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Mitigation of Corrosion Problems in API 5L Steel Pipeline – A Review

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Abstract

The worst nightmare of the oil and gas industry which must not be taken lightly is the issue of corrosion which affects the pipes used for transportation of oil and gas. Corrosion problems need to be properly understood in order to prescribe the necessary kind of treatment that will ensure a long life span for the pipeline. This paper gives a comprehensive review of corrosion problems in API 5L steel pipeline and the ways to mitigate the corrosion problems. Proper control and prevention of corrosion in API 5L steel would ensure long life span of the pipe, uninterrupted flow of products, reduction in shutdown time and generate more revenue for the industry. Oil and gas materials last longer when both inhibitors and protective coatings are used together or when protective coating is used together with cathodic protection.

1. Introduction

Pipelines are extremely important throughout the world in the transportation of gases and liquids over long distances from their sources to the ultimate consumers [1-3]. Pipelines are sometimes buried underground and only makes its presence known at valves, pumping or compressor stations, or terminals [1-4]. Corrosion has led to failure in pipelines which are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage and possibly costly in terms of human safety [4-10]. The fluids in the pipeline are responsible for corrosion, CO_2 and H_2S gases in combination with water are the main cause of corrosion in oil and gas production [6, 11-15]. The main problem associated with API 5L X65 and other steel pipelines used in the transportation of oil and gas are sweet corrosion, sour corrosion and microbiologically influence corrosion (MIC), which leads to pitting corrosion on the surface of the steel pipeline [7, 8, 16-19]. Sweet corrosion is due to the presence of carbon dioxide and water, the carbon dioxide dissolved in the water to form carbonic acid, which reacts with the steel pipeline causing corrosion damage, on the other hand sour corrosion will take place when the fluids in the pipeline include water and hydrogen sulphide, while MIC takes place when sulphate reducing bacteria produce by-products from the organisms which promote several forms of corrosion [7, 8].Corrosion prevention and control is of great importance in the world today, so for several decades, engineers and scientists have been trying to understand better methods of how to prevent and control corrosion of metals. The methods that are normally used to protect corrosion include: Proper selection of materials; good design; application of protective coatings; modifying the corrosive environment; application of inhibitors and cathodic protection [10]. Different methods have been used for corrosion prevention and control of oil and gas pipelines, which includes improvement in the material of construction, application of protective coating, cathodic protection and application of inhibitors to modify the corrosive environment [20]. High strength low alloy carbon steels such as API 5L X65 steel play important roles in oil and gas exploration [21]. It is well known that the corrosion rate of steel in fluid media increases with increasing flow rate, due to the mechanical removal of the passive films on the surface as well as the dissolution or delay of corrosion products growth at different flow rates [22]. Direct contact of pipeline with process media can be prevented by using protective layer or barrier in order to enhance pipe life span. Barrier layer such as paint, coating, lining, a metallic lining or metallic sheets can be used. There are also nonmetallic linings, such as fiberglass, glass flake, epoxy and rubber. Nickel, zinc and cadmium coatings are also preferred at times on certain components. Most of these protective layers do not provide everlasting solutions, but will only extend the life of the pipeline material underneath the barrier to some extent. The paint may flake off due to prolonged exposure to the atmosphere, heat and sunlight. The tape or lining on a pipeline, may become physically damaged, crack and delaminate, exposing the pipeline beneath to corrosive media. However, this method is cheap and less expensive than opting for a costly material of construction for corrosion protection [20]. Cathodic Protection can be used to prevent or mitigate the corroding interface of the steel pipeline by altering the electrochemical condition. Altering the electrical potential field around the pipe causes an alteration in the electrochemical nature of the corroding surface, the rate of oxidation is reduced and the reduction process is accelerated by applying a negative potential and making the pipe a cathode. Corrosion control is enhanced by cathodic protection, which also alters the environment at the pipe surface. The pH of any electrolyte at the pipe surface is increased, the oxygen concentration is reduced and deleterious anions, such as chloride, migrate away from the pipe surface [4]. Use of some inhibitors, such as chromate, has been banned because of toxicity and the environmental hazards they create [23]. Hence there is a need to make use of environmental friendly, non-toxic, extracts of naturally occurring plant materials as corrosion inhibitors also known as green corrosion inhibitors. Extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero-atoms such as phosphorous, nitrogen, sulphur and oxygen. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface, thereby preventing corrosion. Some of the green corrosion inhibitors that have been used in the past are extracts from aloe vera, banana plant juice, mango, orange, passion fruit, cashew peels and tobacco leaves, etc. [23-26].This paper reviews corrosion problems in oil and gas pipeline and its mitigation. Corrosion control and prevention methods such asselection of appropriate materials, use of inhibitors, use of protective coatings and cathodic protection were properly reviewed.

2. **Corrosion problems in oil and gas steel pipeline**

Corrosion is the main problem affecting pipelines in the oil and gas industry. Understanding the electro-chemical nature of corrosion was a major breakthrough, and this made it possible for corrosion to be mitigated to some extent, if electric current sufficient to offset the inherent corrosion current of a particular environment were caused to flow in the opposite direction. The applied direct current is referred to as cathodic protection because it made the pipe the cathode in a galvanic cell. The required current could be supplied by connecting a sacrificial anode in an electrical circuit where soil acted as the electrolyte. Alternatively, commercial current could be directed to the pipe via an anode bed. The application of coating and inhibitors also help to solve the corrosion problem [20, 27, 28].

2.1. Internal corrosion in pipeline

Internal corrosion in oil and gas pipelines is primarily caused by the presence of water together with acid gases (carbon dioxide or hydrogen sulphide) or sulphate reducing bacteria [7]. It can be divided into three broad categories:

- Sweet corrosion
- Mesa corrosion
- Sour corrosion
- Microbiologically influenced corrosion (MIC)

Sweet corrosion: Sweet corrosion occurs when there is carbon dioxide and water in the pipeline. The carbon dioxide dissolves in the water to form carbonic acid, which reacts with the steel pipeline causing corrosion damage. Bare steel in contact with carbonic acid will lead to very high corrosion rate. However, corrosion products form an iron carbonate layer on the metal surface and this in turn reduces the corrosion rate. The system temperature, pressure, concentration of carbon dioxide and the flow rate will also affect the rate of corrosion. The flow rate has an effect because if the flow is sufficiently high that it is fully turbulent there will be no separation out of water, and the inner surface of the pipe will be continuously re-coated with oil making corrosion unlikely [7, 9]:

$$CO_2 + H_2O + Fe \longrightarrow FeCO_3 \text{ (Iron Carbonate)} + H_2 \quad \text{------------------------------} \ (1)$$

Mesa corrosion: Mesa corrosion in the base of the pipeline is caused by sweet corrosion. Severe mesa corrosion forms a long groove internally at the bottom of the pipe. The base of the pipe is more prone to corrosion as this is where the water (and carbonic acid) tends to be collected as it separates out. The characteristic 'mesa' is formed by the corrosion continuing at a more rapid rate at locations where the 'protective' iron carbonate layer is disturbed. At the downstream pipe wall or weld defect, there is always an increase in local turbulence during the flow of oil and gaseous products. This turbulence can disturb the protective layer and result in a local increase in corrosion rate. As the corrosion defect forms there will be increased turbulence at the downstream edge, leading to relatively rapid growth along the pipeline. Material variations, such as weld spatter, can also prevent the formation of a stable iron carbonate layer. This will result in pitting or general corrosion, depending on the extent of the material variation [7, 9].

Sour corrosion: Sour corrosion takes place when the fluids in the pipeline include water and hydrogen sulphide. The presence of hydrogen sulphide can have a number of different effects:

- Metal loss as a result of the presence of hydrogen sulphide follows the same mechanism as that of carbon dioxide corrosion in that hydrogen sulphide dissolves in the water associated with oil products, forming a weak acid. Here the corrosion product is iron sulphide and like iron carbonate, it can be partially protected, thereby reducing the corrosion rate. Small pits are then form due to the iron sulphide film which tends to break down locally.
- Sulphide Stress Cracking (SSC) may take place when a pipe material is exposed to a sour environment and level of stress, i.e. the stress may be residual or applied. Embrittlement of the pipe by hydrogen leads to cracking. SSC is found to attack higher strength materials (actual tensile strength of 550MPa or higher). Hence, provided the line pipe is correctly specified, it is often associated with weld heat affected zones and cold worked sections, which tend to be stronger than the standard line pipe.
- Hydrogen Induced Cracking (HIC) is most likely to affect susceptible steel pipes where iron sulphide film is form and hydrogen is present. Corrosion processes produce hydrogen and HIC takes the form of blisters in the pipe wall around manganese sulphide inclusions left in the steel pipe during manufacturing; it is usually very difficult to remove all the manganese sulphide from the steel pipe. Hence, HIC does not tend to be found at particular locations, such as weldments [7].

$$H_2S + Fe + H_2O \longrightarrow FeS \text{ (iron sulphide)} + 2H + H_2O \text{---------------------} (2)$$

Microbiologically influenced corrosion (MIC): In this case corrosion is influenced by the presence and activities of microorganisms, including bacteria and fungi. MIC has been estimated to be responsible for 20 to 30% of external corrosion on underground pipelines [29]. Microorganisms located at the metal surface do not directly attack the metal or cause a unique form of corrosion. The by-products from the organisms promote several forms of corrosion, including pitting, crevice corrosion, and under-deposit corrosion. Typically, the products of a growing microbiological colony accelerate the corrosion process by either interacting with the corrosion products to prevent natural film forming characteristics of the corrosion products that would inhibit further corrosion, or providing an additional reduction reaction that accelerates the corrosion process. A variety of bacteria which are either aerobic or anaerobic have been implicated in exacerbating corrosion of underground pipelines [30].Obligate aerobic bacteria can only survive in the presence of oxygen, while obligate anaerobic bacteria can only survive in its absence. Another type of bacteria is facultative aerobic bacteria that prefer aerobic conditions, but can live under anaerobic conditions. Common obligate anaerobic bacteria implicated in corrosion include sulfate-reducing bacteria (SRB) and metal-reducing bacteria. Common obligate aerobic bacteria include metal-oxidizing bacteria, while acid-producing bacteria are facultative aerobes. The most aggressive attack generally takes place in the presence of microbial communities that contain a variety of types of bacteria. In these communities, the bacteria act cooperatively to produce conditions favorable to the growth of each species. Obligate anaerobic bacteria can thrive in aerobic environments when they are present beneath biofilms/deposits in which aerobic bacteria consume the oxygen. This is illustrated in Figure 1 below. In the case of underground pipelines, the most aggressive attack has been associated with acid-producing bacteria [29].

2.2. *External corrosion in pipeline*

Differential cell corrosion: Here the oxidation and reduction reactions occur physically at or very near the same location on a metal. An atom is being oxidized while the reduction reaction is occurring at an adjacent atomic site of the pipe. Corrosion of the pipe will normally occur when it is been attacked by acid solution. If the metal oxidation occurs predominantly at one site while the reduction reaction occurs predominantly at another site, this is referred to as a differential corrosion cell. Underground corrosion of pipelines and other structures is often the result of differential corrosion cells of which a variety of different types exist. Differential aeration cells is one of the types of differential cell corrosion, where different parts of a pipe are exposed to different oxygen concentrations in the soil, and cells created by differences in the nature of the pipe surface or the soil chemistry. This behavior is sometimes obvious when excavating an old bare pipeline in which some areas are in excellent condition but other areas only a few feet away are severely corroded [4, 11].

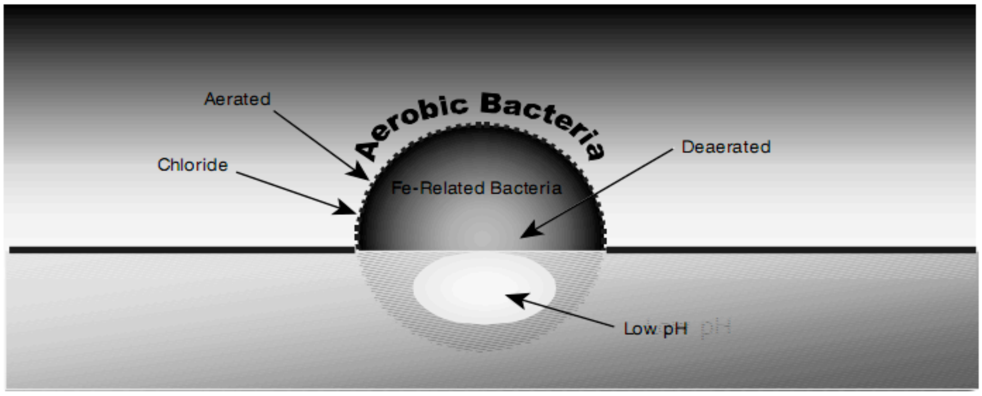

Figure 1: Iron-related bacteria creating a differential oxygen and pH cell on a metal surface (Beavers and Thompson, 2006)

A differential aeration cell: This is most likely the most common corrosion cell found on pipelines or other underground structures. One area of the pipeline is exposed to higher concentrations of oxygen and becomes the cathode in the cell, while another part of the structure is oxygen deficient and becomes the anode. Electrical current leaves the metal surface at the anode, increasing the corrosion rate, and flows to the oxygenated cathodic area, decreasing the corrosion rate. Differential aeration cells as well as other corrosion cells can be autocatalytic in that the chemical and electrochemical reactions, as well as ion migration, tend to produce conditions that promote the continuation of the cells. At the anode, the metal ions produced by the corrosion reactions hydrolyze, reducing the local pH. Corrosive negative halide ions migrate to the anodic sites to maintain charge neutrality. Both of these processes increase the corrosivity at the anodic sites. At the cathodic sites, the reduction reactions increase the pH and improve the protective nature of the corrosion films [4, 12].

Differences in soil properties: Most often there is variation in the moisture content of the soil, the depth from the surface or oxygen barriers such as paved roads can produce differential aeration cells, this is represented in Figure 2, which shows a pipeline passing through two dissimilar soils. The corrosion potential of the pipeline in the clay soil is more negative than the corrosion potential in the sandy soil, resulting in an increase in the corrosion rate of the pipe in the clay and a decrease in the sand. Differences in the oxygen concentration, pH, or concentration of aggressive ions such as chlorides in the soil are other factors that can produce a differential corrosion cell [4, 11, 12].

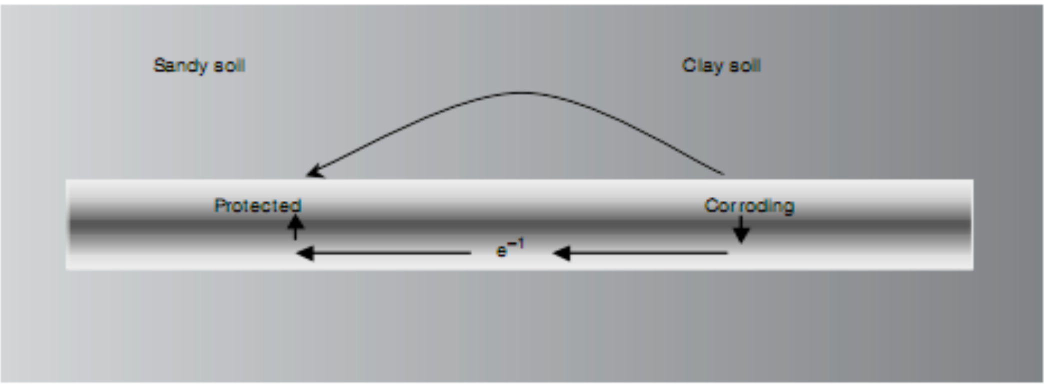

Figure 2: Differential Corrosion Cell created by differences in soils, arrows indicates the direction of ionic and electronic current flow (Beavers and Thompson, 2006).

Galvanic corrosion: This is another example of a differential corrosion cell, in which different metals in contact create potential difference leading to galvanic corrosion. The corrosion potential of different metals depends on the given environment to which it is exposed, i.e. the galvanic series for metals in soils. When these metals are electrically coupled, the metal with the most positive corrosion potential is cathodically polarized, reducing its corrosion rate, while the more negative member of the couple is anodically polarized, increasing its corrosion rate. Galvanic corrosion can be very detrimental to an underground pipe or other structures. Examples include the corrosion of iron in contact with copper or stainless steel fittings. However, galvanic corrosion can be used as an effective means of cathodic protection (CP) [4, 11].

The surface films: Films present on a metal also can alter the corrosion potential and cause differential cell corrosion. Mill scale can be created on pipeline steel during the manufacturing process (hot rolling) and, if not removed, the mill-scale-coated steel will act like a dissimilar metal in contact with non-mill scale-coated pipe steel. The potential of the bare pipe steel surface will be more negative (active) than the mill-scale-coated surface, resulting in severe corrosion of the bare steel surface in low-resistivity soils. A similar condition can occur when new steel pipe is intermixed with old steel pipe. The potential of bright new steel is typically more negative than that of old rusted steel, resulting in rapid corrosion of the new steel unless the new section is electrically insulated from the old section and, or cathodically protected. A similar corrosive condition can occur if, during work on an existing piping system, tools cut or scrape the pipe and expose areas of bright steel. The potential of these bright spots will be more negative than the remainder of the pipe, resulting in accelerated corrosion in low-resistivity soils [4, 13].

The relative size of anodic and cathodic areas: This can have a significant effect on the severity of the differential corrosion cell. In general, the severity of corrosion of the anodic areas increases as the ratio of the anodic to the cathodic area decreases. A high density of current discharge per unit area is created when the anode is small and the cathode is large, the anode will be subject to a high density of current discharge per unit area, with the total amount of current flowing governed by the kinetics of the oxidation and reduction reactions and the soil resistivity. The current collected per unit area on the cathode is relatively low and may not be sufficient to result in any degree of polarization, which would tend to limit corrosion current. In a low-resistivity soil, corrosion can be rapid [4, 11-13].

*Stray current corrosion:*Corrosion of underground pipelines can be accelerated by stray dc flowing in the soil near the pipeline. Sources of direct electrical current include foreign pipelines that are not properly bonded to the pipeline and ground currents from dc sources. Electrified railroads, mining operations, and other similar industries that utilize large amounts of dc sometimes allow a significant portion of current to use a ground path return to their power sources. These currents often utilize pipelines in close proximity as a part of the return path. This stray current can be picked up by the pipeline and discharged back into the soil at some distance down the pipeline close to the current return. Current pickup on the pipe is the same process as cathodic protection, which tends to mitigate corrosion. The process of discharge of a dc off the pipe and through the soil accelerates corrosion of the pipe wall at the discharge point, causing stray current corrosion. The morphology of stray current corrosion tends to be much localized at holidays (defects or holes) in the pipeline coating. Rates of attack can be very high, resulting in rapid perforation of a pipeline [4, 12, 13].In the case of stray current corrosion from a foreign pipeline, the pipeline acts as a return current path for the cathodic protection system on the foreign pipeline. Stray current corrosion occurs where the dc discharges from the pipeline and collects onto the foreign pipeline, as illustrated in Figure 3.

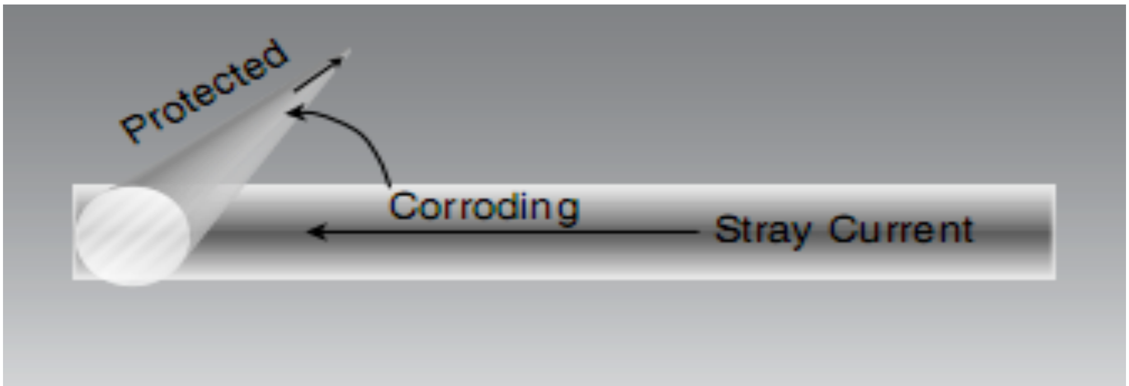

Figure 3: Stray current corrosion caused by foreign pipeline (Beavers and Thompson, 2006)

While relatively rare, cathodic protection rectifiers are occasionally connected backwards, such that dc current is discharged from the pipeline and the impressed current “anode” actually collects rather than discharges current. This can result in severe stray current corrosion of the pipeline [29]. Field experience and laboratory research results indicate that stray alternating current (ac) also can cause accelerated corrosion of underground pipelines [31]. The most common sources of stray ac are induced ac from power lines and pipelines in a common right of way and ground faults from ac power transmission. It is generally agreed that ac-enhanced corrosion rates are only a small fraction of about 51% of those of dc currents. Nevertheless, corrosion damage can be extensive where the ac currents are large [4, 31].

*Stress corrosion cracking:*Stress corrosion cracking (SCC) is as a result of cracking of a material produced by the combined action of corrosion and tensile stress. There are two forms of external SCC on underground pipelines: high-pH SCC (also referred to as classical SCC) and near-neutral-pH SCC (also referred to as low-pH SCC). A characteristic of both forms of SCC is the development of colonies of longitudinal surface cracks in the body of the pipe that link up to form long, shallow flaws. In some cases, growth and interlinking of the stress-corrosion cracks produce flaws that are of sufficient size to cause leaks or ruptures of pipelines. The high-pH form of SCC is intergranular [32], the cracks propagate between the grains in the metal, and there is usually little evidence of general corrosion associated with the cracking. The near-neutral-pH form of SCC is transgranular, the cracks propagate through the grains in the metal and it is associated with corrosion of the crack faces and, in some cases, with corrosion of the external surface of the pipe as well. This form of cracking was first reported on a polyethylene-tape coated pipeline on the TransCanada Pipelines Ltd. (TCPL) system in the 1980s [33, 34].

3. Methods to prevent and control corrosion in oil and gas steel pipeline

Mitigating corrosion to improve pipeline, equipment and plant life continues to be a nightmare for many plant operating staff personnel. Although many methods have been suggested to arrest corrosion, they can be classified broadly into four main categories:

- Selection of appropriate materials.
- Use of inhibitors.
- Use of protective coatings.
- Cathodic protection.

3.1. *Selection of appropriate materials*

When it is observed that the existing pipeline material of construction is prone to corrosive attack, it is advised to select alternative pipeline material to suit the specific need. Generally, the materials used in hydrocarbon applications can be grouped broadly as metals or nonmetals. Each variety of these materials has its specific applications and limitations. The cost of changing the pipeline materials may be high, however, it is worthwhile in terms of life-cycle costing, which may ensure a longer equipment life and lower maintenance cost despite high initial cost. A detailed study of process and operating conditions has to be carried out before selection of a new material [20]. A comprehensive study of flow conditions, corrosion mechanisms involved, and the expected life of pipeline material is important before selecting a specific metal for an application. It is always more important to understand that no single material is a cure for all the corrosion evils. A material that is good for stress corrosion cracking may fail due to fatigue. Another material that can resist high temperature corrosion may fail due to pitting [20]. The vast majority of underground pipelines are made of carbon steel, based on American Petroleum Institute API 5L specifications [35]. Typically, maximum composition limits are specified for carbon, manganese, phosphorous, and sulfur. In some cases, other alloying elements are added to improve mechanical properties. Composition and tensile requirements for common line pipe steels are shown in Table 1 [4].

Table 1: Chemical and tensile requirements of common long seam welded line pipe steels

Grade	**Composition, wt% max**				**Yield strength minimum**		**Ultimate tensile strength minimum**	
	C	Mn	P	S	MPa	Ksi	MPa	ksi
A	0.22	0.9	0.03	0.03	207	30	331	48
B	0.26	1.2	0.03	0.03	241	35	414	60
X42	0.26	1.3	0.03	0.03	290	42	414	60
X46	0.26	1.4	0.03	0.03	317	46	434	63
X52	0.26	1.4	0.03	0.03	359	52	455	66
X56	0.26	1.4	0.03	0.03	386	56	490	71
X60	0.26	1.4	0.03	0.03	414	60	517	75
X65	0.26	1.45	0.03	0.03	448	65	531	77
X70	0.26	1.65	0.03	0.03	483	70	565	82

High yield seamless pipe API 5L

Low carbon and low alloy steels are the most commonly used materials for pipeline. Supplemental (non-mandatory) requirements for minimum toughness levels were introduced into the API Specification 5LX. The latter development is particularly significant because assuring a minimum level of toughness is the key to obtaining line pipe with greatly improved resistance to defects and rapid crack propagation. In the year 2000, a mandatory minimum toughness level was introduced in API Specification 5L [28, 35]. The applicable codes and standards is API 5L, 45th Edition / ISO 3183 (enhanced) high yield seamless pipes, modified to suit offshore structural purposes. Intended for (but not limited to) use in fixed offshore structures, designed to operate in the offshore sector [35].

3.2. Use of inhibitors

Mostly it is necessary to reduce the intensity of corrosive attack by adding inhibitors to reduce the aggressiveness of corrosive media. These chemicals are injected into a medium point to point in the process. The chemicals, their concentration, and the frequency of injection depend on the process medium and, normally, on the recommendations of the inhibitor manufacturer, since these chemicals, although generic in nature, are generally proprietary items. The inhibitors used are normally chromates, phosphates, and silicates. The removal of oxygen from a fluid medium improves the chances of corrosion resistance by materials in contact with the fluid. Controlling and stabilizing the pH value of the medium is another method of combating corrosion. Many varieties of corrosion inhibitors are available in the market, but a judicious approach and the manufacturer's recommendations must be followed while injecting these chemicals in well fluid streams [6, 20].

3.2.1. Inorganic corrosion inhibitors

Adsorption-type inhibitors: These represent the largest class of inhibiting substances. In general, these are compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases the effect is unequal. This class of inhibitors is mostly the amines [36].

Hydrogen-evolution poisons: These substances, such as arsenic and antimony ions, specially retard the hydrogen-evolution reaction. As a consequence, these substances are very effective in acid solutions but are ineffective in environments where other reduction processes such as oxygen reduction are the controlling cathodic reactions [36].

Scavengers: These substances act by removing corrosive reagents from solution. Examples of this type of inhibitor are sodium sulfite and hydrazine, which remove dissolved oxygen from aqueous solutions.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4 \quad \text{---} \ (3)$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \quad \text{---} \ (4)$$

It is apparent that such inhibitors will work very effectively in solutions where oxygen reduction is the controlling corrosion cathodic reaction but will not be effective in strong acid solution [36].

Oxidizers: Such substances as chromate, nitrate, and ferric salts also act as inhibitors in many systems. In general, they are primarily used to inhibit the corrosion of metals and alloys that demonstrate active-passive transitions, such as iron and its alloys and stainless steels [20, 36].

*Vapour-phase inhibitors:*These are very similar to the organic adsorption-type inhibitors and possess a very high vapour pressure. As a consequence, these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with the metal surface. In use, such inhibitors are placed in vicinity of the metal to be protected, and they are transferred by sublimation and condensation to the metal surface. The vapour-phase inhibitors are usually only effective if used in closed spaces such as inside packages or on the interior of machinery during shipment [35, 36].

3.2.2. Organic corrosion inhibitors

Environmental concerns require corrosion inhibitors to be non-toxic, environment friendly and acceptable. Green chemistry serves as a source of environmental friendly green corrosion inhibitors. Corrosion inhibitors are extensively used in corrosion protection of metals and equipment. Organic compounds with functional groups containing nitrogen, sulfur, and oxygen atoms are generally used as corrosion inhibitors. Most of these inorganic compounds are not only expensive but also harmful to the environment. Thus, efforts have been directed toward the development of cost effective and non-toxic corrosion inhibitors. Plant products and some other sources of organic compounds are rich sources of environmentally acceptable corrosion inhibitors. An example of such a system is the corrosion inhibition of carbon steel by caffeine in the absence of zinc. Plant products are a source of environment-friendly green inhibitors such as phthalocyanines [37]. Other organic inhibitors are dibenzylsulfoxide (DBSO), monocarboxylates and amino acids and sodium azelate [38].

3.2.3. *Corrosion inhibitor mechanism*

Corrosion inhibition mechanisms operating in an acid medium differs widely from one operating in a near-neutral medium. Corrosion inhibition in acid solutions can be achieved by halides, carbon monoxide, and organic compounds containing functional group heteroatoms such as nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium, organic compounds with multiple bonds, proteins, polysaccharides, glue, bitumen, and natural plant products such as chlorophyll and anthocyanins [39]. The initial step in the corrosion inhibition of metals in acid solutions consists of adsorption of the inhibitor on the oxide-free metal surface followed by retardation of the cathodic and/or the anodic electrochemical corrosion reactions [39]. Corrosion inhibitors work by forming a protective film which adsorption onto the surface of metal preventing corrosive elements contacting the metal surfaces, as illustrated in Figure 4.

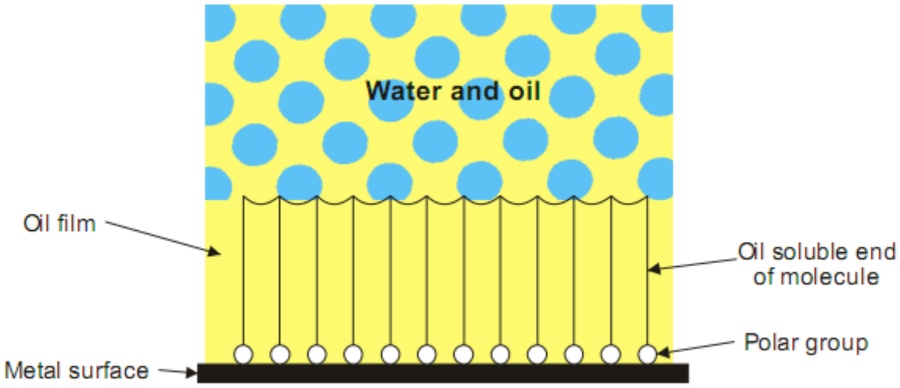

Figure 4: Simple schematic showing how inhibitor film prevents water contacting a metal surface (Palou, *et al.*, 2014).

The action mechanisms of corrosion inhibitors are;

- By adsorption, forming a film that is adsorbed onto the metal surface.
- By inducing the formation of corrosion products such as iron sulfide, which is a passivizing species.
- By changing media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent.

It is well known that organic molecules inhibit corrosion by adsorption, forming a barrier between the metal and the environment. Thus, the polar group of the molecule is directly attached to metal and the non-polar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface [40].An inhibitor may be effective in one system, while in another it is not, therefore, it is convenient to consider the following factors: chemical structure of the inhibitor component; chemical composition of the corrosive medium; nature of the metal surface; operating conditions (temperature, pressure, pH, etc.); thermal stability of the inhibitor – Corrosion inhibitors have temperature limits above which they lose their effectiveness because they suffer degradation of the containing components; solubility of the inhibitor in the system – the solubility of the inhibitor in the system is required to achieve optimum results in the metal surface protection; this depends on the length of the hydrocarbon chain; the addition of surfactants to enhance the dispersibility or solubility of inhibitors; modification of the molecular structure of the inhibitor by ethoxylation to increase the polarity, and thus reach its solubility in the aqueous medium [40]. The main features of an inhibitor are:

- Ability to protect the metal surface.
- High activity to be used in small quantities (ppm).
- Low cost compounds.
- Inert characteristics to avoid altering a process.
- Easy handling and storage.
- Preferably with low toxicity.
- Non-contaminant.
- It should act as an emulsifier.
- It should act as a foaming agent [40].

3.3. Use of protective coatings

Inadequate coating performance is a major contributing factor in corrosion and SCC susceptibility of an underground pipeline. Coatings must be properly selected and applied, and the coated piping must be carefully installed to fulfill these functions [41]. The desired characteristics of the coatings by NACE Standard include: effective electrical insulation; effective moisture barrier; good adhesion to the pipe surface; applicable by a method that will not adversely affect the properties of the pipe; applicable with a minimum of defects; ability to resist the development of holidays with time; ability to resist damage during handling, storage, and installation; ability to maintain substantially constant resistivity with time; resistance to disbanding; resistance to chemical degradation; ease of repair; retention of physical characteristics; non-toxic to environment; resistance to changes and deterioration during above-ground storage and long-distance transportation.The demand to minimize maintenance of metallic structures while optimizing performance requires protective coatings that can self-diagnose and respond to damage and changes in the external environment. Furthermore, the coatings must constitute no hazard to the environment, maintenance personnel and be applied using conventional methods currently used to coat structures for environmental protection. New materials such as nano-structured materials and organic metals present opportunities for engineering damage-responsive coatings and structures. Such materials must be cost effective and non-hazardous [42].

3.3.1. Properties of ideal coating for aqueous corrosion resistance

An ideal coating should have a very hydrophobic surface and should form high barriers to water and electrolytes. Hence there is a need for polymer coatings that are highly cross-linked and that contains silicone or fluorocarbon monomers that promote hydrophobic surfaces. Such coatings should also have controllable gradients in chemical composition to minimize interfacial discontinuities and create a covalent bonded structure from the substrate through to all of the coating layers. Tightly controlled interfacial regions that can be chemically matched to the coating system are another important property in an ideal coating. This provides the basis for water-resistant, adhesion and mechanical property matching with the coating layer to avoid excess stress concentration in the interface, resulting to mechanical delamination [43].

3.3.2. Corrosion mechanism under coatings

When considering corrosion under coatings, adhesion is a very important property. Water molecules can permeate the organic coating and affect the substrate-coating interface, which leads to loss of adhesion. The loss of adhesion, due to water, is attributed to chemical disbondment when chemical interaction of water with covalent, hydrogen or polar bonds and osmotic pressures [44]. The presence of an aqueous electrolyte, with and electrochemical double layer, a cathodic species (oxygen) and an anodic species (metal) can initiate a corrosion reaction. The constant supply of cathodic species, such as water and oxygen, facilitates the corrosion reaction [44].A very good example of corrosion under coatings is the formation of a blister due to cathodic delamination. A complex oxide and hydroxide will be produced after the local corrosion reaction. This will precipitate beneath the polymer, and allows the permeation of water but not of oxygen. This results in the separation of the cathodic and anodic sites. The location of the anodic area is under the precipitate, while the cathodic reaction moves to the edge of the blister, where oxygen may still permeate the coating. The cathodic reaction will increase the pH value at the edge which causes delamination and further growth of the blister [44].

3.3.3. Types of coatings used for steel pipeline

Bituminous enamels: They are formulated from coal-tar pitches or petroleum asphalts and have been widely used as protective coatings for more than 65 years. Coal-tar and asphalt enamels are available in summer or winter grades. These enamels are the corrosion coating; they are combined with various combinations of fiberglass and/or felt to obtain mechanical strength for handling. The enamel coatings have been the workhorse coatings of the industry, and when properly selected and applied, they can provide efficient long-term corrosion protection [4, 5].

*Asphalt mastic:*Pipe coating is a dense mixture of sand, crushed limestone, and fiber bound together with selected air-blown asphalt. These materials are proportioned to secure a maximum density of approximately 2.1 g/cm^3(132 lb/ft^3). This mastic material is available with various types of asphalt. Selection is based on operating temperature and climatic conditions to obtain maximum flexibility and operating characteristics. This coating is a thick (12.7 to 16 mm, or 1/2 to 5/8 in.) extruded mastic that results in a seamless corrosion coating. Extruded asphalt mastic pipe coating has been in use for more than 50 years [4].

Liquid epoxies and phenolics:Many different liquid systems are available that cure by heat and/or chemical reaction. Some are solvent types, and others are 100% solids. These systems are primarily used on larger-diameter pipe when conventional systems may not be available or when they may offer better resistance to operation temperatures in the 95 ^oC (200 ^oF) range. Generally, epoxies have an amine or a polyamide curing agent and require a near-white blast-cleaned surface (NACE No. 2 or SSPC SP10). Coal-tar epoxies have coal-tar pitch added to the epoxy resin. A coal-tar epoxy cured with a low-molecular-weight amine is especially resistant to an alkaline environment, such as that which occurs on a cathodically protected structure. Some coal-tar epoxies become brittle when exposed to sunlight [4].

Extruded plastic coatings:Fall into two categories based on the method of extrusion, with additional variations resulting from the selection of adhesive. The two methods of extrusion are the crosshead or circular die, and the side extrusion or T-shaped die. The four types of adhesives are asphalt-rubber blend, polyethylene copolymer, butyl rubber adhesive, and polyolefin rubber blend. To date, of the polyolefins available, polyethylene has found the widest use, with polypropylene being used on a limited basis for its higher operating temperature. Each type or variation of adhesive and method of extrusion offers different characteristics based on the degree of importance to the user of certain measurable properties [4-6].

*Fusion-bonded epoxy (FBE):*Coatings are heat-activated, chemically cured coating systems. The epoxy coating is furnished in powdered form and, with the exception of the welded field joints, is plant applied to preheated pipe, special sections, connections, and fittings using fluid-bed, air spray, or electrostatic spray methods. Fusion-bonded epoxy coatings were introduced in 1959 and were first used as an exterior pipe coating in 1961 and currently are the coatings most commonly used for new installations of large diameter pipelines [27]. These coatings are applied to preheated pipe surfaces at 218 to 244 ^{o}C (425 to 475 ^{o}F). Some systems may require a primer system, and some require post heating for complete cure. A NACE No. 2 (SSPC SP10) near-white blast-cleaned surface is required. The coating is applied to a minimum thickness of 0.3 mm (12 mils); in some applications, coating thicknesses range to 0.64 mm (25 mils), with the restriction not to bend pipe coated with a film thickness greater than 0.4 mm (16 mils). The FBE coatings exhibit good mechanical and physical properties and are the most resistant to hydrocarbons, acids, and alkalies [4, 5].

*Tape coatings:*Field and mill-applied tape systems have been in use for more than 30 years on pipelines. For normal construction conditions, prefabricated cold-applied tapes are applied as a three-layer system consisting of a primer, corrosion-preventive tape (inner layer), and a mechanically protective tape (outer layer). The function of the primer is to provide a bonding medium between the pipe surface and the adhesive or sealant on the inner layer. The inner-layer tape consists of a plastic backing and an adhesive. This layer is the corrosion-protective coating; therefore, it must provide a high electrical resistivity, low moisture absorption and permeability, and an effective bond to the primed steel surface. The outer-layer tape consists of a plastic film and an adhesive composed of the same types of materials used in the inner tape or materials that are compatible with the inner-layer tape. The purpose of the outer-layer tape is to provide mechanical protection to the inner-layer tape and to be resistant to the elements during outdoor storage. The outer-layer tape is usually a minimum of 0.64 mm (25 mils) thick [4].

Three-layer polyolefin: The three-layer polyolefin pipeline coating was developed in the 1990s as a way to combine the excellent adhesion of FBE with the damage resistance of extruded polyethylene and tape wraps. These systems consist of an FEB primer, an intermediate copolymer layer, and a topcoat consisting of either polyethylene or polypropylene. The function of the intermediate copolymer is to bond the FBE primer with the polyolefin topcoat. Variations in these three-layer systems exist, most notably the use of either polyethylene or polypropylene for the topcoat. Polypropylene offers a higher temperature resistance but is more costly, both as a raw material and because higher temperatures are required for application. Most topcoats are side extruded similar to extruded polyethylene coatings, although at least one product uses flame-spray polyolefin for a topcoat. Another variation in the three-layer systems is the thickness of the FBE primer layer. Early generations of this product utilized a 50–75 mm (2–3 mil) primer which often proved to be inadequate to achieve the desired performance. More recent three-layer systems utilize a 200–300 mm (8–12 mil) primer as a standard thickness [4].

Wax coatings: Have been in use for more than 50 years and are still employed on a limited basis. Microcrystalline wax coatings are usually used with a protective overwrap. The wax serves to waterproof the pipe, and the wrapper protects the wax coating from contact with the soil and affords some mechanical protection. The most prevalent use of wax coatings is the over-the-ditch application with a combination machine that cleans, coats, wraps, and lowers into the ditch in one operation [4-6].

High performance composite coating system: The HPCC is a single-layer, all-powder-coated, multicomponent coating system consisting of a FBE base coat, a medium-density polyethylene outer coat, and a tie layer containing a chemically modified polyethylene adhesive. All materials of the three components of the composite coating are applied using an electrostatic powder coating process. The tie layer is a blend of adhesive and FBE with a gradation of FBE concentration. Thus, there is no sharp and well-defined interface between the tie layer and either of the FBE base coat or the polyethylene outer coat [8].

Low temperature application technology for powder: Coating on High Strength Steel High yield strength steel is often used for constructing oil and steel pipes because it allows the reduction of pipe wall thickness. This technology is applied in frontier areas like the Mackenzie-Beaufort area, the Arctic Islands, and the Labrador basins. Due to the incredibly cold temperatures in these areas, many issues concerning the strength and flexibility of pipelines have developed. Pipes that would be flexible enough to bend and shift whenever frost heaving occurred are necessary to sustain consistent flow. Frost heaving occurs whenever the ground changes from hard during the winter months to soft during warmer temperatures. This has the effect of causing any material that is built underground to shift with it. To address this issue, more flexible and high yield strength grades of steel such as X80 or higher were developed [35]. A coating on the high-strength steel pipes for Frontier areas should withstand the extremely cold temperatures and retain the flexibility needed to protect the pipes. In addition, there is a need for a coating with indentation and impact resistance at −40°C/−50°C. This coating method had been used in frontier oil and gas in Canada [8].

Thermotite flow assurance coating technology: The Thermotite technology consists of a multilayer polypropylene composite FBE as the layer to the steel. Specific requirements for protection or thermal insulation are taken care of through the bespoke system design. Resistance to the effects of compression and creep, typical for deep water and high temperature, can be catered for by adjusting the density and nature of the layers. The three-layer anti-corrosion coating is applied by a side or cross-head extrusion process and the quality tested and approved, prior to the application of the thermal insulation layers (two-layers; PP foam and outer shield). The thermal layers and outer shield or weight coating polypropylene, are applied simultaneously in the thermal insulation lines, by a cross-head extrusion process. The method secures a fixed outer diameter and homogenous foam structure with no air inclusions [4, 8].

3.4. Cathodic Protection (CP)

External corrosion and SCC are electro-chemical phenomena and, therefore, can be prevented or mitigated by altering the electro-chemical condition of the corroding interface. Altering the electrochemical nature of the corroding surface is relatively simple and is done by altering the electrical potential field around the pipe. By applying a negative potential and making the pipe a cathode, the rate of corrosion (oxidation) is reduced (corrosion is prevented or mitigated) and the reduction process is accelerated. This means of mitigating (or preventing) corrosion, cathodic protection, also alters the environment at the pipe surface, which further enhances corrosion control. The pH of any electrolyte at the pipe surface is increased, the oxygen concentration is reduced, and deleterious anions, such as chloride, migrate away from the pipe surface [4]. The CP principle is illustrated in Figure 5 for a buried pipeline, with the electrons supplied to the pipeline by using a dc source and an ancillary anode.

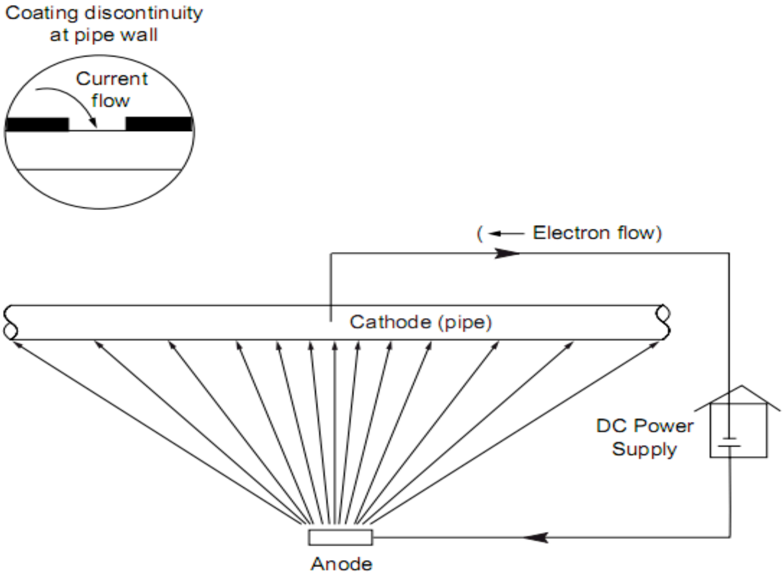

Figure 5: Current flow and distribution in cathodic protection of a pipeline. Note the current flow for a coated pipeline at a coating discontinuity.

In the case of a coated pipeline, it should be noted that current (using the conventional direction) is flowing to the areas as the coating is defective. The non-uniform current flux arising from the particular geometry in Figure 5 is also noteworthy. Furthermore, it should be noted that an electron current flows along the electric cables connecting the anode to the cathode, and ionic current flows in the soil between the anode and cathode to complete the circuit [5].

3.4.1. Types of CP

There are two primary types of CP systems: sacrificial anode (galvanic anode) CP and impressed-current CP. Sacrificial anode CP utilizes an anode material that is electro-negative to the pipe steel. When connected to the pipe, the pipe becomes the cathode in the circuit and corrosion is mitigated. Typical sacrificial anode materials for underground pipelines are zinc and magnesium. Impressed-current CP utilizes an outside power supply (rectifier) to control the voltage between the pipe and an anode (cast iron, graphite, platinum clad, mixed metal oxide, etc.) in such a manner that the pipe becomes the cathode in the circuit and corrosion is mitigated. Schematics of these two types of CP systems are shown in Figure 6 and 7.

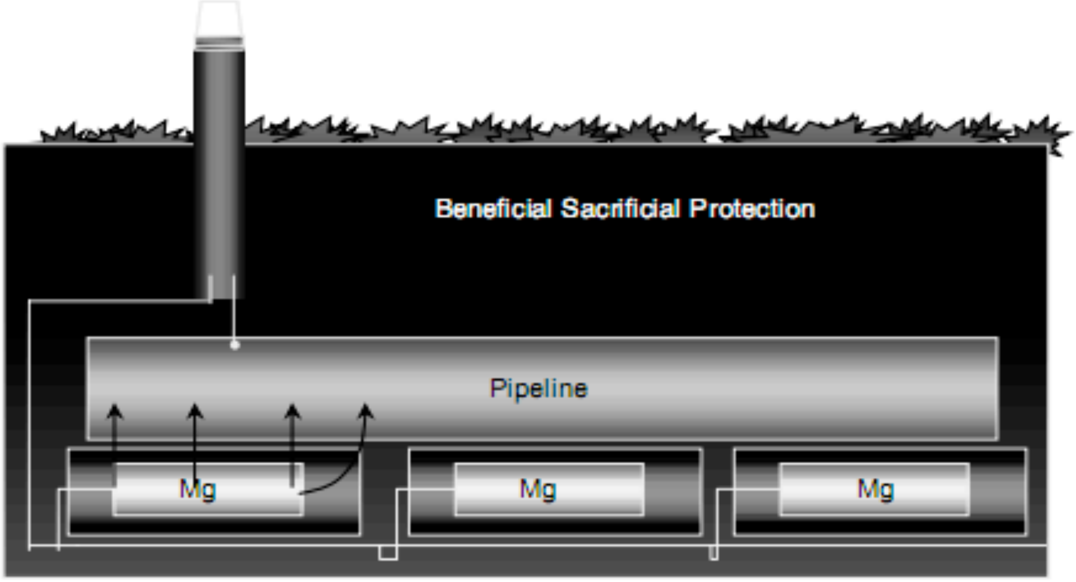

Figure 6: Sacrificial anode CP system with distributed magnesium anodes and an above-ground test station.

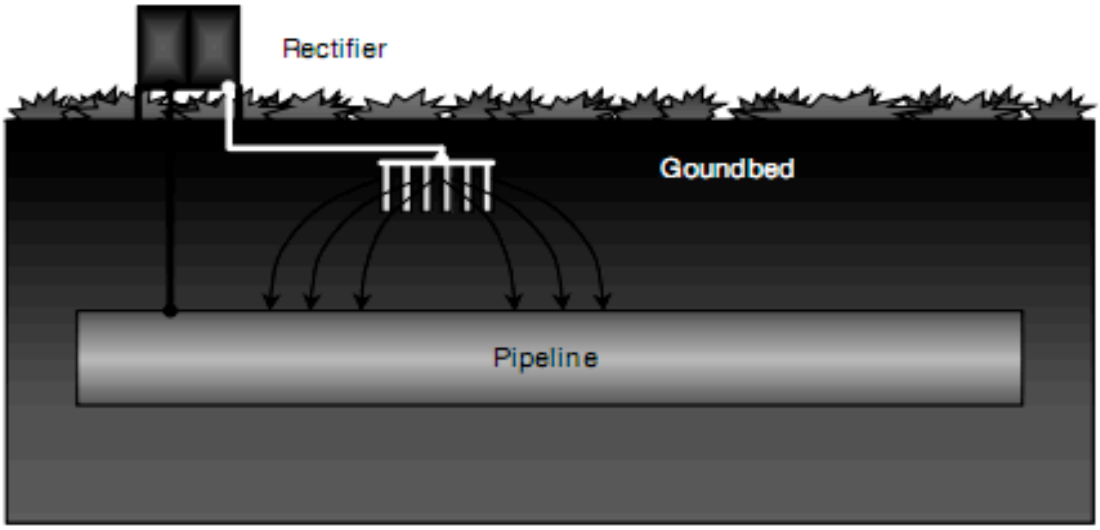

Figure 7: Impressed Current CP system with above-ground rectifier and a single remote anode groundbed.

Cathodic protection is most often used in conjunction with a coating. There are always flaws in the coating due to application inconsistencies, construction damage, or the combination of natural aging and soil stresses. If left unprotected, the pipeline may experience corrosion or SCC where there are coating flaws (holidays). Often the rate of attack through the wall is much higher at the holiday than the general attack of a bare steel surface. The use of a coating greatly reduces the total amount of current required to achieve protection of the pipeline system; therefore, CP and external coatings are utilized together wherever possible. Cathodic protection can be used to control all types of corrosion previously discussed (general, stray current, MIC, and SCC). Sometimes it is difficult to determine the level of CP necessary to mitigate the different corrosion mechanisms and to identify which type of corrosion is present. Stress corrosion cracking presents additional problems. First, the high-pH form of SCC is only found on pipelines protected with CP. The products that result from cathodic reactions occurring on the pipe surface during CP in conjunction with soil chemistry produce the environment necessary for high-pH SCC. Since high-pH SCC propagates only in a very limited potential range, maintaining the potential of the pipe surface outside of this range by proper CP control will prevent growth of the high-pH SCC cracks. In addition, it has been established that proper CP control can inhibit the growth of near-neutral SCC cracks [4, 5].

Conclusions

Corrosion has been the biggest problem with API steel pipeline and other types of pipes used in the oil and gas industry. Oil and gas pipelines which are buried underground and used for the transportation of oil and gas are usually faced with sour corrosion, sweet corrosion, microbiologically influenced corrosion (MIC), differential cell corrosion, stray current corrosion and stress corrosion cracking (SCC). All these various forms of corrosion occurs internally and externally within the pipe and needs to be clearly understood, so as to provide proper control and protection for API steel pipeline and other pipes in the oil and gas industry. The methods necessary for mitigating corrosion problems with API steel pipeline are selection of appropriate materials, use of inhibitors, protective coatings and cathodic protection. Various types of materials have been used in the past as pipeline materials for transporting oil and gas. Proper selection of materials has led to the modern pipeline used in the oil and gas industry today. Although proper selection of materials alone is not enough to combat corrosion in steel pipelines, it is necessary to consider other methods alongside with proper selection of materials, such as the use of inhibitors, protective coating and cathodic protection or a combination of at least two or all the methods, to ensure the corrosion problems are properly mitigated. As far as the oil and gas industry is concerned the cost of mitigating corrosion is little compared to the losses which occur annually in the industry due to the cost of replacing corroded part of the pipeline, loss of oil and gas products and loss of shutdown time when replacing corroded part of pipe. Mitigation of corrosion problems in the oil and gas industry is very important to ensure continuous production and transportation of oil and gas products.

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