Article:

Pessu, F orcid.org/0000-0003-3587-4309, Barker, R orcid.org/0000-0002-5106-6929 and Neville, A orcid.org/0000-0002-6479-1871 (2017) Pitting and uniform corrosion of X65 carbon steel in sour corrosion environments: The influence of CO2, H2S and temperature. CORROSION, 73 (9). pp. 1168-1183. ISSN 0010-9312

https://doi.org/10.5006/2454

Pitting and uniform corrosion of X65 carbon steel in sour corrosion environments:

The influence of CO_2, H_2S and temperature

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Article history: (This style is Article Info subhead)

Received Day Month Year (This style is Article History and Keywords)
Accepted Day Month Year
Available Day Month Year

Keywords: (This style is Article Info subhead)

A. Hydrogen sulfide corrosion
B. Carbon dioxide corrosion
C. Iron sulfide
D. Pitting corrosion
E. Localized corrosion
F. Uniform corrosion.

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ABSTRACT

Localized corrosion of carbon steel pipelines in oilfield environments is a serious concern. In environments containing both CO_2 and H_2S gases, pitting corrosion of carbon steel is considered to be a common occurrence which is particularly complex and still not fully understood. This paper presents a parametric study investigating the pitting corrosion behavior of carbon steel in CO_2-H_2S-containing environments. The work presented is divided into two parts. Part one focuses on understanding the impact of changes in three key process parameters (namely; temperature, absence/presence of 10% H_2S and absence/presence of CO_2 in the gas phase) on FeS film formation process and overall the corrosion behavior of carbon steel with emphasis on general corrosion of carbon steel in a 3.5 wt. % NaCl brine at 30 and 80°C. Part two focuses on understanding the early and later stages of the pitting corrosion process, with consideration afforded to general corrosion and iron sulfide (FeS) film formation mechanisms, kinetics and characteristics. The experiments were conducted based on short term (7 h) and long term tests (168 h) to investigate the early and later stages of evolution of pitting corrosion. Corrosion film properties and morphology are studied through a combination of electrochemical and surface analysis techniques which include scanning electron microscopy (SEM) and X-ray diffraction (XRD). The extent of corrosion damage of the carbon steel is evaluated through the implementation of surface interferometry to study pit depth and geometry. The results show that early stages of pitting corrosion is more likely to occur with the formation of mackinawite at both 30 and 80°C in H_2S systems than in CO_2 systems after 7 h. However, at 80°C extensive uniform corrosion is dominant, leading to the competing effect of iron sulfide (FeS) formation, continuous evolution of pitting corrosion and continuous ferrite dissolution in the presence of CO_2. Results from 168 h tests showed a build-up of FeS on the corroding steel surface with time with the increase in temperature and presence of CO_2 in the gas phase. The build-up of FeS in H_2S-CO_2 containing environments is enhanced by ferrite dissolution. The FeS formed after 168 h is composed mainly of mackinawite at 30°C and mackinawite and pyrrhotite at 80°C after 168 h. The combination of mackinawite (with a different morphology) and pyrrhotite is shown to promote more pitting and localized corrosion at 80°C than for mackinawite alone at 30°C.

INTRODUCTION

In the oil and gas industry, corrosion related failures have been reported to constitute over 25% of total safety incidents [1, 2]. The problem of corrosion in oilfield environments is mainly associated with the presence of dissolved acidic gases in reservoir brines such as CO_2 and/or H_2S [2].

Pitting corrosion remains one of the main modes of corrosion related failures encountered during oilfield production, constituting 12% of all oilfield corrosion incidents[1] and causing a significant impact on the economics of production [1, 2]. This localized mode of corrosion is of particular concern because of its unpredictable nature and the difficulty associated with inhibiting pit growth once it has initiated. Incidents of pitting corrosion failures can be encountered in oil and gas pipelines exposed to CO_2-H_2S containing brines [3, 4]. Although pit initiation in carbon steel materials has been linked to the presence of inclusions [5, 6] and initial preferential ferrite dissolution [7], it is also highly likely that the tendency for pits to initiate and grow in a CO_2-H_2S corrosion environment will be influenced by a combination of environmental and physical factors, as well as the presence of corrosion films[8].

With respect to pitting/localized corrosion of carbon steel in H_2S environments, a clear understanding of the level of influence and/or interaction of the environment on pitting corrosion has remained elusive. Previous studies on the mechanism of corrosion in H_2S-containing environments have been more orientated towards understanding uniform corrosion, with little or no attention associated towards localized/pitting corrosion. However, even contrasting observations appear evident in the literature on the role of H_2S in terms of general corrosion. For example, Videm and Kvarekvål [9], reported the uniform corrosion rate was initially constant with increase in H_2S concentration in mixed H_2S-CO_2 corrosion system from 0.02 mmol.dm^{-3} (~682 ppm) to 0.14 mmol.dm^{-3} (~4771 ppm) at 70°C and pH of 4.2. However, corrosion rate further increased from ~1.3 mm/yr in pure CO_2 to ~ 3mm/yr with ~ 6417 ppm of H_2S gas at 80°C and pH of 4.1. While on the other hand, Zheng et al. [10] and Ma et al. [11] reported a decrease in general corrosion rate of carbon steel in mixed CO_2-H_2S and H_2S-containing environments in the concentration range of 100 ppm to 0.65% H_2S gas and ≤ 0.04 mmol.dm^{-3} (~ 908 ppm), respectively. Furthermore, both Zheng et al. [10, 12] and Tang et al[13] have reported an increase in general corrosion rate of carbon steel with an increase in H_2S concentration in both mixed CO_2-H_2S and pure H_2S-containing environments at 30°C and pH 4 under shear at 1000 rpm RCE speed and at 90°C in 0.25M Na_2SO_4, respectively. These observations indicate the complexity of corrosion behavior of carbon steel in H_2S-containing environments, and together with only a handful of studies considering localized/pitting corrosion in H_2S systems, indicate there are still questions to be answered on the role of H_2S and CO_2 on general and pitting corrosion mechanisms.

Various authors [2, 4] have proposed that the corrosion environment to which carbon steel is exposed has the most influence on the extent of general and pitting corrosion, especially in a relation to the corrosion product formation kinetics, chemistry and morphology. A combination of the fast kinetics of formation of FeS (mackinawite) [11, 14, 15] and the inherent electronic properties of the different form of FeS films [16, 17] have been linked to the initiation and propagation of pitting and/or localized attack.

It appears that to achieve a full understanding of pitting corrosion in H_2S systems, that general corrosion, localized corrosion, the environment and film chemistry/structure must be collectively considered. Consequently, this work seeks to adopt a holistic approach towards understanding the early and later stages of evolution of pitting corrosion in H_2S environments through combined consideration of the evolution of uniform corrosion, corrosion product formation and pitting and/or localized corrosion of carbon steels in H_2S corrosion environments. This is coupled with a parametric approach in which temperature is varied in CO_2, H_2S-N_2 and H_2S-CO_2 systems to assist in isolating the individual effects of the dissolved gases on the aforementioned processes.

Two key sets of experiments were performed in this paper to investigate early stages (based on 7 h tests) of pitting corrosion and later stages (based on 168 h tests). The latter test duration has been explored with emphasis on film formation and chemistry, together with the evolution of localized/pitting corrosion.

Experimental Procedure

The purpose of this work is to assess the corrosion behavior of X65 steel exposed to a 3.5 wt.% NaCl solutions at two different temperatures (30°C and 80°C) under three different gas atmospheres; a pure CO_2 gas system, a 10 mol.% H_2S – 90 mol.% CO_2 gas system and a 10 mol.% H_2S – 90 mol.% N_2 gas system. The emphasis of this study is on corrosion product formation kinetics, quantification of uniform corrosion rates and understanding the evolution of pitting corrosion. This study is based on short duration (7 h) tests and longer duration (168 h) tests. Temperatures and partial pressures of the gases in the gas phase of the corrosion environment are provided in the matrix in Table 1.

Materials: X65 carbon steel samples were used as the working electrodes within a three-electrode cell in every experiment. The steel was in a normalized form and consequently possessed a ferritic/pearlitic microstructure. The nominal composition of the X65 steel is provided in Table 2.

The carbon steel was sectioned into 10 mm x 10 mm x 5 mm samples. Wires were soldered to the back of each samples and embedded in a non-conducting resin. Prior to the start of each experiment, samples were wet-ground up to 1200 silicon carbide grit paper, degreased with acetone, rinsed with distilled water and dried with compressed air before immediate immersion into the test brine. A surface area of 1 cm^2 was exposed to the electrolyte per sample and 5 samples were used per bubble cell in the H_2S corrosion test setup.

Experimental setup: Sweet (CO_2) and sour (H_2S-CO_2 and H_2S-N_2) corrosion experiments were conducted using different bubble cell systems, but with the same sample surface area to brine volume ratio of 5 cm^2 per 1 liter of test solution maintained at the start of all tests. CO_2 corrosion experiments were conducted in two vessels which were each filled with 2 liters of brine and stirred at 200 rpm. The vessels were sealed with 10 samples immersed per vessel and CO_2 was bubbled into the test solution continuously to ensure saturation of the solution. H_2S corrosion experiments were also conducted in two vessels which were each filled with 1 litre of brine, but only 5 samples were present in this case to maintain same surface area to volume ratio as in the CO_2 test. Pre-mixed 10 mol. % H_2S – 90 mol. % CO_2 gas and 10 mol. % H_2S – 90 mol. % N_2 gas were bubbled into the test solution continuously to ensure saturation of the solution.

Brine preparation and solution chemistry characterization: A 3.5 wt. % NaCl brine solution was used for all experiments and stirred at 200 rpm. The test solution for pure CO_2 corrosion experiments was saturated with CO_2 for a minimum of 12 h prior to starting each experiment to reduce oxygen concentration down to 20 ppb, simulating typical oilfield environments. N_2 was used initially to purge the test solution for tests in H_2S-containing environments (H_2S-CO_2 and H_2S-N_2). Prior to commencement of electrochemical measurements for H_2S corrosion tests, the test samples were placed in the N_2 saturated brine solution, after which H_2S-containing gas mixtures were bubbled into the solution for about 20-30 minutes until *in situ* pH is stabilized. All tests were conducted at atmospheric pressure.

In situ electrochemical measurements: Electrochemical measurements were conducted on two samples per test cell and two separate cells were used simultaneously to ensure repeatability. Each sample formed the working electrodes in a three electrode cell which also comprised of an Ag/AgCl reference electrode and a platinum counter electrode. Corrosion rate measurements were conducted using DC measurements with an ACM Gill 8 potentiostat[1]. Linear Polarization Resistance (LPR) measurements were performed by polarizing the working electrode from 15 mV below the open circuit potential (OCP) to 15 mV more positive than OCP at a scan rate of 0.25 mV/s to obtain a polarization resistance measurement (R_p). A scan rate of 0.25 mV/s is considered appropriate since it is a significantly lower than the maximum acceptable scan rate required for accurate LPR measurements [18, 19]. Tafel polarization measurements were performed with an ACM Gill 8 potentiostat at each experimental condition at the end of a 7 h LPR test to determine anodic and cathodic Tafel constants and ultimately the Stern-Geary coefficient, which was subsequently used in conjunction with measured values of R_p to estimate general corrosion rates. Tafel plots were obtained by performing anodic and cathodic sweeps as two separate sweeps on two different samples in the same test cell. Scans always started at the OCP and extended ±250 mV at a scan rate of 0.25 mV/s. Anodic and cathodic sweeps were performed on separate samples to ensure reliable measurements and the cathodic sweep was always performed first.

Tafel polarisation measurements were carried out in separate experiments from the LPR and pitting investigation tests and the samples was not used for pitting analysis.

Characterization of pitting corrosion damage: Pit depth measurements were conducted in alignment with ASTM G46-94 [20]. A NPFLEX 3D[2] interferometer was used in this study for defining the discrete geometry of pits on almost the entire surface area of steel sample. Pits were identified based on carefully chosen thresholds with distinct pit depths, diameters, and areas being quantified. ASTM G46-94 stipulates that an average of the 10 deepest pits and the maximum pit depth (based on relative pit depth measurement after removal of corrosion products) should be used for pit damage characterization for the sample area. A sample surface area of 9 x 9 mm^2 was analyzed for pits from the 10 x 10 mm^2 sample. Consequently, 3D images of regions where the deepest pits exist are identified on the sample surface with a high degree of accuracy and resolution. Visual evidence of pits/cavities has been

[1] ACM Gill 8 is a trademark name for ACM Instruments

[2] NPFLEX 3D is a trademark name for Bruker corporation

provided in terms of the deepest pits identified by the techniques implemented in this work. Such examples are provided later within this paper.

Results and Discussion

Tafel plots and electrochemical observations: FIGURE 1 shows the Tafel plots obtained at the end of the test after 7 h of immersion. The graphs correspond to solutions at temperatures of 30 and 80°C. Tafel polarization measurements were made at the end of LPR measurements for 7 h and showed good repeatability.

Table 3 indicates the measured Tafel constants and the resulting Stern-Geary coefficient values for all test conditions. The Tafel plots shown in FIGURE 1 suggest that the presence of 10 mol. % H_2S gas with CO_2 gas mainly influences the cathodic reactions at both temperatures. This is due to the addition of a direct or heterogeneous cathodic reduction reaction of HS^- [12, 21]. The change in the cathodic reaction process due to the presence of H_2S gas becomes less apparent with increasing temperature. The shape of the cathodic curves in H_2S-containing systems at 80°C suggests that there is still a significant contribution from the reduction reaction of H^+ and/or the buffering effect from H_2CO_3 to the total cathodic current with a shift from CO_2 corrosion system to 10 mol.% H_2S – 90 mol.% CO_2 containing corrosion system.. This is despite the fact that the initial starting pH of the test solution (shown in Table 4) is slightly higher for the H_2S/CO_2 mixture as for the pure CO_2 mixture.

The deductions from the Tafel polarization curves shown in FIGURE 1 has thus far shown strong agreement with the results by several other authors [10]. Zheng et al[10] reported that the main contribution to the cathodic current at 10% H_2S concentration is from the direct reduction of aqueous H_2S species at 30°C and pH of 4. It can also be argued from results shown in FIGURE 1 that the corrosion reaction of steel with H_2S in H_2S-containing environments dominates the reaction mechanism at lower temperature (30°C) and becomes less dominant as the temperature increases (to 80°C) *during the early stages of corrosion*. Referring to Table 4, the pH of un-buffered test solutions also vary slightly for the three gas systems under investigation.

Corrosion rate and corrosion products at 30°C: This section discusses the results based on 168 h experiments at 30 and 80°C with considerations to the early and later stages of the corrosion process. **Figure 2** (a) and (b) show the corrosion potential and corrosion rate measurements at 30°C for tests in 100 mol.% CO_2 gas, 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 corrosion environment over a 168 h. Referring to **Figure 2** (a), the corrosion potential increased with time for all conditions, however, the increase was more significant for tests in 100 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% CO_2 than for test in 10 mol.% H_2S – 90 mol.% N_2. The gradual increase corrosion potential over time to a stable value has been linked to the gradual evolution of networks of cementite in pure CO_2 corrosion system [2, 7, 22], and the establishment of a thin FeS corrosion product layer which suppresses the anodic dissolution reaction in the case of the H_2S environment [8]

Observations after 7 h

Referring to the corrosion rate measurements presented in **Figure 2**(b), the corrosion rate within the first 7 h is steady for the three gas systems. However, the corrosion rate in 100 mol.% CO_2 system (~1.2 mm/yr) is three times higher than in 10 mol.% H_2S – 90 mol.% CO_2 gas system (~0.5 mm/yr) and approximately four times higher than in 10 mol.% H_2S – 90 mol.% N_2 test system (~0.3 mm/yr). This observation is consistent with the findings of Choi et al.[23]. According to Choi et al.[23], it was reported that the corrosion rate was reduced from ~ 1.75 mm/yr to ~0.25 m/yr with the introduction of 100 ppm of H_2S gas into a CO_2 corrosion system at 25°C and pH 4 by the formation of a FeS layer. The corrosion results here also agree well with the Tafel polarization plots shown in **FIGURE 1**(a) which indicate that reduction reactions associated with the presence of H_2S dominate the cathodic current at 30°C and that there is significant suppression of the H^+ reduction reaction(s). In the work of Zheng et al.[10], a decline in corrosion rate after 2 h from ~1.8mm/yr in 100 mol.% CO_2 system to ~1.2 mm/yr in 10 mol.% H_2S – 90 mol.% CO_2 was observed (at 30°C, pH of 5, and 1000 rpm rotating speed). The observation from this study has either been attributed to the establishment of a chemisorbed layer of FeS (Fe-S_{ad}) onto steel surface that displaces aggressive species at the corrosion interface[10] or to the formation of FeS corrosion products (most likely mackinawite) by other authors[11, 14]. For the experiments performed in **Figure 2**, mackinawite is observed for tests containing H_2S, as shown in the SEM images after 7 h in Figure 3. The existence of FeS is confirmed by the x-ray diffraction (XRD) patterns as shown in Figure 3(d). In addition, Figure 3 (a) indicates the initial revealing of the Fe_3C network for the pure CO_2 environment as a result of preferential ferrite dissolution[7]. Figure 3(b) and (c) show the presence of a very thin FeS corrosion product layer, and a 'smudge-like textured' FeS layer with a non-uniform coverage for test samples exposed to 10 mol.% H_2S-90 mol.% CO_2 and 10 mol.% H_2S-90 mol.% N_2, respectively. Polishing marks could still be visible on the corroded steel surface to corroborate the low corrosion rate in these systems. The physical features of FeS at 30°C and after 7 h show a combination of the formation of an adsorbed FeS_{ad} and FeS (mackinawite) layer. The presence of polishing marks in the FeS film formed after 7 h is related to the "solid state" reaction mechanism for the formation of FeS described by Shoesmith et al [14] and the similarities in the crystal cell dimensions of iron and mackinawite[24]. Rickard and Luther III[24], had explained that the Fe-Fe inter-atomic distance in a mackinawite crystal is 2.5967 Å, which is similar to (BCC) ferrite crystal at 2.86 Å. This makes ferrite-rich surface an almost perfect template for the nucleation of mackinawite as shown in Figure 3 (b) and (c). Thus, when a layer of adsorbed FeS from reaction of H_2S or HS^- at the steel surface is formed as reported in the literature [10, 25], it retains the polishing marks of an uncorroded surface, especially at initial stages of the corrosion.

Observation after 168 h

Referring to **Figure 2** (b), the corrosion rate for the X65 exposed to 100 mol. % CO_2 initially increases from ~1.2 to ~1.8 mm/yr before stabilizing at this latter corrosion rate until the end of the test. The initial increase is associated with the evolution of an empty Fe_3C network prior to the establishment of non-protective and nano-crystalline $FeCO_3$ over time [2, 7, 8]. The corrosion rate became constant at ~1.8 mm/yr once an amorphous and/or nano-scale polycrystalline $FeCO_3$ corrosion product was established on the surface as shown in **Figure 4**(a) after 168 h. Identification of $FeCO_3$ is confirmed by the XRD pattern in **Figure 4** (b). The corrosion rate in H_2S-containing corrosion environments; 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 is almost the same and constant throughout the duration of the tests at one-third of the corrosion rate in 100 mol.% CO_2 corrosion environment. As previously mentioned in this paper, the formation of an adsorbed mono-layer of Fe-S_{ads} at the early stages of the corrosion process and the deposition of FeS corrosion product could be responsible for the lower corrosion rate in H_2S-CO_2 and H_2S-N_2 containing corrosion environment over 168 h. Although the kinetics of FeS formation at this temperature (30°C) is also expected to be slow[26]in comparison to higher temperatures (to be shown later for 80°C), the nature of FeS formed is able to keep the corrosion rate in the H_2S corrosion systems constant at low values compared to the pure CO_2 corrosion environment. From the SEM images of **Figure 4** (c) and (e), it is evident that over the course of the 168 h experiments, the lower corrosion rate observed in 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 gas corrosion systems is due to the formation of a FeS corrosion product layer. Although the morphology of the FeS corrosion products in these systems are different in terms of their physical features, these layers are thin and have been identified in this work as mackinawite with no evidence of other forms of FeS at this temperature. SEM image shown **Figure 4** (c) shows significant (but non-uniform) coverage of the steel surface by FeS.

Corrosion rate and corrosion products at 80°C**:** The results in this section focus on the corrosion behavior of carbon steel samples over 7 and 168 h periods. The corrosion potential and corrosion rate over 168 h experiments at 80°C for the three gas systems are presented in **Figure 5** (a) and (b) respectively. Referring to **Figure 5**(a) an initial corrosion potential of -684 mV, -710 mV and -730 mV are recorded for 100 mol.% CO_2, 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2, respectively. These values are consistent with potential expected for H_2S-containing systems in Choi et al.[23] and Morris et al.[27]. After the initial period, the corrosion potential for all three test systems showed very different behavior over the remaining duration of the test. In 100 mol. % CO_2 gas systems, the corrosion potential became stable at -667 mV until the end of this test. This is attributed to the formation of an amorphous/nano-scale polycrystalline and crystalline $FeCO_3$. With test in 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 systems, there is an observed and significant shift in the corrosion potential in the direction of positive potential by approximately 70 mV and 100 mV, respectively. In 10 mol.% H_2S – 90 mol.% CO_2 gas system, the potential is increasing rather gradually from 66 h to the 168 h when compared to 10 mol.% H_2S – 90 mol.% N_2 gas system, where it took up to 100 h before observing a sharp increase in potential.

Observations after 7 h

Within the first 7 h, the magnitude of general corrosion rate increases with time for 100 mol. % CO_2 gas systems, while the corrosion rate is lower and relatively constant in H_2S-containg systems. The latter effect is due to the formation of FeS layer as previously shown in this paper. Evidence of formation of FeS can be seen on the SEM images of **Figure 6**(b) and (c) and the corresponding XRD pattern (**Figure 6** (d)). At 80°C, the contribution of the H^+ reduction reaction to total cathodic current in 10 mol.% H_2S – 90 mol.% CO_2 systems has earlier been shown to be more significant than at lower temperatures. This influence manifests itself as a higher corrosion rate than at lower temperature in H_2S-containing systems and is also an indication for the potential increased contribution from uniform corrosion to total material loss. The FeS corrosion product layer formed in H_2S-containing environments is observed to be non-uniform with localized regions showing cementite due to preferential ferrite dissolution for test in 10 mol.% H_2S – 90 mol.% CO_2. With 10 mol. % H_2S – 90 mol. % N_2, the corrosion product morphology is different from that in 10 mol. % H_2S – 90 mol. % CO_2 and shows evidence of less corrosion of surrounding regions without the FeS films. The results thus far have shown that within the first 7 h of corrosion in H_2S-CO_2 containing systems, there is a competition between ferrite dissolution and FeS precipitation at 80°C. The effect of higher temperature is also likely to influence the kinetics of FeS formation beyond 7 h. The latter involves the loss of Fe^{2+} into the bulk solution preceding surface deposition and is shown from the results from this study to be favored by the presence of CO_2 gas in the gas mixture.

Observations after 168 h

Referring to the corrosion rate data presented in **Figure 5**(b), the corrosion rate is reduced with the formation $FeCO_3$ corrosion product layer from ~5.6 mm/yr to 3.2 mm/yr after 18 h in the 100 mol. % CO_2 corrosion system. The corrosion rate also reduces from a peak at ~2.4 mm/yr to ~0.57 mm/yr for test in 10 mol. % H_2S – 90 mol. % CO_2 and from a peak at ~1.0 mm/yr to ~0.2 mm/yr for test in 10 mol. % H_2S – 90 mol. % N_2. The increase in corrosion potential towards positive values and reduction in corrosion rate in both 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2 gas systems is due to the formation of FeS (mackinawite and pyrrhotite) layers. However, the rate of increase in potential and reduction in corrosion rate is observed to be faster in 10 mol. % H_2S – 90 mol. % CO_2 than in 10 mol. % H_2S – 90 mol. % N_2. This is due to the presence of CO_2 in the gas phase and high temperature. It has previously been shown in this paper that the CO_2 corrosion process helps to increase the availability of ferrous ions. This promotes precipitation of FeS and enhances the build-up of FeS at 80°C. This is evident in the SEM images in **Figure 7**(a)-(c). The XRD patterns in **Figure 7**(d) and (f) also confirm the presence of mackinawite and pyhrrotite forms of FeS. The mackinawite film formed after 168 h is also observed to have a different morphology to that formed after 7 h. Although peaks may have been expected for $FeCO_3$ in the 10 mol. % H_2S – 90 mol. % CO_2 gas system, this was however not the case due to the dominant nature of the FeS formation process. This is because all possible Fe^{2+} that would have contributed towards solution supersaturation for the formation of $FeCO_3$ is likely to be used up for the formation of FeS since theoretically, the solubility of FeS scale is relatively lower than $FeCO_3$ and as a result, FeS is favorably formed. (As an example, the solubility product of makinawite is 3.6 ± 0.2 at 25°C[28], while that of $FeCO_3$ is 9.53 ± 0.04 at 25°C and in 0.7M NaCl [29]). This is also supported by the greater thickness in FeS layer formed in 10 mol. % H_2S – 90 mol. % CO_2 than in 10 mol. % H_2S – 90 mol. % N_2 as shown in **Figure 8**(a) and (b). The average thickness of FeS layer is ~8.2 µm and ~ 5.8 µm for 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2, respectively.

Pitting Corrosion Behavior of Carbon steel in H_2S-containing corrosion systems: Investigation of pitting corrosion in this study is focused on two aspects; early stages and later of pitting corrosion process based on 7 h and 168 h tests respectively. All pitting corrosion data in H_2S-containing corrosion systems are presented with reference to pitting corrosion data in the 100 mol. % CO_2 systems.

Early stages of pitting corrosion process H_2S-containing corrosion systems

This section assesses the early stages of pitting corrosion of carbon steel in H_2S corrosion environments with reference to the early stages of pit evolution in 100 mol. % CO_2 corrosion systems based on 7 h tests. Short term tests were explored to investigate the early stages of pitting corrosion by correlating the fast kinetics of FeS formation and the formation of a non-protective corrosion product and/or breakdown of protective corrosion product layers[4] to the pitting process. It is also important to understand the processes that precede the evolution of pitting corrosion. The early stages of pit evolution is accessed in this study after 7 hours and evaluated against a minimum pit depth threshold of 5µm. The number of measureable pits after 7 h based on this threshold is also taken into account. All pit size analysis and characterization were carried out after removal of corrosion products. A limitation to this method of pitting corrosion analysis is that the transient process of pit initiation and propagation cannot be established. While some authors[4] had defined pitting rate based on ex-situ analysis as used in this work, others[30] have shown from field data that the transient pitting corrosion profile (based on pit depth) is usually complex to such extent that we are not able to establish for certain the point at which the initially formed pit starts to grow. Hence, for the results presented in this section, the concept of pitting process is adopted instead of pit initiation and propagation. Figure 9 presents the size of deepest pits and its relationship with estimated thickness loss due to uniform corrosion. **Figure 10(**a) and (b) present the size of deepest pit and average pit depth based on measurements from over 80% of the steel surface after 7 h, while Figure 9(b) presents the number of measureable pits with depth ≥ 5µm after 7 h. The average pit depth is the average of the 10 deepest pit on an entire exposed surface. Pit depth in this instance is relative to the corroded surface after removal of corrosion products.

Referring to Figure 9 and **Figure 10**, there were no pits on the test sample at 30°C in a 100 mol. % CO_2 system. The size of deepest pit on the surface is ~7.4 μm at 80°C. Similar trends in depth of pit with temperature change in CO_2 systems after 7 h has previously been published[8] in separate tests. It is believed that increase in temperature increases the kinetics of corrosion, the rate of revealing of empty cementite and the kinetics of corrosion product formation. A combination of these and the localized galvanic cell (although not established in this study) that arises due to the formation of non-protective corrosion products [7, 8] is likely the reason why more pits are initiated at 80°C than at 30°C in the CO_2 environment. However, it has also been shown previously[8], that the extent of **initiated pit** at 80°C can be masked by the extensive uniform corrosion of surrounding surfaces such that a complex mix of material degradation mechanism always exist for carbon steel.

For tests in 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2 gas systems, the results **in Figure 9 and Figure 10(a)** also show that depth of initiated pits increased from 100 mol. % CO_2 to 10 mol. % H_2S – 90 mol. % CO_2, and 10mol. % H_2S – 90 mol. % N_2 gas systems (based on the deepest pit), while at the same time the general corrosion rate decreases in the same order of gas systems. This was observed to be similar for both 30 and 80°C. For instance, at 80°C, the depth of deepest pit increases from ~7.4 μm to ~10 μm and then ~15.4 μm for tests in 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 gas systems, respectively. Referring to **Figure 10**(b), the number of initiated pits greater than 5μm is observed to be consistently higher in H_2S-CO_2 system than in H_2S-N_2 system at each temperature. At 80°C, the number of initiated pits is higher in H_2S-CO_2 system than in CO_2 and 2.5 times higher than H_2S-N_2 system. This confirms the synergy between CO_2 and temperature on the early stages of the corrosion process. It manifests in the form of competition between FeS formation and ferrite dissolution to influence the evolution of pitting corrosion process in the presence of H_2S gas. While these results could not prove the direct relationship between size of initiated pits and the presence of CO_2, it does suggest the influence of initial ferrite dissolution (linked to the presence of CO_2) on the number of initiated pits prior to the formation of FeS. In H_2S-N_2 system, it has already been shown in this report that minimum ferrite dissolution precedes FeS formation. This is related to the absence of CO_2 gas in the system (which usually promotes uniform corrosion) and the observation of lower rate of evolution of ferrite and hence a lower number of initiated pits. It is important to note that the deepest pit is usually the most important in terms of understanding the role of these parameters. The observed changes in size of the deepest pit with changing temperature were also the same for all gas combinations. While the minimum threshold for defining a pit is understandably considered vague, examples of the deepest pit on an exposed surface are shown in **Figure 11**(a) and (b), for tests in H_2S-CO_2-containing corrosion system at 30 and 80°C respectively as visual evidence of measurable pits.

It is important to recognize that the propensity for the start of pitting corrosion process to occur in 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2 gas systems correlates with the formation of FeS in H_2S-containing corrosion environments. Deeper pits where also initiated in H_2S-N_2 gas containing system than in H_2S-CO_2 and CO_2 only gas systems. However, at 80°C, more pits were initiated in CO_2 than in H_2S-N_2 and the most in H_2S-CO_2 corrosion system. In CO_2 gas system, high levels of ferrite dissolution enhance the creation of localized anodes. In H_2S-CO_2 gas system the synergy of the corrosiveness of CO_2, the presence of H_2S and formation of FeS appears to indirectly influence the early stages of the pitting process. This is in terms of higher number of created localized anodes (linked to the evolution of Fe_3C[7]) and local galvanic effect from FeS. Ferrite dissolution, which is driven mostly by the CO_2 corrosion component, is also critical in the non-uniform distribution of initially formed FeS as shown in **Figure 6**(a) and (b) for test at 80°C [2, 7]. In H_2S-N_2 corrosion system, synergistic effect explained for the H_2S-CO_2 system is almost non-existent, leading to less of the uneven distribution of FeS as shown in **Figure 6** (c). The FeS layer has more coverage on the surface with less exposed anodic sites due to less initial ferrite dissolution. This translated into a higher size of deepest pit shown in **Figure 9** because of a likely enhanced local galvanic effect and absence of masking effect from uniform corrosion favoured (by the less aggressiveness of the corrosion system due to the absence of CO_2).

The uneven distribution of FeS could be inducing micro-galvanic cells (although not proved in this study) as the driving force for this stage of the pitting corrosion across the surface of the steel, especially once FeS is formed. It has already been established[4] and confirmed in this study that the early stages of pitting corrosion is related to the formation of semi-protective corrosion products. It can therefore be argued that the evidence of measurable pits after 7 h is justifiable since FeS has been shown to form quickly in this study. The electronically conductive nature of FeS[17] is also believed to be capable of supporting the electrochemical processes that precedes the emergence of pits and/or micro-pits [16]. This makes it possible for the FeS layer to support the cathodic reactions while undermining local ferrite-rich pores underneath some of the FeS film. From the results of corrosion product identification and pitting data recorded in this study, it is evident that the formation of FeS (mackinawite) is important to the evolution of pitting corrosion, while the presence of CO_2 in H_2S corrosion environments promotes uniform corrosion and acts in synergy to promote FeS formation.

Increasing the temperature from 30 to 80°C correlates with increase in the depth of initiated pits (relative to corroded surface). This is due to the effect of increasing temperature on the kinetics and nature of FeS formation. However, at 80°C the depth of initiated pit can be also masked due to the competition between continuous ferrite dissolution and FeS formation. The former leads to higher contribution from uniform corrosion to material penetration at 80°C, as already established in a previous publication[8] and masks the depth of initiated pits. The presence of CO_2 also tends to increase total material loss via ferrite dissolution, manifesting mainly in the form of uniform corrosion. This is clearly depicted by the relationship between uniform corrosion and initiated pits as shown in **Figure 9**. The results presented in **Figure 9** and based on 7 h test shows evidence of a synergy between the presence of CO_2 gas in H_2S-containing corrosion systems and temperature.

Later stages of pitting corrosion process H_2S-containing corrosion systems

This section presents and discusses the progression of pitting corrosion with time based on longer duration tests (after 168 h) at 30 and 80°C. The size of deepest pit on an entire exposed surface area and its relationship with estimated thickness loss due to uniform corrosion for the different corrosion environments investigated in this study is presented in **Figure 12**. The average depths of pits are presented in **Figure 12**. Referring to **Figure 12** and **Figure 13**, the size of deepest pit and average pit depth in 100 mol.% CO_2, 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 gas systems increases with increase in temperature after 168 h. This trend highlights the role of temperature and the underlying electrochemical processes on the progression of pitting process. As already mentioned in previous sections, the electrically conductive nature of FeS[17] is capable of supporting the preferential cathodic reaction that could drive localized anodic dissolution. As shown in **Figure 7**(b) and (c), and **Figure 8**(a) and (b) there is evidence to confirm that higher temperature promotes faster formation and build-up of FeS than at 30°C for both 10 mol.% H_2S – 90 mol.% CO_2 and 10 mol.% H_2S – 90 mol.% N_2 gas systems. This also results in the ennoblement of the corrosion potential and reduction in corrosion rate as shown in **Figure 5**(a) and (b). A thicker layer of FeS (composing mainly mackinawite and pyrrhotie) at 80°C is capable of driving the progression of pits depths up to ~146 µm and ~83 µm as recorded at 80°C in both 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2 gas systems respectively than at 30°C (where FeS is mainly mackinawite).

The electrochemical responses presented in **Figure 5**(a) and (b) is representative of the overall exposed surface, including possible localized galvanic cells that manifests as localized corrosion. The corrosion rate is higher in the H_2S-CO_2 gas system than in the H_2S-N_2 gas system at 80°C after 168 h as shown in **Figure 5**. This has also been shown in **Figure 7**(c) and (d) and **Figure 8** (a) and (b) to translate into the formation of thicker and more uneven deposition of FeS in H_2S-CO_2 gas system than in H_2S-N_2 gas system at 80°C. This helps to establish the relationship between the gas systems and the build-up of FeS. In a similar trend, the synergistic effect from the presence of CO_2 gas in the H_2S-CO_2-containing system and temperature is also shown in **Figure 12** and **Figure 13** to directly promote pitting and/or localized corrosion at 30 and 80°C (especially at 80°C). In H_2S-CO_2 corrosion systems, most of the ferrous ions produced during ferrite dissolution are driven by the CO_2 corrosion mechanisms and temperature and consequently consumed for the formation of different forms of FeS such that there is no evidence of $FeCO_3$ in the XRD pattern in **Figure 7**(d) but mostly FeS (mackinawite and pyrrhotite) as shown in **Figure 7**(c). In H_2S-N_2 corrosion system, there is less occurrence of ferrite dissloution process linked to uniform corrosion especially in the absence of CO_2 gas. Hence, there is less build-up of FeS in comparison to H_2S-CO_2 corrosion system as shown in **Figure 8**. This also could also translate to lesser local galvanic effect and hence lower size of deepest pit than in H_2S-CO_2 systems after 168 h as shown in **Figure 12**. **Figure 12** shows that the amount of FeS (non-uniform coverage) is a significant driver of pit progression. This is linked to the potential galvanic effect arising from the conductive properties of FeS.

It is therefore evident that the synergy of the presence CO_2 and higher temperature helps to promote both pitting/localized and uniform corrosion. This synergy is clearly presented as a relationship between pitting/localized corrosion and uniform corrosion in **Figure 12** and is related to the kinetics of Fe dissolution (more uniform corrosion) and hence more FeS formation. This is different to the scenario in the early stages of pitting corrosion process where the synegistic effect of CO_2 and temperature on carbon steel in H_2S-CO_2 system shows no direct relationship with the size of initiated pits. In the H_2S-N_2 gas system, minimum uniform corrosion is observed and hence minimum ferrite dissolution. This also resulted in less build-up of FeS via surface precipitation as shown in **Figure 8**and hence lower depth of measurable pits as shown in **Figure 12** and **Figure 13**. Examples of pits after 168 h at 80°C are shown in **Figure 14**. From the SEM image shown in **Figure 7**(c) and (e), the FeS deposits in H_2S-N_2 corrosion systems are less irregular than in H_2S-CO_2 gas system. This is an indication that while both H_2S-CO_2 and H_2S-N_2 corrosion systems show ennoblement of potential and reduction in corrosion rate, the localized distribution of FeS is also fundamental to the progression of pitting and/or localized corrosion in these systems over time. This also influences the morphology of pitting attack as shown in **Figure 14**.

From the results presented and discussed in this study, it is evident that CO_2 corrosion process manifests predominantly in the form of uniform corrosion. With longer exposure and higher temperature, there is an increase in the cumulative contribution of uniform corrosion over time in H_2S-CO_2-containing corrosion systems. This is a result of the role of CO_2 presence in promoting ferrite dissolution and indirectly enhancing pitting corrosion in H_2S environments. It is also evident that measurable pits (at the early and later stages of pitting process) are not significantly masked by the general corrosion of the surrounding surfaces in H_2S-N_2-containing systems. The presence of H_2S gas in a corrosion environment and formation of FeS reduces the general corrosion rate in H_2S-N_2 and H_2S-CO_2-containing systems, but not necessarily reducing the risk of pitting of carbon steel pipelines.

Conclusions

The corrosion behavior of carbon steel material in CO_2 and H_2S containing brine has been investigated at 30 and 80°C with emphasis on uniform corrosion behavior, film formation characteristics, and pitting corrosion behavior for up to 168 h. The following conclusions were deduced from the results from this study.

- The early stages of pitting corrosion in H_2S-containing environments were found to be influenced by both the formation of FeS (makinawite) corrosion products and temperature. Although a temperature increase was shown to promote pitting corrosion in pure CO_2 environments in the absence of FeS films, the presence of H_2S is able to increase the extent of pitting, most likely through the formation of FeS corrosion product layers which can form rapidly on the steel surface.

- The initiation rate of pits was highest in the combined presence of H_2S and CO_2 compared to the presence of the individual gases alone at both 30 and 80°C. H_2S and CO_2 are able to work synergistically together to provide more substantial FeS films over the same timeframe (over 168 h) compared to purely H_2S systems at the same H_2S content (10 mol.% in this instance).

- The mass of deposits of FeS corrosion products played a significant role in pit growth process. There appears to be a link between the quantity of FeS deposit on the steel surface and the rate of pit progression as the deepest pit were found in systems with the greatest mass of FeS corrosion product at the same temperature. Whether this is achieved through a galvanic effect between the FeS film and the steel surface cannot be confirmed in the present study.

- In the process of evolution of pitting corrosion (both at its early and later stages), the synergistic effect of CO_2 and H_2S is most significant at 80°C. When CO_2 gas is present in conjunction with H_2S, uniform corrosion contribution to material loss is increased much more at 80°C compared to 30°C. This invokes significant FeS formation as well as ferrite dissolution, resulting in the most severe pitting.

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FIGURE CAPTIONS

FIGURE 1: Tafel polarization plots for X65 carbon steel in 3.5 wt.% NaCl solution saturated with 100 mol.% CO_2, 10 mol.% H_2S-90 mol.% CO_2 and 10 mol.% H_2S-90 mol.% N_2 at (a) 30°C and (b) 80°C after 7 h exposure.

Figure 2: Graphs of (a) corrosion potential and (b) corrosion rate of X65 carbon steel in 3.5 wt. % NaCl solutions under three different gas atmospheres at 30°C, over 168 h.

Figure 3: SEM images of corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution saturated with (a) 100 mol.% CO_2, (b) 10 mol.% H_2S- 90 mol.% CO_2 and (c) 10 mol.% H_2S-90 mol.% N_2 at 30°C. (d) XRD pattern for corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution saturated 10 mol.% H_2S- 90 mol.% CO_2 and 10 mol.% H_2S-90 mol.% N_2 at 30°C. Images are for test duration of 7 h. *(Note that the intensity scale is arbitrary)*.

Figure 4: SEM images and XRD patterns of corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution under gas atmospheres composed of (a) 100 mol.% CO_2, (b) XRD pattern for 100 mol.% CO_2 (c) 10 mol.% H_2S- 90 mol.%CO_2 (d) XRD pattern for 10 mol.% H_2S- 90 mol.%CO_2 (e) 10 mol.% H_2S-90 mol.% N_2 and (f) 10 mol.% H_2S-90 mol.% N_2 at 30°C and after 168 h.

Figure 5: Graphs of (a) corrosion potential and (b) corrosion rate of X65 carbon steel in 3.5 wt. % NaCl solutions under three different gas atmospheres at 80˚C, over 168 h.

Figure 6: SEM images of corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution saturated with (a) 100 mol.% CO_2, (b) 10 mol.% H_2S- 90 mol.% CO_2 and (c) 10 mol.% H_2S-90 mol.% N_2 at 80°C. (d) XRD pattern for corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution saturated 10 mol.% H_2S- 90 mol.% CO_2 and 10 mol.% H_2S-90 mol.% N_2 at 80°C for test after 7 h. *(The intensity scale is arbitrary)*.

Figure 7: SEM images and XRD patterns of corrosion product layer on X65 carbon steel in 3.5 wt.% NaCl solution under gas atmospheres composed of (a) 100 mol.% CO_2, (b) XRD pattern for 100 mol.% CO_2 (c) 10 mol.% H_2S- 90 mol.%CO_2 (d) XRD pattern for 10 mol.% H_2S- 90 mol.% CO_2 (e) 10 mol.% H_2S-90 mol.% N_2 and (f) 10 mol.% H_2S-90 mol.% N_2 at 80°C and after 168 h.

Figure 8: Cross-sectional view after micro-machining using the FIB for (a) SEM image shown in Figure 7(c) for 10 mol.% H_2S- 90 mol.% CO_2 and (b) SEM image shown in Figure 7(e) for 10 mol.% H_2S- 90 mol.% N_2 at 80°C.

Figure 9: Summary of relationship between estimated thickness loss due to uniform corrosion and size of deepest initiated pit (relative to corroded surface) as a function of environmental parameters in H_2S-containing corrosion systems after 7 h.

Figure 10: (a) Average pit depth (relative to corroded surface) and (b) Number of pits ≥ 5µm per 1 cm^2 area of carbon steel surface exposed to corrosion system under 100 mol. % CO_2, 10 mol. % H_2S – 90 mol. % CO_2 and 10 mol. % H_2S – 90 mol. % N_2 gas atmosphere as a function of temperature after 7 h. (Error bars are based on the standard deviation from the average of size of 10 deepest pit)

Figure 11: 2D and 3D images of deepest pits (relative to corroded surface) on carbon steel surface exposed to corrosion system under 10mol.% H_2S – 90 mol.% CO_2 for 7 h at (a) 30°C and (b) 80°C.

Figure 12: Summary of relationship between estimated thickness loss due to uniform corrosion and size of deepest propagated pit (relative to corroded surface) as a function of environmental parameters in H_2S-containing corrosion systems after 168 h

Figure 13: Average pit depth (relative to corroded surface) on carbon steel surface exposed to corrosion system under 100mol.% CO_2, 10mol.% H_2S - 90mol.% CO_2 and 10mol.% H_2S - 90mol.% N_2 gas atmosphere for 168 h as a function of temperature. (Error bars are based on the standard deviation from the average of size of 10 deepest pit)

Figure 14: 2D and 3D images of deepest pit (relative to corroded surface) on carbon steel surface exposed to corrosion system under 10mole% H_2S - 90mole% CO_2 after 168 h at 80°C, after 168 h.

Tables

Table 1 Temperature of experiments and associated partial pressures of H_2S and CO_2 gas in different gas combinations at 1.013 bar in the tested brine solution

Temp (°C)	Partial Pressure, p (bar)			
	10 mol.% H_2S – 90 mol.% CO_2		10 mol.% H_2S – 90 mol.% N_2	
	H_2S	CO_2	H_2S	N_2
30	0.097	0.874	0.097	0.874
80	0.055	0.498	0.055	0.498

Table 2: X65 Carbon steel composition (wt. %)

C	Si	P	S	Mo	Mn	Ni	Nb	V	Fe
0.15	0.22	0.025	0.002	0.17	1.422	0.09	0.054	0.057	97.81

Table 3: Tafel constants at different temperatures and gas mixtures; β_a and β_c are the anodic and cathodic Tafel constants, respectively

Temp (°C)	Mole % of combining gases								
	100 mol.% CO_2			10 mol.% H_2S – 90 mol.% CO_2			10 mol.% H_2S – 90 mol.% N_2		
	β_a	β_c	B	β_a	β_c	B	β_a	β_c	B
30	32	200	12	55	11	16	55	170	18
80	58	135	18	58	16	18	47	135	15

Table 4: Average *in situ* pH of test solutions for different gas systems for the first 7 h

Temp (°C)	In-situ pH of test solutions					
	100 mol.% CO_2		10 mol.% H_2S – 90 mol.% CO_2		10 mol.% H_2S – 90 mol.% N_2	
	Start	End	Start	End	Start	End
30	4.00	4.20	4.02	4.03	4.70	4.68
80	3.90	4.78	4.31	4.54	4.74	4.78