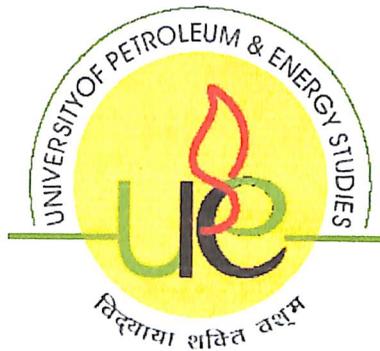


**“DESIGN OF CATHODIC PROTECTION  
SYSTEM FOR A CROSS COUNTRY PIPELINE”**

**By  
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**College of Engineering  
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MAY 2008**

# **DESIGN OF CATHODIC PROTECTION SYSTEM FOR A CROSS COUNTRY PIPELINE**

**A thesis submitted in partial fulfilment of the requirements for the Degree of  
Master of Technology  
(Pipeline Engineering)**

**By  
Hitashu Jain**

**Under the guidance of**

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This is to certify that the work contained in this thesis titled "Design of Cathodic Protection System For a Cross Country Pipeline" has been carried out by Mr. Hitashu Jain under my/our supervision and has not been submitted elsewhere for a degree.

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# ABSTRACT

This project deals with the design of cathodic protection system for Koyali Ratlam of 260 Km long 16" O.D. pipeline. The main function for pipeline is to transport hydrocarbon fluid such as crude oil and natural gas from one location to another location. But, the main problem for pipeline is corrosion attack.

Corrosion is defined as the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material

- Cathodic protection prevents corrosion by converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites by supplying electrical current (or free electrons) from an alternate source CP is often fully effective in preventing any severe corrosion and has a corrosion reducing effect.

This project is focused in design of external corrosion prevention of cross country pipeline using the cathodic protection system based on sacrificial anode and makes a parametric analysis for the CP method to determine parameters that affecting the design such as soil resistivity, protective potential, coating, anode resistance, environment..

The methodology consists of data analysis, calculation and the sensitivity analysis of parameters involved in the design. From the sensitivity analysis found that the major parameters affecting the CP design are soil resistivity, current requirement, anode requirement, weight of anode, current delivering capacity of anode, and coating efficiencies.

The analysis and the concentration of these sensitivity parameters can be implemented to design the excellent CP system

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# NOMENCLATURES

$OD$  - Outside Diameter

$ID$  - Pipe inside Diameter

$I_{corr}$  - Corrosion current

$E_{corr}$  - Corrosion potential

$E_1$  - Rate Potential at point 1

$I_1$  - Cathodic Current at point 1

$I_2$  - Cathodic Current at point 2

$\Delta I$  - Changes value of cathodic current

$A_w$  - Wetted parameter of pipe

$I_c$  - Cathodic Current Demand

$CE$  - Coating Efficiencies

$I'$  - Required current

$A$  - Total area of pipe

$R_T$  - Circuit Resistance

$R_c$  - Structure to Electrolyte resistance

$R_a$  - Anode to structure resistance

$W$  - Minimum net anode mass

$W'$  - Weight of single anode

$E$  - Anode consumption rate

$B$  - Mean coating breakdown factor

$L$  - Total length of pipeline requiring protection

Anode utilization factor  $\mu$

$J$  - Mean current density

$A_s$  - Pipe surface between anodes

$r$  - Anode resistance

$\rho$  - soil resistivity

$A$  - Anode's exposed surface area

$V$  - Potential difference between the anode and the bare steel

$ID'$  - anode inner diameter

$T$  - Anode thickness

$L$  - Anode length

$L'$  - Design life of pipeline

$\hat{I}$  - Length backfill column

$D$  - Diameter backfill column

# ABBREVIATIONS

CP	Cathodic Protection
DNV	Det Norkse Veritas
DC	Direct current
FBE	Fusion Bonded Epoxy
GBSS	Gypsum-Bentonite-Sodium Sulfate
NACE	National Association of Corrosion Engineers (USA)
RP	Recommended practice
UTS	Ultimate Tensile Stress

# TERMS

## **Anode**

Electrode from which electric current flows to an electrolyte (water, soil). On the surface an oxidation process takes place, e.g. metal ions or hydroxyl ions to oxygen and water

## **Backfilling**

Covering of trenched pipeline, which may be natural (by sedimentation) or artificial (by rock dumping or by mechanically returning the seabed material removed during trenching)

## **Bend**

Curved piece of pipe, for offshore use either hot formed from induction bent line pipe joints (mother pipe) or forged items. Bends with small bending radius ( $1.5 \times ID$  or less) are also referred to as elbows, and will normally be forged. To facilitate the welding into pipeline, bends are normally provided with short, straight sections (tangent length).

## **Buckle**

Deformation of pipeline as a result of local actions or stability failure of the pipe section due to external pressure, possibly in combination with bending. The buckling may lead to water entering the pipeline (wet buckle) or not (dry buckle).

## **Cathode**

Electrode into which electric current flows from electrolyte (water, soil). On the surface a reduction process takes place, e.g. water to hydrogen and hydroxyl ions.

## **Cathodic Protection**

Reduction of corrosion rate by shifting the corrosion potential of the electrode toward a less oxidizing potential by applying an external electromotive force.

**Cathodic disbonding**

Loss of bond between barrier coating and steel substrate due to the formation of hydroxyl ions in connection with cathodic protection.

**Coal tar**

Coating material manufactured by distillation (pyrolysis) of rock coal.

**Coating yard**

Onshore facility for the application of pipe coatings and sacrificial anodes to pipe joints.

**Concrete coating**

Pipe coating of reinforced concrete, applied to increase the pipeline weight and/ or protect the steel pipe and its anti-corrosion coating against mechanical damage.

**Corrosion allowance**

Increase of the wall thickness corresponding to the expected corrosion loss, with the objective of ensuring the required wall thickness during the services life.

**Enamel**

Hot applied pipe coating consisting of bitumen or coal tar, reinforced with layers

**Epoxy paint**

Two-components paint consisting of epoxy resin and solvent.

**Galvanic Anode**

A metal, which, because of its relative position in the galvanic series, provides sacrificial protection to metals, those are more noble in the series, when coupled in an electrolyte.

**Galvanic Cathodic**

Protection System: A cathodic protection system in which the external electromotive force is supplied by a galvanic anode.

**Groundbed**

One or more anodes installed below the earth's surface for the purpose of supplying cathodic protection.

**Impressed Current Cathodic Protection System**

A cathodic protection system, which the external electromotive force is provided by an external DC power source.

**Linepipe**

Steel material for welded pipelines

**Rectifier**

A device that converts alternating current to direct current.

**Sacrificial anode**

An anode that connected to structure can offer cathodic protection while it is consumed.

# CHAPTER 1

## INTRODUCTION

### 1 Cathodic Protection

It is a method used to protect metal structures from corrosion. Cathodic protection systems are most commonly used to protect steel, water/fuel pipelines, tanks, ships and offshore oil platforms

#### 1.1 Standards

EN 12068:1999 - Cathodic protection. External organic coatings for the corrosion protection of buried or immersed steel pipelines used in conjunction with cathodic protection. Tapes and shrinkable materials

EN 12473:2000 - General principles of cathodic protection in sea water

EN 12474:2001 - Cathodic protection for submarine pipelines

EN 12495:2000 - Cathodic protection for fixed steel offshore structures

EN 12499:2003 - Internal cathodic protection of metallic structures

EN 12696:2000 - Cathodic protection of steel in concrete

EN 12954:2001 - Cathodic protection of buried or immersed metallic structures. General principles and application for pipelines

EN 13173:2001 - Cathodic protection for steel offshore floating structures

EN 13174:2001 - Cathodic protection for harbour installations

EN 13509:2003 - Cathodic protection measurement techniques

EN 13636:2004 - Cathodic protection of buried metallic tanks and related piping

EN 14505:2005 - Cathodic protection of complex structures

EN 15112:2006 - External cathodic protection of well casing

EN 50162:2004 - Protection against corrosion by stray current from direct current systems

BS 7361-1:1991 - Cathodic Protection

NACE SP0169:2007 - Control of External Corrosion on Underground or Submerged Metallic Piping Systems

NACE TM 0497 - Measurement Techniques Related to Criteria for Cathodic Protection on Underground or Submerged Metallic Piping Systems

### 1.2 Corrosion Mechanism

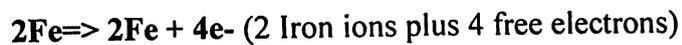
To understand cathodic protection one must first understand the corrosion mechanism.

For corrosion to occur, three conditions must be present.

1. Two dissimilar metals
2. An electrolyte (water with any type of salt or salts dissolved in it)
3. A metal (conducting) path between the dissimilar metals

The two dissimilar metals may be totally different alloys, such as steel and aluminum.

If the above conditions exist, at the more active metal surface (in this case we will consider freely corroding steel which is non uniform), the following reaction takes place at the more active sites:



The free electrons travel through the metal path to the less active sites where the following reaction takes place:



(Oxygen gas converted to oxygen ion - by combining with the four free electrons which combines with water to form hydroxyl ions)

Re-combinations of these ions at the active surface produce the following reaction, which yields the iron corrosion product ferrous hydroxide.



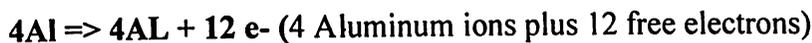
(Iron combining with oxygen and water to form ferrous hydroxide)

This reaction is more commonly explained as current flow through the water from the anode (more active site) to the cathode (less active site).

### **How Does Cathodic Protection Stop Corrosion?**

Cathodic protection prevents corrosion by converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites by supplying electrical current (or free electrons) from an alternate source. Usually this takes the form of galvanic anodes which are more active than steel. This practice is also referred to as a sacrificial system, since the galvanic anodes sacrifice themselves to protect the structural steel or pipeline from corrosion.

In the case of aluminum anodes, the reaction at the aluminum surface is:



And at the steel surface,



(Oxygen gas converted to oxygen ions which combine with water to form hydroxyl ions)

As long as the current (free electrons) is arriving at the cathode (steel) faster than oxygen is arriving, no corrosion occurs.

### **Basic Considerations When Designing Sacrificial Anode Systems**

The electrical current, which an anode discharges, is controlled by Ohm's law; that is:

$$I = E/R$$

Where:

I= Current flow in amps

E= Difference in potential between the anode and cathode in volts

R= Total circuit resistance in ohms

Initially current will be high because the difference in potential between the anode and cathode are high, but as the potential difference decreases due to the effect of the current flow onto the cathode, current gradually decreases due to the polarization of the cathode. The circuit resistance includes

both the water path and the metal path, including any cable in the circuit. The dominant value here is the resistance of the anode. For most applications the metal resistance is so small compared to the water resistance that it can be ignored. In general, long thin anodes have lower resistance than short fat anodes. They will discharge more current, but will not last as long. Therefore a cathodic protection designer must size the anodes so that they have the right shape and surface area to discharge enough current to protect the structure and enough weight to last the desired lifetime when discharging this current.

As a general rule of thumb:

Length of the anode determines how much current the anode can produce, and consequently how many Square feet of steel can be protected.

Cross Section (Weight) determines how long the anode can sustain this level of protection.

### 1.3 Fundamentals of cathodic protection

1) When dissimilar metals are in electrical or physical contact (the former through an electrolyte), galvanic corrosion can take place. The process is similar to a simple DC cell in which the more active metal becomes the anode and corrodes where as the less active metal becomes the cathode and is protected.

2) The galvanic series can be used to predict the metal which will corrode in contact with another metal, based on whether it is cathodic or anodic with respect to another

3) Virtually all modern pipelines are coated with an organic protective coating that is supplemented by cathodic protection systems sized to prevent corrosion at holidays in the protective coating

4) This combination of protective coating and cathodic protection is used on virtually all immersed or buried carbon steel structures, with the exception of offshore petroleum production platforms and reinforced concrete structures

5) Two metals--iron and zinc--separately immersed in a weak mineral acid. The chemical reactions that occur are :

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	Oxidation reaction
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	Reduction reaction
$2\text{H}^+ + \text{Fe} = \text{Fe}^{2+} + \text{H}_2$	Net reaction
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	Oxidation reaction

$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	Reduction reaction
$2\text{H}^+ + \text{Zn} = \text{Zn}^{2+} + \text{H}_2$	Net reaction

6) Both metals corrode, and both corrosion (oxidation) reactions are balanced by an equal reduction reaction, which in both cases involves the liberation of hydrogen gas from the acid environments.

7) The two corrosion reactions are independent of each other and are determined by the corrosivity of hydrochloric acid on the two metals in question.

8) If the two metals were immersed in the same acid and electrically connected, reactions for zinc would then become

$\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$	Oxidation
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	Reduction

9) Almost all of the oxidation reaction (corrosion of zinc) has been concentrated at the zinc electrode (anode) and almost all of the reduction reaction (hydrogen liberation) has been concentrated at the iron electrode (cathode).

10) The oxidation of the zinc anode is much faster. At the same time, most of the corrosion of iron in has stopped, the zinc anode has been used to cathodically protect the iron cathode

11) Of course, some corrosion of the iron may still occur; whether or not this happens depends on the relative sizes of the zinc and iron electrodes

12) Some reduction of hydrogen may still occur on the zinc anode. The anode is the electrode at which a net oxidation reaction occurs, whereas cathodes are electrodes at which net reduction reactions occur.

13) All cathodic protection systems require an anode, a cathode, an electric circuit between the anode and cathode, and an electrolyte

14) Thus, cathodic protection will not work on structures exposed to air environments. The air is a poor electrolyte, and it prevents current from flowing from the anode to the cathode

Metal-metal ion equilibrium (unit activity)	Potential
Ag/Ag <sup>+</sup>	+0.80
Cu/Cu <sup>2+</sup>	+0.34
H <sub>2</sub> /H <sup>+</sup>	(reference) 0
Fe/Fe <sup>2+</sup>	-0.44
Zn/Zn <sup>2+</sup>	-0.76
Al/Al <sup>3+</sup>	-1.66
Mg/Mg <sup>2+</sup>	-2.36
More active or anodic	

# CHAPTER 2

## LITERATURE REVIEW

### Corrosion Prevention

By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced. This can be achieved in several ways:

#### 2.1 Conditioning the Metal

This can be sub-divided into two main groups:

(a) Coating the metal, in order to interpose a corrosion resistant coating between metal and environment. The coating may consist of:

- (i) Another metal, e.g. zinc or tin coatings on steel,
- (ii) A protective coating derived from the metal itself, e.g. aluminum oxide on "anodized" aluminum,
- (iii) Organic coatings, such as plastics, paints, enamel, oils and greases.

The action of protective coatings is often more complex than simply providing a barrier between metal and environment. Paints may contain a corrosion inhibitor, zinc coating in iron or steel cathodic protection

(b) Alloying the metal to produce a more corrosion resistant alloy, e.g. stainless steel, in which ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by an invisibly thin, naturally formed film of chromium oxide  $\text{Cr}_2\text{O}_3$

#### 2.2 Conditioning the Corrosive Environment

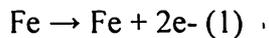
##### (a) Removal of Oxygen

By the removal of oxygen from water systems in the pH range 6.5-8.5 one of the components required for corrosion would be absent. The removal of oxygen could be achieved by the use of strong reducing agents e.g. sulphite. However, for open evaporative cooling systems this approach to corrosion prevention is not practical since fresh oxygen from the atmosphere will have continual access.

## (b) Corrosion Inhibitors

A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, reduces the rate of metal wastage. It can function in one of the following ways:

(i) Anodic inhibitors – as the name implies an anodic inhibitor interferes with the anodic process.



If an anodic inhibitor is not present at a concentration level sufficient to block off all the anodic sites, localized attack such as pitting corrosion can become a serious problem due to the oxidizing nature of the inhibitor which raises the metal potential and encourages the anodic reaction. Anodic inhibitors are thus classified as “dangerous inhibitors”. Other examples of anodic inhibitors include orthophosphate, nitrite, ferricyanide and silicates.

(ii) Cathodic inhibitors – the major cathodic reaction in cooling systems is the reduction of oxygen.



There are other cathodic reactions and additives that suppress these reactions called cathodic inhibitors. They function by reducing the available area for the cathodic reaction. This is often achieved by precipitating an insoluble species onto the cathodic sites. Zinc ions are used as cathodic inhibitors because of the precipitation of  $\text{Zn}(\text{OH})_2$  at cathodic sites as a consequence of the localized high pH. Cathodic inhibitors are classed as safe because they do not cause localized corrosion.

(iii) Adsorption type corrosion inhibitors – many organic inhibitors work by an adsorption mechanism. The resultant film of inhibitor is then responsible for protection, either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming bonds with metal surfaces are amino ( $-\text{NH}_2$ ), carboxyl ( $-\text{COOH}$ ), and phosphonate ( $-\text{PO}_3\text{H}_2$ ) although other functional groups or atoms can form co-ordinate bonds with metal surfaces.

(iv) Mixed inhibitors – because of the danger of pitting when using anodic inhibitors alone, it became common practice to incorporate a cathodic inhibitor into formulated performance was obtained by a combination of inhibitors than from the sum of the individual performances. This observation is generally referred to a ‘synergism’ and demonstrates the synergistic action which exists between zinc and chromate ions.

### **2.3 Electrochemical Control**

Since corrosion is an electrochemical process its progress may be studied by measuring the changes which occur in metal potential with time or with applied electrical currents. Conversely, the rate of corrosion reactions may be controlled by passing anodic or cathodic currents into the metal. If, for example, electrons are passed into the metal and reach the metal/electrolyte interface (a cathodic current) the cathodic reaction rate increases. This process is called cathodic protection and can only be applied if there is a suitable conducting medium such as earth or water through which a current can flow to the metal to be protected. In most soils or natural waters corrosion of steel is prevented if the potential of the metal surface is lowered by 300 or 400 mV. Cathodic protection may be achieved by using a DC power supply (impressed current) or by obtaining electrons from the anodic dissolution of a metal low in the galvanic series such as aluminum, zinc or magnesium (sacrificial anodes). Similar protection is obtained when steel is coated with a layer of zinc. Even at scratches or cut edges where some bare metal is exposed the zinc is able to pass protective current through the thin layer of surface moisture. In certain chemical environments it is sometimes possible to achieve anodic protection, passing a current which takes electrons out of the metal and raises its potential. Initially this stimulates anodic corrosion, but in favorable circumstances this will be followed by the formation of a protective oxidized passive surface film.

### **2.4 Use of paints and coatings**

Painting or coating is the main stay of corrosion prevention for materials not inherently corrosion resistant. This is a matter of economics. Paints and coatings are generally applied at low additional cost to the least expensive structural materials. Minimising the additional cost is an integral part of ensuring the economic viability of painting and coating as a corrosion control solution. Therefore paints and coatings generally do not last as long as the operating lifetime of the material to be protected, the ability to maintain the coating systems is vital.

#### **Factors in selection of paint or coating systems**

When choosing a system, several alternatives may appear to be technically acceptable, and it is necessary to identify relevant factors affecting corrosion control and cost.

The most important of these are:

- High project cost, prestige or failure consequences may warrant choice of high performance materials

- Type of substrate to be coated
- Track record of the selected system for the environmental and operating conditions expected
- Life expectancy of coating to first maintenance • ease of access to substrate work surface
- Quality of applicator and contractor
- Compliance with legislative and environmental requirements
- Delivery logistics
- Maintenance conditions, and compatibility with existing materials

The metal selected for a particular structure or component may be stable in the environment to which it is exposed without any further protective scheme. Clearly this is the ideal situation, but it is only likely to be achieved in very mild environments or by the use of expensive materials, and usually will be due to the formation of a protective film by reaction between the metal and environment. Thus it is rarely the case that a metal is completely inert in an environment in which it does not appear to corrode, but rather is there some initial reaction that produces an inert corrosion product, often invisible to the eye, and which adheres to the metal surface effectively separating the latter from the environment. Whilst economic considerations or other requirements such as strength level, may determine that the metal employed in a given structure is reactive to the environment to which it is to be exposed, it should be remembered that corrosion is a surface phenomenon and that if the surface can be rendered resistant the nature of the bulk of the metal is of little consequence; this is, of course, the idea behind the use of metallic coatings. The latter can be applied in a variety of ways, with varying implications for the design, including fabrication, of structures. Some of them have been mentioned already in relation to the electrode position of metallic coatings, but there are others. Metal spraying, involving the feeding of metal through a flame to produce a finely divided form which is then projected by a gas stream on to the surface to be coated, is best suited to relatively large structures, such as structural steelwork, whilst metal coatings produced by dipping objects into baths of molten metal are restricted to components capable of immersion in the size of bath available. Cladding is a method of attaching sheets of corrosion resistant metal to an underlying core, by bonding a sandwich of the relevant materials by rolling or by detonation of an explosive charge, and is widely used to produce aluminium-clad aluminium alloys and stainless steelclad mild steel. The fabrication of structures from such materials in plate or sheet form can raise problems at joints, where sectioning of the composite plate can expose the less corrosion resistant core metal;

more complicated geometries can sometimes be clad by explosive forming. The primary objective of metallic coatings is to provide a layer of metal resistant to corrosion by the environment concerned, such coatings may acquire defects resulting in the exposure of the underlying metal and the establishment of a bimetallic couple. In such circumstances the nature of the metal coating is no longer of importance only in relation to the environment involved, but also from the viewpoint of its electrochemical properties relative to those of the metal exposed at the coating defect. Thus, a defect in a tin coating applied to mild steel will result in enhanced corrosion of the exposed steel, due to the bimetallic coupling, whilst mild steel exposed at a defect in a zinc coating will be protected from corrosion by the same environment which, in the absence of the zinc, would be markedly reactive towards the steel. The latter is said to be cathodically protected by the zinc acting as a sacrificial anode and the protection arises because the electrode potential of the steel in the galvanic cell is reduced to a value where the steel is immune, i.e. it acts as the cathode in the galvanic cell. For such protective action the zinc does not need to be in physical contact with the steel, so long as there is electrical contact between the two metals and the resistance of the circuit is not too high, since the essential feature of cathodic protection is that the electrode potential of the steel is lowered to a value where the steel is immune from corrosion. This is the form in which cathodic protection is applied to structures as diverse as the hull of a ship or a buried pipeline, with sacrificial anodes of zinc (or of aluminium or magnesium for the protection of steel) dispersed to ensure that the whole of the surface to be protected is below the protection potential. The same result can be achieved without the use of sacrificial anodes, which themselves generate the current necessary for the protection but are thereby consumed and need to be replaced at appropriate intervals of time. Inert anodes, which may be of a variety of conducting materials, can be used for cathodic protection in conjunction with a source of direct current, i.e. a battery, rectifier or generator. The principles are essentially the same as with sacrificial electrodes, each system having its advantages for particular applications but sometimes with both being used to protect the same structure e.g. a buried pipeline can be protected at river crossings with sacrificial electrodes and elsewhere with an inert electrode system. All the above refers to modifying the metal in one way or another, i.e. by changing its composition to a more corrosion resistant one or by altering its electrode potential, but in so far as corrosion involved an environment as well as a metal it also may be possible to control corrosion through modification of the environment. The complete removal of a corrosive environment from contact with a metal will not frequently be possible, especially where the environment constitutes

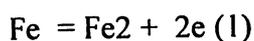
part of the process for which the plant was constructed or where the environment is extensive. But in the same way as a change in metal may result in the formation of a protective film by reaction with an environment, so an appropriate change in the latter to produce a favourable reaction upon a given metal should be possible. This is the principle involved in chemical inhibition, i.e. the addition of chemicals to an environment to inhibit corrosion that would otherwise occur. The nature of the additions will need to vary according to the metal and environment concerned, but in general, they are substances that react with one or other of the products of the corrosive reactions, or they are absorbed onto the metal surface, to produce an insoluble protective film. The addition of caustic alkali to boiler feed waters to render them non-corrosive to mild steel has already been mentioned and is a typical example of the application of inhibition, operating in this case by the formation of thin adherent films of iron oxides. Chromate additions to water will achieve the same result, but by the formation of a chromium oxide film, as with stainless steels where the chromium is derived from the alloying addition made to the steel. Such inhibitors, and there are many others in addition to those just mentioned, are not only effective in preventing general or pitting corrosion, but can be equally effective in preventing or retarding other forms of corrosion, such as stress corrosion or corrosion fatigue. The formation of chemically resistant films can be achieved by means other than the incorporation of inhibitors into corrosive environments, i.e. they can be formed, usually by immersion in concentrated solutions, before exposure. Thus, phosphate and chromate films can be formed on a variety of metals, whilst a black oxide film can be developed to give some protection to steels by immersion in nitrate-hydroxide solutions. Such chemical conversion films will not provide indefinite protection in all environments and the advantage of the formation of such films by incorporating inhibitors into the environment is that there will be a supply of inhibitors present for further reaction should the initially formed film be impaired for any reason. The formation of some films, including many of those that are most efficient in their inhibitive action, is associated with an increase in the electrode potential of the metal over that which would prevail for the same environment without inhibitor present. In the same way as cathodic protection can be related to a lowering of potential, involving the use of externally applied cathodic current, so the observation that chemical inhibition is sometimes associated with an increase of potential suggests that it may be possible to form protective films by the application of anodic current from an external source. (The possible conflict here that corrosion can be prevented by adequately lowering or raising the electrode potential of the metal is countered by the observation that corrosion in many systems of

metal and environment only occurs over a restricted range of potentials.) The anodic formation of protective films is indeed possible and the best known example is probably that involving the anodising of aluminum products, to produce a very stable oxide film sometimes used as a decorative, as well as corrosion resistant film. But there are some combinations of metal and environment, such as stainless steels and titanium alloys in oxidizing media, which can be anodically protected in situ, in the same way as protective films are formed by the presence of an inhibitor in an environment. This technique of anodic protection has been applied mostly in chemical process plant, but it has also been applied in the transportation of dangerous chemicals that would otherwise involve the use of costly metals for containing vessels. There may appear to be little connection between the chemical inhibition of corrosion and the most widely employed of all corrosion control procedures, namely the use of organic coatings in the form of paints, but in fact there is a very strong connection. The popular conception of how paints protect a coated metal is that the paint film physically prevents contact between the metal and environment, but this is demonstrably not the case. The corrosion of unpainted mild steel in a typical industrial atmosphere to form rust consumes 0.11g of water for each square centimetre of surface exposed per year of exposure, together with 0.03g of oxygen. Now if the permeabilities to water and oxygen of a typical thickness of a film of linseed oil based paint are measured it will be found that about 0.2g of both water and oxygen will pass through 1 cm<sup>2</sup> of the film in 1 year. Thus the permeability of the film is such that it will permit more water and oxygen to pass than would be required to account for the observed corrosion rate of even bare steel and so the paint cannot be acting simply as a physical barrier. In which case its function must be essentially chemical and it is not accidental that those paints which are most effective in preventing corrosion contain inhibitive pigments, sometimes identical with those substances added to aqueous solutions as inhibitors. The formulation of paints and the design of painting schemes must be related to the conditions of use, i.e. to the metal to be protected and the conditions of exposure. Although painting is one of the oldest methods of corrosion control, it is only relatively recently that the mechanism of its protective action has begun to be understood, leading to the design of much improved painting schemes and typified by schemes employed on the Forth Rail Bridge and the relatively new Forth Road Bridge. The proximity of these indicates the similarities in their exposure conditions but the painting schemes are very different indeed. The Rail Bridge has a red lead priming coat followed by a linseed oil based paint and has a lift cycle of about 2.5 years. The modern Road Bridge has a much more sophisticated

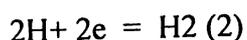
scheme involving the cleaning of the steel surfaces by grit blasting, followed by a layer of sprayed metallic zinc, an etch primer, a coating of phenolic resin containing zinc chromate and finally two coats of a phenolic paint containing dispersed iron oxide. Thus the chemistry and electrochemistry of the system have been designed to combat the potential corrosion problems and the life cycle should be about 15 years. The correct formulation of paints will not provide maximum benefits unless the metal surface to be painted is correctly prepared in the first instance; indeed adequate surface preparation is vital for any of the methods of corrosion control involving the deposition of surface films. Accessibility to surfaces is clearly vital for both operations and whilst this is usually recognized in the general sense it is frequently forgotten in terms of detail. Riveted or bolted joints and other relatively sharp changes in profile frequently provide contours that are not easily cleaned nor adequately coated, with the inevitable early breakdown of a protective system. Sharp edges or corners also present problems, since the surface tension of the liquid paint and the shrinkage that occurs during its drying both tend to produce marked thinning of the paint film at sharp corners. Clearly, as with so many aspects of design, smooth contours and the avoidance of sharp details should be the aims, and where these cannot be achieved fillers, such as jointing compounds, mastic and plastisols, should be used. The latter are particularly useful also in protecting the inaccessible parts of riveted joints and are extensively used in aircraft construction, because of the inadequate elasticity of paint films applied over some joints and the almost inevitable ready ingress of corrosive media once the paint film is broken.

## **2.5 Principle of cathodic protection**

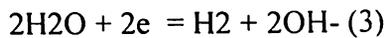
Corrosion in aqueous solutions proceeds by an electrochemical process, and anodic and cathodic electrochemical reactions must occur simultaneously. No net overall charge builds up on the metal as a result of corrosion since the rate of the anodic and cathodic reactions are equal. Anodic reactions involve oxidation of metal to its ions, e.g. for steel the following reaction occurs.



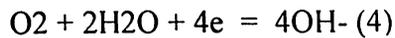
The cathodic process involves reduction and several reactions are possible. In acidic water, where hydrogen ions ( $\text{H}^+$ ) are plentiful, the following reaction occurs.



In alkaline solutions, where hydrogen ions are rare, the reduction of water will occur to yield alkali and hydrogen.



However, unless the water is reduction of oxygen is the most likely process, again producing alkali at the surface of the metal.



Reactions (1) and (2) where anodic and cathodic sites are nearby on the surface of a piece of metal. We can change the rate of these two reactions by withdrawing electrons or supplying additional electrons to the piece of metal. It is an established principle that if a change occurs in one of the factors under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change. Thus, if we withdraw electrons from the piece of metal the rate of reaction (1) will increase to attempt to offset our action and the dissolution of iron will increase, whereas reaction (2) will decrease. Conversely, if we supply additional electrons from an external source to the piece of metal, reaction (1) will decrease to give reduced corrosion and reaction (2) will increase. The latter case will apply to cathodic protection. Thus, to prevent corrosion we have to continue to supply electrons to the steel from an external source to satisfy the requirements of the cathodic reaction. Note that the anodic and cathodic processes are inseparable. Reducing the rate of the anodic process will allow the rate of the cathodic process to increase. These principles may be expressed in a more quantitative manner by plotting the potential of the metal against the logarithm of the anodic and cathodic reaction rates expressed as current densities. The corrosion current,  $I_{\text{corr}}$ , and the corrosion potential,  $E_{\text{corr}}$ , occur at the point of intersection of the anodic and cathodic i.e. where anodic and cathodic reactions rates are equal. If electrons are "pumped" into the metal to make it more negative the anodic dissolution of iron is decreased to a negligible rate at a potential  $E_1$ , whereas the rate of the cathodic current is increased to  $I_1$ . Hence, a current  $I_1$  must be supplied from an external source to maintain the potential at  $E_1$  where the rate of dissolution of the iron is at a low value. If the potential is reduced, the current required from the external source will increase to  $I_2$ . Further protection of the metal is insignificant, however, and the larger current supplied from the external source is wasted. The metal is then said to be over-protected. In aerated neutral or alkaline solutions the cathodic corrosion process is usually the reduction of oxygen. The kinetics of this cathodic process are controlled by the rate at which oxygen can diffuse to the surface of the metal, which is slower than the rate of consumption of oxygen by the cathodic reaction. Thus, the rate of this reaction does not increase as the potential of the metal is made more negative but remains constant unless the rate of supply of oxygen to the surface of the

metal is increased by, for example, increase fluid flow rate. A current of  $I_1$  is initially required to maintain the metal at the protection potential  $E_1$ . However, if the flow rate is increased the limiting current for the reduction of oxygen is increased (dotted line) and the current required to maintain the metal at the protection potential is increased by  $\Delta I$ . Thus, the current density required to maintain the correct protection potential will vary with service conditions. Clearly, cathodic current density is not a good guide as to whether a structure is cathodically protected. The correct protection potential must be maintained if corrosion is to be prevented. If the structure is over-protected and the potential is reduced to a potential region where reduction of water (reaction 3) can take place, further current will be required from the external source and current will be wasted. In Fig 3 reducing the potential from  $E_1$  to  $E_2$  will increase the current required from the external source from  $I_1$  to  $I_2$  as a result of an increased rate of reduction of water. Excessive negative potentials can cause accelerated corrosion of lead and aluminium because of the alkaline environments created at the cathode. These alkaline conditions may also be detrimental to certain paint systems, and may cause loss of the paint film. Hydrogen evolution at the cathode surface may, on high-strength steels, result in hydrogen embrittlement of the steel, with subsequent loss of strength. It may also cause disbanding of any insulating coating: the coating would then act as an insulating shield to the cathodic protection currents.

# CHAPTER 3

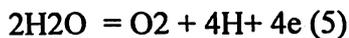
## THEORETICAL DEVELOPMENT

### 3.1 Methods of applying cathodic protection

Cathodic protection may be achieved in either of two ways. By the use of an impressed current from an electrical source, or by the use of sacrificial anodes (galvanic action).

#### 3.1.1 Impressed current

The arrangement for protecting a buried pipeline The buried pipe receives current from a DC power source via an auxiliary inert electrode buried in the ground. The pipe becomes the cathode and the auxiliary electrode the anode. The auxiliary electrode sometimes consists of scrap iron. In this case the iron will dissolve from the anode by reaction (1) and the electrode is described as a consumable anode. If the anode is a noble metal or an electrochemically inert material, the surrounding environment will be oxidized and in water reaction



will occur. In solutions, however, chlorine may be produced at the anode. This may present problems in confined spaces. For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes or continuous ribbons of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide, platinum and coated wire and other

### Properties of impressed-current anodes

Anode material	Max volts*	Typical anode current density A m <sup>-2</sup>
Platinum / niobium	100	250 – 1500
Lead / silver / antimony	100	250 – 1000
High silicon iron	100	10 – 100
Graphite	-	20

Dependent on the environment

A typical ICCP system for a pipeline would include an AC powered rectifier with a maximum rated DC output of between 10 and 50 amperes and 50 volts. The positive DC output terminal is connected via cables to the array of anodes buried in the ground (the anode groundbed). For many applications the anodes are installed in a 60 m (200 foot) deep, 25 cm (10-inch) diameter vertical hole and backfilled with conductive coke (a material that improves the performance and life of the anodes). A cable rated for the expected current output connects the negative terminal of the rectifier to the pipeline. The operating output of the rectifier is adjusted to the optimum level by a CP expert after conducting various tests including measurements of electrochemical potential. Telephone wiring uses a form of cathodic protection. A circuit consists of a pair of wires, with forty-eight volts across them when the line is idle. The more positive wire is grounded, so that the wires are at 0 V and -48 V with respect to earth ground. The 0 V wire is at the same potential as the surrounding earth, so it corrodes no faster or slower than if it were not connected electrically. The -48 V wire is cathodically protected. This means that in the event of minor damage to the insulation on a buried cable, both copper conductors will be unaffected, and unless the two wires short together, service will not be interrupted. If instead the polarity were switched, so that the wires were at 0 V and +48 V with respect to the surrounding earth, then the 0 V wire would be unaffected as before, but the +48 V wire would quickly be destroyed if it came into contact with wet earth. The electrochemical action would plate metal off the +48 V wire, reducing its thickness to the point that it would eventually break, interrupting telephone service. This choice of polarity was not accidental; corrosion problems in some of the earliest telegraphy systems pointed the way. A range of materials

have been used as non-consumable anodes for impressed-current systems. The sort of properties required by these anodes are

- a. good electrical conduction,
- b. low rate of corrosion,
- c. good mechanical properties, able to stand the stresses which they may be subjected to during installation and in service,
- d. readily fabricated into a variety of shapes,
- e. low cost,
- f. able to withstand high current densities at their surfaces without forming resistive barrier oxide layers, etc.

The following materials have been used as anodes: magnetite, carbonaceous materials (graphite), high silicon iron (14-18% Si), lead/lead oxide, lead alloys, platinised materials (such as tantalum, niobium, titanium). Platinum, with its high resistance to corrosion, would be an ideal anode material but has the major disadvantage of very high cost. In practice, voltages up to 100 V and high current densities are possible on impressed-current anodes. Thus, large areas of a structure can be protected from a single anode and, because of the high driving voltage; the anode can be placed remote from the structure.

Cathodic protection can be also applied if the metal to be protected is coupled to the negative pole of a direct current (DC) source (*schematic*), while the positive pole is coupled to an auxiliary anode. Since the driving voltage is provided by the DC source there is no need for the anode to be more active than the structure to be protected. There are basically three types of anode materials:

Inert or non consumable anodes

Semi-consumable anodes

Consumable anodes

All items to be protected shall be electrically connected and should have a welded or brazed connection to an anode. For bolted or clamped assemblies without an all welded brazed electrical grounding, the electric resistance should be less than 0.10 ohm. Coating on contact surfaces shall be removed prior to assembly.

## Non Consumable Anodes

This type of anode supports other anodic reactions on their surfaces. In environments where water and chloride ions are present, chlorine evolution and oxidation of water are possible.

### Platinized substrates:

Platinum is the ideal permanent impressed current anode material. It is one of the most noble metals and in practically all environments forms a thin invisible film which is electrically very conductive. In addition, the exchange current densities of most anodic reactions on the Pt surface are greater than on other anode materials. Due to its high cost, platinum is applied as a thin coating (1-5 ohm m) on metallic substrates such as titanium, niobium and tantalum.

Platinized titanium is often used. To avoid the dissolution at locations on the surface, the operating voltage of the anode is limited by the anodic breakdown potential of titanium which is in the range of 9 to 9.5 V in the presence of chlorides. Hence the maximum recommended operating voltage of platinized titanium anodes is 8 V. The corresponding maximum current density output is approximately  $1 \text{ kA m}^{-2}$ . For cathodic protection systems where operating voltages are relatively high, niobium and tantalum based anodes are generally selected. This is because these two substrates have anodic breakdown potentials greater than 100 V in chloride containing electrolytes. The wastage rate of platinized anodes is approximately  $8 \text{ mg A}^{-1} \text{ y}^{-1}$ .

The rate of platinum consumption has been found to accelerate in the presence of AC current ripple. Most wastage was observed to occur with AC frequencies of less than 50 Hz. The repeated oxidation/reduction processes result in the formation of a brownish layer of platinum oxide. To avoid the occurrence of this phenomenon, a single or a three phase full-wave rectification is recommended. The consumption rate of platinized anodes is also adversely affected by the presence of organic impurities such as sugar and diesel fuel.

**Magnetite:** Magnetite is a cheap and naturally occurring material. It has an electrical conductivity of  $1.25 \text{ ohm}^{-1} \text{ m}^{-1}$ . Due to its brittleness, the anode is cast as a hollow cylinder and closed at one end. The inner surface is then copper plated and the cylinder is filled with polystyrene. Epoxy resin is used to fill any remaining space. The anode cable is soldered to the copper plate. Magnetite anodes have been successfully used in the cathodic protection of buried structures and those immersed in

seawater. The maximum operating current density is  $0.115 \text{ kA m}^{-2}$  and the anode consumption rate is approximately from 1 to  $4 \text{ g A}^{-1} \text{ y}^{-1}$ .

Lida: This is a recently developed anode. It is claimed that it has superior mechanical, consumption and electrochemical properties compared with conventional anodes. The anode is composed of an inert metal oxide, ruthenium oxide coated titanium. The operating current density is  $0.8 \text{ kA m}^{-2}$  and the consumption rate is in the range of  $0.8 \text{ mg A}^{-1} \text{ y}^{-1}$ .

### **Semi-Consumable Anodes**

Semi-consumable anodes such as graphite and high silicon iron have been in service since the first industrial electrochemical systems were built.

**Graphite:** Graphite anodes are widely used. Carbon has been used as an anode in chlorine production since the end of the nineteenth century. Graphite, which is less porous and more electrically conductive, is now preferred for use in impressed anode materials. However, graphite can still be highly porous, with the porosity being exacerbated by gas evolution. For this reason, graphite is often impregnated with resins to reduce solution ingress and improve mechanical strength. Graphite anodes are inert when chlorine evolution is occurring, chlorine being produced efficiently at low polarizations. But if oxygen formation predominates, as in low chlorine media, graphite is oxidized to carbon dioxide. *Graphite deterioration also increases with decreasing pH and increasing sulfate ions concentration.*

To eliminate the possibility of galvanic corrosion caused by detached pieces, graphite is not recommended for use in closed systems. In addition, graphite suffers high consumption rates in water at temperatures above  $50^{\circ}\text{C}$ . Consumption rates measured for graphite depend on the environment and thus range from 0.045 in water to  $0.45 \text{ kg A}^{-1} \text{ y}^{-1}$  in freshwater. Similarly the corresponding operating current densities vary from 2.5 to  $10 \text{ A m}^{-2}$ . The maximum operating voltage for graphite anodes is only limited by excessive consumption rate and brittleness of the material. The main disadvantages of graphite compared to other impressed anodes are low operating current densities and inferior mechanical strength. Graphite is generally used in conjunction with carbonaceous back-fills in soil based impressed anode systems.

### High silicon iron (HSI) alloys:

These anodes are widely used. HSI anodes contain about 14.5% silicon and certain alloys have 4.5% chromium. Chromium has now replaced molybdenum as an alloying element in this type of anode. The high silicon content ensures that the alloy forms a protective film containing silicon dioxide,  $\text{SiO}_2$ . A prerequisite for the formation of this film is that the anode must initially corrode during the first few hours of operation. The mechanism of this passivating film is not well understood. The high electrical conductivity of the film is believed to be due to the presence of iron oxides. Silicon dioxide is highly resistant to acids but it is readily dissolved in alkaline conditions. High silicon iron anodes are extremely hard and cannot be machined easily. They are generally cast and then stress relieved by annealing. Although brittle these anodes have superior abrasion and erosion characteristics compared to graphite. High silicon iron anodes are widely used usually in conjunction with carbonaceous backfills in soils. The maximum operating current density is determined by the type of alloy and the environment. For instance, in groundbeds with backfills the current density is limited to between 10 and 20  $\text{A m}^{-2}$  because of problems caused by gas entrapment. In marine environments, a high iron chromium anode can be operated up to 50  $\text{A m}^{-2}$ . As for graphite, the maximum operating voltage is limited by excessive consumption and brittleness of the material. The consumption rate of these anodes is influenced by the operating current density and the nature of the environment. Generally, a lower current density reduces the consumption rate. Wastage rates range from 0.10 to 0.50  $\text{kg A}^{-1} \text{y}^{-1}$ . Sulfate ions in particular have been noted to enhance the dissolution rate of these materials.

### Lead alloys:

The function of lead as an impressed current anode depends on the formation of a protective and electrically conductivity film (10<sup>1</sup>-10<sup>2</sup>  $\text{Sm}^{-1}$ ) of lead dioxide,  $\text{PbO}_2$ . This film is non-stoichiometric oxide and exists in two forms:

alpha -  $\text{PbO}_2$  (orthorhombic)

beta -  $\text{PbO}_2$  (tetragonal).

Lead dioxide is surprisingly stable in the presence of chloride ions. The insoluble lead chloride,  $\text{PbCl}_2$ , is believed to be responsible for healing the defects in the film. This ensures that  $\text{Pb/PbO}_2$  behaves as an inert electrode and hence allowing at high polarization the evolution of chlorine and

oxygen. To form an adherent and stable film of  $\text{PbO}_2$ , lead is generally alloyed with Ag and Sb. A typical alloy composition is Pb 6 Sb 1 Ag.

Owing to the low overvoltage of chlorine evolution on the surface of these anodes, lead alloys are mostly used in seawater applications. Maximum operating voltage and current density of these anodes are 24 V and  $1 \text{ kA m}^{-2}$  respectively. The consumption rate is in the range  $1\text{-}10 \text{ g A}^{-1} \text{ y}^{-1}$ . It should be added that lead alloy anodes are sometimes used with platinum pins. It has been found that a platinum microelectrode inserted into the surface of the lead enhanced the formation of  $\text{PbO}_2$ . It is also worthwhile noting that the performance of lead alloy anodes (with and without Pt pins) is adversely affected at operation

### **Consumable Anodes**

Examples of this type of anode include scrap iron or steel and cast iron. The anode is deliberately dissolved to provide the electrons required to polarize the structure. Consumable anodes can be used in buried or under immersed conditions. They have consumption rates of approximately  $9 \text{ kg A}^{-1} \text{ y}^{-1}$  and maximum current densities are in the order of  $5 \text{ A m}^{-2}$ . Due mainly to their high consumption rate the use of such anodes is rather rare unless a redundant source of iron or steel is readily available such as an old ship beached below low tide, a disused pipeline, well string etc. However, since such structures are frequently massive, they represent a very low resistance to earth and therefore can make the cathodic protection engineer's life much simpler.

#### **3.1.2 Sacrificial anodes**

To understand the action of sacrificial anodes for cathodic protection it is necessary to have in mind the galvanic series of metals. When the tendency for metal to go into solution as metal ions increases (leaving an excess of electrons on the metal surface), i.e.



the metal becomes more electronegative. Thus, since zinc, aluminum and magnesium are more electronegative than steel they are increasingly able to supply electrons to the more electropositive steel when in electrical contact in water, and will effect cathodic protection of the steel surface. Clearly, if steel was coupled to copper ions, steel would supply electrons to copper which would

become cathodically protected, and the corrosion of the steel would be enhanced. Electrons are supplied to the steel pipe, via the electrical connection, and a corresponding amount of anode material goes into solution as metal ions, according to the laws of electrolysis. Some anode material is lost by self-corrosion, and the anodes are not converted to electrical energy with 100% efficiency. Zinc, aluminum and magnesium are the metals commonly used for sacrificial cathodic protection. The driving voltage of sacrificial anodes is now compared with impressed-current anodes, and sacrificial anodes must be located close to the structure being protected. Although almost any piece of zinc etc could provide cathodic protection over a short period of time, cathodic protection schemes are usually required to operate over periods of several years. Anodes can lose their activity and become passivated, developing a non-conducting film on their surfaces so that they no longer are able to supply current. This can be avoided by careful control of the concentrations of trace impurities in the anode materials, and by alloying. For zinc anodes the level of iron, for example, must be kept below 0.005% for satisfactory long-term operation of the anodes. To prevent passivation of aluminum anodes, alloying with, for example, indium has been found to be successful. The previously successful alloy with mercury is now disliked on environmental grounds.

### **Sacrificial Anode Material**

The galvanic series shows that magnesium heads the list as the most anodic metal and is widely separated from iron in the galvanic series. Magnesium coupled to iron provides sufficient galvanic potential to provide positive protection. An important feature of a sacrificial anode system is that it is inherently a safer system than impressed cathodic protection systems because the normal potentials generated are insufficient to damage coatings present on the surface to be protected. Because of the low potentials generated, sacrificial systems can be used only in low-resistance soils, i.e., with a resistivity less than 3000 ohm cm.

Magnesium anodes

Zinc anodes

Aluminum anodes

### Properties of sacrificial anodes

Anode material	Density g cm <sup>-3</sup>	Potential volts Cu/CuSO <sub>4</sub>	Amp-hrs per kg	Typical anode current density A m <sup>-2</sup>
Zn	7.1	-1.10	780	0.5 – 2
Al	2.7	-1.15	2700	0.6 – 2.5
Mg	1.7	-1.55	1230	1.5 – 5.6

### Anode Efficiency

A prospective sacrificial anode must possess a large number of electrons per unit mass and should deliver these electric charges efficiently. Thus the electrical output of an anode is given by current capacity. The value of the current capacity is determined by the electrochemical equivalent, the density and the efficiency of the anodic material. The electrochemical equivalent, which is dependent on the atomic weight and valence, is a characteristic of the anode material. However efficiency is determined by a number of factors including nature of the environment, operating current density and metallurgical microstructure. It is apparent that if the cathode reaction rate on the anode is low then the efficiency will be high, so that there is minimum self corrosion. Similarly large operating currents will yield high anode efficiency. It should be added that the type of corrosion attack experienced by the anode also significantly affects the magnitude of the anode efficiency. For instance, severe pitting and intergranular attack may result in a chunk of the anode to become detached without complete consumption of the electric charge in that piece.

### 3.2 Selection of cathodic protection system

In the design of a cathodic-protection scheme, a decision must be made as to whether the scheme should be a sacrificial anode or impressed-current system or a mixture of the two systems.

Sacrificial anode systems have the advantage of being

- (a) Simple to install,
- (b) Independent of any source of electric power,
- (c) Suitable for localized protection,
- (d) Less liable to cause interaction on neighboring structures.

It is difficult to over-protect the structure and moderately easy to obtain a uniform electrode potential across the structure. The most severe limitation of the sacrificial anode is the small driving force which restricts its use to conductive environments or well-coated systems. To protect a large structure, such as a pipeline, with sacrificial anodes, a large number of them would need to be distributed along it, involving a multiplicity of electrical connections and considerable installation work.

The advantages of the impressed-current system include

- (a) The large driving force available can protect a large, even uncoated, structure in high resistivity environments,
- (b) Comparatively few anodes are needed,
- (c) The voltage may be adjusted to allow for environmental and coating changes!

The impressed-current system may allow considerable over-protection, however, and considerable variation of potential over the structure is difficult to avoid. Generally, sacrificial anode schemes have found favor for small well-coated low-current demand structures or for localized protection, with impressed-current schemes being utilized for large complex structures which may be bare or poorly coated. However, it has been found economic to provide galvanic protection to large uncoated platforms and similar structures where the cost of coating is prohibitive. In addition, the galvanic anodes offer easily installed robust systems which, being independent of a power source, provide protection immediately on "float-out" of the structure.

### 3.3 Design parameters

Important parameters in the design of cathodic protection systems

#### 3.3.1 Protection potentials

In practice, the structure-to-electrolyte potentials are measured using a standard reference electrode based on copper/copper sulphate, silver/silver chloride, or pure zinc. The reference electrode should be very close to the surface whose potential is being measured. For steel in an aerobic electrolyte of nearly neutral pH a commonly accepted protection potential is -850 mV; when exposed to sulphate-reducing bacteria a potential of -950 mV would be required. Both values are referred to a copper/copper sulphate electrode. Values for lead and aluminum must be carefully controlled to avoid damage by excess alkali which could build up at the surface of the metals if the protection potentials are too negative.

#### Potential required for cathodic protection

Metal	Potential (Cu/CuSO <sub>4</sub> )
Steel	-850 mV
Steel (sulphate reducing bacteria)	-950 mV
Copper alloys	-500 to -650 mV
Lead	-600 mV
Aluminium	-950 to -1200 mV

### 3.3.2 Current density

The current density required to maintain the protection potential is very dependent on local conditions. Increased availability of oxygen at the surface of the metal will directly increase current density. Increased availability of oxygen may occur because of increased concentration of oxygen in the environment, increased water flow or turbulence. Thus, current densities to structures in sea water, rivers, etc are likely to vary continuously. The pH of the environment will also be important. The presence of coatings, marine fouling, and calcareous deposits will have a profound effect on current density. Having decided on the appropriate current density, the total anode current can be determined from the area of the structure. The size of the anodes can then be determined if a sacrificial anode scheme is to be employed, taking into account the working life of the protected structure.

#### Current densities required to protect steel

Environment	Current density A m <sup>-2</sup>
Acidic solutions	350 – 500
Saline solutions	0.3 – 10
Sea water	0.05 – 0.15
Saline mud	0.025 – 0.05

### 3.3.3 Coatings

The provision of an insulating coating to the structure will greatly reduce the current demand for cathodic protection. When first applied, coatings will often contain flaws, and in service, further defects will develop over a period of time. The use of coatings and cathodic protection takes advantage of the most attractive features of each method of corrosion control. Thus, the bulk of the protection is provided by the coating and cathodic protection provides protection to flaws in the

coating. As the coating degrades with time, the activity of the cathodic protection system develops to protect the deficiencies in the coating. A combination of coating and cathodic protection will normally result in the most economic protection system.

#### **3.3.4 Anode resistance**

One of the most important parameters in the design of cathodic protection systems is the electrical resistivity of the environment. Resistivity's encountered for pipeline environments vary from 1 ohm cm for brackish river water to greater than 500,000 ohm cm in non-porous granite. Measurement of the resistivity of the environment and calculation of the electrical resistance between the anodes and the structure due to the electrolyte must be made at an early stage in the design of the scheme to ensure that adequate current output will be obtained from the anodes over the design-life of the structure (by application of Ohm's Law). Established methods for determining the resistivity of soils and water are available and will not be dealt within these notes. Exact calculation of the electrical resistances between anodes and structure due to the electrolyte is rarely possible. Ground beds, as cathodic protection electrodes set in the earth are called, can be considered to lie in a semi-infinite electrolyte and the resistances of electrodes to infinite earth or sea water have been calculated for a number of anode shapes. Thus, if the anodes are remote from the structure, these anode resistances can be used, together with the difference between the required protection potential and the anode potential, to determine current output of anodes using Ohm's Law. If, however, the anodes are positioned close to the structure, then some correction to the resistance is required. When current flows from a small anode to a large metal structure, the current density is at a maximum near the surface of the anode. Hence a major portion of the potential drop between anode and structure occurs in the vicinity of the anode. This factor probably enables values of anode-resistance to infinite-earth to be used reasonably successfully even when anode and structure are not well separated. A further consequence of this factor is that surrounding an anode with a backfill of conducting material greatly reduces the anode resistance in resistant soils. In practice, the distribution of current to a structure is difficult to control. If we consider the protection of a pipe by an anode, it should be clear that there will be a higher current density at the point on the pipeline nearest the anode than elsewhere. The effect is to ensure that the ends of the pipe are protected, the centre of the pipe, nearest the anode, must be overprotected to some degree. The effect can be

minimized by using several anodes spaced along the pipe, but this will greatly increase installation costs.

### **3.3.5 Temperature**

Higher temperatures generally increase corrosion rates. However, corrosion needs a liquid phase and, if drying occurs source of heat may be electrical heating elements, motors etc

### **3.3.6 Environment**

The type of environment to which a material is exposed is a major factor in determining the type and severity of corrosion undergone. Minor constituents of the surroundings can be critical, aggravating or suppressing corrosive attack. Geographical location is also important, as is the influence of weather and season at the time of construction, repair, etc.

#### **Natural environments**

##### *Air*

Rural (farming, fertilizers, ammonia) Coastal, marine (chloride) Industrial, urban (sulphur dioxide, and acid rain)

##### *Waters*

Rivers, lakes, wells, water pipelines, dams; sea water (tidal, "splash zone")

#### **Chemical environments**

Urban and industrial atmospheres Environmental pollutants creating aggressive mists Interior of reaction and storage vessels in chemical plant.

#### **Other environments**

Embedded metals may react with non-metallic materials such as wood, plastics, and concrete. The porosity of some of these media allows contact with stagnant water..

#### **Incident radiation**

Sunlight, ultraviolet light and thermal radiation, can activate short-lived reactive chemical species from contaminants in the environment, aggravating corrosion

## **Relation to design**

The primary objective of this section is to indicate how some of the parameters with which the design engineer is normally concerned, e.g. geometry, stress, fluid and heat transfer, can themselves influence corrosion. In the present context total design is implied i.e. not only the shape of the component or structure, but the material, its fabrication and the relation of these to the environment in which it is to be used. It is also convenient to distinguish between static and dynamic situations especially in order to emphasise some of the problems unique to the latter.

### **3.4 Static situations**

**Use of dissimilar metals in electrical contact** It is well known that in cells or batteries two dissimilar substances immersed in an appropriate electrolyte will provide a source of electrical energy. The generation of the latter in, for example, the Daniel cell involves the dissolution of the zinc electrode whilst copper is deposited from the electrolyte on to the copper electrode. If the two electrodes are not electrically coupled then the rate of dissolution of the zinc or the deposition of the copper will be very markedly reduced whilst immersed in the same electrolyte. Any two metals, providing they are sufficiently dissimilar in the electrochemical sense, in electrical contact will undergo essentially similar responses in that the dissolution, or corrosion, of one of the metals will be accelerated by contact with the other metal. The extent of such galvanic or bimetallic corrosion depends upon a number of factors but, it depends critically upon the metals coupled, reflecting their different electrochemical characteristics.

The extent to which corrosion of a given metal is aggravated or mitigated by coupling to a dissimilar metal depends not only upon the relative electrochemical characteristics of the two metals concerned, but also upon other factors, such as their relative exposed surface areas, the nature of the electrolyte and the temperature. Copper rivets inserted into a steel joint of relatively larger surface areas have caused only a slight increase in corrosion of the steel, whereas steel rivets in contact with a large area of copper have suffered severe corrosion. The distribution of corrosion in the vicinity of bimetallic joints is a complex subject, depending upon factors such as the conductivity of the electrolyte, whereby the corrosion is localised very close to the joint or more evenly distributed according to whether the resistive path is high or low, respectively. Changes in temperature can produce variable effects. zinc acts as a sacrificial anode when connected to iron under those exposure conditions. However, the zinc-iron couple can reverse its polarity, with the iron becoming

anodic to zinc in certain fresh waters when the temperature exceeds about 60 °C. Clearly this could be a problem of significant practical importance in such components as galvanised steel domestic water heaters. Notwithstanding these various potential problems it would be incorrect to assume that corrosion is the invariable result of coupling dissimilar metals and therefore that bimetallic couples must always be avoided in any engineering design. It is a matter of common observation that dissimilar metals can often be coupled without adverse effect and guidance is available for those couples that are likely to result in corrosion. Where other considerations result in the necessity for coupling dissimilar metals despite the corrosion hazard the latter can often be avoided by suitable metallic or paint coatings on the metals or by the use of electrical insulation at the joint. Soldering and brazing are methods of joining metals that will more frequently involve bimetallic junctions than will welding or the use of mechanical fasteners. Because of the relative area effect, it is usually preferable for the solder or brazing alloy, which frequently has a relatively small exposed area, to be more electropositive (or cathodic) than the parent metal. Joints between steel components are therefore likely to suffer less serious corrosion if prepared with a silver solder than if a zinc-rich alloy is used. Possibly the greatest corrosion hazard arising from the presence of soldered joints relates not so much to the bimetallic coupling but to the flex that may be allowed to remain upon exposed surfaces. Fluxes containing chlorides are particularly liable to promote subsequent corrosion, if not thoroughly washed away following the making of the joint, and it is preferable to use one of the noncorrosive fluxes now available. In welded joints, the difference in the electrochemical characteristics of the weld and parent metals are usually much less marked than with soldered or brazed joints, but problems can arise.

Welded joints are more likely to result in stress corrosion cracking, if the residual stresses introduced by welding are not subsequently relieved, also structural changes in the heataffected zone of the parent metal may lead to certain localised forms of corrosion involving selective leaching that is essentially galvanic in origin. The 18 Cr 8 Ni austenitic stainless steels are particularly prone to this form of corrosion, known as weld decay, and which involves intergranular corrosion along the austenitic grain boundaries in certain environments. The heating cycle to which the parent metal is subjected adjacent to the weld can result in the precipitation of chromium carbide in the grain boundaries where, because the carbide contains much more than 18 per cent chromium, a zone of metal impoverished in chromium is formed. Since the corrosion resistance of the steel derives from the formation of a chromium-rich protective film, the corrosion resistance of the chromium depleted

grain boundary regions is diminished and preferential attack occurs. The solution to this problem is either to use a stabilised steel containing titanium or niobium, which have stronger affinities for carbon than has chromium so that chromium depletion does not occur, to use a stainless steel with a carbon content restricted to a maximum of 0.03 percent, or to heat the whole of the welded assembly to a temperature high enough to take the carbides back into solution and cool fairly rapidly to prevent their reprecipitation. Both stabilised and low carbon steel are readily available, but they must be specified where required. A common mistake is to assume that it is sufficient to order 'stainless steel'. In fact there are a considerable number of alloys commonly known as stainless steel and, except where the conditions are relatively mild, the individual alloys can be very different in corrosion behaviour. While the weld decay problem is well understood and the precautions reasonably well known, other similar examples exist where this is less than the case. The corrosion resistance of the high nickel alloys (Hastelloys and high nickel austenitic steels) can also be impaired if the initial heat treatment is not correct or if they encounter a dangerous heating cycle during welding or hot working operations. In some cases the impaired corrosion resistance is confined to a narrow zone on either side of the weld. An example is with some austenitic steels in hot strong nitric acid, which from its morphology is known as knife line attack. Like weld decay, this form of corrosion is due to precipitation reactions during the heating cycle – it can be minimised by the use of a low carbon or niobium stabilised steel, but under extreme conditions the best course is to use a completely different material, such as titanium. This is another example of the extent to which localized corrosion, involving relatively little metal dissolution, can result in the deterioration of an engineering structure to a markedly greater degree than would have been the case had the same amount of metal dissolution been spread uniformly over the whole of the exposed surfaces. Intergranular corrosion along sensitised grain boundaries is not a peculiarity of stainless steels, since some of the high strength aluminium alloys, for example, can show similar effects. The types of corrosion frequently referred, when referring to the preferential leaching of zinc from brasses, as graphitisation, when relating to the selective attack upon the metallic components of grey cast irons, or as dealloying, when a generic term is required, have features in common with the forms of corrosion mentioned above. Dezincification can occur uniformly over an exposed surface or it may take a more localized form, known, respectively, as layer-type and plug-type. The environmental conditions that favour dezincification of brasses are stagnant or slowly running water, elevated temperatures, poor aeration and extremes of acidity or alkalinity. The selective removal of the zinc

leaves a porous film of copper adhering to the component and therefore associated, in the absence of other deposits, with a change of colour from the characteristic yellow of brass to the red of copper. More importantly, there is a marked deterioration in strength associated with these changes, which are best avoided by the use of alloys less susceptible or immune from this type of failure. Thus, lowering the zinc content of the brass or adding a small amount of arsenic in its preparation will be beneficial, or, for the more severely corrosive conditions, the use of cupronickels may be advisable. The graphitisation of grey cast iron pipes buried in certain soils involves selective leaching of the metallic phases and leaves a weak mass of graphite and corrosion products that retain the shape of the pipe, until some relatively small pressure change, frequently associated with ground movement, causes a fracture. Its avoidance sometimes lies in the use of spheroidal, rather than flake, irons or the application of other corrosion prevention methods, such as cathodic protection. Many of these and other examples of selective leaching have their origins in the same galvanic processes as are readily understood when dissimilar metals are placed in electrical contact whilst immersed in an electrolyte. They held make the essential point that corrosion is not prevented simply by avoiding contact between dissimilar metals, important though that is in its own right, and that galvanic cells may be generated at chemical heterogeneities distributed on a micro scale and indeed, as indicated below, by the operation of additional agencies.

The importance of geometrical factors in corrosion :

One of the commonest causes of corrosion, especially in static structures such as frameworks, is poor geometrical detail that results in the entrapment of corrosive environment. Detail should be such that moisture and dirt are not trapped, involving the use of adequate drainage holes if necessary. Nor is this simple point relevant only to such structures, since tanks and other containers frequently need to have their contents removed and if this is not carried to completion the consequence can be severe corrosion. Possibly of even greater significance, if only because they are more likely to be overlooked in design, are crevices or smaller geometrical discontinuities frequently related to the method of fabrication. It is obvious that poorly fitting joints are likely to retain any corrosion substance with which they come into contact, but even when the preparation of the joint is sound its detailed can have a marked influence upon the incidence of corrosion. Thus, upward facing ledges, from overlapping plates or protruding welds, allow the collection of debris that will aggravate corrosion at the underlying surfaces. This is because corrosion reactions may frequently involve oxygen dissolved in the aqueous phase and those surfaces to which oxygen does not have

ready access will undergo marked attack, in contrast to those regions to which a plentiful supply of oxygen is available. but it can occur over large distances as, for example, with a buried pipeline passing through soils of varying oxygen content in regions displaced by distances measured in miles. Nevertheless, corrosion resulting from variations in the oxygen available for electrochemical reaction most frequently involves local changes arising from deposits that shield parts of exposed surfaces and crevice corrosion provides an obvious instance. In fact crevice corrosion, although frequently involving oxygen, can also arise from local changes in the concentration of other substances involved in some corrosion reactions. It is important to remember that crevices are not just created at metal-metal joints. Special care must be taken when bolting metals to moisture retaining materials like wood, which may itself release corrosive substances. Something akin to the localised conditions involved in crevice corrosion can occur due to the collection of condensation on downward facing members, causing particularly damaging corrosion to load bearing joints.

### **3.5 Dynamic situations**

In dynamic situations a number of additional physical factors may become important because of their effects upon the breakdown of the protective film that would otherwise form by reaction between the metal and environment. These may involve relative motion of the metal and environment, changes in stress or heat transfer leading to a variety of forms of corrosion failure but upon all of which the design engineer may exercise influence.

#### **Relative motion of metal and environment**

An example was given earlier of erosion-corrosion of brass condenser tubes due to high velocity, turbulent, cooling water impinging upon the surfaces of the tubes where they passed through poorly fitting baffle plates. This problem, involving the destruction of what would otherwise be a protective film is of widespread occurrence and severity, depending upon the metal and its environment, their relative velocities, the presence or otherwise of suspended matter and so on. However, since both corrosion and its prevention are frequently dependent upon the rate of supply of chemical species to a metal surface, the effect of increased velocity of an environment with respect to the metal with which it is in contact is not invariably to aggravate corrosion. Thus, the shielding of surfaces by deposits, already mentioned as a cause of corrosion, is less likely in high velocity solutions than when the latter are stagnant. By the same token, where the rate of corrosion is controlled by the rate of supply of some substance, e.g. oxygen, to a metal surface, it is to be expected that the corrosion

rate will increase with flow rate, simply because the rate of supply of the critical species controlling the overall reaction rate is increased. This is readily apparent in the results of corrosion in steel pipes conveying natural water, where the controlling parameter is the transfer of oxygen to the metal surface. The semi-empirical equation developed from this work to give the amount of corrosion

$$W = 5.21 \text{ Re}^{0.535} [(0.96t + 0.31)^{0.5} - 0.56]$$

where Re is the Reynolds Number based on the initial pipe diameter and t is the time in days. This, and like expressions for other systems of metal and environment, are only valid for the particular controlling conditions to which they refer, but it makes the general point that increases in flow velocity, proportional to Re, can significantly increase the amount of metal corroded in unit time. Of course, in the same way, when corrosion prevention is achieved by the addition of inhibitors to the environment, a subject discussed later, the effectiveness of the inhibitor is related to its supply to the metal surface and so it can be more efficient in flowing than in stagnant conditions. Nevertheless, it is most frequently the case that the high velocity impingement of liquids upon metal surfaces, the turbulence that can be created at geometrical features causing a change in flow direction or the cavitation that occurs in liquids due to sharp pressure changes, may all promote a degree of corrosion in excess of that which would be observed in the absence of such aspects in a design. The scouring action by solid particles suspended in a fluid which disrupts an otherwise inactive surface is an obvious possible cause of enhanced corrosion that will increase with relative velocity. But gaseous bubbles, created by sudden rarification of pressure or the entrainment of air, can have essentially similar effects if they are large enough and collapse at the metal-liquid interface imparting 'hammer blows' or shock waves to damage the metal surface. This mechanical damage may be sufficient to erode a surface in the absence of any corrosive reaction, but if the damage exposes metal that is reactive to the environment concerned then corrosion will further enhance the surface deterioration. The problem may be particularly acute in ships' propellers, water turbines, pump impellers and the like, if the design and material of construction are inadequate. Marked variations in the extent of attack over adjacent parts of a surface exposed to the same environment are observed where pipework fails by erosion-corrosion due to changes in velocity at a bend. A detailed examination of the shape of pits resulting from such velocity effects will usually indicate undercutting of the metal on the downstream side. Where turbulence results from small protrusions, e.g. deposited matter, weld spatter, the pitting frequently takes the horse-shoe shape. Such features of the pitting associated with the various types of erosion-corrosion together with the fact that the

pits are usually clean and devoid of corrosion products, allow this mechanism of failure to be distinguished from pitting corrosion in stagnant or low velocity conditions. A significant contribution to the avoidance or diminution of erosion-corrosion can be made by the designer in view of the influence of shape or geometry upon this mode of failure. In general, design features that decrease fluid velocities and streamline the flow will be beneficial, as will increase in section thickness at vulnerable areas if the problem cannot be completely overcome. The incorporation into the design of readily replaceable parts is sometimes necessary, as are baffle plates to avoid impingement of fluids on to critical parts if inlet ports cannot be located to avoid the problem. Although all of the methods of corrosion prevention are, in principle, available for controlling erosion-corrosion, the selection of resistant alloys coupled with attention to design details is one of the commonest ways of alleviating the problem. A resistant alloy can only be defined in relation to its conditions of exposure, i.e. the composition, temperature and velocity of the environment. It should be remembered however, that whilst for some systems of metal and environment corrosion rates may increase virtually linearly with flow rate, this is not invariably the case. Thus, in some cases the corrosion rate may decrease with increasing velocity, as for example when 17-19 per cent Chromium 9-13 per Nickel stabilised stainless steel is in contact with white fuming nitric acid at about 40 °C, due to the dispersion of otherwise aggressive corrosion products that enhance corrosion in stagnant conditions. In other cases, the corrosion rate may initially increase with fluid velocity later passing through a maximum and falling to a relatively low rate at high velocities, as is observed for a number of materials immersed in relatively pure waters free from aggressive ions. Clearly, in view of these variable effects, it is especially important to recognise any potential problems arising from fluid velocity effects at the design stage, so that the material selection can be made in the context of the details of the service condition. An example that illustrates the need for attention to detail during design is the use of mild steel for storage of sulphuric acid. Corrosion is rapid in weak acid, but in strong (70 per cent or above) acid a protective layer of ferrous sulphate is formed that reduces the corrosion rate under static conditions to an acceptable level. The corrosion rate is however increased by liquid velocity or increase in temperature. Hence while mild steel is the accepted material for acid storage tanks problems can arise. One problem associated with the effect of the strength of the sulphuric acid is related to the affinity of strong acid for water. The film of acid left on the side of the tank as it is emptied tends to become corrosive because it picks up moisture from air sucked into the tank, and if the tank is not to be refilled within a few days it is

common practice to include a drying agent in the tank vent. For the same reason, the outlet pipe should be positioned to facilitate complete draining of the tank when this is required. The position of the acid inlet is also critical, as if acid enters near the tank wall the local turbulence causes locally increased corrosion. Experience has shown that local thinning due to this cause can extend from top to bottom of the tank (because the liquid level varied as the tank was filled and emptied) and in one case a full 3,000 ton tank split from top to bottom in this locally thinned region, causing serious damage. In large tanks the inlet should be arranged at least 2 m from the tank wall; in smaller tanks good practice is to introduce wear plates in the vicinity of the inlet. Another phenomenon occasionally encountered is deep grooving caused by hydrogen gas bubbles continually following the same path and accelerating corrosion by virtue of the local movement of the acid. This can be particularly dangerous in horizontal tanks, or in manholes on the side of vertical tanks. Mild steel is, despite the problems mentioned, generally a satisfactory material for sulphuric acid tanks. A relatively recent development is the use of anodic protection, which prevents all of the above types of corrosion; as it allows the metal thickness to be reduced, an anodically protected tank can actually be cheaper and has the additional bonus that the acid remains purer because it contains less dissolved iron.

### **Stresses and corrosive effects**

If a normally protective film overlying a metal surface is disrupted by plastic deformation in the underlying metal then reactive metal may be brought into contact with an aggressive environment and corrosion, in one form or another, will ensue. The instances of stress corrosion cracking mentioned earlier are examples of corrosion resulting from the conjoint action of stress and a reactive environment upon metals, but such conjoint action can take other forms. Thus, if the corrosive reaction is not sufficiently localised to retain the geometry of a crack, by the rate of attack being essentially the same in the depth and width direction, then pits or fissures, rather than cracks, will result. Alternatively, if stress is applied in a cyclic manner, so that rupture of a protective film, corrosion and reforming of a film occur in a repetitive fashion, then failure may occur by corrosion fatigue. The latter is one of the commonest modes of material failure, involving crack initiation and growth under the influence of a repetitively applied stress of appropriate amplitude and frequency, as with fatigue in the absence of any environmental interaction, but with the crack initiation and/or propagation stages facilitated by corrosion. From the engineering viewpoint the most significant effects of the corrosive reactions are that, comparatively, they lower the minimum stresses above

which such failure occurs and they also usually increase the crack velocity, either of which will result in a reduced life for components. For initially plain specimens, corrosion fatigue is often assessed in laboratory tests by varying the initial stress amplitude (S) and observing the number of stress cycles (N) necessary to produce total failure, resulting, when produced in the presence of a corrosive substance, with a similar curve produced with the specimens in contact with air. (The implicit assumption that laboratory air is not corrosive frequently may not be valid.) The application of linear elastic analysis to crack growth problems in general has involved corrosion fatigue, the essential difference from the older approach of is employed to determine the crack extension per stress cycle ( $da/dN$ ) as a function of the maximum stress intensity ( $K_{max}$ ) or the stress intensity range per cycle ( $\Delta K$ ). The results indicate that in the absence of corrosion there is a limiting value of  $K$ ,  $K_{TN}$ , below which fatigue crack growth does not occur, and that in the presence of a corrosive substance this is lowered to  $K_{CF}$  and the crack growth rate is increased above that observed in the inert condition for the same stress intensity. For a wide variety of materials, the limiting stress intensity range for corrosion fatigue

$$\Delta K_{CF} = (2.7 \pm 0.3) 10^{-5} E.$$

where  $\Delta K$  is measured in  $MN \cdot m^{-3/2}$  and the modulus  $E$  is in  $MN/m^2$ . For steels, with module of about  $2.105 MN/m^2$ ,  $\Delta K_{CF}$  is in the region of only 5 to 6  $MN/m^{-3/2}$ , indicating the importance of geometrical discontinuities in facilitating corrosion fatigue crack growth. The importance of avoiding notches, especially with sharp profiles, in structures subjected to cyclic loading is well known if fatigue is to be avoided, but in the presence of a corrosive environment this is frequently even more important. The significance of crevices from the corrosion viewpoint has already been mentioned, but such geometrical features are not only important in relation to their influence upon oxygen distribution, since there are many other electrochemical reactions that can be stimulated by localised changes in ion concentration, and geometrical discontinuities in general will frequently facilitate localised concentration changes. Although the corrosion fatigue properties of materials vary with the environmental conditions, the latter are much less specific for corrosion fatigue than they are for stress corrosion, especially in relation to their influence upon  $\Delta K_{CF}$ . Crack growth rates at stress intensity range above  $\Delta K_{CF}$  are sensitive to the composition of the environment, as is apparent from the results for a Titanium – 6 per cent Aluminium – 4 per cent Vanadium alloy immersed in various environments, but the  $\Delta K_{CF}$  values do not appear to be particularly influenced by the nature of the test solution. However, for initially plain surfaces, fatigue properties as

measured by the stress below which total failure is not observed can be markedly influenced by changes in the environment. S-N curves for a mild steel in various aqueous solutions and shows the deleterious effect of chloride addition to water, especially in the presence of oxygen. The difference between the behaviour of plain and notched surfaces is probably largely related to the varying effects of different environments in producing pitting on initially plain specimens. Where the environment promotes pitting it will produce an increase in the stress intensity for the same loading conditions, as well as allowing local electrochemical changes within the confines of the pits that could not occur at a plain surface, either of which mechanisms would facilitate corrosion fatigue crack growth. In a somewhat similar fashion the frequency of stress cycling and the stress wave form may influence corrosion fatigue, in ways that are not apparent in fatigue in the absence of environmental reaction. Metal dissolution is, of course, time dependent, so that the longer the period of a stress cycle the greater is the extent to which dissolution can occur during that cycle. It may be expected therefore that, in general, the effects of corrosion upon crack growth will be greater the lower the frequency, and this is frequently found to be the case. Similarly, prior exposure of a structure to corrosive influences in the absence of stress cycling can influence subsequent behaviour when repetitive stresses are applied, if pitting occurs during the prior exposure period. There are similarities between certain aspects of failure by corrosion fatigue and by stress corrosion. Thus, particularly at very low stress cycle frequencies ( $< \sim 0.01$  Hz), failure by these two modes can be indistinguishable and some of the effects upon corrosion fatigue of corrosion reactions leading to pitting, mentioned above, are also observed in stress corrosion. At first sight it may appear odd that failure resulting from fluctuating or dynamic stresses can have similarities to failure under the static stress situation that is assumed to exist in relation to stress corrosion failure, and indeed with the latter it may be difficult to understand why crack propagation should occur at all, when the stress may be appreciably below the yield stress or the stress intensity well below the fracture toughness value. It should be remembered however that corrosion, even in the absence of stress, can be sufficiently localised to produce the geometry of a crack, so long as dissolution is concentrated at the advancing front and there is relatively little dissolution on the sides of the discontinuity. The presence of stress will help to concentrate the dissolution at the crack tip, since it is there that the stress intensity will be maximal and where plastic deformation, resulting in the disruption of otherwise protective films, will be concentrated. The influence of a pre-existing sharp discontinuity (notch or crack) in facilitating stress corrosion crack propagation therefore may be expected to be

dramatic, as it is in corrosion fatigue, and this is found to be so. For example, certain titanium alloys can be made to fail by stress corrosion when immersed in sea water if the specimens are pre-cracked, but the same alloys in the same environment will not crack if statically loaded as plain specimens. Clearly, in relation to alleviating both stress corrosion and corrosion fatigue failure it is important to avoid sharp changes in section, whether these relate to design features or to surface defects in a structure. Whilst this will invariably be beneficial it will not ensure immunity from such failures, since stress corrosion or corrosion fatigue cracks can be started at initially plain surfaces. Where the stresses are high enough to promote even a small amount of plastic deformation in the metal the attendant disruption of a protective surface film to expose bare metal frequently will be sufficient to initiate the dissolution reactions. This may be particularly important at start-up or shut-down of plant where, although the design stresses may be well below any stress thought likely to induce plastic deformation, thermal stresses may operate in this way. The significance of residual fabrication stresses, if not previously relieved, should not be overlooked in this respect, since they will normally be of yield stress magnitude if produced by welding. Even if such stresses are static, in the sense of being associated only with elastic strains at the relevant time, subsequent localised corrosion by pitting or intergranular penetration will initiate plastic deformation due to the enhanced stress level at the tip of the discontinuity and this can sustain the corrosive attack. Obviously for any stresses below the level that will initiate localised corrosion at an initially plain surface, the local stress intensity can be raised to a dangerous value if corrosion penetrates the metal to a sufficient extent, and the problem in service is the same as that at the design stage, namely to avoid significant changes in section. The various protective treatments discussed later can be employed to this end, but it is also sometimes possible to introduce compressive stresses into the surfaces of components, by shot or hammer peening or surface rolling, that will at least delay the incidence of stress corrosion or corrosion fatigue cracks, because such cracks will form only in the presence of tensile stresses of appropriate magnitude. However, surface compressive stresses will only remain effective so long as the deformed layer that constitutes the inhomogeneous deformation which introduces the stresses in the first place remains intact. Pitting or general corrosion leading to removal of this layer, usually not much thicker than about 0.1 mm, will relieve the compressive stresses and so remove the protection with consequent failure. Situations can arise, both in relation to stress corrosion and corrosion fatigue, where slow crack growth by either of these mechanisms will occur during service and questions then arise as to the point in time when the structure should be regarded as unsafe. The

approach then used is based essentially upon the maximum allowable defect size in a structure to avoid any crack growth. For comparison between materials it is convenient to consider 'design stresses', to allow for the different properties of the different materials, and, since the designer is usually interested in the residual strength of a cracked structure, it is convenient also to convert the fracture toughness values to critical crack lengths. Apart from the more obvious ways of tackling the problems of stress corrosion and corrosion fatigue, through appropriate material selection, the specification of resistant surface coatings or control of the environment, the designer can markedly influence the incidence of such modes of failure by other devices. Attention to the details of manufacturing methods, to minimise residual stresses resulting from grinding, joining, interference fits or misfits in assembly usually will be worthwhile, as will relief of fabrication stresses by thermal treatment where possible or the introduction of surface compressive stresses by rolling. Finally the avoidance of sharp changes in section, that may relate either to some aspect of the design or to some surface defect arising in manufacture, will invariably be beneficial, as will any measures taken to avoid the incidence of geometrical discontinuities, such as pits, during service.

#### **Temperature and heat transfer in relation to corrosion**

Most electrochemical reactions proceed at faster rates with increasing temperature, approximating to a doubling of rate for each 10 °C rise in temperature whether the corrosion process involves dissolution leading to general attack or to a more localised form such as cracking. In general therefore lower temperatures will be beneficial, but there are exceptions. The reversal of polarity of the iron-zinc bimetallic couple with increasing temperature has already been mentioned and there are other instances of equally sharp changes in the nature or extent of corrosion as temperature is increased. It is a matter of common experience that bare steel immersed in tap water at room temperature will corrode at a relatively high rate producing the familiar orange-brown rust as a corrosion product. An identical piece of steel immersed in the same tap water but at the boiling point of the latter will develop a black, adherent, film of corrosion product that is sufficiently protective to reduce the corrosion rate very considerably. This change in the nature of the corrosion products and their degree of protectiveness is not peculiar to the system mentioned nor indeed should it be assumed that where there is such a change it will be invariably beneficial. Thus, for example, the stress corrosion cracking of mild steels in nitrate solutions is unlikely at 20 °C but occurs with alarming ease at 100 °C, and this largely related to the effect of temperature upon the nature of the

corrosion products involved, rather than its influence upon crack tip dissolution rate and hence crack velocity. The earlier statement that corrosion rates will approximately double for each 10 oC rise in temperature is only valid providing the details of any part of all of the reactions involved do not change, which will usually mean that the statement is valid only over restricted range of temperature change. The above assumes isothermal conditions but in many practical situations heat transfer occurs across the metal-solution interface and although in many such cases it is still the temperature at the interface that is critical, rather than the fact that heat transfer occurs across it, nevertheless there are circumstances in which the latter can be important. These circumstances will arise when concentration changes occur in the solution in contact with the metal at the interface across which heat transfer occurs. Heat is transferred through a thin layer of superheated liquid on a metal surface, the temperature gradient rising to about 10 oC as the heat transfer rate increases and the boiling point of the liquid is approached. Convection currents then transfer the heat from this thin film to the bulk liquid. When the heat flux rises to a sufficiently high value, bubbles of vapour begin to nucleate at points on the metal surface and the liquid starts to boil, with the bubbles becoming detached and, by stirring, further assisting in the transfer of heat, Further increase in the temperature of the metal surface causes the rate of boiling to increase and the bubbles become so numerous that they form a continuous film of water vapour between the metal and bulk liquid. The vapour film acts as a thermal insulator, so that the heat flux initially falls as the temperature difference across it increases, but later rises again as the latter continues to increase and film boiling occurs. The more important aspects of these events from the corrosion viewpoint are that, by the stirring effects involved, the transport of material to and from the metal surface will differ from that which occurs in stagnant conditions, with the implications mentioned in the context of relative motion of metal and environment, and that, by evaporation into a bubble, concentration of dissolved solids in the film of water between the bubble and metal surface may occur. Some of the solids dissolved in water, e.g. sodium hydroxide, produce a protective film on mild steel at low concentrations but can be corrosive if sufficiently concentrated, or if the concentrated substance is not itself corrosive, it can deposit on the metal surface reducing heat transfer and raising the metal temperature so that steam, produced from water penetrating the deposit or scale, may react with the steel, if the temperature achieves values in the region of 400 oC. The effects of scales and/or corrosion products in reducing thermal conduction leading to higher temperatures in the underlying metal can lead to other modes of failure. Thus, if local hot spots are developed in a tube wall, thermal stresses will be

generated and these can result in plastic deformation, apparent as bulges. (The temperature differences required to produce such effects in a mild steel tube are in the region of only 100 oC.) If the local stress and temperatures are high enough and sustained then the tube may fail by creep, i.e. by the formation of intergranular voids and cracks. Evidence of such local hot spots is usually apparent in the microstructure of the steel. There is an additional way in which thermal gradients over a metal surface immersed in an electrolyte can induce failure and this arises because of the possibility of a thermogalvanic cell being generated between the hot zone, acting as anode, and the colder regions acting cathodically. The detailed mechanisms involved in thermogalvanic cells are complex and it should not be assumed that temperature variations over a metal surface will result invariably in corrosion from such a source, which is just as well in view of the impossibility of designing any heat exchanger without some temperature gradients. However the problem does arise in some of the commonly used metals in certain environments, especially if the hot, anodic area is small in comparison with the colder, cathodic area. The concentration of corrosive substances at metal interfaces through which heat transfer occurs can take place in circumstances that are not always easily recognised. Thermal insulation used for lagging pipework would not usually be regarded as a particularly hazardous material from the corrosion viewpoint, but it can contain a few parts per million of chloride and the ingress of water can leach this chloride transporting it to the covered metal surface where concentration can occur due to the heat transfer. If the chloride reaches an appropriate concentration and the material being lagged is an stainless steel then stress corrosion cracking can occur, and there have been many such failures in service. To the engineering designer the lesson to be learned from these various examples is that corrosion usually will be prevented by avoiding unnecessarily high temperatures, especially if these are variable over a surface. Perhaps most importantly where heat transfer conditions are involved consideration should be given to the possibilities of solution concentration, especially in crevices and under scales or other thermal insulation whether present by accident or design or as the result of the service conditions.

### **The metal as a part of a design**

In the totality of an engineering design the metal and its fabrication are important parts, but the detailed choices may be determined by considerations other than those involving corrosion. Thus the strength/weight ratio, elastic modulus, electrical or thermal conductivity or other considerations may determine the nature of the metal or alloy to be used in a particular application. Similarly the

physical properties of the alloy, the size of the structure, the number of components and so on, will usually determine the mode of fabrication, with economic considerations applied overall. Where likely corrosion problems may only be considered as part of the design after these primary requirements have been met, the freedom of action in relation to corrosion prevention will necessarily be somewhat restricted. But even where likely corrosion problems are of primary concern in material selection it is important to realise that, say, the use of a stainless steel instead of a mild steel will not always diminish corrosion problems, because the modes and rates of corrosion are not constant for a given material, but rather they are dependent upon the environment to which it is exposed. Clearly any of the stainless steels would provide better life than mild steel in hot concentrated nitric acid, but in hydrochloric acid only the 12 per cent Chromium 12 per cent Nickel steel is significantly better than the mild steel, which in the sulphuric acid is better than any of the stainless steels, which in the sulphuric acid is better than any of the stainless steels, costing about an order of magnitude more per unit weight. These differences are largely related to the differing oxidising characteristics of the acids, the corrosion resistance of stainless steels mainly depending upon the formation of a protective chromium oxide film upon their surfaces, so that in the absence of an adequate supply of oxygen, as with the hydrochloric acids, the chromium addition is of little benefit. Essentially the same point can be seen in relation to the atmospheric corrosion of metals, that good corrosion resistance in a particular atmosphere is no guarantee of good resistance in other circumstances corrosion resistance over mild steel in industrial and rural atmospheres to the development of an adherent rust film due to the incorporation of low-concentrations of certain alloying elements, but the relative improvement in those atmospheres is not nearly so marked in a marine atmosphere. When immersed in water significantly better than mild steel and its use is not recommended in such conditions, although there are examples of it having been so used, no doubt because of its corrosion resistance in other situations and the assumption that this will be good irrespective of the environment. The same point can be made in relation to other forms of corrosion; thus additions to ferritic steels are beneficial with respect to stress corrosion cracking resistance in carbonate environments, but are detrimental in hydroxide solutions, and so on. The general point to be grasped is that in specifying the operating conditions for a component or structure it is vital that the environmental conditions be defined with as much precision as any other parameters, such as stress, temperature etc. Only by so doing can the selection of a material from the corrosion resistance viewpoint be made satisfactorily

### **Galvanic series of some metals in water**

Electropositive

Platinum

Titanium

Stainless steel

Monel

Copper

Lead

Iron, cast iron, or steel

Cadmium

Zinc

Aluminium

Magnesium

Electronegative

### **3.6 Factors that control the corrosion rate**

Certain factors can tend to accelerate the action of a corrosion cell.

These include:

(a) Establishment of well-defined locations on the surface for the anodic and cathodic reactions. This concentrates the damage on small areas where it may have more serious effects, this being described as "local cell action". Such effects can occur when metals of differing electrochemical properties are placed in contact, giving a "galvanic couple". Galvanic effects may be predicted by means of a study of the Galvanic Series which is a list of metals and alloys placed in order of their potentials in the corrosive environment, such as sea water. Metals having a more positive (noble) potential will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it. The Galvanic Series should not be confused with the Electrochemical Series, which lists the potentials only of pure metals in equilibrium with standard solutions of their ions. Galvanic effects can occur on metallic surfaces which contain more than one phase, so that "local cells" are set up on the heterogeneous surface.

Localised corrosion cells can also be set up on surfaces where the metal is in a varying condition of stress, where rust, dirt or crevices cause differential access of air, where temperature variations occur, or where fluid flow is not uniform.

(b) Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion. Sodium chloride is encountered. Quite small concentrations of sulphur dioxide released into the atmosphere by the combustion of fuels can dissolve in the invisibly thin surface film of moisture which is usually present on metallic surfaces when the relative humidity is over 60-70%. The acidic electrolyte that is formed under these conditions seems to be capable of stimulating both the anodic and the cathodic reactions. In practical terms it is not usually possible to eliminate completely all corrosion damage to metals used for the construction of industrial plant. The rate at which attack is of prime importance is usually expressed in one of two ways:

- (1) Weight loss per unit area per unit time,
- (2) A rate of penetration, i.e. the thickness of metal lost.

If suitable water treatment with corrosion inhibitors is used a life of at least twenty years might be expected. This, of course, is ignoring the fact that at some time before the metal corrodes where its required mechanical strength is not attained. When designing equipment for a certain service life engineers often add a "corrosion allowance" to the metal thickness, permitting a certain amount of thinning before serious weakening occurs, the factors influencing the rate of attack are:

(a) the condition of the metal surface

Corrosion debris and other deposits - corrosion under the deposits, with a possibility of pitting (severe attack in small spots)

(b) the nature of the environment

pH - in the range of 4-10 corrosion rate is fairly independent of pH, but it increases rapidly when the pH falls below 4. Oxygen content - increase in oxygen concentration usually gives an increase in corrosion rate. Flow rate - increased water flow increased oxygen access to the surface and removes protective surface films, so usually increases corrosion, but can sometimes improve access for corrosion inhibiting reactants. Water type - very important, in general low corrosion rates are found with scale-forming (hard) waters. Aggressive ions which accelerate corrosion are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  but quite complex interactions may occur between the various dissolved species in natural waters.

### 3.7 Corrosion related measurements

#### 3.7.1 Corrosion Coupon Test

This is the test to determine the corrosion rate of any metal in a given liquid, due to chemical corrosion. The metal is cut into small pieces of a standard size—the coupons or chips. The coupons are then immersed in and rotated through a bath of the test liquid in a manner specified by a certain standard. The corrosion rate is determined by the loss of weight of the coupon with time. Stress corrosion is tested using a different standard, such as ASTM G30–97.

#### 3.7.2 Soil Resistivity Measurement

The electrical resistivity of the soil around a pipe affects the corrosion of the pipe. It is often measured as part of the work related to cathodic protection. From Ohm's law in physics, when a voltage  $V$  is applied across the two ends of a conducting cylinder of length  $L$  and cross-sectional area  $A$ , a current  $I$  will flow through the conductor such that where  $\rho$  is the resistivity of the conductor, and the quantity  $R = \rho L/A$  is the resistance of the conductor. When  $R$ ,  $L$ , and  $A$  are given in ohm, cm, and  $\text{cm}^2$ , respectively, the unit of resistivity is ohm-cm. The foregoing concept can be applied to soil. Dry soil has high resistivity and is noncorrosive, whereas wet soil (especially those containing salts) has low resistivity and is corrosive. Depending on their resistivity, soil can be classified as in

#### Corrosion Classification of Soil

Classification	Soil Resistivity (ohm-cm)
Noncorrosive	>10,000
Mildly corrosive	2000–10,000
Moderately corrosive	1000–2000
Corrosive	500–1000
Very corrosive	<500

The most common way to measure the resistivity of soil is the Wenner method (also called four-pin method), which involves placing four electrodes into ground, separated at an equal distance  $L$ . A current source such as a battery is connected to the two outer electrodes to generate a current  $I$  through the two electrodes. If a voltage  $V$  is measured between the two inner electrodes, the resistivity of soil is  $\rho = 2 \pi L V/I$

When using the above equation to calculate soil resistivity, the distance  $L$  must be much longer than the buried length of each electrode, i.e.,  $L \gg b$ . The current source can be either a DC (direct current) or AC (alternating current). The electrodes can be made of various materials such as iron or copper sulfate. The value measured is the average resistivity of the soil layer over a depth approximately the same as the distance  $L$  between neighboring electrodes. Although different manufacturers make Wenner-type resistivity meters of different designs, the fundamental principle used is the same. Soil resistivity is one of the most important factors in selecting a groundbed location. The number of anodes required, the length and diameter of the backfill column, the voltage rating of the rectifier and power cost are all influenced by soil resistivity. In general, the lowest and most uniform soil resistivity location with relation to depth should be utilized for a deep groundbed site.

**Average resistivity's of some soils**

Environment	Resistivity (ohm cm)
Brackish river water	1
Sea water	25
Town supply water	1000 – 1200
Alluvial soils	1000 – 2000
Clays	1000 – 5000
Gravel	10000 – 25000

Sand	25000 – 50000
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Soil resistivity is measured in ohm-cm and is obtained by various means. A long-standing practice utilizes the Wenner four pin method. The deep groundbed designer should also call upon experience gained from other cathodic protection installations in the area. Earlier survey records often provide area resistivity. Many times the designer may obtain an estimate of average soil resistivity from a knowledge of rectifier output from the groundbed that is to be replaced.

CP Station	Soil Resistivity (ohm-m)	No. of Anode	Type of Anode Bed	Ground Resistance (ohm)	Anode to Backfill resistance (Ohm)	Cable resistance (Ohm)	Total current of each ground Bed (Amp)	Rating of CP station (Volt/ Amp)	Total circuit Resistance (ohm)	
									Actual	Allowed
1	50	15	V	0.843	0.041	0.112	75	50/50	0.983	1
2	50	15	V	0.843	0.041	0.112	75	50/50	0.983	1
3	50	15	V	0.843	0.041	0.112	75	50/50	0.983	1
4	50	10	H	0.793	0.041	0.112	50	50/50	0.946	1

Assume that it is desired to obtain soil resistivity in an area where another groundbed is operating at 22 volts and 40 amperes. In this technique, it is preferred to use operating data when the groundbed was first installed since the size and condition of the bed is known more precisely. It is known that the active column length of the operating bed is 49 m with a diameter of 15.2 cm. Experience has shown that the resistance of the backfill column to earth is approximately 85% of the total circuit resistance. In the example above the total circuit resistance by Ohm's law is:

$$R_T = \frac{V}{I} = \frac{22V}{40A} = 0.55\Omega$$

Then the backfill to earth resistance  $R_A$  is approximately:

$$R_A = 0.55 \times 0.85 = 0.47 \text{ ohm}$$

The H. B. Dwight relationship can be used to determine the backfill to earth resistance

$$R_A = \frac{\rho}{2\pi L} \left( \ln \frac{4L}{r} - 1 \right)$$

Where:

$R_A$  = groundbed resistance (ohm)

soil resistivity, ( $m$ )

$L$  = active bed length, ( $m$ )

$r$  = active bed radius, ( $m$ )

Since  $R_A$  is known, the above equation can be rearranged to solve for the resistivity:

$$\rho = \frac{R_A 2\pi L}{\left( \ln \frac{4L}{r} - 1 \right)}$$

The value of soil resistivity can be determined by substituting the known values for groundbed resistance indicated above as 0.47-ohm, the groundbed length and diameter.

$$\rho = \frac{\pi(0.47)(49)(2)}{\ln \frac{(4)(49)}{0.152} - 1} = 23.5$$

The estimated value of 23.5 ohm m can then be used in the new design with reasonable confidence.

If existing groundbed data is not available, soil resistivity must be estimated by other techniques. Soil resistivity generally relate to the salinity or purity of the water or moisture, which historically

has permeated the soil and remains there to one degree or another. The following broad guidelines relate USA areas and soil type conditions with its resistivity.

Area and/or Soil Type	Resistivity Range (ohm cm)
Brackish water lowlands, poor or slow drainage, coastal areas	150 -1,200
Coastal plains, low elevation	600 - 1,500
Central coastal areas, satisfactory to good drainage	1,200 - 5,000
South central, Midwest and central, Farm and range lands	3,500 - 10,000
West central desert plains, mountains	5,000 - 25,000
Eastern and northeast high country, Excellent drainage, dry and arid	10,000 - 25,000

### 3.7.3 Pipe-to-Soil Potential

The potential difference between a buried pipe and the soil around it is very important in the study of corrosion. this potential is measured by connecting a high-impedance voltmeter or potentiometer between the pipe and a special electrode (half cell) placed in contact with the soil above the pipe. The electrode used can be one of many types, such as the copper sulfate electrode, hydrogen electrode, calomel electrode, zinc electrode, etc., with the copper sulfate being the most commonly used. The copper sulfate (CuSO<sub>4</sub>) electrode, is made of a copper rod immersed in a saturated water solution of copper sulfate. The electrode has a porous plug bottom, which must make a good contact with the soil when the electrode is used. while the copper rod of the electrode must be connected to one end of a voltmeter, the other end of the voltmeter is connected to the pipe through a welded (or soldered) lead. A high impedance voltmeter is required to draw insignificant current from the pipe to the electrode. The wire used to connect the pipe to the voltmeter should be well insulated. The pipe-to-soil potential should be measured at various locations along a pipeline. The pipe is considered in good shape (noncorroding) if the pipe-to-soil potential is higher than -0.85 V. In places where the potential is lower than -0.85 V, cathodic protection is needed.

### 3.7.4 Line Current Measurement

Another quantity that is often measured in corrosion detection is the line current, which is the current measured between two points along a pipeline. The electrical circuit for measuring the line current. It is normally measured between points separated at distances a few hundred feet apart. The existence of line current indicates that corrosion is in progress in the pipe. With line currents measured at regular intervals along a pipe, the location of corrosion cells along the pipe can be determined. Note that line current measurements cannot detect corrosion cells that are of small dimension, as in the case of an anode on the bottom of a cathode in the same cross section of a pipe.

### 3.7.5 Current Requirement Test

In designing Galvanic and Impressed current cathodic protection system the total current requirement is tested so that adequate current is provided to protect the structure. Complete cathodic protection is achieved when the structure potential is  $-0.85$  volt with respect to a copper-copper sulfate reference electrode. Current requirement tests are done by actually applying a current using a temporary test setup, and adjusting the current from the power source until suitable protective potentials is obtained. Figure shows a temporary test setup. In this setup, batteries can be used as the power supply, in series with heavy-duty adjustable resistors. The resistors can be adjusted to increase the current until the potential at the location of interest, such as point A in figure, is at  $-0.85$  volt with respect to a copper-copper sulfate reference cell. The current supplied is the current required for cathodic protection. The effectiveness of the insulating joints is also be tested. The potentials at points B and C are measured, first with the current interrupter switch closed, then with it open. If there is any difference between the two readings at either point, the joint is not insulating completely.

Equipment needed for the test are

- A small DC power system is used (10 A).
- A temporary anode ground bed is installed.
- Potential loggers are installed at selected test locations to monitor potentials
- A current is applied and the potential is measured

- The current that brings the potential of the whole pipe below the protective potential is used the required current for protection

**Short Line Method:** The short line method is used when an isolated section of pipeline is available for testing. In the short line method, the test current is applied then interrupted. The difference between the applied and interrupted current is  $I$ . The change in structure-to-electrolyte potentials at the two test points ( $E_1$  and  $E_2$ ), which occur when the current is interrupted, are measured. If the ratio between  $E_1$  and  $E_2$  is greater than 1.6, a correction factor from Table 6 is applied by multiplying  $E_2$  by the correction factor. Coating conductance (micromhos/ft) is then calculated using the following formula:

$$I \times 10^6 / \{ \{ (E_1 + E_2/2) / 2 \} \times \text{length (ft)} \}$$

Where

$E_1$  = pipe-to-electrolyte potential with current off

$E_2$  = pipe-to-electrolyte potential with current on

**Long Line Method.** The long line method is used when a section of structure cannot be effectively isolated or when the  $E_1/E_2$  ratio in the short line method exceeds 3.0. In the long line method the test current is applied and the current flowing through the pipe is determined at the two IR drop test points. The structure-to-electrolyte potential at the two test points is measured with the current on. The test current is interrupted and the change in current at the two IR drop test points ( $I_1$  and  $I_2$ ) as well as the change in potential at the two potential test points ( $E_1$  and  $E_2$ ) are measured. As in the short line method, if  $E_1/E_2$  is greater than 1.6,  $E_2$  should be multiplied by the correction factor found in Table 6. If the ratio is greater than 3, the test section should be shortened. The coating conductance (micromho/ft) is then calculated using the following formula:

$$(I_1 - I_2) \times 10^6 / [ E_{\text{avg}} \times \text{length (ft)} ]$$

### Sacrificial Anodes

The earliest experiments on cathodic protection were performed with zinc anodes that were electrically connected to copper plates immersed in seawater. As can be seen on the galvanic series, such an arrangement would produce a cathode (copper) and an anode (zinc). In the *large galvanic cell so formed*, the zinc cylinder corroded away in a manner to protect the copper substrate. This method of cathodic protection can be used with other combination of metals providing the necessary current to the metal to be protected. When two metals are electrically connected to each other in an electrolyte e.g. seawater, electrons will flow from the more active metal to the other, due to the

difference in the electrical potential, the so called "driving force". When the most active metal (anode) supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce electrons, which the least active (cathode) will receive through the metallic connection with the anode. The result is that the cathode will be negatively polarized and hence be protected against corrosion. To calculate the rates at which these processes occur, one has to understand the electrochemical kinetics associated with the complex sets of reactions that can all happen simultaneously on these metals.

Anode material

Anode efficiency

Protective current requirements

### **3.8 Protective Current Requirements**

Assumptions of protective current requirements and bare metal areas. To obtain a starting point, certain general assumptions have been found helpful:

For bare metal in the ground, a current of 11 to 22 mA/m<sup>2</sup> of bare metal surface has been found adequate, except under extreme or unusual conditions. This value must then be modified to suit the particular conditions.

For coated pipe, the current required is difficult to estimate without field tests. The primary reason is the unknown condition of the protective coat which can vary from nearly 0% to 98% coverage. For a fairly new protective coat properly applied, assume 2 percent bare and 22 mA/m<sup>2</sup> for use in tentative calculations. Field test may show that this figure should be modified.

Bare pipelines can usually be protected by 11 to 22 mA/m<sup>2</sup>. This is seldom justifiable economically for extensive or long lines, however, and the necessary protection is usually afforded by the application of cathodic protection to localized areas called "hot spots."

Bare steel tanks are treated the same as bare pipelines. Inside steel surfaces in contact with fresh water at zero or low velocities require from 22 to 65 mA/m<sup>2</sup>, depending on the nature of the water. The low value is used for water which is scale forming. That is, the water will form a calcareous coating on the surface of the metal.

Protecting steel surfaces in contact with water in motion presents another problem. Water in motion produces a scouring effect which prevents the formation of the above-mentioned coating and even the formation of a hydrogen film. Therefore, surfaces exposed to water in motion require a higher current density. The amount required is hard to predict. In this case, an experimental determination of the current requirement should be made.

### **3.9 Groundbed Design**

For underground structures requiring cathodic protection, the location and nature of the site where the anode is placed needs careful consideration. A low soil resistivity, which would otherwise be classified as a highly corrosive soil, is not the only factor which determines the location of the anode. Other factors to be considered include the presence of foreign metallic structures, accessibility and availability of a power source. The location which is specifically prepared to house a single or a combination of anodes is called a groundbed.

**Impressed anode groundbeds:** Once a location is selected and the soil resistivity is determined, the engineer needs to design the type of groundbed and choose anode material and combination. Types of groundbeds are classified as: shallow vertical, shallow horizontal or deep well. Anode materials used for underground impressed current systems are generally graphite or high silicon cast iron. In the groundbed, it is preferred for the anode to be surrounded by a carbonaceous backfill. The backfill particles help to reduce anode resistance to earth, extend anode life by allowing anodic reactions to occur on their surface and provide a porous structure so the gases produced can escape.

#### *Shallow Vertical Groundbed:*

The individual or multiple anode groundbed resistances can be determined.

#### *Shallow Horizontal Groundbeds:*

Sometimes due to unfavorable soil conditions shallow horizontal groundbeds are preferred. Again earth resistances can be determined by calculation.

### *Deep Well Groundbeds:*

Where soil resistivity at the surface are very high, a series of vertical anodes are sometimes installed in deep well groundbeds (up to 100 m and more deep). To determine the depth of the well it may be necessary to carry out a soil resistivity survey. Using the four-pin method, soil resistivity variation with depth can be determined by changing the pin spacing. Deep well groundbeds can take different forms.

A basic design incorporates the use of a steel casing to prevent the collapse of the drilled hole. Several anodes attached together with a rope are placed inside the casing. The remaining space is then filled with carbonaceous material. Once the groundbed becomes operative the steel casing will be consumed. After the pipe corrodes away the anode and backfill become active. Deep wells are generally fitted with a vent to allow gases to escape. Gas entrapment tends to increase the groundbed resistance. It should be added that in certain rock formations anodes have been installed satisfactorily without a steel casing. Although deep well groundbeds provide good current distribution they are expensive to construct because of the cost of the drilling. Careful design is also necessary because anode failures cannot be easily rectified.

### *Sacrificial Anode Groundbeds:*

In certain situations, for example in reducing stray current effects, a sacrificial system may be specified to protect underground structures. The backfill used with these anodes is different from that described for impressed anodes. A typical backfill contains a mixture of clay and gypsum. The function of this chemical backfill to provide conditions favorable to anode dissolution. It also helps to reduce the groundbed resistance. Groundbed resistances can be calculated using the same procedure adopted for impressed current anodes. Individual galvanic anodes in a horizontal groundbed are generally not used. For this type of groundbed a continuous galvanic anode strip is found to be practical.

**Remote and Close Groundbeds:** Since a groundbed is a source of current, there is a field (potential) gradient associated with it. When the voltage gradient in the soil near the structure is far from the voltage gradient of the groundbed, the groundbed is referred to as remote. However when the voltage gradient in the soil near the structure overlaps with that of the groundbed, the groundbed is referred to as close. This is because the groundbed is near enough to interfere significantly with the field gradient around the structure.

### 3.10 Backfill Materials

The type of backfill used in a groundbed depends on whether the cathodic protection system is sacrificial or impressed.

**Chemical backfills:** The chemical backfill used with galvanic anodes provides an environment which is conducive for anode dissolution. A typical mixture is 75% powdered gypsum (calcium sulfate), 20% granular bentonite and 5% sodium sulfate. This mixture has a resistivity of 50 ohm cm and is suitable for use in high resistivity soils. The function of the bentonite is to absorb water and expand, thus ensuring good contact between anode and soil by lowering groundbed resistance. A 75% bentonite 25 % gypsum mixture (250 ohm cm) is recommended for low moisture soils.

**Carbonaceous backfills:** Impressed current anodes are usually surrounded by a carbonaceous backfill. Types of materials used include coke breeze, calcined petroleum coke and natural graphite. The dual purpose of the carbonaceous backfill is to reduce the groundbed resistance by increasing the effective size of the anode and to provide a surface on which oxidation reactions could occur. The latter function prolongs anode life. To ensure good electrical contact, the backfill must be tamped around the anode. Resistivity of carbonaceous backfills are in the order of 50 ohm cm.

Particle size and shape are also important when specifying a backfill. Both parameters determine the contact area between anode and earth whilst influencing the porosity of the column which is important for gas ventilation. A general purpose coke breeze is for use in shallow horizontal and vertical groundbeds. It has a resistivity of 35 ohm cm. For deep well applications a special calcined petroleum coke breeze is available. It has a resistivity of 15 ohm cm and can be pumped.

#### Galvanic Series

Galvanic series relationships are useful as a guide for selecting metals to be joined, will help the selection of metals having minimal tendency to interact galvanically, or will indicate the need or degree of protection to be applied to lessen the expected potential interactions. In general, the further apart the materials are in the galvanic series, the higher the risk of galvanic corrosion, which should be prevented by design. Conversely, the farther one metal is from another, the greater the corrosion will be. However, the series does not provide any information on the rate of galvanic corrosion and thus serves as a basic qualitative guide only. Once you have finished reading the material on this

page you can check your skills with a self test. Non-uniform conditions along the surface of a metal can also cause different energy potentials. For example, the portion of an anchor embedded in concrete typically has lower energy potential than the portion exposed to soil. The use of the galvanic series has to be done with caution and a basic knowledge of the environments that is a necessary part of this serious form of corrosion. The following documents provide different points of view regarding the ranking of metals and coatings in practical schemes for preventing galvanic corrosion.

### Galvanic

The following galvanic lists metals in the order of their relative activity in water environment. The list begins with the more active (anodic) metal and proceeds down to the least active (cathodic) metal of the galvanic series. A "galvanic series" applies to a particular electrolyte solution, hence for each specific solution which is expected to be encountered for actual use, a different order or series will ensue. In a galvanic couple, the metal higher in the series (or the smaller) represents the anode, and will corrode preferentially in the environment. Listed below is the latest galvanic table from MIL-STD-889 where the materials have been numbered for discussion of characteristics. However, for any combination of dissimilar metals, the metal with the lower number will act as an anode and will corrode preferentially.

### Galvanic Compatibility

Often when design requires that dissimilar metals come in contact, the galvanic compatibility is managed by finishes and plating. The finishing and plating selected facilitate the dissimilar materials being in contact and protect the base materials from corrosion.

For *harsh environments*, such as outdoors, high humidity, and salt environments fall into this category. Typically there should be not more than 0.15 V difference in the "Anodic Index". For example; gold - silver would have a difference of 0.15V being acceptable.

For *normal environments*, such as storage in warehouses or non-temperature and humidity controlled environments. Typically there should not be more than 0.25 V difference in the "Anodic Index".

For *controlled environments*, such that are temperature and humidity controlled, 0.50 V can be tolerated. Caution should be maintained when deciding for this application as humidity and temperature do vary from regions.

### **DANGERS TO BE AVOIDED**

Consideration must also be given to spark hazards created by the introduction of electric currents into structures situated in a hazardous atmosphere. Any secondary structure residing in the same electrolyte may receive and discharge the cathodic-protection direct current by acting as an alternative low-resistance path. Corrosion will be accelerated on the secondary structure at any point where current is discharge to the electrolyte. This phenomenon is called "interaction". Interaction may occur, for example, on a ship that is moored alongside a cathodically protected jetty, or on a pipeline or metal-sheathed cable that crosses a cathodically protected pipeline. Interaction may be minimized by careful design of the cathodic-protection system, in particular, by design of a scheme to operate at the lowest possible current density and by maintaining the greater separation between the protected structure and the secondary structure, and between the ground beds or anodes and the secondary structure. It is an advantage of sacrificial-anode schemes that they are not prone to creating severe interaction problems and therefore are popular for protection in congested and complex locations. Methods and procedures are available for overcoming interaction, and testing must be carried out in the presence of all interested parties, so that the choice of remedial measures may be agreed if and when the acceptable limit of interaction is exceeded.

# CHAPTER 4

## EXPERIMENTAL/COMPUTATIONAL

### 4.1 Design Formulas

Formula	Parameter
<p><b>Surface area of pipeline (S<sub>a</sub>)</b></p> $S_a = \pi \times D \times L$	<p><b>Where</b></p> <p>S<sub>a</sub> = Surface area of Pipeline (m<sup>2</sup>)  D = Diameter of Pipe (m)  L = Length of Pipe (m)</p>
<p><b>Current Requirement I<sub>t</sub></b></p> $I_t = S_a \times C_d \times S_m / 1000$	<p><b>Where</b></p> <p>I<sub>t</sub> = CP Current Requirement (Amp)  S<sub>a</sub> = Surface Area (m<sup>2</sup>)  C<sub>d</sub> = CP Protective Current Density  C<sub>d</sub> = 0.05 mA/m<sup>2</sup> for PE Coating  C<sub>d</sub> = 0.5 mA/m<sup>2</sup> for CTE Coating  S<sub>m</sub> = Safety Margin (1.3)</p>
<p><b>Anode requirement by weight</b></p> $W = I_t \times C_a / U_f$	<p><b>Where</b></p> <p>I<sub>t</sub> = CP Current Requirement (Amp)  C<sub>a</sub> = anode consumption rate  U<sub>f</sub> = utilization factor</p>

<p><b>Anode to earth resistance for multiple anodes</b></p> $R = 0.159 \times \rho / NL [ \ln 8(L/D) -1 + 2(L/S) \times \ln (0.656N) ]$	<p><b>Where</b></p> <p>R = Resistance to Earth in Ohm of the Vertical Anode in Parallel</p> <p><math>\rho</math> = Soil Resistivity (ohm meter)</p> <p>N = No. of Anode in Parallel</p> <p>L = Length of Prepackaged Anode (m)</p> <p>D = Diameter of Prepackaged Anode (m)</p> <p>S = Anode Spacing (m)</p>
<p><b>Anode to earth resistance for single anode</b></p> $R = 0.159 \times \rho / L [ \ln 8(L/D) -1 ]$	<p><b>Where</b></p> <p>R = Resistance to Earth in Ohm of the Vertical Anode in Parallel</p> <p><math>\rho</math> = Soil Resistivity (ohm meter)</p> <p>N = No. of Anode in Parallel</p> <p>L = Length of Prepackaged Anode (m)</p> <p>D = Diameter of Prepackaged Anode (m)</p> <p>S = Anode Spacing (m)</p>
<p><b>Anode to backfill resistance</b></p> $R_v = 0.159 \times \rho / L [ \ln 8(L/D) -1 ]$	<p><b>Where</b></p> <p><math>R_v</math> = Resistance of Vertical Anode to backfill</p> <p><math>\rho</math> = Resistivity of backfill material (ohm meter)</p> <p>N = No. of Anode in Parallel</p> <p>L = Length of bare Anode (m)</p> <p>D = Diameter of bare Anode (m)</p>

<p><b>Cable resistance</b></p> $R_c = (R_t \times L_t) / N$	<p><b>Where</b></p> <p><math>R_c</math> = total Resistance of anode tall cable  <math>R_t</math> = Resistance of anode tall cable  <math>N</math> = number of anodes</p>
<p><b>Driving voltage of anode</b></p> $V_t = V_c - V_p$	<p><b>Where</b></p> <p><math>V_t</math> = driving potential of anode  <math>V_c</math> = closed circuit potential of anode  <math>V_p</math> = polarized potential</p>
<p><b>Current delivering capacity of anode</b></p> $I_a = V_t / R_t$	<p><b>Where</b></p> <p><math>I_a</math> = current delivering capacity  <math>V_t</math> = closed circuit potential of anode  <math>R_t</math> = ground bed resistance</p>
<p><b>Number of anodes by current requirement</b></p> $N = I_t / I_a$	<p><b>Where</b></p> <p><math>N</math> = Number of anodes  <math>I_t</math> = total current requirement  <math>I_a</math> = anode output</p>

## ANODE SPACING

### NO. OF ANODES

IN PARALLEL	5 Feet	10 Feet	15 Feet	20 Feet	25 Feet
2	0.652	0.576	0.551	0.538	0.530
3	0.586	0.460	0.418	0.397	0.384
4	0.520	0.385	0.340	0.318	0.304
5	0.466	0.333	0.289	0.267	0.253
6	0.423	0.295	0.252	0.231	0.218
7	0.387	0.265	0.224	0.204	0.192
8	0.361	0.243	0.204	0.184	0.172
9	0.332	0.222	0.185	0.166	0.155
10	0.311	0.205	0.170	0.153	0.142
11	0.292	0.192	0.158	0.141	0.131
12	0.276	0.180	0.143	0.132	0.122
13	0.262	0.169	0.139	0.123	0.114
14	0.249	0.160	0.131	0.116	0.107
15	0.238	0.152	0.124	0.109	0.101
16	0.226	0.144	0.117	0.103	0.095
17	0.218	0.138	0.112	0.099	0.091
18	0.209	0.132	0.107	0.094	0.086
19	0.202	0.127	0.102	0.090	0.082
20	0.194	0.122	0.098	0.086	0.079
22	0.182	0.114	0.091	0.079	0.073
24	0.171	0.106	0.085	0.074	0.067
26	0.161	0.100	0.079	0.069	0.06

### 4.3 Design calculations

#### 1) Surface area of pipeline (Sa)

$$S_a = \pi \times D \times L$$

$S_a$  = Surface area of Pipeline (m<sup>2</sup>)

$D$  = Diameter of Pipe (m)

$L$  = Length of Pipe (m)

Pipeline section	Diameter (mm)	Pipeline length (m)	Surface area (m <sup>2</sup> )
From 0 to 260.25 KM	406	260250	331945.4

#### 2) Current Requirement

$$I_t = S_a \times C_d \times S_m / 1000$$

$I_t$  = CP Current Requirement (Amp)

$S_a$  = Surface Area (m<sup>2</sup>)

$C_d$  = CP Protective Current Density

$C_d$  = 0.05 mA/m<sup>2</sup> for PE Coating

$C_d$  = 0.5 mA/m<sup>2</sup> for CTE Coating

$S_m$  = Safety Margin (1.3)

Pipeline section	Diameter (mm)	Pipeline length (m)	Surface area (m <sup>2</sup> )	Protective current density (μA)	Current required (ampere)
From 0 to 260.25 KM	406	260250	331945.4	75	32.36

#### 3) Anode requirement by weight

$$W = I_t \times C_a / U_f$$

$I_t$  = CP Current Requirement (Amp)

$C_a$  = anode consumption rate (7.6 Kg/ Amp-year)

$U_f$  = utilization factor (0.85)

Anode size (mm)	Individual anode weight (Kg)	Total anode requirement (Kg)	Total anode requirement (numbers)
80 mm (D) X 900mm(L)	7.9	902.27	118.7

#### 4) Number of anodes required by ground bed resistance calculations includes

##### 4.1. Anode to earth resistance for multiple anodes

$$R = 0.159 \times \rho / NL [ \ln 8(L/D) - 1 + 2(L/S) \times \ln(0.656N) ]$$

R = Resistance to Earth in Ohm of the Vertical Anode in Parallel

$\rho$  = Soil Resistivity (10 ohm meter)      N = No. of Anode in Parallel ( 3)

L = Length of Prepackaged Anode (1.5 m)    D = Diameter of Prepackaged Anode (0.185 m)

S = Anode Spacing (3 m)

By putting values in the above formula we get the ground bed to electrolyte resistance = 1.412 ohms

##### 4.2.1 Anode to backfill resistance

$$R_v = 0.159 \times \rho / L [ \ln 8(L/D) - 1 ]$$

R<sub>v</sub> = Resistance of Vertical Anode to backfill  $\rho$  = Resistivity of backfill material (0.5 ohm meter)

N = No. of Anode in Parallel    L = Length of bare Anode (0.9 m)

D = Diameter of bare Anode (0.08 m)

R<sub>v</sub> = 0.315 ohms

**4.2.2 Horizontal Distributed Ground Bed Resistance:** The total resistance which a ground bed offered to the current which flows from the anode. This is the resistance offered if the all anode are horizontally installed in soil.

$$R = 0.159 * \rho_s / L_{Pa} [\ln \{ \{ 4 * L_{Pa}^2 + 4 * L_{Pa} (S_2^2 + L_{Pa}^2)^{0.5} \} / d_{Pa} S_2 \} + S_2 / L_{Pa} \{ (S_2^2 + L_{Pa}^2)^{0.5} / L_{Pa} \} - 1]$$

$\rho_s$  = Soil Resistivity (ohm meter)

$L_{Pa}$  = Length of Prepackaged Anode bed (m)

$d_{Pa}$  = Diameter of Prepackaged Anode bed (m)

$S_2$  = Twice Depth of Anode Area(m)

Hence the total resistance if the all anode are horizontally installed in soil is 1.6 ohms

### 4.3. Cable resistance

$$R_c = (R_t \times L_t) / N$$

$R_c$  = total Resistance of anode tall cable  $R_t$  = Resistance of anode tall cable

$N$  = number of anodes (3)  $R_c = 0.0062$  ohms

### 4.4. Current delivering capacity of anode

$$I_a = V_t / R_t$$

$I_a$  = current delivering capacity  $R_t$  = ground bed resistance

$V_t$  = closed circuit potential of anode  $(1.75 - 0.90) = 0.85v$

Therefore total current output per ground bed with 3 anodes is 0.578 A

#### 4.5. Number of anodes by current requirement

$$N = It/I_a$$

N = Number of anodes      It = total current requirement

I<sub>a</sub> = anode output

Hence number of anodes required by resistance will be 213

And total number of anodes required using 7.6 Kg Mg anode (each) will be 119

#### 4.6 Life of anode

$$Life = \frac{M \times u \times \xi}{I \times 8760}$$

M = Net Mass of anode (904.4 m)

u = utilization factor (0.85)

ξ = anode material electrochemical capacity (950Ah/Kg)

I = current output from anode (5.19 A)

So, the life of the Anode is for the design is = 22 to 23 years

#### 4.7 Total number of stations required for 260Km long pipeline

Number of stations = total number of anodes used at all stations/  
number of anodes used by per station

Number of stations = 119/3 = 40

## **Coating**

Coating is the process of applying a different material on another material to prevent it from its surrounding. Coating of pipe is to isolate the pipe line from soil and seawater and to provide a high resistance path between anodic and cathodic area. To do so coating must contain such properties.

### **Properties of Coating Material:**

- Low permeability to water and salt.
- Low permeability to oxygen.
- Good adhesion to pipe steel.
- Adequate temperature stability.
- Resistance to cathodic disbondment.
- Non toxic and environmental friendly.

Some of the coating which is used in the onshore and the off shore pipeline are

- Asphalt enamel
- Coal tar epoxy
- Fusion bond epoxy
- Three layer polyethylene/polypropylene coating
- Concrete weight coating.

The application of these coating is decided by the soil condition, fluid to be transported, Operating condition (temperature, pressure), outside force etc.

### **Type of Coating Material**

**Coal Tar Coating/Asphalt Enamel Coating:** These coating are flood coating applied as a molten material a rotating pipe. These coating are 5-6 mm thick, but these are poor adhesion to steel. So to make a proper adhesion much roughened steel is prepared at time of surface cleaning.

While coating the pipe a surface is cleaned first, then molted coal tar/asphalt is applied on the surface and then one or two layer of glass reinforced fiber mating are applied on it. These are generally cheap coating having operating range 65-75<sup>0</sup>C for coal tar coating and 70-80<sup>0</sup>C for asphalt coating.

**Poly Ethylene Coating:** It is 3-4 mm thick coating. In this coating epoxy primer is applied on the pipe, followed by poly ethylene based adhesive on which the poly ethylene wrap is applied .Such coating is also known as 3PE or 3LPE coating.

Polyethylene has a high electrical resistance, very low moisture uptake, long life expectancy. The upper temperature tolerance of polyethylene wrap is about 65<sup>0</sup>C. The main problem occur in this is the undercoating corrosion, resulting from blisters, and inadequate CP current access because of high electrical resistance.

**FBE Coating:** FBE Coating are thin film coating, 0.5-0.6 mm thick. The epoxy has a strong chemical bond to the steel that provided good adhesion. FBE coating in seawater can withstand temperature between 85-95<sup>0</sup>C.

## Coating Damage

Damage may occur by careless or improper use of corrosion control and inadequate cathodic protection techniques.

**Mechanical Damage:** Probe bars for corrosion testing must not be driven into the soil to make contact with coated pipe. Damage that results from excavation of adjacent facilities must be repaired. Installation of test leads, bonding conductors, or anode leads will require coating removal. After leads have been attached, coating must be repaired.

**Electrical Damage:** Electrical damage to a coating may be caused by excessive voltage from a holiday detector or by excessive structure-to-earth potential applied by an impressed current system. The following empirical formula defines the voltage to be applied by the holiday detector

$$V = KT^{1/2}$$

V = peak voltage output (kilovolts)

T = thickness of coating in mils (do not include wrappers)

K = a constant depending on type of coating (1.0 for so mastic, 1.25 for coal tar, 1.5 for epoxy or plastic).

The voltage will pinpoint the holidays, but will not further damage the coating. Measuring the holiday detector voltage in the field requires a special high-voltage pulse voltmeter. The above formula will determine the output voltage capacity of the holiday detector needed.

**Cathodic Protection Damage/Cathodic Disbondment:** In some conditions, apply excessive amounts of cathodic protection to a coated pipeline and damage the coating. There is a limiting polarization potential, called the "hydrogen over-voltage potential", beyond which free hydrogen will be developed. Gas bubbles will form on and break away from pipe metal exposed at coating defects. A developing

hydrogen gas bubble can exert tremendous pressure. When this pressure is created at a coating void, there is a stripping action which can increase the area of exposed metal and result in rapid deterioration of what may have initially been an excellent coating. Polarization potential can be measured at a given location on a coated pipeline by measuring the pipeline-to-earth potential immediately (within the first second or two) after simultaneously interrupting the current output from all cathodic protection current sources affecting that portion of the pipeline. If, on steel pipelines, this potential is below approximately 1.2 volt (measured between pipe and soil as contacted by a copper-copper sulfate reference electrode), danger of coating damage is slight. If the current-off polarization potential is at or slightly above this figure, free hydrogen may be produced and possible coating damage could be expected. It is possible to cause extensive damage through improper rectifier operation. This results from maintaining excessive structure-to-electrolyte potential.

The following empirical formula specifies the maximum ferrous structure-to-earth potential at all points on a structure which will not cause coating damage.

$$E = (125\rho^{0.3} + 600)$$

**E = Potential in Millivolt**

**$\rho$  = Resistivity in ohm-cm**

#### **Miscellaneous Coating Damage:**

Damage or defects in coatings may also be caused by

- Damage to coating by subsequent construction (probe bars for pole installation, etc.)
- Cracks from excessive thermal or mechanical stresses.
- Action of chemicals in the earth surrounding a pipeline.
- Action of bacteria in the soil surrounding a pipeline.
- Flaws in the coating materials as applied.
- Failure to properly field-coat joints when extensions or modifications are made to a coated pipeline.

**Coating Aging:** As coatings age, they become less effective as electrical insulators. As the coating loses its insulating properties, it allows current to flow out of the surface of the structure and corrosion to take place under the coating film. For this reason, the amount of current needed to give adequate cathodic protection becomes greater. It is also possible for disbanded areas of coating to actually shield cathodic protection current from reaching the surface of the pipe, resulting in undetected corrosion. It is important that any breaks in a coating be carefully repaired before the structure is placed in service. During the life of the structure, any breaks found in protective coatings must be repaired.

**Current density for cathodic protection of underground structures**

Natural soil	10 – 30 ma/m <sup>2</sup>
Mud	25 – 40 ma/m <sup>2</sup>
Fresh water	10 – 40 ma/m <sup>2</sup>
Sea water	50 – 125 ma/m <sup>2</sup>

**Current density required for cathodic protection**

Effective coating resistance in ohm/m <sup>2</sup>	Current density in $\mu$ A
Bare pipe	25
100	7.5
500	2.5
1000	1.25
5000	1.0
7500	0.75
50000	0.50
100000	0.25

### Coating conductivity versus coating quality

Coating conductivity (micro mhos/m <sup>2</sup> )	Coating quality
1 – 100	Excellent coating in high resistivity soil
100 – 500	Good coating in high resistivity soil
500 – 1000	Excellent coating in low resistivity soil
1000 – 2500	Good coating in low resistivity soil
2500 – 5000	Average coating in low resistivity soil
5000 – 10000	Poor coating in low resistivity soil
Above 10000	Very poor coating in low resistivity soil

### Design Calculation for a section of pipeline from chainage 1.5 to 41.85 Km

Chainage (Km)	Soil resistivity (ohm – m)	Anode to earth resistance (ohm)	Cable resistance (ohms)	Current output of each groundbed (Ampere)	Length of pipeline protected
1.5	8.45	1.542	0.0123	0.497	3996.97
4.87	8.23	1.502	0.0123	0.506	4093.13
7.8	8.08	1.475	0.0123	0.518	4161.4
10.9	19.13	2.602	0.0082	0.313	2518.03
14.9	4.73	1.591	0.0246	0.442	3550.21
16.6	3.82	1.285	0.0246	0.525	4221.5
19.69	3.96	1.332	0.0246	0.510	4102.17
22.69	7.12	1.3	0.0123	0.580	4658.63
30.772	5.35	0.977	0.0123	0.743	5974.92
34.772	8.82	1.952	0.0123	0.483	3884.96
37.513	9.21	1.4	0.0123	0.542	3884.96
41.851	6.21	1.681	0.0123	0.460	4360.15

# CHAPTER 5

## RESULTS AND DISCUSSION

Most of the cross country oil and gas pipelines are made up of steel which have a tendency to corrode with environmental conditions after few years. The life of a cross country pipeline can be increased by preventing or reducing the effect of corrosion which can be achieved with the help of a cathodic protection system.

For a koyali Ratlam Pipeline project

Total length of the pipeline is 260.250 Km

outside diameter of pipeline is 406 mm

- 1) I have calculated total current requirement that need to be supplied to the pipeline to provide cathodic protection to prevent corrosion in future which is 32.36 Ampere hence this much current is sufficient to protect 260.250 Km of pipeline (406 mm outside diameter) from corrosion.
- 2) Total number of anodes required to supply 32.36 A of current are 119
- 3) Total weight of anodes required is 902.27 Kg where individual anode weight should be 7.9 Kg
- 4) Anode to earth resistance for multiple anodes = 1.412 ohms
- 5) Anode to backfill resistance = 0.315 ohms
- 6) Cable resistance = 0.0062 ohms
- 7) Current delivering capacity of anode = 0.578 A
- 8) Number of anodes by current requirement = 213

# CHAPTER 6

## CONCLUSIONS

Pipelines are the economic and safest mode for the transportation of large quantities of fluid (liquid or gas). Modern pipelines that are being laid for the transportation of oil and gas are made up of generally steel and steel have a tendency to corrode with time and environmental conditions. Corrosion occurs through electrochemical reactions that occur due to the potential difference between the anode and the cathode. This potential difference can be caused by differences in the environment, differences in the metal, or by external electrical sources of DC current. There are various methods to protect pipelines from corrosion. Both coating and cathodically protected pipeline can be considered as a long life pipeline. Cathodic protection is one of the best ways to prevent or even reduce corrosion. By this method strength is provided by supplying current to the pipeline which results in an increase in the life of pipelines.

## REFERENCES

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- 4) Google search
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- 6) Corrosion control by pea body

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