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The Fundamentals of Corrosion and Scaling

A Handbook for Petroleum and Environmental Engineers

George V. Chilingar
Ryan Mourhatch
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PREFACE

This volume on the Fundamentals of Corrosion and Scaling for Petroleum and Environmental Engineers is a timely contribution to the petroleum industry. This text was designed for use as a primer, a university textbook, and a reference guide, making it appropriate for both the university students and practicing engineers.

The text begins with an overview of the chemical and physical fundamentals of corrosion and scaling, starting at an intuitive level and proceeding into complexities of rate-driven chemical reactions that are encountered in actual field operations. The text proceeds into corrosion mitigative measures including chemical, mechanical, and biological control of important corrosive gases: O_2, CO_2, and H_2S. Extensive review is presented with regard to protective coatings and multimillion-dollar industry of cathodic protection—using abundant examples and applications obtained from the present-day oilfield practice and past case histories. Particular emphasis is placed on the prediction of scale formation in injection water. The chapter on corrosion and scale prevention in waterflood operations focuses on the water-handling facilities, where water is treated and injected at rates typically exceeding over one million barrels per day, for example. The book is concluded with the chapter on Economics, followed by an extensive glossary, and sample problems and questions for students.

Dr. George V. Chilingar has been serving as a professor of Petroleum Engineering at the University of Southern California (USC) since 1954. This volume is the sixty-fifth published book in the field of Petroleum Engineering, Environmental Engineering, and Geology. This most

recent text is a compendium of Dr. Chilingar's course notes and practical experience in corrosion engineering that has successfully guided hundreds of his students in their practice of corrosion prevention.

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CHAPTER 1
INTRODUCTION TO CORROSION

1.1 INTRODUCTION

In 1978, the National Bureau of Standards reported to the U.S. Congress that the cost of corrosion in the United States in 1975 was 70 billion dollars plus or minus 30%, and that about 15% of this loss was avoidable. This economic loss represented about 4% of the gross national product. In 1983, Cron and Marsh also stated that the cost of corrosion in the United States in 1975 was ≈$70 billion of which $10 billion was considered avoidable. The writers estimate that the cost of corrosion and scaling in United States in 2007 was around 400 billion dollars.

The principles of corrosion must be understood in order to effectively select materials and to design, fabricate, and utilize metal structures for the optimum economic life of facilities and safety in operation.

Corrosion in various forms is the major cause of drill pipe failures, for example, which add significantly to drilling costs. The trends toward (1) drilling of deeper wells, (2) use of higher-strength steels, (3) presence of higher stresses, and (4) use of lower-pH drilling fluids contributes to increased susceptibility of metals to failure due to corrosion.

Corrosion is the principal cause of damage to metals in wells and production facilities. Corrosion damage results in costly maintenance of these facilities (repairs and replacements) in addition to the loss of production.

1.2 DEFINITION OF CORROSION

In 1946, The American Electrochemical Society had defined corrosion as the "destruction of a metal by chemical or electrochemical reaction with its environment." The destruction of metals by corrosion occurs by: (a) direct chemical attack at elevated temperatures in a dry environment, and (b) by electrochemical processes at lower temperatures in a water-wet or moist environment. Corrosion occurs because metals tend to revert to more stable forms in which they were found in nature initially, i.e., oxides, sulfates, sulfides, or carbonates.

Inasmuch as the corrosion mechanism is the same for all metals and alloys, differing only in degree, it is useful to examine the mechanism of corrosion of iron.

Corrosion attacks metals in drilling and producing operations through electrochemical processes in the presence of electrolytes and corrosive agents in drilling, completion, packer, and produced fluids.

In the case of electrochemical reaction, the magnitude of electrochemical potential for a particular metal determines the tendency of the reaction to proceed, whereas the resistance offered by the corrosion products to the continued progress of the reaction determines the rate of corrosion.

1.3 INTRODUCTION TO ELECTROCHEMISTRY

Chemical reaction is caused by an external voltage (voltage caused by a chemical reaction) as in an electrochemical cell. In general, electrochemistry deals with oxidation and reduction reactions. The following electrical terms are widely used in electrochemistry and corrosion science:

Electric potential (E) is defined as the capacity of an electric field to do work; it is measured in volts (1 volt = 1 joule/coulomb; joule = 10^7 ergs [energy or work]; coulomb = quantity of electricity; ampere = 1 coulomb/sec). Electric potential can be described as follows:

$$E = \frac{I}{R}$$

Electric current (I) is a movement of electrically charged particles, and is measured in amperes as follows:

$$I = \frac{E}{R} \quad \text{(Ohm's Law)}$$

Resistance determines the amount of current through the object for a given voltage across. The resistance (R) is measured in ohms (volt/ampere).

Electric charge is the quantity for electric charge in coulombs (1 coulomb is the amount of electric charge transported by a current of 1 ampere in 1 second):

$$C = I \times t$$

where I is the electrical current in amperes and t is the time in seconds. Faraday is the larger unit for the electric charge (one Faraday is approximately equal to 96,500 coulombs).

Electrical energy is the energy made available by the flow of electric charge through an electrical conductor. The SI unit of electrical energy is the joule:

$$1\,\text{J} = 1\,\text{kgm}^2/\text{s}^2$$

Electric power: the unit of electric power is watt (W) (one watt is one joule per second):

$1\,\text{W} = 1\frac{\text{J}}{\text{sec}} = 1\,\text{V} \times 1\,\text{A}; 1\,\text{HP} = 746$ watts (one would work at the rate of 1 horsepower by running up the stairway at a speed of 5–6 stairs a second).

Interrelationship among electrical potential (E), electrical current (I), and resistance (R) in a metallic circuit is presented in Figure 1.1: $E = IR$.

In an electrical circuit, there are four main resistances to the current flow between the anode and cathode: R_m = resistance between anode and cathode along the metallic path; R_a = resistance at the anode due to surface films and retardation of anodic reactions (retardation of current flow; polarization); R_e = resistance of electrolyte path; and R_c = resistance at the cathode due to surface films and retardation of cathodic reactions (retardation of current flow; polarization). Thus, the total cell resistance R_t is equal to:

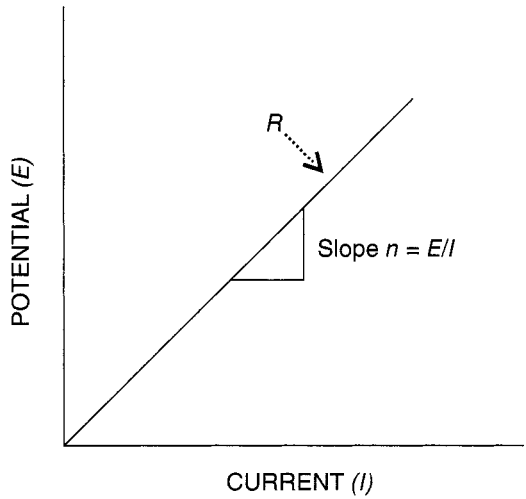


Figure 1.1 Interrelationship among electrical potential (*E*), current (*I*), and resistance (*R*).

$$R_t = R_m + R_a + R_e + R_c \tag{1.1}$$

1.4 CORROSION AGENTS IN DRILLING AND PRODUCING OPERATIONS

The components in fluids that promote the corrosion of steel in drilling and producing operations are oxygen, carbon dioxide, hydrogen sulfide, salts, and organic acids. Destruction of metals is influenced by various physical and chemical factors that localize and increase corrosion damage.

The conditions that promote corrosion include:

1. Energy differences in the form of stress gradients or chemical reactivities across the metal surface in contact with corrosive solution.
2. Differences in concentration of salts or other corrodants in electrolytic solution.
3. Differences in the amount of deposits, either solid or liquid, on the metal surfaces, which are insoluble in the electrolyte solutions.

4. Temperature gradients over the surface of the metal in contact with corrosive solution.
5. Compositional differences in the metal surface.

1.5 REQUIREMENTS FOR ELECTROCHEMICAL CORROSION

Corrosion continues provided electrically conductive metal and solution circuits are available to bring corrodants to the anodic and cathodic sites.

Four conditions must be present to complete the electrochemical reactions and corrosion circuit:

Presence of a driving force or electrical potential. Difference in reaction potential at two sites on the metal surface must be sufficient to drive electrons through the metal, surface film, and liquid components of the corrosion circuit.

Presence of an electrolyte. Corrosion occurs only when the circuit between anodic and cathodic sites is completed by an electrolyte present in water.

Presence of both anodic and cathodic sites. Anodic and cathodic area must be present to support the simultaneous oxidation and reduction reaction at the metal–liquid interface. Metal at the anode oxidizes.

Presence of an external conductor. A complete electron-electrolytic circuit between anodes and cathodes of the metal, through (a) the metal surface films, (b) surrounding environment, and (c) fluid–solid interfaces, is necessary for the continuance of corrosion.

In the environment surrounding the metal, the presence of water provides conducting paths for both corrodants and corrosion products. The corrodants may be a dissolved gas, liquid, or solid. The corrosion products may be: (1) ions in solution, which are removed from the metal surface; (2) ions precipitated as various salts on metal surfaces; and (3) hydrogen gas.

The conditions needed to promote many types of corrosion can be found in most industrial facilities. The basic electrochemical reactions, which occur simultaneously at the cathodic and anodic areas of metal causing many forms of corrosion damage, are as follows:

1. **At the cathode**, the hydrogen (or acid) ion (H^+) removes electrons from the cathodic surface to form hydrogen gas (H_2) (Figure 1.2):

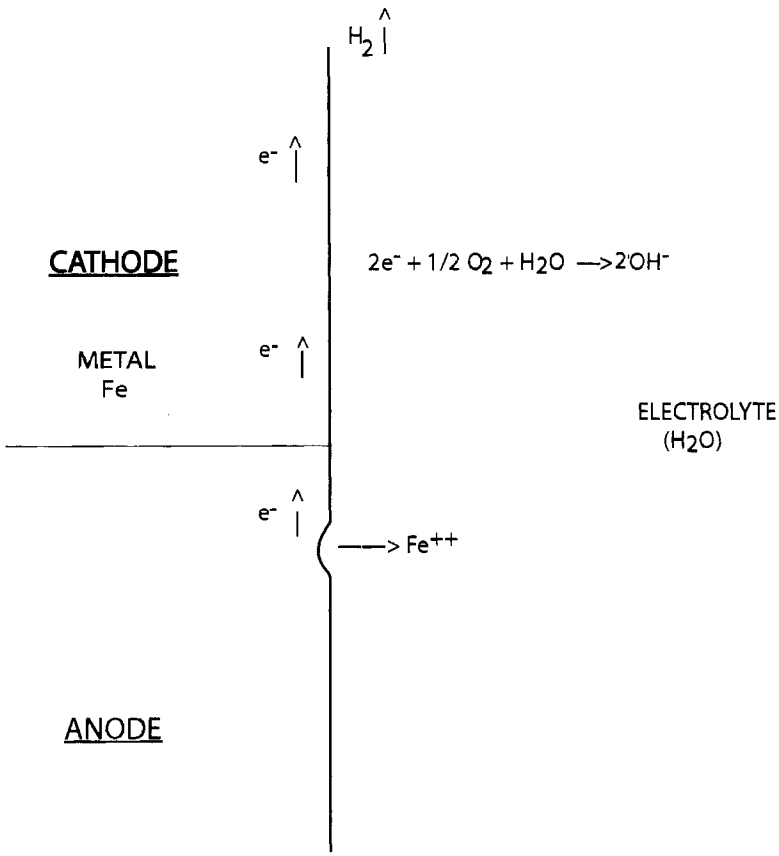


Figure 1.2 Schematic diagram of electrochemical reactions.

$$2e^- + 2H^+ \rightarrow 2H^0 \rightarrow H_2 \quad \text{(in acidic solution)} \tag{1.2}$$

If oxygen is present, electrons are removed from the metal by reduction of oxygen (Figure 1.3):

$$4e^- + O_2 + 4H^+ \rightarrow 2H_2O \quad \text{(in acidic solution)} \tag{1.3}$$

$$4e^- + 2H_2O + O_2 \rightarrow 4OH^- \quad \text{(in neutral or in alkaline solution)} \tag{1.4}$$

2. **At the anode**, a metal ion (e.g., Fe^{2+}) is released from its structural position in the metal through the loss of the bonding electrons and passes into solution in the water as soluble iron or reacts with another component of the environment to form scale. The principal reaction is:

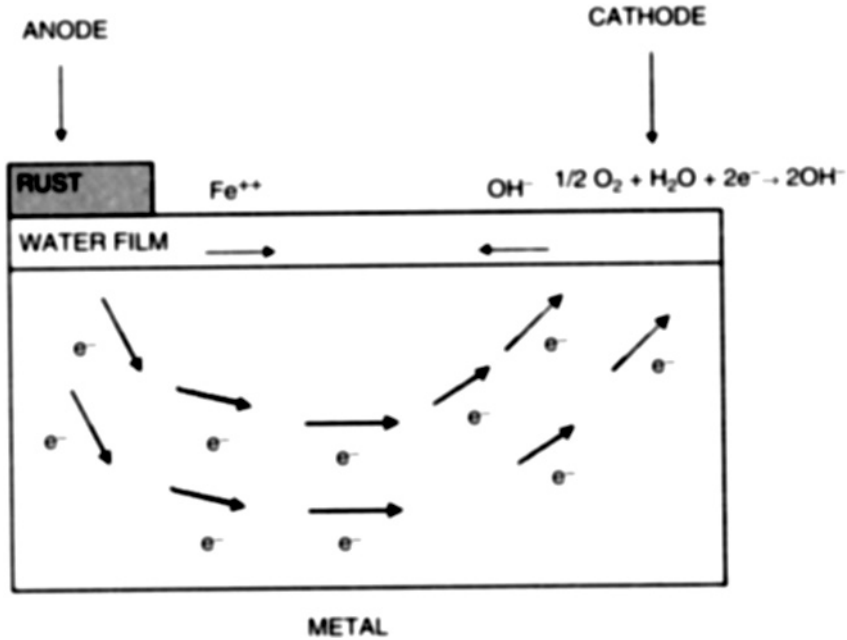


Figure 1.3 Schematic diagram of electrochemical process.

$$Fe - 2e^- \rightarrow Fe^{2+} \tag{1.5}$$

Illustration of galvanic corrosion is presented in Figure 1.4.

Thermodynamic data indicate that the corrosion process in many environments of interest should proceed at very high rates of reaction. Fortunately, experience shows that the corrosion process behaves differently. Studies have shown that as the process proceeds, an increase in concentration of the corrosion products develops rapidly at the cathodic and anodic areas. These products at metal surfaces serve as barriers that tend to retard the corrosion rate. The reacting components of environment may be depleted locally, which further tends to reduce the total corrosion rate.

The potential differences between cathodic and anodic areas decrease as corrosion proceeds. This reduction in potential difference between electrodes upon current flow is termed polarization. The potential of anodic reaction approaches that of the cathode and potential of the cathodic reaction approaches that of the anode. Electrode polarization by corrosion is caused by: (1) changing the surface concentration of metal ions, (2) adsorption of hydrogen gas at cathodic areas, (3) dis-

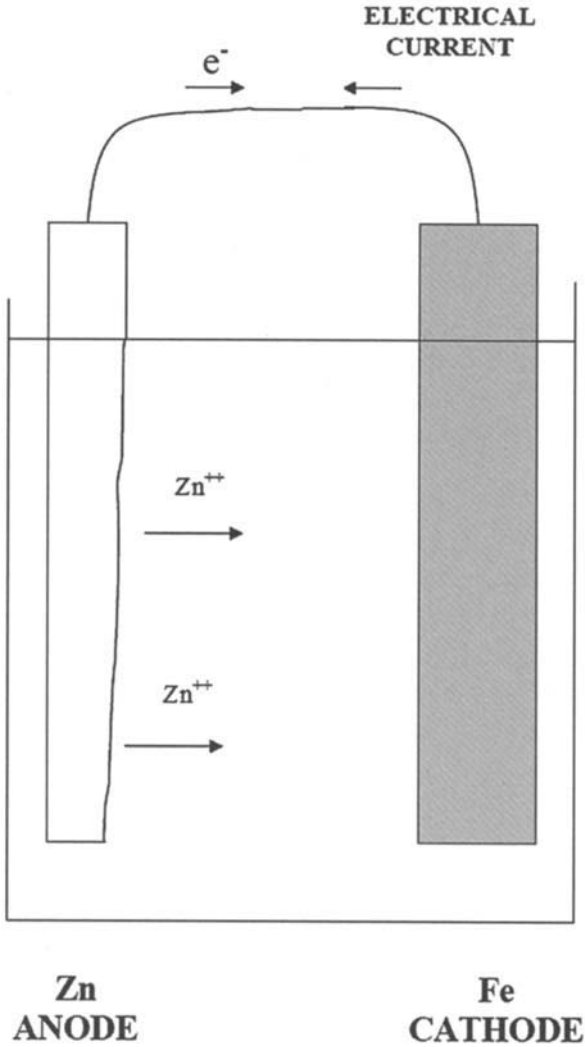


Figure 1.4 Corrosion cell showing flow of electrons and electrical current. Corrosion occurs at the anode.

charge of hydroxyl ions at anodes, or (4) increasing resistance of electrolyte and film of metal-reaction products on the metal surface. Changes (increase or decrease) in the amount of these resistances by the introduction of materials or electrical energy into the system will change the corrosion currents and corrosion rate.

A practical method to control corrosion is through the cathodic protection, whereby polarization of the structure to be protected is accomplished by supplying an external current to the corroding metal. Polarization of the cathode is forced beyond the corrosion potential. The effect of the external current is to eliminate the potential differences between the anodic and cathodic areas on the corroding metal. Removal of the potential differences stops local corrosion action. Cathodic protection operates most efficiently in the systems under cathodic control, i.e., where cathodic reactions control the corrosion rate.

Materials may cause an increase in polarization and retard corrosion by adsorbing on the surface of the metals and thereby changing the nature of the surface. Such materials act as inhibitors to the corrosion process. On the other hand, some materials may reduce the polarization and assist corrosion. These materials, called depolarizers, either assist or replace the original reaction and prevent the buildup of original reaction products.

Oxygen is the principal depolarizer that aids corrosion in the destruction of metal. Oxygen tends to reduce the polarization or resistance, which normally develops at the cathodic areas, with the accumulation of hydrogen at these electrodes. The cathodic reaction with hydrogen ion is replaced by a reaction in which electrons at the cathodic areas are removed by oxygen and water to form hydroxyl ions (OH^-) or water:

$$4e^- + O_2 + 4H^+ \rightarrow 2H_2O \quad \text{(in acid solution)} \tag{1.6}$$

$$4e^- + 2H_2O + O_2 \rightarrow 4OH^- \quad \text{(in neutral and alkaline solution)} \tag{1.7}$$

Polarization of an electrode surface reduces the total current and corrosion rate. Though the rate of metal loss is reduced by polarization, casing failures may increase if incomplete polarization occurs at the anodes. For example, inadequate anodic corrosion inhibitor will reduce the effective areas of the anodic surfaces and thus localize the loss of metal at remaining anodes. This will result in severe pitting and destruction of metal.

Resistance to corrosion process generally does not develop to the same degree at the anodic and cathodic areas. These resistances reduce the corrosion rate, which is controlled by slowest step in the corrosion process. Electrochemical corrosion comprises a series of reactions and material transport to and from the metal surfaces. Complete under-

standing of corrosion and corrosion control in a particular environment requires knowledge of each reaction that occurs at the anodic and cathodic areas.

1.5.1 Components of Electrochemical Corrosion

The various components that are involved in the process of corrosion of metal are: (1) the metal, (2) the films of hydrogen gas and metal corrosion products, (3) liquid and gaseous environment, and (4) the several interfaces between these components. Metal is a composite of atoms that are arranged in a symmetrical lattice structure. These atoms may be considered particles that are held in an ordered arrangement in a lattice structure by bonding electrons. These electrons, which are in constant movement about the charged particles, move readily throughout the lattice structure of metal when an electric potential is applied to the system. If bonding electrons are removed from their orbit about the particle center, the resulting cation will no longer be held in the metal's crystalline structure and can enter electrolyte solution.

Electrochemical corrosion is simply the process of freeing these cations from their organized lattice structure by removal of the bonding electrons. Inasmuch as certain of the lattice electrons move readily within the metal under the influence of electrical potentials, the locations on the surface of the metal from which the cations escape and the locations from which the electrons are removed from the metal need not be and generally are not the same. Corrosion will not occur unless electrons are removed from some portion of the metal structure.

All metals are polycrystalline with each crystal having a random orientation with respect to next crystal. The metal atoms in each crystal are oriented in a crystal lattice in consistent pattern. The pattern gives rise to differences in spacing and, therefore, differences in cohesive energy between the particles, which may cause preferred corrosion attack. At the crystal boundaries the lattices are distorted, giving rise to preferred corrosion attack. In the manufacture and processing of metals, in order to gain desirable physical properties, both the composition and shape of crystal may be made nonuniform, distorted, or preferably oriented. This may increase the susceptibility of the metal to corrosion attack.

Undistorted single crystals of metals experience comparatively little or no corrosion under the same conditions, which may destroy commercial pieces of the same metal. Compositional changes in metal alloy

crystals and crystal boundaries, which are present in steels and alloys, can promote highly localized corrosion.

1.6 CHEMISTRY OF CORROSION AND ELECTROMOTIVE FORCE SERIES

Oxidation takes place when a given substance loses electrons or a share of its electrons. On the other hand, reduction occurs when there is a gain in electrons by a substance. A substance that yields electrons to something else is called a reducing agent, whereas the substance that gains electrons is termed an oxidizing agent. Thus, electrons are always transferred from the reducing agent to the oxidizing agent. In the example below, two electrons are transferred from metallic iron to cupric ion:

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \tag{1.8}$$

Examples of oxidation and reduction processes are presented below:

$$Zn^0 \rightarrow Zn^{2+} + 2e^- \quad \text{(Oxidation)} \tag{1.9}$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \quad \text{(Reduction)} \tag{1.10}$$

The emf series is presented in Table 1.1. Potentials given are those between the elements in their standard state at 25°C and their ions at unit activity in the solution at 25°C. A plus (+) sign for E^0 shows that, for the above conditions, the reduced form of the reactant is a better reducing agent than H_2. On the other hand, a negative (–) sign indicates that the oxidized form of the reactant is the better oxidizing agent than H^+. Thus, in general, any ion is a better oxidizing agent than the ions above it.

Any metal will displace any other metal (in ionic form), occupying a lower position in the activity series, from a solution of any salts of the latter metal, if the metal to be displaced is not very far above hydrogen. In the latter case, there will be a preponderance of hydrogen gas evolution. Examples below demonstrate this:

$$Ca^0 + Sn^{2+} \rightarrow Ca^{2+} + Sn^0 \tag{1.11}$$

$$Ca^0 + Zn^{2+} \rightarrow Ca^{2+} + Zn^0 \tag{1.12}$$

Table 1.1 Electromotive force series.

Electrode reaction	Standard electrode potential E^0 in volts, 25°C
$Li = Li^+ + e^-$	+3.05
$K = K^+ + e^-$	+2.922
$Ca = Ca^{++} + 2e^-$	+2.87
$Na = Na^+ + e^-$	+2.712
$Mg = Mg^{++} + 2e^-$	+2.375
$Be = Be^{++} + 2e^-$	+1.85
$Al = Al^{3+} + 3e^-$	+1.67
$Mn = Mn^{++} + 2e^-$	+1.029
$Zn = Zn^{++} + 2e^-$	+0.762
$Cr = Cr^{3+} + 3e^-$	+0.74
$Ga = Ga^{3+} + 3e^-$	+0.53
$Fe = Fe^{++} + 2e^-$	+0.44
$Cd = Cd^{++} + 2e^-$	+0.402
$In = In^{3+} + 3e^-$	+0.34
$Tl = Tl^+ + e^-$	+0.336
$Co = Co^{++} + 2e^-$	+0.277
$Ni = Ni^{++} + 2e^-$	+0.25
$Sn = Sn^{++} + 2e^-$	+0.136
$Pb = Pb^{++} + 2e^-$	+0.126
$H_2 = 2H^+ + 2e^-$	0.00
$Cu = Cu^{++} + 2e^-$	−0.345
$Cu = Cu^+ + e^-$	−0.522
$2Hg = Hg_2^{++} + 2e^-$	−0.789
$Ag = Ag^+ + e^-$	−0.80
$Pd = Pd^{++} + 2e^-$	−0.987
$Hg = Hg^{++} + 2e^-$	−0.854
$Pt = Pt^{++} + 2e^-$	−1.20
$Au = Au^{3+} + 3e^-$	−1.50
$Au = Au^+ + e^-$	−1.68

$$Ca^0 + 2H^+ \rightarrow Ca^{2+} + H_2\uparrow \tag{1.13}$$

$$Fe^0 + Be^{2+} \rightarrow \text{no reaction} \tag{1.14}$$

1.6.1 Actual Electrode Potentials

In the emf series, each metal will reduce (or displace from solution) the ion of any metal below it in the series, providing all of materials have

unit activities. The activity of a pure metal in contact with a solution does not change with the environment. The activity of an ion, however, changes with concentration, and activity of a gas changes with its partial pressure.

An electrode reaction, in which a metal M is oxidized to its ion M^{n+}, liberating n electrons, may be represented by the relation: $M = M^{n+} + ne^-$. The actual electrode potential of this reaction may be calculated from the standard electrode potential by use of the following expression:

$$E = E^0 - \frac{RT}{nF}\ln(M^{n+}) \tag{1.15}$$

where E = actual electrode potential at the given concentration (volts), E^0 = standard electrode potential (volts), R = universal gas constant; 8.315 volt coulombs/K, T = absolute temperature (K), n = number of electrons transferred, F = Faraday, 96,500 coulombs, M^{n+} = concentration of metal ions.

At 25°C, 3.303 RT/F = 0.05915 and the formula becomes

$$E = E^0 - \frac{0.05915}{n}\log_{10}(M^{n+}) \tag{1.16}$$

The actual electrode potential for a given environment may be computed from the above relation. Table 1.2 shows how the actual electrode potentials of iron and cadmium vary with change in concentration of the ions. It is apparent from Table 1.2 that iron will reduce cadmium when their ion concentrations are equal, but the reverse holds true when the concentration of cadmium ion becomes sufficiently lower than that of the ferrous ion.

The standard electrode potentials are a part of the more general standard oxidation–reduction potentials. Many books on physical chemistry contain a general expression for calculating the actual oxidation–reduction potential from the standard oxidation–reduction potential.

1.7 GALVANIC SERIES

Dissimilar metals exposed to electrolytes exhibit different potentials or tendencies to go into solution or react with the environment. This

Table 1.2 Variation in actual electrode potentials of iron and cadmium with change in concentration of ions.

Reaction	Activity (moles/kg water)			
	1	0.1	0.01	0.001
	Actual electrode potential (volts)			
$Fe = Fe^{2+} + 2e^-$	+0.440	+0.470	+0.499	+0.529
$Cd = Cd^{2+} + 2e^-$	+0.402	+0.431	+0.461	+0.490

behavior is recorded in tabulations in which metals and alloys are listed in order of increasing resistance to corrosion in a particular environment. Coupling of dissimilar metals in an electrolyte will cause destruction of the more reactive metal, which acts as an anode, and provides protection for the less reactive metal, which acts as a cathode.

1.7.1 Cathode/Anode Areal Ratio

When the ratio of area of cathodes to that of anodes (C/A ratio) is high, the corrosion rate at anodes will be high. On the other hand, when the C/A ratio is low, the corrosion rate at anodes will be low. Thus, in the case of Figure 1.5.a, the steel rivets will be heavily corroded and the two plates will soon fall apart when immersed in seawater.

In the case of Figure 1.5.b on the other hand, there will be only slight corrosion of both copper rivets and steel plates upon immersion in seawater.

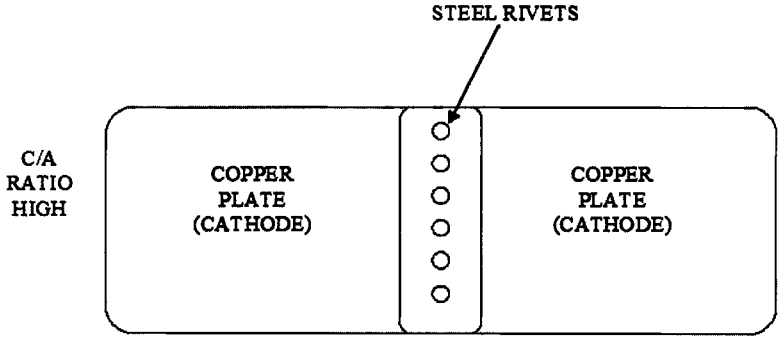
1.7.2 Polarization

Electrochemical cells in which a chemical reaction produces a current can be called primary cells.

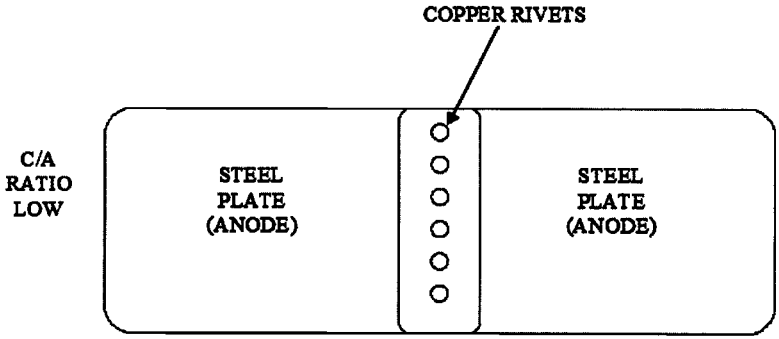
In many primary cells, hydrogen liberated at the cathode soon coats the cathode with bubbles. This diminishes the surface at which electrons can be accepted and, thus, results in an increased resistance to the current flow, i.e., *polarization* (see Figure 1.6).

If some good oxidizing agent is placed in contact with the cathode to accept electrons more readily than does oxonium ion (H_3O^+), hydrogen gas liberation will occur. This is called *depolarization*.

a. Copper plates connected by steel rivets (C/A ratio is high).



b. Steel plates connected by copper rivets (C/A ratio is low).



c. C/A ratio versus corrosion rate at the anode.

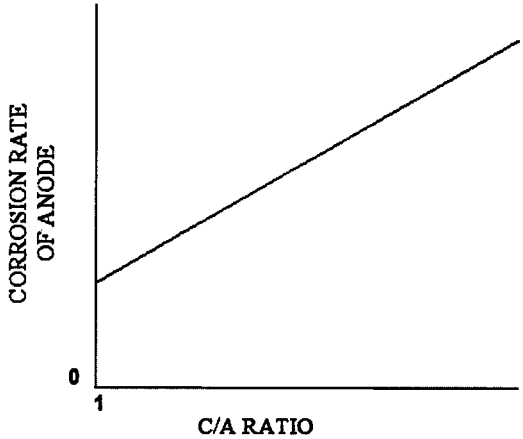


Figure 1.5 Effect of ratio of the area of cathodes to the area of anodes on corrosion rate.

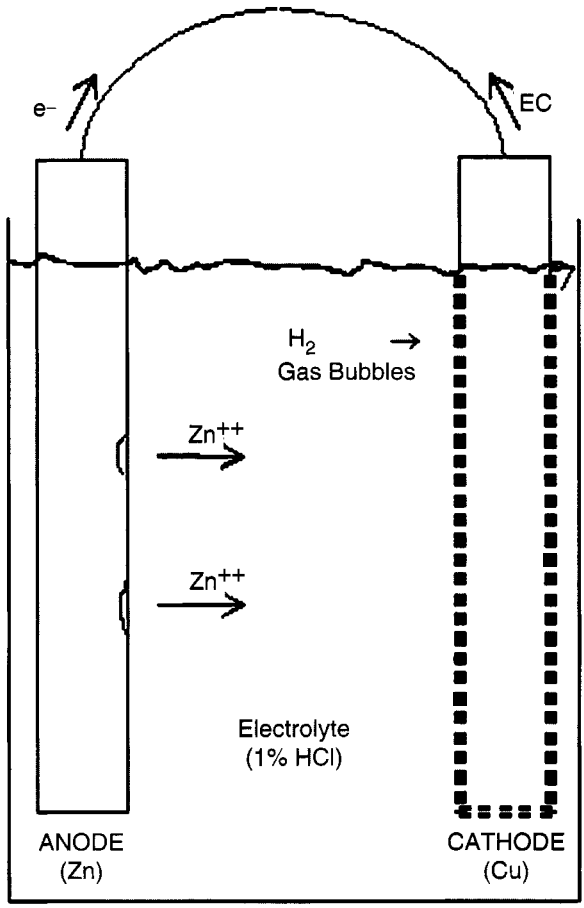


Figure 1.6 Zn–Cu cell and polarization.

Excellent treatment of the subject can be found in Jones (1988, p. 162), who presented polarization diagram of zinc corroding in acid (Figure 1.7).

1.8 CORROSION OF STEEL

In most corrosion problems, the important differences in reaction potential are not those between dissimilar metals, but are those that exist between separate areas interspersed over all the surface of a single

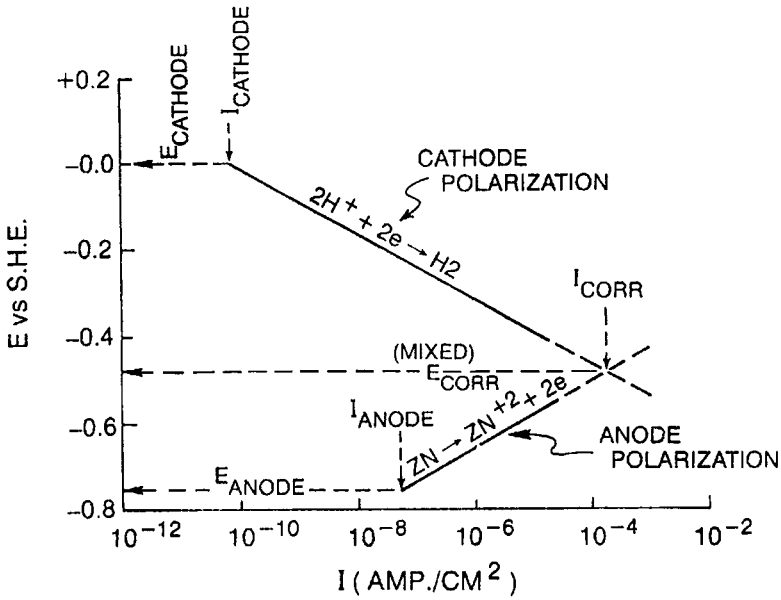


Figure 1.7 Polarization diagram of zinc corroding in acid. (After Jones, 1988, p.163, figure 1A.3) *Ecorr* = mixed (corrosion) potential where oxidation and reduction are occurring equally, i.e., zinc dissolution is equal to hydrogen gas evolution.

metal. These potential differences result from local chemical or physical differences within or on the metal, such as variations in grain structure, stresses, and scale, inclusions in the metal, grain boundaries, and scratches or other surface condition. Steel is an alloy of pure iron with small amounts of carbon present as Fe_3C and trace amounts of other elements. Iron carbide (Fe_3C) is cathodic with respect to iron.

Inasmuch as in typical corrosion of steel the anodic and cathodic areas lie side by side on the metal surface, in effect it is covered with both positive and negative sites. During corrosion, the anodes and cathodes of metals may interchange frequently.

1.9 GASEOUS CORRODANTS

Gaseous corrodants include oxygen, hydrogen sulfide, and carbon dioxide.

1.9.1 Oxygen

Oxygen dissolved in drilling fluids is a major cause of drill pipe corrosion. As a depolarizer and electron acceptor in cathodic reactions, oxygen accelerates the anodic destruction of metal. The high-velocity flow of drilling fluids over the surfaces of drill pipe continues to supply oxygen to the metal and is destructive at concentrations as low as 5 ppb. The presence of oxygen magnifies the corrosive effects of the acid gases (H_2S and CO_2). The inhibition of corrosion promoted by oxygen is difficult to achieve and is not practical in the drilling fluid system. Removal of oxygen from the drilling fluid by physical deaeration, followed by chemical removal of residual oxygen, is recommended.

Oxygen corrosion of drill pipe also occurs while the pipe is out of the hole. Pitting can develop rapidly under particles of mud solids that are left on the pipe. Pits provide the sites for further local attack of the drill pipe while it is in service. Proper cleaning with fresh water for the removal of salts and mud solids is recommended. Cleaned drill pipe should be sprayed with a protective coating prior to storage.

The control of corrosion in water-handling facilities requires the complete exclusion and removal of oxygen from the water throughout the facilities. Oilfield brines, which usually exhibit an oxygen demand, should react with dissolved oxygen in the water. Unfortunately the brines usually contain soluble organics which interfere with the reaction. Oxygen scavenger with appropriate catalysts is usually required for the complete removal of oxygen from the waters.

Oxygen enters the produced brines by exposure to air through open tank hatches, pump seals, flotation and filtration systems, and other points throughout water-handling facilities. Oxygen can enter produced fluids in low-pressure pumping wells and in gas- and oil-gathering systems.

The strong depolarization properties of oxygen create localized attack of metal at the areas of lower oxygen concentration, such as in crevices, pits, and in areas under deposits on the metal. Even in trace quantities, oxygen in brines can create severe pitting of metal.

Inhibition of oxygen-induced corrosion in production facilities has been difficult to attain. Corrosion control effort should be directed to both the exclusion of oxygen from production and water-handling facilities and the complete removal of oxygen from oilfield waters.

The method used to remove dissolved oxygen from water is either mechanical or chemical.

Mechanical methods are useful in reducing dissolved oxygen to values less than 1 ppm. The water is then treated chemically for complete removal of oxygen. A common mechanical method used in the oil field to strip dissolved oxygen from water is by countercurrent flow of water with oxygen-free gas through a trayed stripping column. The process was described by Weeter (1965). Oxygen content can be reduced economically by vacuum deaerators to about 0.3 ppm. According to Cron and Marsh (1983, p. 1037), vacuum is best obtained by the use of steam injectors in series. Chemical scavengers for the removal of oxygen are sodium sulfite, bisulfites, and hydrazine:

$$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4 \tag{1.17}$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{1.18}$$

The reaction rates are complex in many water systems and are affected by temperature, pH, hydrogen sulfide content, and the presence of catalysts. Snavely and Blount (1969) and Snavely (1971) have shown that:

1. SO_2 or Na_2SO_3 is not effective for scavenging oxygen from sour waters, and H_2S must be removed prior to treatment.
2. Hydrozine is not sufficiently reactive for scavenging O_2 at ambient temperatures, except in the presence of Cu^{2+}.

Although stoichiometrically 8 ppm of Na_2SO_3 is required to react with 1 ppm of dissolved oxygen, in actual practice 10 ppm is used. In the case of hydrazine, 1 ppm is required to scavenge 1 ppm of oxygen. Tests of oxygen scavenger reaction rates and chemical scavenger and catalyst requirements should be made in each case.

1.9.2 Hydrogen Sulfide

Hydrogen sulfide is most damaging to drill pipe by promoting sulfide cracking or embrittlement as discussed in Chapter 2. General corrosion attack by hydrogen sulfide is also significant and is influenced by the presence of carbon dioxide, oxygen, and salts. The nature of the attack on metal is related to the alloy composition and strength of steel. The

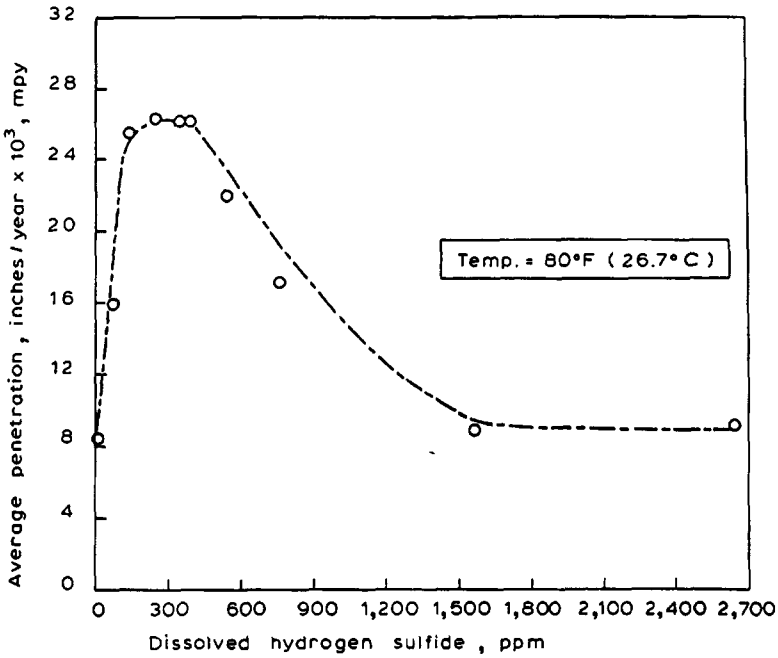


Figure 1.8 Corrosive action of hydrogen sulfide on steel in distilled water at 80°F (After Watkins and Wright, 1953, p. B-55, figure 5; courtesy of *Petroleum Engineer*).

corrosion of mild steel in distilled water containing hydrogen sulfide was illustrated by Watkins and Wright (1953) (Figure 1.8). The data in Figure 1.8 indicate that high concentration of hydrogen sulfide may inhibit corrosion of mild steel.

High concentrations of hydrogen sulfide are catastrophic; however, in the case of high-strength steels, producing rapid embrittlement. The influence of hydrogen sulfide, brine, and carbon dioxide mixtures upon corrosion rates of mild steels is illustrated in Figure 1.9 (Meyer et al., 1958).

Obviously, the removal of dissolved gases (oxygen, hydrogen sulfide, and carbon dioxide) from drilling fluids is an important step in minimizing corrosion damage to drill pipe. The primary object of removing hydrogen sulfide from drilling fluids is the safety of personnel, because H_2S is extremely toxic. The limit for repeated exposure is 10 ppm. Exposure to concentration of 800+ ppm may result in death. Drilling

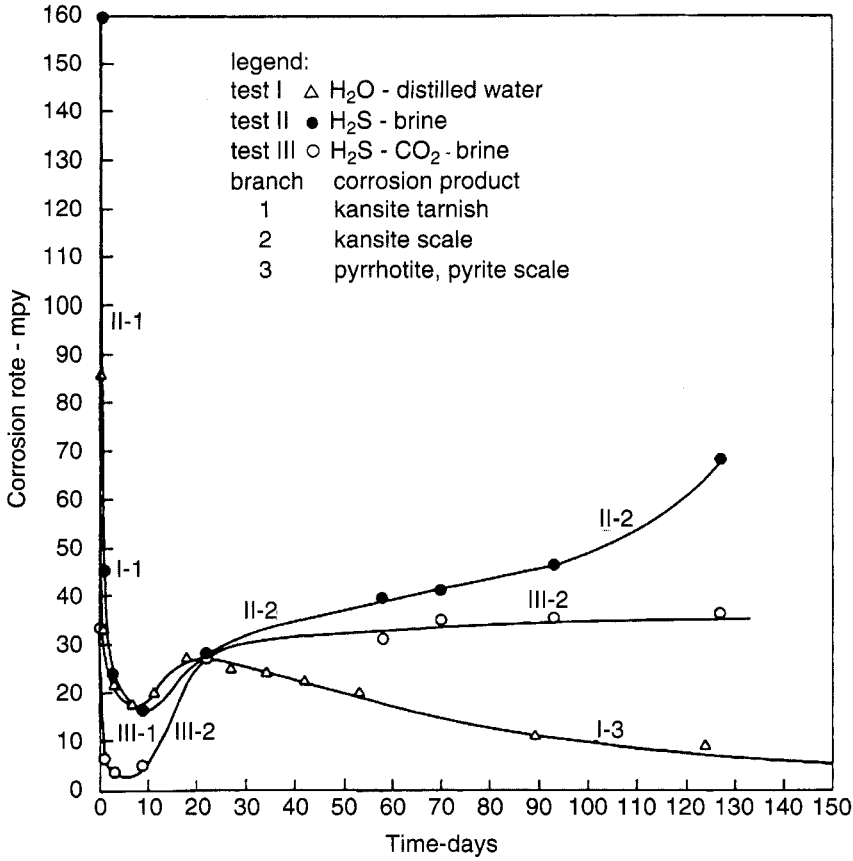


Figure 1.9 Corrosion rates of 1,020 mild steel from tests I, II, and III in mixtures of hydrogen sulfide, carbon dioxide, and brine (Modified after Meyer et al., 1958, p. 113t, figure 7; courtesy of *Corrosion*).

fluids must, therefore, be treated to neutralize hydrogen sulfide gas as it enters the drilling fluid by flow from the formation or from the drilled cuttings. If presence of hydrogen sulfide is expected, the pH of drilling fluids should be held above 10. The reactions with caustic soda are as follows:

$$\text{pH} = 7.0: H_2S + NaOH \rightarrow NaHS + H_2O \tag{1.19}$$

$$\text{pH} = 9.5: NaHS + NaOH \rightarrow Na_2S + H_2O \tag{1.20}$$

Hydrogen sulfide scavengers are also added to drilling fluids for the purpose of pretreatment or removal of this gas. These materials include (1) carbonate, chromate, and oxides of zinc; (2) iron oxide; and (3) copper carbonate. Copper carbonate should not be used for the purpose of pretreatment or in excess of the sulfide requirement due to the possible corrosive effects.

Ironite®Sponge®, which is the product of reaction (controlled oxidation) using highly reactive, specially formulated chemical-grade iron powder as the raw material, can be used as an H_2S scavenger. It consists mainly of Fe_3O_4 and is characterized by high surface area (10 m^2/kg or approximately 50,000 sq ft/lb). The specific gravity of the dry material is around 4.5–4.6 g/cm^3, and particle size ranges from 1.5 to 50.0 μm, with 90% being between 2 and 20 μm. Inasmuch as the material retains very little magnetism, it is not attracted to drill pipe or casing. Ironite®Sponge® reacts with H_2S according to the following equations:

$$Fe_3O_4 + 4H_2S \rightarrow 3FeS + 4H_2O + S \tag{1.21}$$

$$FeS + S \rightarrow FeS_2 \tag{1.22}$$

$$Fe_3O_4 + 6H_2S \rightarrow 3FeS_2 + 4H_2O + 2H_2 \tag{1.23}$$

The first two reactions predominate in basic environment, whereas the third reaction occurs in acidic environment. One pound of material (0.453 kg) reacts with 0.7 lb (0.318 kg) of H_2S. The speed of reaction can be expressed by the following equation:

$$\frac{dS}{dt} = -3{,}000 \times (S_t)^2 \times (H^+)^{1.06} \times (I) \tag{1.24}$$

where S_t = total dissolved sulfides in filtrate, ppm; t = time, min; H^+ = hydrogen ion concentration, moles/L; I = Ironite Sponge concentration, lb/bbl (0.351 × kg/m^3).

Replacement of water-base drilling fluids with oil-base systems provides protection to drill pipe by eliminating the electrolyte that is essential to corrosion. The oil-base systems contain some emulsified water, alkalinity of which must be maintained. The H_2S gas, which is carried by oil-base drilling fluid, must be removed by gas separators and vacuum degassers. The removed gases must then be neutralized for the protection of personnel.

Hydrogen sulfide causes failure of production equipment by acid attack and hydrogen penetration of steel, which results in blistering and cracking as discussed in Chapter 2. Hydrogen sulfide forms iron sulfide scale, which is cathodic to the metal and promotes localized attack under the scale and the penetration of hydrogen into the metal.

The control of corrosion in H_2S environments requires:

1. The proper selection of materials including the use of low-hardness steels with a maximum hardness of Rockwell C-22.
2. The application of inhibitors.
3. The complete exclusion and removal of oxygen from waters in petroleum production.

The transmission of sour or acid gases should be preceded by drying to a dew point, which is below the minimum temperature of exposure within the facilities.

1.9.3 Carbon Dioxide

Carbon dioxide is present in most formation fluids as a component of formation gases and in solution in water and oil. Carbon dioxide dissolves in water and oil. Upon dissolution in water carbon dioxide forms carbonic acid:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{1.25}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{1.26}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{1.27}$$

As the partial pressure of carbon dioxide increases, more acid ions are formed and the water becomes more corrosive. The relationship of the partial pressure of carbon dioxide and the corrosion rate of steel is illustrated in Figure 1.10.

According to Cron and Marsh (1983, p. 1034), the characteristic appearance of CO_2 corrosion is deep, rounded pits with sharp edges. CO_2 corrosion is especially prevalent in areas of turbulence. The partial pressure of CO_2 can be used as a yardstick to predict corrosion. The following relationships have been found:

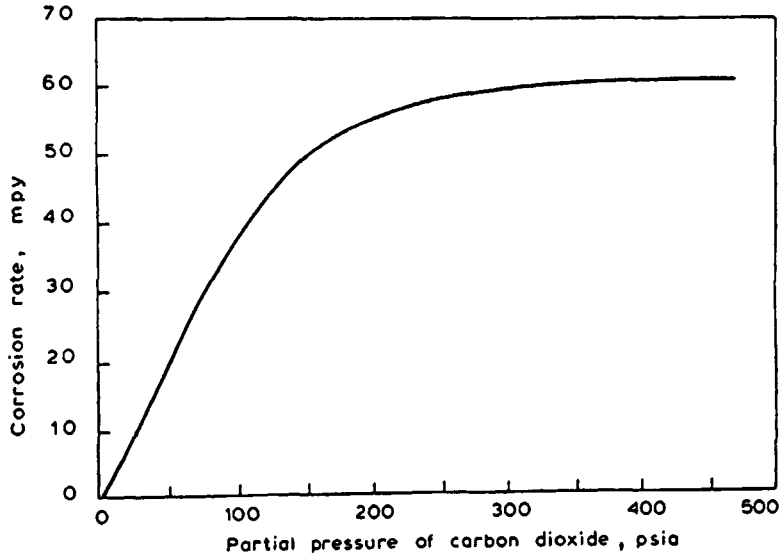


Figure 1.10 Relationship between corrosion rate of steel and partial pressure of CO_2 (After Rhodes and Clark, 1936; courtesy of *Industrial and Engineering Chemistry*).

1. A partial pressure of CO_2 above 30 psi usually indicates that corrosion will occur.
2. A partial pressure of 3 to 30 psi indicates that corrosion may occur.
3. A partial pressure below 3 psi indicates that corrosion generally is not serious.

Carbon dioxide is usually removed from drilling fluids by degassers and adjusting the pH. Alkalinity is preferably adjusted with caustic soda, to avoid scaling or precipitation of carbonates.

1.9.4 Alkalinity of Environment

The pH (hydrogen ion activity) of water influences the corrosion rate of steel. The effect of pH on the corrosion of steel is dependent upon metal composition, stresses, oxygen concentration, and the type of acid that controls the pH. The effect of pH on corrosion of steel in water containing 5 ppm of oxygen is shown in Figure 1.11.

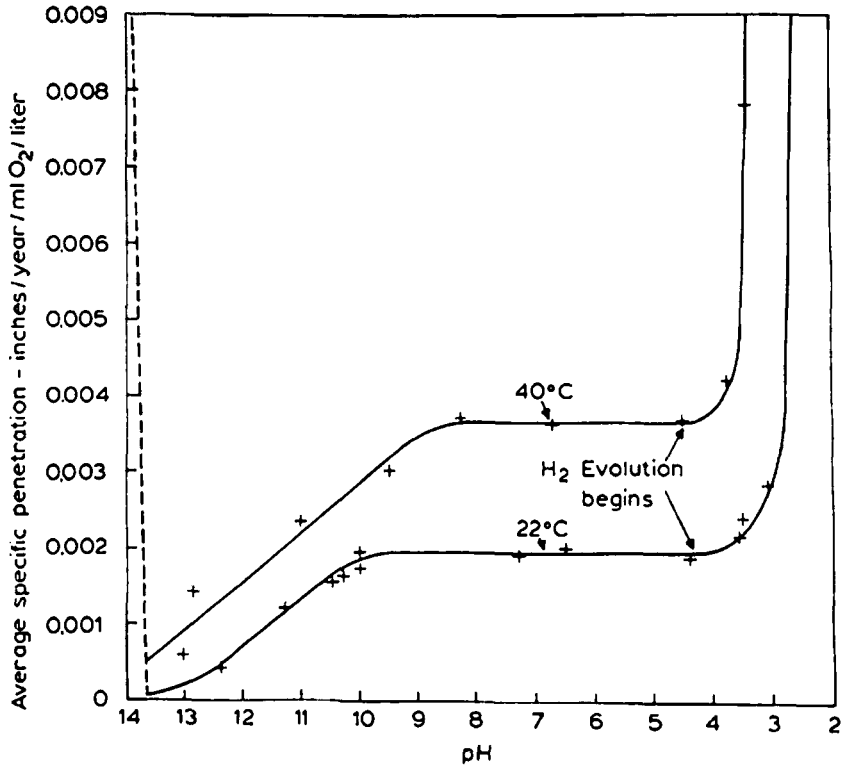


Figure 1.11 Effect of pH on corrosion of mild steel (Modified after Whitman et al., 1924; also see Uhlig, 1948, p. 129, figure 2; courtesy of *Industrial and Engineering Chemistry*).

In a high alkaline range, the corrosion reaction is under anodic control and proceeds at high rates:

$$O_2 + Fe - 2e \rightarrow FeO_2^{2-} \tag{1.28}$$

In the neutral range and in mild alkaline solutions, the corrosion rate is under cathodic control, which provides some corrosion protection. Ferrous hydroxide, which provides a protective layer on the metal surface, forms in this environment. The actual corrosion rate is dependent upon the diffusion of oxygen to metal surface. Corrosion increases with increasing oxygen concentration and abrasion and in the presence of turbulent, high-velocity flow, which is often imposed on drill pipe.

In the acid pH range, corrosion is under anodic control and the metal composition influences the corrosion rates extensively. Trace elements in steel and stresses affect the corrosion damage. The type of acid in solution determines the pH at which corrosion increases rapidly with evolution of hydrogen gas. As shown in Figure 1.11, hydrogen evolution starts at pH near 4, with corrosion accelerating as pH is reduced. Hydrogen evolution at pH of about 4 occurs in the presence of strongly dissociated acids.

Carbonic acid from the solution of carbon dioxide reacts with iron at a pH of 6 with the evolution of hydrogen gas causing severe corrosion. This illustrates the importance of pH control throughout the system where carbon dioxide is present. Relationship of failure by embrittlement (sulfide cracking) to pH is illustrated in Figure 1.12.

Figures 1.11 and 1.12 illustrate the importance of pH influence on the rate of corrosion. The most important corrosion control measure is to remove oxygen, carbon dioxide, and hydrogen sulfide (soluble gases) from the system. The effectiveness of both corrosion inhibitors and pH is enhanced by the removal of soluble gases.

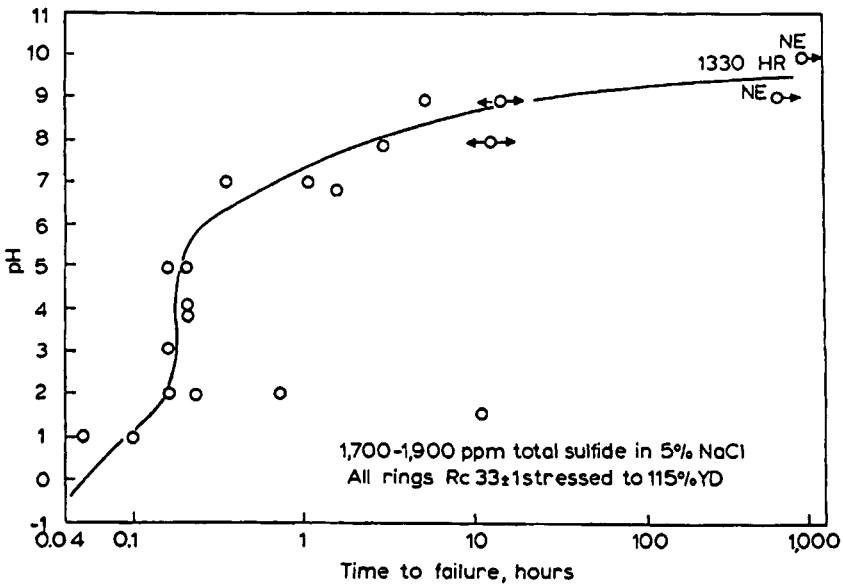


Figure 1.12 Relationship between the pH and time to failure (After Hudgins, 1969, p. 43, figure 3; courtesy of *Materials Protection,* National Association of Corrosion Engineers).

1.10 CATHODIC PROTECTION

Cathodic protection (CP) can be described simplistically as follows:

Inasmuch as corrosion is due to the loss of electrons, sending a current of electrons (DC current) toward the structure to be protected will stop the corrosion. By analogy, if an individual is a "big spender," eventually he will go broke. But, if a "friend" continuously supplies him with additional funds (equal to those he spends), then this individual would not go broke. (See Chapter 4 for detailed analysis of CP.)

Cathodic protection is not a practical method for control of corrosion of drill pipe or the internal surface of well casings. Cathodic protection, however, is applied successfully for the corrosion control of external casing surfaces.

The first step in the control of external casing corrosion is to provide a complete cement sheath and bond between the pipe and the formation over all external areas of the casing strings. This practice is essential to successful well completions.

1.11 ROLE OF BACTERIA IN CORROSION

The influence of sulfate-reducing bacteria in the corrosion process has been the subject of extensive investigations. The subject is complex and the reader is referred to the comprehensive treatment of the subject by Davis (1967) (also see Chilingar and Beeson, 1969). Microbial corrosion has not been significant in the corrosion of drill pipe. Sulfate-reducing bacteria have produced serious corrosion to well casing as reported by Doig and Wachter (1951).

Pitting occurred on the external surface of casing where drilling fluid was present between the casing and the wall of the hole. The low pH of the mud and presence of organic nutrients were favorable for growth of sulfate-reducing bacteria. The pH favorable for bacterial growth ranges from 5 to 9. Bacteria will thrive in areas of stagnant flow even in high-pH systems, however, provided other requirements, i.e., temperature and contents of organic nutrients, salts, and oxygen, are satisfied. Sulfate-reducing bacteria are anaerobic and thrive only in the absence of oxygen. In an aerated mud system, oxygen is depleted in stagnant areas, e.g., along the walls of mud pits and behind casing. This allows sulfate-reducing bacteria to grow with evolution of H_2S:

$$H_2SO_4 + 8H + \text{bacteria} \rightarrow H_2S + 4H_2O \tag{1.29}$$

Thus, hydrogen atoms formed at cathodic areas of metal are removed and utilized to reduce sulfates to sulfides. The end products are live bacteria and corroded iron. The bacterial attack of organic additives of drilling fluids may result in excessive use of mud chemicals and a rapid reduction of pH. The mud will become more corrosive under these conditions. Thus, bacteria must be controlled by the use of high pH (e.g., 10.5) or bactericides.

1.12 CORROSION IN GAS-CONDENSATE WELLS

Corrosion in gas-condensate wells presents serious problems which cannot be predicted accurately. A rigorous corrosion control program, with conscientious monitoring of equipment condition and failures, properties of produced fluids, and corrosion rates, is required to maintain corrosion control.

Analysis of the problem by NGAA (1953) and the NACE Committee on Condensate Well Corrosion (1979) provided a few guidelines for control of corrosion. The NGAA (1953) statistical studies showed that corrosion was likely in condensate wells with:

1. Depths greater than 5,000 ft.
2. Bottomhole temperatures above 160°F.
3. Bottomhole pressures above 1,500 psi.
4. CO_2 partial pressures above 30 psi.

As the gas wells were drilled deeper than ≈10,000 ft, the corrosion problem became more complex. As a result of laboratory and field studies, Hilliard (1980) has noted that the effects of gas composition, pressure, temperature, velocity, and composition of produced water modify the simple relationships between these factors and the corrosion of steel. For example, corrosion due to CO_2 decreases at high temperatures due to a passivation effect. Temperature has not been related clearly to the CO_2 partial pressure, composition of water, or other properties. Hydrogen sulfide at low concentrations reactivates the corrosion.

Presence of water or electrolyte in contact with metal is essential for corrosion to proceed. Water may contact tubing in a gas well from the bottom to the wellhead or be present in a limited area within the well as a result of condensation of vapor. Corrosion in deep gas wells is difficult to monitor except by iron count, caliper logs, and inspection.

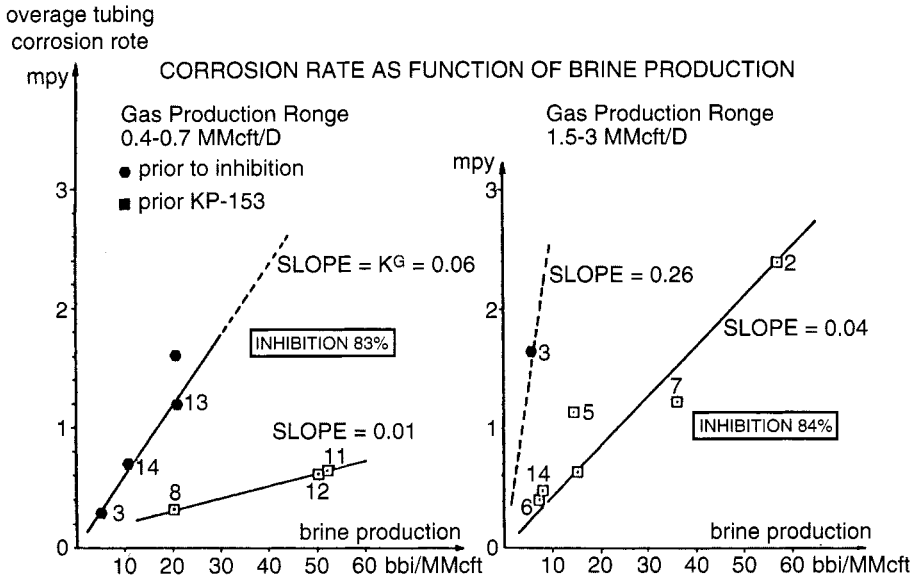


Figure 1.13 Relationship between corrosion rate and brine production (After Gatzke and Hausler, 1983; courtesy of NACE).

Corrosion monitoring at the surface does not reveal behavior that is representative of conditions within the well.

Gatzke and Hausler (1983) described an empirical relationship between corrosion rate and production rates of water and gas. The corrosion rates are derived from iron counts and the interior areas of tubing. Figures 1.13 and 1.14 illustrate the relationship between corrosion rate and brine and gas productions.

Adequate placement of corrosion inhibitors in deep hot gas wells is complicated by problems of evaporation of carrier fluid and removal of inhibitor by the flow of produced condensate and gas. Methods of inhibitor application are:

1. Squeezing of inhibitor into the formation, which may impair well productivity.
2. Batch treatment down the tubing, which may not reach the corrosive areas in deep wells.
3. Continuous injection of inhibitor through a separate line to bottom.

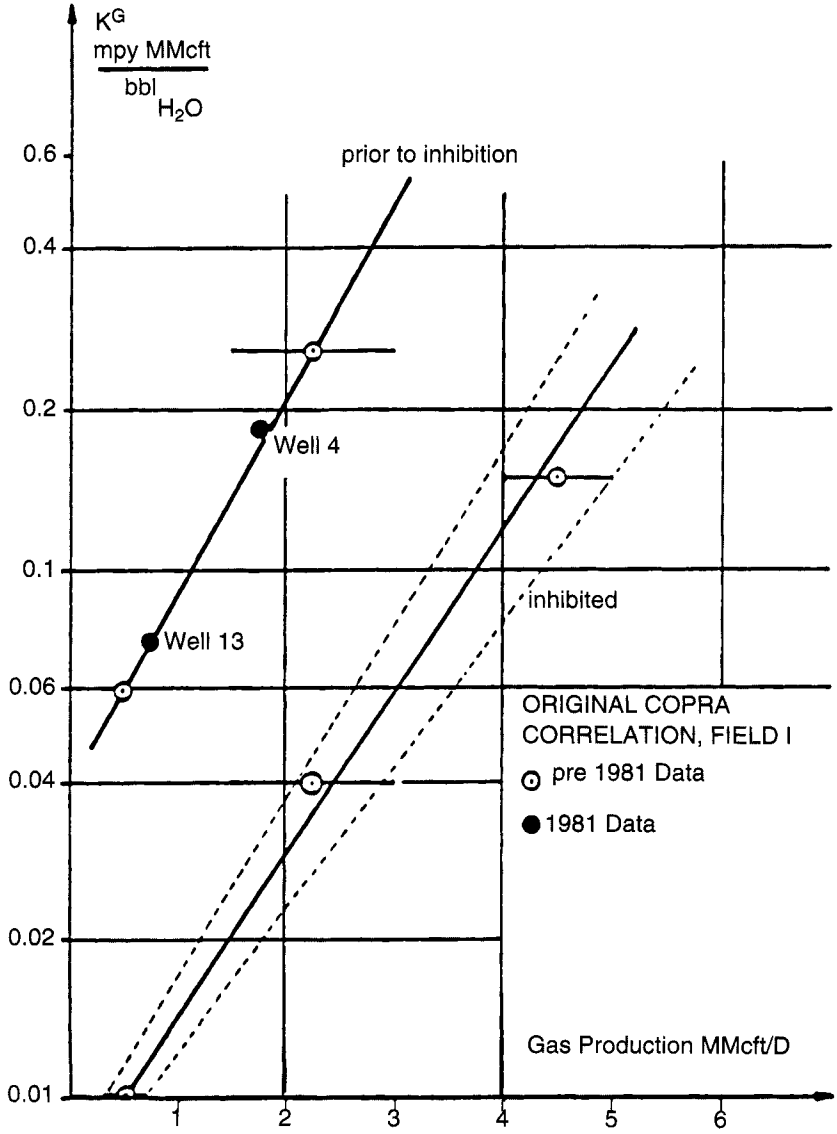


Figure 1.14 Relationship between corrosion rate and gas production (After Gatzke and Hausler, 1983; courtesy of NACE).

The continuous injection method with appropriate inhibitor and carrier fluid is the most effective procedure. An excellent discussion of corrosion characteristics and control practices in deep hot gas wells was presented by Annand (1981).

1.13 CORROSION RATE MEASUREMENT UNITS

The units used in measuring corrosion rate are presented below:

1. Mils penetration per year = *mpy*

$$\text{mil} = 0.001 \text{ inch}$$

For steel:

$$mpy = \frac{2{,}831 \times W}{A \times T} \tag{1.30}$$

where W = loss in specimen weight in grams, T = exposure time in days, and A = area of specimen in in^2.

2. Millimeters per year = mm/yr = $\dfrac{mpy}{40}$
3. Micrometers per year = μm/yr = $mpy \times 25.4$
4. Milligrams per square decimeter per day = $mdd = mpy \times 5.47$

Recommendation

For an excellent and comprehensive treatment of corrosion and scaling, the reader is referred to the classical book of Lloyd W. Jones (1988) entitled *Corrosion and Water Technology for Petroleum Producers*, Tulsa, OK: OGCI Publications. Also, the classical paper by Cron and Marsh (1983) entitled "Overview of Economics and Engineering Aspects of Corrosion in Oil and Gas Production" [*Journal of Petroleum Technology*, 35(6): 1033–1041] is strongly recommended.

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CHAPTER 2
TYPES OF CORROSION

2.1 INTRODUCTION

It is a great challenge to classify the types of corrosion in a uniform way. One can divide the corrosion on the basis of appearance of corrosion damage, mechanism of attack, industry section, and preventive methods. There are many types and causes of corrosion. In the oil and gas production industries, corrosion is usually classified into four different types. This classification is mostly based on the types of corrosion in the oil field (see Oxford and Foss, 1958):

1. Sweet corrosion
2. Sour corrosion
3. Oxygen corrosion
4. Electrochemical corrosion

One can also classify corrosion types as follows (see http://www.corrosiondoctors.org/Forms/fretting.htm):

1. Uniform attack
2. Pitting corrosion
3. Crevice corrosion
4. Galvanic corrosion
5. Erosional corrosion
6. Fretting corrosion
7. Cavitation

8. Intergranular corrosion
9. Stress corrosion
10. Dealloying (selective leaching)
11. Environmental cracking
12. Fatigue
13. Exfoliation

According to Bertness et al. (1989, p. 559), destruction of metal is influenced by various physical and chemical factors which localize and increase corrosion damage.

The conditions which promote corrosion include:

1. Energy differences in the form of stress gradients or chemical reactivities across the metal surface in contact with corrosive solution.
2. Differences in concentration of salts or other corrodants in electrolytic solution.
3. Differences in the amount of deposits, either solid or liquid, on the metal surfaces, which are insoluble in the electrolytic solutions.
4. Temperature gradients over the surface of the metal in contact with corrosive solution.
5. Compositional differences in the metal surface.

In this chapter, the authors tried to cover all of the above conditions and types of corrosion, giving a brief introduction for each. One should realize, however, that in practice usually more than one type of corrosion takes place.

2.2 SWEET CORROSION

Sweet corrosion is a common type of corrosion and can be defined as the deterioration of metal due to contact with carbon dioxide, fatty acids, or other similar corrosive agents, but excluding hydrogen sulfide H_2S. One can recognize the sweet corrosion by pitting on the steel. Carbon dioxide systems are one of the most common environments in the oilfield industry where corrosion occurs. Carbon dioxide reacts with the moisture in the environment and forms a weak carbonic acid (H_2CO_3) in water, which then reacts with metal (however, this reaction occurs very slowly):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{2.1}$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \tag{2.2}$$

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2\uparrow \tag{2.3}$$

Corrosion rates in a CO_2 system can reach very high levels (thousands of mils per year), but corrosion can be effectively inhibited. The reaction of CO_2 with water will decrease pH*, which will cause corrosion. With increasing solubility of carbon dioxide in water, corrosion will increase. The solubility is determined by the temperature, pressure, and composition. Pressure increases the solubility, whereas temperature decreases the solubility. Sweet corrosion always occurs in gas-condensate wells. Condensate wells produce water with pH below 7 at the wellhead and commonly as low as 4 at the bottom of some wells (see Oxford and Foss, 1958). This is due to:

1. High CO_2 contents of gas; usually up to 3%.
2. High total pressure, ranging from 1,000 to 8,000 psi at the wellhead.
3. Presence of organic acids, such as acetic acid (CH_3COOH).

Erosion by high-velocity gas stream aggravates the corrosion.

2.3 SOUR CORROSION

The deterioration of metal due to contact with hydrogen sulfide and moisture is called sour corrosion. Although hydrogen sulfide is not corrosive by itself, it becomes a severely corrosive agent in the presence of water. The general equation of sour corrosion can be expressed as follows:

$$H_2S + Fe + H_2O \rightarrow FeS_X + 2H + H_2O \tag{2.4}$$

One can recognize the sour corrosion by the black deposit, i.e., iron sulfide deposit on the surface of steel. The scale tends to cause faster corrosion because the iron sulfide plays the role of cathode, whereas the steel acts as the anode where corrosion occurs. Sour corrosion results in deep pitting on the equipment. Also, hydrogen released in the

*$pH = -\log[H_3O^+]$.

above reaction can embrittle the steel (cause a sulfide stress cracking [SSC]). The presence of CO_2 and/or O_2 aggravates sour corrosion. The incidents of sour corrosion in refineries vary according to the sulfur content of oil blends used. Amine units are the hot spots for sour corrosion. The following refinery units are the places where sour corrosion is considerable (http://www.ionscience.com/Pages/HydroApp.htm#Bac):

1. Amine columns
2. CDU lower reflux circuits
3. Catalytic crackers
4. Coker gas recovery systems
5. Diesel drier overhead accumulators
6. Fuel gas mixing drums and knockout drums
7. Flame knockout drums
8. Compressor suction drums
9. Gas compressors
10. Hot wells
11. Gas/oil pre-saturators, strippers, and absorbers
12. Hydrocracker reactor effluent air coolers
13. High-pressure sour gas separators
14. Low-pressure sour gas separators
15. Off-gas knockout pots
16. On-site flare knockout drums
17. Recycle gas knockout drums
18. VBU flare knockout drums
19. Sour fuel gas knockout drums
20. Sour gas gathering lines, absorber towers, knockout drums, flash drums
21. Sour water strippers
22. Sour flare lines
23. Vacuum off-gas knockout drums

2.4 CLASSES OF CORROSION

Numerous types of steel destruction can result from the corrosion process, which are listed under the following classes of corrosion:

Uniform attack. The entire area of the metal corrodes uniformly resulting in thinning of the metal. This often occurs to drill pipe, but usually

is the least damaging of different types of corrosive attacks. Uniform rusting of iron and tarnishing of silver are examples of this form of corrosion attack.

Crevice corrosion. Crevice corrosion is an example of localized attack in the shielded areas of metal assemblies such as pipes and collars, rod pins and boxes, tubing, and drill pipe joints. Crevice corrosion is caused by concentration differences of corrodants over a metal surface. Electrochemical potential differences result in selective crevice or pitting corrosion attack. Oxygen dissolved in drilling fluid promotes crevice and pitting attack of metal in the shielded areas of drill string and is the common cause of washouts and destruction under rubber pipe protectors.

Pitting corrosion. Pitting is often localized in a crevice but can also occur on clean metal surfaces in a corrosive environment. An example of this type of corrosion attack is the corrosion of steel in high-velocity seawater, low-pH aerated brines, or drilling fluids. Upon formation of a pit, corrosion continues as in a crevice but, usually, at an accelerated rate.

Intergranular corrosion. Metal is preferentially attacked along the grain boundaries. Improper heat treatment of alloys or high-temperature exposure may cause precipitation of materials or non-homogeneity of the metal structure at the grain boundaries, which results in preferential attack. Weld decay is a form of intergranular attack. The attack occurs in a narrow band on each side of the weld owing to sensitizing or changes in the grain structure due to welding. Appropriate heat-treating or metal selection can prevent the weld decay. Ringworm corrosion is a selective attack which forms groove around the pipe near the box or external upset end. This type of selective attack is avoided by annealing the entire pipe after the upset is formed.

Galvanic or two-metal corrosion. Galvanic corrosion may occur when two different metals are in contact in a corrosive environment. The attack is usually localized near the point of contact.

Selective leaching. Selective leaching occurs when one component of an alloy is removed by the corrosion process. An example of this type of corrosion is the selective corrosion of zinc in brass.

Cavitation corrosion. Cavitation damage results in a sponge-like appearance with deep pits in the metal surface. The destruction may be caused by purely mechanical effects in which pulsating pressures cause vaporization with formation and collapse of bubbles at the metal surface. The mechanical working of the metal surface causes

destruction, which is amplified in a corrosive environment. This type of corrosion attack, example of which are found in pumps, may be prevented by increasing the suction head on the pumping equipment. A net positive suction head should always be maintained not only to prevent cavitation damage, but also to prevent possible suction of air into the flow stream. The latter can aggravate corrosion in many environments.

Erosion–corrosion. The combination of erosion and corrosion results in severe localized attack of metal. Damage appears as smooth groove or hole in the metal, such as in a washout of the drill pipe, casing, or tubing. The washout is initiated by pitting in a crevice which penetrates the steel. The erosion–corrosion process completes the metal destruction. The erosion process removes protective films from the metal and exposes clean metal surface to the corrosive environment. This accelerates the corrosion process. Impingement attack is a form of erosion–corrosion process, which occurs after the breakdown of protective films. High velocities and presence of abrasive suspended material and the corrodants in drilling and produced fluids contribute to this destructive process. The combination of wear and corrosion may also remove protective surface films and accelerate localized attack by corrosion. This form of corrosion is often overlooked or recognized as being due to wear. The use of inhibitors can often control this form of metal destruction. For example, inhibitors are used extensively for protection of downhole pumping equipment in oil wells.

Corrosion due to variation in fluid flow. Velocity differences and turbulence of fluid flow over the metal surface cause localized corrosion. In addition to the combined effects of erosion and corrosion, variation in fluid flow can cause differences in concentrations of corrodants and depolarizers, which may result in a selective attack of metals. For example, selective attack of metal occurs under the areas which are shielded by deposits from corrosion, i.e., scale, wax, bacteria, and sediments, in pipelines and vessels.

Stress corrosion. The stress corrosion is produced by the combined effects of stress and corrosion on the behavior of metals. An example of stress corrosion is that local action cells are developed due to the residual stresses induced in the metal and adjacent unstressed metal in the pipe. Stressed metal is anodic, whereas the unstressed metal is cathodic. The degree to which these stresses are induced in pipes varies with (1) the metallurgical properties, (2) cold work, (3) weight of the pipe, (4) effects of slips, notch effects at tool joints, and (5)

presence of H_2S gas. In the oil fields, H_2S-induced stress corrosion has been instrumental in bringing about sudden failure of drill pipes.

2.4.1 Stress-Induced Corrosion

Because of extra energy supplied by the stress, the portion of the same metal exposed to a higher stress acts as anode. This can be demonstrated by placing a bent nail into seawater (Figure 2.1). The initial points of corrosion attack (formation of rust) will be the more stressed areas, i.e., the head, the point, and middle portion of the nail as shown in Figure 2.1, with discoloration of water with rust in the vicinity.

In general, the more stressed part of a metal structure acts as anode where corrosion occurs. Thus, "stress begets rust!"

Hydrogen collects on the pipe as a film of atomic hydrogen which quickly combines with itself to form molecular hydrogen gas (H_2). The hydrogen gas molecules are too large to enter the steel and, therefore, usually bubble off harmlessly.

In the presence of sulfide, however, hydrogen gradient into the steel is greatly increased. The sulfide and higher concentration of hydrogen atoms work together to maximize the number of hydrogen atoms that enter the steel. Once in the steel, atomic hydrogen is converted to

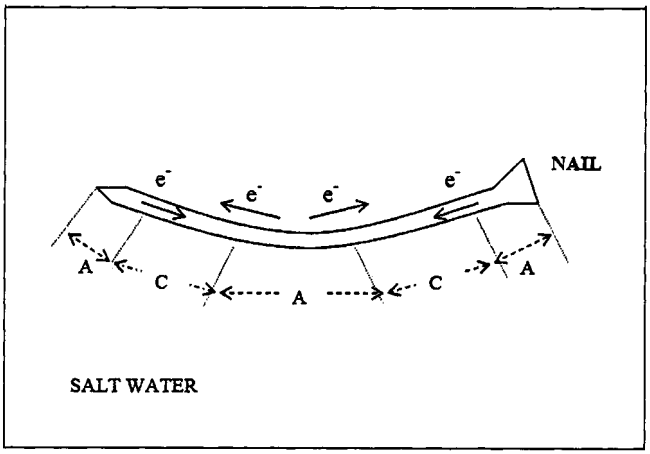

Figure 2.1 Bent nail in seawater showing the flow of electrons (and electrical current)–stress cell.

molecular hydrogen, which gives rise to a high stress in the metal (hydrogen-induced stress). Presence of atomic hydrogen in steel reduces the ductility of the steel and causes it to break in a brittle manner.

The amount of atomic hydrogen required to initiate sulfide stress cracking appears to be small, possibility as low as 1 ppm. Sufficient hydrogen must be available, however, to establish a differential gradient required to initiate and propagate a crack. The H_2S concentration as low as 1–3 ppm can produce cracking of highly stressed and high-strength steels (Wilhelm and Kane, 1987).

According to Cron and Marsh (1983, p. 1035), very low concentrations of H_2S (0.1 ppm) and low partial pressures (0.001 atm) can cause SSC. The time to failure is decreased with increasing concentration of H_2S and increasing stress. Maintaining a high temperature prevents cracking, because SSC does not occur at temperatures above ≈180°F.

Stress-corrosion cracking can occur in most alloys, and the corrodants which promote stress cracking may differ (few in number for each alloy). Cracking can occur in both acidic and alkaline environments, usually in the presence of chloride ion and/or oxygen.

Engineers should monitor the condition of tubular goods (casing, pipelines, etc.) in areas that are subsidence-prone due to fluid (oil, water) withdrawal (see Chilingarian et al., 1995). Faults and fractures form as a result of subsidence, which can cause appreciable *stress* in the casing for example. In turn, stressed metals are corrosion-prone.

2.5 TYPES OF CRACKING IN DRILLING AND PRODUCING ENVIRONMENTS

Hydrogen embrittlement (sulfide cracking) and corrosion fatigue are two forms of cracking that are associated with drilling and producing environments.

2.5.1 Hydrogen Embrittlement (Sulfide Cracking)

Hydrogen embrittlement occurs as a sudden cracking of metal, caused by the entrapment of hydrogen within the lattice structure. The cracking of the metal may proceed in a stepwise rupturing manner. The corrosion process in an acid environment produces atomic hydrogen:

$$Fe + 2H^+ \rightarrow Fe^{2+} + 2H^0 \quad \text{(atoms)} \tag{2.5}$$

$$Fe - 2e^- \rightarrow Fe^{2+} \quad \text{(anode)} \tag{2.6}$$

$$2H^+ + 2e^- \rightarrow 2H^0 \quad \text{(cathode)} \tag{2.7}$$

Some of the hydrogen atoms that are formed in the cathodic reaction penetrate the metal with subsequent formation of molecular hydrogen. The remaining hydrogen atoms combine to form molecules of hydrogen gas at the metal surface. The adsorption of hydrogen atoms by the metal causes a loss in ductility and cracking of high-strength steels.

Materials, which interfere with the pairing of atoms of hydrogen to form hydrogen gas at cathodic areas of metal, enhance the penetration of atomic hydrogen into the steel. Hydrogen sulfide in drilling fluids supplies sulfide ions, which prevent the pairing of hydrogen atoms to form hydrogen gas. Thus, the penetration of atomic hydrogen into steels is promoted by the presence of hydrogen sulfide. The time to failure by hydrogen embrittlement is shortened by increasing:

1. Concentration of hydrogen sulfide
2. Stress
3. Strength and hardness of steel

This behavior is illustrated by Hudgins et al. (1966) in Figures 2.2 and 2.3. The embrittlement (sulfide stress cracking [SSC]) occurs generally in steels with yield strengths above 90,000 psi or above Rockwell C-20–22 hardness. Lower-strength steels are not subject to SSC; however, they are subject to hydrogen blistering.

2.5.2 Hydrogen Blistering

Hydrogen penetration of low-strength steel may cause blistering, which appears as bumps on the metal surface. The hydrogen atoms form hydrogen molecules at points of defect in the metal. The hydrogen gas cannot penetrate into nor escape from the crystalline structure. The pressure of hydrogen gas increases sufficiently to part the metal, create a void, and raise a blister on the steel surface.

2.5.3 Corrosion Fatigue

Cyclic stresses at high levels cause fatigue failure of metal. In a corrosive environment, the progress of fatigue is accelerated by

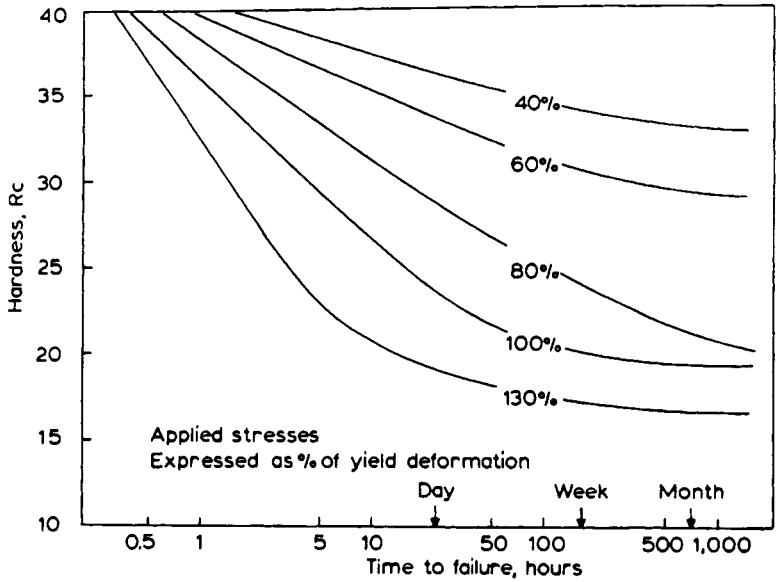

Figure 2.2 Relationship (approximate) between hardness and time to failure at different applied stresses, expressed as percentage of yield deformation, for carbon steels in 5% NaCl solutions containing 3,000 ppm H_2S (After Hudgins, 1969, p. 42, figure 1; courtesy of *Materials Protection*).

electrochemical corrosion. Corrosion fatigue is the combined action of corrosion and fatigue (cyclic stressing), which results in early fracture of metal. Corrosion fatigue is the principal cause of drill pipe failures. By establishing limits to the stresses repeatedly applied to metal, failure by metal fatigue in a noncorrosive environment can be avoided. The endurance limit is the maximum cyclic stress level which can be applied to a metal without a fatigue failure. In an environment with continued corrosion, instead of exhibiting an endurance limit, metal will fail due to the growth of corrosion fatigue cracks. The time to failure or number of stress cycles necessary to cause failure is decreased with increasing severity of corrosive environment and level of stress as illustrated in Figure 2.4.

Corrosion fatigue is enhanced by corrodants in a corrosive environment which cause pitting of steel, such as oxygen and acid gases (H_2S and CO_2), which are often present in drilling and produced fluids. Increasing the strength of steels will not improve the resistance to corrosion fatigue. Instead, it may shorten the number of cycles to failure.

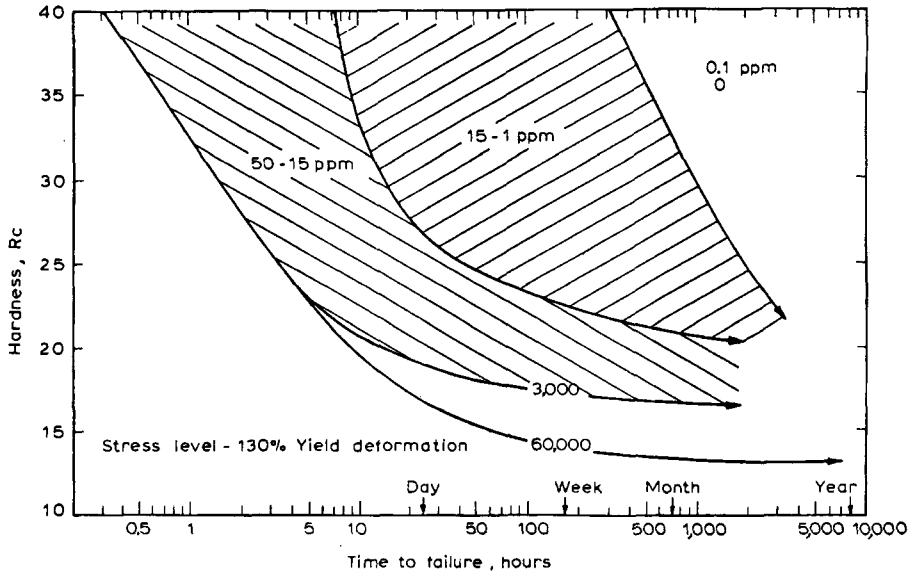

Figure 2.3 Relationship (approximate) between hardness and time to failure for carbon steels in 5% NaCl solution containing various concentrations of H_2S. Stress level = 130% of yield deformation (After Hudgins, 1969, p. 43, figure 2; courtesy of *Materials Protection*).

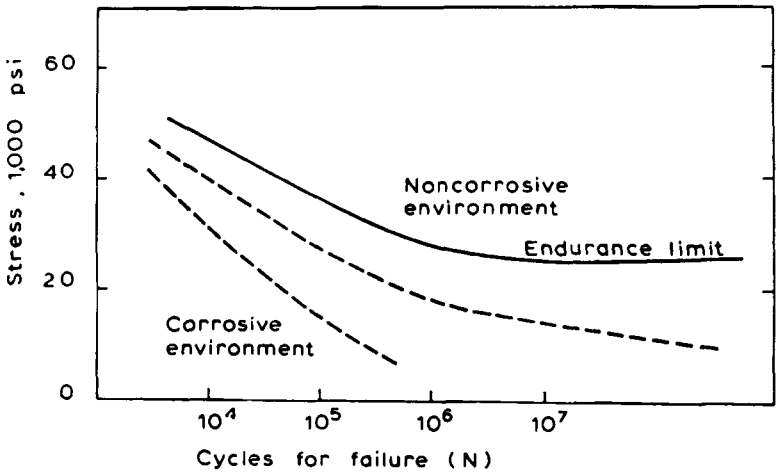

Figure 2.4 Relationship between endurance strength of steel stress and number of cycles needed for the occurrence of failure in corrosive and noncorrosive environments (After Bertness, 1957, p.131, figure 1; courtesy of *Division of Production, American Petroleum Institute*).

High-strength steels are more susceptible to pitting than the low-strength steels.

Notches, such as the ones caused by tongs or slips, and corrosion under protectors will accelerate corrosion fatigue failure. The relationship of fatigue to environment, tensile strength, and surface condition of steel is illustrated in Figure 2.5.

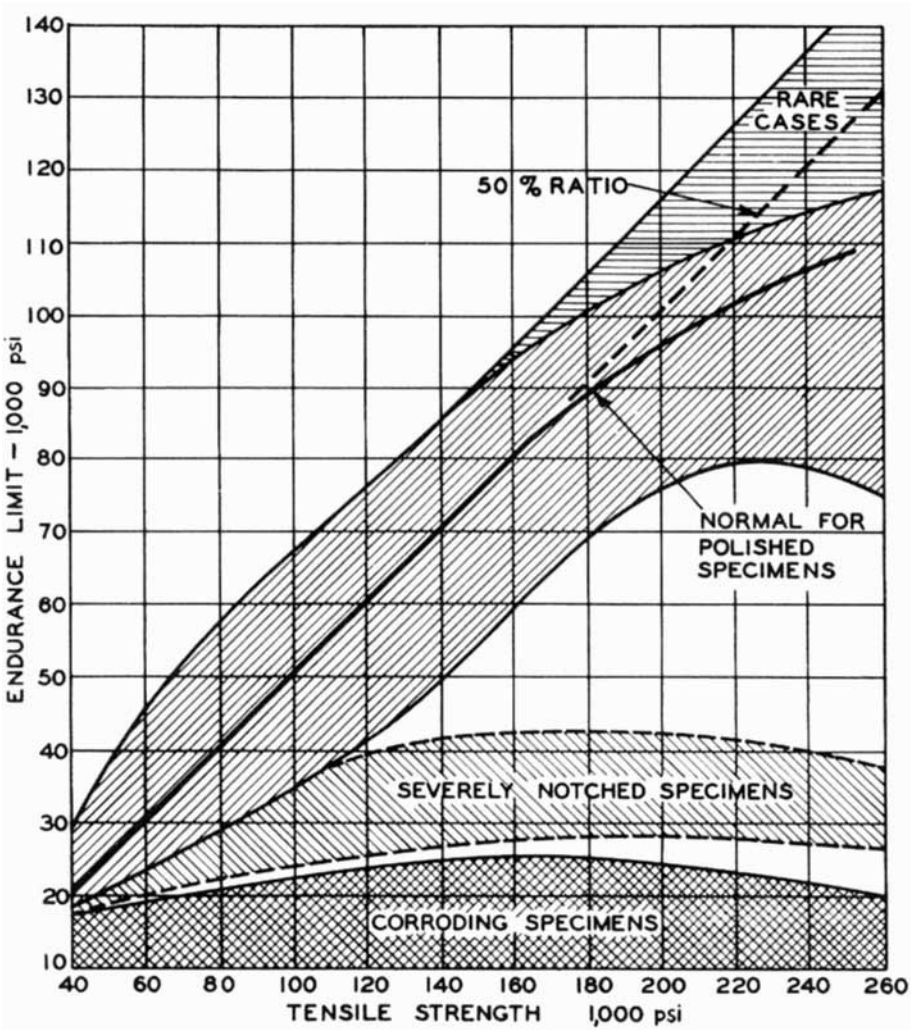

Figure 2.5 Relationship between endurance limit and tensile strength for polished, notched, and corroding specimens (applied to ordinary corrodible steels) (After Battelle Memorial Institute, 1949, p. 78, figure 93; courtesy of John Wiley and Sons, Inc.).

Inhibitors, which reduce the corrosion and the entry of corrosion-generated hydrogen into the rods, can reduce the frequency of corrosion fatigue failures provided that stress is within a reasonable range. Examples of field test of inhibitors for control of corrosion fatigue are discussed by Martin (1980, 1983) (also see Chapter 4).

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CHAPTER 3
MICROBIAL CORROSION

3.1 INTRODUCTION

The term microorganism encompasses five major groups of organisms (Bryant et al., 1989, p. 423):

1. Viruses
2. Fungi
3. Algae
4. Protozoa
5. Bacteria

These are organisms that exist as individual cell or undifferentiated aggregates of cells (cells that are not differentiated into tissues that have distinct functions). The size of microbial cells is so small that a microscope is required for observation. The viruses are the smallest form of recognized microbial life. They are not cells because they differ in many respects from the multifunctional cells: the viruses are much simpler in structure containing only protein and nucleic acid surrounded by a lipid or protein membrane and they do not reproduce by growth followed by division as cells do. Viruses must use other living cells in order to reproduce (Bryant et al., 1989).

A second division of microorganisms is the eukaryotic microbes which include:

1. Fungi
2. Algae
3. Protozoa

Eukaryotic microbes are distinguished from viruses and bacteria by virtue of possession of true nucleus, which is enclosed by a membrane that contains the genetic material of the cell (the deoxyribonucleic acid [DNA]), organized into structures known as chromosomes. Eukaryotic microorganisms also have specialized organelles in their cells, such as Golgi bodies that conduct specialized functions of transport of materials within the cell and secretion of materials to the exterior (Gaudy and Gaudy, 1980). Although eukaryotic microbes are probably responsible for some microbial plugging problems of injection wells, they are not important to enhanced oil recovery processes at this time; therefore, the reader is referred to the literature for additional information on them (Bryant et al., 1989).

The third division of microorganisms that can be distinguished by its physical characteristics is the prokaryotes. The prokaryotes are in general about 10 times smaller than eukaryotes and the structural features within the cells are not distinguishable with an optical microscope. The intracellular features of some prokaryotes can be observed by staining, but an electron microscope is required for detailed structural observation. The only food utilized by prokaryotes (or bacteria) comprises soluble molecules that can be assimilated through the cell wall. On the other hand, the eukaryotic protozoa contain a flexible membrane that can surround particles of food to form a vacuole where digestion of the food takes place (Bryant et al., 1989).

Bacteria have two distinctive structural features: (1) a rigid cell wall that determines the shape of the organisms, which may be either cylindrical or spherical; and (2) flagella which are responsible for the movement of mobile organisms. Differences in the cell walls of bacteria furnish the basis for classification into two broad groups: gram-positive and gram-negative bacteria. The cell wall of gram-positive bacteria consists of multiple layers of peptidoglycan, cross-linked through amino acid bridges, and teichoic acids bonded to the peptidoglycans. The three-dimensional network of molecules provides a strong (rigid) structure. The wall of the gramnegative bacteria also contains peptide glycan; however, the wall is very thin and surrounded by a lipid layer of lipoprotein and lipopolysaccharide, sometimes referred to as the outer membrane. Different bacterial morphologies are shown in Figure 3.1.

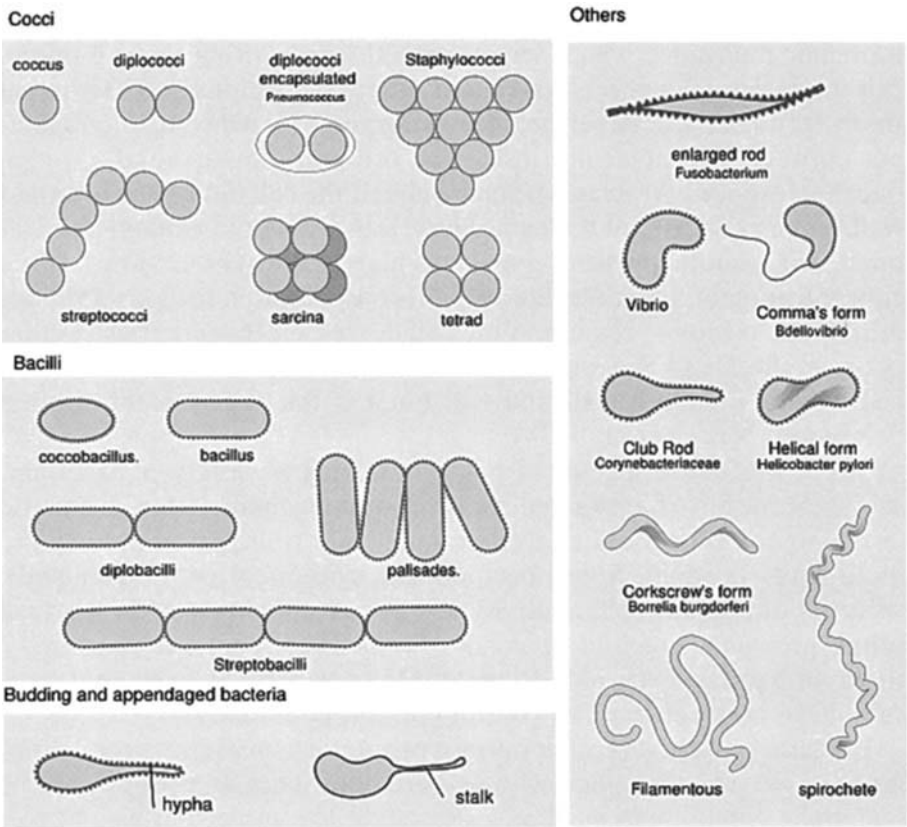

Figure 3.1 Schematic diagrams of bacterial morphology (http://en.wikipedia.org).

The Gram stain test is conducted by applying crystal violet, which is adsorbed by the bacteria. Next, a solution of iodine is added, which forms an iodine-dye complex. Then the mixture is treated with ethanol, which removes the iodine-dye complex form the gram-negative cells where the complex is not chemically bound. Finally, a red stain is applied, which colors the gram-negative bacteria (which could not retain the dye complex) red. The two types of bacteria are then easily distinguished under the microscope: gram-positive bacteria appear purple and the gram-negatives are pink in color. Retention of iodine-dye complex is related to the structure of the cell wall; it is retained by the gram-positive bacteria that contain the thick, multilayered, cross-linked walls described above (Nester et al., 1978; Gaudy and Gaudy, 1980).

The bacterial cytoplasm is a concentrated solution of organic and inorganic molecules, which are prevented from leaving the cell by the cell membrane; however, water and other small molecules can move freely through the semipermeable membrane. This concentration gradient between the molecules inside the cell and the surroundings produces an osmotic pressure within the cell. If the cell did not have a rigid wall that can withstand the osmotic pressure, it would expand and will burst. The osmotic pressure may be as high as 2.5 MPa (25 atm). If the concentration of low-molecular-weight compounds in the surroundings is high, the osmotic pressure in the cell decreases. Indeed, bacteria that occur in the Dead Sea water (containing approximately 30% salt) do not have a rigid cell wall and will burst if the salt concentration is decreased (Nester et al., 1978).

There are many species of bacteria having a variety of sizes and shapes. Some have flagella that are used for movement within an aquatic environment. Bacteria that are not mobile are transported only by the motion of the fluid. Some bacteria are cylindrical (or rod-shaped), whereas others are spherical. Some exist as individual cells, whereas others grow in aggregates or chains of cells. They range in size from 0.2 to about 5 μm and are able to penetrate consolidated rocks that typically have pores as large as 100 μm (Bryant et al., 1989).

Bacteria possess several important properties: small size, exponential growth rate when supplied with essential nutrients, and production of metabolic compounds, such as gases, acids, low-molecular-weight solvents, surfactants, and polymers. Various types of bacteria also tolerate harsh environments similar to those encountered in subsurface geological formations, such as high salinity, high pressure, and high temperature. Also, many bacteria are anaerobic (grow in the absence of oxygen).

3.1.1 Microbial Growth and Metabolism

Populations of microbes are found everywhere in nature; in fact, they are even found in areas that will not support any other form of life. The actual species growing in particular environment comprise those that have been able to successfully adapt to the prevailing environmental and nutritional conditions and the extremes of variations of those conditions. They also have been the most successful in competition with other microbes that may have entered the particular ecosystem. There may be several species living in an area, apparently as a homogeneous

population. On closer inspection by division of part of the material supporting the growth (soil, decaying matter, etc.) into squares of approximately 100 μm^2, however, one will often find that only one species occupies this microzone where it has been able to competitively exclude all other microbes. The combined effects of all of the species in a given zone develop a symbiotic relationship that results in recycling of essential chemical compounds and elements required for maintenance of life. The population will usually remain stable as long as the environmental and nutrient conditions do not undergo drastic changes. Small changes of the environmental conditions, however, can result in rapid changes of the relative populations of the species living in particular zone (Bryant et al., 1989).

Utilization of nutrients in the environment to maintain metabolism and growth depends on the enzyme inventory of a given species of bacteria. Enzymes are protein molecules endowed with the specific characteristics of organic catalysts. They lower the chemical activation energy of metabolic materials (substrate) in the surroundings, allowing them to undergo various organic reactions at low temperatures, which are compatible to the living organisms. The enzymes are true catalysts in that they remain unchanged by the reaction, which causes a rearrangement of substrate molecules or decompositions into smaller units. The enzymes increase the rates of reaction, as well as facilitate low-temperature reactions. In the absence of the enzyme, the same reaction will only take place at an elevated temperature, which may be too high for living organisms to tolerate (Bryant et al., 1989).

The relationship among the rate of reaction, temperature, and activation energy is expressed by the Arrhenius equation (Levenspiel, 1972):

$$\log(K) = \log(A) - \frac{E}{2.3RT} \tag{3.1}$$

where K = reaction rate constant; A = constant, mol/L; E = activation energy, cal; R = gas constant (1.987 cal/deg-mol); and T = temperature, K.

Equation 3.1 is used to determine the activation energy by conducting the reaction at various temperatures and measuring the rate of product formation. The rates of reaction are then plotted versus the reciprocal of the absolute temperature. The activation energy is obtained from the slope of the line, whereas the constant A is the vertical intercept.

Differentiation, as to whether one or another type of bacteria will survive in a given environment containing food resources, depends on the types of enzymes associated with a given species. This is due to the fact that the enzymes have a high degree of specificity with regard to the substrates with which it will interact as a catalyst. Thus, one type of bacteria can assimilate paraffin hydrocarbons, whereas another cannot do so. In the majority of cases, the enzymes remain within the cell and the substrates must penetrate the cell wall, with the aid of a protein which is made specifically for transportation of substrates through the cell wall. This special protein is called permease. In some cases, enzymes are present on the outside of the cell wall, or may even be released as free molecules into the solution surrounding the microbe. Nevertheless, it is the enzyme inventory of the given species, and the permease, which control the type of substrate that can be utilized by the microbes and the rate of transport into the cell. Excretion of molecules from the cell also appears to be a controlled-type process (Nester et al., 1978).

The catalytic function of enzymes depends on the presence of special groups and the spatial configuration of other groups on the protein. Any change of these special functional groups results in a decrease, or complete termination, of catalytic activity with fatal consequences to the microorganism. A change of pH above or below the optimum for the microbes, will change the functional groups enough to slow down their activity. With a more severe change of pH (±2 to 4 pH), the functional groups may be destroyed (denatured) (Bryant et al., 1989).

The temperature of the environment also has a profound influence on the microbe. As indicated by Equation 3.1, with increasing temperature the rate of reaction also increases; but an optimum temperature level exists for any given species. When the temperature is raised above the optimal level, the microbial rate of metabolism decreases and finally stops as the proteins making up the enzymes are denatured. Most of the enzymes cannot withstand temperatures greater than 70°C; however, a few enzymes which are possessed by thermophilic microbes, remain active at temperatures up to 100°C (Moses and Springham, 1982).

Bubela (1983) found that an increase of pressure increased the optimum metabolic temperature and rate of growth of rod-shaped bacteria (6–8 μm long and 3–4 μm in diameter). At atmospheric pressure (101 kPa), the optimum growth temperature was 50°C with a mean generation time of 17 hours, but when the pressure was increased to 20 MPa, the maximum growth rate occurred at 65°C with a mean generation time of 12 hours. The morphology of the microbes also changed from rod-shaped to coccoidal (about 5 μm in diameter). Cores from

offshore wells in Brazil's Namorado oil field at a depth of more than 3,000 m (about 30 MPa pressure) contained large population of *Desulfovibrio* and clusters of coccoidal (spherical) bacteria. When the coccoidal bacteria were grown at one atmosphere pressure in the laboratory, they reverted to rod-shaped morphology, indicating either *Clostridium* or *Bacillus* (Petzel and Williams, 1986). Similar results were discussed by Marquis (1983). Moses and Springham (1982) reported that bacteria have been found to be catalytically active at 179 MPa and that other bacteria were found to raise their optimum growth temperature from 65 to 85°C, when the pressure of the growth medium was increased from 101 kPa to 60 MPa. Thus, it is evident that denaturization of some enzymes is inhibited by an increase of pressure.

Another environmental factor is the salt concentration (NaCl and $CaCl_2$) of water. A difference in concentration of the surroundings and the cytoplasm within the cell produces a large osmotic pressure difference which can result in dehydration of the cell followed by growth inhibition or death of the cell. This is the basis of high salt or sugar concentrations used for preservation of foods. Some bacteria, however, can tolerate a low concentration of salt within the cell walls, which diminishes the osmotic pressure. Others, called halophiles, may actually require high salt concentrations for growth. Grula et al. (1983) readily grew *Clostridium* in salt concentrations up to 75,000 ppm and 45°C, which are representative of conditions that are encountered in petroleum reservoirs that are generally less than 1,000 m deep.

Three divisions of microbes are based on their ability to utilize oxygen. Aerobic bacteria contain enzymes that can decompose peroxides, which are formed as part of the metabolic processes involving oxygen, but the strict aerobes cannot grow in an oxygen-free environment. The facultative bacteria contain a group of enzymes that allow growth in both aerobic and anaerobic environments. The strict (obligate) anaerobes cannot utilize oxygen because they do not contain the appropriate complement of enzymes that are necessary for growth in an aerobic environment (Bryant et al., 1989).

Many biological reactions in microbes will occur only if adenosine triphosphate (ATP) is present for interaction with enzymes, because even though the activation energy of the reaction is lowered by the enzymes, ATP is required to furnish additional energy. This leads to another method of classification of microbes on the basis of their ability to use carbon dioxide as a source of carbon for synthesis. Autotrophic bacteria can use carbon dioxide as their source of carbon and they can make ATP from oxidation of inorganic compounds, deriving their

energy from the sun (photosynthesis) or from metabolism of inorganic compounds. The other class of microbes, known as heterotrophic microbes, must have preformed organic compounds as both their source of carbon and for energy (Nester et al., 1978; Gaudy and Gaudy, 1980; Moses and Springham, 1982).

In assessing microbial nutrient requirement and their metabolic products, it is more appropriate to classify the microbes according to their ability to utilize oxygen, as discussed previously. Numerous cultures (pure and mixed) are capable of synthesizing a variety of biochemical products using petroleum fraction and substrates. The range of metabolic products from microbial consumption of petroleum is very broad, depending on (Bryant et al., 1989):

1. Pressure
2. Temperature
3. Salinity
4. pH
5. Presence or absence of oxygen
6. Supporting nutrients available for cell metabolism (nitrogen, phosphorus, minerals, etc.).
7. The specific bacterial cell interaction with petroleum (Donaldson and Clark, 1982).

Obligate aerobes are organisms that must have oxygen for their metabolism and growth, but they can exist dormant in the absence of oxygen. The bacteria decompose sugars to carbon dioxide, water and, often, acids: $C_6H_{12}O_2 + 8O_2 = 6CO_2 + 6H_2O$ + energy. When the microbes are furnished with hydrocarbons and an ample supply of oxygen, a wide variety of products will result which depend on:

1. The type of microbe
2. Environmental conditions
3. The specific type of hydrocarbon substrates

The products may be carbon dioxide, low-molecular-weight acids, phenols, or biopolymers (proteins, polyanionic, lipids, glycolipids, or polysaccharides). The compounds are waste product from the microorganisms and some may even be toxic if accumulated in the surrounding fluid.

Obligate anaerobes cannot utilize free oxygen; in fact, small quantities of oxygen (10 ppm) are even toxic to some anaerobes. Spores pro-

duced by some anaerobes, however, can remain dormant for long periods in aerobic environment, germinating when they enter anaerobic environments. The anaerobes use low-molecular-weight organic compounds, such as sugars, as a source of carbon and energy. In the process of metabolism, the microbes release various products. Sugars undergo anaerobic fermentation yielding acids, alcohols, ketones, aldehydes, carbon dioxide, and hydrogen. Some species of anaerobic genus *Clostridium* have been found to produce all these compounds (Grula et al., 1983). These anaerobes also may reduce sulfur occurring as inorganic sulfates, or as part of the molecular structure of organic compounds, to hydrogen sulfide. Petroleum reservoirs have been known to become sour (produce large quantities of H_2S with the hydrocarbons) when infected by *Desulfovibrio* bacteria from injected water in secondary recovery (Crawford, 1983). Anaerobes also can produce chemicals, some of which are surface-active agents that lower the oil–water interfacial tension and promote emulsification of oil. The anaerobic bacteria also may produce biopolymers (primarily polysaccharides).

Facultative bacteria can change their metabolism for growth either in an oxidizing or reducing environment. Their products of metabolism are quite similar to those described above. They may produce hydrogen sulfide from organic sulfides and inorganic sulfates, and reduce the low-molecular-weight compounds (sugar, aldehydes, etc.) to methane, hydrogen, and carbon dioxide. In some environments, they produce biosurfactants and biopolymers.

The three classes of bacteria mentioned above are generally mesophilic (existing within a temperature range of 20–50°C). There are also thermophilic and caldoactive bacteria that can live at temperature ranging from 40 to 100°C. They reduce sugars and other carbohydrate compounds to methane and carbon dioxide, while reduction of sulfur compounds yields hydrogen sulfide. They are used in the secondary (anaerobic) treatment of sewage (Bryant et al., 1989).

3.2 MICROBES ASSOCIATED WITH OILFIELD CORROSION

A great deal of the early work by microbiologists working with petroleum was oriented toward the control of the deleterious effects of microorganisms in oil fields. Numerous reports of the presence of microbes in reservoirs have been published (Crawford, 1983; Lazar and Constantinescu, 1985; Singer, 1985). These reports discuss the microbial

population increases that occur with application of secondary oil recovery methods where the injected water is exposed to the atmosphere in open ponds. Lazar and Constantinescu (1985) found abundant microbial flora indigenous in oil field formation waters, which included species of *Bacillus*, *Pseudomonas*, *Micrococcus*, *Mycobacterium*, *Clostridium*, and *Escherichia*. Spore-forming bacilli and some cocci were usual bacteria found in deep reservoirs, whereas aerobic pseudomonades and facultative anaerobes were the dominant species in shallow reservoirs. Pseudomonades are one of the most difficult microbes to control in industrial water systems; they exhibit a high rate of growth and can produce a slime that apparently protects them from biocides to some extent and also results in plugging of the reservoir rock pores (Chakrabarty, 1982). *Escherichia* is reported to contain hydrogenase, an enzyme that utilizes molecular hydrogen and may be associated with cathodic hydrogen depolarization, causing corrosion of steel casings and pipes in the oil field. Natural mixed population of microorganisms growing in oil wells and in petroleum reservoirs produce chemicals that corrode production equipment and plug reservoirs. Sulfate-reducing bacteria cause a sweet crude to turn sour (produce hydrogen sulfide), which has happened in Wilmington Field in California (Gates and Parent, 1976).

Several patents deal with biocides that are recommended for injection into reservoirs to control indigenous microbial flora. Some examples of these biocides include formaldehyde, benzene, toluene, and several quaternary ammonium compounds (Jack and Thompson, 1983). Other processes involve the use of physicochemical methods for bacterial control, including treatment of refinery waste waters and filtering of injection water to remove microorganisms.

Many corrosion problems in the oil field are caused by hydrogen sulfide produced in situ by *Desulfovibrio*. The hydrogen sulfide also reacts with iron in the reservoir, producing ferrous sulfide which oxidizes to ferric sulfide in the produced water.

Bacteria that form slime (some form of polysaccharides), such as *Achromobacter* sp. and *Flavobacterium* sp., will adhere to each other forming a large mass. They also adhere to the walls of the pores, causing severe plugging problems at injection wells (McCoy and Costerton, 1982).

Ivanov and Belyaev (1983) showed that a population of aerobic bacteria around the injection well, which is receiving oxygen and nutrients dissolved in the injected water, produce low-molecular-weight oxygen compounds. The latter are utilized as essential food for growth

by *Desulfovibrio* and other anaerobic bacteria in the oxygen-depleted region beyond the vicinity of wellbore.

3.3 MICROBIAL INTERACTION WITH PRODUCED OIL

Microorganisms have been shown to be normal inhabitants of interstitial waters (Singer, 1985). Microbial metabolism on petroleum in the subsurface, particularly where surface waters carry oxygen and nutrients to the oil deposit, can reduce the value of the crude oil because the aerobic bacteria use the paraffins as carbon source (Crawford, 1983). A staff report in *World Oil* (Anonymous, 1972) claimed that 10% of the world's crude oil has been destroyed, and another 10% considerably reduced in value by microorganisms.

Singer et al. (1983) reported that microbial oxidation of specific sulfur- or nitrogen-containing components of crude oil is feasible. Microorganisms that oxidize specific sulfur- and nitrogen-containing aromatic compounds in crude oils have been isolated. These isolates exhibit a specificity for sulfur- and nitrogen-containing aromatic compounds. They are unable, however, to oxidize or grow on a variety of other hydrocarbons, including aliphatic alkanes, cycloalkanes, and mono-polynuclear hydrocarbons. Isolates identified to date can metabolize only under strictly aerobic conditions. In a related study, Fedorak et al. (1983) found that several isolates of pure and mixed bacterial cultures could degrade the aromatic compounds in Prudhoe Bay oil.

Inasmuch as MEOR is gaining in popularity, corrosion engineers should become more familiar with microbial corrosion (see Donaldson et al., 1989a,b).

3.4 MICROORGANISMS IN CORROSION

Involvement of microorganisms is the main distinction between abiotic corrosion and microbial corrosion, which forms a biofilm layer at the metal–solution interface. Microorganisms change the surrounding environment of the metal surface and consequently enhance and facilitate the corrosion process.

The two main categories of microorganisms are:

1. Prokaryotes
2. Eukaryotes

The most common microorganisms found in the oil field waters are presented in Table 3.1.

3.4.1 Prokaryotes

Bacteria are prokaryotic microorganisms. The bacteria involved in corrosion process are a part of the sulfur cycle in nature. Aerobic *Thioba-*

Table 3.1 Microorganisms in oil field waters.

Microorganism	Definition, activity, control
Sulfide-producing bacteria	Most important is *Desulfovibrio desulfuricans*, the sulfate reducer that metabolizes sulfate ions ($SO_4^=$) in water to form H_2S. Controlled by limiting aerobic bacteria growth and biocides treatment. Thermophilic *Clostridium nigrificans* sulfide producer; also *Clostridium tetani.*
Iron bacteria	Composed of bacteria cells, surrounded by gelatinous iron oxide excretion. Controlled via chemical treatment of producing sand; detergent–acid treatment. *Gallionella, Crenothrix*, and *Sphaerotilus* are common genera.
Slime formers	Aerobic and facultative bacteria and fungi. Controlled by elimination of dissolved oxygen and treatment with biocides. *Pseudomonas, Flavobacterium, Nocordia, Aspergillus, Aerobacter*, and *Micrococcus* are common genera.
Sulfur oxidizers	Oxidize sulfur and produce sulfuric acid. Aerobic bacteria. Examples of genera are *Beggiatoa* and *Thiobacillus*. Controlled best by removing the sulfur nutrient.
Algae and diatoms (plants)	Grow in open and sunlit waters; green-color slimes. Controlled by copper compounds.
Protozoa	Live on smaller organisms in the contaminated, open aqueous environments. Controlled with biocides.

Modified after Jones (1988, p. 130).

cillus is a well-known bacteria causing corrosion. Due to their metabolic activity, they oxidize sulfur and produce sulfuric acid. They proliferate in the soils near sulfur plants and in conduits with sour produced water. According to Videla (1996, p. 34), there are two types of process involved in the sulfur cycle:

1. Assimilatory sulfate reduction
2. Dissimilatory sulfate reduction

In the assimilatory sulfate reduction, sulfate is used by microorganisms as the sulfur source in metabolic process involving reduction of sulfates to organic sulfides. On the other hand, in the dissimilatory sulfate reduction, sulfate is used as the terminal electron acceptor to produce hydrogen sulfide in the anaerobic respiration. *Desulfovibrio desulfuricans* is one of the most famous corrodants of the former category (Figure 3.2).

Iron-oxidizing bacteria are microorganisms that are involved in the corrosion process. These bacteria generally oxidize Fe^{2+} to Fe^{3+}, which usually precipitates as ferric hydroxide. The families of microorganisms include:

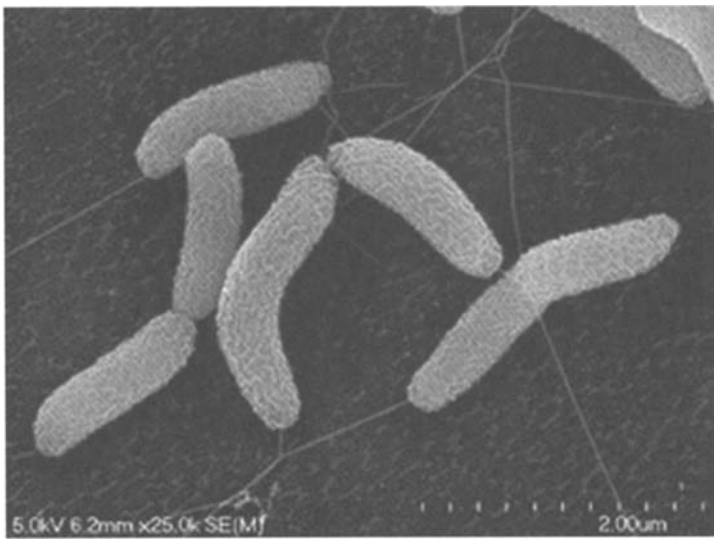

Figure 3.2 SEM photograph of *Desulfovibrio desulfuricans* (http://www.lbl.gov/Publications/Currents/Archive/Apr-30-2004.html).

1. *Caulobacteraceae*
   (a) *Gallionella*
   (b) *Siderophacus*
   (c) *G. ferruginea*

2. *Clamidobacteriaceae*
   (a) *Sphaerotilus*
   (b) *Leptothrix*

3. *Crenothiaceae*
   (a) *Crenothrix*
   (b) *Clonothrix*

3.4.2 Eukaryotes

As mentioned before, the main eukaryotic microorganisms are fungi, algae, and protozoans. The most well-known fungus associated with microbial corrosion is *Hormoconis resinae*, which can grow on wide range of organic compounds including hydrocarbons. According to Videla (1996, p. 41), the *Hormoconis resinae* (1) facilitate the formation of pits at the fixation points of tank walls, (2) produce organic acids (which are corrosive to aluminum), (3) consume nitrates, and (4) create redox conditions for passivity breakdown.

In the case of algae, corrosion occurs as a result of metabolic production of oxygen (algae produce oxygen when exposed to light photosynthesis). Some species produce organic acids. Corrosion generally occurs as blockage of pipes in cooling water towers, creating pH changes which affect water treatment efficiency (Videla, 1996). Among the algae associated with microbial corrosion, the most relevant are *Navicula*, *Oscillatoria*, and *Ulothrix* (see Figure 3.3).

3.5 DIFFERENT MECHANISMS OF MICROBIAL CORROSION

According to Videla (1996), microbial corrosion involves different kinds of mechanisms:

1. Production of compounds, due to metabolic bacterial activities, which change the medium to a corrosive one.

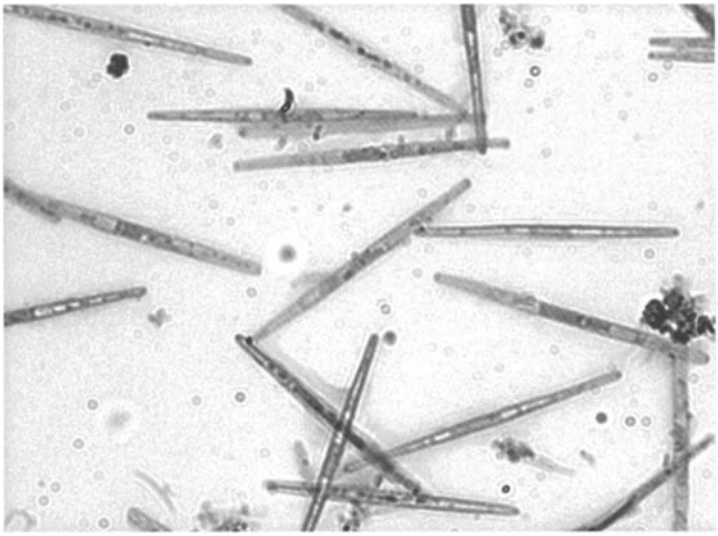

Figure 3.3 *Navicula* corrosive algae (www.acadweb.wwu.edu/courses/envr429-rm/).

2. Respiration characteristics.
3. Consumption of corrosion inhibitor.
4. Acceleration of corrosion reaction rate at the anode and cathode.
5. Removal of the protective film on metal surfaces.

Microorganisms can produce surfactants, inorganic acids, carboxylic acids, or sulfide ions (in the case of sulfate-reducing bacteria [SRB]), which will convert the environment to highly corrosive.

Microorganisms can also increase the corrosion rate at the anode and cathode. At the anode, organic acid production by different types of fungi causes corrosion, whereas sulfide anions are produced as a consequence of dissimilatory reduction of sulfates by SRB in anaerobic conditions. In the case of sulfate-reducing bacteria, the production of H_2S at cathode will facilitate corrosion.

As shown in Figure 3.4, sulfate reducers can also proliferate under a layer of aerobic organism slime deposit in aerated water.

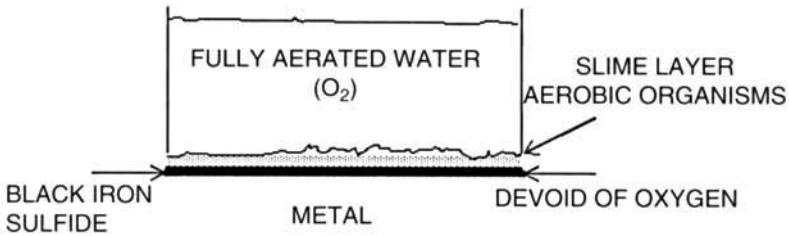

Figure 3.4 Schematic diagram of sulfide corrosion under aerobic slime deposit. Corrosion of iron by H_2S, generated by sulfate reducers.

3.6 CORROSION INHIBITION BY BACTERIA

Some bacteria can also inhibit corrosion. The inhibition generally occurs as a result of biofilm formation on the surfaces of metals or alloys, which slows down anodic and/or cathodic reactions. The biofilm increases the electrolyte resistance of the circuit.

Microorganisms' respiratory metabolic processes can also modify the oxygen concentration, at the metal–solution interface (see Videla, 1996, p. 122).

There are three types of bioinhibitors:

1. Bioinhibitors with oxidizing properties
2. Bioinhibitors dissolving oxygen to form a biofilm
3. Adsorption-type bioinhibitors

Guiamet et al. (1987) and Videla et al. (1988) have reported that *Serratia marcescens* decreases the medium corrosiveness.

3.7 MICROBIAL CORROSION CONTROL

Methods for controlling the microbial corrosion include:

1. Use of biocides
2. Use of corrosion inhibitors
3. Cathodic protection
4. Material selection

Inasmuch as most of the corrosion inhibitors are either expensive or harmful to humans and ecosystem, only few chemicals are being used in oil field and water transport systems. Some of these chemicals are presented in Table 3.2.

Abiocide is a chemical substance capable of killing different forms of living organisms. Biocides are used in the fields of agriculture, forestry, and mosquito control. There are two main categories of biocides:

1. Antimicrobials: include germicides, antibiotics, antibacterials, antivirals, antifungals, antiprotozoans, and antiparasites (also spermicides)
2. Pesticides: include fungicides, herbicides, insecticides, algicides, molluscicides, miticides, and rodenticides

Biocides can also be added to other materials (typically liquids) to protect the material from biological infestation and growth. For example, certain types of quaternary ammonium compounds (quats) can be added to pool water or industrial water systems to act as an algicide, protecting the water from infestation and growth of algae. Chlorine can be added in low concentrations to water as one of the final steps in wastewater treatment as a general biocide to kill microorganisms, algae, etc. It is often impractical to store and use poisonous chlorine gas for water treatment, so alternative methods of effectively adding chlorine are used. Adding hypochlorite solutions to pools, etc. is one possible solution. Hypochlorite can gradually release chlorine into the water (see Henry and Heinke, 1996, for details). Even more

Table 3.2 Bacterial control agents.

Bacterial control agents
Alkyl-aryl quaternary ammonium chlorides
Chlorine-hypochlorites[a]
Aldehydes
Chlorinated phenols
Fatty amines and salts
Alkyl thiocarbamates
Acrolein

After Jones (1988, p. 134).
[a] See Henry and Heinke (1996) for details.

convenient are compounds such as sodium dichloro-s-triazinetrione (dihydrate or anhydrous), sometimes referred to as dichlor, and trichloro-s-triazinetrione, sometimes referred to as trichlor. These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to pool water or industrial water systems, the chlorine atoms hydrolyze from the rest of the molecule forming hypochlorous acid (HOCl), which acts as a general biocide killing germs, microorganisms, algae, etc. Halogenated hydantoin compounds are also used as biocides (http://en.wikipedia.org/).

Chlorine gas hydrolyzes in water to form hypochlorous acid (prime disinfecting agent):

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \tag{3.2}$$

Hypochlorous acid, in turn, dissociates into H^+ and hypochlorite (OCl^-):

$$HOCl \leftrightarrow H^+ + OCl^- \tag{3.3}$$

HOCl plus OCl^- are called *free available chlorine*, available for disinfection.

Disinfection of water by ozone (O_3) is called *ozonation*. Ozone is a powerful oxidizer of inorganic and organic impurities and is effective against *Cryptosporidium*.

Ultraviolet (UV) radiation is not very effective for turbid effluents and is relatively expensive compared to chlorination. Its advantage is the fact that no chemical residues are left after treatment.

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CHAPTER 4

CORROSION CONTROL AND DETECTION

4.1 INTRODUCTION TO CORROSION CONTROL

It is impossible to stop corrosion attack completely. Therefore, the primary objective of a corrosion engineer is to slow down and to decelerate corrosion by protecting the materials and equipment in the most practical and economical way possible. In oil industry, several corrosion control methods were implemented widely on all fronts. Chemical inhibition, cathodic protection, corrosive gases removal, coatings, material selection and design, etc., are different methods that will be discussed in this chapter as corrosion control measures. The economic aspects are discussed in Chapter 8. (See Jones, 1988.)

4.2 CATHODIC PROTECTION

Cathodic protection involves supplying electrons to the metal to make the corrosion potential more negative. Complete protection is achieved when all the surface area of the metal acts as a cathode in the particular environment.

The increase in electronegative potential can be achieved by use of sacrificial anodes (magnesium, aluminum, and zinc) or by an impressed direct current. The potentials required for protection differ with the environment and the electrochemical reactions that are involved. For example, Blount (1970) noted that iron corroding in neutral aerated soil has a reduction potential of 0.579 V. The potential is limited by the

activity and solubility of ferrous hydroxide. If iron is exposed to H_2S in oxygen-free environment, the potential is increased to 0.712 V and is controlled by the solubility of ferrous sulfide.

The theory of cathodic protection is illustrated in Figure 4.1, which shows that the polarization of cathodic areas of steel must be extended until the potential E_c of the cathodic surfaces reaches the potential E_a of the anodic surfaces. The current that is applied in cathodic protection (I'') must exceed the equilibrium corrosion current (I') of the metal in its corrosive environment without cathodic protection.

Measurements of potential are made by use of reference half cells. The copper–copper sulfate half cell is widely used for potential measurements of pipe in soils. The criteria for protection of iron with this half cell are −0.85 V in aerated soil and −0.98 V in an H_2S system. A schematic diagram of cathodic protection is presented in Figure 4.2.

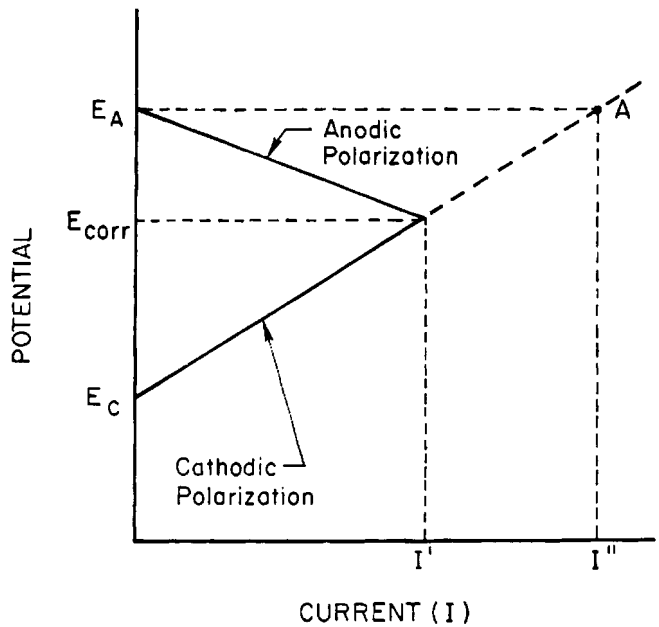

Figure 4.1 Diagram illustrating the theory of cathodic protection. I'' = current required to produce complete cathodic protection. Current must exceed equilibrium corrosion current I' to provide any protection. Corrosion will cease when the flow of cathodic current (I'') increases cathodic polarization to the open circuit potential (E_A) of the anode as shown at point A.

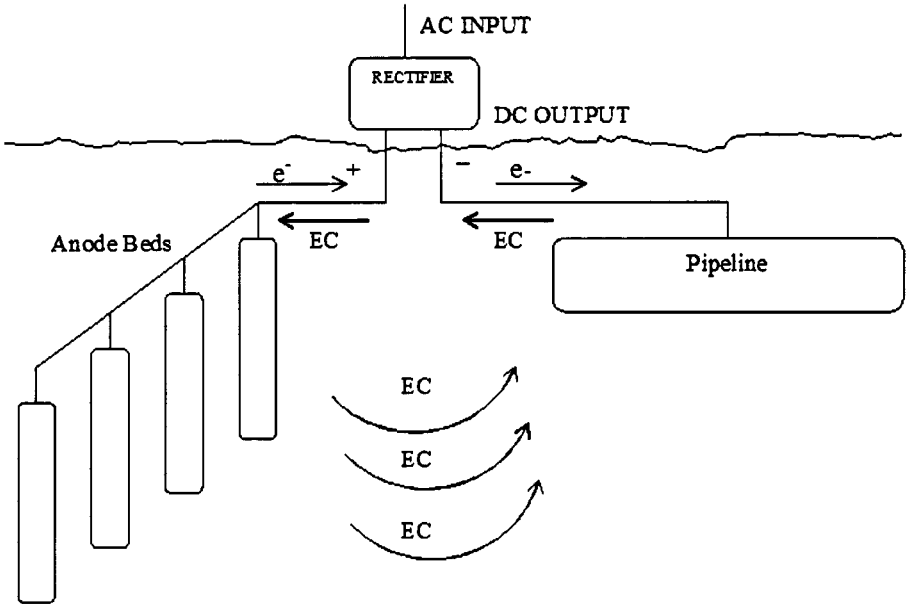

Figure 4.2 Schematic diagram of cathodic protection of a pipeline.

The current density requirements to maintain protective potentials will vary with the environment. Pipe in soil or water, and vessel and tank interiors may develop protective resistances on the surfaces by an increase in pH and the precipitation of scales with the application of cathodic protection.

The current density required for cathodic protection is related to the velocity and supply of corrodants to the metal surface. For example, protective potential can be achieved in a calm seawater environment with 3–5 mA/ft^2, whereas 70 mA/ft^2 or more is required in the high-velocity waters of Cook Inlet in Alaska, as noted by Bertness and Blount (1989).

In general, the current density required for cathodic protection of steel structures in seawater ranges from about 5 to 80 mA/ft^2. In the mud zone, a current density of only 1–4 mA/ft^2 is required (Cron and Marsh, 1983, p. 1039).

In the case of impressed-current cathodic protection, alternating current is converted to direct current by rectifiers. As compared to the galvanic cathodic protection, electrical current is purchased as needed and fewer anodes are used. In addition, renovation and repairs are not

as difficult as the replacement of an entire galvanic system (Cron and Marsh, 1983, p. 1039).

The disadvantages of impressed-current system are the delay in initiating cathodic protection after placement of platform on the seafloor. In cathodically protecting offshore pipelines, sacrificial anodes (e.g., zinc) can be placed in the form of bracelets along the pipeline at certain intervals. A newly developed aluminum alloy is also operative in mud. Larger sacrificial anodes can also be placed alongside the pipe and connected to the pipe with a cable. Cron and Marsh (1983, p. 1037) pointed out the insulation is an economical practice and should be used universally except when flowlines are incorporated into a cathodic protection system (e.g., on offshore platforms). Decision as to whether to use cathodic protection or not is reached after studying the leak frequency curve, expected well life, and leak repair costs. Protection cost is around US\$0.60/yr/ft^2 of surface allowing for installation, maintenance, and operating costs.

Cron and Marsh (1983, p. 1036) showed that in pipelines, casings, etc., the log of cumulative leaks is sometimes a linear function of time. Cathodic protection can be used only for preventing the external corrosion of casing and not the internal corrosion.

In the case of mooring chain links, much corrosion can be prevented through use of a cathodic protection. Individual links, however, must be bonded to a cable for electrical continuity. As pointed out by Cron and Marsh (1983, p. 1041), aluminum anodes in sufficient number attached to the buoy can protect the chain and the buoy.

Because of the differences in availability of dissolved oxygen, long cell action may be set up between the lower parts of casing (and the surface flowlines) and upper parts of the casing. Thus, it is indispensable either to apply cathodic protection to surface structures, as well as to the casing, or to insulate the casing completely from the large surface structures.

Comprehensive monitoring of potential of cathodic protected structures is required to maintain effective control of corrosion. Polarization tests are recommended for determining the current requirements for complete protection of well casings and pipelines as discussed by Kubit (1968).

By studying different types of corrosion cells, one will realize that as soon as the cell starts to conduct current, polarization (Figure 4.6) takes place (see Chapter 1), in which the potential difference of each cell is reduced until it reaches the quasiequilibrium state. Different equilibrium states are illustrated in Figures 4.3, 4.4, and 4.5 (see Parker and Peattie, 1999).

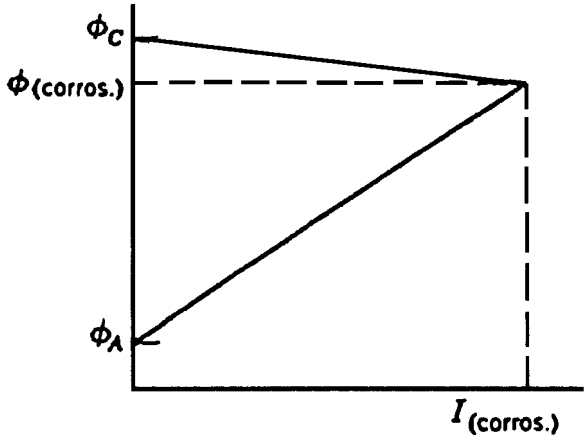

Figure 4.3 Anodic control (after Parker and Peattie, 1999, p. 151, figure B-1; courtesy of Elsevier).

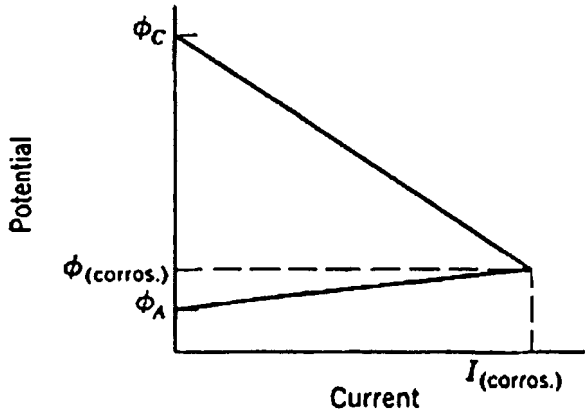

Figure 4.4 Cathodic control (after Parker and Peattie, 1999, p. 151, figure B-2; courtesy of Elsevier).

4.3 CONDITIONS FOR THE STEADY STATE OR LIMITING CORROSION RATE

Steady state exists when energy decrease in the corrosion process is equal to the sum of energies dissipated in the various parts of the electrochemical system.

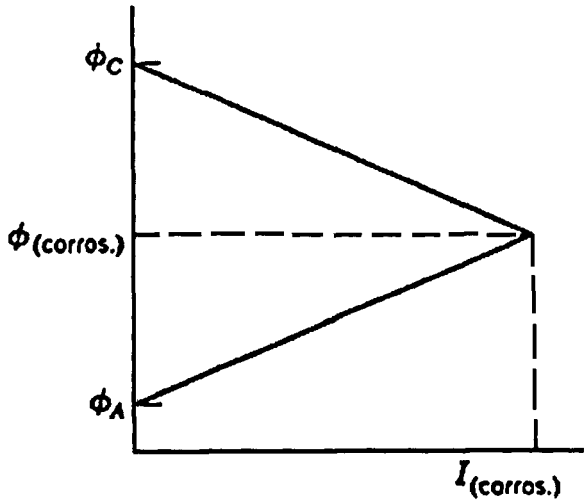

Figure 4.5 Mixed control (after Parker and Peattie, 1999, p. 151, figure B-3; courtesy of Elsevier).

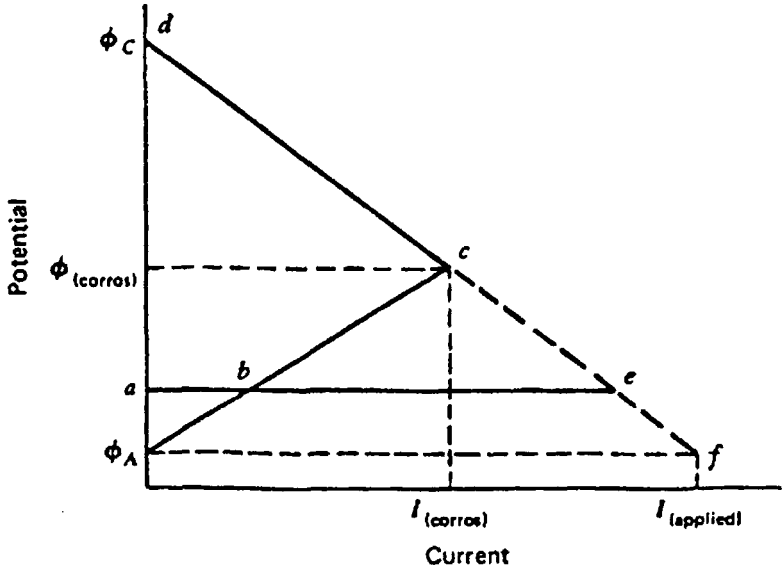

Figure 4.6 Polarization diagram illustrating principle of cathodic protection (after Parker and Peattie, 1999, p. 151, figure B-4; courtesy of Elsevier).

$$\text{At equilibrium}, -\Delta F = 0 = \Sigma NEF$$

where $-\Delta F$ = decrease in the free energy of corrosion reaction; N = number of equivalent taking part in the reaction; F = Faraday = 96,000 coulombs; E = potential.

This leads to the following equation:

$$E'_R = E_A + E_C + E_{IR_i} + E_{IR_e}$$

where E'_R = reversible, emf of the couple; E_A = total polarization of the anodic areas; E_C = total polarization of the cathodic areas; E_{IR_i} = internal *IR* drop of cell; E_{IR_e} = external *IR* drop of cell.
The total polarization at the anodic areas (E_A) is equal to the sum of:

1. *IR* drop through films which may cover the anodic surface
2. Concentration polarization at the anode
3. Possible anodic overvoltage due to some slow process in the overall anodic reaction.

The total polarization at the cathode areas E_C is the sum of:

1. *IR* drop through films
2. Concentration polarization at the cathode
3. Cathodic overvoltage

The internal *IR* drop of the cell (E_{IR}) is the product of the current flowing times the resistance of the electrolyte between cathode and anode areas.

The external *IR* drop of the cells (E_{IR}) is the product of current flowing times the resistance of the metal between anode and cathode areas. Inasmuch as the external resistance R_e is usually very small, the E_{IR} may be neglected.

Figure 4.7 shows that all the dissipative terms are function of current density, and how they limit the corrosion rate.

The corrosion process is under (1) anodic control, if the major factor is E_A, and (2) cathodic control, if the major factor is E_C. Inhibitors function by increasing the magnitude of one or more of these dissipative or irreversible effects, although they usually have little effect upon E_{IR_i}.

If an inhibitor increases E_A, it is an anodic inhibitor, whereas if an inhibitor increases E_C, it is a cathodic inhibitor. These effects are illustrated in Figure 4.8, where the process in the absence of inhibitors is

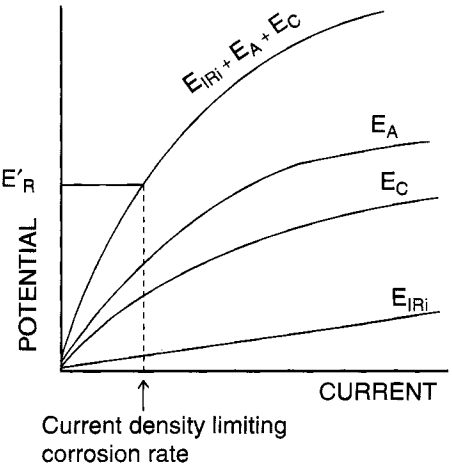

Figure 4.7 Effect of current density on dissipative terms.

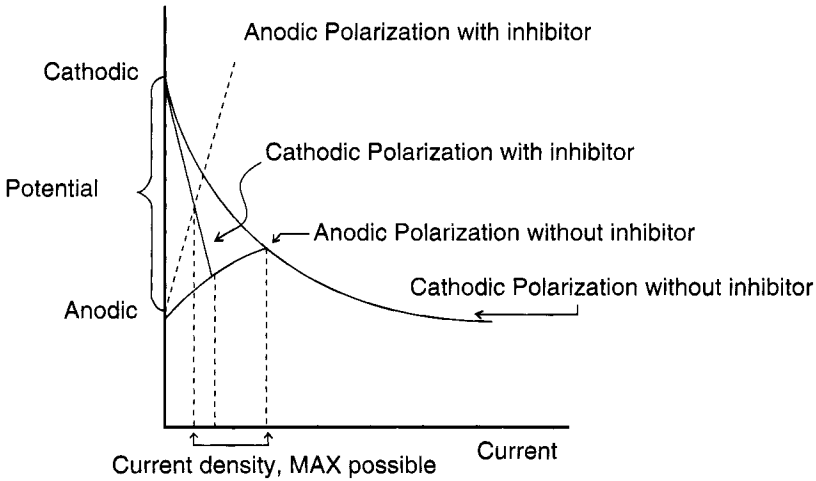

Figure 4.8 Effect of inhibitors on potentials.

under cathodic control mainly, but an anodic inhibitor might bring the process under mixed or anodic control.

4.3.1 Dangerous Inhibitors

An insufficient concentration of an anodic inhibitor in a system that is under cathodic control will intensify the attack on small, localized areas, which leads to pitting and early perforation. The concentration of anodic inhibitor required depends on the concentration of ions such as chloride or sulfate, which interfere with the formation of passivating films. Other factors that are considered in determining the required concentration include:

1. Composition of the environment
2. Agitation of the liquid
3. Stresses in the metal
4. Composition of the metal
5. Contact with dissimilar metal
6. Temperature

4.4 INHIBITORS AND PASSIVATORS

As pointed out by Jones (1988, p. 21), the technology of corrosion inhibition is largely an art. An inhibitor is a chemical substance or a mixture that decreases corrosion when added to an environment (usually in small concentration). A passivator, on the other hand, is an inhibitor which appreciably changes the potential of a metal to a more noble value (cathodic value).

Anodic inhibitors for iron in water are soluble hydroxides, chromates, phosphates, carbonates, and silicates. These substances increase anodic polarization, probably by helping to form (or to repair) a protective film on the metal surface.

Cathodic inhibitors for iron partially immersed in water are magnesium, zinc, and nickel salts. In aqueous medium, as O_2 is reduced at cathodic areas, the pH is increased, resulting in the precipitation of $Mg(OH)_2$, $Zn(OH)_2$, or $Ni(OH)_2$ over the cathodic surfaces as a fairly adherent porous deposit. Thus, the reaction is slowed down because O_2 must diffuse through these deposits in order to reach the cathodic surfaces. In waters containing CO_2, the calcium salts act similarly by

precipitating $CaCO_3$ on the cathodic areas as a result of increasing pH.

An insufficient concentration of an anodic inhibitor in a system that is under cathodic control intensifies the attack on small, localized areas. This results in pitting and early perforation. The required concentration of anodic inhibitor depends on the concentrations of ions such as chloride or sulfate, which interfere with the formation of passivating films. Other factors that are considered in determining the required concentration of anodic inhibitor include:

1. Agitation of the liquid
2. Composition of the environment
3. Stresses in the metal
4. Composition of the metal
5. Contact with dissimilar metal
6. Temperature

Certain inhibitors change the electrochemical potential of a metal to more cathodic or noble value. These inhibitors are called passivators, and they are frequently anodic inhibitors. The cathodic inhibitors are not likely to act as passivators. The iron will stay bright indefinitely in water containing a sufficient amount of chromate (anodic inhibitor).

The pigments that are used in priming paints usually contain passivators. For example, zinc chromate is a pigment which is soluble enough in water and diffuses through the paint film, bringing a small concentration of chromate ions ($C_rO_4^{2-}$) to the metal surface. An appreciably less soluble chromate, such as lead chromate, does not have this property.

The chromate ions form a thin protective film on the surface. This film is composed of an insoluble iron compound such as iron chromate or a ferric-chromic oxide mixture. According to the electron configuration theory, the chromate ions form an adsorbed layer on iron. This film adsorbs and shares electrons of the surface iron atoms and satisfies secondary valence forces; however, it does not disrupt the metal lattice. Thus, the metal surface becomes less reactive and more noble in the galvanic series (see Jones, 1988).

Sodium nitrite ($NaNO_2$) is used as a passivator in oil pipelines and renders the iron several tenths of a volt more noble than it was originally. The nitrite ion is oxidizing in nature and, therefore, acts like chromates or other oxidizing passivators to reduce corrosion.

Organic inhibitors are used for corrosion control in producing operations. Generally the inhibitor affects both the anodic and cathodic reactions by adsorption on the metal surface.

The use of electrochemical methods to evaluate corrosion inhibitors under laboratory and field conditions was discussed by Martin (1979, 1982). One should always keep in mind the fact that some inhibitors can change the wettability of rocks, which is of great importance to reservoir engineers.

The reader is referred to the excellent discussion of fundamentals of inhibitors by Hackerman and Snavely (1971).

4.4.1 Classification of Inhibitors

Based on functional behavior, inhibitors can be grouped as follows (see Jones, 1988, and NACE, 1979):

1. *Reactive inhibitors* involving chemical reaction with metal or environment.
2. *Adsorptive inhibitors* which form some type of film on the metal surface to be protected.
3. *Precipitation inhibitors* which cause formation of precipitates on the surface of metal, creating a protective film.

The corrosion process can be slowed down by:

1. Enhancing the anodic or cathodic polarization, or both.
2. Causing reduction in ion diffusion to metal surface.
3. Improving the electrical resistance at the metal–electrolyte interface.
4. Increasing the hydrogen overvoltage.

Often inhibitors are classified into organic and inorganic.

Inhibitors Used in Beam Pumping

In beam pump-style pumping units, it is important to consider corrosion inhibitors while selecting an optimum subsurface pump. Corrosion inhibitors can increase the service life of the pump and reduce the pump failure costs (Axelson, 1999).

There are several methods used to inject the inhibitor into a producing well. Two basic types are:

1. Batch treatment
2. Continuous treatment

In batch treatment, an inhibitor is added periodically. The most successful batch treatment is when inhibitor can be introduced into the production column. The advantage of batch treatment is that the tubing and pump are exposed to high concentration level of inhibitor and, thus, have the best chance of being covered by a protective film.

Another type of batch treatment is to (1) introduce the inhibitor in the well, (2) flush the inhibitor around the bottom of well, and (3) circulate out through the production column.

In the continuous treatment method, the inhibitor is introduced continuously by means of a pump which can be electrical or gas-driven. The pump can also be operated by the beam unit itself. The inhibitor must be flushed down the annulus so that it can be commingled with produced fluid and returned through the production column.

It is important to remember that some inhibitors can change the wettability of reservoir rocks (e.g., from water-wet to oil-wet). Thus, the reservoir engineer should be aware of this fact.

In conclusion, in the opinion of the authors, actual field service is the best way of choosing the right inhibitor. Obviously, laboratory tests should also be conducted.

1. Organic inhibitors

Organic inhibitors contain carbon-to-carbon groups (–C–C–) in their molecules. Some of the organic inhibitors have oil-wetting preference. The polar amine group (Figure 4.9) adsorbs on the metal to be protected, forming an oily water-repellant (hydrophobic) surface film. The oil films can act as barriers by replacing and repelling water from the metal surface.

Oleic imidazoline (and its derivatives), used in oil field pipelines, constitutes an example of organic chemical inhibitor (Figure 4.10).

Table 4.1 shows some common types of organic and inorganic inhibitors (see Jones, 1988, and NACE, 1979).

2. Inorganic inhibitors

Inorganic inhibitors include crystalline salts (e.g., sodium chromate, sodium silicate, and sodium phosphate), which dissociate in water

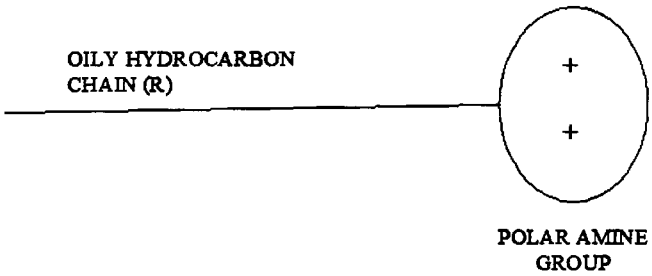

Figure 4.9 Schematic diagram of "semi-polar" organic inhibitor. R = hydrocarbon portion of the molecule.

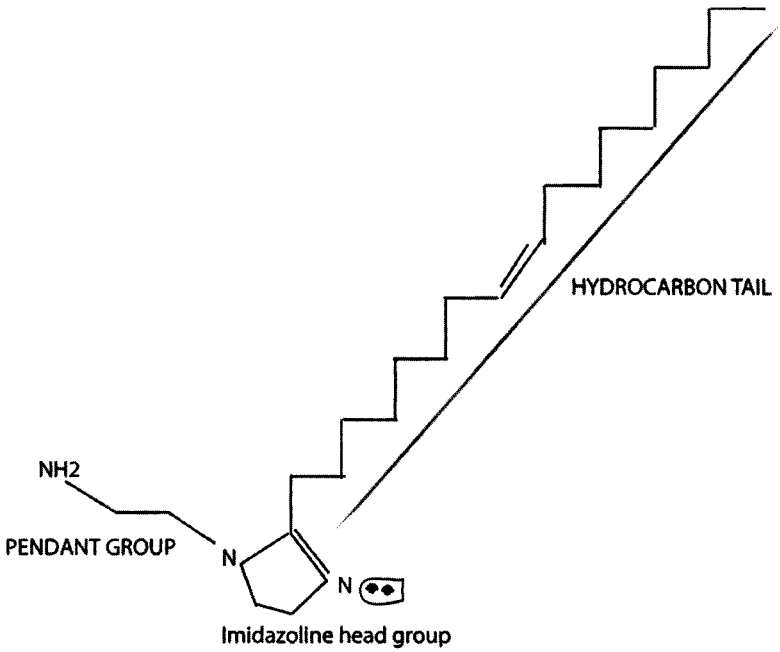

Figure 4.10 Oleic imidazoline–organic chemical inhibitor (used widely in oilfield pipelines).

Table 4.1 Common inhibitors.

Inhibitor Class	Example
Organic, anionic	Sodium phosphonates
Organic, cationic	$R{\cdot}NH_2$, $R_2{\cdot}NH$, $R_3{\cdot}N$, and $[R_4N]^+$ R = hydrocarbon portion of molecule
Inorganic anions	Sodium chromate (CrO_4^{--}) Sodium silicate (SiO_3^{--}) Sodium phosphate (PO_4^{--}) Sodium molybdate (MoO_4^{--})
Mixed-charge inhibitors	Zinc cation (Zn^{++})

Also, see Jones (1988, p. 21).

forming cations and anions. Only the negative anions are involved in reducing corrosion. Thus, they are called inorganic-anionic inhibitors. If zinc is used instead of sodium, they are called inorganic mixed-charge inhibitors. The primary use of inorganic inhibitors is in cooling water towers.

4.5 COATING

Many paints, coatings, and high-performance organic coatings have been developed to protect the equipment from environmental damage and corrosion. Coating is widely used to protect the carbon and low-alloy steels. Organic coatings are able to absorb the corrosive agents (O_2, CO_2, organic solvents, and water vapor).

In order to achieve a long-term protection in designing corrosion-resistant coatings, one should consider the following:

1. Component design
2. Coating formulation
3. Component function
4. Coating protection

Coatings usually contain between 15 to 20 ingredients with their own range of functionality. In designing coatings, one should consider the following (http://www.corrosiondoctors.org):

1. Permeability: The coating layer should be impermeable to corrosive agents, have high dielectric constant, and have a good adhesion to the underlying layer.
2. Cathodically protective pigments: Cathodic protection of coatings is usually achieved by adding a primer. The main function of these additives is to shift the potential of the environment to a less corrosive cathodic potential.
3. Inhibition: Inhibitive coatings react with a certain environment to provide a protective layer on the metallic surfaces.

After applying the coatings to the surface, coating should convert into a dense, solid, and adherent material. The material called binder is used to achieve this. It provides uniformity and coherence to the coating system. The ability of a binder to form a dense film is controlled by its molecular size. Binders that have the highest molecular weight will form films upon evaporation, whereas binders with smaller molecular weight will generally react in situ. The common binders used are presented in Table 4.2.

Only in very few cases, the failure of a coating is due to corrosion of coating itself caused by (Heitz et al., 1992):

1. Formation of blisters
2. Reduction or loss of adhesion

Table 4.2 Common binders used in coating (http://www.corrosion-doctors.org).

Binder Class	Example
Oxygen-reactive binders	Epoxy esters
Lacquers	Acrylics
Heat-conversion binders	Hot melts
Co-reactive binders	Epoxies
Inorganic binders	Post-cured silicates

3. Cathodic disbonding
4. Pitting corrosion of the base material

4.6 DETECTION OF CORROSION

There are several methods of detecting corrosion. Corrosion can be prevented or reduced if corrosive environments are recognized. Early detection of active corrosion will allow initiation of control measures and usually will prevent serious damage. To identify active corrosion before a catastrophic failure damage occurs, factors that increase its rate should be examined. If any of these factors are present, corrosion rate should be measured. If the metal loss is not significant, it may be cheaper to allow the corrosion to continue than to combat it (Allen and Roberts, 1982).

The first step in control is identification of the factors causing corrosion. Visual inspections may be enough, but usually one needs to do more testing to verify conclusions obtained from the visual inspection (see Table 4.3).

Water, corrosive gases, air, contact of dissimilar metals, high fluid velocities, and concentration cell corrosion are some of the factors that enhance the corrosion.

The following tests could be conducted to identify types, cause, and severity of corrosion (Allen and Roberts, 1982):

4.6.1 Chemical Tests

Chemical tests may enable one to determine (1) the type and severity of corrosion, (2) the type and amounts of acid gases (H_2S, CO_2), and (3) oxygen dissolved in water, gas stream, vapor zones, and gas blankets. Scale, such as iron oxide, formed by corrosion can be analyzed chemically (see Allen and Roberts, 1982).

4.6.2 Microbial Tests

Bacteria-related corrosion can be detected by testing oil field water. Most oil field waters contain either aerobic or anaerobic bacteria. Sulfate reducers (anaerobic bacteria), which reduce sulfates to sulfides, are usually responsible for the bacteria-related corrosion in oil field

Table 4.3 Characteristic appearance of corrosion.

Appearance	Cause
Round-bottom connecting pits with sharp sides and bright bottoms. Grey deposit.	CO_2
Transverse fracture with little or no pitting. Black deposit. (Sulfide stress cracking due to excessive metal hardness.)	H_2S
Small conical pits with steep sides and smooth edges. Black deposit.	H_2S
Small conical pits with steep sides and smooth edges, with transverse cracks.	H_2S, tensile stress
General thinning with sharp feathery or web-like residual metal. Little or no deposits.	Mineral acid
Shallow widespread pitting or deep pitting or deep pits under rust nodules. Rust deposits.	O_2
Abraded or worn areas with numerous small pits.	Erosion by solids or metal rubbing in the presence of H_2S, CO_2, or O_2.
Single isolated pits in a row on one side.	Current discharge. Electrolytic corrosion.

Modified after Jones (1988, p. 96).

operations. Upon appearance of black iron sulfide in water or detection of a "rotten egg" odor, one should test for the presence of sulfate-reducing bacteria.

4.6.3 Electrochemical Tests

Electrochemical tests are used to check surface lines, well casing, and other buried steel structures for corrosion.

4.6.4 Pipeline Tests

Pipeline tests can detect areas of high corrosion. 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 (e.g., in brine-polluted areas) will be conducive to rapid corrosion (Allen and Roberts, 1982).

Before proposing routes for pipelines, resistance of soil can be measured along the proposed routes to locate areas of low soil resistivity (high corrosive areas, "hot spots"). Pipelines can then be either protected or laid in the least corrosive areas (for details, see Parker and Peattie, 1999).

4.7 MEASUREMENT OF CORROSION

Four methods are commonly used for evaluation of corrosion:

1. Inspection
2. Corrosion-rate test
3. Chemical-rate test
4. Examination of history of equipment performance

Different techniques are used depending on the cause of corrosion. The rate of corrosion can be determined by:

1. Visual inspection
2. Caliper surveys
3. Casing thickness logs

4.7.1 Visual Inspection

Careful examination with the naked eye gives indication of corrosion phenomena. One should first remove the impurities and coatings on the surface of equipment under inspection. For the parts that are inaccessible to the naked eye, an endoscope is used. An endoscope is an instrument that allows visual examination of the interior of hollow components. Depending on application, it is either rigid or flexible (Allen and Roberts, 1982).

4.7.2 Caliper Surveys

Caliper surveys are run for inspection of the internal surface of tubing or casing. Mechanical feelers contact the inside metal surface and detect

metal loss due to pitting, metal thinning, or rod wear. Caliper surveys are most useful if they are conducted periodically to determine the progression of pits or the metal loss of an area (Allen and Roberts, 1982).

4.7.3 Casing Thickness Logs

The casing thickness is measured by the casing inspection tool. The tool measures total thickness of metal at any point in the casing, pipeline, or tank. If the loss of metal inside the casing has been measured with an internal caliper, then the external metal loss can be calculated from the casing thickness data (see Jones, 1988, p. 95, for details).

Ultrasonic instruments are used for determining pipe or tank wall thickness. Piezoelectric transducers are used to generate a sound wave. The time interval between the input and received electrical pulses is a function of metal thickness, because the speed of sound in a certain metal is constant. The face of transducer must make contact with the metal.

4.7.4 Radiography

Radiographic imaging involves passing X-rays or gamma rays through valves, elbows, etc., in order to provide visual evidence of defects (pits, cracks, etc.) due to corrosion damage.

4.8 NONDESTRUCTIVE TEST METHODS

Ultrasonic or radioactive devices, which are used to measure the wall thickness and detect thinning of metal, may not detect small pits.

The Audio-Gauge and Penetron tools measure thickness of pipelines and tank walls with access to only one side. The Audio-Gauge tool measures sound travel time through the metal, whereas the Penetron tool measures intensity of gamma rays scattered by the metal. The principal limitation is that measurement of corrosion or change in metal thickness is made at only one point. Measurement is usually to the nearest 0.001 inch.

The list of different nondestructive test methods is presented below (Allen and Roberts, 1982):

1. Visual inspection
2. Surface defect examination
3. Eddy current inspection
4. Heat flux methods
5. Ultrasonic inspection
6. Radiographic inspection

4.8.1 Metal 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 finite 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 (Allen and Roberts, 1982).

4.8.2 Other Corrosion Rate Monitors

Other corrosion rate monitors include:

1. Test nipples
2. Various corrosion meters
3. Hydrogen probes and patches, and galvanic probes (for details, see Jones, 1988).

Iron content analysis of produced and injection waters is discussed in Chapter 7.

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CHAPTER 5
CASING AND PIPELINE CORROSION

5.1 INTRODUCTION

At a certain stage during the drilling of oil and gas wells, it becomes necessary to line the walls of borehole with steel pipe which is called casing. Casing serves numerous purposes during the drilling and production history of oil and gas wells, which include (Rahman and Chilingarian, 1995):

1. Keeping the hole open by preventing the weak formations from collapsing, i.e., caving of the hole.
2. Serving as a high-strength flow conduit to surface for both drilling and production fluids.
3. Protecting the freshwater-bearing formation from contamination by drilling and production fluids.
4. Providing a suitable support for wellhead equipment and blowout preventers for controlling subsurface pressure, and for the installation of tubing and subsurface equipment.
5. Providing safe passage for running wireline equipment.
6. Allowing isolated communication with selectively perforated formation(s) of interest.

5.2 TYPES OF CASING

When drilling wells, hostile environments such as high-pressured zones, weak and fractured formations, unconsolidated formations, and slough-

ing shales, are often encountered. Consequently, wells are drilled and cased in several steps to seal off these troublesome zones and to allow drilling to the total depth. Different casing sizes are required at different depths. The five general casings used to complete a well are (Rahman and Chilingarian, 1995):

1. Conductor pipe
2. Surface casing
3. Intermediate casing
4. Production casing
5. Liners

As shown in Figure 5.1, these casings (pipes) are run to different depths and one or two of them may be omitted depending on the drilling conditions. In offshore platform operation, it is also necessary to run a cassion pipe.

5.2.1 Cassion Pipe

On an offshore platform, a cassion pipe usually 26 to 42 inches in outside diameter (OD), is driven into the seabed to prevent washout of near-surface unconsolidated formation and to ensure the stability of the ground surface upon which the rig is seated. It also serves as a flow conduit for drilling fluid to the surface. The cassion pipe is tied back to the conductor or surface casing and usually does not carry any load (see Rahman and Chilingarian, 1995).

5.2.2 Conductor Pipe

The outermost casing string is the conductor pipe. The main purpose of this casing is to hold back the unconsolidated surface formations and prevent rocks from falling into the hole. The conductor pipe is cemented back to the surface. It is either used to support subsequent casing and wellhead equipment or the pipe is cut off at the surface after setting the surface casing. Where shallow water or gas flow is expected, the conductor pipe is fitted with a diverter system above the flowline outlet. This device permits the diversion of drilling fluid or gas flow away from the rig in the event of a surface blowout. The conductor pipe is not

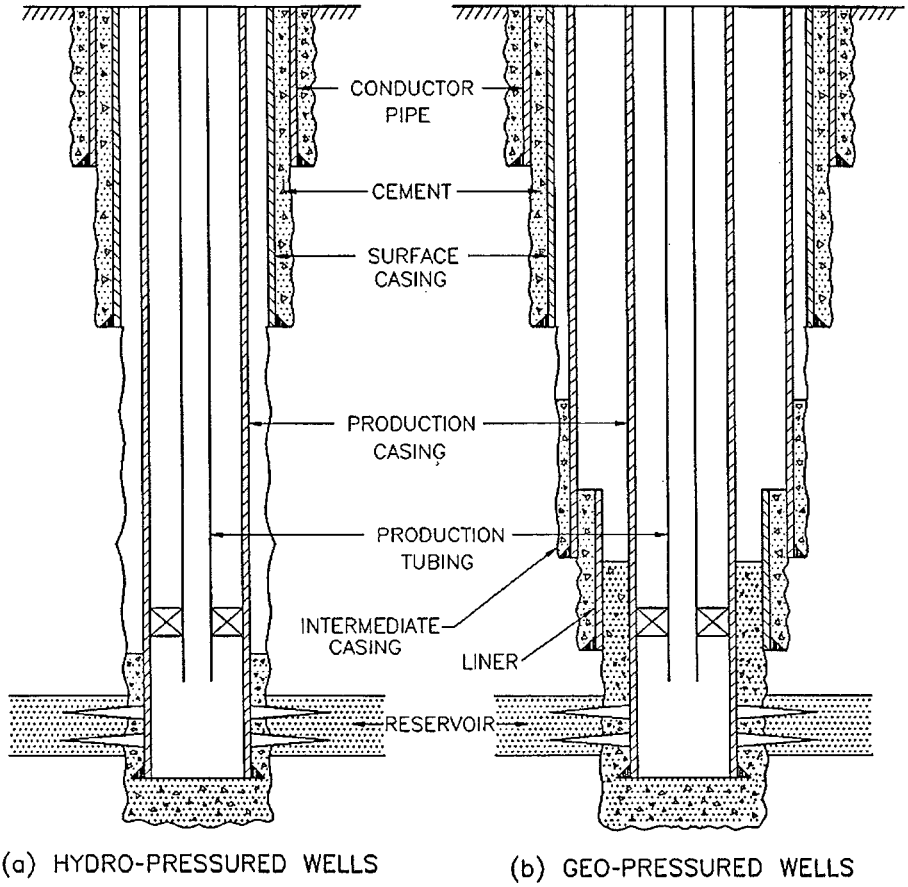

Figure 5.1 Typical casing program showing different casing sizes and their setting depths (after Rahman and Chilingarian, 1995, p. 2).

shut-in in the event of fluid or gas flow, because it is not set-in deep enough to provide any holding force.

The conductor pipe, which varies in length from 40 to 500 ft onshore and up to 1,000 ft offshore, is 7 to 20 inches in diameter. Generally, a 16-inch pipe is used in shallow wells and a 20-inch in deep wells. On offshore platforms, conductor pipe is usually 20 inches in diameter and is cemented across its entire length (Rahman and Chilingarian, 1995).

5.2.3 Surface Casing

The principal functions of the surface casing string include: (1) to hold back unconsolidated shallows formations that can slough into the hole and cause problems, (2) isolate the freshwater-bearing formations, (3) prevent contamination of the latter by fluids from deeper formations, and (4) to serve as a base on which to set the blowout preventers. It is generally set in competent rocks, such as limestone or dolomite, so that it can hold any pressure that may be encountered between the surface casing seat and the next casing seat.

Setting depths of surface casing vary from a few hundred feet to as much as 5,000 ft. Sizes of the surface casing vary from 7 to 16 inches in diameter, with $10\frac{3}{4}$ and $13\frac{3}{8}$ inches being the most common sizes. On land, surface casing is usually cemented to the surface. For offshore wells, the cement column is frequently limited to the kickoff point (see Rahman and Chilingarian, 1995).

5.2.4 Intermediate Casing

Intermediate or protective casing is set at a depth between the surface and production casings. The main reason for setting intermediate casing is to isolate the formations that prevent the well from being drilled to the total depth. Troublesome zones include those with abnormal formation pressures, lost circulation, heaving and sloughing shales, and salt sections. When abnormal formation pressures are present in a deep section of the well, intermediate casing is set to protect formations below the surface casing from the pressures created by drilling fluid specific weight required to balance the abnormal pore pressure. Similarly, when normal pore pressures are found below sections having abnormal pore pressure, an additional intermediate casing may be set to allow for the use of more economical, lower specific weight drilling fluids in subsequent sections. After penetrating the lost circulation zone, unstable shale, or salt section, intermediate casing is required to prevent well problems while drilling below these sections (Rahman and Chilingarian, 1995).

Intermediate casing varies in length from 7,000 ft to as much as 15,000 ft and from 7 to $11\frac{3}{4}$ inches in outside diameter. It is commonly cemented up to 1,000 ft from the casing shoe and hung onto

the surface casing. Longer cement columns are sometimes necessary to prevent casing buckling.

5.2.5 Production Casing

Production casing is set through the prospective productive zones except in the case of openhole completions. It is usually designed to hold the maximal shut-in pressure of the producing formations and may be designed to withstand stimulating pressures during completion and workover operations. It also provides protection for the environment in the event of failure of the tubing string during production operations and allows for the production tubing to be repaired and replaced (Rahman and Chilingarian, 1995).

Production casing varies from $1\frac{1}{4}$ to $9\frac{5}{8}$ inches in diameter, and is cemented far enough above the producing formations to provide additional support for subsurface equipment and to prevent casing buckling.

5.2.6 Liners

Liners are the pipes that do not reach the surface, and are suspended from the bottom of the casing string above. Usually, they are set to seal off troublesome sections of the well or through the producing zones for economic reasons. Basic liner assemblies are shown in Figure 5.2. They include drilling liner, production liner, tieback liner, scab liner, and scab tieback liner (Brown-Hughes Co., 1984).

1. **Drilling liner:** Drilling liner is a section of casing that is suspended from the existing casing (surface or intermediate casing). In most cases, it extends downward into the openhole and overlaps the existing casing by 200 to 400 ft. It is used to isolate abnormal formation pressure, lost circulation zones, heaving shales and salt sections, and to permit drilling below these zones without having well problems.
2. **Production liner:** Production liner is run instead of full casing to provide isolation across the production or injection zones. In this case, intermediate casing or drilling liner becomes part of the completion string.

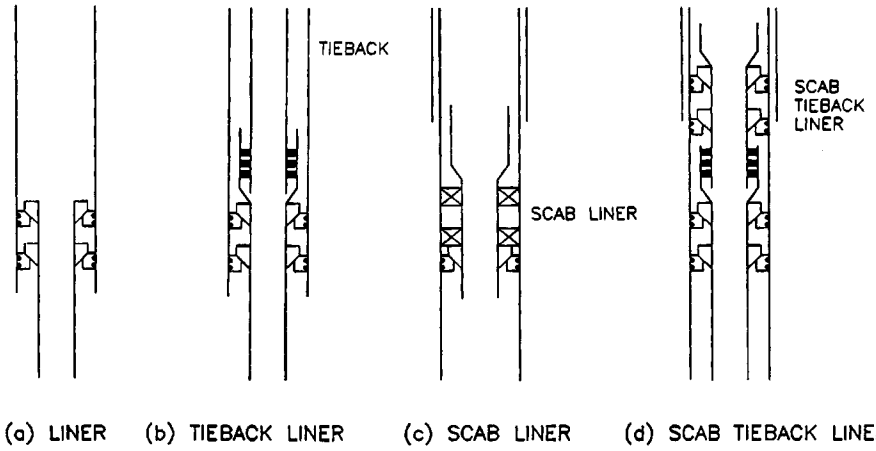

Figure 5.2 Basic liner systems (after Brown-Hughes Co., 1984).

3. **Tieback liner:** Tieback liner is a section of casing extending upwards from the top of the existing liner to the surface. This pipe is connected to the top of liner (Figure 5.2b) with a specially designed connector. Production liner with tieback liner assembly is most advantageous when exploratory drilling below the productive interval is planned. It also gives rise to low hanging weights in the upper part of the well.
4. **Scab liner:** Scab liner is a section of casing used to repair existing damaged casing. It may be cemented or sealed with packers at the top and bottom (Figure 5.2c).
5. **Scab tieback liner:** Scab tieback liner is a section of casing extending upward from the existing liner, but which does not reach the surface and is normally cemented in place. Scab tieback liners are commonly used with cemented heavy wall casing to isolate salt sections in deeper portions of the well.

Possible leaks across the hanger and the difficulty in obtaining a good primary cement job due to the narrow annulus must be taken into consideration.

5.3 CORROSION OF STEEL

In many corrosion problems, the important differences in reaction potentials are not those between dissimilar metals but those which exist between separate areas interspersed over all the surface of a single metal. These potential differences result from local chemical or physical differences within or on the metal, such as variations in grain structure, stresses, scale, inclusions in the metal, grain boundaries, scratches, or other surface conditions. Steel is an alloy of pure iron and small amounts of carbon present as Fe_3C with trace amounts of other elements. Iron carbide (Fe_3C) is cathodic with respect to iron (Rahman and Chilingarian, 1995).

Inasmuch as in typical corrosion of steel anodic and cathodic areas lie side by side on the metal surface, in effect it is covered with both positive and negative sites. During corrosion, the anodes and cathodes of metals may interchange frequently.

5.3.1 External Casing Corrosion

The external casing corrosion may be caused by the presence of one or combination of the following (Rahman and Chilingarian, 1995):

1. Presence of corrosive formation water (having high salinity).
2. Presence of bacterially generated H_2S
3. Presence of electrical currents
4. Presence of corrosive completion fluids
5. Presence of faults which cross the borehole (this gives rise to weak, damaged steel zones susceptible to corrosion).

Electrolytic corrosion is the main source of casing corrosion. The current flow may originate from (1) potential gradients between the formations traversed by the casing, (2) potential difference between the well casing and long flowline, or (3) electrical grounding systems and connecting flowlines.

The origin of stray currents is not easy to determine. The use of voltmeter across an open flowline-to-wellhead flange, however, will show whether or not the electrical current is entering the well, i.e., whether or not electrons are leaving the casing.

5.3.2 Casing Corrosion Inspection Tools

A variety of tools and interpretation techniques are employed to monitor corrosion because a large amount of information is required for interpretation from both single and multiple casing. Four types of tools are considered here (Cryer et al., 1987):

1. Electromagnetic casing corrosion detection
2. Multi-finger caliper tool (mechanical)
3. Acoustic tool
4. Casing potential profile tool

Electromagnetic Corrosion Detection

In essence, electromagnetic corrosion detection tools consist of a number of electromagnetic flux transmitters and receivers that are linked by the casing string(s) in much the same way as the core in transformer links the primary and secondary coils (see Rahman and Chilingarian, 1995).

For a qualitative measure of the average circumferential thickness of multiple casings (Cryer et al., 1987), the phase shift between the transmitted and received signals is measured. The phase shift related to the thickness of the casing is as follows:

$$\phi = 2\pi t\sqrt{\mu\sigma f}$$

where t = combined thickness of all casings, σ = combined conductivity of all casings, μ = combined magnetic permeability of all casings, and f = tool frequency.

By increasing f, the depth of investigation can be reduced to include only the inner casing and values of σ and μ can be determined. Increasing f still further provides an accurate measure of the ID of the inner casing string. All three measurements can be made simultaneously to provide an overall view of material losses.

For more detailed analysis of the inner casing string, a multiarmed pad-tool can be used which generates a localized flux in the inner wall of the casing by means of a central, high-frequency, pad-mounted signal coil. Flux distortions, measured at the two adjacent receivers or "measure" coils, are indicative of inner pipe corrosion.

In a second measurement, electromagnets located on the main tool body generate a flux in the inner casing. Again, the presence of corrosion will induce a flux leakage, which is measured by the two measure coils. This measure is a qualitative evaluation of total inner casing corrosion.

Multi-Finger Caliper Tool

The multi-finger caliper tool consists of a cluster of mechanical feelers that are distributed evenly around the tool. Each of these feelers gives an independent measurement of the radius. The small size of feelers allows small anomalies in the inner casing wall to be detected and measured. The multi-finger caliper gives an accurate construction of the changes in the internal diameter of the casings (Watfa, 1989, in Rahman and Chilingarian, 1995).

Acoustic Tool

The acoustic tool consists of eight high-frequency ultrasonic transducers. The transducers act as receiver and transmitter, as two measurements are obtained from each transducer: (1) internal diameter, which is measured from the time interval of signal emission to the echo return; and (2) the internal casing thickness.

Casing Potential Profile Curves

Corrosion damage to the casing can be detected easily using the casing potential profile tool. This tool measures the voltage drop (*IR* drop) across a length of casing (e.g., 25 ft) between two contact knives (see Figure 5.3).

Logging (from bottom to the top) is done at intervals equal to the spacing of the knife contactors. Voltage (*IR*) drops are then plotted versus depth (casing potential profile). As shown in Figure 5.3, readings on the left (–) side of zero indicate that current flows down the pipe, whereas positive values (+) show that flow is upward. Consequently, the curve sloping to the left from the bottom indicates corroding zone (anode), where electrons are leaving the casing (see Jones, 1988).

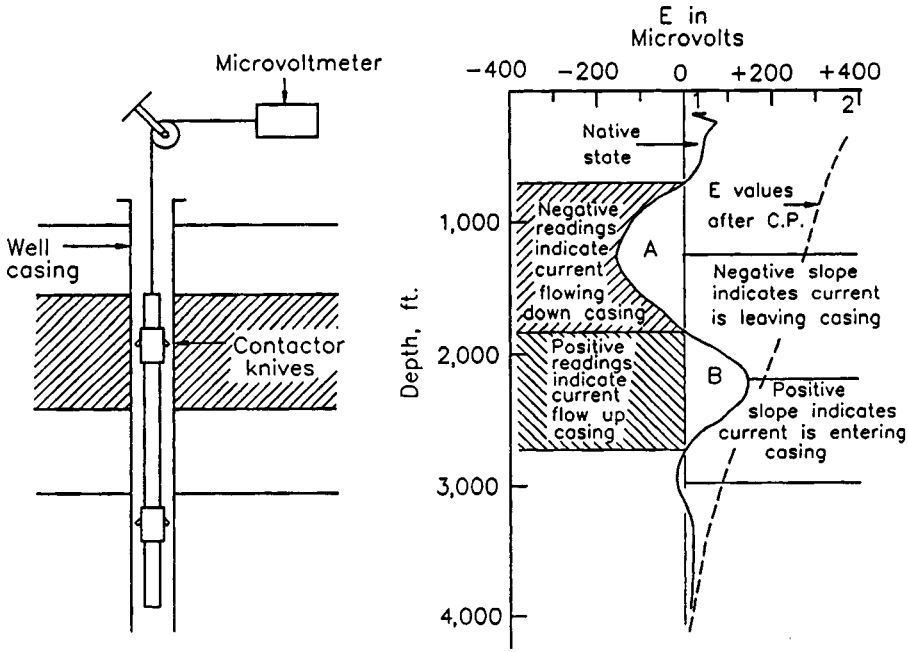

Figure 5.3 Casing potential profile test equipment and example of plotting data (after Jones, 1988, p. 66, figure 1.8-2; courtesy of OGCI Publications, Tulsa, OK).

5.4 PROTECTION OF CASING FROM CORROSION

As pointed out by Jones (1988), the primary causes of external casing corrosion are: (1) corrosion by completion fluids, (2) aggressive formation water, (3) bacterially generated H_2S, and (4) electrical currents.

Casing can be protected by one or combination of the following:

1. Cathodic protection
2. Using wellhead insulator (electrical insulation of well casing from the flowline).
3. Cementation (placement of a uniform cement sheath around casing).
4. Placing completion fluids around casing which has not been cemented (these fluids should be oxygen-free, high-pH, and thixotropic).
5. Proper choice of steel grades

5.4.1 Wellhead Insulation

Use of electrical insulation stops current flow down the casing from the surface and reduces both internal and external casing corrosion. Dielectric insulation materials for both screw and flange joints are commonly used to insulate casing from flowlines. Insulation of wells by connecting them to a single battery is often recommended. It should be noted that when the flowline is at high potential due to cathodic protection, it may induce interference corrosion. In this case, the insulating joints may be partially shunted or wellhead potential elevated by attaching a sacrificial anode (Figure 5.4). Heat-resistant material should be selected for hot, high-pressure wells to prevent failure of insulation materials (also see Jones, 1988, p. 64).

5.4.2 Cementation

In addition to wellhead insulation, the best available procedure of reducing casing failure due to external corrosion is placement of a uniform cement sheath opposite all formations, containing aggressive waters, e.g., formation waters rich in chlorine and sulfate. Diffusional

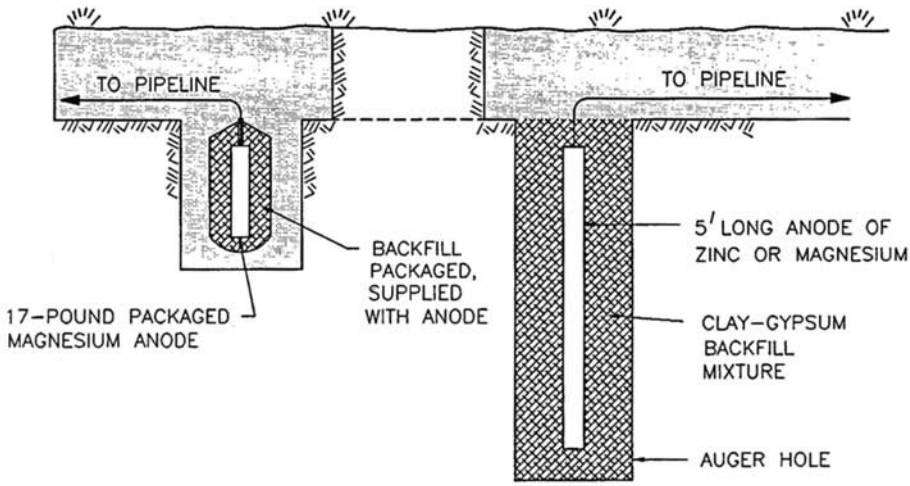

Figure 5.4 Installation of galvanic anodes (after NACE, Houston, TX, Control of Pipeline Corrosion, 1979, figure 8-6).

supply of chlorine and sulfate ions to the surface of the casing can be inhibited by reducing porosity and permeability of the cement sheath. Most API oil well cements contain tricalcium alumina, which forms complex salts of calcium chloroaluminate upon contact with chlorine ions, and calcium sulfoalumina hydrates upon contact with sulfate ions. Both of these reaction products lead to the formation of porous and permeable set cement. Upon long exposure (2–5 years) to these environments, the cement matrix begins to deteriorate and ultimately collapses, leaving the casing without any protection (Rahman and Chilingarian, 1995).

Full-length cementing of surface casing and production casing is advisable, especially for deep wells. Pozzolan blended ASTM type I cement (API Class B or C), which is resistant to chlorine and sulfate attack and at the same time develops strong cement matrix, can be used, for example. Additives such as fuel ash, blast furnace slag, or silica flour are added to the cement to improve its properties (porosity, permeability, and strength).

5.4.3 Completion Fluids

Casing that is not cemented should be protected by oxygen-free, high-pH, and thixotropic completion fluid. Residual dissolved oxygen initiates corrosion pitting and promotes subsequent bacterial growth. Oxygen contained in most completion fluids is best controlled by chemical conversion to harmless reaction product. Common scavengers used to remove oxygen are zinc phosphate and zinc chromate. These inhibitors are used at concentrations of 500–800 mg/L.

Completion fluids must have a high pH, because hydrogen availability increases at low pH and this initiates hydrogen-induced stress cracking. Completion fluids should be thixotropic in order to suspend solids and maintain the required hydrostatic head of the fluid column. This reduces the stresses on casing due to collapse and buckling loads.

As discussed earlier, both hydrogen and sulfide components of hydrogen sulfide are instrumental in bringing about sudden failures in casings. Hydrogen sulfide may enter the completion fluid from (1) formations that contain H_2S, (2) bacterial action on sulfur compounds commonly present in completion fluids, (3) thermal degradation of sulfur-containing fluid additives, (4) chemical reactions with tool joint thread lubricants that contain sulfur, and (5) thermal degradation of organic additives.

Scavengers and film-forming organic inhibitors are utilized in the treatment of water-based completion fluids. Common inhibitors used to remove H_2S from completion fluid are iron sponge, zinc oxide and zinc carbonate, and sodium or potassium chromate. Iron sponge is a highly porous synthetic oxide of iron and reacts with H_2S to form iron sulfite, whereas zinc oxide and zinc carbonate remove H_2S by forming precipitates of sulfide. Chromates remove H_2S by oxidation process.

Film-forming organic inhibitors have been found very effective in protecting casing from contaminants. They are typically oily liquid or wax-like solids with large chains or ring with positively charged amine nitrogen group on one end (Jones, 1988). Their structure can be represented as follows:

$R \cdot NH_2$	$R_2 \cdot NH$	$R_3 \cdot N$	$[R_4 \cdot N]^+$
Primary	Secondary	Tertiary	Quaternary

where R represents the hydrocarbon chain or ring portions of the molecule.

In water, the amine groups take on additional hydrogen that gives them a net positive charge. Thus, the polar amine group is adsorbed to the casing and the hydrocarbon portion forms an oily, water-repellant surface film. The amine inhibitors actually work best where H_2S is present and O_2 is absent, because they can react with H_2S to form a complex compound which helps to build a protective film (for details, see Jones, 1988).

5.4.4 Steel Grades

Susceptibility to stress corrosion cracking of high-strength steel is large. In order to avoid stress corrosion cracking, a variety of materials have been introduced to oilfield casing. They include martensitic stainless steel, austenitic-ferrite stainless steel, high-alloy austenitic stainless steel, nickel-base alloys, and titanium alloys. Chromium-containing martensitic stainless steel has also been used because of its resistance to corrosion in carbon dioxide environments. A stainless steel with 9–12% chromium has a high level of corrosion resistance. These grades of casing and tubing have been offered with an AISI 420 composition (13% chromium) and 80,000 psi minimum yield strength. The results were good (Wilhelm and Kane, 1987).

According to API classification casing grades, which have been found applicable to oilfield conditions where H_2S is present and ambient temperatures are encountered, are: J-55, C-15, N-80, MOD (modified) N-80, SIO-95, and P-110 (Kane and Greer, 1977). Susceptibility to stress cracking decreases as the temperature increases. Hence, as the temperature increases with depth, higher-strength steel grade can be utilized, e.g., SOO-140. Field experience also suggests that large concentration of H_2S affects P-110 casings (for details, see Jones, 1988).

5.4.5 Casing Leaks

In repairing the casing leaks, one can either:

1. isolate the leak with a packer (inexpensive), or
2. replace the casing (very expensive)

Casing leaks can cause loss of production and, possibly, eventual loss of a well. The log of cumulative leaks is often a linear function of time (Figure 5.5). The curve is often an approximate one, because in many cases casing leaks can go undetected for long time. In many cases, however, the extrapolation of the leak frequency versus time curve is surprisingly accurate and can aid in economic analysis (feasibility of cathodic protection).

As pointed out by Cron and Marsh (1983), it is important to determine whether the leaks are due to external or internal corrosion, because cathodic protection can prevent only the external corrosion. In their classical paper, Cron and Marsh (1983, p. 1036) also stated that electrical insulation at wellhead may interrupt a current as high as several amperes. It is important to insulate the casing completely from the large surface structures or apply cathodic protection to these structures as well.

5.4.6 Cathodic Protection of Casing

Cathodic protection is used in many oil fields to protect the casing against external corrosion. Corrosion occurs at the anode, as electrons leave the anodic area and move toward the cathodic areas. If electrons are forced into the anodic areas, corrosion will not occur.

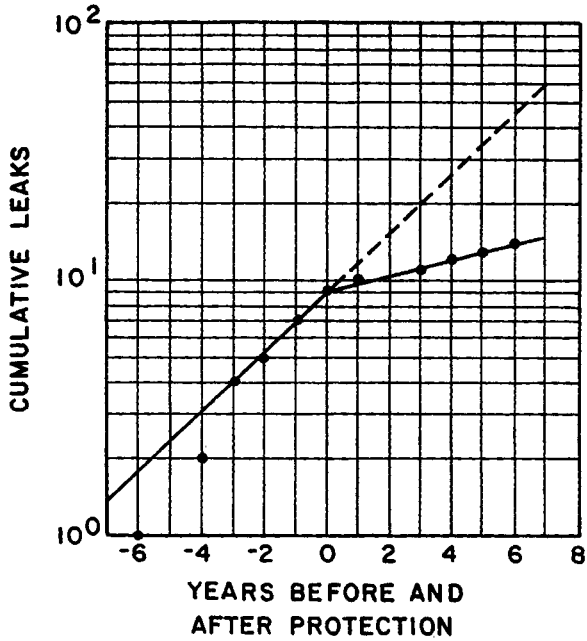

Figure 5.5 Leak frequency, Clairmont Field, Kent County, TX (after Kirklen, 1973, figure 4; courtesy of the SPE).

The first step in the control of external casing corrosion is to provide a complete cement sheath and bond between the pipe and formation over all external areas of the casing strings.

Cathodic protection involves supplying electrons to the metal to make the potential more negative. Complete protection is achieved when all the surface area of the metal acts as a cathode in the particular environment.

The increase in electronegative potential can be achieved by use of sacrificial anodes (magnesium, aluminum, and zinc) or by an impressed direct current. The potentials required for protection differ with the environment and the electrochemical reactions which are involved. For example, Blount (1970) noted that iron corroding in neutral aerated soil has a reduction potential of 0.579 V. The potential is limited by the activity and solubility of ferrous hydroxide. If iron is exposed to H_2S in oxygen-free environment, the potential is increased to 0.712 V and is controlled by the solubility of ferrous sulfide.

Measurements of potential are made by use of reference half cells. The copper-copper sulfate half cell is widely used for potential measurements of pipe in soils. The criteria for protection of iron with this half cell are –0.85 V in aerated soil and –0.98 V in an H_2S system.

The two types of cathodic protection most commonly used are:

1. Galvanic
2. Impressed current

When anodes (e.g., aluminum) are electrically coupled to steel (immersed in the same electrolyte), cathodic protection current is generated. As a result of oxidization of aluminum, electrons are forced into the steel, because electrochemical potential of aluminum is higher than that of steel. Inasmuch as aluminum is consumed in the process, it is called a "sacrificial anode."

In the case of impressed-current cathodic protection, rectifiers are used to convert alternating current to direct current. The negative side of the direct current is connected to the casing, whereas the positive side is connected to the buried anodes. The anode material in this case is essentially inert (see Figure 5.6).

Interference bond on an insulating flange at a cathodically protected casing is shown in Figure 5.7. In the absence of bond, the interference current on the electrically isolated flowline would leave through the soil at point A, causing corrosion of the flowline (Jones, 1988).

As shown in Figure 5.7, the insulating flange electrically isolates the casing from the surface equipment. This confines the cathodic protection current to the casing.

Structure Potential Measurement

The relative potential values of buried pipes in the soil must be measured to (Jones, 1988):

1. Determine if protection is needed
2. Determine the location of anodes
3. Determine how much current must be supplied
4. Check if the protection has been achieved or not

Relative potential is usually measured in comparison to a reference electrode, which is usually ($Cu/CuSO_4$) electrode in soils, whereas Ag/

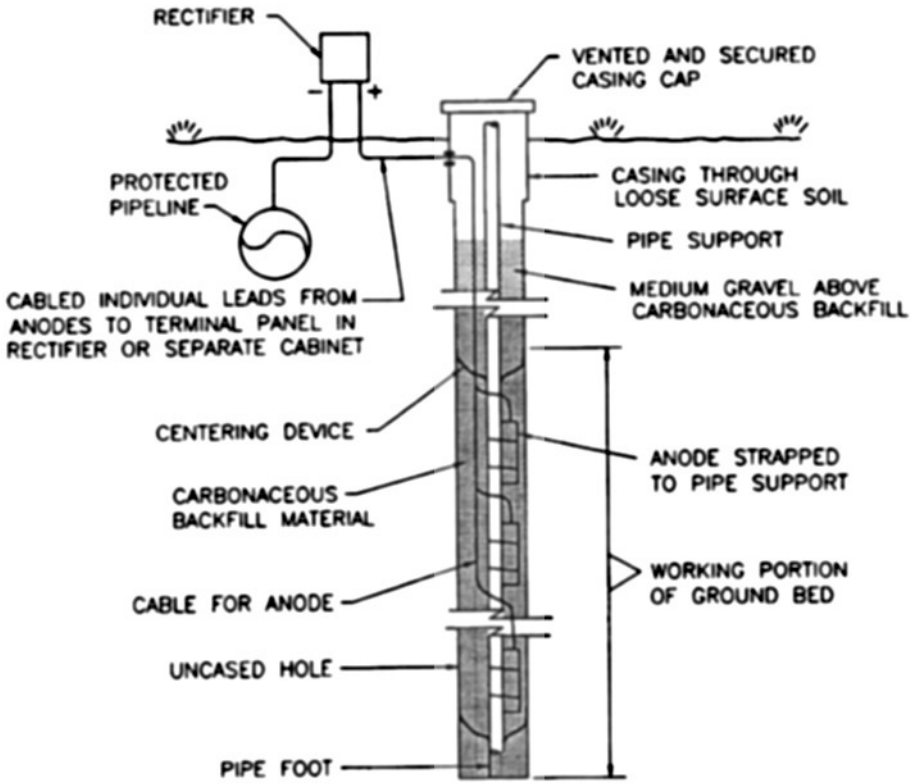

Figure 5.6 Deep well ground bed design using anode and carbonaceous backfill in openhole (courtesy of NACE, Houston, TX, Control of Pipeline Corrosion, 1979, figure 8-12). Can be used for either a pipeline or casing.

AgCl half cell is used in seawater. The reference electrode is connected to positive (+) terminal of a potentiometer and the pipeline is connected to the negative (–) terminal (see Figure 5.8).

Several pipe-to-soil potentials over the distance along the pipeline are measured, and consequently plotted to determine the hot spots, where the pipe is more subject to corrosion. Usually, these occur in zones of lowest soil resistivity (Jones, 1988).

Soil Resistivity Measurements

To determine if the cathodic protection may prevent corrosion of buried pipeline in the soil, one must measure the resistivity of the soil. The

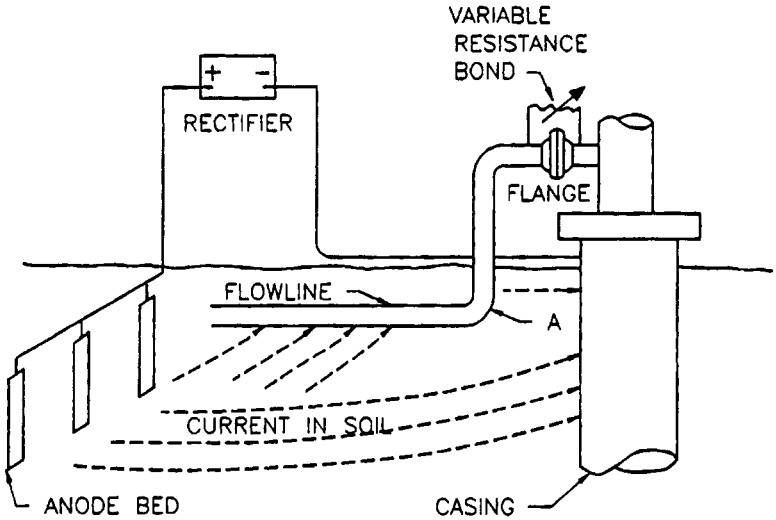

Figure 5.7 Adjustable interference bond across an insulating (isolating) flange connecting a buried flowline to cathodically protected casing (after Jones, 1988, p. 34, figure 1.4-6; courtesy of the OGCI Publications, Tulsa, OK).

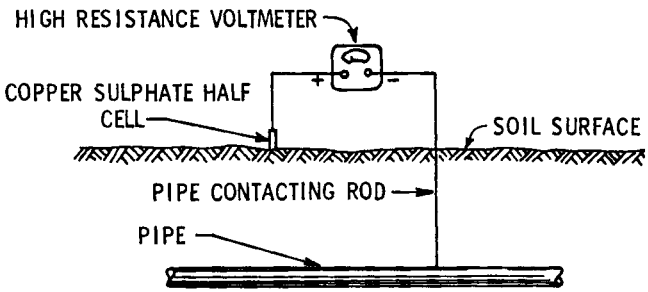

Figure 5.8 Measurement of pipe-to-soil potential on a pipeline (after Jones, 1988, p. 32, figure 1.4-4; courtesy of OGCI Publications, Tulsa, OK).

unit of soil resistivity is ohm-centimeter. According to Parker and Peattie (1999), the resistivity of soil is numerically equal to the resistance of a cube of the soil 1 cm in dimensions, as measured from opposite faces:

$$\rho = \frac{\frac{R}{L}}{A},$$

where ρ = resistivity in ohm-cm, R = resistance in ohms, L = length in cm, and A = area in cm^2.

Measuring the soil resistivity for use with pipe-to-soil survey helps to detect anodic hot spots along the pipelines and to choose locations to place anode beds. The corrosivity of soils is inversely proportional to their resistivities. In other words, low resistivity means high probability of corrosion (see Tables 5.1 and 5.2).

The Wenner method (four-terminal method) is commonly used to measure the resistivity at greater depth (Figure 5.9). For details on measuring resistivity, one should consult Parker and Peattie (1999).

An example of soil resistivity profile along a pipeline is shown in Figure 5.10. Point of low resistivity A is probably an anodic hot spot. In the case of bare pipelines, sacrificial anodes are attached at the anodic hot spots. Then the potentials along the line are resurveyed. More anodes are added as needed until a fairly uniform potential profile is obtained (Jones, 1983, p. 36). For a complete protection of a coated pipeline, an anode ground bed with a power supply is installed.

Table 5.1 Classification of soil corrosivity by resistivity.

Soil resistivity in ohm-cm	Corrosion tendency
>25,000	Not corrosive (if uniform)
10,000–25,000	Mild
5,000–10,000	Moderate
1,500–5,000	Corrosive
<1,500	Very corrosive

Modified after Jones (1988, p. 36).

Table 5.2 Corrosion of steel in soil.

	Corrosion (mpy)	Type	Soil resistivities (Ω-cm)
Desert sand (Arizona)	5	Noncorrosive	Above 10,000
Sandy loam (New England)	21	Mildly corrosive	2,000 to 10,000
California clay	137	Very corrosive	Below 500
Tidal marsh	100	Corrosive	500 to 1,000
Average of 44 soils	61	Moderately corrosive	1,000 to 2,000

After Romanoff (1957).

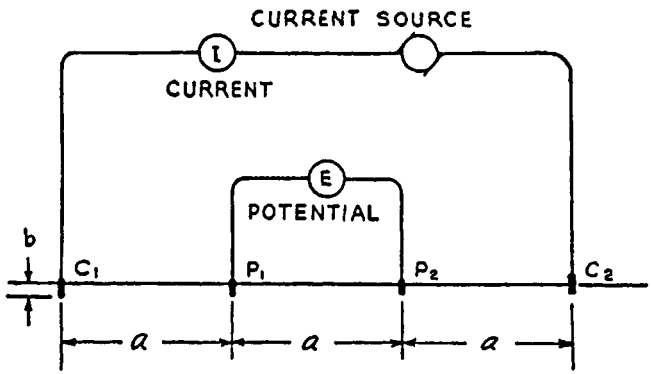

Figure 5.9 Wenner method (four-terminal method) of measuring soil resistivity. Distance "b" (depth of electrode) is smaller than distance "a" (electrode spacing) (after Parker and Peattie, 1999, p. 4, figure 1-4; courtesy of Elsevier). $\rho = 2\pi\alpha\left(\frac{E}{I}\right)$ The resistivity is "averaged" to a depth approximately equal to "a" (electrode spacing).

The rule of thumb in estimating the current requirement in the case of coated pipeline is (Jones, 1988, p. 36):

$$\text{Total pipeline surface area (ft}^2) \times 2\text{mA} \times 0.02$$

It is assumed that 2% of the pipeline is bare or not adequately coated.

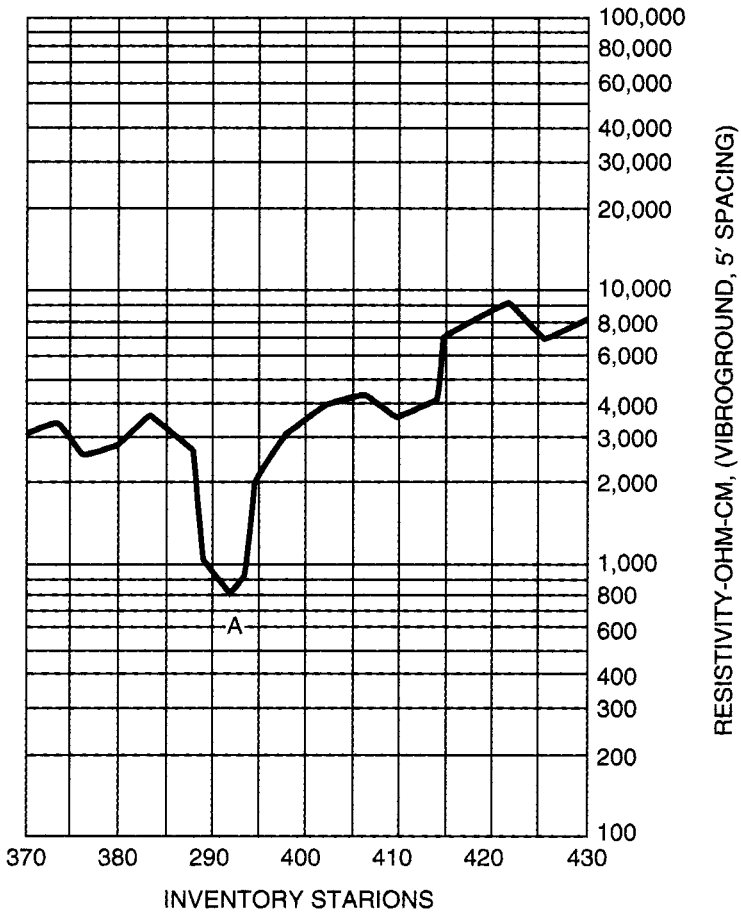

Figure 5.10 Soil resistivity profile along a pipeline. Resistivity values are plotted on the ordinate (log scale), whereas distances along pipeline are plotted on the abscissa (after Parker and Peattie, 1999, p. 9, figure 1-8; courtesy of Elsevier). A = anodic hot spot.

Impressed current systems are preferred over sacrificial anodes when the current requirement exceeds 2–3 amps.

5.5 INTERACTION OF OLD WITH NEW PIPELINE

When two pipelines (one old and one new) are interconnected, corrosion leaks will develop more in the new pipeline. The old pipeline being

protected by some chemical deposits (scales) will act as cathode, whereas the new pipeline will act as anode (Figure 5.11). Thus, in this case the "old" pipeline is better than the "new" one.

If a section of the old pipeline is replaced by a new one, corrosion will occur to a greater extent in the newly installed pipeline. Inasmuch as the old pipeline is protected by some deposits, it will act as a cathode, whereas the new pipeline will become an anode (Figure 5.12).

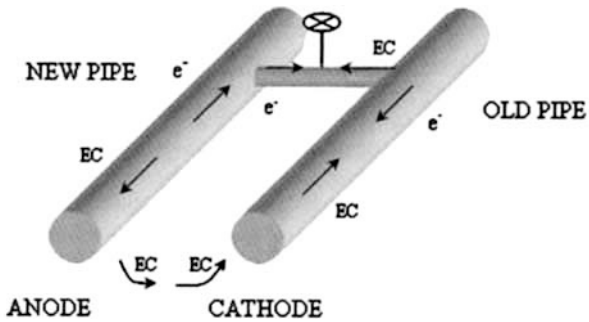

Figure 5.11 Flow of electrons and electric current between the interconnected new and old pipelines.

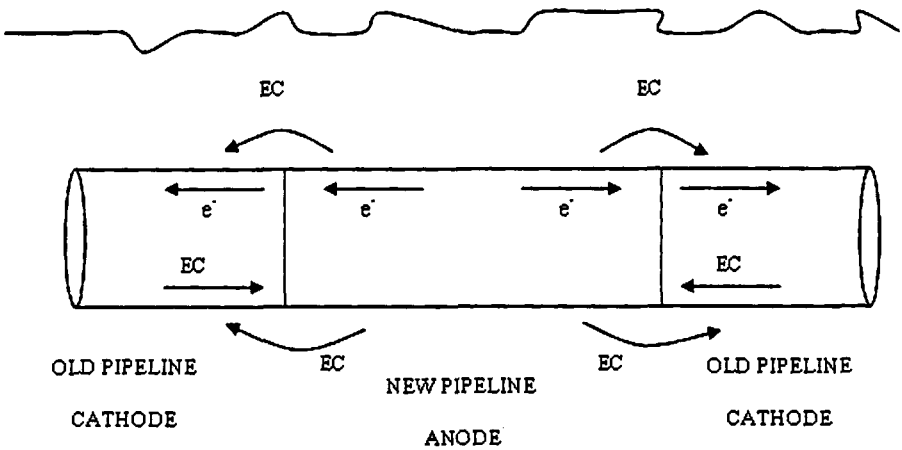

Figure 5.12 Flow of electrons and electric current when a section of old pipeline is replaced by a new pipeline.

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CHAPTER 6
SCALING

6.1 HARDNESS AND ALKALINITY

Hard water is water that has a high content of metal ions, mainly calcium (Ca), magnesium (Mg), and iron (Fe). Total hardness was originally defined as the amount of soap needed to produce foam (Jones, 1988). The total hardness of water (in terms of mg/L of $CaCO_3$), is determined from a water analysis by converting the mg/L of Ca^{++}, Mg^{++}, and Fe^{++} to $CaCO_3$ equivalent in mg/L, whereas the total alkalinity is determined by converting mg/L of HCO_3^-, $CO_3^=$, and OH^- to mg/L of $CaCO_3$, as shown in the following example:

Example 6.1: For a sample of water containing the following ions, calculate the total hardness and the total alkalinity (in terms of $CaCO_3$, mg/L):

ions	Concentration(mg/L)
$CO_3^=$	0
OH^-	0
HCO_3^-	122
Ca^{++}	105
Mg^{++}	56
Fe^{++}	18

Solution: The concentrations in mg/L are converted to mg/L of equivalent $CaCO_3$ by multiplying the concentration of each ion by the ratio of equivalent weight of $CaCO_3$ (50) to the equivalent weight of individual ion. Thus, the total hardness (as $CaCO_3$) is equal to:

$$Ca^{++} + Mg^{++} + Fe^{++} = \left(105 \times \frac{50}{20}\right) + \left(56 \times \frac{50}{12.2}\right) + \left(18 \times \frac{50}{27.9}\right) = 524.2\,\text{mg/L}$$

Inasmuch as the water in this case does not contain OH^- or $CO_3^=$ ions, the alkalinity is due entirely to HCO_3^- anion.

Thus, the total alkalinity = $122 \times \frac{50}{61} = 100\,\text{mg/L}$

6.2 MINERAL SCALES

The term scale refers to any hard deposit on the surface of equipment in the presence of water. The types of scale possible in water systems, depending upon circumstances, are presented in Table 6.1, whereas Table 6.2 shows solubilities of various scales in water.

Scales may be found at any point in water injection system. The prevention of scale formation is of utmost importance. Carbonate, hydroxide, oxide, and sulfide scales may be removed by acidizing, whereas sulfate, phosphate, and ferricyanide scales are not soluble in acid. The latter are very difficult, if not impossible, to remove by means other than mechanical.

Dependence of solubility of gypsum and anhydrite scales on temperature is presented in Figure 6.1.

6.2.1 Calcium Carbonate Scale

Calcium carbonate scaling is a function of pH, temperature, ionic strength* of the solution, calcium cation concentration, and bicarbon-

*The ionic strength of a solution is a function of the concentration of ions in a solution and is defined as $I = \frac{1}{2}\sum(C_i Z_i^2)$, where C_i is the molar concentration of the *i*th ionic species, and Z_i is the number of net electrical charges associated with the *i*th species (see Nazaroff and Alvarez-Cohen, 2001, p. 47).

Table 6.1 Scale formation.

Cause of scale formation	Chemical name	Mineral name
Loss of dissolved gases	Calcium carbonate	Calcite, aragonite
Solution of gases	Ferric hydroxide	Goethite
	Ferrous sulfide	Amorphous iron sulfide
Commingling of waters	Barium sulfate	Barite
	Strontium sulfate	Celestite
	Calcium sulfate[a]	
	Calcium carbonate	Calcite Aragonite
Heating without evaporation	Calcium carbonate	Calcite, aragonite
	Calcium sulfate	Gypsum, anhydrite
	Mixed iron oxide	Magnetite
Incompatible chemicals	Calcium phosphate	Hydroxyapatite
	Ferrous ferricyanide	

[a] $CaSO_4 \cdot 2H_2O$ (dihydrate or gypsum), $CaSO_4 \cdot \frac{1}{2} H_2O$ (hemihydrate), $CaSO_4$ (anhydrite).

After Wright and Chilingarian (1989, p. 326).

Table 6.2 Solubility of various scales in distilled water.

Scale	Temperature (°F)	Solubility (mg/L)
Sodium chloride	77	318,300.0
Gypsum	77	2,080.0
Calcium carbonate	77	53.0
Barium sulfate	77	2.3

Modified after Allen and Roberts (1982, p. 175).

ate anion concentration. Table 6.3 presents factors for conversion of ion concentration (mg/L or meq/L) to ionic strength. The chemistry of calcium carbonate deposition can be understood by examining the following formulas:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{6.1}$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \tag{6.2}$$

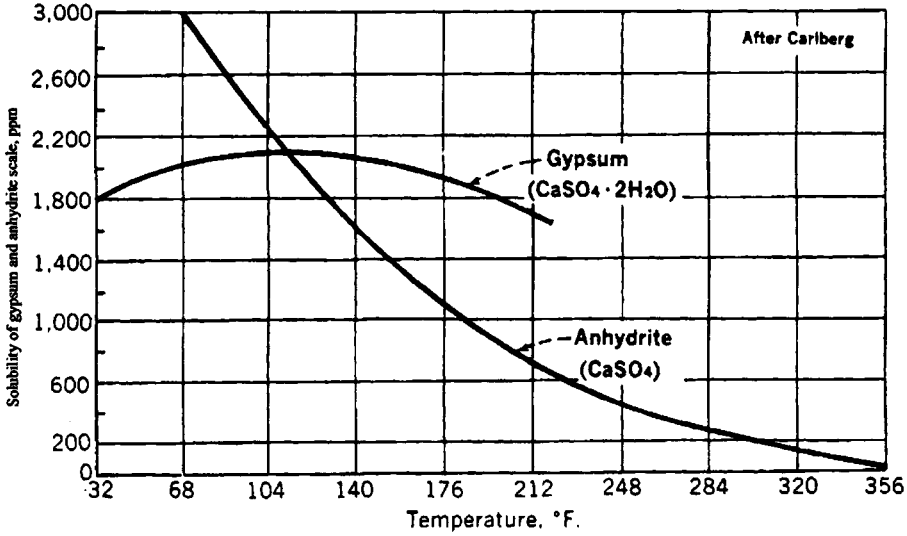

Figure 6.1 Relationship between temperature and solubility of gypsum and anhydrite scales in freshwater (after Carlberg et al., 1962, in Allen and Roberts, 1982, p. 175).

Table 6.3 Factors for converting ion concentration (mg/L or meq/L) to ionic strength.

Ion	mg/L	meq/L
Na^+	2.2×10^{-5}	5×10^{-4}
Ca^{++}	5.0×10^{-5}	1×10^{-3}
Mg^{++}	8.2×10^{-5}	1×10^{-3}
Cl^-	1.4×10^{-5}	5×10^{-4}
$SO_4^=$	2.1×10^{-5}	1×10^{-3}
HCO_3^-	0.8×10^{-5}	5×10^{-4}

Concentrations must be multiplied by the factors shown (after Jones, 1988, p. 119).

$$HCO_3^- + OH^- \rightarrow CO_3^= + H_2O \tag{6.3}$$

$$CO_3^= + Ca^{++} \rightarrow CaCO_3 \downarrow \tag{6.4}$$

As pressure decreases during production, CO_2 is released and $CaCO_3$ precipitates:

$$Ca(HCO_3)_2 \rightarrow CO_2 \uparrow + H_2O + CaCO_3 \downarrow \tag{6.5}$$

Deposition of calcium carbonate will occur if reaction 6.3 and 6.4 are shifted to the right. The following may cause the equilibria to shift to the right:

1. An increase in temperature
2. Decrease in pressure
3. A loss of dissolved carbon dioxide
4. An increase in pH

Langelier (1936) was the first scientist to develop the scale prediction formula:

$$pH_S = (pK'_2 - pK'_S) + pCa^{++} + pAlk \tag{6.6}$$

where pK'_2 and pK'_s = empirical constants, $pCa^{++} = -\log[Ca^{2+}]$, and pAlk = $-\log$[alkalinity].

Stiff and Davis (1952) have simplified the work of Langelier (1936) on scaling index of oilfield waters, i.e., their tendency to deposit calcium carbonate scale. They defined the stability index (*SI*) as follows:

$$SI = pH_{(actual)} - pH_S \tag{6.7}$$

or:

$$SI = pH - pCa - pAlk - K \tag{6.8}$$

where: $pH_s = pCa + pAlk + K$; $pCa = -\log[Ca^{2+}]$; $pAlk = -\log$[alkalinity]; and K is a constant, which depends on temperature and total dissolved solids (TDS). If stability index is positive, the water is oversaturated with $CaCO_3$ and scale formation is possible. The stability index predicts the future behavior of water with no estimate of the past scaling.

Calcium carbonate scale formation may be prevented by any one of the following techniques:

1. Lowering the pH until the stability index becomes zero or slightly negative.
2. Adding a scale inhibitor
3. Removing the calcium ion by any one of the following means:
   (a) Ion exchange, in the case of freshwater.
   (b) Precipitation.
   (c) Chemical treatment: chelation, sequestration, and peptization.
   (d) Dilution to lower the solubility limit.

Figure 6.2 shows the effect of temperature on solubility of $CaCO_3$ in freshwater.

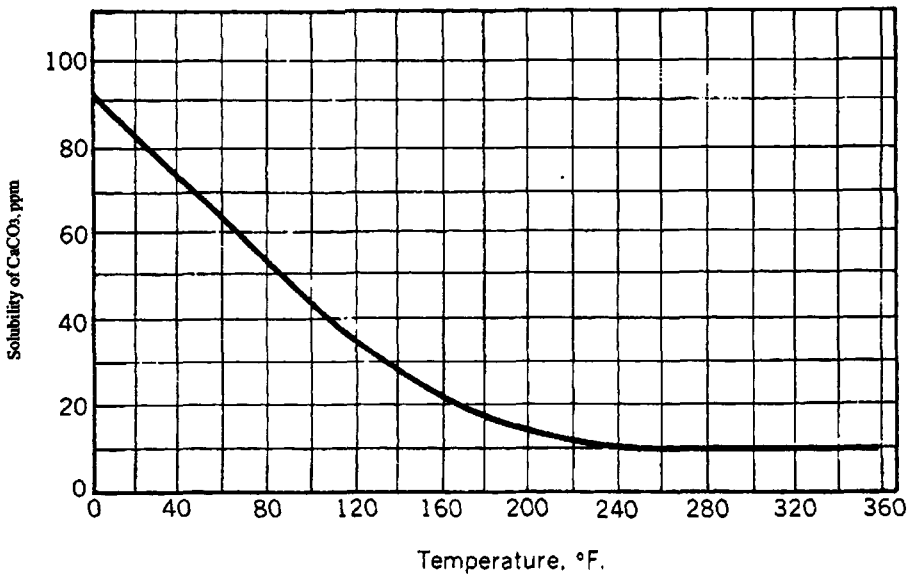

Figure 6.2 Relationship between solubility of $CaCO_3$ and temperature (after Carlberg et al., 1962, in Allen and Roberts, 1982, p.172).

6.2.2 Sulfate Scales

The sulfate scales that occur in waterflood operations are as follows:

1. Barium sulfate
2. Calcium sulfate (anhydrite or gypsum)
3. Strontium sulfate

These three types of scales are normally caused by commingling of two different waters, e.g., one containing sulfate ion and the other containing barium, strontium, or calcium ion. Calcium sulfate scale also may occur when temperatures are raised sufficiently to decrease the solubility of calcium sulfate to the point when precipitation occurs (see Wright and Chilingarian, 1989, p. 327). When mixing of incompatible waters cannot be avoided, one may follow one of the following procedures:

1. Allowing precipitation, and then filtering out precipitates.
2. Adding a scale inhibitor.
3. Removing the barium, strontium, or calcium ion by ion exchange in the case of freshwater.
4. Sequestering or chelating the barium, strontium, or calcium ion.
5. Diluting the offending ion to below solubility limit.

According to Allen and Roberts (1982), the most common form of calcium sulfate scale deposited downhole is gypsum ($CaSO_4 \cdot 2H_2O$). Figure 6.3 shows solubility of gypsum scale at zero and 1,980 psig at 95°F at various concentrations of sodium chloride.

6.3 PREDICTION OF SCALE FORMATION

There are different methods to predict the scale formation, which depend mostly on the type of precipitant and nature of chemical reactions involved. Becker (1998) has used electromotive forces method (emf), which is based on Nernst and Gibb's free energy equation as follows:

$$\in = \in^0 - (RT/nF)\ln\left(\frac{a_{red}}{a_{ax}}\right)$$

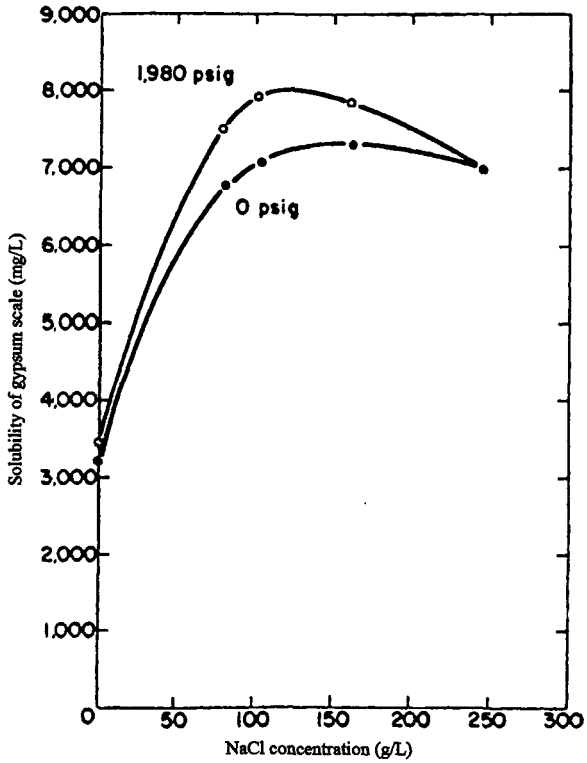

Figure 6.3 Relationship between NaCl concentration (g/L) and solubility of gypsum scale at 95°F (after Fulford, 1968, courtesy of Society of Petroleum Engineers).

where $\in$ = actual electrode potential at the given concentration; $\in^0$ = standard electrode potential; R = universal gas constant; T = absolute temperature in degrees Kelvin; n = charge number of the electrode reaction; F = Faraday constant (96,500 coulombs); a = chemical activities raised to the power corresponding to stoichiometry of reaction.

The spontaneity of the reaction is then determined by using Gibb's free energy equation:

$$\Delta G = -nF\in$$

where the negative value of ΔG shows that reaction will occur spontaneously and scale will form, whereas a positive value of ΔG indicates that scale will not form.

The age and method of collecting samples may have a bearing on the water analysis value obtained. For example, an aged sample of water may show different values than a fresh sample for pH, bicarbonate content, and CO_2. The best procedure is to measure water properties immediately after sampling (see Allen and Roberts, 1982).

Example of Prediction of $CaSO_4$ and $CaCO_3$ Scales

Jones (1988) proposed an elegant method which is mostly based on the type of scales and scaling index (see examples below). On assuming a mixture of 50 vol% seawater and 50 vol% produced water (see Table 6.4), determine *SI* for $CaSO_4$ and $CaCO_3$. In the case of $CaCO_3$, assume that water mixture is saturated with a gas containing 5 mol percent CO_2 at 1 bar total pressure.

Table 6.4 Examples of water analysis.

Ion	Sample 1		Sample 2		Sample 3	
	Seawater		Formation water		Produced water	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Na^+	11,144	484.5	31,602	1,374	28,543	1,241
K^+						
Ca^{++}	464	23.2	18,662	933.1	14,010	700.5
Mg^{++}	1,350	111	2,838	232.6	2,470	202.5
Fe^{++}						
Ba^{++}						
Sr^{++}						
Cl^-	19,900	562.1	89,499	2521.1	75,500	2,126.8
$SO_4^=$	2,600	54.1	410	8.5	432	9
HCO_3^-	149	2.5	617	10.1	502	8.2
$CO_3^=$	0		0		0	
OH^-	0		0		0	
TDS	35,607		143,559		121,457	
Sp. Gr.	1.026		1.104		1.088	
pH	7.8		6.2		7.4	
O_2	3.8					
H_2S			139		190	

Modified after Jones (1988, p. 112).

For $CaSO_4$:

$$Na^+ \Rightarrow 0.5 \times (484.5) + 0.5 \times (1{,}241) = 862.75 \text{ meq/L}$$

$$Ca^{++} \Rightarrow 0.5 \times (23.2) + 0.5 \times (700.5) = 361.85 \text{ meq/L}$$

$$Mg^{++} \Rightarrow 0.5 \times (111) + 0.5 \times (202.5) = 156.75 \text{ meq/L}$$

$$Cl^- \Rightarrow 0.5 \times (562.1) + 0.5 \times (2{,}216.8) = 1{,}344.45 \text{ meq/L}$$

$$SO_4^= \Rightarrow 0.5 \times (54.1) + 0.5 \times (9) = 31.55 \text{ meq/L}$$

After converting all concentrations to meq/L, one can follow the following steps (Jones, 1988):

For $CaSO_4$:

1. The concentration (meq/L) of $CaSO_4$ in water is numerically equal to the lowest value of either Ca^{++} or $SO_4^=$:

$$[CaSO_4] = 31.55 \text{ meq/L}$$

2. The excess common ion (*ECI*) is obtained by subtracting the lowest meq/L of either Ca^{++} or $SO_4^=$ from the other:

$$ECI = 361.25 - 31.55 = 330.3 \text{ meq/L}$$
(common ion in excess of $[CaSO_4]$

3. On adding the concentrations of Na^+ and Mg^{++}, one obtains *NM*:

$$NM = 826.75 + 156.75 = 1{,}019.5 \text{ meq/L}$$

4. Determine the ratio of *NM* to *ECI* (*R*):

$$R = \frac{NM}{ECI} = 3.086$$

5. Determine K_s:

$$K_s = [CaSO_4] - R = 28.4$$

If $K_s \leq 6$, water is undersaturated with $CaSO_4$ at 60°C and Step (6) is followed.

If $K_s \geq 9$, water is oversaturated with $CaSO_4$ at 60°C and Step (7) is followed.

If K_s ranges from 6 to 9, water is near saturation.

If $R < K_s$, Step (7) is followed, whereas if $R > K_s$, $[CaSO_4]$ is approximately equal to the solubility at 60°C and SI for $CaSO_4$ is near zero.

6. For undersaturated waters ($K_s \leq 6$):

$$S_{60} = [CaSO_4]\left(\frac{936}{NM} + \frac{NM}{2{,}808}\right)$$

where S_{60} is the solubility of $CaSO_4$ (meq/L) in water at 60°C. Inasmuch as in the example presented $K_s > 9$, Step (7) is followed.

7. Determine $M = \dfrac{R}{[CaSO_4]} = 0.0978$

If $M > 0.12$, $S_{60} = 1.2K_s$
If $M \leq 0.12$, $S_{60} = 0.68K_s$
Inasmuch as M in this problem is <0.12,
$S_{60} = 0.68(28.4) = 19.3$

8. Thus, SI can be determined:

$$SI = [CaSO_4] - S_{60} = 31.55 - 19.3 = 12.25$$

Inasmuch as SI is positive, scale will probably form.

One should remember that an increase in ECI value reduces the solubility, whereas an increase in the NM value increases the solubility. At higher temperature, waters, which are undersaturated at 60°C, may become oversaturated.

For $CaCO_3$:

The following steps are followed in the case of $CaCO_3$:

1. Determine the ionic strengths using Table 6.3:

$$Na^+ \Rightarrow 0.431$$

$$Ca^{++} \Rightarrow 0.361$$

$$Mg^{++} \Rightarrow 0.156$$

$$Cl^{-} \Rightarrow 0.6722$$

$$SO_4^{=} \Rightarrow 0.031$$

$$HCO_3^{-} \Rightarrow 0.002$$

Thus, the total ionic strength (sum of the above) is equal to 1.653.

2. Determine K from Figure 6.4 $\Rightarrow$ 2.5
   Determine pCa from Figure 6.5 $\Rightarrow$ 0.75
   Determine pAlk from Figure 6.5 $\Rightarrow$ 2.25

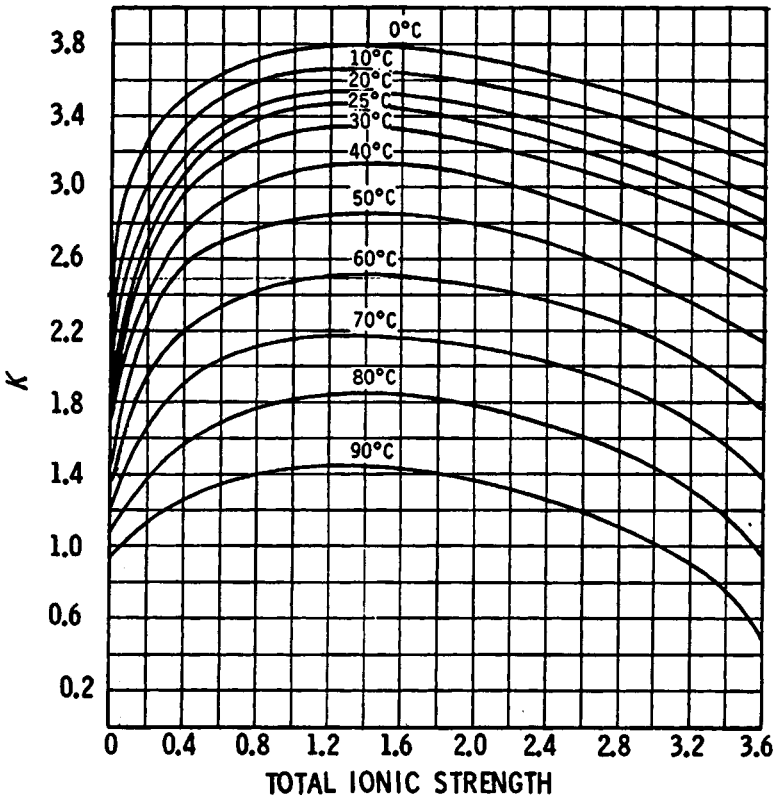

Figure 6.4 Determination of K for various ionic strengths (modified after Stiff and Davis, 1952).

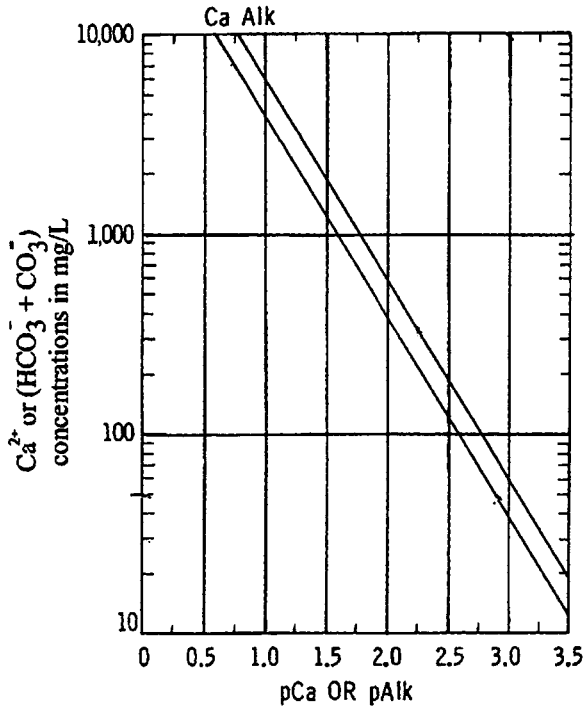

Figure 6.5 Determination of pCa and pAlk from concentrations of $[HCO_3^- + CO_3^=]$ and Ca^{++} (after Langelier, 1936).

3. Thus,

$$pH_S = K + pCa + pAlk = 5.5$$

4. Determine ratio R' (assuming that the gas in contact with water contains 5 mol% CO_2 at total pressure of 1 bar):

$$R' = \frac{(\text{mg/L } HCO_3^-) \times 0.82}{(\text{mol fraction } CO_2) \times S_f} = \frac{325.5 \times 0.82}{0.05 \times 40} \approx 133.4 \qquad (6.9)$$

where mole fraction of CO_2 is determined from gas analysis and S_f is the solubility factor determined from Figure 6.6. At a temperature of 60°C and a pressure of 1 bar, $S_f = 40$.

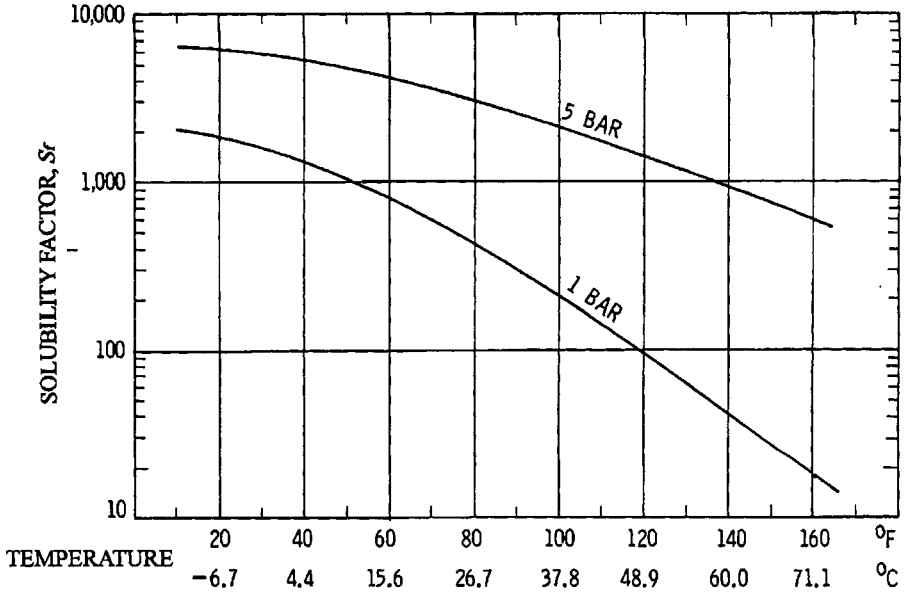

Figure 6.6 Variation of S_f with temperature and pressure (modified after Jones, 1988, p. 121).

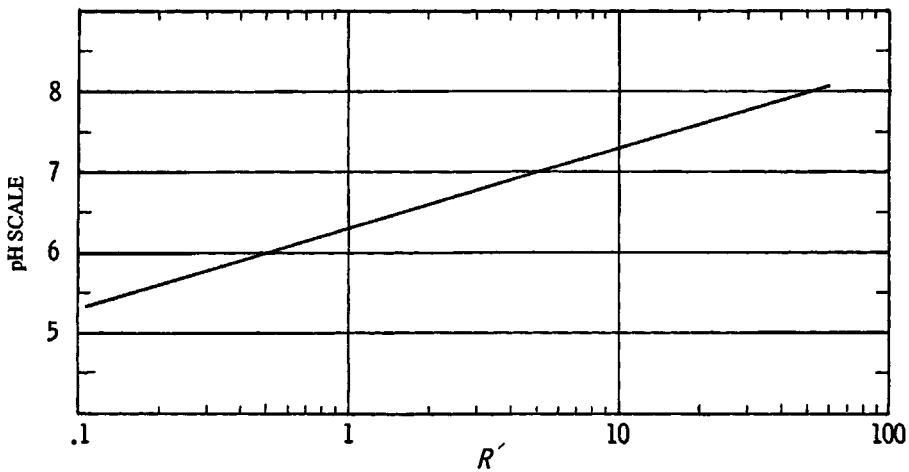

Figure 6.7 Relationship between pH and R' value (modified after Jones, 1988, p. 122).

5. Determine pH from Figure 6.7 (R' versus pH):

$$pH = 9$$

pH decreases with increasing concentration of CO_2 in water.

6. Determine SI:

$$SI = pH_{(actual)} - pH_S$$

$$SI = 9 - 5.5 = 3.5$$

Inasmuch as SI is positive, $CaCO_3$ scale will probably form.

6.4 SOLUBILITIES OF VARIOUS SULFATES AND CARBONATES

Barium sulfate scales usually contain some strontium sulfate. Predominantly $SrSO_4$ scale also occurs in many parts of the world, e.g., Saudi Arabia, North Sea, and Gulf of Suez.

The solubilities of $BaSO_4$ and $SrSO_4$ in oilfield waters are presented in Figure 6.8. With increasing *ECI* (common ion concentration), the solubilities of $BaSO_4$ and $SrSO_4$ decrease.

6.5 SOLUBILITY OF CALCITE, DOLOMITE, AND MAGNESITE AND MIXTURE OF THESE CARBONATES

The solubility of calcite, dolomite, and magnesite (and mixture of these components) in water at $P_{CO_2} \approx 1$ atm and temperatures ranging from 0 to 70°C are presented in Figure 6.9. The amounts of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ (expressed in millimoles per 1,000 g of solution) are plotted on the abscissa and ordinate, respectively.

The points of intersection between bisectrix and dolomite saturation curves show the composition of solutions saturated with pure dolomite, whereas the solubilities of pure $CaCO_3$ and $MgCO_3$ are shown on the ordinate and abscissa, respectively. On the other hand, the solubilities of mixtures of dolomite + calcite and dolomite + magnesite (two phase) are shown by the junction (nodal) points.

The curve connecting these junction points to the left of bisectrix represents solubility of mixtures of dolomite and calcite, whereas the

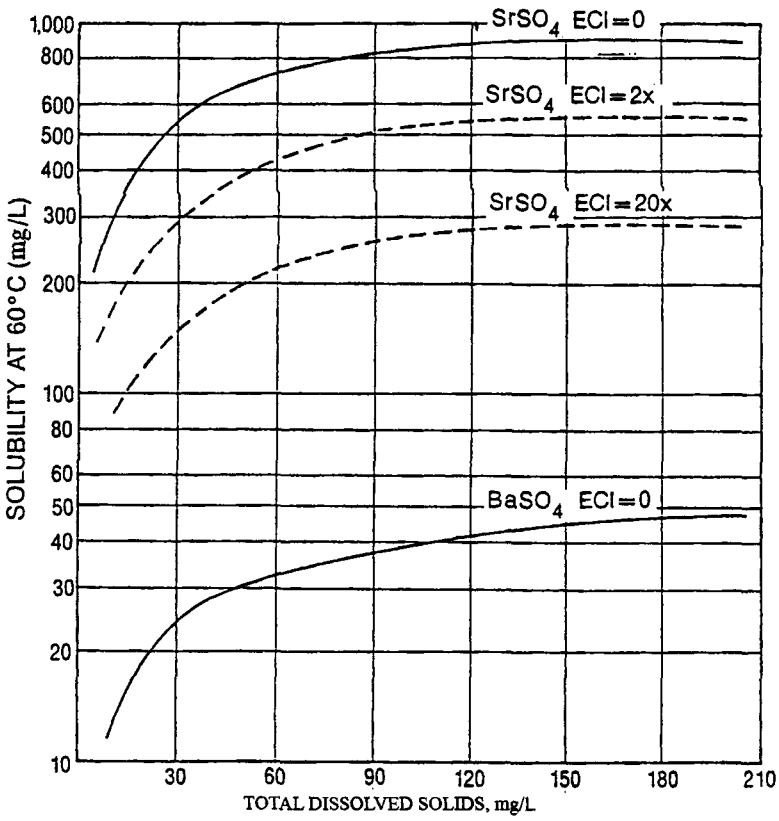

Figure 6.8 Relationship between the total dissolved solids (TDS) and approximate solubilities of strontium sulfate and barium sulfate in oilfield brines at 60°C (modified after Jones, 1988, p. 124).

one at the right of bisectrix represents mixtures of dolomite and magnesite. In all cases, the magnesite had the highest solubility, whereas dolomite was the least soluble.

6.6 RELATIVE PERMEABILITY CONCEPTS

The effective permeability of a porous medium to a fluid is a measure of the ability of the medium to transmit this fluid at the existing saturation, which is usually less than 100%. In the majority of formations,

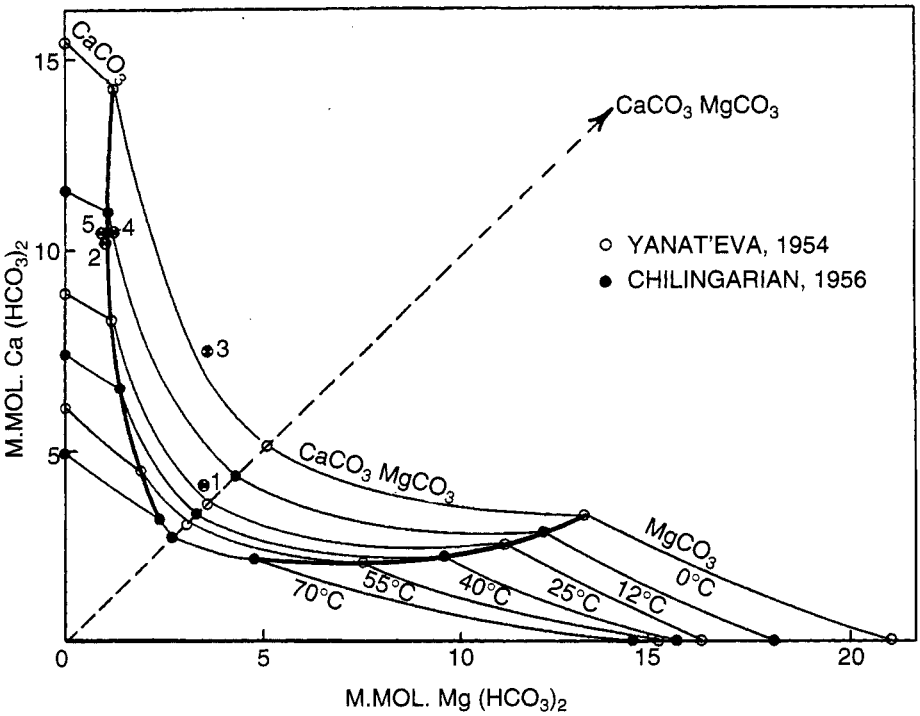

Figure 6.9 Solubility of $CaCO_3$-$MgCO_3$-H_2O system at $P_{CO2} \approx 1$ atm and temperatures ranging from 0 to 70°C. Points between ordinate and 45°-line represent solubility of calcite–dolomite mixtures, whereas those between the 45°-line and abscissa represent dolomite–magnesite mixtures (after Chilingarian, 1956, p. 2770, and Yanat'eva, 1954, p. 777).

there is a simultaneous existence of more than one phase: (1) oil and gas; (2) oil and water; and (3) oil, gas, and water.

The concept of effective permeability implies that all but one phase are immobile. Inasmuch as part of effective pore space is occupied by another phase, a correction factor must be used. Permeability is measured by an arbitrary unit called "Darcy," which is named after Henry d'Arcy. The permeability is equal to one Darcy if 1 cm^3 of fluid per second flows through 1 cm^2 of cross section of rock under a pressure gradient of 1 atm/cm, the fluid viscosity being 1 cP.

The magnitude of effective permeability depends on wettability, i.e., on whether the rock is oil-wet or water-wet. The nature, distribution, and amount of immobile phase affect effective permeability.

The relative permeability to a fluid is defined as the ratio of effective permeability at a given saturation of that fluid to the absolute permeability at 100% saturation. The terms $k_{r0}(k_0/k)$, $k_{rg}(k_g/k)$, and $k_{rw}(k_w/k)$ denote the relative permeability to oil, to gas, and to water, respectively (k is the absolute permeability, often the single-phase liquid permeability). The relative permeabilities are expressed in percent or as a fraction.

In waterflooding projects or in natural water-drive pools, the relative permeabilities to oil and to water are of great importance. When water and oil flow together, the relative permeabilities are affected by many factors, which include:

1. Relative dispersion of one phase in the other
2. Time of contact with pore walls
3. Amount of polar substances in the oil
4. Degree of hardness of water
5. Relative amount of carbonate material in porous medium
6. Temperature

The relative permeability to the continuous phase (dispersion medium) is greater than the relative permeability to the discontinuous (dispersed, internal) phase. With increasing degree of dispersion, the relative permeability increases for both continuous and discontinuous phases. The degree of dispersion increases with decreasing interfacial tension and increasing time of coalescence of dispersed-phase droplets. Sticking (attachment) of the dispersed phase to solid surfaces depends on:

1. Interfacial tension
2. Angle of contact
3. Time necessary for the coalescence of droplets and lenses.
4. Thickness of dispersion medium (continuous phase) layer attached to solid surface.

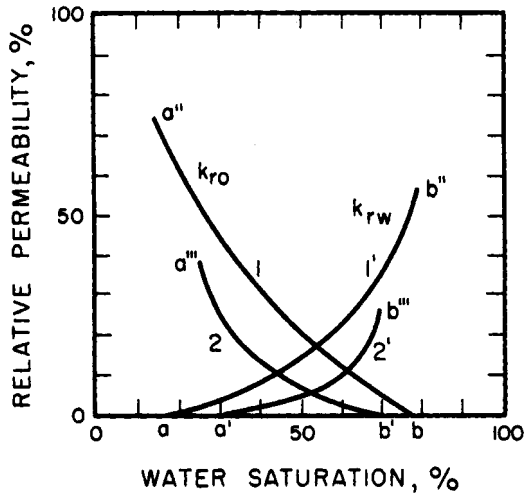

Figure 6.10 Relative permeabilities to oil and to water for polar oil + alkaline water (curves 1 and 1′) and for polar oil + hard water (curves 2 and 2′) (after Babalyan, 1956, p. 145).

6.6.1 Effect of Water Hardness on Relative Permeability Curves

According to Babalyan (1956), in the case of polar oil, the water and oil production is greater when the water is alkaline than when the water is hard.*

This is due to the change in the critical saturations of both phases (Figure 6.10). As shown in Figure 6.10, the relative permeability curves

*For alkaline water:

$$\frac{r\mathrm{Na}^+}{r\mathrm{Cl}^-} > 1;\ \frac{r\mathrm{Na}^+ - r\mathrm{Cl}^-}{r\mathrm{SO}_4^{=}} > 1;\ r\mathrm{Na}^+ + r\mathrm{Cl}^- > r\mathrm{SO}_4^{=};\ r\mathrm{HCO}_3^- > r\mathrm{Ca}^{++} + r\mathrm{Mg}^{++};$$

$$r\mathrm{Na}^+ + r\mathrm{K}^+ > r\mathrm{Cl}^- + r\mathrm{SO}_4^{=}.$$

For hard water:

$$\frac{r\mathrm{Na}^+}{r\mathrm{Cl}^-} < 1;\ \frac{r\mathrm{Cl}^- - r\mathrm{Na}^+}{r\mathrm{Mg}^{++}} > 1;\ r\mathrm{Cl}^- + r\mathrm{SO}_4^{=} > r\mathrm{Na}^+ + r\mathrm{K}^+.$$

(r = % equivalents)

of oil + alkaline water lie above those of oil + hard water, because the following is true in the case of alkaline waters:

1. Low interfacial tension between oil and water
2. Low values of contact angle
3. Slow coalescence of oil droplets in water
4. Greater degree of dispersion of oil in water

In the case of hard water, on the other hand, the oil becomes a dispersed phase at higher water saturation in a porous medium than in the case of alkaline waters. The intensity of the transformation of oil into a dispersed phase is greater in alkaline than in hard waters.

In the case of nonpolar oil, the attachment of oil to solid surfaces is negligible in the presence of both alkaline and hard waters. When nonpolar oil flows with either alkaline or hard waters, there is no change in critical saturations and hence the recovery of oil and water is the same in each case. The relative permeability curves with alkaline water, however, lie above those with hard water (Figure 6.11).

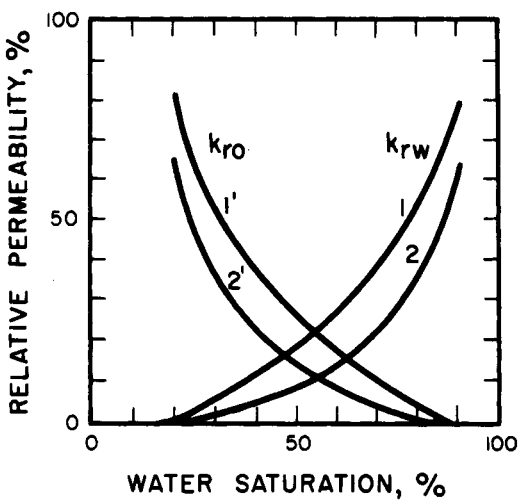

Figure 6.11 Relative permeability curves for nonpolar oil with alkaline water (curves 1 and 1′) and for nonpolar oil with hard water (curves 2 and 2′) (after Babalyan, 1956, p. 149).

6.6.2 Effect of Water Chemistry on Oil Recovery

Bernard (1967) investigated the relative effectiveness of fresh and salt waters in flooding oil from cores containing clays. Experimental results indicated that when hydratable clays are present, more oil is produced with freshwater flood than with a brine flood (Bernard, 1967). The freshwater flood, however, is accompanied by lowering in permeability and development of relatively high pressure drop. It is probable that the results obtained by Bernard are owing to the effect of chemistry of water on relative permeabilities (Figure 6.10), as previously discussed. Thus, oil recovery can be increased by adjusting chemistry of injection waters (relative proportions of Na^+, Cl^-, $SO_4^=$, HCO_3^-, Ca^{++}, and Mg^{++} ions; Na^+/Cl^-, $[Na^+ - Cl^-]/SO_4^=$, Ca^{++}/Mg^{++}, Ca^{++}/Na^+, Ca^{++}/Cl^-, $[Cl^- - Na^+]/Mg^{++}$ ratios; pH; etc.). In 1968 again, Chilingar stressed the importance of utilization of alkaline flooding in oil production.

Although some readers may consider the information presented in Section 6.6 "out-of-place" in this book, this information can be of great value to engineers involved in treating injection waters in waterflooding (secondary recovery) operations. It should also be remembered that some corrosion inhibitors change the wettability of reservoir rocks.

6.7 SCALE INHIBITION

According to Jones (1988, p. 126), classes of scale inhibition chemicals include:

1. Sodium polyacrylate polymers
2. Amino-phosphates
3. Phosphate esters of amino-alcohols

The scale inhibitor chemical is usually prediluted with water in a concentration of 1–2 vol%. The treating rate ranges from 2 to 10 mg/L.

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CHAPTER 7
WATER QUALITY CONTROL*

7.1 INTRODUCTION

There has been a rapid increase in the utilization of secondary recovery of oil (waterflooding). According to Wright and Chilingarian (1989), about 50% of the oil production in the United States was by waterflooding. There is a rough rule of thumb that 10 barrels of water must be injected into the formation for each barrel of oil produced. Using this rule, one comes up with a staggering total for the volume of water to be injected into petrolifenous formations. This rapid increase in water injection is focusing attention upon water quality for subsurface injection. This chapter is devoted to setting standards for water quality, the means by which standards may be met, and the problems arising during the handling of water. The objective of water treatment was stated simply by Hockaday (1958) as follows: "The major consideration of water quality for subsurface injection is that the water must be only good enough to enable the water injection program to be carried out to completion at a minimum cost." This means simply the water must have quality that enables injection of the water into the subsurface formation at the desired injection rate without prohibitive pressures. In addition, water must not cause more corrosion than can be economically tolerated during the time necessary to recover the oil. Thus, water

* Originally written by the famous petroleum engineer Charles C. Wright and George V. Chilingarian in 1989.

quality control is concerned mainly with (1) injection suitability and (2) corrosion control. Unfortunately, these main considerations are interrelated in many ways and cannot be dealt with separately. This is discussed in detail in subsequent sections. Detailed specifications are important in order to maintain a given water quality necessary for completion of a specific project. In setting water quality specifications, one must be careful not to lose sight of the primary purpose of the water quality control, because unnecessarily high standards result in extra cost without compensating return.

7.2 INJECTION SUITABILITY

Injection suitability of water means that desired volume of water can be forced into the subsurface formation at economical pressures. Rising injection pressure may be caused by one or more of the following causes:

1. Fill-up of the formation (filling up of void spaces)
2. Swelling of formation clays (see Rieke and Chilingarian, 1976), resulting in decreased permeability.
3. Formation and deposition of insoluble material in the pores of formation.
4. Increase in oil saturation, resulting in decreased permeability to water.
5. Movement of formation fines caused by solubilization of cementing agents. The fines subsequently lodge in pore throats and canals, causing a reduction in permeability.
6. The presence of suspended solids in the water, which either lodge in restrictions in pore channels or strain out on the formation face and, thus, cause a reduction in permeability.

The first cause is outside the purview of this chapter, but must be remembered because rising pressures do not have to be caused by water quality. The remaining causes are dealt with in detail.

7.2.1 Clay Swelling

There probably is more misinformation about clay swelling in reservoir rocks than on any other phase of water injection. This situation has arisen because of the following:

1. Each species of clay mineral reacts to a different degree with foreign waters.
2. The degree of swelling of a clay mineral is a function of the following (Grim, 1962): (a) the total ionic strength of the water, (b) the relative ratio of monovalent cations to divalent cations, (c) the pH of the water, (d) the specific cations present, and (e) the presence of polar organic compounds.
3. The rate of change from high ionic strength to low ionic strength of water (Crawford, 1966).
4. The analytical determination of the presence of clay minerals and their residence time in a reservoir rock is not a simple determination (Morris et al., 1959; Hewitt, 1963).

Mobile fines give rise to the same reduction in permeability as the swelling of clays (Hewitt, 1963). The work of Von Engelhardt and Tunn (1955) (see Figure 7.1) shows the effect of varying salinity on three

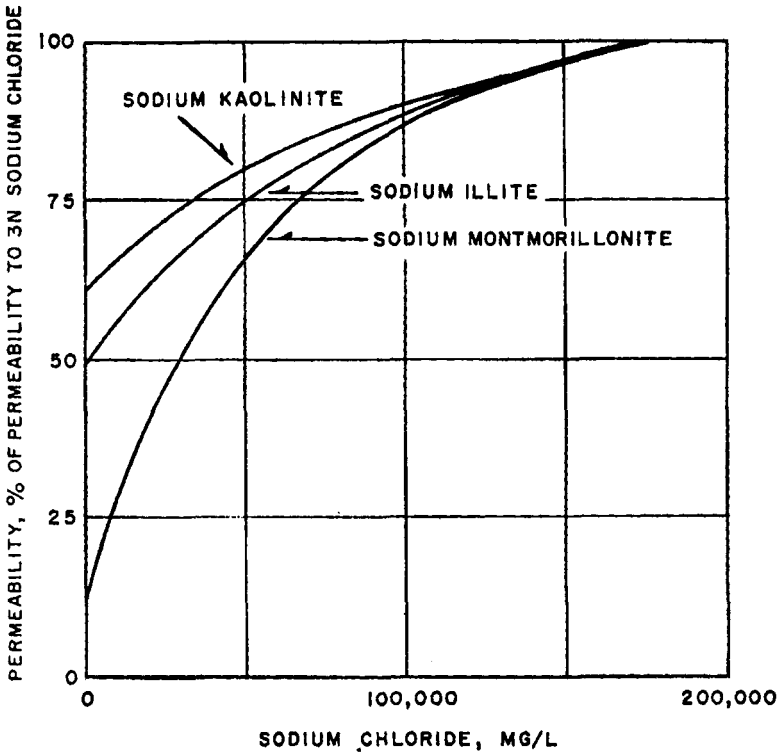

Figure 7.1 Effect of NaCl concentration in water on permeability of quartz sand containing 4% clay (after Von Engelhardt and Tunn, 1955).

basic clay types. Sodium-montmorillonite causes the greatest reduction in permeability because it exhibits greatest swelling, whereas sodium-illite and sodium-kaolinite cause far less reduction in permeability as the salinity of the flooding water is decreased.

One should also remember that the Na/Ca ratio of injection water should be lower than the Na/Ca ratio of formation water, because Ca-base clays swell less than the Na-base clays.

7.2.2 Formation and Deposition of Insoluble Material in the Formation

Jones and Neil (1960) and Jones (1964) showed the importance of making salinity reduction change in steps of not greater than 10-fold dilution (Table 7.1).

Jones (in Crawford, 1966) stated that minimum clay swelling occurs if at least 10% of the salts in solution consists of divalent cations salts. Sometimes, as little as 5% is effective in inhibiting clay swelling. This is true even if the water is fresh. The two mechanisms by which insoluble material may be formed and deposited within the formation are: (1) the reaction of injection water with formation water to form precipitates, and (2) a time-dependent reaction within the injection water, which results in formation of insoluble material after the water has entered the formation.

These mechanisms are not important when formation permeability is high. If the precipitates are deposited sufficiently far from the well-

Table 7.1 Effect of water salinity on the permeability of sandstone core.

Series	Water		Core permeability (mD)
	Sodium chloride (ppm)	Calcium chloride (ppm)	
1	52,600	5,500	225
	5,260	550	235
	526	55	215
	263	27	220
	105	11	215
2	52,600	5,500	220
	105	11	40

bore, there may be only a negligible effect on injectivity due to the radial dispersion, which governs. On the other hand, a low-permeability formation may be damaged by these mechanisms because the deposition will take place at or near the wellbore face.

7.2.3 Increase in Oil Saturation

The main concern with oil entering the formation lies in its extreme effect on water permeability in the regions of low oil saturation. An example of relative permeability (to oil and to water) curves is presented in Figure 7.2.

Increased oil saturation around the wellbore in a water injection well is far more common than usually realized (Table 7.2). This additional

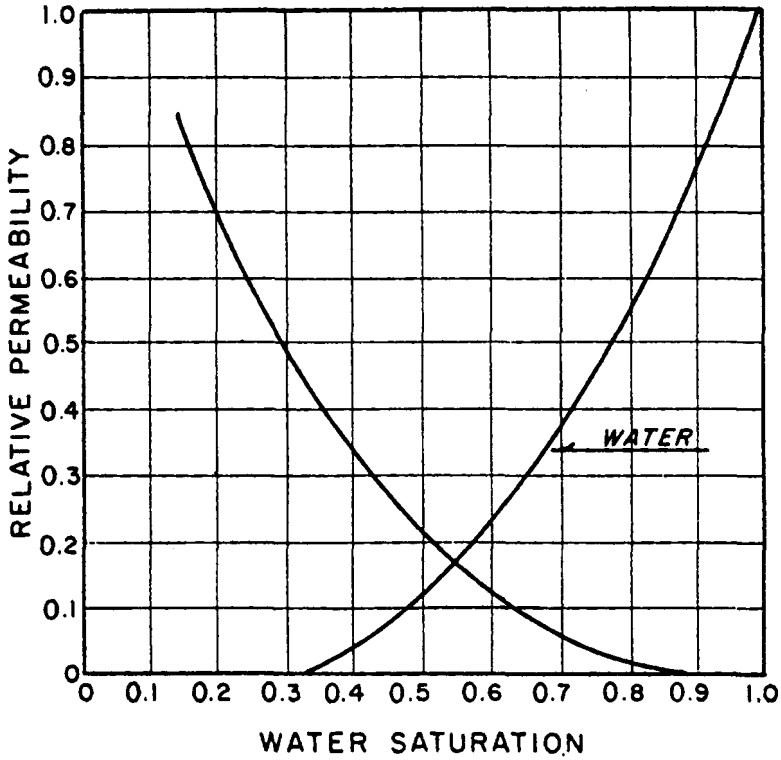

Figure 7.2 Example of relative permeability curves (left: to oil; right: to water).

Table 7.2 Cumulative volume of oil entering injection well with injection rate of 1,000 barrels per day.[a]

Oil content in water (ppm)	Period of time			
	1 day	1 month	1 year	5 years
1	0.048 gal	1.4 gal	18 gal	2.1 bbl
10	0.48 gal	14 gal	180 gal	21 bbl
100	4.8 gal	140 gal	1,800 gal	210 bbl

[a]Assumptions: Specific gravity of water = 1.02; sp. gr. of oil = 0.9.

oil may have one or more of the following origins: (1) oil suspended in water used in waterflooding, (2) plunger-lubricating oil, (3) oil carrier used with treating chemical, (4) formation oil entering during periods of backflow, (5) oil used as oil blanket to exclude air, and (6) oil removed from tubing or piping which was used in a producing operation and transferred to injection operations.

It is important to ascertain the source of oil entering a water injection well, as it may be possible to prevent its entry. As mentioned before, the main concern with oil entering the formation lies in its extreme effect on water permeability in the regions of low oil saturation (Figure 7.2).

Field experience in some areas indicates that 20–30 ppm of oil can be tolerated in the injection water (Amstutz, 1956). Other areas show rising injection pressures whenever any oil is allowed to reach the formation in the injection wells. Operating procedure should be established, which will result in the smallest possible amount of oil entering the injection well (Lewelling and Kaplan, 1959). Plunger-lubricating oil has been found entering the water at about 0.02-ppm concentration from a well-maintained pump. This best-case condition however, does not apply all the time. It is common to find several gallons of plunger-lubricating oil in the pipe downstream of the positive displacement pump after it has been on stream a number of months. Overlubrication, improperly fitted wipers, worn wipers, and similar causes allow more oil to enter the water.

7.2.4 Suspended Solids

Suspended solids are defined as material suspended in the water as compared with the dissolved solids which are in true solution in the

water. Among the many materials found as suspended solids in water are: (1) oil, (2) clay, (3) silt, (4) sand, (5) algae, (6) scale, (7) corrosion products: iron sulfide and iron hydroxide, (8) bacteria, (9) bacterial growths, and (10) precipitates formed due to commingling of incompatible waters (see Cerini et al., 1946; Amstutz, 1956; and Wright, 1965).

Several different schemes have been used in classifying suspended solids. Common classifications are:

1. Inorganic material (nonhydrocarbons)
2. Organic material (hydrocarbons)

This classification is convenient because the differentiation is easily made by determining the solubility of the material in a powerful hydrocarbon solvent. Suspended solids can be classified into:

1. Adherent
2. Nonadherent

Although this classification is hard to apply, it enables one to determine how harmful the suspended solids may be. Adherent solids are defined as those materials that either stick to solid surfaces on contact, such as oil, or form a coating over solid surfaces, such as scale. This classification is very valuable in water quality determinations, because the amount of adherent solid deposits is directly proportional to the amount of material available to form deposits. Using this criterion, one can classify the suspended solids as follows:

1. Adherent solids: (a) oil and (b) scale
2. Nonadherent solids: (a) silt and (b) sand
3. Either adherent or nonadherent solids depending upon composition and circumstances: (a) clay, (b) algae, (c) corrosion products, (d) bacteria, (e) bacterial growth, and (f) precipitates formed due to commingling of incompatible waters.

7.2.5 Movement of Formation Fines

Pore channels in reservoir rocks are tortuous and irregular in size along their length. Frequently, formation fines (mineral fragments, crystals, clays, etc.) are loosely cemented to the walls of pore channels. Any change that disturbs this cementation may allow these particles to

travel down the pore channels until they reach a restriction (pore throat and/or canal). If particles lodge in the restriction, permeability is reduced. The cumulative effect of movement of many particles is a drastic loss in injectivity. Some of the causes of destruction of cementation of formations are:

1. Significant changes in the salinity of water, either increase or decrease.
2. Change in pH
3. High injection rates

7.2.6 Sources of Suspended Solids

Some of the sources of suspended solids include:

1. Failure of sand control measures in water supply wells
2. Overtreatment with chemicals
3. A chemical incompatible with water or with another chemical in use in the water.
4. Air leakage into a closed system, yielding ferrous and ferric hydroxides and aerobic bacteria.
5. Commingling of incompatible waters
6. Overloading or improper operation of wash tanks where the water supply is produced water, resulting in excessive oil in the water.
7. Post-flocculation after filtration
8. Filter breakthrough

Suspended solids may cause the following problems:

1. Suspended solids are the raw materials for the formation of deposits on the interior surfaces of a system.
2. Suspended solids may be large enough to plug pore channels, causing a decrease in permeability and a consequent increase in pressure (decrease in injected volume).
3. In due time, suspended solids, large enough to be strained out of the water by the porous formation face, will build a filter cake and reduce the permeability, leading to an increase in the injection pressure (decrease in injected volume).

Adherent solids are the greatest offender in all three cases. Nonadherent solids, however, also are very detrimental if accompanied by

enough adherent solids to glue them together. It is often stated that suspended solids are not detrimental if they are small enough in size to enter the formation (Amstutz, 1956). This observation is valid only if no adherent solids are present.

An appreciation for the cumulative volume of suspended solids in a liner, if none of the solids enter the formation, may be gained by examining Table 7.3. This is the extreme case, however. Injectivity falloff occurs long before fill heights occur, as noted for 2,500 bbl/day injection rate in Table 7.3. The factors that determine the ability of the suspended solids to enter the formation include:

1. The size of the pores and pore channels in the formation
2. The size distribution of the suspended solids
3. The tendency of the suspended solids to agglomerate
4. The presence of oil, grease, or film-forming chemicals, which bind or glue the suspended solids together.

If suspended solids consisting solely of sand are strained out on the formation face, they cause no loss of injectivity until the formation face is appreciably covered by fill. On the other hand, if suspended solids consisting of clay and silt are strained out on the formation face, they form a filter cake causing very serious loss of injectivity. Suspended solids consisting of fine silt and heavy oil have the same effect as clay and silt.

The best generalization that can be made about suspended solids is that the fewer solids there are in the water, the better the water. If at all possible, the water should be kept completely free of particulate matter. One should always assume that the suspended solids will be

Table 7.3 Cumulative volume of suspended solids.[a]

Suspended solids concentration in injection water (ppm)	Height of fill in feet after 1 year in 5.5-inch, 15.5-lb/ft liner		
	500 bbl/day	1,000 bbl/day	2,500 bbl/day
1	5.3	10.5	26.3
5	26.2	52.3	131
10	52.5	105	263

[a]Assumptions: (1) None of solids enter the formation; (2) solids have a specific gravity of 2.5; (3) solids settle to a porosity of 40%.

screened out on the rock face and, thus, cause an increase in injection pressures (Baker, 1958; Spencer and Harding, 1959).

7.3 CORROSION

Corrosion is a costly item in waterflooding and must be dealt with immediately when detected. The onset of corrosion is usually insidious and the operator is lulled into a false sense of security.

One must understand the cause of corrosion in order to prevent it or stop it after it has started. It is relatively easy to protect a new, clean system, whereas it may be very difficult, if not impossible, to protect a corroded, dirty system, because protective chemicals seldom can penetrate deposits or enter deep pits filled with corrosion products. Corrosion in waterflooding operations is caused by:

1. Galvanic action
2. Stray currents
3. Dissolved gases
4. Bacterial action

Any mechanism for corrosion or any combination of mechanisms (sometimes all) may be present in a given water system at the same time.

The basic principles applying to all corrosion in water systems can be summarized as follows:

1. The metal cannot corrode unless the aqueous environment is in contact with the metal.
2. Condition in the aqueous environment must allow the cathode and the anode reactions to proceed.
3. It is not necessary for the cathode and anode to have different composition (metal).
4. The cathode and the anode must be electrically connected by a conductor.

It is customary to refer to the cathode and the anode as a cell. The types of corrosion cells in a water system are as follows (Unz, 1960):

1. **Concentration cells.** The concentration cell occurs when the same metal or two pieces of the same metal electrically connected together

are immersed in electrolytes having different compositions. The following are the two types of concentration cells:

a. The first and most important concentration cell is the differential aeration cell in which the difference in oxygen concentration produces a potential difference.
b. The second one is known as the salt concentration cell in which a difference in electrolyte (salt) concentration produces a potential difference.

2. **Dissimilar electrode cells.** Dissimilar electrode cells are considered galvanic cells where dissimilar metals are joined together. There are dissimilar areas of the metal brought about by heat treatment or other processes, grains of metal in contact with other grains, or even one metal crystal in contact with another metal crystal of different orientation (Barnard, 1959; Baumann and LaFrenz, 1963; also see Figure 7.3).
3. **Differential temperature cell.** The differential temperature cell occurs whenever the electrolyte in the cathode cell is at a different temperature than the electrolyte in the anode cell. Boilers and heat exchangers are typical examples of this type of cell.

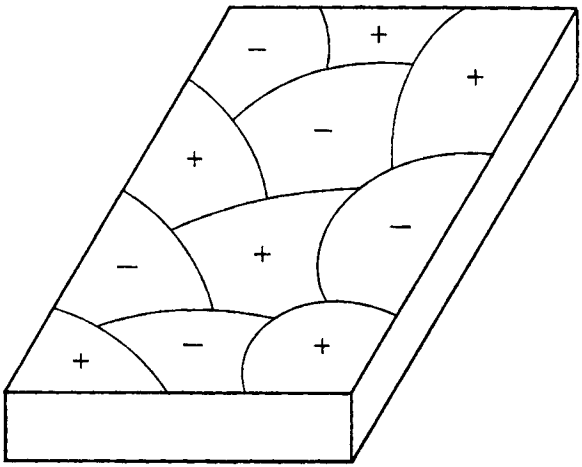

Figure 7.3 Schematic of metal surface arrangement of local action cells (after Unz, 1960).

7.3.1 Some Causes of Waterflood Corrosion

The two basic principles of corrosion can be stated as follows:

1. Metal cannot corrode unless the aqueous environment is in contact with the metal.
2. Conditions in the aqueous environment must allow anode electrode reactions to proceed.

Galvanic corrosion (contact of dissimilar metals) is not considered here (see Chapter 2 on Types of Corrosion). The effect of dissolved gases (carbon dioxide, hydrogen sulfide, and oxygen) on corrosion in a waterflood system is discussed below.

7.3.2 Carbon Dioxide

Carbon dioxide is the most common or prevalent cause of corrosion in a waterflood system. Carbon dioxide dissolved in water gives rise to bicarbonates and, with increasing pH, to carbonates.

A solution saturated with carbon dioxide, at equilibrium with carbon dioxide in the atmosphere, has a pH of approximately 4.2. A solution of sodium bicarbonate has a pH of approximately 8.5, whereas a solution of sodium carbonate has a pH of approximately 10.5 to 11.

The action of carbon dioxide upon metal is primarily an acid attack with or without pitting. There is also an indirect relationship between carbon dioxide and corrosion, however, in that loss of carbon dioxide from solution allows calcium carbonate scale to form with the attendant danger of establishment of differential concentration cells and/or anaerobic bacterial growth (within or underneath the scale). At any given pH, dissolved carbon dioxide causes significantly more corrosion than mineral acid, such as hydrochloric or sulfuric acid. This is due to the availability of more acid at that pH from the nonionized carbonic acid present, which replaces that consumed by the corrosion process. In the case of hydrochloric acid, there is no undissociated acid to draw upon.

7.3.3 Hydrogen Sulfide

In the direct attack of metal by hydrogen sulfide in freshwater, a protective tarnish film of mackinawite (Milton, 1966) ages and grows with

availability of hydrogen sulfide to the formation of crystallites of pyrrhotite (Fe_7S_8). This is followed by increasing corrosion and pitting. In brine solutions, the hydrogen sulfide gives rise to slowly growing mackinawite film and increasing corrosion rate increasing with time. Later, as the film becomes thick, the corrosion rate slows down as a layer of pyrite (FeS_2) is formed.

An indirect danger is that hydrogen sulfide causes depolarization of the cathode, owing to precipitation of ferrous sulfide.

Saturation with carbon dioxide, as well as with hydrogen sulfide, retards the development of the mackinawite tarnish and scale, resulting in lower corrosion rates. In contrast, as the mackinawite scale thickens in the absence of carbon dioxide, even higher corrosion rates result. There is a considerable amount of variation in corrosion rates with hydrogen sulfide depending upon the corrosion product. The nature of the corrosion product is influenced by the electrolyte composition.

7.3.4 Oxygen

Oxygen is a prevalent, most serious cause of waterflood corrosion. The corrosion rate caused by oxygen increases with increasing salinity until a level of approximately 1% NaCl is reached. Above this salt concentration, the corrosion rate falls off directly as the solubility of oxygen decreases with increasing salt concentration. Thus, the reduction in corrosion rate is caused by the reduction in the amount of available oxygen, and not by passivation. Similar effects are noted with other types of salt solutions.

The corrosion rate in the pH range of 4–10 is governed by the diffusion of oxygen to the surface of the metal through the oxide or hydroxide film. The barrier to diffusion is the ferrous hydroxide, which is continuously supplied by corrosion as it is taking place. Under this layer of ferrous hydroxide, the approximate pH is 9.5 (the pH of saturated solution of ferrous hydroxide). The ferrous hydroxide is dissolved below a pH of 4 and the metal surface is placed in direct contact with the electrolyte. At these low pH ranges, there is a rapid corrosion because of hydrogen evolution and oxygen depolarization. The corrosion rate drops sharply above a pH of 10 because of passivation in the presence of oxygen and alkali.

7.3.5 Interactions of the Gases

According to Dalton's law of partial pressures, the total pressure by a mixture of gases is equal to the sum of the partial pressures of each of the constituent gases. The partial pressure is defined as the pressure each gas would exert if it alone occupied the volume of the mixture at the same temperature.

Henry's law applies in conjunction with Dalton's law. The mass of a gas dissolved by a given volume of solvent at a constant temperature is proportional to the pressure of the gases with which it is in equilibrium.

Owing to its higher absorption coefficient, oxygen occurs in the dissolved gases in water at significantly higher ratio than in the air with which the water is in equilibrium. Both carbon dioxide and hydrogen sulfide, however, are far more soluble in water than oxygen.

Generally speaking, the gases are less soluble in aqueous solutions of electrolytes than in distilled water. This is known as the salting out effect. The salting out effect of a given salt is almost independent of the nature of the gas. Generally, the salting effect of an ion from a dissolved salt is larger, the greater the charge the ion carries and the smaller the size of the ion.

In the preceding discussion on solubility of oxygen and gases in water, equilibrium is assumed to be brought about by agitation. In case of quiescent water, as in a tank, diffusion is the governing factor and it may be relatively rapid. Oxygen may be introduced into the water by diffusion alone when the surface of the water in the tank is in contact with air.

It is frequently stated that: "Air is excluded by use of an oil blanket on top of the water." Unfortunately, oxygen has a reasonable diffusion rate through oil. Oxygen can pass through the interface into the water, although at a slower rate than if the water were in contact with the air directly. Furthermore, often the oil blanket will be transported to the injection well.

It is important to note that the corrosion rate of carbonic acid is reduced by the addition of small amounts of hydrogen sulfide, owing to the formation of uniform film of mackinawite over the metal surface. As the hydrogen sulfide concentration is increased, large crystallites appear on the surface. The number of crystallites increases with increasing hydrogen sulfide concentration until the entire surface is covered. These crystallites are believed to be an initial layer of pyrrhotite (Fe_7S_8) overlain by pyrite (FeS_2). Generally, only mackinawite is expected to occur in brine.

7.3.6 Bacterial Corrosion (See Chapter 3)

Corrosion is also caused by bacterial activity. Bacterial growth may be responsible for accelerating oxygen corrosion by the establishment of differential aeration cells. Bacterial growth may cause the depolarization of the differential aeration cells leading to much more violent corrosion. This is particularly true in the case of sulfate-reducing bacteria, as the hydrogen formed by metabolic activity can depolarize one-half of the cell by precipitation of ferrous ion as ferrous sulfide. Bacteria can depolarize the other half of the cell by removing the hydrogen evolved.

In the absence of dissolved oxygen, bacterial corrosion proceeds whenever environmental conditions are favorable and an infection has been established. The corrosion rate tends to be slow initially. Gradually, the corrosion rate accelerates with time, as the bacterial growth alters the environment to a more favorable set of conditions for growth under deposits or slime. Bacterial corrosion is typically characterized by extreme pitting and corrosion products consisting of mixed iron oxides and iron sulfides.

Unfortunately, as mentioned earlier, the entry of air into an otherwise anaerobic system containing bacterial growth causes an additive corrosion. The corrosion, due to the air, is being accelerated by the bacterial growth, depolarizing the actual concentration cells. This results in far more violent corrosion than is expected from the air alone or from the bacterial growth alone.

A brief summary of the causes of corrosion in a waterflood system is presented here. Actually many factors lead to establishment of the differential concentration cells, such as the formation of deposits and scales. Nonetheless, these cells are not formed unless the environmental conditions are conducive and dissolved gases are present.

7.4 USE OF SEAWATER FOR INJECTION PURPOSES

Seawater is chosen as the injection fluid for one or more of the following reasons:

1. Seawater is the only available water.
2. Seawater is the only available brine.
3. Seawater is less expensive than water from alternate sources.

Seawater rarely can be used as taken from the sea. Extensive processing is necessary to avoid future failure. Seawater, while easily injectable into almost all formation, can mean expensive lifting costs later. Sweet oil fields have been converted to sour oil fields simply by supplying sulfate ion to the ever-present sulfate-reducing bacteria. The resulting sulfide production in the oil formation means that at some point in the future, the produced gas must be sweetened before sale. Corrosion will be accelerated in the producing well due to the presence of increasing amounts of hydrogen sulfide.

Most sweet production is associated with water that contains barium and strontium ions. If they are present in more than trace amounts, formation of barium sulfate and/or strontium sulfate scale is possible in the producing wells and facilities. Prevention of scaling requires continuous chemical treatment, which is costly.

Where alternate sources of water are available, the costs of seawater must include these hidden costs that will show up later on the oil production side of operation. To do otherwise will be to invite financial disaster.

7.4.1 Characteristics of Seawater

The composition of seawater is not uniform around the world, as shown by a few examples of extremes below:

Location	Total dissolved solids (mg/L)
Open ocean	33,000
Indian Ocean	35,000
Persian Gulf	42,000–44,000
A site on Saudi Arabian coast W of Bahrain	56,000
Half Moon Bay, Saudi Arabia	67,000

Similar examples can be cited elsewhere in tropical or semitropical areas where extensive solar evaporation occurs and there is limited replenishment from the open ocean.

There are some characteristics of seawater that are the same regardless of location:

1. Oxygenated, usually near saturation.
2. At or exceeding calcium carbonate saturation.

3. Neutral or alkaline pH
4. High sulfate ion content
5. High magnesium ion content
6. Contains living organisms ranging from unicellular to plants and fish.
7. Shows seasonal changes in quality.
8. May contain oil.

7.4.2 Dissolved Oxygen

The dissolved oxygen content of seawater can be dependent upon location of the intake in the water column. Seawater at the surface may be saturated and even supersaturated in oxygen due to wave action, whereas deeper in the column the seawater may be well below saturation or still near saturation depending on the presence or absence of mixing currents. Seawater taken right at the bottom may be substantially depleted of dissolved oxygen due to reaction with the organic matter that rains down from above.

Decision as to where in water column it is best to position the intake should be taken only after sampling from top to bottom under all expected conditions.

7.4.3 Calcium Carbonate Saturation

Seawater in tropical and semitropical areas is at the saturation point with respect to calcium carbonate and may even show supersaturation for samples at or reasonably near the surface.

Any operation that is performed on seawater such as pumping, will cause a temperature rise. Serious consideration must be given to either stabilize the seawater by lowering the pH or to add a scale inhibitor to prevent the formation of calcium carbonate scale.

7.4.4 pH of Seawater

Seawater is neutral or slightly alkaline in the open ocean, whereas near the shore or in evaporation basins in tropical areas, it has higher values of pH, particularly in the summer (pH of 8.1–8.2 is not uncommon). These higher pH values may give trouble in the treatment of seawater.

The pH has a decided influence on the efficiency of chlorination, as well as on the rate of reaction of oxygen with sulfite ion (in the oxygen-scavenging stage).

7.4.5 High Sulfate Ion Content

Seawater, while primarily a chloride brine, has an appreciable sulfate ion content. Normal seawater has around 2,400 mg/L sulfate ion, whereas sulfate content of concentrated seawater from tropical or semitropical areas can reach 4,800 mg/L.

As mentioned earlier, the sulfate ion provides an environment for growth of sulfate-reducing bacteria. In addition, the sulfate ion promotes the formation of barium and/or strontium sulfate scale in producing wells when breakthrough occurs in formations containing barium and/or strontium ion.

The high sulfate ion content also precludes the use of certain treating chemicals, because they are soluble in sodium chloride brines but insoluble when significant amounts of sulfate ion are present.

7.4.6 Magnesium Ion

The magnesium ion in seawater is present in far greater concentration than the calcium ion. The magnesium ion will exchange for sodium ion on the clays (if present) in the formations being injected. The magnesium hardness may affect solubility of some treating chemicals.

7.4.7 Marine Life

Seawater has sufficient nutrients to permit growth of marine organisms. The growth can be very prolific if there is organic contamination in the nearby area. Marine growth includes anaerobic to aerobic bacteria, attachment organisms, shellfish, algae, plankton, and fish.

Shellfish growth can be sufficient to plug large-diameter pipes if growth is permitted. Growth has been measured in inches per year.

Seaweed also should not be ignored. At certain times of the year, seaweed has been known to plug traveling screens at some locations.

7.4.8 Seasonal Changes in Composition of Seawater

Seawater composition is significantly influenced by the time of the year (seasonal). Changes that are encountered include:

1. Temperature cycles from winter to summer
2. Variation of dissolved oxygen (cycles) with temperature, although not a direct relationship as might be expected from solubility limits.
3. Possible blooming of the algae
4. Possible occurrence of red tide with absence of oxygen
5. Planktonic organisms suddenly can greatly increase apparent solids content in seawater (Mitchell and Finch, 1978).
6. Storms can greatly increase the content of suspended solids.

7.4.9 Oil Content

It is very common to find small amounts of dispersed hydrocarbons in seawater. These dispersed hydrocarbons are usually the heavy ends, which are agglomerating the solids.

Oil contents can be quite high when the location is near shipping lanes. Hopefully, with the increased emphasis on not discharging tank bottoms, this source of pollution should decrease.

There is always the possibility of an oil slick in the event of a major tank discharge or accident. Normal practice is simply to shut down the intake until the oil is gone.

7.5 SELECTION OF WATER INTAKE LOCATION

There are three main types of intake:

1. Shallow well into a seawater aquifer
2. Intake from shore
3. Offshore intake

The freedom of choice as to the type of seawater intake is usually non-existent due to the location of project. Where the possibility of choice exists, a study should be made to determine the most economic choice.

7.5.1 Shallow Well in Seawater Aquifer

Water supply wells drilled into a prolific shallow seawater aquifer can offer significant advantages where possible. Properly completed shallow wells will produce water essentially free of both dissolved oxygen and suspended solids. This eliminates the need for the installation of deaeration and filtration facilities and offers substantial savings in both capital investment and operating costs. It is essential to complete these supply wells in such a manner that the casing–tubing annulus can be selected to prevent air entry (Wright, 1972).

7.5.2 Intake from Nearshore Area

An intake from nearshore area requires considerable investigation of local conditions prior to selection of the exact site in order to prevent future problems. Some of the elements of the investigations are:

1. Subsea contours
2. Shoreline currents
3. Tide extremes
4. Effect of storms
5. Character of ocean bottom
6. Cleanliness of water versus position in water column

The following example shows that compromises have to be made due to local conditions: A large waterflood in South America has its seawater intake located in the mudflat area of a large bay. The intake is out of water at low tide. Inasmuch as pumping can be conducted only between mid-tide and high tide, the intake is shut in one-half of the time. The water from the intake is pumped into large storage pits onshore so as to provide sufficient water for continuous operation of the treatment plant. The reasons behind this type of operation were:

1. Extending the intake trestle to deep water would have cost more than onshore storage.
2. Moving the intake location to an area where the mudflats did not exist would have increased pipeline cost to the field more than the cost of onshore storage and intermittent intake operation.

7.5.3 Offshore Intake

Platform operation that necessitates an offshore intake greatly simplifies the preliminary investigations because there are only two main considerations:

1. The water must be sampled from top to bottom of the water column to ascertain where the cleanest water can be obtained during the maximum amount of time.
2. The intake must be located upstream from the waste discharges from the platform (sanitary, kitchen, drilling fluid, etc.) as much of the time as possible. It is important to check influence of currents, tides, and storms.

7.6 DESIGN OF WATER INTAKE

The purpose of the intake is to insure that the cleanest possible water is continuously supplied to the treatment plant. The elements of a good intake facility are:

1. Trash screen
2. Fine screen
3. Chlorination

7.6.1 Trash Screen

The trash screen can be as simple as parallel bars spaced to prevent entry of large fish and trash. Large facilities are usually equipped with traveling rakes to remove the trash so that a dam does not build up.

7.6.2 Fine Screen

The fine screen is used to remove seaweed, fish, and small trash. These substances can blind the filter or foul the deaerator. The fine screen can be as simple as a wire-wound section of perforated pipe for a small-volume platform intake. Large shore-based installations usually have large-diameter rotating drum screens with high-pressure jet washers to

continuously clean the screen. Units are installed in multiples with at least one spare, so that one unit may be shut down for maintenance without shutting down the entire operation.

Units must be sized to handle the maximum amount of solids which could be encountered and still deliver the maximum amount of water that the treatment plant requires.

Materials of construction are quite important because the environment is the worst possible, i.e., intermittent submergence with full wetting in aerated saline water followed by full aeration. Any crevices present will set the stage for crevice corrosion if the metal is susceptible.

7.6.3 Chlorination

The purpose of chlorination is to prevent the growth or attachment of marine organisms to the submerged surfaces. In the absence of chlorination, algae and shellfish grow on the submerged surfaces. Shellfish growth can be of the order of several inches per year and can be costly to control if allowed to become established.

Chlorination, which can be accomplished by either adding chlorine or by adding hypochlorite (generated separately or in-line), can be either continuous or intermittent. Daily high-concentration slugs are common, although the preferred treatment is a continuous low-level dosage.

Chlorination is not as simple as it would appear when dealing with seawater in warm climates. There is a pH effect that limits the effectiveness of chlorine due to ionization constant of hypochlorite.

7.6.4 Filtration

A design decision must be made whether to filter before or after deaeration. There are advantages and disadvantages of using either method.

The advantages of filtering before deaeration is that deaerator will receive only clean water and, therefore, will not foul as quickly. Thus, a maximum deaerator effectiveness will be maintained for a much longer time.

The advantages of deaeration first is that the filters will be exposed only to oxygen-free water and, therefore, will not need to be lined and

cathodically protected. Furthermore, there should be minimum deterioration of water quality downstream of the filters because oxygen is not present to cause corrosion.

7.6.5 Deaeration of Seawater

Deaeration of seawater is essential because oxygen is the major cause of corrosion in any seawater operation. Removal of all of the dissolved oxygen enables operation with a bare steel system. Deaeration can be accomplished by the following methods:

1. Chemical treatment
2. Vacuum deaeration
3. Countercurrent gas stripping

Vacuum deaeration and countercurrent gas stripping are normally followed by scavenging of the residual oxygen traces by chemical means. Oxygen traces will be present unless the water temperature is high enough to permit complete deaeration.

Chemical treatment is normally the choice for very small and for temporary systems. Vacuum deaeration is the preferred method when sweet gas is not available or has high value.

Countercurrent gas stripping is usually the simplest and the most economical method when sweet gas is available. One system, however, exists that utilizes nitrogen gas obtained on site from a cryogenics plant that throws away the oxygen. It was the economic choice in one case described by Matheney (1980), because the size of the installation was large enough to make the cryogenics plant economical.

7.6.6 Oxygen Scavenging

Oxygen scavenging is done by reacting residual oxygen with sulfite ion in the presence of suitable catalyst. The sulfite ion can be supplied in several different forms:

1. Sodium sulfite is the preferred and most economical form when dry material is required for mixing on location.
2. Potassium sulfite has been the preferred form when sulfite solutions are shipped due to higher solubility of potassium salts, permitting a higher concentration product.

3. Ammonium bisulfate is sometimes a preferred form because of its far greater stability in stock solution form. The low pH of strong ammonium bisulfite solution inhibits the reaction of oxygen with the stock solution.
4. Sulfur dioxide is used wherever available in small cylinders. One large seawater treatment plant receives molten sulfur and burns it to produce sulfur dioxide on site, for use in scavenging oxygen and for pH adjustment in scale control.

Normally, cobalt is the best catalyst for the sulfite ion–oxygen reaction. At times, however, there is sufficient ferrous ion present in the seawater to catalyze the reaction. Sometimes, chlorination of the seawater (to stop marine growth) releases natural catalysts and, therefore, catalysts are not required. Reaction times can also be influenced by the pH of the water. This influence should be carefully examined, therefore, because it may affect the sequence of chemical treatment.

7.6.7 Stabilization of Seawater

Seawater is normally considered to have neutral pH. In tropical areas due to heavy evaporation in some basins and bays, however, the pH can be as high as 8.2.

Calcium carbonate in seawater is at or near saturation, whereas in tropical areas at the surface and in evaporation basins supersaturation can occur. Thus, seawater must be treated to prevent the formation of calcium carbonate scale. All the processing that is done to seawater to prepare it for injection and the injection process itself contribute to a rise in temperature which, in turn, causes the seawater to become more unstable.

Stabilization can be achieved by lowering the pH slightly. Sulfur dioxide, carbon dioxide, and sulfuric acid have been used for this purpose. Alternatively, scale inhibition can be employed. Common practice is to employ a scale inhibitor until the injection wells have been cooled down by sufficient water injection to permit the control of scale by slight lowering of the pH.

7.6.8 Temperature of Seawater

It should be remembered that the temperature of seawater will be nearly constant only if taken from deep zones (±300 ft) away from the

coast. The temperature of surface waters and waters in shallow coastal area can change substantially from winter to summer.

In any event, the temperature of seawater is significantly below that of practically all petroliferous formations. Thus, the injection of seawater will result in cooling of the formation, which will reduce oil recoveries by raising the viscosity of the oil. Another effect is the reduced amount of seawater that can be injected as compared to hot well water, due to higher viscosity of seawater caused by the lower temperature.

7.6.9 Biocidal Treatment of Seawater

After deaeration and oxygen scavenging, seawater may become devoid of chlorine. Consequently, some form of biocidal treatment becomes necessary.

There are several methods of controlling microorganisms, including surfactants, pigging, acidizing, and bactericidal treatment. Microorganisms grow on surfaces and do not constitute a problem in free-flowing water. Thus, any means of keeping all of the interior walls of the system clean will control microorganisms.

The preferred method is to use routine pigging and weekly to semi-weekly slug treatments by an effective bactericide. Where water temperatures are very low, such as in the North Sea, time between slug treatments can be extended significantly. The keys to successful microbiological control are:

1. Routine pigging
2. Routine monitoring of growth of microorganisms
3. Regular use of a bactericide compatible with seawater

It is important to point out that culture media made up in accordance with API RP 38 (API, 1965) rarely give satisfactory results if used to evaluate seawater. It is necessary to substitute actual seawater for the synthetic brine (API RP 38) in order to obtain satisfactory sensitivity.

7.6.10 Corrosion Inhibition

In the case of seawater, corrosion inhibitors are not required. Inasmuch as the pH of seawater is either neutral or slightly basic, in the absence of oxygen and biological growth the corrosion rate will be very low (usually 1 mpy or less).

Inasmuch as seawater is highly conductive, galvanic corrosion will occur unless care is taken to prevent the use of improper metallurgy. Crevice corrosion will be common in susceptible areas due to growth of anaerobic bacteria shielded from treatments.

In conclusion, it can be stated that there are enough differences between seawater and oil field waters that care must be taken in both the design and operation of a seawater injection system. In order to avoid a costly system, the peculiarities of seawater must be considered in the basic design (including metallurgy).

7.7 TEST METHODS USED IN WATERFLOODING OPERATIONS

The following test methods are used in waterfloodin.g operations:

Test	Method
Dissolved oxygen method	Membrane-shielded electrode, ASTM D 88881 (ASTM, 1982b)
pH	Glass electrode, ASTM Method D 1293-78 (ASTM, 1982b)
Membrane filter test	0.45-μm membrane filter, 4-ft waterhead (Wright and Cloninger, 1963), 0.45-μm membrane filter, 20-psi waterhead (NACE, 1973)
Total sulfides	Methylene blue with preconcentration to 1/10 volume (APHA, 1980)
Iron count	API RP 45 (API, 1968)
Sulfate-reducing bacteria	API RP 38, with modification that oilfield water is substituted for distilled water and salt (API, 1965)
Aerobic plate count	API RP 38, with modification that oil field water is substituted for distilled water and salt (API, 1965)
Direct microscopic count	API RP 38 (API, 1965)
Salinity	Mohr method (APHA, 1980)
Geochemical analysis	API RP 45 (API, 1968)

7.7.1 Dissolved Oxygen

Until about 1963, dissolved oxygen could not be measured with confidence below 0.12 ppm in seawater systems. At that time, a

dissolved oxygen meter became available with probable accuracy of 0.05 ppm.

At the present time, it is possible to connect the meter to a recorder and continuously record the oxygen content of the water. The reasons for the importance of oxygen content include:

1. Oxygen in water stimulates bacterial growth even when bactericides are being used. Often the bactericide must be fed to the system at significantly higher treatment levels to restore control, even though the oxygen entry has been eliminated.
2. The corrosion inhibitors in use are not capable of protecting against oxygen corrosion. Corrosion by oxygen is greatly accelerated by the presence of dissolved salt.
3. Dissolved oxygen may cause serious corrosion in the anaerobic areas under deposits or scale, because of development of differential aeration cells.

Schaschl and Marsh (1963) stated that "Isolated steel corroding by local cell action in well-aerated soil of low resistivity is a potential cathode for long cell action. If such steel is connected to steel in poorly aerated soil, long cell action will occur; the anodic cell will supply electrons to the cathodic steel. The net result is that the steel in the deaerated zone will corrode faster than if it is isolated, and it will cathodically protect the cathodic steel. Thus, if long cell action occurs under this circumstance, the local cell action corrosion rate at the aerated zone is suppressed."

"A pebble or a piece of wood in contact with steel in an aerated zone can set up a vigorous long cell in which the adjacent steel is the cathode and the steel area under the foreign object is the anode. With a low anode/cathode area ratio, corrosion rate at anodic area can be extremely high, particularly if the drained soil mechanism is operating at the cathodic area."

7.7.2 pH Change

The pH changes seldom are significant in the portion of waterflood water available for testing. The pH changes are important, however, because an increase in pH results in an increased tendency to deposit calcium carbonate scale.

A decrease in pH is rare, but occurs in the case of existence of an unusual combination of factors, allowing prolific growth of sulfur-

oxidizing bacteria. These bacteria convert hydrogen sulfide into sulfuric acid.

7.7.3 The Membrane Filter Test

The membrane filter test (Wright and Cloninger, 1963; Barkman and Davidson, 1972; NACE, 1973) is designed to determine the amount and type of solids suspended in the water. The filter retains all solids larger than 0.45 μm and practically all solids larger than 0.2 μm. The solids collected usually are comprised of one or more of the following:

1. Silt
2. Clay
3. Oil (usually plunger-lubricating oil)
4. Insoluble chemicals
5. Bacteria
6. Ferric hydroxide (precipitated due to the air entry)
7. Ferrous sulfide (corrosion product)
8. Calcium carbonate (scale)

The rate of water flow through the membrane is measured and the slope of flow rate-versus-time line is determined. The slope is a mathematical expression of the rate at which the membrane filter is plugged. The filter has a permeability of about 13 milidarcys, which is usually very low in comparison with the permeability of formations that are being waterflooded. Changes in the slope allow one to detect changes in the suspended solids in the water. The test is a very sensitive one and, usually, these data give the first warning that something has happened in the system.

An interpretation is made only after analyzing the solids collected on the filter. The results are then compared with the history of waterflood operation. The physical nature of the solids has considerable influence on the plugging rate; e.g., a few milligrams of oil as discrete droplets will not plug the filter, whereas the same amount of oil present as films over the other solids will result in plugging. Similarly, the degree of dispersion of iron oxide will affect the degree of plugging. Hydroxides of iron plug the membrane quickly. The amount and nature of solids in the water are influenced by the following:

1. Flow velocity
2. Presence or absence of organic binders, such as oil, film-forming chemicals, and slime.
3. Bacterial growth
4. Temperature
5. Air entry into the system

7.7.4 Total Iron Count Increase

The iron count increase is a measure of the amount of iron that has gone into solution. The total iron count increase measures not only the iron in solution, but also the iron in suspension, such as ferric hydroxide and ferrous sulfide. The iron count increase is not a reliable indicator, because much of the iron lost due to corrosion accumulates in deposits along the walls of the pipe. When iron count increases are large, trouble is to be expected.

7.7.5 Sulfate-Reducing Bacteria

Sulfate-reducing bacteria can be found growing under a wide variety of conditions. The salinity and temperature ranges are quite extreme. If secondary evidence suggests the presence of sulfate-reducing bacteria, one should either treat the system as if they were present or seek the services of a competent microbiologist experienced in working with sulfate-reducing bacteria.

Sulfate-reducing bacteria have been discussed with total sulfides. One is concerned with the actual counting of the bacteria, as contrasted with a measurement of one of their metabolic products, hydrogen sulfide. Present culturing techniques should be improved, because only a fraction of the live bacteria is counted. Thus, the determined number of sulfate-reducing bacteria in a sample shows only the minimum number present. There may be many more bacteria present. Inasmuch as the bacteria thrive only on surfaces, the bacteria counted in the water are only those eroded with deposits from the surfaces of the system or those traveling through the system.

Postgate in a monograph entitled "The Sulphate-Reducing Bacteria" (Postgate, 1979) stated that there are two well-established genera of sulfate-reducing bacteria, each with several members. Postgate's classification may be summarized as follows:

Sulfate-reducing bacteria	
Spore formers	Non-spore formers
Desulfotomaculum	*Desulfovibrio*
nigrificans	*desulfuricans*
orientis	*vulgaris*
ruminis	*salexigens*
antarticum	*africanus*
acetoxidans	*baculatus*
	gigas
	thermophilis

Sulfate-reducing bacteria constitute a potential problem in any system. Bacteria can double their numbers every 20 minutes under favorable conditions. Thus, any increase in number of sulfate-reducing bacteria across the system gives a strong danger signal, as the bacteria can get out of control quickly.

7.7.6 Total Bacteria

Aerobic Plate Count (Total Bacteria)

Aerobic plate counts are made even if one is dealing with oxygen-free systems. Most of the bacteria in waterfloods are facultative bacteria capable of growing under air-free or aerobic conditions. Many laboratories culture the bacteria under aerobic conditions because this is the simpler way.

The reasons for the concern for the presence of total bacteria are as follows:

1. Higher levels of bactericides are needed to kill sulfate-reducing bacteria in the presence of significant numbers of other bacteria.
2. The decay of total bacteria constitutes food for sulfate-reducing bacteria, giving a more favorable environment for bacterial growth.
3. A layer of aerobic bacterial growth constitutes an excellent screen in an otherwise hostile environment, allowing sulfate-reducing bacteria to thrive.
4. Bacterial growth can establish differential concentration cells giving rise to pitting.

Deep Agar Test (Total Bacteria)

Total bacteria determined by deep agar test are the bacteria other than sulfide-producing ones growing in deep agar tubes. These bacteria are counted easily and require no additional setup. One is concerned with the total bacteria determined by deep agar test and the total bacteria determined by aerobic plate counts for the same reasons. Total bacteria are most likely facultative aerobes, which require a low oxygen content for their rapid growth.

Membrane Filter Count Test (Total Bacteria)

Water is filtered through a membrane filter in the membrane filter count test. The bacteria collected on the filter are fixed, stained, and counted under a microscope. This technique is used periodically to check the culturing techniques. The number of bacteria is compared with that grown in culture media.

Iron bacteria are identified and counted separately in the membrane filter test, because they do not grow in the culturing tests. Iron bacteria are undesirable because their long, filament-like bodies mat together, forming an organic deposit wherever they lodge in a system. This organic deposit constitutes an excellent environment for sulfate-reducing bacteria, as well as setting up differential concentration cells.

7.7.7 Corrosion Coupons

Insulated Corrosion Coupons

Corrosion coupons are installed at selected locations adjacent to injection wells. An effort is made to install them at the lowest volume injection well furthest from the plant. These coupons are $3/4 \times 3 \times 1/8$ inches in size and are prepared from cold-rolled ANSI 1018 or 1020 mild steel. Thus, they represent an infinitesimal percentage of the surface exposed in the system. For details concerning the preparation of corrosion coupons, one should consult ASTM Method G1-72 (ASTM, 1982a) and NACE Recommended Practice 07-75 (NACE, 1975).

Inasmuch as the insulated coupon is electrically insulated from the system, theoretically its corrosion rate is related only to the corrosivity of the water. Experience has shown, however, that the corrosion attack

on the insulated coupon in a dirty system is similar in type and rate to that on the noninsulated coupon. Evidence indicates that the electrical insulation is nullified by a conductive film, which is probably associated with bacterial growth.

Corrosion coupons show significantly higher corrosion rates than adjacent spools or tubing. Probably, the following factors are involved:

1. The mild steel coupon is more susceptible to corrosion than the alloy steel used in the system.
2. The coupon is a clean specimen freshly installed in a dirty system. It is exposed for a relatively short time and, therefore, the initial corrosion is magnified by use of the time multiplier.
3. The method of exposing the coupon by placing it in the center of the pipe creates a zone of turbulence. The effect of this turbulence is unknown. It is known, however, that the amount and nature of the deposits on a coupon are not the same as those found on the pipe walls. The coupon has a thinner deposit, probably because of both high velocity of water and short exposure time. The deposit tends to be high in organic matter and low in solids content.

Noninsulated Corrosion Coupons

The same comments apply to the noninsulated coupons as to the insulated coupons. The noninsulated coupon is electrically connected to the system. Thus, a galvanic cell is deliberately set up with the higher probability that the noninsulated coupon is anodic to the system. It should be recognized that the corrosion rate obtained is not representative of the system.

Pitting corrosion appears first on the noninsulated coupons, probably because the galvanic cell setup provides an ideal environment for bacterial growth. The trend of the results of successive tests is carefully examined: the lower the corrosion rate on the noninsulated coupons, the better protected the system is.

Exposure Time of Corrosion Coupons

Exposure periods of 30, 60, and 90 days are recommended in the case of corrosion coupons. Thirty-day exposure period enables the quick

correction of problems of air entry, low pH, and gross bacterial contamination, which give large to excessive corrosion rates in 30 days. Sixty- and ninety-day exposure periods enable detection of pitting corrosion in a relatively clean system, which shows low corrosion rates without pitting on 30-day exposure. Detection of long-term pitting enables implementation of corrective action before significant damage is done.

7.7.8 Significance of Various Tests

In the conventional approach to water quality and corrosion control testing, use is made of many tests as described above. Some of these results are direct indication of factors affecting corrosion, whereas others give indirect indications:

Direct indicators	Indirect indicators
(a) Corrosion coupons	(a) Total sulfide increase
(b) Iron count increase	(b) pH and Eh changes
(c) Dissolved oxygen	(c) Membrane filter test
(d) Polarization probes	(d) Cultured corrosion coupons
	(e) Bacterial counts:
	(1) Sulfate-reducing
	(2) Aerobic plate count
	(3) Total bacteria
	(4) Membrane filter direct microscopic test

Indirect indicators deal with changes in the water, with the exception of cultured corrosion coupons. These changes in the water are caused or influenced by the environment at or near the metal surface–water interface. An understanding of what is measured and how that variable is influenced by the system enables one to interpret the test better. Water tests, to be meaningful, must measure the changes that have occurred in the water. The assumption that the water source is uniform and uncontaminated can be dangerous. The significance of various tests is presented in Table 7.4.

Originally, the iron count was expressed solely as parts per million of iron found in the water. Later, one examined the increase in iron count across the system. This method was better, but needed to be improved. Then iron count increases were expressed as pounds per day

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Table 7.4 Significance of various tests.

Test	Measurement	Significance
Direct measurement of corrosion		
Polarization probes	Corrosion rate	Pessimistic if allowed to become coated with deposits.
	Pitting tendency	Pessimistic if allowed to become coated with deposits.
Corrosion coupons		
Insulated	Corrosion rate	Believed to be pessimistic.
	Pit frequency	Believed to be pessimistic.
	Pit depth	Believed to be pessimistic.
Noninsulated	Corrosion rate Pit frequency Pit depth	Not a measure of system corrosion, but a measure of galvanic corrosion and bacterial depolarization.
Cultured	Corrosion rate Pit frequency Pit depth	Not a measure of system corrosion, but a measure of the presence and activity of causing or accelerating bacterial growth.
Indirect measurement of corrosion		
Iron count increase	Soluble and insoluble iron salts in the water	An averaging of iron losses between the two points where measurements are made, diminished by the amount of insoluble iron deposited on the walls of the pipe.
Direct measurement of bacterial growth		
Bacterial counts	Sulfate reducers Total bacteria, deep agar Aerobic plate count Direct microscopic count	Represent the populations in the water, but only suggest that bacteria are growing in the deposits. A negative answer is not conclusive.

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Table 7.4 Continued

Test	Measurement	Significance
Indirect measurement of bacterial growth		
Total sulfide increase	Soluble and insoluble sulfide salts in the water	The sulfide comes from bacterial reduction of sulfate ion. Amount of sulfide is related to the amount of bacterial activity and extent of infection. Answer is somewhat optimistic, due to precipitation of sulfide in deposits as ferrous sulfide. Test is an averaging of sulfide generated between the two points sampled.
Redox potential	Eh	Average measurement of all bacterial activities between the two points sampled. It is influenced by all bacteria, not just sulfate-reducers. Detects air entry in a closed system.
Tests relating to the environment		
Dissolved oxygen	Oxygen	Determines the oxygen content to 0.01 ppm in the water at the point of sampling.
Membrane filter test	Slope Amount of solids Composition of solids	Determines amount of solids and their probable tendency to cause deposits.

per 1,000 sq ft of metal surface exposed to the water. This permitted one to make direct comparison between portions of a system and between systems. A better way of expressing the rating, however, is as mils/year corrosion rate. The comparison of two different ways of expressing iron counts is shown in Table 7.5.

All iron count increases should be expressed as mils/year corrosion rate. This enables a direct understanding of the magnitude of the increase.

Table 7.5 Comparison of iron count units.

Iron count increase (lb/day/1,000 sq ft)	Corrosion rate (mils/year)	Rating
0	0	None
0.001–0.011	0.01–0.09	Very low
0.012–0.11	0.10–0.99	Low
0.12–0.59	1.00–4.9	Moderate
0.60–1.1	5.0–9.9	High
1.2	10.0	Excessive

Table 7.6 Revised rating chart of sulfide increase.

Sulfide increase (lb/day/ 1,000 sq ft)	Equivalent deposit thickness (inches)	Rating
0	0	None
0.001	0.072	Very low
0.002–0.004	0.014–0.028	Low
0.005–0.009	0.036–0.065	Moderate
0.01–0.019	0.072–0.137	Large
0.02 and over	0.14 and thicker	Excessive

Originally, the total sulfides were expressed as parts per million sulfides in the water. Later, engineers examined the increase in total sulfides across the system. This technique was better, but it still needed to be improved, as did the iron count method. Much later, total sulfides increases were expressed as pounds per day per 1,000 sq ft of surface. This permitted one to make direct comparison between portions of a system and between systems. As in iron counts, pounds of sulfides per day per 1,000 sq ft of surface was used as a unit. A considerable amount of introspection led to the concept that sulfate-reducing bacteria cannot thrive without having space in which to grow. This space is provided only by deposits.

Deposit thickness was then related to bacterial populations and to probable rate of sulfide generation. This resulted in the conversion of sulfide increases to probable deposit thickness. Probable deposit thickness is a term that can be visualized and, therefore, carries more meaning to the petroleum engineer (Table 7.6).

The use of rating chart for sulfide increases presented in Table 7.6 is based on the assumption that essentially all the sulfide generated in the

system is released to the water. This assumption is fairly reliable when there is no oil in the system to coat and bond ferrous sulfide to the pipe. It is also assumed that strong film-forming chemicals, such as the nitrogenous corrosion inhibitors and bactericides, are absent.

When a film former and/or oil is present, much of the ferrous sulfide created in a system is plated out as deposits. But not all the sulfides are plated out; some sulfides always remain in the water. The sulfide is present as colloidal ferrous sulfide or an excess of sulfide over and above that required to tie up the ferrous ion.

A sharp increase in total sulfides may be expected whenever chemical treatment is changed and earlier deposits are stripped off the walls of the pipe. The degree to which this occurs is a function of the nature of bonding material and the ability of the new treatment to disrupt the bond.

The problem with bacteria counts is that the number obtained cannot be visualized in terms of field application. It must be remembered that the bacteria that are counted in a water sample represent the sum of two components:

1. The bacteria entering the system and traveling through.
2. The bacteria eroded off the walls of the pipe from actively growing deposits.

Thus, to obtain an insight into the significance of a bacteria count, one must translate the number of colonies per milliliter into a universally usable number. Increase in the number of colonies per square foot of interior pipe surface is a usable measure.

The increase in bacteria expressed as number of colonies per square foot of surface has the same limitation as iron counts and sulfide increases, i.e., assuming uniform conditions between the two points sampled. Localized hot spot condition cannot be detected except by sampling at closer distances along the system.

High numbers of general bacteria colonies per square foot of surface have the same significance as a thick average deposit thickness, as determined by using the sulfide increase test. Simply stated, it means that the system is dirty. Remedial measures can be the same as those in the case of high sulfide increases.

The rationale of developing the numerical rating for increase in bacteria per sq ft per day is as follows:

The industry yardstick for numbers of general bacteria that do or do not constitute a problem was developed some 40 years ago. It was

determined that there was no loss of injectivity in a waterflood when the general bacteria counts were 10,000 colonies per milliliter or lower. When the general bacteria counts became 100,000 colonies per milliliter or larger, there was loss of injectivity. This observation has become the rule of thumb for most oil field personnel.

In preparing a classification, a flow rate of 3 ft/sec was assumed in a 6-inch diameter injection line 1 mile long. The assumptions are reasonable because the end result is in several orders of magnitude, whereas any errors in the assumptions would be substantially less than one order of magnitude (see Table 7.7).

The waterflood rating chart (Table 7.7) was developed to enable interpretation of the test data, which are usually determined during waterfloods. One can categorize the tests as shown in the following outline:

1. Measurement of actual corrosion:

Direct	Indirect
(a) Corrosion rate, insulated coupons (b) Pit depth, insulated coupons (c) Pit frequency, insulated coupons	(a) Iron count increase

2. Measurement of factors leading to corrosion:

Direct	Indirect
(a) Polarization probe (b) Sulfate-reducing bacteria	(a) Total bacterial count (b) Total sulfide increase (c) Direct microscopic count (d) Dissolved oxygen

3. Direct measurement of actual loss of injectivity: well injectivity.
4. Measurement of factors leading to loss of injectivity:

Direct	Indirect
(a) Membrane filter slope (flow rate-versus-time line) (b) Filtered solids	(a) Aerobic plate count (b) Total bacteria, deep agar (c) Direct microscopic count (d) Dissolved oxygen

Table 7.7 Waterflood rating chart.

Rating	1	2	3	5	10	20
Total sulfide (S) increases: equivalent deposit thickness, inches	$S < 0.007$ None	$0.007 < S < 0.014$ Very low	$0.014 < S < 0.035$ Low	$0.035 < S < 0.072$ Moderate	$0.072 < S < 0.14$ Large	$S > 0.14$ Excessive
Iron-count (Fe) increases: equivalent mils/year	$Fe < 0.01$ None	$0.01 < Fe < 0.1$ Very low	$0.1 < Fe < 1.0$ Low	$1.0 < Fe < 5.0$ Moderate	$5 < Fe < 10$ Large	$Fe > 10$ Excessive
Increase in sulfate-reducing bacteria, colonies/mL	None	Sporadic random appearance Questionable	Absent more times than present Acceptable	Present more times than absent Moderate	Always present 1–9/mL Large	Greater than 9 col/mL Excessive
Increase in total bacteria count (B), colonies/sq ft/day	$B < 10^7$ Negligible	$10^7 < B < 10^8$ Very low	$10^8 < B < 10^9$ Low	$10^9 < B < 10^{10}$ Moderate	$10^{10} < B < 10^{11}$ Large	$B > 10^{11}$ Excessive
Corrosion rate, 30 days, insulated coupons mils/year (mpy)	$mpy < 0.01$ None	$0.01 < mpy < 0.1$ Very low	$0.1 < mpy < 1$ Low	$1 < mpy < 5$ Moderate	$5 < mpy < 10$ High	$mpy > 10$ Excessive
Pit depth, 30 days, insulated coupons, mils	0 None	1 Shallow	2–3 Minor	4–5 Moderate	6–10 Deep	10+ Excessive
Pit frequency, 30 days, insulated coupons, pits/sq in.	0 None	1 Very low	2 Low	3 Moderate	4 High	5+ Excessive
Permeability (k) of filter cake, mD	$k > 4$ Excellent	$4 > k > 0.4$ Very good	$0.4 > k > 0.04$ Acceptable	$0.04 > k > 0.004$ Moderate	$0.004 > k > 0.0004$ Fair	$k < 0.0004$ Poor
Suspended solids (SS) increase, mg/sq ft/day	$SS < 170$ Excellent	$170 < SS < 350$ Very good	$350 < SS < 520$ Acceptable	$520 < SS < 870$ Moderate	$870 < SS < 1{,}300$ Fair	$SS > 1{,}300$ Excessive

After Wright (1963) and Collins and Wright (1982).

Relative importance of the various tests is presented in Table 7.8. There are two kinds of tests: (1) those that measure the actual corrosion, and (2) those that measure the environment conducive to corrosion.

No system is safe unless results of all tests are favorable. The system is rated as "reasonable" or "in trouble," depending upon whether the present time or the future is considered. Often a system requires 2 or 3 months to fully respond to a certain action. The crux of the problem is that one is trying to interpret tests run at the wellhead and predict the nature of conditions in the injection well. On examining the results of various tests, one may reach the following conclusions:

1. If deposits and/or scale are building up at the wellhead, they are building up in the well.
2. If bacterial growth is occurring at the wellhead, it is occurring in the well.
3. If corrosion is occurring at the wellhead, corrosion is occurring in the well.
4. If oxygen is present in the water at the wellhead, corrosion is occurring in the well.

Table 7.8 Relative value of tests.[a]

Test	Corrosion indicator	Ability of test to predict future corrosion
Dissolved oxygen	1	5
Polarization probe		
Corrosion rate	1	5
Pitting rate	1	5
Corrosion coupons		
Corrosion rate	1	5
Pit depth	1	5
Pit frequency	1	5
Iron count increase	2	4
Sulfate-reducing bacteria	3	1
Total bacteria	4	2
Total sulfide increase	3	1
Membrane filter slope (flow rate-versus-time line)	5	3
Filtered solids	5	3

[a] Scale: 1 = best.

Usually, one is restricted to making measurements at the wellhead where the water has traversed only 10% of the system. One must, therefore, infer, interpret, or guess what the actual conditions in the well are. A trend, with time, toward conditions conducive to corrosion may be bad, even if the actual values are low. In addition, conditions such as deposit and/or scale formation that cannot easily be reversed must be prevented.

Bacterial growth can be controlled easily in the absence of deposits and/or scale. In addition, corrosion inhibitors perform best when the system is clean. Consequently, in interpreting the test results, one must give considerable weight to any test indicating the buildup of deposits. The tests presented in Table 7.9 give some clues as to the existing conditions. The tests indicating corrosion and deposit buildup are the most significant.

Possibly, one could minimize the interpretative difficulties by making determination on surfaces exposed in the system. It may be practical to expose a surface for 30 days or longer, remove it from the system, and make the following determinations:

1. Amount of deposit
2. Nature of deposit
3. Composition of deposit (water, hydrocarbons, and nonhydrocarbons).

Table 7.9 Significance of various tests.

Test	Remarks
Membrane filtration test	
Slope of flow rate-versus-time line	Measures the plugging ability of solids; it is directly related to their ability to form deposits.
Filtered solids	Measures the amount of solids in the water available to form deposits.
Total bacteria count	When the count is above 10,000 per mL, there is a strong probability of slime growth.
Total sulfide increase	Measures the activity of sulfate-reducing bacteria in deposits and indirectly indicates the thickness of deposits.
Corrosion coupons	The presence and amount of deposit on the coupon is related to the presence and amount of deposits in the system.

The significance of various tests can be summarized as follows:

1. The insulated coupon test directly measures corrosion. The disadvantage of this test is that it represents only the conditions present at that one location, which is an infinitesimal fraction of the surface area of the system.
2. Noninsulated and cultured coupons tests elucidate the mechanism of corrosion by providing a more favorable environment for corrosion.
3. Dissolved oxygen and total sulfide increase tests directly measure factors that cause or accelerate corrosion. The dissolved oxygen test is direct and realistic. The sulfide increase test can be optimistic, due to binding of sulfides in the deposits as ferrous sulfide.
4. Two tests measure bacterial growth in the system. The bacterial counts represent only those bacteria eroded away from deposits. Thus, a negative answer is always questionable. The redox potential change is an averaging test, which indirectly indicates the amount of total bacterial activity between two points, or indicates air entry in a closed system. This test is reliable in the presence of large differences, but is not reliable when small differences exist.
5. The membrane filter test measures the amount and kind of solids in the water. Proper interpretation of this test allows the correction of conditions which cause deposition, before significant deposits are formed.

There are many useful tests, but their quantitative significance is hard to determine, because most of the tests are indirect measurements of processes taking place in the system and only partially measure the dynamics at the metal surface–water interface. Inasmuch as one is measuring the change that has occurred in the water, it must be determined where the change took place. Conceivably the following alternatives are possible: (1) The entire system between sampling points contributed uniformly to the change. (2) Only 10% or less is responsible for the change, and 90% or more of the system between the sample points did not contribute to the change. Under these circumstances, a given change can be interpreted as catastrophic or negligible in nature, depending upon whether one assumes that 10% or less of the system or the entire system caused the change. Interpretation of water tests, therefore, is fraught with many apparent contradictions between predictions and actual field results.

7.7.9 Reporting of Test Data

An immediate verbal report of test data is made whenever conditions warrant correction. A written report of the findings, together with recommendations, is made as soon as the laboratory phase of the testing is completed, except the test for sulfate-reducing bacteria. The latter report includes preliminary bacterial counts after 1 or 2 weeks of incubation. Final bacteria counts are made at the conclusion of 4 weeks of incubation, as prescribed in API RP 38 (1965).

Test data are plotted on time series graphs. This graphical presentation is examined monthly and enables a quick detection of trends. This is very valuable, because if water is sampled only once a month, erroneous conclusions can be reached if judgment is based on analysis of a single sample.

7.8 COPRA CORRELATION

If one assumes that the corrosion iron loss occurs over the entire length of the tubing string, the iron count data can be used to calculate the uniform overall corrosion rate by using the following formula (Chambers and Hillegeist, 1975; Gatzke and Hausler, 1984):

$$CR_u = (C_{Fe} \times Q_{H_2O})/(0.082Ld)$$

where CR_u is the uniform corrosion rate in mpy; C_{Fe} is the iron count in produced water in ppm; Q_{H_2O} is the total water production in bbl/day; L is the length of tubing in ft; and d is the inside diameter of tubing in inches.

Inasmuch as the corrosion rates in flowing gas wells depend on gas/water ratios, Burke and Hausler (1985) developed COPRA correlation (corrosion rate—production rate) in order to predict the actual fluid corrosivity and to evaluate the inhibitor treatments. They used the following formula:

$$K_G = CR_{Fe}/R_{wg}$$

where K_G is the normalized (or relative) average corrosion rate; CR_{Fe} is the uniform corrosion rate computed from iron counts or coupon tests; and R_{wg} is the ratio of water production in bbl to gas production

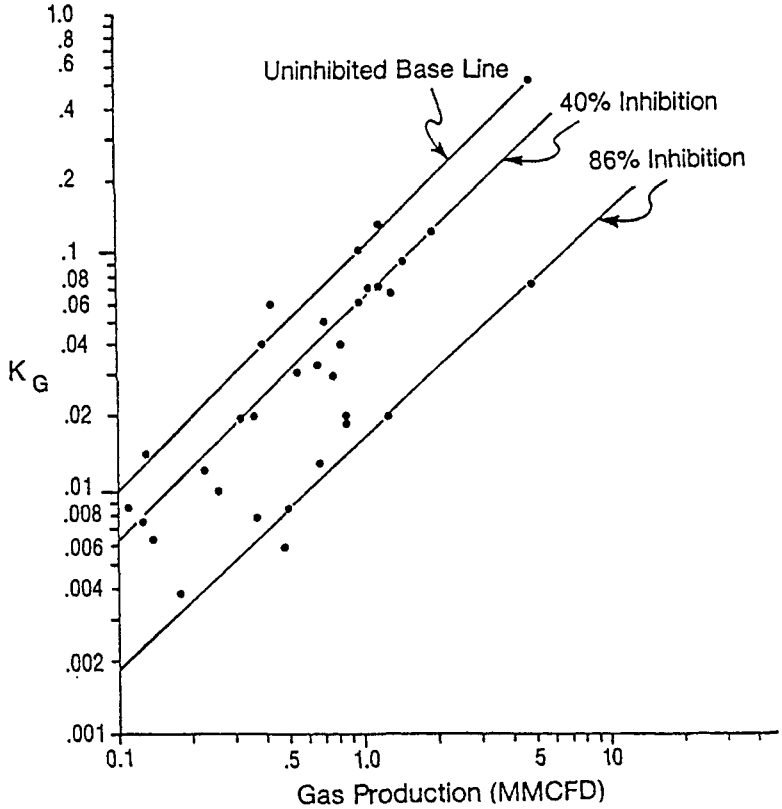

Figure 7.4 Corrosion rate–production rate correlation for a group of gas wells before and after initiation of a corrosion inhibitor program (after Burke and Hausler, 1985; also see Jones, 1988, p. 94).

in MMcf. The K_G is then plotted versus the gas production rate (Figure 7.4). The slope of the line indicates corrosivity of a group of wells regardless of water/gas ratios.

7.9 PREPARATION OF WATER FOR SUBSURFACE INJECTION

There is a limited choice of deciding how to prepare water for subsurface injection, because the nature of the effluent has a decided bearing on the problem. The choice is very limited in specific instances. Some

treatment processes (see Wright and Davies, 1966) are common to all sources of water, whereas others are peculiar to one or more sources. Figure 7.5 is a schematic of a Mid-Continent waterflood installation. The major treatment processes for water injection are as follows:

1. Oil removal
2. Gas removal
3. Solids removal

All other treatment processes are subsidiary to these three main processes.

7.9.1 Oil Removal

Oil removal is basic to all treatment processes involving oil field water, although the necessary completeness of oil removal may vary widely. There is an economic limit or dividing line for each lease when the amount of oil removal for the value of the oil recovered ceases to be profitable.

The ease of removing oil from water is greatly influenced by chemical treatment and the physical handling of the oil–water mixture before it reaches the injection water system. Frequently, the operator may

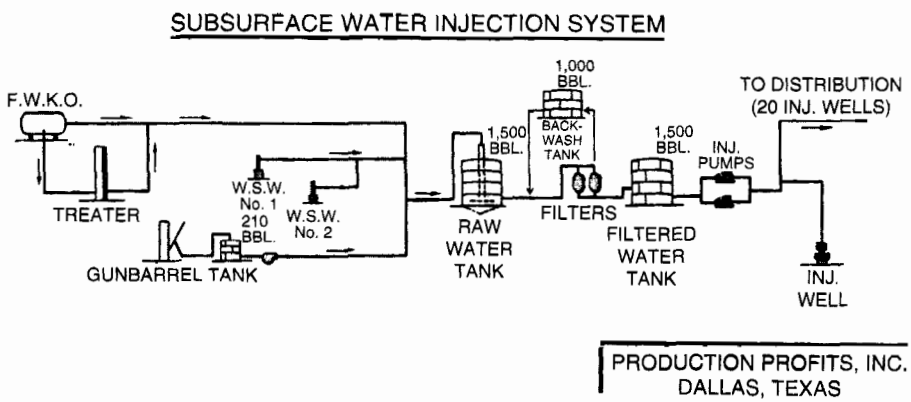

Figure 7.5 Schematic of a Mid-Continent waterflood installation (courtesy of Production Profits, Inc.).

make a minor change in the chemical treatment or the physical handling of the oil–water mixture before it reaches the injection water facility. This change may result in a considerable increase in the cost of injection water facility.

The treatment and handling of oil and water from the point where they leave the formation to the ultimate injection of the water must be viewed as an integrated process. All changes, mechanical or chemical, must be reviewed for their total effect on the system, not just the immediate problem at hand. The following examples illustrate the need for integrated approach:

1. Overtreatment of producing wells with certain types of scale inhibitors will stabilize the dispersion of oil in water, making oil removal in the injection water system more difficult.
2. Certain types of corrosion inhibitors act as oil-in-water emulsifying agents and will cause oil-in-water emulsions to appear in the injection water facility when used in slug treatment.
3. Some emulsion breakers used today, which give rise to very clean oil, produce very stable oil-in-water emulsions in the injection water facility.

There are three practical methods of removing oil from water, each one having its distinct place in water treatment: gravity separation, flotation, and filtration.

7.9.2 Gravity Separation

In gravity separation, the oil and water mixture is allowed to separate into two distinct phases, owing to the difference in specific gravity between the oil and water. This process, which is highly effective with low-specific-gravity oils (high °API)*, becomes less effective or even impossible with high-specific-gravity oils (low °API).

The separation is significantly aided by temperature. Temperature reduces the viscosity of the dispersion medium (water) and further increases the specific gravity differential between the oil and water (Figure 7.6). The less the specific gravity difference between the oil and

* °API = (141.5/sp. gr. at 60°F) − 131.5.

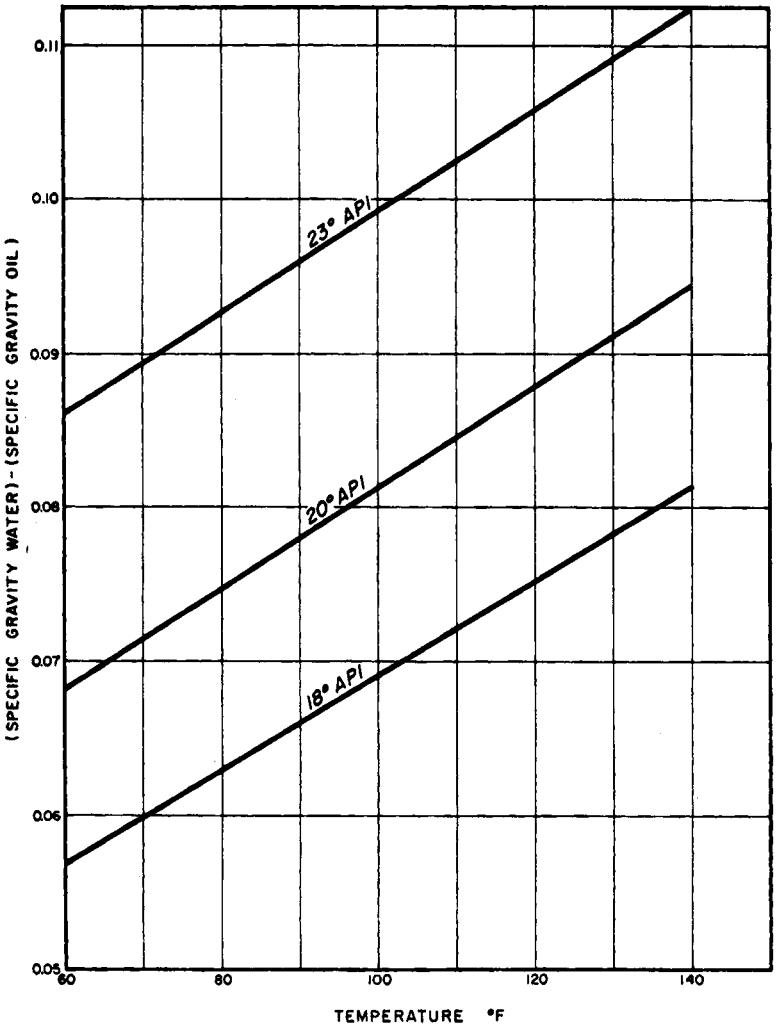

Figure 7.6 Effect of temperature on specific gravity difference between water and oil.

the water, the lower the rising velocity of oil and, therefore, the longer the residence time required in the separator.

The subject of gravity separation has been covered in detail in an API manual in 1963 (API, 1963). The following references should be consulted when the engineer is dealing with tanks, API gravity separators, or open ponds, because the principles are the same in all cases: API

(1951), Ingersoll (1951), Johnston and Campbell (1957), Brunsmann et al. (1962), and Chilingarian et al. (1989). Usually, utilization of these principles gives a high degree of success in oil removal. The causes of difficulty of oil removal in the unusual case may be the presence of emulsions or the lack of sufficient specific gravity difference between oil and water. When the gravity separator does not give the desired degree of oil removal or it is not feasible or economical to use a properly designed gravity separator, one must use the flotation equipment.

7.9.3 Flotation

There are two distinct types of flotation processes: dissolved gas flotation and froth flotation. Froth flotation is an adaptation of a beneficiation process long used in the mining industry. Froth flotation requires the addition of a chemical to stabilize the froth, which is mechanically formed by "beating" air or gas into the water. Froth flotation is less sensitive to overloading than dissolved gas flotation; however, it has other shortcomings. These may limit the application of froth flotation to a specific system and field trials are highly recommended.

Aside from the manner in which the gas bubbles are formed in the water, the two types of flotation processes are similar. Dissolved gas flotation is a process in which gases are dissolved into the water under pressure. Upon subsequent release of pressure, the evolving bubbles become attached to particulate matter and/or oil, and float to the surface where they may be skimmed off (Katz, 1958, 1960; Simonsen, 1962; API, 1963; Chilingarian et al., 1989). Flotation is a highly efficient method of removing suspended oil from water when the load is less than 100 ppm and emulsions do not exist. Increasing amounts of oil are left in the water as the incoming load increases. The flotation process has the following shortcomings:

1. Emulsions are seldom resolved.
2. Suspended solids may interfere with oil removal.
4. High incoming oil contents give rise to more oil in the output.
5. The process is very sensitive to (a) velocity or throughput, (b) gas/water ratio, and (c) recycle ratio.

When the flotation cell is overloaded or when emulsions are present and cannot be prevented by remedial measures upstream, one must use supplementary chemical treatment with flotation cell. Certain clays are

good adsorbents of oil. Adding these clays as a slurry to the flotation cell, followed by a polyelectrolyte, results in a very clear water discharge. Alum, alone or with coagulant aids, also helps an overloaded flotation cell or one receiving emulsions. Physicochemical theory of coagulation of colloids has been discussed by Black (1948, 1960), Stumm and Morgan (1962), Riddick (1964), and Hudson (1965).

Filtration is necessary when the last traces of oil must be removed from the water and when gravity separation and/or flotation are inadequate. Filtration is also used when solids must be removed.

7.9.4 Removal of Solids (Filtration)

Filtration must be viewed as a cleanup or "polishing" operation, as it is not economical for removal of large amounts of solids or oil from water. The choice of a filter is based upon the following factors: (1) quality of effluent desired, (2) amount of suspended solids, (3) nature of suspended solids, (4) capital cost versus operational cost, (5) space available, (6) weight of installation (offshore platform loading considerations), (7) flexibility of operation desired, (8) salvage value, (9) degree of mobility of equipment desired, (10) variability in quality of incoming water, and (11) degree of reliability of operation required.

Conley (1965) has presented an excellent discussion on the interrelation of the various components of a water treatment plant, showing how to determine the optimum treatment practice and optimum sizing of the various components for greatest economy.

The classic concept of water filtration is the use of the slow sand filter in which a layer of solids (filter cake) is built upon the top layer of sand. This layer is known as the "Schmutzdecke." (It is composed of the solids causing the turbidity in the water, and bacterial growth.) The filter cake concept applies only to the slow sand filter. The rapid sand filters build a collected solids zone inside the top layers of the filter media.

In the past, all domestic water plant installations have had sand filters, either slow or rapid. A revolution in water filtration has occurred in the last five decades. This revolution had its origin in the need for mobile treatment plants for use by the armed forces during World War II. Portable diatomaceous earth filters were devised and used extensively by the armed forces. In recent years, the utility of these diatomaceous earth filters has led to a determined assault on the problems of water filtration.

The following types of filters are discussed here: (1) slow sand filters, (2) rapid sand filters, (a) gravity sand filters, (b) pressure sand filters, and (3) diatomaceous earth filters. Each filter has its proper place in water treatment.

7.9.5 Slow Sand Filters

The slow sand filters have been replaced by the rapid sand filters in most installations, because the slow sand filter requires very large surface area for its operation, is inflexible, and is not backwashable. Regeneration of the filter bed required physical removal of the top layer of sand with "Schmutzdecke," which was done with shovels.

7.9.6 Rapid Sand Filters

Rapid sand filters are divided into two main types: (1) gravity filters and (2) pressure filters. The principles of the two types of filters are identical. The pressure filter is operated at elevated pressures, thus prolonging the filter cycle and/or increasing the rate of flow of water through the filter. Gravity filters are commonly operated at 2 GPM/sq ft*, whereas pressure filters are operated at 3 GPM/sq ft and higher.

The rapid sand filter is operated with clarification ahead of the filter. This step reduces the load on the filter, allowing longer filter runs and high-quality effluent at higher flow rates. Rapid sand filters have a layer of sand on layers of graded gravel and do not utilize a "Schmutzdecke" layer for the filtration action. Instead, the particulate matter is adsorbed on the sand in the layers below the surface. A considerable amount of support for the adsorption of solids (causing turbidity) as the predominant removal mechanism of rapids and filters was gained from the report of O'Melia and Crapps (1964) in their study on the chemical aspects of filtration.

Rapid sand filters are customarily operated with sand on top of a graded gravel bed. A considerable amount of interest, however, has been shown in some areas in the use of sized coal in place of sand. Coal has the advantage of lower density, occupying greater volume per unit

* GPM or gpm = gallons per minute; 1 gal = 0.003785 cu m = 3,785.43 cu cm.

weight and, more important, requiring lower velocity of the backwash water to suspend the coal bed during the washing or scrubbing cycle. Coal, however, is soft and abrades rapidly with reduction in particle size. This results in losses during the backwash cycle and, consequently, coal replacement is much more frequent than that of sand.

A skid-mounted bank of three high-rate rapid sand filters ready for shipment to the field is presented in Figure 7.7. Figure 7.8 is a cutaway drawing of a high-rate rapid sand filter showing the internals and the media. Figure 7.9 shows the inlet distributor, whereas Figure 7.10 shows the bottom drain collector for a high-rate rapid sand filter. The openings are spaced to obtain an equal flow through each.

7.9.7 High-Rate Rapid Sand Filters

High-rate rapid sand filters have been developed in the 1960s (Udwin, 1971). Rates exceeding 10/gal/min/sq ft with effluent quality of less than 0.2 mg/L of suspended solids are not uncommon. The high filtration rate is achieved by optimizing inlet and discharge header flows in order

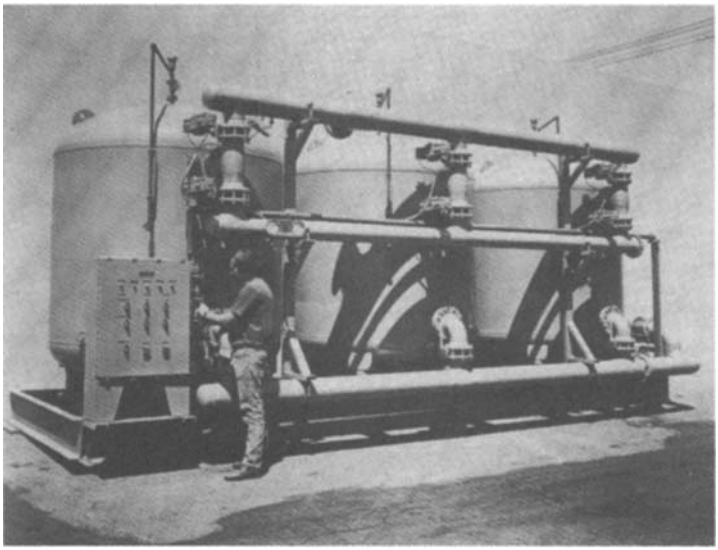

Figure 7.7 Skid-mounted bank of three high-rate rapid sand filters (courtesy of Serck Baker, Inc.).

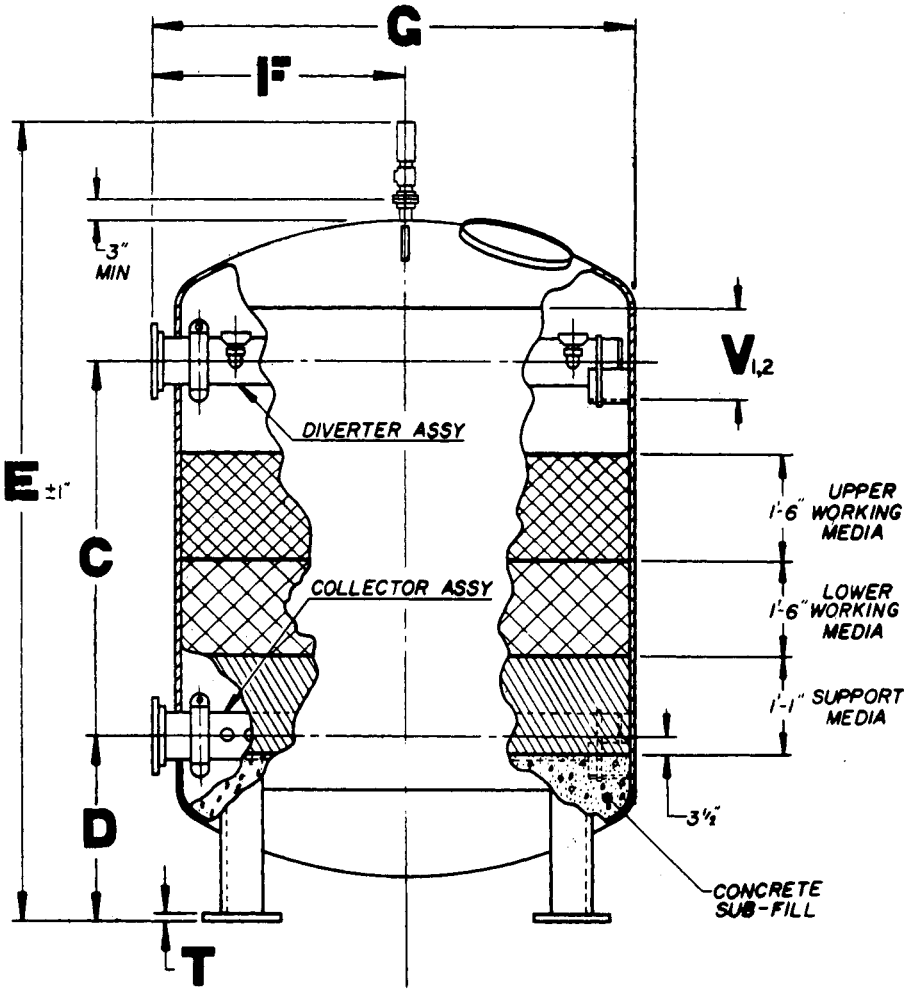

Figure 7.8 Cutaway drawing of a high-rate rapid sand filter (courtesy of Serck Baker, Inc.).

to obtain uniform flow through the entire filter bed. Dual-media beds are common and some triple-media beds are in use.

Dual-media may consist of coal on top of sand or coal on top of garnet. Triple-media beds consist of all three, i.e., coal, sand, and garnet. A combination of particle size and specific gravity serves to adjust the mass of the particles of each media so that minimal intermixing of the layers takes place during backwashing. The use of multiple media

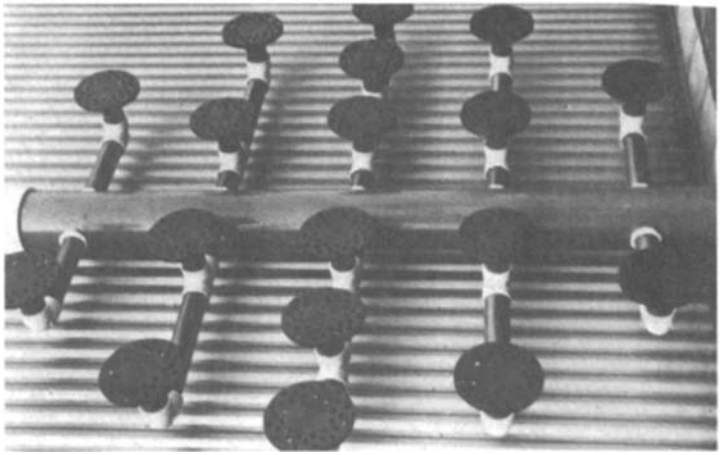

Figure 7.9 Inlet distributor for a high-rate rapid sand filter (courtesy of Serck Baker, Inc.).

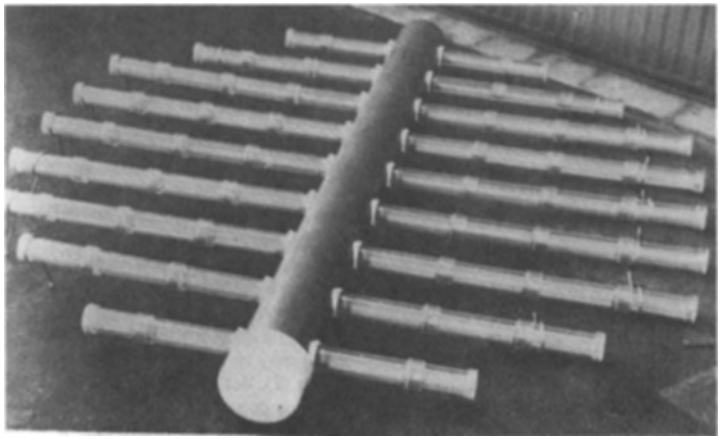

Figure 7.10 Bottom drain collector for a high-rate rapid sand filter (courtesy of Serck Baker, Inc.).

permits either higher bed loadings or longer filter runs. Normally, the coarsest particles are at the inlet of the filter bed.

Other types of high-rate rapid sand filters have been developed and promoted. A popular type is the upflow filter in which the inlet is at the bottom and the flow of water is up through the bed. Whereas advan-

tages are claimed for upflow filters, one must be aware of their sensitivity to hydraulic shock, which can cause unloading of collected solids into the filter effluent. In another type of filter, the inlet is at the center, with flow occurring both upwards and downwards from the middle of the bed.

It is strongly advised that filters be purchased based on either field trial or performance under identical circumstances. There have been too many failures when filters were purchased on the basis of "specifications" alone, without trial.

7.9.8 Diatomaceous Earth Filters

Diatomaceous earth filters consist of a screen or screens upon which a foundation of cellulose fibers and diatomaceous earth is laid (called "precoat"). Once the precoating is in place and functioning, water filtration is commenced with a continuous addition of diatomaceous earth slurry called filter aid, body feed, or slurry feed. Whereas diatomaceous earth is the customary choice, expanded perlite is preferred in some areas, owing to its local availability or availability at a lower price than diatomaceous earth. A task group of the American Water Works Association led by Baumann (1965) prepared a report on diatomite filters, with many references. This report covers in detail the design, installation, and operation of diatomite filters in large-scale plants. It should be consulted for general background information.

Baumann and LaFrenz (1963) reported on the extreme need for optimizing filter design, as water production costs can be four to five times higher than necessary if other than optimum conditions are used for flow rate, terminal head loss, and body feed. Automatic operation proved to be most economical for all waters and plant sizes. Maintenance of an automated plant, however, can be a problem if qualified personnel are not readily available.

In a paper presented by Bell (1962), a considerable amount of information is made available about various aspects of design relating to hydraulic velocities, septum considerations, adequacy of filter cleaning, precoating technique, and principles of continuous slurry feeding.

7.9.9 Selection of Diatomite

Several grades of diatomite are available for use as a filter aid. The principal difference among the various grades of diatomite is particle

size distribution, which gives rise to differences in filtration properties. The finest size filter aid, which gives the lowest flow rate, is used for removing tight emulsions and ultrafine colloids. The coarsest grade of diatomite (high flow rate), on the other hand, produces water of good clarity when the "turbidity" is due to relatively coarse particles.

The common shortcoming of inadequately prepared diatomaceous earth is short filter cycles, resulting from the rapid buildup in filtration pressure. The final selection of a filter aid should be made only on the basis of field trials, inasmuch as one is striving to optimize the following variables: filtration pressure, filter effluent clarity, filter cycle time, and rate of flow through the filter.

When diatomaceous earth filters are properly run, they deliver high-quality water. One can routinely obtain filtered water having 0.2 ppm suspended solids. Unfortunately, it is very easy to plug wells on using improperly operated diatomaceous earth filters. Some of the causes of filter failure are as follows:

1. Leaving open the line to high-pressure pumps when backwashing and precoating filter. As a result, large amounts of fiber and diatomaceous earth are injected into the wells.
2. Dropping off of the filter cake and precoat from the screen, in whole or in part, owing to temporary shutdown of the filter or to a momentary pressure surge. Subsequent operation of the filter results in all slurry feed and all suspended solids going through the filter into the high-pressure pumps and/or into the wells.
3. Inadequate precoating of the screens which may leave holes in precoating. This results in the same condition as described in (2), but to a lesser degree.
4. Leaving a backwash valve open, partially or completely, after backwashing the filter. This results in partial or complete bypassing of the filter. This is worse than having no filter at all, because, in addition to bypassing the filter, filter aid is supplied continuously to the water.
5. Mechanical damage to the septum allowing precoat and body feed to pass through.

Frequently, it is advisable to install strainers or in-line filters downstream of a diatomaceous earth filter to prevent mistakes or problems that could result in plugging of wells.

7.10 REMOVAL OF DISSOLVED GASES

In addition to oil and solids removal, sometimes dissolved gases also must be removed. The commonly encountered dissolved gases and resulting problems are as follows:

Gas	Problem
(1) Hydrogen sulfide	Corrosion, precipitation of iron sulfide
(2) Oxygen	Corrosion, bacterial growth
(3) Carbon dioxide	Corrosion

Undesirable dissolved gases may be removed from water by (1) aeration, spraying or cascading; (2) vacuum degassing; (3) countercurrent gas stripping; and (4) chemical treatment, in the case of presence of oxygen or low amounts of hydrogen sulfide. The choice of the specific method is determined by the amount of containment and economics.

Spreading water (in order to create large surface areas for contact with air) may release unwanted gases, such as carbon dioxide and hydrogen sulfide, and take on less objectionable gases, such as oxygen. The equipment to be used may be slat-type cooing towers, spray nozzles, or high-speed breakers to achieve mechanical division.

7.11 EQUIPMENT CONSIDERATIONS

Equipment required for the collection, treatment, and distribution of injection water for oil fields is a major consideration when determining the economic feasibility of various processes. Inasmuch as the water is usually aggressive and may require treatment with aggressive chemicals, careful consideration should be given to the use of corrosion-resistant materials, low-maintenance operations, and to a fairly high degree of automation for reduction of plant upsets and operating labor costs.

7.11.1 Pipelines

Pipelines in the past have been normally made of bare steel. Massive replacement and/or high maintenance costs of bare steel pipelines have led many operators to alternatives. Some have concluded that properly

treating the water requires more commitment than they or their personnel are willing to give. Thus, they have decided that pipelines must be made from a corrosion-resistant material, having resistance greater than that of steel. The following alternatives have been used:

1. Internally plastic-lined steel pipeline with special attention to joints.
2. Fiberglass-reinforced plastic pipe, prefabricated and joined in the field.
3. Plastic pipelines, such as PVC, may be satisfactory if the temperature of produced water is low, the pipelines are not subject to external or internal shock, and the pressures are low.
4. Cement–asbestos pipelines, which are resistant to corrosion if made of type-5 cement and are autoclave-cured. In special cases, the pipeline may be epoxy lined. Again there is a pressure limitation.
5. Cement-lined pipe.

In general, consideration should be given to the convenience of rapid dismantling and relocation of the lines, as in the case of cement–asbestos pipelines, to the types of epoxies and plastics to be used based on the actual tests with the fluids handled, and to the requirements and costs of additional facilities, such as cathodic protection of steel pipelines.

The design of the pipeline should take into consideration: (a) the possibility of hydraulic shock and surge, which may rupture the pipeline; (b) the venting of air pockets; (c) methods of testing for leaks; (d) the use of cleanout pigs for removal of scale and other fouling materials; and (e) the use of surface-mounted pipelines with attendant expansion problems versus buried and restrained pipelines. Many instances of hydraulic rupture of steel pipelines are known, where an inadequate analysis of pipeline transients was made during the design phase. Cases are also known where thermal expansion has caused inadequately buried pipelines to literally jump out of the ground.

7.11.2 Separators

The type of separators selected depends upon the origin and volume of suspended materials to be removed, the aggressiveness of waters, and the value of the land on which they are to be located.

7.11.3 Volume and Origin of Suspended Material to be Removed

Normally, when the waters are to be injected for secondary recovery, the content of suspended solids must be low, in some cases below 0.2 ppm. When produced waters are combined with seawater, a heavy precipitate of barium sulfate may be formed. The settling of this precipitate may require a large sedimentation pond with up to 72-hour retention time. This will also enable gravity separation of oil suspensions.

Sedimentation ponds are made of reinforced concrete having sufficient depth to allow a reasonable collection of sediment before being taken out of service for cleaning. Generally, two or more separate ponds should be provided so that when one is removed from service (less than 5% of the time), the other may carry the throughput at an increased velocity, at a reduced rate, or a combination of both.

The retention time may be varied and can be determined by a maze of two or more baffles within a single pond, so that their arrangement can be changed for different lengths of retention time as conditions vary. The ponds should be made of corrosion-resistant concrete (such as type-5), or sulfate-resistant concrete when using seawater. For additional protection, the ponds should be lined with a coal–tar epoxy or similar coating. Current environmental regulations should be consulted as special linings and other requirements may be specified to eliminate the possibility of groundwater contamination. Bottoms of the ponds should be designed so that the greatest depth is at the point of maximum precipitation and, when ponds are drained, the sediment can be hydraulically flushed out to a sludge pond.

The internal baffles guiding the flow through a number of passes can be built of wood or similar low-cost material, which need not support a hydraulic load, because the level is equalized on all sides. Oil, which gravitates to the surface, can be skimmed near the end of the flow path by continuous adjustable-height gravity skimmer.

It may be necessary to prevent algae formation. This can be accomplished by blocking out the passage of sunlight into the sedimentation basin. One method is to have interlocking, opaque, polyfoam, plastic panels, which float on the surface and can be easily removed for pond maintenance purposes. In case where entrained gases must be released or waters from different sources must be mixed before entering the sedimentation pond, the use of gravity cooling tower, wood slat-type aerators, and eduction-type mixing nozzles may be considered.

Standard API separators should be considered when a lengthy time period is not required for settlement and separation, a closed system is

desirable, and the land area is costly. There are standard models for various conditions made by a number of manufacturers. The materials used in construction, however, should be carefully considered as to their resistance to corrosion.

7.11.4 Aggressiveness of Waters

Inasmuch as all waters, including distilled water, have some degree of corrosiveness, a major economic consideration is the choice of materials in pumps, pipes, valves, fitting, tanks, filters, etc. One must take into account the desired life of the facility, changing conditions affecting the aggressiveness of the water, and the chemical treatment of the water for corrosion control in comparison to the increased cost of using more corrosion-resistant materials.

7.11.5 Value of Space on Which Facilities Are to Be Located

An additional consideration in facility design is the value or limited area of the land or space on which it is to be located. In some cases, sedimentation ponds may be planned on a multilevel basis instead of being spread over a large, single-level area. This also holds true for pumping and filtration equipment. The equipment may be placed below grade, as well as on-grade and stacked for multilevel operation. This is a major consideration for offshore structures where platform loading is critical.

7.11.6 Filtration Equipment

Dependable filtration for the removal of suspended solids from water before injection is most important, particularly for reservoirs that have low permeability. The filtering process is most often upset when large blocks of solids are carried through, with subsequent reduction in efficiency. In general, the trend is toward more completely automated systems where differential flows and pressures are measured and, at predetermined levels, the filters are backwashed or recharged as often as necessary to maintain the desired quality of effluent. Generally, filtration systems are of three types: (1) clarification systems, (2) in-line flocculation systems, and (3) filter-aid filters.

7.11.7 Clarification

Clarification systems include flocculation, sedimentation, and sand bed filtration. Basically, they are the same as those used in filtration of domestic water in municipal plants. They are always necessary when the amount of suspended solids is high (15 ppm or above), as these quantities of solids impose an impractical economic load on the in-line flocculation or filter aid-type filters. Clarification-type filtration may be used when the reduction of suspended solids content is not extremely critical, with the effluent having more than 1 ppm. Usually, these facilities consist of reinforced concrete basins. The water is passed (1) through compartments, where chemicals are added in subsequent stations for flocculation and decantation; (2) through basins for sedimentation; and (3) into gravity sand beds or other media filters.

These systems should have parallel chambers and, particularly, filters, so that one section can be removed from service and one filter regenerated at a time, while the system operates at slightly reduced rates. The sand filters should be automatically backwashed on demand, based on differential pressure through the bed. A number of manufacturers build complete fittings and appurtenances for these systems. One disadvantage of this system is that it is open throughout and subject to oxygen uptake, which later must be removed by deaeration and chemical scavenging. Pipes and fittings may be constructed from conventional cast iron, but the trend is toward use of fiberglass epoxy or plastic materials throughout.

7.11.8 In-line Flocculation Systems

In-line flocculation technique was developed with progress in the state of the art of high-rate rapid sand filters. It has been found that filter media alone will only remove particles down to about 20 μm in size. A polyelectrolyte is required to remove finer particles. A coagulant and/or polyelectrolyte are added to the water a short distance upstream of the filter to gather and/or attach the suspended solids to the filter media. Although shorter filter cycles result, the capital and operating costs of clarification facilities are eliminated. This system works well when the solids loading is low. The benefits become questionable when filter cycles drop to significantly less than 12 hours. One must plan for the worst case and not the average solids loading, in order to prevent plant shutdowns during high loadings.

7.11.9 Filter-aid Filters and In-line Flocculation Filters

Filter-aid or in-line flocculation filters are considered essential for maintaining a closed system from source water to injection well and also for any system requiring injection water with less than 1 ppm of suspended soils. As mentioned before, when the source water has a high turbidity, the removal of the majority of suspended solids should be done by means other than these filters.

The following should be taken in consideration in designing filter-aid filters:

1. The source and quality of filter aid are important consideration. Generally, diatomaceous earth and perlite are the two media available. The life of the filter cake varies greatly, depending upon product quality.
2. The sizing of the filters depends upon the total throughput and the total amount of solids to be removed. The solids affect the life of the filter cake and must be evaluated, in order to obtain reasonable backwashing cycles.
3. Tank shells, piping, and fittings are generally made of stainless steel, although plastic or rubber linings are economically feasible for the interior shell of large units. Filter frames may be of metal mesh. Hard rubber or plastic cores are becoming popular, however, owing to their lower cost and lack of distortion. Metal screens, on which diatomaceous earth cake is formed, are being replaced by a finely woven plastic cloth, which is relatively inexpensive and comparatively easy to replace in the field.
4. There is a trend toward complete automation, which, most likely, will preclude upsets from human error.
5. As a positive control on solids breakthrough in the filter system, a positive-stop (i.e., in-line) filter should be installed on the downstream side of the system. General equipment selection (two or more filters, the optimum being three) should be such that one filter can be taken out for backwash, while the remaining one can carry the same or slightly reduced total throughput at temporarily increased flow rates per square foot of filter area. The optimum rate for filtration as presently accepted was about 2 GPM/sq ft, although manufacturers are developing high-rate filters with filtration rate of 20 GPM/sq ft.

7.12 DEGASSING EQUIPMENT

7.12.1 Deaeration Equipment

The dissolved oxygen content of many waters for injection is far above limits, which should be maintained for control of corrosion. The most feasible method of removing this dissolved oxygen down to the limits, where effective treatment can be completed by chemical scavengers, is by passing the water through a deaeration column. Materials in the column for all wetted surfaces must be resistant to the corrosive atmosphere.

The interior shell of the column should be lined with a plastic material, whereas the trays and appurtenances should be constructed from stainless steel. The two or more trays are packed with Raschig Rings made from a ceramic or plastic material, creating the desired dispersion of water into large surface areas.

Oxygen removal may be accomplished by vacuum pumps exhausting from the top of the column, and creating a negative pressure for flashoff of the oxygen. When sweet field gas is available, it can be used as an upward counterflow to the water. Gas will scrub the oxygen and carry it out of the top of the column to a flare point or where gas can be used. This column also can serve as a small-capacity surge tank between the supply to the filters and the discharge to the injection pumps. Level control should be provided to throttle the inlet or outlet to maintain a liquid level within a predetermined range. Again, consideration should be given to providing two or more deaerating columns so that one can be removed from service and repairs, while the others are operating at an increased throughput.

A diagram of a countercurrent stripping tower for the removal of dissolved oxygen is presented in Figure 7.11 (see Jones, 1988, for details).

Generally, the deaerator reduces the dissolved oxygen content to 0.5 ppm or less. Following the deaerator with a chemical scavenger, the oxygen content can be reduced to 0.1 ppm or less, resulting in excellent corrosion control. Air should not be allowed to enter the system beyond this point. In addition, all vessels, such as chemical mixing tanks or surge tanks, must be blanketed with an oxygen-free gas.

7.13 CHEMICAL MIXING AND FEED EQUIPMENT

All chemicals used in treating the water, i.e., bactericides, oxygen scavengers, alum, polyelectrolytes, bentonite, etc., should be provided with

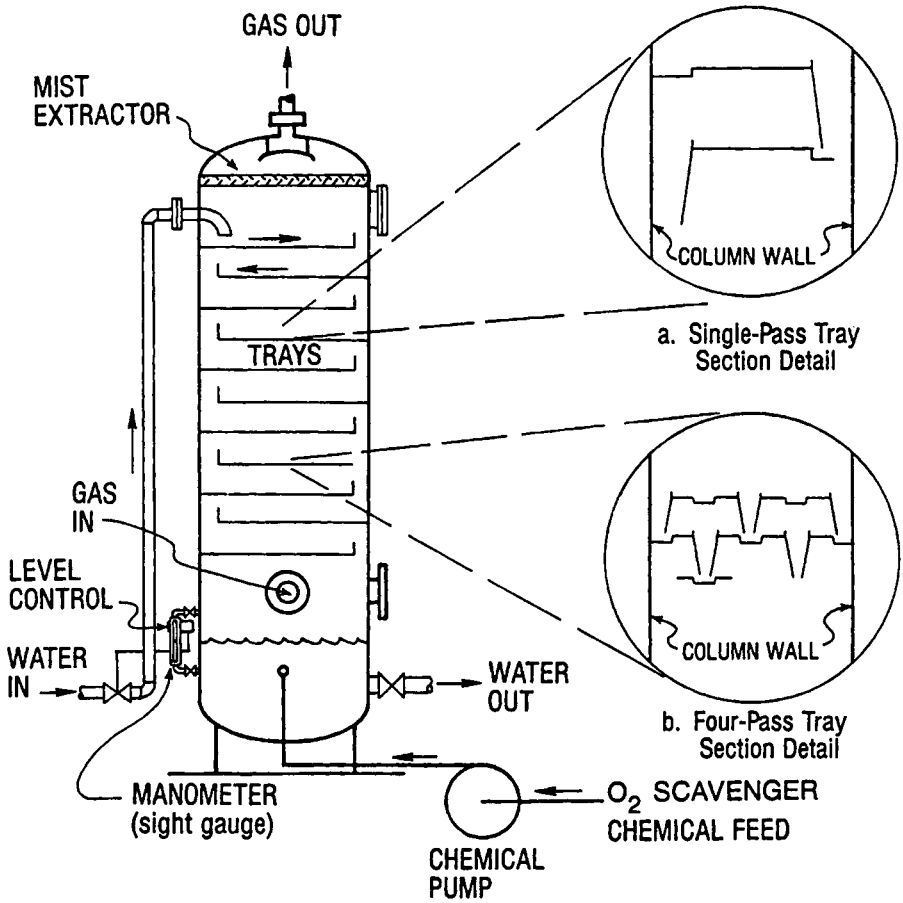

Figure 7.11 Cross section of the countercurrent stripping tower for the removal of dissolved oxygen. Gas devoid of oxygen is moving upward, whereas water to be treated moves downward (after Jones, 1988, p. 49; courtesy of OGCI).

a mix hopper having a transfer arrangement to a feed tank. In the case of sodium sulfite, the tanks should be closed and blanketed to prevent oxygen contamination. All chemicals should be fed into the system through a variable metering-type injection pump. Materials selected should be corrosion resistant to chemicals in concentrated and dilute states, which sometimes differ, and should be determined prior to construction. Discharge lines from sources of certain chemicals, such as alum, polyelectrolytes, and bentonite, should have outlets to a number

of water treatment chambers so that the progressive feed can be varied to meet operating conditions. In general, all equipment should be constructed from a combination of chemical-resistant plastic and stainless steel.

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CHAPTER 8
ECONOMICS OF CORROSION

8.1 INTRODUCTION

The National Bureau of Standards (1978) reported to the U.S. Congress that the cost of corrosion in the United States in 1975 was 70 billion dollars plus or minus 30% and that 10–45% of this loss was avoidable by the corrosion control technology. This economic loss represented about 4% of the gross national product. At the present time, the per capita direct plus indirect cost of corrosion for U.S. residents is approximately $2,000.00 per person.

In 1999, a 2-year study was mandated by the U.S. Congress in the Transportation Equity Act for the 21st Century (TEA-21 Act) to revisit the old Battelle/NBS study and extend it by making recommendations on corrosion management strategies. This study was administered by the Federal Highway Administration (FHWA) and was performed by a team led by CC Technologies in collaboration with NACE International, the world's largest organization studying corrosion. Objectives of this study were to estimate the total economic cost of metallic corrosion in the United States and to provide cost-effective, rational strategies to minimize corrosion's impact. Although the study covered a large number of economic sectors, including the electric power industry, the emphasis was placed on the transportation infrastructure, conveyance, and storage.

The result indicated that the corrosion management and corrosion control has been improved during the past several decades, but there is a need for improvement. According to the study done by CC Tech-

nologies Laboratories, Inc. (with support from the FHWA and NACE), the direct cost of corrosion in the United States in 2002 was around $276 billion which is 3.1% of the U.S. gross domestic product (GDP).

The principles of corrosion must be understood in order to effectively select materials and to design, fabricate, and utilize metal structures for the optimum economic life of facilities and safety in operation (see http://www.corrosioncost.com [J. Gorman, M. Arey, G. Koch, 2001]).

The cost of corrosion by industry sector is presented here.

The cost of corrosion can be defined in different ways, e.g., the cost of corrosion can be defined as the corrosion cost as a fraction of the total cost of the following:

1. Design
2. Manufacturing
3. Operation
4. Maintenance
5. Technology development
6. Asset value loss

Many small companies do not have systematic method for collecting data on losses due to corrosion, which has made it difficult to develop consistent broad-reaching approaches to solving major corrosion problems.

Because of the corrosion industry fragmentation, it is difficult to disseminate and utilize the information on the best corrosion prevention practices. In addition, it is difficult to access suppliers of corrosion control technologies. Therefore, it is hard to implement corrosion management and preventive methods (see www.corrosionsource.com).

8.2 DIRECT AND INDIRECT COST OF CORROSION

The direct cost of corrosion comprises two main components:

1. The costs of design, manufacturing, and construction (includes the cost of labor and equipment): (a) Material selection (such as stainless steel to replace carbon steel); (b) increased wall thickness of structures for corrosion allowance; (c) material used to mitigate or prevent corrosion (such as coatings, sealants, and corrosion inhibitors); and (d) cathodic protection.

2. The cost of management: (a) Corrosion-related inspection; (b) corrosion-related maintenance; (c) repairs due to corrosion; (d) replacement of corroded equipment; (e) inventory of backup components; and (f) rehabilitation loss of productivity.

According to an NBS study, the Direct Cost of Corrosion is defined as the total direct annual corrosion costs incurred by owners and operators of structures, manufacturers of products, and suppliers of services. Indirect costs include (a) lost productivity because of outages, delays, failures, and litigation; (b) taxes and overhead on the cost of corrosion portion of goods and services; and (c) indirect costs of nonowner/operator activities. The study conservatively estimated the indirect cost to be equal to the direct cost, for a total of $552 billion in 2002. This represents 6% of the GDP (see www.corrosionsource.com).

According to Cron and Marsh (1983), indirect costs of corrosion include:

1. Lost revenue
2. Lost productivity
3. Lost efficiency
4. Product contamination
5. Overdesign
6. Delays
7. Lawsuits

8.3 MAJOR INDUSTRIAL CATEGORIES OF CORROSION COSTS

For analyzing the cost of corrosion in the United States, the economy was divided into five major categories or sectors:

1. Infrastructure
2. Utilities
3. Transportation
4. Production and Manufacturing
5. Government

Total cost of corrosion in 2002 of the different industry sectors of the United States was $137.9 billion per year, which is broken down in Table 8.1.

Table 8.1 Cost of corrosion in different industry sectors.

Industry Sector	Cost of Corrosion (in billion dollars)	Percentage
Infrastructure	22.6	16.4
Utilities	47.9	34.7
Transportation	29.7	21.5
Production and Manufacturing	17.6	12.8
Government	20.1	14.6

Modified after Koch et al. (2002).

8.3.1 Infrastructure

Infrastructure provides organizing structure and support for the system or organization it serves, whether it is a city, a nation, or a corporation. As the infrastructure reaches the end of its lifetime (aging), the emphasis is on extending its life. The most destructive for infrastructure is corrosion. According to Koch et al. (2002), the infrastructure can be divided into five categories as follows:

1. Highway bridges
2. Gas and liquid transmission pipelines
3. Waterways and ports
4. Hazardous materials storage
5. Airports and railroads

The direct infrastructure cost of corrosion was estimated at $22.6 billion (16.4% of total annual cost; Table 8.2).

Gas and Liquid Transmission Pipelines

There are more than 400,000 miles of pipelines in the United States, which transfer natural gas, crude oil, and hazardous liquids. The direct cost of corrosion of pipelines is approximately $7 billion per year.

Table 8.2 Cost of corrosion in various industry sectors.

Infrastructure	Cost of Corrosion (in billion dollars)	Percentage
Highway bridges	8.3	37
Gas and liquid transmission pipelines	7	31
Waterways and ports	0.3	1
Hazardous materials storage	7	31

Modified after Koch et al. (2002).

Table 8.3 Utilities cost of corrosion.

Utilities	Cost of Corrosion (in billion dollars)	Percentage
Gas distribution	5	10
Drinking water and sewer systems	36	75
Electrical utilities	6.9	14
Telecommunication	0.48	1

Modified after Koch et al. (2002).

8.3.2 Utilities

Utilities sector has the largest annual direct cost of corrosion among industry sectors. Utilities sector is divided into the following subsections. (See Koch et al., 2002.)

Gas Distribution

There are 1,700,000 miles of natural gas distribution pipelines, which are made mostly of steel, cast iron, or copper. The direct cost of corrosion in gas distribution pipelines is $5 billion per year (Table 8.3).

Electrical Utilities

There are several kinds of power plants in the United States:

1. Fossil fuel
2. Nuclear
3. Hydroelectric
4. Cogeneration
5. Geothermal
6. Solar
7. Wind

The annual direct cost of corrosion in electrical utilities sector was approximately $6.9 billion in 2002.

8.3.3 Production and Manufacturing

Production and Manufacturing sector is the most important part of industry. This sector is further subdivided as follows:

1. Mining
2. Oil and gas exploration and production
3. Petroleum refining
4. Chemical, petrochemical, and pharmaceutical production
5. Pulp and paper
6. Agricultural production
7. Food processing
8. Electronics
9. Home appliances

Most of production equipment has mechanical parts, which are mostly made of metallic parts. The primary life-limiting factors for equipment are wear and corrosion. Maintenance painting is heavily relied upon to prevent corrosion.

There are many chemicals used in production section that are corrosive. Costs of corrosion in this section include:

1. Maintenance costs
2. Replacement costs
3. Installation costs

4. Delay in production
5. Labor costs
6. Protection costs
7. Research and development

The total annual direct cost of corrosion for Production and Manufacturing sector was $17.6 billion in 2002, which constitutes 12.8% of the total direct cost of corrosion in industry. The further breakdown of expenditures is presented in Table 8.4.

In the United States, there are more than 160 refineries, which in 2002 supplied more than 18 million barrels per day of refined petroleum products.

Oil and Gas Exploration and Production

In oil and gas production, the direct cost of corrosion is lower compared to the indirect costs. The only exception where direct costs exceed the indirect costs is in offshore production.

There are three major corrodants that cause serious problems in oil industry: oxygen dissolved in drilling fluids, seawater, and produced water; CO_2; and H_2S.

Table 8.4 Production and manufacturing cost of corrosion

Production and Manufacturing	Cost of Corrosion (in billion dollars)	Percentage
Mining	0.1	1
Oil and gas exploration and production	1.4	8
Petroleum refining	3.7	21
Chemical, petrochemical, and pharmaceutical production	1.7	10
Pulp and paper	6	34
Agricultural production	1.1	6
Food processing	2.1	12
Home appliances	1.5	9

Modified after Koch et al. (2002).

Cost of Corrosion in Drilling

Corrosion fatigue is responsible for most of drill pipe failures. Fatigue strength (endurance limit) can be defined as the unit stress that a metal can endure for a large number of cycles of stresses. Stress levels are usually expressed as a percent of yield strength (see Jones, 1988).

Pits form on the inside of drill pipe as a result of corrosion due to presence of dissolved oxygen. These pits increase the stress and initiate a fatigue crack, which is propagated to failure upon cyclic stressing.

As pointed out by Cron and Marsh (1983), the economic impact of drill pipe corrosion is immense. The cost of a joint is ≈$12,000, but the fishing job in the case of pipe break-off will cost ≈$40,000/day rig time. If the fish cannot be recovered, then the well is lost, resulting in a multimillion-dollar loss. Thus, a corrosion-control program should be initiated initially: "an ounce of prevention is better than a pound of cure!"

Often, drilling fluids are used as packer fluids in the annular area of wells after completion. If not properly treated, this drilling fluid can cause costly corrosion problems late in the life of a well. Water-base and oil-emulsion drilling fluids (oil-in-water) may attack the metal surfaces in contact with it in the casing if not properly treated. The type of corrosion involved is electrochemical corrosion.

Numerous conditions encountered during drilling operation cause corrosion to the drilling equipment. Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are commonly encountered in drilling deep wells. Hydrogen sulfide, which reacts with iron at the pipe surface, forms iron sulfide (FeS), liberating two hydrogen atoms that permeate steel and lead to corrosion. Carbon dioxide, which forms carbonic acid (H_2CO_3) in water, has a similar reaction with steel, i.e., iron carbonate forms, releasing hydrogen atoms that attack steel (Magcobar Services, 1972, Corrosion, Sect. 19). Oil-base drilling muds are very effective in reducing corrosion to the drilling equipment, because the continuous oil phase prevents the completion of the galvanic cell, which is necessary for corrosion to take place (Magcobar Services, 1972, Corrosion, Sect. 19). Certain chemicals, when added to the oil-base muds, make the steel surface oil-wet and protect it against corrosion. Because of different drilling conditions, drilling fluid cost varies widely. The most important factors that affect the cost of drilling are as follows:

1. The type of formation to be drilled
2. Hole size

3. Total depth
4. Logistics

Special drilling fluid systems are available either for reducing the severity of or eliminating corrosion. The cost of the drilling fluid, however, is increased as a result. For example, the use of oil-base drilling fluid in place of water-base mud eliminates the problems of cement and salt contaminations; however, it is very costly to change ("switch") the mud type.

The cost of drilling fluid increases with increasing size and depth of the well because of the higher volume of the fluid required. Logistics is also responsible for high drilling fluid cost, because materials that have to be transported a long distance will cost more than those that are available locally. Consequently, there are no typical drilling fluid costs. For example, drilling fluid cost alone for different wells in the west Texas area drilled to a depth of 15,000 ft can vary from $20,000 to over $30,000 (1977 prices, Allen, 1977, p. 4).

8.4 CORROSION-CONTROL ECONOMICS AND PREVENTIVE METHODS

For each type of corrosion, there are different methods of corrosion control (see Chapter 4). Technological advancement in corrosion control and preventive methods had a big impact on corrosion economics during the past few decades. According to an NBS (National Bureau of Standards) study, there are many preventive methods:

1. Increase awareness of corrosion costs and potential cost savings.
2. Change the misconception that nothing can be done about corrosion.
3. Change policies, regulations, standards, and management practices to increase corrosion cost savings through sound corrosion management.
4. Improve education and training of staff in the recognition of corrosion type.
5. Implement advanced design practices for better corrosion management.
6. Develop advanced life-prediction and performance-assessment methods.
7. Improve corrosion technology through research.

In corrosion control economics, two factors must be considered in calculations: (1) cost and (2) service life.

Corrosion control offers many alternatives, with different return on investment:

1. Replacing parts and do nothing about corrosion
2. Cathodic protection
3. Inhibitors
4. Coating and painting
5. Water deaeration
6. Dehydration
7. Chemical treatments
8. Different alloys
9. Nonmetallic materials

In their classical paper, Cron and Marsh (1983) gave a good example of corrosion control in an area of uncertainty. They considered an oil field with some tubing failures. The alternatives were:

1. Install the coated tubing.
2. Inject a corrosion inhibitor.
3. Keep replacing the tubing, with consequent deferred production and risk of losing the well.

First, one has to develop the past history by plotting the log of cumulative leaks versus the time. The extrapolated leak curve ("straight line") will give (estimate) the probable cost of no corrosion control (alternative A, 3 above). Next, the operator will choose an inhibitor (alternative B, 2 above), which can be 70% effective. As a result, corrosion rate will be cut to 30% of its uninhibited rate. The extrapolated leak curve ("line") will show this reduction in corrosion damage. The lowered cost due to decrease in leaks is then compared with the cost of inhibitor. The *ROI* (return on investment) is equal to the lowered cost per year divided by the investment cost. For a simple comparison of alternatives A and B, Cron and Marsh (1983, p. 1035) offered the following formula:

$$ROI = \frac{(Op\ Cost_A + Dep_A) - (Op\ Cost_B + Dep_B)}{(Inv\ Cost_B - Inv\ Cost_A)} \tag{8.1}$$

The depreciation (*Dep*) can be determined using the formula below:

$$Dep = \frac{Inv\ Cost}{Years\ of\ Life} \tag{8.2}$$

One can evaluate other alternatives similarly. As pointed out by Cron and Marsh (1983), consistent record keeping is necessary to determine the effectiveness of any program.

8.5 GALVANIC VERSUS IMPOSED DIRECT ELECTRICAL CURRENT IN CATHODIC PROTECTION

In deciding whether to use the impressed-current or galvanic cathodic protection system, one has to make an elaborate economic study. It is very difficult to put a dollar value on the advantages and disadvantages of each system (Tables 8.5 and 8.6). In the case of offshore operations,

Table 8.5 Advantages and disadvantages of galvanic protection.

Advantages	Disadvantages
Permanently activated system, depending on the life of anodes.	Inflexibility of system once installed.
Maintenance required is minimal.	Many anodes are required.
Not vulnerable to electric failures.	In the case of offshore operations, additional weight to the platform.
Not vulnerable to mechanical failures.	Distribution of current is difficult to change.
Not vulnerable to storm damage.	In the case of offshore operations, it is costly to replace or repair anodes.
Installation cost per anode is low.	
No dependence on external power source.	
In the case of offshore operations, the system is not vulnerable to storms.	
In the case of offshore operations, the system becomes effective right after immersion of platform.	

See Cron and Marsh (1983).

Table 8.6 Advantages and disadvantages of impressed-current cathodic protection.

Advantages	Disadvantages
Flexible system, easy to change or repair.	Electric power is required.
Replacement costs are low.	Expensive to install each anode.
Testing is required in few places only.	In the case of offshore operations, the interconnecting cables are vulnerable to damage.
System can be easily deactivated.	System can be deactivated accidentally.
Fewer anodes are used.	

the costs of the two systems are within ≈35% of each other (Cron and Marsh, 1983, p. 1040).

In the case of aluminum sacrificial anodes, the alloying elements are zinc, tin, mercury, and indium, which insure the uniform dissolution of aluminum. According to Cron and Marsh (1983, p. 1039), a 725-lb aluminum anode will generate a current of ≈5.3 amps in the Gulf of Mexico. If galvanic efficiency is 95%, the electrical output of this anode is 1,280 amp-hr/lb with a life of ≈20 years.

In the case of offshore operations, the water depth and vulnerability to storm damage are the deciding factors in choosing protection system.

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APPENDIX A
SAMPLE PROBLEMS AND QUESTIONS

A.1 SAMPLE PROBLEMS[1] AND QUESTIONS[2] (SOLUTIONS AND ANSWERS ARE PROVIDED)

1. A plant engineer must protect the inside of a water tank from corrosion by using cathodic protection. The tank, which is a vertical cylinder 10 ft high and 8 ft in diameter, contains water to a depth of 8 ft. The engineer installed suitable anodes in the tank and connected them to the negative terminal of a rectifier output. By inspection, water analysis, and former experience, he determined that a total current of 5.06 A would stop the corrosion. Assuming that this current would equal the sum of all corrosion currents (local cell currents) due to corrosion, and if cathodic protection were not applied, what would be the tanks life in years? The original tank wall thickness is 0.300 inch and the tank has to be scrapped when the wall thickness is reduced to 0.200 inch. Both the tank bottom and walls in contact with the water are being corroded. Assume uniform corrosion and that iron corrodes as $Fe \rightarrow Fe^{2+} + 2e^{-}$. The charge on electron is 1.59×10^{-19} C (C = A × sec). One ampere flowing for 1 second dissolves anodically, or deposits cathodically, 1.11800 mg of silver.

[1] Courtesy of Professor Emeritus J. S. Smatco of Chemical Engineering Department at the University of Southern California, Los Angeles, CA.
[2] The help extended by Malvina Lerma is greatly appreciated.

Avogadro's number = 6.06×10^{-23}.
Density of steel = 7.8 g/cc.

Solution:
Amount of steel corroded:

(a) Bottom of tank = $V_b = \frac{n \times 8^2}{4} \times \frac{0.100}{12} = 0.419 \text{ft}^3$.

(b) Sides = $V_s = (2 \times \pi \times 4) \times \frac{0.100}{12} \times 8 = 1.676 \text{ft}^3$.

(c) Total volume corroded = $V_b + V_s = 0.419 + 1.676 = 2.095$ ft^3.

(d) Weight of steel corroded = 2.095 × 28,400 × 7.8 = 465,000 g. One Faraday (= 96,500 C) will corrode 1 g-equ of a metal. 1 g-equ of iron = 55.85/2.
Current = 5.06 A = 5.06 C/sec.

Duration of corrosion = $\frac{465{,}000 \times 96{,}500}{(55.85/2) \times 5.06}$ = 31.8×10^7 sec = $31.8 \times 10^7 (1/3{,}600 \times 365 \times 24)$ = 10 yrs.

2. A steel water tank was to be protected by cathodic protection with DC current applied so that the tank would have negative polarity. The tank was 12 ft tall, open at the top, and was 10 ft in diameter. The wall thickness was 0.38 in. The practical life of the tank was considered at an end when thickness of any part reached 0.18 in. The current flow was adjusted so that 0.05 A/ft^2 was impressed.

Accidentally, connections were made backwards and the tank was made anodic. The error was not noted for 2 years, the blame going to an imperfect system and corrosive solutions. Assuming that the reaction is $Fe \rightarrow Fe^{2+} + 2e^-$ at 100% efficiency and that 26.8 A-hr is capable of dissolving 27.93 g of iron, how much iron dissolved in 2 years? What was the wall thickness after 2 years? What fraction of the tank's life was used up?

Solution:
Wall area (wetted) = $10\pi \times 12 = 377$ ft^2.
Area of tank bottom = $\pi \times 5^2 = 78.54$ ft^2.
Total area = 377 + 78.54 = 455.54 ft^2.
Specific weight of Fe = 7.8 × 62.4 = 490 lb/ft^3.

Electrochemical equivalent of Fe = $\frac{27.93 \times 1{,}000}{455.54 \times 26.8} = 2.297\,\text{lb}/1{,}000\,\text{A-hr}$.
2 yrs = 2 × 24 × 365 = 17,500 hrs.
Current flow = 455.54 × 0.05 = 22.78 A.
A-hr in 2 yrs = 22.78 × 17,500 = 398,000.
Fe dissolved = $\frac{398{,}000 \times 2.297}{1{,}000} = 915\,\text{lb}$ or 915/490 = 1.868 ft^3.
Thickness loss = 12 × 1.868/455.54 = 0.0492 in.
Fractional life = (0.0492 × 100)/(0.38 − 0.18) = 24.6%.
Wall thickness after 2 yrs = 0.380 − 0.0492 = 0.331 in.

3. A sacrificial magnesium anode is used to protect a section of a steel gas pipeline. It weighs 70 lb and must be replaced when the remaining magnesium reaches 10 lb in weight. During the protection job, only one-half of the magnesium corrodes in such a way as to deliver current to the pipe. The other half is self-corroded without any benefit to the pipe. How long would this anode last, if 3 A flows continuously?
   Atomic weight of Mg = 24.32.
   1 Faraday = 96,500 C = 26.8 A-hr.

Solution:

Wt. loss of anode usefully = $\frac{70-10}{2} = 30\,\text{lb}$ or 30 × 454 = 13,550 g.
Corrosion reaction: $Mg \rightarrow Mg^{2+} + 2e$.
1 Faraday = 96,500 C = 26.8 A-hr and is the electricity produced by 1 g-equ of usefully corroding Mg.
Amount of g-equ corroded = $\frac{13{,}550}{24.32/2} = 1{,}114$.
A-hr = 26.8 × 1,114 = 29,900.
hr/yr = 24 × 365 = 8,760.
Life = 29,900/(8,760 × 3) = 1.13 yrs.

4. A steel vessel has a 0.5-in.-thick wall. During use, it corrodes. Its internal area is 40 ft^2. Assuming a uniform corrosion rate, the following facts are to be noted: The plant chemist found that the product, processed in the vessel, contained 1.0 g of $Fe(OH)_3$ in 150 gal of solution processed during each run; 24 runs per day were made. Steel has a density of 7.7 g/cc. Find the corrosion rate expressed as $mg/m^2/day$ (mmd); also as inch penetration per year

(ipy). What is the life of this vessel if it is considered worn-out when the average wall thickness reaches 0.375 inch?

Solution:
Area = 40 × 0.0929 = 3.72 m^2.
$Fe(OH)_3$ produced per day = 1.0 × 24 = 24 g.
Wall thickness loss = 0.5 − 0.375 = 0.125 in. or 0.125 × 2.54 = 0.318 cm.

Mol wt. $Fe(OH)_3$ = 106.85.

$$\text{Fe metal loss/day} = \frac{55.85}{106.85} \times 24 = 12.55 \text{ g/day}.$$

$$\text{Corrosion rate} = \frac{12.55 \times 1{,}000}{3.72} = 3{,}375 \text{ mg/m}^2\text{/day}.$$

Wt. loss/year = 12.55 × 365 = 4,580 g/year.

$$\text{Vol. loss/year} = \frac{4{,}580}{7.7} = 595 \text{ cm}^3.$$

$$\text{Thickness loss/year} = \frac{595}{3.72 \times 10^4} = 0.016 \text{ cm or } \frac{0.016}{2.54} = 0.0063 \text{ ipy}.$$

$$\text{Life} = \frac{0.125}{0.0063} = 19.85 \text{ yrs}.$$

5. A coated and wrapped steel pipeline (500 miles long) having 18-in O.D. is to be protected by cathodic protection. Sacrificial magnesium anodes are used to supply the electric current. The specific resistivity of the soil is 1,000 Ω-cm. The anodes are grouped in stations, each station having five anodes weighing 17 lb each. The five anodes of each station are "planted" on 10-ft centers in a string paralleling the pipeline, and 10 ft away from the pipeline. Under these conditions, a current density of 0.01 mA/ft^2 of pipe surface is obtained. The anode stations are placed 2 miles apart, and the anodes in each station are connected in parallel with 10 PVC (polyvinyl chloride) covered copper wire. These clusters are then connected by a 4 PVC covered copper cable to welded stud on the pipe. Each anode is surrounded by backfills composed of 5% Na_2SO_4, 20% bentonite clay, and 75% gypsum. Installation costs per mA-yr equal magnesium cost per mA-yr; magnesium costs of $0.55/lb (1998 costs). Assuming that only one-half of the planted magnesium actually yields useful current for protection, find:
   (a) Current flow per station
   (b) Life of installation
   (c) Magnesium weight loss per station per year

(d) Cost of installation
(e) Cost of protection per ft^2 of pipe per year

Solution:
Number of stations = 500/2 − 1 = 249.
Wt. of Mg per station = 5 × 17 = 85 lb.
Total weight of Mg for pipeline = 85 × 249 = 21,165 lb.
Total cost for Mg = 21,165 × 0.55 = $11,640.75.
Area of pipe protected by one station = 1.5 × 3.1416 × 5,280 × 2 = 49,800 ft^2.
Current per station = 49,800 × 0.01 = 498 mA.
Electricity generated per year = 498 × 24 × 365 = 4,365 × 10^3 mA-hr or 4,365 A-hr.
Inasmuch as 26.8 A-hr is produced by 24.32/2 g of Mg at 100% efficiency, then electrochemically useful Mg = 4,365 × 24.32/26.8 × 2 = 1,980 g/station or 5.72 lb/station.
Actually, twice as much magnesium corrodes per year; therefore, the lifetime = 85/2 × 5.72 = 7.41 yrs.
There are two possible interpretations concerning installation costs per year:

(a) If installation cost is equal to the cost of Mg effective in producing current only, it would be $11,640.75/2 = $5,820.37. Installation cost + Mg cost = 5,820.37 + 11,640.75 = $17,461.12.
(b) If installation cost is equal to the total cost of Mg used, then it would be $11,640.75.

Installation cost + Mg cost = 11,640.75 + 11,640.75 = $23,281.50. Interest charges, maintenance cost, overhead, and inspection costs should be added to the above figures.

According to (a): yearly costs/ft^2 of pipe = $\frac{17{,}461.12 \times 100}{49{,}800 \times 250 \times 7.41}$ = 0.019cents/ft^2/year.

According to (b): $\frac{23{,}281.50 \times 100}{49{,}800 \times 250 \times 7.41} = 0.025$ cents/ft^2/year.

6. Use the rule of thumb to estimate the current requirement in a coated pipeline that is 5,000 ft long and 24 inches in diameter. Assume that 2% of the pipeline area is bare or not adequately coated.

Solution:
$2\ \text{mA} \times [2 \times (24/12/2) \times \pi \times 5{,}000] \times 0.02 = 1{,}256\ \text{mA}$.

7. What are inhibitors and how do they slow down the corrosion process? (List at least one method.)

Answer: Inhibitors are chemicals that coat or film a metal surface to protect it from its environment. The film slows down the corrosion process by (a) increasing either anodic or cathodic polarization or both, (b) reducing diffusion of ions to the metal surface, (c) increasing electrical resistance at the metal electrolyte interface, or (d) increasing hydrogen overvoltage.

8. List two reasons why relative potential values must be measured around buried or immersed structures.

Answer: The values are needed to determine: (a) whether the protection is needed or not, (b) where the anodes should be placed, (c) how much current must be supplied, and (d) whether or not protection has been achieved.

9. How does one remove unwanted gases from a fluid?

Answer: (a) Countercurrent stripping with an inert gas, (b) vacuum deaeration, and (c) chemical treatment.

10. Explain how metals are heat-treated for hardening.

Answer: Heat treatment determines a metal's grain structure. According to Jones (1988), hardening involves heating to a critical temperature and then cooling. The grain structure after heating is called *austenite*. Upon rapid cooling (quenching), *austenite* is converted to *martensite*, with a brittle, hard, needle-like grain structure. In order to reduce the amount of *martensite* and achieve a more uniform hardness (without internal stresses), the quenched steel is reheated to a temperature below 1,360°F (732°C) for a certain period of time and then cooled at a controlled rate.

11. When does sulfide stress cracking (SSC) occur?

Answer: SSC occurs when the water contains hydrogen sulfide (or certain other sulfur compounds) and the metal is under tensile stress. Generally, SSC occurs in the absence of air.

12. How does one combat H_2S in drilling fluids?

Answer: (a) Maintain drilling fluid density and hydrostatic head sufficient to minimize in-flow of formation fluid, (b) maintain drilling fluid at pH 10 or higher, (c) use sulfide scavengers, or (d) use drilling fluid in which oil is the continuous phase.

13. List most likely locations of oxygen gas entry into a water injection system.

Answer: (a) Through holding tank vent hatches and (b) at packing glands on the suction side of water pumps.

14. If an old and a new pipe are interconnected, which one will act as an anode? Why?

Answer: Inasmuch as chemical or electrochemical reactions take place on a metal surface, it behaves differently than the clean metal. A film only a few molecules in thickness formed on metal may give rise to a potential $\approx$0.3 volt different from that of a metal devoid of film. This potential difference is sufficient to create an active corrosion cell. Such films form on stainless steels increasing their resistance to corrosion.

Steel in soils exhibits change in potential with time. Old steel (steel which has been in the ground for several years) is cathodic with respect to the new steel, identical in composition.

15. List gases that are responsible for corrosion.

Answer:
Oxygen, hydrogen sulfide, and carbon dioxide.

16. List the three essential steps in order to achieve a good coating job.

Answer:
(a) Selection of a suitable coating
(b) Proper surface preparation
(c) Careful application

17. List the main coatings and plastics most widely used in the oil industry.

Answer:

(a) Hydrocarbon base
(b) Resin base
(c) Combinations of (a) and (b)
(d) Metallic
(e) Cement and concrete sheathing
(f) Composite inorganic

18. What properties of a metal determine its suitability in production operations?

Answer:

(a) Resistance to failure by cracking
(b) Adequate strength
(c) Resistance to general and localized corrosion

19. What is cavitation and where does it usually occur?

Answer:

Cavitation involves the repeated formation and collapse of gas or vapor bubbles, resulting in a localized and intense metal loss. Cavitation occurs in water injection pumps with inadequate pressure on the suction feed-line. It also occurs in flowlines and tubing handling water with dissolved gas at turbulent velocities. Cavitation occurs when the vapor pressure exceeds the outside pressure (boiling).

20. What is the major cause of drillstem corrosion?

Answer:

Dissolved oxygen.

21. What are the major causes of external casing corrosion?

Answer:

(a) Electrical current
(b) Bacterially generated H_2S
(c) Aggressive formation waters
(d) Attack by corrosive completion fluids

22. What is the current density required for cathodic protection in various parts of the world (see Cron and Marsh, 1983)?

Reference: Cron, C. J. and Marsh, G. A., 1983. Overview of economic and engineering aspect of corrosion in oil and gas production. *J. Petrol. Technol.*, June: 1033–1041.

Answer:

Area	Current density, mA/ft^2
Lake Maracaibo, Venezuela	50–80
Cook Inlet, Alaska	25–50
North Sea	8–16
Nigeria	8
Persian Gulf	6–8
Gulf of Mexico	6–8
Mud zones	1–4

23. How does one protect platform against corrosion in the:
    (a) immersed zone,
    (b) splash zone,
    (c) atmospheric zone, and
    (d) mud zone.

Explain why.

Answer: Steel structure placed offshore is subjected to a severely corrosive environment:

Atmospheric Zone: According to Cron and Marsh (1983), the corrosion rate of bare steel in the marine atmosphere can be 30 mil/yr or higher. The corrosion rate depends on (1) steel composition, (2) rainfall, (3) ultraviolet light from the sun, and (4) degree of exposure to wind.

Thus, it is of utmost importance to coat the steel, the effectiveness of which depends on quality of surface preparation (removal of mill scale, rust, and dirt; sandblasting; etc.).

According to Cron and Marsh (1983), the coating should contain zinc particles and zinc silicate, which provide a protection similar to the metallic zinc coating (galvanization).

In the case of spillage possibility, the coating must be covered by another coating of vinyl or epoxy.

Splash zone: The part of platform, which occurs alternatively above and below the waterline (due to tide and waves), is called the splash zone.

The uniform corrosion rate in the splash zone is ≈15 mil/yr, whereas the pitting penetration may reach 100 mil/yr.

Cron and Marsh (1983) mentioned the use of rubber-like coating with a thickness of $\frac{1}{4}$ to $\frac{1}{2}$ in. Another approach is to apply a thin layer of Monel (70% nickel and 30% copper) as a protective sheath.

Due to lack of continuous electrolyte, the cathodic protection is only partially effective.

Immersed zone: The immersed zone of platform, which is below the waterline at lowest tide, is subject to pitting corrosion (as high as 100 mil/yr), as well as general wastage (Cron and Marsh, 1983).

Cathodic protection can prevent pitting, corrosion of welds, and corrosion fatigue.

Sacrificial anodes, which can be made of zinc, magnesium, and aluminum, can weigh 300–800 lb. They can have different shapes (rod, ribbon, cylinder, pencil, and bracelet) and can last for ≈20 years.

Mud zone: The zone below the mud line, where the platform was driven into the sea bottom, is called mud zone.

Inasmuch as there is no agitation and the presence of a reducing environment, only 1–4 mA/ft^2 current density is required for cathodic protection. Allowance, however, should be made for the cathodic protection of casing, which is in electrical contact with the platform (Cron and Marsh, 1983).

Reference: Cron, C. J. and Marsh, G. A., 1983. Overview of economic and engineering aspect of corrosion in oil and gas production. *J. Petrol. Technol.*, June: 1033–1041.

For additional information, the reader is referred to the following references:

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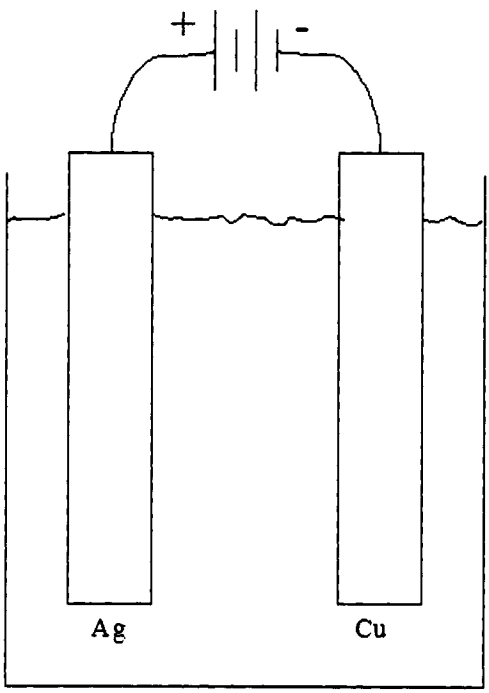
A.2 SAMPLE QUESTIONS AND PROBLEMS (NO SOLUTIONS)

1. What methods and precautions are used in order to control corrosion in EOR in situ combustion operation?
2. Define electrode polarization and explain the factors affecting the reaction kinetics in electrochemical polarization.
3. What is the current density required for cathodic protection in mud zone worldwide? Is it lower or higher than that in Cook inlet in Alaska, for example? Why?
4. Draw the polarization diagram of zinc corroding in acid. Explain in detail.
5. List and explain the main types of corrosion.
6. List the most important factors in oil- and gas-well corrosion.
7. Define an "inhibitor" and a "passivator."
8. What factors determine the required concentration of inhibitors?
9. Explain why the chromate inhibitors stop corrosion. Would they work in the presence of reducing agents and why?
10. Describe the effect of abrasion on corrosion.
11. Briefly discuss the economics of cathodic protection.
12. What is the corrosion test plate or "coupon?"
13. How would you recognize "sweet corrosion?"
14. How would you recognize "sour corrosion?"
15. List five main subdivisions of corrosion.
16. List five methods of preventing corrosion.
17. Describe in detail the role played by the bacteria (aerobic and anaerobic) in corrosion, including iron organisms.

18. List the corrosion problems encountered in condensate wells.
19. Draw a schematic diagram of Fe corrosion caused by moisture in an atmospheric environment proving that "rust begets rust."
20. List the methods used to monitor corrosion.
21. Explain the terms *fatigue strength* and *corrosion fatigue*.
22. List 10 factors influencing corrosion: 5 factors associated mainly with the metal and 5 factors with the environment.
23. Describe methods of controlling the corrosion of (a) casing and (b) tubing.
24. Calculate E^0 for $Fe \rightarrow Fe^{3+} + 3e^-$
    $Fe \rightarrow Fe^{2+} + 2e^-$ $E^0 = 0.440$ volts
    $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $E^0 = -0.771$ volts
25. What is the life of a 700-lb aluminum anode, which generates a current of 5.1 A in seawater? Galvanic efficiency = 94%.
26. List requirements for injection waters.
27. Design a test for testing plugging characteristics of injection water.
28. Describe methods used in removing the suspended matter in injection water.
29. What is meant by the expression: "chemically unstable water?"
30. Describe four methods of treating unstable water in waterflooding.
31. Using chemical equations, show why calcium carbonate often precipitates during the production of oilfield waters.
32. Using chemical equations, show why the aeration of water may cause the precipitation of ferric hydroxide.
33. What is a "surfactant?" List three major types of surfactants, giving examples.
34. List the three main factors to be considered prior to initiating a waterflood project.
35. What are the primary differences between the surface waters and deep well waters?
36. List four types of plugging in waterflood operations and means of preventing (or minimizing) each one.
37. A sample of water has 1,000 mg/L of sodium, 5 mg/L of potassium, 90 mg/L of calcium, 150 mg/L of HCO_3^-, 20 mg/L of magnesium, and 4 mg/L of iron. What is the total hardness and total alkalinity of the sample expressed as $CaCO_3$?
38. Define the Langelier's Stability Index (*SI*) and list the parameters that influence it.
39. Calculate *SI* for both $CaSO_3$ and $CaSO_4$ for a mixture of 30% seawater and 70% (by volume) produced water (Table 6.4). The tem-

perature of this mixture is 60°C. The water is saturated with a gas containing 7 mol % CO_2 at 5 bar total pressure.

40. Should Ca/Na ratio of injection water be higher or lower than Ca/Na ratio of formation water? Why?
41. Explain the process of hydrogen embittlement.
42. Determine the total dissolved solids (*TDS*) in a water sample having a specific gravity of 1.3.
43. At an injection rate of 100 cubic meter/day, how many cubic centimeters of compacted solids will be deposited by water containing 40 mg/L *TSS* (total suspended solids) in 30 days?
44. Does the stressed portion of a pipeline act as a cathode or as an anode? Why?
45. What is the effect of temperature on steel corrosion in the case of oxygen corrosion?
46. In an aqueous solution, which one of the following reactions will result in greater hydrogen gas evolution? Why?
    (a) $Ca + Mg^{2+} \rightarrow Ca^{2+} + Mg^0$ $E_{Ca} = +2.87$, $E_{Mg} = +2.375$
    (b) $Ca + Sn^{2+} \rightarrow Ca^{2+} + Sn^0$ $E_{Sn} = +0.136$
47. In the diagram below, show the direction of flow of electrical current and electrons. Show location of anode and cathode. (Electroplating)



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APPENDIX B
GLOSSARY

(Main sources: American Petroleum Institute [API], Bulletin D11; Chilingarian, G. V. and Vorabutr, P., 1981. *Drilling and Drilling Fluids*, Developments in Petroleum Science, 11. Amsterdam: Elsevier, 767 pp.)

Absorption—The penetration of molecules or ions of one or more substances into the interior of a liquid or solid. For example in a hydrated bentonite, the planar water, which is held between the structural layers is absorbed.

Acid—Any chemical compound containing hydrogen capable of being replaced by positive elements or radicals to form salts. Acid is a compound which, on dissociation in solution, yields hydrogen ions; it lowers the pH. Hydrochloric acid, tannic acid, and sodium acid pyrophosphate (SAPP) are examples. A substance that can donate a proton (H^+).

Acidity—The relative acid strength of liquid (pH < 7).

Actual electrode potential—In the emf series, each metal will reduce (or displace from solution) the ion of any other metal below it in the series, providing all of materials have unit activities and the metal to be displaced is not very far above hydrogen. The activity of a pure metal in contact with a solution does not change with the environment. The activity of an ion, however, changes with the concentration, whereas the activity of a gas changes with its partial pressure.

Adhesion—The molecular attraction or force exerted across the surfaces of contact between unlike liquids and solids, which resists their separation.

Adsorption—A surface phenomena exhibited by a solid (adsorbent) to hold or concentrate gases, liquids, or dissolved substances upon its surface (adhesion property). For example, the water held to the outside surface of a hydrated bentonite is adsorbed water.

Aeration—Injection of air or gas in varying amounts into a fluid.

Aerobic—Refers to the process (or life) that occurs in the presence of oxygen.

Aerosol—Liquid or solid particles suspended in air or gas.

Aggregate—A group of two or more individual particles held together by strong forces. Aggregates are stable to normal stirring, shaking, or handling as powder or suspension. They may be broken by drastic treatment such as ball milling a powder or by shearing a suspension.

Aggressive waters—Waters that have a potential to corrode metals. Inasmuch as all waters, including distilled water, have some degree of corrosiveness, a major economic consideration is the choice of materials used in pumps, pipes, valves, fittings, tanks, filters, etc.

Alloy—Alloy is a metal that is composed of more than one metallic element. A combination of different metals.

Alkali—Any compound having marked basic properties. Sodium and potassium are *caustic alkalies*.

Alkalinity—It is measured by the maximum number of equivalents of an acid with which a base can react to form a salt. In water, alkalinity is determined by the contents of carbonates, bicarbonates, hydroxides, and, occasionally, borates, silicates, and phosphates.

Ampere—The unit of electrical current = 1 coulomb per second.

Anaerobic—Refers to a process that occurs in the absence of oxygen. Also refers to life in a medium devoid of oxygen.

Anion—A negatively charged atom or radical (such as Cl^-, OH^-, and $SO_4^=$) in solution of an electrolyte. Anions move toward the anode (positive electrode) under the influence of an electrical potential.

Anode—The electrode in a corrosion cell which corrodes. Oxidation occurs at the anode.

Anolyte—The electrolyte adjacent to anode.

API gravity—The weight per unit volume of crude oil (or other related fluids) as determined by using the formula recommended by the American Petroleum Institute:

API—141.5/sp.gr.60°F – 131.5

where: sp.gr.60°F is the specific gravity compared to water at 60°F.

Atom—The smallest nearly indestructable particle, which can enter into chemical combination or can exist alone.

Atomic number—Designates the place of element in the periodic table. This number represents the net positive charge in the nucleus of an atom and is also equal to the number of protons within the nucleus.

Austenitic—A nonmagnetic (face-centered) cubic iron alloy.

Bacteria—Single-celled microorganisms that lack chlorophyll.

Base—A compound, which ionizes in the aqueous solution to yield excess of hydroxyl ions, increasing pH. Base is formed when a metallic oxide reacts with water. Bases increase the pH. Examples are caustic soda and lime. Any anion that can combine with a proton to form an anion acid (e.g., HCO_3^-) or a neutral molecule acid (e.g., H_2CO_3) can be regarded as a base.

Basicity—pH value above 7. Ability to neutralize or accept protons from acids.

Biochemical oxygen demand (BOD)—A standardized measure of the amount of oxygen consumed in the biological processes that break down the organic matter in water. BOD represents the quantity of the oxygen in mg/L required to biodegrade organic matter by aerobic biochemical action.

Biodegradable—Decomposable as a result of the activity of microorganisms.

Biological oxidation—The process by which microorganisms consume the complex organic materials, decomposing them. This process is also called *biochemical oxidation*.

Biomonitoring—Measuring bacterial activity (bacterial count).

Brass—An alloy of zinc and copper (>60%).

Brine—Water containing a high concentration of common salt (sodium chloride) and other chlorides and sulfates.

Bronze—An alloy of copper and tin (<12%).

Buffer—A substance or combination of substances in solution, which offer resistance to changes in pH upon the addition of acid or base.

Calcium hydroxide $Ca(OH)_2$—The main constituent in cement (≈60%); also the active ingredient of slaked lime. It is often referred to as *lime*.

Calcium sulfate—Anhydrite: ($CaSO_4$); plaster of Paris ($CaSO_4 \cdot 1/2H_2O$); and gypsum ($CaSO_4 \cdot 2H_2O$).

Cast iron—An alloy of carbon (2–4%) and iron. In the case of *gray cast iron*, fractures appear gray, whereas in the case of *white cast iron*, the fractures have metallic white appearance.

Cathode—Reduction in a corrosion cell always occurs at the cathode (negative electrode). No corrosion occurs at the cathode.

Cathodic polarization—Polarization occurring at the cathode.

Catholyte—Electrolyte adjacent to the cathode.

Cation—The positively charged ion in the solution of electrolyte. Under the influence of an electrical potential, it moves toward the cathode.

Caustic embrittlement—Metal embrittlement due to contact with an alkaline solution.

Caustic soda—NaOH.

Cavitation corrosion—Cavitation damage results in a sponge-like appearance with deep pits in the metal surface. The destruction may be caused by pulsating pressures caused by the formation and collapse of bubbles ("boiling") at the metal surface. The mechanical working of the metal surface is amplified in a corrosive environment. Cavitation may be prevented by increasing the suction head on the pumping equipment. By maintaining a net positive suction head, cavitation damage is prevented. This also prevents possible suction of air into the flow stream, which can aggravate corrosion in many environments.

Cement—A mixture of calcium aluminates and silicates prepared by combining lime and clay while heating. Slaked cement contains about 62.6% calcium hydroxide.

Centipoise, cP—A unit of viscosity which is equal to 0.01 Poise. 1 P = 1 g/m-sec, whereas 1 cP = 1 g/cm-sec. The viscosity of water at 20°C is 1.006 cP (1 cP = 0.000672 lb/ft-sec).

Chemical oxygen demand (COD)—A measure of the amount of oxygen required to oxidize organic matter and oxidizable inorganic compounds in water.

Chromate—A compound in which chromium has a valence of 6, e.g., sodium bichromate. Chromate is widely used as an anodic corrosion inhibitor, often in conjunction with lime.

Clarification—The removal of turbidity and suspended solids by settling (often aided by centrifugal action) and chemically induced coagulation.

Clay—A hydrous silicate of alumina, formed by the decomposition of feldspar and other aluminum silicates.

Concentration cell—The emf of concentration cell (electrolyte cell) is due to the difference in concentration of electrolyte (or active metal) at the cathode and anode.

Connate water—Water that was entrapped within sediments upon deposition. Later this water was modified by diagenetic/catagenetic alteration, infiltration of meteoric water, etc.

Reference: Larsen, G. and Chilingar, G. V., 1967. *Diagenesis of Sediments, Development in Sedimentology* 8, Amsterdam: Elsevier, 551 pp.

Copolymer—A molecule which is formed upon linking of two or more unlike polymers.

Corrosion—In 1946, the American Electrochemical Society had defined corrosion as the destruction of a metal by chemical or electrochemical reaction with its environment.

Corrosion fatigue—Reduction in fatigue durability by a corrosive environment. Cyclic stresses at high levels cause fatigue failure of metal. In a corrosive environment, the progress of fatigue is accelerated by electrochemical corrosion. Corrosion fatigue is the combined action of corrosion and fatigue (cyclic stressing), which results in early fracture of metal. Corrosion fatigue is the principal cause of drillpipe

failures. By establishing limits to the stresses repeatedly applied to metal, failure by metal fatigue in a noncorrosive environment can be avoided.

Endurance limit—The endurance limit is the maximum cyclic stress level that can be applied to a metal without a fatigue failure. In an environment with continued corrosion, instead of exhibiting an endurance limit, metal will fail due to the growth of corrosion fatigue cracks.

Corrosion due to variation in fluid flow—Velocity differences and turbulence of fluid flow over the metal surface cause localized corrosion. In addition to the combined effects of erosion and corrosion, variation in fluid flow can cause differences in concentrations of corrodants and depolarizers, which may result in selective attack of metals. For example, selective attack of metal occurs under the areas that are shielded by deposits from corrosion, i.e., scale, wax, bacteria, and sediments, in pipelines and vessels.

Coulomb—The unit of electrical quantity; quantity of electricity that will deposit 0.001118 g metallic silver on the cathode, when the current is passed through a solution of silver nitrate.

Coupon—Corrosion coupons are installed at selected locations to injection wells. An effort is made to install them at the lowest-volume injection well furthest from the plant. These coupons are commonly 3/4 × 3 × 1/8 inches in size and are prepared from cold-rolled ANSI 1018 or 1020 mild steel. Thus, they represent an infinitesimal percentage of the surface exposed in the system. For details concerning the preparation of corrosion coupons, one should consult ASTM Method G1-72 (ASTM, 1982) and NACE Recommended Practice 07-75 (NACE, 1975).

Inasmuch as the insulated coupon is electrically insulated from the system, theoretically its corrosion rate is related only to the corrosivity of the water. Experience has shown, however, that the corrosion attack on the insulated coupon in a dirty system is similar in type and rate to that on the noninsulated coupon. Evidence indicates that the electrical insulation is nullified by a conductive film, probably associated with bacterial growth.

Crazing—A network of cracks which appear on a surface.

Crevice corrosion—Crevice corrosion is an example of localized attack in the shielded areas of metal assemblies, such as pipes and collars,

rod pins and boxes, tubing, and drillpipe joints. Crevice corrosion is caused by difference in concentration of corrodants over a metal surface. Electrochemical potential differences result in selective crevice or pitting corrosion attack. Oxygen dissolved in drilling fluids promotes crevice and pitting attack of metal in the shielded areas of drillstring and is the common cause of washouts and destruction under the rubber pipe protectors. Crevice corrosion (contact corrosion) commonly occurs at the contact of metal with a nonmetallic material.

Current density—Current density is defined as the total number of amperes passing through a unit area (usually 1 cm^2) of an electrode.

Darcy—A unit of permeability (ease of flow through a porous medium). Permeability is equal to 1 Darcy when a pressure of 1 atm on a sample 1 cm long and 1 cm^2 in cross section will force a 1-cP-viscosity liquid through the sample at a rate of 1 cc/sec.

Dehydration—Removal of free or combined water from a compound.

Depolarize—Increasing the corrosion reaction rate by removing the polarizing corrosion products, etc., from the electrodes.

Desalinization—Salt removal from the sea or brackish water.

Diffusion—The spreading, scattering, or mixing of a substance (gas, liquid, or solid) upon its passage through a porous medium.

Dissociation—The splitting up of a compound or element into two or more simple molecules, atoms, or ions. Applied usually to the effect of heat or solvents upon dissolved substances. Sometimes, it is defined as the reversible decomposition of complex molecules into simple ones, sometimes of different kind.

Drilling fluid (also mud)—A circulating fluid (e.g., clay dispersed in water) used in rotary drilling to (1) remove the cuttings; (2) lubricate the bit; (3) form a filter cake on the walls of borehole (prevent formation damage); (4) cooling of the bit, drillpipe, and drillcollars, etc. (see Chilingarian and Vorabutr, 1981).

Reference: Chilingarian, G. V. and Vorabutr, P., 1981. *Drilling and Drilling Fluids*, New York, NY: Elsevier Science Pub. Co., Inc., 802 pp.

Dynamic—The state of being active (in motion), as opposed to static.

Electrical energy—The energy made available by the flow of electric charge through an electrical conductor. The SI unit of electrical energy is the joule:

$1\ \text{J} = 1\ \text{kg m}^2/\text{s}^2 = 10^7\ \text{ergs}$

Electric charge (quantity)—The quantity for electric charge in coulombs. 1 coulomb = amount of electric charge transported by a current of 1 ampere in 1 second:

$Q = I \times t$

where I is the electrical current, in amperes and t is the time in seconds. Faraday ($\approx$96,500 coulombs $\approx 6.06 \times 10^{23}$ electrons) is the larger unit for the electric charge.

Electric current (*I*)—Movement of electrically charged particles. It is measured in amperes, i.e., the amount of current sent by 1 volt through a circuit having resistance of 1 ohm:

$I = \dfrac{E}{R}$ (Ohm's law)

Electric potential (*E*)—The capacity of an electric field to do work. It is measured in volts (1 volt = 1 joule/coulomb; 1 joule = 10^7 ergs (energy or work); coulomb = quantity of electricity; ampere = 1 coulomb/sec). Electric potential E is equal to $I \times R$.

Electric power—The unit of electric power is watt (W) (1 watt = joule/second). 1 W = 1 J/sec = 1 V × 1 A; 1 HP = 746 watts (one would work at the rate of 1 horsepower by running up the stairway at a speed of 5–6 stairs a second).

Electrolysis—Chemical changes in an electrolyte upon passage of electrical current.

Electrolyte—Solution containing substance that dissociates into the positive and negative ions and conducts an electric current. Acids, bases, and salts dissolved in water constitute electrolytes.

Electrostatic—Static electricity (electricity at rest).

Electromagnetic—Electricity in motion, inducing magnetic phenomena.

Electromotive force—A measure of energy delivered (work done) by a current-inducing process for each coulomb transferred. Electromotive force is a term used to characterize electrical devices, such as

voltaic cells, thermoelectric devices, electrical generators and transformers, and even resistors.

Emulsion—A liquid mixture of two (or more) liquids that do not dissolve in each other. One liquid is held in suspension, or dispersion, in the other liquid by mechanical agitation or by adding small amounts of emulsifiers. Emulsions may be chemical, mechanical, or a combination of the two. Commonly, there are oil-in-water or water-in-oil types.

Equivalent weight—Formula (or atomic) weight of an element, compound, or ion divided by its valence. Elements always combine in quantities proportional to their equivalent weights.

Erosion–corrosion—The combination of erosion and corrosion results in severe localized attack of metal. Damage appears as smooth groove or hole in the metal, such as in a washout of the drillpipe, casing, or tubing. The washout is initiated by pitting in a crevice which penetrates the steel. The erosion– corrosion process completes the metal destruction.

The erosion process removes protective films from the metal and exposes clean metal surface to the corrosive environment. This accelerates the corrosion process.

The combination of wear and corrosion may also remove protective surface films and accelerate localized attack by corrosion. This form of corrosion is often overlooked or recognized as being due to wear. The use of inhibitors can often control this form of metal destruction. For example, inhibitors are used extensively for protection of downhole pumping equipment in oil wells.

Eukaryotes—The main eukaryotic microorganisms are fungi, algae, and protozoans. The most well-known fungus associated with microbial corrosion is *Hormoconis resinae*, which can grow on wide range of organic compounds including hydrocarbons. According to Videla (1996, p. 41), the corrosiveness of the *Hormoconis resinae* is due to facilitating the formation of pitting areas at the fixation points of tank walls. They produce organic acids, which are corrosive to aluminum, consume nitrates, and create redox conditions for passivity breakdown. Reference: Videla, H. A., 1996. *Manual of Biocorrosion*. CRC Press, Inc., Lewis Publishers: 273 pp.

Fermentation—Decomposition process of certain organic substances, e.g., starch in which a chemical change is brought about by enzymes,

bacteria, or other microorganisms. "Souring" is a common term used for fermentation.

Filtration—The process of separating suspended solids from the liquid by forcing the latter through a porous medium.

Flotation (floatation)—Removal of oil, solids, and colloidal materials from produced water, for example. There are two main types of flotation: (1) dissolved gas flotation and (2) froth flotation. The basic principle involved is the attachment of gas bubbles (air is not recommended) to the dispersed colloidal material, oil droplets, and solids, with resulting increase in their buoyancy. Thus, sludge is collected at the top of the tank by a rotating arm, for example, and then discharged to a sludge basin (for details, see Jones, 1988).

Foam—A foam is a two-phase system (similar to an emulsion) in which the dispersed phase is a gas or air.

Foaming agent—A substance that produces fairly stable bubbles at the air-liquid interface due to aeration, agitation, or ebullition.

Galvanic or two-metal corrosion—Galvanic corrosion occurs when two different metals are in contact in an electrolyte medium. Usually, the attack is localized near the contact points.

Galvanize—Coating a metal with zinc.

GYP (Gypsum)—$CaSO_4 \cdot 2H_2O$.

Hardness (water)—The hardness of water is due principally to the calcium and magnesium ions (but also iron) present in the water and is independent of the accompanying acid ions. The total hardness is expressed in terms of mg/L of calcium carbonate, but the use of equivalents is increasing.

Hard water—Water containing ions (Ca^{++}, Mg^{++}, Fe^{++}) that interfere with the action of soap (see API RP 13 B.).

Heterogeneous—Refers to a substance that consists of more than one phase and is not uniform, such as dispersed colloids and emulsions. It has different properties in different parts.

Homogeneous—A substance or fluid that has the same properties (or composition) throughout.

Humic acid—Organic acids derived from humus, which is formed as a result of partial decomposition of vegetable or animal matter (also, organic portion of soil).

Humidity (critical)—Corrosion rate increases sharply after critical relative humidity is reached.

Hydrate—A substance containing water combined in the molecular form (such as $CaSO_4 \cdot 2H_2O$). A substance containing water of crystallization.

Hydration—The process of taking up water by means of absorption and/or adsorption.

Hydrogen blistering—Penetration of atomic hydrogen (H°) into a low-strength steel may cause blistering (internal fracturing), which appears as bumps on the metal surface. The hydrogen atoms change to molecular hydrogen at points of defect in the metal. Although the hydrogen gas cannot penetrate into the crystalline structure, its pressure may increase sufficiently to pry apart the metal, create a void, and raise a blister on the steel surface.

Hydrogen embrittlement (sulfide stress cracking–SSC)—Sudden cracking of metal caused by the entrapment of hydrogen within the lattice structure.

Hydrogen sulfide—A malodorous gas with a characteristic odor of rotten eggs. Some produced crude oils and formation waters may contain hydrogen sulfide. In the presence of an aqueous phase, H_2S is corrosive to tubular goods and wellhead assembly. In very low concentrations, this toxic gas can cause death.

Hydrolysis—Hydrolysis is the reaction of salt with water to form an acid or base. Hydrolysis of soda ash (Na_2CO_3), for example, increases the pH of water.

Hydrophile—A substance usually in a colloidal state (or an emulsion), which is wetted by water; i.e., water adheres to it.

Hydrophilic—A substance that has an affinity for water (water-wet).

Hydrophobe—A substance (usually in a colloidal state) not wetted by water (oil-wet).

Hydrophobic—Refers to a substance that repels water (oil-wet).

Hydroxide—A basic compound containing the OH^- radical. When dissolved in water, it increases the pH of solution.

Hydroscopic—The property of a substance enabling it to absorb water from the air.

Impingement attack—Impingement attack is a form of erosion–corrosion process, which occurs after the breakdown of protective films. High velocities and presence of abrasive suspended material and the corrodants in drilling and produced fluids contribute to this destructive process.

Inhibitor (corrosion)—Any additive that slows down or prevents corrosion upon its addition to the system.

Interfacial tension—The force necessary for breaking the surface between two immiscible liquids. With lowering of the interfacial tension between the two phases of an emulsion, the deemulsification becomes easier.

Intergranular corrosion—Corrosion preferentially attacks the metal along the grain boundaries. Improper heat treatment of alloys or exposure to high temperature may cause precipitation of materials (or non-homogeneity of the metal structure) at the grain boundaries, which gives rise to preferential attack.

Weld decay is a form of intergranular attack. The attack occurs in a narrow band on each side of the weld owing to sensitizing or changes in the grain structure due to welding. Appropriate heat treating or metal selection can prevent the weld decay.

Ringworm corrosion is a selective attack which forms a groove around the pipe near the box or external upset end. This type of selective attack is avoided by annealing the entire pipe after the upset is formed.

Interstitial water—Water present in the pores (interstices, voids) of rocks.

Ion—When dissolved in water, acids, bases, and salts are more or less dissociated into electrically charged ions, due to loss or gain of electrons. The valence of an ion is equal to the number of charges borne by it.

Ionic mobility—The speed of ions toward or away from the electrodes.

Ionic strength—The ions shown to be present by water analysis are converted to a common basis called *ionic strength*, to account for differences in the influence of different ions on constant K in Stiff and Davis (1952) equation (see Chapter 6).

Reference: Stiff, H. A. and Davis, L. E., 1952. A method for predicting the tendency of oilfield waters to deposit calcium carbonate. *Petroleum Trans., AIME*, 195: 213.

Jones effect—The net surface tension of salt solutions first decreases with an increase of concentration, then passes through a minimum, and finally increases with increasing concentration.

Joule—Joule is the SI unit of energy (work). One joule is the work done (energy expended) by a force of one Newton moving an object 1 meter along the direction of force. 1 Joule = 10^7 ergs. When 1 Joule of energy is expended for each coulomb of current (between two points of circuit); there is a potential difference of 1 volt between these two points. Joules (work/energy) = volts × coulombs.

Kinematic viscosity—The kinematic viscosity of a fluid is equal to the ratio of dynamic viscosity (e.g., cP) to the density (e.g., g/cc). In several common viscometers, the kinematic viscosity is measured in terms of the time of efflux (in seconds) of a fixed volume of liquid through a standard capillary tube (or orifice).

Lime—Commercial form of $Ca(OH)_2$.

Lipophile—A substance (usually colloidal) easily wetted by oil.

Lipophilic—Having an affinity for oil (oil-wet).

Live oil—Crude oil that contains gas and has not been stabilized or weathered.

Molecular weight—The sum of the atomic weights of all the constituent atoms in the molecule of a compound.

Molecule—When atoms combine, they form a molecule. In the case of an element or a compound, a molecule is the smallest unit that chemically still retains the properties of the substance in mass.

MPY (*mpy*)—Mils per year. Measure of the rate of corrosion penetration. 1 mil = 0.001 inch.

Neat cement—A slurry composed of portland cement and water.

Neutralization—A reaction in which the hydroxyl ion of a base and the hydrogen ion of an acid unite to form water, with the other product being a salt.

Normal solution—A solution having a concentration of 1 gram-equivalent of a substance per liter of solution.

Oil-base drilling fluid—In the oil-base drilling fluids, oil is the continuous phase, whereas water is the dispersed phase. Oil contains blown asphalt and usually 1 to 5% water (emulsified), with caustic soda or quick lime and an organic acid.

Oil content—The oil content in any fluid in volume %.

Oil-in-water emulsion—A drilling fluid in which the oil content is usually kept between 3 to 7% and seldom over 10% (but it can be considerably higher). The oil is emulsified into fresh- or saltwater using an emulsifier. Sometimes, CMC, starch, or gum may be added to the fresh- and saltwater muds.

Ohm—The electrical resistance of a circuit when an electromotive force of 1 volt maintains a steady current of 1 ampere.

Oxygen (aeration) cell—The emf of electrolytic cell is due to difference in concentration of oxygen at one electrode compared with that at another electrode (electrodes of same material).

Parts per million (ppm)—Unit weight of solute per million unit weights of solution (solute + solvent).

Passivators—Chemicals that change the electrochemical potential of a metal to a more cathodic or noble value. Such inhibitors are called passivators. Cathodic inhibitors are not likely to act as passivators, whereas anodic inhibitors frequently do. For example, the iron will stay bright indefinitely in water containing sufficient chromate.

Permeability—A measure of the ability of rock to transmit a fluid under conditions of laminar flow. Unit of permeability is the Darcy.

pH—The strength of an acid or base can be represented by the molar concentration of hydrogen ion: $pH = -\log[H_3O^+]$. Water solutions with $pH < 7$ are acidic, whereas those with $pH > 7$ are alkaline (basic). The pH numbers range from 0 to 14, with 7 being neutral.

Pitting corrosion—Pitting is often localized in a crevice, but can also occur on clean metal surfaces in a corrosive environment. An example of this type of corrosion attack is the corrosion of steel in high-velocity seawater, low-pH aerated brines, or drilling fluids. Upon formation of a pit, corrosion continues as in a crevice, but, usually, at an accelerated rate.

Polarization—Increased resistance to the flow of current. For example, liberation of hydrogen gas at the cathode, covering it with a layer of

bubbles, diminishes the surface at which the electrons can be accepted.

Polymer—Polymer is the product of polymerization, a reaction in which identical molecules combine, giving rise to new carbon-to-carbon linkages.

Porosity—Volume of pores (voids) divided by the bulk volume. Absolute porosity refers to the total amount of pore space in a rock, regardless of whether the pores are intercommunicating or not. Effective porosity refers to the volume of intercommunicating pores. The writers of this book define *effective porosity* as the "effective porosity", as used in the United States, minus the irreducible fluid saturation (immobile fluid).

Potential (electrical)—Force driving an electric current through a closed circuit.

Preservative—Any material used to prevent starch, gum, or any other substance from fermenting through bacterial action. Paraformaldehyde is a common preservative.

Prokaryotes—Bacteria are prokaryotic microorganisms. Most of the bacteria involved in the corrosion process are a part of the sulfur cycle in nature. *Thiobacillus* is one of the best-known bacteria in causing corrosion. It is an aerobic microorganism (due to their metabolic activity), which produces a high-acidity environment favorable for corrosion.

Resistance—Determines the amount of current through a circuit for a given voltage across. The resistance (R) is measured in ohms (volt/ampere).

Resistivity—The electrical resistance offered to the passage of a current, expressed in ohm-centimeters; the reciprocal of conductivity. The unit of resistivity (ohm-cm) is equal to the resistance in ohms of a cube of rock 1 cm on each side. $\rho = R/L/A$, where ρ is the resistivity in ohm-cm, R is the resistance in ohms, L is the length in cm, and A is the cross-sectional area in cm^2. Freshwater drilling fluids usually have a high resistivity, whereas the saltwater drilling fluids exhibit a low resistivity.

Saturated solution—Saturated solution contains (at a given temperature) as much of a solute as it can retain. At 68°F, 126.5 lb of salt are required per 1 bbl of freshwater to achieve saturation.

Scaling Index (*SI*) (Langelier–Stiff and Davis)—$SI = pH_{actual} - pH_s$ where:

$pH_s = pCa + pAlk + K$
pH_s = pH water would have if it were exactly saturated with $CaCO_3$.
K = constant that depends on TDS and temperature.
pCa^{++} = negative logarithm of the calcium ion concentration, mols/L.
pAlk = negative logarithm of total alkalinity.
Negative *SI* indicates no precipitation, whereas positive *SI* indicates that scale will probably form.

Selective leaching—Selective leaching occurs when one component of an alloy is removed as a result of corrosion. An example of this type of corrosion is the selective corrosion of zinc in brass.

Silt—Non-swelling rock particles ranging in size from $\frac{1}{256}$ to $\frac{1}{16}$ mm (see Figure B.1).

Soap—Salt (sodium or potassium) of a high-molecular-weight fatty acid. If a metal other than sodium or potassium is involved, the soap is called a *metallic* soap.

Sodium bicarbonate ($NaHCO_3$)—A material used extensively for treating cement contamination and occasionally other calcium contamination in drilling fluids.

Sodium bichromate ($Na_2Cr_2O_7$)—Correctly called *sodium dichromate.*

Sodium hydroxide (NaOH)—Commonly called "caustic" or "caustic soda." It is primarily used to impart a higher pH.

Solubility—The degree of dissolution of a substance in a particular solvent.

Solute—A substance that is dissolved in another (the solvent).

Solvent—Liquid in which solute is dissolved.

Specific heat—The heat (in calories) required to raise the temperature of 1 g of a substance by 1°C.

Stainless steel (passive)—Iron alloyed with 13% or more of chromium.

Standard hydrogen electrode (SHE)—A platinized platinum electrode dipping into a solution of hydrogen ions (activity = 1.000), as the H_2 gas bubbles over the electrode at a pressure of 1 atm (see Jones, 1988, p. 161).

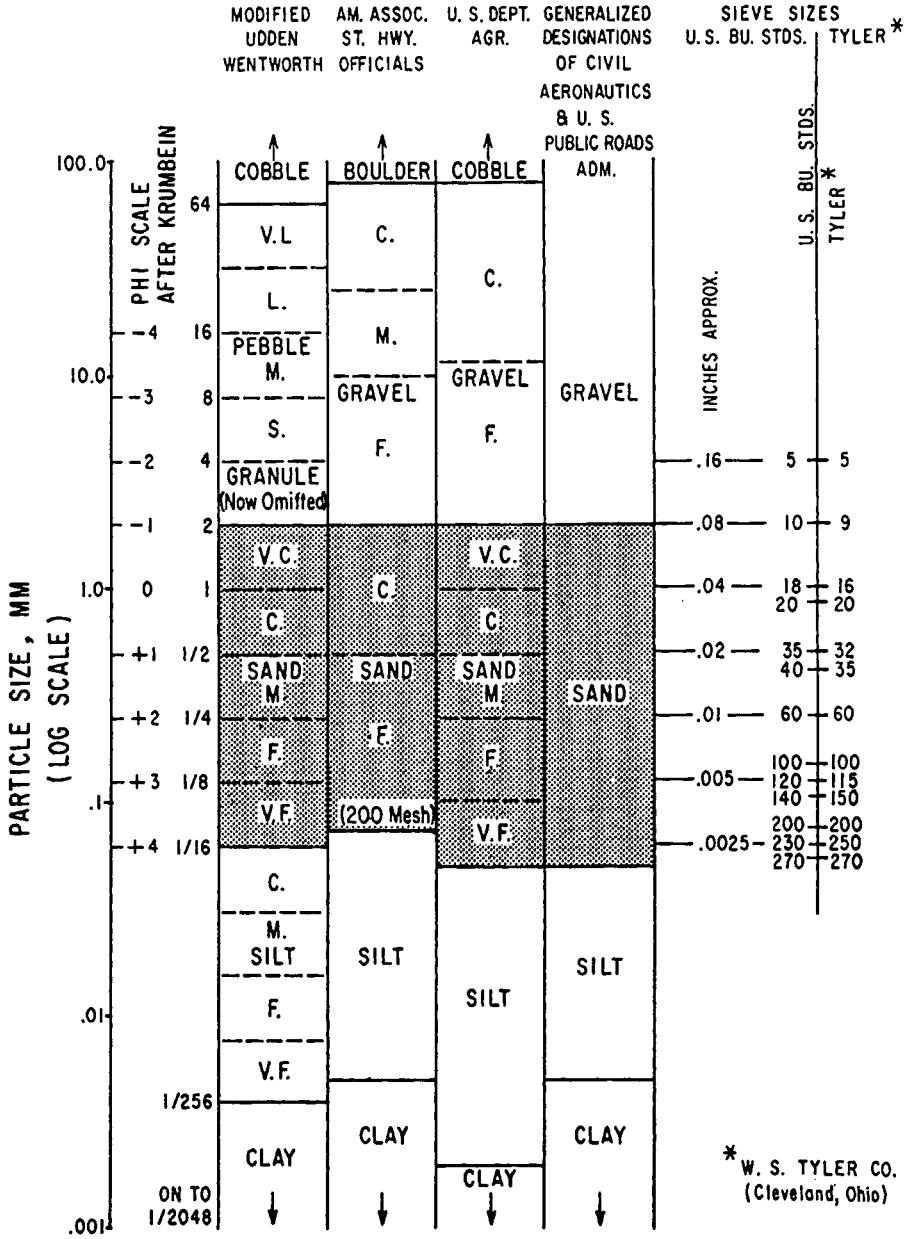

Figure B.1 Comparison between various particle size classifications and sieve size. (After Chilingarian and Wolf, 1975, p. 39.) Reference: Chilingarian G. V., Wolf, K. H., and Allen D. R. Introduction. In: G. V. Chilingarian and K. H. Wolf, 1975. *Compaction of Coarse Grained Sediments*, 1. Developments in Sedimentology ISA, Amsterdam: Elsevier, 552 pp.

A common reference electrode, potential of which is assigned the value of 0.000 volt (see Figure B.2).

References: Jones, L. W, 1988. *Corrosion and Water Technology for Petroleum Producers*. Tulsa, OK: Oil and Gas Consultants International, Inc. (OGCI Publications), 202 pp.

Deming, H. G., 1946. *Fundamental Chemistry*. London: John Wiley & Sons, 756 pp.

Steel—An alloy of iron and carbon.

Stress corrosion—Stress corrosion cracking of metals is produced by combined action of corrosion and tensile stress. The term stress corrosion cracking often is applied to all cracking that is related to stress and corrosion: (1) stress corrosion fatigue, (2) hydrogen embrittlement and blistering, (3) sulfide cracking, (4) corrosion fatigue, (5) stress alloying, and (6) caustic embrittlement.

Although stress corrosion cracking can occur in most alloys, the corrodants that promote stress cracking may differ and be few in number for each alloy. Cracking can occur in both acidic and alkaline environments; usually in the presence of chlorides and/or oxygen.

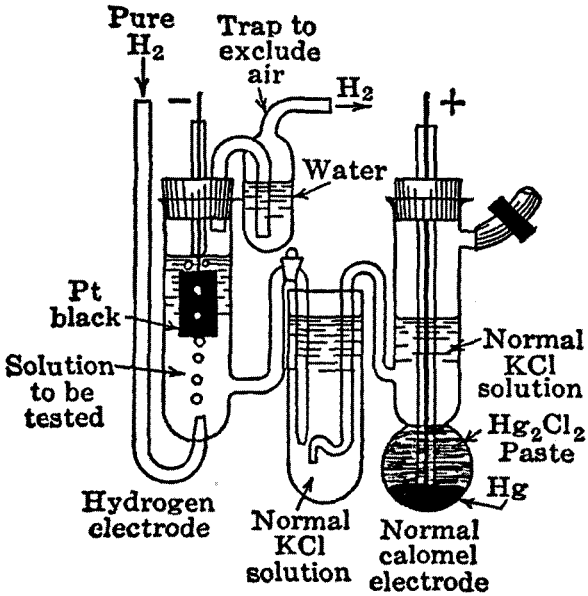

Figure B.2 The hydrogen electrode (see Deming, 1940, p. 501).

Surfactant—A material that tends to concentrate at an interface of two fluids and reduce the interfacial tension. It controls the degree of emulsification, aggregation, dispersion, foaming, defoaming, wetting, etc.

Surface tension—The force in dynes/cm acting at the interface between a liquid and its own vapor, which tends to maintain the area of the surface at a minimum. The surface tension of a liquid is approximately equal to the interfacial tension between the liquid and air. The term *interfacial tension* refers to the force acting at the interface between two liquids or a liquid and a solid.

Thinner—Refers to organic additives (tannins, lignites, lignosulfonates, etc.) and inorganic agents (sodium acid pyrophosphate [SAPP], tetraphosphate, etc.), which reduce the viscosity of drilling fluids.

Uniform attack—Uniform corrosion of the entire area of the metal, resulting in thinning of the metal. This often occurs to drillpipe, for example. Usually, it is the least damaging of the different types of corrosion. Examples of this form of corrosion are uniform rusting of iron and tarnishing of silver.

Unit charge—The charge on the electron.

Volt—The potential difference across a conductor when a current of one ampere dissipates one watt of power. 1 volt = 1 joule per coulomb.

Water-base drilling fluid—Clay (swollen) dispersed in water constitutes a conventional drilling fluid.

Watt—Power of 1 joule per second.

Wetting—The affinity (adhesion) of a liquid to the surface of a solid.

Wetting agent—Additive to a liquid which increases the spreading of liquid on the surface of a material.

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APPENDIX C
CONVERSION OF UNITS

Multiply	→ by →	To Obtain
Acre (ac)	4.3560×10^4	sq ft
	6.272640×10^6	sq in.
	1×10^5	sq links (Gunter's)
	4.046856×10^3	sq m
	1.5625×10^{-3}	sq mi
	4.840×10^3	sq yd
Acre-foot (ac-ft)	4.3560×10^4	cu ft
	1.233482×10^3	cu m
	1.613333×10^3	cu yd
	3.259×10^5	gal
Atmosphere (atm)	1.01325	bars
	7.6×10	cm of Hg at 0°C
	1.03326×10^3	cm of H_2O at 4°C
	1.01325×10^6	dynes/sq cm
	3.38995×10	ft of H_2O at 39.2°F
	1.46960×10	psi
Bar	9.86923×10^{-1}	atm
	7.50062×10	cm of Hg (0°C)
	1×10^6	dynes/sq cm
	1.45038×10	psi
Barrel	1.589828×10^{-1}	cu m
	5.614583	cu ft

Multiply	→ by →	To Obtain
British thermal unit (Btu)	2.519958×10^{2}	cal, g
	1.05435×10^{10}	ergs
	2.50201×10^{4}	ft-poundals
	7.77649×10^{2}	ft-lb
	3.92752×10^{-4}	hp-hr
	1.05435×10^{3}	J
	2.92875×10^{-4}	kW-hr
	1.05435×10^{3}	W-sec
Calorie, gram (cal, g)	3.968321×10^{-3}	Btu
	4.184	J
Centimeter	3.280840×10^{-2}	ft
	3.937008×10^{-1}	in.
	1×10^{-2}	m
	1×10^{7}	μm
	6.213712×10^{-6}	mi
	1.093613×10^{-2}	yd
Centimeter-gram (cm-g)	1×10^{-5}	m-kg
	7.233014×10^{-5}	lb-ft
Centimeter of mercury at 0°C	1.315789×10^{-2}	atm
	1.33322×10^{4}	dynes/sq cm
	3.937008×10^{-1}	in. of Hg, 0°C
	1.93368×10^{-1}	psi
Centipoise (cP)	1×10^{-2}	g/(cm-sec)
	2.419088	lb/(ft-hr)
	6.71969×10^{-4}	lb/(ft-sec)
	2.089×10^{-5}	lb-sec/sq ft
Cubic centimeter	3.531467×10^{-5}	cu ft
	6.102374×10^{-2}	cu in.
	1×10^{-6}	cu m
	2.641720×10^{-4}	gal
	9.99972×10^{-4}	l (L)
	3.381402×10^{-2}	oz
	1.056688×10^{-3}	qt
Cubic centimeter per second (cu cm/sec)	2.118880×10^{-3}	cu ft/min
	1.585032×10^{-2}	gal/min
Cubic foot (cu ft)	2.295684×10^{-5}	ac-ft
	2.831685×10^{4}	cu cm
	7.480520	gal
	2.831605×10	L
	9.575065×10^{2}	oz
	2.992208×10	qt

Multiply	→ by →	To Obtain
Cubic inch (cu in.)	1.638706×10	cu cm
	5.787037×10^{-4}	cu ft
	2.143347×10^{-5}	cu yd
	4.329004×10^{-3}	gal
	1.638661×10^{-2}	L
	5.541125×10^{-1}	oz
	1.731602×10^{-2}	qt
Cubic meter (cu m)	8.107132×10^{-4}	ac-ft
	1×10^{6}	cu cm
	3.531467×10	cu ft
	6.102374×10^{4}	cu in.
	1.30795	cu yd
	2.64172×10^{2}	gal
	9.99972×10^{2}	L
Cubit	4.572×10	cm
	1.5	ft
	1.8×10	in.
Day (mean solar)	2.4×10	hr (mean solar)
	1.44×10^{3}	min (mean solar)
	8.64×10^{4}	sec (mean solar)
	2.739726×10^{-3}	yr (calendar)
Decimeter	1×10	cm
Dyne	1.573663×10^{-2}	grains
	1.019716×10^{-3}	g
	1×10^{-5}	newtons
	7.233014×10^{-5}	poundals
	2.248089×10^{-6}	lb
Erg	9.48451×10^{-11}	Btu
	2.39006×10^{-8}	cal, g
	9.86923×10^{-7}	cu cm-atm
	3.48529×10^{-11}	cu ft-atm
	1	dyne-cm
	6.24196×10^{11}	electron V
	7.37562×10^{-8}	ft-lb
	1.019716×10^{-3}	g-cm
	1×10^{-7}	J
	2.77777×10^{-14}	kW-hr
	9.868995×10^{-10}	l-atm
	1×10^{-7}	W-sec

Multiply	→ by →	To Obtain
Foot (ft)	3.048×10	cm
	9.99998×10^{-1}	ft (U.S. survey)
	1.2×10	in.
	3.048×10^{-1}	m
	1.89393×10^{-4}	mi
	3.33333×10^{-1}	yd
Foot per second (ft/sec)	1.09728×10^{5}	cm/hr
	1.8288×10^{3}	cm/min
	3.048×10	cm/sec
	6.818182×10^{-1}	mi/hr
	1.136363×10^{-2}	mi/min
Gallon (gal)	3.068883×10^{-6}	ac-ft
	3.174603×10^{-2}	bbl
	3.785412×10^{3}	cu cm
	1.336805×10^{-1}	cu ft
	2.31×10^{2}	cu in.
Gravitational constant	9.80621×10^{2}	cm/sec^2
	3.21724×10	ft/sec^2
Hectogram	1×10^{2}	g
	2.679229×10^{-1}	lb
Hectoliter (hL)	1.00028×10^{5}	cu cm
	3.531566	cu ft
	2.641794×10	gal
	1×10^{2}	L
	3.381497×10^{3}	oz
Horsepower boiler (hp boiler)	1.31548×10	hp (mechanical)
	1.31495×10	hp (electrical)
Horsepower (electric)	7.46×10^{9}	erg/sec
	1.0004	hp (mechanical)
	7.46×10^{-1}	kW
Horsepower (metric)	9.85923×10^{-1}	hp (electrical)
	9.8632×10^{-1}	hp (mechanical)
Inch (in.)	2.54×10^{8}	Å
	2.54	cm
	8.33333×10^{-2}	ft
	2.54×10^{-2}	m
	2.77777×10^{-2}	yd
Inch of mercury at 32°F	3.34211×10^{-2}	atm
	3.38639×10^{-2}	bars
	3.38639×10^{4}	dynes/sq cm
Inch per minute (in./min)	1.524×10^{2}	cm/hr
	5	ft/hr
	9.46969×10^{-4}	mi/hr

Multiply	→ by →	To Obtain
Joule (absolute) (J)	9.48451×10^{-4}	Btu
	2.39006×10^{-1}	cal, g
	1×10^{7}	ergs
	2.37304×10	ft-poundals
	7.37562×10^{-1}	ft-lb
	3.72506×10^{-7}	hp-hr
	9.99835×10^{-1}	J (Int.)
	1	W-sec
Joule (Int.)	1.000165	J (abs.)
Joule per second (absolute) (J/sec)	5.69071×10^{-2}	Btu/min
	1.43403×10	cal, g/min
	1.34102×10^{-3}	hp (mechanical)
	1	W
Kilogram	9.80665×10^{5}	dynes
	3.215074×10	oz
	7.093163×10	poundals
	2.679229	lb
	6.852177×10^{-2}	slugs
Kilogram per cubic meter (kg/cu m)	6.242796×10^{-2}	lb/cu ft
	3.612729×10^{-5}	lb/cu in.
Kilogram-meter	2.34048	cal, g (mean)
	9.80665×10^{7}	ergs
	$7.23301 \times$	ft-lb
	3.65304×10^{-6}	hp-hr
Liter (L)	1.000028×10^{3}	cu cm
	3.531566×10^{-2}	cu ft
	6.102545×10	cu in.
	2.641794×10^{-1}	gal
	3.381497×10	oz
	2.113436	pt
	1.056718	qt
Liter per minute (L/min)	3.5315666×10^{-2}	cu ft/min
	2.641794×10^{-1}	gal
Meter (m)	1×10^{2}	cm
	3.280839	ft
	3.937008×10	in.
	1×10^{-3}	km
	6.213712×10^{-4}	mi
	1.093613	yd
Meter per hour (m/hr)	$3.280840 \times$	ft/hr
	6.213712×10^{-4}	mi/hr

Multiply	→ by →	To Obtain
Meter per minute (m/min)	5.468066×10^{-2}	ft/sec
	3.728227×10^{-2}	mi/hr
Micron μm	1×10^{-4}	cm
	3.28084×10^{-6}	ft
	3.93701×10^{-5}	in.
	1×10^{-6}	m
Mile (mi)	1.609344×10^{5}	cm
	8×10	chains (Gunter's)
	5.28×10^{3}	ft
	6.336×10^{4}	in.
	1.609344	km
	1.70111×10^{-13}	light yr
	1.609344×10^{3}	m
	1.76×10^{3}	yd
Millibar	1×10^{-3}	bars
Milligrams	1×10^{-3}	g
Milliliter (mL)	1.000028	cu cm
	6.102545×10^{-2}	cu in.
	1×10^{-3}	L
	3.381497×10^{-2}	oz
Millimeter (mm)	1×10^{-1}	cm
	3.28084×10^{-3}	ft
	3.937008×10^{-2}	in.
	1×10^{-3}	m
Newton	1×10^{5}	dynes
	2.248089×10^{-1}	lb
Newton-meter	1×10^{7}	dyne-cm
	7.375621×10^{-1}	lb-ft
Ounce (oz)	4.80×10^{2}	grains
	3.110349×10	g
	8.33333×10^{-2}	lb
	3.428571×10^{-5}	tons
Part per million (ppm)	1×10^{-3}	g/L
Pint	4.731765×10^{2}	cu cm
	1.671007×10^{-2}	cu ft
	2.8875×10	cu in.
	6.188915×10^{-4}	cu yd
	1.25×10^{-1}	gal
	4.731632×10^{-1}	L
	1.6×10	oz
	5×10^{-1}	qt

Multiply	→ by →	To Obtain
Pound (apoth or troy) (lb)	3.732417×10^{2}	g
	1.2×10	oz
	8.228571×10^{-1}	lb (avdp)
	3.673469×10^{-4}	tons (long)
	3.732417×10^{-4}	tons (metric)
	4.114286×10^{-4}	tons (short)
Pounds (avdp)	1.215277	lb (apoth or troy)
Quart (U.S., liq) (qt)	9.463530×10^{2}	cu cm
	3.342014×10^{-2}	cu ft
	5.775×10^{1}	cu in.
	2.5×10^{-1}	gal (U.S., liq)
	3.2×10^{1}	oz (U.S., liq)
	2	pt (U.S., liq)
	8.326747×10^{-1}	qt (British)
	8.59367×10^{-1}	qt (U.S., dry)
Radian	1.591549×10^{-1}	circumference
	5.729578×10	deg (angular)
	3.437747×10^{3}	min (angular)
	6.366198×10^{-1}	quadrants
	2.062648×10^{5}	sec (angular)
Square foot (sq ft)	2.295684×10^{-5}	ac
	9.290304×10^{2}	sq cm
	1.44×10^{2}	sq in.
	3.587006×10^{-8}	sq mi
	1.111111×10^{-1}	sq yd
Square inch (sq in.)	6.4516	sq cm
	6.9444×10^{-3}	sq ft
	2.490977×10^{-10}	sq mi
Square meter (sq m)	2.471054×10^{-4}	ac
	1×10^{4}	sq cm
	1.076391×10	sq ft
	1.550003×10^{3}	sq in.
	3.861022×10^{-7}	sq mi
	1.19599	sq yd
Ton (metric)	1×10^{3}	kg
	2.204623×10^{3}	lb (avdp)
	9.842065×10^{-1}	tons (long)
	1.102311	tons (short)
Tun	2.52×10^{2}	gal

Multiply	→ by →	To Obtain
Watt (W)	3.41443	Btu/hr
	8.60421×10^2	cal, g/hr
	1×10^7	erg/sec
	4.42537×10	ft-lb/min
	1.34102×10^{-3}	hp
	1	J/sec
	1×10^{-3}	kW
Watt (Int.) (W)	1.000165	W
Watt-hour (W-hr)	3.41443	Btu
	3.40952	Btu (mean)
	8.60421×10^2	cal, g
	3.6×10^3	J
Yard (yd)	9.144×10	cm
	3	ft
	3.6×10	in.
	9.144×10^{-1}	m

C.1 TEMPERATURE CONVERSION FORMULAS

To obtain	Formula
°F (Fahrenheit)	$(°C \times 1.8) + 32$
°C (Centigrade)	$\frac{°F+40}{1.8} - 40$
°C	$(°F-32) \times 0.5555$
K (Kelvin)	$°C + 273.16$
°R (Rankine)	$°F + 459.688$

C.2 APPROXIMATE EQUIVALENTS

Rough Rules:

The authors of this book believe that a good engineer should be familiar with both SI and FPS systems of units, and should be able to convert easily from one to the other.

1 m = little over a yard = 1 yard + 10%.

1 mm ≈ about the thickness of 11 leaves of this book.

1 kg = 2 lb plus 10%.

1 liter = a quart plus 5%; volume occupied by 1 kg of water.
1 mL = volume occupied by 1 g of water–within 0.0027%, equal to 1 cm^3.
1 cm^3 = volume of 20 drops of water.

C.3 THEORETICAL ASPECTS

Conversion of units of time and length is simple. For example, 1 year (calendar) = 365 days (mean solar) = 525,600 minutes (mean solar) = 3.1536×10^7 seconds (mean solar); and 1 yard = 3 feet = 36 inches = 91.44 centimeters.

The units of force and mass, however, are not as easily converted and understood. The earth exerts a gravitational force on all bodies. The magnitude of this force, called weight, is equal to the mass of the body multiplied by the gravitational acceleration, or:

$$F = mg$$

where:
F = weight or force in pounds; m = mass of the body in slugs; g = gravitational acceleration, which at sea level is about 32.2 ft/sec^2.

For example, the density (mass per unit volume), ρ, of water having a specific weight, γ, of 62.4 lb/cu ft is:

$$\rho = \gamma/g = \frac{62.4 \text{ lb/cu ft}}{32.2 \text{ ft/sec}^2} = 1.94 \text{slug/cu ft}$$

In the opinion of the writers, it is critical to use different terms for the specific weight, γ, and for the density, ρ.

Example: Dynamic Viscosity Conversion Factor
Dynamic or absolute viscosity, μ, may be defined as the (shearing stress)/(rate of shearing strain) ratio assuming a linear distribution of velocity between two plates (one plate moving with respect to the other) with fluid in between:

$$\mu = \frac{F/A}{V/h} \tag{C.1}$$

$$\mu = \frac{\tau}{V/h} \tag{C.2}$$

where:
F = the force required to maintain flow (to slide the fluid layers relative to each other, which is accomplished by overcoming the internal fluid friction); A = area of moving plate in contact with the fluid; V = velocity of upper plate if lower plate is stationary; h = distance between the two plates; τ = shearing stress or F/A.

The symbols M, L, F, and T represent the fundamental dimensions of mass, length, force, and time, respectively; thus:

$$\mu = \frac{F/L^2}{(L/T)/L} = \frac{FT}{L^2} \tag{C.3}$$

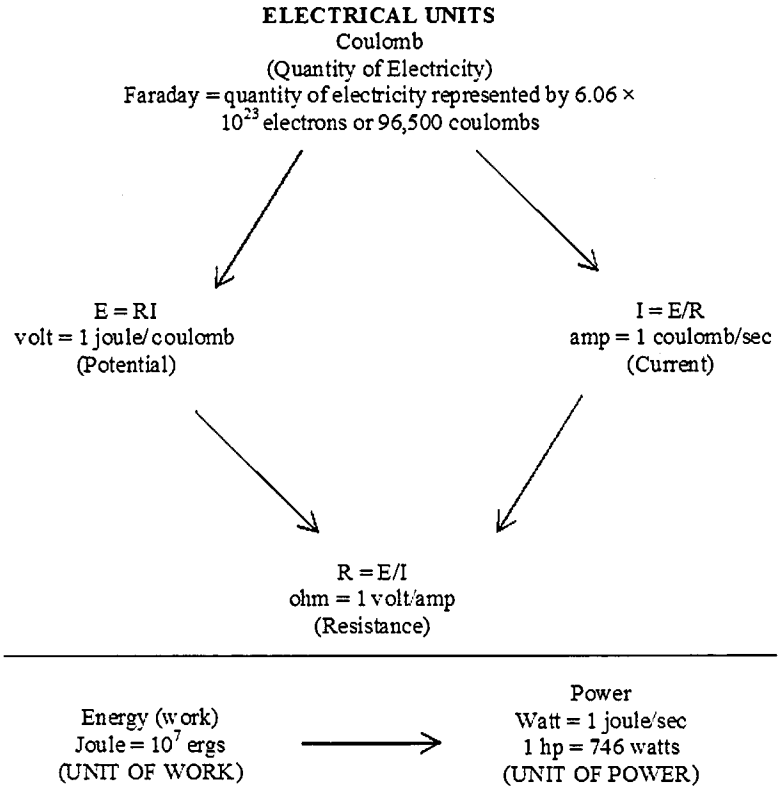
Inasmuch as force equals mass times acceleration [$F = (ML/T^2)$], the dimension of dynamic viscosity is:

$$\mu = \frac{(ML/T^2)T}{L^2} = \frac{M}{LT} \tag{C.4}$$

Thus, dynamic or absolute viscosity can be expressed in lb-sec/ft^2 or slug/ft-sec, whereas in the metric system:
1 (dyne-sec/cm^2) = 1 (g/cm-sec) = 1 Poise
Inasmuch as 1 in. = 2.54 cm and 1 dyne = 2.248×10^{-6} lb,

$$\begin{aligned} 1\,\text{Poise} = 1(\text{dyne-sec/cm}^2) &= \frac{\text{dyne}(2.248\times10^{-6}\,\text{lb/dyne})\text{sec}}{\text{cm}^2\left[(2.54\times12)^2\,\text{ft}^2/\text{cm}^2\right]} \\ &= 2.089\times10^{-3}\ (\text{lb-sec/ft}^2) \\ &= 2.089\times10^{-3}\ (\text{slug/ft-sec}) \end{aligned}$$

The absolute viscosity of water at 20°C is around 1 centipoise, which is equal to 0.01 of a Poise, named in honor of French scientist Poiseuille.



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