

Corrosion Behavior of Sucker Rods used in Offshore for Petroleum Production

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Abstract - The corrosion of sucker rods is one of the major problems in the petroleum industries. Usually, the sucker rods made of certain grade of steel and these steels are prone to corrosion in the aggressive environment due to presence of carbon dioxide and sulphide in the crude oil. In the present study the API CT L-80 grade steel has been used. The corrosion behavior study of this steel has been carried out at different temperature (30-120°C) at a constant partial pressure of carbon dioxide alone and with addition of little amount of H₂S. The corrosion behavior of steel increases with increasing temperature and due to the presence of small amounts of H₂S. Under these operating conditions, iron sulphide film interferes with the formation of iron carbonate scale, which is less protective. The simultaneous presence of CO₂ and H₂S in produced fluids can make a very aggressive environment, which may lead to severe corrosion sucker rod. CO₂ and H₂S have been shown to produce competing films at temperature between 30 and 120°C and it was observed that FeS is more aggressive than FeCO₃ at 90°C. The phases formed on the surface of material were analyzed by using SEM and XRD.

Key words: CO₂ corrosion, sucker rod, iron carbonate, SEM, XRD

INTRODUCTION

Corrosion of sucker rods are one of the major problems encountered with produced fluids which accounts for about one-half of the failures. Corrosion is the destructive result of an electrochemical reaction between the steel used in making sucker rods and the operating environment to which it is subjected. Simply, corrosion is nature's way of reverting a man-made material of a higher energy state (steel), back to its basic condition (native ore) that found in nature. The elemental iron in steel combines with moisture or acids, to form other compounds such as iron oxide, sulfide, carbonate, etc. The biggest problem in condensate systems is corrosion of the steel. Condensate corrosion is primarily caused by the acidity of carbon dioxide (CO₂) [1-3]. In certain few applications, dissolved oxygen can contribute to corrosion in the condensate. If not properly protected against the acidity of CO₂, any of the condensate components including pipelines, drilling and transmission

will fail leading to system outage, production loss and the potential loss of lives. In addition, the by-products of corrosion such as iron oxides and sulphides are returned to the steam pipelines and deposited on the internals that reduces efficiency. Usually, some form and concentration of water is present in all the wells which is corrosive due to presence of considerable quantities of dissolved impurities and gases. Usually, carbon dioxide (CO₂) and hydrogen sulfide (H₂S) are the most common acidic gases present in all the wells [1-3]. These gases are highly soluble and tendency to readily dissolve in water results in lowering the pH of the electrolyte or solution. The corrosivity of the water is a function of the amount of these two gases present in solution. The water with low pH values is more corrosive due to accelerating higher acidity to the steel surface. All downhole environments are corrosive to some degree to greater extent depends on the nature and presence of acidic gases. Some corrosive fluids may be non corrosive as the corrosion penetration rate recorded in mils of thickness lost per year (mpy) is very low that not cause any corrosion problems. However, most producing wells are plagued with corrosive gases which cause corrosion problems in most currently manufactured sucker rods. In most of the literature reported that sucker rod corrosion cannot be completely eliminated but it can be controlled or protected using effective chemical inhibitors as per specification of API Specification 11BR and NACE Standard RPO195. Corrosion on steel surface may occurs very aggressively when the sucker rods immersed in the corrosive fluids. The further rate of the reaction depends on the formation speed and nature of surface films that formed on the surface due to corrosion. Usually, the reaction rate slows down as obstructive film of corrosion deposit formed that acts as scale coats and retards the corrosion penetration rate that tends to slow down corrosion. However, if this deposit is cracked continuously by any means such as bending movement, abrasion then aggressive local corrosion continues on the area with the scale removal and cause surface damage resulting in bruises, nicks, bends corrosion which results in deep corrosion pitting. The downhole sucker rod equipments are high tensile strength steel and it may be protected from corrosion using considerably applying inhibitors on the metal surface. Usually, batch type treatments are frequently used to apply significant amount of inhibitors to control the corrosion. In many literatures reported that, application of 40 parts per

million (ppm) of corrosion inhibitors effectively batch treat once a week reduces the corrosion rate significantly.

2.0 LITERATURE REVIEW

In petroleum industry the corrosion problems associated with offshore and onshore particularly in lifting of crude oil from offshore and their storage and transmission depends on medium consisting of multiphase crude oils. These are mainly consists of hydrocarbons, gases and water. Also the corrosivity of pipeline depends on the nature of the crude oils i.e. either in sweet environments or in sour environments. The presence of two immiscible fluids i.e water and hydrocarbons poses special problems in corrosion monitoring and thus determine the rate of corrosion. Generally corrosion of the underground pipelines which is carrying the crude oils and gases is closely associated with the water which may be in the suspended form or in condensed form. The crude oils or gases themselves do not take part in the electrochemical reaction, while it act as the vehicle for the transportation of water and other corrodents such as oxygen, carbon dioxide in sweet environment, and hydrogen sulphide in the case of sour environment. Many reports indicated that in rare cases the crude oils may participate in the corrosion process. In 1975, De Waard and Milliams showed the effect of partial pressure of CO_2 and temperature on the rate of corrosion on steel coupon sample [1]. Later on De Waard, Milliams and Lortz in 1991 improved the model using correction factors for the non ideality of CO_2 at high pressure, formation of iron carbonate scale and change in pH and Fe^{++} ion levels [2]. Further in 1995, based on some limited flow studies, DE Warred, Lortz and Dugstadin proposed semi empirical model which combine the contribution of flow independent kinetics of the corrosion reaction with flow dependent mass transfer of dissolved CO_2 [3-4]. In Fig.1 showed the different analysis zones of the coupon sample. In order to identify the possible mechanism of damage that affects the integrity of the coupon material it is divided into three important zones through which the fluids enters, out and interacts [1]

Zone 1: Transverse area in the direction of the operation fluids

Zone2: Transverse area in opposite direction to fluid flow

Zone 3: Contact area between the coupon and fluids

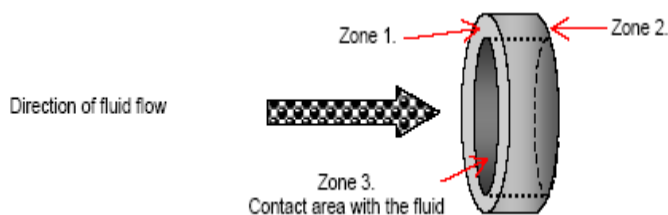


Fig.1: Micrograph shows different zone of coupon carrying fluids

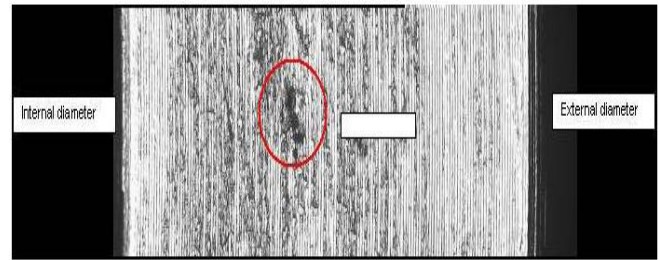


Fig.2: Micrograph shows localized defects near internal diameter at the circumference (360°)

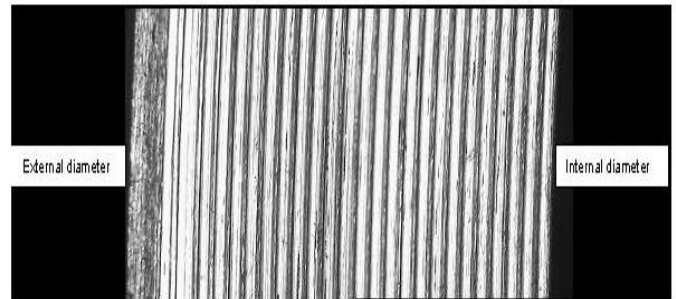


Fig.3: Micrograph shows no defects zone 2

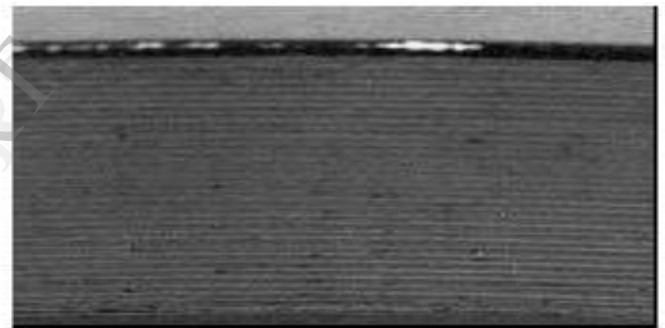


Fig.4: Micrograph shows some scratches in zone 3

The below scale shows the variation in reaction rate with varying concentration of hydrogen ion. The pH indicated is in logarithmic scale and each pH increment of 1.0 represents a tenfold change in hydrogen ion concentration. The pH of pure water free with dissolved gases is 7.0 while pH less than 7 are increasingly acidic and pH more than 7 are increasingly alkaline.

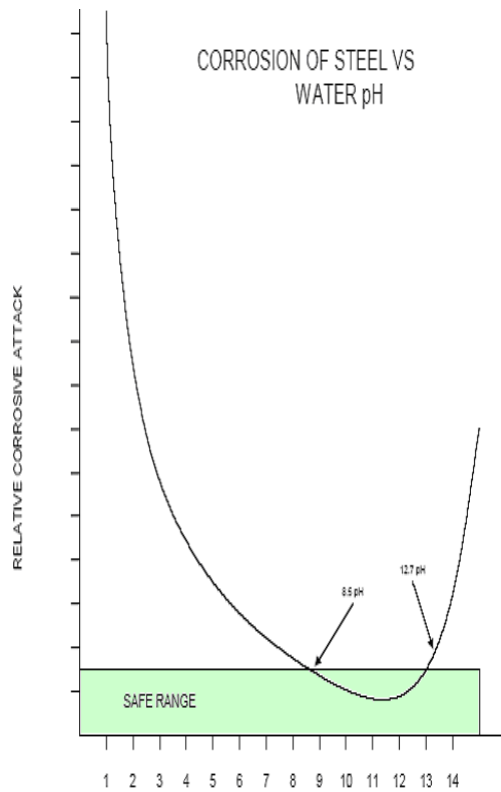
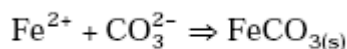


Fig.5: Graph shows the relationship between corrosion rate and pH.

2.1 Mechanism of failure

2.1.1 CO₂ Corrosion

CO₂ combines with water to form carbonic acids (H₂CO₃) which have the tendency to lower the pH of the water. These carbonic acids are very aggressive to steel and results in large areas of rapid metal loss that can completely erode sucker rods and couplings. The severity of corrosion depends on the concentration of partial pressure of CO₂ and temperature. As the partial pressure of CO₂ and temperature increases the severity of corrosion also increases [1-3]. It has been observed that the CO₂ corrosion pits are round in shapes, deep with steep walls and sharp edges [3]. The pitting is usually interconnected in long lines while it is occasionally singular and isolated. The pit bases are filled with gray deposit of iron carbonate scale which is a loosely adhered surface film generated from CO₂ corrosion. In CO₂ corrosion of carbon steel, when the concentration of Fe²⁺ and CO₃²⁻ ions exceed the solubility limit, they can precipitate to form solid iron carbonate as indicated below



When iron carbonate precipitates at the steel surface it can slow down the corrosion process by presenting a diffusion barrier for the species involved in the corrosion process.

The precipitation will occur when the concentration of both the ions exceeds the solubility product (K_{sp}), which is a function of temperature and ionic strength. In most cases

nucleation is the initial stage of precipitation which can be disregarded and assumed that the rate of precipitation is controlled by the crystal growth rate. Many theories reported that the mechanism and kinetics of crystalline film growth lead to quadratic dependence on supersaturation and given as follows;

$$R_{gr} = k_{gr}(S - 1)^2$$

where R_{gr} is the growth rate and k_{gr} is the constant of growth rate. The super saturation is defined as

$$S = \frac{C_{\text{Fe}^{2+}} \cdot C_{\text{CO}_3^{2-}}}{K_{sp}}$$

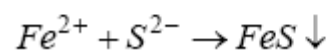
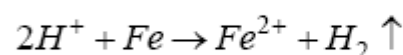
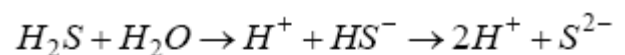
for appreciable rates of precipitation, supersaturation (S) has to be significantly larger than unity and the kinetic constant K_{gr} has to be large. Actually at low temperature little iron carbonates film forms even at higher supersaturation as a result of the slow kinetics of the precipitation reaction (low K_{gr}). However the metal surface corrodes away under the film which is quantified through a nondimensional parameter called scaling tendency and represented as;

$$ST = \frac{R_{gr}}{CR}$$

the above equation indicates the relative rate of precipitation and corrosion prior to any film formation expressed in same volumetric units.

2.1.2 H₂S corrosion

H₂S corrosion is also known as sour corrosion and in combination with CO₂ it accelerates the rate of reaction in many folds. In presence of even small concentration of H₂S in the wells it causes corrosion on steel and deposit a tightly adhering black scale on the metal surface which is insoluble and cathodic to steel and tends to accelerate corrosion penetration rates. The second corrodent generated by H₂S is iron sulfide scale. H₂S pitting is usually small, random, and scattered over the entire surface of the rod. It is round in shapes, deep with steep walls and beveled edges. A third corroding mechanism is hydrogen embrittlement, which causes fracture on the metal surface with granular or brittle appearance. Reactions with H₂S takes place as;



2.1.3 Chloride Corrosion

Corrosion in steel equipment made for downhole applications such as sucker rods due to presence of chloride is a major apprehension for the petrochemical industries. Corrosion, from waters with high concentrations of chlorides, has the tendency to be more aggressive to carbon steel sucker rods than to alloy steel sucker rods. The corrosivity of water increases as the concentration of chlorides increase. Corrosion due to high concentration of chloride contributes to an increase in corrosion related sucker rod failures. Chloride corrosion tends to evenly pit the entire surface area of the sucker rod with shallow, flat-bottomed, irregular shaped pits. Pit shape characteristics include steep walls and sharp pit edges. In presence of high concentrations of chlorides in wells create difficulty in reaching and protecting the steel surface of sucker rods.

2.1.4 Oxygen Enhanced Corrosion

Oxygen enhanced corrosion is most prevalent on couplings and a few instances on rod upsets. Oxygen enhanced corrosion is rarely seen on the rod body. The rate of oxygen enhanced corrosion is directly proportional to the dissolved oxygen concentration, chloride content of the produced water and presence of other acidic gases. Dissolved oxygen can cause severe corrosion at extremely low concentrations and evaporate large amounts of metal. In fact, aggressive oxygen enhanced corrosion can erode couplings without harming the sucker rods on either side. Pitting is usually shallow, flat-bottomed, and broad-based with the tendency of one pit to combine with another. Pit shape characteristics may include sharp edges and steep sides if accompanied by CO₂ or broad, smooth craters with beveled edges if accompanied by H₂S. Corrosion rates increase with increased concentrations of dissolved oxygen.

3.0 Experimental Methods

The materials used for the experiments were supplied by Oil and Natural Gas Company Limited (ONGC) Mumbai and Essar Steel Limited Gujarat, India. The chemical composition of alloys, as obtained by inductively coupled plasma and atomic emission spectroscopy (ICP-AES) technique, are shown in Table 1. The as received material was in the plate form of size 300x200x20 mm. The specimens of dimension 12x10x2.5 mm were prepared with a hole of 1.5 mm diameter drilled near the top edge to facilitate suspension inside of an autoclave. The samples were polished upto 800 grit emery papers, washed in distilled water and then cleaned in acetone and air dried. Experiments were carried out at four different temperatures (30, 60, 90 and 120°C) at a constant partial pressure of CO₂ (50 psi) in a closed loop machine with a liquid flow velocity of 1.5 m/s. Initial weight of the L-80 grade steel coupon sample was measured and suspended in specimen holder inside of autoclave. The galvanic corrosion between sample and autoclave vessel was strictly avoided using Teflon tape in Ni-Cr thin wire. The vessel was deaerated by

purging argon gas for 1-2 hours to maintain the oxygen impurity below 40 ppm. The oxygen level was measured by using the oxygen meter. The vessel temperature was increased to the testing condition by using silicon control rectifier (SCR), which supplies the heat to the solution and then charged the pressure of CO₂ from the cylinder to maintain vessel pressure of 50 psi. The actual temperature of the solution and pressure inside the vessel were observed by digital display unit of the control panel. The pressure loss during the operation was avoided by using the proper teflon tape. Each experiment was conducted using the same procedures for a total period of 96 hours at different temperature with fresh sample. The exposed samples were washed by distilled water then finally measured the weight in digital weighing machine upto accuracy of four digits. The corrosion rate of each sample was measured in mils per year (mpy). The corrosion products formed on the metal surface were analyzed by using X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques as shown in Fig.

4.0 Results and Discussion

The corrosion rates of samples as a function of temperature up to 90°C increases linearly and then decreases with increasing temperature as shown in Fig.5. The results indicate that the corrosion rate slowly increases with increasing temperature in case of carbon dioxide, while it is faster and more steeper in addition of hydrogen sulphide. At low temperature (30-60°C), the corrosion process slowly increases results in the formation porous iron carbonate beneath the oxide layer. As the temperature increases the cracks initiates beneath the oxide layer and finally spallation occurs around 90°C and the corrosion process increases severely. Further, increase in temperature (120°C), the solubility of iron carbonate decreases due to precipitation of iron carbonate on the metal surface and thus formation of dense and adherent protective film. The compact layer form on the metal surface prevent to further corrosion reaction. It has been observed that as the CO₂ pressure increases in the solution the corrosion rate increases due to local depletion of bicarbonate (HCO₃⁻), which favors the cathodic reaction. Many authors reported that iron carbonate precipitate on the metal surface with high rate of Fe⁺⁺ dissolution and the additional bicarbonate produced by the cathodic reduction of CO₂ []. It has been also reported that for the precipitation of FeCO₃ super saturation with Fe⁺⁺ is required which is 5-10 times higher than the thermodynamic values of solubility [7].

Surface Morphology

The surface morphology in Fig. 10 and 11 shows that L-80 grade steel is not protective in nature at the temperature of 90°C in both CO₂ and H₂S medium due to the initiation and formation of cracks on the metal surface. The L-80 grade steel shows higher corrosion rate in case of presence of little amount of H₂S with CO₂ above curve in Fig.5 above while less aggressive in the case of CO₂ alone. This higher rate has been observed due to freely entry of the corrosive ions through the pores of the oxide and sulphide layers.

However at the higher temperature beyond 90°C the dissolution of Fe^{++} ions occurs homogeneously and precipitate and thus more iron carbonate film accumulate on the metal surface causes decrease in corrosion rate. The solubility of iron carbonate decreases with increasing temperature and. The iron carbonate film precipitates on the metal surface becomes tight and adherent and finally acts as a barrier between the environment and the metal surface results in protects the metal for further corrosion. The corrosion rate obtained by the weight loss method at 120°C significantly decreases due to the formation of dense protective film of iron carbonate film as shown in Fig. The phases formed over the metal surface at both CO_2 and H_2S medium were obtained by using XRD analysis. The XRD analysis indicates the formation of different phases such as $FeCO_3$, Fe_3O_4 , Fe_2O_3 and H_2S are shown in Fig. 8 and 9. In Fig. 8 the $FeCO_3$ film formed at the surface are not prompt, where the peaks of iron carbonate shown sharp indication of the protection of metal from the further corrosion. At higher temperature the magnetite (Fe_3O_4) film formed and shows little protection over the surface.

Table 1: Chemical composition of L-80 grade steel in (wt%)

Elements	Wt%
C	0.29
Mn	1.36
S	0.025
P	0.030
Si	0.26
Ni	0.015
Cr	0.02
Mo	0.002
Al	0.01
Cu	0.17

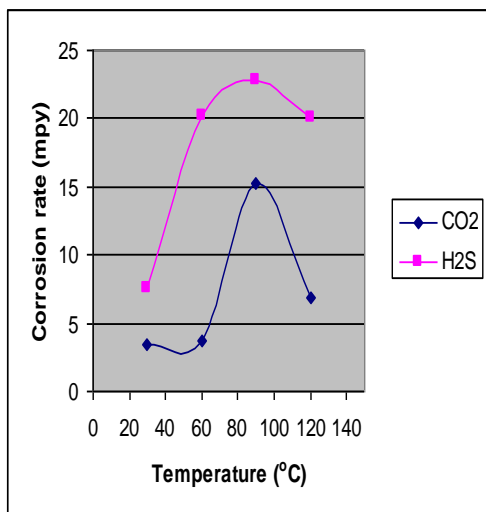


Fig.6: Corrosion rate of steel in CO_2 and H_2S medium



Fig.7: Physical appearance of exposed samples (a) CO_2 and (b) H_2S medium

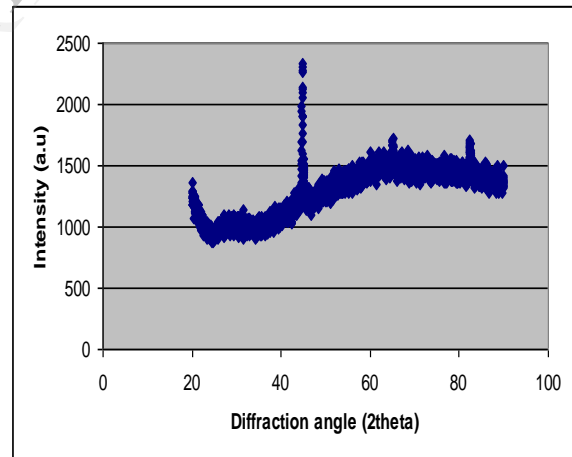


Fig. 8: XRD pattern of L-80 grade steel in CO_2 medium

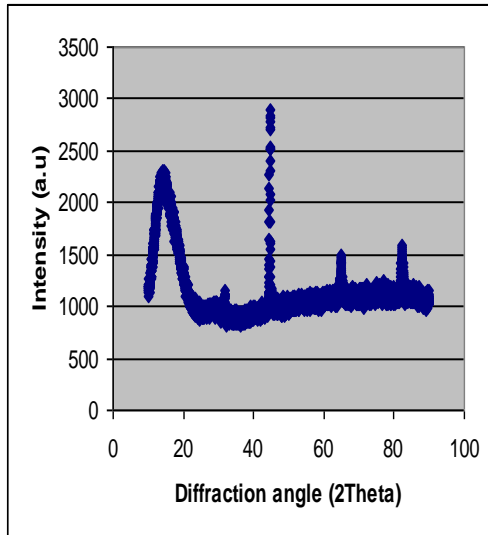


Fig. 9: XRD pattern of L-80 grade steel in H₂S medium

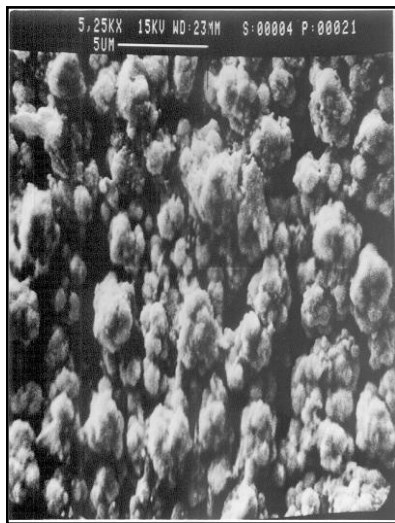


Fig. 10: SEM micrograph of L-80 grade steel in CO₂ medium



Fig. 11: SEM micrograph of L-80 grade steel in H₂S medium

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