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An Overview of Corrosion in Oil and Gas Industry: Upstream, Midstream, and Downstream Sectors

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1.1 Introduction

The oil and gas industry is normally divided into three major components: upstream, midstream, and downstream. The upstream sector explores, locates, and produces crude oil and natural gas from both underground and underwater fields, which are referred to as onshore and offshore fields, respectively. For this, the upstream sector is sometimes referred to as exploration and production (E&P). Types of wells handled in the upstream sector include oil, gas, and water. The midstream sector involves the transportation (by pipeline, rail, barge, oil tanker, or truck), processing, storage, and wholesale marketing of crude or refined petroleum products. Pipelines and other transport systems are used to move crude oil and natural gas from production sites to refineries and petrochemical plants. Natural gas pipeline networks gather gas from natural gas producing wells and from separation and purification plants and deliver it to downstream sector and customers, such as local utilities. Midstream operations often overlap with some elements of the upstream and downstream sectors. For example, the midstream sector may encompass natural gas processing plants that purify the raw natural gas as well as removing and producing elemental sulfur and natural gas liquids (NGLs). The third component is the downstream sector that includes crude oil refineries, petrochemical plants, and petroleum products distribution. One major component of the downstream sector is the refining of crude oil into gasoline, diesel, jet, and other fuels. In addition, the downstream industry provides thousands of products such as jet fuel, heating oil, asphalt, lubricants, synthetic rubber, plastics, fertilizers, antifreeze, pesticides, pharmaceuticals, natural gas, and propane.

At the early stages of crude oil production from a newly discovered field, the produced fluids streams are normally dry. Water, however, is required for corrosion to occur at low temperatures. As a result, the majority of equipment used in oil production were conveniently constructed from the relatively low cost carbon steel that has the required strength for pressure containment. It is very common that the life of these installations exceed 50 years without the need to apply any corrosion control measure as long as the streams remain dry or dominated by the

hydrocarbon phase. Nothing remains the same with the passage of time. As oil and gas fields matured, the amount of produced water increased either naturally or due to recovery by waterflooding, for example. This increase in water content called for employing an effective and practically easy to apply corrosion control method.

Corrosion inhibition has been the method of choice that allowed production from fields that were about to be abandoned because of the increase in corrosion activity. The accumulated experience of using carbon steel with corrosion inhibition encouraged extending this approach even to environments with aggressive corrosion conditions such as wells with higher H_2S contents. Batch and continuous corrosion inhibitor treatments became two of the most common methods to control internal corrosion of carbon steel piping and equipment in oil and gas production, transportation, and processing. A large number of commercial corrosion inhibitors are available, and new products are being continuously developed by chemical manufacturers. Several international standards have been developed [1] and are being developed [2] for corrosion inhibitor evaluation and selection.

Corrosion encountered in the production of oil and gas is very costly and it involves direct and indirect costs associated with lost time, the replacement of materials of construction, and the continuous involvement of personnel in corrosion management as well as safety and environmental consequences. In 2016, NACE International released the "International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT)" study, which estimates the global cost of corrosion to be approximately US$2.5 trillion. The study reviewed cost of corrosion studies performed by several countries including, Australia, China, Finland, Germany, India, Japan, Kuwait, Sweden, the United Kingdom, and the United States. Based on these studies, the annual corrosion costs in each nation ranged from approximately 1–5% of their gross national product (GNP). These studies do not include the cost of corrosion failures consequences on safety and environment. The IMPACT study found that significant savings between 15% and 35% of the cost of damage can be realized by implementing corrosion control practices that are equivalent to reducing the global corrosion cost by US$375–875 billion annually.

1.2 Corrosion in Upstream Production Operations

The upstream sector [3] includes exploration, drilling, completion, production, processing, and workover of both oil and gas fields. Simplified process flow diagrams for oil and gas production are shown in Figure 1.1 along with typical midstream processing facilities [4].

Exploration involves searching for oil and gas reserves both conventional and unconventional. Drilling for these reserves could be in the vertical direction only or combined with horizontal–lateral–drilling. The drilled wells are completed using casings only or with production tubing, and different types of valves. The production casing or tubing are perforated to allow flow from the reservoir.
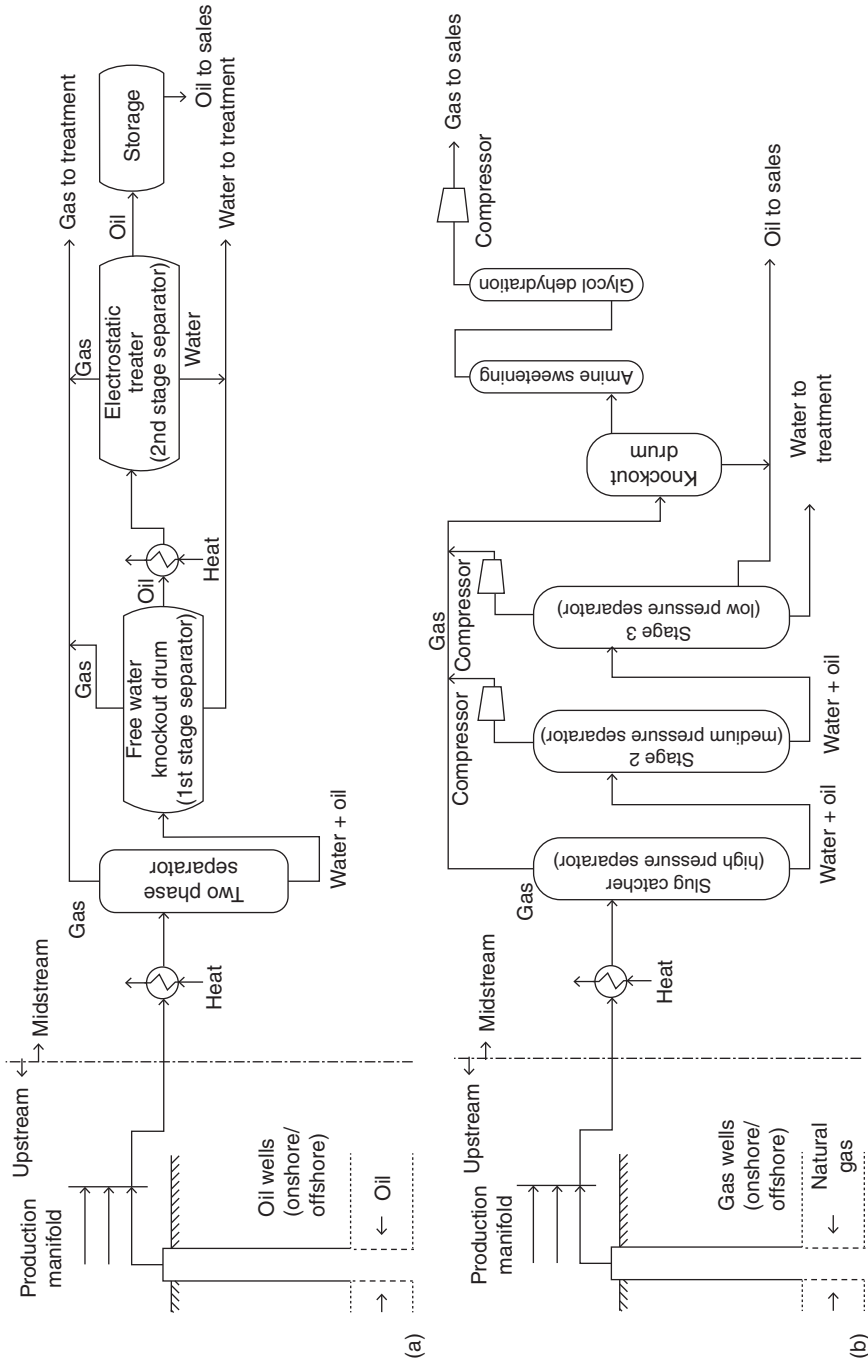
Figure 1.1 Simplified upstream and midstream process flow diagrams for (a) oil wells and (b) gas wells. Source: Adapted from Baker Hughes 2013 [4].
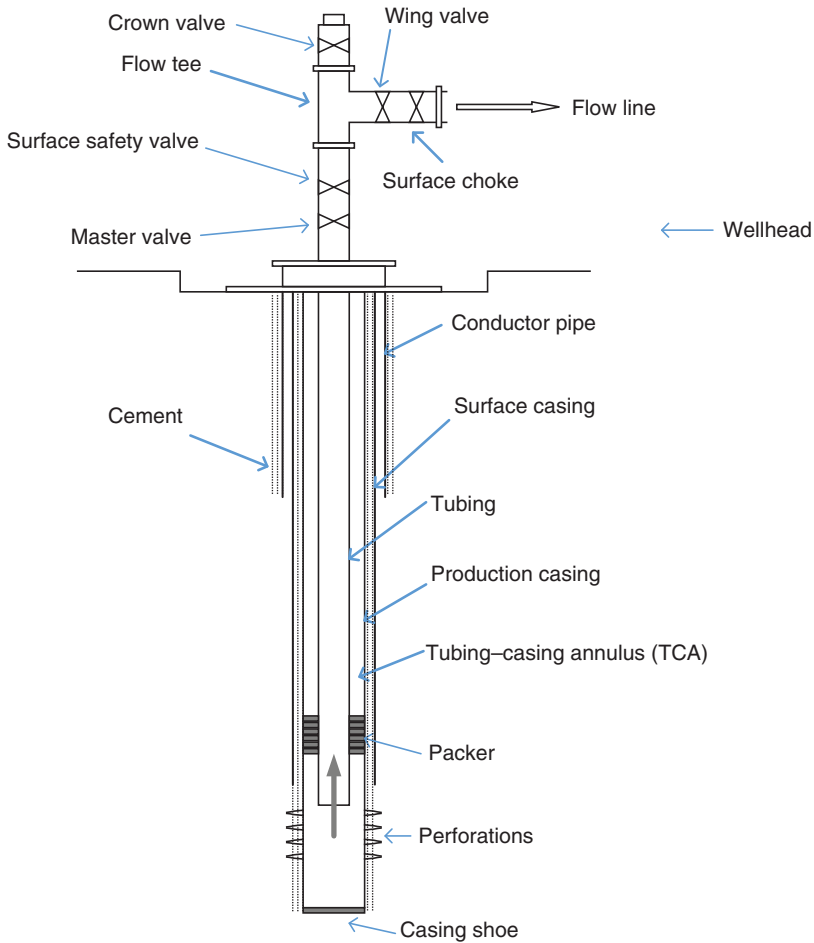
Figure 1.2 Schematic of a typical oil well.

To control flow, different valves are installed within the well, at the wellhead, and at the assembly on top of the well head – usually called the Christmas tree. The fluids from the wells are transported using flowlines and trunklines to processing facilities to separate gas, oil, and water. The wells are worked over in case of drop in production due to plugging, for example, or if a major well component fails. A schematic of a typical oil well is shown in Figure 1.2.

Hydrocarbon reservoirs can be gaseous, liquid, or both. A natural gas reservoir under initial conditions contains a single gaseous hydrocarbon phase. If the gaseous hydrocarbon phase contains heavier ends that become liquid at the surface, the reservoir is classified as a gas condensate reservoir. An oil reservoir, on the other hand, can be either two-phase (gas–liquid) or single liquid phase. A gas well produces from a natural gas reservoir and an oil well produces from an oil reservoir. Natural gas reservoirs are usually at higher temperatures than crude oil reservoirs. This implies higher downhole temperatures in gas wells than in oil wells. Two main characteristics of the wells are the bottomhole temperature

(BHT) and the bottomhole pressure (BHP). BHT is the temperature at the center of the perforated interval, while BHP is the pressure at the center of the perforated interval under shut-in conditions. The pressure can reach to more than 90 MPa (∼13 000 psi) and the temperature to more than 200 °C (∼390 °F).

A reservoir or a well are classified as sweet when carbon dioxide (CO_2) is present with no or very little hydrogen sulfide (H_2S). They will be classified as sour if H_2S is present at noticeable amounts. CO_2 and H_2S are called acid gases. Due to the different corrosion damage mechanisms, sweet and sour wells usually have different corrosion control strategies from drilling to transportation. The gas could be non-associated when produced alone or associated when produced with oil. Condensate wells are gas wells with condensed liquids as well. A characteristic quantity is the gas–oil ratio (GOR), which is the ratio of produced gas to produced oil at standard conditions.

At the beginning of their production life, oil and gas wells could be dry, i.e. no formation water, or have low water cuts. Normally, the water cut increases with time as the well matures, so does damage due to corrosion attacks. The scaling tendency and the potential of emulsion formation are dependent on the type of formation water. A comprehensive geochemical analysis of formation water is essential for reservoir characterization. Reservoirs are also characterized by permeability and porosity or pore classification and distribution. Permeability is a measure of the ease of fluid flow through a body of porous material under a standard pressure differential. Porosity is a measure of the reservoir pore volume, distribution, and connectivity. These three parameters generally govern the reservoir productivity.

Drilling could be for conventional oil or natural gas, or water, and could be onshore or offshore. The drilled wells can be on any depth from surface to 6000 m. The drilling process is facilitated using drilling fluids that are recirculated as the drill bit digs through the different formations that could be, for example, sandstone or limestone. To reach different parts of the formation, the wellbore can be drilled vertically or directionally – which is an intentional deviation from vertical all the way to horizontal drilling. During drilling, casings are placed to prevent the well from collapsing and to allow for deeper drilling. The drilling fluids recipes include corrosion inhibitors among other chemical additives. Corrosion inhibitors are added to the drilling fluid formulation to prevent attack of the casing. Well completion is the type of method used to connect the formation with the wellbore that could take different forms like a perforated cemented casing or an open hole.

Water wells, on the other hand, are drilled either to supply water or to inject water into crude oil reservoirs as a mean to increase their pressure and, therefore, to sustain oil production. The first type is called water supply wells, while the latter is called water injection wells. There are also water disposal wells that are used to reinject access water back into the formation.

1.2.1 Causes of Corrosion in Upstream Environments

Upstream production facilities include producing wells, wellhead valve assemblies, flowlines and trunklines, and oil and gas processing facilities. The corrosives encountered in actual production formations include CO_2, H_2S,

polysulfides, organic acids, and elemental sulfur. Oxygen (O_2), if present, is usually introduced into the formation from external sources.

Additional unique parameters encountered in oil and gas production are the extreme temperatures and pressures. In deep gas wells, the temperatures can reach up to 230 °C (450 °F), and the partial pressures of CO_2 and H_2S can reach up to 20.7 MPa (3000 psi) and 48 MPa (7000 psi), respectively. In oil and gas wells, higher water cuts and higher temperatures and pressures would lead to more corrosive conditions. Downhole corrosivity is also a function of the amount of salts (e.g. chlorides) dissolved in the water phase.

Oxygen could be introduced to the production formations by:

(a) Drilling muds, which are used during drilling of wells.
(b) Dense brines, which are sometimes used to fill the annulus between the production tubing and the casing, i.e. casing-tubing-annulus (CTA).
(c) H_2O and CO_2, which are injected to assist oil lifting.
(d) Hydrochloric acid (HCl), which is injected to stimulate the well by enhancing formation permeability.

A common trend in older oil and gas production fields is the extensive use of carbon and low-alloy steels driven by their relatively low cost and availability. Corrosion-resistant alloys (CRAs) have only been recently used and very selectively.

1.2.1.1 Oxygen

In oil production, corrosion attack of internal surfaces by oxygen is very aggressive. Normally, oxygen is not present at depths greater than approximately 100 m (330 ft) below surface. Oxygen contamination is more likely to occur in facilities used for processing and handling of produced oil that operate near-ambient pressure. Oxygen ingress could occur through leaking pump seals, casing and process vents, open hatches, and open handling as in mud pits and during drilling. Oxygen has some unique properties. It is a strong oxidant with relatively fast reduction kinetics according to the following reaction, as an example:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{1.1}$$

Oxygen has low solubility in water and brines, and this explains why the mass transport of oxygen is the rate-limiting step in the corrosion reactions of carbon and low-alloy steels in non-acidic environments. This also explains the localized attacks in crevices and under deposits that are attributed to the limited mass transport in oxygenated systems.

The concentration of dissolved oxygen is between 7 and 8 ppm under ambient equilibrium conditions between air and water. The corresponding corrosion rate at this concentration and under stagnant conditions is about 0.25 mm/yr (10 mpy). Under highly turbulent flow conditions, it could reach as high as 150 mm/yr (600 mpy) assuming continuous oxygen replenishment. By scavenging oxygen to 7–8 ppb, the corrosion rate can be reduced to less than 0.01 mm/yr (0.4 mpy). Formation of the magnetite (Fe_3O_4 or $Fe_3H_2O_4$) corrosion

product film lowers the corrosion rate further by shifting the reaction to become controlled by the following slower anodic step:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1.2}$$

1.2.1.2 Hydrogen Sulfide, Polysulfides, and Sulfur

H_2S is a weak acid, readily soluble in water, and is a source of hydrogen ions. These properties of H_2S favor iron oxidation. Under equilibrium conditions of 1 atm of H_2S and in the absence of buffering ions, the pH of dissolved H_2S in water is 4. Under high H_2S partial pressures, typically in gas formations, pH values of as low as 3 have been estimated. One of the products of H_2S corrosion reactions is the formation of iron sulfide, which promotes entry of atomic hydrogen into steel by slowing down the recombination reaction as per the following series of reactions:

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+ \tag{1.3}$$

$$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+ \tag{1.4}$$

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

$$xFe^{2+} + yS^{2-} \rightarrow Fe_xS_y \tag{1.6}$$

$$H_3O^+ + e^- \rightarrow H^0 + H_2O \tag{1.7}$$

$$H^0 + H^0 \rightarrow H_2 \uparrow \quad \text{(recombination reaction)} \tag{1.8}$$

Absorption of atomic hydrogen could promote hydrogen-induced cracking (HIC), stress-oriented HIC (SOHIC) in low strength steels, and sulfide stress cracking (SSC) of high strength steels, i.e. steels with yield strength greater than 690 MPa (100 ksi).

H_2S reacts with elemental sulfur to form sulfanes according to the following reaction:

$$H_2S + nS^0 \rightarrow H_2S_n \quad \text{(where } n > 2\text{)} \tag{1.9}$$

This occurs in, for example, gas wells with high partial pressures of H_2S, where sulfanes can then flow from the well and could redeposit elemental sulfur as the pressure drops. Similar to H_2S, sulfanes are a free acid form of polysulfides.

Iron sulfide corrosion products have low water solubility and, therefore, precipitate rapidly on the steel surface forming a barrier that shields velocity effects. In the presence of these iron sulfide films, corrosion inhibitors could function satisfactorily even at velocities up to 30 m/s (100 ft/s). Iron sulfide films can be protective or non-protective. At lower temperatures and low H_2S partial pressures, a protective iron sulfide film usually develops. This is normally promoted by the absence of chloride ions and oxygen. At high temperatures and pressures, a less protective iron sulfide film is usually formed, mainly pyrrhotite $FeS_{1.15}$ [5]. In some deep sour gas wells, localized corrosion occurred under pyrrhotite deposits that took the shape of a barnacle. The presence of an iron chloride layer, $FeCl_2$, at

Table 1.1 Differences between CO_2 and H_2S systems.

Parameter	H_2S	CO_2
Solubility in water	Relatively fast	Relatively slow
Velocity effects	Relatively unimportant	Relatively important
Corrosion rates	Low values	High values (~1000s mpy)
Presence of Cl^- ions	Important	Unimportant

the interface between the pyrrhotite and the steel surface promoted iron dissolution by maintaining a localized acid environment.

Because of the shielding effect of the iron sulfide corrosion product films, velocity effects (i.e. high stream velocities tend to strip out corrosion inhibitor molecules adsorbed on the steel surface limiting their applicability; while this velocity effect diminishes in the presence of an iron sulfide corrosion product layer) are usually not encountered in sour systems.

1.2.1.3 Carbon Dioxide

CO_2, like H_2S, is a weak acid. Unlike H_2S, however, CO_2 must hydrate to carbonic acid (H_2CO_3) before it becomes acidic. The hydration reaction of CO_2 to H_2CO_3 is a relatively slow reaction compared with H_2S hydration. Table 1.1 gives some differences between CO_2 and H_2S systems.

Corrosion of steel by hydrated CO_2 leads to deposition of a protective iron carbonate (siderite, $FeCO_3$) scale that reduces the rate of corrosion. The corrosion rates of bare carbon steel exposed to aqueous CO_2 can be calculated using the following equation [3]:

$$\log R = A - \frac{2320}{t + 273} - \frac{5.55\,t}{1000} + 0.67 \log P_{CO_2} \tag{1.10}$$

where

R is the corrosion rate (refer to the Table 1.2 for units)
t is the temperature (°C)
A is a constant (refer to Table 1.2 for values)
P_{CO_2} is the partial pressure of CO_2 (refer to Table 1.2 for units)

Different models that account for the conditions in the field have been developed. Some models were derived based on empirical or semi-empirical assumptions, and others were developed based on mechanistic derivations.

Table 1.2 Values of "*A*" appearing in Eq. (1.10).

R	P_{CO_2}	*A*
mm/yr	atm	7.96
mpy (mils/yr)	psi (pounds/square inch)	8.78

Elevated temperatures favor the formation of protective $FeCO_3$ scale since higher temperatures result in decreased scale solubility, decreased CO_2 solubility, and accelerated precipitation kinetics. Increased pH and non-turbulent environments also contribute to the formation of protective $FeCO_3$ scale. In systems containing both H_2S and CO_2, iron sulfide corrosion products dominate when the H_2S/CO_2 ratio exceeds about 1/200 [5]. Pitting mechanisms are found in O_2- and H_2S-containing systems, while general corrosion occurs in CO_2-containing systems.

1.2.1.4 Strong Acids

Strong acids are pumped into wells for dissolving scales and increasing formation permeability. Normally, HCl (15 and 28 wt%) is used for limestone formations, while addition of hydrofluoric acid (HF, 3 wt%) is necessary for sandstone formations. In situations where corrosion inhibitors are not effective in minimizing attacks by HCl, formic acid (HCOOH, 12 wt%) is used especially in deep sour gas wells. In addition to chemical inhibitors, corrosion control of these strong acid solutions is achieved by limiting exposure time to 2–12 hours.

1.2.1.5 Concentrated Brines

Concentrated brines, also called completion brines, are dense halide solutions used to equilibrate formation pressures during production operations. Examples include halides of calcium, zinc, and magnesium. Concentrated brines can be corrosive due to dissolved oxygen or entrained air. They can also be corrosive due to hydrolysis of metallic ions as shown in the following reaction:

$$Zn^{2+} + H_2O = ZnOH^+ + H^+ \tag{1.11}$$

To avoid exposure to zinc chloride ($ZnCl_2$) brines, calcium bromide ($CaBr_2$) brines with densities above $1.7 \, g/cm^3$ (14 lb/gal) are also used but these are more expensive.

1.2.2 Corrosion Types in Petroleum Production Operations

The main types of corrosion found in petroleum production operations include:

(a) *Stray-current corrosion*: This type of corrosion is usually associated with cathodic protection (CP) systems.
(b) *Under-deposit (Crevice) corrosion*: This is a type of localized corrosion normally associated with the presence of oxygen that can become more intense in the presence of chloride ions. This type of corrosion requires the presence of crevices or surface deposits like sand, sludge, corrosion products, or bacterial slime to develop differential concentration cells characterized by oxygen-rich and oxygen-deficient regions.
(c) *Galvanic corrosion*: This type of corrosion occurs when two dissimilar metals are present where the more active metal becomes the anode and the less active metal becomes the cathode. The situation becomes more aggravated when the cathode-to-anode area ratio is large accelerating the metal dissolution reaction taking place at the anode.

(d) *Microbiologically-influenced corrosion (MIC)*: The most common example of MIC in oil and gas production is the generation of H_2S by sulfate-reducing bacteria (SRB) in an H_2S-free systems. Other types of bacteria also contribute to MIC such as acid-producing bacteria (APB) and iron-oxidizing bacteria (IOB).

(e) *Mechanical and mechanical/corrosive effect*: The list of mechanical and mechanical/corrosive effects includes cavitation, erosion, erosion–corrosion, and corrosion fatigue.

1.2.3 Corrosion Inhibitors for Oil and Gas Production

Methods to control the previously mentioned types of corrosion could involve materials selection, coatings, CP, inhibitors, nonmetallic materials, and environmental control. The discussion in this section will be limited to corrosion inhibition [6]. The most commonly used type of corrosion inhibitor for oil and gas production is the film-forming amine molecules and their salts. These inhibitors allowed production from otherwise highly corrosive primary production oil wells and gas wells and from secondary-recovery wells that use waterflooding.

Important characteristics that must be considered before using a corrosion inhibitor in the field are its pour point, solubility, emulsion tendencies, and performance. Pour point is the lowest temperature at which the inhibitor remains liquid. Filming-amine corrosion inhibitors have the general structure of an organic chain with a polar head and, therefore, are neither completely soluble in hydrocarbons nor in aqueous phases. Different degrees of oil–water emulsions can result specially with corrosion inhibitor batch treatments. Tight-emulsions are difficult to break, which can interrupt the operations of surface equipment. To alleviate this, either the inhibitor is made non-emulsifying or emulsion breakers should be added to the inhibitor package. Before conducting field trials, the performance of the inhibitor should be evaluated in the laboratory where the rotating cage method is commonly used for this purpose.

1.2.3.1 Oil and Gas Wells

Wells in oil and gas production can be categorized into oil wells, gas wells, and water wells. Oil wells produce hydrocarbons, and water and can be further subdivided into naturally flowing wells and artificially lifted wells. Artificial lifting can be achieved using gas-lifting, electric submersible pumps (ESPs), rod-pumps, and hydraulic pumps. Gas wells can produce dry gas or gas-condensate containing liquid hydrocarbons in addition to gaseous hydrocarbons. Water supply wells produce aquifer water that is reinjected into water injection wells for waterflooding or tertiary recovery. Water injection wells are also used for disposal. These types are reflected in the schematic shown in Figure 1.3.

Each well type can be either sweet when dominated by CO_2 or sour when measureable amount of H_2S is present. In addition to CO_2, sweet corrosion can be caused by formic acid (HCOOH), acetic acid (H_3CCOOH), or other short-chain organic acids present in produced gas and/or liquids.

Newer oil and gas wells are drilled at deeper depths where the BHT can reach up to 205 °C (400 °F) and the BHP can exceed 138 MPa (20 000 psi). Generally, the
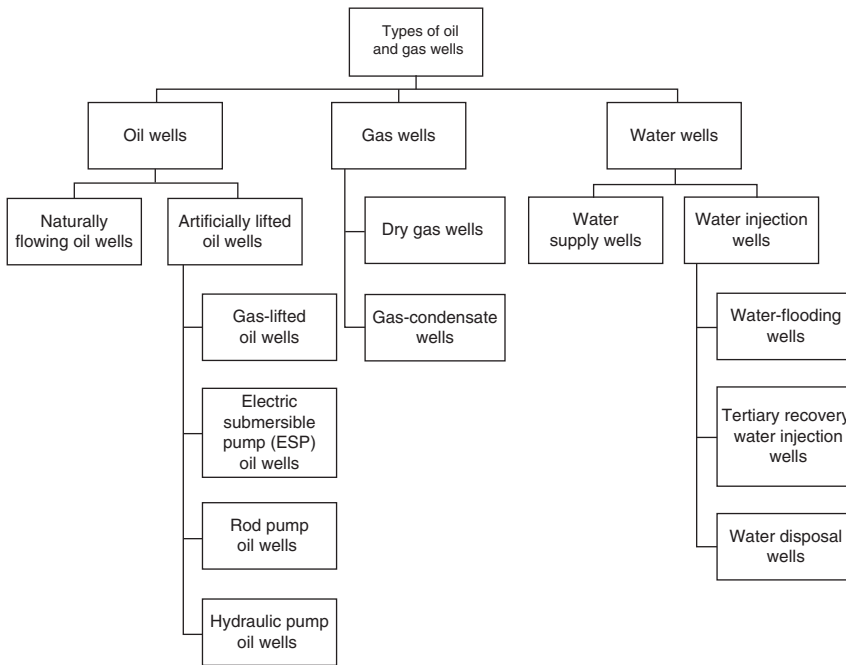
Figure 1.3 Schematic of types of oil and gas wells.

higher the temperature encountered in a well, the more difficult it is to control corrosion. As in regular chemical reactions, corrosion reaction rates generally double for every 10 °C (18 °F) increase in temperature. Higher pressures lead to higher concentrations of dissolved acid gases that increase the corrosivity of the water. Based on field experiences of sweet wells, the following general rules were developed based on CO_2 partial pressures, PP_{CO_2}:

- PP_{CO_2} <48 kPa (7 psi) are considered noncorrosive.
- PP_{CO_2} between 48 and 207 kPa (7 and 30 psi) indicate corrosion.
- PP_{CO_2} >207 kPa (30 psi) usually indicate severe corrosion.

Other factors that influence the corrosivity of produced fluids are water composition and amount, velocity or flow regime, and the presence of solid particles such as sand. The higher the chlorides, the more corrosive is the water. At a certain water percent, oil wells invert from oil continuous phase to a water-wet phase. Depending on velocity and co-existing fluid phases, the flow regime can take different forms such as bubble flow, slug flow, churn flow, and annular flow. Production of fine sand particles can lead to removal of corrosion inhibitor film and erosion depending on velocity. In these cases, sand control to prevent sand from traveling with the produced fluid is necessary. This could be accomplished using sand screens, for example, at the source.

1.2.3.2 Inhibitor Selection
Selection of the correct inhibitor depends on the type of system to be protected whether a pumping oil well, a gas-lift well, a gas well, a water flood system, or

a flow line. For example, if a conventional inhibitor is injected upstream of a gas compressor, the heavier components could deposit and foul the valves of the compressor. Both temperature and pressure should be considered when selecting an inhibitor. Higher temperature and pressure could lead to polymerization and sludge formation. The pressure levels will determine the corrosivity of CO_2 and H_2S. The inhibitor thermal stability should be assessed during the course of corrosion inhibitor evaluation.

Factors that influence inhibitor selection include identifying the problem to be solved, identifying the corrosive species, pressure and temperature, velocity, production composition, water/oil ratio, salinity of water, and acidity of water and oil. Parameters to be considered when evaluating an inhibitor are whether the system is sweet or sour, the service pressure and temperature, water composition and water cut, and the type of corrosion inhibitor treatment, e.g. batch or continuous treatments. Factors that affect the dosage and frequency of treatment include the severity of corrosion, the total amount of produced fluid, the percentage of water, the nature of corrodent, and the type of chemical selected.

1.2.3.3 Practical Challenges with Inhibition

There exist several practical challenges with inhibition, and these are foaming, emulsions, scale removal and plugging, and safety and handling. Foaming could occur in places where the streams containing inhibitors are agitated with a gas. Examples include a gas separator, a counter current stripper, or an aerator. Compatibility of inhibitors with metals should be considered. For example, amine-based inhibitors protect steel but attack copper and brass surfaces. The reduction of nitrate inhibitors produces ammonia (NH_3), which causes stress corrosion cracking (SCC) of metals made of copper and brass. It is, therefore, important to know the metallic components of a system and ensure the compatibility of the inhibitor with each exposed metal.

1.2.3.4 Inhibitor Application Methods

There are two important properties to consider when selecting a corrosion inhibitor application method. First is that the corrosion inhibitor initial concentration must be sufficient to cover the entire exposed surface of the steel structure. The second property is that if portions of the corrosion inhibitor get stripped away, a new film should form spontaneously. The common types of the corrosion inhibitor application methods are batch, continuous, and squeeze treatments:

(a) *Batch treatment*: This can be further subdivided into standard batch, extended batch, annular slug, tubing displacement, and between pigs batch.
(b) *Continuous treatment*: This method is used on producing wells, injection wells, pipelines, and flow lines. For continuous corrosion inhibitor treatment, Table 1.3 gives the general criteria for selecting the treatment dosage.
(c) *Squeeze treatment*: Caution must be exercised when applying this method not to damage or plug the formation.

There are several methods for applying corrosion inhibitors to oil and gas production systems, and each has its advantages and disadvantages. Continuous

Table 1.3 General criteria for selecting treatment dosage.

Corrosion severity	Recommended dosage rate (ppm)^a
Mild corrosion	10–15
Moderate corrosion	15–25
Severe corrosion	>25

a)   These concentrations are based on total produced fluid.

treatment via a capillary treater string – drip feed – is considered an effective corrosion inhibition method. This is most feasible if a capillary tube already exists, since installing a new one is costly. A treater string delivers corrosion inhibitor through a small diameter stainless steel tube that runs in the annulus from the wellhead all the way to the depth of the packer. If the annulus is open to the tubing, then the chemical can be continuously injected into the annulus. This variation of the method is known as slip-stream flushing. The inhibitor concentration should range from 25 to 100 ppm in the produced fluid.

Because organic chemical inhibitors might not condense on the tubing wall until they reach high up on the tubing string, they are not recommended for temperatures above 150 °C (302 °F), which sometimes can be extended to 170 °C (338 °F). For this method, each well requires one injection device that limits its use in unmanned offshore platforms. Water-soluble inhibitors used in continuous injection of water containing systems are typically quaternary amines, amine salts, or salted imidazolines. Chemical scavengers are added to these if oxygen is present. Oil-soluble inhibitors tend to be long-chain primary amines, imidazolines, fatty acids, and phosphate esters.

Other treatment methods should be considered for existing wells without an installed treater string or if the annulus is not open to the tubing. In a squeeze treatment, the corrosion inhibitor is squeezed into the formation and is allowed to flow back. This method has the drawbacks of formation plugging and premature drop in corrosion inhibitor concentration due to chemical losses into the formation. Batch treatment is the third method, which has the drawback of using excessive amounts of the corrosion inhibitor.

An improved version of batch treatment is the tubing displacement method in which a reduced amount of chemical is used compared with the batch treatment. The chemical pill is displaced in the tube to the depth of the packer using dead crude. In terms of performance, the tubing displacement method comes next to the continuous treatment method. Batch treatment inhibitors are usually oil soluble in order to achieve better persistency against water-wetting. Other corrosion inhibitor methods with limited applications make use of artificial lift systems and umbilical. Gumming and valve plugging are common challenges with the use of artificial lift systems.

Dosage for corrosion inhibition of surface facilities, flowlines, and trunklines is typically between 10 and 50 ppm for continuous treatment. Sulfur inhibition is essential to prevent excessive corrosion and to prevent plugging of downstream

facilities. In case of elemental sulfur deposition, dosages as high as 2500 ppm are used for continuous treatment, along with batch treatment to prevent contact of water and sulfur with the internal surface of the pipe wall. Corrosion rates as high as 30 mm/yr (1200 mpy) have been experienced. Batch treatments are implemented to dissolve existing sulfur deposits where high sulfur solubility solvents are used. Examples of these are carbon disulfide (CS_2), di-alkyl-disulfide (DADS), dimethyl-disulfide (DMDS), and aromatic solvents that can dissolve less sulfur but is less expensive and easier to operate.

Waterflooding systems involve water intake units or water supply wells, surface-gathering lines and tanks, water-treating equipment, surface water pumps and transport lines, and downhole tubing of water injection wells. The primary causes of corrosion in these facilities are oxygen contamination and acid gases. As discussed before, oxygen can be removed by mechanical means and using oxygen scavengers. If these two methods are not applicable due to small amount of water, for example, then oxygen corrosion inhibitors can be used. A zinc amino methyl phosphonate and an organic sulfophosphate corrosion inhibitors are available for produced water handling systems. Of the acid gases, H_2S is found to be more problematic than CO_2 in water handling systems. Iron sulfide corrosion products can lead to scaling issues in water supply wells and to deposition and under-deposit corrosion in surface lines. Iron sulfide solids could lead to plugging of water injection wells and to difficulties in the oil–water separation process.

A sweet system could become sour due to the action of the SRB that reduces sulfate (SO_4^{2-}) to H_2S. An ideal temperature for SRB growth is $40 \pm 6\,°C$ ($100 \pm 10\,°F$). Maintaining a non-static and clean system and injecting bactericides are common methods used to control MIC. For cleaning surface lines, scrapers are used, which require provisions in the design and construction for scraper launchers and receivers. Many of the bactericides are surface-active cationic materials that restrict its use with other chemicals. Scale inhibitors, for example, are anionic chemicals, and therefore the two types of chemicals should be used with care if mixed together. Corrosion monitoring and inspection are an integral and critical parts of any effective corrosion control program.

1.2.3.5 Oxygen Removal

Oxygen is one of the main causes of corrosion in oilfield water. The presence of dissolved oxygen significantly reduces the inhibition effectiveness of film-forming corrosion inhibitors. Both mechanical and chemical means can be used to remove dissolved oxygen. In the mechanical means, oxygen is removed physically by employing, for example, counter-current gas stripping or vacuum de-aeration. In the chemical means oxygen is removed by reacting with scavengers. Common oxygen scavengers include:

- *Sodium sulfite*:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \tag{1.12}$$

- *Ammonium bisulfite*:

$$2NH_4HSO_3 + O_2 \rightarrow (NH_4)_2SO_4 + H_2SO_4 \tag{1.13}$$

- *Sulfur dioxide*:

$$SO_2 + H_2O + \tfrac{1}{2}\,O_2 \rightarrow H_2SO_4 \qquad (1.14)$$

Mechanical means are used to remove large quantities of dissolved oxygen, while chemical scavenging becomes practical when small quantities of oxygen exist. Both methods could be coupled to ensure complete removal of dissolved oxygen. One important feature of oxygen is its solubility in hydrocarbons that is 5–25 times higher than its solubility in oilfield waters. It is, however, more economical to exclude oxygen than to remove it. This can be achieved by using gas blankets on water supply wells and water storage tanks and by continuously maintaining the integrity of valve stems and pump packing.

1.2.4 Problems Encountered and Protective Measures

1.2.4.1 Drilling Fluid Corrosion

1.2.4.1.1 Causes of Corrosion The main environmental causes of corrosion in drilling fluids are O_2, CO_2, H_2S, dissolved salts (ionic strength), temperature, and low pH. The physical conditions include metal composition, metal properties, string design, and stress. Combined physiochemical accelerators include stress corrosion and erosion–corrosion. Micro-organisms also cause corrosion in drilling environments.

The major forms of attack are:

- Under-deposit (crevice) corrosion
- Corrosion fatigue
- SCC
- Erosion–corrosion (abrasion)
- Uniform attack
- Galvanic corrosion

Corrosion rates of 0.5–2 lb/(ft^2 yr) (2.4–9.8 kg/(m^2 yr)) with no pitting are considered acceptable for drill pipes.

1.2.4.1.2 Oxygen Corrosion Control To control oxygen in drill muds, 10 mg/l sulfite ion should be added continuously for each 1 mg/l of oxygen. A residual sulfite concentration of 100 mg/l should continuously be maintained in the drilling fluid. Interfering side reactions that prevent the oxygen–sulfite reaction should be prohibited. Filming inhibitors typically used during drilling becomes less effective in the presence of oxygen.

1.2.4.1.3 H_2S Corrosion Control H_2S causes two forms of corrosion by attacking the surface, and these are under-deposit (crevice) corrosion and SSC. Methods to control these attacks include selecting resistant materials, removing H_2S using chemical scavengers, and reducing stress. Sources of H_2S could be indigenous like from the formation itself or generated by thermal degradation of mud products or SRB. H_2S could also be introduced through make-up water.

Film-forming amine-type inhibitors are recommended for the drill string to provide protection from hydrogen embrittlement. To minimize corrosion fatigue and hydrogen embrittlement of the drill pipe, oil-soluble filming inhibitors can be applied directly on the drill pipe. Cationic filming inhibitors should be used with care since they can flocculate the anionic clays in drilling systems, therefore damaging the mud properties. SSC of the drill pipe is controlled by selecting materials with acceptable hardness and yield strength and by controlling the drilling fluid. The likelihood of SSC is reduced if the temperature is above 80 °C (175 °F).

1.2.4.1.4 *CO$_2$ Corrosion Control* CO_2 causes selective corrosion mainly by an under-deposit electrochemical cell action. Corrosion control of CO_2 is similar to H_2S through applying oil-soluble, film-forming corrosion inhibitors that can be applied by spraying the outside of the drill pipe and batch treatments for the internal surfaces to penetrate deposits and reach the under-laying pits.

1.2.4.1.5 *Scale and Deposit Control* Conditions that lead to under-deposit pitting attack of exposed metal are mainly mineral scale, corrosion by-products, and mud. Scale inhibition is an effective mean to prevent and remove these deposits. Examples of effective scale inhibitors include organic phosphonate, phosphate esters, acrylic, acrylamide, and maleic acid. For corrosion protection, high treatment levels, up to 1000 mg/l, are used. Because of the inhibitors dispersing properties, these high levels may alter mud properties, and, therefore, the proposed recipe should be evaluated before applying.

1.2.4.2 Primary Production

There are two types of oil producing wells, and these are flowing wells and artificial lift wells. Artificial lift wells can be further subdivided into wells that use downhole hydraulic pumps, gas-lift wells, and rod-pumped wells.

1.2.4.2.1 *Artificial Lift Wells*

Downhole Hydraulic Pumps For these types of wells, the pumps operate by pumping clean crude oil using a surface pump in a string of tubing to operate a downhole hydraulic pump. Corrosion control is achieved using CRAs and chemical inhibition that include corrosion and scale inhibitors and demulsifiers.

Gas-Lift Wells In gas-lift wells, a pressurized gas (nitrogen for example) is injected into the annulus and through a gas-lift valve into the tubing. The drop in density allows the oil to flow by the reservoir pressure. CRAs are usually used for the gas-lift valves, while corrosion inhibitors are used to protect the tubing. The corrosion inhibitors are added at the surface to the gas-lift stream, which would protect the tubing surface above the gas-lift valve. If the tubing surface below the valve experiences corrosion, then corrosion inhibitors can be injected using either batch or squeeze treatments. The inhibitor selected for this type of application is usually oil-soluble and water-dispersible.

Rod-Pumped Wells Corrosion in rod-pumped wells can be caused by several mechanisms. Galvanic corrosion could develop between dissimilar metals or by differences in metallurgy due to cold working. Pitting could occur due to artificially induced stress raisers during pumping operations, e.g. corrosion attack could result from stray current leaking from surface equipment or from a CP system. Oxygen corrosion could occur on rods stored outdoor or from oxygen entry into the wellbore through the annulus. Oxygen corrosion commonly takes place in the lower part of the well that includes the casing, the pump, the tubing, and the lower part of the rod string. Because the oxygen gets depleted by corrosion reactions, the upper part of the well experiences less attack by oxygen. Under-deposit corrosion could develop when the rods are in the hole.

CO_2 corrosion is aggravated by the presence of oxygen and organic acids. Organic acids aggravate CO_2 corrosion by dissolution of the protective iron carbonate scale. H_2S corrosion could lead to metal loss and pitting. The presence of oxygen would increase the corrosion rate and could form elemental sulfur from reacting with iron sulfide. The presence of organic acids would increase corrosion by dissolving the iron sulfide scale and by lowering the pH (<6). The bottom of the pit could be a stress raiser and could lead to cracking. SSC occurs in the presence of H_2S. SSC initiates and propagate at the grain boundaries. Mechanical damage could also develop by rod-to-tubing abrasion that could also lead to galling, i.e. removal of large portions of metal. The flow velocities in pumped wells are usually not high enough to influence corrosion. However, high velocities are experienced at flow-restricted areas that could lead to increased corrosion rates.

In addition to coating, control of rod corrosion can be achieved by ensuring sound mechanical operation and by employing an effective corrosion inhibition program. There are several methods of corrosion inhibitor treatment of a well, and these are batch, continuous, squeeze, tubing displacement, weighted inhibitors, and use of sticks or encapsulated inhibitors.

1.2.4.2.2 Flowing Wells In flowing wells, the velocities and pressures are higher than in artificial lift wells. Typical example is gas condensate wells that may produce gas, hydrocarbons, formation water, acid gases (CO_2 and H_2S), and organic acids. Corrosion in this case is a function of the amount of produced formation or condensed water, the CO_2 and H_2S concentrations in water, and the amount of dissolved oxygen that would not be present in the production stream unless artificially introduced. Corrosion damage mechanisms in these wells are associated with CO_2, H_2S, and O_2.

Corrosion by CO_2 can cause severe pitting and the presence of organic acids can increase the corrosion rate. Corrosion by H_2S can lead to metal loss, pitting, hydrogen embrittlement, and SSC. Oxygen, if present, will cause pitting of ferritic stainless steels. Most gas wells are completed with low-alloy steels coupled with coatings and corrosion inhibition. Wireline operations could damage the protective film, and therefore corrosion inhibition should be applied afterward. Important characteristics when selecting an inhibitor are low inhibited corrosion

and pitting rates. Other important characteristics are strong film persistency, should be non-damaging to producing formation when squeezed, and should lead to minimal system upsets that could result from emulsion stabilization caused by the added corrosion inhibitor. Corrosion inhibitor treatment methods of the flowing well include tubing displacement, which is a variation of batch treatment, continuous injection, and squeezing.

1.2.4.2.3 Monitoring Monitoring is essential to evaluate the corrosivity level of the streams both before and after treatments. Common methods used for corrosion monitoring are iron count analysis, corrosion coupons, electrical resistance probes, linear polarization instruments, a side-stream test loop, and caliper surveys. A recommended industry practice was developed for preparing, installing, and interpreting coupons, namely, NACE SP0775 [7]. Other corrosion monitoring methods include hydrogen probes, galvanic probes, electromagnetic logging devices, and chemical analysis of produced water for alloying metals such as manganese and chromium. Moreover, collection of field data is a valuable source of information that should include record of failure data.

1.2.4.3 Corrosion in Secondary Recovery Operations

Secondary recovery is also referred to as waterflooding where water generally exacerbates corrosion problems. The facilities in secondary recovery operations consist of producing wells, producing flowline, separation facilities, tanks, injection pumps, injection lines, and injection/disposal wells.

1.2.4.3.1 Types of Corrosion Problems

Producing Wells Dissolved acid gases (H_2S and CO_2) are the main cause of corrosion in producing wells. The presence of organic acids can exacerbate H_2S and CO_2 corrosion. The increased amount of water due to waterflooding will also increase corrosion. The water cut may increase to 90% or more. During waterflooding, sweet fields containing only CO_2 might become sour due to H_2S generation by SRB growing in the formation. Corrosion problems related to H_2S could develop such as pitting under SRB deposits and SSC of high-strength materials. If different sources of water are used, deposition of mineral scales such as $CaCO_3$, $CaSO_4$, or $BaSO_4$, may increase. These could cause wear and under-deposit corrosion.

Producing Flowlines Corrosion in flowlines usually occur at the bottom of the line if flow rates are low enough to allow water drop-out that would make the bottom of the flowline continuously water-wet. Severe pitting is often observed under sludge or scale deposits that accumulate in flowlines under these conditions.

Oil/Water Separation Facilities Separation facilities normally utilize heat to aid in the oil/water separation process. Scale deposition would reduce the heat transfer in these facilities, which could lead to severe under-deposit corrosion due to increased localized temperatures. In direct fired heaters, creep rupture type of failure can occur if spots under deposited scale reach high temperatures. If the separation equipment is open to the atmosphere, oxygen ingress can cause increased corrosion in the water phase.

Tanks/Water Storage   Acid gases (CO_2 and H_2S) carried over with produced water cause corrosion in the water storage tanks. Under-deposit corrosion is a serious issue under accumulated sludge in tank bottoms. These areas also favor SRB growth. Tank roofs if not properly protected can fail because of condensation. As water condenses on the roof, it will absorb corrosive gases that will lead to pitting attack of the tank roof. In addition to acid gases, oxygen entry will increase their rate of attack dramatically.

Injection Pumps   In addition to normal corrosion mechanisms, pumps can fail by cavitation and erosion. If 304 and 316 stainless steels are used, they could fail by chloride SCC in produced brines if temperatures are above 52–65 °C (125–150 °F). Pumps are subjected to cyclic stresses that could lead to fatigue failures at spots of increased stress concentrations like grooves and pitted areas.

Injection Flowlines and Wells   The corrosion mechanisms are basically the same as for producing wells tubulars and flowlines, namely, H_2S, CO_2, and organic acids corrosion. Under-deposit corrosion in the bottom of the lines and corrosion under scale and under SRB colonies can occur. Oxygen contamination will significantly increase corrosion except for SRB, which are basically anaerobic. Corrosion can still occur in areas of restricted oxygen entry like under scales and sludge. Aerobic bacteria slime can become anaerobic, which can then support SRB growth.

1.2.4.3.2   *Corrosion Mitigation Methods*

Producing Wells   Corrosion control methods for primary and secondary recoveries are similar. The production methods used can be beam lift, ESP, or gas lift. The selected corrosion control method will depend on the type of production method, well design, and economics. In all types of producing wells, corrosion inhibitors are used to protect tubulars and other downhole equipment.

Corrosion methods used to inject corrosion inhibitors downhole are squeeze treatment, batch treatment, and continuous treatment. An effective corrosion inhibitor should be selected for the targeted environment whether CO_2 dominated, H_2S dominated, or both. Laboratory tests should be performed to aid in the selection process. A corrosion inhibitor package can be formulated to be oil-soluble, oil-insoluble, water-dispersible, water-soluble, etc. Tests should be performed to make sure that the corrosion inhibitor will not produce stable emulsions. Tests in this case should be performed using actual well fluids. The inhibitor dosage and the frequency of treatment are usually increased during secondary treatment.

The treatment should be adjusted based on corrosion monitoring data. The most common mean of monitoring is by installing corrosion coupons in the flowlines close to the wellhead. Downhole corrosion monitoring has been difficult. Short sucker rods and short joints to production tubing can be used for downhole corrosion monitoring. NACE SP0775 [7] provides information on the preparation, installation, and evaluation of corrosion coupon data. Downhole equipment should be inspected for corrosion that is considered a valuable source of information. Corrosion inhibitors become less effective where wear takes place as in rod

pumps, for example. NACE MR0176 [8] provides guidelines for selecting pump materials.

ESP wells and rod-pumped wells are usually treated in the same way. Because of the ESP configuration, inhibitors placed in the annulus cannot reach pump parts in the production zone above the fluid intake, e.g. the motor housing. Other means of corrosion protection should be employed for these parts. Continuous corrosion inhibitor treatment using small diameter tubing (capillary) to inject the inhibitor below the housing can be used. CRAs are used for parts of the pump that cannot be reached by the corrosion inhibitor. Coatings can be used on production tube internals since ESPs do not cause wear.

Gas-lift wells are usually treated by atomizing a corrosion inhibitor solution into the gas stream. This will provide protection only above the valve used to inject the lift gas. Other means should be used to protect regions below the injection valve.

Producing Flowlines   Corrosion inhibitor carried-over from downhole is usually sufficient to provide protection for the flowlines close to the wellhead. Additional protection can be obtained through batch or continuous treatments.

Oil/Water Separation Facilities   To protect these facilities, supplemental corrosion inhibitor injection is used. In addition to corrosion inhibitors, coatings and CP are used. Removal of scale and debris should be done periodically specially from locations with heat transfer surfaces. Higher grade alloys are used where under-deposit corrosion is a problem.

Tanks/Water Storage   Tanks can be protected using internal coatings, CP, and/or non-metallic liners. Tanks should be cleaned regularly to remove accumulated sludge and debris that are precursors for under-deposit corrosion and SRB problems. Tanks are considered the first source of oxygen contamination in injection systems. Usually inert gas blanketing is used to exclude oxygen.

Injection Pumps   Corrosion of injection pumps and ancillary equipment is prevented using CRAs. To prevent pitting of these equipment, it is recommended to flush them regularly with deaerated and inhibited fresh water.

Flowlines and Injection Wells   Corrosion management of flowlines and injection wells is usually accomplished using corrosion inhibitors injected on a continuous basis. Corrosion damage mechanisms observed in these facilities include CO_2 and H_2S attacks, MIC, oxygen ingress, and scale and sludge deposition. The types of corrosion inhibitors selected for these applications can be oil-soluble/water-dispersible, or water-soluble chemicals. Internal coatings and nonmetallic linings are also used.

Injection well tubulars can be both bare steel or internally coated coupled with corrosion inhibition. Nonmetallic liners or tubulars, such as fiber-reinforced plastic (FRP), have been used in several locations. High cost is preventing use of CRAs. To stimulate water injection wells after a drop in their injectivity, inhibited solutions of strong acids are used. This include 15 wt% HCl for limestone formations and 12 wt% HCl with 3 wt% HF for sandstone formations. Laboratory

evaluation of the formulated acid recipe is performed to ensure that the resulting corrosion rate of steel test specimens is less than 245 g/m^2 (0.05 lb/ft^2).

1.2.5 CO_2 Injection

Following primary and secondary recovery options of crude oil using, respectively, assisted-lifting and waterflooding, tertiary recovery is possible by injecting CO_2. Injecting CO_2 gas requires less pressure than other gases, and it readily dissolves in oil resulting in up to 10-fold reduction in the viscosity of heavy crudes. Before use, collected CO_2 is purified and compressed, and in some cases transported in pipelines to the point of injection. Handling CO_2 would, however, lead to attack of carbon steel materials and dissolution and transport of scales. The dissolved scales may redeposit in surface equipment. A CO_2 overall production facility consists of a CO_2 source well, a wellstream heater and contactor to remove water, scrubber, compressor, and transportation pipeline.

   To protect the tubing and wellhead of a CO_2 source well from corrosion, continuous downhole injection of water-soluble filming amine inhibitors is used. Alternatively, these wells could be completed with 316L and 304L stainless steels, or FRP. Dehydration of the steam is performed to prevent corrosion and hydrate formation at low temperatures. Water and CO_2 could be injected using the same system. In the case of CO_2 injection, the water content should be kept below 50 ppm to keep corrosion to the minimum. For water lines, cement lining, and corrosion inhibition are used to mitigate corrosion. Corrosion control of the tubing materials for the oil producing wells could be achieved using internal coatings and/or inhibition or by using 9Cr–1Mo and 13%Cr steels. For corrosion monitoring of producing wells, the linear polarization technique could be used along with weight-loss coupons, iron counts, and caliber surveys.

1.2.6   Corrosion of Oil and Gas Offshore Production Platforms

Offshore drilling and production platforms could reach to water depths of more than 305 m (1000 ft). Platform corrosion can be divided into four zones: soil, seawater, splash zone, and marine atmosphere. Severe corrosion is usually found in the splash zone, which is controlled using coating or sheathing with Monel alloy. Factors that contribute to seawater corrosivity are salinity, temperature, oxygen content, velocity, conductivity, and biofouling.

   Atmospheric corrosion can be minimized using coatings. Coatings and CP are used to control corrosion of the steel structures immersed in seawater. CP normally extends to protect the piles in the mud. CP is also effective in eliminating corrosion fatigue resulting from cyclic stresses due to environmental factors. Regular inspection of the platform is essential to ensure both structural integrity and personnel safety.

1.2.7   Corrosion of Gathering Systems and Tanks

Gathering systems cover all production facilities from the wellhead choke valve to the sales point of oil and/or gas. These include flowlines and trunklines, separation, dehydration, and gas processing. The scope of this discussion will be

limited to internal corrosion of gas and oil systems, which is a function of composition of produced fluids, temperature, pressure, and flow regime. A gas stream is considered sour if the partial pressure of H_2S is greater than 0.34 kPa (0.05 psia); otherwise it is sweet. In a sweet system, CO_2 corrosion mechanisms are assumed to predominate, which are usually more severe than H_2S corrosion at lower temperatures.

1.2.7.1 Sweet Gas Corrosion

Several solutions can be used to mitigate sweet gas corrosion. For flowlines, low-alloy steel with corrosion allowance or internal coatings can be used. CRAs such as 316 or duplex stainless steels can also be used. These materials, however, require attention toward chloride SCC at elevated temperatures. Application of CRA liners is also commonly used. In case downhole tubulars of gas wells are protected using corrosion inhibitors, then the inhibition effect will extend to flowlines. Turbulent flow and mixing and lower temperatures at the flowlines will ensure effective inhibition. The corrosion inhibitor can be injected at the surface as well. Batch treatments are required when the flow velocity is low and continuous injection may be required when the velocity is high.

1.2.7.2 Sour Gas Corrosion

Materials in sour gas services must be resistant to SSC. At temperatures normally encountered in flowlines, sour corrosion rates are normally lower than sweet corrosion rates. Moreover, sour corrosion is not flow-dependent when protective iron sulfide films are formed. An acceptable corrosion rate is anticipated when:

(a) The hydrocarbon liquids are above 100 barrels per 28 300 m³ (1 MSCF) of gas.
(b) The water content of the liquid phase is less than 10 vol%.
(c) The flow is turbulent, which will ensure water entrainment in the hydrocarbon phase.

Corrosion inhibition might be necessary in streams where the mentioned criteria is not satisfied. The logic discussed for protection of flowlines and facilities handling sweet gas is also applicable for sour gas streams.

1.2.7.3 Oil Wells Corrosion

Most crude oil wells contain H_2S that in addition to oil makes corrosion control easier than in gas systems containing CO_2 only. Corrosion becomes an issue when the water cuts exceed 30 vol%. Inhibition of downhole equipment, however, should provide sufficient inhibition for flowlines. If the oil velocity is low allowing water to drop-out in the flowlines then other means of corrosion control should be implemented. This includes pigging to remove settled water and deposits and to distribute the corrosion inhibitor over the entire internal surface of the flowline. Usually low-carbon steel is used for the construction of gas–oil separation plants (GOSP) and free water knockout systems. Mainly CP is used for corrosion control of saltwater handling facilities. Internal organic coatings are also used if temperature permits. For large tanks, galvanizing is used.

1.3   Corrosion in Midstream Sector

The midstream sector includes gas plants, liquefied natural gas (LNG) production and regasification, and oil and gas pipeline transport systems. Gas plants separate hydrocarbons and fluids from the pure natural gas to produce "pipeline quality" dry natural gas. Natural gas associated with crude oil consists of mixtures of hydrocarbons such as ethane, propane, butane, and pentanes, which are known as "natural gas liquids." NGL is used as feedstock for oil refineries or petrochemical plants and as sources of energy. Non-associated natural gas, on the other hand, contains water vapor, H_2S, CO_2, helium, nitrogen, and other compounds.

If the gas has sufficient pressure, then it is fed directly into the pipeline network or recompressed if pressure is lost during separation. Gas turbines are used to operate compressors used to compress and pump the natural gas through the pipeline. Compression includes other supporting equipment such as scrubbers (to remove liquid droplets) and heat exchangers. LNG liquefaction and regasification facilities handle light-end hydrocarbons, mainly methane, which cannot be compressed to liquid state at ambient temperatures. Natural gas is transported over long distances by liquefying it at $-162\,°C\,(-260\,°F)$ using one or more cooling stages. LNG is transported using special insulated tank carriers and at the receiving end, a regasification terminal heats the LNG for pipeline distribution. For separation and dehydration facilities processing inhibited sweet streams, low-alloy steel with corrosion allowance is usually sufficient. If this is not sufficient, then use of 316 stainless steels materials or cladding might be required. Low-alloy steel with corrosion allowance is used in the construction of sour gas processing facilities, separators, and sweeting systems.

The main component of the midstream sector is pipelines [9–11], which provide a very convenient mean of transporting gases and liquids over long distances. Worldwide, pipelines networks cover very long distances that exceed 3.5×10^6 km. In Canada alone, the pipeline inventory is more than 800 000 km consisting of gathering lines, feeder lines, transmission lines, and distribution lines. These types are explained schematically in Figure 1.4.

Pipeline systems transport crude oil, multiphase fluids, condensate, liquid petroleum products, NGL, oilfield water, oilfield steam, liquid or dense phase CO_2, and gas. Multiphase fluids consist of oil, gas, and water, which are in liquid and/or vapor forms in different combinations produced from one or more oil wells or recombined from oil wells fluids. A pipeline system consists of pipelines, pump stations, and other facilities required for the measurement, processing, storage, gathering, transportation, and distribution of oil or gas industry fluids. The pipe components include the pipe itself, fittings, flanges, valves, bolting, and gaskets. Joining of pipes, components, and non-pressure-retaining attachments to piping is performed using arc welding, gas welding, and mechanical methods. Pipelines sizes range from 6 to 48 in. (15–120 cm) in diameter.

New pipelines are pressure tested after installation and before operation using either gas or liquid. In case of liquid, the medium or the complete piping should be treated to protect against corrosion and other types of damage. Corrosion inhibitor, biocide, and oxygen scavenger can be added if water is used as the test
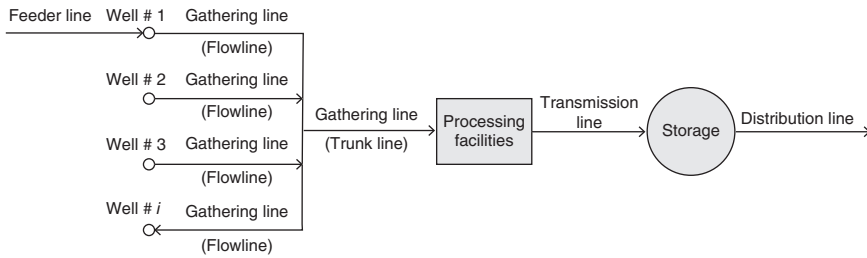
Figure 1.4 Gathering line, feeder line, transmission line, and distribution line represented schematically.

medium. A pressure-testing plan is developed and implemented for each pressure test. Pipelines can be offshore or onshore, and onshore pipelines can be exposed to the atmosphere or buried. Pipelines may be attacked by either external or internal corrosion or both. Buried transmission and distribution pipelines are protected from external corrosion mainly by the use of a suitable dielectric coating combined with CP or by the use of CRAs. Protective coating systems and CP are also used for submerged piping. Coatings and CP systems are inspected during and after installation and are inspected and maintained regularly thereafter.

A pipeline is susceptible to internal corrosion if it contains a corrosive gas phase with water dew point above the pipeline operating temperature or if it contains a liquid phase with free water alone or combined with other corrodents such as O_2, H_2S, CO_2, suspended or dissolved solids, and bacteria. Methods to control internal pipeline corrosion include:

- Removal of water by scraping or pigging.
- Treatment of residual water or dehydration.
- Injection of environmentally acceptable corrosion inhibitors and biocides.
- Removal of dissolved gases by chemical or mechanical means.
- Gas blanketing.
- Internal coating or lining.
- Design considerations.

Corrosion/erosion allowance is added during the design stage to the pipeline wall thickness that is calculated based on the targeted service conditions for pressure containment. To ensure the effectiveness of the applied corrosion control methods, monitoring techniques are used and these could include:

- Monitoring of physical and chemical operating conditions.
- Corrosion monitoring devices such as weight-loss coupons, corrosion probes, and hydrogen probes.
- Non-destructive inspection such as ultrasonic thickness measurements.
- Visual inspection of the internal surfaces of sections cut from the failed pipe.
- Internal electronic inspection equipment.

Detailed records of internal and external corrosion control programs are maintained including failures and corrective actions. Examples of conditions that could impact the integrity of existing pipelines systems include mechanical

damage, manufacturing defects, corrosion and SCC, and coating damage or deterioration.

One of the most serious issues with hydrocarbon-containing pipeline systems is leaking and leak detection. Leaking of hydrocarbon fluids has major safety, environmental, and financial consequences. Leak-detection surveys and analyses are performed regularly. In case of service modifications or piping pressure re-rating, pressure-testing should be repeated before the line is put back to service. The preceding discussion applies to low-temperature pipelines that operate in the range of metal temperatures from −70 °C (−94 °F) to 230 °C (446 °F).

High-temperature pipelines operate at metal temperatures exceeding 230 °C (446 °F) that include steam distribution pipelines. High-temperature pipelines are susceptible to external corrosion under insulation and internal corrosion/erosion mechanisms such as caustic embrittlement and oxygen pitting.

1.3.1 Control of Internal Corrosion in Carbon Steel Oil Pipeline Systems

Worldwide, the majority of pipelines are constructed of carbon steel materials. This section addresses carbon steel pipelines used for transporting oil, natural gas, and water for sweet and sour services [10]. The primary corrosion mechanism leading to failures in these pipelines is pitting corrosion along the bottom of the line. The most common contributing factors to these failures are water holdup, CO_2, H_2S, bacteria, velocity, solids deposition, and oxygen ingress. Both batch and continuous chemical inhibitor treatments are widely used to control corrosion caused by most of these factors.

To ensure the effectiveness of these treatments, several corrosion monitoring and inspection techniques are employed. Common direct and indirect corrosion monitoring techniques include:

- Gas (H_2S and CO_2) and oil analysis.
- Water analysis-complete geochemical analysis.
- Production monitoring, e.g. pressure, temperature, flow rates, and water cut.
- Corrosion coupons.
- Bio-spools.
- Electrochemical monitoring, e.g. electrochemical noise, linear polarization, and electric resistance.

For inspection, magnetic flux leakage (MFL) is the most common inline inspection technique. Other techniques include:

- Non-destructive examination (NDE) using ultrasonic inspection and radiography.
- Visual inspection using video camera and borescopes.
- Destructive examination of sections cut out form the pipeline.

The repair and rehabilitation techniques include:

- Pipe section replacements.
- Installing repair sleeves.

- Installing thermoplastic liners.
- Replacement with composite or plastic pipeline.
- In-kind replacement of the entire pipeline.

1.3.2 Control of Internal Corrosion in Carbon Steel Gas Pipeline Systems

The emphasis in this section is on carbon steel pipelines transporting gas where internal corrosion is the main contributing factor leading to failures and leaks [11]. The primary corrosion mechanism leading to failures in these pipelines is pitting corrosion along the bottom of the line or at the water–gas interface. Other less common corrosion mechanisms are top-of-the-line corrosion (also known as vapor-phase corrosion), SSC, and HIC. Standard test methods and materials requirements have been developed for SSC and HIC [12–14]. The most common contributing factors to internal corrosion in gas pipelines are H_2S, CO_2, oxygen ingress, bacteria, water holdup, chlorides, solids deposition, methanol, polysulfides, elemental sulfur, and the critical gas velocity.

Both batch and continuous corrosion inhibitor chemical treatments are employed, which require application on a clean pipeline surface for effective adsorption. To ensure an effective treatment, the same corrosion monitoring techniques highlighted in Section 1.3.1 are applicable here too. Analysis of chloride levels in water samples gives insight into tendency toward localized corrosion. The use of hydrogen probes in gas lines is important to monitor for hydrogen-related damages. For inspection, repair, and rehabilitation, the same techniques mentioned in Section 1.3.1 can be used here as well.

1.3.3 Control of Internal Corrosion in Carbon Steel Water Pipeline Systems

This section discusses carbon steel pipelines handling water where, similar to oil and gas, internal corrosion is the primary cause of pipeline failures and leaks [15]. Carbon steel water pipelines convey fresh or produced water. The types of transported water include fresh source water (also known as aquifer water), produced water for waterflooding, disposal water, or steam condensate. Similar to oil and gas, pitting is the main corrosion mechanism leading to failures of uncoated carbon steel pipelines. Pitting usually takes place along the bottom of the line and to a lesser extent at other circumferential positions. Common features in these water services are:

- Presence of water that contains corrodents such as O_2, $CO_2(aq)$, $H_2S(aq)$, bacteria, chlorides, scale, or solids.
- Low or intermittent flow where water and deposits can accumulate.

Other types of failures can be attributed to poor coating systems and linings or joining systems. In these situations, corrosion attack can be aggravated due to the partially exposed steel surfaces that lead to a large cathodic to anodic area ratio accelerating anodic dissolution. The most common contributing factors to internal corrosion in water pipelines are oxygen ingress and contamination, $CO_2(aq)$,

$H_2S(aq)$, microorganisms, scale formation, and solid accumulation. Both batch and continuous corrosion inhibitor chemical treatments can be employed where batch treatment can be more effective for better adsorption on the pipeline steel surface. Similar techniques discussed in the previous Section 1.3.1 can be employed for corrosion monitoring, for corrosion inspection, and for repair and rehabilitation.

1.3.4 Chemical Inhibition of Internal Corrosion in Carbon Steel Pipeline Systems

Pipelines constructed from carbon steel are usually the lowest life-cycle cost option for hydrocarbon services consisting of any combination of the following phases: oil, gas, condensate, and water. Chemical inhibition is integrated into the corrosion control program for carbon steel pipelines based on the calculated corrosion allowance. The first step is to determine the uninhibited corrosion rate under actual field conditions either based on available data from similar fields or by conducting laboratory tests and corrosion modeling. Maintaining a database of existing field and laboratory data is a common practice that becomes beneficial when designing new pipeline systems.

Corrosion models have application limits that should be reviewed before performing corrosion rate calculations. The application limits could include parameters such as ranges of allowed partial pressures of acid gases, temperature range, pressure range, types of production fluids, CO_2/H_2S ratio assumptions, and corrosion mechanisms. To facilitate managing large pipeline network, pipelines are grouped into similar corrosion circuits based on the prevailing type of service. For each corrosion circuit, failure modes are assigned along with required corrosion control options and recommended corrosion monitoring and inspection techniques. The next step is to select a target inhibited corrosion rate that also depends on inhibitor system availability and the required corrosion allowance. The recommended inhibited corrosion rate values based on temperature ranges of new designs and inhibitor testing programs are [16]:

- For temperature ranges up to 70 °C (104 °F), the inhibited corrosion rate should be less than or equal to 0.05 mm/yr (2 mpy).
- For temperature ranges >70 °C (104 °F) and ≤120 °C (248 °F), the inhibited corrosion rate should be less than or equal to 0.1 mm/yr (4 mpy).
- For temperature ranges >120 °C (248 °F) and ≤150 °C (302 °F), the inhibited corrosion rate should be less than or equal to 0.2 mm/yr (8 mpy).
- For temperature ranges above 150 °C (302 °F), the inhibited corrosion rate would depend on the results of the laboratory testing program.

The next step is to conduct laboratory assessments of the proposed corrosion inhibitors that could be required due to any of the following reasons:

- To determine the corrosion inhibition efficiency of candidate chemicals and rank them based on their performance.
- To study the impact of the service water on the inhibitor performance.
- To assess the effect of velocity on the inhibitor performance since inhibitors are normally applicable to velocities up to 20 m/s (approximately 66 ft/s).

- To determine if the oil in the field has natural inhibition effects.
- To study the effect of corrosion product film formation on inhibition.

   The inhibitor selection program should include the following tasks:

- Determining limits of the service operating window to select representative inhibitor test conditions.
- Identifying the required corrosion inhibitor application method(s), i.e. batch, continuous, squeeze, or a combination.
- Developing an acceptance criteria for the tested inhibitors that could include:
   - Absence of localized corrosion attacks especially at the pipeline welds that may require obtaining test samples from the actual pipeline.
   - An inhibited general corrosion rate of less than a targeted value.
   - A maximum concentration value of the corrosion inhibitor, for example, 100 or 200 ppm, to arrive at the targeted inhibited general corrosion rate.
   - Compatibility with other chemicals in the system.
- Studying the corrosion inhibitor impact on downstream facilities.
- Establishing test procedures for residual chemical analysis of the selected chemical (these procedures are usually provided by the chemical manufacturer).
- Recommending suitable corrosion monitoring techniques.

1.4   Corrosion in Downstream Sector

The downstream sector includes petroleum refining and petrochemical operations [17]. Refining utilizes atmospheric and vacuum distillation columns to separate crude into fractions or cuts. Refineries are designed and constructed based on the type of crude oil feedstock whether light, medium, or heavy, e.g. a successful refinery has the ability to accept any type of available crude. In addition to distillation, other refining processes include catalytic cracking, hydrocracking, hydrotreating, and reforming. Product distribution terminals to bulk customers such as airports and gasoline stations are also included in the refinery operations.

   Petrochemical plants produce many chemical compounds and are divided into three main primary product groups:

- Olefins that include ethylene, propylene, and butadiene. These are the main sources of plastics (polyethylene, polyester, polyvinylchloride), synthetic rubber, and industrial chemicals.
- Aromatics that include benzene, toluene, and xylenes. These are also sources of plastics (polyurethane, polystyrene, acrylates, nylon). These are also used in producing synthetic detergents, and dyes.
- Synthesis gas (syngas) is formed by the steam reforming reaction between methane and steam to produce a mixture of carbon monoxide (CO) and hydrogen. Syngas is utilized to make methanol used as a solvent and chemical intermediate and NH_3 used in producing fertilizers, for example. Syngas is also used in the Fischer–Tropsch process to produce synthetic diesel.

Corrosion problems can significantly increase the cost of operating and maintaining these refineries and petrochemical plants. High costs are associated with scheduled shutdown for turnaround and inspection (T&I) and even higher costs for unscheduled shutdowns for repairing corroded piping and equipment. During these periods the equipment will be opened to the atmosphere exposing the internal components to air and moist. If not planned properly, exposure of corroded metal surfaces to air and moisture could lead to pitting corrosion and SCC. Repairing these damages could extend the shutdown period even further. A facility with a robust maintenance and corrosion management program, however, would result in an optimized shutdown period that would lead to substantial cost savings.

The types of fluids and streams in refining and petrochemical operations involve flammable hydrocarbons, toxic or explosive gases, and strong acids and caustics. These factors along with elevated temperatures and pressures impose restrictions on selecting suitable materials for construction.

1.4.1 Materials of Construction

The majority of components in refineries and petrochemical plants are fabricated from carbon steel [17]. In refineries, these include fractionation towers, separator drums, heat-exchanger shells, storage tanks, and most piping. Low-alloy steels are used for higher-temperature applications such as furnace tubes. In petrochemical plants, stainless steels are widely used in, for example, fabricating linings, tray components in fractionation columns, piping, heat-exchanger tubes, reactor cladding, and tubes and tube hangers in furnaces. Cast irons are used in pumps and valve components where their high hardness reduces the corrosive effects of high velocities resulting from impingement, erosion, and cavitation.

Copper and aluminum alloys are used in water-cooled condensers and coolers at most refineries. The other major use of aluminum is in vacuum towers where it provides resistance to naphthenic acid corrosion. Nickel alloys are resistant to strong acids and bases like sulfuric acid (H_2SO_4), HCl, HF, and caustic solutions. High-nickel alloys are used where polythionic acid corrosion is a problem like in flare stack tips. Titanium is used in overhead coolers and condensers tubes because it resists attacks by aqueous chlorides, sulfides, and sulfur dioxide (SO_2). Titanium is also used when handling seawater or brackish water like in multistage flash distillation.

If during welding of carbon steel, localized hard zones were developed with hardness values exceeding 200 HB, SSC might occur if the steel is exposed to aqueous sulfide solutions. Heat-treatment is, therefore, required in these situations to prevent SSC from occurring. Compressors and pumps are subject to fatigue failures. Most equipment fabricated from carbon steel operate in the temperature range from ambient to 425 °C (800 °F). Refinery and petrochemical plant equipment that operate at low temperatures include liquefied-propane storage, ammonia storage, solvent dewaxing units, and liquefied petroleum gas (LPG) handling facilities.

General corrosion, which is a uniform metal loss, is accounted for by specifying corrosion allowance. This type of corrosion can be easily detected by NDT

techniques. The most practical approach to prevent pitting corrosion is to avoid process conditions that lead to pitting. SCC is the most serious type of failure that is also difficult to detect. Materials standards developed by industry are used to select the proper SCC-resistant material for each application [18].

1.4.2 Corrosion in Refineries and Petrochemical Plants

Corrosion in refineries and petrochemical plants can be classified into low-temperature and high-temperature corrosion. Low-temperature corrosion occurs below approximately $260\,°C$ ($500\,°F$) in the presence of water, while high-temperature corrosion occurs above this temperature and does not require the presence of water. The discussion here will be limited to low-temperature corrosion that is relevant to corrosion inhibition [17].

The majority of corrosion problems in refineries and petrochemical plants are caused by water, H_2S, HCl, HF, H_2SO_4, and caustic. Organic acids such as H_3CCOOH are also a problem in petrochemical plants. Air could enter during shutdown or turnarounds and could cause corrosion and fouling specially in equipment operating under vacuum conditions. Traces of oxygen could also enter with the boiler feedwater.

In refining and/or petrochemical process units, corrosion could be caused by process chemicals such as H_3CCOOH, aluminum chloride catalysts, organic chloride solvents, HCl, H_2SO_4, caustic, amines, and phenol. Acetic acid is used in the synthesis of organic intermediates such as terephthalic acid. Aluminum chloride is used as a catalyst in butane isomerization, ethylbenzene production, and polybutene production. Organic chlorides are used as solvents to remove wax deposits and metal-degreasing and are usually reinjected back to the crude feed. Both aluminum chloride and organic chlorides could generate HCl. HF is sometimes used in alkylation processes instead of H_2SO_4. Acids become corrosive in the presence of water.

Carbon steel is used in the construction of H_2SO_4 alkylation units where a protective iron sulfate ($FeSO_4$) film is responsible for the corrosion resistance. Flow velocities are restricted to below $1.2\,m/s$ ($4\,ft/s$) to avoid breakdown of the $FeSO_4$ film. Esters produced as by-products in the alkylation reactions may decompose in reboilers to produce SO_2. The SO_2 can combine with water to produce the corrosive sulfurous acid (H_2SO_3) in the upper section and overhead system of the fractionation towers.

Caustic is used in refineries and petrochemical plants to neutralize acids. Caustic corrosion could occur in crude distillation units if $40\,wt\%$ caustic is injected into hot, desalted crude oil transfer line. Corrosion by amines occurs in gas-treating and sulfur recovery units where corrosion is actually caused by dissolved H_2S or CO_2, and by amine degradation products. Carbon steel is the principal material of construction for amine units. Since filming-amine corrosion inhibitors are not effective in these cases, proprietary oxidizing corrosion inhibitors are used. Phenol (carbolic acid) is used to convert heavy distillates into lubricating oils. Phenol corrosiveness comes from its acidity in the

presence of water. To control HF corrosion, filming-amine corrosion inhibitors are injected into the overhead systems of the different towers.

SCC could occur in refining and petrochemical process units in the presence of chlorides, caustic, ammonia, amine, and polythionic acid. Other forms of corrosion that occur in refineries and petrochemical plants include corrosion fatigue and erosion–corrosion where corrosion inhibitors are used to assist in controlling these types of corrosion. Cavitation and impingement are examples of erosion–corrosion damage mechanisms that are seen in refinery and petrochemical equipment and units.

1.4.3 Corrosion Inhibitors in Refinery and Petrochemical Plants

Corrosion control methods in refinery and petrochemical service include materials selection, design changes, process changes, corrosion inhibitors [19], protective coatings, and refractory linings. Small concentrations of filming-amine corrosion inhibitors are added to control corrosion in various process units. Filming-amine corrosion inhibitors have an upper temperature application limit of approximately 175 °C (350 °F). This limit is set by desorption of the inhibitor film from the metal surface rather than by thermal degradation of the inhibitor. Higher temperatures lead to faster rates of desorption than adsorption of inhibitor film rendering it ineffective. The main use of these inhibitors is to protect overhead condensing equipment such as the overhead system of crude unit distillation columns. Surfactants are added to the corrosion inhibitor package to induce water dispersibility.

To establish corrosion protective films, higher inhibitor dosages are injected for several days at the beginning of the treatment. The dosage is subsequently trimmed down to the lower recommended rate to optimize expenses and to avoid generating any emulsion issues in downstream units due to excessive surfactant concentrations. An increase in the amount of foulant materials in downstream equipment could be seen at the beginning of the treatment. This is due to the corrosion inhibitor dissolving deposits and corrosion products accumulated prior to the treatment. These inhibitors can also cause foaming in amine units.

Traces of oxygen in the boiler feed water are removed using oxygen scavengers such as hydrazine and sodium sulfite since mechanical means would be uneconomical.

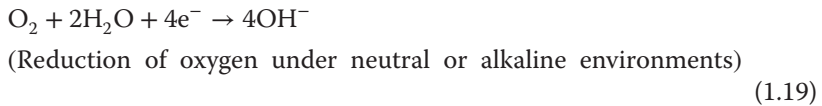### 1.4.4 Corrosion Control of Water-Recirculating Systems

Water-recirculating systems [20] are used to remove excess heat from heat transfer surfaces. There are three types of these systems: once-through, open recirculating, and closed recirculating systems. In once-through systems, the cooling water passes only once through the plant heat exchangers. In open recirculating systems, the cooling water is reused and makeup water is added to compensate for evaporative losses. In this type of system, the water is saturated with oxygen. In closed recirculating systems, corrosion by-products can accumulate and foul heat transfer equipment.

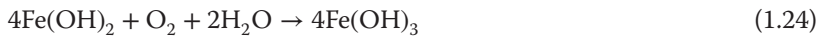**1.4.4.1 Typical Corrosion Reactions in Water-Recirculating Systems**

Corrosion reactions in water cooling systems are electrochemical in nature and consist of two half-reactions. For common heat transfer materials, the anodic oxidation half-reactions for Fe, Cu, and Al-based metals are as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1.15}$$

$$Cu \rightarrow Cu^+ + e^- \tag{1.16}$$

$$Al \rightarrow Al^{3+} + 3e^- \tag{1.17}$$

The cathodic reduction half-reactions are:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
(Reduction of oxygen under acidic environment) $\tag{1.18}$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
(Reduction of oxygen under neutral or alkaline environments)
$$\tag{1.19}$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$
(Hydrogen evolution) $\tag{1.20}$

$$Cu^{2+} + 2e^- \rightarrow Cu$$
(Metal deposition) $\tag{1.21}$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
(Reduction of metal ions) $\tag{1.22}$

Interactions of the two half-reactions lead to the formation of several corrosion products:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{1.23}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \tag{1.24}$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{1.25}$$

The hydrated ferric oxide (Fe_2O_3) is the common red rust. Protective metal oxides are also formed:

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O$$
(Cuprous oxide) $\tag{1.26}$

$$Al^{3+} + OH^- \rightarrow Al(OH)_3 \tag{1.27}$$

$$2Al(OH)_3 \rightarrow Al_2O_3 \cdot 3H_2O$$
$$\text{(aluminum oxide)} \tag{1.28}$$

Corrosion forms common in heat transfer equipment are:

- General corrosion or uniform attack
- Galvanic corrosion
- Erosion–corrosion
- Crevice corrosion
- Pitting corrosion

1.4.4.2 Water Corrosivity

Factors that influence the corrosivity of water include dissolved gasses, temperature, suspended solids, pH, dissolved salts, scaling tendency, fouling deposits, and bacteria. Dissolved gases commonly encountered in water-recirculating systems are O_2, CO_2, Cl_2, and NH_3. Corrosivity due to dissolved oxygen has already been discussed in previous Sections 1.2.1.1 and 1.4.4.1. In the absence of dissolved oxygen, however, a uniform protective film of magnetite (Fe_3O_4) is formed:

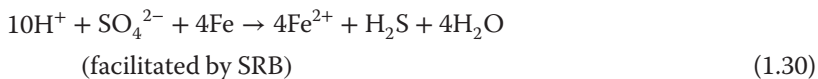$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{1.29}$$

Increasing the temperature will tend to increase rates of corrosion reactions. This will also increase the formation of protective corrosion products films that will suppress the corrosion rates. Deposition of suspended solids in low-flow areas will lead to crevice corrosion. Normally, the pH in an open recirculating cooling system is 6.5–9; in closed systems the pH is 8.5–9; while in boilers the pH is 11. Carbon steel is sensitive to pH, while copper alloys are not as sensitive due to the formation of a protective cuprous oxide film. Increasing the pH can lead to precipitation of $CaCO_3$ in waters of moderate calcium levels. As dissolved salts increase, the water conductivity increases extending the effects of galvanic corrosion over longer distances. Soft waters are more corrosive than hard waters. Hard waters are high in calcium, which precipitates forming a protective $CaCO_3$ film. Chlorides tend to interfere with the formation of surface passive films leading to pitting attack. Both stainless steels and copper alloys are susceptible to chloride attacks.

The most common scale found in water cooling systems is $CaCO_3$ where it will be highest at the hottest areas along the heat transfer surfaces. Indices have been developed to indicate the $CaCO_3$ tendency to deposit, which can be controlled by the addition of acids or specific chemicals such as polymeric inorganic phosphates and polycarboxylates. Calcium sulfate is the second common chemical found in cooling water systems that usually exists as gypsum ($CaSO_4 \cdot 2H_2O$). This scale can be controlled using polyacrylates.

Another scale found in recirculating cooling water systems is calcium phosphate [$Ca_3(PO_4)_2$], which is difficult to control. This scale results from phosphates addition in chemical treatment. Special copolymers have been used to control this type of scale. Another scales that are difficult to remove from heat transfer surfaces are silicate scales such as calcium silicate ($CaSiO_3$) and magnesium silicate ($MgSiO_3$). The most effective mitigation approach for these scales is to

maintain SiO_2 concentration below 150 mg/l in the recirculating cooling water. Fouling deposits include diverse materials that are suspended in water, which can be controlled by maintaining high flow rates (1.5–2.5 m/s, or 5–8 ft/s), by using mechanical means such as coarse filters or side-stream filters, by chemical treatment, and by performing periodic cleaning.

Biological growth or biofouling can interfere with the flow of water and with heat transfer in heat exchangers and these interferences contribute to corrosion. Biofilms by impeding heat transfer and flow will lead to an increase in pumping energy demands. Classes of microorganisms found in water-recirculating systems are algae, fungi, and bacteria that can lead to under-deposit, crevice, and pitting corrosion. SRB can result in corrosion rates of carbon steel as high as 2.5 mm/yr (100 mpy) where the following general reactions take place:

$$10H^+ + SO_4^{2-} + 4Fe \rightarrow 4Fe^{2+} + H_2S + 4H_2O$$
$$\text{(facilitated by SRB)} \tag{1.30}$$

$$H_2S + Fe^{2+} \rightarrow FeS + 2H^+ \tag{1.31}$$

Other bacteria present in cooling systems are the nitrifying bacteria, the iron-depositing bacteria, and slime-forming bacteria. Biocides, both oxidizing and non-oxidizing, are used to control bacterial growth.

1.4.4.3 Corrosion Control

Corrosion control of water systems can be accomplished using CRAs, or by applying protective coatings and installing sacrificial anode CP. An effective chemical treatment or corrosion inhibitor program must possess the following important properties:

- Provide corrosion protection to all exposed metal surfaces.
- Effective at low concentrations.
- Does not cause undesirable deposits on metal surfaces.
- Applicable under wide range of pH, temperature, water quality, and heat flux.
- Prevent scale formation and disperse deposits
- Have no or negligible toxicological effects when discharged.

For once-through systems, preventing corrosion by selecting CRAs could be more cost-effective than other methods of corrosion control. Addition of corrosion inhibitors could be justified economically for the two other water cooling systems, namely, open recirculating system and closed recirculating system. Corrosion inhibitors in these cases are classified based on their interactions with the two electrochemical half-reactions of corrosion process, which are either anodic or cathodic. In addition to anodic and cathodic corrosion inhibitors, mixed inhibitors are chemicals that suppress both anodic and cathodic reactions. Examples of anodic inhibitors are chromates, nitrites, molybdates, and phosphates, while examples of cathodic inhibitors include polyphosphates, phosphonates, and multicomponent systems such as zinc chromate, and zinc phosphonates. For copper-based alloys, three cathodic inhibitors from the azole group have been used, and these are mercaptobenzothiazole (MBT), benzotriazole, and tolyltriazole.

1.5   Conclusions and Outlook

Corrosion control using chemical inhibition will remain an attractive option due to low cost and ease of application with the film-forming amines type of corrosion inhibitors having the largest share in the oilfield industry. Normally these corrosion inhibitors are considered mixed type that function by suppressing both anodic and cathodic reactions. Corrosion inhibitors can be applied using three main types of treatment methods: batch, squeeze, and continuous. The squeeze treatment method is applicable to upstream sector only, while batch and continuous treatment methods are applicable to all sectors. Each method has advantages and disadvantages and some limitations. The type of method selected will depend on the system being treated, while a combination of methods could be more cost-effective, e.g. applying batch treatment initially followed by continuous treatment.

Treating upstream facilities could help in protecting downstream facilities by the corrosion inhibitor being carried over in the stream. Tight oil–water emulsions could be experienced in the surface separation facilities if excessive amounts of the corrosion inhibitor are added, and therefore the total process should be considered when designing a corrosion inhibitor treatment program. Depending on the type of service, the corrosion inhibitor solubility and dispersibility should be tailored based on the phases present in the stream and their proportions. A continuous hydrocarbon phase would require a water-dispersible corrosion inhibitor, while an aqueous continuous phase would require a water-soluble corrosion inhibitor.

Challenging applications are inhibition of top-of-the-line corrosion, under-deposit corrosion, and services with high temperatures or velocities. Several chemical manufacturers are developing multifunctional oilfield chemicals encompassing corrosion and scale inhibitors as well as biocidal properties. This is especially desirable for offshore applications where the system footprint and operational logistics are very demanding. Many research centers are active in developing environmentally suitable chemicals that soon could become mandatory in some regions of the world.

Defining application windows or Integrity Operating Window (IOW) with similar corrosivity for corrosion inhibitor treatments is more practical than testing chemicals for specific service conditions. Similar facilities can be grouped into corrosion circuits or corrosion loops. For every corrosion circuit or corrosion loop, the corrosion damage mechanisms will be identified along with recommended corrosion control programs including plans for corrosion mitigation, monitoring, and inspection. To develop chemicals suitable for an application window, both chemical manufacturers and end users should work together.

Standard and new laboratory test methods are also being developed and revised for better simulation of the service conditions in the field. Traditionally, H_2S partial pressures are used to simulate service conditions in the field that could be over conservative in some cases as indicated by the actual materials performance in the field. Fugacities and corresponding concentrations/activities of the dissolved acid gases have been proposed as a better representation of the field conditions than partial pressures. Modeling of sour corrosion is another topic of active

research where prediction of the iron sulfide corrosion product film in terms of its protective properties is the main challenge. In addition, iron sulfide deposition and removal by chemical means require further research.

Currently, there is no inhibitor that can prevent precipitation of FeS. FeS may plug injection wells and may make oil–water separation difficult. The transition from sweet to sour corrosion is usually defined by the CO_2 to H_2S ratio where several values have been proposed in the literature. A more rigorous derivation of these values and their relation to the dominating corrosion mechanisms and pitting tendencies would be beneficial to the industry.

New corrosion challenges continue to evolve with time such as transportation and use of liquefied CO_2 for enhanced oil recovery applications and shale (unconventional) gas production. For these new and existing challenging applications, the limits are being pushed to use high-strength, low-alloy carbon steels. In some applications, nonmetallic materials, such as FRP and graphene-based materials, could be used as an alternative. There are several disadvantages restricting FRP use, however, and these include low temperature service limit, low resistance to fatigue and mechanical damage, low strength, high combustibility, difficulty in attaining joint integrity, and possible attack by CO_2 and unsaturated hydrocarbons.

New coatings based on graphene and 2D materials are being developed where corrosion inhibitor molecules could be incorporated in the matrix. Release of these corrosion inhibitor molecules is triggered once the protective film is disrupted allowing them to spontaneously protect the exposed metal surfaces.

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