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A Critical Review on Corrosion and its Prevention in the Oil field Equipment

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Abstract

Corrosion in the petroleum industry is one of the crucial failure has to take in consideration in the design of the oilfield equipment due to not only reducing economic losses but also to safe and protect the resources. Thus, various experimental and numerical studies were performed to understand the mechanisms and rules of corrosion types occurred in the oil and gas production fields and determine the factors affecting these types. The current investigation is aimed to comprehensively review different types of corrosion took place in the oilfield and flow line equipment and how they can be prevented. The effect of diverse harsh working environmental representing by the existence of high content of corrosive gases (e.g., carbon dioxide (CO_2)and hydrogen sulfide (H_2S)) is also considered. Additionally, different types of protection methods used to prevent the corrosion or at least reduce the corrosion rate including inorganic inhibitors (e.g., anodic and cathodic protection methods), organic inhibitors (e.g., film former or coating) and maintain the environmental conditions (e.g., scavengers and biocides) are considerably presented.

Keywords: sweet corrosion, sour corrosion, oxidation corrosion, corrosion inhibitors, petroleum industry, review.

1- Introduction

Corrosion of metal in oil and gas well production systems is a serious problem and a dangerous mode of failure due to the fact that corrosion may not only cause economic losses but may also bring with it problems of protection and safety of resources. Thus, understanding the mechanisms of corrosion occursin the oil and gas systems at all stages from down hole to surface equipment and processing facilities is crucial in order to make a rational corrosion prevention design and benefit the exploration and development of oil and gas fields [1]. To understand this concept, it is essentially understanding the operating environments of the oilfields production systems and standing on the factors affecting the corrosion problem. So, some oil and gas wells have adverse operating environments representing by presence of corrosive materials such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S)and chloride anions which exacerbate the corrosion. Also, most oil and gas wells include co-produced water injected during water flooding and condensate water with high-concentration chloride ions and acetic acid as well as oxygen that enters the well during well construction and down hole operations like acidizing [2]. Hence, water is always an element of oil and gas reservoirs and therefore there is a potential of corrosion. The relative amount of the produced water is usually known as "water cut" and it is defined as:

$$\text{Water cut} = \frac{water\ production}{Oil\ plus\ water\ production} \times 100\ \% \qquad \ldots.\ (1)$$

Qing et al.[3] proposed a combined technology of the corrosion inhibitor huff & puff and a selective water shutoff agent (gel treatment) to solve the problem of a high water cut and serious corrosion in the oil wells. The technology showed a successful multi-purpose of decreasing the water cut, inhibiting the corrosion in the pipe string and then increasing the oil production.

In addition to the above mention edparameters, there are others considerably affect the corrosion severity in the oil and gas production systems. They are in situ pH value, fluid dynamics, temperature, pressure and gas to oil ratio. The material selection and its structure, galvanic coupling, stray currents and microbes areother important components affecting the corrosion prevention design[4].Numerous review articles[5-13] have broadly summarized previous published experimental and numerical studies conducted the most common types of corrosion occurrences in the petroleum industry systems and their mechanisms such as electrochemical corrosion, chemical corrosion, environment-assisted fracture, stress corrosion and flow- and phase change–induced corrosion. It was noted from the literatures that general corrosion and localized corrosion are commonly occurred in tanks, casings and tubing, and internal corrosion or corrosion/erosion occurred in the wellhead assembly, operating pipelines and other equipment due to stress corrosion cracking (SCC). It was also noted that galvanic corrosion is rarely occurred in the wells consists of tubing string made of corrosion-resistant alloy in contact with lower-grade steel casing associated with crevice corrosion in the occluded area between tubing and casing due to the use of different dissimilar materials. Other studies [14-17]reviewed the use of protection ways in the oil and gas industry in which corrosion inhibitors (CIs) and catholic or anodic protections can possibly being used for preventing the corrosion problem or reducing its rate. Several kinds of corrosion inhibitors could restrict the occurrence of corrosion for a short time period and most others could not completely inhibit the corrosion. The operation factors those affecting the selection criteria of the corrosion protection and corrosion inhibition were also discussed. However by yet, there is no overview study explaining the behavior of corrosion and its types and mechanisms in the oil and gas industry in the relation of production environmental conditions and how they can be prevented.

This research aims to explicitly identify the role of oil environmental factors(e.g., flow, pressure, temperature, oil phase and water phase) and the rate at which the corrosion occurs in the oil and gas equipment. The influence of the produced water content i.e., anionic species (e.g., chlorides, sulfides, sulfates, carbonates and bicarbonates) and cationic species (e.g., ferrous, ferric, magnesium, strontium, calcium and barium)on the type of corrosion is discussed. In additions, the effect of other oil components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), Oxygen (O_2), solids and microbes as well as the pH value, organic acids and mercury on the initiation of corrosion and its mechanism is also explained.

2. Types of corrosion in the oil and gas equipment

Generally speaking, all of the facilities used in oil and gas production systems have the potential of the corrosion failure. Two types of corrosion are normally occurred in oil and gas well production systems, are internal corrosion and external corrosion. Internal corrosion takes place in the inner walls of the tubing, casing, wellhead assembly, field equipment and the operating pipeline. External corrosion takes place in the outer wall of the casing and cement sheath contacting with the produced water that contains corrosive components or with the produced oil that contains high content of CO_2, H_2S, and elemental sulfur and the high-salinity formation water [2]. The sedimentation of the elemental sulfur and hydrate and scale formation may block the flow passage resulting in complicated down hole operations and then irregular production. When studying and analyzing the corrosion in the oil wells, working environmental conditions, corrosive media or gases in produced fluid and their concentrations, the material selected and its structure, and so on are required to be understood for indicating the severity of corrosion is related to which and indicating the interaction among them. In light of that, Table **(1)** showing different categories of corrosion related failures registered through the Britoil operations from 1978-1988.

Table (1) Frequencies of different categories of corrosion [5]

Type of failure	Frequency (%)
CO_2 related corrosion	28
H_2S related corrosion	18
Preferential weld	18
Pitting corrosion	12
Erosion/Corrosion	12
Galvanic corrosion	6
Crevice corrosion	3
Stress corrosion	3

From the table, it can be noted that CO_2 related, H_2S related and preferential weld corrosion had the major frequencies and the crevice corrosion and stress corrosion had the minor frequencies of corrosion related failure in the oil wells. As example, ahigh concentration ofcorrosive gases(H_2S or CO_2) and a total pressureis not high may have an effect is not moresevere than that of a lowconcentration of corrosive media and a high totalpressure. In general, the more severe corrosion is with the higher partial pressureof corrosive gases. Systemwith high total pressure may also have partial pressureof H_2S or CO_2 and thus it may generate moresevere corrosion than that of a system with a low total pressure and highcontents of H_2S orCO_2.

2.1 Oxygen (O_2) related corrosion

Oxygen is one of the primary chemical kinds that responsible for the corrosion in oil production equipment. The O_2 causes corrosion in diverse areas including instant pitting due to dissolved oxygen corrosion, water injection tubing shown in Figure (1) and surface processing. The corrosion in the surface processing often occurs during oil treatment as much of this is typically performed near to ambient pressure which allows for easier ingress of oxygen through leaking seals, vents, etc. Moreover, the chemical agent is responsible for much of external corrosion in the oil and gas facilities.Liu et al. [18] studied the influence of produced water with high salinity and corrosion inhibitors on the corrosion of water injection pipe under the static or dynamic condition. It was found that the pipe corrosion was mainly resulted from the dissolved O_2, $Ca^{2+}$and other inorganic salts in produced water.

2.1.1 Factors affecting the O2 related corrosion

When the oxygen attacks the carbon steel surface, there are two reactions occur, one is the cathodic reaction where the oxygen is directly involved in, and the other is the anodic reaction that leads to dissolve the iron.

Cathodic reaction (orReduction reaction): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Anodic reaction (or Oxidation reaction): $Fe \rightarrow Fe^{+2} + 2e^-$

Fig.(1) Corrosion in water injection tubing [6]

The flux of the dissolved oxygen at the cathodic sites or the corrosion rate is typically controlled by cathodic reaction (O_2 reduction) which is affecting by three primary parameters, are concentration of O_2 in the solution, mass transfer of O_2 to the surface, and temperature. Increasing the value of any one of the first two parameters frequently leads to increase the corrosion rate due to raising of the surface oxygen flux [7].The maximum allowable concentration of O_2in the oil and gas systems that maintaining a good corrosion controlis 20 ppb (part per billion) which means that if the dissolved O_2 concentration is greater than 20 ppb then control methods should be applied. However, under the circumambient conditionsor under turbulent conditions (greater mass transport), water in equilibrium with air contains about 6-8 part per million (ppm)O_2 and this concentration is enough to induce a significant corrosion rate[7].To estimate the O_2 related corrosion rates of carbon steel in the oil and gas equipment, the following equation can be used[8]:

$$I_{lim} = 4\,F.K.C \ldots\ldots\ldots (2)$$

where$I_{lim}$is the limiting current density of the cathodic reaction, F is the Faraday constant, K is the mass transfer coefficient and C is the bulk concentration of O_2.In the oil and gas production equipment, local diversity in oxygen concentration could result in a localized corrosion through the formation of differential aeration cell as shown in Figure (2). The oxygen concentration inside the celldepletes and becomes Anode relative to the environment outside which becomes cathode and corrodes. Moreover, Figure (3**)** shows another exampleof localized corrosion that occurred in the external surface pipeline due to the differential aeration where the pipe is sitting on the ground where it is in contact with the earth [10].Also, Hua et al [19] evaluated the corrosion behavior of X65 carbon steel in supercritical CO_2-saturated water and water-saturated/unsaturated supercritical CO_2at 80 bar and 50 °C to simulate conditions of CO_2 transportation in carbon capture and storage applications. It was shown that corrosion occurred when under-saturated water was present in the system and a localized corrosion was a fundamental consideration in all environments, particularly in water-containing CO_2 systems. However, no dissolution of the steel was observed at water contents below 1600 ppm at the considered conditions.

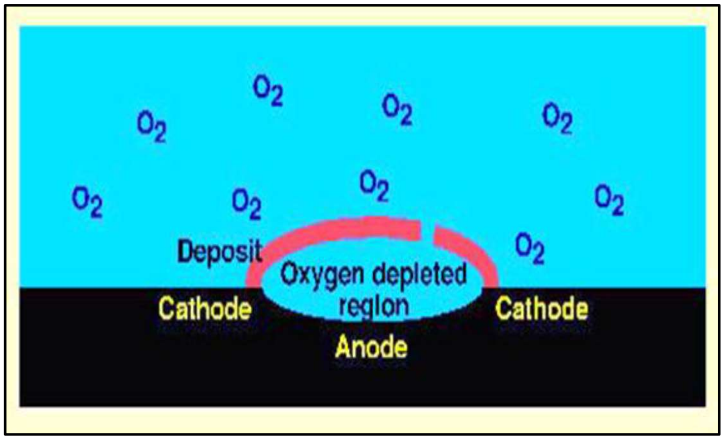

Fig. (2) Local corrosion beneath deposit[9]

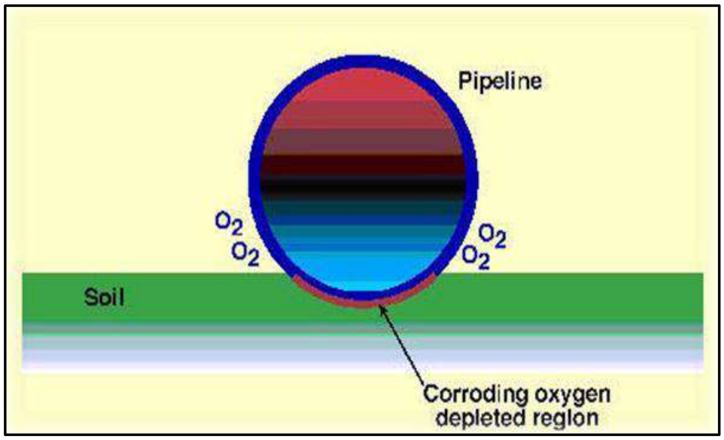

Fig. (3) External differential aeration cell[10]

2.2 Sweet corrosion

In oil and gas production equipment, carbon dioxide (CO_2) is the primary cause of corrosion commonly known as sweet corrosion. It makes from carbon steel and tends to form acidic solutions when mixes with water (corrodible substrate). The corrodant is H+, derived from carbonic acid (H_2CO_3) and the dissolution of CO_2 in the produced brine. The CO_2gas can be found either as natural component of the reservoir or it is introduced during some operation like injection of the CO_2 into the reservoir through the enhanced recovery operations. If the CO_2isa dry gas, it would not be corrosive [2].

2.2.1 Mechanism of sweet corrosion

To understand the mechanism of sweet corrosion in carbon steel, it essentially understands the formula of Anodic reaction and cathodic reaction occurrence of Fe in strong acids. The accepted mechanism of anodic dissolution for Fe is [20]:

$Fe + H_2O \longrightarrow FeOH + H^+ + e^-$

$FeOH \longrightarrow FeOH^+ + e^-$(rate determining step)

$FeOH^+ + H^+ \longrightarrow Fe^{2+} + H_2O$

The initial step of sweet corrosion with presence of $CO_2$is:

$Fe + CO_2 \longrightarrow Fe\text{-}CO_2$ (Adsorbed Surface Complex)

The resulted adsorbed surface complex then reacts with water (H_2O) to give Fe^{2+}(aq) and a weak acid (H_2CO_3) that can provide the cathodic reactant H^+ during dissociation. So, the mechanism of Cathodic reaction is:

$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$

$2H_2CO_3 + 2e^- \longrightarrow H_2 + 2HCO_3^-$

The dissociation of H_2CO_3 in solution leads to produce hydrogen ion for cathodic reaction or the H_2CO_3 itself could be adsorb at the cathode and beingdirectly reduced.

$H_2CO_3 + e^- \longrightarrow H + HCO_3^-$

2.2.2 Factors affecting sweet corrosion

Although a number of studies considering the CO_2 corrosion have been done under varying environmental factors such as pressure, temperature, pH value. The correct cathodic reaction pathway is still controversial subject and uncertain. The corrosion mechanism with the change of the pH shown in Figure (4), indicated that when pH is lower than 4the direct hydrogen ion reduction is dominate while the reduction of adsorbed H_2CO_3 becomes important when the pH is in the range of 4-7[21].

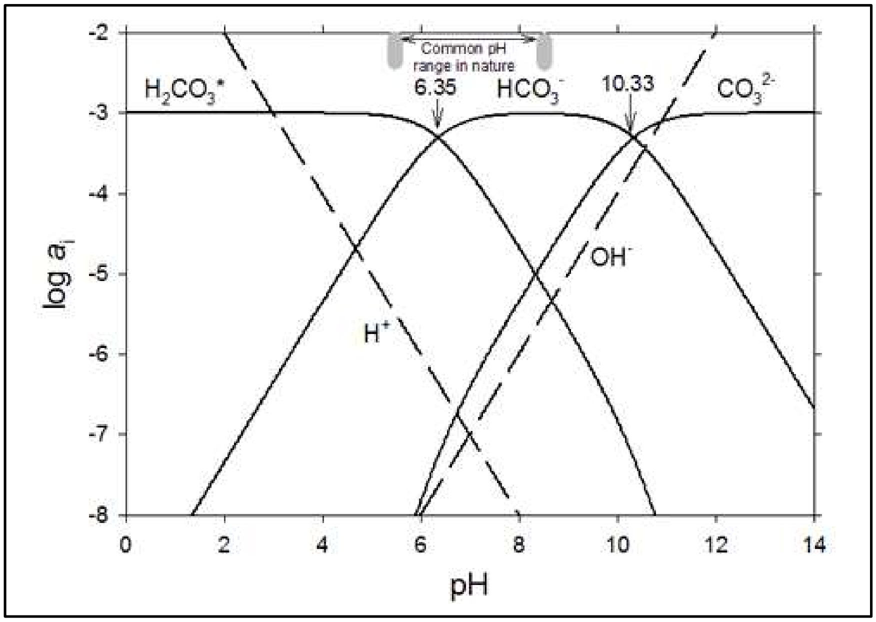

Fig.(4) Showing Bjerrum plot of the activity (concentration) of the various ions in the CO_2-H_2O system as a function of the pH value. $H_2CO_3$is sum of $CO_{2(aq)}$ and $H_2CO_{3(aq)}$)[21]

If the partial pressure of CO_2 (P_{CO2}) increases, the rate of corrosion increases due to increasing the amountof the $H_2CO_{3(aq)}$ and $CO_{2(aq)}$.

$CO_{2(g)} \leftrightarrow CO_{2(aq)} + H_2O_{(L)} \leftrightarrow H_2CO_{3(aq)}$

The corrosion rate is categorized as serious corrosion when $P_{CO2} > 0.2$ MPa, mild corrosion when $P_{CO2} = 0.02–0.2$ MPa, and No corrosion with $P_{CO2} < 0.02$MPa [2].

The rate of sweet corrosion in mild steel is also influenced by solid corrosion products such as siderite ($FeCO_3$). The $FeCO_3$ can significantly delay the corrosion rate by forming a film protective layer acts as a barrier for the species diffusion involved in the corrosion. The layer is nonconductive and so it does not act as a cathode. The degree of protection depends upon environment and characteristic of the carbon steel [22].

Temperaturealso plays a role in changing the rate of CO_2 corrosionwhere at lower tempertures (<70^{o} - 90^{o}C), the rate increasesdue to increasing the mass transfer and decreasing the $FeCO_3$protective scale. At high tempertures (>80^{o} - 100^{o}C), the corrosion rate often decreases due to losing the solubility of iron carbonate that leading to form the $FeCO_3$protective scale.

The fluid composition or the ratio of water/oil/gas and their flow rate are also effected the severity of CO_2 related corrosion. For instance, there is no corrosion occurred at lower water cut ratio i.e., water wetting does not occur or an oil layer prevents contacting water with the carbon steel surface. However, a higher corrosion rate is occurred at a high water cut ratio due to increasing the flow rate and increasing reactant flow/protective film dissolution [22, 23]

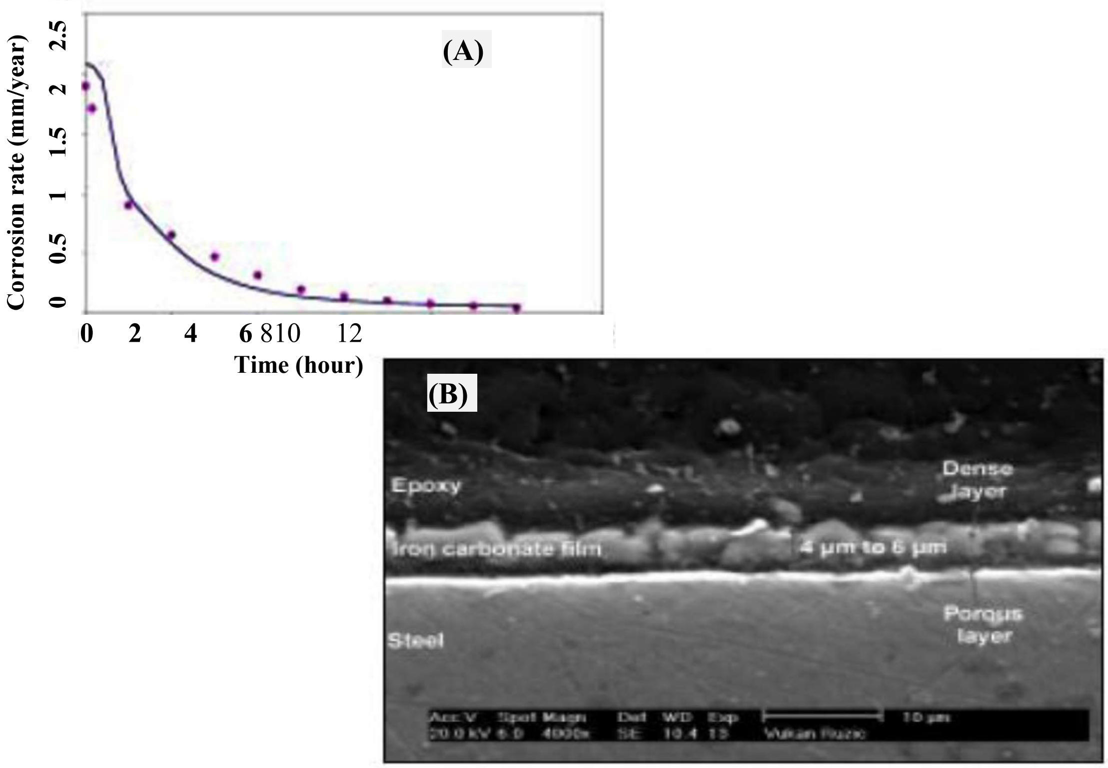

Fig.(5): (A) Plot of the corrosion rate as a function of time for steel sample exposed for 10 hours at temperature of 80^{o}C, pH is 6.6 and the partial pressure of $CO_2$is 0.54 bar; and (B) SEM image of steel sample with $FeCO_3$ film after exposed for 10 hours[23]

In line with that, Kadukova et al. [24] investigated the main effects of three different environmental factors i.e., soil characteristics, water presence, and location on the biocorrosion behavior inburied natural transmission gas pipelines. It was found that biocorrosion or microbiallyinfluenced corrosion (MIC) is one of the major indication of pipeline failure that affecting the operation and maintenancecosts of petroleum underground pipeline industry. Sanders et al.[25] studied the influence of the formation of calcium carbonate scale on the occurrence of the CO_2 corrosion. Surface scaling rarely occurs in the pipework during oil and gas production when no corrosion exists. Lua et al.[26]also investigated the effect of different severe environmental factors (high pressure and high temperature)on the performance of high strength 15Cr martensitic stainless steel in—live acid (10% HCl + 1.5% HF + 3% HAc + 5.1% corrosion inhibitor) and in spent acid and formation water containing CO_2. The results showed that corrosion of stainless steel in-live acid was most serious uniform corrosion than that in spent acid and formation water containing CO_2. Additionally, the actual operational parameters of subsea multiphase pipeline such as dynamic, high temperature autoclaveon their internal corrosionusing the partial pressure of CO_2, velocity of the corrosion medium, temperature, and corrosion timewere conducted by Peng and Zeng[27]. It was noticed that CO_2caused a severe localized corrosion with an increased rate as the partial pressure and velocity increased. Thatcorrosion rate increased first and then decreased with increasing temperature.

Using polarization curve technique, electrochemical impedance spectroscopy, weight loss test, scanning electron microscope and X-ray diffraction, corrosion behavior of N80 carbon steel that contacts with formation water containing CO_2 was studied by Zhu et al.[28]. The effects of temperature and acetic acid concentration on that corrosion behavior were also studied. Increasing temperature not only enhanced the dissolution of steel substrate, but also promoted the precipitation of $FeCO_3$ which was the main corrosion product. The addition of acetic acid enhanced localized corrosion attack on N80 carbon steel and there was a transition region between CO_2 corrosion control and HAc corrosion control.Similarly, Zhang et al. [29] also investigated the effect of HCO_3concentration on sweet corrosion of steel X65 using polarization measurement of potentiodynamic scans and weight-loss method under high pressure and high temperature. The corrosion rate decreased with the increase of HCO_3 concentrationwhile the value of pH for the solution increased.

In additions, number of experimental studies have conducted the CO_2 corrosion with presence of corrosion films formed on X52 pipeline steel by voltammetry using different switching potentials and immersion in simulated acid sour media (NACE ID182)[30] , and formed on 3 % Cr-steel pipes after corrosion in simulated CO_2-enhanced oil recovery brines[31]. It was observed that a thin layer of $FeCO_3$ and FeO is formed onthe steel surface which acts as initial pseudo-passive layer and consequently gives indications for long-term corrosion performance.

While Barmatov et al.[32] claimed that the corrosion rate of low carbon steel fully coated with an inhibitor film formed through the immersion in 4 M HClslightly increases with increasing flow velocity which can be attributed to a partial erosion of the inhibitor film. When the coverage is in the lower range, the corrosion occurs at the diffusion limit and an increase in flow velocity causes a strong decrease in corrosion rate due to an increased rate of mass transport of the corrosion inhibitor to the metal surface.

2.2.3. Types of Sweet Corrosion

In oil and gas equipment, the sweet corrosion generally involves several types of localized and general corrosion as shown in Figure (6). Within the localized corrosion, a simple metal dissolution followed by pitting is normally occurredthat resultsdue to the breakdown of the protective passive film on the metal surface. The pitting leaves distinctive patterns such as "mesa-type"corrosion that occurs in low to medium flow regimes and attributable to the metallurgical processing used in manufacturing the tubing, groves and channels. Tapered and smooth side pitting corrosion that occurs in stagnant to moderate flow conditions. Ringwormcorrosion is caused when welding is not followed by full-length normalizing of the tubular after processing and "raindrop attack" occurs when gas condenses wells or water condenses on metal [2, 4].

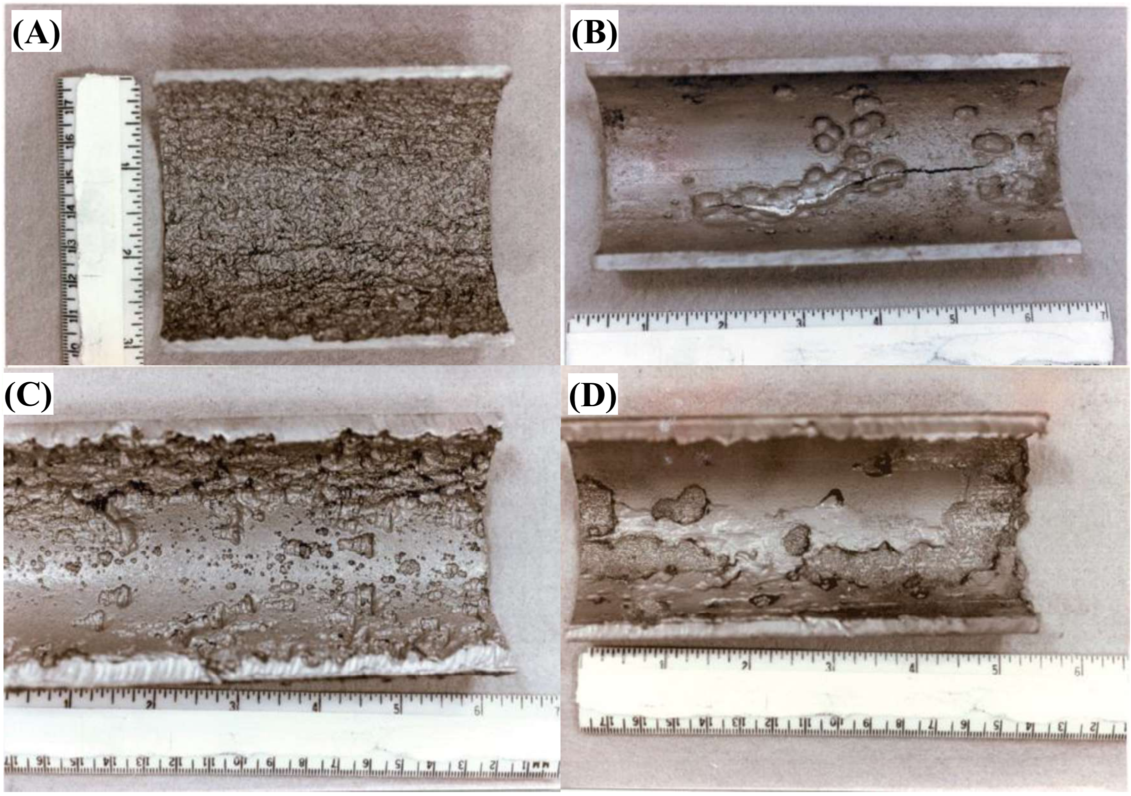

Fig.(6) Types of sweet corrosion, (A) General corrosion, (B) Pitting corrosion, (C) Raindrop attack, and (D) Mesa-type corroison[4]

2.3 Sour corrosion

Hydrogen sulfide (H_2S) is a toxic and the main corrosive gas responsible on the occurrence of H_2S related corrosion (sour corrosion).

2.3.1. Mechanism of sour corrosion

When H_2S is souble in water, several reactions of carbon steel are occurred as follows [2]:

$Fe \longrightarrow Fe^{2+} + 2e^{-}$(Anode)

$2H^{+} + 2e^{-} \longrightarrow H_{2(g)}$(Cathode)

$H_2S_{(g)} \longleftrightarrow H_2S_{(aq)} \longleftrightarrow H^+_{(aq)} + SH^-_{(aq)}$

$Fe_{(s)} + H_2S_{(aq)} \longrightarrow FeS_{(s)} + H_{2(g)}$ (Solid state reaction)

At the anode Fe^{2+} ions are produced from carbon steel and it react to form solid corrosion products such as iron sulfide (FeS) which is black in colure and it can form a protective scale reducing the corrosion rate [2]. The $FeCO_3$ precipitates out of solution not as solid corrosion product.

2.3.2. Factors affecting sour corrosion

The H_2S corrosion rate is controled by a number of interdependent factors rather similar to these of the CO_2 related corrosion are:

- H_2S partial pressure: Increasing the partial prssure of H_2S with decreasing pH likely leads to a cathodic cracking mechanism and then the occurance of sulfide stress cracking (SSC) which is a form of hydrogen embrittlement. When the H_2S partial pressure is less than 0.3 kPa (0.05 psi) so the SSC would not be a problem.
- Temperature: At lower temperature, general and pitting corrosion rate are often acceptable due to presence of protective FeS film while at higher temperature about110°C,FeS film is not protective and it will be porous.
- Steel composition and microstructure:This has a direct effect on corrosion rate since steel composition can affect passive film stability and phase distribution (e.g., Chromium in stainless steel), minor alloying elements can cause local changes in passive film forming element (e.g., Carbon in stainless steel causing sensitization), and impurity elements can segregate to grain boundaries and cause local crack tip chemisrty changes as the carck intersect them like manganese sulfide in steel [33]. For further information, a review article was concluded the role of materials developments for supercritical water reactors focusing mainly on the nuclear reactor applications and changing the chemical composition and microstructure of the near surface regions on the corrosion and degradation mechanisms and the selection criteria of materials. In additions, fluid composition and flow is also a factor affecting the corrosion rate.

Using electrochemical impedance spectroscopy (EIS), the effect of sulfate reducing bacteria (SRB) on the corrosion of the Q235carbon steel was investigated in the crevice under the simulated disbonded coating in the soil-extract solutions (SES) by Xu et al.[34]. The results showed that the corrosion rate is inhibited in the SES with SRB during the stationary phase of SRB, but enhanced during the death phase. The comparison of the polarization (Rp) and the charge transfer resistances (R_t) has indicated that the biofilm seriously influences the reactive procedure of metal/solution interface. SRB is found in the pits on the surface of the steel as shown in Figure (7).

Fig.(7) Corrosion pit in a sour regime

Also, the hydrogen permeation of X80 pipeline was conducted under superficial stress and cathodic protection by mechanical abrading in the presence of sulfate-reducing bacteria (SRB)[35]. The mechanical abrading process tends to increase the surface area ratio and introduce compression stresses on the steel surface. The effects of five different factors named pressure of CO_2, pressure of H_2S, temperature, content of Cl^-, and water cutand the relative anti-corrosion methods on the corrosion rate of the sulfur-resistant tubing were also studied by Qiu et al.[36]. It was found thatCO_2 pressureis the major corrosion factor.

2.3.3 Types of sour corrosion

In addition to general corrosion and pitting corosion as types ofH_2S related corrosion, there are other types of cracking induced H_2S related corrosions shown in Figure (8), including gsulfide stress cracking (SSC), step wise cracking (SWC) (or hydrogen-Induced cracking (HIC) or hydrogen pressure induced cracking (HPIC)), and stress oriented hydrogen induced cracking (SOHIC) [2,33]. The sulfide stress cracking (SSC) is formed due to presence of atomic hydogen in solid solution in bulk that decreases the ductility and deformability. Also, tensile stress can easily form cracks which are running perpendicular to the stress direction.

The step wise cracking (SWC) or hydrogen-induced cracking (HIC) occurs in susceptible steels exposed to aqueous environments containing hydrogen sulphides. The HIC is intially induced due to accumulates of H_2 at trap sites(e.g., voids associated with inclusions)forming local cracks and blisters that grow strains surrounding the substrate and neighbours which then form a linked array and cause equipment failure. The stress oriented hydrogen induced cracking (SOHIC) is occurred due to interaction between tensile stress and hydrogen induced blisters and cracks. Ladder-like crack arrays form running approximately perpedicular to stress dirction [37].

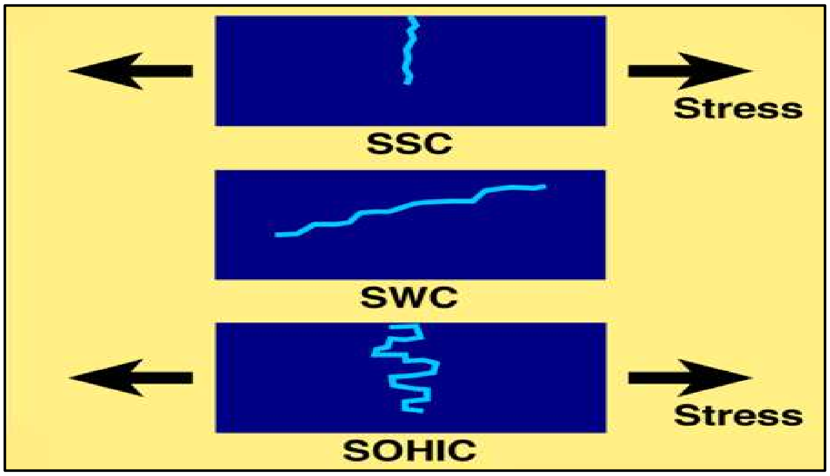

Fig. (8)Types of cracking in a sour environment

Ren et al[38] evaluated the use of single piece of C110 carbon steel of casing or tubing and combinational metals of C110 steel and G3 alloy of string connected by a thread joint under different stresses in deep sour gas wellsunder high-pressure (65 MPa) and high-temperature (120°C) autoclave containing brine water for seven days and dissolved H_2S, $CO_2$and elemental sulfur.The results showed that complex corrosion can occur around the contact partincluding general, galvanic, and stress corrosion and the sour corrosion of C110 steel in the vapor is similar to that in solution.

3. Corrosion Inhibition

There are several methods can be applied to delay the corrosion in oil and gas industry including methods based on modification of the environment(e.g., adjusting the pH, de-humidification of the air, and the addition of inhibitors), methods based on modification of the metal (e.g., adding of alloying elements, and heat treatments), and methods based on protective coating (e.g., coating by a reaction product either chemical or electrochemical treatment of metal surface, organic coating such as paints, resins, inorganic coating, and metal coating).

3.1. Definitionof corrosion inhibitors

Corrosion inhibitors are chemical substances or reagents which when added in small concentrations to the system will minimize or prevent corrosion.Corrosion inhibitors are capableto convert an active corrosion processinto a passive process without disruption of a process. Corrosion inhibitorsare used internally withcarbon steel pipes and vessels as an economic controlalternative to alloys and stainless steels, or externally as coatings on non-metallic components [39, 40].

3.2.Importance of corrosion inhibitors

The importance of corrosion inhibitors is to control the corrosion process in many environments, however there aresome certain exceptionslike equipment subjected toturbulent flow, systems operating above the stability limitsof inhibitor, and equipment subjected to high velocitybeyond 4 m/s[39]. Thus, several factors need to be considered in order to improve the efficiency of inhibition such as regular cleaning of pipelines by using pigging process, reduce the stagnation of fluid due to shut down of the well and regular monitoring the efficiency by analysis the inhibitor concentration.

3.3.Classification of corrosion inhibitors

There are three main kinds of liquid-phase corrosion inhibitors named anodic, cathodic and mixed. Corrosion inhibitors areselected on the basis of solubility or dispersibilityin the fluids which are to be inhibited. The following considerations have to be addressed in order to obtain the proper selection of the corrosion inhibitors [39]:

- Magnitude of suppression of uniformand localized corrosion,

- Effect of temperature and concentration onthe performance of inhibitors.

- How long the effectiveness is required.

- Understanding if there is a bimetallic coupling to other metals joined to the main system.

- Understanding the existing condition of the system to be protected.

- Effect of inhibitor on heat transfer characteristics.

- Toxicity and pollution problems.

- Economically and technically competitive with other considered inhibitors.

Corrosion inhibitors can be classified according to their mechanism and composition as follows [40]:

- Organic or inorganic.
- Anodic or cathodic.
- Adsorption or film forming.
- Oxidizing or non-oxidizing, and
- Safe or dangerous inhibitors.

3.3.1. Anodic inhibitors

Anodic inhibitors (or passivating films) are compounds,work to delay the anodic reactionas shown in Figure (9), by shifting the corrosion potential to more positive value[42]. It works to form a protective passive oxide film that will act as a barrier for metal dissolution. Anodic inhibiters are being either oxidizing (e.g., chromate and nitrite, etc.) or non-oxidizing (e.g., phosphates, tungstates, benzoate and molybdate, etc.)[39, 40].For effective and typical performance of anodic inhibitor, critical concentration of anodic inhibitor has to be determined (see Figure 10). However, if there are aggressive ions such as chlorine and sulfite, it may tend to increase the critical inhibiter concentration. This type of inhibiter is sensitive to metal identification such as benzoate functions for steel but not zinc.

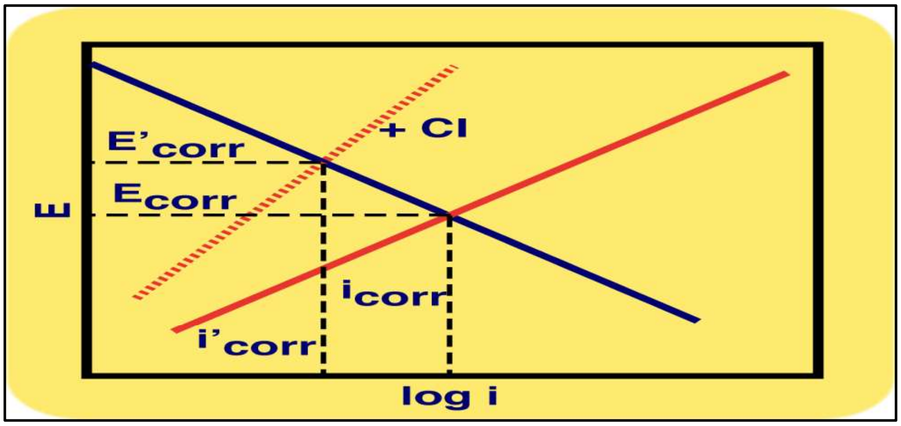

Fig.(9)Anodic Inhibitor[40]

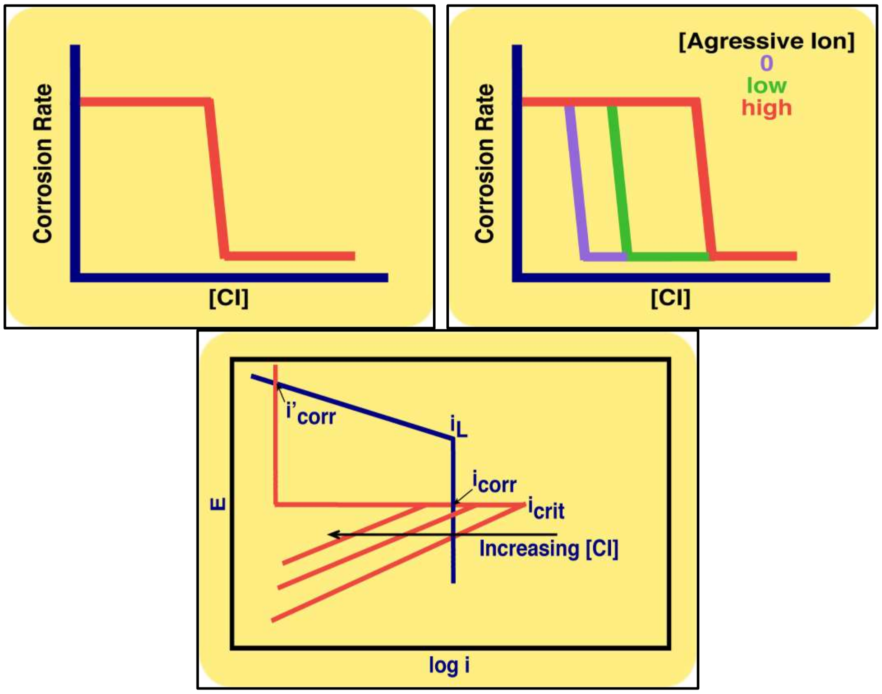

Fig.(10) Showing the critical concentration of anodic inhibitor[40]

3.3.2. Cathodic inhibitors

Cathodic inhibitors work to either delay the cathodic reactions Figures (11 & 12) or to precipitate on the cathodic areas by increasing the circuit resistance andrestricting the reducible speciesdiffusion into the cathodic parts. There are two major cathodic reactionsare hydrogen reaction and oxygen reaction. The reduction of hydrogen ions shown belowresults in forming an electronically non-conducting surface filmlike salt of divalent metals, phosphates and chromate [39,41].Andoxygen reduction where the oxygen is diffusingto the metal/electrolyteinterface. When an inhibitorlike zinc or magnesiumis added tothe system, reacts withthe hydroxyl ion and precipitates insoluble compoundswhich would, in turn, stifle the cathodicsites on the metal [39].

$2H^+ + 2e^- \leftrightarrow H_2$ (Hydrogen reduction)

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$(Oxygenreduction)

$Zn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Zn\ (OH)_{2(S)}$

Examples of cathodic inhibitors are Cu $(HCO_3)_2$, $ZnSO_4$, Cr_4 $(SO_4)_3$, NiSO4, polyphosphate, and aminoethylene phosphate [39].

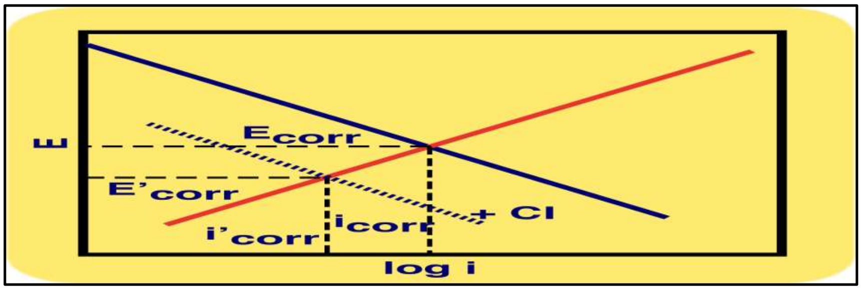

Fig.(11) Cathodic Inhibitor[40]

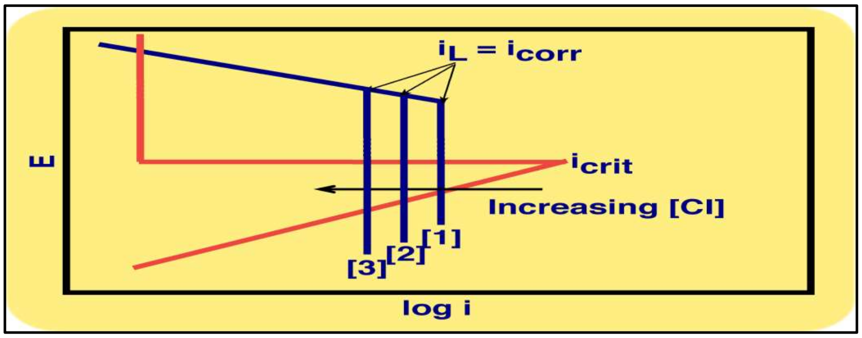

Fig.(12) Showing the critical concentration of cathodic inhibitor [40]

The role of synergistic effect of corrosion inhibitors on water injection pipe under dynamic condition was evaluated [18]. The pipe corrosion was mainly resulted from the dissolved oxygen, Ca^{2+} and other inorganic salt in produced water. The HZ-2 inhibitor prepared by the proportion of oleic acid imidazoline and phosphonic acid salt of 2:1was the best corrosion inhibitors, which significantly reduced the corrosion rate. While, Lua et al. [26] found that acidizing corrosion inhibitor had a good matching ability with the high strength martensitic stainless steel in reducing the uniform corrosion rate where it is mainly changed the anodic process of stainless steeland moved the corrosion potential to a positive direction, which in turn, significantly decreased the corrosion current density.

3.3.3 Mixed corrosion inhibitors

Mixed inhibitors are organic compounds that cannot be designatedspecifically as anodic or cathodic. The effectiveness of mixed inhibitors is related to what extent they adsorb and cover the metal surface. The metaladsorptiondepends on the structure of the inhibitor, the surface charge, and the type of electrolyte [43].

Mixed organicinhibitorscontaining nitrogen and/or sulfur, like amines, triazoles, alkythiourea. Mixed inhibitors protect the metal in three different ways: physical adsorption, chemisorption andfilm formation. Physical adsorption is a result of electrostatic attraction between theinhibitor and the metal surface. When the metal surface is positively charged, physical adsorption ofnegatively charged (anionic) inhibitors is facilitated.Chemisorption (or chemically adsorb) is the most effective mixed inhibitors that takes place more slowly than physical adsorption. Chemisorption involvescharge sharing or charge transfer between the inhibitor molecules and the metal surface.

The process of film formation is effective onlywhen the films are adherent, not soluble, and prevent access of the solution to the metal.Thick film likeair formed films on steel surface, may lose its adhesion due to mechanical damage if its thicknessreaches the critical point. Protective films may be nonconducting called ohmic inhibitors because they increase theresistance of the circuit, thereby inhibiting the corrosion or conducting (self-healing films).The process of film formation is complexand the properties of films are dependentupon its composition, thickness, temperature, solubilityand other physical forces[39,43]. For example, Al_2O_3filmproduced by anodizingis highly resistant to corrosion and so it producesa very high resistance. Additionally, scavengers are other kinds of inhibitors substances, work to remove the corrosion reagents like oxygen from the aqueous solution as per reactions given below. These substances are often negative inhibitors because they remove the undesired species. Examples of them are sodium sulfite and hydrazine [40].

$2Na_2SO_4 + O_2 \rightarrow 2Na_2SO_4$ (Sodium sulfite)

$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$ (Hydrazine)

Katariya et al. [44] assessed the effect of coating mild steel with Zeolite ZSM-5 on the corrosion resistance against varying concentrationsof different organic acids (acetic acid, formic acid and citric acid) at temperatures up to 60 °C under stagnant and stirred conditions. The results showed that for 6 h duration of contact between zeolite coatingand acid solutions, corrosion inhibition efficiency up to 98% is achieved. The extent of mild steel corrosion decreased in the order of formic acid > citric acid > acetic acid, and corrosion resistance though only slightly, decreased with solution temperature and concentration. Maria et al.[45] studied the effect of mechanical shear stresses generated by the movement of the environment on the steelsurface that interferes with the formation of the filmcorrosion inhibitors. The authors addressed some developedideas explaining the influence of flow on the corrosion process associated with carbon dioxide (CO_2). For further understanding the corrosion inhibitors, criteria for selecting corrosion inhibitors, mechanisms of corrosion inhibition and types of corrosion inhibitorused for managing corrosion in oil and gas industry, many review article are helpful[7,16].

Conclusion

Corrosion failure considers as a major cause of structural deterioration in oil and gas structuresand pipelines where it may cause structural failure, leakage, product loss, environmental pollution and the loss of life. This paper is aimed to broadly review the major types of corrosion occurred in oil and gas systems and the appropriate ways of corrosion inhibitions. The review is mostly focused on sweet corrosion and sour corrosion as well as factors affecting their rates. Pitting corrosion in addition to general and localized corrosion is regarded as the most hazardous corrosion in the petroleum equipment. The CO_2corrosion pits may often be hemispherical deep pits with steep edge localized corrosion. Several types of cathodic, or anodic or mixed inhibitors could inhibit the occurrence of localized corrosion for a short periodtime while most of them could not completely inhibit the localized corrosion. There are a wide variety of bacteria such as sulfate, iron and CO_2-reducing bacteria, sulfur, iron and manganese-oxidizing bacteria, also microorganisms producing organic acids or mucilage are responsible for most failures of buried pipelines bio corrosion and cables, but sulfate reducing bacteria (SRB)are responsible for over 75% of the corrosion in productive oil.

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