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Corrosion Damage of Steel of Floating Oil Storage Tanks

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Abstract
One of the major problems that oil tankers steel face is the corrosion phenomenon that affects all steel structure of the tanker, consequently causes damage to these metals and changes in their chemical and physical properties. This paper aims to investigate the steel damage due to Microbiological induced corrosion (MIC) that occurs in marine and oil industries such as offshore platforms, production plant, pipelines, and floating storage tanks. The bacteria most frequently associated with corrosion of steel are those generate sulphides and these are commonly called sulphate-reducing-bacteria (SRB). Under favourable conditions these bacteria can produce prodigious quantities of sulphide which can precipitate out as metal sulphides, dissolved sulphide or hydrogen sulphide that eventually damage the steel structure. Therefore, this research investigates the corrosion of steel structure of floating oil tanks due to the SRB. Its mechanism and cause are discussed. Severe corroded areas on the bottom shell of the steel tank of the floating oil storage tank were observed. Most of defected areas are related to SRB as the black and red colors associated with the rotten eggs smells were found. This is due to the presence of sulphate and hydrogen in the crude oil. Under favorable conditions, the growth of the SRB and the reduced sulfate reacts with hydrogen exists in the crude oil lead to chemical compounds such as hydrogen sulphide (H_2S) that react with the steel to produce ferrous sulphides and in the presence of water may produce ferrous hydroxides, eventually causing metal loss in the form of pitting corrosion.

1. Introduction

A wide range of bacteria can exist in all areas of oil production facilities including the production plant, pipelines, the water injection plant, the reservoir and, of course, in the cargo tanks on board the oil tanker used to transport the oil. Most microbes produce corrosive acidic compounds. Optimal microbial proliferation and subsequent corrosion inevitably relates to a population of differing but mutually inter-dependent bacterial species rather than individual species. Biocorrosion is an electrochemical process of metal dissolution initiated or accelerated by bacteria and other microorganisms through their metabolic activities [1]. The interaction of bacteria with the metal surface may also result in the formation of biofilms, which can severely affect the kinetics of cathodic and/or anodic reactions in an electrochemical process [2]. Moreover, a synergistic interaction of microorganisms may occur, resulting in biofilms and metabolic products that enhance corrosion processes [3].

The bacteria most frequently associated with corrosion of steel are those that generate sulphides and these are commonly called sulphate-reducing-bacteria (SRB). Under favourable conditions these bacteria can produce prodigious quantities of sulphide which can precipitate out as metal sulphides, dissolved sulphide or hydrogen sulphide. MIC is an electrochemical mode of corrosion that results from microbes that react with the surface and lead to corrosion or influence other corrosion processes of metallic materials [4]. MIC is a form of corrosion produced by living organisms such as bacteria, algae or fungi, those organisms cannot be seen with the unaided human eye, and they are often associated with the presence of tubercles organic substances. MIC encourages the increase in the corrosion rates of a preexisting surface corrosion due to the presence of bacteria that accelerate the rates of the anodic and cathodic corrosion reaction. MIC specifically Sulfate-reducing bacteria (SRB) have been found one of the major corrosion reported cases in oil, gas, and refineries industries [5].

2. Mechanisms of Sulfate-Reducing Bacteria (SRB)

The Sulfate-reducing bacteria (SRB) derive their energy from organic nutrients by oxidizing it or molecular hydrogen (H_2) reducing (SO_4) to (H_2S). SRB's fundamentally are anaerobic which mean that they do not require oxygen for growth and activity, as a result as an alternative to oxygen, and these bacteria use Sulfate. SRB usually grows in the pH range between 4 and 9.5. Sulfate-reducing bacteria (SRB) are most well-known as the bacteria that are associated with high bacterial corrosion rates [6].

The main characteristic of SRB is the use of a sulphate ion as the final electron acceptor in their bioenergetic process. In their metabolic process, sulphate ions are reduced to sulphide ions, which can be present in three forms: H_2S (soluble), HS^- and $S2^-$, depending on the pH of the environment [7]. SRB are anaerobic microorganisms generally found in anoxic environments, such as soil sediment, oil fields and the anaerobic reactors used in wastewater treatment [8]. In oil, gas and shipping industries, SRB are particularly aggressive, generally causing pitting corrosion in metal equipment, which results in high corrosion costs [9].

A theory of "Cathodic Depolarization" suggests that only SRB that are hydrogease-positive are able to consume protons to generate molecular hydrogen and accelerate direct electron transfer between the hydrogenase and the metal [10]. An alternative mechanism considers the formation of an iron/iron sulphide galvanic cell, in which the iron sulphides (FeSx) formed by the precipitation of the biogenic sulphide with ferrous ions act as sites for the reduction of H+ ions to molecular hydrogen, enhancing the corrosion [11, 12]. SRB are nonpathogenic and anaerobic bacteria, but SRB can act as a catalyst in the reduction reaction of sulfate to sulfide [9]. It means they are able to make severe corrosion of metals in a water system by producing enzymes, which can accelerate the reduction of sulphate compounds to H2S [10, 11]. However, to occur this reduction, three components namely SRB, sulphates, free electrons as an external energy source must be present and the water temperature must be less than approximately 65°C [12]. Mild steel, Stainless steel and carbon steel are the most commonly exploited materials in the petroleum realm which are known to undergo from MIC.

The typical electrochemical corrosion depends only on the material, and its chemical medium, however, in SRB-MIC a third element that is the microorganisms in the biofilm should be considered. Figure 1 shows the basic factors that lead to SRB-MIC [7].

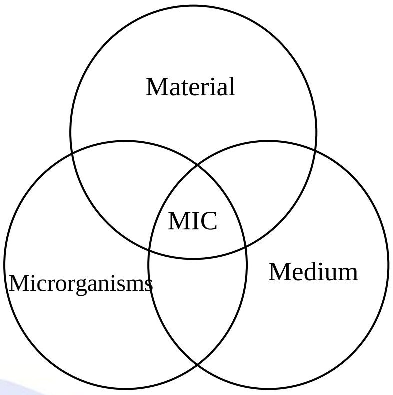

Figure 1 Factors involved in SRB-MIC corrosion.

Another mechanism starts when SRB attach themselves to metallic surfaces, and they start to form a thin film known as "biofilm" that consists of cells immobilized at a substratum, frequently embedded in an organic matrix of microbial origin. The Biofilms are believed to contain typically about 95% water [8]. The importance of biofilms driven from the fact that it represents the predominant form of life of bacteria in natural environments. In other words, the biofilm is the consequence of the development of microbial communities on submerged surfaces in aqueous environments. They usually grow as a general phenomenon that can be observed in almost all media, and at a temperature range between -12 °C to 115°C and in almost all ranges of PH (from 0 to 13) [6]. Upon formation of biofilm, the cathodic polarization theory as postulated by Kuhr and Vlugt, are the most applicable explanation whereby protons may act as an electron acceptor at the cathode in the absence of oxygen, the typical reactions of this theory are provided below:

1. Metal: Anodic reaction $4Fe \rightarrow 4Fe^{2+} + 8e^-$
2. Solution: Cathodic reaction $8H^+ + 8e^- \rightarrow 8H+4H_2$
3. Cathodic Reaction: water dissociation $8H_2O \rightarrow 8H^+ + 8OH^-$
4. Micro-Organism: $SO_4^{2-} + 4H_2 \rightarrow H_2S- + 2H_2O+2OH^-$ (Microbial Depolarization).
5. $Fe^{2+} + H_2S \rightarrow FeS$ (Corrosion Products) $+ 2H^+$
6. $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$ (Corrosion Products)

7. $4Fe + SO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$ (Overall Reaction).

The schematic process of corrosion of ferrous metal due to SRB by the cathodic depolarization theory is shown in Figures 2. It shows iron corrosion mechanism that is based on CDT. In real condition SRB are attached to metal surface but for convenience the bacterial cells are shown separately. At the cathodic site, reducing agents designated as [H] from the iron flow to the bacteria and are used for reduction of sulfate $(So_4)^{2-}$ to sulfide (H_2S).at the anodic site, only one fourth of the dissolved Fe^{2+} reacts stoichiometrically with H_2S to form FeS. In the presence of CO_2 and bicarbonate as common in marine environments, the remaining Fe precipitates $FeCO_3$, in the absence of bicarbonate the more soluble $Fe(OH)_2$ is formed, the total reaction of corrosion is as follows:

$4Fe + SO_4^{2-} + 3HCO3^- + 5H^+ \Longrightarrow FeS+3FeCO3+4H2O$

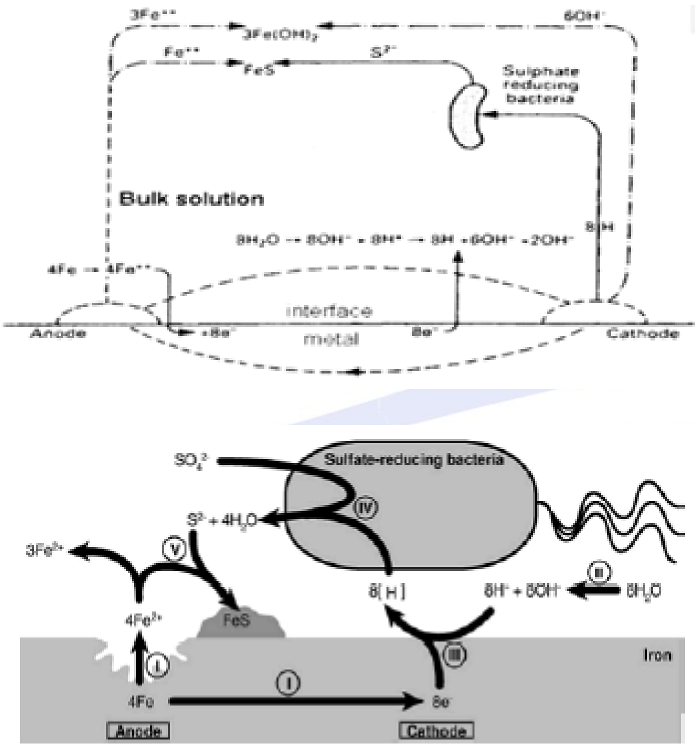

Figure 2 Scheme of iron corrosion by SRB based on cathodic depolarization theory [10].

3. Factors affecting SRB growth

There are many factors that make materials more vulnerable to SRB-MIC as follows:

1. Welding

Welding process produces an altered microstructure with altered mixed composition at fusion and heat affected zones, causing the material more susceptible to SRB.

2. Material Selection

Most common materials used in wide range of industries are susceptible to MIC/SRB with varying degrees and probabilities including carbon and low alloy steels, 300 Series SS and 400 Series, aluminum, copper and some nickel base alloys. For example, the SRB is the main bacteria considered responsible for the microbial corrosion of carbon steel. It has a corrosion rate of between (0.7-7.4) mm/year [3]. However, other studies show that the corrosion rate to be (0.2-0.7) mm/year [8] and all scenario observed depends on the concentration of FeS involved. While in stainless steel, the SRB leads to pitting and crevice corrosion and as a percentage of total corrosion failures for stainless steel systems due to SRB-MIC may be as high as 20% [11].

Copper: SRB-MIC leads to pitting and in the presence of high chloride concentrations, the copper chloride gets deposited between the copper metal and the cupper film resulted in pitting corrosion leads to the final pin-hole failure [12].

3. Excessive water washing

Crude oil cargoes can cause a waxy layer to form on the cargo tank steel structures and this layer helps to inhibit corrosion. However, washing mediums such as hot and cold sea water can remove this protective layer and thus allow the corrosion process to start. The integrity of the protective layer is also reduced by an increased frequency of crude oil washing.

4. High sulphur content of cargo oil

Crude oils that contain high concentrations of sulphurous constituents can cause high levels of general and pitting corrosion when these components react with entrained or residual sea water to form acidic compounds. In addition, sulphur is cathodic by nature and can promote the formation of an active corrosion cell.

5. Water in cargo oil tanks

Residual water in cargo oil tanks can originate from a number of sources and when it settles out from the cargo can cause electrolytic or microbial influenced corrosion of structural components, particularly on after end tank bottom plating around the suction bell mouths where water tends to accumulate due to the trim of the ship.

6. High Temperature

The double bottom spaces of a double hull tanker act as a thermal barrier which effectively insulates the cargo tanks from the cooling effect of the sea. Consequently, the cargo tank structure is less subject to temperature change reflecting changes in ambient sea temperature and tends to remain close to the cargo loading temperature. After cargo discharge, the steel structure remains at an elevated temperature for some time until such times as it is cooled by ambient air or adjacent ballast tanks being filled by water. The temperature differential between sea and cargo tanks during the ballast voyage has been reported as high as 150^{o}C. High temperatures lead to an increase in general corrosion. It has been reported that the corrosion rate doubles for every 100^{o}C increase in temperature. High temperatures can also lead to an increased bacterial growth rate and consequent increase in microbial influenced corrosion rates. Wing tanks of single hull tankers also provide an insulating thermal barrier for centre cargo tanks.

4. SRB in Floating Oil Storage Tanks

This section presents a corrosion inspection of a floating oil storage tank. It is well known that when bacteria find a place on steel surface they can grow and a corrosion pit develop at the site. Pitting corrosion in tanks contaminated with sulphate reducing bacteria (SRB) is caused when substantial aerobic populations of microorganisms inhabit the tank and create the conditions necessary for SRB proliferation. The environmental conditions preferred by SRB include zero dissolved oxygen, water and the presence of soluble organic nutrients. Aerobic micro-organisms use up oxygen and the oxygen deficient zone formed is anodic in relation to adjacent relatively oxygen rich zones thus causing anodic corrosion pits to develop. Temperatures above ambient suit most SRB and they are known to inhabit sea water and the produced water associated with crude oil from older reservoirs where the necessary nutrients for their growth may be found.

Figure 3-A shows a blisters and coating failure as the initiation process that leads to SRB corrosion. The black colour for the coating and steel surface is an evidence of the presence of the SRB corrosion causing bottom plate coating failure. Underneath blisters, oxidation occurred and steel become brown as shown in Fig 3-B. An evidence of the presence of Hydrogen Sulphied was also observed due to the brown colour and rotten eggs smells.

A B

Figure 3 Coating failure due to the presence of the SRB on the bottom plate.

The SRB corrosion is observed as localized pitting under deposits that shield the organisms. The Damage is often characterized by pits in carbon steel as in Figures 4 and 5. The figures show blistering precedes the coating failure and initiation of pitting corrosion. This blistering occurred as a result of deficiency of coating binding to the tank surface which allows the crude oil contents to react or enter in the coating-surface interface at weak positions of the coating. The presence of the SRB that produces sulfate can be the cause which reacts hydrogen leading to chemical compounds as H_2S that react with the steel to produce ferrous sulphides or ferrous hydroxyl, eventually causing metal loss in the form of pitting corrosion. The localized pitting initiation observed varies between 1-3 mm in depth. Furthermore, these pittings can act as stress corrosion cracking (SCC) initiator; because the “roots” of pits act as “stress magnifies” so that the applied stress becomes multiplied several times, resulting in stresses far more than the tensile yield strength, thus producing failure [7].

Figure 4 Initiation of pitting corrosion.

Figure 5 Coating defects and pitting corrosion.

The environmental conditions preferred by SRB include zero dissolved oxygen, water and the presence of soluble organic nutrients are exist in oil tanks. It would appear that, as crude oil is often loaded at temperatures higher than ambient air and sea temperatures, during the loaded passage the temperature of the cargo tank structure is being maintained at higher levels than normal due to the insulating effect of the double hull spaces. The presence of the SRB that produces sulfate which reacts with hydrogen exists in the crude oil leading to chemical compounds that react with the steel causing metal loss in the form of pitting corrosion. The environmental conditions preferred by SRB include higher tank temperatures, coupled with residual water in the cargo tank can offer favourable conditions for SRB anaerobic bacteria to proliferate, and activate the formation of corrosive cells on the surface of the inner bottom. Water exists on the surface of the bottom tank plates accelerates the chemical reaction process producing ferrous oxides that destroy the metal surface.

The high coating thickness and rapid curing of the coating, before evaporation of solvents results in excess solvent inside the coating. Later, when the solvent evaporated, this caused a material loss leading to contraction and stress inside the coating. In addition a high coating film thickness amplified the effect. The stress may result in cracking, or cause the coating to loosen from concave shaped surfaces. Underneath the loosened coating, pitting corrosion with up to 10 to 15 percent wall thickness reduction was observed. It is believed that the pitting was initiated by Sulphur Reducing Bacteria (SRB).

6. Conclusions

Mechanism of Sulfide--Reduced-Bacteria (SRB) based corrosion has to be well understood in order to get better result in corrosion inhibition. Various possible mechanisms of SRB corrosion in steel-oil/water interface were considered. Depending on the environmental condition, one mechanism or a combination of several mechanisms can occur. It was shown that corrosion defects in the form of pitting corrosion was observed in bottom steel plates of crude oil tanks due to the presence of Sulfide-Reduced-Bacteria (SRB) as a result of the hydrocarbon content of the crude. The process could possibly began with blistering, coating failure at less density areas, then bare steel becomes exposed to crude oil where the SRB produced sulfate reacts with hydrogen leading to chemical compounds that react with the steel causing metal loss in the form of pitting corrosion. Therefore, to protect steel plates from SRB corrosion a proper protection system should be used, and coating systems should be selected and applied adequately.

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