Corrosion in the Oil Industry

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In

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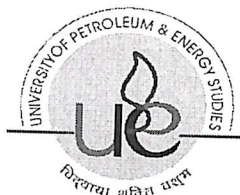
Certificate

This is to certify that the project report on "Corrosion in the Oil Industry" submitted to the University of Petroleum & Energy Studies, Dehradun, by Mr. Harsh Kumar, in partial fulfillment of the requirement for the award of degree of Bachelor of Technology in Applied Petroleum Engineering (Academic Session 2003-2007) is a bonafide work carried out by him under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

Date: 30-04-2007

Dr. T. Chandrashekhar

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EXECUTIVE SUMMARY

Corrosion may seem an unexciting subject, but international and state oil companies now need to place much higher priority on both the technology and management of its causes, monitoring its effects, controlling its various outcomes and undertaking remedial work. Extraordinarily for its potential consequences, it is one of the few phenomena where widely-used inspection techniques remain out of step with the reality of the chemical processes involved. Companies unwilling to address this will have both their reputation and value compromised.

This report contains a detailed description of various forms of corrosion ailing the oil & gas industry worldwide and the ways to detect and mitigate such corrosion with special emphasis on cathodic protection, detailed design parameters for installation of a CP system are discussed and various design formulae are cited. H_2S corrosion has been studied at a greater depth using the knowledge of thermodynamics to obtain the rate of H_2S corrosion under varying conditions of S^{2-} concentrations and temperature. The effect of formation rock content on corrosion has also been studied through the potentials attributed and developed due to them.

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GLOSSARY OF CORROSION TERMS

- **Adsorption-** Adsorption occurs at the interface or boundary of a solid or liquid which is in contact with another medium. (Different than absorption).

- **Anode-** The electrode of an electrolytic cell at which a net oxidation reaction occurs. In corrosion processes the anode is the electrode that has the greater tendency to go into solution.

- **Bactericide-** An agent destructive to bacteria.

- **Cathode-** The electrode of an electrolytic cell at which a net reduction reaction occurs. In corrosion processes, the cathode is usually the area that is not attacked.

- **Cathodic Protection-** Reduction or prevention of corrosion of a metal surface by making it cathode, *for* example, by the use of sacrificial anodes or impressed currents.

- **Concentration Cell-** An electrolytic cell, the emf of which is due to differences in the composition of the electrolyte at anode and cathode areas.

- **Corrosion-** The deterioration of a substance, usually a metal, because of a reaction with its environment.

- **Corrosion Fatigue-** Reduction of fatigue durability by a corrosive environment.

- **Couple-** A pair of dissimilar electronic conductors in electrical contact.

- **Dezincification-** Corrosion of a zinc containing alloy, usually brass, involving loss of zinc, and a residue or deposit in-situ of one or more less active constituents, usually copper.

- **Electron-** Negatively charged particles, always with the same mass and charge, one of the structural units of atoms.

- **Electrochemical Equivalent-** The weight of an element or group of elements oxidized or reduced at 100 percent efficiency by a unit quantity of electricity.

- **Electrolyte-** An ionic conductor.

- **Erosion-** Deterioration by the abrasive action of fluids, usually accelerated by the presence of solid particles of matter in suspension. When deterioration is further increased by corrosion, the term erosion-corrosion is often used.

- **Galvanic Cell-** A cell in which chemical change is the source of electric energy. It usually consists of two dissimilar conductors in contact with each other and with an electrolyte or two similar conductors in contact with each other and with dissimilar electrolytes.

- **Inhibitor-** A chemical substance which retards corrosion when added to an environment in small concentration.

- **Ion-** An electrically charged atom or group of atoms. (They are formed when salts disassociate in solution).

- **Intergranular Corrosion-** Corrosion which occurs preferentially at grain boundaries.

- **Sacrificial Protection-** Reduction or prevention of corrosion of metal in an environment acting as an electrolyte by coupling it to another metal which is electrochemically more active in that particular electrolyte.

- **Stress Corrosion Cracking-** Spontaneous cracking produced by the combined action of corrosion and static stress (residual or applied).

INTRODUCTION

Corrosion

Corrosion may seem an unexciting subject, but international and state oil companies now need to place much higher priority on both the technology and management of its causes, monitoring its effects, controlling its various outcomes and undertaking remedial work. Extraordinarily for its potential consequences, it is one of the few phenomena where widely-used inspection techniques remain out of step with the reality of the chemical processes involved. Companies unwilling to address this will have both their reputation and value compromised.

Corrosion in the oil field appears as leaks in tanks, casing, tubing, pipeline and other equipment. Base metal disappears as corrosion changes it to another type of material.

Why Metals Corrode

Metal ores are mostly oxides and sulfides which are more stable than pure metals. Energy is required to reduce the ore and produce metal, as in the blast furnace. Most metals are like fuels; they tend to combine with oxygen, sulfur, and other elements. These combining reactions of metals produce heat or some other form of energy and change the metals back to more stable compounds. Metals such as .zinc and magnesium are more reactive and release more energy when they corrode than metals such as silver and gold, the so-called noble metals. Silver and gold do not corrode readily but are too expensive to be used as a means of reducing corrosion.

How Metals Corrode - The Basic Corrosion Cell

Corrosion cells may occur at:

- Points where dissimilar metals connect
- Points of internal stress
- Places where there are differences in corroded ion concentration
- On either side of the bending axis on pieces of bent metal
- Stresses from the manufacturing process, or even wrench marks
- Places where there are dings, scratches, stress, or other
- imperfections have disrupted the uniformity of the metal surface
- Places where there are differences in oxygen concentration

By recognizing corrosion when it does occur, and by understanding the mechanisms involved, we may begin to eliminate corrosion by design. The basic galvanic corrosion mechanism follows the principle of a battery typical battery requires two dissimilar metals connected together and immersed in an electrolyte. All metals have a tendency to dissolve or corrode to a greater or lesser degree. In this case, the metal with the greater tendency to corrode forms the negative pole and is called the anode. When the two are connected, the other metal forms the positive pole, or cathode. Loss of positive metal ions from the anode causes a release of free electrons. This process is called oxidation. The buildup of electrons generates an electrical potential, causing them to flow through the conductor to the cathode. At the cathode, excess electrons are neutralized or taken up by ions in the electrolyte. This process is called reduction. As long as reduction reactions predominate, no metal is lost at the cathode. The anode will continue to corrode as long as the electric circuit is maintained and the metal ions are removed from solution by combining with other elements to make up corrosion products. Anodes and cathodes can form on a single piece of metal made up of small crystals of slightly different compositions. (They can be next to each other or separated by large distances–sometimes tens of kilometers.) The electrolyte may simply be water.

For example, pure iron [Fe] in steel has a tendency to dissolve, going into solution as Fe++. As each Fe++ ion is formed, two electrons are left behind, giving that area of the metal a small negative charge. If nothing happens to remove Fe++ ions around the anodic site, the tendency to dissolve will diminish. In oil production, Fe++ ions are removed by reacting with oxygen [O2], hydrogen sulfide, or carbon dioxide. The corrosion products are precipitates or scales of rust [Fe2O3], iron sulfides [FeSx] or iron carbonate [Fe2CO3]. Excess electrons flow away from the anodic region to a site where they form a cathode, and where reduction occurs. Reduction of oxygenated water forms hydroxyl ions [OH_]. If oxygen is not present, but CO2 or H2S is, then the dominant cathode reaction is the reduction of hydrogen ions to produce hydrogen gas. If the electrolyte is salt water, chlorine gas is produced

Since the corrosion product of iron is often iron oxide, one might think that corrosion is merely a reaction between iron and oxygen gas as:

$$4\ Fe^{o}\ +\ 3\ O_2\ \rightarrow\ 2\ Fe_2O_3$$
(Iron)   (Oxygen)   (Iron Oxide)
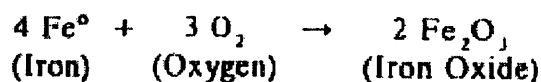
Or between iron and hydrogen sulfide:

$$Fe^\circ + H_2S \rightarrow FeS + H_2^\circ$$

(Iron) (Hydrogen (Iron (Hydrogen
Sulfide) Sulfide) Gas)
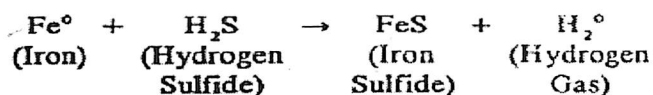
Iron does not react with dry oxygen or dry hydrogen sulfide at ordinary temperatures except to form a very thin, invisible film which protects the iron from further attack. Corrosion occurs only when water is present. Corrosion is an electrochemical process. Two different electrochemical reactions occur simultaneously at two different places on the metal surface, and electric current flows between these two places, called the anode and cathode.

For example, in the corrosion of iron in a weak acid solution, iron goes into solution as ferrous ions at the corroding or anodic surface, leaving two negative electrons in' the metallic iron:

$$Fe^\circ \rightarrow Fe^{++} + 2 \text{ (electrons)}$$

(Iron) (Ferrous ion) (Remain in iron)
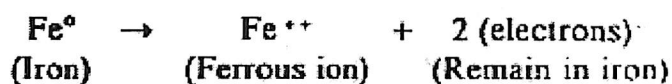
The negative electrons in the metal move toward non-corroding or cathode areas, or the positive current moves away from the cathode and towards the anode. Hydrogen ions in the solution are plated out at the cathode, forming hydrogen gas which bubbles off:

$$2 H^+ + 2 \text{ (electrons)} \rightarrow H_2^\circ$$

(Hydrogen (Hydrogen
ion) gas)
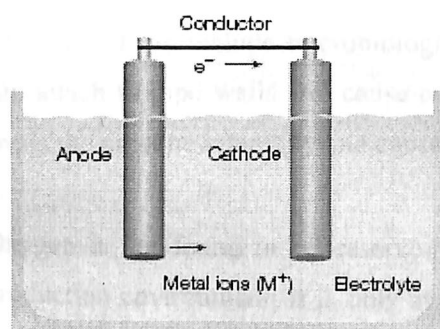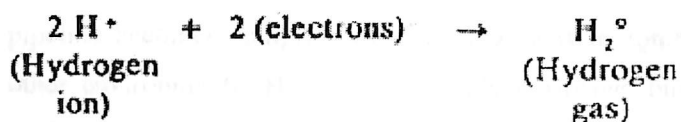
Figure 1 Corrosion Cell
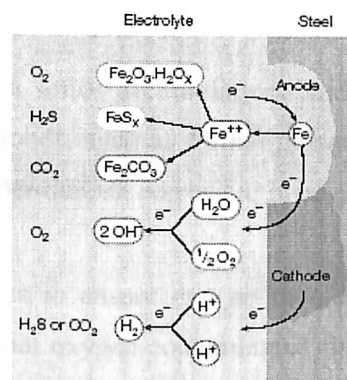
Figure 2 Corrosion on a Steel Surface

Corrosion in Oil Field Environments

Corrosion—the deterioration of a metal or its properties—attacks every component at every stage in the life of every oil and gas field. From casing strings to production platforms, from drilling through to abandonment, corrosion is an adversary worthy of all the high technology and research we can throw at it.

Oil field production environments can range from practically zero corrosion to severely high rates of corrosion. Crude oil at normal production temperatures (less than 120 °C) without dissolved gases is not, by itself, corrosive. The economics of controlling corrosion in many oil fields are dependent on efficient separation of crude oil from other species. While the rates may vary, the species causing the most problems are nearly universal.

CO_2 and H_2S gases, in combination with water, define most of the corrosion problems in oil and gas production. Water and carbon dioxide—produced or injected for secondary recovery can, for example, cause severe corrosion of completion strings.

The mechanisms of CO_2 corrosion are generally well defined; however, the reality inside a pipeline becomes complicated when CO_2 acts in combination with H_2S, deposited solids, and other environments. H_2S can be highly corrosive, but can, in some cases, form a protective sulfide scale that prevents corrosion.

Other problems include microbiological activity and the solids accumulation. Microorganisms can attach to pipe walls and cause corrosion damage. Solids, such as formation sand, can both erode the pipeline internally and cause problems with under-deposit corrosion, if stagnant.

Oxygen is not found in oil reservoirs and much is done to ensure that no oxygen enters the production environment; it is only at the drilling stage that oxygen-contaminated fluids are first introduced. Drilling muds, left untreated, will corrode not only well casing, but also drilling equipment, pipelines and mud handling equipment. In many such cases, a few parts per million (ppm) of oxygen will enter the pipelines, greatly exacerbating corrosion problems.

Acid used to reduce formation damage around the well or to remove scale, readily attacks metal.

External corrosion problems in oil and gas production normally are similar to those found in the pipeline industry, but since the lines are shorter and smaller in diameter, their economic impact on the total cost of production is limited. Completions and surface pipelines can be eroded away by high production velocities or blasted by formation sand.

Atmospheric corrosion of structures and vessels is a problem for offshore fields and those operating near marine environments. Improvements in the quality of protective coatings for offshore environments have dramatically reduced the frequency of repainting platforms and tanks.
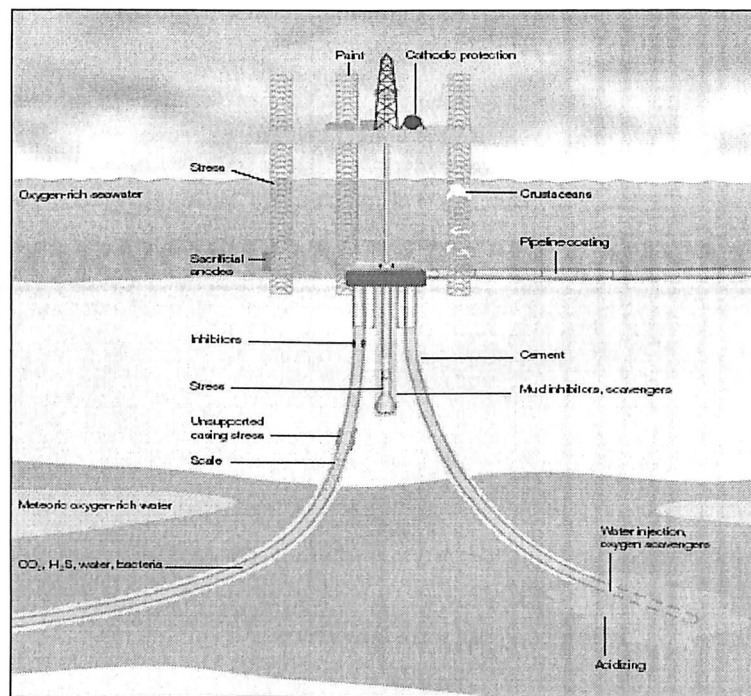
Figure 3 Corrosion in the Oil and Gas Industry

CORROSION MECHANISMS

Corrosion encountered in petroleum production operations involves several mechanisms. These have been grouped into electrochemical corrosion, chemical corrosion and mechanical and mechanical/corrosive effects.

Electrochemical Corrosion

Galvanic Corrosion (Two Metal)—Two dissimilar metals in a conductive medium develop a potential difference between them. One becomes anodic, the other cathode. The anode loses metal ions to balance electron flow. Because metals are made up of crystals, many such cells are set up, causing intergranular corrosion. Problems are most acute when the ratio of the cathode to anode area is large.

Crevice Corrosion—Much metal loss in oilfield casings is caused by crevice corrosion. This localized form of corrosion is found almost exclusively in oxygen-containing systems and is most intense when chloride is present. In the crevice, metal is in contact with an electrolyte, but does not have ready access to oxygen. At the start of the reaction, metal goes into solution at anodic sites and oxygen is reduced to hydroxyl ions at cathodic sites. Corrosion is initially uniform over the entire area including the crevice. As corrosion continues in the crevice, oxygen becomes depleted and cathodic oxygen reduction stops. Metal ions continue to dissolve at anodes within the crevice, producing an excess of positive charges in solution. Negatively charged chloride (or other anions) now migrate to the developing anodes to maintain electroneutrality. They act as a catalyst, accelerating corrosion.

At this point, crevice corrosion is fully established and the anodic reaction continues with ferrous ions [Fe++] going readily into solution.
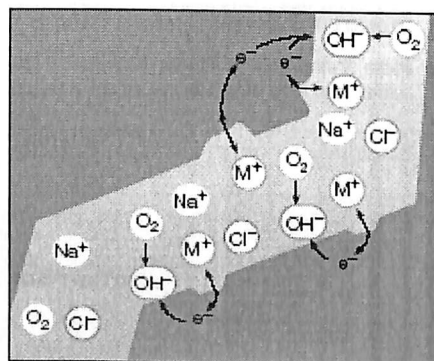
Figure 4 Crevice Corrosion

This type of corrosion often starts at drillpipe joints, tubing collars or casing collars. The gap in the joint becomes devoid of oxygen and anodic. In salty water the corrosion is promoted by the migration of negatively charged chlorine ions [Cl-] to the crevice.

Pitting corrosion is another form of crevice corrosion where a small scratch, defect or impurity can start the corrosion process. Again, a buildup of positive charges occurs in a small pit on the metal surface. Chlorine ions from a saline solution migrate towards the pit. These, coupled with the formation of hydrogen ions, act as a catalyst causing more metal dissolution.

Stray-Current Corrosion—Extraneous AC and DC currents in the earth arriving at a conductor will turn the point of arrival into a cathode. The place where the current departs will become anodic, resulting in corrosion at that point. A DC current is 100 times more destructive than an equivalent AC current. Only 1 amp per year of stray DC current can corrode up to 20 lbm [9 kg] of steel. Cathodic protection systems are the most likely sources of stray DC currents in production systems.
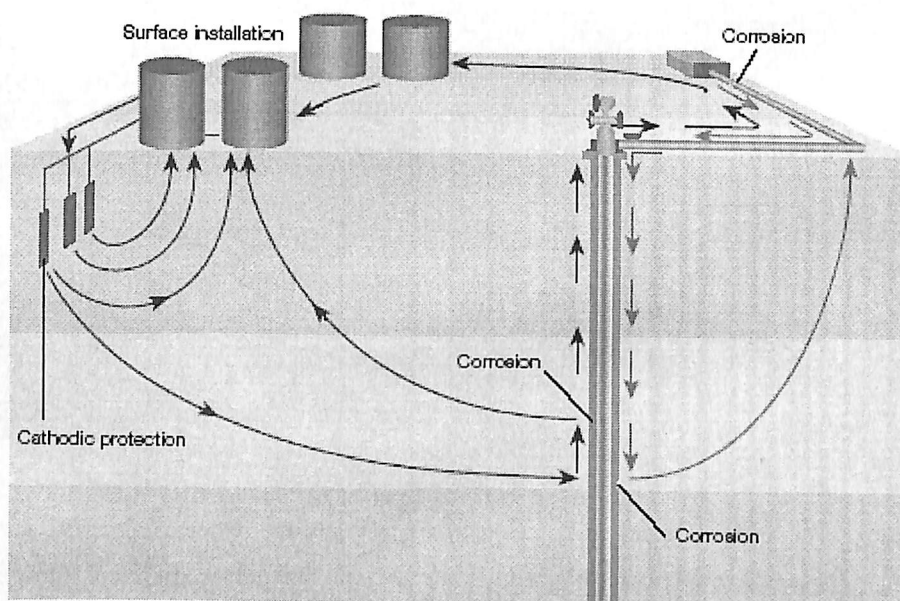
Figure 5 Stray Current Corrosion

Current paths are shown between surface installation, electrical machinery, pipelines and a well. Current leaving the casing sets up an anodic area and corrosion.

Chemical Corrosion

Hydrogen Sulfide, Polysulfides and Sulfur—

$$Fe^0 + H_2S + Moisture = FeS + H_2^0$$
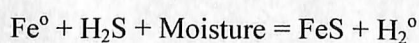
Hydrogen sulfide [H2S] when dissolved in water, is a weak acid and, therefore, it is a source of hydrogen ions and is corrosive. (The effects are greater in deep wells, because the pH is further

reduced by pressure.) The corrosion products are iron sulfides [FeSx] and hydrogen. Iron sulfide forms a scale that at low temperatures can act as a barrier to slow corrosion. The absence of chloride salts strongly promotes this condition and the absence of oxygen is absolutely essential. At higher temperatures the scale is cathodic in relation to the casing and galvanic corrosion starts. In the presence of chloride ions and temperatures over 300°F [150°C] barnacle type corrosion occurs, which can be sustained under thick but porous iron sulfide deposits. The chloride forms a layer of iron chloride [FeCl2], which is acidic and prevents the formation of an FeS layer directly on the corroding steel, enabling the anodic reaction to continue. Hydrogen produced in the reaction may lead to hydrogen embrittlement. Hydrogen sulfide prevents the formation of the hydrogen gas molecule. Atomic hydrogen diffuses into the grain boundaries of the metal and/or inclusions and reacts with itself to form the larger size, molecular hydrogen. These larger molecules of hydrogen are trapped and cause excessive pressure within the steel, resulting in splitting, blistering or cracking and in the loss of ductility and yield strength. Embrittlement is especially severe in higher strength steels having hardness greater than Rockwell "C" 22 and in equipment subject to cyclic loading, such as sucker rods.
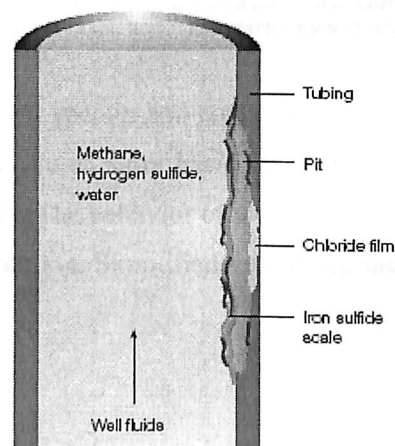
Figure 6 Barnacle type Corrosion

As tubing corrodes in a hydrogen sulfide and water environment, iron sulfide scale builds up. This is porous and is also cathodic with respect to the steel tubing. An intervening layer of iron chloride [FeCl2] is acidic and prevents precipitation of FeS directly onto the steel surface. This establishes a pit-forming corrosion cell.

Hydrogen Embrittlement
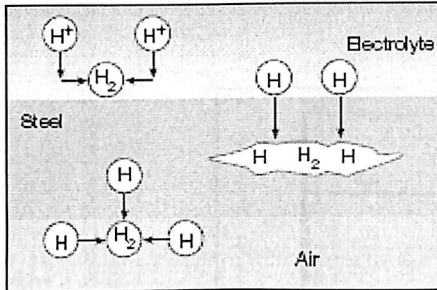
Sulfide Stress Corrosion
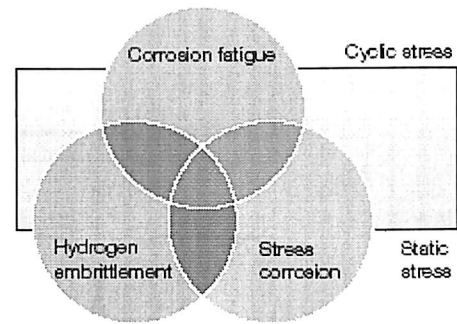
Stress Corrosion Cracking
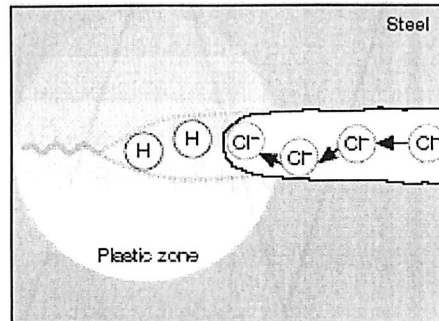
Figure 7 Hydrogen Embrittlement & Stress Corrosion

When H2S is present, corrosion cells generate FeS and atomic hydrogen. The layer of FeS promotes the movement of hydrogen into the metal (first), and accumulations generate tremendous pressure. This leads to embrittlement and, if combined with static or cyclic stress, can lead to failure of the metal by corrosion fatigue or stress corrosion (second). Stress corrosion cracking (third) starts at a pit or crevice. The zone around the tip of the crevice becomes plastic under stress allowing a crack to develop. Chlorine ions, which act as a catalyst to corrosion, can migrate into the crack accelerating the process. The development of the crack within the plastic zone is another site for hydrogen embrittlement.

For H2S in water, the particular sulfur species and concentration are functions of pH. At acid pH, the predominant species is H2S, while at more basic pH, S is the main constituent. HS- is the dominant species at intermediate pH. The behavior of metals in solutions containing H2S depends largely on the specific species in solution. Simplified total reactions for each species as a function of pH follow.

$$Fe + H_2S = FeS + 2H^\circ \text{ (acidic)},$$
$$Fe + HS^- = FeS + H^+ + 2e \text{ (neutral)},$$
$$\text{and } Fe + S^= = FeS + 2e \text{ (basic)}.$$
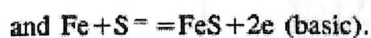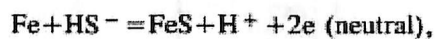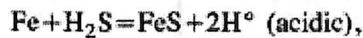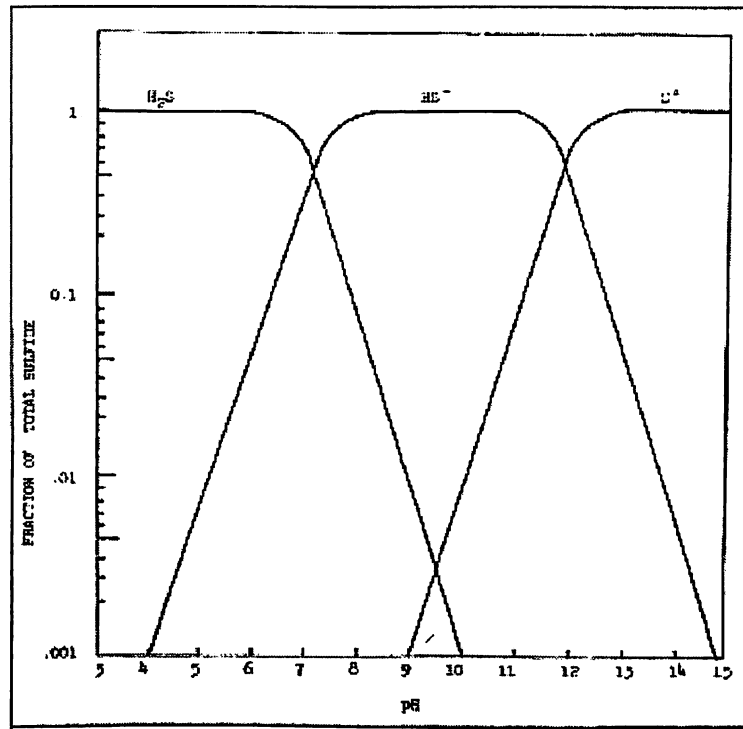
Figure 8 Sulfur Species as a Function of pH
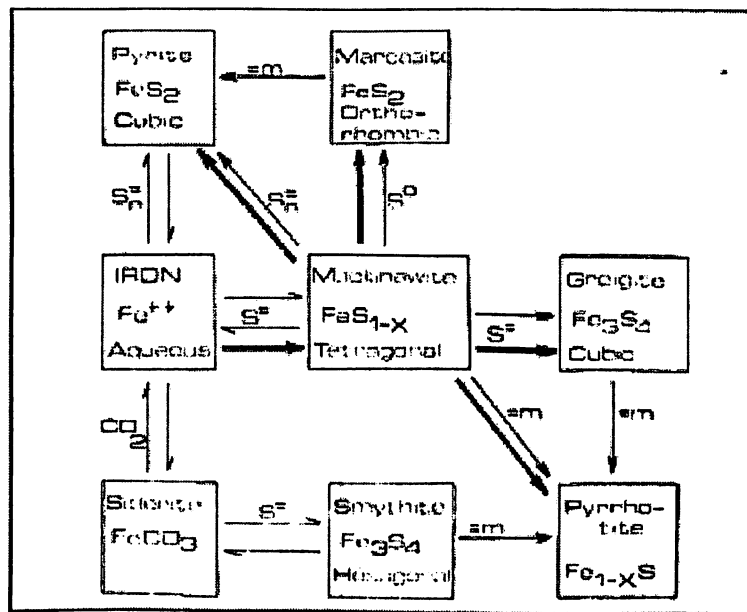
Figure 9 Common Forms of Iron Sulfide Formed during H2S Corrosion of Steel
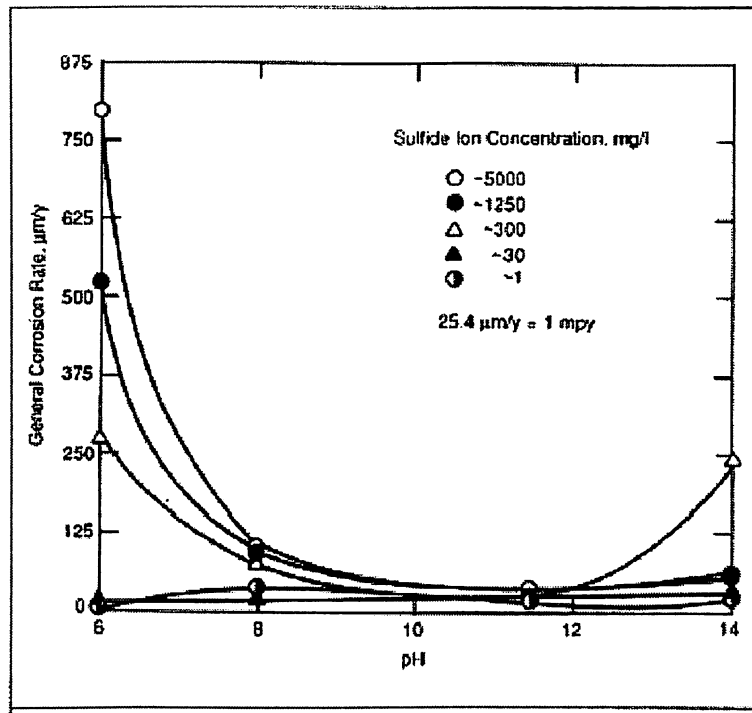
Figure 10 General Corrosion Rate for Carbon Steel as a Function of Sulfide-ion Concentration and pH

Clearly, the corrosion rate diminishes significantly as the pH increases above pH 8. This is why high-pH drilling muds are beneficial for the resistance of drilling equipment to H_2S; the corrosion rate of steels in H2S is also a function of the entire environment, including other gases and water chemistry. Fig. 11 describes the typical corrosion experienced on carbon steel as a function of other constituents in the total environment.
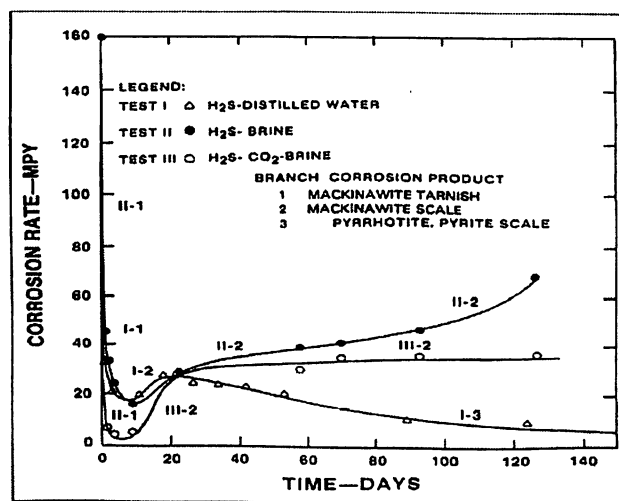
Figure 11 Corrosion Rate of Carbon Steel as a Function of H2S Environment

Carbon Dioxide—

Like H2S, carbon dioxide [CO2] is a weakly acidic gas and becomes corrosive when dissolved in water. However, CO2 must hydrate to carbonic acid [H2 CO3]—a relatively slow process— before it becomes acidic. This corrosion is found most frequently in gas wells where carbon dioxide is present. The carbonic acid formed, produces corrosion pits in the exposed metal. The corrosion product is iron carbonate (siderite) scale. This can be protective under certain conditions. Siderite itself can be soluble. Conditions favoring the formation of a protective scale are elevated temperatures, increased pH as occurs in bicarbonate bearing waters and lack of turbulence, so that the scale film is left in place. Turbulence is often the critical factor in the production or retention of a protective iron carbonate film. Siderite is not conductive, so galvanic corrosion cannot occur. Thus corrosion occurs where the protective siderite film is not present and is fairly uniform over the exposed metal. Crevice and pitting corrosion occur when carbonic acid is formed. Carbon dioxide can also cause embrittlement, resulting in stress corrosion cracking. The top portions of the tubing and surface flow lines are most susceptible to this type of corrosion. Corrosion rates are usually higher with high wellhead pressures, because more carbon dioxide will dissolve in the water vapor at higher pressures, creating a stronger acid. A yardstick to predict the corrosiveness of gas wells is based on partial pressure of carbon dioxide. This is calculated as partial pressure = total wellhead pressure X %CO2. If the partial pressures are above 30, the well stream is probably corrosive; 7 to 30 may be corrosive and 0 to 7 is non corrosive. This principle does not always apply when salt water is produced because dissolved salts can cause corrosion rates to increase considerably.
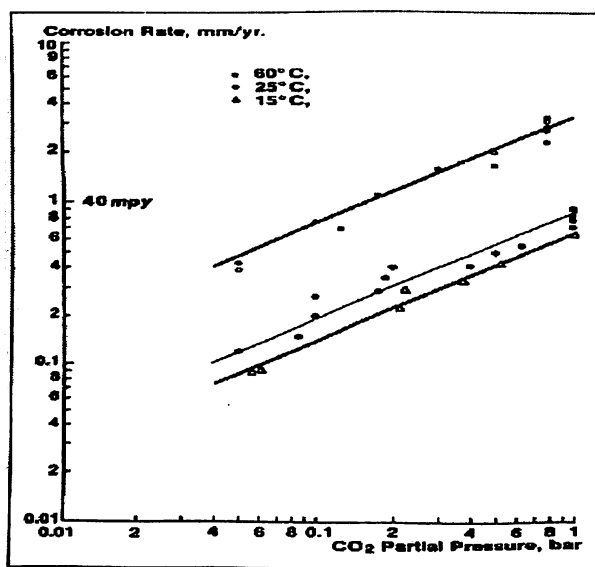
Figure 12 Steel corrosion as a function of P_{CO_2} and T

Oxygen Corrosion—

Oxygen dissolved in water causes very rapid corrosion. This corrosion forms a scale which may vary from dense and adherent to lose, porous and thick. Downhole oxygen corrosion in production wells is usually caused when air enters the casing – tubing annulus. In a water-injection system, air may enter the fluid system at many places. In pumping wells, iron oxide corrosion occurs in casing, tubing, pump and lower sections of the rod string. Rust usually causes even-depth pitting. Corrosion rate increases three-fold when oxygen dissolved in water increases from less than 1ppb to 0.2 ppm. Serious corrosion has been indicated in hydrogen-sulfide bearing water containing as little as 0.09 ppm oxygen, with corrosion problems eliminated after oxygen is removed. The oxygen content should be below 50 ppb for good corrosion control. Trace amounts of oxygen-the amounts- that get in through leaky pump packing:-faulty gas blankets, faulty flanges and leaky control valves can cause a special type of corrosion known as concentration cell corrosion. This can destroy equipment in a very short time in less than 3 days oxygen can penetrate a 3-ft layer of oil on top of water in a storage tank. Trace amounts of oxygen get through a gas blanket and set up a concentration cell, the most severe type of corrosion. The most corrosive environment in oil field operations is caused by trace amounts of oxygen entering into a sour brine system. This environment can destroy equipment in six months.

Of the three dissolved gases, oxygen is by far the most aggressive of the group. If either or both of the other two gases are dissolved in the water, it drastically increases their corrosivity. The higher the concentration of dissolved gases in solution the higher the corrosion tendency.
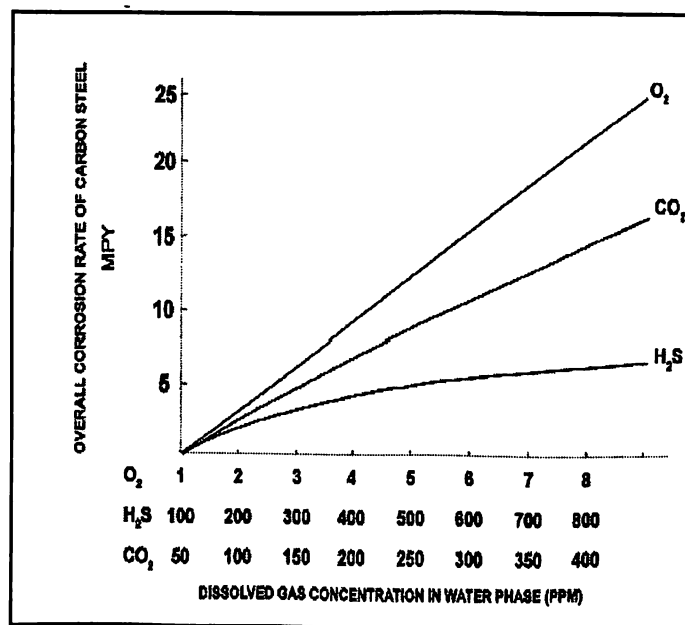
Figure 13 Rate of Corrosion with Different Environments

Oxygen accelerates the corrosion process in two ways:

- First it acts as a "depolarizer". This means that it will easily combine with hydrogen atoms at the cathode and allow the corrosion reaction to proceed at a rate limited primarily by the rate oxygen can diffuse to the cathode. Without oxygen, the energy it takes to evolve hydrogen gas from the cathode is a major bottleneck in the corrosion reaction and keeps it slowed down.

- Second, the oxygen oxidizes the ferrous ions to ferric ions, which forms the insoluble ferric hydroxide (above pH=3).

Any time there is a difference in the oxygen content of water in two areas of a system, attack will take place preferentially in the area exposed to the lowest oxygen concentration. An oxygen concentration cell. Therefore even solids, scale, corrosion by-product which may cause areas of low oxygen concentration, can cause pitting. Dissolved O2 can cause severe corrosion at concentrations of 40 ppb (parts per billion); most operations try to limit the oxygen content to 20-30 ppb in water sources.

Morphology - Oxygen corrosion has a pitting effect on metal. These pits start small, very deep, with sharp, ice-pick hole-like bottoms – accelerate rapidly.

Figure 14 Pitting Corrosion by Oxygen Concentration Cell

Second, the oxygen oxidizes the ferrous ions to ferric ions, which forms the insoluble ferric hydroxide (above pH=3).

Flow

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

oxygen molecule + water molecules + electrons $\longrightarrow$ hydroxyl ions

$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$

ferrous ion $\longrightarrow$ ferric ion + electron

Fe^{++} Fe^{++}
Fe^{++} Fe^{++}
Fe^{++}

O_2 O_2
O_2 O_2 O_2

$H^+H^+H^+H^+H^+H^+H^+H^+$ $H^+H^+H^+$

Pipe Wall   **Anodic Area**   **Cathodic Area**

Figure 14 Pitting Corrosion by Oxygen Concentration Cell

$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$

ferric ion + hydroxyl ions $\rightarrow$ ferric hydroxide

Fe^{++} Fe^{++}
Fe^{++} Fe^{++}
Fe^{++}

O_2
O_2 O_2 O_2
O_2

$H^+H^+H^+H^+H^+H^+H^+H^+$ $H^+H^+H^+$

Pipe Wall   **Anodic Area**   **Cathodic Area**

Figure 14 Pitting Corrosion by Oxygen Concentration Cell

Strong Acids (direct chemical attack)—

Strong acids are often pumped into the wells to stimulate production by increasing formation permeability in the near wellbore region. For limestone formations, 5 to 28% hydrochloric [HCl] acid is commonly used. For sandstones, additions of hydrofluoric acid—normally up to 3%—are necessary. In deep sour wells where HCl inhibitors lose effectiveness, 9% formic acid has been used. Corrosion control is normally achieved by a combination of inhibitor loading and limiting exposure time, which may range from 2 to 24 hr. If corrosion-resistant alloys are present (austenitic and duplex stainless steels), concern for stress-corrosion cracking (SCC) and inhibitor effectiveness may rule out the use of HCl. In addition to spent acid, other stagnant columns such as drilling and completion fluid, may also be corrosive.

Concentrated Brines—

Dense halide brines of the cations of calcium, zinc, and, more rarely, magnesium are sometimes used to balance formation pressures during various production operations. All may be corrosive because of dissolved oxygen or entrained air. In addition, these brines may be corrosive because of acidity generated by the hydrolysis of metallic ions. Corrosion due to acidity is more severe with dense zinc brines. More expensive brines of calcium bromide are now often used at densities above 14 lbm/gal [1.7 gm/cm3] to avoid long-term exposure to zinc chloride [ZnCl2] brines.

Biological Effects—

The most important biological effect is the generation of H2S by sulfate-reducing bacteria. These anaerobic bacteria metabolize sulfate ions (using an organic carbon source) and produce hydrogen sulfide. They can thus introduce H2S into an H2S-free system. Colonies of SRBs can also form deposits that lead to crevice corrosion with produced H2S accelerating corrosion, because it is known to be an anodic stimulant. In low-flow rate systems, hard rust nodules or tubercles can form creating differential oxygen cells, which lead to crevice corrosion.
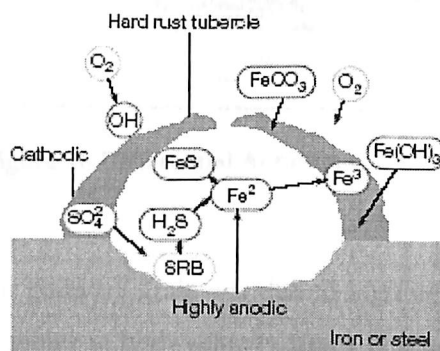
Figure 15 Rust Tubercle

Tuberculation is a complex localized process that forms a nodule-like structure. It often forms in a region of low fluid velocity where a deposit of sludge or rust can shield a part of the metal and reduce the oxygen available to that area. The portion of steel exposed to water with low oxygen concentration becomes anodic and corrodes at a faster rate than the rest.

Mechanical and Mechanical/Corrosive Effects

Differential Aeration Cell-

A corrosion attack will occur where steel is subjected to changing conditions. This is responsible for most of the metal loss in underground steel. Examples are pipelines passing through different soils, well casings penetrating strata of various compositions, or flow lines crossing abandoned salt water pits. Steel contacted by varying amounts of air (oxygen) experiences very rapid corrosion. This type of corrosion is called differential aeration cell. The area of steel starved of oxygen is anodic to the adjacent area of steel and corrodes.
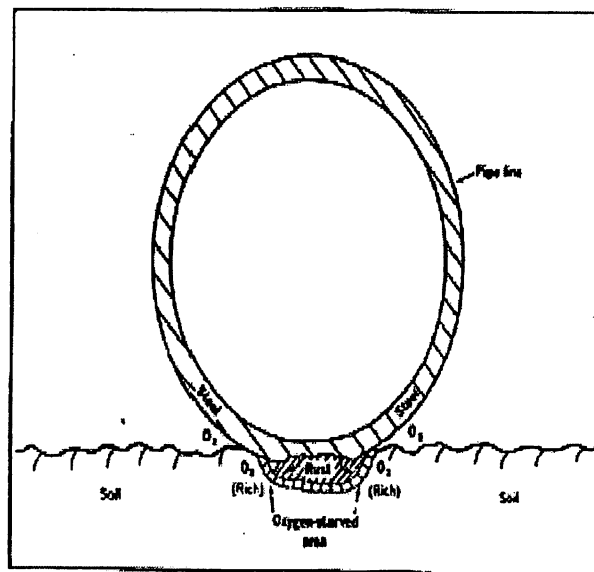
Figure 16 Differential Aeration Corrosion

Cavitation—

This type of metal loss—often grain by grain—is due to high-pressure shock waves, generated from the collapse of minute bubbles in high-velocity fluids impinging on nearby metal surfaces. Cavitation metal loss is usually found on pump impellers developing too low a suction pressure.

Erosion—

This is direct metal removal by the cutting action of high-velocity abrasive particles. Erosion failures (washouts) are seen in drillpipe when leaks (loose connections or a corrosion fatigue crack) allow drilling mud to flow through the wall under high pressure. Erosion of flowlines at bends and joints by produced sand is probably the other most common occurrence of metal erosion in the petroleum industry. Cavitation is a special form of erosion corrosion that

frequently, occurs in centrifugal pumps. Gas or vapor bubbles form and then collapse, thereby breaking the protective films at the metal surface.

Erosion Corrosion—

When erosion removes the protective film of corrosion products, corrosion can occur at a faster rate. Erosion corrosion may play a role in CO_2 corrosion. Under mild flow conditions, sand may also cause erosion corrosion. This type of corrosion is also seen in anchor chains where corrosion between links proceeds quickly.

Corrosion Fatigue—

This results from subjecting a metal to alternating stresses in a corrosive environment. At the points of greatest stress, the corrosion product film becomes damaged allowing localized corrosion to take place. Eventually this leads to crack initiation and crack growth by a combination of mechanical and corrosive action. Because of this combined action, corrosion fatigue is greater at low stress cycles that allow time for the corrosion process. Welded connections on drillships, drilling and production rigs and platforms are subject to this type of corrosion. One oil field study found that 90% of rod breaks occur at dents, nicks, or bends, with the cause of breaks being attributed primarily to improper handling. Although a majority of sucker rod breaks are due to fatigue, a rod string can give many years of trouble-free service; if handled properly and not overloaded. The load limit or endurance limit is determined by API. If a rod string is allowed to corrode, higher stresses are set up because of pits. Proper use of the corrosion inhibitor will prevent pitting.

Sulfide Stress Corrosion—

Production of hydrogen results from sulfide stress cracking (SSC). SSC occurs when a susceptible metal is under tensile stress and exposed to water containing hydrogen sulfide or other sulfur compounds—generally under anaerobic conditions. Corrosion cells generate FeS and atomic hydrogen. The amount of metal loss is small and the FeS layer thin. The layer of FeS promotes the movement of hydrogen into the metal, usually into impurities at the grain boundaries. Penetration of hydrogen into the body of the metal reduces ductility. Accumulations of hydrogen at imperfections generate tremendous pressure. For hard high-strength steel the combination of lack of ductility and internal stress superimposed on the tensile stress causes the metal to break and crack. Penetration of molecular hydrogen can also lead to blistering.

Chloride Stress Cracking (CSC)—

While under tensile stress, austenitic stainless steels can fail by cracking when exposed to saline water above 200°F [95°C].

Stress Corrosion Cracking (combined with SSC, CSC and corrosion fatigue)—

CSC is an example of a broad range of stress-corrosion cracking, defined as corrosion accelerated by tensile stress. This type of corrosion starts at a pit or notch, with cracks progressing into the metal primarily along grain boundaries. SCC requires the presence of a tensile stress and a corrosive environment. Other factors, however, can distinguish see from ssc. The principal contributing factors to see are the environment (pH, Specific ion, concentration of ion, temperature, and applied stress) and materials (yield strength, alloying, microstructure, and heat treatment). Almost every alloy is subject to catastrophic cracking when stressed in a specific environment. All aggressive environments do not crack all alloys; instead, certain chemical species and alloy combinations produce SCC. Such ions as hydroxides, chlorides, and nitrates may cause cracking of carbon and low-alloy steels. Table below shows some of the solutions and compounds that cause ssc in various alloys. This list is incomplete because specific ions or environments are added continually as new alloy/environment combinations that produce scc are encountered in field operations and the laboratory. The concentration of a specific ion is also a factor. As the concentration increases, susceptibility to SCC increases, even if all other factors remain the same. Temperature is one important factor in determining the susceptibility of an alloy to see and in distinguishing the failure mechanism between ssc and SCC. For SCC, an alloy's susceptibility usually increases with increasing temperature, while for ssc, an alloy's maximum susceptibility occurs near room temperature. Fig. 3.47shows this behavior for carbon steel exposed to NaOH. The logarithmic scale for time to failure shows the significant effect small changes in temperature have on the life of steel in this environment. Applied stress and yield strength factors are identical for ssc and SCC behavior. Increasing the applied stress and the yield strength, however, reduces alloys' resistance to SCC.

Table 1 Material / Environment Combinations for which SSC may occur

Material	Environment
Aluminum alloys	$NaCl-H_2O_2$ and $NaCl$ solutions, seawater, air, and water vapor
Copper alloys	Ammonia vapors and solutions, amines, water, and water vapor
Gold alloys	$FeCl_3$ and acetic acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	$NaCl-K_2CrO_4$ solutions, rural and coastal atmospheres, and distilled water
Monel	Fused caustic soda and hydrofluoric and hydrofluosilicic acids
Nickel	Fused caustic soda
Ordinary steels	$NaOH$, $NaOH-Na_2SiO_2$, calcium, ammonium, and sodium nitrate solutions; mixed acids ($H_2SO_4-HNO_3$); HCN and acidic H_2S solutions; seawater; and molten Na-Pb alloys
Stainless steels	Acid chlorine ($MgCl_2$ and $BaCl_2$) and $NaCl-H_2O_2$ solutions, seawater, H_2S, $NaOH-H_2S$ solutions, and condensing steam from chloride waters
Titanium alloys	Red-fuming nitric acid, seawater, N_2O_4, and methanol-HCl

*Fontana, M. and Green, H. Corrosion Engineering, McGraw-Hill Inc., 1967. Reproduced with permission from McGraw-Hill.
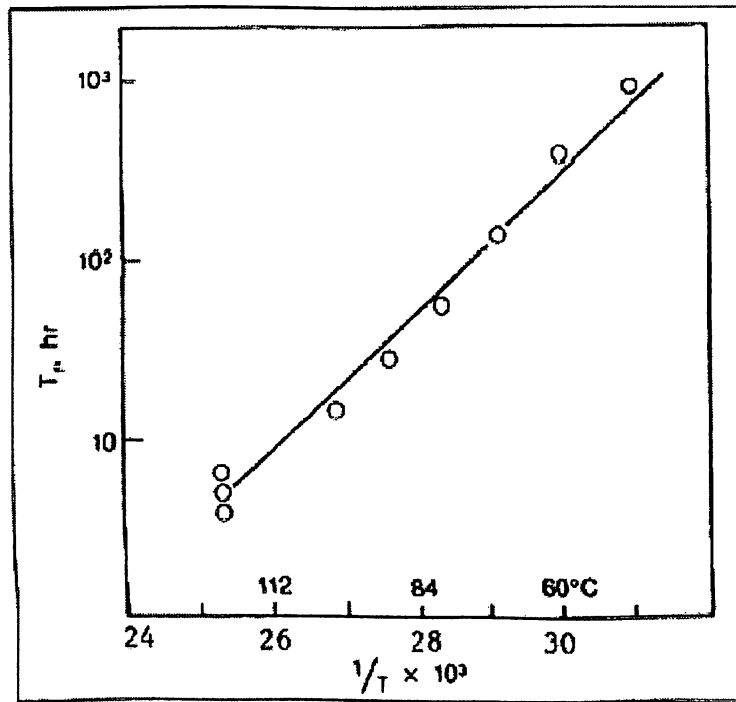
Figure 17 Effect of Temperature on SCC of Steel in boiling 33% NaOH

Effect of Chlorides

- The chloride concentration in Produced water from hydrocarbon formation can vary from zero to few ppm for condensed water to saturation in formation waters having high total dissolved salts/solids.(TDS).
- In naturally de-aerated production environments, corrosion rate increases with increasing chloride ion content over the range 10,000 ppm to 100,000 ppm.
- The magnitude of this effect increases with increasing temperature over 60°C.
- This combined effect results from the fact that chloride ions in solution can be incorporated into and penetrate surface corrosion films which can lead to destabilization of the corrosion film and lead to increased corrosion.
- This phenomenon of penetration of surface corrosion films increases in occurrence with both chloride ion concentration and temperature.
- Chlorides are often specified in ppm NaCI. It should be noted that ppm chlorides can be obtained as 0.63 x ppm NaCI.
- Typically, brines with low chloride content (i.e. <10,000 ppm) are less aggressive than those having higher chloride contents provided that they are compared at the same pH.
- Presence of chlorides can affect the effectiveness of chemical corrosion inhibitors. Therefore, a careful selection of inhibitors and inhibition procedures must be performed where high levels of chlorides (>30,000 ppm) are present.

Effect of Fluid flow Velocity

- Affects both the composition and extent of corrosion product films.
- Typically, high velocities (> 4 m/s for non-inhibited systems) in the production stream lead to mechanical removal of corrosion films and the ensuing exposure of the fresh metal surface to the corrosive medium leads to significantly higher corrosion rates.
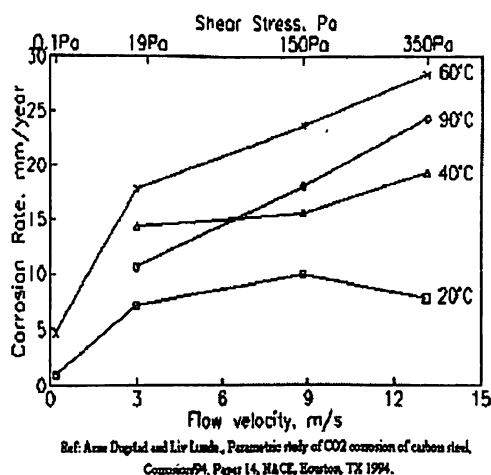
Figure 18 Corrosion Rate as a Function of flow velocity and temperature

Effect of Oil Type

- A systems is called as oil dominated or gas dominated on the basis of the gas/oil ratio (GOR) of the production environment. If the environment has a GOR < 890 m3/m3(5000 scf/bbl in English units), the tendency for corrosion and environmental cracking is often substantially reduced.

- This is caused by the possible inhibiting effect of the oil film on the metal surface, which effectively reduces the corrosivity of the environment. However, *the inhibiting effect is dependent on the oil phase being persistent and acting as a barrier between the metal and the corrosive environment.*

- The persistence of the oil phase is a strong factor in providing protection, even in systems with high water cuts. In oil systems with a persistent oil phase and up to 45 percent water cut, corrosion is fully suppressed, irrespective of the type of hydro-carbon. Relative wettability of the oil phase versus the water phase has a significant effect on corrosion. Metal surfaces that are oil wet show significantly lower corrosion rates.

Gas to Oil Ratio

In oil and gas production, where the environment has a GOR < 890 m^3/m^3(5000 scf/bbl in British units), the tendency for corrosion and environmental cracking is substantially reduced. This is caused by the inhibiting effect of the oil film on the metal surface, which effectively reduces the corrosivity of the environment. However, the inhibiting effect is dependent on the oil phase being persistent and acting as a barrier between the metal and the corrosive environment. If GOR is not

known, it is recommended that a value greater than 5000 scf/bbl or 890 m³/m³ (in SI units) be used.

Water to Gas Ratio

- To have corrosion in oil and gas systems, aqueous water is required.
- In many production applications where essentially dry hydrocarbons are being produced, the full corrosivity of the hydrogen sulfide and/or carbon dioxide will not be present.
- In such systems, a dry gas is considered as that which contains no more than 2 BBL water/MSCF gas (or 11.3m3/Millionm3).
- For Water to Gas Ratio with less than or equal to this amount, the corrosive severity is substantially reduced.
- Care should be taken to evaluate presence of possible locations where water can separate from the hydrocarbons and form a continuous water phase. Under such conditions, substantial corrosion can exist.

DETECTION AND MEASUREMENT OF

CORROSION

Finding corrosive Environments

Corrosion can be prevented or reduced if a corrosive environment is recognized. Early detection of active corrosion will allow initiation of control measures and usually will prevent serious damage.

How can active corrosion be identified before a catastrophic failure or irreparable damage occurs?

Look for factors that increase rates. If any of these factors are present, measure corrosion rate. If metal loss is not significant, it may be cheaper to allow the corrosion to continue than to combat it.

Identify Potential Sources of Corrosion-The first step in control is the identification of corrosion causing factors. Visual inspections may be adequate. Chemical, bacteriological, or electrochemical tests are usually made to verify conclusions. Here are factors which contribute to corrosion:

1. Water must be present before corrosion can start. The water may be oil field brine, fresh water, water spray, vapor or condensation

2. Acid gases, hydrogen sulfide and carbon dioxide, in gas or oil wells form acids when dissolved in water. Also, hydrogen sulfide may be generated by sulfate reducing bacteria in waters containing dissolved sulfates.

3. Air (oxygen) enters oil field systems by "breathing" of vessels, through casing – tubing annulus, from packing leaks at pumps and valves, from faulty gas blankets, and other sources. Trace amounts of air cause severe pitting.

4. Dissimilar metals in physical contact can cause galvanic corrosion. Some common occurrences are brass valves in steel lines, brass polished rod liners, and bronze pump impeller in steel case.

5. High fluid velocities or turbulence can remove protective films. This can be a' problem in high capacity gas wells, high speed centrifugal pumps, throttling valves, chokes, and heat exchangers.

6. *Concentration cell corrosion* occurs in many situations:

Pipelines: External corrosion of lines crossing cultivated fields, brine-polluted areas, caliche beds, and roads.

Internal corrosion of lines handling fluids with considerable suspended corrosion products, loose

scale, or other solids.

Well Casings: External corrosion caused by faulty electrical insulation between wellhead and flow line or gas gathering line. Oil wells with known casing leaks should be checked for external corrosion.

Internal corrosion is frequently caused by "breathing" of air if the casing-tubing annulus is open to the atmosphere.

Vessels: External corrosion of tanks set on soil foundations, buried drain lines beneath tanks, and crevices where moisture can collect between tank and supports.

Tests for Corrosive Conditions

Chemical Tests- *Type* and amount of acid gases or oxygen dissolved in water or in gas streams, vapor zones, and gas blankets can be determined by chemical tests which provide a clue to the type and severity of corrosion. Scale such as iron oxide formed by corrosion, can be analyzed chemically. The composition will usually indicate probable cause.

Tests for Bacteria- *Most* oil field waters contain either aerobic or anaerobic bacteria. Sulfate reducers, anaerobic bacteria which digest sulfate in water to produce hydrogen sulfide are the primary cause of bacteria-related corrosion in oil-field operations. If black iron sulfide suddenly appears in water, or a "rotten egg" odor is detected, test for sulfate reducing bacteria.

Electrochemical tests are used to check surface lines, well casings, or other buried steel structures.

Tests or Pipelines- Soils contain moisture and will conduct electricity . Corrosion cells develop along a pipeline and metal loss occurs as current flows from anodic to cathodic areas. Low electrical resistance of soil as in brine polluted areas, will allow rapid corrosion. Resistivities of soils can be measured along proposed routes to locate areas of low soil resistivities and high corrosivity. Pipe can then be either protected or laid in the least corrosive areas. Plastic pipe may be more economical in very corrosive areas.

Test Of Current Flow in Well Casings- Electrical current flowing in the casing may be corrosion current or current from a cathodic protection system. Whatever the current source, a

voltage or IR drop occurs along the outside of the casing due to current flow and resistance of the pipe. If the casing string is the same grade and weight, the resistance, R is constant and voltage drop is proportional to current flow. Voltage changes in the casing are measured with a logging tool with two sets of contactor knives spaced 25 ft apart. Polarity of the voltage reading between the two logging tool contacts indicates whether the current is flowing from the casing to the earth or from the earth to the casing at any point. A series of readings provides a casing potential profile, Figure 20.

The reflections on Curve No. I at points A and B show where current leaves the pipe and metal loss occurs. In Curve No.2, cathodic protection has been applied and current is not leaving the pipe at any point. The casing is fully protected. The potential profile is the best approach to find active corrosion on the outside of the casing and to show effectiveness of cathodic protection. Many high-resistivity formations such as anhydrites will not permit cathodic current to pass from near-surface anodes, so lower portions of a casing string may not be protected. The casing potential profile log will detect such conditions. An anode placed near the bottom of a hole is better than a shallow ground bed to protect casing. A deep well anode distributes current further downhole.
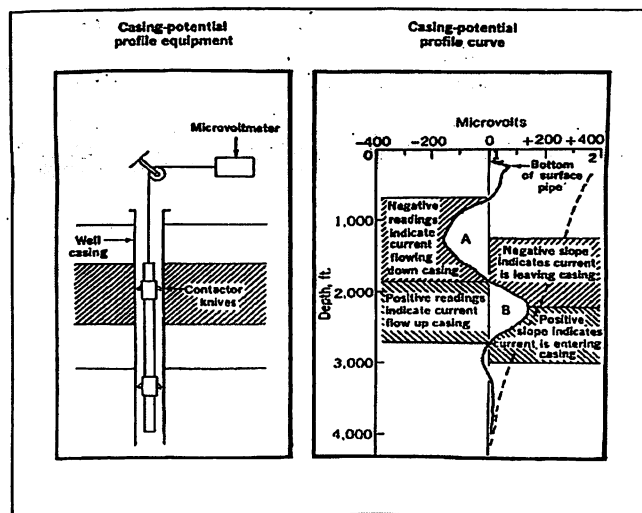
Figure 19 Casing potential profile.

Measurement of corrosion Rate.

Where factors favorable for corrosion are found, the next step is to determine corrosion rates. Rate measurements are usually made over an extended time because single tests do not provide absolute values of damage. A comparison of the several tests gives a more accurate appraisal of corrosive rate. With this information a decision can be made whether corrosion control can be economically justified.

Four techniques are used commonly for evaluating active corrosion: inspection, corrosion-rate tests, chemical-rate tests, and equipment-performance history. A specific technique may be more suitable depending on the cause of the corrosion, the equipment involved, and operating conditions. Frequently a combination of techniques will provide the most useful information. Following are the principal means of determining corrosion rate.

Visual Inspection- Out-of-service equipment can be inspected to determine corrosion damage. All of the equipment can be scanned rather than local areas, as is the case with most other techniques. *Good* records and descriptions are essential for future reference and comparison.

Caliper Surveys- Caliper surveys are run to inspect the internal surface of tubing or casing. Mechanical feelers contact the inside metal surface and will detect metal loss due to pitting, metal thinning or rod wear. Better detail is obtained with instruments where all feelers record, such as the Kinley tool. This allows the determinations at any point of pits, general metal reduction, mashed areas, kinks, or "dog-legs." When tools are run through internally-coated tubing, precautions are necessary with some types of caliper to prevent pipe coating damage. Caliper surveys are most useful if they are conducted periodically to determine the progression of pits or area metal loss. Periodic surveys are useful in determining the effectiveness of corrosion inhibitor treatment.

Casing Thickness Log- The first tool to measure casing thickness was the Casing Inspection Tool, designed by Shell Development Company. This instrument records the phase shift in the magnetic, field between an exciter coil and pickup coil as the tool is lowered or raised on an electric cable in the casing. The tool measures total thickness of metal at any point in the casing. If loss of metal on the inside of the casing has been measured with an internal caliper, then external metal loss can be calculated from casing thickness log data.

A typical casing thickness log is shown in Figure 21, where collar kicks to the right indicate the greater thickness of metal in casing collars, and the kicks to the left indicate a loss of metal from the casing.
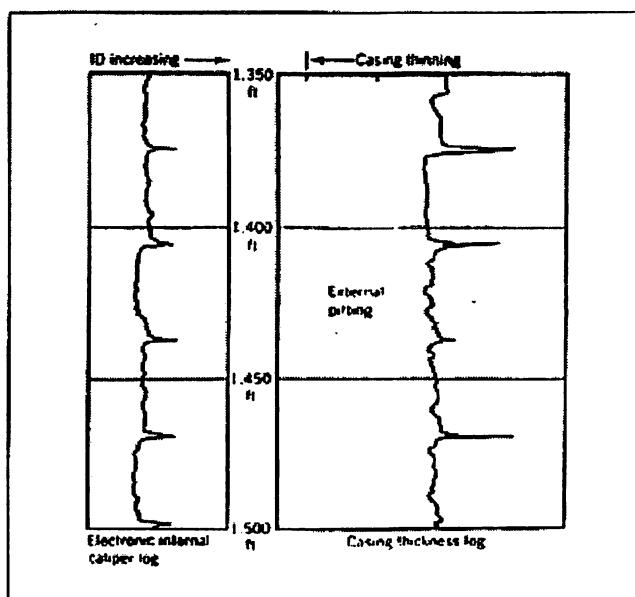
Figure 20 Typical casing thickness log.

Evaluation of Drill Pipe Corrosion- Several tools designed for the detection of flaws, pits, and cracks in drill pipe are available through Tuboscope and others.

Non-Destructive Tests- Ultrasonic or radioactive devices are used to measure wall thickness and detect thinning of metal, but they may not detect small pits. These tests can be made with equipment on stream.

Meal Loss Rate Tests Using Coupons- Weight loss tests are the most common of all rate measurement tests. A small metal coupon, usually low carbon steel, is exposed in the fluid system where corrosion may be active. The coupon is left for a definite period of time and then removed, cleaned and weighed to determine the amount of metal loss. Weight-loss, area of coupon, and exposure time are used to calculate corrosion rate which is reported in mils per year (MPY) of metal loss. Appearance and presence of pitting should be included in reporting corrosion of coupons. Arrangements can also be made, as shown in Figure 22, to insert coupons in a pipe or vessel under moderate pressure through a valve. The fitting shown in Figure 22 can also be used for installing a pressure gauge, thermometer, or for sampling fluid in the line. Coupons were extensively used for many years because there was no better method for estimating internal corrosion.

However, other methods are now available. Coupons must be accurately weighted before exposure. There must be no corrosion of the coupon while it is stored or being transported to and

from test location. Grease or oil cannot be present on the un-corroded coupon because it will not corrode properly when exposed. After being exposed, the coupon must be cleaned of all corrosion products without any attack of the metal. Coupons are then weighed and corrosion rate is calculated.

Determination of corrosion rates through coupons can be inexpensive, if the number of coupons used in a system is large and personnel for processing coupons are available. Some inhibitor suppliers provide coupons, and then clean and weigh them after exposure.

The principal disadvantages of coupons are:
1. the time required to obtain results,
2. they show corrosion only at the point of installation

Metal in the coupon is not identical with metal in the pipe line; therefore, corrosion rate of coupon may not be identical with that of the pipe. However, if corrosion is negligible in coupon placed near the center of the pipe and often near an elbow, corrosion of the pipe may also be negligible. Similarly, if injection of an inhibitor reduces coupon corrosion rate to a negligible value, similar results may be expected on the vessel or pipe. Deposition of corrosion products sometimes causes corrosion rates to decrease with time.
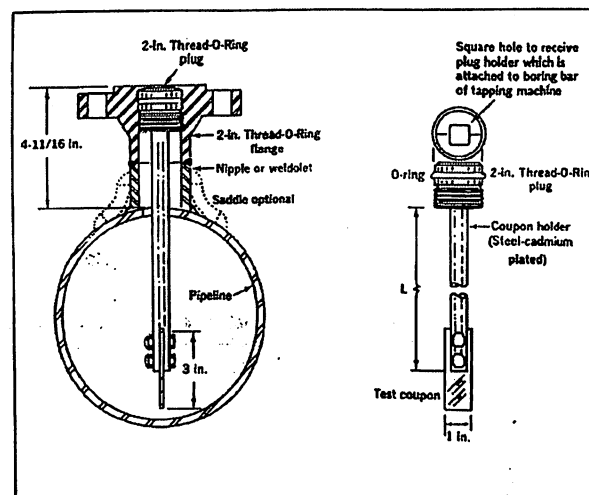
Figure 21 Fitting for in-stream corrosion test coupon.

Electrical Resistance Method (Corossometer)- The Corrosometer is used principally in gas streams because it does not have to be submerged in water to function. The Corrosometer measures electrical resistance and is an adaptation of the Wheatstone bridge. This bridge consists

of four resistances, with two of the resistances in the probe and two in the instrument box. One of the probe resistances, a small strip, wire, or tube of steel or other metal, is exposed to the corrosion environment; changes in resistance with corrosion provide a very precise measure of corrosion rate. Probe elements may be obtained in various sizes and thicknesses. By taking two readings of the instrument and applying characteristic corrections for the particular probe, corrosion rate may be determined to the nearest micro inch (millionths of an inch). The corrosion rate can then be expressed in mils (thousandths of an inch) per year or other convenient units.

The Corrosometer is about 6 in. X 8 in. x 16 in. It is connected through a cable to a probe installed in a pipe or vessel through a threaded fitting. Any number of probes may be installed in various locations. All probes can be observed at convenient time intervals with one instrument. The instrument may be supplied with power from 110V AC or from internal batteries. The Corrosometer appreciably reduces total time required to obtain reliable results. For example, if a corrosion inhibitor treatment is to be evaluated, several probes can be installed at various places in the system and observed until each one shows a definite straight line corrosion rate. Then without moving or changing any of the probes, inhibitor injection is started. Continued measurement of corrosion rates at each probe will show the time required for the inhibitor to reach each probe and inhibitor effectiveness at each location in percent reduction of corrosion. Inhibitor injection can then be stopped and the persistence of inhibitor observed at each location.

Disadvantages of the Corrosometer are:
1. It is somewhat expensive.
2. It is a sensitive and delicate instrument not easily repaired. However, the instrument and measurments can be checked easily *for* accuracy.
3. Untrained operators may have difficulties in instrument operation.
4. This method is usually limited to the measurement of uniform corrosion because it is not too satisfactory *for* measurement of pitting type of corrosion. Also, misleading results can be given if a deposit forms on the probe.

Electrochemical Method- (Corrosion Rate Meter)- The corrosion rate meter measures corrosion current and corrosion rate, because metal loss is directly proportional to current flowing from the test electrode. With the corrosion rate meter, an external current is applied from the auxiliary electrode to the test electrode to change its potential by about 10 mill volts. The applied current is related to metal loss corrosion rate. The instrument gives direct readings in MPY and the readings represent instantaneous corrosion rates. Very low rates are detected. Certain designs

of the instrument can record data *for* multi-test points on a continuous basis. This is useful to study changes throughout a system caused by introduction of oxygen scavengers, inhibitors, air leaks, or other changes. The test probes must be submerged in liquid and probe positioning must be done with care in a flowing stream to avoid "shadowing" of one electrode by another. Short-circuiting of electrodes with corrosion products or solids must be avoided. Uniform corrosion is indicated although some progress has been made in predicting pitting.

Chemical Test for Corrosion Rate-*The* measurement of iron dissolved in a produced water stream can indicate a metal-loss rate. The corrosion product must be water soluble. Therefore the test is applicable primarily to CO, corrosion in which water soluble ferrous bicarbonate (FeHCO3) is the *corro*sion product. This type of corrosion is usually associated with gas wells and wells producing sweet crude. Corrosion products such as iron sulfide and iron oxide are insoluble in water and cannot be reliably used to evaluate corrosion rate. The iron content is measured in parts per million and then converted to iron loss in pounds per day using the water production rate of the test well and the Monograph shown in Figure 23. A low corrosion rate is an iron loss of less than 0.2 lb per sq ft per year of exposed metal. Iron loss rates may not correlate with equipment failures. With uniform corrosion, the loss may be high and damage small. With pitting corrosion, the loss could be low and damage severe. A common practice is to supplement this data with tubing caliper surveys run in key wells at intervals of one to two
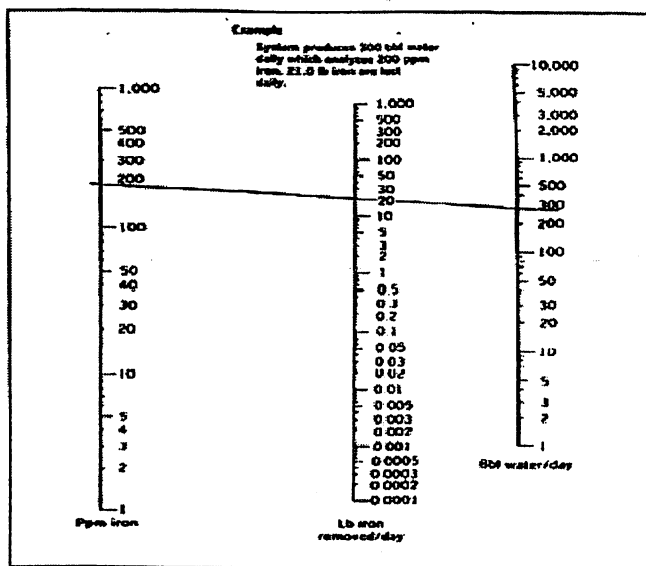
Figure 22 **Monograph for determining iron loss**

Corrosion Records-In any production operation a study of corrosion records can be started at any time if records of purchases and repairs due to corrosion are available. A preliminary study may show that leaks and repairs are confined to certain parts of the system. *For* example, most flow line leaks may occur at road crossings or near tank batteries or wells. Control measures might then be limited to vulnerable places and most leaks might be prevented at minimum cost. If records of repair and replacement costs due to corrosion are available, the operator can determine how much can be spent to prevent corrosion. The record of casing leaks provides a basis for estimation of future leaks and determination of economic incentives to reduce the leaks. When very extensive systems are involved, corrosion surveys and records can be kept on IBM cards or other computer records. Computers can be employed effectively in studying any corrosion problem where a large mass of data is involved. Failure plots of rods, tubing, and pump greatly enhance the analysis of problems in rod pumped wells. These plots will permit the recognition of failure patterns which can be used to differentiate between corrosion and mechanical problems. Plots of leaks versus time on semi-log paper or log-log paper (Figure 24) provide a good method of predicting future failure frequencies and evaluating the effectiveness of measures to reduce corrosion. Figure 24 shows the casing leak history in one large field, before and after installation of insulating plastic nipples between the wellheads and the flowlines. The insulated nipples were installed during 1944, and by 1946 or 1947 it was apparent that casing leaks had been appreciably retarded. Based on the projection to 1970 with and without insulated nipples, casing leaks were reduced about 95%.This great reduction will occur after isolating the well casing from the flowline if most of the external casing corrosion is caused by current flowing from the flowline into the well casing. In this illustration a definite trend of casing leak frequencies had been established before application of insulated nipples between the flowlines and the wellheads. Afterwards, the trend was reduced, indicating the effectiveness of the protection. Also, pin, pointing of line leaks on an aerial map will indicate "hot-spots" which may need attention. Generally, other measurements such as pipe-to-soil potential surveys are made in conjunction with this mapping to define the problem. This technique can be applied to surface line leaks.
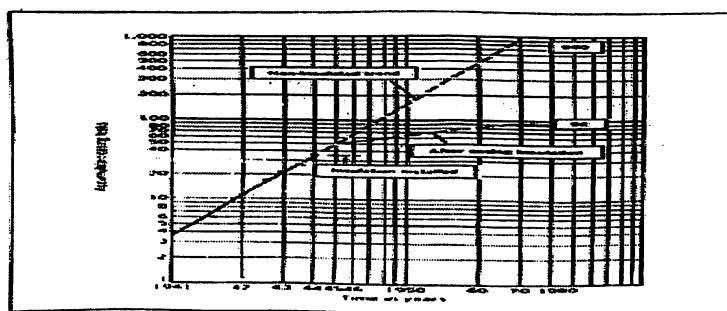
Figure 23 Comparison of casing leaks with and without insulated joints

CORROSION CONTROL

It is usually impossible or too expensive to stop all corrosion. Corrosion may sometimes be allowed to proceed at an acceptable rate if the projected economic loss from corrosion is less than the cost of corrosion control. For example, in many areas lease production equipment may not be coated for corrosion control if damage occurs at a slow rate, various vessels should be internally coated where corrosion is causing serious damage. Corrosion inhibitors are used widely but are generally less than 90% effective. The degree of corrosion control is also influenced by safety aspects, governmental regulations and environmental considerations. There are a number of ways to minimize corrosion in oil field operations including: materials selection, engineering design, inhibitors, coatings, removal of corrosive gases, and cathodic protection.

Select Proper Materials to Reduce Corrosion Rate

Metals and Alloys- Iron and steel are the most commonly used metals in oil field operations because of their lower cost, ease of fabrication, and strength. However, there are numerous applications where high-priced alloys are more economical than the use of steel. For example, various expensive alloys are used in sucker rod pumps because other means of corrosion control are relatively ineffective. Selection of metals is affected by corrosive environment as well as physical requirements. When hydrogen sulfide is present, the effect of hydrogen embrittlement on strength and durability of a metal is the primary concern. Acceptable and unacceptable metals to resist embrittlement in an H2S environment are shown in Table 2.

Low-carbon steels ,including J-55, C-75, N-80 and SOO 90 are used widely in hydrogen sulfide environments, and additional protective measures are normally required. The other acceptable alloys, Listed in table 2 are expensive and are used only where economically justified. Unacceptable alloys because of embrittlement tendencies are shown in Table 2; also high strength carbon steel Class D sucker rods with Rockwell hardness of Rc23 to 28 may experience embrittlement problems. In carbon dioxide and oxygen environments, embrittlement is not a problem, and metals are selected for metal loss control. Expensive alloys to resist CO2 and O2 corrosion are shown in Table 3. Economics usually favor the use of low carbon steel with suitable protective measures for carbon dioxide exposure. For oxygen problems, low carbon steels and air exclusion is the cheapest approach. If oxygen cannot be excluded or removed the higher priced alloys may be justified. Galvanic corrosion is primarily a metals selection problem. A simple solution is to use similar metals.

Other means of controlling this problem are:

1. select metals close together in the galvanic series,

2. use inhibitors,

3. use proper coatings,

4. electrically insulate,

5. use cathodic protection, or

6. Select metals so that anodic area is large compared to cathodic area.

Table 2 Selection of Alloys for H.S Environment

Acceptable Alloys

1. Low and Medium alloy, carbon steels < 1% nickel, not finished, max. R$_c$22
2. J-55, C-75, Q&T N-80, SOO-90
3. 300 series stainless steel Annealed, max. R$_c$22
4. Incoloy 800 (Ni-Cr-Fe)
5. Incoloy 825 (Ni, Fe, Cr, Mo)
6. Inconel 600 (Ni, Cr)
7. Inconel X-750 (Ni-Cr-Al)
8. Monel 400 (Ni-Cu) Annealed
9. K-monel 500 (Ni-Cu-Mo)
10. Hastelloy C (Ni-Cr-Mo)
11. MP35N (Co-Ni, Cr, Mo)
12. Stellites (Co-Cr-W)
13. Colomonoys (Ni-Cr-B)
14. Cemented Carbides (Tungsten Carbide)

Unacceptable Alloys

1. Low and medium alloy steels > 1% nickel or cold finished
2. Free machining steels > .08% sulfur
3. Stainless steel
   Cold finished or precipitation hardened
4. K-monel
   Cold finished

Table 3 Acceptable Alloys for CO. and 0, Environments

Carbon Dioxide	Oxygen
Stainless Steels Except Free Machining Monels (Ni-Cu) Nickel-Iron (Ni-resist) Al-Bronze (Cu-Al)	Stainless Steels Monels Nickel-Iron Al-Bronze

There is a tendency to overemphasize galvanic corrosion. Many couples of metals that are relatively close together in the galvanic series, Table 4, rarely cause troubles. However, the iron

compound (ferrite), that makes steel strong and hard, is cathodic to the pure iron constituent. Metals close to steel in the galvanic series do not significantly aggravate the problem.

Table 4 Galvanic Series of Metal and Alloys in Aowing Sea Water

Magnesium and magnesium alloys
Zinc
Commercially pure aluminum (1100)
Cadmium
Aluminum 2024 (4.5 Cu, 1.5 Mg, 0.6 Mn)
Steel or iron
   Cast iron
Chromium stainless steel 13% Cr (active)
Ni-Resist Cast Iron (high Ni)
18-8 stainless steel (active)
   18-8 Mo stainless steel (active)
Lead-tin solders
Lead
Tin
Nickel (active)
   Inconel (active)
Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
   Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
Brasses (Cu-Zn)
   Copper
      Bronzes (Cu-Sn)
         Cupronickels (60-90 Cu, 40-10 Ni)
            Monel (70 Ni, 30 Cu)
Silver solder
Nickel (passive)
   Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
Chromium stainless steel 11-30% Cr (passive)
   18-8 stainless (passive)
   18-8 Mo stainless (passive)
Hastelloy C (62 Ni, 17 Cr, 15 Mo)
   Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
Silver
Titanium
Graphite
Gold
Platinum

Non-Metals- Most non-metals have much lower strength than steel and may have severe temperature limitations. Plastics, cement-asbestos, ceramics and cement are frequently used in oil field operations. Plastics are organic materials with plasticizers, inert fillers, and hardeners which give improved mechanical and physical properties. Those most commonly used are listed in Table 5. Plastic pipe is being used extensively, particularly fiberglass pipe reinforced with epoxy resin. This type of pipe has been replacing PVC pipe because of the improved strength and higher temperature rating. Epoxy resin is superior to other resins as reinforcement material based on

temperature resistance and strength. Table 6 is summary of pipe properties with various reinforcement resins. Cement-asbestos pipe is a mixture of Portland brines. The primary application of cements has been in SWD sumps, holding ponds, plant drainage systems, cement-lined tubing, and tank bottom re air. They are attacked by acids and are weak in tension.

Table 5 Plastics Used in Oil Field Operations

Thermoplastics		
Type	Trade names	Applications
Fluorocarbons	Teflon Kel-F	Seals. tubing Valve diaphragms
Polypropylene	Moplen Pro-Fax Excon	Valves. pipe, insulation
Polyvinyl chloride	PVC	Valves. pipe, linings
Vinyls	Tygon Prioflex Vinylite Saran	Piping, tubing packaging
Thermosetters		
Epoxies	Epoxy	Fiberglass pipe, glue, grout

Table 6 A Comparison of Various Types of Fiberglass-Reinforced Plastic Pipe

	Epoxy	Vinyl-Epoxy	Polyester
Max. Working Pressure psig	300 .	150	(Not recommended)
Max. Temperature, °F	150	150	(Not recommended)

Corrosion Control Through Original Design

Large savings in future repair and maintenance are usually possible through proper planning for corrosion control when structures and other equipment are being designed and installed. Because all metals have an inherent tendency to corrode, corrosion is normal rather than abnormal and will usually occur unless preventive measures are taken. A new installation should be designed to last

the life of the project but avoid over-design. Many times, future failures are inadvertently built into system design. Often when the design is adequate, corrosion may be unusually severe. Many types of corrosion can be eliminated or minimized by proper engineering design. Here are some of the more prevalent corrosion problems resulting from improper design

1. Crevices cause concentration cell corrosion.
2. Fluid velocity - If it is too slow solids settle and shelter bacteria. Trace amounts of oxygen set up concentration cells. If it is too high, protective films are eroded .Recommended velocities are shown in Table 7,
3. Dissimilar metals coupled together cause galvanic corrosion.
4. Poor drainage of lines and equipment may cause concentration-cell corrosion.
5. Improper selection of metal may result in sulfide embrittlement.
6. Air-exclusion equipment is undersized.
7. Pump suction conditions may promote cavitation.
8. Flow lines or gas-gathering lines are either not insulated from the well, or insulation is not maintained.

Table 7 Flow Velocities in Oil Field Lines To Minimize Corrosion Recommended Maximum and Minimum

Type service	Type fluid	Flow Velocities, Ft/sec	
		Minimum	Maximum
Injection lines— cement lined	Liquid	—	5
Injection lines— plastic lined	Liquid	—	10
Injection tubing	Liquid	2	10
Heat exchangers	Liquid	5	10
Flow lines & tubing	Gas	—	80-100

These are only a few examples of corrosion problems resulting from poor design. The more obvious conditions that may cause corrosion should be avoided. Installation of insulating flanges or fiberglass reinforced plastic nipples should be standard procedure at the wellhead in flowlines and gas-gathering lines.

Galvanic Cells and Corrosion-Resistant Metals- Two different metals, immersed in the same electrolyte (salt or acid solution), will have an electrical potential difference between them, and, if the two metals are connected together, current will flow from one metal to the other. This system is called a galvanic cell; it is the basic arrangement of the dry cell battery. The galvanic series of metals in aerated sea water is shown in Table 4. Metals such as magnesium, zinc, or aluminium shown in the upper part of the table are called "active" metals; those on the lower end of the table, such as nickel and monel are called "passive" metals. Definite values of the electric potentials are not given because metals and alloys do not have definite and fixed potentials in sea water. Metals shown in Table 4 will not have the same relative electrical potentials or be in the same order in the galvanic series in other corrosive media. As an extreme example, serious pitting of admiralty brass tubes in a cooling system was observed adjacent to steel baffles. It would be expected that steel would be anodic, but observation of corrosion showed that in this particular cooling fluid, which contained sulfides, ammonia, and other material, the admiralty brass was anodic and the corroding electrode. On immersing in aerated sea water, each metal or alloy will corrode at the relative rate characteristic of that metal as shown in Table 4, with metals higher in the table being anodic and corroding at a faster rate than those lower in the table. If any of the two metals in the series are connected together and immersed in sea water, this action will occur:

1. Electric current will flow in such a direction between the two metals as to reduce corrosion on the less active metal and increase corrosion on the more active metal.
2. Flowing current is greater and corrosion rate increases when metals are more widely separated in the galvanic series. .
3. Corrosion rate per unit area of the corroding metal is almost proportional to the total area of the noncorroding metal.

As an example of galvanic corrosion, if iron or mild steel and copper are immersed in aerated sea water, steel, the more active metal, will corrode at the rate of about 5 mils per year. If steel is joined to an equal area of copper, corrosion rate of steel will be nearly doubled to about 10 mils per year. If the relative area of the steel compared to the copper is very small, the metal loss per year per unit area of steel is very high. The copper is cathodically protected and does not corrode when joined to steel. Destructive galvanic cells are sometimes built into pump stations, tank farms and other installations. With improper design these galvanic cells may actually accelerate corrosion. For example, at one time many states in the U.S. required that metallic structures be adequately grounded for protection against lightning. Rods or steel pipes, ¾ to 1-in. in diameter

and about 8 ft long, are driven into the ground and connected to the structure. These rods are usually copper clad to prevent corrosion. It may appear that steel tanks, resting on the earth, should be grounded in this manner. Calculations have shown that the electrical resistance to ground of the required number of rods in parallel is much higher than the electrical resistance to ground of the tank bottoms. Therefore, the rods do not protect the tanks against lightning but do introduce a galvanic cell which increases the corrosion rate of steel, tank bottoms. When an important structure, .such as a large saltwater pump, is being designed or purchased, a qualified corrosion engineer should check the design so as to avoid harmful galvanic cells.

It is usually possible

1. to provide adequate grounding for protection against lightning and accidental failures of electrical insulation,
2. to eliminate harmful ,galvanic cells,
3. to provide the most suitable protective coatings to reduce corrosion, and
4. to arrange circuits so that cathodic protection can be installed economically if and when required.

Galvanic cells contribute to the corrosion of many structures. But, either through design or accidental choice, galvanic couples are often an advantage. The gates and seats of valves are often faced with monel or stainless steel, both of which are strongly cathodic to the surrounding steel valve body. In addition to erosion resistance, the critical seat and gate surfaces are cathodically protected by the steel body. The relative area of the steel is large so the galvanic couple causes only a slight increase in the corrosion rate per unit area of the steel, and the steel body is so heavy that it seldom fails, In these applications where dimensions must remain exact, where fluid velocities and mechanical abrasion are problems, and where corrosion cannot be controlled with inhibitors or coatings, the more expensive corrosion resistant metals can be used to advantage. In cathodic protection through the use of sacrificial anodes including sacrificial metallic coatings, corrosion is transferred from the steel to the more active metal whose only function is to corrode and protect the steel.

Insulating Flanges or Nipples- Insulating flanges, couplings, or nipples in a pipe line can be installed and tested during construction at a much lower cost than after the pipe line is in operation. During construction it is not always possible to determine where the insulating joints will be needed; when in doubt, insulating flanges or nipples should usually be installed. They can

be easily shorted out if not needed. Insulating threaded bushings, unions, or flange joints can be purchased. Insulating materials for most flange joints are also available from the corrosion service companies. Figure 25 shows a cross section of a typical insulating flange joint. Reinforced fiberglass insulating joints, usually 10 in. in length, are being used currently in preference to flanges because flange washers or insulating sleeves often become lost or damaged if the flange is broken out frequently. A pressure tight insulating nipple is an indication of satisfactory insulation. However, the use of insulated nipples is frequently limited by pressure ratings, particularly in the larger sizes.
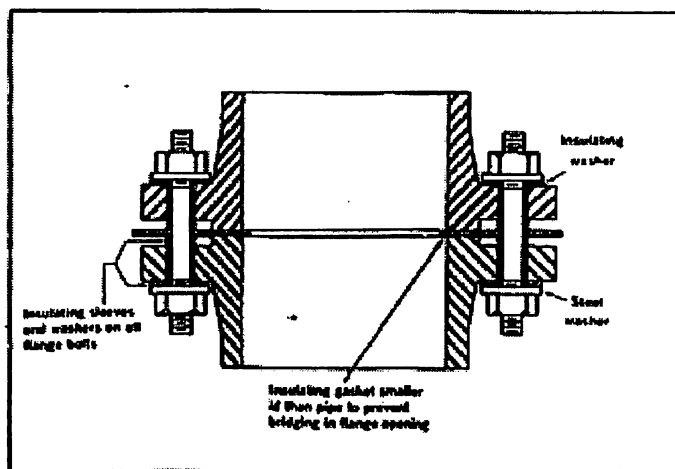
Figure 24 Cross section of Insulating flange Joint

Protective Coatings-

The application of protective coatings can be carried out during construction. Some coatings should be applied at the pipe mill. After uncoated lines have begun to leak, the installation of cathodic protection has often been difficult and expensive. If lines are coated, cathodic protection may not be necessary or, if needed, installation is much less expensive than for uncoated lines. Cathodic protecting protects the outside of the pipe only.

Protection of Casing from Corrosive Water Zones-

During completion of oil and gas wells, cementing all strings to the surface is one approach but it is often quite expensive. An alternate and somewhat less expensive procedure is to cement only through corrosive saltwater zones. Casing should be centralized through these corrosive zones to be protected. Low pH saltwater mud behind the casing may be replaced with mud containing lime and no organic matter to provide a permanent alkaline environment and to prevent growth of sulfate-reducing bacteria. During a completion where a tubing packer is used, consideration

should be given to possible need for injection of inhibitor to protect the casing-tubing annulus and also the inside of the tubing if a downhole control valve is provided. Where H2S cracking of high strength steel is a problem, the primary approach is to restrict the yield strength to 90,000-100,000 psi range.

Selection of Coatings

Coatings prevent or restrict contact of the metal with corrosive liquids or gases. Paints, plastics, cement, rubber, and ceramics have been used to provide such barriers. Also, some types of coatings cathodically protect the base metal. Hundreds of different coatings are available but they can be broadly grouped by their composition into three categories: inorganic, organic, and metallic.

Organic Coatings- These are the most ,used coatings in oil field operations and fall into two broad classes:

1. Paint- is applied as relatively thin films (about 5 mils) for atmospheric exposure, inside drill pipe and tubing.
2. The heavier, usually bituminous coatings are applied to buried or submerged structures

In addition to corrosion protection, paints also improve the appearance of steel structures, and this is usually their most important function. All paint coatings look about the same when first applied. However, there is a wide difference in their durability and protective value, depending largely on the kind of paint and also on the preparation of the surface and method of paint application.

Labor is usually the largest item in the cost of a paint job, so the best possible paint and the best method of application usually results in the lowest maintenance cost over a period of years.

Cement- This is used extensively as a lining for pipe in salt water service and particularly in tubing in water injection wells. Cement lining of pipe costs about 50% less than plastic-coating pipe but pipe requires special handling and welding. If installed properly, it gives long trouble-free service. Acidizing through cement-lined pipe is not recommended. However, when absolutely required, the acid should be pumped at a rate of ¼ bbl/minute in 2-in. lined pipe.

Metallic Coating- For corrosion control in oil production operations, the only metallic coatings of importance are zinc and alumunium on steel. Chromium coatings are used on some pumps but their primary value in this application is hardness and resistance to wear. Cadmium-plated bolts are fairly common in offshore operations. The hot-dip process is the most economical method for applying zinc and aluminum coatings, although both can be applied by metal spray. Electroplating is used to coat threaded couplings with zinc because molten zinc would fill the threads. The durability or life of zinc coatings depends only on thickness rather than on the method of application. Zinc and aluminum coatings are used to some extent on buried or submerged structures where corrosion is moderate but their best application is in the atmosphere where galvanizing and "inorganic zinc" provide the best and most economical protection.

When properly applied, "inorganic zinc" or zinc silicate coating is superior to any organic paint for atmospheric exposure. Inorganic zinc is normally used as an undercoat for more decorative organic paint coatings, although the zinc silicate coating will provide adequate corrosion protection without the coat of paint for long periods in most atmospheric conditions.

Internal Protection of Pipe- Thin coatings have been developed to provide effective internal protection to drill pipe and tubing. Internal coating of pipe is relatively expensive because the pipe must be carefully cleaned by sandblasting, and several paint coats must be applied, each coat being baked at a controlled temperature. These coatings can be applied only to new pipe or used pipe in good condition at the supplier's plant. Cement-lined pipe is frequently used in saltwater lines and water injection lines.

Protection of Underground and Submerged Pipe and Structures

The appearance of coatings for buried pipe lines and similar structures is not important. However, pipe lines are not easily accessible so the first coating must usually last for the life of the pipe line. Buried and submerged structures are continuously exposed to moisture, and coatings should be resistant to penetration by and absorption of water. Cathodic protection is often applied to these structures, so the coating should maintain the highest possible electrical resistance. Coating effectiveness is often determined by measuring electrical resistance of the coating. . High-softening-point coal tar and asphalt enamels containing mineral fillers to improve physical properties, have been widely used with reasonable success. A shield of asbestos felt and reinforcement of felt or fiberglass improves the strength and durability of the coating. Equipment is available for applying these coatings either at the mill or in the field. Coaltar enamels, usually applied hot while spinning the pipe have been widely used in potable water lines, generally with

excellent results. Coaltar enamels should be equally satisfactory in water injection lines, provided the welded joints can be properly coated. Cement linings are also suitable for water injection lines, provided the linings are properly applied and the joints are properly welded and coated. Cold-applied tapes and hot-applied plastic-base coatings have been improved to the point where they appear to be quite satisfactory for external coatings. All buried or submerged pipe lines should be adequately coated. Mill-coated pipe can be obtained in all sizes and quantities. If anticipated use of a particular line is short, coating may be justified by the increased salvage value of the coated pipe. External coatings for tank bottoms differ somewhat from pipelines. Concrete and asphalt mastic have been widely used for pads and tanks. These pads probably retard but can not prevent corrosion because moisture and oxygen can collect between the pad and the tank bottom. Where the soil is dry and well drained, a sand pad is preferred. It will then be possible to apply cathodic protection if necessary although current requirements may be high. A coal-tar enamel coating, applied to tank bottoms at the time of construction, should provide satisfactory protection. Proper surface preparation, coating thickness, and holiday-free condition are essential to the success of a coating. The coatings should be inspected for holidays before pipe or other equipment is installed in field. Small holidays concentrate corrosion in a small area, resulting in rapid penetration of the equipment wall. Widely used coatings and their application are listed in Table 8.

Table 8 Coatings for Pipe and Vessels

Pipe		Vessels
External	Internal	Internal
Coal Tar	Cement (Lined)	Coal Tar Expoxy
Asphalt	Epoxy	Coal Tar
Vinyl (Tape)	Coal Tar—Epoxy	Epoxy
Coal Tar—Epoxy	Phenolics	PVC (Liner)
Polyethylene (Tape)	Polyurethane	Polyesters
Polyester	Polyesters	
Epoxy	PVC (Liner)	

Inhibition with Chemicals

Chemical inhibition is widely used to reduce corrosion. Inhibitors control corrosion in tanks, flow lines, tubing, well casing, waterflood equipment, and gas plants. However, other control methods such as coatings and cathodic protection are often more effective. There are two general types of inhibitors based on chemical composition:

1. Inorganic inhibitors which include chromates, phosphates, nitrites, arsenic and other chemicals.
2. Organic inhibitors which include a wide variety of high molecular weight compounds.

Inorganic inhibitors are used in closed cooling systems in high temperature acidizing of gas wells, and in the treatment of steel surfaces in preparation for painting. Sodium chromate is extremely effective in closed fresh water systems, but it promotes pitting if used in insufficient concentrations in salt solutions. At least 5,000 ppm sodium chromate is required to prevent pilling in salt solutions. Organic inhibitors have wide application in petroleum production. They provide an effective means for controlling corrosion in gas condensate wells –and sour oil wells-and in acidizing oil and gas wells. Their composition is often not available to the user. Therefore, the oil company has no reliable way to predict whether or not a particular inhibitor will be effective in a given application. It is necessary to depend on the supplier to recommend an inhibitor and then to determine, perhaps first in laboratory tests, the relative effectiveness of an inhibitor and whether it is compatible with the fluids in a specific well. Most of the more effective chemicals used in oil and gas wells, service wells, and lease equipment are long-chain nitrogen compounds. With this type inhibitor, a film formed on the wall of the pipe or vessel increases resistance to corrosion current. The film can be formed and maintained on metal surfaces by continuously adding the inhibitor to a flow stream or it can be created by "slugging" the flow stream with a concentration of at least 1,000 ppm of inhibitor for 1 hour with frequent retreatments to maintain the film. Film efficiency depends on inhibitor concentration and. contact time with the metal surface. In slug treatments the ability of the inhibitor to adhere to the metal determines the frequency of retreatments. Several techniques are used for application of inhibitors in oil wells and gas wells.

Gas-Well Inhibition- CO_2 in the gas stream is the most usual cause of corrosion in gas wells. Corrosion usually occurs in the top portion of the tubing string and in surface flow lines where water vapor condenses on the walls of the pipe. However, if formation water is being produced, the corrosion can be scattered over the entire tubing string. Also, hydrogen sulfide can be present in gas wells. Corrosion will occur wherever water is present, either as condensation or water produced from the formation. If no water is present no corrosion occurs. In conjunction with an inhibition program, corrosion rates are monitored to evaluate the effectiveness of the chemical and the application method. Corrosion rate tests for monitoring include iron counts, corrosion coupons, corrosometer, and caliper surveys. If hydrogen sulfide is the major cause of corrosion,

iron counts and caliper surveys are not suitable for rate measurements since the iron sulfide is insoluble, forms a scale on the tubing wall, and covers corrosion pits. The exception to these conditions is in gas wells where there is enough carbon dioxide to keep iron in solution when sampling. If a tubing caliper is needed in wells with iron sulfide scale in the tubing, tubing is usually acidized before making the survey.

There are three primary types of treatments for gas-well inhibition:

1. batch down tubing,
2. tubing-displacement method, and
3. nitrogen squeeze.

Batch Down Tubing for Gas Wells- The tubing is treated with 0.3 gal of active inhibitor per - 1000 sq ft of metal surface. A water - or oil- soluble inhibitor is used as a 10% solution by volume of the inhibitor fluid. The proper volume is pumped into- the tubing and the well shut-in for 24 hours. Frequency of retreatment is based on corrosion rate tests. This treating method has the lowest cost per application, even if the carrier fluid, usually oil or condensate, must be purchased. It is preferred for weaker wells because less hydrostatic pressure is imposed on the formation than when using tubing displacement, and the wells can unload the fluid more readily.

Tubing Displacement Method for Gas Wells- The tubing is filled completely with a 2% solution of an oil soluble inhibitor and shut-in for four hours. This is a more effective method and provides a longer film life. It is more expensive if the carrier must be purchased and presents an unloading problem in low pressure wells. Corrosion rates are monitored to determine the frequency of retreatment.

Nitrogen Squeezes for Gas Wells- *Four* barrels or more of a 25% solution of an oil-soluble inhibitor is atomized into a nitrogen gas stream by jet nozzles. The atomized slug of inhibitor and nitrogen is then displaced with nitrogen gas down the tubing. The total tubing volume is over-displaced by about three equivalent barrels. Total volume of nitrogen will depend on wellhead pressure-the higher the pressure the more nitrogen required due to compressibility of the gas. The well is shut-in about 12 hours, and then the nitrogen gas is blown to the atmosphere prior to returning the well to production. This treatment has the greatest cost per application but may be economical for weaker wells that cannot unload small fluid columns imposed by the batch method. Corrosion rates are monitored to determine the frequency of retreatment.

Oil Well Inhibition- Corrosion in rod-pumped wells is directly related to water cut of produced fluid. Wells producing more than 30% water frequently have serious corrosion problems. If hydrogen sulfide is present, corrosion is more severe. When used properly, corrosion inhibitors are about 90% effective in rod-pumped wells. The chart in Figure 10-9 presents a preferred approach to select the method for corrosion inhibition in oil wells.
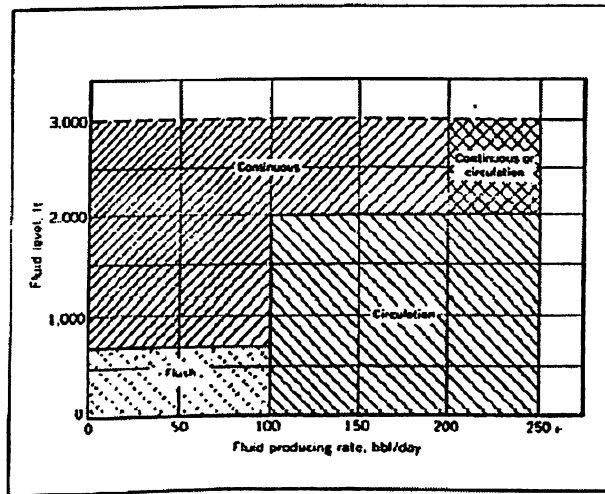
Figure 25 Selecting the method for corrosion inhibition in oil wells.

There are six methods for oil-well inhibition:

Batch flush is applicable to low-volume low pressure wells producing less than 100 bbl of fluid per day, and with a working fluid level of 700 ft or less above pump. With this treatment, one to 2 gal of inhibitor in water is dumped down the casing-tubing annulus and flushed with ½ bbl of water per 1,000 ft of casing. This procedure exposes the well equipment to an inhibitor concentration of at least 1,000 ppm in the produced fluid for one hour or longer. A high degree of protection, usually results.

Circulation method is used in moderate to low working fluid level wells where produced volumes are greater than 50 bbl/day. With this method a slug of 3 to 5 gal of inhibitor is injected down the casing -tubing annulus and then all produced fluid is diverted down the annulus for some time period of effective treatment, the inhibitor concentration at the wellhead should be upto 1000ppm for a one-hour period. The required volume of inhibitor and circulation time is related to the working fluid level, casing-tubing annulus volume, and pump displacement. Larger volumes of inhibitor are required for high fluid level wells because the inhibitor slug is increasingly diluted as it falls through fluid in the annulus. The circulating time to move the

inhibitor slug to the pump suction will be affected by the fall rate through the vapor zone fluid level, casing-tubing annulus volume, and pump displacement.

Continuous injection is frequently employed in high working fluid level wells. With this system, a small quantity of inhibitor is injected continuously into the casing-tubing annulus along with a side stream flush *of* I to 2 barrels of produced fluid per day. The produced fluid should have a concentration of 25-50 ppm of inhibitor.

Squeeze injection is employed if production tubing is set on a packer. A quantity of inhibitor is selected to yield an average concentration of 20 ppm in the water produced during the life of the treatment usually 3 to 6 months. The well is shut-in for 24 hrs to permit the inhibitor to adsorb on the formation rock. The inhibitors slowly removed from the formation rock by produced fluid and returns to the well to protect the tubing, pump, rods, and flow line for several months.

The drop method involves the dropping ,of a weighted material containing corrosion inhibitor down the well. The weighted corrosion inhibitor falls through the fluid column to the bottom, and the inhibitor is released slowly *to* provide about 25 ppm concentration in the produced fluid.

Automatic chemical injectors provide automatic treatment including proper chemical additions where the batch flush or circulating methods are used to treat pumping wells. The injector saves labor if the treatment frequency is greater than once each week and reduces the chance of missed or delayed treatment. Maintenance of this equipment is important because malfunctions may result in a well being without treatment for a considerable period of time. This could cause irreparable damage particularly to rod strings.

Each application method has its advantages and disadvantages. The operator should consider all data on each well prior to selecting an inhibitor, the method of treatment, and the amount of inhibitor required. Fluids containing arsenic inhibitor should not be disposed of in areas where livestock fish and game may reach the fluid.

Cathodic Protection

CP is a technique to reduce the corrosion rate of a metal surface by making it the cathode of a electrochemical cell.

Because coating defects are unavoidable and can thus permit corrosion, pipeline surface protection is not complete with coatings alone; supplementary cathodic protection is necessary.

Cathodic protection, on the coated pipe is needed only on the minute areas of steel exposed to the earth at holidays rather than the whole surface of an uncoated structure. The electrical energy required to cathodically protect a bare structure may be thousands of times as great as the energy required to protect the same structure when it is well coated.

Cathodic protection can be applied by two methods:
1. impressed current cathodic protection and
2. galvanic cathodic protection.

Basic principle of cathodic protection:

If current is to be forced to flow onto the pipe on areas that were previously anodic, the driving voltage of the cathodic protection system must be greater than the driving voltage of the corrosion cells being overcome.

The original cathodic areas on the pipe collect current from the anodic areas. Under cathodic protection, these same cathodic areas (which were not corroding in the first place) usually collect even more current from the cathodic protection system. For the cathodic protection system to work, current is discharged from an earth connection (ground-bed). In discharging current to earth, the ground-bed materials are subject to corrosion. Because the sole purpose of the ground beds is to discharge current to the earth, it is desirable to use materials that are consumed at much lower rates (pounds per ampere per year) than are the usual pipeline metals.

Cathodic protection does not necessarily eliminate corrosion. It' does, however, remove corrosion from the structure being protected and concentrates the corrosion at another known location. At this known location, the current discharging structure (ground bed) can be designed for a reasonably long life. It is also easily tested and replaced at the end of its useful life without endangering the pipeline system being protected.

Criteria for cathodic protection:

The most widely accepted Universal Criteria for Cathodic Protection has been derived using Thermodynamics.

The Nernst equation :

$$\text{❖} \quad E = E_0 - \frac{RT}{nF} L_N \frac{O_x}{R_{ed}}$$

Where,

E is actual half cell potential

E0 is Standard potential

T is absolute temperature

R is Gas constant

n is number of electrons

Ox product of all activities of Products

Red is product of all activities of all reactants

The other Criteria are :

- A 300 mV voltage shift on applying (cathodic protection)current to steel structures. The voltage shift is measured between the pipe surface and a saturated copper copper sulphate [CSE] reference electrode contacting the (common) electrolyte. This criteria emanates from the premise that natural potential of Steel in soil is (-) 550 mV w.r.t. CSE and raising it by 300 mV brings it to Protective potential limit (-) 850mV. However, his criteria is utilized for structures not in contact with dissimilar metals.

- Cathodic Polarization voltage shift of 100 mV. Measured between the structure surface and a saturated copper copper sulphate [CSE] reference electrode, in the common electrolyte. The Polarization voltage shift is measured by Interrupting the (cathodic)Protection current and measuring the polarization decay.

Cathodic protection rectifiers:

The rectifier is the most common source of DC power that can be used for cathodic protection. This device simply converts AC power to low voltage DC power. It is available in a. wide range of voltage and current ratings and is usually provided with a means of adjusting the DC output voltage to the required level. Other power sources such as thermoelectric units, batteries, solar units or wind chargers may also be used to supply the direct current required for cathodic protection.

Sacrificial Anodes such as Zn, Mg, for soil and Al for sea water are used as Anodes due to their Electrochemical characteristic.

S.No.	Material		[P-S-P] w.r.t.CSE	Amp.-Hour Per Kg.	Kg. per Amp.-Hour
1.	Magnesium	[Mg]	(-) 1.05 to (-)1.7	1,200	7.5
2.	Zinc	[Zn]	1.10	780	11.25
3.	Aluminium	[Al]	1.10 to 1.15	1,800 t0 2,800	4.38 to 3.15

The ground-bed (anode bed/**Sacrificial Anode**) is the point of current discharge into the earth from the rectifier. Corrosion will take place at the anodes, which will eventually require replacement.

Two types of ground-beds are commonly used by the industry

1. The conventional type and
2. The deep well type.

With the conventional type, the anodes are installed horizontally in a straight line 2 to 1 m below ground level. In the deep well type, the anodes are installed in a well 60 to 120 m below ground level. Each type has pallicular advantages and disadvantages but both types discharge the rectifier current into the earth.
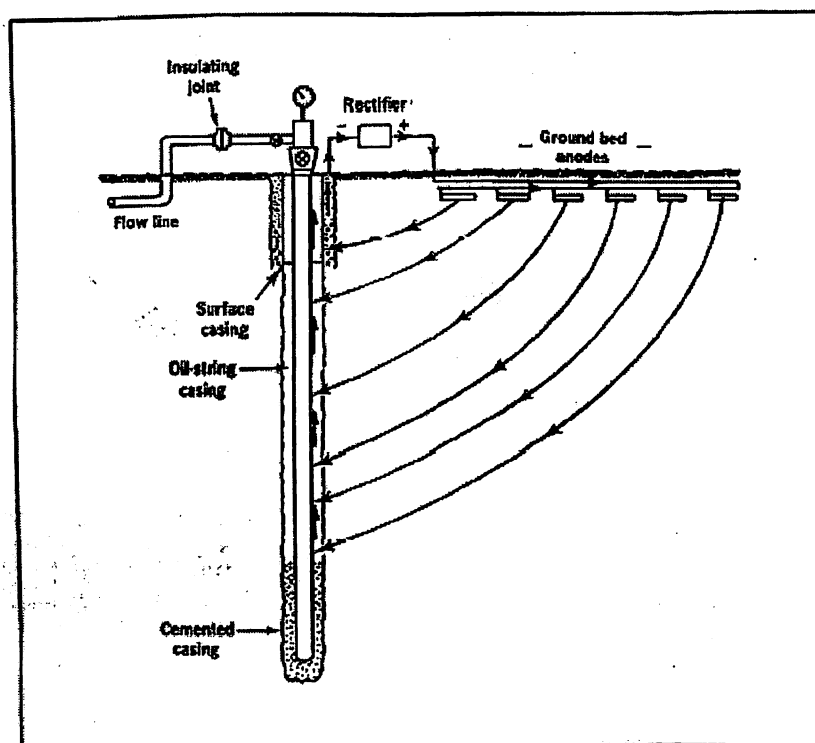
Figure 26 Typical cathodic-protection installation for a well casing.

Impressed Current Cathodic Protection [ICCP] System is used For longer service life as this has a better protective current giving capability and can be adjusted as per demand from the in service [pipeline/tank] system due to changes such as environment, weather etc. A typical Schematic of [ICCP]system is shown below :
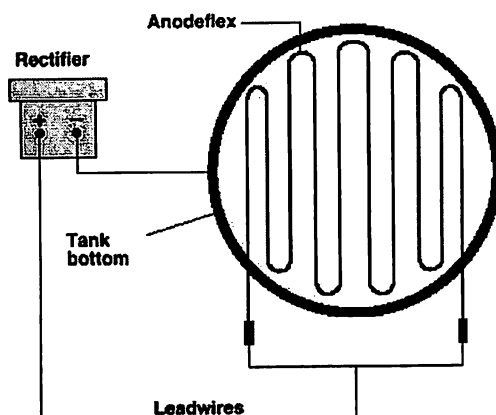
Figure 27 ICCP System

The [ICCP] system is powered by a dedicated power source such as a AC Input DC Output Transformer Rectifier unit (TRU) or a AC,DC Input and DC Output TRU where the chances of AC input failure are probable abundantly. Other power sources such as a Cathodic Protection Power Supply Module [CPPSM] which has a DC Input [derived from a Thermo Electric Generator or A Close circuit Vapor Turbo generator [CCVT] and DC output, Solar Photo-Voltaic Panels, Battery/D.G. Back up etc. are also used.

A wide range of Impressed Current Anodes are available and are selected as per rate of corrosion / consumption, cost, weight, size, degree of risk in use, required lifetime, prior performance etc.

Group	Material	Very Approximate	
		Consumption Kg./Amp.-Year	Current Density Amp./M^2
Actively Corroding or consumable	Iron	9.5	05
Partially Passive or Semi Consumable	Lead Si-Fe-Cr Cast Graphite Magnetite	0.03-0.09 0.20 – 1.0 0.50 – 1.0 0.005 – 0.020	300 50 10 100
Fully Passive or non Consumable	Platinum [Pt] Mixed Metal Oxide [MMO],Cable Anodes	0.001 < 0.006	1,000 600

Effectiveness of Cathodic Protection (CP)

Stopping the Development of Pipeline Leaks

CP, properly designed and maintained, can control pipeline corrosion effectively on steel systems has been demonstrated in countless instances. Criteria for determining whether adequate corrosion control has been achieved and the field-monitoring techniques required for the assessment of these criteria Are discussed separately. The proof of the effectiveness of CP is most apparent where protection has been applied to old piping systems that had been developing leaks at a rapidly increasing rate. Suitable protection systems can stop the development of further leaks in dramatic fashion.
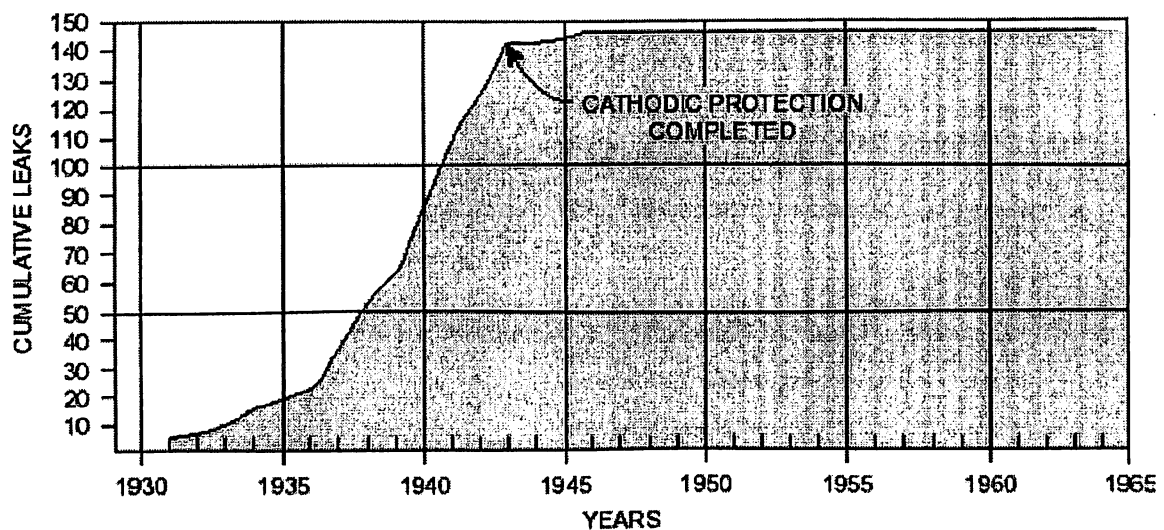
Figure 28 Effectiveness of CP in Stopping the Development of Leaks

Presence of Stray Current

Where stray current corrosion is a factor, CP alone may not be the best method of controlling corrosion. The stray currents can be man-made or natural direct currents from sources other than galvanic corrosion cells on the pipeline itself. The applicability of CP depends to a great extent on the severity and degree of variation of the stray currents picked up and discharged by the pipeline. Low level steady-state (static) currents or currents that vary within reasonable narrow limits may be controlled with CP systems. Larger stray currents, particularly those showing wide variation and reversals in direction of flow (dynamic stray currents), usually require special analysis and corrective measures.

Comparison between Galvanic and Impressed Current CP System

Galvanic	Impressed Current
They are independent of any source of electrical power	(1) Requires a mains supply or other source of electric power
Their usefulness is generally restricted to the protection well-coated structures or the provision of local tection, because of the limited current that is nomically available.	(2) Can be applied to a wide range or structures including, if necessary, large, uncoated structures.
Their use may be impracticable except with soils or ters with low resistivity.	(3) Use is less restricted by the resistivity of the soil or water.
They are relatively simple to install; additions may be de until the desired effect is obtained.	(4) Needs careful design although the ease with which output may be adjusted allows unforeseen or changing conditions to be catered for.
Inspection involves testing, with portable. Instruments, each anode or between adjacent pairs of nodes.	(5) Needs inspection at relatively few positions; instrumention at points of supply can generally be placed where it is easily reached.
They may be required at a large number of positions. eir life varies with conditions so that replacements may required at different intervals of time at different parts t system.	(6) Requires generally a small total number of anodes
They are less likely to affect any nearby neighbouring structures because the output at any one point is low.	(7) Requires the effects on other structures that are near the groundbed of protected structures to be assessed but interaction is often easily corrected, if necessary.
Their output cannot be controlled but there is a dency for their current to be self-adjusting because if ditions change such that the metal tobe protected omes less negative, driving e.m.f., and hence current, reases. Possible, by selection of material, to ensure that metal cannot reach a potential that is sufficiently ative to damage paint.	(8) Requires relatively simple controls and can be made automatic to maintain potentials within close limits despite wide variations of conditions. Since the e.m.f. used is generally higher than with galvanic anodes the possible effects of ineffective control or incorrect adjustment, for example, damage to paintwork or coatings, are greater.
Their bulkiness may restrict flow and/or cause bulence and restrict access in circulating water systems. ry introduce drag in the case of ships' hulls.	(9) Allows or more compact anodes by the use of suitable materials: drag is negligible.
) They may be bolted or welded directly to the surface e protected thus avoiding the need to perforate the tal of ships' hulls, plant to be protected internally, etc.	(10) Requires perforation in all cases on ships' hulls, plant etc., to enable an insulated connection to be provided.
)Their connections are protected cathodically	(11) Requires high integrity or insulation on connections to the positive side of the rectifier which are in contact with soil or water: otherwise they will be severely corroded. (12) Requires the polarity to be checked during commissioning because misconnection, so that polarity it reversed, can accelerate corrosion.
) They cannot be misconnected so that polarity is ersed.	

CATHODIC PROTECTION DESIGN ASPECTS

Site Data Requisite for Cathodic Protection Design:

MS Pipelines, storage tanks are laid underground, whereas, above grade tank bottoms and Mounded bullets external surface are in contact with corrosive (soil) environment and are, therefore, amenable to Soil side Corrosion. It is, therefore, necessary to Provide adequate Corrosion control measures to ensure metal integrity for Safe & Economic Operation throughout the Design [service] Life of the facility. The need for external Corrosion control is usually based, as per **NACE 0169 96** clause 3.2 Recommended practice, on Data obtained from one or more of the following :

1. General information [Topographic] of terrain along which the pipeline/facility is to be routed.

2. Measurement of soil resistivity [ρ] along ROW and at Anode bed plots. Each selected Anode bed plot shall be sub-divided into sub-plots. Size of the subplots shall depend upon investigation of soil resistivity upto requisite depth. Each of these sub-plots shall be investigated individually. Sufficient observations at each of these plots should be recorded. This to obtain sufficient information about sub-soil stratification and water table depth wherever possible. The number of sub-plots shall be decided at site. Number, location, demarcation and size of sub-plots shall be individually decided for each ground bed plot location. One or more plots may be selected and surveyed at each CP station to finalize suitable ground bed location.

3. Soil / water analysis for Chemical & Microbial loading.

4. Survey for investigating possible sources of stray currents so that requisite mitigative measures are included in the CP design.

5. Where a site survey is not possible the C P contractor shall ensure that requisite data is available for him to fulfill requirements of the CP Design.

6. Survey for knowing the location of existing Cathodic Protection system to maintain appropriate clearance between the existing and upcoming C P Systems Prior to CP

Additional Data To Be Collected:

The following data shall be collected to generate design data for evaluation of interaction/ interference possibilities due to presence of other services in ROW/ in close vicinity:

i. Route and types of foreign service/pipeline/storage facility in and around or crossing the right of way (including those existing and those which are likely to come up during contract execution or any abandoned pipelines).

ii. Diameter, wall thickness, pressure, pipeline coating against corrosion, soil cover used in case of pipelines.

iii. Details of the existing pipeline/storage facility cathodic protection systems protecting the services i.e. location, rating, type of protection, anode beds, test station locations and their connection schemes.

iv. Graphical representation of existing structure/pipe-to-soil potential [PSP]records, T/R unit current/ voltage input/output ratings, present current/Potential Input/Output Data etc for the existing pipelines.

v. Remedial measures existing on foreign pipeline/ services to prevent interaction.

vi. Possibility of integration/ isolation of existing CP systems, which may involve negotiations with owners of other existing pipeline services.

vii. Crossing and parallel running of electrified and non-electrified traction (along with information regarding operating voltage, type AC/DC etc.) as well as abandoned tracks near ROW having electrical continuity with the tracks in use.

viii. Crossing or parallel running of any HT AC/DC overhead line (existing/proposed) along with details of distance from pipeline, voltage, type AC/DC, distance from pipeline of earthing of towers etc.

ix. Voltage rating, number of cores and sheathing details of underground power cables, along ROW or in its vicinity.

x. Information on existing and proposed DC/AC power sources and system having earth as return path, in the vicinity of the entire pipeline route such as HV DC sub stations, fabrication yards with electric welding etc.

xi. Conduct necessary potential gradient survey for any existing anode ground bed that may interfere with the CP system being designed.

xii. Any other relevant information that may be needed in designing and implementing proper protection scheme for the proposed CP System.

Selection of Type, Size, Spacing of CP:

The Cathodic Protection system should meet the following Objectives:

1. Deliver & Distribute sufficient Protective Current to ensure that the selected & specified Protection Criteria is achieved all over the structure being protected throughout the design life of the underground pipeline/storage tank/structure.

2. To provide complete Protection to the underground pipeline/storage tank/structure throughout it's Intended Design Life.

3. Minimize the effects of Interference Currents on existing neighboring Metallic structures such as underground Pipelines/tanks/rutor steel in concrete or any of the existing installations.

4. Locate all components, parts of the CP system so as to minimize the possibility of their dissolution[except normal Anode consumption] or damage.

5. Ensure that the system does not jeopardize the Integrity of the buried structure during its service life.

This Objective is achieved by Developing the Design Engineering Package based on the NACE / BS / BIS Codes and Standards and Recommended Practices, Good Engineering Practices, besides conforming to the Safety requirements stipulated under the Statutory regulations such as from C C E [Nagpur],O I S D [Ministry Of Petroleum & Natural Gas, Govt. Of India],Indian Petroleum Rules, N F P A,API model Code for safe practices etc.

DESIGN FORMULAE :

Design formulas to be utilized are as hereunder:

Surface Area (Sa)

$$S_a = \pi . d. l$$

Where, d is pipe diameter
l is pipe length

Current Requirement

$$I_t = S_a . C_d . S_f$$

Anode Weight Required

$$W_t = I_t . O . Y / U_f$$

Where Wt is Anode Weight required
O is Anode consumption rate
Uf is utilization factor

Ground bed Resistance

$$R_b = \frac{0.159 \times \rho}{N \times L} (\log_N \frac{8 \times L}{D} -1+ \frac{2 \times L}{S} \log_N 0.656N)$$

where
Rb = Ground bed Resistance
Of several Anodes
ρ = Soil Resistivity in Ohm-Cms
N = Number of Anodes

L = Length of Anode Bed

S = Anode Spacing

D = Outer Diameter of Anode bed

And

$$R_h = \frac{0.159 \times \rho}{L} \left\{ Log_N \frac{4L^2 + 4L(S^2 + L^2)^{1/2}}{dS} + \frac{S}{L} - \frac{(S^2 + L^2)^{1/2}}{L} - 1 \right\}$$

where

Rh is resistance of Horizontal Anode bed

ρ is resistivity of backfill material

L is length of anode

d is diameter of anode

S is twice depth of anode

No specific formula for horizontal anodes in parallel is known.

[Refer : Peabody Ed. By Bianchetti :"Control Of Pipeline Corrosion" NACE 2001]

Internal Resistance Of Anode

$$R_a = \frac{0.159 \times \rho}{L} \left(\frac{2.3 \log 8 \times L}{d} - 1 \right)$$

where

d = Anode Diameter

L = Length of Anode

Cable Resistance :

$$R_C = (L_P \times R_p) + (L_n + R_N)$$

Where

Ln is Length of Anode Cable

RN is Resistance of Cable

LP is length of Cathode cable

RP Resistance of Cathode Cable

Total Circuit Resistance :

$$R_T = R + R_V / N + R_C$$

Where,

RC is Cable resistance

R is Resistance to electrolyte of ground bed (Ω)

RV is Singe Anode to backfill resistance.

Cross-section area of pipe [A]

$$A = \ddot{e} \, x \, t \, x \, (D - t)$$

where

t is thickness of pipe [M]

D is Diameter of Pipe [M]

Linear Resistance of pipe [RS]

$$R_S = \rho_S \, x \, 1 / A$$

Where

ρS is resistivity of steel pipe

1 is unit length of pipe

A is cross Section area of pipe

Coating Leakage Resistance of pipe [Rl]

$$[R_l] = R_p / Sak$$

Where

Rp is Coating Resistance of pipe

Sak is surface area of 1 km of pipe

Attenuation Constant [α]

$$\alpha = [R_S / R_l]^{\frac{1}{2}}$$

Voltage At Drain Point

$$E_d = P/S(min.) \quad - \quad P/S(Nat.)$$

where

Ed = Pipe to Soil Potential at furthest point from drain point

P/S(min.) = Minimum acceptable Pipe to Soil Potential

P/S(Nat.) = Natural Pipe to Soil Potential

Attenuation

$$E_{dp} = E_d \times Cosh \, aL$$

where

Edp = Potential at drain point

Ed = Potential at furthest point

a = Attenuation Factor

L = Distance

The spacing between consecutive CP Stations is accordingly decided.

Weight and Number of Anodes:

1. **Wetted area of steel:** from direct measurement/drawing

2. **Total current I (A) needed :**

   I = Area (m2) X Current Density (mA/m2)/1000

3. **Weight of anode material required :**

   = Area (m2) X Current Density (mA/m2) X Design Life (yrs) X 8670/[1000 X Material Capacity (AhKg-1)]

4. **Minimum Number of Anodes :**

   = Current Density X Area/[1000 X Anode Output (A)]

5. **Weight Requirement :**

   =Number of Anodes X Individual Net Weight

6. **Current Requirement :**

   = Number of Anodes X Individual Anode Current Output

Spread Protection:-

$$2L = \sqrt{\frac{8.\Delta U_L}{\pi. D.J.R'}}$$

L = Spread Protection (m)

D =Diameter *of* the pipeline (m)

J = Protection current density (Nm2).

R' = Resistance *of* the pipe (ohm/m).

ΔU_L = 0.3 V maximum potential difference between potential at drain point (X = 0) and potential at end of protection spread (X = L).

Voltage Drop along the pipe:

$\Delta U = R' \times L (i + \Delta i/2)$

Where:

L = Length *of pipeline* section (m).

R' = Resistance *of* pipe (ohm/m).

M = Current entering pipeline section over length L (A).

I = Constant current in section L (A).
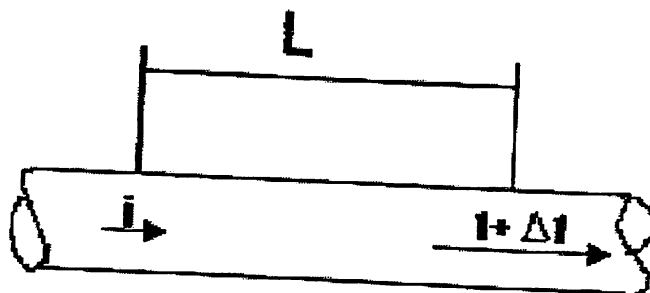
Required Protective Current

$$2I_0 = 2 \pi D * L * J$$

Where:

I_0 = Protective current on one side of the cathodic protection stations (A).

D = Diameter of the pipeline (m).

J = Protective current density *(Nm2)*.

L = Spread of protection (m) of one sides of the cathodic protection station, limited by an insulating joint or with arrangement equidistant to neighbor cathodic protection stations.

Calculation of Anode Life:

$$L = E * C * M / i$$

Where :

Anode output current	I(A)
Anode weight	m(kg)
Efficiency	E(%)
Capacity	*C(Ah/kg)*
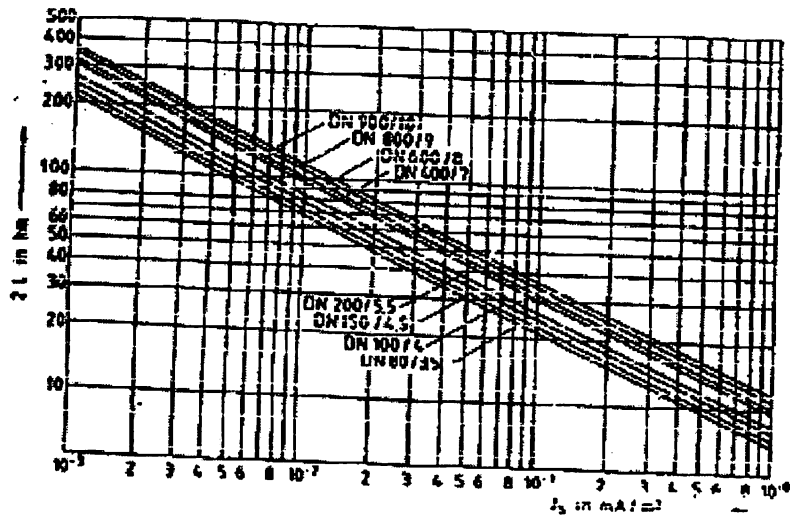
Figure 29 Spread protection as a function of current density and pipe dimension
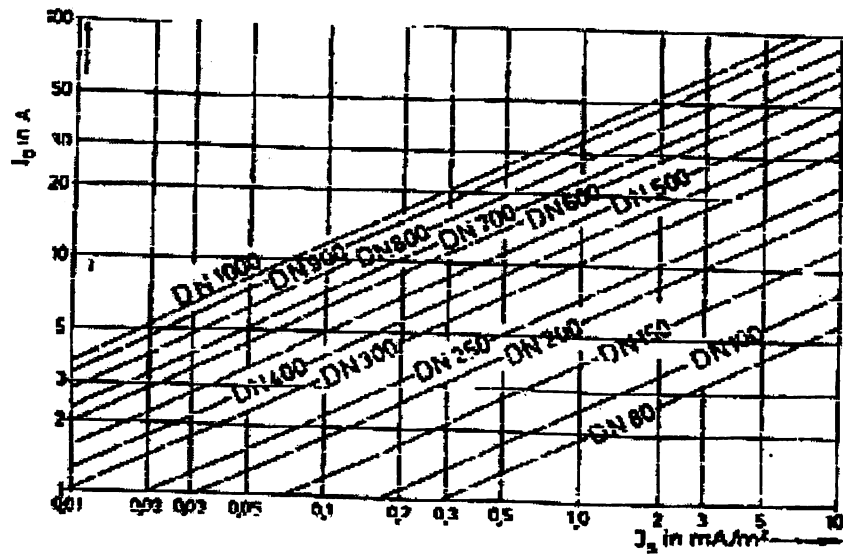
Figure 30 Required current Demand as a function of current density and pipe dimension

Identifying the Causes and Applying Controls

There are many sources of corrosion and many more methods of slowing the process down. This section looks at different parts of the industry and identifies typical corrosion problems and some of the solutions.

Offshore structures—

On surface equipment, the simplest solution is to place an insulating barrier over the metal concerned. Offshore installations are often painted with zinc-rich primers to form a barrier against rain, condensation, sea mist and spray. The zinc primer not only forms a physical barrier, but also acts as a sacrificial anode should the barrier be breached. Offshore structures are also protected in other ways. The zone above the high tide mark, called the splash zone, is constantly in and out of water. The most severe corrosion occurs here. Any protective coating or film is continually eroded by waves and there is an ample supply of oxygen and water. Common methods of controlling corrosion in this zone include further coating and also increasing metal thickness to compensate for higher metal loss. The part of the structure in the tidal zone is subjected to less severe corrosion than the splash zone and can benefit from cathodic protection systems at high tide. Cathodic protection works by forcing anodic areas to become cathodes. To achieve this, a reverse current is applied to counteract the corrosion current. The current can be generated by an external DC source—impressed cathodic protection—or by using sacrificial anodes. The rest of the structure—exposed to less severe seawater corrosion—is protected by cathodic protection. However, crustaceans and seaweed attach to the submerged parts adding weight that may increase stress related corrosion. This mechanism occurs when the combined effects of crevice, or pitting, corrosion and stress propagate cracks leading to structural failure. However, a covering of life does restrict oxygen reaching metal, and so reduces corrosion. Other forms of structural stress are also important. Low-frequency cyclic stress— resulting from factors such as waves, tides and operating loads—can allow time for corrosion within cracks as they are opened. Modeling and accounting for these stresses are therefore an extremely important part of corrosion prevention.
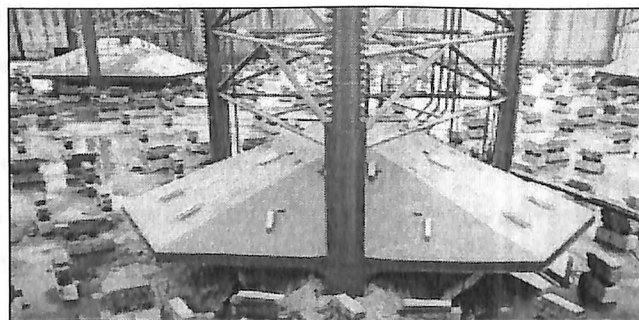
Figure 31 Sacrificial anodes on the leg and spud tank of Sedco Forex's Trident IV jackup rig.
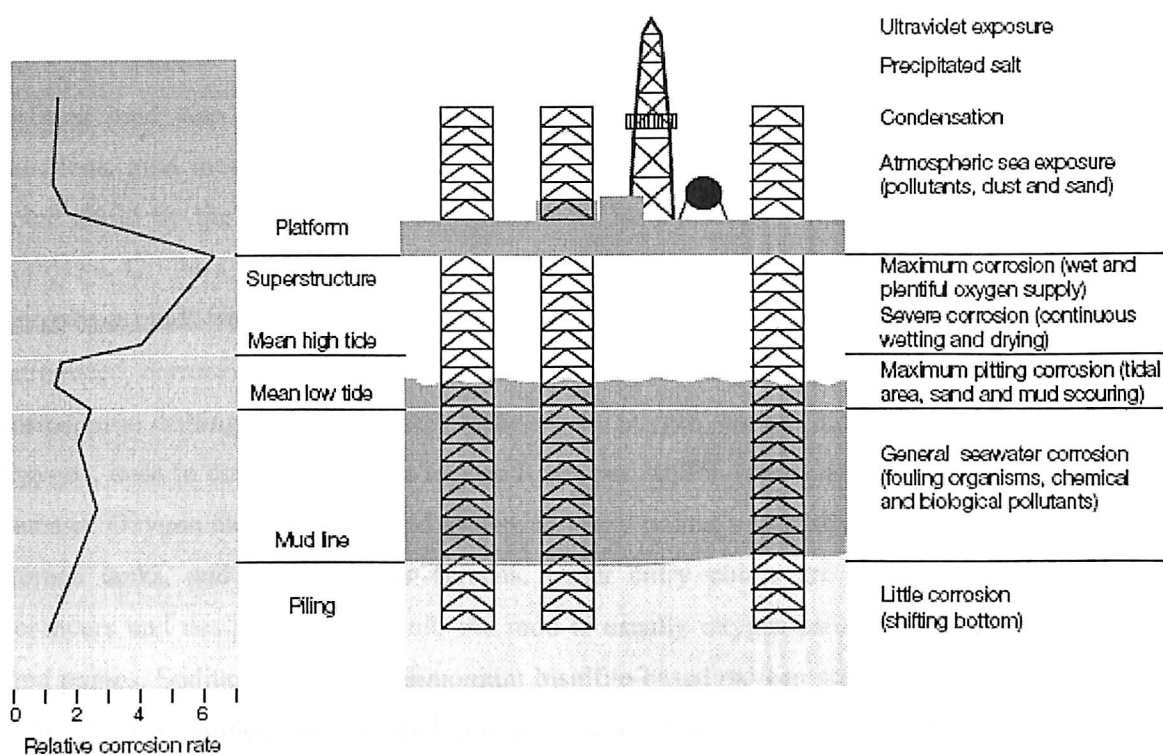
Figure 32 Diverse Corrosive Environments Attacking an Offshore Rig

The bottom of a jackup rig or production platform sinks into the seabed and is attacked by H2S produced by sulfate-reducing bacteria (SRB). However, cathodic protection also shields this part of the structure and, because of reduced oxygen supply, the protection current required tends to be less than for the rest of the rig.

Drillpipe corrosion—

While a well is being drilled, stress is applied not only to the rig structure, but also to the drilling equipment. Drillpipe is probably the most harshly treated of all equipment. It is exposed to formation fluids and drilling mud, subjected to stress corrosion and erosion by cuttings. Joints of drillpipe are made from hardened high-strength steel and are likely to suffer from fatigue failures started by deep corrosion pits caused by oxygen, either from the mud itself or from being stacked wet. Drillpipe is sometimes coated internally, with baked resins or fusion bonded epoxies, to counteract corrosion. Once this coating has disappeared, however, corrosion can be rapid. A common area where drillpipe leaks or washouts occur is in the threaded drillpipe connections called tool joints. The threads provide ideal places for crevice corrosion, which can also occur in scars left on the tool joints by makeup tongs. A special grease, commonly known as dope, lubricates the threads and helps prevent corrosion.

Mud corrosion—

Drilling mud also plays a key role in corrosion prevention. In addition to its well-known functions, mud must also remain no corrosive. A greater awareness of corrosion problems has come about by the lower pH of polymer muds. Low pH means more acidic and hence more corrosive. Oil-base muds are usually no corrosive and, before the introduction of polymer muds, water-base muds were used with relatively high pH of 10 or greater. So when polymer muds were introduced, corrosion from mud became more apparent. Dissolved gases are the primary cause of corrosion in drilling fluids. The most common are oxygen, carbon dioxide and hydrogen sulfide. Oxygen, even in concentrations as low as 1 part per million (ppm), is capable of causing serious damage. Oxygen can enter the mud system at many points, especially at the surface mixing and storage tanks, and at the shaker screens. Other entry points are at the centrifugal pumps, desanders and desilters. As a result, the mud is usually oxygen-saturated before it reaches the mud pumps. Sodium sulfite- or ammonium bisulfite-based oxygen scavengers, such as Dowell's IDSCAV, are routinely used in mud systems. These chemicals bond with oxygen in the mud to reduce its corrosivity. Maintaining high pH is important in controlling corrosion rates by neutralizing acids caused by H2S or CO2. Hydrogen sulfide can enter the mud system directly from the formation or from thermally degraded mud products, SRBs or makeup water. Scavengers, such as sodium chromate, zinc chromate, and sodium nitrite, can quickly remove H2S. Dowell's film forming inhibitors IDFILM, help protect the drillstring and casing. Triazine compounds are used in products such as Dowell's IDCIDE as biocides to control bacteria.
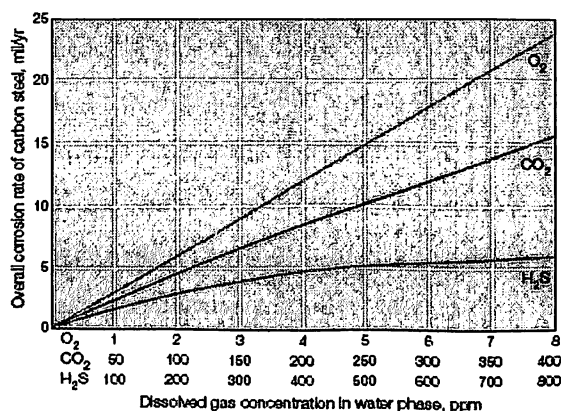
Figure 33 Comparison of Corrosion Rates of Steel

Measurements of the corrosion rates of a carbon steel exposed to different concentrations of O2, CO2 and H2S gases dissolved in water, show that O2 is about 80 times more corrosive than CO2 and 400 times more corrosive than H2S
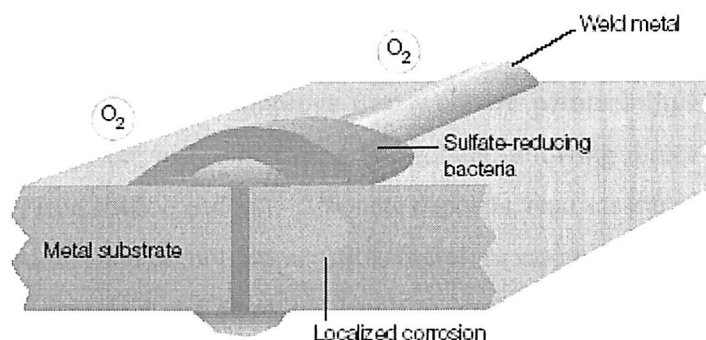
Figure 34 Localized Bacterial Corrosion

Colonies of sulfate-reducing bacteria (SRB) form a deposit under which crevice corrosion develops. The SRBs introduce H2S into the system, which causes the corrosion.

Hydrogen sulfide will induce sulfide stress cracking so any mechanical measures to reduce stress such as decreasing torque or weight-on-bit will limit this type of failure. Surprisingly, high temperature reduces sulfide stress cracking. So if H2S is detected, it is better to take advantage of high downhole temperatures and treat the mud with the drillstring in the hole. Corrosion control of CO2 is similar to H2S control in that pH must be raised to reduce the acid effects, and drillpipe should be coated with inhibitors. Carbon dioxide can enter the mud system several ways— directly from the formation, by thermal degradation of organic materials, as carbonates from barite or bentonite, chemical over-treatment with soda ash, or bicarbonate of soda. Calcium hydroxide can be used to precipitate carbonates to reduce CO2 levels.

Completion—

After casing has been put in a well, it is usually cemented in place. Cement itself provides primary external protection against corrosion, especially near the surface where circulating aquifer water supplies unlimited oxygen. As a recent study on casing leaks in the Wafra field in Kuwait discovered, the type of cement used is also important. Severe corrosion occurred in wells where construction and permeable light cement were used instead of the usual Portland class G cement with additives. Leakage rates were higher in shallow zones where high sulfate concentrations caused the construction cement—which is nonsulfate resistant—to break down, exposing the exterior of the casing to corrosive aquifer water.

Completion design also plays an important role in preventing internal corrosion. Reducing sand production by gravel packing prevents sand blasting that causes erosion corrosion. Erosion corrosion will be more pronounced on equipment that restricts flow such as nipples, valves or sharp pipe bends. Once erosion has removed protective coatings, other forms of corrosion can start. The velocity of produced fluids has the same effect as produced sand with erosion occurring

at places of turbulence and cavitation. Stimulation programs may, inadvertently, promote internal corrosion. Depending on lithology, highly corrosive hydrochloric acid [HCl] with additions of hydrofluoric [HF] acid are used to improve near-wellbore permeability. These acids can also remove scale buildup on the inside of casing and tubing, allowing direct attack on bare metal. (Scale, produced by iron sulfide and iron carbonate deposits, restricts the corrosion process. Other types of scale are porous and do not protect.) It is therefore essential to use inhibitors and to flow the well to remove spent acid and allow pH levels to increase. Inhibitors are mixed with acid to provide a protective film over exposed completion strings. The first generation of acid inhibitors was based on highly poisonous arsenic products, but over the years less toxic and more environmentally appropriate products have been developed. The type and amount of inhibitor used— inhibitor loading—depends not only on the acid and its strength, but also on the metal it is protecting, the working temperature range and the protection time desired. Inhibitor loadings are determined by measuring the corrosion of samples of casing or tubing— coupons—in a corrosion-test autoclave that duplicates the well-treating environment.

Corrosion During Production—

Corrosion can continue inside the casing and along completion strings and pipelines during the life of a well. Gas condensate wells may produce gas, hydrocarbons, formation water, acid gases (CO2 and H2S) and organic acids. Wells that produce formation water, or allow it to condense, are likely to corrode; this may occur anywhere in the tubing string, wellhead or flowline. Higher temperatures accelerate the corrosion rate, as does faster flow. Corrosion increases with water salinity up to about 5% of sodium chloride. Above this, the solubility of oxygen in the water decreases reducing corrosion rates. In fact, when the salt content is above 15%, the rates are lower than with fresh water. When after and acid gases are present, the corrosion rates rise rapidly. Water dissolves CO2 or H2S and becomes acidic. In highly corrosive environments, carbon steel can be protected by corrosion inhibitors during production. Like acid corrosion inhibitors, these adhere to casing and completion strings to form a protective film. Inhibitors can be continuously introduced into a producing well by a capillary tube run on the outside of the tubing as part of the completion design. Other methods include batch treatment where inhibitor is pumped down the tubing regularly, say every six weeks, or squeeze treatments, where inhibitor is pumped into the formation. To protect wells and pipelines from external corrosion, cathodic protection is used. In remote areas sacrificial ground beds may be used for both wells and pipelines. A single ground bed can protect up to 50 miles [80 km] of pipeline. In the Middle East, solar panels have been used to power impressed current cathodic protection systems. Other

methods include thermoelectric generators fueled directly from the pipeline. To protect several wells, a central generator may be used and a distribution network set up. Wells should be insulated from pipelines so that protection systems do not cause unwanted anodic regions and stray current corrosion. Under the right conditions, iron sulfide and iron carbonate scales—the corrosion products when H2S or CO2 are present— provide protective coatings. The composition of production fluids, however, may change during the life of a reservoir so relying on natural protection may not be wise.

DETERMINING THE RATE OF H$_2$S CORROSION

A THERMODYNAMIC APPROACH

Corrosion Reaction Mechanism
in the Presence of
Sulphate Reducing Bacteria [SRB]

1. Anodic Reaction:

   $4Fe = 4Fe^{2+} + 8e^-$

2. Dissociation of water:

   $8H_2O = 8H^+ + 8OH^-$
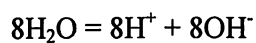
3. Cathodic Reaction:

   $8H^+ + 8e^- = 8H$

4. Cathodic depolarization by bacteria:

   $SO_4^{2-} + 8H = S^{2-} + 4 H_2O$

5. Corrosion product (a):

   $3Fe^{2+} + S^{2-} = FeS$

6. Corrosion product (b):

   $3Fe^{2+} + 6OH^- = 3Fe(OH)_2$

7. Overall Reaction:

   $4Fe + SO_4^{2-} + 4H_2O = 3Fe(OH)_2 + FeS + 2OH^-$
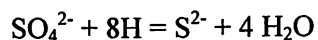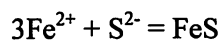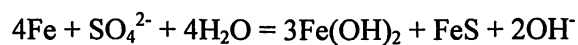
8. The dissolution of Mackinawite reduced H2S and HS- solutions can be expressed as:

   $FeS + H_2S = Fe^{2+} + 2HS^-$
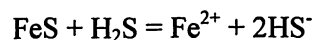
This reaction is based on the assumption that for the conditions of, 25 °C to 95 °C and pH 3.2–8.2, the dominant aqueous iron. Although a general dissolution reaction including iron hydrosulphide complexes would provide a better description of the overall dissolution reactions in the Fe–S system, the simplified Reaction 8 was adopted. This was based on the results of Davison 1991.

The solubility equilibrium is written for the nominal, FeS, with unit activity assumed for the solid and the standard state of the aqueous species is the ideal 1 m solution. Thus, the equilibrium constant, $K_{eq, FeS}$ for Reaction _5. can be calculated from:

$$K_{eq, FeS} = [FeS]/[Fe^{2+}][S^{2-}]$$

For the values of $[Fe^{2+}]$, consider a unit area on a pipe of the following specifications:

Pipe Specifications:

OD = 14"

Lb/ ft = 170.37

WT = 1.250"

Considering unit area of height 1 m,
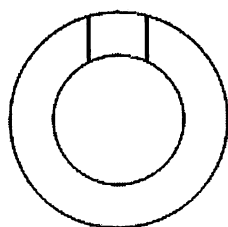
SA = 2 * π * r * H

= 2 * 3.14 * 0.14605 * 1

= 0.91765 m² [= 0.92 m²]

Net Curved Surface Area for a 100Km Pipeline = 2 * π * r * H

= 2 * 3.14 * 0.14605 * 100,000

= 91.765E+03 m²

Volume = π * r² * H

= 3.14 * (0.14605)2 * 1

$$= 0.0670 \text{ m}^3$$

$C_{Fe2+} = N_{Fe2+} / \text{Volume}$

$$= 4.539E+03 / 0.0670$$

$$= 67.7592E+03 \text{ mole/m}^3$$

Also, according to the Nernst Equation:

$$E = E_0 - \frac{RT}{nF} L_N \frac{O_x}{R_{ed}}$$

Therefore,

From the Anodic Reaction (1),

$E = 0.44 - [0.0591 / 8] * \log [67.7592E+03 / 1]$

E = 0.40431 V

Where E is the Cell Potential.

Inference:

For a CATHODIC PROTECTION system to be successful for the above taken case, it should be able to overcome 0.40431 V which is being generated by the corrosion cell as cell potential.

The values for the equilibrium constant K $_{FeS}$ are plotted vs. T (^oC) in Fig. 37, Also shown in this figure is the best-fit line through all low pH equilibrium constants and the temperature dependent equation:

$\log K_{FeS} = [2848.779/T] - 6.347$............1

Corrosion in the Oil Industry

where T is in Kelvin.
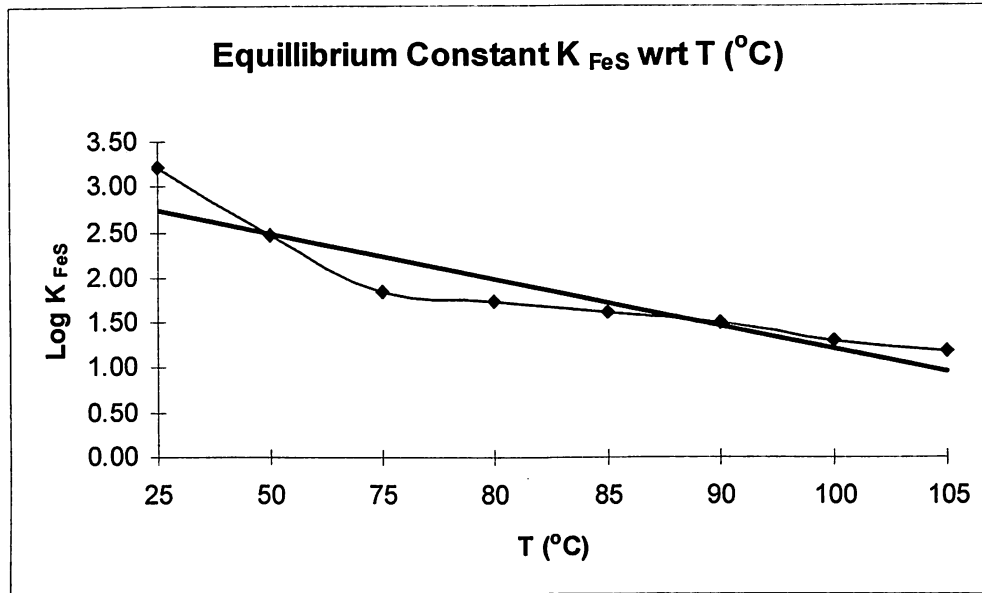
Figure 35 Log K vs T

Temp (°C)	K_{FeS}
25	1.63E+03
50	2.97E+02
75	6.90E+01
80	5.29E+01
85	4.08E+01

For the values of [S^{2-}], we take the H_2S data of BHN field of ONGC, which is as follows:

Batchwise H₂S Levels for BHN
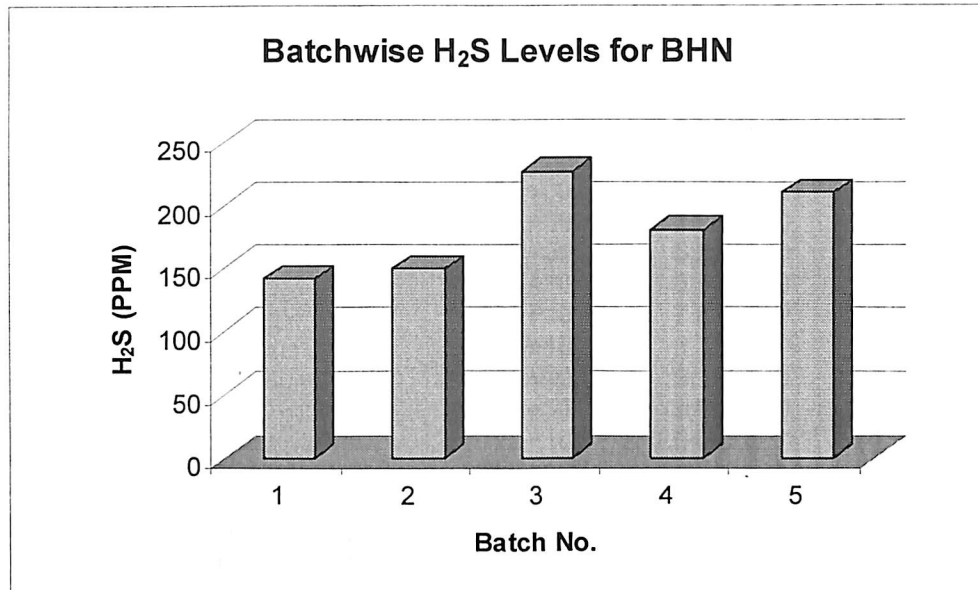
Figure 36 H$_2$S Levels For BHN field

The [S^{2-}] values were normally kept independent, well covering the BHN field H$_2$S limits.

[FeS] values were then obtained, using the relation :

[FeS] = K $_{eq, FeS}$ * [S $^{2-}$] * [Fe^{2+}] mol/m^3

Where **[Fe^{2+}] = 67.7592E+03** mol/m^3

But,

[FeS] = N$_{FeS}$ / Volume

Where,

N$_{FeS}$ = Weight / Molecular Weight

Volume = 0.0670 m^3

Molecular Weight = (55.847 + 32) = 87.847

Therefore,

Weight of FeS formed = [FeS] * 0.0670 * 87.847

The Rate of Corrosion is given by:

A = 12 * W / [T * Area (m^2) * Density (kg/m^3)]

Calculations to find the corrosion rate at varying temperatures and H$_2$S concentrations were done

S. No.	Temp (°C)	K_{FeS}	[S] (ppm)	[FeS] mol/m^3	Weight FeS	A (mpy)	mm/y
1	25	1.63E+03	0	0	0.00E+00	0.00E+00	0.00E+00
2	25	1.63E+03	20	2.21E+09	1.30E+10	5.94E+00	1.48E+02
3	25	1.63E+03	40	4.42E+09	2.60E+10	1.19E+01	2.97E+02
4	25	1.63E+03	60	6.63E+09	3.90E+10	1.78E+01	4.45E+02
5	25	1.63E+03	80	8.84E+09	5.21E+10	2.38E+01	5.94E+02
6	25	1.63E+03	100	1.11E+10	6.51E+10	2.97E+01	7.42E+02
7	25	1.63E+03	120	1.33E+10	7.81E+10	3.56E+01	8.91E+02
8	25	1.63E+03	140	1.55E+10	9.11E+10	4.16E+01	1.04E+03
9	25	1.63E+03	141	1.56E+10	9.17E+10	4.19E+01	1.05E+03
10	25	1.63E+03	149	1.65E+10	9.69E+10	4.42E+01	1.11E+03
11	25	1.63E+03	160	1.77E+10	1.04106E+11	4.75E+01	1.19E+03
12	25	1.63E+03	180	1.99E+10	1.1712E+11	5.35E+01	1.34E+03
13	25	1.63E+03	183	2.02E+10	1.19072E+11	5.43E+01	1.36E+03
14	25	1.63E+03	200	2.21E+10	1.30133E+11	5.94E+01	1.48E+03
15	25	1.63E+03	210	2.32E+10	1.3664E+11	6.24E+01	1.56E+03
16	25	1.63E+03	220	2.43E+10	1.43146E+11	6.53E+01	1.63E+03
17	25	1.63E+03	227	2.51E+10	1.47701E+11	6.74E+01	1.69E+03
18	25	1.63E+03	250	2.76E+10	1.62666E+11	7.42E+01	1.86E+03
19	25	1.63E+03	300	3.32E+10	1.95199E+11	8.91E+01	2.23E+03
20	25	1.63E+03	350	3.87E+10	2.27733E+11	1.04E+02	2.60E+03
21	25	1.63E+03	400	4.42E+10	2.60266E+11	1.19E+02	2.97E+03
22	25	1.63E+03	450	4.97E+10	2.92799E+11	1.34E+02	3.34E+03
23	25	1.63E+03	500	5.53E+10	3.25332E+11	1.48E+02	3.71E+03
24	25	1.63E+03	550	6.08E+10	3.57865E+11	1.63E+02	4.08E+03
25	25	1.63E+03	600	6.63E+10	3.90399E+11	1.78E+02	4.45E+03
26	25	1.63E+03	650	7.19E+10	4.22932E+11	1.93E+02	4.83E+03
27	25	1.63E+03	700	7.74E+10	4.55465E+11	2.08E+02	5.20E+03
28	25	1.63E+03	750	8.29E+10	4.87998E+11	2.23E+02	5.57E+03
29	25	1.63E+03	800	8.84E+10	5.20532E+11	2.38E+02	5.94E+03
30	25	1.63E+03	850	9.40E+10	5.53065E+11	2.52E+02	6.31E+03
31	25	1.63E+03	900	9.95E+10	5.85598E+11	2.67E+02	6.68E+03
32	25	1.63E+03	950	1.05E+11	6.18131E+11	2.82E+02	7.05E+03
33	25	1.63E+03	1000	1.11E+11	6.50664E+11	2.97E+02	7.42E+03

Corrosion Rate @ 25°C
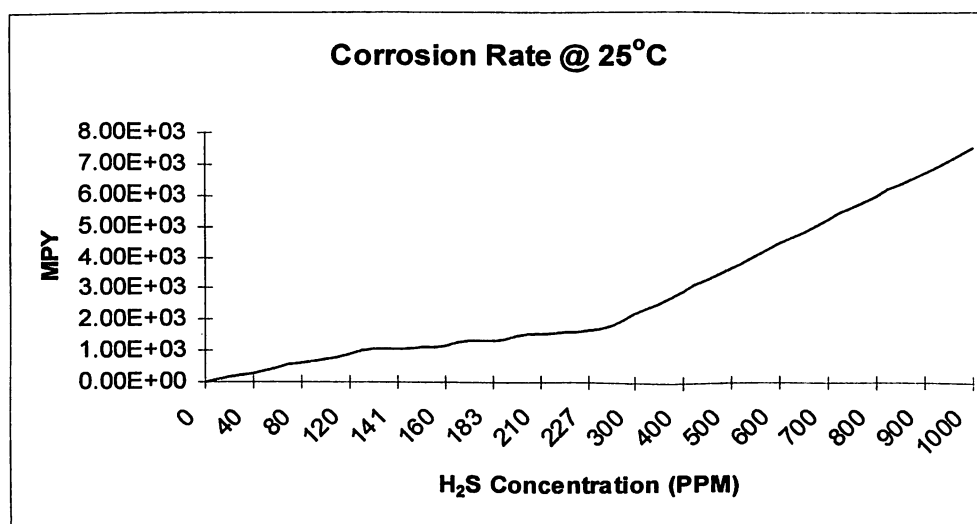
S. No.	Temp (°C)	K $_{FeS}$	[S] (ppm)	[FeS] mol/m^3	Weight FeS	A (mpy)	mm/y
1	50	2.97E+02	0	0	0	0.00E+00	0.00E+00
2	50	2.97E+02	20	4.02E+08	2.37E+09	1.08E+00	2.70E+01
3	50	2.97E+02	40	8.05E+08	4.74E+09	2.16E+00	5.41E+01
4	50	2.97E+02	60	1.21E+09	7.11E+09	3.24E+00	8.11E+01
5	50	2.97E+02	80	1.61E+09	9.48E+09	4.32E+00	1.08E+02
6	50	2.97E+02	100	2.01E+09	1.18E+10	5.41E+00	1.35E+02
7	50	2.97E+02	120	2.41E+09	1.42E+10	6.49E+00	1.62E+02
8	50	2.97E+02	140	2.82E+09	1.66E+10	7.57E+00	1.89E+02
9	50	2.97E+02	141	2.84E+09	1.67E+10	7.62E+00	1.91E+02
10	50	2.97E+02	149	3.00E+09	1.76E+10	8.05E+00	2.01E+02
11	50	2.97E+02	160	3.22E+09	1.90E+10	8.65E+00	2.16E+02
12	50	2.97E+02	180	3.62E+09	2.13E+10	9.73E+00	2.43E+02
13	50	2.97E+02	183	3.68E+09	2.17E+10	9.89E+00	2.47E+02
14	50	2.97E+02	200	4.02E+09	2.37E+10	1.08E+01	2.70E+02
15	50	2.97E+02	210	4.23E+09	2.49E+10	1.14E+01	2.84E+02
16	50	2.97E+02	220	4.43E+09	2.61E+10	1.19E+01	2.97E+02
17	50	2.97E+02	227	4.57E+09	2.69E+10	1.23E+01	3.07E+02
18	50	2.97E+02	250	5.03E+09	2.96E+10	1.35E+01	3.38E+02
19	50	2.97E+02	300	6.04E+09	3.55E+10	1.62E+01	4.05E+02
20	50	2.97E+02	350	7.04E+09	4.15E+10	1.89E+01	4.73E+02
21	50	2.97E+02	400	8.05E+09	4.74E+10	2.16E+01	5.41E+02
22	50	2.97E+02	450	9.06E+09	5.33E+10	2.43E+01	6.08E+02
23	50	2.97E+02	500	1.01E+10	5.92E+10	2.70E+01	6.76E+02
24	50	2.97E+02	550	1.11E+10	6.51E+10	2.97E+01	7.43E+02
25	50	2.97E+02	600	1.21E+10	7.11E+10	3.24E+01	8.11E+02
26	50	2.97E+02	650	1.31E+10	7.70E+10	3.51E+01	8.78E+02
27	50	2.97E+02	700	1.41E+10	8.29E+10	3.78E+01	9.46E+02
28	50	2.97E+02	750	1.51E+10	8.88E+10	4.05E+01	1.01E+03
29	50	2.97E+02	800	1.61E+10	9.48E+10	4.32E+01	1.08E+03
30	50	2.97E+02	850	1.71E+10	1.01E+11	4.59E+01	1.15E+03
31	50	2.97E+02	900	1.81E+10	1.07E+11	4.87E+01	1.22E+03
32	50	2.97E+02	950	1.91E+10	1.13E+11	5.14E+01	1.28E+03
33	50	2.97E+02	1000	2.01E+10	1.18E+11	5.41E+01	1.35E+03

Corrosion Rate 50 °C
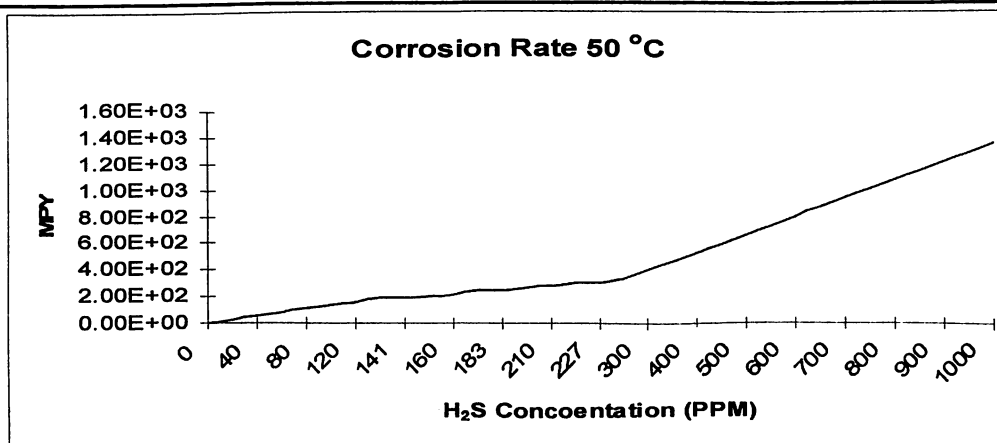
S. No.	Temp (°C)	K FeS	[S] (ppm)	[FeS] mol/m³	Weight FeS	A (mpy)	mm/y
1	75	6.90E+01	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2	75	6.90E+01	20	9.36E+07	5.51E+08	2.51E-01	6.28E+00
3	75	6.90E+01	40	1.87E+08	1.10E+09	5.03E-01	1.26E+01
4	75	6.90E+01	60	2.81E+08	1.65E+09	7.54E-01	1.88E+01
5	75	6.90E+01	80	3.74E+08	2.20E+09	1.01E+00	2.51E+01
6	75	6.90E+01	100	4.68E+08	2.75E+09	1.26E+00	3.14E+01
7	75	6.90E+01	120	5.61E+08	3.30E+09	1.51E+00	3.77E+01
8	75	6.90E+01	140	6.55E+08	3.85E+09	1.76E+00	4.40E+01
9	75	6.90E+01	141	6.60E+08	3.88E+09	1.77E+00	4.43E+01
10	75	6.90E+01	149	6.97E+08	4.10E+09	1.87E+00	4.68E+01
11	75	6.90E+01	160	7.48E+08	4.41E+09	2.01E+00	5.03E+01
12	75	6.90E+01	180	8.42E+08	4.96E+09	2.26E+00	5.65E+01
13	75	6.90E+01	183	8.56E+08	5.04E+09	2.30E+00	5.75E+01
14	75	6.90E+01	200	9.36E+08	5.51E+09	2.51E+00	6.28E+01
15	75	6.90E+01	210	9.82E+08	5.78E+09	2.64E+00	6.60E+01
16	75	6.90E+01	220	1.03E+09	6.06E+09	2.76E+00	6.91E+01
17	75	6.90E+01	227	1.06E+09	6.25E+09	2.85E+00	7.13E+01
18	75	6.90E+01	250	1.17E+09	6.88E+09	3.14E+00	7.85E+01
19	75	6.90E+01	300	1.40E+09	8.26E+09	3.77E+00	9.42E+01
20	75	6.90E+01	350	1.64E+09	9.64E+09	4.40E+00	1.10E+02
21	75	6.90E+01	400	1.87E+09	1.10E+10	5.03E+00	1.26E+02
22	75	6.90E+01	450	2.11E+09	1.24E+10	5.65E+00	1.41E+02
23	75	6.90E+01	500	2.34E+09	1.38E+10	6.28E+00	1.57E+02
24	75	6.90E+01	550	2.57E+09	1.51E+10	6.91E+00	1.73E+02
25	75	6.90E+01	600	2.81E+09	1.65E+10	7.54E+00	1.88E+02
26	75	6.90E+01	650	3.04E+09	1.79E+10	8.17E+00	2.04E+02
27	75	6.90E+01	700	3.27E+09	1.93E+10	8.80E+00	2.20E+02
28	75	6.90E+01	750	3.51E+09	2.07E+10	9.42E+00	2.36E+02
29	75	6.90E+01	800	3.74E+09	2.20E+10	1.01E+01	2.51E+02
30	75	6.90E+01	850	3.98E+09	2.34E+10	1.07E+01	2.67E+02
31	75	6.90E+01	900	4.21E+09	2.48E+10	1.13E+01	2.83E+02
32	75	6.90E+01	950	4.44E+09	2.62E+10	1.19E+01	2.98E+02
33	75	6.90E+01	1000	4.68E+09	2.75E+10	1.26E+01	3.14E+02

Corrosion Rate 75 °C
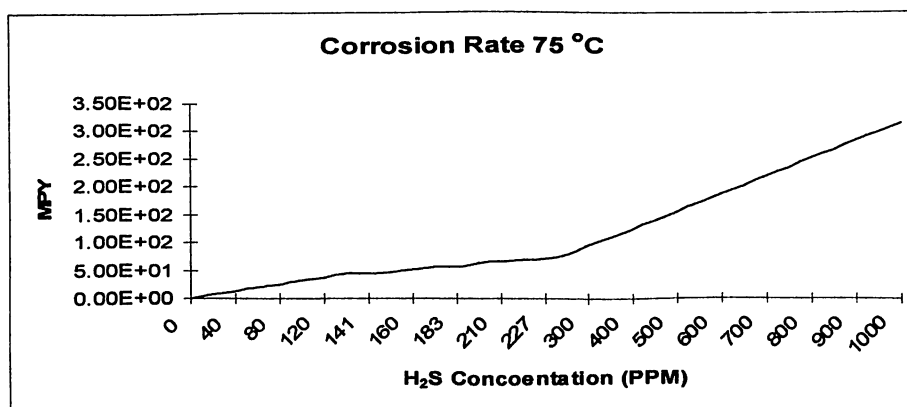
S. No.	Temp (°C)	K_{FeS}	[S] (ppm)	[FeS] mol/m^3	Weight FeS	A (mpy)	mm/y
1	80	5.29E+01	0	0	0.00E+00	0.00E+00	0.00E+00
2	80	5.29E+01	20	7.16E+07	4.22E+08	1.92E-01	4.81E+00
3	80	5.29E+01	40	1.43E+08	8.43E+08	3.85E-01	9.62E+00
4	80	5.29E+01	60	2.15E+08	1.27E+09	5.77E-01	1.44E+01
5	80	5.29E+01	80	2.87E+08	1.69E+09	7.70E-01	1.92E+01
6	80	5.29E+01	100	3.58E+08	2.11E+09	9.62E-01	2.41E+01
7	80	5.29E+01	120	4.30E+08	2.53E+09	1.15E+00	2.89E+01
8	80	5.29E+01	140	5.02E+08	2.95E+09	1.35E+00	3.37E+01
9	80	5.29E+01	141	5.05E+08	2.97E+09	1.36E+00	3.39E+01
10	80	5.29E+01	149	5.34E+08	3.14E+09	1.43E+00	3.58E+01
11	80	5.29E+01	160	5.73E+08	3.37E+09	1.54E+00	3.85E+01
12	80	5.29E+01	180	6.45E+08	3.80E+09	1.73E+00	4.33E+01
13	80	5.29E+01	183	6.56E+08	3.86E+09	1.76E+00	4.40E+01
14	80	5.29E+01	200	7.16E+08	4.22E+09	1.92E+00	4.81E+01
15	80	5.29E+01	210	7.52E+08	4.43E+09	2.02E+00	5.05E+01
16	80	5.29E+01	220	7.88E+08	4.64E+09	2.12E+00	5.29E+01
17	80	5.29E+01	227	8.13E+08	4.79E+09	2.18E+00	5.46E+01
18	80	5.29E+01	250	8.96E+08	5.27E+09	2.41E+00	6.01E+01
19	80	5.29E+01	300	1.07E+09	6.33E+09	2.89E+00	7.22E+01
20	80	5.29E+01	350	1.25E+09	7.38E+09	3.37E+00	8.42E+01
21	80	5.29E+01	400	1.43E+09	8.43E+09	3.85E+00	9.62E+01
22	80	5.29E+01	450	1.61E+09	9.49E+09	4.33E+00	1.08E+02
23	80	5.29E+01	500	1.79E+09	1.05E+10	4.81E+00	1.20E+02
24	80	5.29E+01	550	1.97E+09	1.16E+10	5.29E+00	1.32E+02
25	80	5.29E+01	600	2.15E+09	1.27E+10	5.77E+00	1.44E+02
26	80	5.29E+01	650	2.33E+09	1.37E+10	6.25E+00	1.56E+02
27	80	5.29E+01	700	2.51E+09	1.48E+10	6.74E+00	1.68E+02
28	80	5.29E+01	750	2.69E+09	1.58E+10	7.22E+00	1.80E+02
29	80	5.29E+01	800	2.87E+09	1.69E+10	7.70E+00	1.92E+02
30	80	5.29E+01	850	3.04E+09	1.79E+10	8.18E+00	2.04E+02
31	80	5.29E+01	900	3.22E+09	1.90E+10	8.66E+00	2.17E+02
32	80	5.29E+01	950	3.40E+09	2.00E+10	9.14E+00	2.29E+02
33	80	5.29E+01	1000	3.58E+09	2.11E+10	9.62E+00	2.41E+02

Corrosion Rate 80 °C

MPY vs H$_2$S Concoentation (PPM)
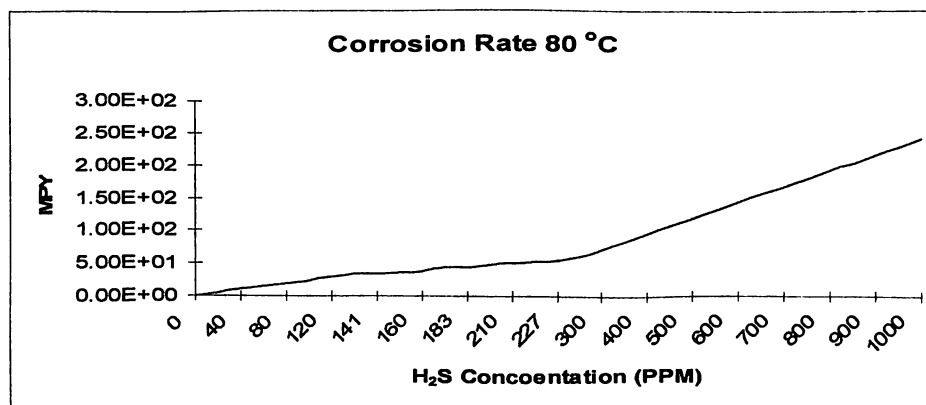
S. No.	Temp (°C)	K $_{FeS}$	[S] (ppm)	[FeS] mol/m^3	Weight FeS	A (mpy)	mm/y
1	85	4.08E+01	0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2	85	4.08E+01	20	5.53E+07	3.25E+08	1.48E-01	3.71E+00
3	85	4.08E+01	40	1.11E+08	6.51E+08	2.97E-01	7.42E+00
4	85	4.08E+01	60	1.66E+08	9.76E+08	4.45E-01	1.11E+01
5	85	4.08E+01	80	2.21E+08	1.30E+09	5.94E-01	1.48E+01
6	85	4.08E+01	100	2.76E+08	1.63E+09	7.42E-01	1.86E+01
7	85	4.08E+01	120	3.32E+08	1.95E+09	8.91E-01	2.23E+01
8	85	4.08E+01	140	3.87E+08	2.28E+09	1.04E+00	2.60E+01
9	85	4.08E+01	141	3.90E+08	2.29E+09	1.05E+00	2.62E+01
10	85	4.08E+01	149	4.12E+08	2.42E+09	1.11E+00	2.77E+01
11	85	4.08E+01	160	4.42E+08	2.60E+09	1.19E+00	2.97E+01
12	85	4.08E+01	180	4.97E+08	2.93E+09	1.34E+00	3.34E+01
13	85	4.08E+01	183	5.06E+08	2.98E+09	1.36E+00	3.40E+01
14	85	4.08E+01	200	5.53E+08	3.25E+09	1.48E+00	3.71E+01
15	85	4.08E+01	210	5.80E+08	3.42E+09	1.56E+00	3.90E+01
16	85	4.08E+01	220	6.08E+08	3.58E+09	1.63E+00	4.08E+01
17	85	4.08E+01	227	6.27E+08	3.69E+09	1.69E+00	4.21E+01
18	85	4.08E+01	250	6.91E+08	4.07E+09	1.86E+00	4.64E+01
19	85	4.08E+01	300	8.29E+08	4.88E+09	2.23E+00	5.57E+01
20	85	4.08E+01	350	9.67E+08	5.69E+09	2.60E+00	6.50E+01
21	85	4.08E+01	400	1.11E+09	6.51E+09	2.97E+00	7.42E+01
22	85	4.08E+01	450	1.24E+09	7.32E+09	3.34E+00	8.35E+01
23	85	4.08E+01	500	1.38E+09	8.13E+09	3.71E+00	9.28E+01
24	85	4.08E+01	550	1.52E+09	8.95E+09	4.08E+00	1.02E+02
25	85	4.08E+01	600	1.66E+09	9.76E+09	4.45E+00	1.11E+02
26	85	4.08E+01	650	1.80E+09	1.06E+10	4.83E+00	1.21E+02
27	85	4.08E+01	700	1.93E+09	1.14E+10	5.20E+00	1.30E+02
28	85	4.08E+01	750	2.07E+09	1.22E+10	5.57E+00	1.39E+02
29	85	4.08E+01	800	2.21E+09	1.30E+10	5.94E+00	1.48E+02
30	85	4.08E+01	850	2.35E+09	1.38E+10	6.31E+00	1.58E+02
31	85	4.08E+01	900	2.49E+09	1.46E+10	6.68E+00	1.67E+02
32	85	4.08E+01	950	2.63E+09	1.55E+10	7.05E+00	1.76E+02
33	85	4.08E+01	1000	2.76E+09	1.63E+10	7.42E+00	1.86E+02

Corrosion Rate 85 °C
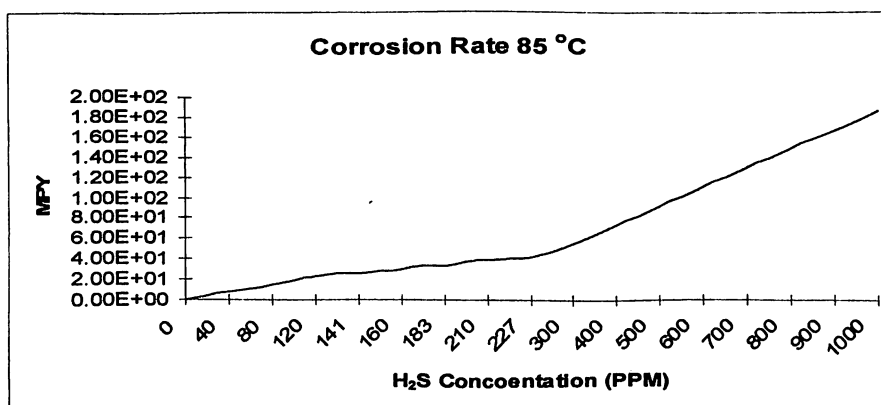
Observations

- It was observed that the rate of corrosion with varying concentrations of H_2S at different temperatures follows a similar trend.

- The rate of corrosion increases at a slightly decreasing rate till a specific H_2S concentration is reached after which, an exponential increase in the rate was observed in all the studied cases of varying temperatures.

- It was observed that although the rate followed a similar trend in all the cases, the net weight of metal lost due to corrosion at maximum (studied) H_2S levels decreased with increase in temperature.

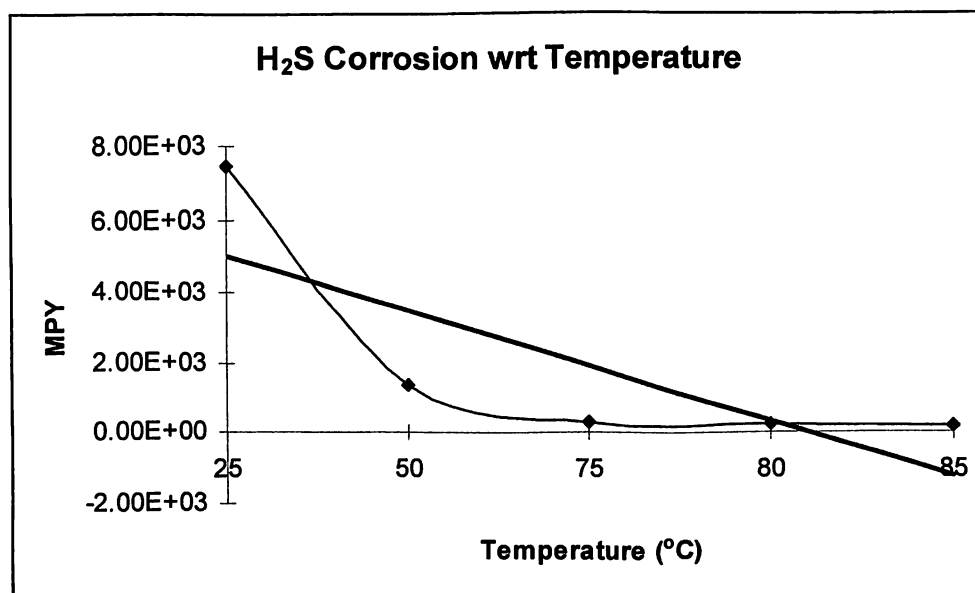| S. No.	Temp ($^{\circ}C$)	K $_{FeS}$	[S] (ppm)	[FeS] mol/m^3	Weight FeS	A (mpy)	mm/y
1	25	1.63E+03	1000	1.11E+11	6.50E+11	2.97E+02	7.42E+03
2	50	2.97E+02	1000	2.01E+10	1.18E+11	5.41E+01	1.35E+03
3	75	6.90E+01	1000	4.68E+09	2.75E+10	1.26E+01	3.14E+02
4	80	5.29E+01	1000	3.58E+09	2.11E+10	9.62E+00	2.41E+02
5	85	4.08E+01	1000	2.76E+09	1.63E+10	7.42E+00	1.86E+02

Figure 37 H$_2$S Corrosion w.r.t Temperature

- On comparing the results obtained with standard values of corrosion rate, as given below, it was found that H_2S corrosion falls in the "Severe" range.

Safe	< 5 mpy
Moderate	5 – 50 mpy
Severe	>50 mpy

Where:

mpy = Mills Per Year

1 mpy = 25 mm / year

Inference:

- For any given H_2S concentration, rate of corrosion increases exponentially after a certain value.

- Corrosion shows a declining trend with increase in temperature.

The second point might be of conflict to the popular belief that any increase in temperature results in an increase of corrosion rate. In this case too, corrosion will increase with temperature, however, the results show otherwise due to the fact that in case of H_2S corrosion, at higher temperatures, a mackinawite (FeS) layer is formed on the corrosion cell such that it reduces the rate of corrosion due to its impervious nature which does not allow the corrosion fluid (H_2S) to come in contact with the metal and thereby reduces corrosion rate.

The molar Gibbs free energy for Reaction 5 can be calculated directly from the equilibrium constants derived from Eq. _12. following the expression:

$$G^o_r = -RT \ln K_{FeS}$$

Where R is the gas constant (8.3141 J/K mol).

For a linear temperature dependent reaction, the first derivative of Eq.67 with respect to temperature provides a constant enthalpy, ΔH^o, while the second r derivative, the heat capacity,

ΔC^o, is zero. In turn the entropy, ΔS^o, can be calculated from ΔH^o and ΔG^o and is also constant. The functions calculated from 25 °C to 105 °C are summarized in Table 5.

$R = 8.3141 \ J/K \ \text{mol}.$

$\Delta G_r^o = -2.303RT \log K_{FeS}.$

$\Delta H_r^o = -2.303R * 2848.779.$

$\Delta S_r^o = (\Delta H_r^o - \Delta G_r^o)/T$

T (°C)	Log K $_{FeS}$	G° J/mol	H° J/mol	S° J/mol
25	3.21	-1.83E+04	-5.45E+04	-1.22E+02
50	2.47	-1.53E+04	-5.45E+04	-1.22E+02
75	1.84	-1.23E+04	-5.45E+04	-1.22E+02
80	1.72	-1.16E+04	-5.45E+04	-1.22E+02
85	1.61	-1.10E+04	-5.45E+04	-1.22E+02
90	1.50	-1.04E+04	-5.45E+04	-1.22E+02
100	1.29	-9.22E+03	-5.45E+04	-1.22E+02
105	1.19	-8.61E+03	-5.45E+04	-1.22E+02

Figure 3 Equilibrium constants and thermodynamic functions for the dissolution of mackinawite (FeS) between 25 °C and 105 °C

Effect of Formation Type & Content on Corrosion Rate

Formation	$G^o_{f,298}$	$H^o_{f,298}$	Log K	K
Pyrite (FeS$_2$)[a]	-1.60E+05	-1.72E+05	-28.0814	8.29E-29
Troilite (FeS)[a]	-1.01E+05	-1.01E+05	-17.7588	1.74E-18
Greigite (Fe$_3$S$_4$)[b]	-2.90E+05	-	-50.8945	1.27E-51
Mackinawite (FeS)[b]	-9.33E+04	-	-16.3514	4.45E-17
Amorphous FeS (FeS)[b]	-8.91E+04	-	-15.6154	2.42E-16

[a] Robie et al (1978)
[b] Berner (1967)

From the relation:
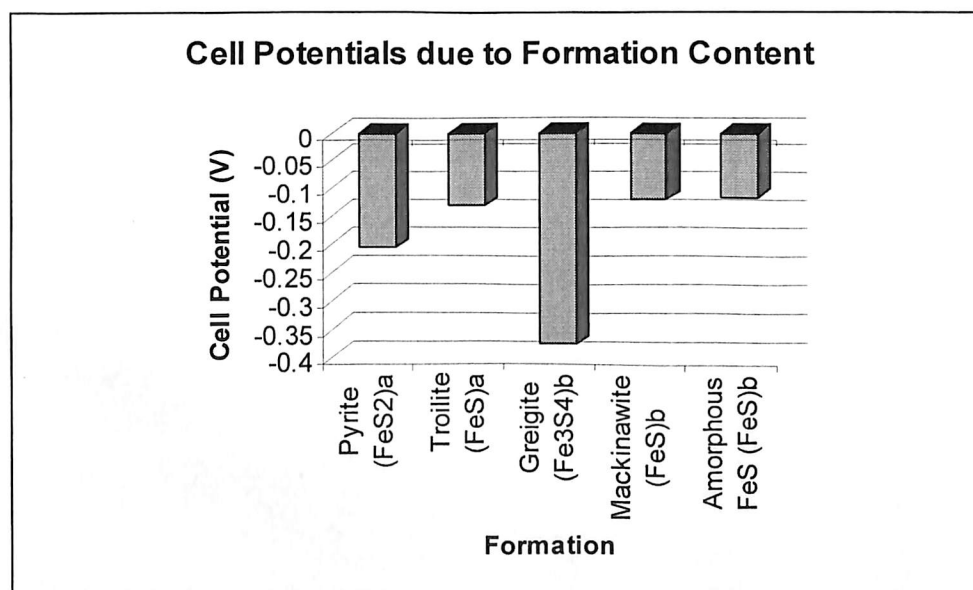
log k = n * F * E / (2.303 * R * T)

Where

n = no. of electrons participating

F = 96500 C

E = Cell Potential

R = 8.314

T = Temperature (K)

Figure 38 Cell Potentials Due To Formation Content

[a] Robie et al (1978)
[b] Berner (1967)

Formation	E_{298K}
Pyrite (FeS_2)[a]	-0.20755
Troilite (FeS)[a]	-0.13125
Greigite (Fe_3S_4)[b]	-0.37616
Mackinawite (FeS)[b]	-0.12085
Amorphous FeS (FeS)[b]	-0.11541

[a] Robie et al (1978)
[b] Berner (1967)

Inference:

- Depending on the type and content of the formation rock encountered, the cell potentials developed solely due to the formation and content will change as shown above.

- This is of utmost importance while designing a CP system for surface facilities handling such crude as it should be able to overcome this potential in addition to the cell potential developed due to the corrosion cell at the metal surface itself and must be accounted for.

RESULTS & CONCLUSION

It was observed that the rate of corrosion with varying concentrations of H_2S at different temperatures follows a similar trend. The rate of corrosion increases at a slightly decreasing rate till a specific H_2S concentration is reached after which, an exponential increase in the rate was observed in all the studied cases of varying temperatures. Although the rate followed a similar trend in all the cases, the net weight of metal lost due to corrosion at maximum (studied) H_2S levels decreased with increase in temperature due to the fact that at higher temperatures, a mackinawite (FeS) layer is formed on the corrosion cell such that it reduces the rate of corrosion

On comparing the results obtained with standard values of corrosion rate, it was found that H_2S corrosion falls in the "Severe" range for the system at hand.

The study carried out on the effect of formation rock content on the rate of corrosion showed that that the formation content greatly affects the corrosion rate and must be accounted for while designing a CP system for surface facilities handling such crude.

Corrosion control is an important consideration. The periodic monitoring techniques and analytical assessment of corrosion severity is very important and critical since it provides the direction to ensure proper utilization of materials and corrosion control methodologies. Therefore, correct and appropriate condition assessment techniques should be used to avoid premature failure and ensure maximum safety.

The oil industry, recognizing this need has invested heavily in material and personnel to try to tame corrosion and prevent metal from returning to its natural state. New oil fields benefit from predevelopment planning and the growing knowledge of all aspects of corrosion control and monitoring. Older fields will continue to benefit from the expertise of the corrosion engineer and the constant monitoring required to prevent disaster.

SCOPE FOR FUTURE WORK

During the course of the project work, some interesting factors came into light which affect corrosion rate to a large extent but have unfortunately been neglected till now. Future work on the topic of "Corrosion in The Oil Industry" may include:

1. Effect of Ionic Mobility on Corrosion Rate
2. Effect of Transport Number on Corrosion Rate
3. Effect of Diffusion Constant on Corrosion Rate
4. Cost of Corrosion
5. Corrosion Modeling & Simulation using:
    o Intercorr - PREDICT
    o Intercorr - SOCRATES
    o Inercorr – PREDICT PIPE

The end of something is the beginning of something new..........

Literature Cited

- Allen, E.T., Crenshaw, J.L., Johnson, J., Larsen, E.S., 1912. The mineral sulphides of iron with crystallographic study. American Journal of Science 23, 169–236.

- Atkin, B.P., Sommerfield, C., 1994. The determination of total sulphur in geological materials by coulometric titration. Chemical Geology 111, 131–134.

- Ba°gander, L.E., Carman, R., 1994. In-situ determination of the apparent solubility product of amorphous iron sulphide. Applied Geochemistry 9, 379–386.

- Barnes, I.K., Clarke, F.E., 1969. Chemical properties of ground water and their corrosion and encrustation effects on wells. U.S. Geological Survey Professional Paper 498D, 58.

- Benning, L.G., Barnes, H.L., 1998. In situ determination of the stability of iron monosulphide and kinetics of pyrite formation. Mineralogical Magazine 62A, 151–152.

- Benning, L.G., Wilkin, R.T., Konhauser, K.O., 1999. Iron monosulphide stability: experiments with sulphate-reducing bacteria. In: A′ rmannsson, H._Ed.., Proceedings of the International

- Symposium on the Geochemistry of Earth's Surface, 5th, 1999. pp. 429–432,

- Balkema Berner, R.A., 1964. Stability fields of iron minerals in anaerobic marine sediments. Journal of Geology 72, 826–834.

- Berner, R.A., 1967. Thermodynamic stability of sedimentary iron sulphides. American Journal of Science 265, 773–785.

- Berner, R.A., 1970. Sedimentary pyrite formation. American Journal of Science 268, 1–23.

- Boesen, C., Postma, D., 1988. Pyrite formation in anoxic environments of the Baltic Sea. American Journal of Science 288, 575–603.

- Jones., 1982. Corrosion Control, 200-232, 305.

- L.L Shreir. Corrosion Volume 1, 152-178

- L.L Shreir. Corrosion Volume 2, 702-712

- Tutty and Denualt Second-Order Kinetics for EC Reactions at Special Micro Electrode Institute of Mathematics and Application Journal of Applied Mathematics. 53,95 – 109,1994.

WebPages Referred

- http://www.foe.co.uk/campaigns/climate/
- http://thinkprogress.org/2006/08/07/bp-alaska/trackback/
- http://www.efcweb.org/
- http://priceofoil.org/
- http://www.nace.org/
- http://www.intercorr.com/
- http://www.google.com/

Technical Papers Referred

- S. M Kapila. Corrosion under anaerobic conditions [Technical Paper]
- ONGC – IOGPT Reports, H_2S study of BHN field
- ONGC – IOGPT Reports, H_2S study of BHS field
- Corrosion in the Oil Industry, Denis Brondel Montrouge, France Randy Edwards Columbus, Ohio, USA Andrew Hayman Clamart, France Donald Hill Tulsa, Oklahoma, USA Shreekant Mehta St. Austell, England Tony Semerad Mobil Sumatra, Indonesia
- Corrosion Problems in Oil Industry Need More Attention, Dr A K Samant, Suptdg. Chemist, Mud Services, Assam Asset, Sivasagar, Assam.
- Controlling internal corrosion in oil & gas pipelines, Rolf Nyborg (2005)
- PPTS Advisory For Operators: Internal Corrosion And Crude Oil
- Pipeline Incidents/Accidents Frequencies and Causes, Roger Little.
- Active Corrosion Control Cathodic Protection Design Aspects, Dr.M.B.Mishra