rates of pitting can occur.

Lead
Lead is frequently used as an external shield in underground electrical and communication cables. Lead may pit in these underground environments, aggravated by stray electrical currents.

Control of Pitting Corrosion
Pitting corrosion can be controlled in several ways including:

1. Materials selection
   Selection a pit-resistant material for the subjected environment.
2. Modification of environment
   The propensity of an environment to induce pitting sometimes can be modified by deaeration, elimination of certain species, inhibition, etc. Keeping the surface clean can help to control pitting.
3. Protective coatings
   Coatings can be effectively used in specific instances, such as on threaded fasteners. On boldy-exposed surfaces, there is always the possibility of concentrating attack at imperfections in the coating, unless the coating is a metalic film sacrificial to the substrate.
4. Electrochemical techniques
   Cathodic protection has been used effectively to control pitting on boldly-exposed surfaces. Anodic protection is generally not recommended where pitting attack may occur.
5. Design
   Increased cross-section area or corrosion allowances are not a practical method againest pitting attack or severe localized corrosion.

5.2.2.4 Crevice Corrosion

Defination
Crevice corrosion is a form of localized attack in which the site of attack is an area where free access to the surrounding environment is restricted. As crevice corrosion is caused by differences in the concentration of materials inside and outside the crevice, crevice corrosion is also called concentration cell corrosion. This form of localized attack can occur at crevices where materials meet in such a way that the environment can

enter the joint between them but the flow of material into and out of the joint is restricted. These crevices may either be metal to metal or metal to nonmetal. Crevices can also be formed under deposits of debris or corrosion products.

Crevice corrosion can be recognized by the localization of attack either at the enterance of the crevice or deep within the crevice. When corrosion occure deep within the crevice, it often revealed only after a failure has occurred.

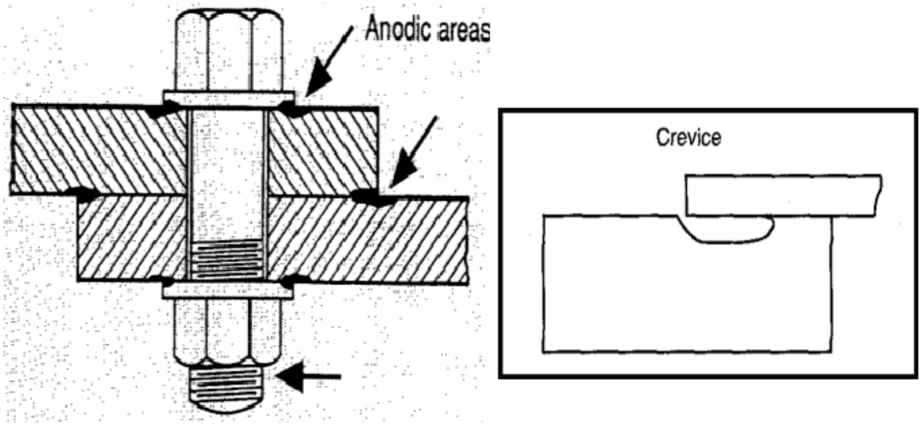


Fig. 5-10 Crevice Corrosion

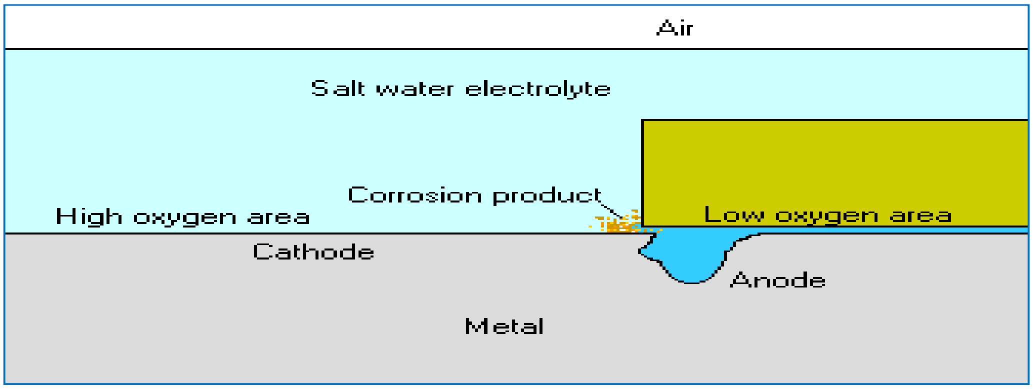


Fig. 5-11 Crevice Corrosion

Fig. 5-12 Crevice Corrosion (Extensive corrosion between the flange faces) and (corrosion of the bolts)

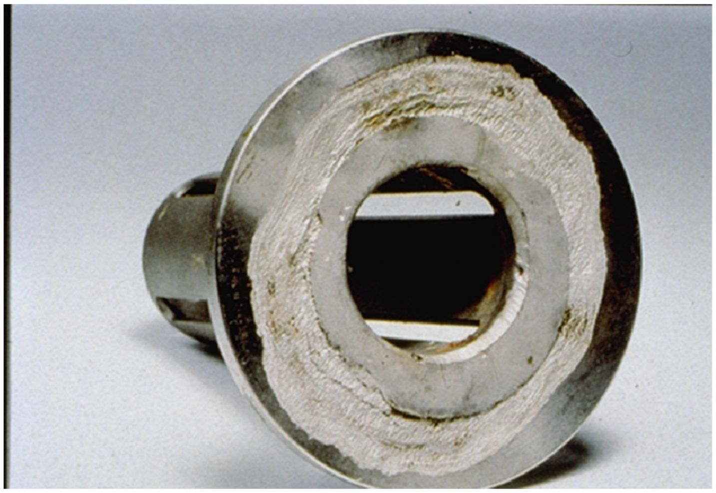


Fig. 5-13 Crevice Corrosion

Mechanism

There are two basic mechanisms of crevice corrosion:

- Oxygen concentration cell corrosion
- Metal ion concentration cell corrosion

In Oxygen concentration cell crevice corrosion, the difference in oxygen concentration between the areas outside and outside the crevice causes a potential difference between these areas. Oxygen concentration primarily affects the activity of the cathodic reactions involved in corrosion. Where the cathodic activity is high, the area will act as a cathode with respect to areas where the cathodic activity is low. In many natural environments, the most common cathodic reactions are the reduction of oxygen or water.

Water reduction $2H_2O + O_2 + 4e^- \rightarrow 4(OH)^-$

Oxygen reduction $O_2 + 4H^- + 4e^- \rightarrow 2H_2O$

In both of these reactions, oxygen appears as a reactant. A basic principle in chemistry is the law of mass action, which says that an increase in the concentration of reactants will increase the reaction. The law which states that the build-up of reaction products will tend to stifle the reaction. The Nernst equation is a mathematical expression of this basic concept. In both of the above cases, an increase in oxygen content will tend increase the cathodic reaction, whereas a decrease in oxygen content will tend to reduce the cathodic reaction. An area with a more active cathodic reaction will tend to act as a cathode with respect to area with a less active cathodic reaction.

The area within a crevice will become depleted quickly in oxygen because of corrosion reaction and other reaction that consume oxygen. Thus, the area within a crevice will become anodic with respect to the outside area, where the high oxygen content drives the cathodic reaction. (Refer to figures 5-11 and 5-14).

As a result, concentration cell corrosion from oxygen concentration results in corrosion concentrated deep within the crevices, as shown in figures 5-10 to 5-14.

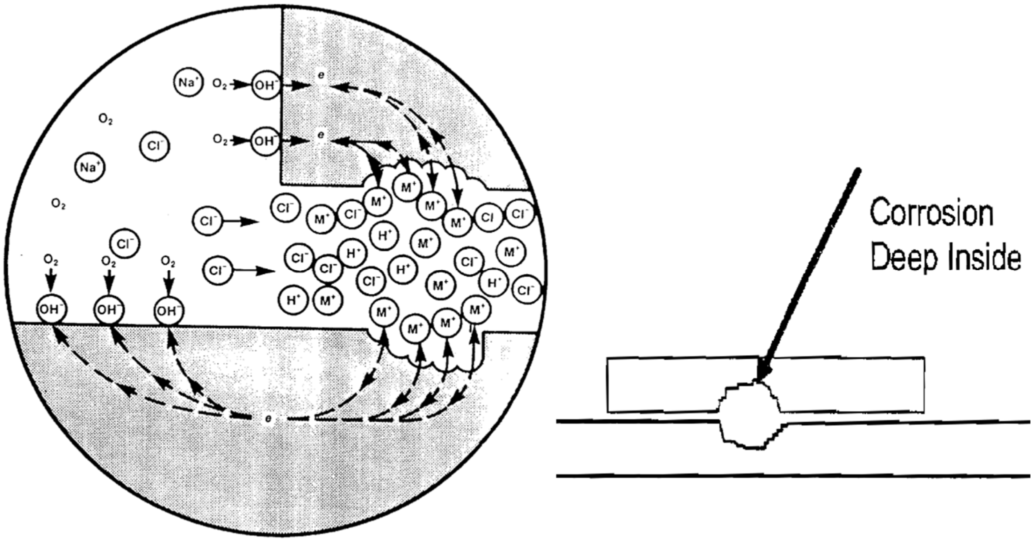


Fig. 5-14. Oxygen concentration cell crevice corrosion

As with pitting, the initial driving force of an oxygen concentration cells causes corrosion to initiate, but that corrosion can be further accelerated by the accumulation of acidic hydrolyzed salts within the crevice.

In metal ion concentration cell corrosion, the difference in potential between the inside and the outside of the crevice is caused by a difference in metal ion concentration. The Nernst equation can be used to better understand concentration cell corrosion. By comparing the potentials at high and low concentration with the standard potentials, the potential difference between these areas can be calculated.

Say that the reaction is $Cu^0 \rightarrow Cu^- + 2e^-$ and the low concentration of Cu^{++} is 0.01 and the high concentration of Cu^{++} is 0.1. The potential of the cell created between theses areas is:

$$E_{high\,-low} = -(0.059/2)\ \log\ (00.01/0.1) = +0.295\ V$$

In this case, the positive potential indicates that the potential of the surface in contact with the high concentration of metal ions is more positive than the surface in contact with the low concentration of metal ions.

In an electrochemical cell, the surface with a more positive potential will act as a cathode. The area of the cell exposed to the high metal ion concentration that exists inside the crevices will act as a cathode with respect to the area with low metal concentration outside the crevice. In metal ion concentration cell crevice corrosion, the corrosion is usually concentrated at the enterance to the crevice, as shown in figure 5-15.

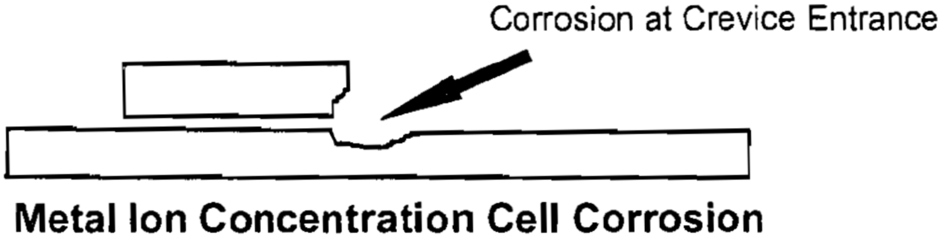


Fig. 5-15. Metal ion concentration cell crevice corrosion.

Localized corrosion, similar in appearance to crevice corrosion, can occur because of restricted access of corrosive solution to certain areas of the surface. For example, in structures exposed to atmosphere, the surfaces within the crevices may be subjected to considerably longer period of wetting than boldly-exposed surfaces, which tend to dry easily. The mechanism of this attack is not concentration cell corrosion; the attack occurs primarily because of difference in time of wetness.

Types

Cevices corrosion can occur under many circumstances such as:

- In metal-to-metal crevices, such as thread fasteners, couplings, or joints.
- In metal-to-nonmetal crevices under gasket or wet insulation (the later is sometimes called “Poultice” attack)
- Under deposits of debris or corrosion products.

Metal ion or oxygen concentration corrosion cell can occur in both metal-to-metal and metal-to-nonmetal crevices.
In case of corrosion under debris or corrosion products, the deposit can either be inert (e.g,. sand) or electrochemically active (e.g., carbonaceous material or magnetite. In case of electrochemically-active deposits, the crevice attack is further accelerated by differential potential between the deposit and the underlying metal.

Crevice Corrosion- Performance of Metals and Alloys

Crevice corrosion occurs most commonly on passive film protected metals, such as:

- Aluminum and aluminum alloys
- Stainless steel and nickel-based alloys
- Titanium and titanium alloys
- Zirconium and zirconium alloys
- Copper alloys

Aluminum and Aluminum Alloys

Aluminum and aluminum alloys are attacked by crevice corrosion in many environments. Crevice corrosion of aluminum alloys in marine environments is particularly common. The most common form of crevice corrosion on aluminum alloys is due to oxygen concentration cells.

Stainless Steel and Nickel-based Alloys

Although resistance varies with composition, many stainless steels are susceptible to crevice corrosion. Crevice corrosion of stainless steel in marine environments is particularly common. Crevice corrosion on stainless steels is caused most commonly by oxygen concentration cells. Molybdenum addition increase the resistance to of stainless steels to crevice corrosion in many environments.

Many nickel alloys are subjected to crevice corrosion in a manner analogous to austenitic stainless steel. The molybdenum-bearing varieties seem to be more resistant and distinctly superior to the stainless steels, but even the highly-resistant alloys may be attacked under sever conditions.

Titanium and Titanium Alloys

Titanium depends on a passive film for its resistance. It can suffer sever crevice corrosion in hot brines and other environments where conditions inside a crevice area allow breakdown of the passive film.

Zirconium and Zirconium Alloys

Zirconium and zirconium alloys are reactive metals similar to titanium. They can corrode in crevices where corrosive species such as Fe^{+3} or Cu^{++} accumulate or concentrate.

Copper Alloys

Copper alloys are subjected to metal ion concentration cell corrosion in many environments. This form of crevice corrosion is often not a significant problem as it occurs at the enterance of the crevice, where some corrosion damage is acceptable. Crevice corrosion deep within crevices is usually a greater problem, particularly in the case of seals, where corrosion inside the crevice can cause leaks.

Control of Crevice Corrosion

The control of crevice corrosion is complicated by the difficulty of affectively reaching the environment within the crevice. The principle option for control of crevice corrosion are:

- Material Seleection
- Design
- Cathodic Protection

Material selection is an obvious way to control crevice corrosion: Simply use materials less subject to this problem. However, this means of control is often made difficult because it is nearly impossible to predict the severity of the crevices that will actually be created in the service environment. To determine which alloys are resistant, some type of testing is required. To be valid, the test must reproduce the actual crevice environment, including the depth and tightness of the crevice. Many test crevices tend to be more severe than those actually encountered in field application. As a result, alloys are more resistant than required are selected for use. While this is conservative practice, the more resistant materials are usually more expensive and the extra expense may not be justified.

Design is used to control crevice corrosion, primarily by eliminating crevices. Ways to eliminate crevices will be covered in more details in this book. Some of the ways in which design can eliminate crevices are:

1. Using butt-welded joints instead of lap-welded or bolted joints
2. Sealing of lap joints where they can not be avoided
3. Avoiding skip welds
4. Providing a complete drainage
5. Avoiding materials that can hold moisture in contact with substrate
6. Providing surfaces that can be kept clean easily and kept free of debris.

Cathodic protection is very effective in controlling crevice corrosion.
Cathodic protection makes the potential of the outside more negative; thus, the difference in potential between the inside and the outside of the crevice is reduced.
Cathodic protection also produces alkalinity on the protected surface outside the crevices. This alkalinity can diffuse into the crevice and reduce the acidic effect of hydrolyzed slats inside the crevice.

5.2.2.5 Filiform Corrosion

Defination

Filiform corrosion is a special form of oxygen cell corrosion occuring beneath organic or metalic coatings on material. The attack results in a fine network of random “threads” of corrosion product developed beneath the coating material.

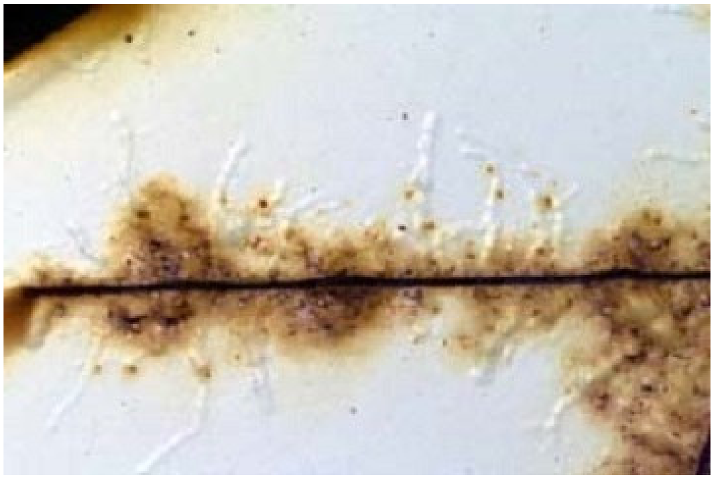


Fig. 5-16. Filiform corrosion on painted steel

Fig. 5-16. Filiform corrosion on steel drum lid

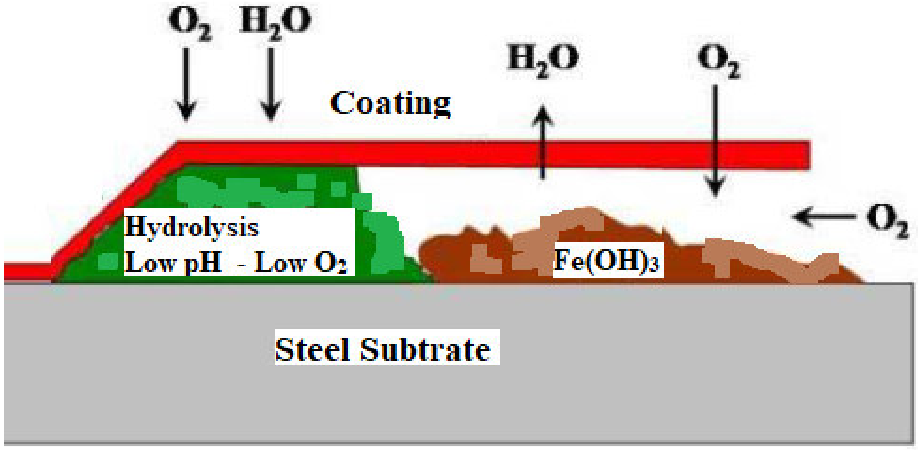


Fig. 5-17. Filiform corrosion mechanism

Such attack developed beneath coating in a high humidity (>60% RH) environment on such items as coated cans, office furniture, cameras, aircraft structures, auto interiors and exteriors, and a host of other common products.

Mechanism

The mechanism of filiform corrosion is similar to that of crevice corrosion in that It is driven by the potential difference between the advancing head of the attack and the area behind the head of the advancing attack. In filiform corrosion, the head of the advancing filament (about 0.1 mm wide) becomes anodic, with low pH and a lack of oxygen, as compared to with the cathodic area immediately behind the head , where oxygen is available through semipermeable film. Corrosion proceeds as the cathode follows behind the anodic area. Water and oxygen in the cathodic area convert the anodic products to the usual oxides of the metal.

The cause of the filiform corrosion appears to be associated with mild surface contamination of solid particles deposited from the atmosphere or residue on the metal surface after processing. Such surfaces exposed to humid atmospheres will often suffer filliform corrosion.

Filiform corrosion does not normally result in significant corrosion of the metal surface. It can decay the adhesion of the paint film, resulting in the eventual attack of the metal.

Filiform Corrosion – Performance of Metals and Alloys

Filiform corrosion can occur under semipermeable coatings on steel, zinc, aluminum, and magnesium alloys exposed to high-humidity (>60% RH) environments.

Control of Filiform Corrosion

This type of corrosion, particularly on painted surfaces, can be prevented by proper cleaning and preparation of the metallic surface and then applying the coating only to a thoroughly-cleaned and dried surface.

5.2.2.6 Pack Rust Corrosion

Pack rust is a form a localized corrosion typical of steel components that develop a crevice into an open atmospheric environment. This expression is often used in relation to bridge inspection to describe built-up members of steel bridges, which are showing signs of rust packing between steel plates.

Fig. 5-18. Pack rust corrosion

5.2.3 Galvanic Corrosion (Bi-metallic corrosion)

5.2.3.1 Introduction

Galvanic corrosion is a form of corrosion which occurs because of the potential differences between metals. Galvanic corrosion occurs through the action of the electrochemical cell.

5.2.3.2 Definition

Galvanic corrosion is defined as corrosion accelerated by the potential differences between different metals when they are in electrical contact and exposed to an electrolyte.

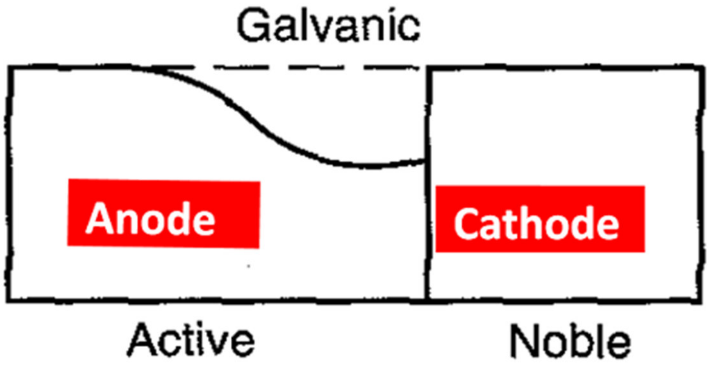


Fig. 5-19. Galvanic corrosion

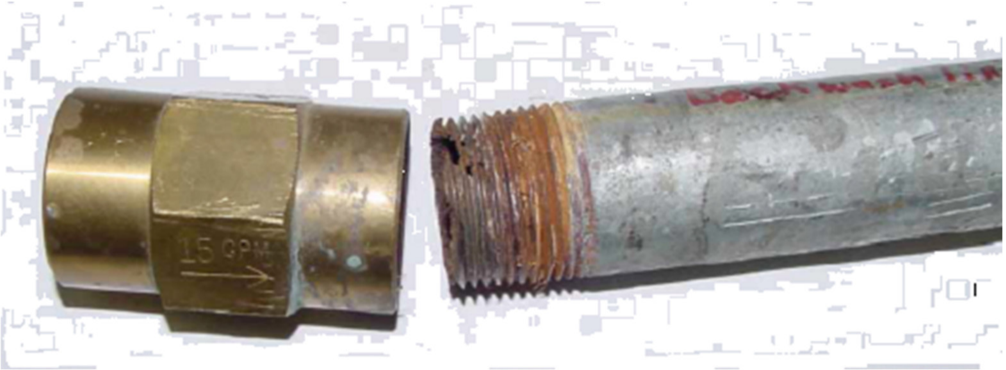


Fig. 5-20. Galvanic corrosion in steel connected to copper joint.

Fig. 5-21. Galvanic corrosion in steel connected to copper.

Galvanic corrosion can also occur between a metal and an electrically-conductive nonmetal such as graphite. Carbon in plastics and elastomers may aslo be electrochemically active and can cause galvanic corrosion. Such corrosion products as magnetite (Fe_3O_4) and sulfides can also be electrochemically active and are cathodic with respect to most metals. Ions of more noble metal may be reduced on the surface of a more active metal (e.g., copper on aluminum). The resulting metallic deposit provides cathodic sites for further galvanic corrosion of the more active metal.

The electrical contact between the dissimilar materials may be through either direct contact, or an external conductive path.

In galvanic corrosion, the rate of attack of one metal or alloy is usually accelerated, while the corrosion rate of the other is usually decreases.

Galvanic corrosion can be recognized by either increased corrosion of the anodic material, or decrease corrosion of the cathodic material. Galvanic corrosion is often pronounced, where dissimilar materials are immediately adjacent to each other at the sharp edges or corners.

5.2.3.3 Mechanism

Electrochemical Process

The mechanism of galvanic corrosion is the classical electrochemical cell. As discussed previously, the electrochemical cell requires four factors to be present.

- **Anode**

The anode is the site where metal is lost and electrons are produced.

- **Cathode**

The cathode is the site where the electron produces at the anode are consumed.

- **Metallic path.**

The metallic pass conducts electrons from the anodic sites to the cathodic sites.

• Electrolyte

The electrolyte provides reactants for the cathodic reactions and allow the flow of ions.

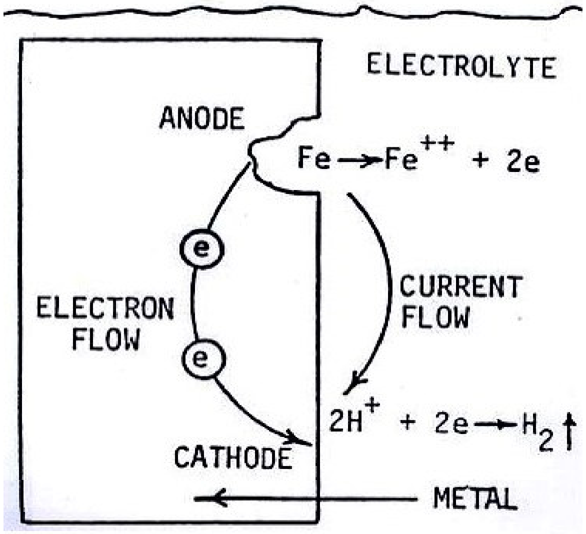


Fig. 5-22. Corrosion cell.

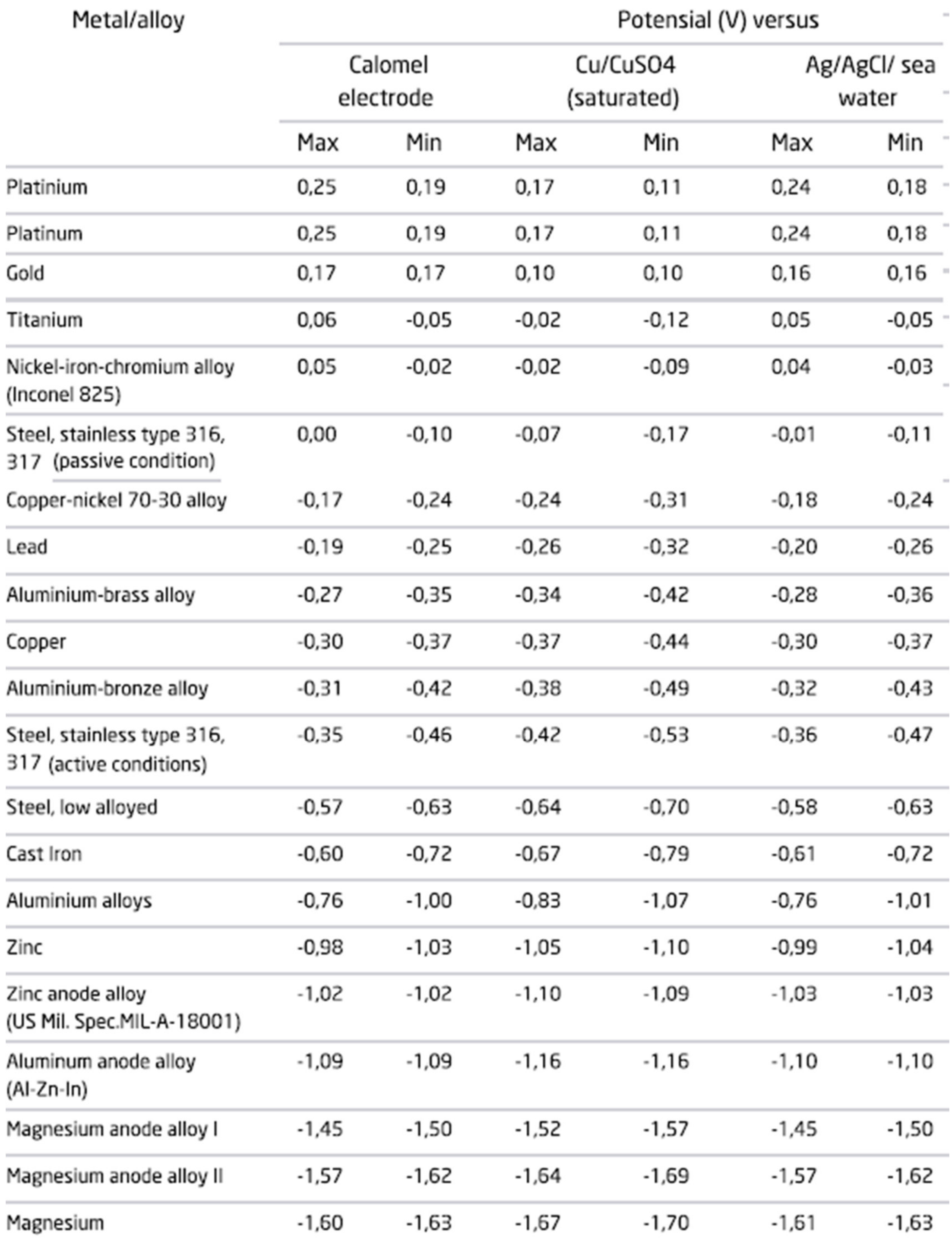
For galvanic corrosion to occur, all this four components must be present and active.

In galvanic corrosion, electrons flow through a metalic path from sites where anodic reactions are occuring to sites where they allow cathodic reaction to occur. Electrical current flows through the electrolyte to balance the flow of electrons in the metalic path.

Galvanic corrosion is driven by the potential differences between metals or electrically conductive nonmetals when exposed to an electrolyte. Nonmetals include such electrically conductive materials as graphite. In some cases, the cathodic member of a galvanic couple can be a deposit formed by the deposit of metal ions from solution onto the anodic metal surface.

5.2.3.4 Galvanic Series

A galvanic series is simply a listing of metals in the order of their potential in a specific electrolyte. A galvanic series for seawater is shown below.



Metal/alloy	Potensial (V) versus					
	Calomel electrode		Cu/CuSO4 (saturated)		Ag/AgCl/ sea water	
	Max	Min	Max	Min	Max	Min
Platinium	0,25	0,19	0,17	0,11	0,24	0,18
Platinum	0,25	0,19	0,17	0,11	0,24	0,18
Gold	0,17	0,17	0,10	0,10	0,16	0,16
Titanium	0,06	-0,05	-0,02	-0,12	0,05	-0,05
Nickel-iron-chromium alloy (Inconel 825)	0,05	-0,02	-0,02	-0,09	0,04	-0,03
Steel, stainless type 316, 317 (passive condition)	0,00	-0,10	-0,07	-0,17	-0,01	-0,11
Copper-nickel 70-30 alloy	-0,17	-0,24	-0,24	-0,31	-0,18	-0,24
Lead	-0,19	-0,25	-0,26	-0,32	-0,20	-0,26
Aluminium-brass alloy	-0,27	-0,35	-0,34	-0,42	-0,28	-0,36
Copper	-0,30	-0,37	-0,37	-0,44	-0,30	-0,37
Aluminium-bronze alloy	-0,31	-0,42	-0,38	-0,49	-0,32	-0,43
Steel, stainless type 316, 317 (active conditions)	-0,35	-0,46	-0,42	-0,53	-0,36	-0,47
Steel, low alloyed	-0,57	-0,63	-0,64	-0,70	-0,58	-0,63
Cast Iron	-0,60	-0,72	-0,67	-0,79	-0,61	-0,72
Aluminium alloys	-0,76	-1,00	-0,83	-1,07	-0,76	-1,01
Zinc	-0,98	-1,03	-1,05	-1,10	-0,99	-1,04
Zinc anode alloy (US Mil. Spec.MIL-A-18001)	-1,02	-1,02	-1,10	-1,09	-1,03	-1,03
Aluminum anode alloy (Al-Zn-In)	-1,09	-1,09	-1,16	-1,16	-1,10	-1,10
Magnesium anode alloy I	-1,45	-1,50	-1,52	-1,57	-1,45	-1,50
Magnesium anode alloy II	-1,57	-1,62	-1,64	-1,69	-1,57	-1,62
Magnesium	-1,60	-1,63	-1,67	-1,70	-1,61	-1,63

Table. 5-3. Galvanic series of metals in seawater.

Galvanic corrosion affects the anode in the couple by increasing its corrosion rate. The form of this corrosive attack may be by general attack, pitting, or some other form of corrosion. Galvanic activity does not control the form of corrosion, which occurs at the anode; it only increases the rate of attack.

Galvanic corrosion affects the cathode of the couple in several ways.In general, the corrosion that would normally occur if the cathode were exposed to the environment by itself will decrease when it is coupled to a more active material. In some cases, however, the cathode can be adversely affected. Hydrogen embrittlement, a form of corrosion that will be discussed later in this section, can result. In addition, the alkaline cathodic reaction products formed in a galvanic cell can adversely affect some materials such as aluminum. Metals that are chemically vulnerable in both acidic and alkaline environments, known as amphoteric materials, can be affected at the cathode in a galvanic corrosion cell. Such attacks are called amphoteric effects.

5.2.3.5 Galvanic Corrosion Rates

The extent of accelerated corrosion resultin from galvanic coupling is affected by the following factors:

1- The potential difference between the metals or alloys.
2- The specific nature of the environment
3- The polarization behaviour of the coupled materials
4- Spatial effects, such as area, distance, and cell geometry
5- Resistivity of the electrolyte

1- Potential Difference

The potential difference between material causes current flow when dissimilar materials are coupled in a suitable electrolyte. The direction of current flow depends on which metal is more active. The more active metal becomes the anode, while the less active metals becomes the cathode. The magnitude of the driving force for galvanic attack in this couple is the difference in potential between these electrodes.

To determine the specific effects between specific materials in a specific environment, it is necessary to know the galvanic series for those materials in the environment of interest. Such an empirically-developed galvanic series of metals and alloys may be useful for predicting galvanic relationships of metals and alloys according to their potentials, measured in a specific electrolyte. It allows one to determine which metal or alloy in the galvanic couple is more active in the environment of interest. The difference is measured potential between two metals or alloys in this galvanic series can give a prediction of the probable magnitude of corrosive effects.

Most commonly when someone mention “the galvanic series”, it is in reference to a table which has been constructed from measurements in seawater. With certain exceptions, this series is broadly applicable in other natural waters and in uncontaminated atmospheres.

In general, electrode potentials are sensitive to the following factors:

- Electrode composition
- Electrolyte composition
- Temperature
- Degree of agitation
- Presence of depolarizers, inhibitors, or both
- Surface condition of electrodes
- Metallurgical conditions of the electrodes

Any differences in these factors between the environments for which a galvanic series was developed and the intended service environment can cause a reordering of materials in the series.

2- Nature of Environment

Galvanic corrosion can occur under either immersion or atmospheric conditions. Under immersion conditions, galvanic effects cover essentialy the exposed surface of anode and cathode. Because the effect of the electrolyte resistance, galvanic effects are usually concentrated where the anode and cathode are closer together. In atmospheric exposures, the resistance effects in the electrolyte limit the range of galvanic effects to the area where the two electrodes are in contact (when this area is filled with electrolyte) and for a very short distance around the contact area. This distance is usually in the order of 1 mm to 2 mm.

3- Polarization

As shown in chapter 2, polarization of the anodic and cathodic areas, can have a very larg effect on the intensity of the anode’s corrosion. If neither the anode nor the cathode polarizes significantly, the amount of current flow will be large; and the resulting galvanic will also be large.

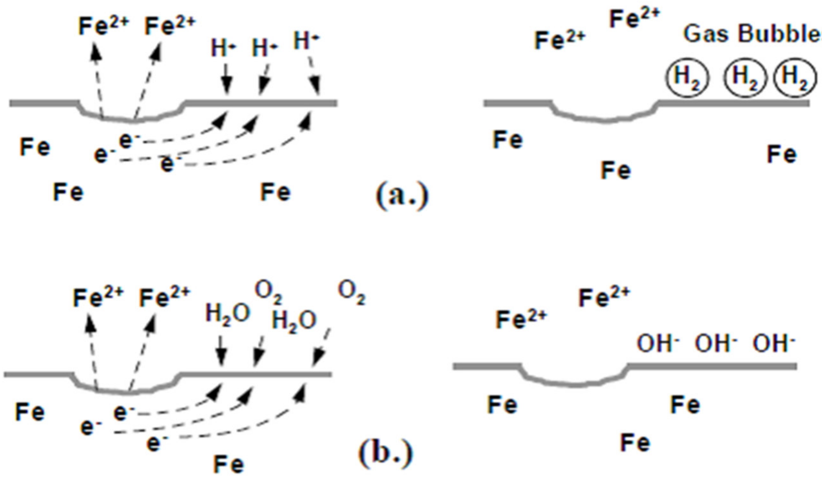


Fig. 5-23. Cathodic polarization due to accumulation of H_2 gas (A), and accumulation of OH^- ions (B) in case of cathodic reaction in the presence of oxygen.

4. Spatial Effects, Area, Distance, and Cell geometry Effects

Area Effects

Area effects in galvanic corrosion involve the ratio of surface areas of the cathode to the anode. As discussed in chapter 2, the galvanic corrosion, which occurs when the exposed area of the anode is small with respect to the exposed area of the cathode under immersion conditions, the intensity of the attack on the anode can be very high.

Conversely, if the exposed area of the anode is large with respect to the exposed area of the cathode, the acceleration of corrosion at the anode may be negligible. In atmospheric environments, since the affected area is only the wetted contact area and few millimeters beyond, the effective are ration is effectively 1 to 1. Figures 5-24 to 5-26, illustrate the anode/cathode area effect.

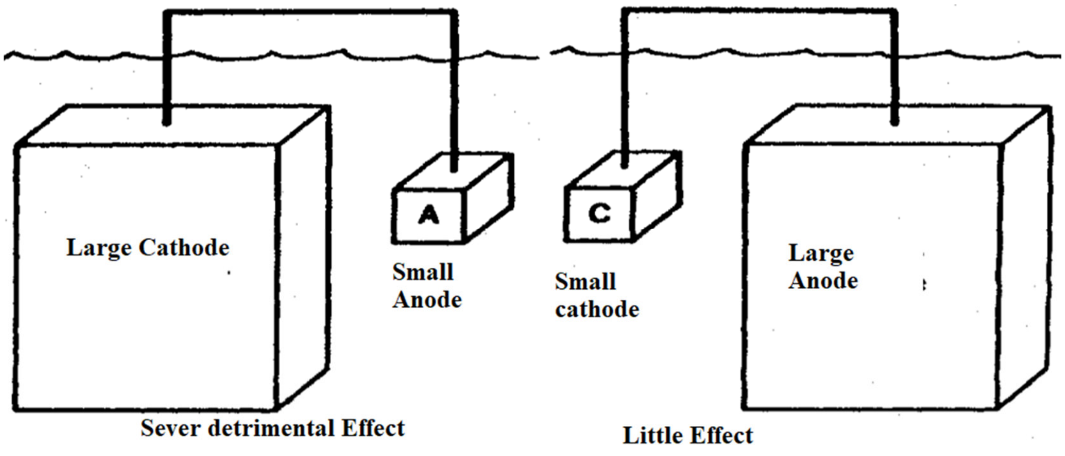
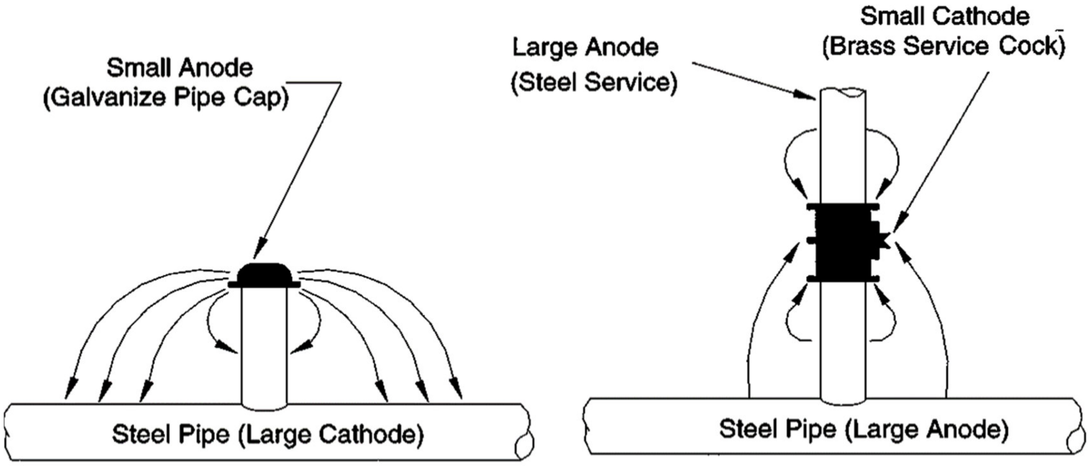


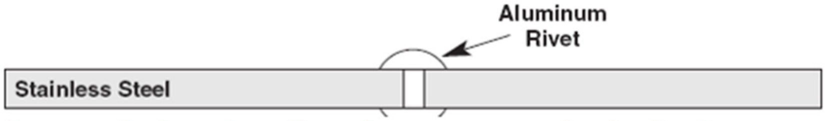
Fig. 5-24. Effect of anode/cathode area ratio



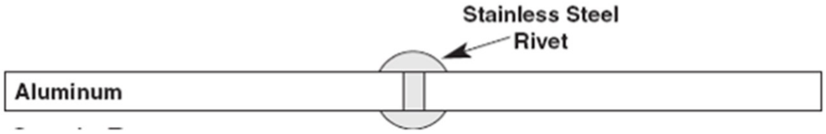
Small Anode - Large Cathode. (Corrosion At Anode Severe).

Small Cathode - Large Anode. (Relatively Mild Corrosion At Anode).

Fig. 5-25. Effect of anode/cathode area ratio



Large cathode and small anode, severe corrosion in aluminum



Large anode and small cathode, low corrosion in aluminum

Fig. 5-26. Effect of anode/cathode area ratio

Distance Effects

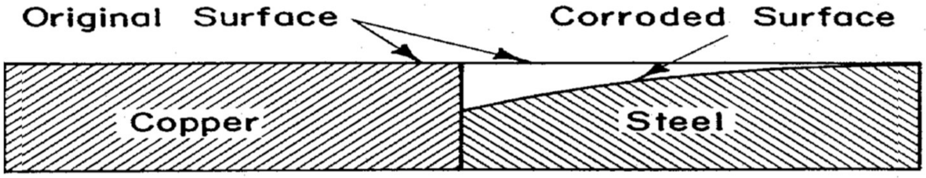
In a galvanic couple under immersion conditions, most of the corrosion occurs near the junction because of the effects of electrolyte resistivity. In high resistivity electrolytes, this effect at the junction between the anode and the cathode is more pronounced than in low-resistivity electrolytes.

Geometric Effects

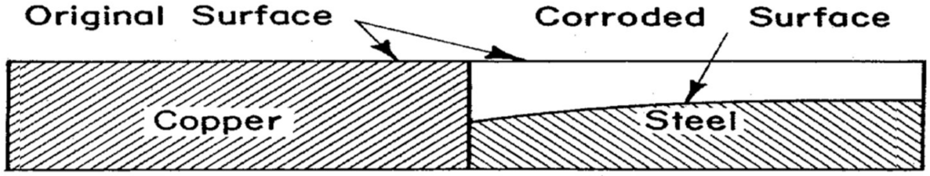
Cell geometry exerts an effect to the extent that current will not readily flow around obstacles. For example, the interior pipe cannot be protected by application of an external current. At the anode, because of current gradient effects, galvanic corrosion tends to be concentrated on sharp points or edges.

5. Electrolyte Resistivity Effects

Since the electrolyte is the element in the circuit, which allows galvanic current flow, the resistivity of the electrolyte will affect the flow of current in the cell. All other things being equall, less corrosion current will flow in a cell that has a high-resistivity electrolyte than in one with low-resistivity electrolyte. Because the corrosion of the anode is a direct function of this current, galvanic corrosion is usually less intense in electrolytes with higher resistivity.Refer to figure 5-27.



Extent of Corrosion of steel in contact with copper in a tap water environmet



Extent of Corrosion of steel in contact with copper in seawater environment

Fig. 5-27. Effect of electrolyte resistivity on galvanic corrosion.

5.2.3.6 Predicting Galvanic Attack

While it is fairly easy to predict the likelihood of galvanic attack and to identify which metal is likely to suffer increased attack as an anode, exact predictions of changes in corrosion rate is difficult.

Potential measurements can be used to develop a galvanic series for a specific environment if one is not available. Only those metals that are candidates for evaluation need to be included in the series. It should be pointed out that metals and alloys forming passive films will exhibit varying potentials with time; therefore, it will be difficult to position them in the series with certainty.

It is possible to predict galvanic corrosion rates by measuring the current flow in a model couple that reproduced the relative area and other important factors is the proposed application. It is important to remember that the rate may change with time , so long-term current flow must be evaluated to make a good prediction of actual service performance. In performing there tests, a specialized ameter with “zero effective” resistance is used to measure the current flow between the anode and the cathode in the external circuit. It is important that a zero resistance ammeter be used for these measurements, because even a small resistance inserted into the circuit can significantly reduce the current flow.

Measurements of the polarization characteristics of the candidate materials in the service environment can also be used to predict galvanic corrosion rates. The polarization curves are plotted on Evans diagrams that predict total current flow, and the current density on the anode can be calculated.

In most cases, these methods can be used to predict galvanic corrosion tendencies (i.e,. to identify anode and cathode) relatively well. They also give good relative prediction of galvanice corrosion rates. There can be significant differences between the predicted rates using this method and the actual rates experienced in service. The best method for predicting galvanic corrosion rates is to expose model couple of the candidates materials in the intended service environment and compare the galvanic corrosion rate with the rates of the uncoupled materials.

5.2.3.7 Galvanic Attack – Performance of Metals and Alloys

The performance of specific metals and alloys can be estimated from their position on the galvanic series. In general, metals higher (i,e,. more negative) in the galvanic series will be affected by contact with a wider variety of materials that are more positive (less negative) in the galvanic series. Of course, it is the relative position of the materials making up a specific couple that must be evaluated dor each application where galvanic corrosion is a concern.

Magnesium and magnesium alloys occupy an extremely active position in most galvanic series and therefore, are highly susceptible to galvanic attack. Magnesium is widely used as a sacrificial anode in cathodic protection.

Aluminum and aluminum alloys also occupy active positions in the galvanic series. In “chloride-bearing” solutions, aluminum alloys are susceptible to “galvanically-induced” localized corrosion, especially dissimilar-metal crevices. In this type of environment, severe galvanic effects are observed when aluminum alloys are coupled with more nobel metals and alloys. Galvanic effects are also observed in the presence of deposited heavy metals such as copper, mercury, or lead. Some aluminum alloys are used for sacrificial anodes in seawater. An active aluminum aloy is used to “clad” aluminum, protecting it against pitting in some applications.

Zink is an active metal, susceptible to galvanic attack. It is widely used for galvanic anodes in cathodic protection as a sacrificial coating applied by hot-dip galvanization or electroplating and as pigment in certain types of coatings.

Carbon low-alloy stells are fairly active materials and require protection againest galvanic attack by more noble materials. Galvanic attack on carbon and low-alloy steels, when are anodic in a galvanic corrosion cell, is usually in the form of general attack.

Galvanic attack of stainless steels is difficult to predict because of the influence of passivity. In the common galvanic series, a nobel position is assumed by stainless steels when in the passive state, while the less noble position is assumed in the active state. This dual position in chloride-bearing aqueous environments has been the cause of some serious design errors. More precise information on the galvanic behaviour of stainless steels can be obtained using polarization curves, critical potentials, and the mixed potential of the galvanic couple.
In chloride bearing environments, “Galvanically-induced” localized corrosion of some stainless steels occurs in couples with copper or nickel (and their alloys) and other more noble materials. Couples of stainless steel and copper alloys are often used with impunity in fresh-water cooling systems. Iron and steel tend to protect stainless steel in aqueous environments when galvanically coupled. The passive behaviour of stainless steels makes them easy to polarize so that galvanic effect on other metals or alloys tend to be minimized. Because of the passive film on both alloys, galvanic corrosion between stainless steel and aluminium in seawater is much less severe that would be anticipated by their difference in position on the galvanic series, particularly if the anode/cathode area is favorable.

Nickel and its alloys are not reaily polarized and, therefore, will cause accelerated corrosion to more active materials such as aluminum and ferrous alloys. In chloride bearing solutions, nickel is somewhat more noble than copper, and the cupronickels lie some where in between. Nickel and its alloys are similar to copper alloys in their effects on stainless steels. In some environments, the cast structure of a nickel weld may be anodic to the parent metal. With the chromium-nickel alloys, the combination of a passive surface with the inherent resistance of the nickel-based alloys (e.g., Allloys 600, 625, C276) places them in more noble positions in the traditional galvanic series. In chloride bearing solutions, Alloy 600 is reported to occupy two positions because of the existance of active and passive states in a manner similar to stainless steels. These alloys are readily polarized, and galvanic effects on other less noble metals and alloys tend to be minimized.

Lead and tin form oxide films that can shift their potentials, to more noble value. In some environments, they may occupy more noble positions than one might expect. For example, the tin coating in tin cans is anodic to steel under the anaerobic conditions within the sealed container, but it becomes cathodic when the can is opened and exposed to air.

Copper and its alloys occupy an intermediate position in the galvanic series. They are not readily polarized in chloride-bearing aqueous solutions and, therefore, may cause severe accelerated corrosion of more active metals such as aluminum , its alloys, and ferrous metals.

Titanium, Zirconium, and tantalum are extremely noble because of their passive films. In general, these alloys are not susceptible to galvanic attack, and their ease of polarization tends to minimize adverse galvanic effects on other metals or alloys. Because of the ease with which they pick up hydrogen in the atomic state, they may themselves become embrittled in galvanic couples if the anodic member corrosed rapidly, with H_2 evolution proceeding at a very rapid rate.

"Noble metals" such as gold and silver do not cathodically polarize rapidly and, therefore, can have marked effect in galvanic couples with other metals or alloys. This effect is observed with gold and silver coating on copper, nickel, aluminum, and their alloys.

Graphite, either in pure form or as an additive to plastics and elastomers, can have an adverse effect on most other materials when they are galvanically coupled. Graphite has a very low position on the galvanic series and does not polarize readily. Thus, its effect on other materials can be severe.

5.2.3.8 Control of Galvanic Attack

Galvanic corrosion can be controlled in several ways, including:

1. Design
2. Material selection
3. Electrical isolation
4. Barrier coatings
5. Cathodic protection
6. Modification of environment

1. Design

Unfavourable area ratios should be avoided. Use metal combinations in which the more active metal or alloy surface is relatively large. Revets, bolts and other fasteners should be of a more noble metal than the nmaterial to be fastened.

Avoid dissimilar metal crevices such as those that occur at threaded connections. Crevices should be sealed, preferably by welding or brazing, through putties are sometimes used effectively.

Provide an appropriate corrosion allowance of the more active member.

2- Material Selection

combinations of metals or alloys widely separated in the relevant galvanic series should be avoided, unless the more noble material is easily polarized. Metallic coatings can be used to reduce the separation in the galvanic series.

3- Electrical Isolation

The joint between the dissimilar metals can be insulated to break the electrical continuity. Use of nonmetallic inserts, washers, fittings, and coatings at the joint between the materials will provide sufficient electrical resistance to eliminate galvanic corrosion.

When electrical isolation is used to control galvanic corrosion, it is important to verify that isolation has actually being achieved. In atmospheric exposures, this can been verified using a simple ohmmeter. When both members of the couple are exposed to such an electrolyte as liquid or soil, resistance tests are not useful because low resistance will be read through the electrolyte even if the metals are effectively isolated. In these cases, more sophisticated instruments that discriminate between electrical metallic conductivity and electrolytic conductivity must be used.

4- Barrier Coatings

Innert barrier coatings, organic or vitreous, can effectively isolate the metals from the environment. Note that it is potentially dangerous to coat only the anodic member of the couple. This reduces its area and severely accelerated attack can occur at "holidays", or "pores, in the protective coating. When using barrier coatings to control galvanic corrosion, always coat the cathode. Further protection may also be achieved by coating the anode.

5- Cathodic Protection

Metals, such as magnesium or zink, may be introduced into the galvanic assembly. The most active member will corrode, while providing cathodic protection to the other metals even when the other metals are electrically coupled. Impressed current cathodic protection systems provide the same effect.

6- Modification of Environment

In particular cases, it is possible to greatly reduce galvanic attack between widely dissimilar metals or alloys. Use of corrosion inhibitors is effective in some instances. Elimination of cathodic depolarizers (e.g., deaeration of water, or the use of oxygen scavengers such as sodium sulfite) can be effective in some aqueous environments.

5.2.4 Environmental Cracking

5.2.4.1 Introduction

Environmental cracking is an important form of corrosion. Unlike many other forms of corrosion, where the corrosion occurs over long periods of time, and such failures as leakage and structural collapse can be prevented through inspection, environmental cracking can occur very rapidly and result in a failure before inspection can identify damage.

Definition

Environmental cracking is the brittle failure of an otherwise ductile material, resulting from the combined action of corrosion and tensile stress.

Mechanism

The combined action of a tensile stress and a corrosion reaction is the principle characteristic of the environmental cracking phenomenon. In the absence of either the tensile stress or the corrosive environment, cracking will not occur. Failures resulting from this localized form of corrosion can be unanticipated and catastrophic because they occur in metals selected for their good corrosion resistance (e.g., stainless steel).

5.2.4.2 Recognition of Environmental Cracking

In environmental cracking, tight cracks are at right angle of the direction of maximum tensile stress. Single and multiple cracks can occur. A group of multiple cracks on the metal surface is commonly observed. Corrosion products can be found in the cracks, but the metal surface is usually clean, with no evidence of corrosion except for the fine network of cracks. Environmental cracks other than corrosion fatigue are often generally branched. They can either be intergranular and propagate along the metal grain boundaries, or transgranular, and propagate across the grains.

5.2.4.3 Controlling Cracking Factors

Many factors control whether or not a material will be susceptible to environmental cracking in a given situation. These factors includes:

- Tensile stress
- Alloy composition and structure
- Corrosion environment
- Corrosion potential
- Temperature

5.2.4.4 Types of Environmental Cracking

The following types of environmental cracking will be discussed in this chapter:

1- Stress corrosion cracking (SCC)
2- Hydrogen-induced cracking (HIC)
3- Liquid metal embrittlement (LME)
4- Corrosion fatigue (CF)

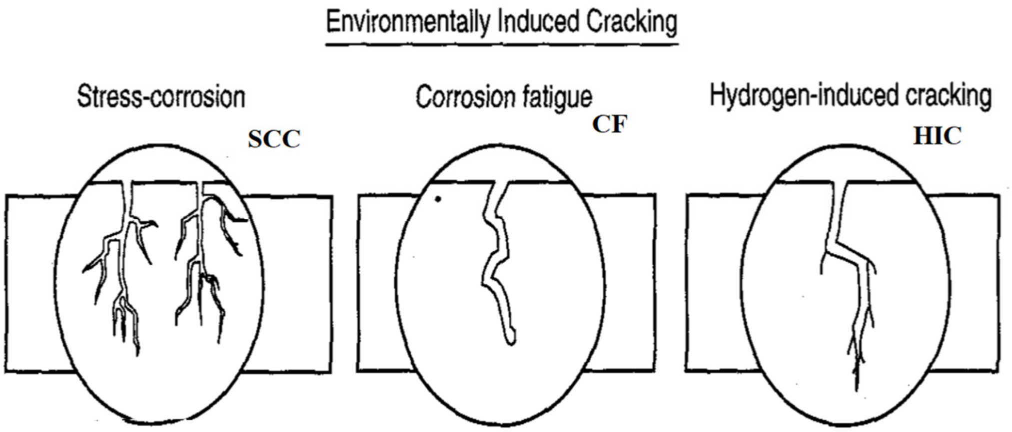


Fig. 5-28A. Environmental induced cracking.

1- Stress Corrosion Cracking (SCC)

Definition

Stress corrosion cracking is a brittle failure mode in an otherwise ductile metal, resulting from combined action of tensile stress and a specific corrosion environment.
Note that only a specific corrosive media promote stress corrosion cracking of an alloy system (e.g., caustic with carbon steel, chlorides with stainless steel, and ammonia with copper alloys).

All metals are potentially subject to SCC. The conditions necessary for stress corrosion are:
a - Suitable environment
b - Tensile stress
c - Sensitive metal
d - Appropriate temperature and pH values

Recognition

Stress corrosion cracking can be recognized by the brittle failure of an otherwise ductile material when exposed to a specific environment.

Mechanism

Stress corrosion cracking is an anodic process, a fact which is verified by the applicability of cathodic protection as an effective remedial measure.
Usually there is an incubation period, during which time cracking originates at a microscopic level. This is followed by actual propagation. Eventually, the cracks may be self-arresting to a large extent, as in the typical multi-branched trans-crystalline stress corrosion cracking, apparently because of localized mechanical relief of stresses.

We can say that stress corrosion cracking occurs in metals exposed in an environment where, if the stresses were not existing or even much lower, there would be no damage. Likewise, SCC would not occur if the structure, subject to the same stresses, where the environment that did not contain the specific corrodent for the material.

The term stress corrosion cracking implies the formation of cracks and, as indicated above, usually little metal loss or general corrosion is associated with it. If there is a severe general corrosion, stress corrosion cracking usually will not occur. The failure of stress bolt rusted away until it eventually cannot sustain the applied load is not classified as being due to stress corrosion. However, if products from general corrosion are trapped so as to cause stress in a structure, they can cause stress corrosion cracking.

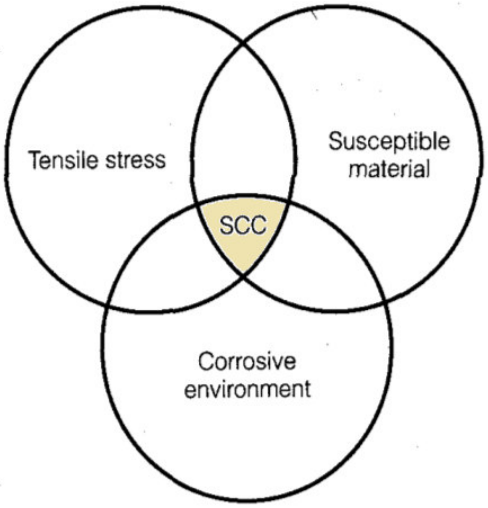


Fig. 5-28B. Simultaneous tensile stress, susceptible metallurgical condition, and critical corrosive solution required for stress corrosion cracking.

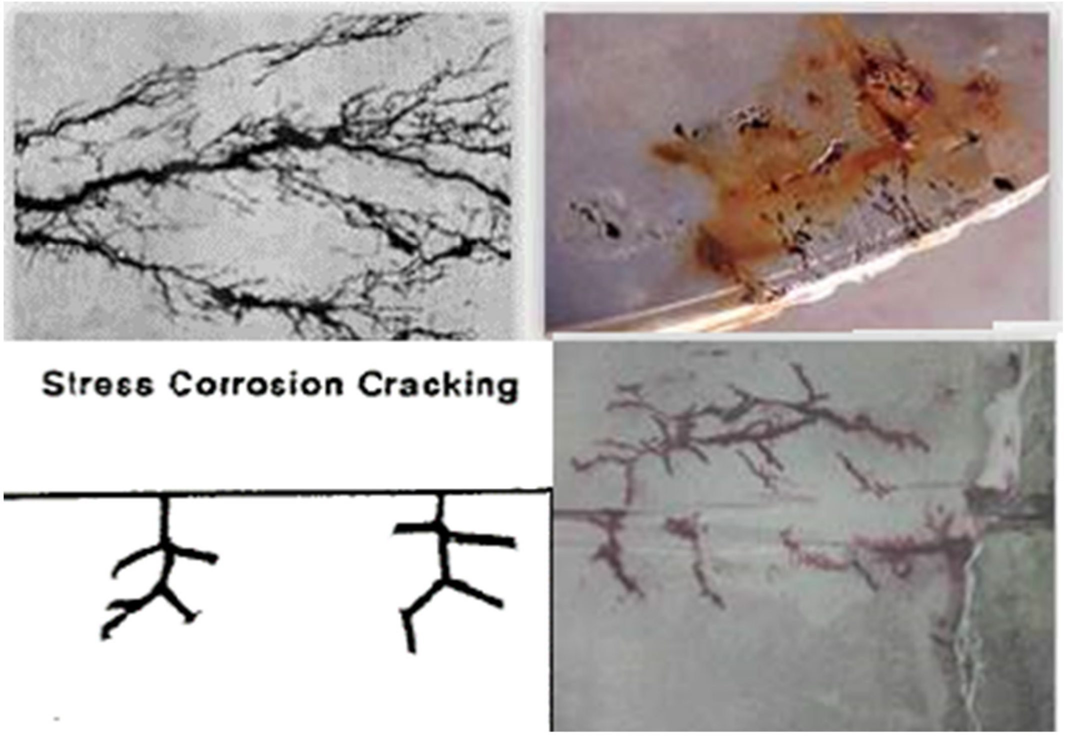


Fig. 5-29. Stress corrosion cracking.

Fig. 5-30. SCC on Stainless Steel Expansion Joint - Alkaline Water in Steam Line.

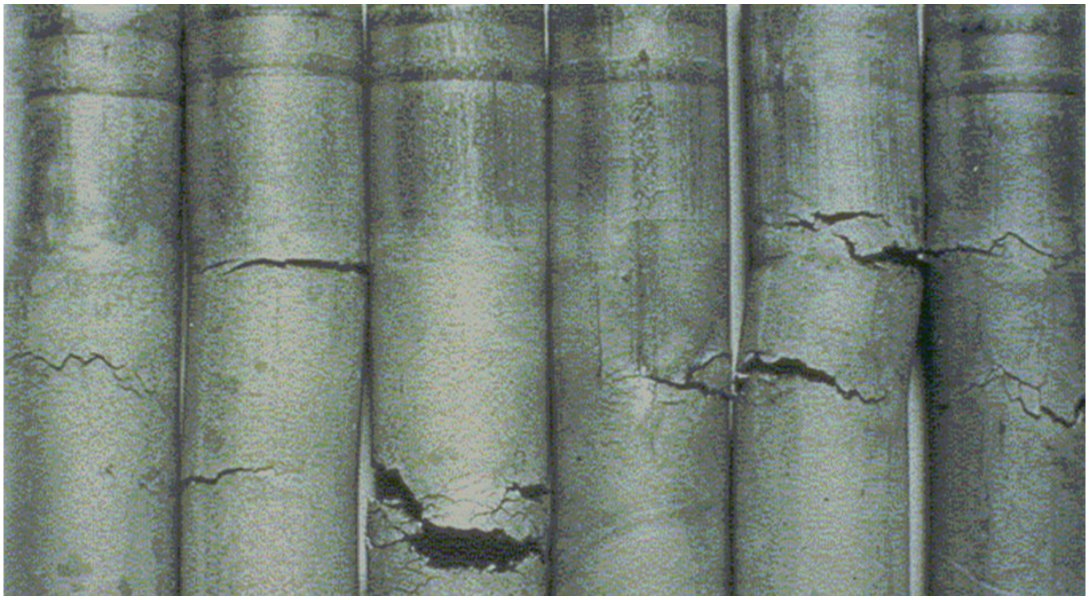


Fig. 5-31. SCC Stainless Steel Tubes in Vertical Condenser.

Fig. 5-32. Chloride induced stress corrosion cracking

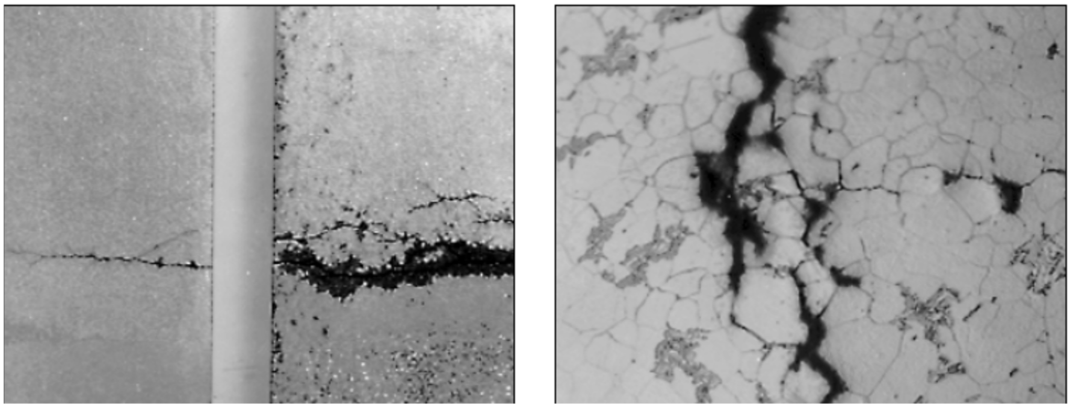


Fig 5-33. .Stress Corrosion Cracks Adjacent to Welds. Carbon steel test specimens exposed to calcium-ammonium nitrate fertilizer solution at 140°F. Note intergranular pattern of cracks. Magnification of left photograph is 1.5X; right is 500X.

Fig 5-34. SCC of Aluminum Brass Bolt - Steam with Traces of Ammonia.

SCC: Performance of Metals and Alloys

We will discuss the susceptibility of various alloys groupings to stress corrosion cracking.

These metal-environment combinations are illustrative only, and this is not to be considered as a final comprehensive listing.

Carbon and Low-Alloy Steels

Carbon steels containing sufficient residual or applied tensile stress are susceptible to stress corrosion cracking by caustics, anhydrous ammonia, nitrates, cyanides, bicarbonates, mixture of carbon monoxide-carbon dioxide-water, and many other corrosive species. Both intergranular and transgranular modes of cracking are encountered.

High strength steels [e.g., those with strengths above about 900 MPa (130,000 psi)] are susceptible to SCC in the same environment as carbon steel. As the material strength increases, so does its susceptibility to cracking.

Stainless Steels

Martensitic Grades

Stress corrosion cracking of martensitic stainless stells has been reported to be in hot concentrated caustic solutions. SCC has been reported in hardened martensitic stainless steels in some salt atmospheres.

Ferritic Grades

The ferritic grade tend to be resistant to chloride stress corrosion cracking, although they will suffer environmental cracking in hot concentrated caustic. The superferritics are resistant in caustic evaporators, but their performance is probably influenced by oxidizing contaminants in caustic.

Austenitic Grades

Transcrystalline stress corrosion cracking is induced in 18-8-type austenitic grades and related alloys by chlorides, and by hot concentrated caustic. The more highly-alloyed grades of higher nickel content have increasing resistance to chlorides, but not to caustic.

Precipitation-Hardened Grades

Depending on the heat treatment, precipitation-hardened grades may or may not be resistant to chloride stress corrosion cracking. In general, the heat treatments that give alloys a very high strength cause a susceptibility to chloride stress corrosion cracking.

Superaustenitic Grades

There are a number of more highly-alloyed austenitic grades, that have improved resistance to chloride stress corrosion cracking, but that remain susceptible to SCC in caustic and other corrosive species.

Nickel and Chronium-Nickel Alloys

Certain nickel alloys are subject to stress corrosion cracking by hydrofluoric acid vapors in the presence oxygen and by hydrofluorosilicic acid.
Chromium-nickel alloys are subjected to stress corrosion cracking by concentrated caustics and acid chlorides (e.g., aluminum chloride) at high temperatures when stressed above the yield point.

Titanium

Commercial titanium alloys are subjected to stress corrosion cracking in hot salt (Sodium chloride above 275 ^{0}C), 10% hydrochloric acid at slightly above room temperature, and nitrogen tetroxide or red fuming nitric acid. Cracking can be controlled by changing the environmental composition in the latter two cases.
Various chlorinated and fluorinated organic solvents have been reported to cause stress corrosion cracking, but methanol (methyl alcohol) has been the prime problem. Stress corrosion cracking by methanol can be inhibited by adding small amounts of water (2000 ppm), but is dependent on the level of chloride contamination.

Aluminum

High strength alloys are susceptible to stress corrosion cracking in the presence of moisture, particularly if chlorides are present.
The most susceptible grades are the copper-bearing, magnesium-bearing, and zinc-bearing alloys. Proper thermal treatment or tempering can lessen susceptibility. There appears to be no threshold stress level for the susceptible combinations of alloys and environments.

Copper Alloys

High strength copper alloys (e.g., brasses hardened by cold work, welded silicon or aluminum bronzes) are susceptible to stress corrosion cracking by ammonia, sulfur dioxide and nitric acid or other nitrogen-containing compounds. Cupronickels appear to be practically immune to ammonia cracking. Pure steam can cause cracking of silicon bronzes.

Alloy	**Environment**
Aluminum alloys	Air with water - Potable waters - Seawater, NaCl solutions NaCl-H_2O_2 solutions
Carbon steels	Caustic NaOH solutions - HCN solutions Calcium, ammonium, and sodium nitrate solutions Acidified H_2S solutions - Anhydrous liquid ammonia - Carbonate/bicarbonate CO/CO_2 solutions - Seawater
Copper alloys	Ammoniacal solutions - Amines - Nitrates
Nickel alloys	Caustic alkaline solutions - High-temperature chloride solutions - High-purity steam- Hydrofluoric acid -Acidic fluoride solutions

Stainless Steels Austenitic	Hot acid chloride solutions - NaCl-H_2O_2 solutions - NaOH-H_2S solutions- Seawater - Concentrated caustic solutions - Neutral halides, Br^-, I^-, F^-
Stainless Steels Austenitic (sensitized)	Polythionic acids - Sulfurous acid - Pressurized hot water containing >2 ppm dissolved oxygen
Stainless Steels Ferric	H_2S, NH_4Cl, NH_4NO_3, hypochlorite solutions
Stainless Steels Martensitic	Caustic NaOH solutions
Titanium alloys	Red-fuming nitric acid Hot salts, molten salts N_2O_4 - Methanol/halide

Table 5- 4. Alloy–Environment Combinations Causing Stress Corrosion Cracking

2. Hydrogen-Induced Cracking (HIC) and Sulfide Stress Cracking

Description

Hydrogen-induced cracking (HIC) results from combined action of tensile stress and hydrogen in the metal. Atomic hydrogen produced on the metal surface by a corrosion reaction “nascent hydrogen” can be absorbed by the metal and can promote environmental cracking. Higher-strength alloys (i.e., those of a tensile strength of 1034 MPa (150000psi) are more susceptible to this mode of cracking than are lower strength alloys. Sulfide stresses cracking is a specific form of hydrogen induced cracking wherein the presence of sulfides suppresses the evolution of hydrogen.

Recognition

Hydrogen-induced cracking results in the brittle failure of otherwise ductile materials when exposed to an environment where hydrogen can enter the metal.

Mechanism

Hydrogen-induced cracking is a cathodic phenomenon wherein the normal evolution of hydrogen at cathodic sites is inhibited, and the atomic hydrogen (H^0) in the cathodic reaction enters the metal. “Poisons” in the environment, such as sulfides or arsenides, can inhibit formation and evolution of molecular hydrogen (H_2) at cathodic sites.

Atomic hydrogen on the metal surface (nascent hydrogen) can diffuses into the metal instead of evolving as gaseous cathodic reaction product.

Anodic protection lessens and cathodic protection aggravates the cracking. Field application of cathodic protection have been responsible for cracking failures in the pipelines and ship propellers.

In cases of ordinary corrosion process that the nascent atomic hydrogen is produced at the local cathodes combines together to form molecular hydrogen. If in highly stressed conditions and in the presence of certain chemical species that act as a negative catalyst (poisons) for conversion of atomic to molecular hydrogen, these cathodes are subjected to HIC. The normal formation and evolution of molecular hydrogen is suppressed; and the nascent atomic hydrogen diffuses into the interstices of the metal, instead of being evolved as a gaseous cathodic reaction product.

Cyanides, arsenides, antimonides, phodphides, and sulfides poison the conversion of atomic to molecular hydrogen. One commonly encountered species is hydrogen sulfide (H_2S).

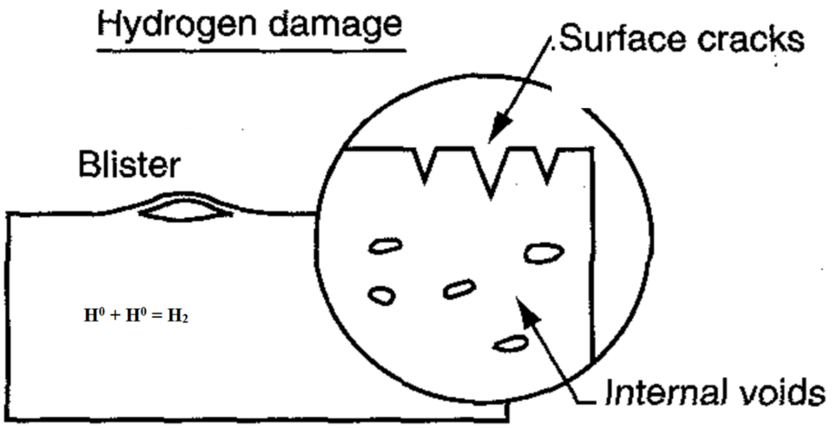


Fig 5-35. Hydrogen damage.

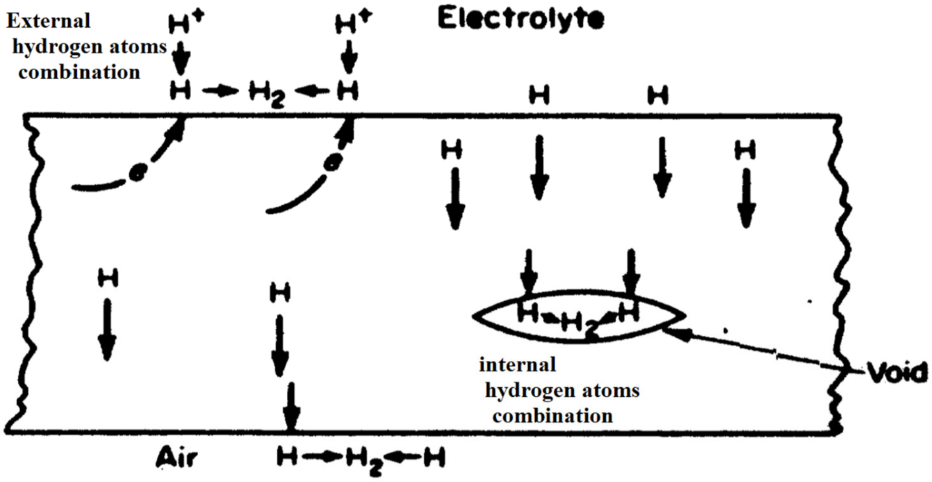


Fig 5-36. Hydrogen damage.

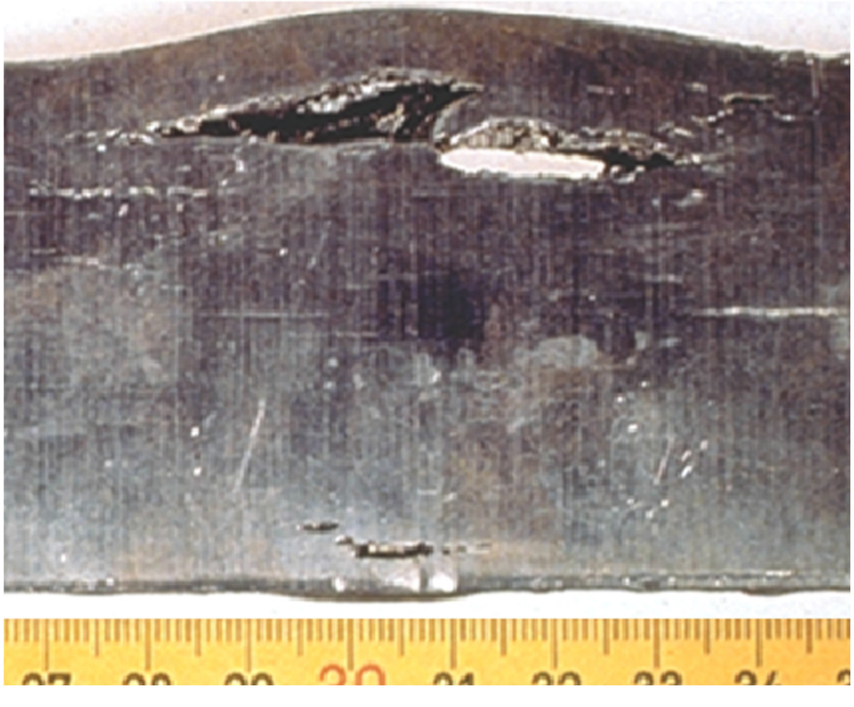
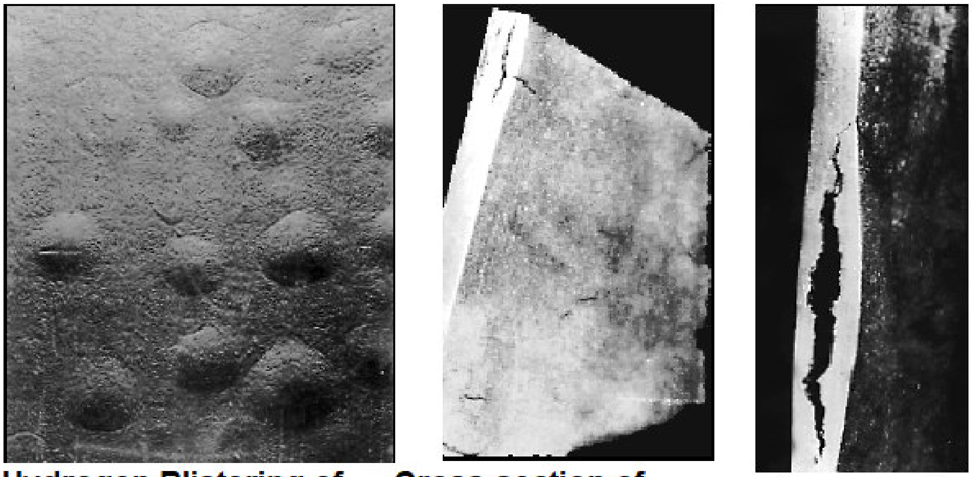


Fig 5-37. Hot Hydrogen Attack of Carbon Steel Plate - Naphtha + Hydrogen at 500 C



Hydrogen Blistering of Carbon Steel Plate.

Cross-section of Hydrogen Blister which has Cracked Through the Surface of the Plate at the Apex of theBlister.

Cross-section of Hydrogen Blister which has Cracked at the Edge

Fig 5-38. Hydrogen damage.

Sulfide Stress Cracking (SSC)

Sulfide stress cracking is a type of hydrogen-induced cracking in which sulfide is the primary poison for hydrogen evolution. Processes or conditions involving wet hydrogen sulfide are called sour services, and the high incidence of sulfide-induced HIC has resulted in the term sulfide stress cracking (SSC). Whether or not the "poison" on the metal surface is a sulfide, the presence of hydrogen sulfide in the metal creates the conditions for cracking under stress. The presence of sulfide, or any other inhibiting ions, simply implies that a greater volume of hydrogen will penetrate the metal during a given time, producing more rapid cracking of the steel. The result is the same; hydrogen-induced cracking.
The sulfide stress cracking of medium-strength steels has been a continuing source of troubles in oil fields. Similar problems are encountered wherever wet hydrogen sulfide is encountered (e.g., acid gas scrubbing systems, wastewater treatment).

NACE MR0175, "Sulfide Stress Corrosion Cracking Resistant Material for Oil Field Equipment"

Failures have occurs in the field when storage tank roofs have been saturated with hydrogen by corrosion and have been subjected to a surge in pressure, resulting in a brittle failure of the circumferential welds.

Factors affecting HIC Includes:

- Temperature
- Hydrogen concentration
- Strength level
- Cold work

Maximum susceptibility to HIC occurs near room temperature, with increasing temperatures causing a reduction in susceptibility. Generally, as the tensile strength of the alloy increases, the HIC susceptibility also increases. In addition, cold work can cause increased susceptibility.

This pattern in that of common hydrogen embrittlement, a temporary loss of ductility when steel becomes saturated with atomic hydrogen (as in pickling, electroplating). Ductility may be restored, without permanent damage to the alloy, by heating for a short term at about 200 ^{o}C (400 ^{0}F) to drive out the hydrogen

Examples of potential sulfide cracking failures in upstream operations include:
- Cracking of high-strength tubing or casing, e.g., N-80 or P-110 in a sour oil or gas well
- Cracking of high-strength 12 Cr (Type 410 stainless steel) valve trim or other 12 Cr components in a sour well or process stream.
- Cracking of a hard piping or pipeline welds in a line carrying sour crude and brine or wet sour gas
- Cracking of high-strength drill pipe, tool joints, and other drilling tools exposed to sour gas

HIC – Performance of Metals and Alloys

HIC performance of various alloy groupings is discussed below.

Aluminum

Some aluminum alloys are susceptible to HIC.

Carbon and Low-Alloy Steels

If sufficiently hardened by cold work, heat treatment, or welding, HIC can occur from nascent hydrogen. This type of cracking is promoted by the presence of specific poisons from dimerization of atomic hydrogen (sulfide, arsenic, etc.).

Hot hydrogen attack (decarburization) can also occur in steel exposed to hydrocarbons or hydrogen rich environments at high temperature [approximately 260 ^{0}C (500 ^{0}F)]. In this form of attack, the hydrocarbon breaks down on the metal surface and the hydrogen enters the steel. Methane forms by reacting with the carbon of metastable carbides. Pressure builds up and cause cracking.

The main weakness of the high-strength steels, such as low-alloy martensite-forming grades, is the susceptibility to cracking by atomic hydrogen. The hydrogen may be nascent, as in corrosion by moist environments contaminated with salts or cathodic poisons or atomic hydrogen, as in case of galvanic couples or impressed current cathodic protection.

Stainless Steels

Martensitic Grades
In the hardened condition, these alloys are subjected to hydrogen-induced cracking, including sulfide stress cracking, in a manner similar to other high strength steels.

Ferritic Grades
Cracking by atomic hydrogen has been reported in cathodic protection installations with a driven impressed current potential in excess of -850 mV versus a copper-copper sulfate electrode.

Austenitic Grades
Hydrogen-induced cracking is observed primarily in the severely cold-worked material in marine atmospheres.

Precipitation-Hardened Grades
Precipitation-hardened stainless steels are cracked by nascent or atomic hydrogen, particularly in sour (hydrogen sulfide) service. Their susceptibility is determined by the steel’s specific thermal history and resultant hardness.

Nickel-Based Alloys
Severely cold-worked nickel alloys have failed by HIC when in a galvanic couple, with steel in the presence of small amounts of hydrogen sulfide.

Chromium-nickel alloys can suffer hydrogen-induced cracking, but generally under severe conditions, such as in the presence of a combination of severe cold work, high stress, and galvanic coupling in the presence of hydrogen sulfide and chlorides.

Copper Alloys

It is possible for atomic hydrogen which has resulted from impressed currents to cause HIC. (e.g., in cathodic protection of manganese bronze ship propellers).

Titanium/Zirconium/Tantalum

Titanium, zirconium, and tantalum can be functionally destroyed by the formation of hydrides caused by absorption of atomic hydrogen. These metals are subjected to HIC.

An Over view of NACE MR0175 Document and recommendation

NACE (National Association of Corrosion Engineers) Standard MR-01-75, *Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment, is the* industry standard which provides guidelines for the selection of materials for sour environments.

MR-01-75 defines a sour gas environment follows:

- The gas being handled is at a total pressure of 65 psia or greater.
- The partial pressure of H_2S in the gas is greater than 0.05 psia.

It also defines a sour oil or multiphase system as one which has a partial pressure of H_2S in the gas phase greater than 0.05 psia. However, in addition to this partial pressure criterion, if an oil well meets all four of the following criteria, it **is not considered** sour.

- The maximum gas/liquid ratio is 5000 SCF per bbl.
- The gas phase contains a maximum of 15% H_2S.
- The partial pressure of H_2S in the gas phase is not higher than 10 psia.
- The surface operating pressure is a maximum of 265 psia.

MR-01-75 contains curves that provide a convenient method of determining whether or not a gas well or an oil well is sour. By knowing the total pressure and the H_2S concentration of the gas in the well, you can readily determine from the graph if it falls within the sour (i.e., cracking susceptibility) region.

The definition of sour or non-sour, as outlined in MR-01-75, is intended only to make clear where metals are subject to sulfide cracking at temperatures near ambient. It does not address all aspects of materials selection for sour environments, such as weight loss corrosion, and stress corrosion cracking. In addition, its definition of sour does not consider H_2S toxicity and personnel protection.

The classification curve depends on (H_2S Partial pressure and In situ pH Value).

The H_2S partial pressure is calculated as follows:

- Partial pressure of H_2S = total system pressure x mole fraction of H_2S in gas.
  For example, in a well with a bottom hole pressure of 2500 psig and a gas containing 2% mole H_2S,
  Partial pressure= 2500 x 0.02 = 50 psig.
- The In situ pH is the calculated pH at operating conditions; it depends on water chemistry, temperature, pressure, and CO_2 content. The in situ pH can be calculated using computer software, using Oddo and Tomson method, or using NACE MR0175 guide Annex D.

3. Liquid Metal Embrittlement (LME)

Definition

Liquid metal embrittlement (LME) is defined as the decrease in strength or ductility of a metal or alloys as a result of contact with a liquid metal.

Recognition

A normally ductile material that is under tensile stress while in contact with a liquid metal may exhibit brittle fracture at low stress levels.

Mechanism

Unlike fracture by stress corrosion cracking, initiation of the failure by LME is not time dependent. Cracking begins immediately upon the application of stress if the liquid metal has wet the solid material. Crack growth will continue as long as sufficient liquid metal covers at least part of the fracture surface and some vapor reaches the apex of the crack.

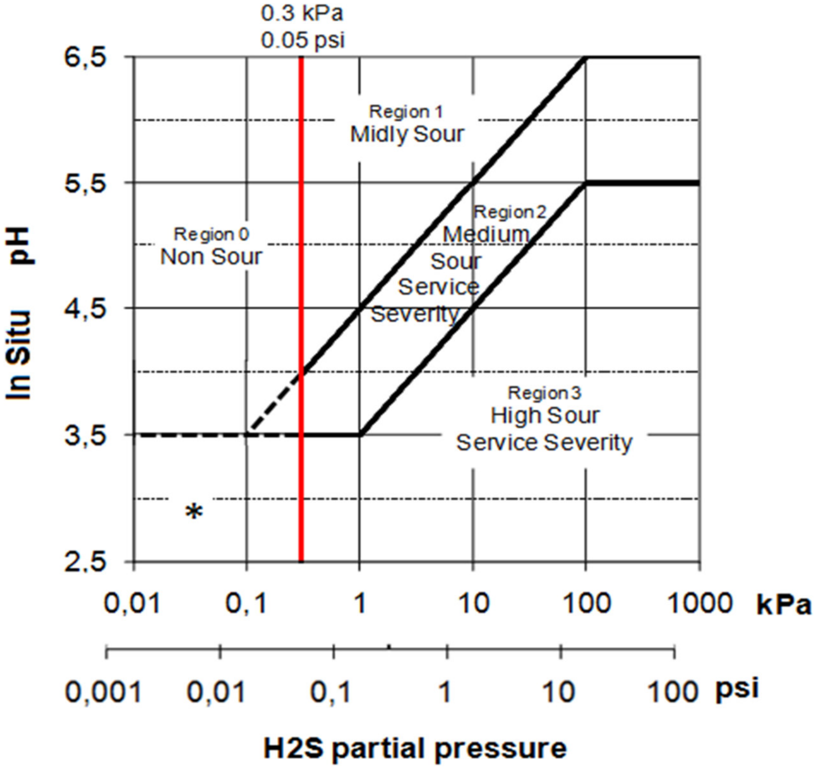


Fig 5-39. Classification of environment sourness's.

Region 0; Sweet Service - *No specific requirements needed (no hardness restriction according to in-house design codes)*

Region 1; Mild Sour Service - *Minor or inexpensive precautions are requested . (e.g. up to grade P110 with restricted yield - maximum hardness 300 HV "Vickers hardness" = approx. 285 Brinell hardness "BHN")* Refer to Annex.A.

Region 2; Intermediate Sour Service - *Increasing precaution are required (e.g. up to grade N80 - maximum hardness 280 HV = approx. 266 Brinell hardness "BHN")*

Region 3; Severe Sour Service - *Important precautions are mandatory. (e.g. NACE MR0175 approved list - maximum hardness 250 HV = approx. 238 Brinell hardness "BHN").*

LME – Performance of Metals and Alloys

LME may be encountered in most common structural metals and alloys. Given the right combination of liquid metal, stress level, and temperature, most alloys exhibit some degree of susceptibility to LME.

One fascinating aspect of LME is the specificity of the embrittling agent. For example, gallium, which causes severe embrittlement of aluminum and its alloys, has no significant effect on other materials such as low carbon steels, stainless steels and copper alloy.
Stainless steels, in general, are quite resistant to degradation when contacted by liquid metal, while materials such as plain carbon steels and copper-based alloys are severely embrittled.
From an engineering standpoint, zinc poses a significant problem for low-alloy and stainless steels. Zinc is widely used in painting as a protective coating, as in the case of hot-dip galvanized steel. Fortunately, zinc is encountered as a liquid metal only during welding and brazing, or in case of a fire.

Carbon and Low-Alloy Steels

Carbon and low-alloy steels are susceptible to LME in a number of environments in addition to those containing zinc. Research conducted in the temperature range between 450 ^{0}F and 1600 ^{0}F (approximately 230 ^{0}C to 875 ^{0}C) showed that such steels can suffer embrittlement when in contact with the followin liquid metal systems: copper, zinc, cadium, lead-tin solders, brass, and indium. The embrittling effect of lithium is also well known.

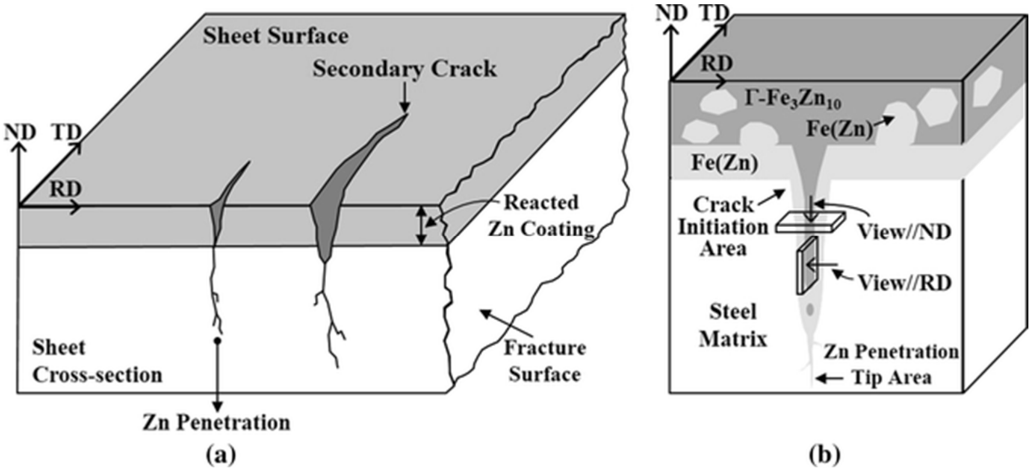


Fig 5-40. Liquid metal embrittlement.

Additionally, the higher the strength of the steel, the greater the degree of embrittlement. For example, high strength steels are embrittled at room temperature by mercury-sodium amalgams. Such amalgams have no effect on a low strength carbon steel, such as 1010 carbon steel.

Stainless Steels

The family of stainless steels, including martensitic, ferritic, duplex, precipitation-hardening, and austenitic stainless steel, is quite resistant to LME. Only molten zinc, aluminum, and cadmium produce adverse effects.

Aluminum and Aluminum Alloys

Aluminum alloys can fail rapidly by LME in the presence of mercury, gallium, indium, tin, and alkali metals (with the exception of lithium). As with low-alloy steels, the higher the strength, the more severe the embrittlement.

Copper and Copper Alloys

Mercury cause severe LME of brasses and bronzes; tin, lead and alloys of tin and lead also embrittle brasses. Copper and copper-base alloys other than brasses are also embrittled by mercury, bismuth, and lithium.

Nockel and Nickel-Based Alloys

Mercury and liquid lead rapidly corrode nickel-base alloys, but do not cause embrittlement. Nickel-base alloys, however, maybe severely embrittled by sulfur diffusing along grain boundaries from a nickel, nickel-sulfite eutectic.

Titanium and Titanium Alloys

The deformation of titanium and titanium alloys in contact with mercury will result in sever embrittlement. Molten cadmium may also cause embrittlement. In addition, several titanium alloys have been found to suffer brittle fracture at room temperature when intimate contact with solid cadmium. In all cases, the protective outside film must be ruptures before embrittlement will occur.

Magnesium Alloys

Liquid sodium and liquid zinc are the only low melting point metals known to cause LME of magnesium alloys.

4. Corrosion Fatigue

Definition

Corrosion fatigue results from the combined action of a cyclic tensile stress and a corrosive environment. A tensile component of cyclic stress is required.

Description

Corrosion fatigue is characterized by the premature failure of a cyclically-loaded part. This failure may occur at a lower stress, or in a fewer number of cycles in the corrosion environments than it would in an inert environment.

Mechanism

Corrosion fatigue continues to be a serious cause of failure and necessitates major expenditures by industry for repair. For example, the petroleum industry encounters major trouble with corrosion fatigue in crude oil production. The exposure of drill pipes and sucker rods to brines and sour crudes results in failures that are expensive both from the standpoint of replacing equipment’s, as well as from the loss of production during the time required for replacing the broken section.

Corrosion Fatigue – Performance of Metals and Alloys

Aluminum Alloys

Fatigue strengths of most aluminum alloys are lower in corrosive environments such as salt waters than in air. The more corrosion-resistant alloys, are more fatigue resistant.

Copper Alloys

Copper alloys are often used in applications where repeated stresses are encountered. Combination of high-fatigue limits and high-corrosion resistance in the service environment enhance corrosion resistance. Therefore, copper and copper alloys are usually used in applications as springs, switches, diaphragms, bellows, automobile gasoline and oil lines, and tubes for condensers and heat exchangers.

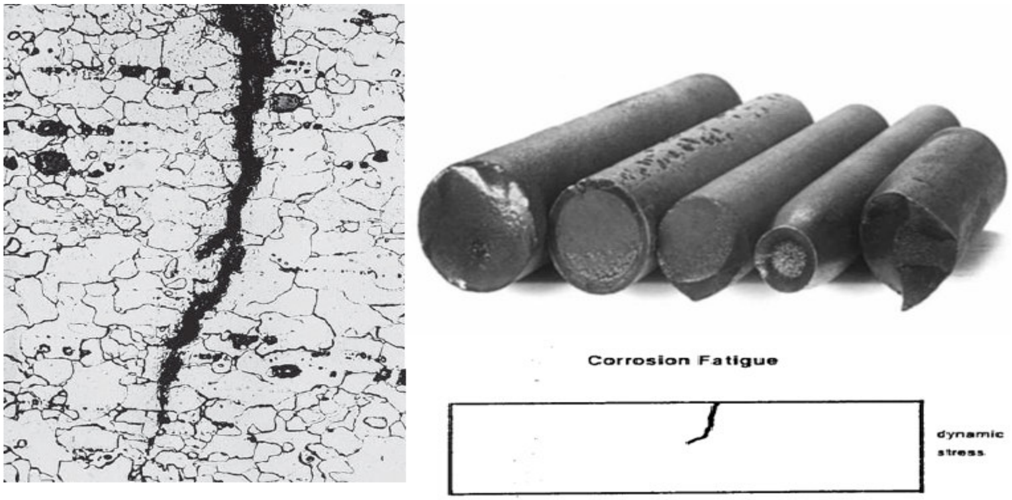


Fig 5-41. Corrosion fatigue.

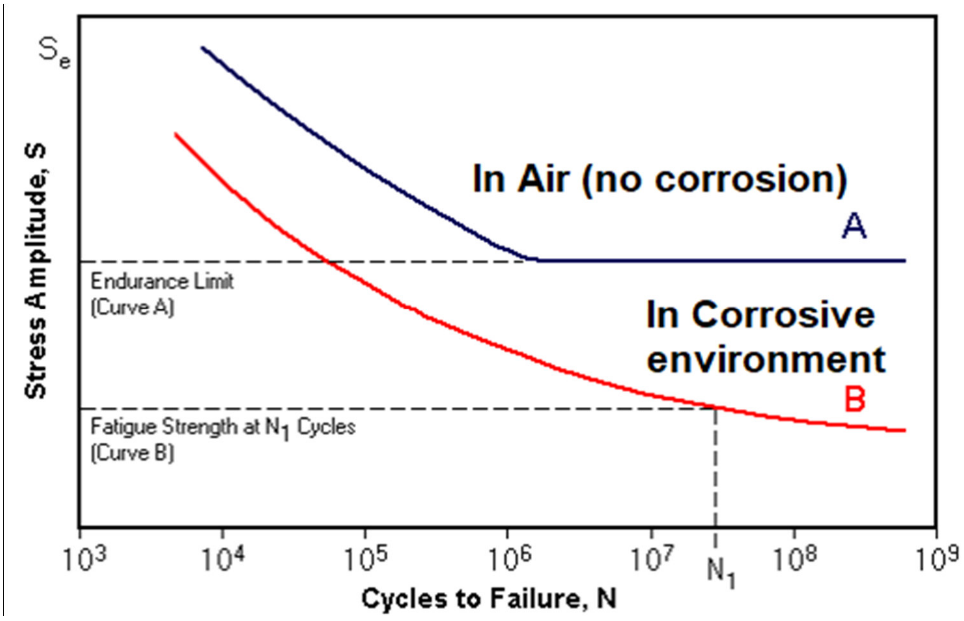
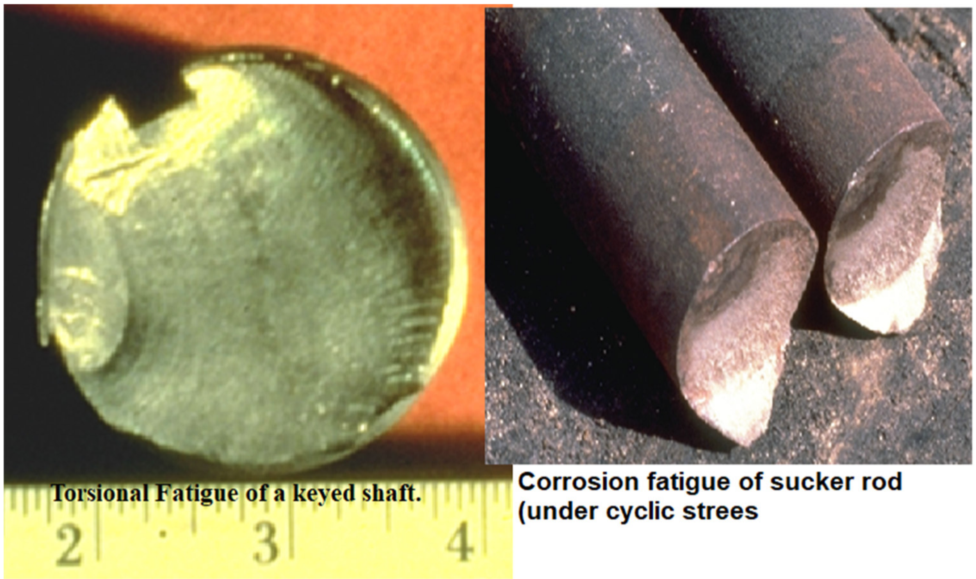


Fig 5-41. Corrosion fatigue in air and in corrosive environment- The relation between stress applied and number of cycles to failure.



Torsional Fatigue of a keyed shaft.

Corrosion fatigue of sucker rod (under cyclic strees

Fig 5-41. Corrosion fatigue.

Carbon and Low Alloy Steels

The Corrosion fatigue resistance of steels will be greatly influenced by the corrosion behavior of the steels in service environment. Time, stress, intensity, number of cycles, and the rate of cyclic stress will significantly affect corrosion fatigue. The rate of damage tends to increase if any of these conditions increases. Higher-strength steels do not necessarily exhibit higher corrosion fatigue tendencies, even if the service environment is corrosive. More corrosive environments, such as brackish water, have been shown to reduce apparent corrosion fatigue limits.

The use of inhibitors and zinc-plated steels can improve corrosion fatigue resistance.

Stainless Steels and Nickel Alloys

These materials have inherently higher corrosion fatigue limits than ordinary steels, with the presence of chromium and molybdenum being a significant contributor to this resistance. Generally, the resistance of corrosion fatigue will parallel the relative resistance to such localized corrosion as pitting or crevice corrosion, because localized breakdown of the passive film prompts the failure in both cases. In many instances, corrosion fatigue cracks will emanate from the bases of pits initiated in the corrosion environment.

Titanium Alloys

Corrosion fatigue of titanium alloys is not considered common. Fatigue in fretted areas has been documented in some rotating aircraft components.

Control of Environmental Cracking

Environmental cracking can be controlled in many ways, including:

1- Design

The design can be changed to lower the tensile stresses to below the threshold level controlling stress corrosion cracking, or to a level significantly less conductive to cracking, controlling other environmental cracking phenomena. If an alloy is susceptible to cracking in a given environment, the tensile stresses must be reduced to control cracking. The total resultant stress from residual stresses, thermal stresses, and stresses from operating loads and pressure must be considered.

A second design consideration for control of environmental cracking is to avoid geometries in which solutions can be concentrated, or in which species can accumulate. Dead spaces where steam blanketing or water evaporation can occur are potential failure sites. Solutions with bulk chloride concentrations of 1 ppm can become concentrated to high chloride levels in crevices and other restricted geometries.

A third consideration is the compatibility of materials throughout the system. Contact of dissimilar metals can polarize one into the potential range for environmental cracking. Chlorides leached from insulations, or formed by hydrolysis of organic chlorides in elastomeric seals or plastic devices, can cause stress corrosion cracking of austenitic 18-8 stainless steels. Ammonia introduced to control pH and minimize the corrosion of steel can promote stress corrosion cracking of copper alloys in adjacent equipment.

The overall design should be reviewed for material compatibility. A fix of corrosion in one part of the process must not cause environmental cracking elsewhere in the system.

2- Material selection

A common fix of the environmental cracking problem is to substitute a more resistant alloy for the one that has failed. It is important to identify the critical species causing the environmental cracking. Recall that specific alloy systems are subjected to specific types of attack in specific environments.
Another example of changing materials to control cracking is the substitution of lower strength steel for high strength steel when hydrogen-induced cracking causes a failure.
In addition to complete shifts from one alloy system to another, minor compositional changes within the alloy system may help control environmental cracking.

3- Modification of environment

Environmental cracking sometimes can be controlled by eliminating the critical species from the environment, or by lowering its concentration to levels, which will not promote cracking. Unfortunately, the concentration that will promote SCC depends on the alloy and the temperature and experimental data are often required to identify safe concentration limits. When the concentration of critical species is to be controlled, care must be taken to ensure that species are not increased in concentration during service by evaporation or by localized boiling.

In some environment-alloy combination, it is possible to reduce environmental cracking by eliminating oxygen or oxidizing agents. Oxygen removal can be accomplished by reducing dissolved oxygen with a scavenging agent such as sodium sulfite.

Minor constituents in the solution can also affect the concentration and temperature range over which cracking is observed. These minor constituents can be beneficial or detrimental.

Another approach in modifying the environments is to prevent an aqueous solution from contacting the alloy. Stress corrosion cracking in gas storage and transmission service is controlled by dehumidifying the gases. If the water concentration decreased and the dew point lowered sufficiently, no condensation will occur, and environmental cracking is prevented. Carbon steel may successfully contain a dry mixture of carbon dioxide and carbon monoxide. In a wet mixture of these gases, carbon steel may fail rapidly by stress corrosion cracking. In ductwork and other high temperature systems, the temperature is purposely maintained above the dew point of the gas mixture to prevent condensation; and therefore, cracking is controlled.

4- Protective coatings

Coatings have been used to control environmental cracking, although the protection afforded is only as good as the integrity of the coating. Barrier coatings that effectively isolate the metal from an aqueous environment can help control environmental cracking.

Metallic coatings also have been used to control environmental cracking. An outer layer of a resistant alloy may be clad to a high-strength alloy substrate. The alloy surface effectively prevents contact of the aggressive environment with the high strength substrate, which is susceptible to cracking.

A combination of control techniques is illustrated by the application of primer systems that contain environmental cracking inhibitors to buried gas transmission pipe lines. Environmental cracking is controlled both by isolation of the steel from ground waters by the coating system and by the inhibitor which protect the substrate at flaws in the coatings.

5- Electrochemical techniques

Cathodic protection can be used to control some forms of environmental cracking; however, cathodic protection can contribute to hydrogen-induced cracking and must be used with care.

Both anodic and cathodic protection have been used to polarize an alloy to a potential out of the range that will promote stress corrosion cracking. In anodic protection, the alloy is polarized to a potential more oxidizing than the stress corrosion cracking range. Steel in caustic solutions may be protected by anodic protection. In cathodic protection the metal is polarized to a potential more reducing than the cracking potential range. Polarization may be controlled by galvanic action of dissimilar metals or by impressed currents.

Conversely, changing the potential can be detrimental and can promote environmental cracking. A common instance of this is in cathodic protection of high strength steel for corrosion control. Because hydrogen is generated on the steel surface, the cathodic protection may induce hydrogen embrittlement. Polarization to more reducing potentials by cathodic protection results in greater concentrations of hydrogen in the steel and greater susceptibility to cracking. Failures of galvanized high-strength bolts have resulted from this effect.

6- Reduction in residual surface stress

Residual stress from metal fabrication and unit construction are reduced by two principal methods: Stress-relieving heat treatment or shot-penning, sometimes referred to a as a mechanical stress relief. In the first case, a fabricated item is heated to a temperature high enough for residual stresses to relax. In the second case the metal is mechanically peened at an intensity sufficient to cause residual compressive stresses at the surface. Both of these methods can effectively reduce surface stresses. In some cases, the residual surface stress can be reduced below the level required for environmental cracking.

A summary of environmental corrosion is in the following tables.

Type	**Mechanism**	**Factors**	**Appearance & Detection**	**Source of Hydrogen**	**Control Methods**
High-Temperature Hydrogen	H° diffuses into steel, reacts	Occurs in carbon and C-1/2 Mo steels above	Detected with UT or at high	At high temperature and high	Controlled by upgrading

Attack (Section 440)	with carbon, forms methane, and creates an internal pressure which causes cracks and fissures.	450°F and 100 psig H2. Cr-Mo (low alloy) steels have greater resistance.	magnification under a microscope prior to failure.	pressure, hydrogen has an equilibrium between H2 and H°. As H° is formed some diffuses into the steel.	material as specified in API 941. Cr and Mo additions to steel increase resistance.

Table.5-5.Temperature Related Hydrogen Damage Mechanisms in Steel Plate and Piping

Type	**Mechanism**	**Factors**	**Appearance & Detection**	**Source of Hydrogen**	**Control Methods**
Hydrogen Blistering	H° formed during corrosion diffuses to internal discontinuities (non-metallic inclusions), recombines to H2, creates internal pressure, and forms a blister.	The presence and density of non-metallic plate-like inclusions.	Forms circular blisters on ID of vessels. Detected internally with visual inspection or externally by UT thickness gauge.	H° forms on surface by corrosion, in the presence of hydrogen recombination poison (H2S or HF acid), and diffuses into steel. It is accelerated by cyanides or ammonia.	Can be eliminated in H2S service by coating with stainless steel. Performance can be improved by using low sulfur steel or corrosion controls (water wash or APS).
Hydrogen Induced Cracking (HIC) or Stepwise Cracking	An advanced degree of hydrogen blistering, in which pressure in blisters causes cracks to grow in the through wall direction between internal discontinuities	The presence and density of non-metallic inclusions and blisters.	Surface breaking cracks at center or edge of blisters, can be detected with WFMT or visually, if severe. Subsurface cracks can be detected with shear wave UT.	Same as hydrogen blisters.	Same as hydrogen blisters.
Stress Oriented Hydrogen Induced Cracking (SOHIC)	Similar to HIC, but weld residual stresses cause crack growth in the through wall direction between internal discontinuities.	Residual stresses in the HAZ and the presence of nonmetallic inclusions.	Surface breaking cracks in the weld HAZ, can be detected with WFMT.	Same as hydrogen blisters.	Same as hydrogen blisters, plus stress relief will improve resistance.

Table.5-6. Summary of Hydrogen Damage Mechanisms.1 of 2. Defect Related Hydrogen Damage Mechanisms in Steel Plate

Note H2 - Molecular Hydrogen, H° - Atomic Hydrogen, UT - Ultrasonic Testing, WFMT - Wet Fluorescent Magnetic Particle Testing,
HAZ - Heat Affected Zone, Rc - Rockwell “C” Hardness, BHN - Brinell Hardness

Type	Mechanism	Factors	Appearance & Detection	Source of Hydrogen	Control Methods
Sulfide Stress Cracking (SSC)	H° diffuses into a region of high stress (crack tip or internal flaw) in hard steel and causes crack growth. Cracking can occur quickly.	High strength & hardness (>Rc 22 in HAZ or >BHN 200 for the weld metal for steel).	Surface-breaking cracks, often in the weld or HAZ. Can be detected with internal WFMT. Can also crack steel machinery.	H° forms on surface by corrosion, in the presence of H2S, and diffuses into steel.	Avoid the use of overly strong or hard materials. Upgrade to materials listed in NACE MR-01-75. PWHT improves weldment performance.
Hydrogen Stress Cracking (HSC)	Same as sulfide stress cracking.	Same as sulfide stress cracking.	Same as sulfide stress cracking.	H° forms on surface by corrosion, in the presence of hydrogen recombination poison other than H2S (HF acid), and diffuses into steel.	Same as sulfide stress cracking. In HF service Monel is a common upgrade, but is susceptible to cracking.
Hydrogen Embrittlement or Hydrogen Assisted Cracking	H° which enters at high temperatures and high hydrogen partial pressures, from corrosion, or from any source reduces the material's ductility and resistance to crack growth.	High strength and high hardness steels are affected. The degradation of the properties is transitory. The normal properties return if the hydrogen diffuses out.	No change in appearance until failure. Mechanical property tests while the material is hydrogen charged are needed for detection.	H° can come from any source including electroplating, corrosion, or high temperature hydrogen and rapid cooling.	Avoid high stresses and stress concentrations while material is hydrogen charged. Bake out hydrogen at 600°F to restore properties.
Hydrogen Cracking of Welds (Delayed Cracking, Cold Cracking, or Under bead Cracking)	H° diffuses to a region of high stress (crack tip or internal flaw) and causes crack growth in the HAZ.	High strength & hardness (>Rc 22 in HAZ or >BHN 200 for the weld metal).	Cracking will occur at the weld toe after the weld has cooled, up to 48 hours after welding. Can be found using WFMT.	H° diffuses to the HAZ from the base metal (if the vessel has been in corrosive service and not baked-out prior to welding) or during welding.	Apply proper preheat. Clean and degrease base metals before welding. Bake out metal before welding. Use clean, dry low hydrogen electrodes.

Table.5-6. Summary of Hydrogen Damage Mechanisms.2 of 2.- Property Related Hydrogen Damage Mechanisms Plate and Pipe

Note H2 - Molecular Hydrogen, H° - Atomic Hydrogen, UT - Ultrasonic Testing, WFMT - Wet Fluorescent Magnetic Particle Testing,
HAZ - Heat Affected Zone, Rc - Rockwell “C” Hardness, BHN - Brinell Hardness

5.2.5 Flow Assisted Corrosion

Introduction

In this section, we will consider principal varieties of related attack due to flow of a substance across a surface.

The surface may be either stationary (e.g., a valve seat) or moving (e.g., a pump impeller or propeller).

Definition

Flow assisted corrosion is defined as the combined action of corrosion and fluid flow.

Types

The types of velocity phenomena we will discuss are:

1. Erosion-corrosion
2. Impingement
3. Cavitation

1- Erosion-Corrosion

Description

Erosion-corrosion occurs when the velocity of the fluids sufficient to remove protective films from metal surface.

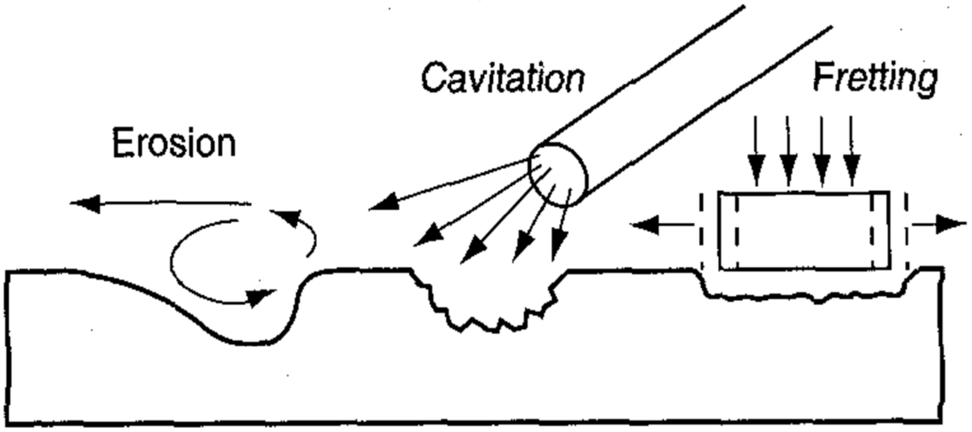


Fig. 5- 42. Erosion, cavitation, and fretting.

Recognition

Erosion-corrosion often causes localized attack where surface discontinuities cause flow aberrations and turbulence. This phenomenon often occurs at weld beads.

Fig. 5- 43. Erosion corrosion.

Mechanism

Erosion-corrosion can occur in flowing liquids or gases with or without abrasive particles. In this form of attack, the velocity of the flow is sufficient to remove weakly-adhered corrosion products from the surface, reducing their protective effect, and may also remove substrate. This results in acceleration of corrosion process.

The fluid dynamics in erosion-corrosion by liquids can be an important factor in determining the rate of material removal. Turbulence of flow is also important. Velocity alone can explain a sudden increase in surface damage.

When erosion-corrosion occurs, the effect of velocity on the corrosion rate usually exhibits a breakaway phenomenon, wherein a maximum velocity can be withstood without removal of the protective films. Above this limiting breakaway velocity, the corrosion rates increases very rapidly. The resistance of protective films to removal plays a significant role in determining the breakaway velocity for a given alloy-environmental system.

Erosion by particles in acorrosive medium may not proceed by complete removal of the corrosion product. At elevated temperatures, the corrosion product may be ductile and may flow with the particle impact. This results in the removal of good deal of corrosion product and little base of metal. The erosion debris, if collected and examined, will show characteristic rounded particles rather than the flakes characteristic of metal debris.

Although not necessarily an electrochemical corrosion mechanism, elements of mechanical erosion are often encountered and recognizable features should be defined.

Mechanical erosion is caused by hard particles impacting on the surface and results in cratering of the metal surface. The plastic deformation of each impact extrudes metal around the particles, the extrusions are broken off by later impact. Erosion by particle impact in influenced by the angle of impact. For ductile metals, the removal rate maximizes at impacting angle of about 20^0 to 30^0. Other factors contributing to erosion rate are particle velocity, hardness, angularity, and the temperature of the environment. The sensitivity of the ductile materials to the angel of impingement causes localization of erosion damage along the flow path. As material is removed from the surface, the impingement angel changes locally, and the small areas in which the erosion efficiency is highest erode faster than other areas. A characteristic ripple pattern is shown.
In some cases, it is difficult to discriminate between erosion corrosion and velocity effect corrosion resulting from non-uniform mass transfer effects, which are due to the greater availability of reactive material and the reduction in dissolved ion concentration because of flow.

If erosion-corrosion can be identified and there is no evidence of particle impingement, one possible solution is to reduce the flow rate, or remove flow-disturbing surface discontinuities.

Erosion – Corrosion – Performance of Metals and Alloys
Almost any material will be affected by the combined effects of velocity and corrosion if the velocity is high enough.

Aluminum and Aluminum Alloys

Aluminum and aluminum alloys,in general, are not very resistant to erosion-corrosion in enviromnets where the are subject to corrosion, such as in potable water and seawater. Limiting velocities are usually in the order of 0.75 m/s (2 ft/s) or less.

Carbon and Low-Alloy Steels

Carbon and low-alloy steels, in general, are not very resistant to erosion-corrosion in environments where they are subject to corrosion, such as in potable water and seawater. Limiting velocities are usually in the order of 1 m/s (3 ft/s) or less.

Stainless Steels and Nickel-Based Alloys

Stainless steels and nickel-based alloys generally show good resistance to erosion-corrosion.

Copper Alloys

Copper alloys, generally, are resistant to erosion-corrosion attack. They are widely used for piping systems and heat exchangers tubes. They do have limiting velocities, which must not be exceeded. These velocities are usually in the order 2 to 4 m/s (6to 12 ft/s).

2- Impingement

Description

Impingement is localized erosion- corrosion caused by turbulence or impinging flow. Entrained air bubbles tend to accelerate this action, as do suspended solids. This type of corrosion occurs in pumps, valves, and orifices, on heat exchanger tubes, and at the elbows and tees in pipelines.

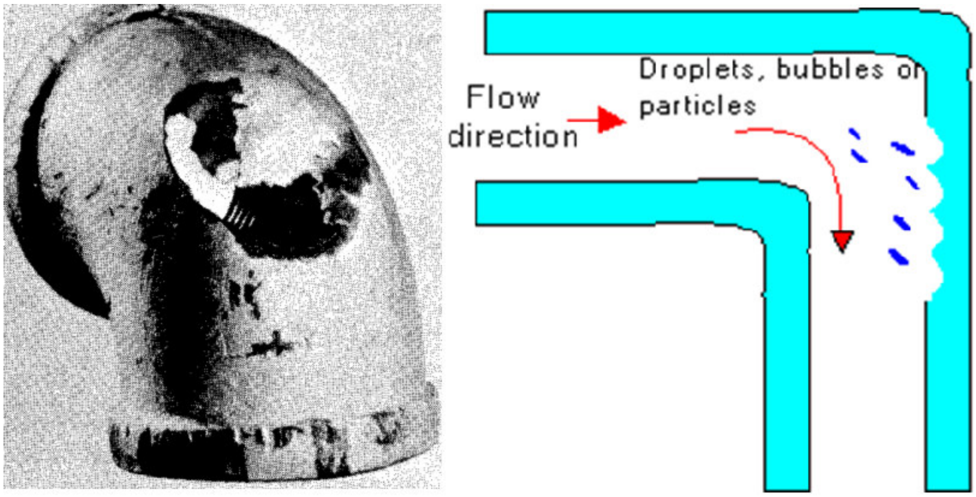


Fig. 5- 44. Erosion corrosion.

Recognition
Impingement corrosion usually produces a pattern of localized attack with additional features. The pits or grooves tend to be undercut on the side away from the source of flow.

Mechanism

The mechanism of impingement is similar to that of erosion-corrosion, as flow removes the protective films responsible for the corrosion resistance of the material. In impingement, however, the flow is either turbulent or directed at roughly right angles to the materials, whereas, in erosion-corrosion, the flow is roughly parallel to the surface.

When a liquid is flowing over a surface (e.g., in pipe), there is usually a critical velocity below which impingement does not occur and above which it increase rapidly. Impingement attack first received attention because of the poor behavior of some copper alloys in seawater.

In practice, impingement and cavitation may occur together, and the resulting damage can be the result of both. Impingement may damage a protective oxide film and cause corrosion, or it may mechanically wear away the surface film to produce a deep groove.

Water Drop Impingement

Water drop impingement is a form of mechanical erosion in which the eroding medium is high-velocity water drops. Any liquid drops at high velocity can produce analogous effects. Usually, the source of the drops is condensate, as in case of steam turbines. Drops also occur in natural atmospheres, such as by rain. Raindrop erosion is a practical problem associated with high-speed jets, and helicopter rotor blades.

Some similarities exist between solid-particle and water-drop impact damage. The impact creates sufficient contact stress to cause yielding of the surface and attendant crater formation. Impact can also cause disintegration and lateral jetting of fragments of the impacting particle, whether drop or solid. Solid particles will tend to cut the surface and, therefore, are more sensitive to impingement angle than are water drops. Water drop impact causes damage by the momentary high pressure pulse induced during collision. The pressure, known as water hammer pressure, is a functional of the drop velocity relative to the surface, the density of the liquid, and the velocity of sound in the material being eroded.

Water drop impingement damage on a ductile material produces rounded craters of uniform size and often craters within craters. The surface often looks something like a fracture surface, since it has ductile, dimpled characteristics. Solid particle impingement causes angular pits, conforming to the shape of the particle; and imbedded particles may be found in the surface. This is the positive way to distinguish between water drop erosion and hard particle erosion. Identifying differences between water drop impingement damage and cavitation erosion is very difficult; it is often impossible to distinguish between the two.

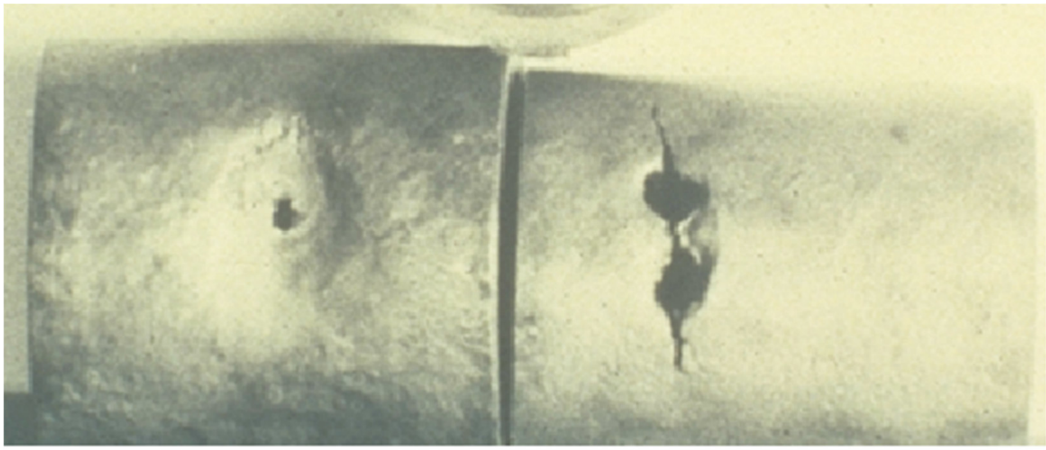


Fig. 5- 45. Water Drop Impingement of boiler tube.

Impingement – Performance of Metals and Alloys.

The interaction between the medium and the surface produces a film which either protects the surface from the material removal process, or is vulnerable to fracture and chipping by impacting particles or liquid drops. Removal of protective or passivation films by shear forces from high velocity flowing fluid or turbulence can accelerate galvanic actions, especially when only a small area of substrate is exposed (small anode/large cathode). In this case, the corrosion resistance of the alloy will be similar to that in film-free liquid immersion corrosion. The rate of corrosion may be accelerated by the flow, but the resistance to the specific corrosive environment will be the same for each metal alloy.

Aluminum and Aluminum Alloys

Aluminum alloys, in general, are not very resistant to impingement in environments where they are subject to corrosion (e.g., in potable water and seawater).

Carbon and Low-Alloy Steels

Carbon and low-alloy steels, in general, are not very resistant to impingement in environments where they are subject to corrosion (e.g., in potable water and seawater).

Stainless Steels and Nickel-Based Alloys

Stainless steels and nickel-based alloys generally show good resistance to impingement.

Copper Alloys

Copper alloys, in general, are not very resistant to impingement environment where they are corrode, such as in potable water and seawater. Otherwise, they are resistant to velocity attack. They are widely used for piping systems and heat exchangers tubes, where impingement effects can be reduced through design.

Titanium/Zirconium/Tantalum

Titanium, zirconium, and tantalum have good resistance to velocity effects in general.

3- Cavitation

Description

Cavitation is a mechanical damage process caused by collapsing bubbles in a flowing liquid.

Recognition

Cavitation usually results in the formation of deep aligned pits in area of turbulent flow.

Mechanism

Cavitation is caused when a protective films are removed from a metal surface by high pressures generated by the collapse of gas or vapor bubbles in a liquid. Where the energy input to produce cavitation is sufficiently high, there will be no significant contributions to the process either by hard particle impact or by corrosion.

The steps through which this process is thought to occur are:

1- Bubble formation in an area of low pressure (downstream valves or pump suction line).
2- Bubble moves to a higher-pressure areas.
3- Bubbles collapse, and impinge the metal surface with a force may reach 100,000 psi, removing the protective film, and may cause mechanical damage to the targeted area.

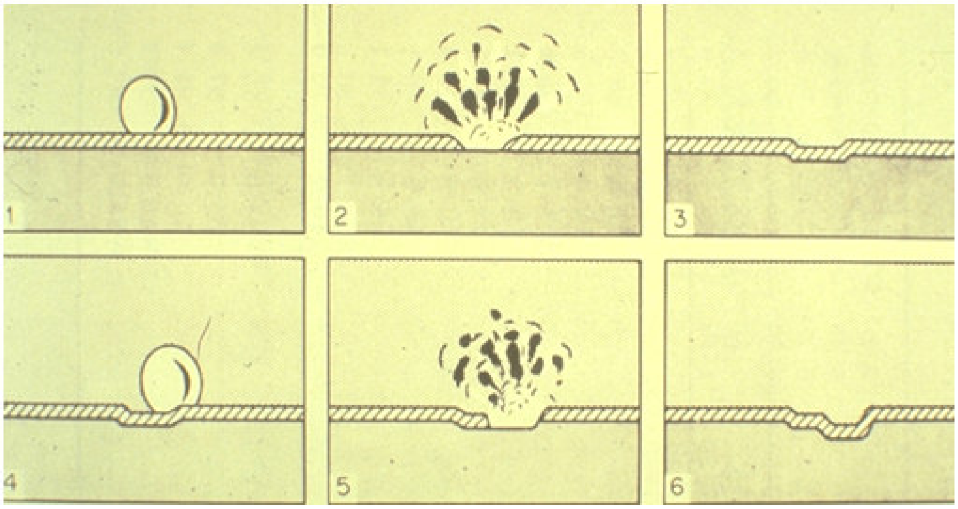


Fig. 5- 46. Schematic of Cavitation

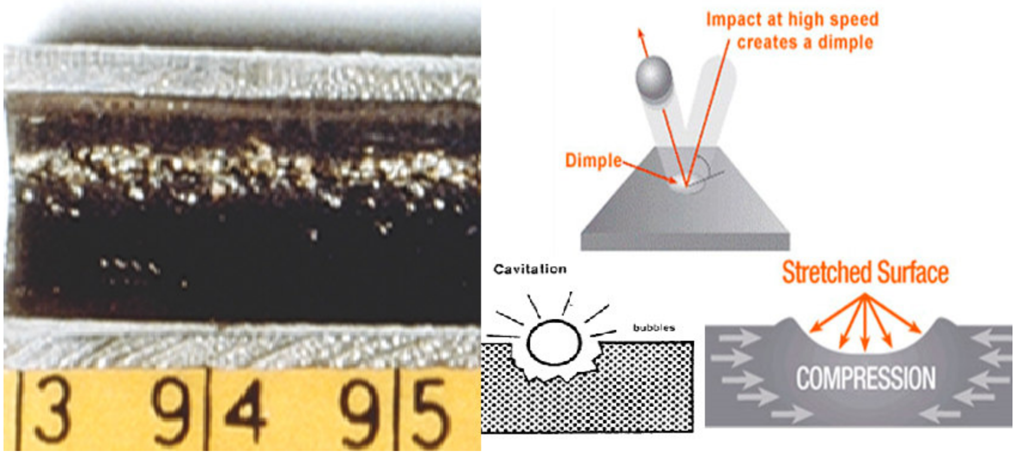


Fig. 5- 47. Cavitation in Carbon Steel Pipe in Steam Cooler - Steam Condensed Causing Cavitation.

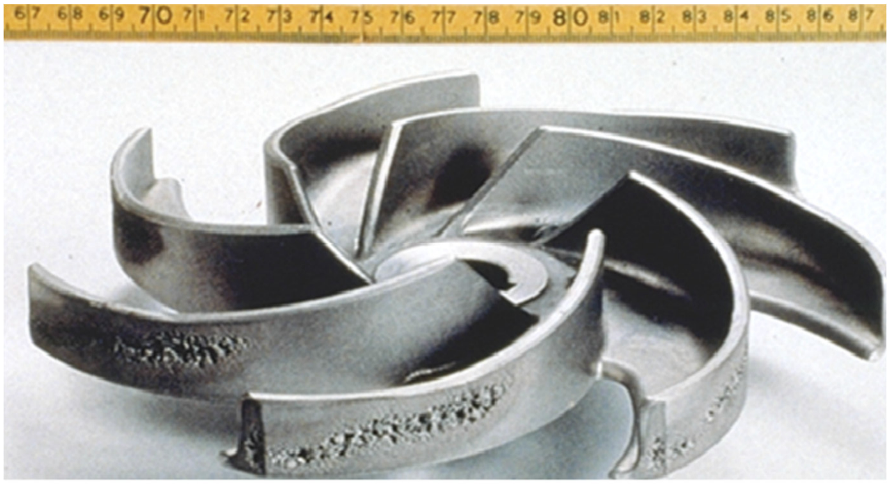


Fig. 5- 48. Cavitation of Stainless Steel Pump Impeller in Vacuum Evaporation System for Evaporated Milk - Cavitation Damage on Discharge Side of Impeller

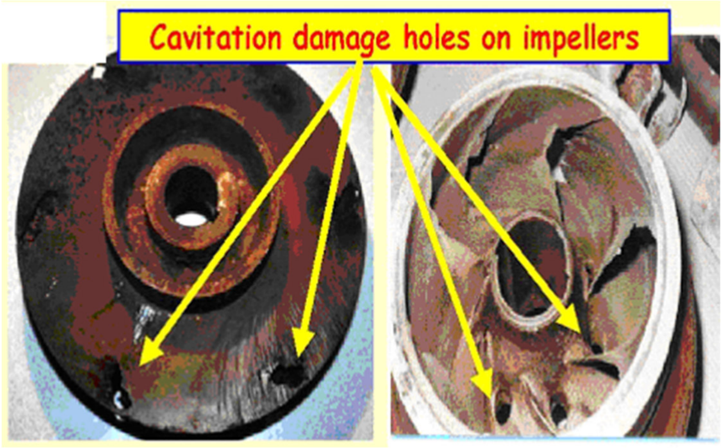


Fig. 5- 49. Cavitation of steel Pump Impeller

Cavitation Corrosion – Performance of Metals and Alloys

In general, alloys with higher strength are more resistant to cavitation corrosion than lower-strength materials. Cavitation damage should be considered as two separate phenomena. When cavitation damage is caused primarily by corrosion following the removal of protective films, the corrosion portion of the damage may predominate. The cavitation itself is usually incapable of mechanically damaging and removing the underlying metal. Under these conditions, the corrosion behavior of the material is important. Under extreme cavitation conditions, the cavitation itself is capable of damaging and removing the metal directly, and corrosion effects are significant.

Aluminum and Aluminum Alloys

Aluminum alloys, in general, are not very resistant to cavitation damage because their low-strength.

Carbon and Low-Alloy Steels

Carbon and low-alloy steels, in general, are not very resistant to cavitation damage unless the cavitation is incapable of directly damaging and removing the steel. In this case cathodic protection, or the use of corrosion inhibitor, can reduce the effect of cavitation.

Stainless Steels and Nickel-Based Alloys

Stainless steels and nickel-based alloys generally show better resistance cavitation than many materials because of their relatively high strength and the relative resistance of their protective films to mechanical damage. However, they are susceptible to cavitation under extreme conditions.

Copper Alloys

Copper alloys, in general, are not very resistant to cavitation because of their low strength. Impingement is more likely in environments where they may corrode, such as such as in potable water and seawater. Otherwise, they are resistant to velocity attack. They are widely used for piping systems and heat exchangers tubes, where cavitation or impingement effects can be reduced through design.

Titanium/Zirconium/Tantalum

Titanium, zirconium, and tantalum have good resistance to velocity effects in general.

Control of Flow Assisted Corrosion

Flow assisted corrosion can be controlled in many ways including:

1- **Design**

Velocity effects can be controlled through design, primarily by controlling the flow velocity and flow patterns. Flow velocity should not exceed the limiting velocities for the material selected. Smooth flow is always preferable to turbulent flow from the standpoint of velocity effect corrosion. Entrained gases and solids should be eliminated from flow whenever possible. Pressure should be considered when cavitation damage is possible.

2- Material selection

Selecting a material according to the resistance to the expected flow velocity and flow regime is widely used to control velocity effect corrosion. As mentioned above all conditions within the system (e.g., periods of stagnation) must be considered when selecting materials.

3- Modification of environment

In some cases, corrosion inhibitors can effectively control velocity effect corrosion. Some inhibitors can reduce the corrosion rate of the areas from which the protective films have been removed.

Another beneficial effect of some inhibitors is that they can increase the resistance of the protective film to velocity effects.

4- Protective coatings

Protective coatings can be used to control velocity effects. Rubber linings are particularly effective in reducing erosion-corrosion effects when solid materials are contained within the flow stream. Of course, the bond of the protective coating to the material is an important factor in their use in controlling velocity effects. Metal coatings applied by cladding or weld overlay, are widely used to control velocity effect corrosion.

5- Cathodic protection

Cathodic protection can effectively control the corrosion of metals, even when the metals are not covered with protective films. Thus, velocity effect corrosion can be controlled by cathodic protection. The recuired electrical current for cathodic protection in high velocity flow is usually much greater than the current required at low flow velocities.

5.2.6 Intergranular Corrosion

Definition

Intergranular corrosion is the preferential attack at, or adjacent to, the grain boundaries of a metal.

Description

As described previously, almost all engineering metals are composed of individual crystals, or grains, which meet at areas of relative impurity and misalignment called grain boundaries. Corrosion that occurs preferentially at, or adjacent to these grain boundaries results in a very large effect compared to the actual amount of metal removed at the grain boundaries. In some cases, individual grains are loosened and lost from the material. In other cases, the localized loss of grains boundary material results in localized attack similar in appearance to cracking.

Recognition

Intergranular corrosion is usually produces surfaces that are granular in appearance. It may also take the form of localized areas with the appearance similar to cracking.

Mechanism

Intergranular corrosion occurs when the grain boundaries, or the areas directly adjacent to the grain boundaries, are anodic to the surrounding grain materials. Grain boundaries may be anodic to the surrounding metal through many mechanisms. They may be anodic because of difference in impurity level between the grains and the grain boundaries. They may be anodic because of the effective strain energy of the misalignment of atoms in the grain boundaries. The grain boundaries, or adjacent areas may be anodic because of the formation of precipitates due to improper heat treatment.

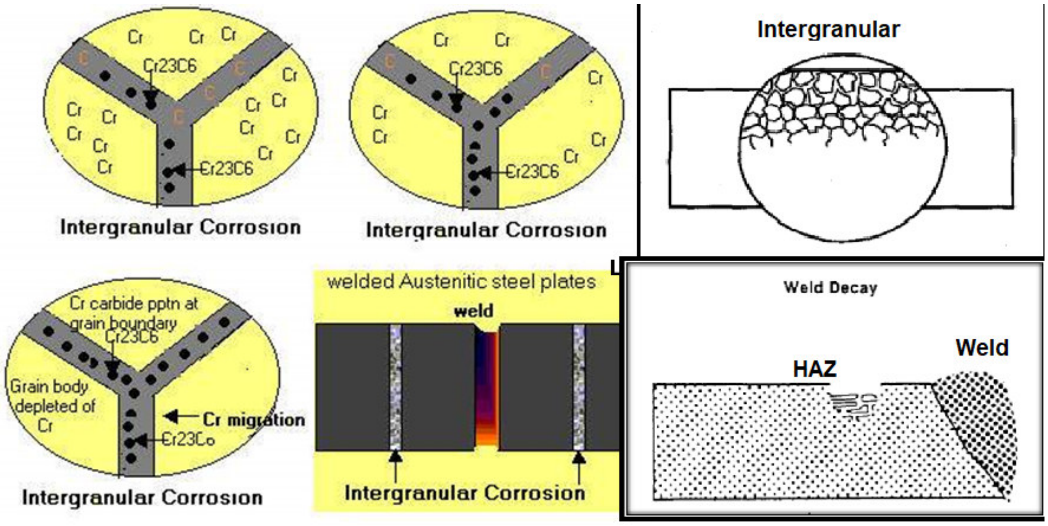


Fig. 5- 50. Intergranular corrosion

Intergranular Corrosion – Performance of Materials

Although several metals and alloy systems are subject to intergranular corrosion, we will concern primarily with stainless steels and aluminum alloys.

Intergranular Corrosion of Stainless Steel

Intergranular corrosion of stainless steel is most frequently caused by three types of metallurgical effects that cause the grain boundaries to become anodic relative to the surrounding material.

The three types of effects are:

1- General sensitization
2- Weld decay
3- Knife line attack

1- General Sensitization

Austenitic stainless steels, when they are cooled slowly through a temperature range of approximately 500 ^{0}C to 850 ^{0}C (932 ^{0}F to 1562 ^{0}F) or are otherwise maintained for some time in that range, can become susceptible to intergranular attack if subjected to specific corrodents. The grain boundaries are said to be “sensitized”. This sensitization is the cause of formation of chromium carbides, depleting grain boundaries and the areas adjacent to grain boundaries of chromium. The sensitized areas do not have sufficient chromium content to produce stable passive film. They become anodic with respect to the surrounding passive material. As will be described later in more detail, sensitization of stainless steels can be prevented by:

a- Avoiding heating in the sensitizing range
b- Heat treatment to eliminate chromium carbides
c- Use of material with very low carbon content
d- Use of stabilized material which contains alloy additions that preferentially combine with carbon rather than the combination of carbon and chromium.

If ferritic stainless steels are quenched rapidly, they can also become sensitized.

2- Weld Decay

Weld decay occurs in the heat-effected zone about 6 mm from the actual weld and parallel to it. Weld decay is the same as sensitization, except it occurs locally because of the effects of welding, rather than over the entire substrate.

Weld decay results in uniform thinning adjacent to the weld, where grains of metal have been removed because of intergranular attack.

3- Knife Line Attack

Knife line attack occurs in narrow zone near the interface of the weld pool and base metal. Knife line attack occurs only in certain stabilized grades of stainless steel at the weld temperature, which is higher than the temperature at which sensitization occurs. In general sensitization and weld decay, the chromium has a higher affinity for carbon than for the titanium or niobium which has been added to stabilize the material. Therefore, when the weld cools in the narrow weld zone, chromium carbides precipitates in the fusion line. Resistance to corrosion is lowered adjacent to the weld.

Aluminum and Aluminum Alloys

The chemical composition, mechanical working, and heat treatment of aluminum alloys have been developed to minimize intergranular corrosion. During welding this careful balance can easily be upset and the alloy can become susceptible to intergranular attack. Both the weld filler materials and the welding process, particularly the control of the heat input, must be carefully controlled to minimize the adverse effects of welding on the intergranular corrosion of aluminum alloys.

Certain aluminum alloys are subject to a form intergranular attack known as “exfoliation”. The appearance of the exfoliation is layered or leafed in character, consisting of alternating strata of corroded and uncorroded metal. Corrosion products resulting from the attack force the uncorroded layers upward from the surface, thus imparting the characteristic appearance of exfoliation.

Fig. 5- 52. Exfoliation of aluminum.

Although many aluminum alloys are resistant to intergranular corrosion, others are not, particularly aluminum alloy systems containing magnesium, copper, or both.

Development of intergranular corrosion of aluminum in an aqueous environment depends on the presence of chloride. Such conditions are a concern, for example, in seawater and other chloride-containing environments. Intergranular corrosion of aluminum is thought to occur in susceptible aluminum alloys as a result of the formation of precipitates along grain boundaries.

Copper and Copper Alloys

Copper and many copper alloys are susceptible to intergranular corrosion in environments containing amines or ammonia. Copper-nickel alloys are more resistant than other copper alloys in these environments.

Nickel and Nickel-Based Alloys.

Commercially pure nickel is subject to intergranular oxidation at elevated temperatures.

Nickel-copper alloys have reportedly suffered intergranular corrosion in certain hydrofluoric acid and chromic acid solutions.

Intergranular corrosion can occur in the nickel-molybdenum alloys in hot hydrochloric acid and sulfuric acid, especially (due to the precipitation of molybdenum rich constituents) because these acids precipitate molybdenum rich constituents.

Nickel-chromium alloys of the Inconel variety are subjected to intergranular corrosion because of Cr_7C_3 precipitation and are not intended for service where this could be a problem. Some nickel-chromium alloys have been stabilized against this type of attack and are effective in normal welding type construction for corrosive service. These alloys, however, are potentially subjected to Knife line attack (in the case of titanium-stabilized alloys) and to attack of intermetallic phases in highly oxidizing acid solutions.

In the molybdenum-bearing grades, intergranular corrosion is caused by molybdenum carbides and by molybdenum rich intermetallic compounds, rather than chromium carbides. This problem has been countered by stabilization and by reduction of the carbon content. These types of alloys have also experienced problems oxidizing chloride solutions (e.g., ferric chloride, hypochlorites) and in oxidizing and reducing acids.

Control of Intergranular Corrosion

Intergranular corrosion can be controlled in several ways including:

1- **Material selection**

Alloys can be selected for their resistance to intergranular corrosion in the specific service environment. For the stainless steels, alloy variations low in carbon content (the "L" grades) can be used, as well as grades containing stabilizing additions of such elements as titanium and niobium.

2- **Design/fabrication**

If the material is not resistant to the effects of welding on intergranular corrosion, the welds may be eliminated by using another joining technique. In some cases, the joints themselves can be eliminated in the design. Other fabrication process requiring heating of the metal must be properly controlled.

3- **Modification of the environment**

In some cases, the environment can be modified so that the affected grain boundaries are no longer anodic with respect to the adjacent material. This may be accomplished by adding corrosion inhibitors, or by removing aggressive ions (such as chlorides) where aluminum alloys are used.

4- **Use of proper welding procedures**

Proper welding procedures can minimize or eliminate the effects at grain boundaries that lead to intergranular corrosion. Welding procedures which minimize intergranular corrosion, once developed, must be followed carefully to obtain the desired effects.

5- **Heat treatment**

Proper heat treatment can eliminate intergranular corrosion either by preventing grain boundary effects in the first place, or by removing the adverse effects of improper heat treatment or welding. This commonly consists of a heat treatment called a "solution heat treatment" which dissolves the undesirable constituents at the grain boundaries. This heating is usually followed by a rapid cooling to prevent reformation of undesirable precipitates at the grain boundaries.

5.2.7 Dealloying

Definition

Dealloying is a corrosion process in which one constituent of an alloy is removed preferentially, leaving an altered residual structure.

Description

Most engineering metals are alloys that consists of mixtures of elements. In some cases, such as in the case of zinc and copper alloyed to produce a brass, one element used is anodic with respect to the other elements in the alloy and can selectively corrode by galvanic action.

The phenomenon was first reported in 1866 on brass (i.e., copper-zinc) alloys.

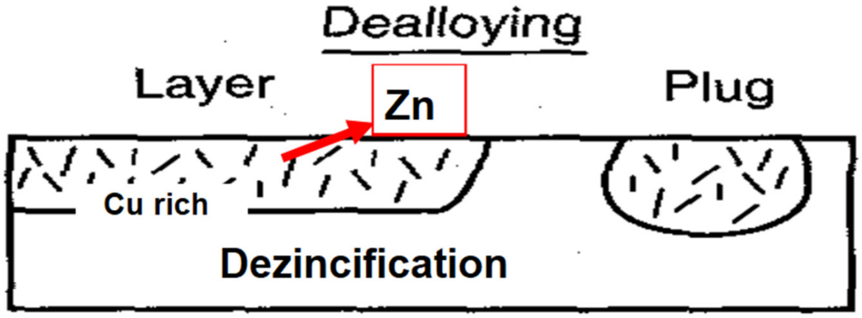


Fig. 5- 52. Dealloying.

Recognition

Dealloying is commonly detectable as a color change, or a drastic change in mechanical strength. Brasses will turn from yellow to red and cast irons from silvery gray to dark gray. Gray iron that has suffered graphitic corrosion can be cut with a penknife.

Difficulties may be encountered where deposit, colored environments, or accessibility make inspection hard. Problems will be experienced in detecting dealloying in most methods of automated inspection, because no volume change occur and because the density difference can be masked by precipitated salts, corrosion products, etc., within the dealloying region.

Various laboratory techniques, such as cross-sectioning the part in question, will normally provide evidence of color changes. Metallographic examination at high magnification and x-ray spectroscopy can provide positive identification.

Fig. 5- 53. Left Layer-type dezincification in brass bolts. The brass on the top right dezincified leaving a porous copper plug on the surface. Right bottom: dezincification of Mixing Tap Orifice - Potable Water.

Mechanism

The dealloying mechanism can be either a selective removal of one or more alloy constituents, leaving a residual substrate, or dissolution of the entire alloy, with one or more constituents deposited. Laboratory investigation have shown that both processes can occur simultaneously under certain conditions. In either case, the corrosion results in a residual metal with essentially the same surface profile and volume as the parent metal. Typically, up to 30% or more of the original metal will have corroded away, and the residual “sponge” or”plug” will have virtually no mechanical strength.

Dealloying – Performance of Metals and Alloys

Copper Alloys

Was originally observed in brasses and termed “dezincification” to connote the loss of zinc from the original copper-zinc alloy. Other terms, such as “destanification”,”denickelification”, and “dealuminification” have been used to indicate the loss of other alloying constituents.

Brasses

Red brasses of 15% zinc or less are usually resistant in their conventional applications in aqueous or atmospheric service. Yellow brasses, including inhibited “aluminum brass” and admiralty brass, are resistant in such moderate environments as potable water or fresh cooling waters if they contain tin plus arsenic, antimony, or phosphorus.

Bronzes

Phosphor (tin) bronzes have been subject to destanification (i.e., dealloying of tin from the alloy) in severe chemical environments.

Aluminum bronzes (copper-aluminum alloys) are sometimes subject to dealuminification.

Silicone bronzes have been subjected to desiliconificationin isolated cases involving high temperature steam plus acidic species.

Cupronickels have occasionally been reported to suffer dealloying under conditions of localized corrosion.

Cast Iron

Dealloying of cast irons usually proceeds uniformly inward from the surface, leaving a porous matrix of carbon.

Graphitic corrosion, or graphitization, is a form of dealloying caused by the selective dissolution of iron from some cast irons, usually gray cast iron.

In the dealloying of gray cast iron, the iron corrodes leaving the graphite matrix. In this instance, more than 80% of the original alloy may have been lost due to corrosion, with no apparent change in volume or thickness. There is no outward appearance of damage, but the effected metal loses weight and becomes porous and brittle. Depending on alloy composition, the porous residue may retain appreciable tensile strength and have moderate resistance to erosion. For example, a completely graphitized buried cast iron pipe may continue to hold water under pressure until jarred by workman’s shovel.

Graphitization occurs in salt waters, acidic mine waters, dilute acids, and soils especially those containing sulfates and sulfate-reducing bacteria.

The presence of sulfates and sulfate-reducing bacteria in soil stimulates this form of attack. The addition of several percent of nickel to cast iron generally reduces susceptibility to graphitization. It is possible to produce graphitization in the laboratory by immersing gray cast iron in a very dilute sulfuric acid.

Control of Dealloying

Control of dealloying can be accomplished in several ways, including:

1- Material selection

Control of dealloying is normally achieved by using an alloy that is more resistant to this form of corrosion, such as:

- Inhibited brasses instead of ordinary brasses
- Ni-resist cast iron instead of gray cast iron
- Nodular or malleable cast iron instead of gray cast iron

2- Modification of environment

It is sometimes possible to control dealloying corrosion by changing the environment, especially in regard to the parameters of acidity/alkalinity. For example, acidic waste waters that cause graphitic corrosion of cast iron can be controlled by proper treatment. Corrosion inhibitors can also control dealloying in some metal-environment systems.

3- Protective coatings

Protective coatings may be useful in some specific instances.

4- Electrochemical techniques

Cathodic protection has been demonstrated to control dealloying.

5- Design

Control of temperature is often used to control dealloying. Minimizing hot-wall effects in heat exchangers can be beneficial in controlling dealloying of some materials.

5.2.8 Fretting Corrosion

Definintion

Fretting corrosion is defined as metal deterioration caused by repetitive slip at the interface between two surfaces in contact.

Description

Fretting usually involves the relative motion of tow surfaces that were not intended to move in that fashion.

Recognition

Fretting corrosion occurs at the interface between two surfaces which can move with respect to each other. Surfaces effected by fretting corrosion are often free of corrosion products and show a burnished appearance.

Mechanism

Fretting corrosion occurs when motion between two surfaces either removes protective films, or, combined with the abrasive action of corrosion products, mechanically removes material from the surface in relative motion.

For fretting corrosion to occur, the interface must be under load and the motion (usually of small amplitude) must be sufficient for the surfaces to strike or rub together.

Results of fretting include:

- Metal loss in the area of contact
- Production of oxide and metal debris
- Galling, seizing, fatiguing, or cracking of the metal.
- Loss of dimensional tolerances
- Loosening of bolts or riveted parts
- Destruction of bearing surfaces

The wear process in fretting is not well understood. It is known that the debris produced can be either an oxide, if oxidation conditions exist, or very fine metal particles, if no corrosive medium invades the contact region. The debris can be abrasive and play a role in the fretting wear process.

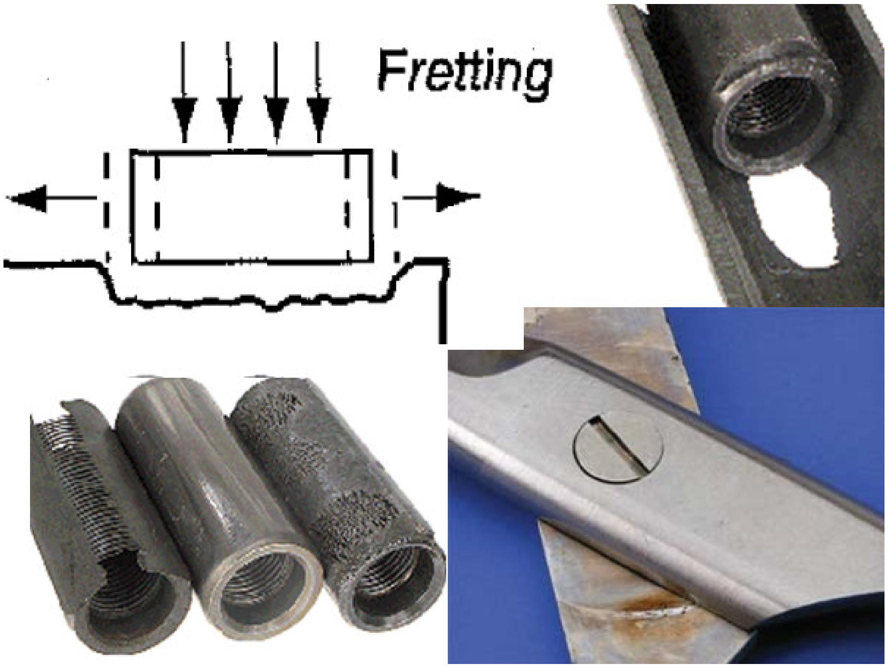


Fig. 5- 54. Fretting.

Fretting Corrosion – Performance of Metals and Alloys

Virtually all materials are subject to fretting corrosion if they are present.

Controls

Techniques for control of fretting corrosion include:

1- **Material selection**

To control fretting corrosion when the motion between the surfaces cannot be eliminated, use mating surfaces of different materials, e.g., soft metal against hard metal.

2- **Design**

In the design of systems, avoid situations in which there can be small relative motion between surfaces. This can be accomplished by roughening the interface, increasing the load.

The environment between the surfaces can be controlled by the use of cements or sealants. These materials can also reduce or eliminate abrasive scrubbing between surfaces.

3- **Use of lubricants**

Lubricants, such as molybdenum sulfide at the faying surface, can be used to control fretting corrosion. The use of such low friction materials as fluorocarbons, either as one surface in the system or as a lubricant, can also be effective in controlling fretting corrosion.

5.2.9 High – Temperature Corrosion

Introduction

High temperature corrosion is a form of material degradation that occurs at elevated temperatures. Direct chemical reactions, rather than the reactions of electrochemical cell, are responsible for the deterioration of metals by high temperature corrosion.

The basis of high temperature corrosion resistance stems from considerations of thermodynamics and kinetics of reactions at elevated temperatures.

Thermodynamics determines the tendency of metals to react in specific environments, considering both the temperature and species present in the environment (oxygen, water, sulfides, hydrogen, etc.).

In the case of kinetics, whether or not a metal is considered corrosion-resistant is dependent not on “whether

it corrosdes", but on "how fast it corrodes". As to what factors determine whether at high temperature corrosion reaction will occur slowly or rapidly, we must consider the characteristics of the corrosion product layer which forms.
The behavior of metals at elevated temperature, and especially their corrosion behavior, is a detailed and a complex subject.

Definition

High temperature corrosion is the deterioration of a metal at temperatures where direct chemical reactions between the metal and the environment cause the material to degrade.
The actual temperature at which high-temperature corrosion becomes important depends upon the material and the environment, but the corrosion usually begins to occur when the temperature is about 30% to 40% of the melting point of the alloy.
It is usually in this range what the mechanical properties are governed by creep strength, and here the first evidence of what we consider to be high-temperature corrosion characteristics appears. Magnesium and aluminum alloys are in high-temperature modes at temperatures as low as 204 ^{0}C (400 ^{0}F), iron and steel at temperatures as low as 426 ^{0}C (800 ^{0}F), stainless steel in the range of 425^0 to 870 ^{0}C (800^0 to 1600 ^{0}F). Titanium on the other hand, loses strength at temperatures as low as 315 ^{0}C (600 ^{0}F), despite its high melting point, 1815 ^{0}C (3300 ^{0}F)

Recognition

High-temperature corrosion is usually associated with the formation of thick oxide or sulfide scales, or with internal reactions that cause internal swelling of the metal at elevated temperatures.

Mechanisms

High-temperature corrosion is dependent on several reactions, including:

1. Oxygen reactions
2. Sulfidation
3. Carburization
4. Decarburization(hydrogen effects)
5. Halide effects
6. Molten-phase formation

1- Oxygen Reactions

Oxygen reactions are the most common and most widely studied high-temperature corrosion reactions. Oxygen reaction concepts are directly applicable to most other gas-metal, high-temperature reactions in which scale is formed. In fact, almost all high temperature corrosion reactions can be classified as oxidation, whether the scale is an oxide, a sulfide, or a halide, because the valence charge of the metal has been increased.
Most metals will react directly with oxygen at high temperatures. When a metal is oxidized at elevated temperatures, an oxide or other compounds may form. This corrosion product layer may act as a barrier between the substrate and the corrosive environment (air, flue gas, molten salt, or any other corrodent).

To be effective in controlling the rate of oxidation, oxide scales must:

- Be physically stable
- Maintain good mechanical integrity
- Be adherent to substrate
- Possess slow-growth kinetics
- Have low volatility

Reaction Rates

Depending on the degree to which the scale formed prevents attack of the base metal, the corrosion reaction can be either a linear or a parabolic function of time. Other rate behaviors with respect to time are also possible.

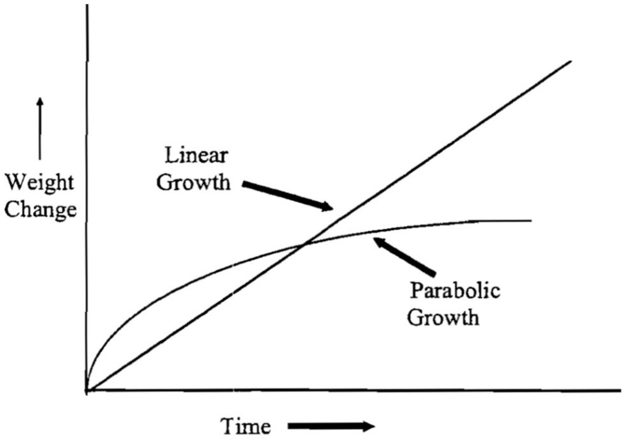


Fig. 5-55. High temperature corrosion rate

A. Linear Behavior

If the oxide film or scale cracks or is porous and the corrosive environment can continue to penetrate readily and react with the base metal, protection will be limited and attack will proceed at a rate determined essentially by the availability of the corrosive species. In this case, the rate will be linear.

B. Parabolic Behavior

If the scale formed in continuous, adherent, and prevents easy access of the corrosive gas to the underlying base metal, a considerable measure of protection may occur and the extent of protection will increase as the scale thickens. In this case, the availability of the corrosive gas will not determine the reaction rate.
Diffusion through the scale will be the slowest and, hence, the rate-controlling step. The diffusing element that controls the reaction rate may be either oxygen moving inward or the metal moving outward.
As the scale thickens, everything else remaining the same, the diffusion rate will decrease, so the rate of scale growth will decrease, and be inversely proportional to its thickness at any point in time.

Oxide Scale Characteristics

As briefly, mentioned, important characteristics of scales with respect to their ability to control high-temperature corrosion include scale thickness and scale adhesion.

A. Scale thickness

Scale thickness can be an important factor. In early stages, the scale is thin and comparatively elastic. It also will have little strength and usually will remain tightly adherent to the base metal . As it thicken, heavy scales tend to be brittle and, therefore, tend to rupture and spall from the surface.

B. Scale Adhesion

A weakly adherent scale is likely to separate locally from the base metal, a phenomenon sometimes termed blistering. Scales can eventually rupture and spall because they have a little strength.

Internal Oxidation

It is also possible for oxidation to proceed without an external scale, provided certain conditions exist.
The alloy must contain, as a minor ingredient, an element that is considerably more reactive than the major constituent. Silicon in copper is one example; chromium in nickel is another.
The rate at which the minor element diffuses toward the surface must be less than that at which the corrosive species diffuses inward.
Internal oxidation is controlled by the concentration of oxygen in surface layers. This quantity must be insufficient to oxides the noble major constituent, but sufficient to oxidize the reactive minor constituent.

2- Sulfidation

When the sulfur activity (partial pressure, concentration) of the environment is sufficiently high, Sulfide phases (in addirtion to oxide phases) can be formed.

In the majority of environments encountered, alumina or chromium sesquioxide should form in the preference to any sulfides, and destructive sulfidation attack occurs mainly at sites where the protective oxide has broken down. Sulfur can be transported through scales. Once it has entered the alloy, sulfur appears to tie up the chromium and aluminum as sulfides. If sufficient sulfur enters the alloy so that all immediately available chromium or aluminum, is concerted to sulfides, the less stable sulfides of the base metal can then form.
It is these base metal sulfides that are often responsible for the observed attack because they grow much faster than the oxides or sulfides of chromium or aluminum. They have relatively melting point, so molten slag phases are often possible.
Once sulfides have formed in the alloy, there is a tendency for the sulfide phase to be preferentially oxidized by the encroaching reaction front (Oxides are more stable than sulfides) and for the sulfur to be displaced inward. This process prompts the formation of new sulfides deeper in the alloy, often in grain boundaries or at the sites of other chromium- or aluminum-rich phases. In this way, finger-like protrusions of oxide/sulfide can be formed from the alloy surface inward, which may act to localize stress or otherwise reduce the load-bearing section.

3- Carburization

Metals, such as steel, when exposed to a suitable carbonaceous gas or liquid at high temperature, may absorb some of the carbon atoms that reach the metal surface. The surface because of its higher carbon content, will respond better to heat treatment and develop a higher surface hardness, while the interior will be softer but tougher, a desirable characteristics for many applications.
Most metals have a significant solubility for carbon, that is they can absorb large amounts of carbon without undergoing any drastic physical change, although some properties (e.g., response to heat treatment) may be altered measurably.
If carbon continue to be driven into the metal, its solubility can be excesses and more dramatic changes will occur. In the more commonly used heat resistant alloys of the iron-nickel-chromium system, precipitation of chromium-rich carbides will occur.
As carburization continues and the quantity of carbides increases, the matrix of the alloy will be depleted of chromium. As discussed previously, chromium is the element that contribute most to a resistance to oxidation and sulfidation. The chromium-depleted matrix will be unable to develop adequate protective scales and will become quite susceptible to these these and other types of attack. Furthermore, the presence of continuous grain boundary carbides will both increase the rate of intergranular attack (because the carbides are more reactive than the matrix) and deteriorate the mechanical properties (because cracks can propagate more readily).
Another possible effect of carburization is metal dusting. This phenomenon occurs in process operations where oxidizing and reducing conditions alternate. When the environment is on the reducing side (CO predominant), shallow carburization of the metal can occur at breaks in the protective oxide film. When the exposure then changes to oxidizing, the high-carbon area of the metal is burned out and the underlying metal is reacted to become new oxide. A depression is left in the metal surface where the carbburized area existed, and the metal oxide is swept downstream as metal dust.

4- Decarbrization (Hydrogen Effects)

Decarbrization or high-temperature hydrogen effect attack is a high-temperature phenomenon that should be distinguished from hydrogen-induced cracking, which occurs at near ambient temperature and is usually associated with an aqueous environment as the source of the hydrogen. At temperatures above the dew point, high-pressure hydrogen is the usual source.

The attack relates to the reaction of hydrogen, with readily reducible carbides, or in some cases oxides, within the alloy to form methane or steam. These gaseous products, under high pressure, will cause small local ruptures which will impair the structural integrity of the metal and lead to early failure.

Hydrogen is a difficult gas to cope with at elevated temperatures because of its ability to diffuse rapidly through metals in atomic form and because of its extreme reactivity. If the hydrogen, during its passage through the metal, encounters such readily-reducible compounds as the carbides previously mentioned, an irreversible reaction will occur.

5- Halide Effects

Halogen gas can form volatile halide layers on metal substrate. When a critical temperature is reached, the halide layer evaporates, leaving the metal substrate exposed to further rapid reaction.
Corrosion by halogens proceeds in essentially the same fashion as corrosion by oxygen, sulfur, or nitrogen. The gas upon contacting the surface will oxidize the metal atoms there and form a halide layer.
The halide scale, while it remains in place, will offer some measure of protection againest continuing attack. The major difference is that metal halide compounds all have very high vapor pressures, so that when some critical temperature is exceeded, the scale will volatize and leave the metal surface exposed for further rapid reaction.

6- Molten-phases formation

In all environments considered up to this point, we have ignored the possibility of corrosion product fusion and have limited the discusion to gas metals reactions with solid, or in the case of halides,gaseous reaction products. In many situations, the corrosion product itself may melt, or contaminants may lower the melting point into the service of temperature range.
The reaction products or harmful contaminants have one thing in common; whether they themselves are solids, liquid, or gaseous, they react with the metal or corrosion products to form fused phase. This phase will destroy the integrity of protective scale by fluxing or dissolving it and leaving the underlying metal available for further corrosion. Frequently the fused phase will attract and concentrate effective corrodents at the place where they do the maximum amount of damage; where the scale is disrupted.
Some familiar examples of contaminants which interfere with the normal development of protective scale during high temperature services are:

a- Leaded gasoline: The composition of leaded gasoline leaves deposits of leadoxide and other compounds on exhaust valves, which can shorten their lives.
b- Residual oils: Combustion of residual oils may interfere with the normal development of a protective scale.
c- Sea salts: The small amounts of sea salt may enter a reactor or gas turbine with the combustion air can initiate a sequence of events culminating in catastrophically high corrosion rates.
d- Welding slag: improbperly or incompletely removes, also may cause difficulty and frequently premature failure.

High-Temperature Corrosion- Performance of Metals and Alloys

Carbon and Low-Alloy Steels

Ordinary carbon and low-alloy steels have been used successfully from room temperature up to 480 ^{0}C (900 ^{0}F) and for short periods of time up to 590 ^{0}C (1100 ^{0}F). At temperature beyond this, ordinary steels tend to corrode rather heavily. There is a trend to resort to cementation (surface diffusion treatment) on carbon and low alloy steels to render them more resistant to corrosion. Depending on the corriveness of the medium involved and the exposure of temperature one or several of the following may be used: Siliconizing, aluminizing, chromizing, or special treatment such as plating, plasma spraying, or cladding.

Alloy Additions

Addition of alloying elements to steels can greatly increase their resistance to some high-temperature environments.
Additions of chromium to steel can cause a sharp decrease in iron corrosion (oxidation) by air at elevated temperatures. On the negative side, chromium additions can make iron less resistant to halide attack. Nickel

additions to iron-chromium alloys not only improve the corrosion resistance, but their mechanical strength as well.

The benificial effect of aluminum additions in suppressing high-temperature corrosion of iron alloys is strong. When amounts of 12% aluminum are added, a considerable reduction in high temperature corrosion is achieved. However, mechanical properties suffer, thus making this approach to corrosion resistance less attractive. Where lower mechanical properties can be tolerated, the use of limited amount of aluminum can be considered.

One approach to simulating aluminum-alloying while causing relatively little effect on mechanical properties is spray metallizing or aluminizing. This high-temperature cementation process diffuses aluminum into iron and produces an effective surface for exposure in air, or sulfur dioxide fumes to temperature in the neighborhood of 1095 ^{0}C (2000 ^{0}F).

Stainless Steels

The most common alloys used for exposure at high temperatures are the stainless steel.

If the medium- or high-alloy steel are used, chromium-bearing stainless steel are generally recommended. Both straight chromium steels and chromium-nickel stainless steel are used up to approximately 870 ^{0}C (1600 ^{0}F). At still higher temperatures, higher nickel and a higher chromium alloys are used. At a temperature somewhat in excess of 1093 ^{0}C (2000 ^{0}F), only alloys with more than 20% Cr can be used. These alloys are relatively safe for short or intermediate periods of time.

During long-term use at high temperatures, a phenomenon known as creep is experienced, during which relatively low loads may cause a metal deform very slowly and possibly fail.

Nickel-based Alloys

Many nickel-based alloys have excelent resistance to high-temperature corrosion, and many have been specifically developed for high temperature application such as blades for gas turbine engines.

Refractory metals

At temperatures higher than can be tolerates by other alloys, it may be necessary to use refractory metals-those that have good high temperature mechanical properties and melting temperature well above 1650 ^{0}C (3000 ^{0}F). Thus, alloys of chromium, niobium, molybdenum, tantalum, rhenium, or tungsten are usually considered for very high temperature service.

Control of High-Temperature Corrosion

1- **Material Selection**
   The selection of materials compatible with the chemical makeup of the environment at the specific service temperature conditions is the most commonly used method for controlling high-temperature corrosion.
2- **Design**
   Design can be used to reduce some factors related to high-temperature corrosion. Stress reduction can reduce the creep that affects scale adhesion and dimentional stability of the metal itself. Reduction of thermal cycling and thermal differentials can also be used to control high-temperature corrosion.

3- **Modification of the Environment**
   In some cases, environmental contaminants can be controlled to reduce high-temperature corrosion. In other cases, materials such as oxygen can be added to improve scale formation when the scales are more stable in high-oxygen environments.

4- **Protective Coatings**
   Protective coatings of high-temperature-resistant metals and alloys applied by weld overlay or electroplating, as well as ceramic coatings, have been successfully used to control high-temperature corrosion in some cases.

Chapter 6

Methods of Corrosion Control

6.1 Design

Corrosion control at the design stage does not just happen- it must be planned. For a major project, as much lead-time will be required for the corrosion aspects of the design as for other consideration. If the technology of the application is established, there has to be careful selection of a known solutions, with meticulous attention to those details that are new.

Design includes consideration of many factors, such as:

1. Material selection
2. Process parameters
3. Construction parameters
4. Geometry for drainage
5. Dissimilar metals
6. Crevices
7. Corrosion allowance / Operation lifetime
8. Maintenance and inspection requirements

6.1.1 Material selection

Material selection because of its importance as a corrosion control method will be considered as a separate topic in this chapter.

6.1.2 Process Parameters

In designing equipment and facilities, it is important to consider the various factors that make up the service conditions, including:

A- Temperature
B- Velocity
C- Pressure
D- Chemistry

A - Temperature:

Temperature factor to be considered include the nominal operating temperature, the maximum operating or the upset temperature, the minimum operating temperature, and temperature during downtime.
In most corrosion reactions, an increase in temperature accompanies by an increase in reaction rate. A rule of thumb suggests that the reaction rate doubles for each 10 ^{0}C (18 ^{0}F) rise in temperature. Although there are numerous exceptions to this rule, it is important to take into consideration the influence of temperature when analyzing why materials fail, and in designing to prevent corrosion.

Nominal Operating Temperature
The nominal design temperature range, is usually the primary concern with regard to corrosion resistance because it is the temperature range that will occur most of the time. Material used for construction are normally selected on the basis of the nominal operating temperature.

Maximum Operating/Upset Temperature

The design engineer must consider the maximum operating temperature to which equipment may be exposed in cases of malfunction. For example, a car radiator operates at temperatures of 80 ^{0} to 90 ^{0}C (176 ^{0}F to 194 ^{0}F), but in the event that some fluid is lost, the temperature may go to 100 ^{0}C (212 ^{0}F); as a result the radiator or coupling hoses may blowout. In the same sense, if a large steam boiler loses its water or steam content, the boiler tubes are no longer cooled by the steam, and the steel tubes may be severely damaged. The maximum operating temperature must be considered, along with the normal operating temperature. In some cases corrosion rates can be very high at the maximum operating temperature, and significant corrosion can

occur during these short periods.
In some cases, corrosion can initiate at elevated temperatures where it would not initiate at normal operating temperatures. This corrosion sometimes continues at the normal operating temperature. Materials having passive films that subject to the initiation of such corrosion. Protective coatings selected to withstand normal operating temperatures can be damaged during periods of higher temperature and may not provide protection during subsequent operation at lower temperatures.

Minimum Operating Temperature

In some cases, particularly when there are considerable gases in the system, the system can be damaged at temperature lower than the nominal operating temperature. Flue stacks and engine exhaust systems are examples of systems that are designed to operate hot without the presence of liquid water. If operated below the dew point, where water condense, corrosion can occur.

Temperatures During Downtime

Temperatures during downtime must also be considered. Although these temperatures are usually lower than the operating temperature, effects such as condensation must be considered during design.

B- Velocity

Flow rates

As discussed previously in this book, velocity and fluid flow can have a great effect on corrosion. Systems should be designed to limit fluid flow velocities to levels that can be tolerated by the materials. Fluid flow velocities are must commonly controlled by the selection of pipe sizes.
Even short periods of high flow can remove surface films and initiate corrosion that can be continued during the period of normal flow.
Low-flow conditions should also be considered, particularly when using stainless steel and other alloys that require oxygen to maintain their passive films.
In most cases, entrapment of air or other gases and solid particles in the fluid flow should be avoided.

Flow Regime

Turbulence greatly increases the effects of fluid flow. Systems should be designed to minimize turbulence. The use of wide-radius elbows (sweeps) is a common method for avoiding turbulence in piping systems. The systems must be installed carefully to ensure that no conditions cause turbulence. The use of improperly fitting gasket can cause turbulence.

C- Pressure

In systems that are completely filled with liquid, pressure usually has little effect on corrosion reactions. However, pressure has a great effect on the consequences of corrosion. High-pressure equipment must be carefully designed to prevent catastrophic failures, and corrosion of such equipment is very important aspect of design. Pressure also is a major factor in stresses in the system, and the effect of these stresses on corrosion, particularly on environmental corrosion cracking, must be considered during design.

If both gases and liquids are in the system, the solubility of the gas in liquid is a function of the pressure in the system. The corrosivity of the liquid and the gas partial pressure must be considered in system design.

Pressure Variations

Pressure variations not only affect the range of environments that must be considered in design, but they can induce cyclic stresses that cause corrosion fatigue.

D- Chemistry

The chemistry of the environment is an important factor in system design. In some cases, wide ranges of chemistry will be encountered; and the system must be designed with consideration of all environments, that may occur. This includes normal operating conditions, deviations, and conditions during downtime. As mentioned previously, a large number of chemical factors influences corrosion, including:

- pH
- Major species
- Minor species
- Nature environment (atmospheric vs immersion)

All these, and other factors in the chemical makeup of the environment, must be considered during design.

6.1.3 Construction Parameters

The locations of specific structures and processes within a facility should be considered. For example, if several buildings are to be constructed, a building that produces corrosive fumes should be located downwind from the others.

In many cases, systems are constructed or assembled under field conditions rather than under controlled shop conditions. Control of field conditions is particularly important with regard to welding and the application of protective coatings. In the field, it may be necessary to weld or apply protective coatings under unusual or awkward conditions. These conditions must be considered in design. Welding and the application of protective coatings may require special field precautions. Failure to properly control conditions can result in a system that is not corrosion resistant as intended.

Welding

Welding is one of the most important parts of fabrication. Too often, rigid material specifications based on optimum performance of the equipment are voided by mistakes in welding. One must start with the convection that no shortcut can be taken in welding integrity and quality. Strict adherence to fabrication codes, joints preparation, welder qualification, selection of compatible welding techniques and electrodes, thermal pre- or post-treatment, and inspection is mandatory. Techniques may range from gas welding to electron beam welding, with an array of possibilities in –between. The appropriate selection of joining methods is a must to ensure optimum performance.

In some cases, post weld heat treatment may be required to restore mechanical properties of the weldment, to improve strength and corrosion-resistance properties in the weld and heat-affected zones, and to reduce residual stresses. When required, these treatments must be carefully specified and carried out. Post weld heat treatment is particularly difficult in field conditions, and most welding requiring post weld heat treatment is done in shop conditions.

Some basic rules apply to most welding:

- Keep the weld design simple
- Insist on approved shop drawings
- Conform to code regulations
- Specify inspection requirements
- Specify “pass/fail” limits for inspection results
- Specify welding procedures in detail
- Specify procedures for storage and handling of welding materials
- Specify the proper filler metal
- Make an inspection agreement with the fabricator
- Ensure fabricator’s capability to do the job
- Ensure qualifications of welders
- Specify post weld heat treatment, if necessary
- Consider post weld shipping of equipment

Accommodating Other Corrosion Control Measures

The overall system design can affect such corrosion control measures as protective coatings and cathodic protections. Examples are sufficient clearance around, over, and under components that are to be coated. The clearance must be sufficient for surface preparations and coating application.
Consideration should be given to clearance for scaffolding, if required. A surface that is easily accessible will

receive a better coating than one that is not. Access for repair of coatings and recoating must also be considered.

Cathodic protection systems must be considered in the overall design, rather than as the afterthought. Locations of Anodes, rectifiers, and other system components should be considered with regard to access for installation and maintenance.

6.1.4 Geometry of Drainage

Design should ensure water or corrodents cannot be trapped. There is innumerable ways to design systems so that water and debris can be trapped and held in contact with surfaces. This greatly increases surface corrosion that is due to increase time of wetness. The illustrative below show common drainage problems.

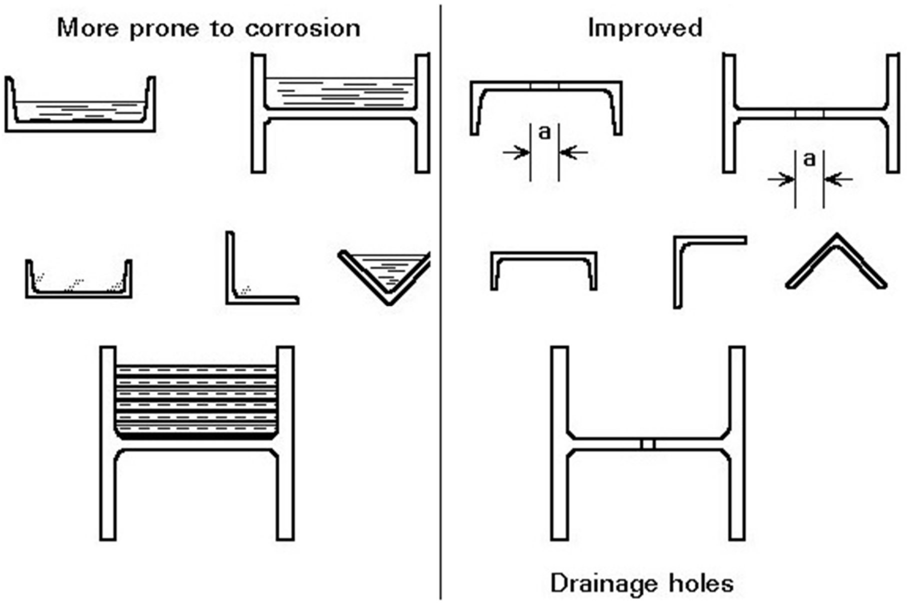


Fig. 6-1. Poor and good designs.

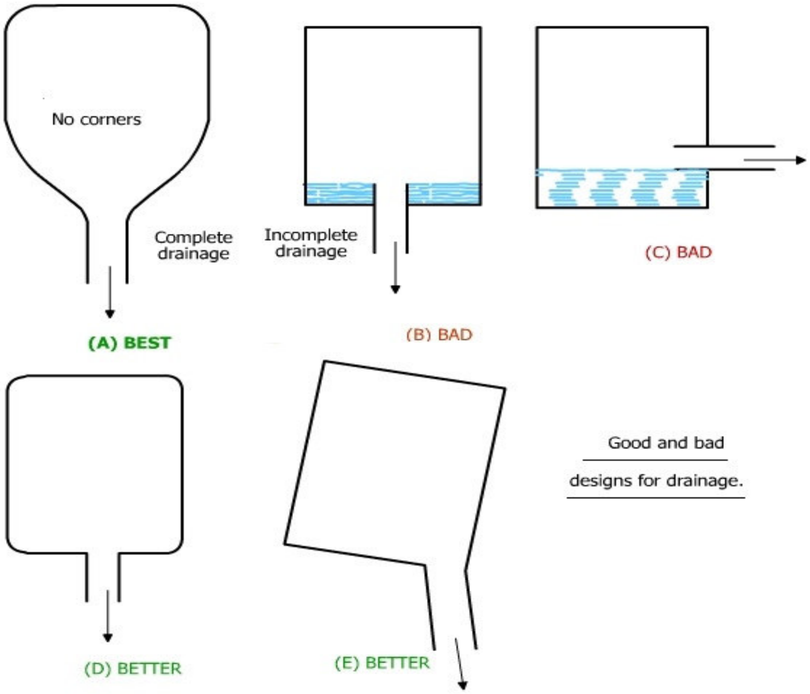


Fig. 6-2. Poor and good designs

6.1.5 Dissimilar Metals

Within a system, it should be ensured that no metal is installed that adversely affect other metals galvanically. For instance, if we install a copper or brass valve in a plain carbon steel system, the copper will be cathodic to the carbon steel, and the steel adjacent to the valve will corrode more rapidly.

As described previously, the area effect in this type of corrosion may be quite pronounced.

If galvanic corrosion is a problem, the following remedial measures may be considered:

- Use Metals compatible in galvanic contact. This may mean the use of metals close together in the galvanic series for the service environment, or use materials with desirable polarization characteristics (e.g., stainless steel or titanium) for cathodic member of the couple.
- Avoid unfavorable cathode/anode ratios. Anode/cathode ratios are often more important than the position of the metals in the galvanic series. Insulate (break the circuit between the two metals) to ensure contact is not restored during service.
- Maintain coatings. It is important for the cathode to be coated carefully and maintained to avoid an unfavorable cathode/anode area effect.

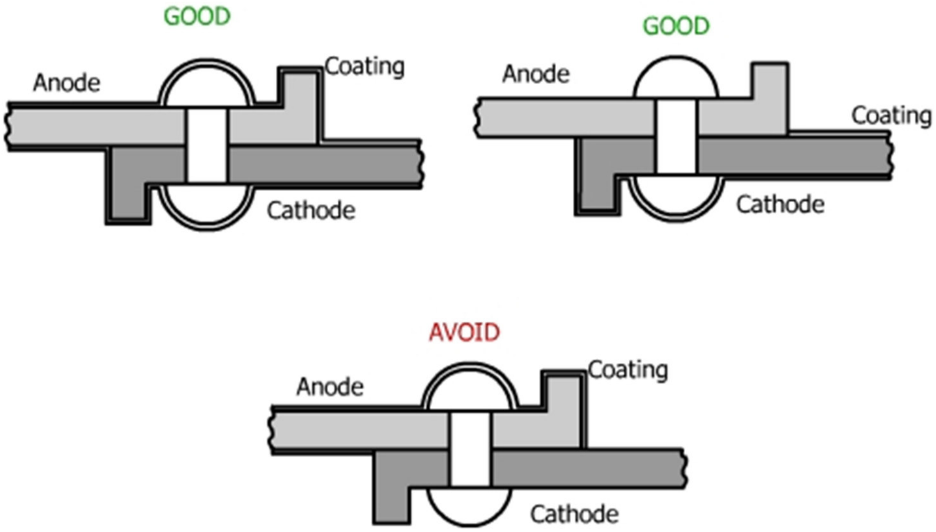


Fig. 6-3. Dissimilar metal coating.

6.1.6 Crevices

Wherever possible, crevices should be minimized. As in case of drainage, there are innumerable ways to create crevices and innumerable illustration of ways to avoid crevices. Like many other corrosion-related design aspects, attention to crevices is an important part of designing a corrosion resistant system. One of the best ways to avoid crevices is to join parts by welding rather than by bolting or riveting. A full penetration butt weld is the type of welded joints that best eliminate crevices.

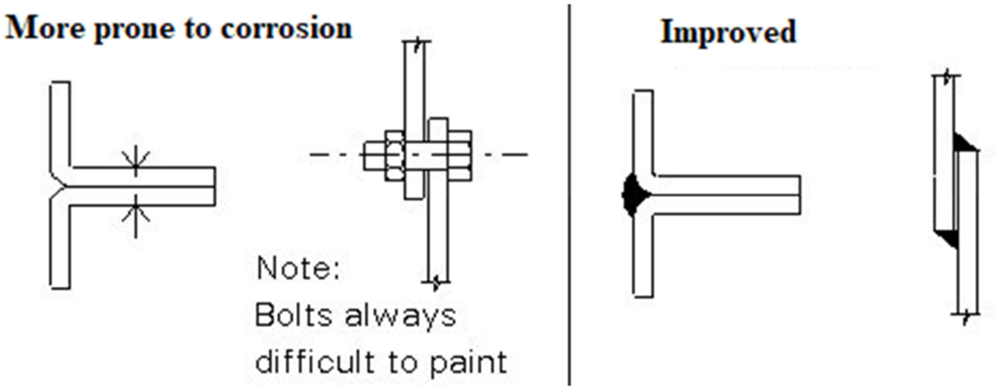


Fig. 6-4. Crevice eliminations.

6.1.7 Corrosion Allowance/ Operation Lifetime

In some cases, it may be more economical to use less corrosion-resistance material and compensate for rate of attack. In most cases, additional material or corrosion allowance, is added to the system to make up for the corrosion likely to occur over the life of the system. This approach assumes that the corrosion is not unacceptable from the standpoint of contamination or appearance and that corrosion is predictable. Use of corrosion allowance is normally only applicable to metal-environment combinations in which uniform corrosion occurs at either a linear rate or a rate that decreases with time. Corrosion allowance is normally used when a specific lifetime for the component can be defined, and the component can be replaced easily if additional system-operating life is desired.

6.1.8 Maintenance and Inspection

Consideration should be given to ease maintenance and inspection by providing adequate access to components. This access may require specific items such as access ports to manholes, or may be simply involve proper location of equipment.

It is important that the designer prepare detailed inspection and maintenance manuals and instructions.

6.1.9 (1) Material selection

One answer to the control of corrosion is to use a more resistant material. Since, there is no such thing as a material resistant to all corrosive situations. In selecting a material, we first need to define the required characteristics of the material, then find a material with as many of these characteristics as possible. If there is no material that have all the required characteristics, we need to find some means of corrosion control or adjust the service conditions to meet the characteristics of the candidate material.

6.1.9.1 Factors That Influence Materials Selection

Selecting an appropriate materials can involve balancing out a large number of factors, such as:

1. Corrosion resistance in the environment
2. Availability of design and test data
3. Mechanical properties
4. Cost
5. Availability / Maintainability
6. Compatibility with other system components
7. Life expectancy of equipment
8. Reliability
9. Appearance

1. Corrosion Resistance in the Environment

Corrosion resistance in the service environment can be very sensitive to the exact chemical and physical characteristics of the environment. Before materials can be selected, the environment must be defined.

Some of the environmental characteristics that need to be defined are :

- Main constituents (identity and amount)
- Impurities (identity and amount)
- Temperature
- pH
- Degree of aeration
- Velocity or agitation
- Pressure
- Estimated range of every variable

The proper material can be selected only after all the pertinent environmental characteristics have been defined.

2. Availability of Design and Test Data

Data on the performance candidate materials in the specific environment must be available for appropriate materials to be selected. Data about the performance of materials in identical service environments is always best to use, but the data is often unavailable. Service data from similar service environments is usually the next best choice for materials selection, as long as enough is understood about the differences between the present environment and the previous service environment.

Data from laboratory tests can be used as a basis for materials selection in applications where the service environment is not too complex and can be easily reproduced in the laboratory. Laboratory tests, however, are usually of short duration. It is often difficult to get reliable laboratory data about the changes in corrosion rates over long periods of time, and short-duration laboratory tests can fail to identify corrosion mechanisms with long-reaction times.

Laboratory tests can fail to identify corrosion mechanisms with long reaction times. Laboratory tests are frequently used as screening test to eliminate materials with undesirable characteristics. The candidate materials are then tested for longer period under conditions that more closely match the anticipated service conditions.

Published corrosion data contains information on materials performance in both laboratory and service conditions. These data must be used carefully. It is particularly important that the reported corrosion measurement was appropriate for the type of corrosion that occurred. For example, the use of corrosion rates based on the weight.

3. Mechanical Properties

Mechanical properties, such as strength and ductility, are important factors in the selection of materials for any application. These data are widely available. Loss of ductility due to environmental cracking is an important consideration that must be addressed in many cases.

4. Cost

Cost is a consideration in the selection of materials. The use of simple cost considerations, such as the cost per kilogram of material, is not sufficient to give a good idea of the actual installed cost. Costs of fabrication often overweight the actual cost of the material used. It is often less expensive to use a material that is easy to fabricate than one that is difficult to fabricate, even if the easy material is higher in cost per kilogram.

Other costs must also be considered in the selection of materials. Annual costs of maintenance, replacement, and repair are important considerations. To properly assess these costs, calculations must consider the time value of money. These economic analysis must be performed to determine the actual cost of material selection options over the life of the system.

5. Availability and Maintainability

The material must be available in the form required. Many materials are available as plates and sheet, but not as pipe or castings, and vice versa. It is sometimes practical to make use of an available form of the material, (e.g., to fabricate a pipe from sheet material), but the cost of fabrication and the effect of fabrication on the material properties must be considered.

Also the availability of material for partially replacement if recommended during inspection or in case of failures.

6. Compatibility with Other System Components

Material selection must be performed based on consideration of the entire system. Incompatibilities, such as those that might cause galvanic corrosion problems, are easy to identify and correct. Other corrosion problems, such as corrosion due contamination by metal ions from other parts of the system, are much more difficult to identify at the design stage. One common problem in this area is when different parts of the system are designed by different groups. Each portion of the system may be well designed. However, they may not be compatible with each other. Design, particularly from the standpoint of corrosion, is a system problem.

7. Life Expectancy of Equipment

In some cases, it is less expensive and more practical to design specific system components for short life, with frequent replacement during overall life of the system. In these case, it is important that inspections and replacement of these components be included in the operation and maintenance manuals for the system.

It is difficult to establish the actual required life of equipment. Frequently the actual service life of the equipment exceeds the nominal “design life” originally assumed. This can lead to situations in which maintenance and repair costs due to corrosion become excessive, or much worse, results in service failures.

8. Reliability

Reliability is also an important factor in materials selection, particularly when failure is a safety or environmental issue, such as in high pressure piping carrying hazardous materials. Reliability outweighs cost and expense, and the use of corrosion resistant materials may be justified.

9. Appearance

Appearance is also an important factor in the design. The human factors of a clean and pleasant environment not only affect the quality of life for workers but, is an important factor in community relations.

6.1.9.2 Comparison with Other Corrosion Control Methods

Materials selection is an important consideration in the design of corrosion-resistant systems; however, it is only one possible option for controlling corrosion. The iron and steel used for the vast majority of structural applications are not corrosion-resistant in many environments and must be protected.

In atmospheric environments, coating are used to protect many materials against corrosion. In underground and immersion conditions, a combination of coatings and cathodic protection is commonly used to augment the resistance of materials that are not inherently corrosion-resistant. Many liquid-handling systems rely on corrosion inhibitors. Of course, these means of augmenting the corrosion resistance of materials has associated costs, and the overall cost and other factors must be considered.

6.1.9.2.1 Candidate Materials

According to the performance of materials and their resistance to many forms of corrosion a selection can be made. Metals and nonmetals are candidates for a wide range of applications.

Metals

When selecting metals, the detailed of the structure of the metal is often as important as the chemical composition of the metal. Proper heat treatment and surface treatments to obtain the desired properties must be specified.

Candidate metals are commonly classified into the following groups:

- Carbon and low-alloy steels
- Stainless steel
- Nickel and nickel-based alloys
- Copper and copper alloys
- Aluminum and aluminum alloys
- Titanium and titanium alloys

Nonmetals:

Candidates nonmetals are commonly classified into the following groups:

- Plastics
- Composites
- Elastomers
- Concrete
- Vitreous materials

6.1.9.2.2 Modification of the Environment (Corrosion Inhibitor)

Modification of the environment is widely used to enhance the inherent corrosion resistance of materials. In liquid-handling systems, the three principal methods of environmental modification are the use of corrosion inhibitors, deaeration, and pH control.

Corrosion Inhibitors

A corrosion inhibitor is a substance which, when added to an environment, decreases the rate of attack by the environment. Corrosion inhibitors are commonly added in small amounts to acids, cooling water, steam, and other environments, either continuously or intermittently, to control corrosion. Corrosion inhibitors generally control corrosion by forming thin films that modify the environment at the metal surface.

Inhibitors form films in several ways: by adsorption, the formation of bulky precipitates, and the formation of a passive layer on the metal surface.

Some inhibitors retard corrosion by adsorption to form a thin, invisible film only a few molecules thick. Others form bulky precipitates that coat the metal and protect it from attack. A third mechanism consists of causing the metal to corrode in such a way that a combination of adsorption and corrosion product forms a passive layer.

Types of Inhibitors

Types of corrosion Inhibitors include:

1. Anodic (Passivating)
2. Cathodic
3. Ohmic
4. Precipitation inducing
5. Vapor phase

1- Anodic (Passivating) Inhibitors

Anodic inhibitors is illustrated in the Evans diagram below. The increase in anodic polarization decreases the corrosion current. And the rate of corrosion at the anode.

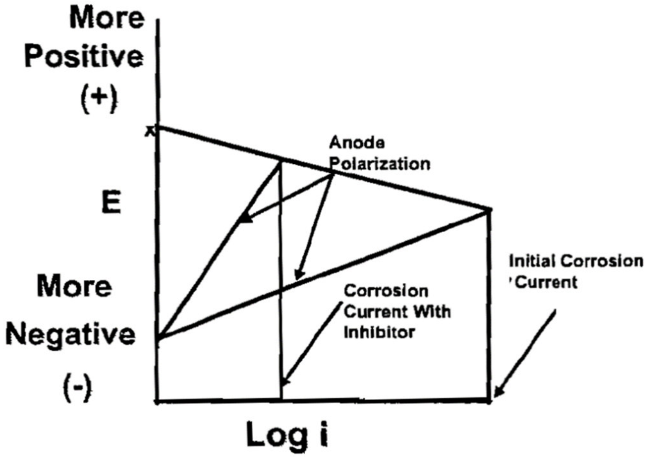


Fig. 6-5. Anodic inhibitor- and anodic polarization

Anodic inhibitors must be used with cautions because they can cause increased localized corrosion if they do not cover the entire anodic surface.

There are two types of anodic inhibitors: Oxidizing and non-oxidizing

Oxidizing inhibitors include chromate, nitrite, and nitrate, which can passivate steel in the absence of oxygen.

Non-oxidizing anodic inhibitors, such as phosphate, tungstate, and molybdate, require the presence of oxygen to passivate steel.

Cathodic Inhibitors

Cathodic Inhibitors cause cathodic polarization. As shown in the Evans diagram below, this decrease the corrosion current and the corrosion rate of the anode.

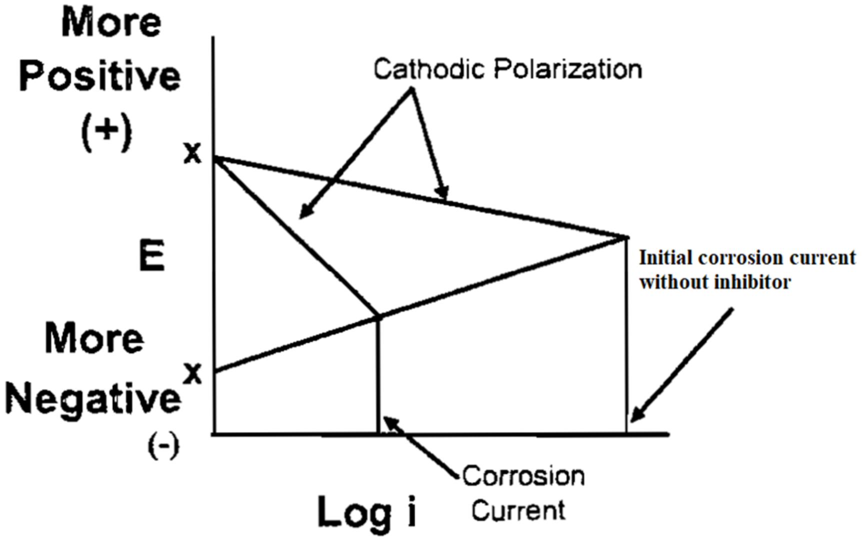


Fig. 6-5. Cathodic inhibitor- and cathodic polarization

There are two main types of cathodic corrosion inhibitors, cathodic poisons and cathodic precipitates. Cathodic inhibitors either slow the cathodic reaction itself, or cause selective precipitation on the cathodic area. The latter method increases the circuit resistance and restrict diffusion of reducible species to the cathodic areas. Where the anodic polarization in unaffected, the corrosion potential is shifted to more negative values.

Cathodic poisons interfere with cathodic reactions, such as hydrogen atom formation or hydrogen gas evolution. The rate of cathodic reaction is slowed; and because anodic and cathodic reactions must proceed at the same rate, the whole corrosion process is slowed.

Examples of cathodic poisons include arsenic, bismuth, and antimony compounds.

A serious draw back in the use of cathodic poisons is that they sometimes cause hydrogen blistering of steel and increase its susceptibility to hydrogen embrittlement. Because the recombination of hydrogen atom is inhibited, the surface concentration of of hydrogen atom is increased; and a greater fraction of the hydrogen produced by the corrosion reaction is absorbed into the steel. Blisters are formed when hydrogen atoms combine to form hydrogen molecules inside the steel. Molecular hydrogen does not diffuse through the steel; therefore, it collects at defects or voids to create pressure, which may reach 7000 MPa (1 million psi) or more.

Cathodic precipitates deposit because of increased pH resulting from the cathodic reaction. The most widely used cathodic precipitation-type inhibitors are the carbonates of calcium and magnesium because they occur in natural water. Their use as inhibitors usually requires only an adjustment of pH. Zinc sulfate ($ZnSO_4$) precipitates as zinc hydroxide $Zn(OH)_2$ on cathodic areas and is also considered an inhibitor.

Ohmic inhibitors

Ohmic inhibitors increase resistance of the electrolyte circuit by forming a film on the metal surface. Because it usually impractical to increase the resistance of the bulk electrolyte. Increased resistance is particularly achieved by the formation of a film on the metal surface. If the film is deposited selectively on anodic area, the corrosion potential shifts to the more positive value; if it is deposited on cathodic areas, the shift is to more negative values; and if the film covers both anodic and cathodic areas, there may be only a slight shift in either direction.

Organic Inhibitors

Organic inhibitors affect the entire surface of the metal. They are adsorbed according to their electrical charge. Cationic organic inhibitors carry a net positive charge and anionic organic inhibitors a net negative charge.

Organic compounds constitute a broad class of corrosion inhibitors designated specifically as anodic, cathodic, or ohmic. Anodic or cathodic effects alone are sometimes observed in the presence of organic inhibitors, but organic inhibitors generally affect the entire surface when present in sufficient concentration. Both anodic and cathodic areas probably are inhibited, but to a various degrees, depending on the potential of the metal, the chemical structure of the inhibitor, and the size of inhibitor molecule.

The typical increase of inhibition with inhibitor concentration, indicates that inhibition is the result of adsorption of inhibitor on the metal surface. The film formed by adsorption of soluble organic inhibitors is only a few molecules thick and invisible.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the metal surface. Cationic inhibitors (positively charged +), such as amines, or anionic inhibitors (negatively charged -), such as sulfonates, will be adsorbed preferentially, depending on whether the metal is charged negatively or positively.

Precipitation Inhibitors

Precipitation inducing inhibitors are film forming compound that have a general action over the metal surface, interfering with both anodic and cathodic reactions.

Common precipitation inhibitors include silicates and phosphates. In waters with a pH near 7.0, a low concentration of chlorides, silicates, and phosphates causes steel to passivate when oxygen is present; hence, these molecules behave as anodic inhibitors. Another anodic characteristic is that corrosion is localized in the form of pitting when insufficient amount of phosphates or silicate are add as inhibitor to saline water.

Both silicate and phosphates form deposits on steel that increase cathodic polarization. Their action is a combination of both anodic and cathodic effects.

Vapor Phase Inhibitors

Vapor-phase inhibitors (VPI), also called volatile corrosion inhibitors (VCI), are compounds transported in a closed system to the site of corrosion by volatilization. In boilers, volatile basic compound are transported with steam to prevent corrosion in condenser tubes. Compound of this type inhibit corrosion by making the environment alkaline or by forming hydrophobic films.

Application of inhibitors

Inhibitors can be used in both aqueous and non-aqueous liquid systems, as well as in gaseous environment.

Aqueous Liquid System

Aqueous systems are the most common corrosive environments to which inhibitors are applied. Water is a powerful solvent capable of carrying many different ions at the same time. Requirements for corrosion inhibitors can vary greatly, depending on the type and the amount of dissolvent species present. Because there no universal inhibitor for water systems, an inhibitor satisfactory for one system may be ineffective or even harmful in another.

Common corrosive species and factors that affects corrosion inhibition are:

1- Oxygen (O_2)

Dissolved oxygen promotes corrosion; if its presence is reduced to very low levels (less than 0.1 ppm) by scavenging compound or by stripping, sufficient control is provided for some systems (e.g., in boilers and hot water supplies). Oxygen can be used to passivate steel by adding a passivating inhibitor.

2- Chloride ions (cl^-)

Steel is more difficult to passivate in the present of chloride ion; therefore, a higher concentration of passivating inhibitor is required if chlorides are present. Non-passivating inhibitors also must be used in higher concentrations because chloride ions are strongly adsorbed by steel.

3- Sulfate ions (SO_4^-)

The effects of sulfates on passivity are similar to those of chlorides, but to a lesser degree.

4- Bicarbonate ions (HCO_3^-)

Calcium (Ca^{++}) and magnesium (Mg^{++}) bicarbonates may be used to form protective precipitates, but at high concentrations they may interfere with the inhibitors by precipitating non-protective deposits. Small concentrations of heavy metal ions, such as copper and mercury, may cause severe interference with inhibitors.

5- Hydrogen ions (H^+)

Hydrogen ions increase corrosion rates and increase the difficulty of passivating steel. Non-passivating organic or cathodic inhibitors are preferred in pickling acids to avoid the consequences of de-passivation.

6- Hydroxyl ions (OH^-)

In alkaline solutions, corrosion of steel is controlled by the rate of oxygen diffusion through the precipitated corrosion products, usually ferrous hydroxide, $Fe(OH)_2$. Steel is passivated in alkaline solutions. Atmospheric metals, such as aluminum, zinc, and lead, corrode in alkaline environments and inhibitors may be required.

7- Effects of Elevated Temperature on Corrosion inhibitors

Elevated temperatures are generally adverse to corrosion inhibition. High temperatures increase corrosion rate, decrease the tendency of inhibitors to adsorb on metal surfaces, increase the driving force for anodic and cathodic reaction, and promote greater solubility of corrosion products.

Non-aqueous Liquid Systems

Corrosion in nonaqueous liquids, such as fuels, lubricants, may be caused by small amounts of water if present. Water is slightly soluble in petroleum products, and its solubility increases with temperature. If a nonaqueous medium is saturated with water and the temperature is lowered then some of the water will separate to attack steel it contacts. Oils that have been subjected to high temperatures in air may contain organic acids that will be extracted by any water present, increasing the rate of attack.

Solubility is an important factor to be considered in evaluating corrosion inhibitors for nonaqueous fluids, because they do not have the same solvent effect as water. Because an inhibitor must be transported through the environment to sites where corrosion occurs, it must be either soluble in the environment or sufficiently dispersed in fine droplets so that the settling does not occur. The inhibitor must not form filter-plugging insoluble products by reaction with metals or components of the nonaqueous fluid.

Gaseous Environments

Gaseous environments include open atmosphere, the vapor phase (head space) in tanks, natural gas in wells, and the empty space in packaging containers.

Again, water and oxygen are the principal corrosive agents, but the main problem in providing inhibition is to transport the inhibitor from a source to the sites where corrosion occur.

Open Atmosphere

Corrosion inhibitors for corrosion in the open atmosphere are applied directly to the metal surfaces to be protected. The most common method is the use of inhibitive pigments in protective coatings.

Vapor phase in tanks

The walls of tanks above a water line are subject to extensive corrosion because the relative humidity is always high and oxygen is plentiful if the tank is vented to the atmosphere. Where water contamination is not a factor, a layer of oil on the surface helps to maintain a low humidity; and as the level is raised and lowered, the walls become coated. The oil may contain an organic inhibitor and an agent (usually an amine) to cause the oil to spread on the metal surface. An oil layer contains about 15% lanolin (wool wax) has been used in ship ballast tanks to control corrosion.

Natural Gas in Wells

Gas wells corrode mostly in the reflux zone, which is a specific area of the well between the bottom and the wellhead, where condensation occurs. As the gas flows up in the well, its temperature drops due to expansion; and this causes condensation when the temperature reaches the water dew point of the gas.

Volatile inhibitors injected into gas wells have been used successfully to inhibit corrosion. Many gas wells today are protected by injecting amine inhibitors continuously, in slugs or by squeezing.

Empty Space in Packaging Containers

Packaged materials may be protected from corrosion in several ways. Packages that cannot be sealed and that contain parts that is not coated with an inhibitor or exposed to volatile inhibitors (e.g., electronic parts) are protected by placing a desiccant, such as silica gel, in the package to maintain humidity at low level.

Vapor-phase inhibitors can be placed in a package in a bulk; alternatively, the article to be protects can be wrapped in paper impregnated with a VPI. These compounds are volatile organics, so the package in which they are used must be well sealed.

Inhibitor Application Techniques

Commonly encountered methods of inhibitor application include continuous injection, batch treatment, squeeze treatment, and coating.

1- Continuous Injection

Continuous injection of corrosion inhibitors is used in systems, where slugs or batch treatment cannot be distributed evenly through the fluid. This method is used for water supplies, oilfield injection water, cooling water, open-annulus oil or gas wells, and gas left wells. Liquid inhibitors are injecting using a chemical injection pump. Most chemical injection pumps can be adjusted to deliver at the desired injection rate.

Another form of continuous application is by the use of slightly soluble form of solid inhibitors. The inhibitor (e.g., glassy phosphate or silicate in the form of cartridge) is installed in a flow line where the inhibitor is leached out by the passage of fluid through the cartridge. Inhibitor sticks or pellets are used in the oil and gas wells to supply the inhibitor continuously by natural slow dissolution.

2- Batch Treatment

In batch treatment, a quantity of inhibitor is added to a closed system to provide protection for an extended period. A familiar example of batch treatment is an automobile cooling system. A quantity of inhibitor is added to provide protection for an extended period. Additional inhibitor may be added periodically, or the fluid may be drained and replaced with a new supply. In most aerated, closed-loop cooling systems, it is important that the inhibitor concentration be measured occasionally to ensure that a safe level is maintained.

Batch treatment is also used in treating oil and gas wells. An inhibitor is diluted with an appropriate solvent and injected into the annulus of open-hole wells or into the tubing of gas wells that have packer. In this application, it is important that the inhibitor contact all the surfaces and that it has good persistence. Most wells require treatment about every 2 weeks.

3- Squeeze Treatment

The squeeze treatment is a method of continuously feeding an inhibitor in an oil well. A quantity of inhibitor is pumped into a well, and then sufficient solvent is added to force the inhibitor into the formation. The inhibitor is adsorbed by the formation, from which it slowly escapes to inhibit the produced fluids. Protection applies in this manner has been known to last for up to 1 year.

4- Coatings

Inhibitors may be used in coatings. One common coating inhibitor is zinc chromate, which passivates steel by providing chromate ions.

Safety Consideration with Inhibitors

Handling

Toxic effects of inhibitors must be considered in processes where the compounds may be inhaled or contacted. Extreme care must be taken to avoid the use of toxic compounds near food-processing equipment, ice plants, and potable water supplies.

When inhibitor solution are prepared for injection, care must be taken to follow label instructions regarding skin contact, eye contact, ingestion, and inhalation. Read all safety information before opening containers of inhibitors.

Disposal

Because a number of inhibitors contain ions and compounds that may be toxic, it is often difficult to dispose of inhibited fluids that have been drained, dumped, or leaked from systems. Chromates are a prime example of this problem. In fact, the use of chromate-containing inhibitors has been reduced in recent years because of the disposal problem. Disposal must be considered during inhibitor selection.

Heat Transfer

Heat transfer is an important consideration in applying corrosion inhibitors. Scaling of heat transfer surfaces, which can reduce heat transfer, should be avoided or held to minimum. Excessive deposits of phosphates, silicates, or sulfates should be avoided; the latter in particular should be avoided because they are difficult to remove by chemical means.

6.1.9.2.3 Water Treatment

Treatment of water is frequently used for corrosion control. Water treatment may be accomplished by physical or chemical methods.

Physical water treatment methods include:

- Removal of solids
- Removal of gases
- Removal of liquids

Removal of solids is normally accomplished be settling or filtration.

Removal of undesirable gases is normally accomplished by deaeration, or in some cases by aeration. Removal of air by deaeration can be accomplished by gas stripping towers, or in boiler systems or steam stripping. Aeration is used to remove hydrogen sulfide and other dissolved gases that can be displaced by air. Removal of liquids is accomplished through the use of skimmers and separators.

Chemical water treatment methods include:

- Softening
- pH adjustment
- Demineralization
- Desalination
- Oxygen scavenging

Softening may be performed using line softening, or sodium zeolite ion exchange methods. Softening is frequently required to prevent scaling by calcium and magnesium salts.

pH adjustment is commonly performed to cause calcium carbonates precipitation. Many natural waters and municipal water supplies contain calcium carbonate ($CaCO_3$) in solutions. This can be made to precipitate by heating (Calcium carbonates solubility decreases with increasing temperature), or by increasing the pH (making the solution more alkaline, where solubility decreases sharply). Calcium carbonate precipitations will form as pH increased. At the correct pH, the deposit will be firm and smooth and similar to the egg-shell. Once protective deposits is formed, the pH of the water must be maintained at the equilibrium level; if allowed to become acidic, it will re-dissolve the protective deposit. If the appropriate pH is exceeded, calcium carbonates will precipitate to form a slimy, porous deposit that does not provide corrosion protection and in fact may increase corrosion by creating concentration cells involving oxygen.

Demineralization removes dissolved minerals from water. It may be accomplished by deionization using ion exchange resins, by reverse osmosis, or by distillation.

Desalination is usually accomplished by reverse osmosis or by distillation to remove dissolved salts.

Oxygen scavengers reduce depolarization by oxygen. Oxygen scavengers are compounds such as sulfites or hydrazine that react with oxygen in a solution and thus reduce the availability of oxygen for corrosion reactions. They may be added alone or combined with other inhibitors.

6.1.9.2.4 Cathodic and Anodic Protection

Cathodic and anodic protection are electrochemical techniques used for corrosion control. Cathodic protection has wide use in a variety of environments, including liquid immersion and soil. Anodic protection has a more limited, but important, application in chemical environments.

Principles

Cathodic protection reduces or eliminates corrosion by making the metal a cathode of an impressed current or attachment to galvanic anode (usually magnesium, aluminum, or zinc).

The cathode in an electrochemical cell is the electrode where reduction (no corrosion) occurs. Before cathodic protection is applied, corroding structures will have both cathodic areas and anodic areas (Those areas where corrosion is occurring). If all anodic areas can be converted to cathodic areas, the entire structure will become a cathode and corrosion will be reduced.

How Cathodic Protection Works

Corrosion occurs where (positive) current discharge from metal to electrolyte at an anode. The objective of cathodic protection is to force the entire system to act as cathode, with current entering the environment and limited corrosion occuring.

The application of direct current to a corroding metal structure can cause it to become entirely cathodic.

To begin with, direct current is associated with the corrosion process on a buried or submerged metallic structure.

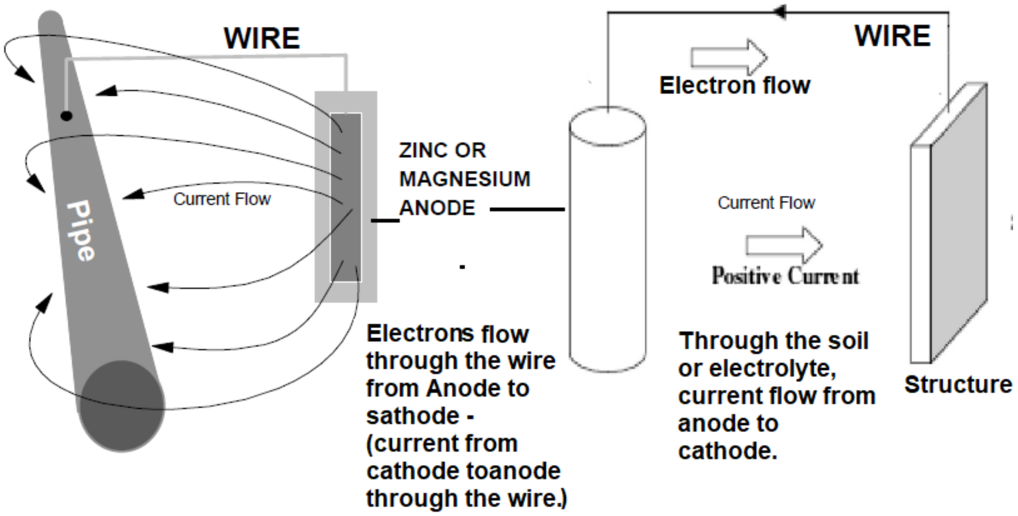


Fig. 6-6. Galvanic (Sacrificial) anode cathodic protection.

As shown, direct current flows from the anodic areas into the soil, through the soil, into the cathodic areas, and back through the pipe itself to complete the circuit. For a given driving voltage (The galvanic potential between the anode and the cathode), the amount of current flowing is limited by factors as the resistivity of the environment (expressed normally in ohm-centimeters) and the degree of polarization at the anodic and cathodic areas.

Corrosion occurs where the current discharges from metal into the electrolyte (soil) at anodic areas. Where current flows from the environment onto the pipe (cathodic areas), there is no corrosion. In applying cathodic protection to a structure, the objective is to force the entire surface exposed to the environment to be cathodic to the environment. When this condition has been attained, corrosion is mitigated.

Galvanic Anode Cathodic Protection Systems

In the galvanic anode system. Pieces of an active metal, such as zinc or magnesium, are placed in contact with the corrosive environment and are electrically connected to the structure to be protected. The galvanic anode corrode preferentially, providing protection to the structure.

A galvanic (sacrificial) anode can be described as a metal that will have a voltage difference with respect to the structure to be protected and will discharge (positive) current that will flow from the environment to the structure.

Requirements for a metal to be a practical anode material include:

- Potential
- Long life
- Efficiency

Materials that are commonly used as galvanic anodes are:

- Aluminum
- Magnesium
- Zinc

The potential difference between the anode and the structure to be protected must be sufficient enough to overcome the anode-cathode cells on the structure to be protected. The anode material must have sufficient electrical energy to permit reasonably long life using a practical amount of anode material.

Anodes must have good efficiency, meaning that a high percentage of the electrical energy content of the anode should be available for useful cathodic protection current output. The balance of the energy that is consumed in self-corrosion of the anode itself should be very small.

Anode materials are cast in many weights and shapes to meet cathodic protection design requirements. Data on available anodes can be obtained from suppliers of cathodic protection materials.

Impressed Current Cathodic Protection Systems

In an impressed current cathodic protection system, an external source of direct-current (DC) power is connected (or impressed) between the structure to be protected and the anodes in a ground bed. The basic configuration of an impressed current cathodic protection system is shown in figures 6- 7.

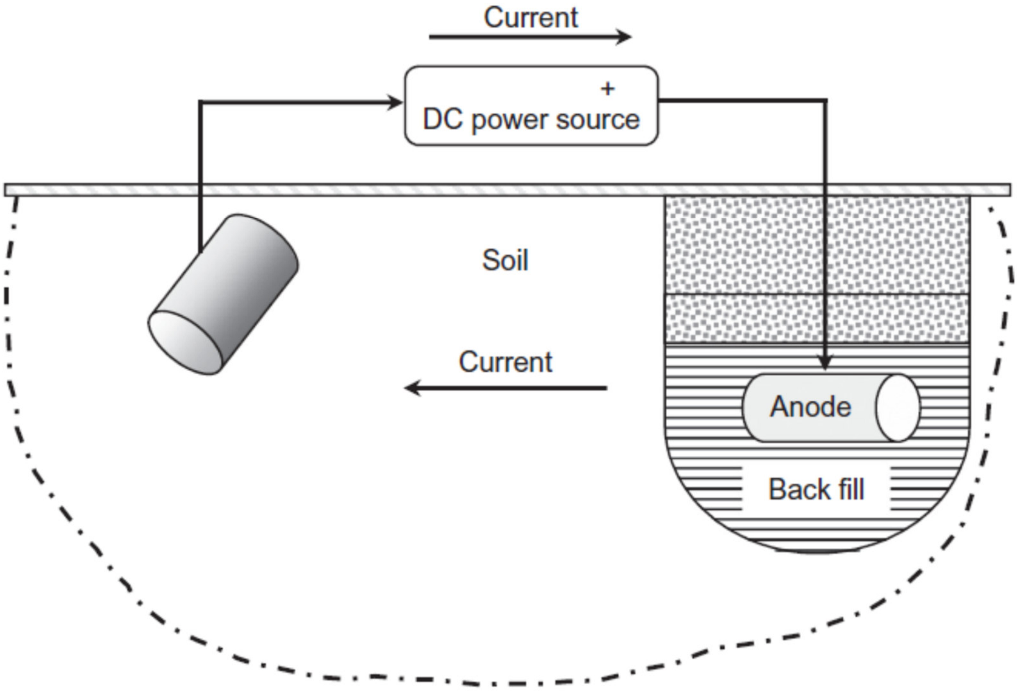


Fig. 6.7 Schematic of cathodic protection system using impressed current.

The positive terminal of the power source must always be connected to the ground bed, which is then forced to discharge as much cathodic protection current as it desirable. If a mistake is made and the positive terminal is connected to the structure to be protected, the structure will become an anode instead of a cathode and will corrode.

Impressed Current System Anodes

Ground bed anodes are forced to discharge current and will corrode. In most cases, it is desirable to use anode materials that are consumed at relatively low rates. The ground beds should be designed to discharge large amounts of current and still have a long life expectancy.

Various materials are used for impressed current anodes. While scrap steel pipe, rail, rod, or other similar iron or steel material may be used, such materials are consumed at a rate of about 20 pounds per ampere-year (1 ampere flowing for one year). This means a relatively large amount of material is needed to achieve the desired operating life for an installation, which may be justified only when it is available as scrap at low cost.

Other types of anodes are consumed at lower rates. Because of the chemical composition of these low consumption anode materials, the anodic reactions involve the production of such gases as carbon dioxide, oxygen, or chlorine from the environment rather than consumption of the anode material itself.

One type of low consumption anode material is a cast iron containing about 14.5% silicon and other alloying elements that are consumed at a low rate (typically, a few tenth of pounds a pound per ampere-year). This material is available commercially in various anode size to meet design requirements.
Another widely used commercially available anode material is carbon or graphite.

Anodes of these materials also consumed at low rates (< 1lb/A-Yr.) and are available in various shapes and sizes.
For marine work, considerable success has been achieved with lead-silver alloys. Although lead can be consumed at around 70 lb/A-Yr, suitable lead silver alloys will form a lead peroxide film on the anode's outer surface reducing the discharge of current to a low consumption rate.
Platinum works very well as a low consumption impressed current anode because it is consumed at an extremely low rate. Because of its cost, it is usually plated onto a less expensive material. Titanium and niobium are used in marine work on ships and hulls and for applications involving the interior parts of such structures as condenser water boxes, internal parts of pumps, and certain pipeline interiors.

Impressed Current Cathodic Protection System Power Sources

When an impressed current system is used, a current supply is necessary. Common current sources are rectifiers and solar cells.

Rectifiers

A rectifier is provided with power from electric utility system lines. It converts alternating current to a lower voltage direct current by means of a stepdown transformer and a rectifying device.

Solar Cells

Solar panels used with and without battery storage facilities have been most successful and can be considered for use in location where electrical power is not available.

Engine generators, fuel cells, wind powered cells, and other sources may also be encountered.

Measurements of Cathodic Protection Effectiveness

Various techniques may be used to determine the degree to which a structure, supposedly under cathodic protection, is actually protected against corrosion.

Structure-to-Environment Potential

Potential measurements are a common means for determining whether protection is in effect. If current flowing into a protected structure, there must be a change in the potential of the structure with respect to the environment. This is because the current flow cause a potential change, which is a combination of the voltage drop across the resistance between the protected structure and the environment and the polarization potential developed at the structure surface.
Reference electrodes such as those discussed earlier in this course may be used to measure the potential to the environment.

Test Coupons

Evidence that cathodic protection is working can be obtained by using coupons of the same metal as that in the protected structure. These are weighted carefully before the current is activated and then electrically connected to the protected structure. The coupons should be placed where they can receive the same exposure to cathodic protection current as does as the structure; then, after a known exposure time, they may be removed and weighed.

Potential Change

The change in potential between when the current is applied and when it is not applied is used as an indication of the degree of cathodic protection.

Design

Design of an effective cathodic protection system is a complex task requiring experience, knowledge, and judgment. In this book we will briefly mention some of the factors which must be taken into consideration when developing a cathodic protection system, including:

1- Regularity requirements
2- Economics
3- Metal to be protected
4- Life requirements
5- Total current requirements
6- Variation in environment
7- Electrical shielding
8- Stray-current effects
9- Temperature
10- Wire and cables
11- Anode backfill
12- Protective coatings

1- Regulatory requirements

Cathodic protection may be required by law for some systems, particularly when corrosion could endanger public safety or the environment. Metallic underground storage tanks and pipes handling hazardous materials are examples of systems where cathodic protection may be required by law.

2- Economics

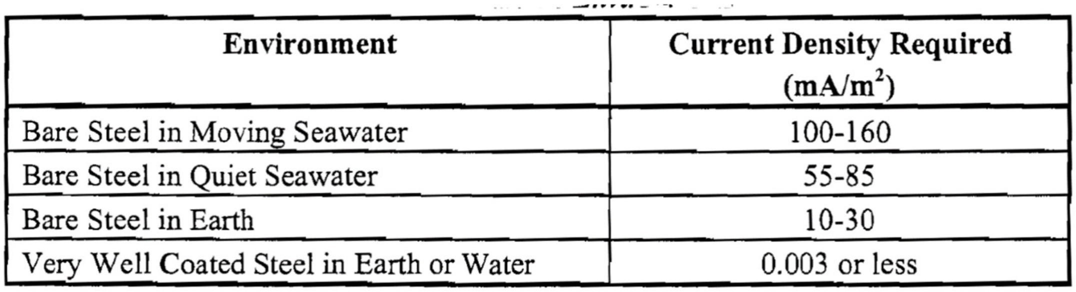
Compared to the cost of protected structure, cathodic protection is low. Costs of cathodic protection include the initial cost of design and installation, the cost of power in impressed current systems, and the cost of inspecting and maintaining the system.

3- Metal to be protected

The nature of the metal to be protected is a factor in cathodic protection systems. Steel is most commonly the metal protected, but other metals cab be protected as well. Amphoteric materials, such as zinc, aluminum, and lead, can be protected under some circumstances.

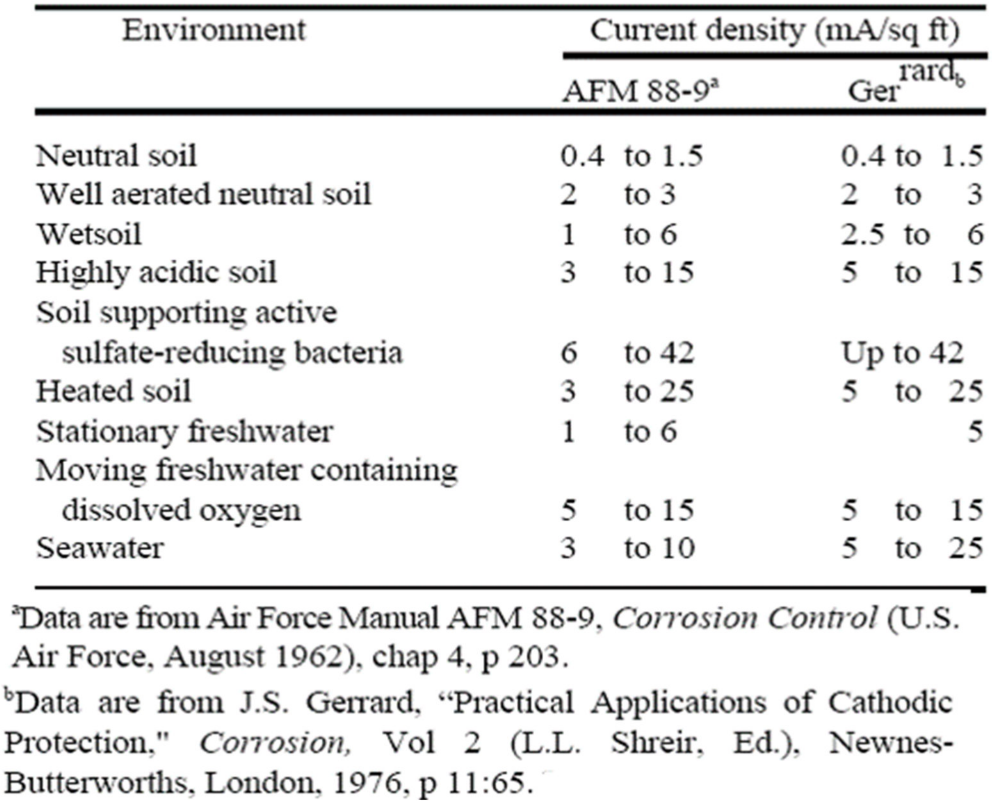
4- Life requirements

Because of the consumption of anodes, cathodic protection systems have a finite life. Impressed-current systems usually have a longer life because of the slow consumption of the anodes. When the anodes are consumed, they can be replaced and the effective protection of the structure can continue.



Environment	Current Density Required (mA/m^2)
Bare Steel in Moving Seawater	100-160
Bare Steel in Quiet Seawater	55-85
Bare Steel in Earth	10-30
Very Well Coated Steel in Earth or Water	0.003 or less

Table. 6-1. Current required for bare and coated steel. “NACE” (mA/m^2).



Environment	Current density (mA/sq ft)	
	AFM 88-9[a]	Gerrard[b]
Neutral soil	0.4 to 1.5	0.4 to 1.5
Well aerated neutral soil	2 to 3	2 to 3
Wetsoil	1 to 6	2.5 to 6
Highly acidic soil	3 to 15	5 to 15
Soil supporting active sulfate-reducing bacteria	6 to 42	Up to 42
Heated soil	3 to 25	5 to 25
Stationary freshwater	1 to 6	5
Moving freshwater containing dissolved oxygen	5 to 15	5 to 15
Seawater	3 to 10	5 to 25

[a] Data are from Air Force Manual AFM 88-9, *Corrosion Control* (U.S. Air Force, August 1962), chap 4, p 203.

[b] Data are from J.S. Gerrard, "Practical Applications of Cathodic Protection," *Corrosion,* Vol 2 (L.L. Shreir, Ed.), Newnes-Butterworths, London, 1976, p 11:65.

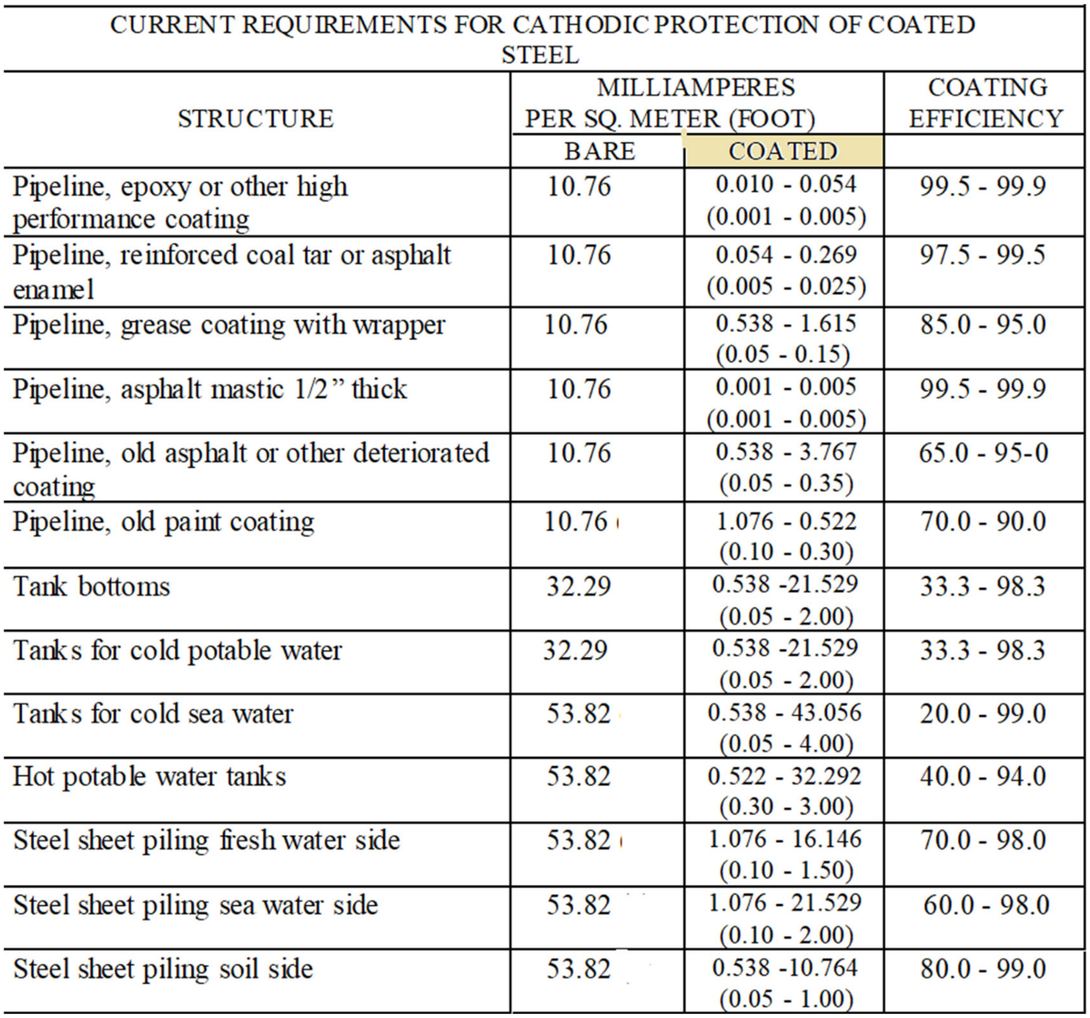
Table. 6-2. Current required for bare and coated steel. (mA/ft^2).

5- Total current requirements

The total amount of current required must be determined during system design. In general, galvanic systems are used to when total current requirements are small, and impressed current systems are used when the total current requirements are large. Refer to tables' 6-1, 6-2, and 6-3, notice the difference between current required for bare steel and for coated steel.

6- Variation in environment

The electrical resistivity of the environment is an important factor in the design of cathodic protection systems. Resistivity is a primary factor in the amount of current and in the design of the ground beds for both galvanic and impressed current systems.



CURRENT REQUIREMENTS FOR CATHODIC PROTECTION OF COATED STEEL

STRUCTURE	MILLIAMPERES PER SQ. METER (FOOT)		COATING EFFICIENCY
	BARE	COATED	
Pipeline, epoxy or other high performance coating	10.76	0.010 - 0.054 (0.001 - 0.005)	99.5 - 99.9
Pipeline, reinforced coal tar or asphalt enamel	10.76	0.054 - 0.269 (0.005 - 0.025)	97.5 - 99.5
Pipeline, grease coating with wrapper	10.76	0.538 - 1.615 (0.05 - 0.15)	85.0 - 95.0
Pipeline, asphalt mastic 1/2" thick	10.76	0.001 - 0.005 (0.001 - 0.005)	99.5 - 99.9
Pipeline, old asphalt or other deteriorated coating	10.76	0.538 - 3.767 (0.05 - 0.35)	65.0 - 95-0
Pipeline, old paint coating	10.76	1.076 - 0.522 (0.10 - 0.30)	70.0 - 90.0
Tank bottoms	32.29	0.538 -21.529 (0.05 - 2.00)	33.3 - 98.3
Tanks for cold potable water	32.29	0.538 -21.529 (0.05 - 2.00)	33.3 - 98.3
Tanks for cold sea water	53.82	0.538 - 43.056 (0.05 - 4.00)	20.0 - 99.0
Hot potable water tanks	53.82	0.522 - 32.292 (0.30 - 3.00)	40.0 - 94.0
Steel sheet piling fresh water side	53.82	1.076 - 16.146 (0.10 - 1.50)	70.0 - 98.0
Steel sheet piling sea water side	53.82	1.076 - 21.529 (0.10 - 2.00)	60.0 - 98.0
Steel sheet piling soil side	53.82	0.538 -10.764 (0.05 - 1.00)	80.0 - 99.0

Table. 6-3. Current required for bare and coated steel. (mA/ft^2 and mA/m^2).

7- Electrical shielding

When the structure to be protected is in an environment with other metallic structures, the other structures can effectively shield the structure to be protected from the cathodic protection current. Design of cathodic protection systems in environments congested with other metallic structures often requires placement of anodes between the structures to ensure proper distribution of current.

8- Stray-current effects

Currents from nearby electrical systems, such as electric rail system, can interfere with the current flow in a cathodic protection system. When present, the cathodic protection system must be designed and adjusted to compensate for these currents. Cathodic protection systems themselves are also a source of these currents. All cathodic protection systems in a given locality must be adjusted to minimize interaction and possible damage to other buried metal structures that are not cathodically protected.

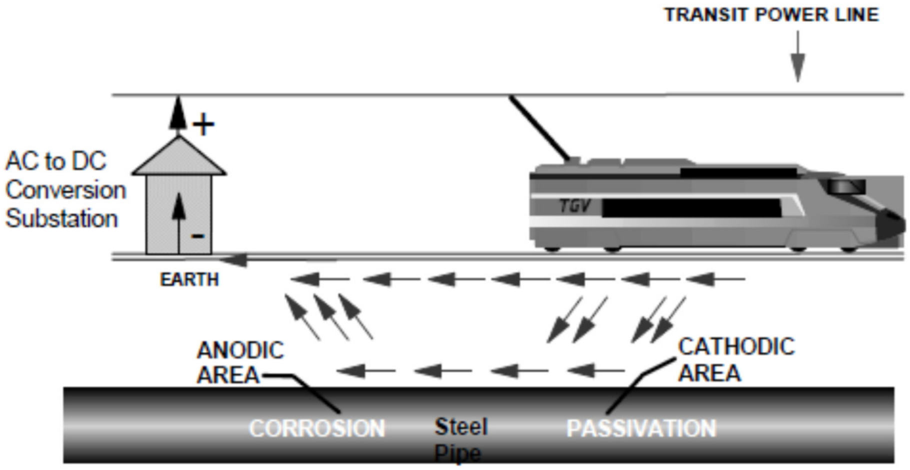


Fig. 6-8. Stray current due to DC source. Current leave the rail road, enters the soil, use the pipe line as a conductive material, then leave the pipe line causing corrosion at the point of current flow out.

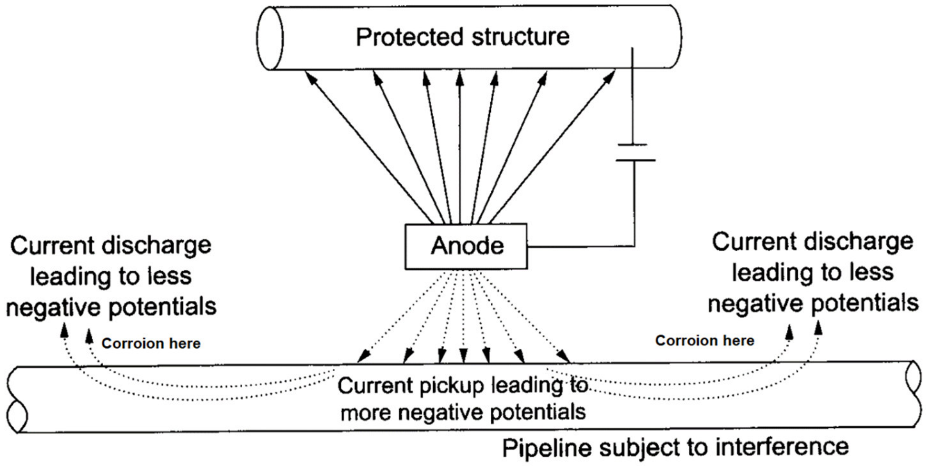


Fig. 6-9. Stray current due to neighbor cathodic protection. Current from anodes enters the soil, use the pipe line as a conductive material, then leave the pipe line causing corrosion at the point of current flow out.

9- Temperature

Temperature of the environment can also affect cathodic protection system by changing the electrical resistivity of the environment or changing the current required for protection.

10- Wire and cables

In galvanic systems, the wire connecting the anodes to the structure is not critical. If there is damage to the insulation on these wires, the anode will cathodically protect the exposed metal. In impressed current systems, the wire connecting the structure to the power source is similarly protected. However, the wire connecting the positive terminal of the power source to the anode bed and interconnecting wires in the anode bed are corroded severely at any break in the insulation on these wires (The metal will act as anode because it is connected to the positive terminal and in contact with environment). Specially insulated wires should be used and carefully placed to avoid system failure.

11- Anode backfill

Backfill is the material placed around the anodes in both galvanic and impressed current systems. In galvanic anode system, these material provide an environment for maximum efficiency, and the low resistivity environment around the anodes ensures adequate current output. In impressed current systems, anode backfill is used to reduce the resistivity of the environment around the anodes and to increase the effective area of the anode. The proper backfill must be used for each system, and the backfill must properly placed to ensure maximum anode performance.

12- Protective coatings

As shown in tables 6-1, 6-2, and 6-3, a well-coated structure will require less current form protection, i.e. less power, less anode weights, and less cables …etc.

13- Maintenance

Cathodic protection systems require periodic inspection and maintenance.

In galvanic anode systems, the two must common problems are the consumption of anodes and damage to connecting wires from digging in the area. Inspection of galvanic cathodic protection usually consists of periodic measurements of the structure to electrolyte potentials to ensure adequate protection and measurements of current output of the galvanic anodes. These measurements are commonly performed at permanently placed test stations, as an integral part of the system. Inspection of galvanic anode systems is usually performed on a semi-annual or annual basis, but the frequency will vary depending on the system, the material contained in the system, and regulatory requirements.
Impressed current systems, failure of the power source and damage to the electrical connections are the most common problems. As noted above, damage to the wire between the rectifier and the ground bed is a common problem. It is common to require monthly inspection of the power sources in impressed current cathodic protection systems. Structure to electrolyte potential measurements to ensure adequate protection is usually performed on a less frequent basis. As in the case of galvanic systems, impressed current systems use permanent stations for most of these measurements.

Selection of cathodic protection system

When selecting a cathodic protection system, the designer should consider the size of the structure and the past project experience in operating and maintaining both types of systems.

Basis for selecting a sacrificial anode system

Advantages:

(i) No need for an external power source
(ii) Less complex installation
(iii) Uniform distribution of current
(iv) Minimum maintenance
(v) Minimum cathodic interference

Limitations:

(i) Current output is limited. It has limited driving potential; therefore, the protection for the bare steel area is limited for each anode.
(ii) Poorly coated structures need more anodes.
(iii) The system is ineffective in high resistive environments.

Basis for selecting impressed current system

Advantages:

(i) The system can be applied with a wider range of voltage and current requirements.
(ii) High current can be impressed with a single ground bed.
(iii) Single installation can protect larger metallic surface.
(iv) Uncoated and poorly coated structures can be effectively protected.
(v) Voltage and current can be varied to meet changing conditions with time.

Limitations:

(i) Overprotection leads to coating damage and hydrogen embrittlement.
(ii) The system is affected by interference problems.
(iii) External power is necessary, thus the system is vulnerable to power failure.

Anodic Protection

Anodic protection is corrosion protection achieved by maintaining an active-passive metal or alloy in the passive region by an externally applied anodic current.

The basis of this type of protection is shown in figure 6- 10.

Solution oxidizing power and corrosion potential are equivalent; therefore, it is possible to achieve passivity by altering the potential of the metal using an appropriate external power supply to apply an anodic current.

Anodic protection can be applied only to metals and alloys possessing active-passive characteristics and can be used only in certain environments because electrolyte composition influences passivity.

A very important caution with respect to the anodic protection is that if the anodic protection current fails for some reason, the protective article could be very rapidly attacked by the corrosive environment.

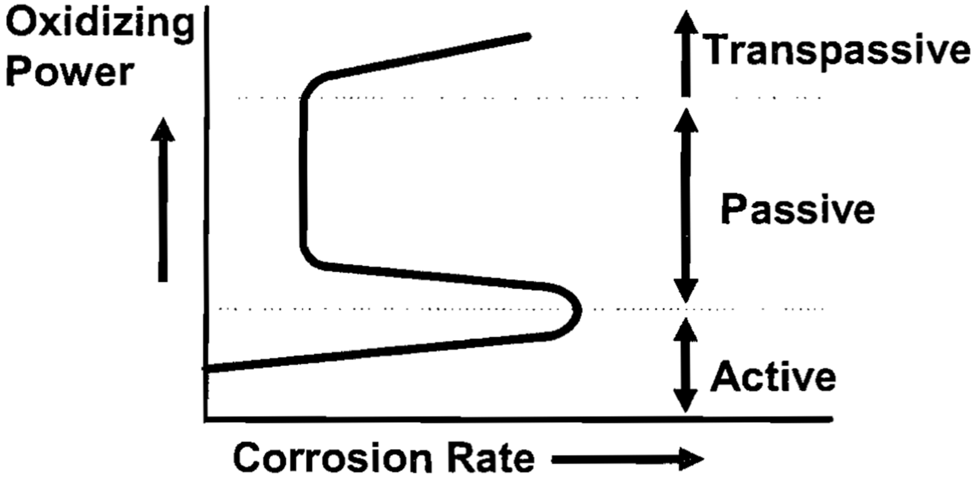


Fig. 6-10.Anodic protection.

Protective Coatings

Putting a barrier between a corrosive environment and the material to be protected is a fundamental method of corrosion control. It is arguably the most widely used method of protecting metals and other substrates.
A protective coating is any material that, when applied to a surface will resist the service environment and prevent serious breakdown of the substrate.
Coatings may be used for a variety of reasons:

- Corrosion Control: Protective coatings may be used as a corrosion control measure.
- Waterproofing: Coatings may be used to prevent the transmission of liquid, or reduce the transmission of water vapor.
- Weatherproofing/Weather Protection: Weatherproofing would include of course waterproofing and other weathering factors such as ultraviolet rays of the sun.
- Biocide Application: In the marine industry, antifouling coatings may be used to reduce the attachment of marine organisms to the hulls of ships and other submerged structures.
- Fireproofing/Fire Retarding: Some coating are used to reduce the effect of fire on the substrate.
- Appearance: Coatings may be used to help attain and maintain the appearance of industrial, commercial, and residential locations
- Color Coding: Even substrates that might not be coated for corrosion reasons, such as stainless steel, may be coated as a part of color coding scheme.

- Sanitation: Coatings may be applied to porous substrates, such as concrete, wood, and plaster, to allow for easier cleaning.
- Safety: Coatings may be applied for reasons of safety such as; to make hazards more visible, and to symbolize the presence of certain type of hazardous substance, process, or equipment.
- Prevention of Product Contamination: Coatings may be applied to prevent contamination of the product contained to preserve, taste, or to prevent odor pickup.
- Friction Reduction: A surface may be coated to reduce friction. An example would be coating the interior pipeline to decrease resistant to flow.
- Wear Resistance: Certain high wear areas (e.g., slurry pipelines, hoppers) may be coated with abrasion-resistant coating to reduce wear of the substrate.
- Heat Transfer: Coating may be used to increase heat transfer (e.g., the use of black paints in solar heating applications) or to cut heat transfer (e.g., the use of white and reflective paints on buildings and other structures).
- Electrical Insulation: Coatings may be used to provide electrical insulation, as in case of coating transformer wire.
- Organic Coatings: Organic coatings are very widely used as protective coatings. They consists of an organic film-forming material called resin. This resin may be dissolved in a solvent, or may be the primary constituent of the vehicle (the liquid part of the coating).

Mechanism of Protection

Three basic mechanisms by which a coating may provide corrosion protections are:

1- Barrier
2- Inhibitive pigments
3- Cathodic protection

1- Barrier

A major purpose of a coating is to protect a substrate form the effect of its environment. One way in which the coating may do this is by acting as a physical barrier between the substrate and its environment.

2- Inhibitive Pigments

Inhibitive coatings contain pigments that react with absorbed moisture vapor within the coating and then react with the steel surface to passivate it and decrease its corrosive characteristics.

3- Cathodic Protection

Coatings can contain active metals (usually zinc) as pigments. These active metals are anodic to steel. In the presence of an electrolyte, a galvanic cell is set up and the metallic coating corroded instead of the metal.

Desirable Properties of a Coating

The following are generally considered to be desirable properties in a coating:

1- Chemical resistance
2- Low-moisture permeability
3- Easy application to substrate
4- Adhesion to substrate
5- Cohesive strength
6- Tensile strength
7- Flexibility/elongation
8- Impact resistance
9- Abrasion resistance
10- Temperature resistance
11- Resistance to cold flow
12- Dielectric strength
13- Resistance to cathodic disbondment

1- Chemical Resistance

Chemical resistance is the ability of a coating to resist deterioration of its properties due to chemicals present within the intended exposure condition.

2- Low-Moisture Permeability

One of the primary barrier function of a coating is to keep moisture away from the substrate. Low moisture permeability is resistance to moisture vapor absorption and moisture vapor transmission.

3- Easy Application to Substrate

The coating must be easily applied to the substrate by methods which will not affect the properties of the substrate. Ease of applications is important property of a coating, especially for critical exposures where the structure may be intricate, with many corners, edges, etc.

4- Adhesion to Substrate

Adhesion is created by the physical and chemical forces that interact at the interface of the coating and the substrate. Adhesion to the substrate is greatly enhanced by good surface preparation and correct application of the coating.

5- Cohesion Strength

Cohesive strength is the ability of a coating to resist internal stress due to curing, thermal expansion/contraction, cold working (forming), etc. It is a measure of the internal strength of a coating and is usually a good indicator of toughness.

6- Tensile Strength

Tensile strength is the ability of a coating to resist breaking/cracking under linear stress. For example, when the substrate heats/cools, the coating can move with it.

7- Flexibility/Elongation

Flexibility is the ability of a coating to withstand deformation of the substrate.

8- Impact Resistance

Impact resistance is the ability of a coating to withstand sudden mechanical shock. Impact resistance is closely related to abrasion resistance.

9- Abrasion Resistance

Abrasion resistance is essential in areas of hard service where damage due to scraping and other abrading actions can occur.

10 – Temperature Resistance

Temperature resistance is the ability of a coating to resist deterioration of its properties due to the extremes of temperature within the intended exposure conditions.

11- Resistance to Cold Flow

Resistance to cold flow (creep) is an important property in high-build thermoplastic coatings, some of which tend to cold flow (flow down or slump) with age.

12- Dielectric Strength

Dielectric strength is essential in that the coating must break the electrical circuit set up during a corrosion reaction. Dielectric strength is also an important factor wherever coatings are to be used with cathodic protection, because in this case, there is a strong excess of electrons on the metal. When the coating is sufficiently dielectric, it breaks the electron circuit and prevent cathodic current flow.

13- Resistance to Cathodic Disbondment

Cathodic disbondment is usually resulted at the cathodically protected coated surface due to excess current (potential is more negative than required for protection – usually happened at structure to soil potential more negative than -1400 mV).

Coating System Selection

Coating system selection is similar to the selection of any material. Many factors need to be considered, including:

1- Types of exposure
2- Operating conditions/ upset conditions
3- Substrate
4- Ambient conditions during application
5- Environmental regulations
6- Cost
7- Application of coating during operation or at shutdown
8- Time constraints
9- New construction/maintenance
10- Shop/field application
11- Design/fabrication considerations

1- Time of Exposure

The type of exposure is an important consideration in coating selection. Coating should be selected with regard to the service environment.

2- Operating Conditions/Upset Conditions

The specific operation condition may be the chief factor in coating selection. For example, if a coating is to be applied to a structure operating at high temperature and exposed to acid fumes, the coating selected will be limited to the one that can withstand the high temperature and has good resistance to acid.

Upset conditions refer to changes in operation that could damage or destroy a coating. For example, a tank properly protected on its interior and containing an acid or alkali might be coated on its exterior with a mildly resistant coating. As long as contents stay in the tank, no harm may come to the coating. If the tank were to overflow, the exterior coating could fail. If this type of upset condition can occur, then the coating selected for the exterior should be highly resistant to the tank’s contents.

3- Substrate

The substrate affects chemical compatibility, thermal compatibility, flexing, and adhesion of the coating. A reaction between the coating and the substrate could be harmful if it lessens adhesion or leads to bleeding.

4- Ambient Conditions During Application

Anticipated ambient conditions during application, such as temperature, relative humidity, and dew point, can affect how well the coating cures. The selected coating must be one that can be applied successfully in the anticipated ambient conditions.

5- Environmental Regulations

In most locations, governmental regulations may restrict the use of certain techniques or material, such as abrasive blasting and solvent emission. Regulations also restrict some coatings to be used in contact with potable water or foodstuffs.

6- Cost

Cost for a given coating project can influence coating selection. The cost of coating material itself is frequently only a small portion of the overall cost of coating, which includes surface preparation, coating application, inspection, scaffolding, etc. It is usually most economical in the long term to use the best coating.

7- Application of Coating During Operations or at Shutdown

If coating application is to be proceed when a unit is in operation, various factors may influence the coating selection, such as metal temperature during operation, application methods permissible during operation, plant personnel who will be present during operation, and safety.

8- Time Constraints

The time allowed to work on or to complete the job can affect coating selection.

9- New Construction/Maintenance

Generally, new construction projects allow for or require a complete coating system. With maintenance work, surface preparation efforts tend to be minimal and the coating may be only touched up. Coatings compatible with those to be maintained must be chosen, and the coating that can tolerate poor surface preparation must be selected.

10- Shop/Field Application

Available surface preparation, application equipment, and techniques vary between shop and field application, affecting the types of coatings which may be selected. In many cases, steel is primed in the shop and topcoated in the field. This avoids field surface preparation, which is often difficult and can yield inferior results.

11- Design/Fabrication Considerations

The structure should facilitate coating operations through good design and fabrication. Fabrication defects may hinder corrosion protection by coatings. It is very difficult to protect the fabrication defects of metals with coatings. To the greatest extent possible.

Common Design Defects

Common design defects include:

1- Inaccessible areas

Inaccessible area are difficult to coat properly. Special attention is requires to ensure proper coating.

2- Fasteners

Riveted and bolted construction can leave gaps and areas that are difficult to coat. Riveted and bolted construction should be replaced by welding whenever is possible.

3- Gaps

Gaps should be avoided

4- Angles

5- Threaded areas

Threaded outlets are very difficult to coat properly, and should be replaced, when possible, by the more easily accessible and treated pad-type outlets.

6- Dissimilar metals

Where dissimilar metals are electrically connected by a metallic, the possibility for severe corrosion exists. Once corrosion starts, it can spread rapidly because of the large exposed cathodic area relative to the small anodic areas present at breaks in the coating. One way to avoid the occurrence of large cathode/anode ratio is to coat the entire alloy. It is important to remember that severe localized corrosion may occur at any breaks in the coating on the anodic material.

Common Fabrication Defects

Common fabrication defects include:

- Imperfect welds
- Weld spatter
- Skip welds
- Rough welds
- Laminations
- Gouges
- Sharp corners

Welds should be continuous, rather than skip welds, sot welds, or intermittent welds.

Weld spatter is difficult to completely coat and highly vulnerable to corrosion. Breakdown of the coating at deposit of weld spatter can quickly spread over a large area. Weld spatter is similar to rough welding surfaces and must be removed prior to coating.

Rough welding surfaces should be avoided. Grinding is necessary to make them smooth. Tiny voids in the weld may be bridged over by coating. Sharp ridges and spikes are difficult to coat, the coating pulls back from the edge of the ridge and is much thinner at that point.

Rough welds should be repaired to remove sharp edges and other irregularities.

Lamination, scabs, rollovers, and other defects of this type must be corrected to avoid any areas inaccessible to coating.

Gouges and other sharp indentations makes coating difficult. These indentations should be rounded so that the entire surface can be coated evenly and completely. Coatings applied to gouges may bridge over a gouge, and creating a void where corrosion can occur.

Coatings tend to pull back from sharp edges. Sharp edges should be rounded. Coatings can bridge over the base of a sharp bend or angle, creating a void that can trap moisture.

Surface Preparation

The majority of coating failures are caused either completely or partially by faulty surface preparation. For this reason, it is highly critical that proper surface preparation be attained.

Many factors in surface preparation affects the life of coatings including:

Residues of oil, grease, and soil, which weaken adhesion on mechanical bonding of paint to the surface

Residue of various chemicals that can induce corrosion

Rust on the surface; rust scale cannot be protected by any coating and cannot maintain adhesion to steel

Loose or broken mill scale which can cause early coating failure, or tight mill scale which can cause later failure

An anchor pattern which may be so rough that it contain peaks impossible to adequately protect with paint, or may not be rough enough, causing coating failure from loss adhesion

Sharp ridges, burrs, edges, or cuts from mechanical cleaning equipment, preventing adequate thickness of coatings over irregularities

Surface moisture which, if painted over, may cause blistering and delamination failure

Old coating which may have poor adhesion or may be incompatible, or may be too deteriorated for recoating

Generally, these conditions should be remedied by appropriate means of surface preparation prior to any coating application

Many tools, techniques, and methods can be used to prepare a surface for coating. A number of standards exist for a various types and degrees for surface preparation.

Coating Application

Many methods of applying a coating have been developed. The most common are manual methods (e.g., brush or roller), spray application, and specialized methods (e.g., dipping used in production facilities).

Manual

Brushing and rolling rank as the easiest and the most commonly used application techniques. Paling is where the coating is “gloved” on. This has application on cables and other hard-to-cover items where appearance is not critical. Concrete, mortars, epoxy, polyester, furan, and other materials may be applied as heavy coatings by hand troweling. The organic materials may be reinforced with glass cloth, while wire mesh might be used for inorganic products.

Spray

Spray application of coating may be accomplished using either conventional air spray, airless spray, electrostatic spray or flame spray.

Conventional air spray is a technique in which an air stream is used to atomize the coating and propel it onto the work piece

Airless spray is a technique in which the coating is pressurized and the tip of the gun is designed to atomize the coating.

With electrostatic spray, electrically-charged particles of coatings are directed through the air toward a surface shoes charge is opposite that the particles. Thus, the coating is attracted to the surface and will tend to deposit with little overspray. It is mainly used in production lines, although some fields use occurs.

In the flame spray method, thermoplastic powders or rods are fed into a suitable flame and impelled toward the surface to be coated. The particles coalesce and solidify to form the coating. Metals are applied in the same manner at much higher temperature.

Production techniques

In hot dipping, the work piece is dipped into a bath of molten metal. When zinc is the material to be applied, the process is called hot-dip galvanizing.

When using the fluidization bed technique, thermoplastic polymer powder is suspended in a tank through which air is pumped so that the particles behave like a liquid. Surfaces to be coated are preheated and run through the bed. The hot surface melts and thermoplastic and fuses the coating, and subsequent cooling produces a uniform plastic sheathing. The coating thickness depends on the temperature of the substrate and the time of exposure.

Parts to be coated by the powder spray method are heated to the appropriate temperature and then moved to an area where a fusible coating powder is sprayed onto the surface. Powder spray is a production line technique that can produce uniform coatings.

Inspection

Inspection should be conducted before, during, and after each step of the coating operation. A wide variety of tests and equipment is available for coating inspection.

Surface Preparation Inspection

Surface preparation includes inspection for such factors as surface cleanliness, anchor profile, and removal of chemicals and other materials that may affect coating performance. Cleanliness of the surface with regard to removal of rust and old coating is usually performed using visual standards. Anchor profile inspection can be performed in several ways. One of the most common is to use a special conforming tape that is pressed into the surface to be inspected and then measured with a micrometer to determine the anchor profile height. One common test for removal of undesirable chemicals is a chemical spot test for soluble iron compounds.

Inspection during coating application involves verification that such conditions as temperature and relative humidity are within the proper limits and that the proper application techniques are used. Wet-film thickness of the coating may be measured during coating application, if required.

Inspection after coating may include tests for complete curing of the coating, usually by measuring the hardness of the coating; tests for coating adhesion, and dry-film coating thickness. Coating continuity may also be measured using high- or low-voltage electrical “holiday detectors”.

Wraps and Tapes

Protective wraps and tapes are frequently used as protective coatings. While very durable, they must be applied carefully to achieve good performance. They may either be hand-applied to small areas or applied mechanically to large structures, such as pipes for underground service. Some tape systems require the use of liquid-applied primer for proper adhesion and performance. Some tapes and wraps are loosely applied and then “heat shrunk” to give a tightly fitting covering.

Insulation

Some coatings are applied as a thermal insulation. When applied directly over a substrate, it is important that these coatings do not absorb moisture and do not contain chemicals that may react with the substrate.

Metallic Coatings

Metallic coatings can be applied to other metals, or to nonmetallic substrates in many ways, including by weld overlaying, hot dipping, electroplating, and cladding. Metallic coatings are relatively from defects, such as pinholes or other holidays, but defects that expose the substrate are usually present. Mechanical damage and corrosion of the coatings can also expose the substrate. Where the substrate is exposed, the galvanic relationship between the coating and the substrate is very important in the protection of the substrate.

Coating Anodic to Base Metal

When coating is anodic to the base metal, the coating will serve as an anode with respect to the base substrate at areas of substrate exposure. The coating can protect the substrate even at defects or damage areas. In immersion of underground service, the size of the defect protected can be large because of the ability of the protective current ro flow through the electrolyte. In immersion service, the ratio of exposed areas is favorable when the majority of the surface is anodic and the exposed cathodic area is relatively small. In atmospheric service, the size of exposed substrate that can be protected is limited.

Anodic coatings, of course, will be slowly consumed in protecting the substrate, and their life span is dependent upon their thickness. The thick coatings obtained by hot dipping will usually give longer life than the thinner coatings applied by electroplating.

Coating Cathodic to Base Metal

If the coating is cathodic to the base metal, the coating will act as a cathode and the substrate will act as an anode whenever the substrate is exposed. Thus the substrate will corrode to protect the coating. This is not desirable. This effect is accelerated by the the relative anode/cathode area ratio. In immersion of underground service, the anode/cathode area ratio can be specially severe. Although less severe in atmospheric service, the area ratio remains unfavorable in most cases.

Chapter 7

Corrosion and Failure Inspection

7.1 Introduction

Some forms of corrosion are relatively easy to detect and monitor; some are difficult, if not impossible. However, because of corrosion's implications for safety and cost, inspection and monitoring are performed frequently.

Inspection is performed to determine whether the equipment or structures exposed to the environments still conform to the safe parameters of the original design. Therefore, one must establish whether corrosion has consumed the "corrosion allowance" originally added to the allowable wall thickness of the equipment, or structure on which mechanical defects, such as cracking, abrasion, etc., may have become evident. Failures initiates by such phenomena may, and often lead to dangerous or unsafe conditions.

Inspection must be carries out in an organized and systematic manner. A number of industries now have computerized programs dealing with the frequency, timing, and recording of equipment conditions. It takes a lot of effort to specify how and how often particular piece of equipment must or should be inspected. Once this is accomplished, a computerized program can be prepared.

The most probable sites of first failure can often be predicted, particularly where fluid flow is a factor. The inspector must have access to the past history of the equipment or of similar units it has replaced.

Inspection groups may include a variety of skilled persons:

- Chemists.
- Metallurgical, mechanical, or chemical engineer.
- Mechanical inspector
- Corrosion technician

Inspections can be either scheduled or unscheduled. Scheduled inspections are planned in advance and are conducted during scheduled downtime when possible. Much of the information is usually obtained prior to plant shutdown by means of "on-stream" inspection, where such techniques as ultrasonic and radiography have been used to determine, if possible the equipment condition in advance. Proper action and replacement of equipment or equipment components can be readied prior to the outage.

Unscheduled inspections usually are performed when a failure occurs. The main purpose of an unscheduled inspection is to determine what needs to be done to resume safe plant operation.

There are many methods of corrosion inspection, including:

1. Visual
2. Radiographic (x-ray)
3. Ultrasonic
4. Electromagnetic
5. Liquid penetrate
6. Magnetic particle

7.1.1 Visual

Visual examination is one of the oldest, simplest, and least expensive of the nondestructive test methods. The object is examined visually or with the aid of a magnifying glass, offen accompanied by discreet probing by a penknife. An experienced inspector can determine much from the appearance of surfaces. Visual examination of inaccessible surfaces can be performed using borescope and remote television cameras.

Advantages of visual inspection

- It can be a very simple but effective test to perform and often does not need expensive equipment.
- Experienced operators and advanced equipment make it possible for visual inspection to be very sensitive.
- It allows discontinuities to be seen and not be just a blip on the screen.
- Many different surface-breaking discontinuities can be found.
- Training and experience times can be short.
- Virtually any component can be examined anywhere on the surface.

Disadvantages of visual inspection

- Many variables can lead to discontinuities being missed.
- At its worst, it relies totally on the human factor.
- Sub-surface discontinuities will not be seen.

7.1.2 Radiographic

This technique is suitable for the detection of internal defects in ferrous and nonferrous metals and other materials. X-rays, generated electrically, and Gamma rays emitted from radio-active isotopes, are penetrating radiation which is differentially absorbed by the material through which it passes; the greater the thickness, the greater the absorption. Furthermore, the denser the material the greater the absorption.

X and Gamma rays also have the property, like light, of partially converting silver halide crystals in a photographic film to metallic silver, in proportion to the intensity of the radiation reaching the film, and therefore forming a latent image. This can be developed and fixed in a similar way to normal photographic film.

Material with internal voids is tested by placing the subject between the source of radiation and the film. The voids show as darkened areas, where more radiation has reached the film, on a clear background. The principles are the same for both X and Gamma radiography.

To produce an X or Gamma radiograph, the film package (comprising film and intensifying screens - the latter being required to reduce the exposure time – enclosed in a light tight cassette) is placed close to the surface of the subject.

The source of radiation is positioned on the other side of the subject some distance away, so that the radiation passes through the subject and on to the film. After the exposure period the film is removed, processed, dried, and then viewed by transmitted light on a special viewer.

Various radiographic and photographic accessories are necessary, including such items as radiation monitors, film markers, image quality indicators, dark room equipment, etc. Where the last is concerned there are many degrees of sophistication, including fully automatic processing units. These accessories are the same for both X and Gamma radiography systems.

Also required are such consumable items as radiographic film and processing chemicals.

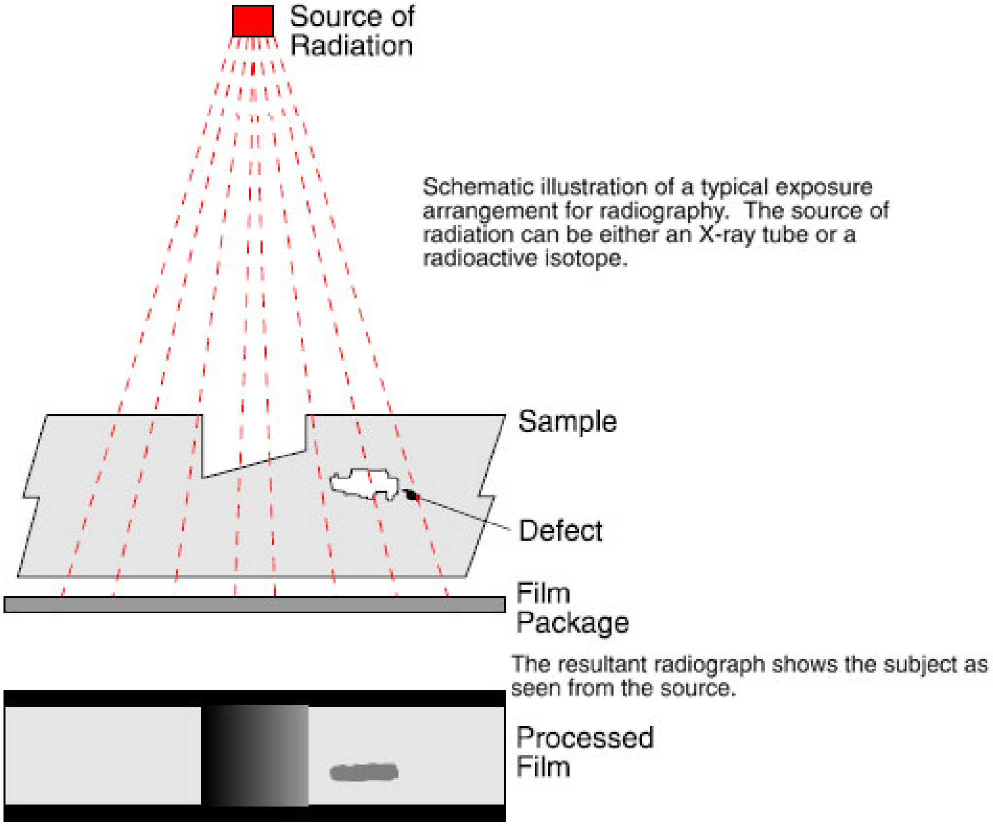
Advantages of industrial radiography

- Radiography can be used with most solid materials.
- Radiography has the ability to detect internal flaws.
- It provides a permanent record of the test.
- It discloses fabrication errors and often indicates necessary corrective action.
- It reveals assembly errors.
- The fact that radiographic examination is being carried out improves the quality of the welding.

Disadvantages of industrial radiography

- Radiography can only detect defects that are in a certain orientation.
- Radiography has difficulty detecting very small defects.
- It is impractical to examine parts of complex geometry.
- It requires two-sided access.
- Radiography requires many safety considerations and obviously, if used incorrectly, can be extremely dangerous.

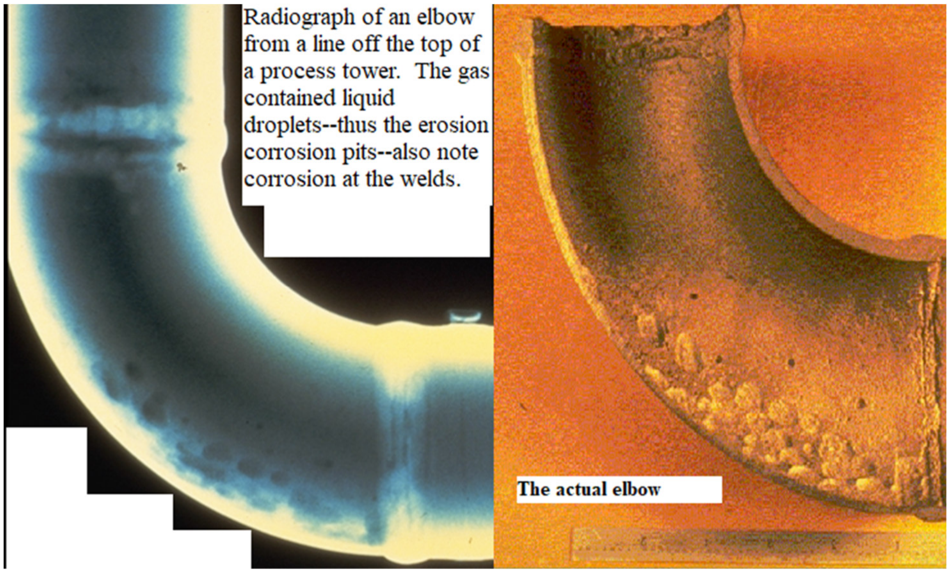
- Generally, radiography is a high-cost NDT method, both in capital items, consumables and manpower.



Schematic illustration of a typical exposure arrangement for radiography. The source of radiation can be either an X-ray tube or a radioactive isotope.

The resultant radiograph shows the subject as seen from the source.

Fig. 7-1. Radiographic.



Radiograph of an elbow from a line off the top of a process tower. The gas contained liquid droplets--thus the erosion corrosion pits--also note corrosion at the welds.

The actual elbow

Fig. 7-2. Radiographic inspection result and actual specie.

7.1.3 Ultrasonic

Ultrasonic equipment is widely used for the nondestructive thickness gauging of an in-service equipment subject to corrosive attack, the detection of laminar discontinuities, and crack detection. Ultrasonic techniques include pulse-echo, transmission, and resonance methods. The pulse-echo technique requires access to only one side of the part being inspected. A single transducer is used to send sound waves into the material and receive the returning echo. Echoes are produced by internal discontinuities and are from the back side of the piece. The echo from the back side of the piece gives the material thickness. The transmission method uses transducers on both sides of the material and is primarily used to detect internal discontinuities. The resonance method uses a single transducer and is primarily used for thickness measurement.

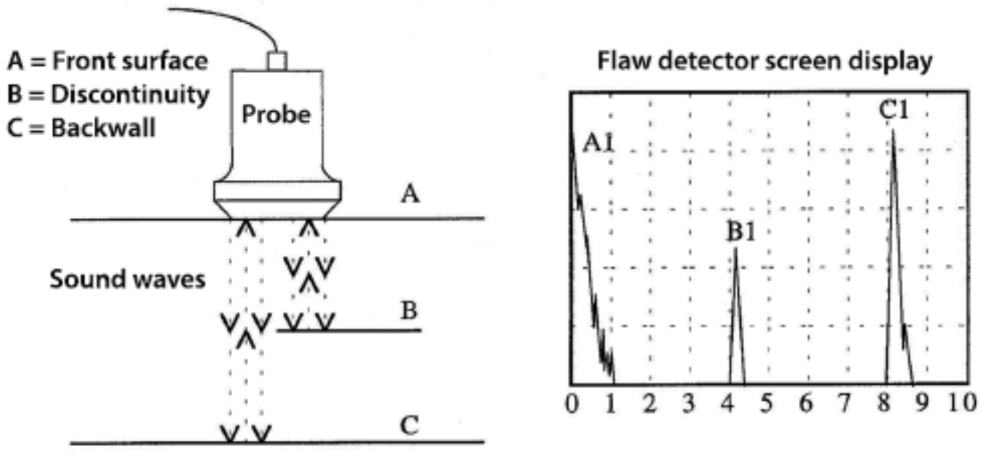


Fig. 7-3. Ultrasonic inspection.

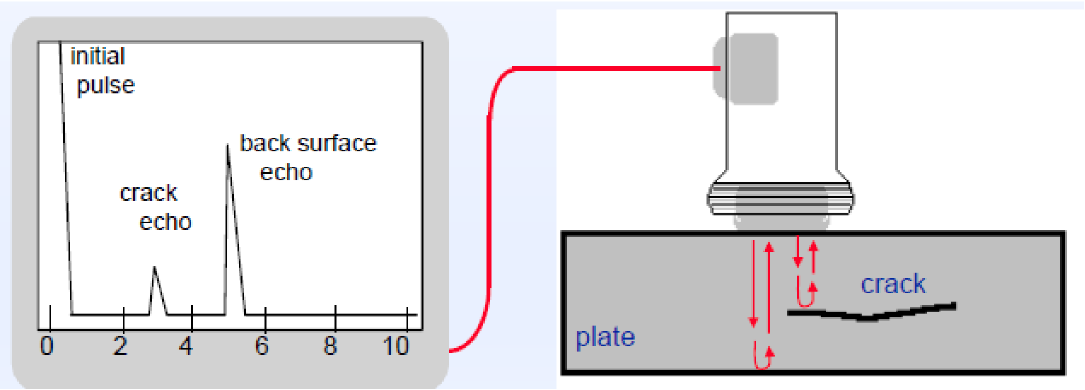


Fig. 7-4. Ultrasonic inspection.

Advantages of ultrasonic inspection

- Excellent penetration of ultrasound into materials allows the detection of deep-lying defects. Parts from a few millimeters thick up to several meters long can be examined.
- The method is very sensitive and can locate very small defects.
- Defects can be sized and the position of internal defects within a component accurately established. The nature, shape and orientation of the defect can be determined.
- With the pulse-echo technique, access to only one side of a component is required.
- The ultrasound reflected back from defects is displayed almost instantaneously, allowing immediate on-site interpretation, and allows the method to be utilized for automatic systems, production monitoring and process control. Electronic monitoring of fast rising and falling defect signals, which an operator may miss, allow for very rapid inspection systems. A permanent record of the inspection can be made for evaluation at a later date.
- The entire volume is scanned from the front to the back surface.
- The technique can be very portable, with flaw detectors and probes being light and compact, allowing on-site inspection of difficult-to-access components possible.
- Signals can be processed by a computer, allowing defects to be characterized and a determination of material properties made. Thickness measurements of metal beneath paint coatings can be carried out with the multiple-echo method without the removal of the protective coatings.

Disadvantages of ultrasonic inspection

- It is often difficult to interpret a defect signal.
- Manual techniques require experienced operators and the training and experience periods can be quite long.
- Preparation and development of inspection procedures is not straightforward and good technical knowledge is needed.
- Irregular-shaped parts and parts with rough surfaces, such as in-service components, are difficult to test, as are cast components with a coarse grain structure.
- Single-crystal probes have a dead-zone in which defects will not be detected.
- Twin-crystal probes are usually focused and can only be used over a certain depth range.
- To allow the efficient transfer of ultrasonic energy between the probe and the component, a couplant must be used. Couplant loss can lead to false interpretation. Techniques have been developed that can be applied without the use of couplant, but they are usually specialized and can only be used under certain conditions.
- The couplant can be a contaminant, which requires removal before further processing can occur, *i.e.* painting/coating.
- Contact testing requires the surface profile to be reasonably good.

7.1.4 Electromagnetic - Eddy Current Inspection Method

Electromagnetic inspection techniques, such as eddy-current testing, are used to detect cracks, to measure the electrical and magnetic properties of the metal, and to detect discontinuities or lack of homogeneity. Eddy-current testing equipment has been developed for the inspection of the internal surfaces of piping and heat exchanger tubes. It can also be used to determine the thickness of nonconductive films, such as paints, over conductive substrates.

The main applications of the eddy current technique are for the detection of surface or subsurface flaws, conductivity measurement and coating thickness measurement.
The technique is sensitive to the material conductivity, permeability and dimensions of a product.
Eddy currents can be produced in any electrically conducting material that is subjected to an alternating magnetic field (typically 10Hz to 10MHz). The alternating magnetic field is normally generated by passing an alternating current through a coil.
The coil can have many shapes and can between 10 and 500 turns of wire.
The magnitude of the eddy currents generated in the product is dependent on conductivity, permeability and the set up geometry. Any change in the material or geometry can be detected by the excitation coil as a change in the coil impedance.
The most simple coil comprises a ferrite rod with several turns of wire wound at one end and which is positioned close to the surface of the product to be tested. When a crack, for example, occurs in the product surface the eddy currents must travel farther around the crack and this is detected by the impedance change. See Fig.7-5.

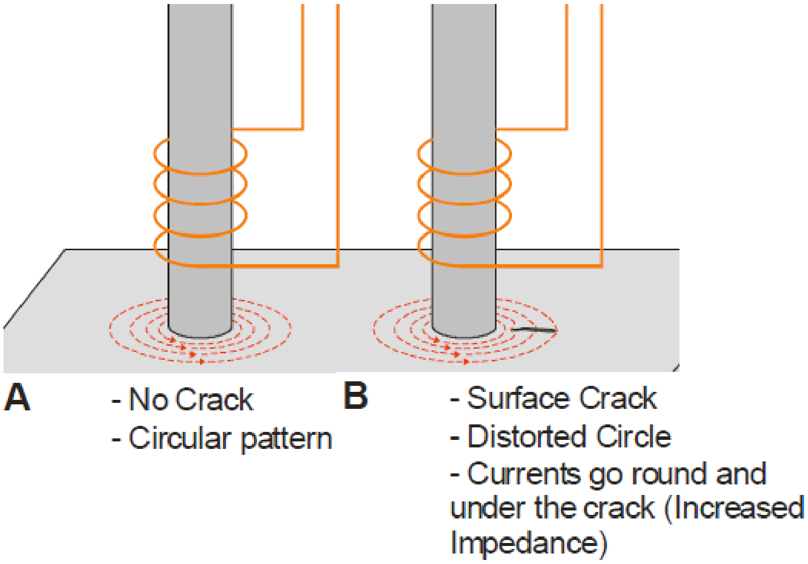


Fig. 7-5 Eddy current inspection

Coils can also be used in pairs, generally called a driven pair, and this arrangement can be used with the coils connected differentially. See Fig.7-6

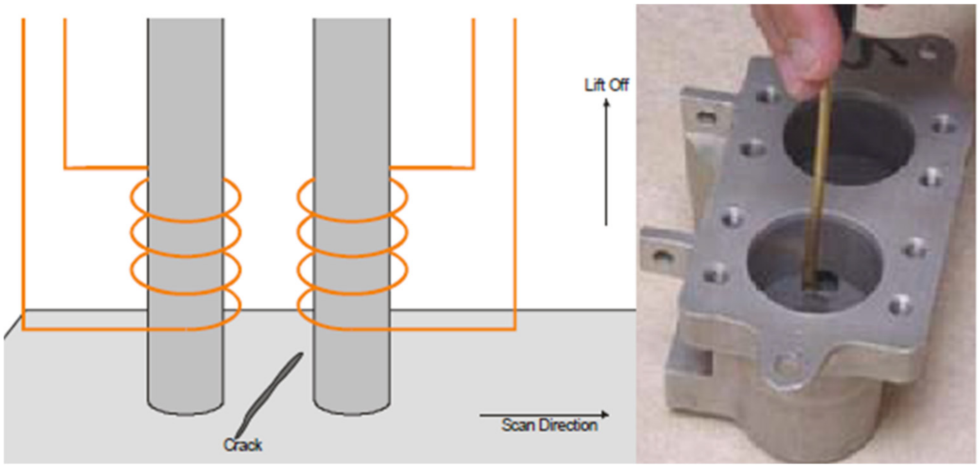


Fig. 7-6. Eddy current inspection

Advantages of Eddy current inspection

- Eddy current testing can be used to locate and measure a variety of physical properties.
- It can be used as an automated high-speed testing process in some aspects, *i.e. encircling* coils.
- Results can be kept as a permanent record in some displays.
- Results can be displayed in numerous ways.
- Eddy current testing gives excellent reproducibility of results.
- Eddy currents are very sensitive to small surface cracks if the correct equipment is used.
- Eddy current testing does not require couplant.

Disadvantages of Eddy current inspection

- Eddy currents can only be used on electrically-conductive materials.
- The permeability of ferromagnetic materials gives inconsistent and false readings.
- The depth of penetration is very limited because of the skin effect of AC fields.
- Only AC fields can generate eddy currents.
- Depending on the equipment used, some features cannot be detected, usually when the indicator is a gradual or a sharp change and whether the equipment is set up to measure such a change.

- When using encircling or internal coils, the part or coil must be accurately centered.
- The indications found are sensitive to orientation, with the most sensitive being when the indication is at 90° to the flow of eddy currents.

7.1.5 Liquid Penetrant

Sometimes flaws may be open to the surface, although they may be impossible to find visually without aid. These include fine cracks caused by stress corrosion, fatigue, grinding, galling, etc. Flaws of this type may be found more easily by applying a liquid dye penetrant that becomes visible when a thin layer of absorptive material, such as chalk, is applied and wicks the penetrant out of the flaws.

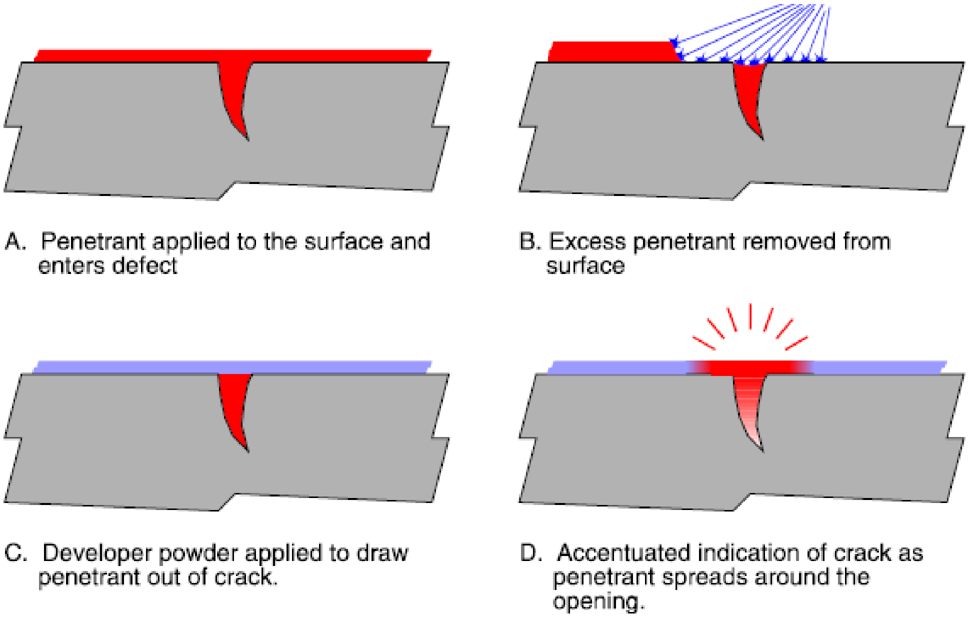


Fig. 7-7. Liquid penetrant inspection.

Advantages of Liquid Penetrant inspection

- An easy method to learn.
- Very versatile and can be used to examine metals and non-metals.
- Sensitive to small surface-breaking discontinuities.
- Very good for high-volume production.

Disadvantages of Liquid Penetrant inspection

- Pre-cleaning has to be thorough.
- Will not detect discontinuities below the surface.
- Rough surfaces or surfaces with porosity can produce excessive background, which will interfere with inspection.

7.1.6 Magnetic Particle Inspection

Surface and near-surface flaws in ferromagnetic materials can also be detected using magnetic particles. A magnetic field is applied to the work piece. The part is therefore, magnetized. Finely milled iron particles coated with a dye pigment are then applied to the specimen. These particles are attracted to magnetic flux leakage fields and will cluster to form an indication directly over the discontinuity. This indication can be visually detected under proper lighting conditions.

Advantages of magnetic particle testing

- Magnetic particle testing is a sensitive method for locating surface and slight sub-surface discontinuities in ferromagnetic materials.
- Indications are produced that can have very good definition of the actual discontinuity.
- The method is relatively simple to learn.
- Components of virtually any size or shape can be tested.
- Cracks which are filled with foreign material may still be detected.
- Discontinuities do not have to be surface-breaking like a crack, for example, non-metallic inclusions may be located.
- Portable equipment can be used to test components *in-situ*, an electrical supply is not necessary in all cases.
- The method is very rapid. An indication of a discontinuity is formed virtually instantaneously.
- Testing is possible in some cases on painted or coated components.

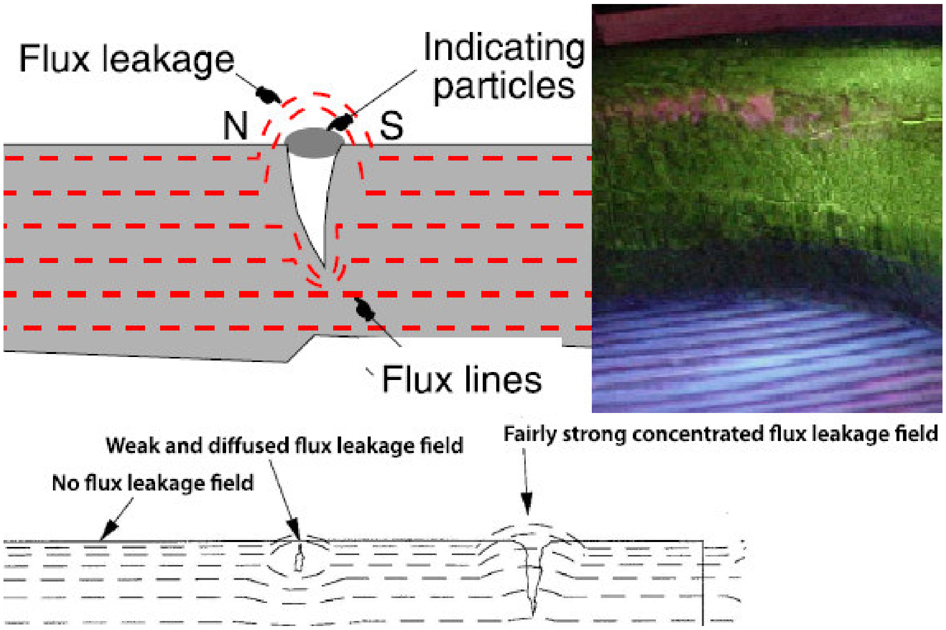


Fig. 7-8. Magnetic particle inspection.

Disadvantages of magnetic particle testing

- Only ferromagnetic parts can be tested.
- To ensure a part is fully tested, it is often necessary to apply two magnetic fields 90° apart in separate operations.
- Residual magnetic fields may be a problem – demagnetization is often required.
- High currents are often needed to magnetize a part, which may lead to arcing between the part and electrical contact, which can burn the part. This can cause parts to be scrapped.
- Post cleaning is usually needed to remove residual consumables.
- Often the part will have been de-greased prior to inspection, leaving the part susceptible to corrosion. Protection after testing is often required.

Chapter 8

Corrosion Monitoring

8.1 Introduction

Corrosion monitoring is a means for continuous or frequent periodic measurements of corrosion activity within a system, with either no interruption or minimal interruption of operations.

There are many methods of corrosion monitoring, including:

1- Specimen exposure
2- Electrical Resistance
3- Electrochemical Methods
4- Water chemistry analysis
5- Deposit analysis
6- Cathodic protection monitoring

8.1.1 Specimen Exposure

Specimen exposure are frequently performed for in-service corrosion testing and monitoring. In-service testing is used to determine the corrosion performance of alternative materials. Specimen exposures are also used to monitor corrosion within the system. Specimen exposures are used to monitor effectiveness of corrosion inhibitors, as well as to monitor the effects of changing operating conditions on the corrosion of material within the system.

Corrosion Coupons

Coupons are small material samples placed into the system to measure or monitor corrosion performance. Coupons may be simple flat specimens that can be mounted for exposure. In some cases, “spool pieces”, which are short pieces of piping or tubing, are inserted into the system, either directly or in a bypass loop.

Coupons are frequently cleaned and weighted prior to exposure. After exposure; they should be visually examined for corrosion activity and for patterns of corrosion products. They can also be photographed at this stage to give a permanent record of their appearance. The specimens are cleaned and weighted to determine mass loss. Then the specimens are again carefully inspected to determine all types of corrosion that had occurred, and photographed again to give permanent record of their clean condition. If localized corrosion has occurred, measurements appropriate to the form of corrosion that has occurred are then performed.

Corrosion coupons are one of the most common methods to monitor internal corrosion is to expose test specimens, or coupons, to the environment. Coupons are pre-weighed pieces of metal that are inserted into a system and then allowed to corrode. The most commonly used coupons are small strips of metal, small cylindrical rods, or flush-mounted discs as shown in Figures 8-1 to 8-4.

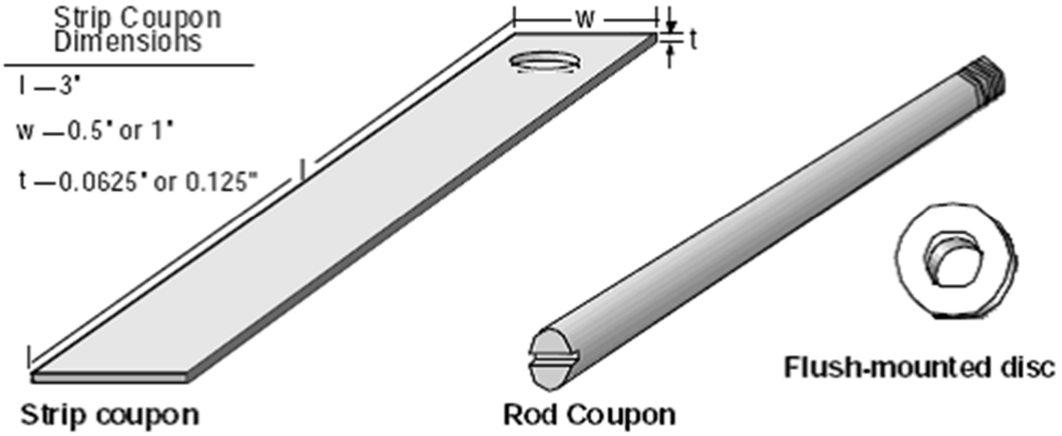


Fig. 8-1. Corrosion coupon types.

Fig. 8-2. Corrosion coupon types.

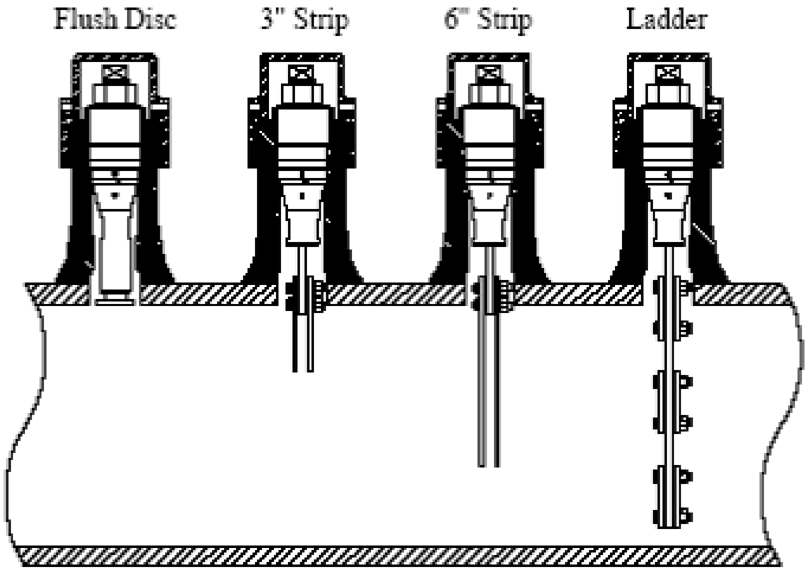


Fig. 8-3. Corrosion coupon types.

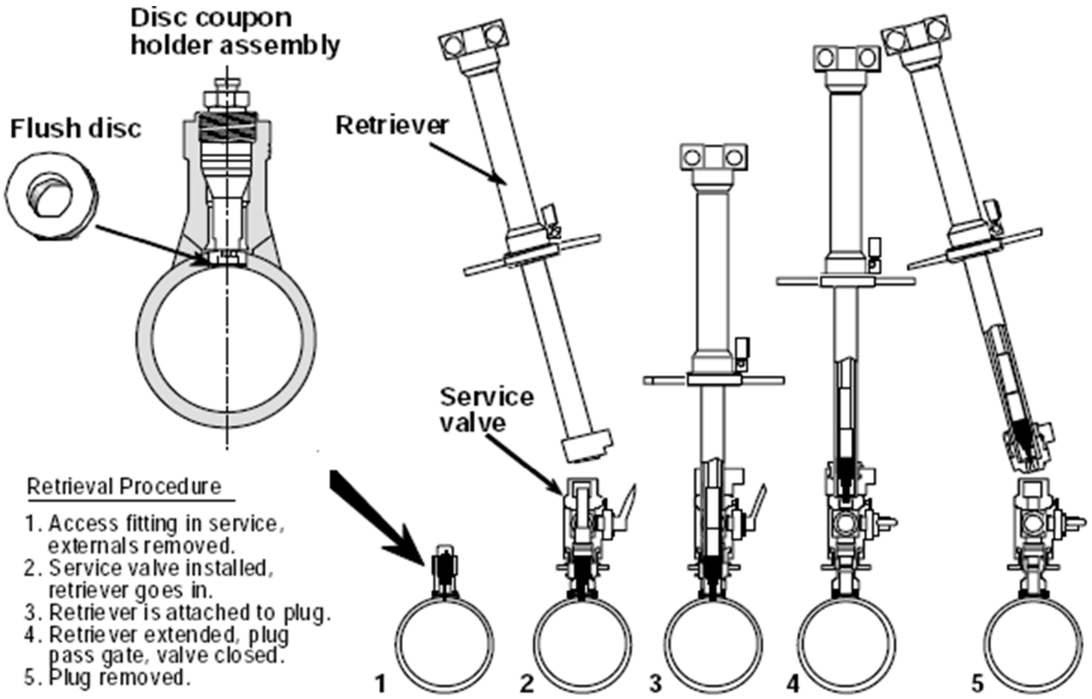


Fig. 8-4. Corrosion coupon Installation.

Strip coupons are used more often. They provide satisfactory corrosion rate data and are applicable for most circumstances. Rod coupons are normally used for locations where installation and retrieval under pressure are not required. Flush-mounted coupons can remain in the system longer than normal corrosion coupons. Each coupon is very carefully weighed and mounted into a coupon holder so that the coupon can be installed at a particular location in the system. Coupon holders are made so that coupons are held fixed and rigid. The corrosion coupons are exposed to a system via access fittings. Access fittings allow the coupons to be placed at many locations in a system and to be inserted and retrieved at any time. Once coupons are inserted into a system, they are allowed to remain for 30, 60, or 90 days.

In gas production systems, coupons are recommended at the wellhead, at the downstream end of the flow line, and between each vessel or separator. In water injection systems, coupons are recommended at each supply well, at each leg in the gathering system, and at the inlet and outlet of each tank, vessel, or pump.

When the coupons are removed from the system, corrosion products and evidence of pitting are noted. The coupon is wiped dry with a clean towel and taken to the laboratory for determination of the corrosion rate.

Corrosion rate is calculated as follows:

$R = W \times 143700 / A\, d\, D$

$T = W \times 393.7 / A\, d$

Where

T = Metal thickness loss in mils (1.0 mill = 0.001 inch.)

W = Weight loss

A = Coupon area cm^2

d = Metal/Alloy density (g/cm^3) - Iron = 7.85 g/cm^3

D = Exposure time (days)

R = Corrosion rate (mils per year – MPY)

1MPY = 0.0254 mm/year.

Relative corrosion Resistance	mpy	Mm/yr	um/yr
Outsttanding	<1	<0.02	<25
Excelent	1-5	0.02 – 0.1	25-100
Good	5-20	0.1-0.5	100-500
Fair	20-50	0.5-1	500 – 1000
Poor	50-200	1-5	1000-5000
Unacceptable	200+	5+	5000+

Table 8-1. Corrosion rate classification.

Pits are measured with either a depth gauge or a micrometer. A measure of pitting severity is the ratio of the deepest metal penetration rate to the average metal penetration rate. The penetration rate is calculated from the overall weight loss of the coupon as follows:

$$\text{Pitting Severity} = \frac{\text{Maximum Piting Rate (mpy)}}{\text{Penetration Rate (mpy)}}$$

where -

$$\text{Maximum Pitting Rate} = \frac{\text{Maximum Pit Depth} \times 365}{\text{Time (days)}}$$

Special Coupons

Special coupons have also been developed to test for specific types of corrosion, including crevice corrosion, environmental cracking, and galvanic effects.

Crevices: Crevices coupons are fitted with a crevice former. The crevice former may be of either the same metal as the coupon or a nonmetallic material. The crevice formed is frequently made to be part of the coupon holding system.

Stress: There a wide variety of stress coupons for determining the resistance of materials to environmental cracking. These include C-ring, bent-beam, and direct- tension specimens. The C-ring specimens are the most frequently used for in-service testing.

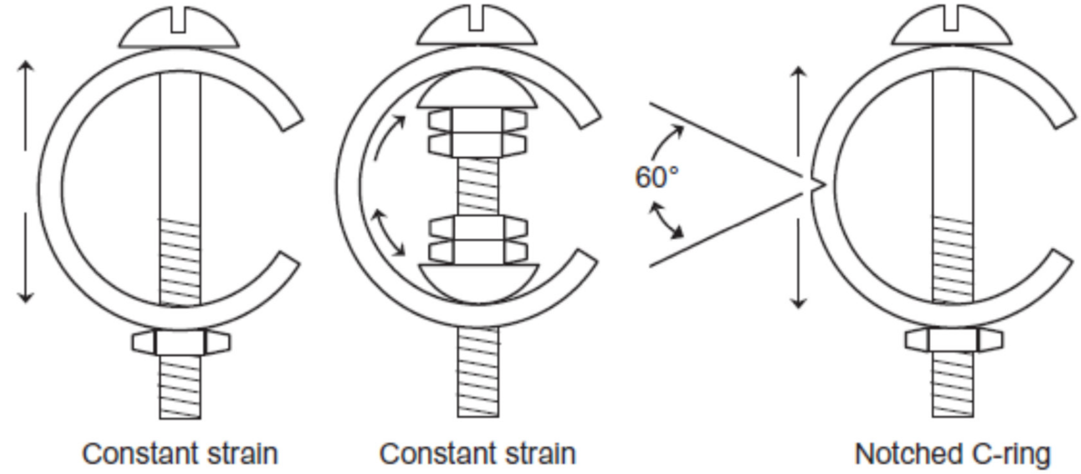


Fig. 8-5. C rings used in constant deformation tests.

Galvanic Couples: Galvanic couples coupons may be as simple as two metals joined together to form a coupon that is exposed and evaluated after exposure. In other cases, both metals, with attached lead wires, are individually exposed to the service environment and the current flow between the samples is measured using a zero-resistance ammeter. One variation of the technique is the placement of a dissimilar metal coupons with an attached lead wire inside a pipe or vessel. The corrosion current between the coupon and the vessel is then monitored, and upset conditions, such as variations of chemistry or application of inhibitors, can be detected by a change in corrosion current.

Corrosion Coupon Advantages

- Cheap, easily applied
- Coupons made of material similar to pipe material.
- Visual examination identifies mode of attack.
- Samples available for scale / deposits analysis
- Source of microbiological data.

Corrosion Coupon Disadvantages

- Corrosion rates averaged over exposure time.
- Corrosion rate calculation assumes general corrosion.
- Data generation rate slow (long-term data acquisition).
- Requests insertion and retrieval under high pressure, which can have safety implications.

8.1.2 Electrical Resistance (ER)

Electrical Resistance Acceptance of the electrical resistance (ER) corrosion monitoring method grew quickly after the correlation with corrosion rates was established in the 1950s. The principle of the widely used ER technique is quite simple, that is, the electrical resistance of a sensing element increases as its cross sectional area is reduced by corrosion damage. The electrical resistance of a metal or alloy element is given by the equation:

$R = r\,L / A$

where

L is the probe element length (cm);

A is the cross-sectional area (cm^2);

r is the specific resistance of the probe metal (Ω cm).

Reduction or metal loss in the element cross section A due to corrosion will be accompanied by a proportionate increase in the element electrical resistance (R). Since temperature influences the electrical resistance of the probe element, ER sensors usually measure the resistance of a corroding sensor element relative to that of an identical shielded element. Commercial sensor elements are in the form of plates, tubes, plates or wires (Figures. 8.6 and 8-7).

Reducing the thickness of the sensor elements can increase the sensitivity of these sensors. However, improved sensitivity involves a trade-off against reduced sensor lifetime. The ER probe manufacturers provide guidelines showing this trade-off for different sensor geometries. These probes usually have a useful life up to the point where their original thickness has been halved with the exception of wire sensors. For ER wire sensors, the lifetime is lower, corresponding to a quarter original thickness loss.

It is obvious that erroneous ER corrosion results will be obtained if conductive corrosion products or surface deposits form on the sensing element.

Iron sulfide formed in sour oil–gas systems or in microbial corrosion and carbonaceous deposits in atmospheric corrosion are relevant examples. The same restriction also applies to electrically conductive environments, (e.g., molten salts or liquid metals).

There are several advantages to the ER corrosion monitoring method. Because probes are relatively small, they can be installed easily and the system wired directly to a control room location or to a portable resistance bridge at the probe location. For systems that are wired directly to control rooms, a computer system can be used to obtain the data and to transform the results in corrosion rate values. On the other hand, it is time consuming and sometimes impossible to take measurements at the probe site with a portable bridge. The temperature-compensation device reacts slowly, and it can be a source of error if the temperature varies when the measurement is taken.

Corrosion rate measurements obtained in short periods of time can also be inaccurate because the method measures only the remaining metal, which produces significant errors by estimating small differences between large numbers.

The ER results provide a good measure of metal loss by general corrosion. However, the probes are less sensitive to effects of localized attack, which increase the element resistance on only a small area of the element, except near the end of probe life on loop element probes, where the localized attack completely corrodes through the element, increasing its resistance to infinity. Special probes have been prepared for sensitivity to crevice corrosion by creating multiple crevices on the measurement element, such as beads on wire loop probes.

Electrical Resistance Testing Advantages

- Direct measurement of metal loss.
- Will work in most environments. Does not require continuous aqueous phase.
- Quicker response than weight loss coupons.
- Data interpretation straight forward.
- Continuously logging probes give high quality data (logging rate as low as 5 min).
- Sensitive to erosion as well as corrosion.

Electrical Resistance Testing Disadvantages

- Sensitive to thermal changes.
- Corrosion rate calculated as uniform corrosion and no information on localized attack.
- Tradeoff between sensitivity and probe life.
- Adversely affected by conductive surface films e.g. FeS in sour conditions
- Crevice corrosion can occur on poorly constructed flush mounted probes.
- Require insertion and retrieval under high pressure.

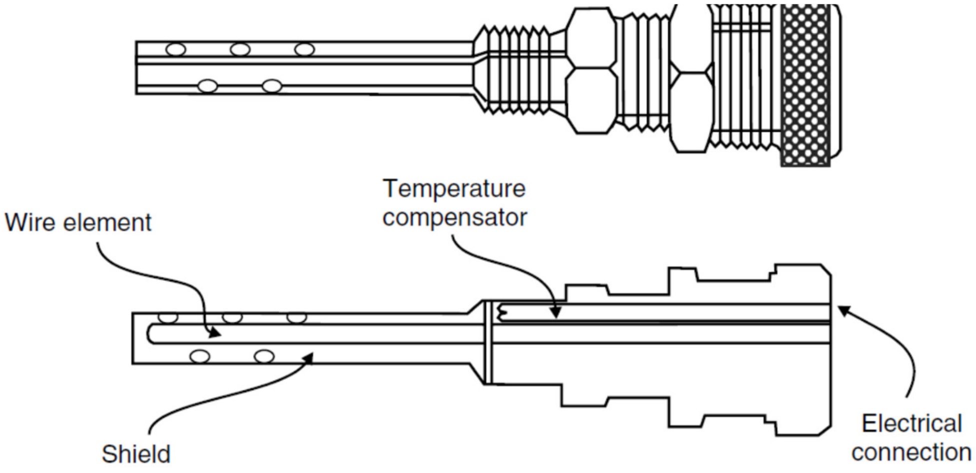


Fig. 8-6 Illustration of an electrical resistance probe

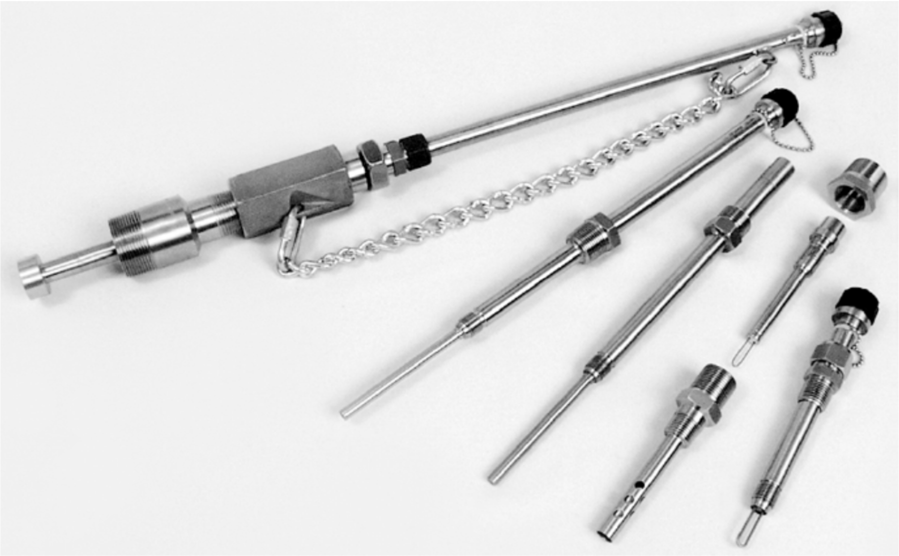


Fig. 8-7. Commercial sensor elements to carry out ER measurements.

Fig. 8-8. ER measuring devices.

8.1.3 Inductive Resistance Probes

Following advances in electronics, signal processing, and measuring techniques, this new metal loss monitoring technology is a derivative of ER corrosion sensing. This corrosion monitoring technology has been developed to combine very high resolution measurement with long probe life and the capability of intrinsically safe operation in hydrocarbon process plant environments.

The thickness reduction of a sensing element is measured by changes in the inductive resistance of a coil embedded in the sensor, figure 8-9. Sensing elements with high magnetic permeability intensify the magnetic field around the coil; therefore, thickness changes affect the inductive resistance of the coil. Sensitivity has been claimed to be several orders of magnitude higher than with comparable ER probes.

The measurements are virtually unaffected by other process variables, such as temperature, hydrostatic pressure, impact loading (slugging), or flow regimes.

The system is also immune to extraneous industrial noise, specifically electromagnetic induction, and thermally induced electromotive force voltages. The inductive resistance sensor elements have very high geometric and physical symmetry providing sensor surfaces with identical metallurgy and microstructures.

Fig. 8-9. Subsea inductive resistance probe IR.

8.1.4 Electrochemical Methods

Several electrochemical test method have been adapted from the original laboratory test to field test procedures that are useful in corrosion monitoring.

Linear Polarization Resistance

In this popular electrochemical technique, a small potential perturbation (typically 10–20 or even 30 mV) is applied to the sensor electrode of interest and the resulting current is measured. The ratio of the potential to current perturbations is known as the polarization resistance, which, according to the next equation is inversely proportional to the uniform corrosion rate.

More specifically, the polarization resistance of a metal is defined as the slope of the potential-current density ($\Delta E/\Delta i$) curve at the free corrosion potential (Fig. 8-10), yielding the polarization resistance R_p that can be itself related to the corrosion current (i_{corr}) with the help of the following
Stern–Geary Eqs.

$$R_p = \beta / i_{corr} = \Delta E / \Delta I$$

where
R_p is the polarization resistance; ohms
i_{corr} is the uniform corrosion current; Ampere
β is an empirical polarization resistance constant (Stern-Geary constant= 0.027 V for “Fe”)

The polarization resistance can be converted into a corrosion rate by the Stern-Geary equation:

$$i_{corr} = \beta / A R_p$$

where
A = Electrode area in cm^2

Stern – Geary Equation to calculate corrosion rate

Corrosion rate (mpy) = $(1.29 \times 10^5 / z D) / (\beta / R_p A)$

Where:

M = Atomic mass (56 for Fe)

z = Electron loss per atom (2 for Fe)

D = density (7,86 g/cm^3)

In a plant situation, it is necessary to use a probe as one of those shown in Fig. 8.11 such that it enters the vessel in the area where the corrosion rate is desired.
An electronic power supply polarizes the specimen from the corrosion potential. The resulting current is recorded as a measure of the corrosion rate. Several commercially available probes and analyzing systems can be directly interfaced with remote computer data-acquisition systems. Alarms can also be used to signal plant operators when high corrosion rates are experienced.
The LPR probes are typically a two or three electrode configuration with either flush or projecting electrodes. With a three-electrode system, corrosion measurements are made on the test electrode. Because these measurements take only a few minutes, the need for a stable reference electrode is minimized. For field monitoring, the reference electrode is typically made of stainless steel or of the same alloy as that being monitored on the test electrode. The auxiliary electrode is also normally of the alloy being monitored. The proximity of the reference electrode to the test electrode governs the degree to which compensation for solution resistance is effective. With a two-electrode system, the corrosion measurement is an average of the rate for both electrodes. Both electrodes would then be made of the alloy being monitored.

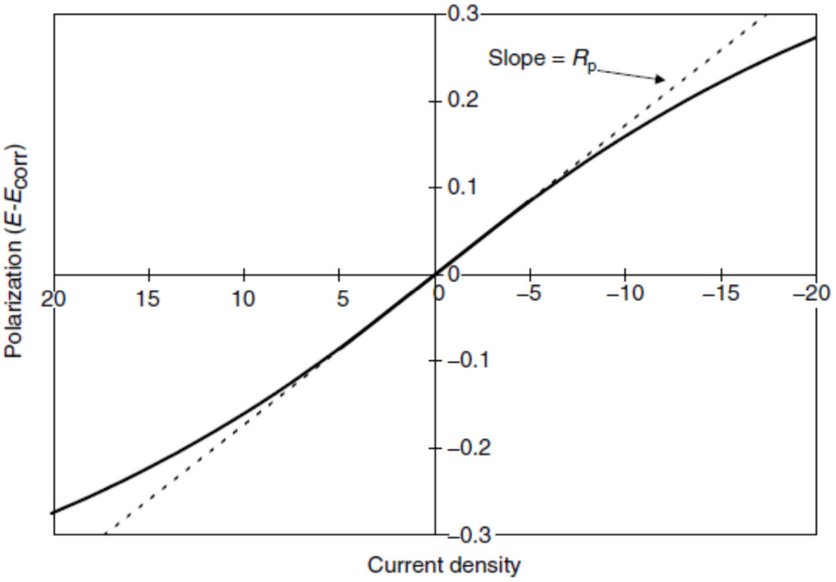


Figure.8-10. Hypothetical linear polarization plot.

Fig. 8-11. Commercial sensor elements to carry out linear polarization resistance (LPR) measurements.

Advantages of LPR Measurements

- Rapid measurement of the corrosivity
- Sensitive to any process changes, flow, pressure, temperature…etc.

Disadvantages of LPR Measurements

- General corrosion rates indicative of trend rather than absolute
- Need continuous water phase (both spatially and time)
- Probes susceptible to fouling by either deposits or partial wetting by hydrocarbon phase

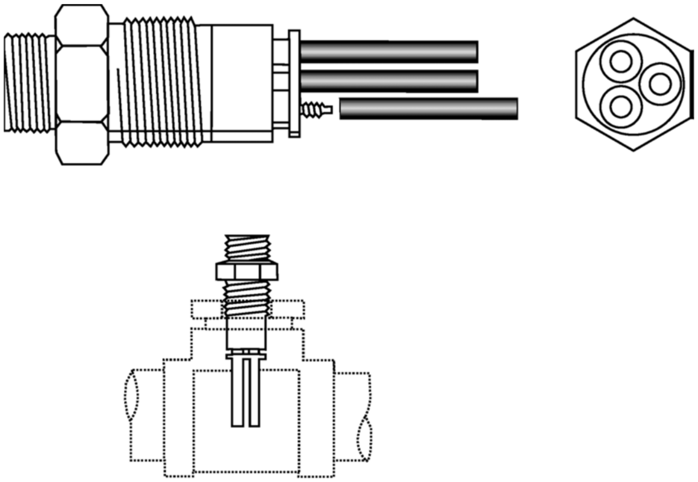


Fig. 8-12. Typical linear polarization resistance probe (*top*) and probe in pipe tee.

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy has been recently applied to field corrosion monitoring. In this technique, the response of the sample to an applied low voltage alternating current signal is measured. By measuring the sample response to signal of different frequencies, many corrosion effects can be determined, including corrosion rate, corrosion mechanisms, and film formation.

Electrochemical noise

Electrochemical noise monitoring is essentially the monitoring of the potential of a sample for small variations, or the monitoring of the variations of the corrosion current between two identical coupons. As corrosion occurs, these variations increase. This technique is particularly sensitive to localized corrosion, such as pitting. If stressed specimens are used, the techniques is also very sensitive to environmental cracking.

8.1.5 Water Chemistry

For water or process streams, chemistry s also determined to detect changes in environment that may affect corrosion. This test is performed on a periodic basis by collection and laboratory analysis of samples, or may be continuous through the use of measurements probes, such as pH electrodes or oxygen probes. Analysis for pH, oxygen content, carbon dioxide content, inhibitor concentration and metal ions in solution are frequently performed. Metal ion content can be used to measure the amount of metal loss within the system and can give an indication of the overall corrosion performance of the various metals in the system, but it cannot determine where the corrosion is occurring or the form of attack.

8.1.6 Deposits

Analysis of deposits can also be used to evaluate corrosion within the system. By determining the chemical makeup of corrosion of corrosion deposits, significant information regarding cause of the corrosion can be obtained.

8.1.7 Suspended Solids

Suspended solids can be evaluated for chemical composition. They may be corrosion products or precipitates from reactions within the system, or thermally deposited scales. The amount of suspended corrosion product can be used to determine the amount of metal being corroded in the system.

8.1.8 Scale

Scale and corrosion products may remain in place within the system and can be removed and analyzed to determine their chemical makeup. The chemical composition of corrosion product scales, as well as their adherence, thickness, and continuity, can be useful in determining corrosion performance and the cause of corrosion failures.

8.1.9 Microbiological Fouling

Microbiological activity can have a significant affect on the corrosion, as well as on other system functions, such as heat transfer. The presence of microorganisms within the system may be monitored by sampling the process stream, by inspection of surface within the system, or by analysis of coupons. Microorganisms can be detected by measuring the loss of nutrient materials from the process stream or by measurements of the buildup from by-products of the microorganisms in the process stream. By-products of microorganisms include hydrogen sulfide, which can be very corrosive.

8.1.10 Cathodic Protection Monitoring

Cathodic protection intervenes in the corrosion process. To stop corrosion, this intervention must be at the proper level and must be continuous. The cathodic protection system is measures periodically to determine the level of protection that is being achieved and to ensure that the protection is as continuous as possible. It is also important to keep good record of these inspections. In some cases, these records are required for regulatory compliances. In any case, they are useful in trouble-shootings problems in the system, as trends within the system are often characteristics of certain types of problems within it. Measurements performed during routine monitoring of cathodic protection systems will be discussed.

Measurements Methods

Structure-to-Electrolyte Potentials

Structure-to-electrolyte potentials are frequently called pipe-to-soil potentials because the technology of cathodic protection was initially developed to protect underground piping systems. The term structure-to-soil potential is more generally applied. Strictly speaking, the potential measured is a structure-to-reference electrode potential.

In measuring structure-to-electrolyte potentials, an electrical connection must be made to the structure being measured. This connection can be through a connection made during the installation of the system and brought to the surface at a test station, or at a point where a portion of the system comes to the surface, such as a service riser. In some cases, metal rods are pushed through the soil to make contact with structure, but this practice is not recommended because of the potential for damage to the structure and coatings.

Connection to the electrolyte (liquid or soil) is made using a reference electrode. The portion of the structure being measured depends on the placement of the reference electrode and not the point of electrical connection with the structure. It is very important that the reference electrode to be placed in the proper location when making structure-to-electrolyte measurements. In general, the proper location is directly over or adjacent to the portion of the structure where potential is being measured; however, the proper location may vary for different systems. The proper location for placement of the reference electrode should be given in the maintenance plan for the system. In some cases, special soil-contact tests are included in the installation.

A voltmeter is used to measure the potential between the reference electrode and the structure. The voltmeter should have a high-input impedance to minimize the current drawn in the measurements circuit.

Criteria

NACE Standard RP0169 gives criteria for the interpretation of structure-to-electrolyte potentials in the cathodic protection of underground or submerged metallic piping systems. Similar criteria are available for other types of systems, such as the interiors of water storage tanks and the external surface of buried storage tanks.

Criteria is defined as a standard for assessment of the effect degree of the cathodic protection system by measuring the potential between the pipeline, and earth to assure weather adequate protection on a buried structure have been attained or not.

Some important definitions:-

- On potential is referred to as an on potential if the measurement is made with the cathodic protection (CP) system energized.

- Off or instant off potential estimates the polarized potential when the measurement is made within one second after interrupting the current output from all CP current sources.
- Polarization or cathodic polarization is defined as the difference between the native potential, and the off potential.
- (IR drop) Difference in potential between on-potential, and off-potential is the error potential created by current flowing through a portion of the resistance.

Steel and Cast Iron

For steel and cast iron piping, The most widely used standard criteria for determining protection:-

1) -850 mv with CP applied criterion.

- The full criterion states that adequate protection is achieved with negative potential of at least 850 mv which with the CP applied(on-potential).
- This potential is measured with respect to $Cu/CuSO_4$ reference electrode (CSE) contacting the electrolyte directly over the structure, to minimize the voltage drop errors in the measurement.
- In case of presence of soil bacteria, or hot pipelines, the potential criteria is adjusted to be -950 mv (CSE).

2) Polarized potential of -850 mv criterion.

- This criterion states that adequate protection is achieved with a negative polarized potential (off-potential) of at least 850 mv relative to CSE.
- Polarized potential is defined as the potential across the structure/electrolyte interface which is measured directly after interruption of all cp current sources (off potential).

3) 100 mv of polarization criterion.

- This criterion states that adequate protection is achieved when the
  Off-potential is a minimum of 100 mv more negative than the native potential(static unprotected potential) relative to CSE.
- This criterion is determined by detecting the native potential of the underground structure at all test location before applying the CP system, then energize CP system, give sufficient time for polarization, finally measure the
  off-potential, and compare it with the native results, if the difference exceeds 100 mv, then the 100 mv criterion has been satisfied.

4) 300 mv potential shift criterion.

- This criterion states that adequate protection is achieved when the
  On-potential is a minimum of 300 mv more negative than the native potential(static unprotected potential) relative to CSE.
- This criterion is determined by detecting the native potential of the underground structure at all test location before applying the CP system, then energize CP system, give sufficient time for polarization, finally measure the on-potential, and compare it with the native results, if the difference exceeds 300 mv, then the 300 mv criterion has been satisfied

Aluminum

For aluminum, the 100 –mV cathodic polarization criteria is the only one that is used. When cathodically protecting aluminum, atmospheric effects are important. Potentials on aluminum structures should never be more negative than -1200 mV. In addition, aluminum cannot be effectively protected at any potential level in alkaline environments where the pH is greater than 8.0

Copper

For copper, the 100 mV cathodic polarization is used.

Dissimilar-Metal Couples

For systems constructed using more than one metal, the criterion for the most anodic material applies to the system.

Chapter 9

Cathodic Protection

9.1 Introduction

The basic principle of cathodic protection (CP) is a simple one.

Through the application of a cathodic current onto a protected structure, anodic dissolution is minimized. Cathodic protection is often applied to coated structures, with the coating providing the primary form of corrosion protection. The CP current requirements tend to be excessive for uncoated systems. The first application of CP dates back to 1824, long before its theoretical foundation was established. This chapter deals mainly with CP related to buried pipelines, an important application field. Other common CP installations include buried tanks, marine structures such as offshore platforms, and reinforcing steel in concrete.

9.1.1 Theoretical basis

The CP principle is illustrated in Fig. 9.1 for a buried pipeline, with the electrons supplied to the pipeline by using a dc source and an ancillary anode. In the case of a coated pipeline, it should be noted that current (using the conventional direction) is flowing to the areas as the coating is defective. The nonuniform current flux arising from the particular geometry in Fig. 9.1 is also noteworthy. Furthermore, it should be noted that an electron current flows along the electric cables connecting the anode to the cathode, and ionic current flows in the soil between the anode and cathode to complete the circuit.

An Evans diagram can provide the theoretical basis of CP. Such a diagram is shown schematically in Fig. 9.2, with the anodic metal dissolution reaction under activation control and the cathodic reaction diffusion limited at higher density. As the applied cathodic current density is stepped up, the potential of the metal decreases, and the anodic dissolution rate is reduced accordingly. Considering the logarithmic current scale, for each increment that the potential of the metal is reduced, the current requirements tend to increase exponentially. In anaerobic, acidic environments the hydrogen evolution reaction tends to occur at the cathodically protected structure, whereas oxygen reduction is a likely cathodic reaction in aerated, near-neutral environments:

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(anaerobic, acidic environments)}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{(near-neutral environments)}$$

The production of hydroxide ions, leading to alkaline surface conditions, should be noted in the oxygen reduction reaction. Pourbaix diagrams are useful to determine the possible cathodic reactions as a function of the potential of the cathodically polarized structure.

Combinations of different thermodynamically stable reactions can occur in practice. The balancing anode reactions depend on the material of the anode and the environment. The following are examples of reactions at the anodes of a CP system:

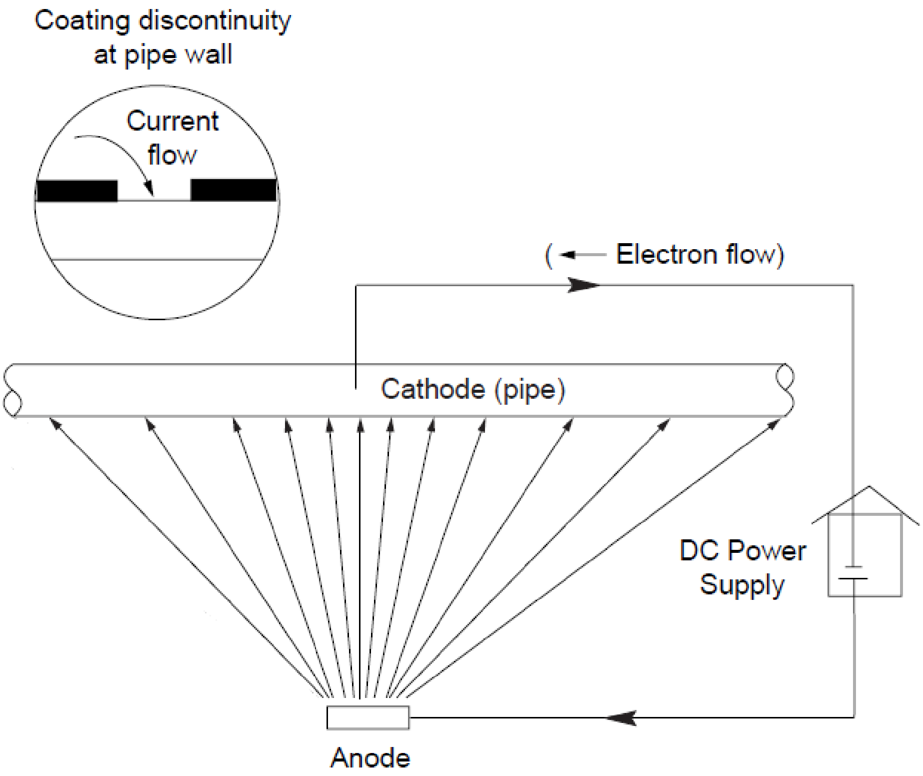


Figure. 9.1. Current flow and distribution in cathodic protection of a pipeline (schematic). Note the current flow for a coated pipeline at a coating discontinuity.

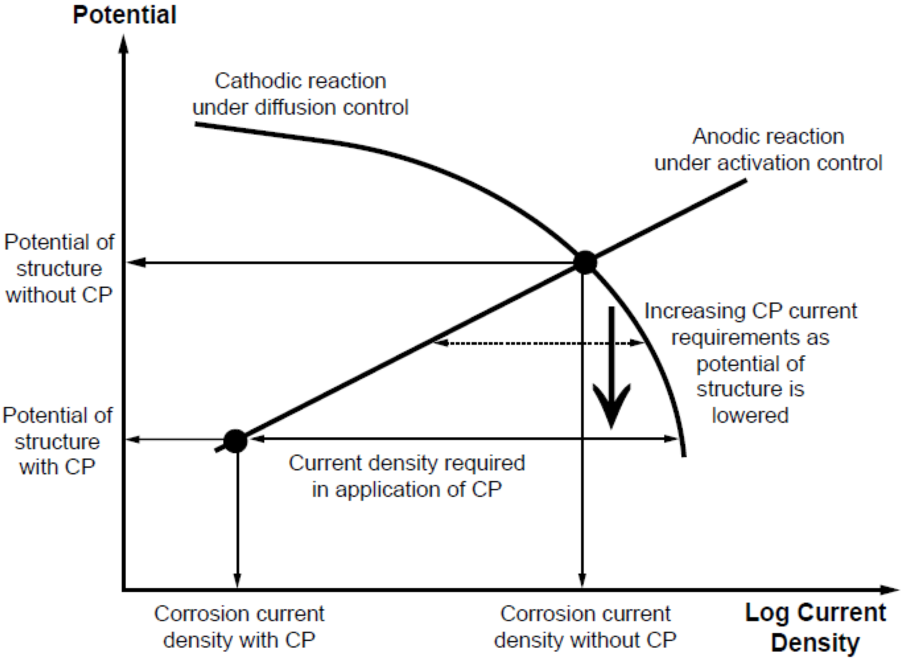


Figure. 9.2. Evans diagram illustrating the increasing CP current requirements as the potential of the structure is lowered to reduce the anodic dissolution rate.

$$M \rightarrow M^{n+} + ne^- \qquad \text{(for a consumable anode)}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{(inert anode)}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(inert anode in brackish environment)}$$

9.1.2 Protection criteria

In practical terms, a decision has to be made concerning the level of cathodic protection current that is applied. Too little current will lead to excessive corrosion damage, whereas excessive current (or “overprotection”) can lead to disbonding of coatings and hydrogen embrittlement.

Furthermore, corroding structures do not have uniform corrosion potentials or protection requirements over their entire surface.

Practical protection criteria need to take such variations into account. The following is a list of protection criteria that have been proposed for buried steel structures:

_ Potential of structure $\leq$ -850 mV w.r.t. saturated Cu/CuSO4 reference electrode (under aerobic conditions)

_ Potential of structure $\leq$ -950 mV w.r.t. saturated Cu/CuSO4 reference electrode (under anaerobic conditions where microbial corrosion may be a factor)

_ Negative potential shift of $\geq$ 300 mV when current is applied

_ Positive potential shift of $\geq$ 100 mV when the current is interrupted

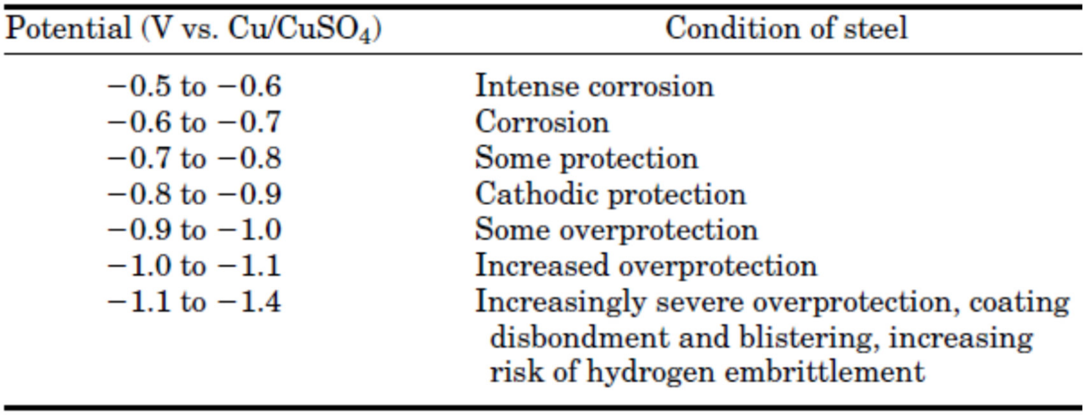
The first criterion is probably the best known and widely used in industry due to its ease of application. Using the Nernst equation and a ferrous ion concentration of 10^{-6} *M* (a criterion commonly used to define negligible corrosion in thermodynamics), a potential for steel of -930 mV w.r.t. Cu/CuSO4 can be derived, which is somewhat more negative than this criterion. The satisfactory performance under the less stringent potential requirement may be related to the formation of protective ferrous hydroxide on the surface. Strictly speaking, potential protection criteria are based on the potential of the structure at the soil interface.

Actual measurements performed by placing the reference electrode some distance away from the structure usually have to be corrected.

The potential shift criteria require measurements with the CP system in the ON and OFF conditions. Ohmic drop errors (see section below) can invalidate the 300-mV shift criterion. The 100-mV shift criterion may be useful for preventing overprotection. Table 11.1, provides further information on desirable and undesirable potential ranges for buried steel.

The harmful effects of overprotection are included in this table.

Different protection criteria are required for different material environment combinations. Other construction materials commonly used in buried applications, such as copper, aluminum, and lead, have different potential criteria than those given for steel above. Table 11.2 provides a comprehensive listing of cathodic protection criteria for different materials and environments. It should be noted that excessively negative potentials can be damaging to materials such as lead and aluminum and their alloys, due to the formation of alkaline species at the cathode.



Potential (V vs. Cu/CuSO$_4$)	Condition of steel
−0.5 to −0.6	Intense corrosion
−0.6 to −0.7	Corrosion
−0.7 to −0.8	Some protection
−0.8 to −0.9	Cathodic protection
−0.9 to −1.0	Some overprotection
−1.0 to −1.1	Increased overprotection
−1.1 to −1.4	Increasingly severe overprotection, coating disbondment and blistering, increasing risk of hydrogen embrittlement

TABLE 9.1 Relationship between Potential and Corrosion Risk for Buried Steel

Material	CP criteria	Standard/reference
Buried steel and cast iron (not applicable to	_850 mV vs. Cu/CuSO4	NACE Standard RP0169-83

applications in concrete)	Minimum negative 300-mV shift under application of CP	NACE Standard RP0169-83
	Minimum positive 100-mV shift when depolarizing (after CP current	NACE Standard RP0169-83
	_850 mV vs. Cu/CuSO4 in aerobic environment	British Standard CP 1021:1973
	_950 mV vs. Cu/CuSO4 in anaerobic environment	British Standard CP 1021:1973
Steel (offshore pipelines)	_850 mV vs. Cu/CuSO4	NACE Standard RP0675-75
	Minimum negative 300-mV shift under application of CP	NACE Standard RP0675-75
	Minimum positive 100-mV shift when depolarizing (after CP current switched off)	NACE Standard RP0675-75
Dissimilar metals	Protection potential of most reactive (anodic) material should be reached	NACE Standard RP0169-83

TABLE 9.2 Cathodic Protection Criteria for Different iron and steel.

9.1.3 Measuring potentials for protection criteria

Strictly speaking, the potential protection criteria outlined above refer to the structure-to-soil potential. However, in practice, it is clearly difficult to measure this potential of, say, a buried pipeline. In principle, a reference would have to be placed in the soil surrounding the pipeline, at an “infinitely” small distance away from the pipeline surface.

When a reference electrode is placed at ground level to measure the potential of the cathodically protected pipeline, this measurement will contain two components: (1) the pipe-to-soil potential and (2) theso-called IR drop (Fig. 9.3). The IR drop error arises from the fact that current is flowing through the soil and that the soil between the pipeline and the reference electrode has a certain electrical resistance.

Unfortunately, when a surface potential reading is made, the IR drop error will tend to give a false sense of security. In the presence of the IR drop, the pipeline potential will actually appear to be more negative than the true pipe-to-soil potential. It is thus hardly surprising that regulatory authorities are increasingly demanding that corrections for the IR drop error be made in assessments of buried structures.

To minimize this fundamental error, it has become customary to conduct so-called instant OFF potential readings, mainly in the case of impressed current cathodic protection systems. On the practical level, in systems involving numerous buried sacrificial anodes such readings are usually not possible. In this approach, the impressed CP current is interrupted briefly to theoretically provide a “true” pipe-to-soil potential reading. This momentary interruption of current theoretically produces a reading free from undesirable IR drop effects. The theoretical basis for this methodology is illustrated in Fig. 9.4. In practice, a so-called waveform analysis has to be performed to establish a suitable time interval following the current interruption for defining the OFF potential. As shown in Fig. 9.4, transient potential spikes tend to occur in the transition from the ON to the OFF potential, which should be avoided in establishing the OFF potential. There is thus no incentive to determine the OFF potential as soon as possible after interrupting the current; rather time should be allowed for the spike(s) to dissipate. The total duration of the OFF cycle is only of the order of 1 s or even shorter.

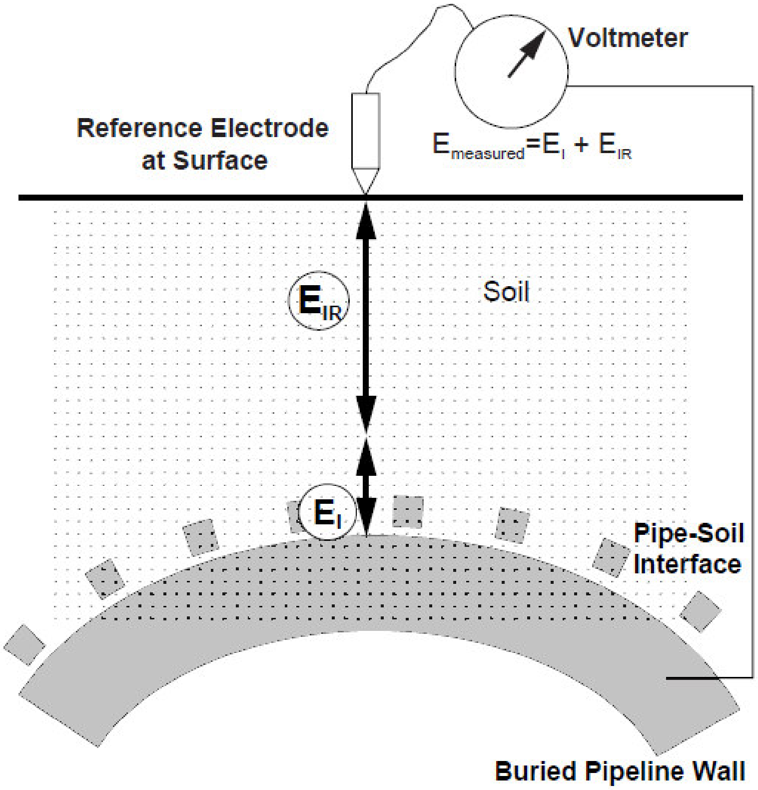


Figure 9.3 Schematic illustration of the IR drop error introduced during pipeline potential measurements at ground level. (*E*IR _ IR drop potential and *E*I _ pipe-to-soil potential.)

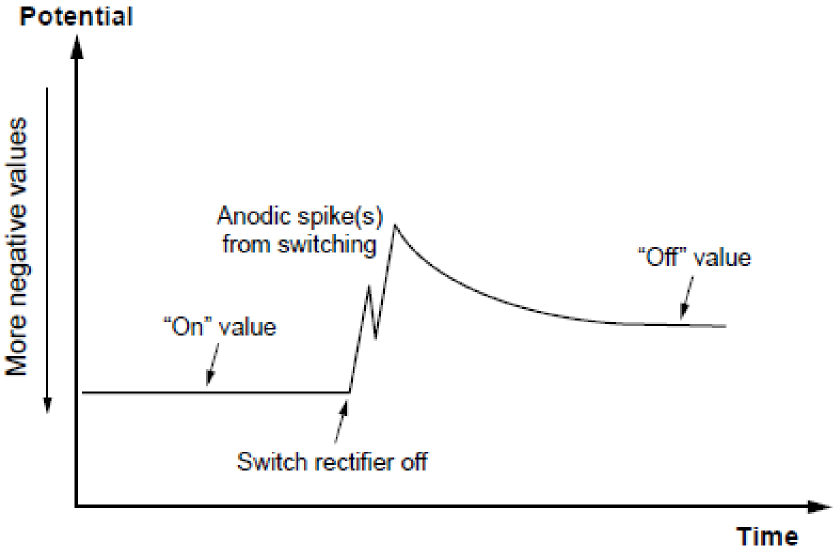


Figure 9.4 Measurement of instant-OFF potentials, by interrupting the CP current supply (schematic).

9.2 Sacrificial Anode CP Systems

Cathodic protection can be applied by connecting sacrificial anodes to a structure. Basically, the principle is to create a galvanic cell, with the anode representing the less noble material that is consumed in the galvanic interaction (Fig. 9.5). Ideally, the structure will be protected as a result of the galvanic current flow. In practical

applications a number of anodes usually have to be attached to a structure to ensure overall protection levels. The following advantages are associated with sacrificial anode CP systems:
_ No external power sources required.
_ Ease of installation (and relatively low installation costs).
_ Unlikely cathodic interference in other structures.
_ Low-maintenance systems (assuming low current demand).
_ System is essentially self-regulating.
_ Relatively low risk of overprotection.
_ Relatively uniform potential distributions.

Unfortunately, these relatively simple systems also have some limitations such as
_ Limited current and power output.
_ High-resistivity environments or large structures may require excessive number of electrodes. Maximum resistivity of 6000 to 10,000
__cm is generally regarded as the limit, depending on coating quality.
_ Anodes may have to be replaced frequently under high current demand.
_ Anodes can increase structural weight if directly attached to a structure.
Typical applications include buried tanks, underground pipelines, buried communication and power cables, water and gas distribution systems, internal protection of heat exchangers and hot water tanks, ships, and marine structures.

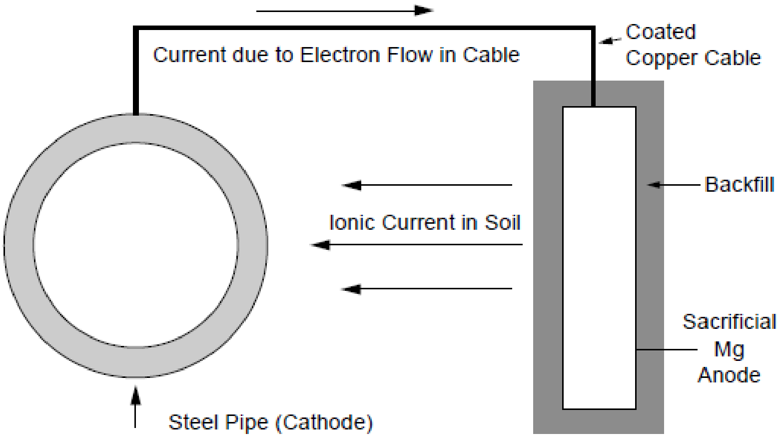


Figure 9.5 Principle of cathodic protection with sacrificial anodes (schematic).

9.2.1 Anode requirements

The anode material must provide a certain driving voltage to generate sufficient current to adequately protect a structure. The driving voltage is defined as the difference in between the operating voltage of the anode and the potential of the polarized structure it is protecting. A fundamental requirement is for the anode to have a stable operating potential over a range of current outputs. This means that the operating potential should lie very close to the free corrosion potential and that the corrosion potential remains essentially unaffected by current flow. With such characteristics, it is said that sacrificial anode systems are self-regulating in terms of potential. Furthermore, over its lifetime, an anode must consistently have a high capacity to deliver electric current per unit mass of material consumed. The capacity is defined as the total charge (in coulombs) delivered by the dissolution of a unit mass of the anode material.
The theoretical capacity can be determined from Faraday's law, and the anode efficiency obtained in practice can be defined as

$$\text{Efficiency} = \frac{\text{actual capacity}}{\text{theoretical capacity}} \times 100\%$$

Ideally an anode will corrode uniformly and approach its theoretical efficiency. Passivation of an anode is obviously undesirable. Ease of manufacturing in bulk quantities and adequate mechanical properties are also important.

9.2.2 Anode materials and performance characteristics

For land-based CP applications of structural steel, anodes based on zinc or magnesium are the most important. Zinc anodes employed underground are high-purity Zn alloys, as specified in ASTM B418-95a. Only the Type II anodes in this standard are applicable to buried soil applications.

The magnesium alloys are also high-purity grades and have the advantage of a higher driving voltage. The low driving voltage of zinc electrodes makes them unsuitable for highly resistive soil conditions.

The R892-91 guidelines of the Steel Tank Institute give the following driving voltages, assuming a structure potential of -850 mV versus CSE:

High potential magnesium. - 0.95 V

High-purity zinc: - 0.25 V

Magnesium anodes generally have a low efficiency at 50 percent or even lower. The theoretical capacity is around 2200 Ah/kg. For zinc anodes, the mass-based theoretical capacity is relatively low at 780 Ah/kg, but efficiencies are high at around 90 percent.

Anodes for industrial use are usually conveniently packaged in bags prefilled with suitable backfill material. This material is important because it is designed to maintain low resistivity (once wetted) and a steady anode potential and also to minimize localized corrosion on the anode.

The current output from an anode can be estimated from Dwight's equation (applicable to relatively long and widely spaced anodes) as follows:

$$i = \frac{2\pi EL}{\rho \ln (8L/D - 1)}$$

Where

i = current output (A)

E = driving voltage of the anode (V)

L = anode length (cm)

ρ = soil resistivity (Ωcm)

D = anode diameter (cm)

The life expectancy of an anode is inversely proportional to the current flowing and can be estimated with the following expression:

$$\text{Lifetime} = \frac{KUeW}{i}$$

Where

Lifetime = anode life (years)

K = anode consumption factor (0.093 for Zn, 0.253 for Mg)

U = utilization factor, a measure of the allowable anode consumption before it is rendered ineffective (typically 0.85)

W = mass of the anode (kg)

e = efficiency of the anode (0.9 for Zn, 0.5 for Mg)

i = current output (A)

9.2.3 System design and installation

The design of CP systems lies in the domain of experienced specialists.

Only the basic steps involved in designing a sacrificial anode system are outlined. Prior to any detailed design work a number of fundamental factors such as the protection criteria, the type and integrity of the coating system, the risk of stray current corrosion, and the presence of neighboring structures that could be affected by the CP system have to be defined.

9.2.3.1 Buried structures in soils.

For structures buried in soil, such as pipelines, the first step in detailed design is usually to determine the resistivity of the soil (or other electrolyte). This variable is essential for determining the anodes' current output and is also a general measure of the environmental corrosiveness. The resistivity essentially represents the electrical resistance of a standardized cube of material.

Certain measurement devices thus rely on measuring the resistance of a soil sample placed in a standard box or tube. A common way to make in situ measurement is by the so-called Wenner four-pin method. In this method, four equally spaced pins are driven into the ground along a straight line. The resistivity is derived from an induced current between the outer pin pair and the potential difference established between the inner pair. An additional type of resistivity measurement is based on electromagnetic inductive methods using a transmitter and pickup coils.

The second design step addresses electrical continuity and the use of insulating flanges. These parameters will essentially define the structural area of influence of the CP system. To ensure protection over different structural sections that are joined mechanically, electrical bonding is required. In complex structures, insulated flanges can restrict the spread of the CP influence.

In the third step the total current requirements are estimated. For existing systems, the current that has to be applied to achieve a certain potential distribution can be measured, but this is not possible for new systems. For the latter case, current requirements have to be determined based on experience, with two important variables standing out: First, the type of environment has to be considered for specifying an adequate level of current density. For example, a soil contaminated with active sulfate-reducing bacteria, leading to microbial corrosion effects, typically requires a higher current density for protection. The second important variable is the surface area that requires protection. The total current requirements obviously decrease with increasing quality of the surface coating. Field-coated structures usually have higher current requirements compared with factory-coated structures. The effective exposed area of coated structures used for design purposes should take coating deterioration with time into account.

Following the above, a suitable anode material can be selected, together with the number of anodes and anode size for a suitable output and life combination. The anode spacing also has to be established to obtain a suitable current distribution over the entire structure.

Provision also has to be made for test stations to facilitate basic performance monitoring of the CP system. There are two basic types of test station. In one type, a connection to the pipe by means of a shielded lead wire is provided at the surface. Such a connection is useful for monitoring the potential of the pipeline relative to a reference electrode.

The reference electrode may be a permanent installation. The second type provides surface access to the anode-structure connection.

The current flowing from the anode to the structure can thereby be conveniently monitored at the surface.

In urban centers test stations are usually recessed into the ground with their covers flush with the pavement. In outlying rural areas test stations tend to be above ground in the form of test posts. It is important to record the location of each test station. In urban areas a locating system based on street names and position relative to lot lines is commonly used. Locations relative to landmarks can be used in rural situations. A more recent option is the Global Positioning System (GPS) for finding test stations in the field. The relevant GPS coordinates obviously have to be recorded initially, before GPS positioning units can be used for locating test stations. Affordable handheld GPS systems are now readily available for locating rural test stations with reasonable accuracy.

Professional installation procedures are a key requirement for ensuring adequate performance of sacrificial anode CP systems.

Following successful design and installation, the system is essentially self-regulating. Although the operating principles are relatively simple, attention to detail is required, for example, in establishing wire connections to the structure. The R892-91 guidelines of the Steel Tank Institute highlight the importance of an installation information package that should be made available to the system installer. The following are key information elements:

_ A site plan drawn to scale, identifying the size, quantity, and location of anodes, location and types of test stations, layout of piping and foundations
_ Detailed material specifications related to the anodes, test stations, and coatings, including materials for coating application in the field
_ Site-specific installation instructions and/or manufacturer's recommended installation procedures
_ Inspection and quality control procedures for the installation phase

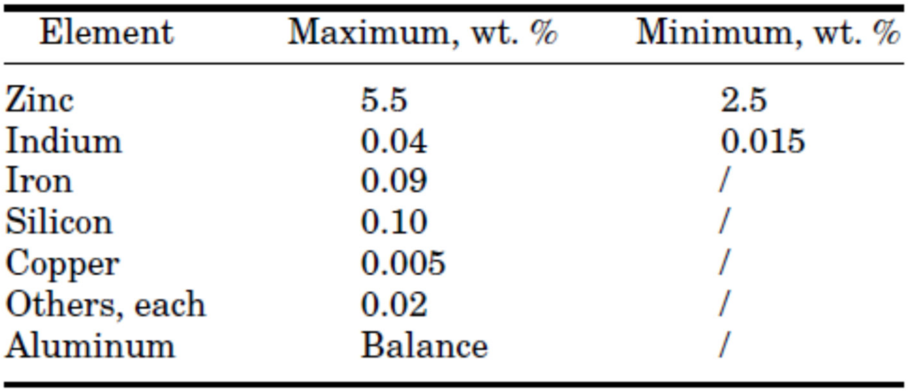
9.2.3.2 Submerged marine structures.

Cathodic protection of submerged marine structures such as steel jackets of offshore oil and gas platforms and pipelines is widely provided by sacrificial anode systems. A commonly used protection criterion for such steel structures is -800 mV relative to a silver/silver chloride-reference electrode. In offshore applications, impressed current systems are more vulnerable to mechanical wear and tear of cabling and anodes. Compared to soils, seawater has a low resistivity, and the low driving voltages of sacrificial anodes are thus of lower concern in the sea. The sacrificial anodes in offshore applications are usually based on aluminum or zinc. The chemical composition of an aluminum alloy specified for protecting an offshore gas pipeline is presented in Table 9.3. Close control over impurity elements is crucial to ensure satisfactory electrochemical behavior. Sydberger, Edwards, and Tiller 4 have presented an excellent overview of designing sacrificial anode systems for submerged marine structures, using a conservative approach. A brief summary of this publication follows.

One of the main benefits of adequate design and a conservative design approach is that future monitoring and maintenance requirements will be minimal. Correct design also ensures that the system will essentially be self-regulating. The anodes will "automatically" provide increased current output if the structure potential shifts to more positive values, thereby counteracting this potential drift. Furthermore, a conservative design approach will avoid future costly retrofits. Offshore in situ anode retrofitting tends to be extremely costly and will tend to exceed the initial "savings." Such a design approach has also proven extremely valuable for requalification of pipelines, well beyond their original design life. A conservative design approach is sensible when considering that the cost of CP systems may only be of the order of 0.5 to 1% of the total fabrication and installation costs.

The two main steps involved in the design calculations are (1) calculation of the average current demand and the total anode net mass required to protect the structure over the design life and (2) the initial and final current demands required to polarize the structure to the required potential protection criterion. The first step is associated with the anticipated current density once steady-state conditions have been reached. The second step is related to the number and size of individual anodes required under dynamic, unsteady conditions.

The cathodic current density is a complex function of various seawater parameters, for which no "complete" model is available. For design purposes, four climatic zones based on average water temperature and two depth ranges have therefore been defined: tropical, subtropical, temperate, and arctic. For example, in colder waters current densities tend to be higher due to a lower degree of surface protection from calcareous layers. One major design uncertainty is the quality (surface coverage) of the coating. In subsea pipelines, the coating is regarded as the primary corrosion protection measure, with CP merely as a back-up system.



Element	Maximum, wt. %	Minimum, wt. %
Zinc	5.5	2.5
Indium	0.04	0.015
Iron	0.09	/
Silicon	0.10	/
Copper	0.005	/
Others, each	0.02	/
Aluminum	Balance	/

TABLE 9.3 Chemical Composition of Anode Material for an Offshore Pipeline

For design purposes, not only do initial defects in the coating have to be considered but also its degradation over time.

In general, because of design uncertainties and simplifications, a conservative design approach is advisable. This policy is normally followed through judicious selection of design parameters rather than using an overall safety factor. Marginal designs will rarely result in underprotection early in the structure's life; rather the overall life of the CP system will be compromised. Essentially, the anode consumption rates will be excessive in underdesigned systems. Further details may be found in design guides such as NACE RP0176-94 and Det Norske Veritas (DNV) Practice RP B401.

9.3 Impressed Current Systems

In impressed current systems cathodic protection is applied by means of an external power current source (Fig. 9.6). In contrast to the sacrificial anode systems, the anode consumption rate is usually much lower. Unless a consumable "scrap" anode is used, a negligible anode consumption rate is actually a key requirement for long system life. Impressed current systems typically are favored under high-current requirements and/or high-resistance electrolytes. The following advantages can be cited for impressed current systems:

_ High current and power output range
_ Ability to adjust ("tune") the protection levels
_ Large areas of protection
_ Low number of anodes, even in high-resistivity environments
_ May even protect poorly coated structures

The limitations that have been identified for impressed current CP systems are
_ Relatively high risk of causing interference effects.
_ Lower reliability and higher maintenance requirements.
_ External power has to be supplied.
_ Higher risk of overprotection damage.
_ Risk of incorrect polarity connections (this has happened on occasion with much embarrassment to the parties concerned).
_ Running cost of external power consumption.
_ More complex and less robust than sacrificial anode systems in certain applications.

The external current supply is usually derived from a transformer-rectifier (TR), in which the ac power supply is transformed (down) and rectified to give a dc output. Typically, the output current from such units does not have pure dc characteristics; rather considerable "ripple" is inevitable with only half-wave rectification at the extreme end of the spectrum. Other power sources include fuel- or gas-driven generators, thermoelectric generators, and solar and wind generators.

Important application areas of impressed current systems include pipelines and other buried structures, marine structures, and reinforcing steel embedded in concrete.

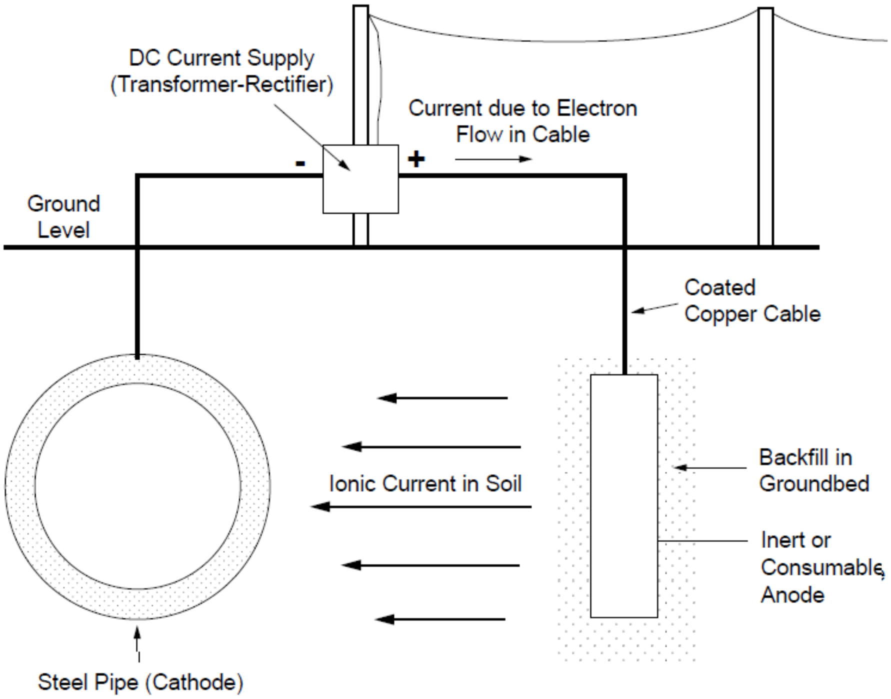


Figure 9.6 Principle of cathodic protection with impressed current (schematic).

9.3.1 Impressed current anodes

Impressed current anodes do not have to be less noble than the structure that they are protecting. Although scrap steel is occasionally used as anode material, these anodes are typically made from highly corrosion-resistant material to limit their consumption rate. After all, under conditions of anodic polarization, very high dissolution rates can potentially be encountered. Anode consumption rates depend on the level of the applied current density and also on the operating environment (electrolyte). For example, the dissolution rate of platinized titanium anodes is significantly higher when buried in soil compared with their use in seawater. Certain contaminants in seawater may increase the consumption rate of platinized anodes. The relationship between discharge current and anode consumption rate is not of the simple linear variety; the consumption rate can increase by a higher percentage for a certain percentage increase in current.

Under these complex relationships, experience is crucial for selecting suitable materials. For actively corroding (consumable) materials approximate consumption rates are of the order of grams per amperehour (Ah), whereas for fully passive (nonconsumable) materials the corresponding consumption is on the scale of micrograms. The consumption rates for partly passive (semiconsumable) anode materials lie somewhere in between these extremes.

The type of anode material has an important effect on the reactions encountered on the anode surface. For consumable metals and alloys such as scrap steel or cast iron, the primary anodic reaction is the anodic metal dissolution reaction. On completely passive anode surfaces, metal dissolution is negligible, and the main reactions are the evolution of gases. Oxygen can be evolved in the presence of water, whereas chlorine gas can be formed if chloride ions are dissolved in the electrolyte. The reactions have already been listed in the theory section of this chapter. The above gas evolution reactions also apply to nonmetallic conducting anodes such as carbon. Carbon dioxide evolution is a further possibility for this material. On partially passive surfaces, both the metal dissolution and gas evolution reactions are important. Corrosion product buildup is obviously associated with the former reaction.

It is apparent that a wide range of materials can be considered for impressed current anodes, ranging from inexpensive scrap steel to high-cost platinum. Shreir and Hayfield identified the following desirable properties of an "ideal" impressed current anode material:

_ Low consumption rate, irrespective of environment and reaction products
_ Low polarization levels, irrespective of the different anode reactions
_ High electrical conductivity and low resistance at the anode-electrolyte interface

_ High reliability
_ High mechanical integrity to minimize mechanical damage during installation, maintenance, and service use
_ High resistance to abrasion and erosion
_ Ease of fabrication into different forms
_ Low cost, relative to the overall corrosion protection scheme

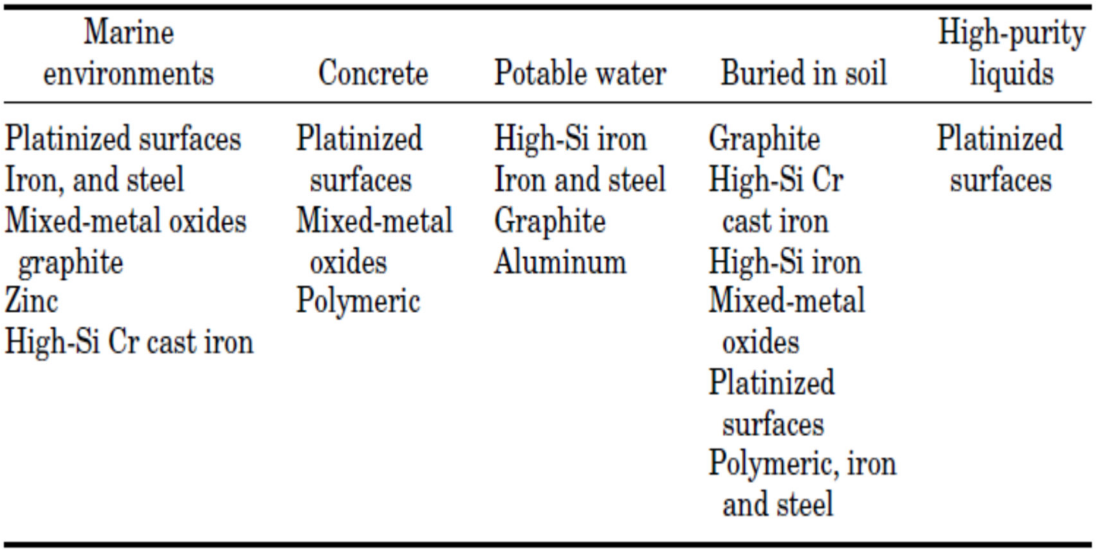
In practice, important trade-offs between performance properties and material cost obviously have to be made. Table 11.4 shows selected anode materials in general use under different environmental conditions. The materials used for impressed anodes in buried applications are described in more detail below.

9.3.2 Impressed current anodes for buried applications

The NACE International Publication 10A196 represents an excellent detailed description of impressed anode materials for buried applications. Further detailed accounts are also given by Shreir and Hayfield and Shreir, Jarman, and Burstein; only a brief summary is provided here.

Graphite anodes have largely replaced the previously employed carbon variety, with the crystalline graphite structure obtained by high temperature exposure as part of the manufacturing process that includes extrusion into the desired shape. These anodes are highly porous, and it is generally desirable to restrict the anode reactions to the outer surface to limit degradation processes. Impregnation of the graphite with wax, oil, or resins seals the porous structure as far as possible, thereby reducing consumption rates by up to 50 percent. Graphite is extremely chemically stable under conditions of chloride evolution. Oxygen evolution and the concomitant formation of carbon dioxide gas accelerate the consumption of these anodes.

Consumption rates in practice have been reported as typically between 0.1 to 1 kg A^{-1} y^{-1} and operating currents in the 2.7 to 32.4 A/m2 range. Buried graphite anodes are used in different orientations in anode beds that contain carbonaceous backfill.



Marine environments	Concrete	Potable water	Buried in soil	High-purity liquids
Platinized surfaces Iron, and steel Mixed-metal oxides graphite Zinc High-Si Cr cast iron	Platinized surfaces Mixed-metal oxides Polymeric	High-Si iron Iron and steel Graphite Aluminum	Graphite High-Si Cr cast iron High-Si iron Mixed-metal oxides Platinized surfaces Polymeric, iron and steel	Platinized surfaces

TABLE 9.4 Examples of Impressed Current Anodes Used in Different Environments

The following limitations apply to graphite anodes: Operating current densities are restricted to relatively low levels. The material is inherently brittle, with a relatively high risk of fracture during installation and operational shock loading. In nonburied applications, the settling out of disbonded anode material can lead to severe galvanic attack of metallic substrates (most relevant to closed-loop systems) and, being soft material, these anodes can be subject to erosion damage.

Platinized anodes are designed to remain completely passive and utilize a surface coating of platinum (a few micrometers thick) on titanium, niobium, and tantalum substrates for these purposes.

Restricting the use of platinum to a thin surface film has important cost advantages. For extended life, the thickness of the platinum surface layer has to be increased. The inherent corrosion resistance of the substrate materials, through the formation of protective passive films, is important in the presence of discontinuities in the platinum surface coating, which invariably arise in practice. The passive films tend to break down at a certain anodic potential, which is dependent on the corrosiveness of the operating environment. It is important that the potential of unplatinized areas on these anodes does not exceed the critical depassivation value for a given substrate material.

In chloride environments, tantalum and niobium tend to have higher breakdown potentials than titanium, and the former materials are thus preferred at high system voltages.

These anodes are fabricated in the form of wire, mesh, rods, tubes, and strips. They are usually embedded in a ground bed of carbonaceous material. The carbonaceous backfill provides a high surface area (fine particles are used) and lowers the anode/earth resistance; effective transfer of current between the platinized surfaces and the backfill are therefore important. Reported consumption rates are less than 10 mg A^{-1} y^{-1} under anodic chloride evolution and current densities up to 5400 A/m2. In oxygen evolution environments reported consumption rates are of the order of 16 mg/A-y at current densities below 110 A/m2.

In the presence of current ripple effects, platinum consumption rates are increased, particularly at relatively low frequencies.

Limitations include current attenuation in long sections of wire.

Uneven current distribution results in premature localized anode degradation, especially near the connection to a single current feed point. Multiple feed points improve the current distribution and provide system redundancy in the event of excess local anode dissolution.

Current ripple effects, especially at low frequencies, should be avoided.

The substrate materials are at risk to hydrogen damage if these anodes assume a cathodic character outside of their normal operational function (for example, if the system is de-energized).

Mixed-metal anodes also utilize titanium, niobium, and tantalum as substrate materials. A film of oxides is formed on these substrates, with protective properties similar to the passive film forming on the substrate materials. The important difference is that whereas the “natural” passive film is an effective electrical insulator, the mixed metal oxide surface film passes anodic current. The product forms are similar to those of the platinized anodes. These anodes are typically used with carbonaceous backfill. Electrode consumption is usually not the critical factor in determining anode life; rather the formation of nonconductive oxides between the substrate and the conductive surface film limits effective functioning. Excessive current densities accelerate the buildup of these insulating oxides to unacceptable levels.

Scrap steel and iron represent consumable anode material and have been used in the form of abandoned pipes, railroad or well casings, as well as any other scrap steel beams or tubes. These anodes found application particularly in the early years of impressed current CP installations. Because the dominant anode reaction is iron dissolution, gas production is restricted at the anode. The use of carbonaceous backfill assists in reducing the electrical resistance to ground associated with the buildup of corrosion products. Periodic flooding with water can also alleviate resistance problems in dry soils.

Theoretical anode consumption rates are at 9 kg A^{-1} y^{-1}. For cast iron (containing graphite) consumption rates may be lower than theoretical due to the formation of carbon-rich surface films. Full utilization of the anode is rarely achieved in practice due to preferential dissolution in certain areas. Fundamentally, these anodes are not prone to failure at a particular level of current density. For long anode lengths, multiple current feed points are recommended to ensure a reasonably even current distribution over the surface and prevent premature failure near the feed point(s).

Limitations include the buildup of corrosion products that will gradually lower the current output. Furthermore, in high-density urban areas, the use of abandoned structures as anodes can have serious consequences if these are shorted to foreign services. An abandoned gas main could, for example, appear to be a suitable anode for a new gas pipeline. However, if water mains are short circuited to the abandoned gas main in certain places, leaking water pipes will be encountered shortly afterward due to excessive anodic dissolution.

High-silicon chromium cast iron anodes rely on the formation of a protective oxide film (mainly hydrated SiO_2) for corrosion resistance.

The chromium alloying additions are made for use in chloride containing environments to reduce the risk of pitting damage. These anodes can be used with or without carbonaceous backfill; in the latter case the resistance to ground is increased (particularly under dry conditions) as are the consumption rates.

Consumption rates have been reported to typically range between 0.1 to 1 kg A^{-1} y^{-1}. The castings are relatively brittle and thus susceptible to fracture under shock loading.

Polymeric anodes are flexible wire anodes with a copper core surrounded by a polymeric material that is impregnated with carbon. The impregnated carbon is gradually consumed in the conversion to carbon dioxide, with ultimate subsequent failure by perforation of the copper strand. The anodes are typically used in combination with carbonaceous backfill, which reportedly increases their lifetime substantially.

Because these anodes are typically installed over long lengths, premature failures are possible when soil resistivity varies widely.

9.3.3 Ground beds for buried structures

From the above description, the important role played by the ground beds in which the impressed current anodes are located should already be apparent. Carbonaceous material (such as coke breeze and graphite) used as backfill increases the effective anode size and lowers the resistance to soil. It is important to realize that, with such backfill, the anodic reaction is mainly transferred to the backfill. The consumption of the actual anode material is thereby reduced. To ensure low resistivity of the backfill material, its composition, particle size distribution, and degree of compaction (tamping) need to be controlled. The latter two variables also affect the degree to which gases generated at the anode installation can escape. If it is difficult to establish desirable backfill properties consistently in the ground, prepackaged anodes and backfill inside metal canisters can be considered. Obviously these canisters will be consumed under operational conditions.

The anodes may be arranged horizontally or vertically in the ground bed. The commonly used cylindrical anode rods may be the long continuous variety or a set of parallel rods. Some advantageous features of vertical deep anode beds include lower anode bed resistance, lower risk of induced stray currents, lower right-of-way surface area required, and improved current distribution in certain geometries.

Limitations that need to be traded off include higher initial cost per unit of current output, repair difficulties, and increased risk of gas blockage.

At very high soil resistivities, a ground bed design with a continuous anode running parallel to a pipeline may be required. In such environments discrete anodes will result in a poor current distribution, and the potential profile of the pipeline will be unsatisfactory.

The pipe-to-soil potential may only reach satisfactory levels in close proximity to the anodes if discontinuous anodes are employed in highresistivity soil.

9.3.4 System design

Just as for sacrificial anode systems, design of impressed current CP systems is a matter for experienced specialists. The first three basic steps are similar to sacrificial anode designs, namely, evaluation of environmental corrosivity (soil resistivity is usually the main factor considered), determining the extent of electrical continuity in the system, and subsequently estimating the total current requirements.

One extremely useful concept to determine current requirements in existing systems is current drain testing. In these tests, a CP current is injected into the structure with a temporary dc power source. Small commercial units supplying up to 10 A of current are available for these purposes. A temporary anode ground bed is also required; grounded fixtures such as fences, fire hydrants, or street lights have been used. Potential loggers have to be installed at selected test stations to monitor the potential response to the injected current. The recorded relationship between potential and current is used to define what current level will be required to reach a certain protection criterion.

An example of results from a current drain test performed on a buried, coated steel pipeline is presented in Fig. 9.7. Once the data loggers and current-supply hardware have been installed, these tests usually only require a few minutes of time.

Following the completion of the above three steps, the anode geometry and material have to be specified, together with a ground bed design. The designer needs to consider factors such as uniformity of current distribution (see separate section below), possible interference effects (see Sec. 11.4.3), the availability of electrical power, and local bylaws and policies with respect to rectifier locations. Once the circuit layout and cabling are defined, the circuit resistance can be calculated and the rectifier can subsequently be sized in terms of current and potential output. Lastly, consideration must be given to the design of ancillary equipment for control purposes and test stations for monitoring purposes. Modern designs include provisions for remote rectifier performance monitoring and remote rectifier output adjustments.

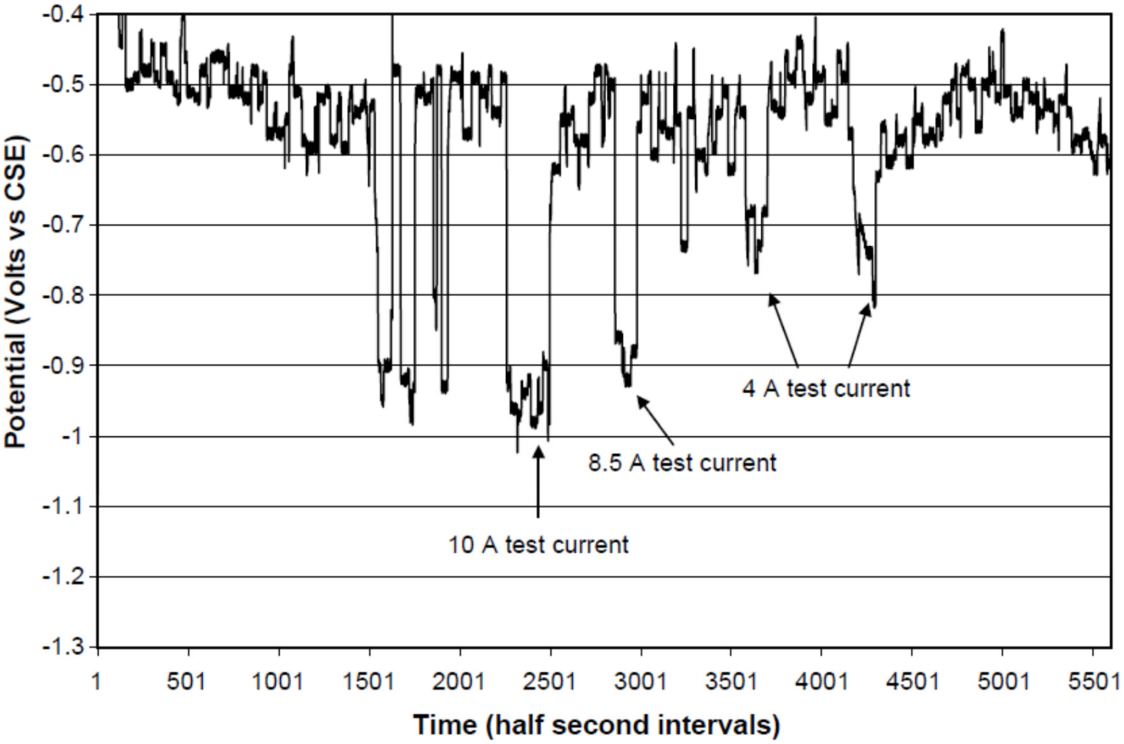


Figure 9.8 Current drain test results for a buried steel pipeline.

9.4 Current Distribution and Interference Issues

9.4.1 Corrosion damage under disbanded coatings

It has already been stated that in buried cathodically protected structures, a surface coating is in fact the primary form of corrosion protection, with CP as a secondary measure. Users of this double protection methodology are sometimes surprised to find that severe localized corrosion damage has occurred under a coating, despite the two-fold pre ventive measures. Such localized corrosion damage has been observed in both sacrificial anode and impressed current CP systems.

Importantly, it may not be possible to detect such problems in structure-to-soil potential surveys.

The phenomenon of coating disbondment plays a major role in this type of problem. The protective properties of a coating are greatly dependent on its ability to resist disbondment around defects. The protective properties of the coating are compromised when water enters the gap between the (disbonded) coating and the metallic surface. A corrosive microenvironment will tend to develop in such a situation.

Depending on the nature of this microenvironment, the CP system may not be able to protect the surface under the disbondment. Only when the trapped water has a high conductivity (e.g., saline conditions) will a protective potential be projected under the disbondment.8 In the absence of protective CP effects, the surface will corrode under the free corrosion potential of the particular microenvironment that is established.

Jack, Wilmott, and Sutherby identified three primary corrosion scenarios that could be manifested under shielded disbonded coatings on buried steel pipelines, together with secondary transformations of the primary sites (Table 9.5). A brief description follows.

Aerobic sites. Under aerobic conditions, oxygen reduction is the dominant cathodic reaction. Corrosion rates thus depend on the mass transport of oxygen to the steel surface. Under stagnant conditions, oxygen diffusion into the solution under the shielded disbondment is the rate-limiting step. The formation of surface oxides is also important for corrosion kinetics. The main corrosion products expected under aerobic conditions are iron (III) oxides/hydroxides.

Anaerobic sites. Hydrogen evolution is a prime candidate for the cathodic half-cell reaction under anaerobic conditions. Corrosion rates therefore tend to increase with decreasing pH (increasing aciditylevels). In the case of ground water saturated with calcium and carbonate, the corrosion product is mainly iron (II) carbonate, a milky white precipitate. On exposure to air this white product will revert rapidly to reddish iron (III) oxides.

Anaerobic sites with sulfate reducing bacteria (*SRB*). Highly corrosive microenvironments tend to be created under the influence of SRB; they convert sulfate to sulfide in their metabolism. Likely corrosion products are black iron (II) sulfide (in various mineral forms) and iron (II) carbonate. SRB tend to thrive under anaerobic conditions.

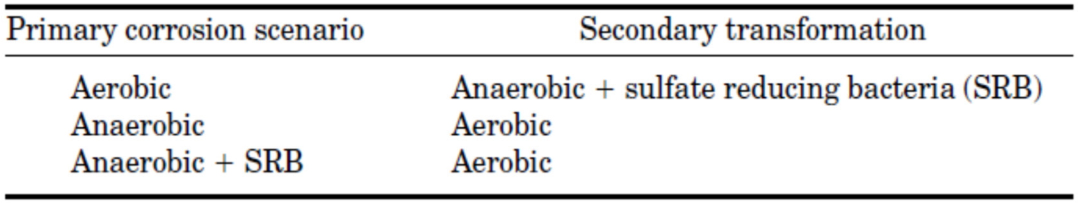
These chemical species will again tend to change if the corrosion cell is disturbed and aerated.

Secondary transformations. Changing soil conditions can lead to transformations in the primary corrosion sites. After all, soil conditions are dynamic with variations in humidity, temperature, water table levels, and so forth. For example, mixtures of iron (II) carbonate and iron (III) oxides and the relative position of these species have indicated dominant transformations from anaerobic to aerobic conditions, with the reddish products encapsulating the white species.

The transformation from anaerobic sites to aerobic sites is a drastic one, with high CP current demand and extremely high corrosion rates.

Iron (II) sulfides are oxidized to iron (III) oxides and sulfur species. In turn, sulfur is ultimately oxidized to sulfate.

The change of aerobic sites to anaerobic sites with SRB leads to reduction of Fe (III) oxides to iron sulfide species. The conversion kinetics are pH dependent. Increasingly corrosive conditions should be anticipated with the formation of sulfide species.



Primary corrosion scenario	Secondary transformation
Aerobic	Anaerobic + sulfate reducing bacteria (SRB)
Anaerobic	Aerobic
Anaerobic + SRB	Aerobic

TABLE 9.5 Primary Corrosion Scenarios and Transformations at “Disbonded” Coating Sites for Steel Pipelines Buried in Alberta Soil

9.4.2 General current distribution and attenuation

In practice, the current distribution in CP systems tends to be far removed from idealized uniform current profiles. It is the nature of electron current flow in structures and the nature of ionic current flow in the electrolyte between the anode and the structure that influence the overall current distribution. A number of important factors affect the current distribution, as outlined below.

One underlying factor is the anode-to-cathode separation distance.

In general, too close a separation distance results in a poor distribution, as depicted in Fig. 9.8. A trade-off that must be made, when increasing this distance, is the increased resistance to current flow. At excessive distances, the overall protection levels of a structure may be compromised for a given level of power supply. Additional anodes can be used to achieve a more homogeneous ionic current flow, where an optimum anode-to-cathode separation distance cannot be achieved.

Resistivity variations in the electrolyte between the anode and cathode also have a strong influence on the current distribution. Areas of low resistivity will “attract” a higher current density, with current flowing preferentially along the path of least resistance. An example of such an unfavorable situation is illustrated in Fig. 9.9. Similar problems may be encountered in deeply buried structures, when different geological formations and moisture contents are encountered with increasing depth from the surface. An indication of resistivity variations across different media is given in Table 9.6.

Another important factor for coated structures is the presence of defects in the protective coating. Not only does the size of a defect affect the current but also the position of the defect relative to the anode. Current tends to be concentrated locally at defects. A fundamental source of nonuniformly distributed CP current over structures results from an effect known as attenuation. In long structures such as pipelines the electrical resistance of the structure itself becomes significant.

The resistance of the structure causes the current to decrease nonlinearly as a function of distance from a drain point. A drain point refers to the point on the structure where its electrical connection to the anode is made.

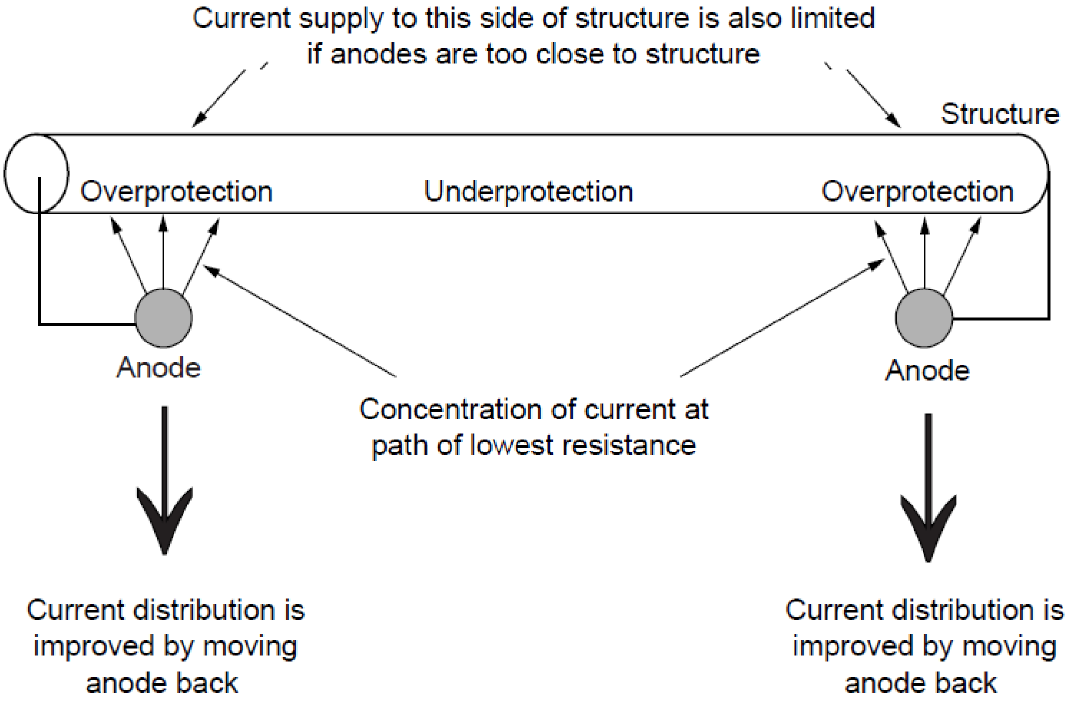


Figure 9.8 Nonuniform distribution of protective current resulting from anode positioning too close to the corroding structure (schematic).

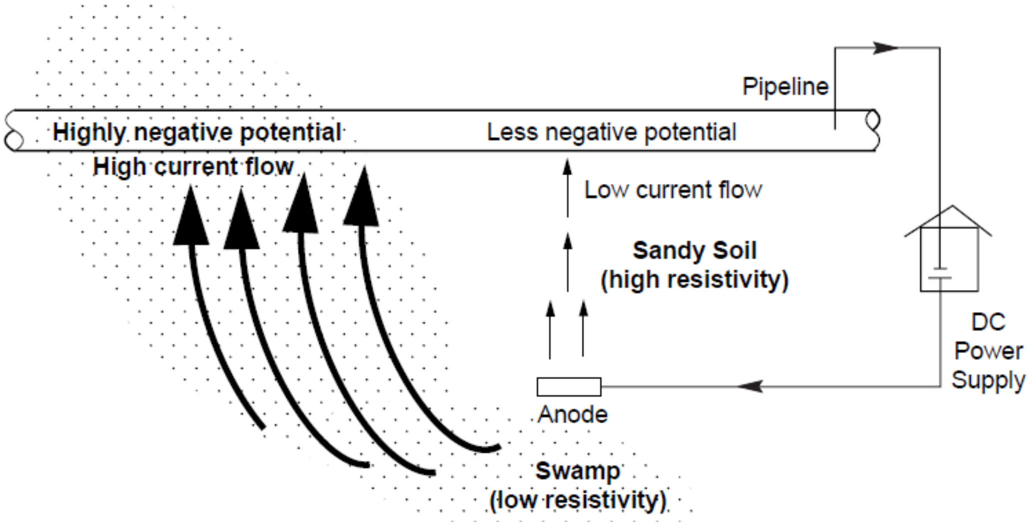


Figure 9.9 Nonuniform current distribution over a pipeline resulting from differences in the electrolyte (soil) resistivity (schematic). The main current flow will be along the path of least resistance.

Soil type	Typical resistivity, Ω·cm
Clay (salt water)	< 1000
Clay (fresh water)	< 2000
Marsh	1000–3000
Humus	1000–4000
Loam	3000–10,000
Sand	> 10,000
Limestone	> 20,000
Gravel	> 40,000

TABLE 9.6 Resistivities of Different Electrolytes

This characteristic decrease in current (and also in potential), shown in Fig. 11.11, occurs even under the following idealized conditions:
_ The anodes are sufficiently far removed from the structure.
_ The electrolyte resistivity is completely uniform between the anode(s) and the structure.
_ The coating has a high and uniform ohmic resistance.
_ A linear relationship exists between the potential of the structure and the current.
Under these idealized conditions the following attenuation equations apply

$$E_x = E_0 \exp(-\alpha x)$$

$$I_x = I_0 \exp(-\alpha x)$$

where *E*0 and *I*0 are the potential and current at the drainage point, and *x* is the distance from the drainage point.
The attenuation coefficient is defined as

$$\alpha = \frac{R_S}{R_K}$$

where *RS* is the ohmic resistance of the structure per unit length and
RK is given by

$$R_K = \sqrt{R_S R_L}$$

where *RL* is known as the leakage resistance and refers to the total resistance of the structure-electrolyte interface, including the ohmic resistance of any applied surface coating(s).

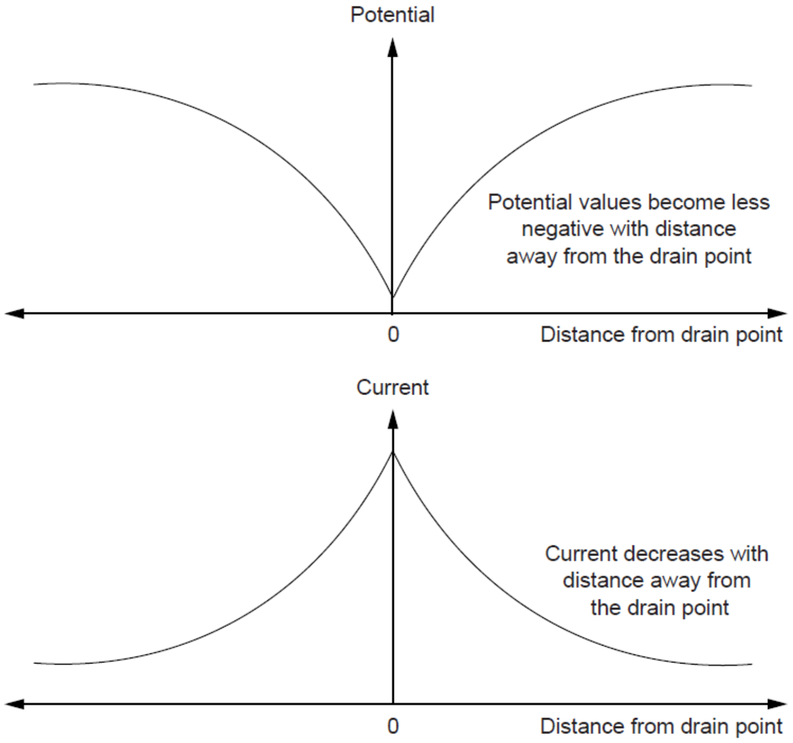


Figure 9.10 Potential and current attenuation as a function of distance from the drain point, due to increasing electrical resistance of the pipeline itself (schematic).

To minimize attenuation, the term should be as small as possible.
This implies that for a given material a high *RK* value is desirable.

Because the ohmic resistance of the structure *RS* is fixed for a given material, the leakage resistance *RL* needs to be considered. The higher the integrity of the coating, the higher *RL* will be. The buildup of calcareous deposits on exposed areas of cathodically protected structures will also tend to increase *RL.* The formation of such deposits is therefore desirable for attenuation considerations. For achieving a relatively uniform current distribution in CP systems, the following factors are thus generally regarded as desirable:
_ Relatively high electrolyte resistance
_ Uniform electrolyte resistance
_ Low resistivity of the structure
_ High quality of coating (high resistance)
_ Relatively high anode to cathode separation distance
_ Sufficiently large power supply in the CP system

9.4.3 Stray currents

Stray currents are currents flowing in the electrolyte from external sources, not directly associated with the cathodic protection system.

Any metallic structure, for example, a pipeline, buried in soil represents a low-resistance current path and is therefore fundamentally vulnerable to the effects of stray currents. Stray current tends to enter a buried structure in a certain location and leave it in another. It is where the current leaves the structure that severe corrosion can be expected. Corrosion damage induced by stray current effects has also been referred to as *electrolysis* or *interference.* For the study and understanding of stray current effects it is important to bear in mind that current flow in a system will not only be restricted to the lowestresistance path but will be distributed between paths of varying resistance, as predicted by elementary circuit theory. Naturally, the current levels will tend to be highest in the paths of least resistance.

There are a number of sources of undesirable stray currents, including foreign cathodic protection installations; dc transit systems such as electrified railways, subway systems, and streetcars; welding operations; and electrical power transmission systems. Stray currents can be classified into three categories

1. Direct currents
2. Alternating currents
3. Telluric currents

9.4.3.1 Direct stray current corrosion.

Typically, direct stray currents come from cathodic protection systems, transit systems, and dc high-voltage transmission lines. A distinction can be made between anodic interference,
cathodic interference, and combined interference.

Anodic interference is found in relatively close proximity to a buried anode, under the influence of potential gradients surrounding the anode. As shown in Fig. 9.11, a pipeline will pick up current close to the anode. This current will be discharged at a distance farther away from the anode. In the current pickup region, the potential of the pipeline subject to the stray current will shift in the negative direction; in essence it receives a boost of cathodic protection current locally. This local current boost will not necessarily be beneficial, because a state of overprotection could be created. Furthermore, the excess of alkaline species generated can be harmful to aluminum and lead alloys. Conversely, in areas where the stray current is discharged, its potential will rise to more positive values. It is in the areas of current discharge that anodic dissolution is the most severe.

Cathodic interference is produced in relatively close proximity to a polarized cathode. As shown in Fig. 9.12, current will flow away from the structure in the region in close proximity to the cathode. The potential will shift in the positive direction where current leaves this structure, and this area represents the highest corrosion damage risk.

Current will flow onto the structure over a larger area, at further distances from the cathode, again with possible damaging overprotection effects.

An example of combined anodic and cathodic interference is presented in Fig. 9.13. In this case current pickup occurs close to an anode, and current discharge occurs close to a cathodically polarized structure. The degree of damage of the combined stray current effects is greater than in the case of anodic or cathodic interference acting alone. The effects are most pronounced if the current pickup and discharge areas are in close proximity. Correspondingly, the damage in both the current pickup (overprotection effects) and discharge regions (corrosion) will be greater.

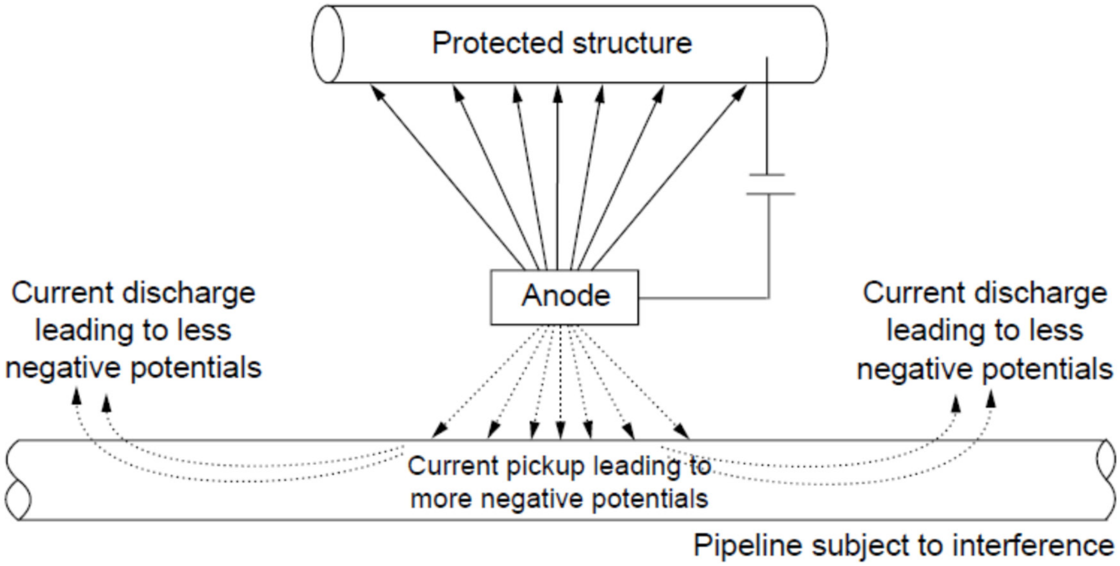


Figure 11.12 Anodic interference example (schematic).

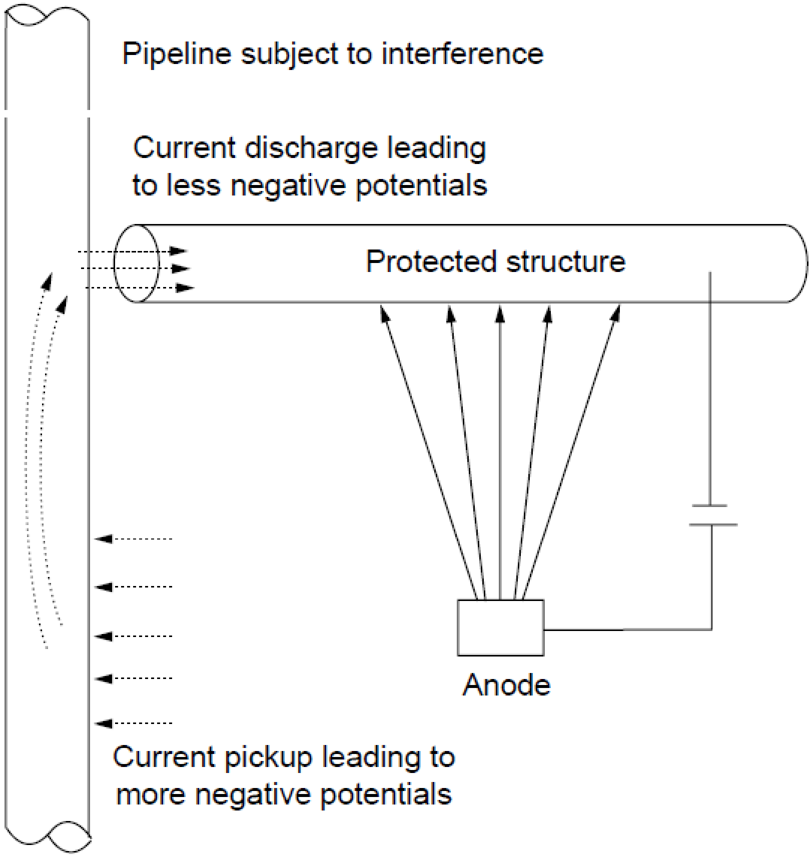


Figure 9.12 Cathodic interference example (schematic).

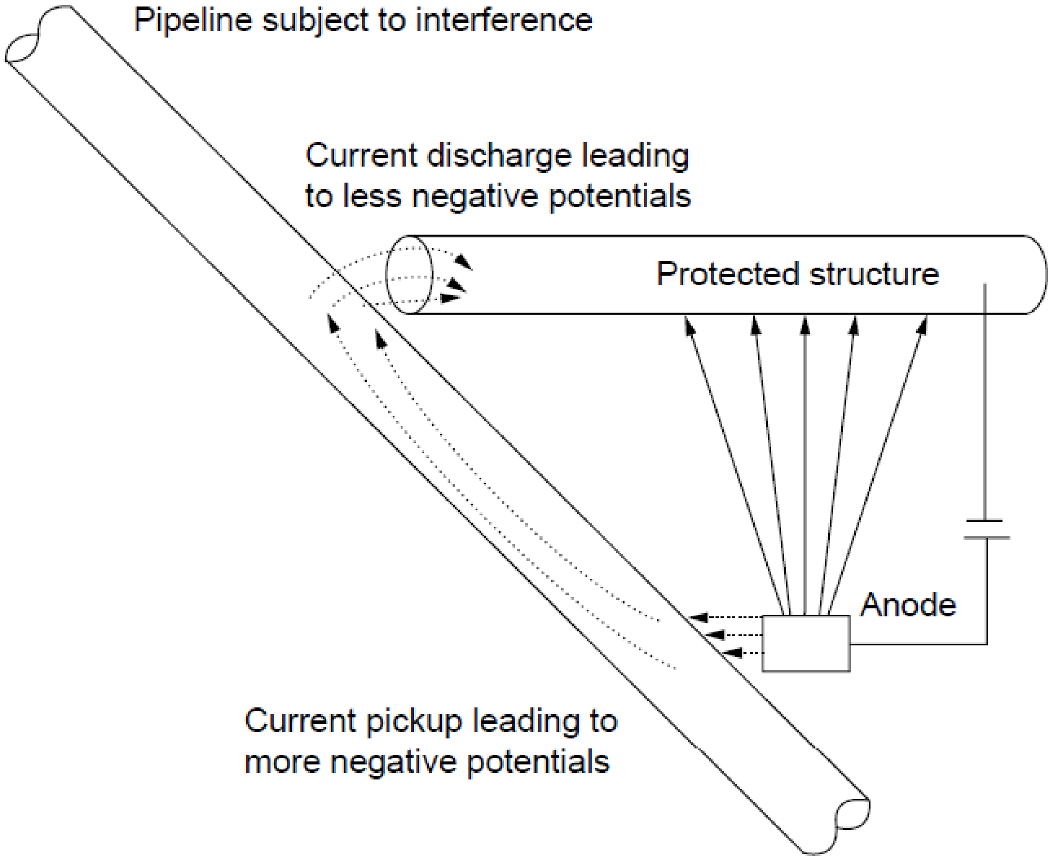


Figure 9.13 Combined anodic and cathodic interference example (schematic).

9.4.3.2 Alternating current.

There is an increasing trend for pipelines and overhead powerlines to use the same right-of-way. Alternating stray current effects arise from the proximity of buried structures to highvoltage overhead power transmission lines. There are two dominant mechanisms by which these stray currents can be produced in buried pipelines: electromagnetic induction and transmission line faults.

In the electromagnetic coupling mechanism, a voltage is induced in a buried structure under the influence of the alternating electromagnetic field surrounding the overhead transmission line. This effect is similar to the coupling in a transformer, with the overhead transmission line acting as the primary transformer coil and the buried structure acting as the secondary coil. The magnitude of the induced voltage depends on factors such as the separation distance from the powerline, the relative position of the structure to the powerlines, the proximity to other buried structures, and the coating quality. Such induced voltages can be hazardous to anyone who comes in contact with the pipeline or its accessories.

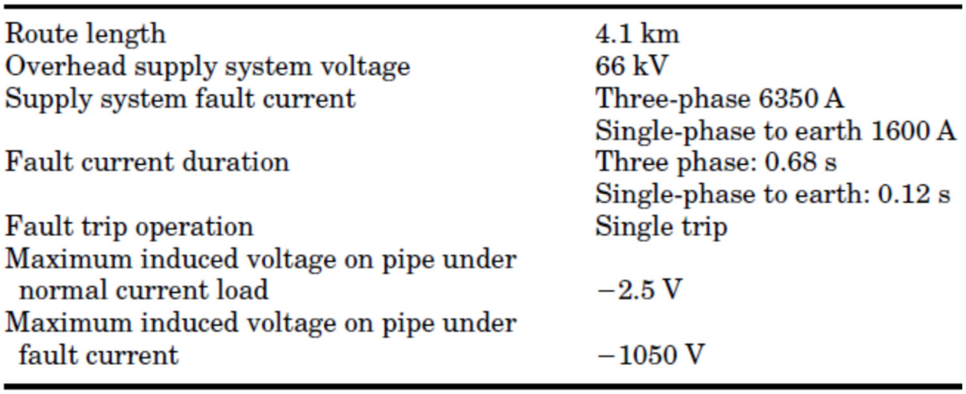
The second mechanism is one of resistive coupling, whereby ac currents are directly transmitted to earth during transmission line faults. Causes of such faults include grounding of an overhead conductor, lightning strikes, and major load imbalances in the conductors.

Usually such faults are of very short duration, but due to the high currents involved, substantial physical damage to coated structures is possible. Ancillary equipment such as motorized valves, sensors, and cathodic protection stations could also be damaged. These faults represent a major threat to human and animal life, even if no contact is made with the pipeline. The example listed in Table 9.7 for a pipeline provides an indication of the relative magnitude of these two mechanisms. Further details, including safety issues, may be found in the publication of Kirkpatrick.

9.4.3.3 Telluric effects.

These stray currents are induced by transient geomagnetic activity. The potential and current distribution of buried structures can be influenced by such disturbances in the earth’s magnetic field. Such effects, often assumed to be of greatest significance in closer proximity to the poles, have been observed to be most intense during periods of intensified sun spot activity. In general, harmful influences on structures are of limited duration and do not remain highly localized to specific current pickup and discharge areas. Major corrosion problems as a direct result of telluric effects are therefore relatively rare.

Geomagnetic activity for different locations is recorded and reported by organizations such as the Geological Survey of Canada. Activity is classified into quiet, unsettled, and active conditions. Furthermore, charts forecasting magnetic activity are available, similar to short and long-term weather forecasts. Such forecast data has proven useful to avoid measurements of pipeline “baseline” corrosion parameters during sporadic periods of high geomagnetic transients.



Route length	4.1 km
Overhead supply system voltage	66 kV
Supply system fault current	Three-phase 6350 A Single-phase to earth 1600 A
Fault current duration	Three phase: 0.68 s Single-phase to earth: 0.12 s
Fault trip operation	Single trip
Maximum induced voltage on pipe under normal current load	−2.5 V
Maximum induced voltage on pipe under fault current	−1050 V

TABLE 9.7 Example of Fault Effect Calculation

9.4.3.4 Controlling stray current corrosion.

In implementing countermeasures against stray current effects, the nature of the stray currents has to be considered. For mitigating dc interference, the following fundamental steps can be taken:

_ Removal of the stray current source or reduction in its output current
_ Use of electrical bonding
_ Cathodic shielding
_ Use of sacrificial anodes
_ Application of coatings to current pickup areas

To implement the first obvious option in the above listing, cooperation from the owners of the source is a prerequisite. In several cases, so-called electrolysis committees have been formed to serve as forums for cooperation between different organizations.

The establishment of an electrical connection between the interfering and interfered-with structure is a common remedial measure.

Figure 9.14 shows how the interference problem presented in Fig. 9.11 is mitigated by an electrical bond created between the two structures.

A variable resistance may be used in the bonded connection. A so-called forced drainage bond imposes an additional external potential on the bond to “assist” stray current drainage through the bond. In practice, for complex systems, the design of bonds is not a simple matter.

Furthermore, stray currents tend to be dynamic in nature, with the direction of current reversing from time to time. In such cases, simple bonding is insufficient, and additional installation of diodes will be required to protect a critical structure at all times.

In cathodic shielding the aim is to minimize the amount of stray current reaching the structure at risk. A metallic barrier (or “shield”) that is polarized cathodically is positioned in the path of the stray current, as shown in Fig. 9.15. The shield represents a low-resistance preferred path for the stray current, thereby minimizing the flow of stray current onto the interfered-with structure.

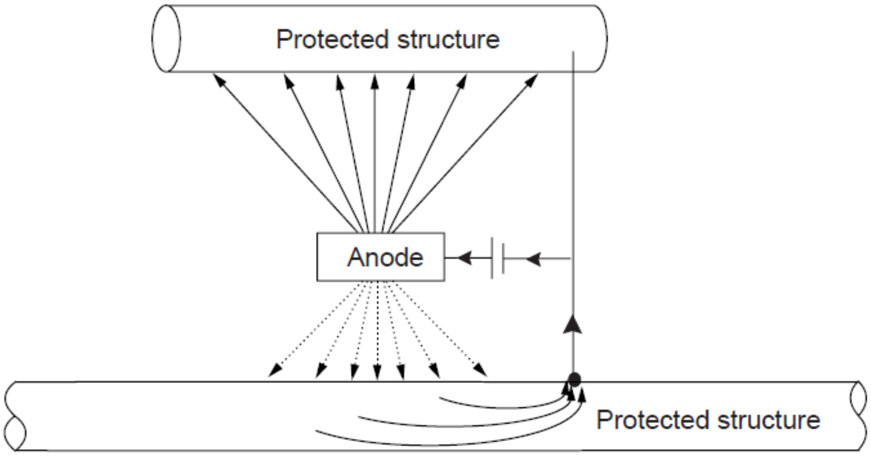


Figure 9.14 Use of a drainage bond to mitigate stray current discharge from the pipeline (schematic).

If the shield is connected to the negative terminal of the power supply of the interfering structure, its effects on the protection levels of the interfering structure have to be considered; these will obviously be reduced for a given rectifier output.

Sacrificial anodes can be installed at the current discharge areas of interfered-with structures to mitigate stray current corrosion. This mitigation method is most applicable to relatively low levels of stray currents. As shown in Fig. 9.16, the current is discharged from these anodes rather than from the structure at risk. The importance of placing the anodes close to the interfering structure is apparent: to minimize the resistance to current flowing from the anodes. The galvanically less noble anodes will generate a cathodic protection current, thereby compensating for small amounts of residual stray currents that continue to be discharged from the interfered-with structure.

The use of protective coatings to reduce stray current damage should be implemented prior to the installation of buried structures. It is usually impractical to apply such coatings after the installation phase. The use of coatings to mitigate the influence of stray currents should only be considered at the current pickup areas. It is not recommended to rely on additional coatings at current discharge areas, because rapid localized corrosive penetration is to be expected at any coating defect. In general, if a macroscopic anode and cathode exists on a structure, coatings should never be applied to the anode alone for corrosion protection. Any discontinuities in the coating covering only the anode represent sites where intense anodic dissolution will occur.

It is much better practice to coat the cathode as a corrosion control method.

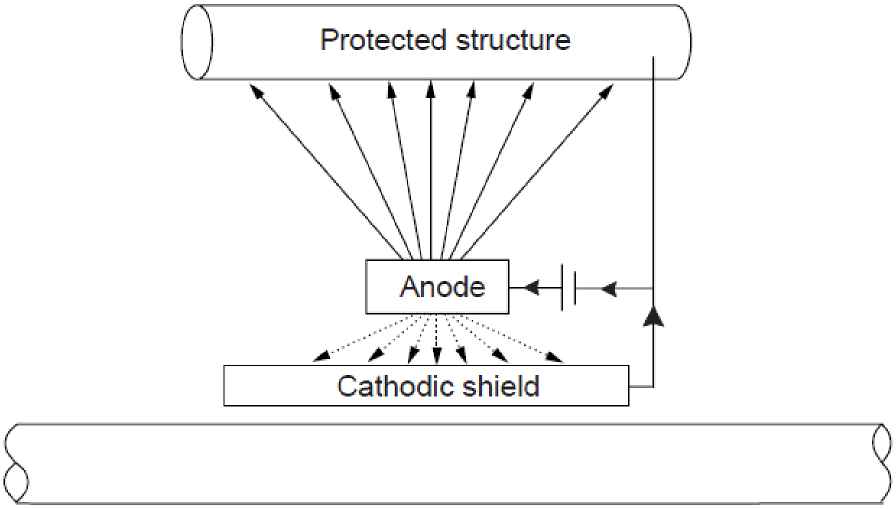


Figure 9.15 Principle of a cathodic shield to minimize anodic interference (schematic).

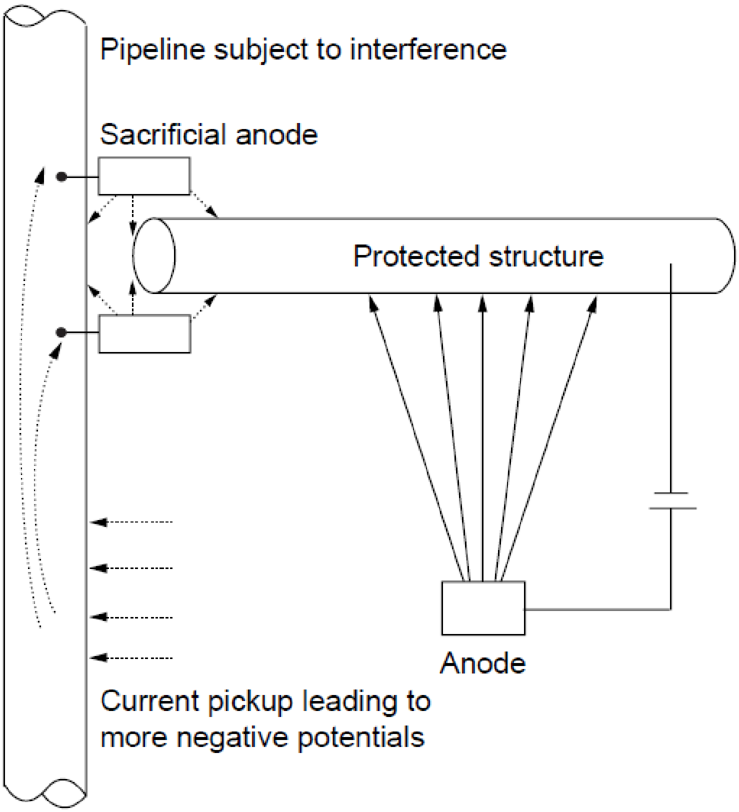


Figure 9.16 Use of sacrificial anodes to mitigate cathodic interference

Ac-induced stray current effects can be reduced by locating buried structures sufficiently far away from power lines. Nonmetallic pipeline construction materials such as high-density polyethylene can be used in some cases, where operating pressures are low. The highest potential shifts occur on metallic structures that have high-integrity coatings.

With high-quality coatings, grounding of the pipeline is clearly limited. Obviously, it is generally not desirable to sacrifice coating quality to reduce the magnitude of these effects. A similar reduction of the induced potential shifts can be achieved with distributed sacrificial anodes attached to the structure. These anodes provide cathodic protection current and reduce the resistance to ground, which is fundamentally desirable to minimizing the ac-induced voltage shifts. The use of such anodes will also tend to mitigate the influence of telluric effects.

9.4.3.5 Stray current case study—dc rail transit systems.

Stray current-induced corrosion damage has been associated with North American dc rail transit systems for more than a century. In the United States alone, there are more than 20 transit authorities operating electrified rail systems in major urban centers. Stray current corrosion problems continue to plague several North American cities where the transit systems are typically installed in high-density urban areas. Examples of stray current corrosion problems in transit systems, excluding foreign structures, are listed in Table 11.8. Obviously such urban areas are associated with underground cables and piping (water and gas) systems that can also be highly susceptible to this form of corrosion damage.

A recent survey of the cost of corrosion in the United States has estimated that some 5 percent of the total cost is attributable to stray current effects, mostly due to electrified transit systems. This percentage includes the damage to utility structures operated outside the direct activities of the transit authorities. In other parts of the world electrified rail systems can represent the dominant form of rail transportation for passengers and freight. Not surprisingly, major stray current corrosion problems have also been associated with these systems, again with serious economic implications.

These stray current problems stem from the fundamental design of electrified rail transit systems, whereby current is returned to substations via the running rails. The ground surrounding the rails can be viewed as a parallel conductor to the rails. The magnitude of stray current flow in the ground conductor will obviously increase as its resistivity decreases. Any metallic structure buried in ground of this nature will tend to “attract” stray current because it represents a very low resistance current path. The highest rate of metal dissolution occurs where the current leaves the structure, and undesirable overprotection effects can occur at the points of current pickup.

Type of damage	Comments
Corrosion of steel base plates and anchors in footings of supports	Caused by stray current discharge into the ground at elevated rail sections
Localized thinning of metal spikes in wooden ties	Lifetimes can be drastically reduced
Loss of rail section	
Reinforcing steel corrosion in concrete structures	Applicable to support structures, platforms, subway walls, tunnels, and surrounding buildings
Corrosion of expansion joint bonds	
Corrosion of steel shells in tunnels	Tunnels generally regarded as wet, highly corrosive areas conducive to stray current corrosion

TABLE 11.8 Examples of Direct Stray Current Damage in Electrified Transit Systems.

A basic stray current scenario is illustrated in Fig. 9.17, where the negative rail has been grounded. Remote from the substation, due to a voltage drop in the rail itself, the rails will tend to be less negative relative to earth, and stray current flows onto the pipeline. Close to the substation, the rails are highly negative relative to earth, and stray current will tend to leave the pipeline and induce corrosion damage. In essence, the moving electrified vehicle represents a moving stray current source.

Considering that the rails are actually often mounted on wooden ties, some readers may wonder why current flow from the rails to the ground is actually possible. Such ties may after all appear to be insulators separating the rails from ground. First, the presence of water (rain) can obviously negate the insulating properties of the wooden ties by directly acting as an electrolyte. Wooden ties obviously always contain moisture and can retain rain water and therefore will never be perfect insulators, even in nominally dry conditions. Second, accumulation of soil and other debris will tend to bridge the ground and the rails, permitting the transfer of current. Third, metallic fasteners (spikes) holding the rails in place tend to act as short circuits for current flow to the ground. Considering these factors, it is apparent that for all practical purposes grounding of the rail can never be completely eliminated. Lastly, in some countries the outdated practices of deliberately bonding neighboring buried utility structures to the rail return current prevail. This approach is generally unsatisfactory because a large amount of stray current enters the ground that cannot be controlled in complex utility systems.

The stray currents tend to be very dynamic in nature, with the magnitude of stray current varying with usage of the transit system and relative position and degree of acceleration of the electrified vehicles.

Fundamentally, the following factors all have an effect on the severity

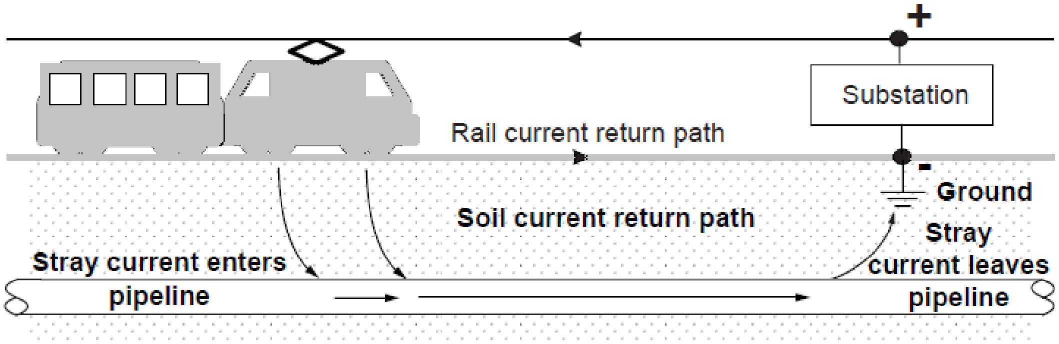


Figure 9.17 Stray current problem associated with an electrified dc transit system.

of stray currents: magnitude of propulsion current, substation spacing, substation grounding method, resistance of the running rails, usage and location of cross bonds and isolated joints, track-to-earth resistance, and the voltage of the traction power system. At a particular location on an affected pipeline, the presence of stray currents can thus usually be identified when fluctuating pipe-to-soil potentials are recorded with time. Figure 9.18 illustrates the fluctuations in pipe-to-soil potentials for a pipeline in close proximity to an electrified rail transit system.

Typically a number of trains would have passed this monitoring point during the data collection period in Fig. 9.18. Positive potential excursions associated with current discharge at the measuring point and negative potential transients related to current pickup are evident.

At greater distances from the stray current source the potential profile is significantly more stable, as indicated by the second potential trace in Fig. 9.18.

Stray current effects are often detected at insulators in pipeline systems, which separate different sections of these systems. An example of stray current effects on two sides of an insulator is presented in Fig. 9.19. The more positive potential profile of pipeline on Side A indicates that current discharge is predominantly occurring, representing an increased corrosion risk. Conversely on Side B, current pickup is the overriding effect. However, it should be noted that stray current flow is very dynamic in this situation, with potential transients in the positive and negative direction recorded on both sides of the insulator. Negative potential excursions on Side A correspond to positive excursions on Side B (and vice versa), indicating current pickup and discharge respectively (and vice versa).

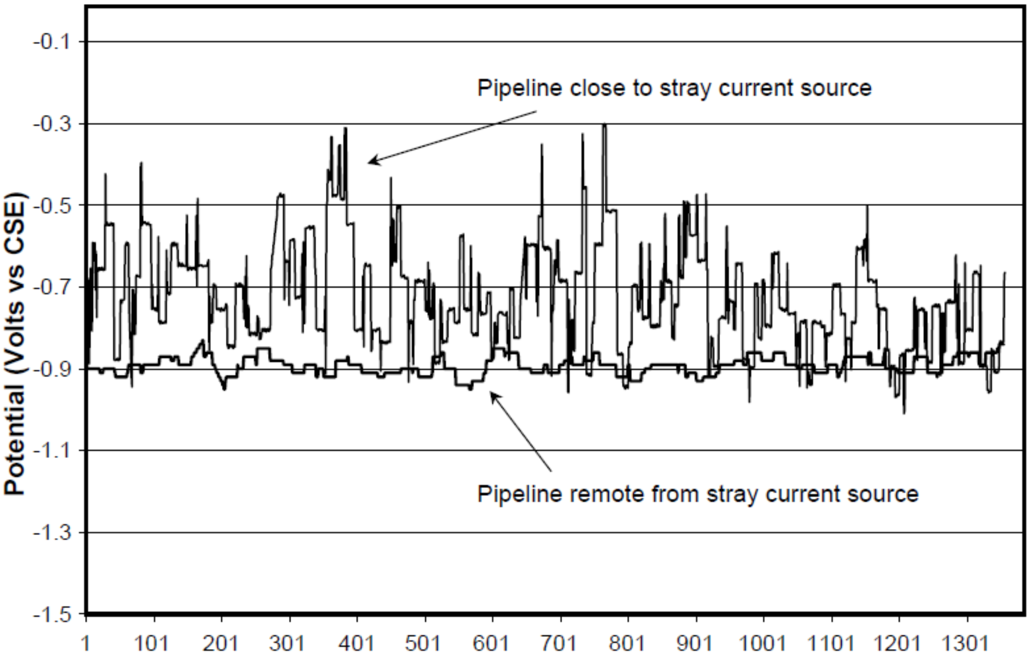


Figure 9.18 Stray current activity on a pipeline revealed by significant potential transients (schematic).

The older dc transit systems generally produce the worst stray current problems due to the following factors:

_ Relatively high electrical resistance of the running rails (smaller rail cross sections, bolted connections, deterioration of connections over time, etc.)

_ Poor isolation from earth of the running rails (intentional grounded negative bus, intimate earth contact, moisture absorbing wood ties, etc.)

_ Widely spaced substations leading to a higher voltage drop in the rails

In modern system designs stray current problems are ameliorated with two fundamental measures: (1) decreasing the electrical resistance of the rail return circuit and (2) increasing the electrical resistance between the rails and ground. The first measure makes current return through the ground less likely. Steps taken in this direction include the use of heavier rail sections, continuously welded rails, improved rail bonding, and reduced spacing between substations. It is desirable to combine substations with passenger stations. At passenger stations current flow is highest due to acceleration of trains. This combination ensures that these peak currents have a very short return path. The rail-to-soil resistance can be increased by using insulators placed between the rails and concrete or wooden ties and by using insulated rail fasteners. Stray current

concerns are particularly relevant when older rail systems are integrated with newer designs. The higher current demand of modern, high-speed vehicles poses increased stray current risks in the older sections.
Apart from the above design improvements in more modern transit systems, several other remedial measures can be considered. Regular rail inspections are important for detecting problems with electrical continuity and faulty insulators. In addressing stray current problems of this nature, communication and cooperation between different organizations and stakeholders is most beneficial. Corrosion control coordinating committees are usually established for these purposes.

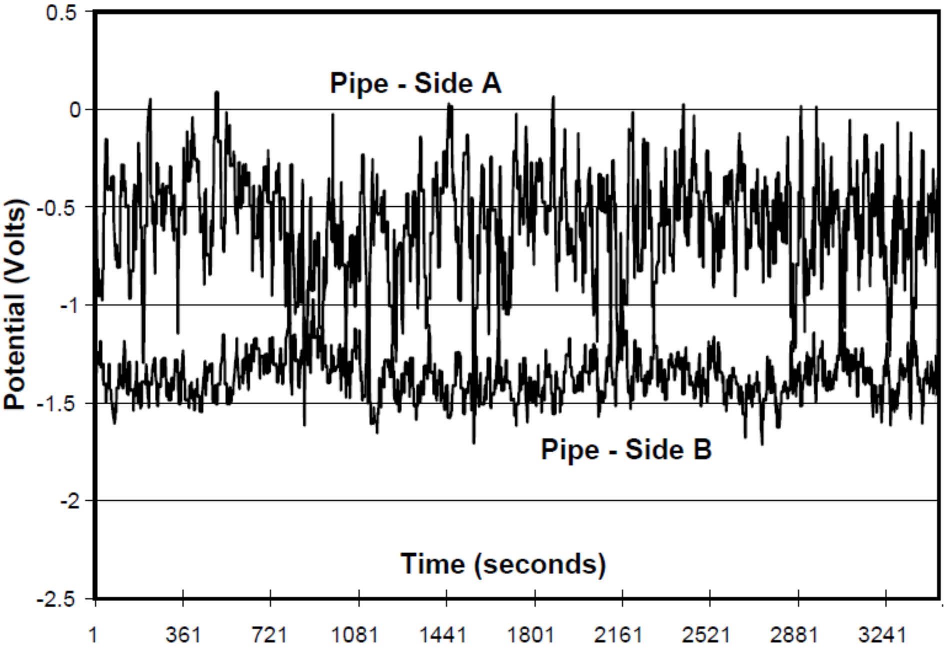


Figure 9.19 Potential fluctuations due to stray current effects on two sides of an insulator in a pipeline. Note the opposite direction of the potential transients on the two sides.

9.5 Monitoring the Performance of CP Systems for Buried Pipelines

Monitoring cathodic protection systems and corrosion damage to pipelines (and other structures) under their influence is a highly specialized subject. This material is therefore presented separately from the general corrosion monitoring chapter, although readers should be able to identify some overlap in basic concepts.
In the discussion of cathodic protection monitoring, two important distinct areas can be identified. The first domain lies in monitoring the condition and performance of the CP system hardware. Monitoring of rectifier output, pipe-to-soil potential and current measurements at buried sacrificial anodes, inspection of bonds, fuses, insulators, test posts, and permanent reference electrodes are relevant to this area.
The second domain concerns the condition of the pipeline (or buried structure) itself and largely deals with surveys along the length of the pipeline to assess its condition and to identify high corrosion-risk areas.

9.5.1 CP system hardware performance monitoring

Because CP systems are expected to operate in demanding environmental conditions over long time periods, it should not be surprising that hardware maintenance is a fundamental requirement for reliable performance. Lightning strikes are also a major damage factor. NACE International has produced an excellent guideline, describing procedures on the basis of monthly, quarterly, and annual monitoring.
According to these guidelines, selected test stations are visited on a monthly basis. The rectifier units and selected sacrificial anode locations are visited, visually inspected, and their output measured. The quarterly procedures are similar, but the number of monitoring points ideally embraces the entire system. These comprehensive steps also apply to annual monitoring, which additionally focuses on the detailed inspection of system components (bonds, shunts, fuses, surge, divertors, distribution boxes, cable connections, mounting, systems etc.).
Considering the geographic expanse of typical CP systems, it is apparent that these tasks and the associated record keeping can be time consuming and labor intensive. An increasing trend toward selective remote

rectifier monitoring, using modern communication systems and computer networks, is emerging to accomplish these tasks with reduced resources. The benefits of this approach were highlighted several years ago. Wireless cell phone and satellite communication systems are available for interrogating rectifiers in remote locations. Importantly, GPS technology represents remote, wireless, low-cost timing devices for performing more specialized recordings with rectifier interruptions. Modern commercial systems presently provide the following remote rectifier monitoring features:

_ Rectifier voltage and current output
_ Standard on structure-to-soil potential data
_ Instant OFF structure-to-soil potential data
_ Depolarization data
_ Ancillary readings from suitable sensors such as temperature and soil parameters
_ Remote adjustment of rectifiers, provided “advanced” control hardware has been installed
_ Alarm and alert notification, if preset operating windows are exceeded

9.5.2 Structure condition monitoring

Monitoring the condition of structures protected by CP is a highly specialized subject. In many cases, condition monitoring requirements are specified by regulatory authorities. Further details of techniques used for assessing the condition of buried pipelines are presented below.

9.5.2.1 Close interval potential surveys.

Close Interval Potentials Survey (CIPS) refers to potential measurements along the length of buried pipelines to assess the performance of CP systems and the condition of the cathodically protected pipeline. The potential of a buried pipeline can obviously be measured at the permanent test posts (Fig. 9.20) but, considering that these may be miles apart, only a very small fraction of the overall pipeline surface can be assessed in this manner. The principle of a CIPS is to record the potential profile of a pipeline over its entire length by taking potential readings at intervals of around 1 m.

Methodology. In principle CIPS measurements are relatively simple.

A reference electrode is connected to the pipeline at a test post, and this reference electrode is positioned in the ground over the pipeline at regular intervals (around 1 m) for the measurement of the potential difference between the reference electrode and the pipeline (Figs. 9.21 and 9.22).

In practice, a three-person crew is required to perform these measurements.

One person walking ahead locates the pipeline with a pipe locator to ensure that the potential measurements are performed directly overhead the pipeline. This person also carries a tape measure and inserts a distance marker (a small flag) at regular intervals over the pipeline. The markers serve as distance calibration points in the survey. The second person carries a pair of electrodes that are connected to the test post by means of a trailing thin copper wire and the potential measuring instrumentation. This person is also responsible for entering specific features as a function of the measuring distance.

Such details (road, creek, permanent distance marker, fence, rectifier, block valve, etc.) serve as useful geographical reference points when corrective actions based on survey results have to be taken. The third person collects the trailing wire after individual survey sections have been completed. (Strictly speaking, the first person may not be required if the distance can be monitored via a counter measuring the length of the unwinding copper wire.)

In practice, CIPS measurements are very demanding on the field crews and require extensive logistical support from both the pipeline operator and the CIPS contractor. Field crews are typically required to move over or around fences (of which there are many in residential areas), roads, highways, and other obstacles and difficult terrain.

Breakage of the trailing copper wire is not uncommon, and special strengthened wire has to be taped down onto road surfaces that are crossed. The rate of progress for a survey thus greatly depends on the terrain to be surveyed. Pawson13 has identified the following responsibilities of a pipeline operator in preparing for a CIPS:

_ Preparation of a detailed technical specification for the survey
_ Establishing and clearing the right of way (the path of the pipeline)
_ Notification of land owners and foreign operators
_ Establishing the sphere of influence of existing rectifiers and foreign structures

_ Checking the condition and establishing functionality of rectifiers, bonds, and isolation
_ Characterizing the effectiveness of the CP systems in difficult terrain (water swamps, etc.)
_ Identification of suitable seasonal and weather windows
_ Specification of the reporting format
_ Ensuring availability of support personnel
_ Specification of qualifications and experience required from the CIPS contractor

The CIPS contractor's responsibilities are

_ Provision of a proposal detailing specification compliance or, where appropriate, the specification of alternate work methods
_ Provision of a sample of the report format(s)
_ Provision of project schedules
_ Utilization of professional crews and equipment (including materials, spares, support, and back-up equipment)
_ Implementation of professional data management and report preparation

A report published by NACE International gives additional guidelines about the nature of information that should be supplied by the pipeline operator and by the contractor. A most important consideration in the potential readings is the IR, or ohmic drop error, that is included in the potential measurements when a CP system is operational.

As discussed earlier, the voltage criteria for protection against corrosion are based on the potential of the pipeline at the interface with the soil. The ON potential measurements taken at the surface do not represent this interfacial potential and include, among other effects, an IR drop from the cathodic polarization of the pipeline. In the presence of the IR drop, the measured ON potentials tend to be more negative than the actual interfacial potential, and a false sense of security may be obtained.

For minimization of IR errors, two current interruption criteria used in practice include a 3-s ON, 1-s OFF cycle and a 0.8-s ON, 0.2-s OFF cycle. The ON period is generally selected to be distinctly longer than the OFF period to limit depolarization of the pipeline. A waveform analysis is also important because the transition between the ON and OFF potential readings is not necessarily smooth; spikes of several hundred millivolts may be encountered in practice, and the measuring instrument should obviously be set up to avoid these transients (refer to Fig. 9.4).

To accomplish the ON-OFF switching for the above potential measurements, a current interrupter has to be installed on the rectifiers.

Modern interrupters are based on solid-state switches and can be programmed to perform switching only when the survey is performed during the day; this feature minimizes the depolarization of the pipeline that may occur gradually due to the cumulative effects of the OFF periods. Importantly, a particular section of a pipeline will typically be under the influence of several rectifiers, and thus a number of rectifiers will have to be interrupted in a synchronized manner to perform the ON and OFF potential readings. Pipeline operators usually specify that at least two rectifiers ahead of the survey team and two rectifiers behind it have to be interrupted in a fully synchronized manner.

In modern practice, this type of synchronous switching of multiple rectifiers is accomplished by controlling the switch intervals and timing with the GPS. The potential recording device can also be synchronized to the rectifier interruption cycle with GPS technology. The GPS is a satellite-controlled radio navigation system that facilitates the determination of position (in three dimensions), velocity, and time.

Users of this system may be based on land, at sea, or in the air, and the system is operational 24 h a day, in any weather conditions and anywhere on earth. The operator of this extremely accurate timing system is the U.S. Department of Defense.

On a single-phase rectifier an interrupter can, in principle, be installed at three locations: the input ac to the rectifier, the transformed ac current, or the dc from the rectifier. The current output of the rectifier to the pipeline should be verified before and after this type of interrupter installation. It will need to be adjusted if the current drawn to power the interrupter unit affects the output to the pipeline.

Figure 9.20 Test station with an electrical connection to the pipeline.

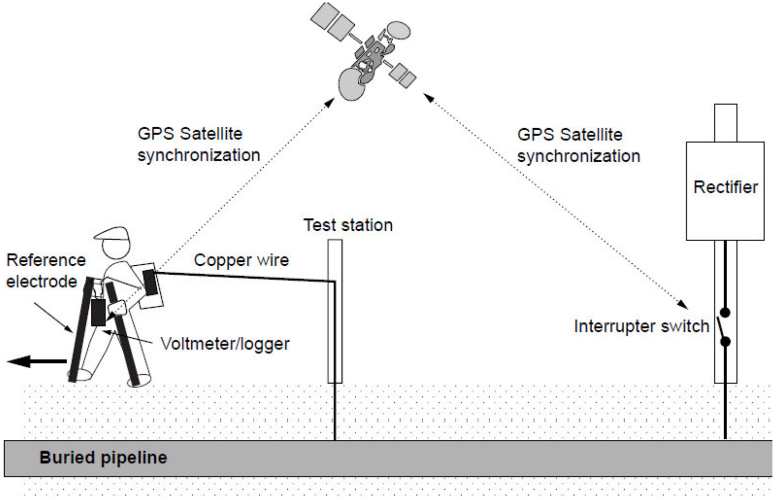


Figure 9.21 CIPS methodology (schematic).

Figure 9.22 CIPS equipment, with the operator starting a survey at a test post.

Data management.

Computers are used to process survey data, with the first processing step being the downloading of data from the field measurement units at the end of each survey day. The data is typically transformed further for presentation in graphical form, together with a “client copy” of a database, using data storage devices such as magnetic disk, tape, or CD-ROM.

An example of graphical CIPS data is presented in Fig. 9.23. In the simplest format, the ON and OFF potentials are plotted as a function of distance. The distance is referred to as a station number, with station number 0-00 representing the starting point of a survey. The usual sign convention is for potentials to be plotted as positive values. The difference between the ON and OFF potential values should be noted. As is usually the case, the OFF potentials are less negative than the ON values. If the relative position is reversed, some unusual condition such as stray current interference is likely to have arisen.

NACE International has drawn up a Standard Recommended Practice [RP0792-92] for the format of computerized close interval survey data.

These guidelines describe a general organization for CIPS data, applicable to both mainframe and personal computers. According to these recommendations, each data file containing the ON and OFF potential values should be supplemented with the following information, in the form of a separate header file or a header incorporated into the data file:

_ Data file name
_ Date
_ ON and OFF time cycles
_ Environmental conditions
_ Survey operator
_ Pipeline identification
_ Interval used in the survey
_ Equipment details
_ Location description
_ Beginning and end stations
_ Direction of survey and type of survey
_ Measuring units
_ Method of connection to the pipeline
_ Additional user-defined information

The provision of comprehensive supporting information is of vital importance because the condition of a cathodically protected pipeline will typically be assessed through a number of surveys, over a number of years. The environmental conditions, measurement instrumentation and technology, and the contractor can therefore easily be different from survey to survey. Meaningful trending and comparison from survey to survey cannot be made if this supplementary information is not available. For example, the potential readings in dry soil may differ from wetter conditions.

Advantages and limitations.

The CIPS technique provides a complete pipe-to-soil potential profile, indicating the status of cathodic protection levels. The interpretation of results, including the identification of defects, is relatively straightforward. The rate of progress of the survey team is independent of the coating quality on the pipeline. When the entire pipeline is walked, the condition of the right-of-way and of the cathodic protection equipment can be assessed together with the potential measurements.

Fundamentally, these surveys do not indicate the actual severity of corrosion damage, because the corrosion potential is not a kinetic parameter. The entire length of the pipeline has to be walked by a survey team and significant logistical support is required. The technique is not applicable to certain terrain such as paved areas, roads, rivers, and so forth.

Pearson survey.

The Pearson survey, named after its inventor, is used to locate coating defects in buried pipelines. Once these defects have been identified, the protection levels afforded by the CP system can be investigated at these critical locations in more detail.

Methodology.

An ac signal of around 1000 Hz is imposed onto the pipeline by means of a transmitter, which is connected to the pipeline and an earth spike, as shown in Fig. 9.24. Two survey operators make earth contact either through metal studded boots or aluminum poles.

A distance of several meters typically separates the operators.

Essentially, the signal measured by the receiver is the potential gradient over the distance between the two operators. Defects are located by a change in the potential gradient, which translates into a change in signal intensity.

As in the CIPS technique, the measurements are usually recorded by walking directly over the pipeline. As the front operator approaches a defect, increasing signal intensity is recorded. As the front person moves away from the defect, the signal intensity drops and later picks up again as the rear operator approaches the defect. The interpretation of signals can obviously become confusing when several defects are located between the two operators. In this case, only one person walks directly over the pipeline, with the connecting leads at a right angle to the pipeline.

In principle, a Pearson survey can be performed with an impressed cathodic protection system remaining energized. Sacrificial anodes should be disconnected because the signal from these may otherwise mask actual coating defects. A three-person team is usually required to locate the pipeline, perform the survey measurements, place defect markers into the ground, and move the transmitters periodically. The operator carrying the receiver should be highly experienced, especially if the survey is based on audible signals and instrument sensitivity settings. Under these conditions, the results are completely dependent on this operator's judgment.

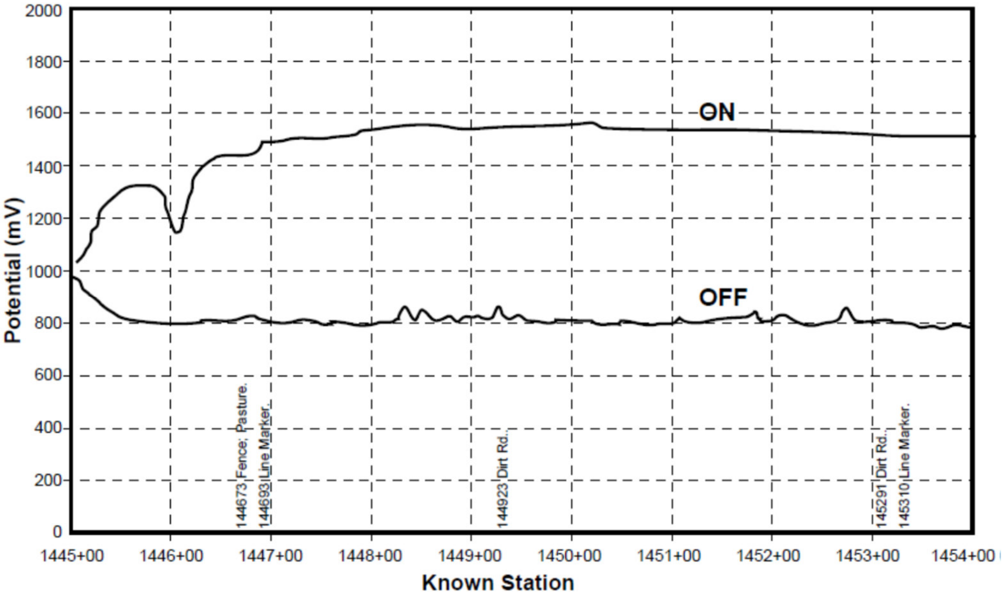


Figure 9.23 CIPS data, showing ON and OFF potential values.

Advantages and limitations.

By walking the entire length of the pipeline, an overall inspection of the right-of-way can be made together with the measurements. In principle, all significant defects and metallic conductors causing a potential gradient will be detected. There are no trailing wires and the impressed CP current does not have to be pulsed.

The disadvantages are similar to those of CIPS because the entire pipeline has to be walked and contact established with ground. The technique is therefore unsuitable to roads, paved areas, rivers, and so forth. Fundamentally, no severity of corrosion damage is indicated and no direct measure of the performance of the CP system is obtained.

The survey results can be very operator dependent, if no automated signal recording is performed.

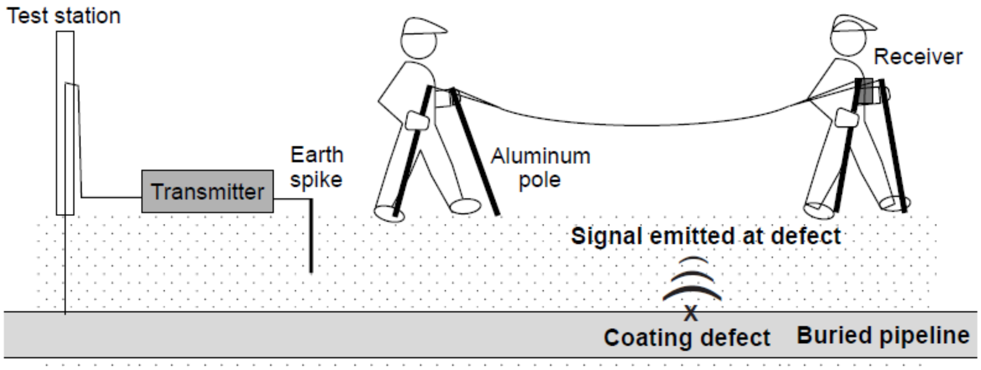


Figure 9.24 Pearson survey methodology (schematic).

Direct current voltage gradient (DCVG) surveys.

DCVG surveys are a more recent methodology to locate defects on coated buried pipelines and to make an assessment of their severity. The technique again relies on the fundamental effect of a potential gradient being established in the soil at coating defects under the application of CP current; in general, the greater the size of the defect, the greater the potential gradient. The DCVG data is intricately tied to the overall performance of a CP system, because it gives an indication of current flow and its direction in the soil.

Methodology.

The potential gradient is measured by an operator between two reference electrodes (usually of the saturated Cu/CuSO4 type), separated by a distance of say half a meter. The appearance of these electrodes resembles a pair of cross-country ski poles (Fig. 9.25). A pulsed dc signal is imposed on the pipeline for DCVG measurements.

The pulsed input signal minimizes interference from other current sources (other CP systems, electrified rail transit lines, telluric effects). This signal can be obtained with an interrupter on an existing rectifier or through a secondary current pulse superimposed on the existing "steady" CP current.

The operator walking the pipeline observes the needle of a millivoltmeter needle to identify defect locations. (More recently developed DCVG systems are digital and do not have a needle as such.)

It is preferable for the operator to walk directly over the pipeline, but it is not strictly necessary. The presence of a defect is indicated by a increased needle deflection as the defect is approached, no needle deflection when the operator is immediately above the defect, and a decreasing needle deflection as the operator walks away from the defect (Fig. 9.26). It is claimed that defects can be located with an accuracy of 0.1 to 0.2 m, which represents a major advantage in minimizing the work of subsequent digs when corrective action has to be taken.

An additional feature of the DCVG technique is that defects can be assigned an approximate size factor. Sizing is most important for identifying the most critical defects and prioritizing repairs. Leeds and Grapiglia15 have provided details on the sizing procedure. An empirically based rating based on the so-called %IR value has been adopted in general terms as follows:

_ 0 to 15%IR ("small"): No repair required usually.
_ 16 to 35%IR ("medium"): Repairs may be recommended.
_ 36 to 60%IR ("large"): Early repair is recommended.
_ 61 to 100%IR ("extra large"): Immediate repair is recommended.

To establish a theoretical basis for the %IR value, the pipeline potential measured relative to remote earth at a test post must be considered.

This potential (V_t) is made up of two components:

$$V_t = V_i + V_s$$

where V_i is the voltage across the pipe to soil interface and V_s is the voltage between the soil surrounding the pipe and remote earth. The %IR value is defined as

$$\%\mathrm{IR} = \frac{V_s}{V_t}$$

Essentially the pipe-to-soil interface and the soil between the pipe and remote earth can be viewed as two resistors in series, with a potential difference across each of them. Although *Vi* cannot be measured easily in practice, *Vs* can be measured relatively easily with the DCVG instrumentation (one reference electrode is initially placed at the defect epicenter, and the voltage change is then summed as the electrodes are moved away from the epicenter to remote earth). In practice, the *Vs* value measured at a test post has to be extrapolated to a value at the defect location. Two test post readings bracketing the defect location and simple linear extrapolation are usually employed.

For effective protection of the defect by the CP system, the *Vs/Vt* ratio should be small. The overall shift in pipeline potential due to the application of CP should be manifested by mainly shifting *Vi,* not *Vs.* Higher %IR values imply a lower level of cathodic protection.

Because the DCVG technique can be used to determine the direction of current flow in the soil, a further defect severity ranking has been proposed. As indicated in Fig. 9.1, current will tend to flow to a defect under the protective influence of the CP system. Corrosion damage (anodic dissolution) at the defect has an opposite influence; it will tend to make current flow away from the defect. Using an adaptation of the DCVG technique, it has been claimed that it is possible to establish whether current flows to or from a defect, with the CP system switched
ON and OFF in a pulsed cycle.

Advantages and limitations.

Fundamentally, the DCVG technique is particularly suited to complex CP systems in areas with a relatively high density of buried structures. These are generally the most difficult survey conditions. The DCVG equipment is relatively simple and involves no trailing wires. Although a severity level can be identified for coating defects, the rating system is empirical and does not provide quantitative kinetic corrosion information. The survey team's rate of progress is dependent on the number of coating defects present.

Terrain restrictions are similar to the CIPS technique. However, it may be possible to place the electrode tips in asphalt or concrete surface cracks or in between the gaps of paving stones.

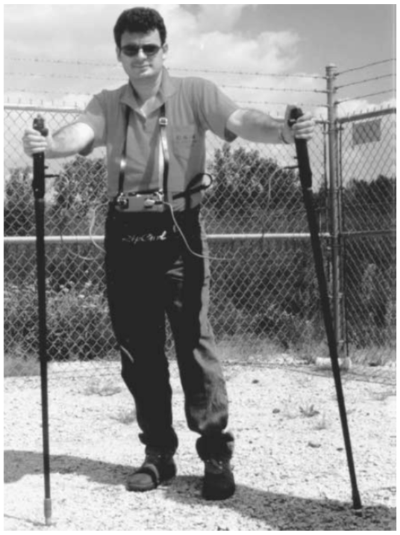


Figure 9.25 DCVG measuring equipment.

Corrosion coupons.

Corrosion coupons connected to cathodically protected structures are finding increasing application for performance monitoring of the CP system. Essentially these coupons, installed uncoated, represent a defect simulation on the pipeline under controlled conditions. These coupons can be connected to the pipeline via a test post outlet, facilitating a number of measurements such as potential and current flow.

A publication describing an extensive coupon development and monitoring program on the Trans Alaska Pipeline System serves as an excellent case study. This coupon monitoring program was designed to assess the adequacy of the CP system under conditions where techniques involving CP current interruption on the pipeline were impractical.

Although the coupon monitoring methodology is based on relatively simple principles, significant development efforts and attention to detail are typically required in practice, as this case study amply illustrates.

Methodology.

Perhaps the most important consideration in the installation of corrosion coupons is that a coupon must be representative of the actual pipeline surface and defect. The exact metallurgical detail and surface finish as found on the actual pipeline are therefore required on the coupon. The influence of corrosion product buildup may also be important. Furthermore the environmental conditions of the coupon and the pipe should also be matched (temperature, soil conditions, soil compaction, oxygen concentration, etc.). Current shielding effects on the bonded coupon should be avoided.

Several measurements can be made after a coupon-type corrosion sensor has been attached to a cathodically protected pipeline. ON potentials measured on the coupon are in principle more accurate than those measured on a buried pipe, if a suitable reference electrode is installed in close proximity to the coupon. The potentials recorded with a coupon sensor may still contain a significant IR drop error, but this error is lower than that of surface ON potential measurements. Instant-OFF potentials can be measured conveniently by interrupting the coupon bond wire at a test post. Similarly, longer-term depolarization measurements can be performed on the coupon without depolarizing the entire buried structure. Measurement of current flow to or from the coupon and its direction can also be determined, for example, by using a shunt resistor in the bond wire. Importantly, it is also possible to determine corrosion rates from the coupon. Electrical resistance sensors provide an option for in situ corrosion rate measurements as an alternative to weight loss coupons.

The surface area of the coupon used for monitoring is an important variable. Both the current density and the potential of the coupon are dependent on the area. In turn, these two parameters have a direct relation to the kinetics of corrosion reactions.

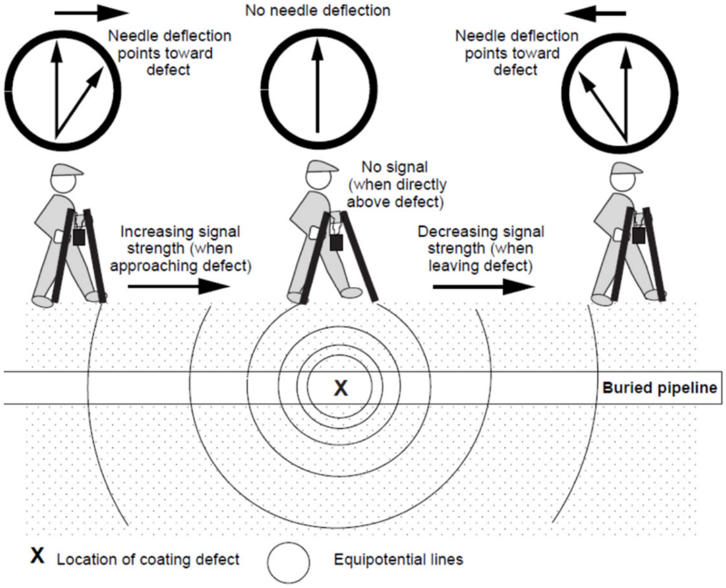


Figure 9.26 DCVG methodology (schematic).

Advantages and limitations.

A number of important corrosion parameters can be conveniently monitored under controlled conditions, without any adjustments to the energized CP system of the structure. The measurement principles are relatively simple. It is difficult (virtually impossible) to guarantee that the coupon will be completely representative of an actual defect on a buried structure. The measurements are limited to specific locations. The coupon sensors have to be extremely robust and relatively simple devices to perform satisfactorily under field conditions.

Annex A

Material Properties and Material Testing

Structural Forms of Steel

Steel is iron with more than 0% carbon but less than approximately 2% carbon. Steel behaves very differently as the amount of carbon increases from 0 % to 2 %. Cast iron contains more than 2 % carbon (up to approximately 6%).

Steel with less carbon is more flexible (ductile) than high carbon steel, but is also weaker. Carbon increases strength, hardness and brittleness.

Structural forms of steel are commonly classified by the amount of carbon in steel. Steel that has very little carbon is called ferrite. Steel that has approximately 0.8% carbon is called pearlite. Steel that has a carbon content above 0.8% contain some cementite. All three of these forms of steel –ferrite, pearlite, and cementite- represent the material at room temperature.

Steel that is heated to elevated temperature is called austenite. When austenite is cooled from upper temperature, it is transformed into other structures (such as ferrite, pearlite, and cementite).

Ferrite

Ferrite is almost pure iron. It has little tendency to dissolve carbon when carbon is added. Therefore, little carbon is in ferrite. Since carbon gives the steel the ability to become strong and hard, ferrite is a very weak steel. Ferrite exists at low temperature only, and it is magnetic.

Cementite

Cementite (also called iron carbide), is actually a compound of iron and carbon. Its chemical formula is Fe_3C. Pure cementite contains 6.67% carbon by weight. However, different amounts of cementite are present in steel that contains between 0.8% and 2.0% carbon.

As the percentage of carbon increases, more and more cementite are present. At 6.67% carbon, the entire mixture is cementite. Bellow approximately 2% carbon, the alloy is still considered steel; above that percentage, it becomes cast iron.

Cementite exists at room temperature, and it is magnetic. After heat treatment. Cementite can become very strong and hard.

Pearlite

Pearlite is a mixture of cementite and ferrite. It exists at room temperature and is magnetic. Under microscope, pearlite appears as a series of layers, resembling an aerial view of newly plowed fields. See figure A- 2. The black ridges are cementite and the white are ferrite. Thus, pearlite is made up of alternating layers of ferrite and cementite. In 0.8% carbon, the ferrite and cementite are sufficiently balanced so the entire microscopic view contains ridges.

If there is less than 0.8% carbon, the steel will be a mixture of ferrite and pearlite, and only contain parts of the view will appear as ridges. If the steel has more than 0.8% carbon, it will be a mixture of cementite and pearlite.

Austenite

Austenite is the structural form of steel that occurs only at elevated temperature. When steel is heated to an elevated temperature and becomes austenite. If it is slowly cooled back to room temperature, steel becomes ferrite, pearlite, or cementite. Refer to figures A-1, A-2, & A-3.

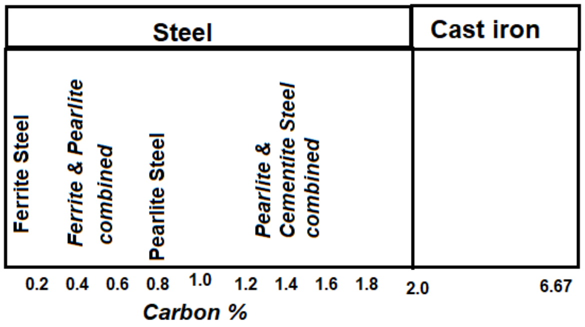


Fig. A-1. Structural forms of steel.

Fig. A-2. Pearlite (left) – Ferrite and pearlite (right).

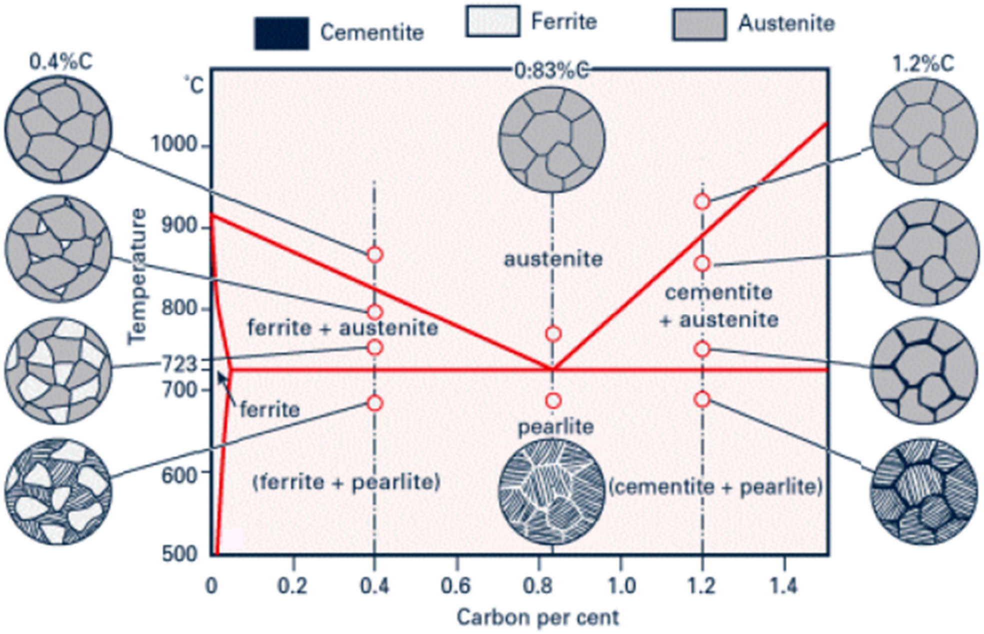


Fig. A-3. Iron carbon phase diagram].

Types of steel

Carbon Steel: (plain carbon steel)

The most common type of steel (90%).

Contains few other alloys.

Less expensive.

Classified into (Low, Medium, and high carbon steel)

Carbon steel is by far the most commonly used material. Carbon steel is essentially all iron, with a small amount (up to a few tenths of one percent) of carbon. Carbon steel is relatively inexpensive, easy to weld, and a “forgiving” material. Its properties are predictable, it rarely fails without warning, and it is strong in service below 1000°F. However, mild carbon steel is normally limited to 800°F because of degradation (called *graphitization) due to the breakdown of iron carbide* after long periods at elevated temperatures. Further, at 950°F, carbon steel is subject to excessive oxidation when exposed to air.

Low Carbon Steel:

Has the ability to become hard and strong like other steel. However, because it does not become very hard, it is easier to machine and work with in the manufacturing plants. Fence wire, Auto bodies, Storage Tanks, large pipe and various types of buildings, bridges and ships.

Low –Carbon Steel
• 0.05-0.35 % Carbon
• Comparatively less strength
• Comparatively less hardness
• Easy machining and forming
• Least expensive
• Largest quantity produced

Table. A-1. Low carbon steel specifications.

Medium Carbon Steel:

Can be heat treated to become more hard and strong. Used in forgings and high strength casting. Applications include wheels, axels, and gears.

Medium –Carbon Steel
• 0.35-0.5 % Carbon
• Hard and strong after heat treating
• More expensive than low carbon steel

Table. A-2. Medium carbon steel specifications.

High Carbon Steel:

Can be heat treated to become more hard and strong. The disadvantage of high hardness in steel and the potential of cracking or becoming very brittle during the hardening process. Used for making tools, knives, railroad wheels.

high –Carbon Steel
• 0.5-1.5 + % Carbon
• Hard and strong after heat treating
• More expensive than low and medium carbon steel

Table. A-3. High carbon steel specifications.

Alloy Steel:

A grade of steel in which one or more alloying elements have been added in larger amounts to produce special properties. They are more expensive. Their types are; low alloy structural, high, stainless ….etc.

Carbon Steel	Alloy Steel
Lower cost - Greater availability	Higher strength – Better wear – Toughness - Special high temperature behavior – Better corrosion resistance – Special electrical properties

Table. A-4 Carbon steel and Alloy steel comparison

Stainless Steels and Nonferrous Materials

Above 11–12% chrome, the alloys form the general class of "stainless steels." As a very rough general rule, the more money you are willing to spend in adding more alloy (more chrome, nickel, molybdenum) the more enhanced corrosion resistance and/or high temperature resistance you can achieve. A steel with more alloy than iron (for example, the nickel-based "Inconels" or "Hastelloys") is a member of the "nonferrous" class of materials.

Steel Alloying Elements

Carbon, Manganese and nickel are added to steel to increase strength. To obtain better corrosion resistance or resistance to atmospheric conditions, chromium or copper may be added. If lead or sulfur is added, the steel will have better machinability. For better physical properties at high temperature Tungsten or molybdenum are recommended.

Alloying Element	Effect on steel	Alloying Element	Effect on steel
Carbon	Hardness, strength, wear	Chromium	Corrosion resistance, hardenability
Lead	Machinability	Manganese	strength, hardenability, more response to heat treatment
Aluminum	De-oxidation	Nickel	Toughness, strength
Silicon	De-oxidation, hardenability	Tungsten	High temperature strength, wear
Molybdenum	High temperature strength, hardenability	Sulfur	Machinability
Titanium	Elimination of carbide precipitation	Vanadium	Fine grain , toughness
Cooper	Corrosion resistance, strength	Phosphorus	Strength

Table A-5. Alloying elements and their effectiveness.

Steel Numbering

For example steel number (4141); (**41,** first two numbers Identifies major alloying element), (**40,** Last two numbers Identifies percentage of carbon - 4% in this case), Table. A-6. Steel numbering system

Steel Numerical Name	Key Alloy	Steel Numerical Name	Key Alloy
10XX	Carbon only	46XX	Nickel- Molybdenum
11XX	Carbon only	47XX	Nickel- Chromium- Molybdenum
13XX	Manganese	48XX	Nickel- Molybdenum
23XX	Nickel	50XX	Chromium
25XX	Nickel	51XX	Chromium
31XX	Nickel-chromium	61XX	Chromium-Vanadium
33XX	Nickel-chromium	86XX	Nickel- Chromium- Molybdenum
40XX	Molybdenum	92XX	Silicone- Manganese
41XX	Chromium- Molybdenum	93XX	Nickel- Chromium- Molybdenum
43XX	Nickel- Chromium- Molybdenum	94XX	Nickel- Chromium- Molybdenum- Silicone
44XX	Manganese- Molybdenum	98XX	Nickel- Chromium- Molybdenum

Metal Grain Size.

The size of the grains of the metal affects metal properties. The heat treatment of the metal determines the grain size.

The following steps would be used to increase the grain size:

– use a higher austenitizing temperature, hold the austenitizing treatment longer, to allow more time for the grains to grow, slowly cool the steel

Large grain size improves some high temperature strength properties (creep), but in most cases a fine grain size is what we really want. To achieve a finer grain size, we would control the austenitizing temperature and time and rapidly cool the steel.

Heat Treating Steels

Steels have a wide range of properties, depending upon how they were formed in the mill, and how they were fabricated into the final product. Virtually all steels start “life” when the mill heats them above approximately 1650°F to develop the high temperature austenite phase. Upon cooling, the austenite transforms to the stable lower temperature ferrite-phase structure.

As carbon steel cools from liquid, it transforms its crystalline structure. More importantly, as carbon steel cools below 1330°F (721°C), it can form a number of different arrangement and types of phases with various iron carbide content and distributions, depending on carbon content and cooling rate.

Heat treatment is a metallurgical process that involves heating or cooling. Heat treatment variations such as quenching, annealing, etc., are all chosen by metallurgists to give specific and predictable properties.

There are many types of heat treatment process like heating, Quenching, annealing, normalizing, tempering and surface hardening.

The practical aspect of this is to be aware that carbon steel, a common material, can be altered during fabrication, subsequent heat-treating and welding operations

The same basic principles apply to alloys. Typical considerations when heat treating and welding include the following:

- Mechanical strength is very important in many machinery applications.
- Weldability is important in vessels, tanks, and piping where shop and field fabrication are common.
- Resistance to brittle fracture (toughness) is critical in low temperature applications, thick wall materials, and services that become saturated with hydrogen.
- Ductile (not hard) steels and welded areas are needed in services subject to wet sour service.

Cooling Rates: Annealing, Normalizing, and Quenching.

A steel is annealed by slowly cooling it from the austenitizing temperature — typically by leaving the steel in the turned-off heat treating furnace.

A moderately fast cooling rate is achieved by normalizing the steel, whereby the steel is cooled in air from the austenitizing temperature.

A very fast cooling rate is obtained by dipping the steel or spraying it with oil — this very rapid cooling is called “quenching.”

Quenching the steel produces high strength and hardness, but also high residual stress and poor toughness. Therefore, for many applications, the steel is given a follow-up heat treatment at 1000 - 1400°F, depending upon the steel or alloy. This is called “tempering.” Tempering reduces strength somewhat, but it greatly improves the ductility and toughness of the steel.

Quenching

Quenching is a controlled cooling process that causes metals to harden. There are several different quenching mediums used to cool metals, including water , Brine , Oil , air , molten salt, and sand.

Water or Brine Quenching	Oil Quenching	Air Quenching
Most drastic	Less drastic	Least drastic
Most hardness and strength	Less hardness and strength	Least hardness and strength
Least resistant to deterioration and cracking	More resistant to deterioration and cracking	Most resistant to deterioration and cracking

Table A-7 . Quenching technique comparison.

Annealing and Normalizing

Annealing is a controlled cooling process at slow cooling rate to attain a high degree of softness.

Normalizing is like annealing but cooling is at relatively higher rate.
They are used to:

- To make the material easier to machine
- To produce the material that is easier to form
- To relieve internal stresses.
- To refine the crystal structure of a part.

Annealing and normalizing generally produce a material that is less hard and less strong. They make the material less brittle and more ductile. Annealing and Normalizing also reduce the amount of internal stresses in a material. This in turn, reduces the tendency of a material to distort or crack.

Annealing and Normalizing	Quenching
• Slow cooling process • Softens and weakens metal • Cause ductility • Reduce internal stress • Helps prevent cracking and distortion	• Rapid cooling process • Hardness and strengthen metal • Cause brittleness • Cause internal stress • Increase chances of cracking and distortion

Table A-8. Quenching and (Annealing and Normalizing) comparison.

Full Annealing	Normalizing	Air Quenching	Oil Quenching	Water Quenching	Brine Quenching
←	Softer	←	Harder	→	→
←	Less stronger	←	Stronger	→	→
←	More ductile	←	More brittle	→	→
←	Less internal stress	←	More internal stress	→	→
←	Less distortion	←	More distortion	→	→
←	Less Quenching	←	More cracking	→	→

Table. A-9. Effects of Annealing, normalizing, and quenching.

Tempering

Tempering is defined as heating the steel to a certain temperature and then cooling it to increase ductility of the steel.

Material properties

Mechanical properties of steel depends on:

1. Carbon content
2. Cooling rate
3. Alloys content
4. Heat treatment

Hardness, ductility and strength are the three properties discussed most often in metallurgy. These three are related to one another. Generally as hardness and strength increase, ductility decreases and the material becomes more brittle.
Since Strength, Hardness and Ductility are desired properties in metals; researchers are working on adding certain alloys to steel to improve hardness and strength without decreasing Ductility.

Metal properties include:

- **Tensile strength.** The limit of the materials ability to carry stress (loads) without failure.
- **Yield strength.** The limit of the materials ability to carry stress (loads) without significant deformation.
- **Strain.** The amount a material deforms compared to its original dimensions. *Elastic strain is recovered when the stress is removed and the material returns to its original dimension; plastic strain results in a permanent deformation.*
- **Ductility.** The ability to deform under stress.
- **Toughness.** The ability of a material to resist brittle fracture in the presence of a notch. Usually measured by impact testing. (See *Brittleness, below.)*
- **Hardness.** Resistance to surface penetration. In general, the harder the material, the more resistance to wear.
- **Thermal stability.** The ability to operate without internal metallurgical changes.
- **Resistance to corrosion.** The ability to operate in various chemical environments without decay of the metal.
- **Resistance to creep.** The ability to operate under stress at high temperature without significant permanent deformation. (Important in furnace tubes and other high temperature applications.)
- **Brittleness.** The tendency to shatter under load without much strain.
- **Weldability.** The ability to be welded without resulting defects such as cracking or excessive hardness (frequently leading to subsequent cracking).
- **Fatigue resistance.** The ability to resist cyclic loads without failure.

Hardness

Hardness is a measure of resistance to deformation (penetration).

There are many hardness measuring instrumentation, methods, and units. All depending on the same technique with different penetration element and measurements such as:

Brinell hardness tester

Vickers hardness tester

Rockwell hardness tester

In all methods the penetrator is pressed into the sample by an accurately controlled test force. The force is maintained for a specific dwell time, normally 10 - 15 seconds. After the dwell time is complete, the penetrator is removed leaving a round indent in the sample. The size of the indent is determined optically by measuring two diagonals of the round indent using either a portable microscope or one that is integrated with the load application device. Equations are used to obtain the hardness number from the depth or area of penetration.

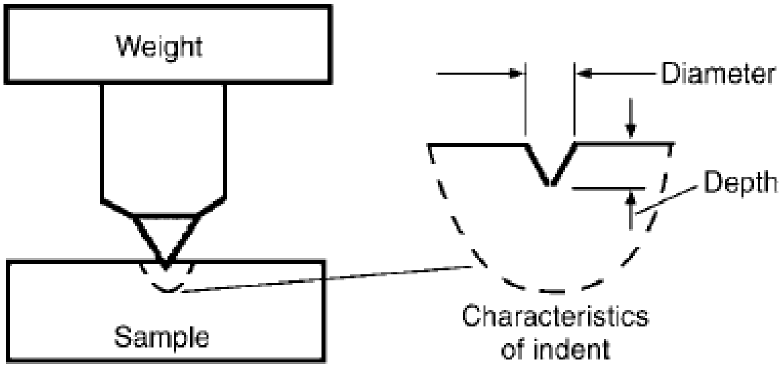


Fig. A-4. Penetrator (Indenter) for Hardness test.

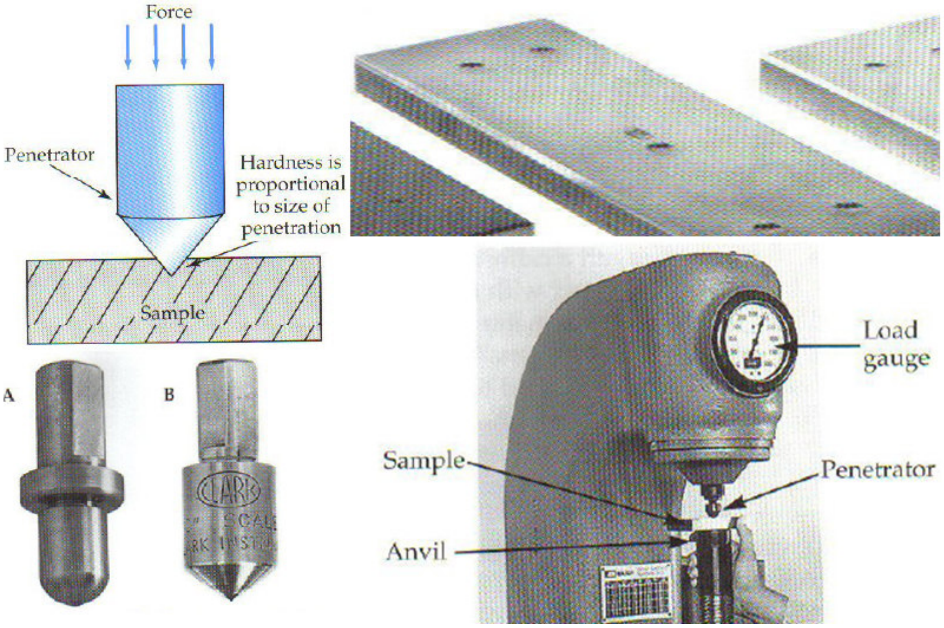


Fig. A-5. Hardness test.

Method	Basis	Penetrator	Load
Rockwell	Depth of penetration	Diamond point 1/16” Ball or 1/8 “ Ball	60-100-150 Kg
Rockwell superficial	Depth of penetration	Diamond point 1/16” Ball or 1/8 “ Ball	15-30-45 Kg
Brinell	Area of penetration	10 mm Ball	500-3000 KG

Table. A-10. Comparison between hardness testing methods.

Brinell Hardness (BHN)	Vickers Hardness (HV)	Rockwell Hardness (HRB)
95	100	56.2
105	110	62.3
114	120	66.7
124	130	71.2
133	140	75.0
143	150	78.7
152	160	81.7
162	170	85.0
171	180	87.1
181	190	89.5
190	200	91.5

Table. A-11. Example of hardness Conversion Table

Increases in hardness values (which results from an increase in C content) will usually be associated with increases in ultimate tensile and yield strength, but there will be reductions in ductility (elongation) expressed as reduction of area and elongation.
Usually in metals, a smaller grain size will lead to some increase in hardness and tensile strength.

Cold Rolled Steel (unquenched)	150 BHN
Quenched Steel	600 BHN
Stainless Steel	150 BHN
Cast Iron	200 BHN
Wrought Iron	100 BHN
Aluminum	100 BHN
Annealed Copper	45 BHN
Brass	120 BHN
Magnesium	60 BHN

Table. A-12. Brinell hardness number for different types of metals

Ductility and Brittleness.

Ductility is the ability of material to stretch without breaking. Usually ductility is more desirable than brittleness. Ductility is measured by percent elongation. Low carbon steel, Aluminum and rubber bands are ductile. Cast iron, glass and uncooked spaghetti are brittle.

Tensile strength

Stress is the amount of effort attempting to fracture an item, the ability to resist that stress is known as strength. If the stress on a part exceeds its strength, the part will break. Stress = force per square unit area resisting that force.

Tensile Strength Testing

Uses an extensometer to apply measured force to a test specimen. The amount of extension can be measured and graphed.

Variables such as strain, stress, elasticity, tensile strength, ductility and shear strength can be gauged. Test specimens can be round or flat

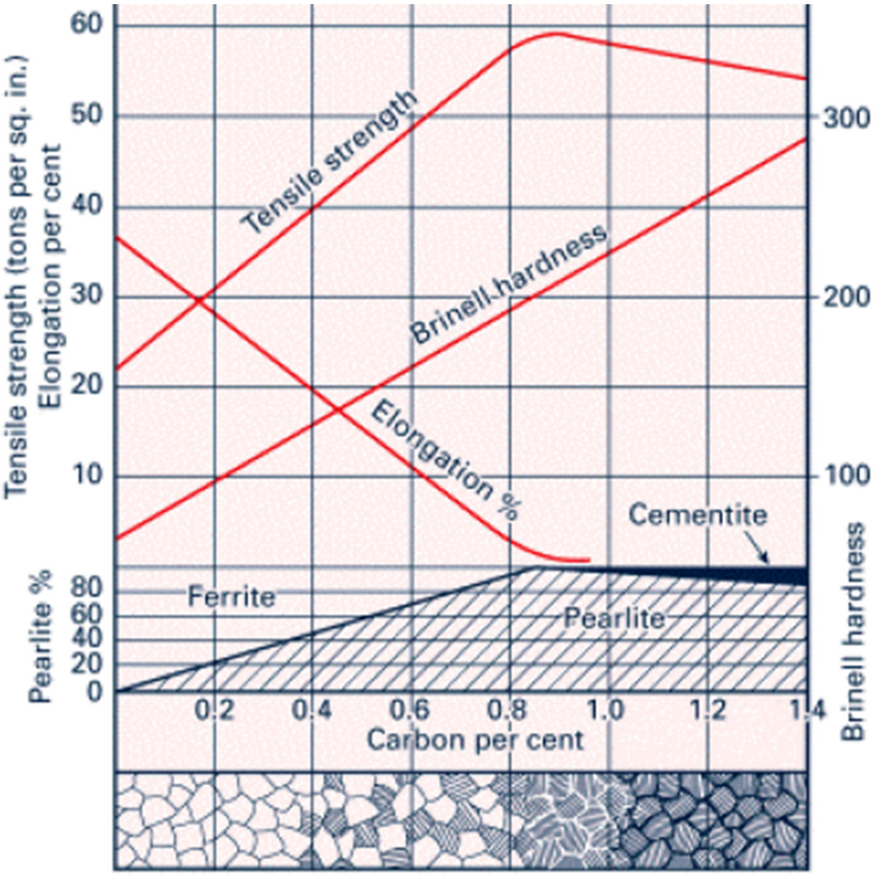


Fig A- 6. Relation between grain size, Tensile strength, hardness, elongation (ductility), and carbon percent.

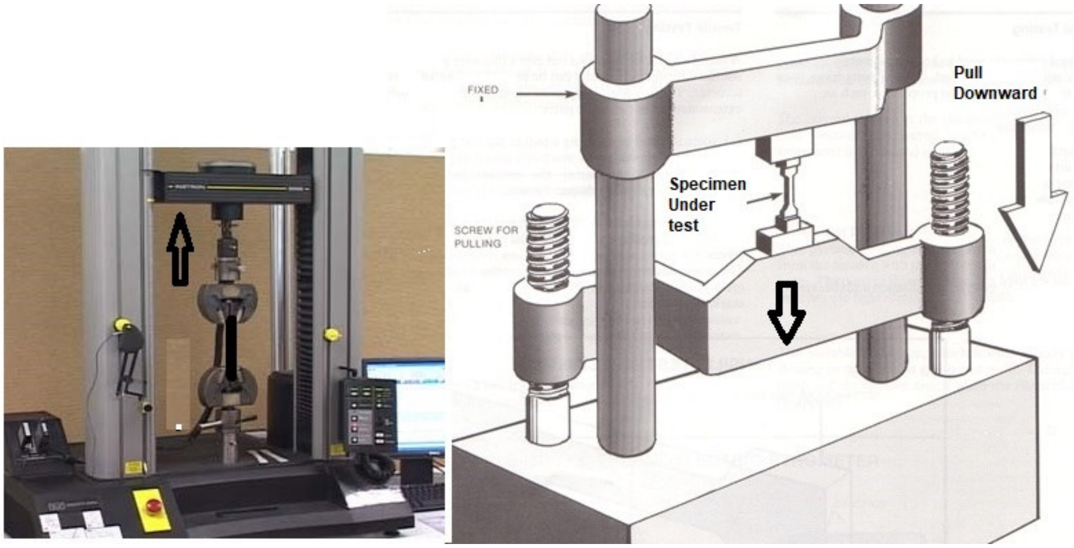
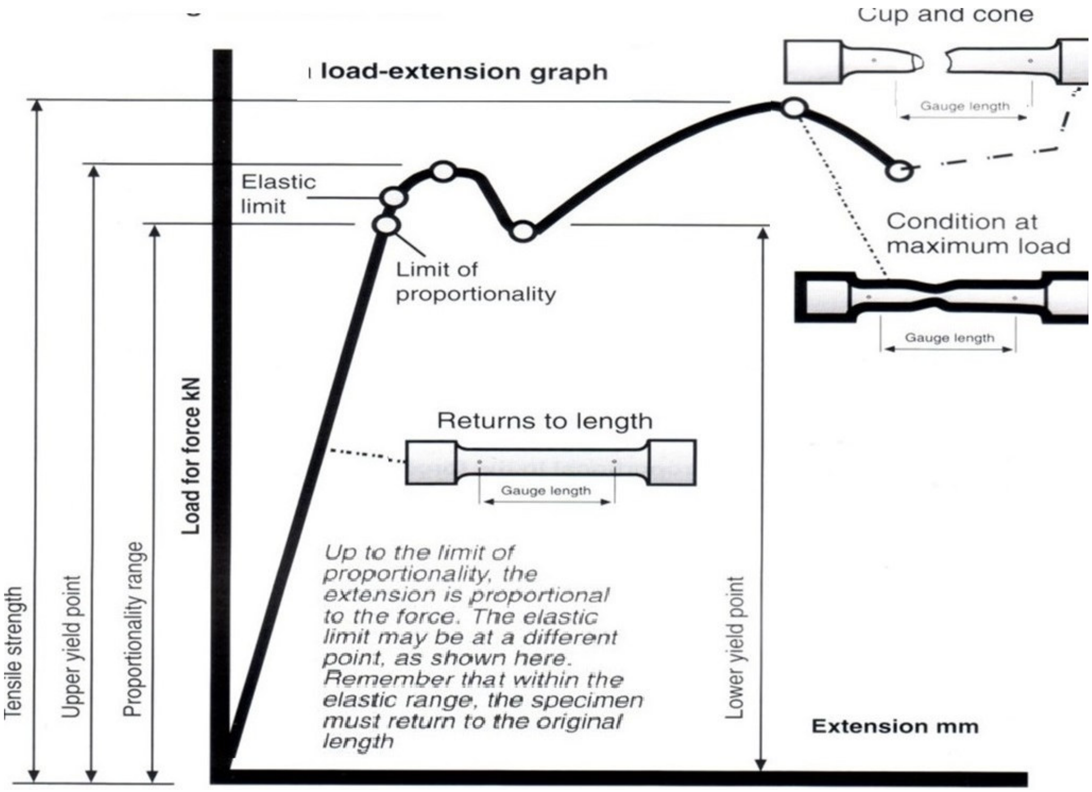


Fig. A-7. Extensometers for Tensile stress test.



Up to the limit of proportionality, the extension is proportional to the force. The elastic limit may be at a different point, as shown here. Remember that within the elastic range, the specimen must return to the original length

Fig. A-8. Strain - stress graph.

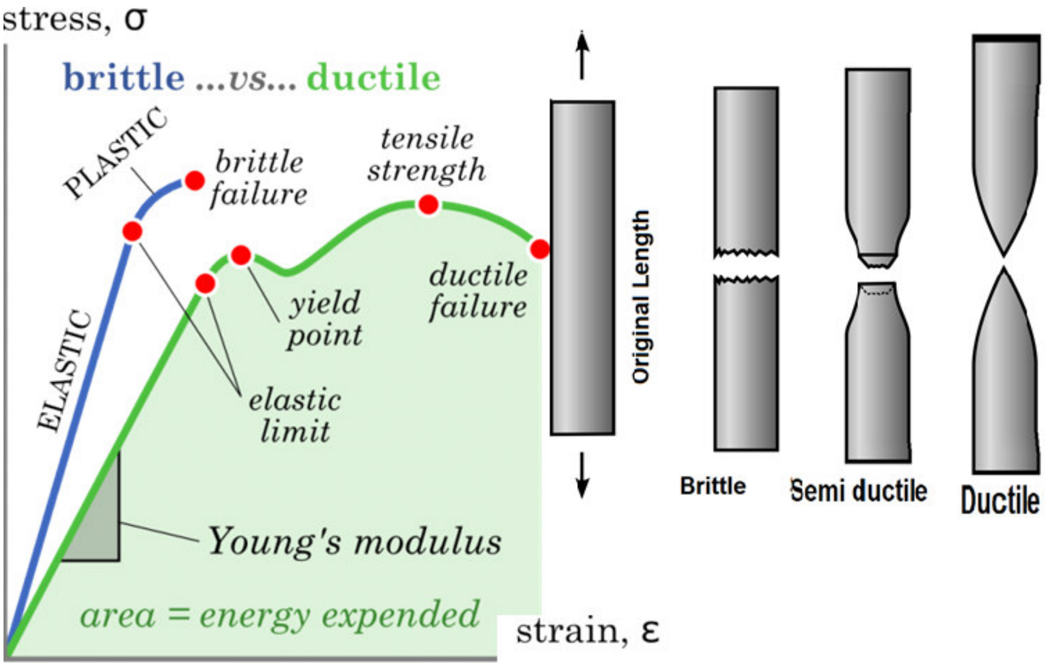


Fig. A-9. Brittle versus ductile strain versus stress graph.

Material	Tensile Strength (psi)	Hardness (BHN)
Steel	60,000 – 200,000	150 - 620
Cast Iron	20,000 – 100,000	140 – 325
Aluminum	20,000 – 60,000	50 – 110
Copper	30,000 – 60,000	40
Bronze	365,000 – 130,000	100-200
Brass	30,000 – 100,000	50 -160

Table. A-12. Tensile strength values for different types of metals

Glossary of Commonly Used Metallurgical Terms

Brittle Fracture. Fracture of metal at relatively low stress levels without significant deformation

Carbide precipitation. The combination of carbon with a metallic element to form a compound. In stainless steel, carbide precipitation can happen at elevated temperatures (including during welding), particularly at grain boundaries. Carbide precipitation can result in degradation of stress corrosion, cracking resistance or strength.

Crystallization. The separation of the solid phase from the liquid phase. Incorrectly used to describe a fatigue failure. A fatigue failure is not crystallization because the failed metal is crystalline before it fails.

Embrittlement. Severe loss of resistance to brittle fracture due to a chemical or mechanical property change.

Graphitization. Decay of carbides to carbon and iron in steel at elevated temperatures causing a loss in strength.

Heat affected zone (HAZ). The area next to a weld that is not melted but has a change in properties from the heat of welding.

Hydrogen embrittlement. Loss of ductility due to the absorption of hydrogen in the metal.

Inclusions. Nonmetallic material contained in a solid metal.

Martensite. The hard brittle structure formed by rapidly cooling steel from high temperatures.

Modulus of elasticity. The relation between stress and strain in the elastic range.

Microstructure. The structure of a material revealed by viewing a polished and etched metal under the microscope.

Recrystallization. Heating in a temperature range where fine grains form. The formation of strain free grains results from cold worked material or a change in crystal structure at high temperature.

Residual stress. The stress left in a material after all loads are removed. Commonly caused by welding or cold working.

Strain hardening. The increase in hardness (strength) because of permanent deformation

Stress relief. Heating a material to a temperature, holding it at that temperature for a length of time, and then followed by slow cooling so that most of the residual stresses are removed.

Annex B

Microbiologically induced corrosion

Introduction

This type of corrosion is caused by bacterial activities.

The bacteria produce waste products like CO_2, H_2S, and organic acids that corrode the pipes by increasing the toxicity of the flowing fluid in the pipeline. The microbes tend to form colonies in a hospitable environment and allow enhanced corrosion under the colony. The formation of these colonies is promoted by neutral water especially when stagnant. Numerous reports of the presence of microbes in reservoirs had been published. Lazar et al, found abundant microbial flora indigenous in oil field formation waters, which included species of Bacillus, Pseudomonas, Micrococcus, Mycobacterium, Clostridium, and Escherichia. Escherichia is reported to contain hydrogenase, an enzyme that utilizes molecular hydrogen and may be associated with cathodic hydrogen depolarization, causing corrosion of steel casings and pipes in the oil field.

Microbiologically induced corrosion (MIC) is recognized by the appearance of a black slimy waste material or nodules on the pipe surface as well as pitting of the pipe wall underneath these deposits.

Figures B-1 and B-2 represent the scanning electron microscopy (SEM) photograph of esulfovibrio desulfuricans and a pipeline affected by MIC corrosion, respectively.

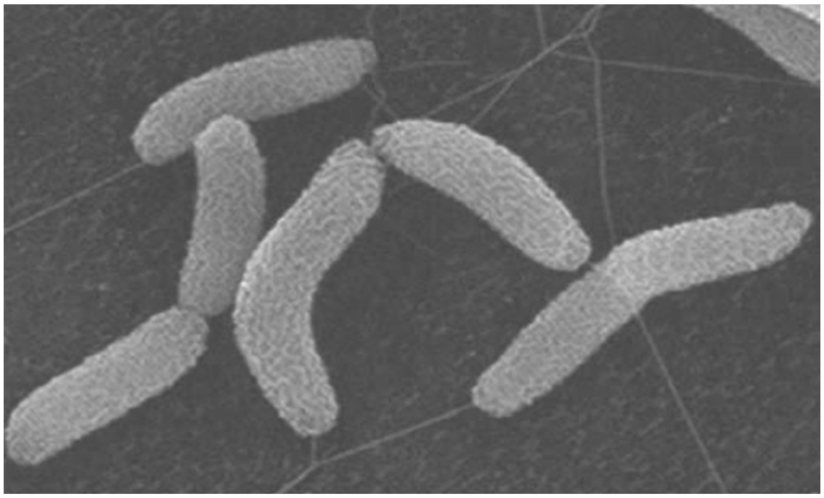


Figure B-1 SEM photograph of D. desulfuricans.

Microbiological activity and redox potential

The soils may become more aggressive in the presence of microbiological activity. Commonly observed bacteria present in the soils are sulfate reducing (Desulpho Vibrio desulpharicans). This bacterium consumes hydrogen and reduces sulfates to sulfide.

$$SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O$$

The product is hydrogen sulfide, which reacts with steel and produces black FeS. Under anaerobic conditions, the reactions are:

$$4Fe + SO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$$

It is clear that hydrogen is consumed and H_2S is formed. The corrosion acceleration by bacteria is twofold. Hydrogen consumption accelerates the corrosion by decreasing the cathodic polarization. Also, iron sulfide formation increases the corrosion rate by forming a galvanic couple with bare steel. Bacteria survive by consuming certain types of adhesives. The favorable conditions for prompting bacteriological activity include a temperature range of about 35-40 ^{0}C and pH between 5.5 and 8.5.

The presence of bacterial activity can be qualitatively established by placing a few drops of hydrochloric acid on the corrosion products. The evolution of H_2S indicates the existence of anaerobic bacteriological activity. Sulfate reducing bacteria and sulfur oxidizing bacteria (Thiobacillus, thioxidants) may also exist in an aerated environment. These bacteria consume oxygen and oxidize sulfides to sulfuric acid (H_2SO_4) during their

metabolic activity. They can produce sulfuric acids with concentrations as high as 10% (i.e., pH 0.5). In general, the microbiological activity can increase the corrosion rate by:
(a) Depolarizing the cathodes.
(b) Creating corrosion products that can be effective cathodes.
(c) Causing damage to coatings and exposing structure to environments.

SRB occur naturally in surface waters, including seawater. Bacteria accumulation can lead to pitting of steel, and the buildup of H_2S increases the corrosiveness of the water, thus increasing the possibility of hydrogen blistering or sulfide stress cracking.

Figure 11 Pipeline affected by MIC corrosion.

References

1- NACE- Basic Corrosion Course . 2014

2- Corrosion, and water technology For petroleum producers, L.W.Jones, OGCI publications, second printing 1992.

3- Applied water technology, dr/ Patton, second edition 1995.

4- An introduction to corrosion, and protection of metals, Gosta Wranglen, prof. dr/ Techn, Chpman and Hall ltd 1985.

5- Pipe line corrosion and cathodic protection, Marshall E.Parker, third edition.

6- Corrosion control in petroleum production,TPC 5, NACE.

7- NACE standard RP-01-69, MR01-75, RP-05-75, RP-01-75.

8- Control of pipeline corrosion, A.W.PEABODY, NACE,2nd edition.

9- CORROSION AND CORROSION CONTROL - An Introduction to Corrosion Science and Engineering. 4th edition. R. Winston Revie. 2008

10- CORROSION ENGINEERING Principles and Solved Problems - BRANKO N. POPOV- 2015

11- Corrosion Prevention and Protection Practical Solutions- V. S. SASTRI- 2007

12- Fundamentals of CORROSION - Mechanisms, Causes, and Preventative Methods -Philip A. Schweitzer - 2009

13- Principles of corrosion engineering and corrosion control= Zaki Ahmed – 2006

14- Metallurgy Fundamentals. D.A.Brandt. J.C.Warner. 2005 Goodheart-Willcox.

15- DOE FUNDAMENTALS HANDBOOK -MATERIAL SCIENCE- 1993.

16- Handbook of Corrosion Engineering - Pierre R. Roberge -2000