# $\mathrm{CO}_2$ TOP OF THE LINE CORROSION IN THE PRESENCE OF $\mathrm{H}_2\mathrm{S}$

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This thesis entitled

# $\mathrm{CO}_2$ TOP OF THE LINE CORROSION IN THE PRESENCE OF $\mathrm{H}_2\mathrm{S}$

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# ALVARO CAMACHO MANUITT., M.S., August 2006, Chemical Engineering. <u>CO<sub>2</sub> TOP OF THE LINE CORROSION IN THE PRESENCE OF H<sub>2</sub>S (134 p.)</u> Director of Thesis: Srdjan Nesic

The objective of this research work is to investigate the main parameters that affect  $CO_2/H_2S$  top of the line corrosion (TLC).

For each experiment, top and bottom of the line weight loss corrosion measurements were performed. Higher general corrosion rates were found for the bottom of the line than for the top of the line.

Tests were conducted on carbon steel (API X-65 or AISI 1020) coupons, using deionized (DI) water as the electrolyte. The experiments were conducted in large scale flow loops at different absolute pressures and a fixed temperature, having test durations from 2 to 21 days. Experimental conditions (temperature, total pressure, pH, H<sub>2</sub>S concentration, superficial gas velocity) were monitored regularly during each experiment.

It was found that the total pressure, partial pressure of  $CO_2$ , partial pressure of  $H_2S$ , and HAc concentration have a strong effect on the general corrosion behavior for both top and bottom of the line. No traces of localized attack could be found either at top nor bottom of the line in the 21 days of experiments in the presence of  $CO_2$  and  $H_2S$ . Longer lasting experiments should be performed in the presence of HAc. Approved:

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# DEDICATION

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### **CHAPTER 1: INTRODUCTION**

This research work was done with the support of four important oil and gas companies. All the problems addressed in this work are of great concern to these companies, as they are closely related to wet gas corrosion as an operational and maintenance issue, and they worked in close collaboration with the author to design the test matrices, experimental techniques, materials to be evaluated, etc.

 $CO_2$  corrosion, or so called "sweet corrosion," is the most prevalent form of attack encountered in oil and gas production. It is also a major concern in the application of carbon and low alloy steels, which are still the principal construction materials due to their economy, availability and strength.  $CO_2$  corrosion phenomena have been widely studied<sup>1-4</sup>, however understanding and control of top of the line corrosion lags significantly behind general knowledge of  $CO_2$  corrosion; this is particularly true when acetic acid (HAc) and/or hydrogen sulfide (H<sub>2</sub>S) are present.

Top of the line corrosion (TLC) occurs in multiphase flow or during wet gas transportation when water vapor condenses on the internal walls of the pipeline due to the heat exchange occurring between the pipe and the surroundings (frozen land, deep-sea water).

Unprocessed vapor flowing through the pipe condenses on the cooler walls where the condensed liquid becomes rich in aggressive species present in the stream; these species include organic acids, carbonic acid and sulfurous acid.

Since TLC happens when condensation occurs, it is typically associated with partially or completely failed thermal insulation. Despite the available corrosion control techniques which are capable of mitigating particular deterioration processes, TLC becomes a problem because of the three different locations that might be found in a pipeline.

Gunaltun<sup>5</sup> reported that the pipe wall can be divided into three parts:

- The bottom of the line, where the corrosion is uniform and its rate can be lowered with the use of inhibitors.
- The sidewall of the pipe, where the condensed water drains to the bottom. The corrosion is also uniform, but inhibitors are not efficient.
- The top of the line, where a protective iron carbonate layer can be formed but inhibitors are not effective, and localized corrosion could occur if the corrosion layer does not offer uniform protectiveness.

As can be appreciated in Figure 1, the key factors affecting TLC can be divided into:

- The condensation process due to the heat exchange
- The dissolution of the aggressive species in the condensed liquid and
- The subsequent attack of the metal surface.

At the top of the line and even at the sides of the pipe, the continuous injection of corrosion inhibitor is impossible due to the lack of carrier liquid.



**Figure 1. Key factors affecting TLC** 

#### **CHAPTER 2: LITERATURE REVIEW**

Some research work<sup>6-11</sup> has been done describing the main parameters influencing TLC due to carbon dioxide (CO<sub>2</sub>). In each case, the influential parameters are the bulk temperature, temperature of the pipe wall, total pressure of the system, partial pressure of CO<sub>2</sub>, gas velocity and condensation rate. All of these parameters influence the corrosion rate (CR) in a complex way, but common behaviors are generally observed:

- At low condensation rates, a protective film of iron carbonate (FeCO<sub>3</sub>) appears on the surface of the pipe exposed to TLC, which lowers the CR. The formation of this film is explained by the iron saturation of the liquid film and the precipitation of corrosion product, which locally lowers the pH<sup>6-11</sup>.
- At high condensation rates, saturation cannot be reached, and the CR can reach several mm/y. The CR is governed by the rate of the corrosive reaction and the rate of condensation. The former increases the amount of iron in the liquid film, while the later decreases this amount. The CR depends on the balance of these two counteracting effects<sup>6-11</sup>.

The effect of organic acids (acetic acid, in the present work) on  $CO_2$  corrosion has been investigated before<sup>12-16</sup>. In  $CO_2$  corrosion, it is known that the presence of acetic acid (HAc) in the liquid phase leads to an increase in the general CR. It is believed that HAc influences the corrosion process in two ways which are practically indistinguishable<sup>10-14</sup>. First, the HAc dissociates to form acetate (Ac<sup>-</sup>) and hydrogen ions (H<sup>+</sup>) <sup>10-14</sup>, acting as a provider of protons (it will decrease the pH of the solution). Secondly, the remaining HAc that did not dissociate (called free acetic acid) is believed to be reduced directly on the metal surface (in the same way as the carbonic acid). The contribution of the proton reduction and the direct reduction of HAc at the metal surface increases the overall cathodic current and enhances the anodic reaction (metal dissolution). It is not conclusive which of these two HAc influences actually occurs.

In a  $CO_2$  environment, the degree of this influence depends on the free acetic acid/carbonic acid ratio. It is also proposed that the presence of Ac<sup>-</sup> could have an effect on the properties of the carbonate layer and change its potential protectiveness through the formation of an iron acetate layer instead of iron carbonate. Regarding TLC, the same observation can be made. HAc is volatile, so it can be transported in the gas phase and condenses with the water on the walls of the pipe.

It has also become increasingly obvious that the number of gas fields with  $H_2S$  where TLC is a problem is on the rise. The effect of small quantities of  $H_2S$  on TLC remains unknown. In the light of a recent TLC failure<sup>5</sup> of a sour wet gas line, better understanding of the  $H_2S$  effect on TLC is needed.

 $H_2S$  and  $CO_2$  are "acid gases", which promote corrosion phenomena in gas transportation and production pipelines by forming weak acids in water. At low pressure, the solubility of both  $H_2S$  and  $CO_2$  can be estimated using Henry's law. The difference in the aqueous phase gases is that aqueous  $CO_2$  must undergo a hydration reaction to form carbonic acid ( $H_2CO_3$ ) before dissociation while aqueous  $H_2S$  is acidic and will directly dissociate into solution<sup>17</sup>.

Vapor-liquid equilibrium reactions for carbon dioxide and hydrogen sulfide are described as<sup>3</sup>:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$
 Eqn. 2.1

$$H_2 S_{(g)} \leftrightarrow H_2 S_{(aq)}$$
 Eqn. 2.2

Henry's law is used to calculate the composition of the vapor-liquid equilibrium:

$$x_{CO_2}H_{CO_2} = pCO_2$$
 Eqn. 2.3  
 $x_{H_2S}H_{H_2S} = pH_2S$  Eqn. 2.4

where  $x_{CO_2}$  and  $x_{H_2S}$  are the mole fractions of CO<sub>2</sub> and H<sub>2</sub>S in solution and *H* is the Henry's constant. *pCO*<sub>2</sub> and *pH*<sub>2</sub>S are the partial pressures of CO<sub>2</sub> and H<sub>2</sub>S.

Although there is no direct reaction between CO<sub>2</sub> and H<sub>2</sub>S, the composition of the solution can be determined through a sequence of chemical reactions and by considering the common ion effect because the H<sup>+</sup> ions. As CO<sub>2</sub> gas dissolves in water, aqueous carbon dioxide ( $CO_{2(aq)}$ ) is hydrated to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>).

$$CO_{2(aq)} + H_2O_{(liq)} \longleftrightarrow H_2CO_{3(aq)}$$
 Eqn. 2.5

The  $H_2CO_3$  dissociates to release a  $H^+$  and a bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) in solution:

$$H_2CO_{3(aq)} \longleftrightarrow H_{(aq)}^+ + HCO_{3(aq)}^-$$
 Eqn. 2.6

The  $HCO_3^-$  also dissociates to release another  $H^+$  and a carbonate ion  $(CO_3^{2-})$ .

$$HCO_{3(aq)}^{-} \longleftrightarrow H_{(aq)}^{+} + CO_{3(aq)}^{2-}$$
 Eqn. 2.7

After H<sub>2</sub>S dissolves in water, it does not need to hydrate with water to form an acid in order to dissociate H<sup>+</sup>. Since it is acidic, H<sub>2</sub>S dissociates to bisulfide ( $HS^-$ ) and sulfide ( $S^{2-}$ ) species in a series of dissociation reactions in solution:

$$H_2 S_{(aq)} \xleftarrow{K_1} H_{(aq)}^+ + H S_{(aq)}^-$$
 Eqn. 2.8

$$HS_{(aq)}^{-} \longleftrightarrow H_{(aq)}^{+} + S_{(aq)}^{2-}$$
 Eqn. 2.9

Since these processes occur in water, all are in dynamic equilibrium with  $H_2O$ ,  $H^+$  and  $OH^-$  ions:

$$H_2O_{(l)} \longleftrightarrow^{K_W} H_{(aq)}^+ + OH_{(aq)}^-$$
 Eqn. 2.10

Although  $H_2S$  gas is about three times more soluble than  $CO_2$  gas, the acid created by dissociation of  $H_2S$  is about three times weaker than carbonic acid. Hence, the effect of  $H_2S$  gas on decreasing the solution pH is approximately the same as  $CO_2$  gas. Unlike dissolved  $CO_2$ , dissolved  $H_2S$  does not need to undergo the slow hydration step in order to become an acid<sup>18</sup>.

The distribution of species is dependant upon the partial pressures of  $CO_2$  and  $H_2S$ , the temperature, and the pH of a known system. Concentration of species can be determined by solving the corresponding equilibrium reactions above.

Ignoring the metal cracking aspects associated with sour corrosion due to the hydrogen permeation into the metal lattice, the  $H_2S$  can affect  $CO_2$  corrosion in various ways. It has been reported that trace amounts of  $H_2S$  does retard the corrosion process at ambient temperature<sup>19</sup> by the formation of a protective FeS film by solid state reaction. On the other hand, the presence of higher concentrations of  $H_2S$  can also lead to the formation of FeS according to the solid state reaction, however the formation and pealing off of this layer can enhance the corrosion process:

$$Fe_{(s)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + H_{2(g)}$$
 Eqn. 2.11

or by precipitation according to:

$$Fe_{(aq)}^{2+} + S_{(aq)}^{2-} \leftrightarrow FeS_{(s)}$$
 Eqn. 2.12

Depending on various environmental factors, different thermodynamically stable types of FeS can be formed. In some cases FeS film can be non protective and result in localized attack. For example, due to the difference in density between the corrosion layer (potentially protective) and the base metal, the formed layer can generate internal stresses itself which can lead to film facture, causing a potential localized attack problem.

Generally, three regimes in  $CO_2/H_2S$  systems can be classified based on the concentration of  $H_2S$  as shown in Figure 2.<sup>20</sup>



Figure 2. Corrosion regimes in CO<sub>2</sub>/H<sub>2</sub>S corrosion defined by Pots, et al.<sup>20</sup>

In the  $H_2S$  dominated system, known as the sour regime, the dissolved  $H_2S$  is a weak acid similar to carbonic acid. As a result, not only does  $H_2S$  lower the pH, but also

it can increase the CR in a similar way as carbonic acid by providing an extra cathodic reaction:<sup>18</sup>

$$H_2S_{(aq)} + e^- \rightarrow H \cdot + HS^{-}_{(aq)}$$
 Eqn. 2.13

this reaction can enhance the corrosion process by itself.

# CHAPTER 3: RESEARCH OBJECTIVES AND EXPERIMENTAL CONDITIONS 3.1 Objectives

This research work has as the main objective the investigation of the most important parameters that affect  $CO_2/H_2S$  top of the line corrosion, primarily, the  $H_2S$  partial pressure (pH<sub>2</sub>S) effect. The influence of other parameters on the  $CO_2/H_2S$  corrosion process were also analyzed:

- Total pressure (P)
- Partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>)
- Partial pressure of H<sub>2</sub>S (pH<sub>2</sub>S)
- HAc concentration
- Material (steel type)
- Test duration

In order to get a better understanding of the effect of the previously mentioned parameters, other variables affecting TLC were kept constant:

- Total pressure of the system (for each test series)
- Temperature
- Gas velocity
- Condensation rate
- pH

This work attempts to evaluate how the previously mentioned parameters affect the general corrosion process and the occurrence of localized attack. Some of the experimental conditions and the actual corrosion rate results had to be normalized to protect the proprietary information in this project.

In the oil and gas production industry, the temperature is considered as "high" when its value is within 60°C and 100°C. The temperature tested in these experiments has a value within this range and was the same for every experiment of each series.

The value of condensation rate above which TLC could happen is  $0.1 \text{ ml/m}^2/\text{s}$ . The condensation rate evaluated in this project is significantly higher than this value, and it was labeled as a "high" condensation rate.

The values of HAc concentration and total and partial pressure of  $CO_2$  and  $H_2S$  were also normalized. Therefore, no units are shown for these parameters in this document.

### **3.2 Test Matrix**

The actual evaluated conditions are commonly found in oil and gas production and were suggested by the sponsor companies of the present project. The different experiments that were performed are listed below, specifying the variables investigated.

The test matrix is divided in three different series, designed by the sponsors of the project, as an answer to problems found in their own fields. The temperature, gas velocity and condensation rate were kept constant for all the experiments series, the rest of the variables were changed according with the specific objective of each series.

### 3.2.1 Series I

Table 1 shows details of the experimental conditions. This set of tests aims at studying the effect of the H<sub>2</sub>S partial pressure on TLC. Different H<sub>2</sub>S partial pressures

were tested from 0 to 1.3. In this series the influence of  $CO_2$  partial pressure (p $CO_2$ ) and  $H_2S$  partial pressure (p $H_2S$ ) together is studied in four different experiments (I-3, I-4, I-5 and I-6). The effect of p $CO_2$  was evaluated in two steps changing it by a factor of 10, while the total pressure was maintained at 30 by adding nitrogen. The test duration was two days and each experiment was repeated once.

Experiment # I-0 I-3 I-1 I-2 I-4 I-5 I-6 Investigating Baseline  $H_2S$  $CO_2/$  $CO_2/$  $CO_2/$  $CO_2/$  $H_2S$  $H_2S$  $H_2S$  $H_2S$ pCO<sub>2</sub> 1.3 1.3 1.3 13 1.3 1.3 13 pH<sub>2</sub>S 0.04 0.13 0.7 1.3 0.7 1.3 0

Table 1. TLC Test matrix, Series I

For this series of experiments the superficial gas velocity was kept constant at 5 m/s, the condensation rate was fixed at a high value and the temperature was high. The liquid phase was deionized (DI) water. The pH is monitored and fixed by the experimental conditions.

For Series I, the material evaluated was an API X-65 carbon steel (coupon extracted from a 13" outside diameter pipe section, thickness:  $1 \frac{1}{2}$ ").

### 3.2.2 Series II

The details of the experimental conditions are shown in Table 2. The main parameters tested were the  $H_2S$  partial pressure (from 0 to 0.4), the free acetic acid concentration (from 0 to 10) and their combination. The gas temperature was high, the partial pressure of  $CO_2$  is 80 and the condensation rate was set at high value. The liquid phase was made of DI water. The pH was monitored and fixed by the experimental conditions. It is important to mention than while experiments II-1, II-2, II-3, and II-4 lasted four days, experiment II-0 (test without H<sub>2</sub>S or HAc) lasted only two days.

Experiment #	II-0	II-1	II-2	II-3	II-4
Investigating	Baseline	$H_2S$	HAc		$H_2S$
pH <sub>2</sub> S	0	0.05	0.05	0.05	0.4
[HAc]	0	0	5 (free)	10 (free)	10 (free)
Duration	2 days	4 days	4 days	4 days	4 days

Table 2. TLC Test matrix, Series II

At the sponsors' request (similarly to changes to total and partial pressure) for Series II the material evaluated was AISI 1020 bought in the form of a solid bar. The total pressure evaluated in this series was 83 while the superficial gas velocity was kept constant at 5 m/s.

In order to compare the performance of the different materials, both steels (API X-65 and AISI 1020) were evaluated under the same  $CO_2/H_2S$  conditions and no acetic acid. That is, experiment II-1 was done twice using steel X-65 first and then steel AISI 1020.

The chemical analyses and mechanical properties of each material are shown in Appendix A, page 128.

The HAc influence was studied in four different experiments where the free acetic acid concentration in the liquid phase in the tank was changed from 0 to 0.40. While keeping the HAc concentration constant, the  $H_2S$  partial pressure was raised in order to evaluate the interaction between the two corrosive agents.

### 3.2.3 Series III

In order to investigate the occurrence of localized attack, longer lasting tests were done; in Series III the effect of  $H_2S$  partial pressure was evaluated in experiments of 2, 7, 14 and 21 days duration. The 2 day experiments were done to compare results with Series I. In Table 3, the tested values of the variables evaluated are shown.

Experiment # III-0 III-1 III-2 III-3 Investigating Baseline  $H_2S$  $pCO_2$ 20 20 20 20  $pH_2S$ 0 0.04 0.7 1.3

Table 3. TLC Test matrix, Series III

For this series, the total pressure was fixed at 30, the temperature was set at a high value, the condensation rate was also high while the superficial gas velocity was 5 m/s. The liquid phase was made of DI water. The pH was monitored and fixed by the experimental conditions. The material tested at these conditions was API X-65.

### **3.3 Experimental Setup**

The experiments were done in two different large scale stainless steel flow loops, the H<sub>2</sub>S flow loop and the TLC I loop, in order to simulate real field conditions.

### 3.3.1 H<sub>2</sub>S flow loop

Figure 3 shows the process and instrumentation diagram of the H<sub>2</sub>S flow loop.

Figure 4 shows a picture of this system.

This system is comprised of 101.6 mm (4") diameter, Sch 80, Hastelloy<sup>©</sup> C-276 (UNS No. 10276) for resistance to corrosion and stress corrosion cracking, two progressive cavity pumps for conveying liquid and gas, and three separate test sections for corrosion monitoring<sup>21</sup>.

The  $H_2S$  flow loop (1950 liters capacity) has a large stainless steel conical bottom tank from where the liquid solution is drawn from the bottom using a progressive cavity pump (PCP), while another PCP is used to pump the gas around the flow loop; the latter suctions the vapor phase from the top of the tank while a small positive displacement pump feeds the gas PCP with the needed liquid for lubrication.

This closed system is horizontally leveled, and it is fully insulated from the environment. Heat is added to the system using two resistance-heaters, which are immersed in the tank.

The gas pump circulates the vapor through a 41 m. long Hastelloy C-276<sup>21</sup> pipeline that is connected back to the tank. Through the loop, a stratified vapor flow is created; such vapor fluid is rich with the corrosive gases present in the system.



Figure 3. Schematic diagram of the H<sub>2</sub>S flow loop



Figure 4. H<sub>2</sub>S flow loop

As mentioned before, the  $H_2S$  flow loop has three test sections. For the present work only the down stream test section is used. In this section (Figure 5) two coupons are flush-mounted at the top of the line while two others are similarly installed at the bottom.



Figure 5. Downstream H<sub>2</sub>S loop test section.

### 3.3.2 TLC I flow loop

The experiments without  $H_2S$  are performed in the TLC I loop which consists of a 30 m. long, 101.6 mm. inner diameter pipe, and has all AISI 316L stainless steel wetted parts. A schematic diagram of this system is shown in Figure 6 and a photograph of the system is presented in Figure 7.



Figure 6. Schematic diagram of the TLC I flow loop

This closed system is horizontally leveled and is fully insulated from the environment. The tank used for liquid storage contains 1 m<sup>3</sup> of water.<sup>22</sup> The concentration of acid present in the water is controlled by injection.



Figure 7. H<sub>2</sub>S flow loop

Heat is added to the system using resistance heaters (Inconel<sup>©</sup> 625), which are immersed in the tank. The power available is 90 kW. A blower provides gas velocities up to 20 m/s. A system of coils is used for the cooling of the gaseous phase, allowing condensation to occur; a gas/liquid separator is used also to catch any liquid carry-over before the test section.

The test section provides four ports, two at the top of the line and two at the bottom of the line, which are available for the measurement of the CR by insertion of flush-mounted corrosion monitoring probes.

### **3.3.3** Measurement Techniques

A weight loss technique was used to calculated the average CR. Prior to exposure each coupon was polished with 600 grain sand paper following the ASTM G 1 -81 Standard<sup>23</sup>, dried with isopropyl alcohol and weighed using a balance with an accuracy of 1/10<sup>th</sup> milligram. After the experiment, the coupons were removed from the loop, its surface was flushed with isopropyl alcohol and dried, then the coupons were weighted again and pictures of the surface were taken for visual examination and to register the appearance of the corrosion layer.

Scanning Electronic Microscopy (SEM) examination is done on every coupon, analyzing the morphology of the corrosion attack and the corrosion layer, and its composition through Energy Dispersive Spectrometry (EDS).

After removing the corrosion layer following the mentioned ASTM G 1 -81 Standard<sup>23</sup>, the weight loss for each specimen was determined and the CR was obtained using the following equation:

$$CR = \frac{\left(W_o - W_f\right) \times \left(\frac{24 \text{ hours}}{1 \text{ day}}\right) \times \left(\frac{365 \text{ days}}{1 \text{ year}}\right)}{\rho \times A \times t} \times \left(\frac{10 \text{ mm}}{1 \text{ cm}}\right)$$
Eqn. 3.1

where

CR = Corrosion rate in mm/yr  $W_o = \text{Initial weight (g)}, \qquad W_f = \text{Final weight (g)}$  t = time elapsed during the experiment in hours  $\rho = \text{Density (7.85 g/cm^3)}$   $A = \text{Area } A = \pi \left[ \left( \frac{\phi_{Ext}}{2} \right)^2 - \left( \frac{\phi_{Int}}{2} \right)^2 \right] \text{cm}^2$ Eqn. 3.2

 $\phi_{Ext}$  = External diameter ( $\phi_{Ext} \approx 3.17 \ cm$ )  $\phi_{Int}$  = Internal diameter ( $\phi_{Int} \approx 0.757 \ cm$ )

The carbon steel coupons used to measured the CR were flat surface disks; only one face of the coupon was in direct contact with the corrosive environment as the other faces are coated with Teflon to avoid electrical contact with the probe holders, with the environment or even with the loops themselves. In Figure 8 the appearance of a typical weight loss coupon used in this project is shown. The coupons are shown as they are prior to exposure and after polishing.



Figure 8. Weight loss coupons with Teflon coating at the back and the side (External diameter = 3.14 cm, Internal diameter 0.757 cm)

### **3.3.4** Experimental Procedure

The general procedure for experiments is as follows. The tank/loop is initially filled with 300 gallons of distilled water. In order to get the desired superficial gas velocity of 5 m/s, the PCP is set at 615 rpm while the lubrication pump is run at 54 MHz.

The solution is then purged with  $CO_2$  gas to deoxygenate to less than 20 parts per billion (ppb) oxygen content; the dissolved  $O_2$  concentration is measured using a colorimetric technique. The ampoules used to measured the oxygen concentration are Vacuettes<sup>®</sup> from Chemetrics.

Heaters were used to reach and maintain the desired temperature. The concentration of dissolved iron (Fe<sup>2+</sup>) was measured before each experiment begins and was monitored during the whole duration of the experiment. The Fe<sup>2+</sup> concentration was measured using a Turner<sup>®</sup> SP-870 spectrophotometer.

Other variables that were regularly monitored during the experiments are pH, temperature, pressure, and H<sub>2</sub>S concentration.

The pH measurements were done with a pH meter provided with a high pressure electrode that was connected to the pH measurement port shown in Figure 9.



Figure 9. pH meter installed in the pH measurement port at the H<sub>2</sub>S loop

The  $H_2S$  concentration was measured using the colorimetric tubes shown in Figure 10, that gives accurate readings of the  $H_2S$  concentration in the gas phase. Depending upon the expected  $H_2S$  concentration, different Gastec® tube ranges were used.

The condensation rate was set by adjusting the cooling water flow through the coiling tube (see Figure 5) by using the needle valves that control the water flow for each test port cooling system. The condensation rate was measured by collecting condensed liquid in a device installed at the end of the test section, as shown in Figure 11. The water

flow rate on the cooling system (see Figure 5) was adjusted to get the specified condensation rate.



Figure 10. Gastec® pump used to measure H<sub>2</sub>S concentration in the gas phase



Figure 11. Condensation rate measurement device

The condensation rate measurement device is provided with two valves, one at the top and one at the bottom. Between the valves and directly connected to the device, a glass pipe with a scale allows measurement of collected liquid over given time. Before making the condensation rate measurement, the device was drained; thus, to make the measurement the upper valve is opened and once is possible to get a reading from the

scale, the chronometer starts; after enough liquid is in the device, another reading is taken and the watch stops.

Due to the toxicity of the  $H_2S \text{ gas}^{24}$ , the condensation rate cannot be measured in the  $H_2S$  loop using the same device described previously. Thus, after setting the desired condensation rate at the Inclinable Loop, the temperature difference between the gas flow and the pipeline wall was measured. Considering this difference as the main driving force for the condensation to occur, the same temperature difference was set at the  $H_2S$  system in order to mimic the condensation rate in the  $H_2S$  loop. The probe used to measure the temperature difference is made with two thermistors that separately measures the gas temperature and the wall temperature simultaneously. The thermistor that measures the wall temperature is at the flat surface of the probe which gets flush-mounted in the pipeline wall, while the gas temperature is measured with the thermistor located at the tip of the probe. The temperature probe is shown in Figure 12.



**Figure 12. Temperature probe** 

Prior to injection of the  $H_2S$  gas, its partial pressure was estimated using an equilibrium calculation. With this result, the  $H_2S$  gas was injected measuring the differential pressure with the gas transducer installed in the loop (Figure 13). The  $H_2S$  concentration in the gas phase is then verified to check the actual concentration
corresponds to the desired condition. If not, more H<sub>2</sub>S was injected until the needed experimental conditions were reached.

Prior to injection of acetic acid (HAc), the desired free acetic acid concentration was calculated through equilibrium equations and using as data inputs the pH of the liquid phase in the tank, the  $CO_2/H_2S$  partial pressures and the Fe<sup>2+</sup> concentration in the liquid phase. The HAc concentration was double checked measuring again the pH after the HAc injection.



Figure 14 - 15 shows some other equipments used in the experimentation.

Figure 13. Pressure transducer installed in the H<sub>2</sub>S loop



Figure 14. Gas mixing panel



Figure 15. H<sub>2</sub>S safety control panel

#### **CHAPTER 4: EXPERIMENTAL RESULTS AND DISCUSSION**

#### 4.1 Series I

In this chapter, the influence of  $H_2S$  partial pressure on corrosion at the top and the bottom of the line of API X-65 carbon steel will be discussed. For this Series, the total pressure and the partial pressure of  $CO_2$  (p $CO_2$ ) were kept constant at 30 and 1.3 respectively.

# 4.1.1 H<sub>2</sub>S influence

Figure 16 shows results related to the influence of  $pH_2S$  on corrosion at the top and the bottom of the line. The numbers shown at each data point represent the number of coupons used to calculate the corrosion rate and the error bars are the maximum and minimum values obtained after the weight loss measurement.



Figure 16. Series I. Effect of the H<sub>2</sub>S partial pressure at the top and bottom of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Surface analyses are presented in Figures 22 to 38)

In the environment without  $H_2S$ , the average corrosion (CR) rate was around 3.3 for top of the line. The measured variables are shown in Appendix B1.

When 40 units of partial pressure of  $H_2S$  are introduced, the top of the line CR decreases to 1.5 and this decrease continues to 0.2 when the partial pressure of  $H_2S$  reaches 1.3 units. However, when the partial pressure of  $H_2S$  is further increased (in this case to 0.7), the trend is inversed and the CR increases to 1.3. However, further increase of the  $H_2S$  partial pressure to 1.3 does not seem to have a clear effect on the top of the line CR which remains at a similar value as measured at 0.7 units of  $H_2S$ .

The same trend (trace amounts of  $H_2S$  retard corrosion) is observed for bottom of the line tests. For bottom of the line conditions, without  $H_2S$ , the average CR is 16.3; average CR decreases to approximately 5.5 units with 0.04 and 1.3 units of  $pH_2S$  and reaches values of 11.5 for 0.7 and 1.0 units of  $H_2S$ .

The higher CR for bottom of the line coupons may be explained by the higher amount of water, present at the bottom. For top of the line coupons, the condensed water hangs on the metal surface for a finite amount of time; during that time, the corrosive gases dissolve into the liquid phase and the corrosion reactions occur, with the subsequent increase of the pH (due to increasing  $[Fe^{2+}]$ ) and promotion of the precipitation of species on the metal surface<sup>3</sup>. The precipitation process leads to formation of a layer that presents a barrier that retards the corrosion reaction.

For bottom of the line conditions, the metal surface is constantly wetted by fresh solution where the pH is controlled by the amount of dissolved acid species and not by the  $Fe^{2+}$  concentration. The differences in water chemistry between top and bottom of the line promote a different CR for each condition.

In order to compare the CR with the scale formation rate (amount of corrosion scale accumulated at the surface) both processes were expressed in the same units of reaction rate. The scale formation rate can also be seen as the amount of iron that ends up as part of the corrosion product layer. Figure 17 shows the comparison of the scale formation rate with the CR for top of the line conditions.

After two days of experimentation, the scaling formation rate (SFR) seems to be more than 30% of the CR, except for experiment I-2 (0.13 pH<sub>2</sub>S), where the calculated general CR was close to 0 (0.2) and the SFR/CR ratio went off of the scale . Also, in Experiment I-2 the scaling formation rate has a value seven times higher than the CR.



Figure 17. Series I. Rate of reaction under the effect of the  $H_2S$  partial pressure at the top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high

# **condensation rate, test duration: 2 days.** (Surface analyses are shown in Figures 22 to 38)

As H<sub>2</sub>S partial pressure increases the SFR/CR ratio tends to increase to values close to 100%. Even though, the SFR stays constant, the CR decreases for higher pH<sub>2</sub>S.

Figure 18 shows the scaling formation rate and the CR comparison for bottom of the line coupons.



Figure 18. Series I. Rate of reaction under the effect of the H<sub>2</sub>S partial pressure at the bottom of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Surface analyses are shown in Figures 22 to 38)

For bottom of the line conditions, the ratio between the SFR and the CR seems to be fairly constant with values below 10%.

The lower SFR/CR ratio for bottom of the line compared with the ratio for top of the line is another indication of the favorable scaling tendency for top of the line.

# 4.1.2 CO<sub>2</sub> influence

Figure 19 presents the influence of the CO<sub>2</sub> partial pressure at the top and bottom of the line. It is seen that the top of the line CR almost doubles if the CO<sub>2</sub> partial pressure is increased by an order of magnitude (from 1.3 to 13) independently of the H<sub>2</sub>S partial pressure. The same trend is observed at the bottom of the line at a lower magnitude of change. However, the bottom of the line results are not conclusive due to the limited number of coupons analyzed for the high H<sub>2</sub>S partial pressure conditions (pH<sub>2</sub>S = 13) and the wide range of corrosion rates found for the lowest pCO<sub>2</sub> evaluated. The error bars of the low pH<sub>2</sub>S overlapped with the values found at higher pH<sub>2</sub>S. For all of these conditions, the bottom of the line corrosion is one order of magnitude higher than for the top of the line.



Figure 19. Series I. Effect of the CO<sub>2</sub> partial pressure at the top of the line. High temperature, P = 30,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Surface analyses are shown in Figures 22 to 38)

Figure 20 shows the comparison between the scaling formation rate and the CR for top of the line coupons under different pCO<sub>2</sub> and pH<sub>2</sub>S. For the experiments performed with 1.3 units pH<sub>2</sub>S at different pCO<sub>2</sub>, the SFR/CR ratio is higher than for the experiments with the lower pH<sub>2</sub>S. The FeS reaction (solid state reaction) occurs more rapidly than the FeCO<sub>3</sub> precipitation<sup>18</sup>, thus as H<sub>2</sub>S concentration (pH<sub>2</sub>S) rises, the scaling formation is expected to occur more quickly. In the same way, increase of pH<sub>2</sub>S promotes higher CRs. When the pH<sub>2</sub>S is equal to the pCO<sub>2</sub> the scaling formation rate is comparable suggesting that all the iron dissolved became part of the resulting corrosion layer (SFR / CR = 100%



Figure 20. Series I. Rate of reaction under the effect of different  $H_2S$  and  $CO_2$  partial pressures at the top of the line. High temperature, P = 30,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Surface analyses are shown in Figures 22 to 38)

Figure 21 presents the scaling formation rate and the CR for bottom of the line coupons under different  $pCO_2$  and  $pH_2S$ .

For bottom of the line conditions, where the FeCO<sub>3</sub> precipitation is not expected due to the lower pH values than for the top of the line, the SFR/CR ratio remains constant at values lower than 8%. This supports the contention that bottom of the line condition is less favorable to scaling formation than top of the line.



Figure 21. Series I. Rate of reaction under the effect of different H<sub>2</sub>S and CO<sub>2</sub> partial pressures at the bottom of the line. High temperature, P = 30,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Surface analyses are shown in Figures 22 to 38)

# 4.1.3 Surface Analysis

In the present section some optical photographs, SEM and backscatter images

together with EDS analyses will be discussed to get a better understanding of the

phenomena.

# 4.1.3.1 Top of the Line

Figure 22 shows optical photographs of the surface of API X-65 carbon steel

coupons from Series I after two days experimentation at the top of the line for pH<sub>2</sub>S from

0 to 1.3.



Figure 22. Series I. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 30,  $V_G = 5$ m/s, high condensation rate, test duration: 2 days. (Corrosion rate are presented in Figure 16, 17, 19 and 20)

For this set of experiments, the temperature was kept constant at a high value and two  $CO_2$  partial pressures were evaluated (1.3 and 13).

The surface of the coupon evaluated in absence of  $H_2S$  (Figure 22a) shows characteristics of *mesa attack*, typical of CO<sub>2</sub> flow induced corrosion. However, when  $H_2S$  is present, the morphology of the resultant corrosion layer changes for all pH<sub>2</sub>S evaluated (see Figure 22b, 22c, 22d and 22e).

The rounded areas present on the surface of the coupons seem to be droplet fingerprints. These fingerprints are present on all the top of the line coupons, showing evidence of the condensation process and the subsequent attack on the metal surface.

In Figure 22f and 22g, the photograph of the coupons exposed to the higher  $pCO_2$  are shown. Comparing pictures 22d with 22f and 22e with 22g, it can be said that when the  $pCO_2$  is increased from 1.3 to 13, no major difference of the morphology of the resultant corrosion layer is found.

Figure 23 to Figure 27 show the SEM photomicrograph of the API X-65 carbon steel coupons surfaces after testing at the top of the line. As mentioned in section 3.1 the experimental condition for Series I are: high temp., pH<sub>2</sub>S of 0, 0.04, 0.13 and 1.3 and  $pCO_2 = 1.3$ . The pictures showed in Figure 23 to 27 are presented in different magnifications.

SEM observation at low magnification (50x, 100x, 200x) remain unchanged for each H<sub>2</sub>S condition and no evidences of localized attack were found at pCO<sub>2</sub> equal to 1.3. The coupon of the test performed in a pure CO<sub>2</sub> environment (Experiment I-0,  $pH_2S = 0$ ) showed the presence of small acicular (needle-like) features (see Figure 27a) distributed uniformly on the surface of the coupon (Figure 26a, and 27a).



Figure 23. Series I. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate , test duration: 2 days (50x) (Corrosion rate are presented in Figures 16, 17, 19 and 20)



same surface examined at higher magnification shows these features (see Figure 27a).

At low magnification the mentioned acicular features are not evident however, the

Figure 24. Series I. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (100x) (Corrosion rate are presented in Figures 16, 17, 19 and 20)



Figure 25. Series I. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (200x) (Corrosion rate are presented in Figures 16, 17, 19 and 20)



Figure 26. Series I. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (500x) (Corrosion rate are presented in Figures 16, 17, 19 and 20)



**Figure 27. Series I. Top of the line. High temperature, P = 30, pCO<sub>2</sub> = 1.3, V<sub>G</sub> = 5 m/s, high condensation rate, test duration: 2 days (2000x)** (Corrosion rate are presented in Figures 16, 17, 19 and 20)

Based on the experimental conditions for experiment I-0, it is likely that the film is composed of FeCO<sub>3</sub>. It has been reported<sup>4</sup> that four different film composition are possible on the carbon steel surface between 5°C and 105°C.

Considering that the test temperature is within the mentioned range, the four possible films are: a transparent film, iron carbide (Fe<sub>3</sub>C), iron carbonate (FeCO<sub>3</sub>) or a combination of Fe<sub>3</sub>C and FeCO<sub>3</sub><sup>3,4</sup>. However, previous work<sup>3,4</sup> confirmed that FeCO<sub>3</sub> or siderite is the main layer formed on carbon steel surfaces in absence of H<sub>2</sub>S.

The morphology of the corrosion layer appears homogeneous and few areas of the coupon show incomplete formation of the film. Back-scatter and EDS analyses of the film on specific areas are shown in Figure 28 and 29, respectively. EDS analysis reveals the presence of C, O and Fe (elements associated with FeCO<sub>3</sub> films) on the area covered with corrosion products (border of the droplet fingerprint). C, O and Mn are present inside the droplet marks. Since Mn is an element present in the carbon steel alloy, it gives a basis to establish that the brighter areas represent the base metal without any film while the dark area is covered by a FeCO<sub>3</sub> layer.

The backscatter images in Figure 28a shows the droplet fingerprint with rounded features on its border. It is important to mention that inside the droplet fingerprint other rounded particles of different size are present.

The lighter-colored area in Figure 28a is determined to be the wetted area. Figure 29 shows the interface area at a higher magnification, which seems to show the darker area of the backscatter image as a non-corroded area of the original metal surface. EDS analysis were performed in both bright and dark areas.



Figure 28. Series I. Backscatter images .Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 17, 19 and 20)



Figure 29. Series I, Experiment I-0. EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $pH_2S= 0$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16 and 17)

If trace amount of  $H_2S$  (0.04, 0.13, 0.7, 1.3 units pH<sub>2</sub>S) are present in the system, the surface topography changes (see Figures 23, 24, 25, and 26). No acicular features are present; the surface coverage seems to be more complete and uniform. The layer seems to be formed of small crystals, of morphology consistent with FeCO<sub>3</sub><sup>15</sup>. However, the composition analysis reveals only the presence of iron sulfide, as will be seen later.

Looking at the interface between a wetted and non-wetted area, and the backscatter images of the same areas presented in Figure 28, it can be concluded that the film composition is uniform across the interface for each pH<sub>2</sub>S tested.

In  $CO_2/H_2S$  environment, the solid state reaction to produce FeS film<sup>18</sup> subdued the growth of the iron carbonate crystals. The condensed water droplet becomes rich in  $S^{2-}$  and  $HCO_3^-$ . Once the aggressive species reach the top of the line wall, the fastest reaction happens first (FeS formation). Other factors (drag forces and gravity) prevent long lasting droplet hanging on the top of the line, giving insufficient time for the FeCO<sub>3</sub> precipitation conditions.

With the addition of further  $H_2S$  (0.13), the overall surface features revealed for  $pH_2S$  of 0.04 units are comparable. The crystal features shown for 0.13 units or higher  $pH_2S$  are similar to those found at  $pH_2S$  equal to 0.04. The main difference in the morphology of the layer is the different particle sizes found with the incremental changes of  $pH_2S$ . The higher the  $H_2S$  partial pressure, the bigger the precipitated features found.

For the highest  $pH_2S$  evaluated (1.3) different zones were revealed. Figures 26f and 27f show different size crystals precipitated. In Figure 30, the mentioned precipitated are presented with the corresponding EDS analysis.



Figure 30. Series I, Experiment III-3. EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days. (Corrosion rate are presented in Figures 16, 17, 19 and 20)

As shown in Figure 30, despite the crystal size or shape, the whole corrosion layer is composed of FeS.

Figure 31 compares the coupons for Experiment I-3 and I-5, where the pCO<sub>2</sub> was changed from 1.3 to 13 at the same pH<sub>2</sub>S (0.7). Despite the more obvious fingerprint on the surface , the layer shows similar characteristics to that previously described: a uniform layer of iron sulfide with the presence of crystals of different sizes.

Figure 32 presents the coupons exposed to 1.3 units  $pH_2S$  and two different  $pCO_2$ . No iron carbonate could be identified even if the shape of the crystals is very characteristic. Despite the increase in  $CO_2$  partial pressure, there is no significant effect on the corrosion product layer. It only affects the general CR as mentioned in section 4.1.2.

# 4.1.3.2 Bottom of the Line

Figure 33 provides the general overview of the surface of the bottom of the line coupons as removed from each experiment and rinsed with isopropanol.

Corrosion product film coverage was complete due to complete fluid coverage of the surface in each case, however, for 13 units  $pCO_2$  conditions (Experiment I-5 and I-6) some ripple were noticeable on the coupon surface (see Figure 37). Analysis of each surface film was conducted through SEM, EDS, and backscatter imaging. As can be appreciated in Figure 34a, SEM details of the corrosion product film formed over two days' exposure without the presence of H<sub>2</sub>S show a uniform film at 200x magnification. Closer inspection of that film reveals important difference in morphology with the coupons analyzed from the top of the line under the same conditions (see Figure 34b).



Figure 31. Series I, Test I-3 and I-5. Top of the line. High temperature, P = 30,  $pH_2S= 0.7$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 19 and 21)



Figure 32. Series I, Test I-4 and I-6. Top of the line. High temperature, P = 30, pH<sub>2</sub>S= 1.3, V<sub>G</sub> = 5 m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 19 and 21)



Figure 33. Series I. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 30,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 18, 21 and 22)

The addition of 0.04 units pH<sub>2</sub>S has affected the corrosion product film as seen in Figure 34c and 35a. Analyzing Figure 35a, where apparent changes in color can be appreciated, does not show a great difference in the film composition by backscatter imaging (Figure 35a). Features of the corrosion product film are fairly similar by visual comparison of the SEM analyses presented in Figure 34c to Figure 34q.

EDS analysis, in Figure 35, shows the presence of sulfides in the film formed when just 0.04 units of  $H_2S$  were present.

With the increase of the  $pH_2S$  to 0.13 units in the gas phase, the surface corrosion product film, shown in Figure 34f-i, is similar to that formed at 0.04 units  $pH_2S$ .

The presence of the original polishing marks on the corrosion layer, revealed at low magnification (Figures 34c, 34f, 34j and 34n) allows to think on the formation of FeS through solid state reaction instead of any precipitation process that can mask the marks on the original bare metal surface.

When the  $H_2S$  partial pressure is further increased to 0.7 or 1.3 units, the polishing marks can no longer be seen.

As shown in the EDS analysis presented in Figure 35, the composition of the films are basically sulfide and the corrosion product film are uniforms.Recalling the scaling formation rate / CR ratio (SFR/CR) presented in Figure 18, SFR/CR ratios were fairly constant for all the conditions evaluated at the bottom of the line. However the largest CR, in the presence of CO<sub>2</sub> and H<sub>2</sub>S, were found at the higher pH<sub>2</sub>S values. That is, the CR was high enough to delete any mark present on the base metal, while for the lower pH<sub>2</sub>S after two days of experiment, some marks remain apparent.



Figure 34. Series I. Bottom of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corr. rate are shown in Figures 16, 18, 21 - 22)



Figure 35. Series I. Bottom of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 18, 21 and 22)

When the CO<sub>2</sub> partial pressure is increased from 1.3 to 13, the surface analysis shows some very peculiar characteristics. First, by looking at the coupons with the naked eye (Figure 33f and 33g) it can be seen that there is some kind of flow influence with the presence of lines on the surface of the coupons (zone B in Figure 36e, 36f, 36g and 36h). It corresponds most probably to directional liquid flow over the coupons.

In the H<sub>2</sub>S flow loop, it is difficult to evaluate how much liquid flows at the bottom of the line during a test and what portion of it comes from carry-over or from pure condensation. However, chemical analyses of these peculiar flow-related surface features show that the composition of the film inside and outside the ripple is different (see backscatter images Figure 37). EDS analysis presented in Figure 37 shows clearly the presence of a sulfide film in both cases but also shows also considerably more element of the steel structure (Ni, C, Si) around the ripple than inside them.

After removal of the corrosion layer, the position of the ripple was still clearly visible and looked less corroded than its surroundings. Therefore, one type of film seems less protective than the other. This process is still mainly not understood and it is difficult to link the increase of  $CO_2$  partial pressure with a flow effect and the presence of two different kinds of film on the metal surface.

In summary, compared to a pure  $CO_2$  environment, the addition of  $H_2S$  (0.04 and 0.13) seems to at first gradually retard the CR. However, when the pH<sub>2</sub>S reaches 0.7, this trend of decrease is reversed and the CR increases again (without reaching, the CR of a pure  $CO_2$  environment).

The same trend is observed at the top and bottom of the line.

It is known that a FeS film is formed rapidly through solid state film formation in a system with wetted metal in the presence of hydrogen sulfide.

The film is known to retard corrosion. It is hypothesized here is that further increase in the H<sub>2</sub>S partial pressure would modify the properties of the film, limiting its ability to retard the CR.



Figure 36. Series I, Test I-3 to I-6. Bottom of the line. High temperature, P = 30, V<sub>G</sub> = 5 m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 18, 21 and 22)



Figure 37. Series I, Backscatter. Test I-5 and I-6. Bottom of the line. High temperature, P = 30,  $pCO_2 = 13$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 2 days (Corrosion rate are presented in Figures 16, 18, 21 and 22)

As shown in Figure 38, the increase in the  $CO_2$  partial pressure from 1.3 to 13 increases the CR as expected (at  $pH_2S = 0.70$  and 1.3) and seems to modify slightly the characteristics of the iron sulfide film.



Figure 38. Series I. Series I. Bottom of the line. High temperature, P = 30,  $pCO_2 = 1.3$ ,  $V_G = 5$  m/s, high condensation rate = 2.5, test duration: 2 days (high magnification) (Corrosion rate are presented in Figures 16, 18, 21 and 22)

# 4.2 Series II

As mentioned in Section 3.2.2, in this series the main parameters tested are the  $H_2S$  partial pressure (from 0 to 0.04) and the free acetic acid concentration (from 0 to 10). The measured variables are shown in Appendix B.2.

## 4.2.1 H<sub>2</sub>S and HAc influence

Figure 39 shows an overview of the average CR results obtained on experiments of Series II. In Series II the material evaluated was an AISI 1020 carbon steel, the total pressure was equal to 83 at a high gas temperature, while the condensation rate and superficial gas velocity were the same as in previous series (5 m/s and high condensation rate respectively). A single coupon was used to calculate the corrosion rate, thus, no error bars are presented for this series.

The measured CR for top of the line with no  $H_2S$  and no HAc in experiment II-0 is 18.3 and decreases to 4.1 units with the addition of 0.05 units of  $H_2S$ . The addition of 5 unit of free HAc in the tank increases the top of the line CR to values of 5.3 with further increases to 7.4 when the free HAc concentration is raised to 10 units in the liquid phase of the tank (notice the logarithmic scale of the graph).

Further increases of the  $pH_2S$  to 0.4 elevates the CR at the top of the line to values of 9.4 for the same free HAc concentration of 10 units.

Comparing Experiments II-0 to Experiments II,2, II-3 and II-4, the addition of H<sub>2</sub>S had retarded the CR at the top of the line, as seen in Figure 39.

The addition of 0.05 units of  $H_2S$  retards the CR in the otherwise pure  $CO_2$  environment. When 5 units of free HAc were added to the system, the CR increases.

Similarly, CR increases were apparent when more  $H_2S$  or HAc was added (Experiment II-3 and II-4). The CR seems to be related to the concentration of the weak acids in solution regardless of whether it is HAc or  $H_2S$ .



Figure 39. Series II. Effect of the H<sub>2</sub>S and HAc at the top and bottom of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Surface analyses are shown in Figure 43 to 50)

Previous testing done in the  $H_2S$  loop has shown that the addition of trace amounts of  $H_2S$  has acted to retard the CR in single phase fluid flow by a solid state reaction on the surface of the corroding material<sup>18</sup>.

From previous testing, it is known that a Mackinawite film is formed rapidly in a system with wetted metal in the presence of  $H_2S^{18}$ . This phenomenon has been observed

in single phase and multiphase flow regimes of 1% NaCl solution and a  $CO_2/H_2S$  gas mixture<sup>17</sup>, but not in condensed water at the top of the line.

Analyzing the bottom of the line results, the addition of 0.05 units of  $H_2S$  for Experiment II-1 had given results expected under these conditions, however the addition of HAc in Experiment II-2 caused an order of magnitude increase in the CR, where the pCO<sub>2</sub> (80) and the pH<sub>2</sub>S (0.05) were the same than Experiment II-1.

A general hypothesis would be that the addition of HAc changes the film-forming characteristics of the H<sub>2</sub>S reaction and limits its ability to retard the CR, as seen in Figure 39. The reason for this hypothesis is that the addition of 5 units of free HAc increased the CR from Test II-1 to test II-2, but the increase to 10 units HAc in Experiment II-3 had no perceptible effect on the CR measured in Experiment II-3. However, for Experiment II-4, when the pH<sub>2</sub>S was increased from 0.05 to 0.4 and the free HAc concentration was kept at 10 as compared to Experiment II-3, the general CR increased showing that the concentration of H<sub>2</sub>S is still a factor in the bottom of the line corrosion of the material.

The scaling formation rate and the CR comparison for top of the line is shown in Figure 40.

For the pure CO<sub>2</sub> environment (Experiment II-0) the scaling formation rate / corrosion rate ratio (SFR/CR) is 35% while the ratio for experiments done with  $H_2S$  and HAc (Experiment II-1 through II-4) is below 8% in every case. In the same way as described in Figure 39, the general CR decreases with the addition of  $H_2S$  and HAc. That behavior suggests that, despite the lesser layer formation over the metal surface in the

presence of  $H_2S$  and HAc, those species gave some protection to the metal under the same pCO<sub>2</sub> (80) for top of the line.



Figure 40. Series II, – Rate of reaction under the effect of the  $H_2S$  and HAc at the top of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Surface analyses presented in Figure 43 to 50)

Figure 41 shows the SFR and the CR comparison for bottom of the line AISI 1020 coupons in Series II.

For bottom of the line the SFR/CR ratio is comparable for all the cases, except for experiment II-1, where the calculated SFR was significantly higher than the CR. The fact that the value of SFR is higher than the CR for experiment II-1 can be explained by the low calculated CR and the possible deposition of materials present in the liquid carried over.


Figure 41. Series II, – Rate of reaction under the effect of the H<sub>2</sub>S and HAc at the bottom of the line. High temperature, P = 83, pCO<sub>2</sub> = 80, V<sub>G</sub> = 5 m/s, high condensation rate, test duration: 4 days (Surface analyses are presented in Figure 43 to 50)

The comparable SFR/CR values found at the bottom of the line, for environments with or without  $H_2S$  and HAc can be explained with the differences in the water chemistry expected for bottom and top of the line. As was explained for Series I, the condensed droplets hangs on the metal surface for a finite amount of time, while the liquid on the bottom is continuously refreshed and its pH is controlled by the dissolved acid species and not by the Fe<sup>2+</sup>.

### 4.2.2 Material evaluation

In order to compare the performance of the two different materials evaluated in this work, experiment II-1 was repeated using API X-65 carbon steel. Figure 42 shows the CR results obtained for both experiments.



Figure 42. Series II. AISI 1020 and API X-65 corrosion performance in presence of  $CO_2$  and  $H_2S$ . High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days

For both materials, the top of the line corrosion was significantly higher than for bottom of the line. Is important to mention that the AISI 1020 had lower CR at both locations.

Despite the fact that both materials are carbon steels used for similar applications, the chemical composition and the microstructure of them are dissimilar. The X-65 had spheroidized iron carbide, while the AISI 1020 had the expected ferritic / pearlitic matrix.

The difference in microstructures, more than difference in composition, could explain the differences in CR performance of the evaluated materials. Ferritic / pearlitic materials have a thermodynamically favored conformation that make them less reactive to the corrosive media. However, the limited number of coupons evaluated made difficult to get conclusive information about the difference in performance of the materials evaluated.

# 4.2.3 Surface Analysis

In this section, the surface characteristics of the coupons exposed to the corrosive environment of Series II are presented.

# 4.2.3.1 Top of the Line

Figure 43 shows optical photographs of the coupons taken immediately after their removal from the loop at the end of the experiments and rinsed with isopropyl alcohol.

Rounded areas, signifying the presence of droplets of condensed liquid, can generally be seen on the surface of the coupons. In general, the coupons exposed to  $CO_2/H_2S$  environments presented a darker film on the coupon surface. This is consistent with iron sulfide as the predominant compound of the corrosion layer<sup>18</sup>.

Figure 44 shows SEM pictures of the coupons submitted to the baseline experimental conditions (no H<sub>2</sub>S and no HAc). The corrosion product layer is presumably formed by FeCO<sub>3</sub>. It is thin, dense and fairly adherent to the metal surface.

Regarding the  $H_2S$  tests, Figure 45 shows the SEM pictures of the corrosion product layer present on the surface of the top of the line coupons at pCP<sub>2</sub> equal to 80,  $pH_2S$  equal to 0.05 for different HAc concentrations. Comparing the resulting coupon surface for Experiment II-1 and II-2, the corrosion layer shows many similarities.

When the free HAc concentration is raised to 10 the corrosion layer does not look as uniform as in the previous experiments. It seems like HAc additions promote localized attack since does not allow an uniform coverage of the layer over the metal surface.

	pCO <sub>2</sub> = 80 (Top of the line)			
	Free Hac = 0	Free Hac = 5	Free Hac = 10	
$pH_2S=0$	(a)			
$pH_2S=0.05$	(b)	(c)		
$pH_2S=0.4$			(e)	

Figure 43. Series II. Morphology of carbon steel AISI 1020 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

However, any conclusions of this kind cannot arise from these experiments since the duration of them was not enough to prove the occurrence of localized attack under the considered conditions.



Figure 44. Series II. Top of the line, Test II-0. High temperature, P = 83,  $pCO_2 = 80$ ,  $pH_2S = 0$ , [Hac] = 0,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

EDS analysis presented in Figure 46 shows the presence of sulfur and iron on the

surface of the coupons for every condition. While only a slight difference in the corrosion

product layer was seen with the addition of acetic acid (0, 5, & 10), the layer seems to

exhibit quite different properties in Experiment II-4 when the pH<sub>2</sub>S was increased from



0.05 to 0.4 showing a more porous surface (see Figure 47).

Figure 45. Series II, Experiments II-1 to II-4. Top of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $pH_2S = 0.05$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

In this test ( $pCO_2 = 80$ ,  $pH_2S= 0.4$  and Free HAc= 10), the layer is not uniform nor homogeneous as shown in Figure 46c and 47. Different areas, showing differences in the film characteristics on the backscatter images, are present. However, EDS analysis did not reveal any difference in the relative composition of the two areas identified. Considering that the coupons currently analyzed are for top of the line, the difference areas, called zone "A" and "B" are the fingerprints of the droplets condensed on the metal surface.



Figure 46. Series II. Backscatter. Top of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

The HAc is a condensable gas while the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are gases at the evaluated

conditions. The difference in characteristic of the droplet fingerprint showed in Figure

46c compared to those found for Series I (see Figure 23) can be explained by considering that the HAc (condensable vapor) prefers the liquid phase while  $CO_2$  and  $H_2S$  have to dissolve into the liquid before they can react with the metal surface.



Figure 47. Series II, Experiment II-4. Top of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $pH_2S = 0.4$ , free [HAc] = 10,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

# 4.2.3.2 Bottom of the Line

Figure 48 shows pictures of the coupons taken immediately after their removal from the loop at the end of the experiments.



Figure 48. Series II. Morphology of carbon steel AISI 1020 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 83,  $pCO_2 = 80$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

For bottom of the line, in a pure CO<sub>2</sub> environment, the corrosion product layer is

very thick and porous as shown in Figure 49.



Figure 49. Series II. Cross section of carbon steel AISI 1020 tested at bottom of the line. High temperature, P = 83, pCO<sub>2</sub> = 80, pH<sub>2</sub>S = 0, free [HAc] = 0, V<sub>G</sub> = 5 m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

Cross-sectional analysis presented in Figure 49 displayed the typical characteristics of an iron carbide layer. That layer could be expected for corrosive conditions where no FeCO<sub>3</sub> precipitation is expected. That is, at bottom of the line the supersaturation conditions for FeCO<sub>3</sub> precipitation were not present<sup>3</sup>.

Once  $H_2S$  is introduced, the characteristics of the corrosion product layer change considerably. SEM analysis related to Experiments II-1 to II-4 are presented in Figure 50 at different magnifications.

In all cases, the layers show similar characteristics. It is amorphous and fairly homogeneous. During the corrosion layer removal process it was concluded that the film is not adherent to the metal surface. The presence of sulfur seen in the EDS analysis (see Figure 46) suggest the FeS presence as the main component of the layer.

In summary, compared to a pure  $CO_2$  environment, the addition of a small quantity of H<sub>2</sub>S (from 0.05 to 0.4 units) decreases the CR both at the top (decrease of up to 78%) and bottom of the line (decrease of up to 99%). The addition of 5 and 10 units of free HAc slightly increases the CR at the top of the line with increasing concentration, but does not seem to affect the CR at the bottom of the line.

Further addition of  $H_2S$  (0.4) continues to increase the CR both at the top and bottom of the line. From previous testing, it is known that a FeS (Mackinawite) film is formed rapidly through solid state film formation in a system with wetted metal in the presence of  $H_2S$ . The film is known to retard corrosion. A general hypothesis would be that the addition of HAc is changing the film forming characteristics of the  $H_2S$  reaction limiting its ability to retard the CR.



Figure 50. Series II. Bottom of the line, Test II-1 to II-4. High temperature, P = 83,  $pCO_2 = 80$ ,  $pH_2S = 0.05$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 4 days (Corrosion rate are presented in Figures 39 to 41)

### 4.3 Series III

The objective of the Series III is to investigate the influence of the partial pressure of  $H_2S$  and the occurrence of localized attack at longer lasting experiments. The experiments of Series III were performed with API X-65 carbon steel at 30 units total pressure, 20 units pCO<sub>2</sub>, high gas temperature, with DI water solution as the liquid phase in the tank.

#### 4.3.1 Corrosion rate

Experiments lasting two days were performed for each condition, installing four coupons (2 at top of the line, 2 at bottom of the line) in the downstream test section of the  $H_2S$  loop. The coupons were removed after two days of experimentation in order to find corrosion effects. The four coupons were replaced 7 days later, one each of top of the line and bottom of the line coupons were removed to get the 7 day samples; after 21 total days two new coupons replaced those removed, then experiments ran for another 14 days of experimentation, all coupons were removed from the loop, allowing corrosion results for 14 and 21 days. The measured variables are shown in Appendix B.3.

The general CR results of Series III are summarized in Figure 51 for top of the line and Figure 52 for bottom of the line. As found in Series I, both at the top and the bottom of the line, the presence of trace amounts of  $H_2S$  retards the general CR compared to a pure  $CO_2$  environment for short-term experiments. This is generally explained by the formation by solid state reaction of a protective FeS film at the surface of the metal.

In the pure  $CO_2$  environment (Experiment III-0) the general CR decreases with time as can be appreciated in Figure 53, where the CR is presented in its differential form, thus subtracts the cumulative effect of corrosion damage from previous days.

While the pure  $CO_2$  environment CR reaches values close to 0 after 18 days of experimentation, the addition of trace amounts of  $H_2S$  retards the initial CR but the attack remains constant for the entire duration of the experiment.



Figure 51. Series III, Effect of the H<sub>2</sub>S concentration at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses are presented in Figures 61 to 74)

In general, for top of the line 0.04 units of  $pH_2S$  decreases the CR to values below 4 for the duration of the experiment. Further increases of  $pH_2S$  further retards the general CR below 2 units. These observation indicate that increase in  $pH_2S$  effectively retards the CR on the metal surface at the top of the line. For bottom of the line, the trend is opposite than for top of the line. While trace amounts of  $H_2S$  (0.04 units  $pH_2S$ ) retards the CR, further increase in  $pH_2S$  leads to a clear accelerate the general CR. Checking Figure 54, where the differential CR is presented for bottom of the line, it seems that the CR decreases rapidly in the first 15 days and then reverses the tendency and increases slightly.



Figure 52. Series III, Effect of the H<sub>2</sub>S concentration at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses are presented in Figures 75 to 89)

Comparing top of the line CR with bottom of the line, as had been seen in Series I and Series II, the general CR is significantly higher at the bottom than for the top. In this Series, where the  $pCO_2$  was kept constant at 20, the general CR at the bottom of the line is one order of magnitude higher than for the top of the line.



Figure 53. Series III, Differential corrosion rate. Effect of the H<sub>2</sub>S concentration at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses are shown in Figures 61 to 74)



Figure 54. Series III, Differential corrosion rate. Effect of the H<sub>2</sub>S concentration at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses are shown in Figures 75 to 89)



Figure 55 - 57 show the comparison between scaling formation rate and CR at the top of the line for each experiment of Series III.

Figure 55. Series III, Experiment III-1. Top of the line. Rate of reaction with time. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses are presented in Figures 62, 69 - 70)



Figure 56. Series III, Experiment III-2. Top of the line. Rate of reaction with time. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.70V_G = 5$  m/s, high condensation rate (Surface analyses are presented in Figures 63, 71 - 72)



Figure 57. Series III, Experiment III-3. Top of the line. Rate of reaction with time. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.30$ ,  $V_G = 5$  m/s, high condensation rate (Surface analyses presented in Figure 64, 73 - 75)

In general, the SFR/CR ratio was below 30% at every time in presence of  $H_2S$  with a minimum value between 7 and 14 days of experiment. It seems like after 7 days, the corrosion reaction is retarded significantly by the barrier formed by the corrosion layer; however, this layer loses its protectiveness and the attack is regenerated, letting the CR increase again.

Figure 58 - 60 show the comparison between scaling formation rate and CR for each experiment of Series III at bottom of the line conditions.

For bottom of the line, the SFR/CR ratio was constant below 30%. The lower SFR / CR ratio was found in pH<sub>2</sub>S equal to 0.7; it seems like that medium pressure gives enough H<sub>2</sub>S to retard the CO<sub>2</sub> corrosion process without excessive H<sub>2</sub>S attack. However,  $pH_2S$  equal to 0.7 did not represent the lowest corrosion rate found with 0.04 pH<sub>2</sub>



Figure 58. Series III, Experiment III-1. Bottom of the line. Rate of reaction with time. High temperature, P = 30, pCO<sub>2</sub> = 20, pH<sub>2</sub>S = 1.3, V<sub>G</sub> = 5 m/s, high condensation rate (Surface analyses are presented in Figures 77, 82 - 84)



Figure 59. Series III, Experiment III-2. Bottom of the line. Rate of reaction with time. High temperature, P = 30, pCO<sub>2</sub> = 20, pH<sub>2</sub>S = 1.3, V<sub>G</sub> = 5 m/s, high condensation rate (Surface analyses are presented in Figures 78, 85 - 86)



Figure 60. Series III, Experiment III-3. Bottom of the line. Rate of reaction with time. High temperature, P = 30, pCO<sub>2</sub> = 20, pH<sub>2</sub>S = 1.3, V<sub>G</sub> = 5 m/s, high condensation rate (Surface analyses are presented in Figures 79, 87 - 89)

# 4.3.2 Surface Analysis

The surface analyses of the coupon exposed to experimental conditions of Series

III is presented in this section

#### 4.3.2.1 Top of the line

Figure 61 to 64 shows pictures of the coupons taken immediately after their removal from the loop at the end of each experiment. Rounded areas, synonymous of the presence of droplets of condensed liquid, can generally be seen on the surface of the coupons.

In all cases, the layer shows a lot of similarities. First, rounded areas related to the

presence of droplets of condensed liquid are seen on the surface of the coupons.

	p(	$CO_2 = 20. \text{ pH}_2\text{S} = 0$ (Top of the line)
2 days	a)	
7 days	(b)	
14 days	(c)	
21 days	( <b>d</b> )	

Figure 61. Series III, Experiment III-0. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51 and 53)



Figure 62. Series III, Experiment III-1. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 55)



Figure 63. Series III, Experiment III-2. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.70$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 56)



Figure 64. Series III, Experiment III-3. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 57)

From previous Series, this observation is not surprising and is usually verified in the top of the line corrosion experiments.

For each condition, is clear that the severity of the attack increases with time. However, no signs of localized attack could be observed on the surface of any coupon.

The rounded shapes are more and more visible as the test duration increases. It is mostly due to the fact that, as the duration of the test increases, the corrosion process under the droplet has more time to have a visible effect on the steel surface. The surface conditions, such as surface tension due to the corrosion product film, could also have a strong effect on the residence time of the droplets or have an influence on the droplet renewal process.

Figure 65 and Figure 66 present SEM pictures and EDS analysis of the corrosion product layer present on the surface of the top of the line coupons for respectively the 2, 7 14 and 21 days experiments without any H<sub>2</sub>S present (Experiment III-0).

The pictures show very common characteristics with a corrosion product layer almost exclusively formed of a dense FeCO<sub>3</sub> layer (see Figure 66).

As mentioned before, it is believed that the vapor condenses at the top of the line and forms droplets that stay attached to the metal surface. Since the gas velocity is fairly low (5 m/s), the liquid at the top is not renewed fast enough and conditions for FeCO<sub>3</sub> precipitation<sup>3</sup> are reached easily. The gas velocity has a strong influence of the condensation process by influencing the flow regime, the residence time of the droplets at the top of the line. No traces of localized corrosion could be observed before 7 days of test. However, few pits were identified on the surface of the coupons after 14 and 21 days of exposure.



Figure 65. Series III, Experiment III-0. SEM and Backscatter images. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51a and 53)



Traces of localized corrosion can be observed very clearly on both coupons exposed to the  $CO_2$  environment with no  $H_2S$ .

Figure 66. Series III, Experiment III-0. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, High condensation rate (Corrosion rates are presented in Figures 51 and 53)

The corrosion product layer was removed following the cited ASTM G-1 standard<sup>23</sup> and the previous observation regarding localized attack was verified (Figure 67 and 68).



Figure 67. Series III, Experiment III-0. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51 and 53)

On the most representative part of the surface (away from the edge and away from the center), no traces of localized corrosion could be seen by naked eye even after 21 days.

With the presence of  $H_2S$ , no FeCO<sub>3</sub> crystals could be seen on the layer even if the pCO<sub>2</sub> is at 20 units (see Figures 70, 72 and 74). Instead of that, an amorphous and fairly homogenous corrosion product layer is seen on the surface of the coupons. EDS analysis shows the presence of sulfur and iron (see Figure 69 to 74). At low magnification (less than 200x) Rounded areas can be seen as part of the surface film formation which is indicative of corrosion caused by condensed droplets on the surface.



Figure 68. Series III, Experiment III-0. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51 and 53)

At the border of a wetted/non-wetted area, EDS and backscatter analysis were obtained to better define the regions. However, no difference could be seen in the composition of the layer.

Figure 75 shows pictures of the weight loss coupons for Experiment III-3 after removal of the corrosion layer following the standard ASTM  $G-1^{23}$  described in section 3.3.3 of the present document. In all cases, the steel surface is uniformly corroded and there is no trace of localized corrosion even after 21 days of test.

Mainly at high magnification, in all cases, some crystal shape features can be observed while the majority of the surface of the coupons is covered by an amorphous and fairly homogenous corrosion product layer. These crystal shape features look very similar to  $FeCO_3$  crystals observed in Experiment III-0. However, they are much smaller than the ones observed in similar experimental conditions but without  $H_2S$ .



Figure 69. Series III, Experiment III-1. SEM and Backscatter images. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 55)



Moreover, EDS analysis shows the presence of sulfur and iron but do not indicate the presence of FeCO<sub>3</sub>.

Figure 70. Series III, Experiment III-1. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 55)



Figure 71. Series III, Experiment III-2. SEM and Backscatter images. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.7$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 56)



Figure 72. Series III, Experiment III-2. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.7$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 56)



Figure 73. Series III, Experiment III-3. SEM and Backscatter images. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 57)



Figure 74. Series III, Experiment III-3. SEM and EDS analysis. Top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 57)

	$pCO_2 = 20$ (Top of the line)		
2 days	a)		
7 days	(b)		
14 days	(c)	Not available	
21 days	( <b>d</b> )		

Figure 75. Series III, Experiment III-3. Morphology of carbon steel API X-65 coupons after remove the corrosion layer, tested at the top of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 51, 53 and 57)
#### 4.3.2.2 Bottom of the line

Figure 76 - 79 shows pictures of the bottom of the line coupons taken immediately after their removal from the loop at the end of each experiment. Where interesting characteristics where found, photographs of the coupons after removal of the layer are shown.

For Experiment III-0 showed in Figure 76, it can be appreciated than all the coupons show very similar characteristics with a thick and porous black layer attached to the metal surface. The cracks observed on Figure 76c and 76d should be consequence of thermal expansion effect when the coupons are removed from the experimental environment. The layer is not adherent to the metal surface and can be removed very easily. The thermal expansion effect observed during the drying process has a stronger effect on the layer if the coupons stayed in the loop for a longer period of time. The corrosion product layer was removed using an inhibited acid solution<sup>23</sup> and absolutely no trace of localized corrosion was observed on the metal surface (see Figures 77 and 79).

Pictures of bottom of the line coupons tested in Experiment III-1 and III-2 are presented in Figure 77 and 78 respectively. They all show very similar characteristics with a shiny colored surface except for the 21 days exposure coupon on Experiment III-1  $(pCO_2 = 1.3, pH_2S = 0.04)$  where a non-uniform layer can be seen (Figure 77d). The marks of polishing can still be seen. It seems therefore that the corrosion product layer is very thin and it can be inferred that this is the consequence of solid state reaction.

For experiment III-3 (Figure 79), where the  $pH_2S$  was increased to 1.3, some peculiar properties of the layer were observed on the 21 days coupon . Entire parts of the

layer unexpectedly peeled off after applying manually very light mechanical stress. These parts appeared not to be adherent to the metal surface. In fact, corrosion was strongly happening underneath the layer, leading to non-uniform attack over the surface of the coupon.



Figure 76. Series III, Experiment III-0. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52 and 54)



During the test, the layer may have been under mechanical stress due to the thickness increase and may have cracked, allowing large sheets of the top layer to peel away.

Figure 77. Series III, Experiment III-1. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 58)

Some liquid has most probably flown under these plaques leading to areas on the coupon showing much more corrosion (Figure 79d). However, the corrosion under the film appears to be uniform.

	$pCO_2 = 20$ . $pH_2S = 0.7$ (Bottom of the line)			
2 days	<b>a</b> )			
7 days	(b)			
14 days	(c)			
21 days	( <b>d</b> )			

Figure 78. Series III, Experiment III-2. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.7$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 59)



This could explain why the corrosion is still occuring after 21 days of testing (as it is seen in pure  $CO_2$  environment) but seems to increase with time.

Figure 79. Series III, Experiment III-3. Morphology of carbon steel API X-65 coupons immediately after removal from the loop, tested at the bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 60)

As said previously, before removing the corrosion film from the coupon exposed to bottom of the line for 21 days under  $pCO_2 = 1.3$  and  $pH_2S = 0.04$ , the layer showed non uniform characteristics, but the surface underneath showed uniform attack. SEM pictures and EDS analysis of Experiment III-0 are presented in Figure 80 and Figure 81.



Figure 80. Series III, Experiment III-0. SEM and Backscatter images. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52 and 54)

An amorphous layer identified to be iron carbide  $(FeC_3)$  is present on the surface of all coupons in Experiment III-0.



Figure 81. Series III, Experiment III-0. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52 and 54)

SEM analysis of coupons of Experiment III-1 are presented in Figure 82 and

Figure 83. All SEM analyses shown are prior to film removal. In all cases, the layer

shows similar characteristics of being both amorphous and homogeneous. It is also very easy to remove and not adherent to the metal surface.



**Figure 82. Series III, Experiment III-1. SEM and Backscatter images. Bottom of the line. High temperature, P = 30, pCO<sub>2</sub> = 20, pH<sub>2</sub>S = 0.04, V<sub>G</sub> = 5 m/s, high condensation rate** (Corrosion rates are presented in Figures 52, 54 and 58)

Corrosion product film coverage was complete due to complete fluid coverage of

the surface in each case. EDS analyses and back-scatter images show that the

composition of the film is mostly identical for all the coupons exposed in Experiment III-1 with the exception, in some extent, of the 21 days long test.



Figure 83. Series III, Experiment III-1. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 58)

The film formed on all coupons in this test was shown by EDS to contain mainly

sulfur and iron. However, for the 21 days long test, some features of the corrosion

product film appears slightly different. As can be appreciated in Figure 84 the EDS analysis show the presence of sulfides in the film formed on all the areas observed.



Figure 84. Series III, Experiment III-1. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.04$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 58)

The pictures shown in Figure 85 and 86 correspond to Experiment III-2, where the  $pCO_2$  was kept constant at 20 while the  $pH_2S$  was set at 0.7 units. SEM analyses showed few similarities with Experiment III-1 where the corrosion layer was mainly composed by FeS and still revealed polishing marks on the surface, evidencing FeS formation by solid state reaction



Figure 85. Series III, Experiment III-2. SEM and Backscatter images. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.7$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 59)

The polishing marks are still evident after 21 days of experiments. When the  $pH_2S$  was increased to 0.7, the film formation is more favorable than any other precipitation process. The apparent pits noticeable in Figure 86 are just small defects on the layer than cannot be considered as localized corrosion due to the high magnification of the picture.

The common rule to define localized attack is that it has to be noticeable at

magnifications lower than 200X.



Figure 86. Series III, Experiment III-2. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 0.7$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 59)

SEM analyses of coupons of Experiment III-3 are presented in Figure 87 and Figure 88. All SEM analyses shown are prior to film removal. In all cases, the layer shows similar characteristics. It is amorphous and fairly homogeneous.



Figure 87. Series III, Experiment III-3. SEM and Backscatter images. Bottom of the line. High temperature, P = 30, pCO<sub>2</sub> = 20, pH<sub>2</sub>S = 1.3, V<sub>G</sub> = 5 m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 60)

Like in Experiment III-2, the polishing marks are noticeable after 21 days of test. Some cracks on the film can be found after 7 days of experiment. The picture taken for the 21 days long experiment coupon shows a breakdown on the film that seems to be product of internal stresses on the film.



Figure 88. Series III, Experiment III-3. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate (Corrosion rates are presented in Figures 52, 54 and 60)

Difference in volume between the base metal lattice and the FeS film can generate the stresses needed to promote breakdowns and further localized attack. Longer experiments are needed to verify that hypothesis. EDS analysis of the film and the layer underneath is shown in Figure 89, evidencing FeS film coverage over the entire surface.



Figure 89. Series III, Experiment III-3. SEM and EDS analysis. Bottom of the line. High temperature, P = 30,  $pCO_2 = 20$ ,  $pH_2S = 1.3$ ,  $V_G = 5$  m/s, high condensation rate, test duration: 21 days (Corrosion rates are presented in Figures 52, 54 and 60)

For Series III, the corrosion layer was easy to remove and not adherent to the

metal surface. For bottom of the line, corrosion product film coverage was complete due to complete fluid coverage of the surface in each case. Some liquid had most probably flowed under the top layer, leading to areas on the coupon showing much more corrosion (Figure 89). However, the corrosion under the film appears to be uniform. It could explain why the corrosion does not stop after 21 days of testing (as it is seen in pure  $CO_2$  environment) but seems to increase with time.

# **CHAPTER 5: CONCLUSIONS**

- Under the tested conditions it was found that the general CR is higher at the bottom of the line than for top of the line.
- At the pCO<sub>2</sub> / pH<sub>2</sub>S tested, H<sub>2</sub>S retards the general CR at both the top of the line and bottom of the line.
- In the CO<sub>2</sub> environments tested, a FeCO<sub>3</sub> corrosion layer is favorably formed at the top of the line, where appropriate conditions can be reached inside the condensed droplet, while a FeC<sub>3</sub> layer is formed at the bottom of the line where the pH is controlled by the pCO<sub>2</sub> and not by the Fe<sup>2+</sup> dissolution.
- Trace amounts of H<sub>2</sub>S generate the formation of FeS film through solid state reaction under the conditions tested.
- For experiments performed, in the presence of H<sub>2</sub>S, it was found that regardless of the value of pCO<sub>2</sub>, the corrosion layer film composition as analyzed by EDS is mainly FeS.
- The extra cathodic reaction promoted by the presence of HAc increases the general CR for both top and bottom of the line, attacking the metal itself and diminishing the protective effect of the H<sub>2</sub>S.
- AISI 1020 carbon steel (ferritic / pearlitic) showed better corrosion resistance than API X-65 (TMCP pipeline steel).
- In a pure CO<sub>2</sub> environment (20 pCO<sub>2</sub>) the general CR tends to decrease to values close to 0 after 18 days of experiment but traces of localized attack were revealed after 14 days of experiment.

- Despite the fact that H<sub>2</sub>S initially retards the general CO<sub>2</sub> CR, it does not stop it completely after 21 days of experimentation.
- No traces of localized attack could be found in 21 days long experiments under any of the CO<sub>2</sub> / H<sub>2</sub>S combinations tested.

## **Future works**

- Pure CO<sub>2</sub> top of the line corrosion tests should be performed over long exposure to better characterize the localized attack.
- The HAc influence should be analyzed further, performing longer term experiments in order to verify the occurrence of localized attack.
- Since the FeS can form different thermodynamically stable structures, more accurate and quantitative surface analyses should be performed on the corrosion layers.

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## **APPENDIX A: Materials characterization**

The chemical analyses of API X-65 and AISI 1020 carbon steels are shown in Table 4. The fourth and fifth columns on this table shows the requirements specified on the standards for both materials<sup>16</sup>.

Element	AISI 1020	API X-65	API 5L X-65	AISI 1020
	Composition	Composition	Standard	Standard
	(wt. %)	(wt. %)	(wt. %)	(wt. %)
С	0.19	0.13	< 0.26	0.13 - 0.23
Mn	0.8	1.16	< 1.40	0.30 - 0.60
Р	0.01	0.009	< 0.03	< 0.04
S	0.023	0.009	< 0.03	< 0.05

Table 4. Chemical analysis of the carbon steels used in the experiments

Figure 90 shows the microstructure of longitudinal and transversal cuts of the API X-65 carbon steel. Figure 91 shows the microstructure of the AISI 1020 carbon steel. In this case, only the face of the coupon that would be in contact with the fluid is evaluated<sup>16</sup>.

The microstructure of the API X-65 is finer in the longitudinal direction, probably as a result of processing. Figure 90 shows a microstructure typical of a micro-alloyed thermo-mechanical controlled processing (TMCP) pipeline steel. Iron carbide could be distributed in spheroidized form instead of a lamellar arrangement. Hardness measurements are recorded in Table 5<sup>16</sup>.

The AISI 1020 microstructure shows a typical ferritic / pearlitic matrix, which is expected for this hypoeutectoid steel (carbon content less than 0.8%). There is a homogeneous distribution of ferrite and pearlite<sup>16</sup>.



Figure 90. Microstructure of the X65 carbon steel. Longitudinal cut (a-b), transversal cut (c-d)

Table 5 shows the hardness results obtained from the two materials tested. Also, by converting these values, approximate tensile strengths were calculated and compared with the values designated for those metals in the standards. The 1020 carbon steel showed a hardness of 84.3 HRB, and the calculated tensile strength is above the minimum requirements of the standard.



Figure 91. Microstructure of the 1020 carbon steel

The X65 showed a difference in hardness with direction. This change in hardness

is consistent with the change in microstructure described previously<sup>16</sup>.

Measurement	AISI 1020	API X-65	API X-65
		longitudinal cut	transversal cut
1	83.5	81.3	60.3
2	84.5	94.4	68.7
3	82.1	98.7	63.3
4	89.1	87.9	78.0
5	83.2	95.4	59.1
6	86.8	89.3	51.1
7	80.9	88.7	66.5
8	80.2	98.9	75.0
9	89.1	93.3	58.5
10	83.2	85.1	67.7
Average	84.3	90.7	64.8
Approx. Tensile	79,000 psi for	90,000 psi for	56,000 psi for
Strength	85HRP	90.7HRB	65.7HRB
Tensile	58,000 nsi (min)	77.000 psi (min)	77.000 nsi (min)
Requirements	36,000 psi (iiiii)	//,000 psi (iiiii)	
Yield Strength	36,000 psi (min)	65,000 psi (min)	65,000 psi (min)

Table 5. Hardness (HRB) results

#### **APPENDIX B: Experimental conditions**

## **B.1 Measured conditions for Series I**

Tables 6 presents different measurements that were taken during the experiments of Series I.

Experiment	pH (tank)	$Fe^{2+}$ in the tank (ppm)	[H <sub>2</sub> S] in the gas phase
I-0	NA	NA	
I-1	5.1	NA	21,000
I-2	5.2	NA	40,000
I-3	4.7	NA	240,000
I-4	4.6	NA	500,000
I-5	4.5	NA	260,000
I-6	4.5	NA	470,000

Table 6. Series I. pH and Fe<sup>2+</sup> concentration measurements

# **B.2** Measured conditions for Series II

Tables 7 presents different measurements that were taken during the experiments of Series II.

 $\mathrm{Fe}^{2+}$  in the tank (ppm) Experiment [H<sub>2</sub>S] in the gas phase pH (tank) I-0 NA NA 6.3 5,500 I-1 (1020) 4.6 I-1 (X-65) 4.6 6.5 5,500 5,500 4.2 I-2 33.7 5,500 I-3 4.3 NA I-4 4.1 NA 40,000

Table 7. Series II. pH and Fe<sup>2+</sup> concentration measurements

# **B.3 Measured conditions for Series III**

Tables 8 to 11 present different measurements that were taken during the experiments of Series III.

Duration	nH (tank)	$Ee^{2+}$ in the tank (nnm)
Duration		
At start	NA	NA
After2 days	4.6	18.7
After9 days	4.9	35.8
After16 days	4.6	33.7
After23 days	4.8	79
After removal of the probes	4.8	79

Table 8. Experiment III-0. pH and Fe<sup>2+</sup> concentration measurements

# Table 9. Experiment III-1. pH and Fe<sup>2+</sup> concentration measurements

Duration	pH (tank)	Fe <sup>2+</sup> in the tank (ppm)
At start	4.2	7.91
After 7 days	4.4	18.7
After 14 days	4.4	18.9
After 21 days	4.6	N/A
After 23 days	4.7	18
After removal of the probes	4.7	18

Table 10. Experiment III-2. pH and Fe<sup>2+</sup> concentration measurements

Duration	pH (tank)	$\mathrm{Fe}^{2+}$ in the tank (ppm)
At start	4.3	9
After 2 days	4.4	N/A
After 7 days	4.5	N/A
After 14 days	4.4	18.1
After 21 days	4.5	20.3
After removal of the probes	N/A	N/A

Duration	pH (tank)	$Fe^{2+}$ in the tank (ppm)
At start	4.3	6.5
After 2 days	4	25
After 8 days	4.1	22.9
After 14 days	4.3	25.3
After 21 days	4.3	26

 Table 11. Experiment III-3. pH and Fe<sup>2+</sup> concentration measurements