

Influence of Hydrogen Sulfide on CO₂ Corrosion in Pipeline Steel

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Abstract— Experiments for the pipeline steel have been carried out in an autoclave consisting with a multiphase dynamic flow loop system at various temperatures and a constant partial pressure of carbon dioxide. A small amount H₂S has been added in the vessel. The temperature of the system was varied from 30-120°C and pressure of carbon dioxide has been maintained constant of 50 psi. All the experiments were carried out in 3.5% brine solution and a constant speed of 0.5 m/s. The study provides an example of the increased corrosion rate under dynamic flow condition due to presence of small amounts of H₂S with carbon dioxide. Under these operating conditions, iron sulfide film interferes with the formation of iron carbonate scale, which is not stable and easily removed from the metal surface and results in less protective. The simultaneous presence of both CO₂ and H₂S in produced fluids made a very aggressive environment, which may lead to severe corrosion for the pipeline steel. Both CO₂ and H₂S have been shown to produce competing films at higher temperature and observed that FeS is more protective than FeCO₃ at 120°C. The phases formed on the surface were analyzed by Scanning Electron Microscope (SEM) and X-ray photoelectron spectroscopy (XPS) technique.

Keywords— Autoclave, Multiphase, Dynamic Loop, Brine, CO₂ and H₂S

I. INTRODUCTION

There are very limited numbers of studies that cover H₂S corrosion or sour corrosion particularly when compared to the CO₂ corrosion or sweet corrosion. Wells with large amounts of H₂S are usually labeled sour; however wells with only 10 ppm and above are sufficient to be labeled sour. In many literatures it has been shown that the maximum concentration of H₂S in brine water is 400 ppm [1-2]. Also, stated that only 0.05 H₂S partial pressures are sufficient for aggressive corrosion in the petroleum industries. Usually, the H₂S corrosion is predominant in production wells, flowlines, and during drilling. The primary problem in presence of H₂S is the metal embitterment due to penetration of H₂ in metal with very complex mechanism. It may involve SH⁻ ion on the metal surface since it is the only dissolved sulfur ion. The extensive literatures are available on sweet corrosion while very few in case of sour corrosion particularly in autoclave system under dynamic flow condition. Most of the researchers reported that addition of small amount of H₂S less than 30 ppm in a CO₂ saturated brine solution can accelerate the corrosion of steel [1]. While this effect may seem to vanish at higher concentration of H₂S and at high temperature more than 80°C due to formation of protective film of iron sulfide on the metal

surface. This effect will be only significant at lower pH value less than 5 as suggested in a study [2]. In general, the reasons behind the H₂S effect on CO₂ corrosion are not completely understood. However, in many reports, it has been speculated that adsorbed sulfide species acts as a catalyst on the metal surface and causes for enhanced rate of corrosion through catalytic effect [2-3]. The simultaneous presence of CO₂ and H₂S in produced fluids makes a very aggressive environment, which leads to severe corrosion due to interference in the formation of iron carbonate scale (FeCO₃) through iron sulfide (FeS) film [4]. Videm and Kvarekval demonstrated that small amounts of H₂S increased the corrosion due to easily disturbed and ultimately removal of iron sulfide film from the surface [4]. This result is of interesting because the iron sulfide film is more easily removable from the pipe wall than the iron carbonate scale and thus leads to pitting corrosion. However, the iron sulfide films have a protective effect at higher temperature in and around 100°C due to formation of a protective film. At high temperature, the iron sulfide film form more easily and deposited at the metal surface which is dense and adhered layer in nature and thus removal of protective scale decreases results in decreased corrosion rate.

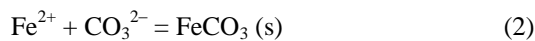
Hydrogen sulfide is a weak acid and when dissolved in water it act as a catalyst in absorption of atomic hydrogen on metal surface and thus promoting sulfide stress cracking (SSC) in high strength steels. The most common type of corrosion may occur in presence of iron sulfide environment is pitting corrosion, sulfide stress cracking, hydrogen blistering and hydrogen embrittlement. Also, the corrosion products formed the different phases include blue-black iron sulfides, pyrite, mackinwaite, magnetite, greigite, kansite, sulfur, and sulfur dioxide. Usually, Iron sulfides are formed during corrosion reactions and play an important role in controlling the corrosion by forming a protective film in absence of oxygen and chloride ion. To reduce or prevent corrosion in drilling, production and flow lines the uses of organic inhibitors are preferable in both sweet and sour environment due to viable and economic consideration. There is a wide variety of corrosion inhibitor formulations available that can be selected and implemented to handle in most environments in oil and gas production systems. Most corrosion inhibitors are typically organic amine-based compounds and these function by establishing a film that protects metal from corrosive fluids. Usually, organic film formers are used in oil, gas, water wells and may be in combination of both water and gas systems, and flowlines.

II. MECHANISM AND KINETICS OF CO₂ CORROSION

A. Carbon dioxide corrosion is also known as sweet corrosion since many decades and it is one of the most important problems in the oil and gas industries. The severity of corrosion depends on many factors such as the concentration of CO₂, temperature, pressure and velocity in the solution. Thus it is essential to characterize both individual parametric effect and interaction in each corrosive environment. Since one of the parameter can alter the reaction rate drastically even in presence of small values. De Waard and Milliams developed a semi-empirical correlation between corrosion rate and CO₂ partial pressure and later simplified in the form of a nomogram expressed as;

$$\text{Log C.R (mm/y)} = 5.8 - 1780/T + 0.67 \text{ Log (pCO}_2\text{)} \quad (1)$$

In CO₂ corrosion of carbon steel, when the concentrations of Fe²⁺ and CO₃²⁻ ions exceed the solubility limit, they can precipitate to form solid iron carbonate according to the reaction as below;



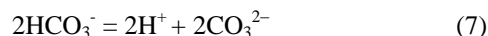
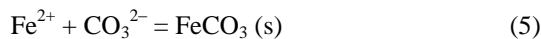
When no solid reaction products are formed on the metal surface the overall anodic dissolution reaction takes place and can be written as below equation;



This reaction proceeds through intermediate reactions involving hydroxyl ions (OH⁻) and its individual rate decreases with decreasing pH and a time will reach where cathodic reaction becomes predominant and it acts as a rate controlling step on the metal surface. In deaerated solution, the usual cathodic reaction is evolution of hydrogen as in equation

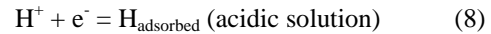


In the CO₂ medium, the rate of cathodic reaction is mainly affected by the partial pressure of CO₂. For their explanation deWaard and Milliams proposed that the evolution of hydrogen ion can occur through carbonic acid as equation as



Thus dissolved CO₂ have the tendency to form weak carbonic acid (H₂CO₃) in the solution which increases the cathodic reaction kinetics by dissociation to bicarbonate and hydrogen ions. However, high concentration of H₂CO₃ or its precursor CO₂ relative to H⁺ ion in the bulk solution increases the rate of overall mass transfer and depolarized the cathodic reaction. The hydrogen is produced through the bicarbonate ions near the surface rather than direct H₂CO₃. In this sense, the carbonic acid acts as catalysts on metal surface. Under stagnant condition, dissolved ferrous ions combine with the

H₂CO₃ to form ferrous carbonate (FeCO₃), while in flow condition some part of the iron carbonate dissolved and thus the reaction rate become faster due to removal of corrosion scale from metal surface. In presence of small amount of H₂S, the metal usually fails due to sulfide stress cracking (SSC), which is a special type of hydrogen-induced cracking [HIC]. The mechanism of HIC can be described as below. First, the hydrogen ion (H⁺) adsorbs and then enters on the metal surface rather than formation of hydrogen molecule.

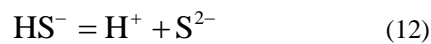


This adsorbed hydrogen recombines to form hydrogen gas then enter into the metal and developing pressure causing cracking. However, the recombination reaction poisons in presence of sulfide ion, which prevent the formation of hydrogen gas. Thus the adsorbed hydrogen moves through the metal, which causes severe corrosion. Hydrogen sulfide is very aggressive in promoting this type of corrosion, because it only not poisoned the recombination reaction of hydrogen molecule, but also provides the hydrogen ions. The hydrogen ion adsorbs on the metal surface usually and reduces the ductility and tensile strength of the material due to its penetration into the metal. Usually, the hydrogen ion reacts with strong carbide former elements such as Ti, Zr, Nb and can produce metal hydrides that may initiate cracking. The sulfide stress cracking usually occurs in high-strength drill pipes, casing tube, flow lines and sucker rods. However, the cracking may not appear at low concentration of H₂S.

III. MECHANISM AND KINETICS OF H₂S CORROSION

H₂S corrosion in pipeline is a well-known phenomenon in petroleum industry because of their severe attack and localized corrosion. Usually, carbon steels are more susceptible to corrosion at the inner surface, even in presence of small amount of H₂S. Brickel et al. indicated that, small amounts of H₂S are responsible for localized corrosion that promotes the sulfide stress corrosion cracking (SSCC), hydrogen induced cracking (HIC) and hydrogen embrittlement (HE). Usually, H₂S causes the sulfide stress corrosion cracking in high strength steel, even at low temperature and low partial pressure. Only very small amount of H₂S (0.005 ppm) can act as a catalyst and enhanced the corrosion on pipe surface. The presence of small amount H₂S in CO₂ saturated solution can significantly enhance the corrosion rate due to severe attack. Additions of small amount of H₂S to carbonic acid solution can reduce the uniform corrosion as shown by T. Kundu et al. [3]. This may be due to the formation of iron sulfide as a corrosion product on the metal surface. The composition of these films are mainly consists of FeS and FeS₂ and their properties depends on the concentration of H₂S in the solution. At low partial pressure of H₂S, the black film may be loose and porous and can be easily skipped off from the metal surface while at higher partial pressure of H₂S the film may be hard and very difficult to remove. However, the more adhered

film may cause severe corrosion at the patches or pores of the film. The H₂S corrosion is more dangerous than the CO₂ corrosion because it fails without notice in short period. According to Rogers and Rowe, the FeS films are cathodic to steel and difficult to polarize and provide a galvanic driving force for localized attack at exposed patches of steel or pores in the film. Corrosion rates are initially low, while the films are being formed and then accelerate rapidly. In a series of field test information indicated that, the corrosion rates of carbon steels are fairly low for 120 days, but after 180 days serious corrosion losses were observed with formation of massive soft black iron sulfide. Kvarekval et al. [2] have investigated the composition and properties of the sulfide films on the steel surface in H₂S-CO₂-H₂O system. They indicated that FeS is the main corrosion product on the metal surface. Also, they reported the higher corrosion rate of carbon steel at higher H₂S partial pressure due to more surface area of the film. The surface area of the film increases with increasing the concentration of FeS, which indicates the formation of a non-protective porous film. However, at lower H₂S partial pressure, blistering may occur as reported by several workers [3-4]. With addition of small amount of H₂S the reactions precede on the metal surface with the dissociation of hydrogen sulfide as follows;



The formed FeS may be protective or not that will depend on the various parameter such as solution temperature, concentration of H₂S, oxygen content etc. At higher temperature and concentration of H₂S the films formed on the surface protect the metal significantly. But at lower concentration the H₂S may not be sufficient to form the film and thus corrosion increases due to localized attack.

IV. EXPERIMENTAL DETAILS

The material used in the current study was obtained and the chemical compositions are given in Table 1. The as-received materials was cut into the rectangular specimen of dimension 20 mm x 12 mm x 2.5 mm with a center hole of diameter 1.5 mm at the top edge of each specimen to facilitate the suspension inside of the autoclave of capacity 2.2 liter. The faces of the sample were initially coarse grounded on a SiC belt grinder machine then consequently machine polished in the successive grades of emery papers (220, 400, 600 800 and 1000). The initial weight and area of the sample was measured using digital weighing machine upto an accuracy of four digit. Four different experiments were carried out at different temperature (30°C, 60°C, 90°C and 120°C) in a multiphase dynamic loop machine at constant partial pressure of 100 psi.

Table 1: Chemical composition of the as received material (in wt %)

Elements	Wt %
C	0.19
Mn	1.22
Si	0.36
S	0.003
P	0.004
Cr	0.07
Mo	-
Cu	0.16

The velocity of fluid was maintained at a constant speed of 1.5 m/s for 96 hours. The oxygen solubility of the system was maintained below 40 ppm using the Ar gas. In the beginning of the test, the actual temperature of the machine was set as 30 °C, 60 °C, 90 °C and 120 °C separately and respectively and then created the actual partial pressure of carbon dioxide by releasing the carbon dioxide gas inside the autoclave. After 96 hours of exposure the sample was taken out from the autoclave washed in distilled water, rinsed in acetone and then dried in air. After cleaning, the coupon weighed again and finally the corrosion rate (CR) of the sample was measured in mills per year using the formula;

$$CR (mpy) = \frac{\{Weight\ loss (gm) * K\}}{Metal\ Density \left(\frac{gm}{cm^3}\right) * Area(A) * Exposure\ Time(hrs.)}$$

The constant value (K) = 5.34 x 10⁵.

The surface morphology of corroded sample was observed using environmental scanning electron microscope (ESEM) at an operating voltage of 15 kV. The phases and elements present on the exposed samples were analyzed by using XPS systems and elements present are shown in Fig. 2.

V. RESULTS AND DISCUSSION

The weight loss data as a function of temperature at a constant partial pressure of carbon dioxide are shown in Fig. 1. The results showed that corrosion rate of the sample increases with increasing temperature. The highest corrosion rate has been observed at a temperature of 90°C due to formation of porous layer of oxides and sulfides on the metal surface. This causes faster reaction and dissolution of the film in the solution results in higher corrosion rate. Also, the results indicated that the corrosion rate decreases at higher temperature near about 100-120°C due to formation of adherent and dense layer of protective film that protects from further reaction of corrosion. At higher temperature the XPS analysis showed that the presence of sulphur, chloride and oxygen ion in the surface of the material. Also presence of iron and oxygen indicated that easily formation of FeCO₃ phase that is predominantly forming over the surface and protective in nature. The physical appearances of exposed sample at aggressive and

protective temperature are shown in Fig. 3 and Fig. 4. The exposed sample at 90°C shown high and depth pits, while at 120°C the appearance of depth pit is comparatively less.

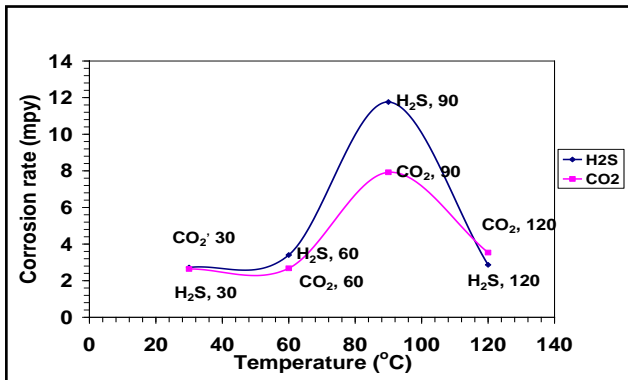


Fig. 1: Weight loss data as a function of temperature at constant CO₂ partial pssure

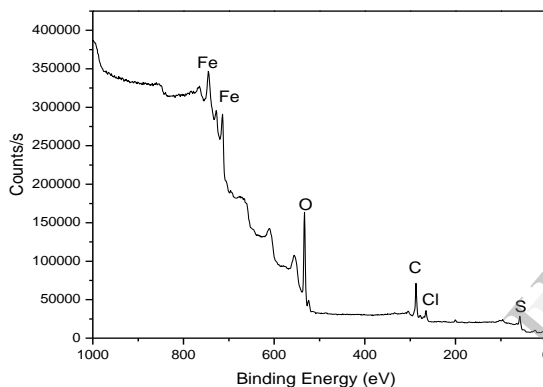


Fig. 2: XPS Patterns of API X-52 grade steel

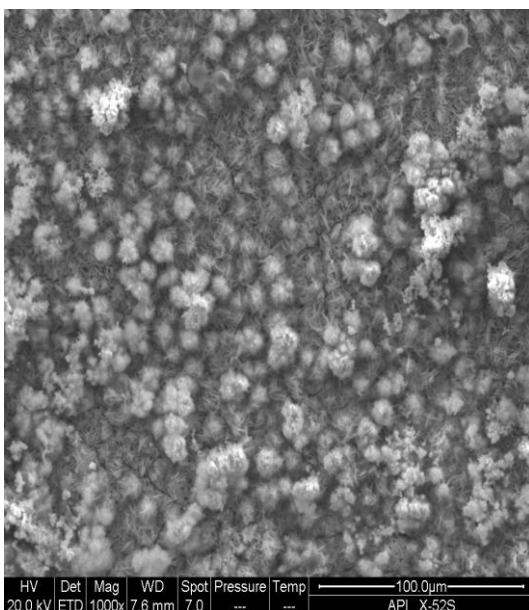


Fig. 3: Surface morphology of exposed samples @ 1000X in CO₂ environment at 120°C

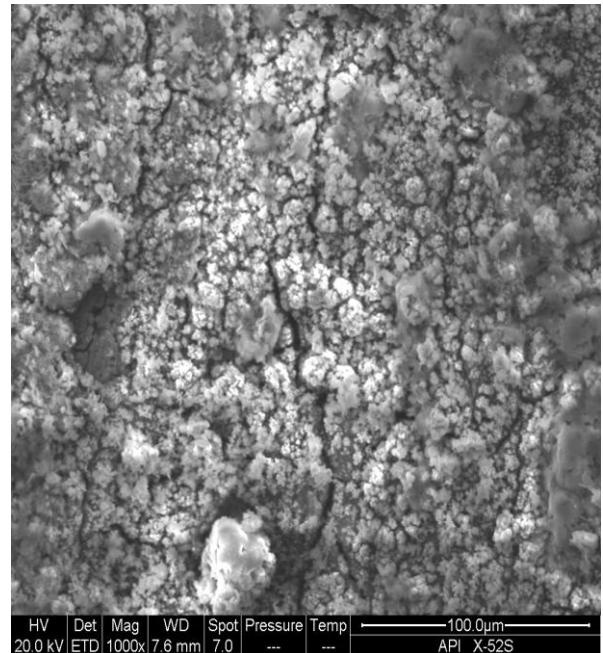


Fig. 4: Surface morphology of exposed samples @ 1000X in H₂S environment at 120°C

VI. CONCLUSIONS

The corrosion rate of pipeline steel increases with increasing temperature upto 90°C due to formation of porous layer results in spallation of the film in the solution. Beyond this temperature the corrosion rate again fall down due to formation of dense and adhered layer of oxide film on the metal surface. At aggressive temperature the layer formed on the surface dissolving continuously and the reaction rate becomes faster and shows higher corrosion rate while at higher temperature the iron carbonate film form which is very dense and compact on the surface results in slower corrosion rate.

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