

TOP OF THE LINE CORROSION IN PRESENCE OF ACETIC ACID AND CARBON DIOXIDE

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ABSTRACT

This paper deals with the phenomena of corrosion by acetic acid and carbon dioxide at the top of a horizontal pipeline under dewing conditions. The effect of different parameters known to influence the Top of the Line Corrosion (TLC), such as the condensation rate and the bulk temperature is studied. The free acetic acid concentration varies from 0 to 1000 ppm, the bulk temperature, is set mainly at 70°C, the condensation rate is varied while the partial pressure of carbon dioxide and the gas velocity are set at a fixed value. The presence of acetic acid increases the corrosion rate both at the top and at the bottom of the line in different ways. The condensation rate influences strongly the top of the line corrosion when it has a small influence at the bottom. Evidences of localized corrosion are found at the bottom of the line. The corrosion at the top is uniform in the experiments conducted.

Keywords: Top of the Line Corrosion, carbon dioxide, acetic acid, condensation rate.

INTRODUCTION

Top of the Line Corrosion occurs in the transportation of wet gas when significant heat exchange between the inside of the pipe and the outside environment is present causing the water vapor carried by the wet gas to condense on the interior wall of the pipe. Due to gravity forces, most of the condensed water drains to the bottom of the pipe and a thin film of condensed water forms on the sides and at the top of the internal pipe walls (see Figure 3). Continuous injections of inhibitors can prevent corrosion at the bottom of the

pipe but at the top and on the sides, it is not possible. Therefore the condensation of wet gas can lead to a very corrosive environment.

In 1999 Gunaltun¹ presented a complete visual inspection of a TLC case under stratified flow regime. He divided the pipe wall in three different areas:

- The bottom of the pipe where the corrosion is uniform and where the rate can be lowered with the use of inhibitors.
- At the sidewall of the pipe where the condensed water drains to the bottom. The corrosion is also uniform but inhibitors are not efficient.
- At the top of the line where a protective iron carbonate layer can be formed in certain cases. Inhibitors are not effective and localized corrosion occurs.

Many papers⁴⁻⁷ have been published describing the main parameters influencing TLC due to carbon dioxide. In each of them, the parameters are the temperature of the gas bulk, the temperature of the pipe wall, the total pressure of the system, the partial pressure of carbon dioxide, the gas velocity and the condensation rate. All of these parameters influence the corrosion rate in a complicated way but a common behavior is generally observed:

- At low condensation rates and at a bulk temperature higher than 70C, a protective film of iron carbonate appears at the surface of the pipe, which lowers the corrosion rate. The formation of this film is explained by the saturation of the liquid film and the precipitation of corrosion product, which locally lowers the pH. This film still exists but is no longer protective at 50 C and below due to the increase of the solubility iron carbonate.
- At high condensation rates, saturation cannot be reached and the corrosion rate can reach several mm/y. The corrosion rate 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 it. The corrosion rate depends on the balance of these two counteracting effects.

In 2002, Vitse^{2, 3} completed a study on the TLC due to carbon dioxide, in the same experimental loop used in this work. He presented several new observations regarding the influences of the TLC parameters:

- The partial pressure of CO₂ has little influence on the corrosion rate respectively at low temperature and high cooling, and at high temperature and low cooling. On the other hand, at high temperature and high cooling, the influence is more significant. It can be explained by the fact that at a low condensation rate it is easier to saturate the liquid film with corrosion products, increasing the pH and retarding the kinetics of the reaction of corrosion by CO₂. At a high condensation, it can be impossible to saturate the liquid film and the pH could be more sensitive to the influence of the partial pressure of CO₂.
- The gas velocity has a direct effect on the condensation rate that in turn can affect the corrosion rate. This is due to the mass transfer limitation for condensation present in the gas phase.
- The condensation rate has a complex influence on the corrosion rate and is influenced by all others parameters. The corrosion rate significantly increases

when the condensation rate reaches a threshold. This observation is in agreement with the theory that the saturation level of corrosion products in the condensed film controls the corrosion rate. If the condensation rate is high enough that it prevents the liquid film from reaching saturation, the corrosion rate consequently depends on the corrosivity of the liquid phase. If the condensation rate is low, saturation can be reached which leads to the formation of an iron carbonate scale, which is protective at high temperature only.

The baseline conditions of the present work are based on two of Vitse's observations: the temperature of the gas at which the most important uniform corrosion rate occurs (70°C) and the value of the condensation rate corresponding to the threshold (called in this study as the "critical condensation rate level")

The effect of organic acid (here acetic acid) on CO₂ corrosion has been investigated by many authors^{8, 9, 10, 12}. In CO₂ corrosion, it is known that the presence of acetic acid increases the corrosion rate. This can be explained by the acetic acid's ability to decrease the pH and to increase the solubility of Fe²⁺, which reduces the thickness of the iron carbonate layer. Regarding the top of the line corrosion, the same observation can be made. Acetic acid is volatile, so it can be transported in the gas phase and condenses with the water on the walls of the pipe. The aggravation of the corrosion will be seen only if the presence of HAc has a significant effect on the pH. In such case, the protectiveness of the corrosion products layers at the top of the line is questionable.

EXPERIMENTAL PROCEDURE

The Institute for Corrosion and Multiphase Technology at Ohio University, Athens Ohio, has build, with a support of the company TOTAL, an experimental flow loop especially designed for the study of the Top of the Line Corrosion. A schematic representation of the loop is presented in Figure 1. The flow loop, mainly made of stainless steel 316, can be divided in three main parts: the tank, the pump and the loop.

- The tank is used for the storage and the heating of the water. It is filled with dionized water and acetic acid is added to reach the specific concentration required in the tests. Two heaters immersed in the water warm the liquid. The mixing of water vapor and carbon dioxide occurs at the upper part of the tank.
- The pump moving the gas is a positive displacement progressive cavity pump. It is continuously lubricated with water from the tank.
- The 4" diameter flow loop is 30 meters long and horizontally leveled. The gas mixture of water vapor and carbon dioxide flows along the pipe and the condensation of water occurs as this mixture contacts the cooled section of the loop. The test section where the measurements are taken, is located 8 meters after the exit of the tank. The test section (Figure 2) is a 1.5 meters long pipe spool. Four probe ports are installed (two at the top, two at the bottom). The copper coils enrolled around the pipe act like a heat exchanger forming the "condensation device". Sample of condensed liquid and pH measurements can be taken at the test section.

The experimental procedure is as follow: the tank is first filled with 1 m³ of de-ionized water and carbon dioxide is injected in the loop at a specific pressure. The water is then heated up to the specific temperature by two electrical resistance heaters. The pump is started and the vapor-gas mixture flows in the loop. If de-oxygenation is needed, the system is flushed until the concentration of oxygen is low enough (150 ppb). When condensation is required, the test section is cooled using the "condensation device" and the condensation rate is set. When the steady state is reached, the corrosion probes are introduced in the test section and the experiments begin. A data acquisition device is used in order to continuously measure the inlet and outlet temperature of the gas and of the cooling liquid at the test section, the total pressure, the condensation rate and the cooling liquid flow rate.

Acetic acid concentration

The acetic acid concentration is adjusted by adding the right amount of pure HAc in the tank. The required amount of acetic acid is first de-oxygenated before introduced in the tank using a high-pressure vessel. The concentration distribution of free HAc and acetate (AC⁻) is back calculated from the value of pH.

Condensation rate measurement

A gas-liquid separator located at the end of the loop allows the measurement of the condensation rate. The flow rate of condensed water is monitored using a pressure transducer. The value of the condensation rate at the test section is back calculated from this measurement. Even if the loop is thermally insulated from the ambient atmosphere, a minimal heat transfer cannot be prevented. It means that condensation will always occur in the loop and that its minimum value is set by the efficiency of the thermal insulation. The lowest level of condensation is named "Low condensation rate". Three condensation rates have been tested in this work, named in increasing order "Low", "Critical", "High" and "Very High".

Corrosion rate measurement

The corrosion rate measurement starts once the system is at equilibrium. Corrosion rate are measured with weight loss coupons made of 1020 carbon steel shown in Figure 4. The weight loss coupons are polished with 600 grain sand paper, dried with isopropyl alcohol and weighed. They are flush mounted to the internal pipe wall of the loop by using a specially designed probe holder. Therefore, only one face of the coupons is in direct contact with the corrosive environment as the others faces are coated with Teflon. One experiment lasts typically around 48 hours. As soon as they are removed from the loop, the coupons surface is flushed with isopropyl alcohol and dried. Then they are weighed again with the corrosion product layer. Some of the coupons are then immediately treated with Clarke's¹¹ solution and brushed in order to remove the corrosion product layer and weighed again. The corrosion rate is calculated from this

weight loss value. The difference in the two latter weight loss measurements (with or without corrosion product layer) gives an indication about the amount of the corrosion products on the coupons. The coupons, which have not been treated with the Clarke's solution, are stored in a dry environment until surface analysis is done.

Test matrix

The test matrix (Table 1) aims at investigating the effect of acetic acid concentration on the corrosion rate. A range from 0 to 1000 ppm of "free" acetic acid (undissociated acetic acid) is studied over various condensation rates. The temperature remains mainly at 70°C and the gas velocity at 5m/s. The pH is not controlled and depends on the operating conditions. The oxygen content in the liquid phase is always kept under 150 ppt. Each experiment lasts 48 hours and is repeated at least two times.

RESULTS

Due to the confidentiality of the results, only normalized values are reported.

The values are calculated at the top and at the bottom by dividing the actual corrosion rate with the maximum corrosion rate observed at that location. At the bottom of the line, the corrosion rate is always an order of magnitude greater than at the top of the line at the same conditions. The normalized results reveal qualitatively the trends in the data and the influence of the key parameters. Error bars are displayed on each graph showing the maximum and the minimum values obtained for the experiments and the number of repeat.

Effect of acetic acid concentration

Top of the line

Figure 5 shows the influence of increasing concentration of acetic acid on the top of the line corrosion rate. Under low condensation rate, the presence of acetic acid, even in low concentrations (here 18 ppm of undissociated HAc) is enough to almost double the corrosion rate. Then the corrosion rate does not change when the concentration of acetic acid increases to 171 ppm.

Under critical condensation rate, the threshold between pure CO₂ and 18 ppm of HAc observed under low condensation rate is not so obvious. In fact, the corrosion rate remains unchanged until a concentration of 1014 ppm of HAc is reached.

Bottom of the line

Figure 6 shows the influence of increasing concentration of acetic acid on the bottom of the line corrosion rate. Under low condensation rate, the corrosion rate does not seem to change comparing a pure CO₂ environment with one containing a small amount of HAc (18 ppm). When the concentration of free HAc reaches 57 ppm, the corrosion triples and remains constant until 171 ppm.

Under critical condensation rate, a change in the corrosion rate is seen comparing a pure CO₂ environment with one containing a small amount of HAc (17 ppm). Then, the corrosion rate is unchanged until a concentration of 1012 ppm of HAc is reached.

Influence of the condensation rate

Top of the line

Figure 7 shows the influence of the condensation rate on the top of the line corrosion rate with a liquid phase containing 171 ppm of undissociated acetic acid.

At a concentration of 171 ppm of undissociated acetic acid, the corrosion rate is not greatly affected by the condensation rate except when the condensation rate reaches a very high level.

Bottom of the line

Figure 8 shows the influence of the condensation rate on the bottom of the line corrosion rate with 171 ppm of undissociated acetic acid. The condensation rate (over a range from low to high) does not influence the corrosion rate. It can be explained by the fact that there is always a significant amount of liquid flowing at the bottom of the pipe. The liquid condenses all over the pipe but, due to gravity forces, it flows to the bottom.

Influence of the gas temperature

Top and bottom of the line

Figure 9 and 10 show the influence of the temperature of the case on the top and bottom of the line. This influence has been studied at a concentration of HAc of 171 ppm, under critical condensation rate and for two different gas temperatures (50C and 70C).

The corrosion rate is higher at 70 C than at 50C and this behavior is observed both at the top and at the bottom of the line.

Corrosion product layer

Understanding the mechanism of creation and removal of protective iron carbonate layer is one of the key points of the top of the line corrosion. Figures 11-14 show some images of corroded weight loss coupons at the top of the line (Figure 11, 12) and at the bottom of the line (Figure 13, 14).

In every experiment at the top of the line, the corrosion products layer shows the same characteristics: the layer is thin and dense, hard to remove. Figure 17 shows a SEM (Scanning Electron Microscope) picture of the corrosion product layer, which confirms the existence of a dense iron carbon film. The weight of the corrosion product layer itself represents between 10 to 65 % of the total weight loss, depending on the experiments.

At the bottom of the line, all the coupons are covered with a black thick layer easily removed. The weight of the layer represents between 3 to 10 % of the overall weight loss.

After removal of the iron carbonate layer, the surface of the steel is studied with SEM.

At the top of the line, there was no evidence of localized corrosion and the corrosion is uniform in all of the experiments. At the bottom of the line, localized corrosion was observed in many experiments. Figure 18, which shows the surface of a weight loss coupon without its corrosion product layer, gives an indication about localized corrosion taking place initially in small pits that agglomerate. The surface is then uniformly corroded at a high rate. Figure 15 and 16 show the surface of carbon steel coupons without iron carbonate layer from the top and the bottom of the line respectively. From the bottom, the surface of the coupon is rough and uneven when at the top it is much smoother.

CONCLUSIONS

An experimental study was conducted to determine the influence of acetic acid on CO₂ top of the line corrosion. At a fixed CO₂ partial pressure, several condensation rates, gas temperatures and acetic acid concentrations were tested and the corrosion rate was monitored using weight loss C1020 coupons.

- The corrosion rate at the bottom is an order of magnitude higher than the top of the line
- At the top of the line, the corrosion rate increases gradually with the concentration of acetic acid.
- At the bottom of the line, a large change in the corrosion rate is seen when acetic acid is added, and then the corrosion rate increases gradually with the acetic acid concentration.
- At the top of the line, the corrosion rate increases when the condensation rate increases.
- At the bottom of the line, the condensation rate has a small influence on the corrosion rate.
- The corrosion rate is higher at 70C than at 50C both at the top and bottom of the line.
- At the top of the line, the corrosion is uniform and no trace of pit is found. A thin and dense iron carbonate layer covers the surface.
- At the bottom of the line, evidence of localized corrosion was found.

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TEST MATRIX

- The partial pressure and the gas velocity remain constant during all the experiments.
- The gas velocity is set at 6 m/s and the gas phase is composed of CO₂, water and acetic acid vapor in equilibrium with the liquid phase.
- Free HAc represents the concentration of undissociated acetic acid in the liquid phase. The concentration of total acetate species (HAc + AC⁻) is presented in parenthesis.
- In most of the experiments, the temperature of the gas is set at 70 C with only one at 50 C (test 11).
- Its real values being confidential, the condensation rate is leveled this way:
Low < Critical << high <<< very high

Test number	1	2	3	4	5	6
Tgas (C)	70		70		70	
Free HAc (ppm)	0		18 (20)		57 (60)	
Condensation rate	Low	Critical	Low	Critical	Low	Critical

Test number	7	8	9	10	11	12
Tgas (C)	70		70		50	70
Free HAc (ppm)	114 (120)		171 (180)			
Condensation rate	Low	Critical	Low	Critical	Critical	High

Test number	13	14
Tgas (C)	70	70
Free HAc (ppm)	171 (180)	1012 (1040)
Condensation rate	Very high	Critical

Table 1: Test matrix

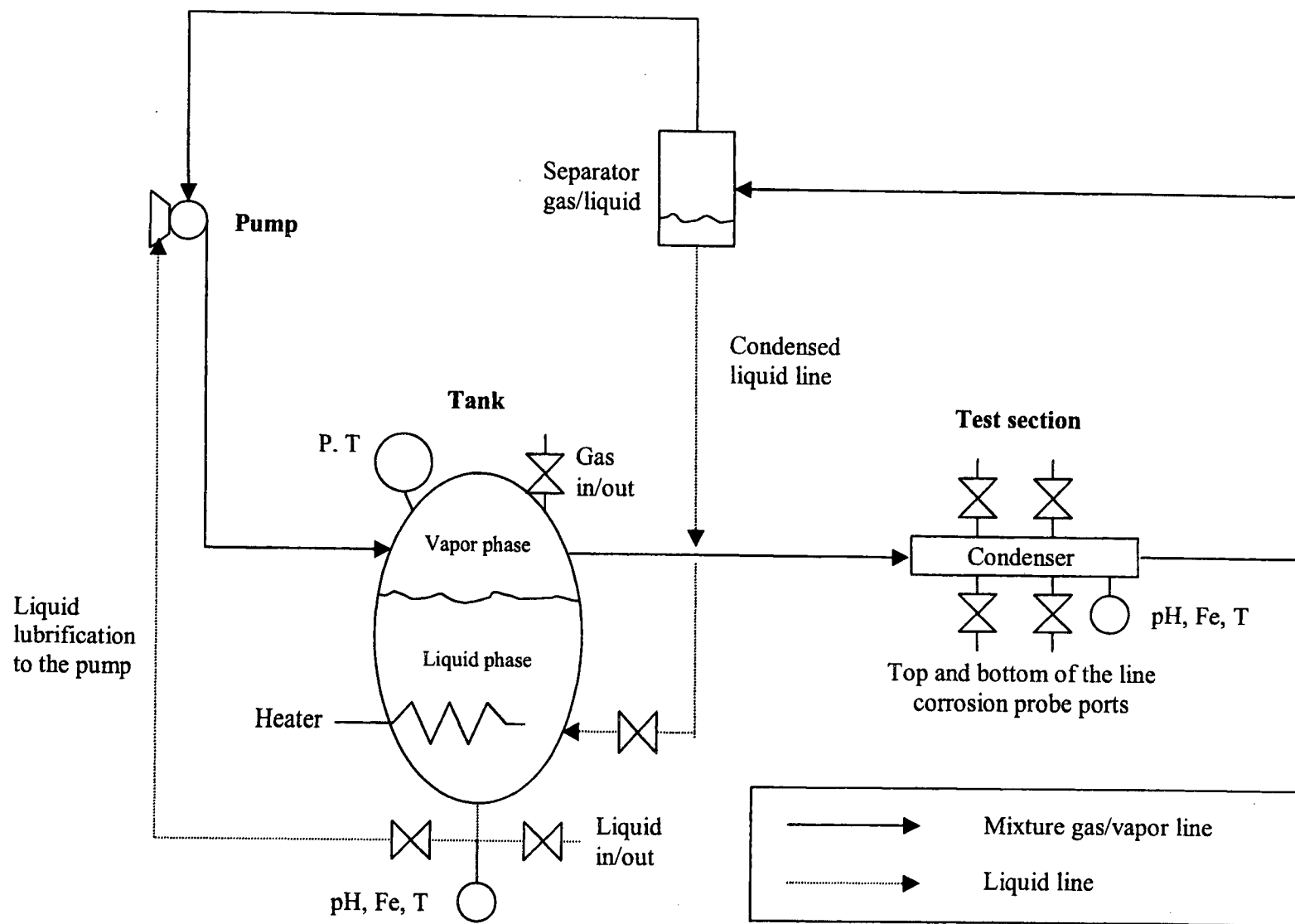


Figure 1: Top of the line corrosion loop schematic

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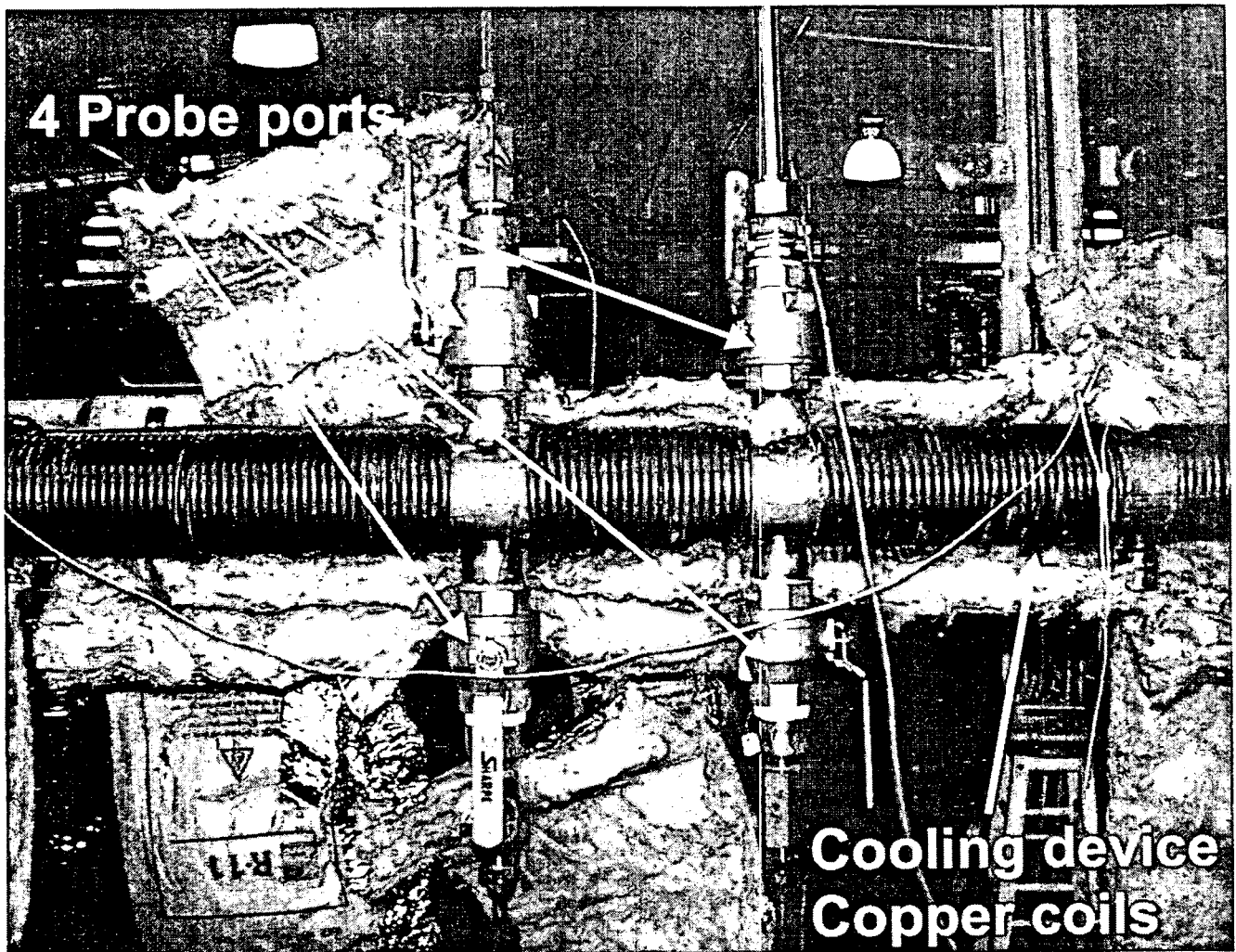


Figure 2: Picture of the test section

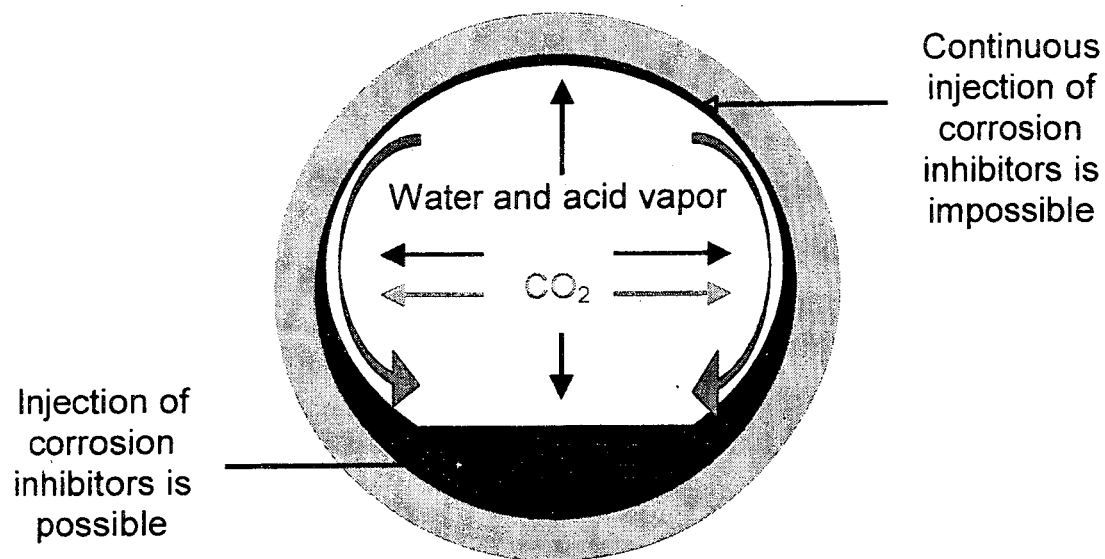


Figure 3: Liquid condensation inside the pipe

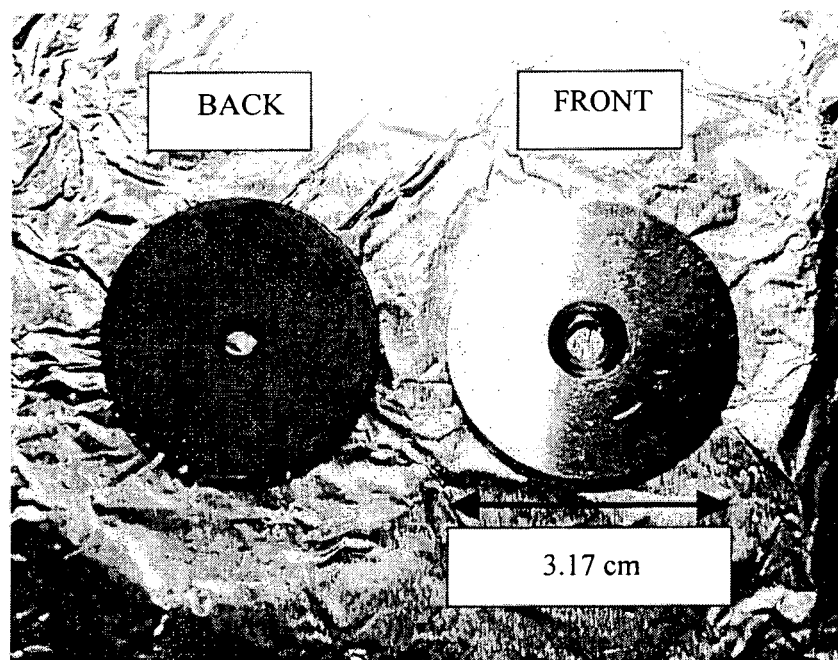


Figure 4: Weight loss coupons with Teflon coating at the back and the side
(External diameter ≈ 3.17 cm)

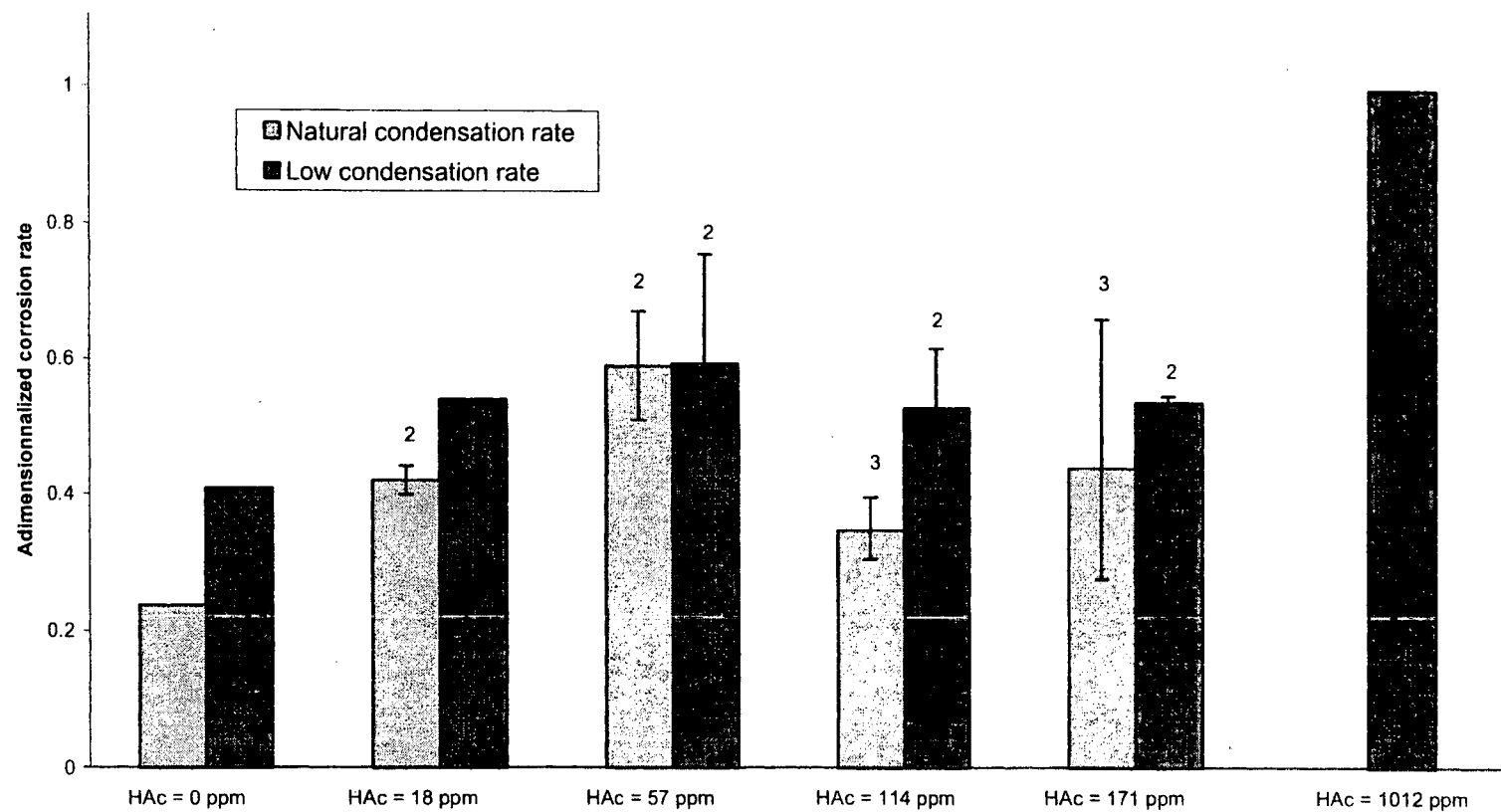


Figure 5: Influence of the concentration of undissociated acetic acid on the corrosion rate at the **top of the line**
 - $T_{\text{gas}} = 70^{\circ}\text{C}$, Gas velocity = 5 m/s, Partial pressure of CO_2 constant -

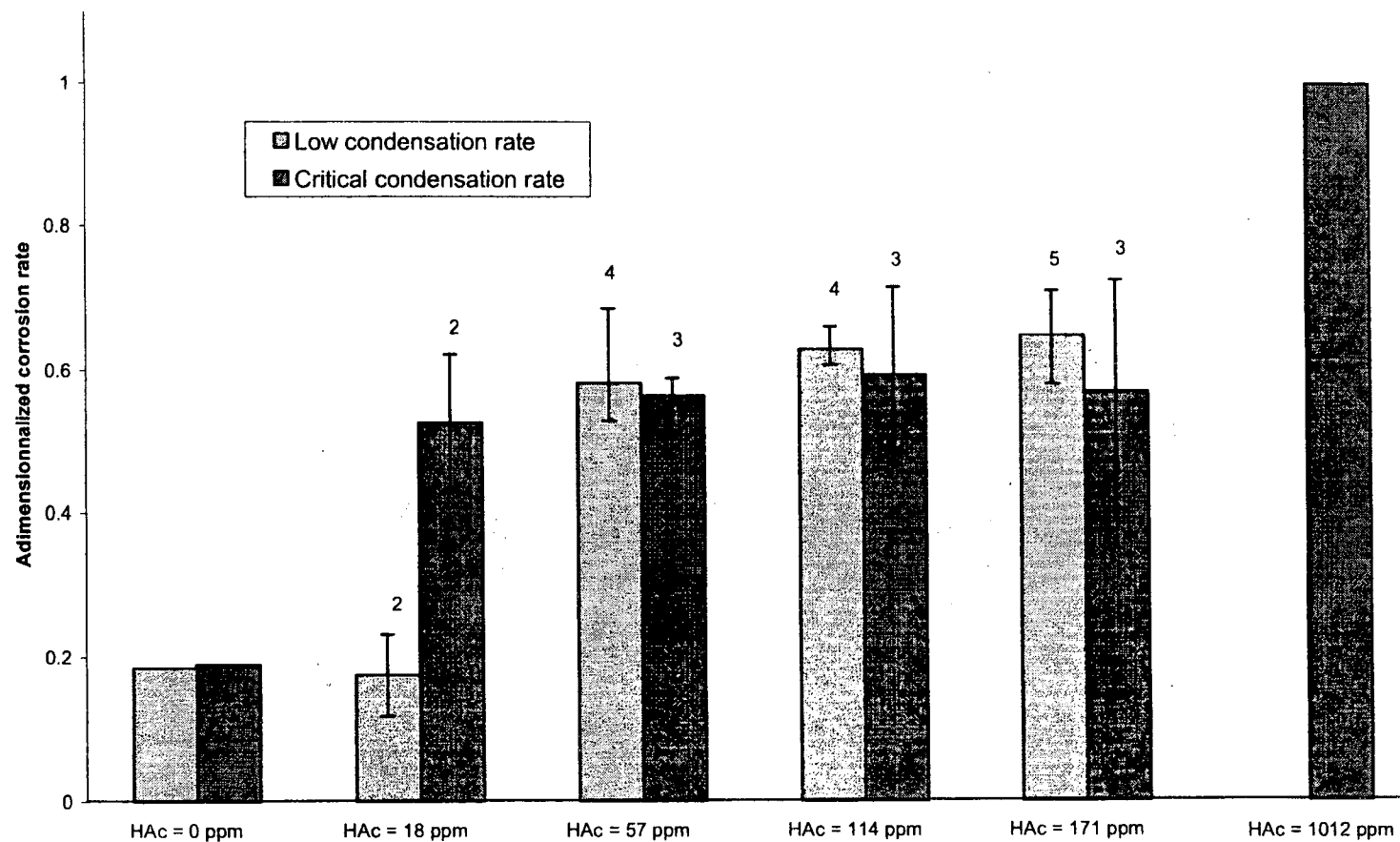


Figure 6: Influence of the concentration of undissociated acetic acid on the corrosion rate at the **bottom of the line**
 - $T_{\text{gas}} = 70^{\circ}\text{C}$, Gas velocity = 5 m/s, Partial pressure of CO_2 constant -

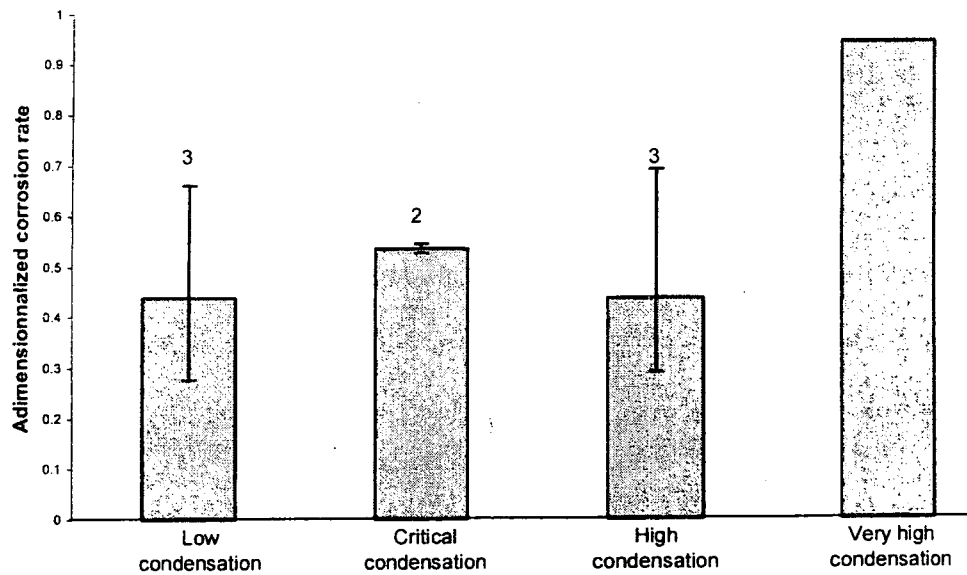


Figure 7: Influence of the condensation rate on the corrosion rate at the **top of the line**
 $T_{\text{gas}} = 70^{\circ}\text{C}$, Gas velocity = 5 m/s, $\text{HAc} = 171 \text{ ppm}$ - Partial pressure of CO_2 constant

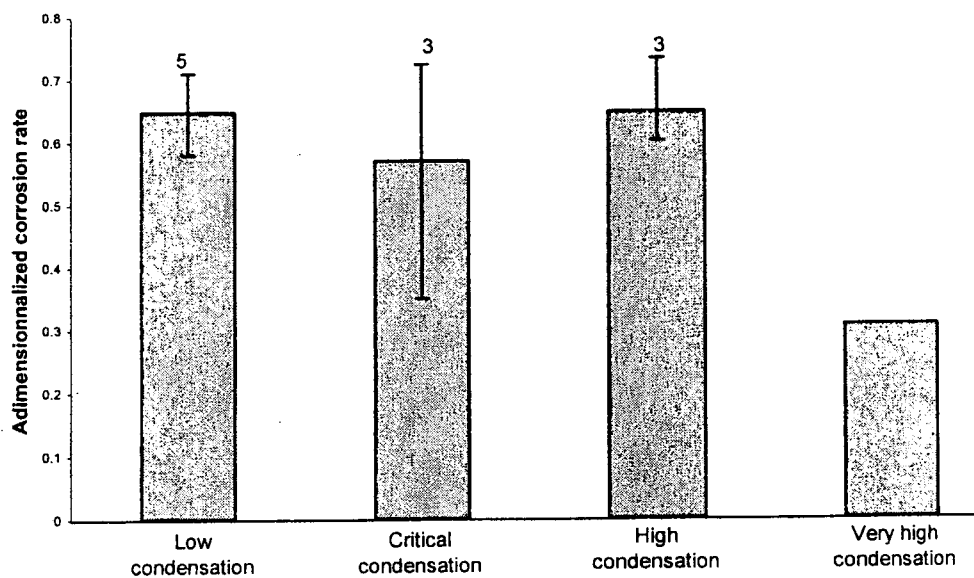


Figure 8: Influence of the condensation rate on the corrosion rate at the **bottom of the line** - $T_{\text{gas}} = 70^{\circ}\text{C}$, Gas velocity = 5 m/s, $\text{HAc} = 171 \text{ ppm}$, Partial pressure of CO_2 constant -

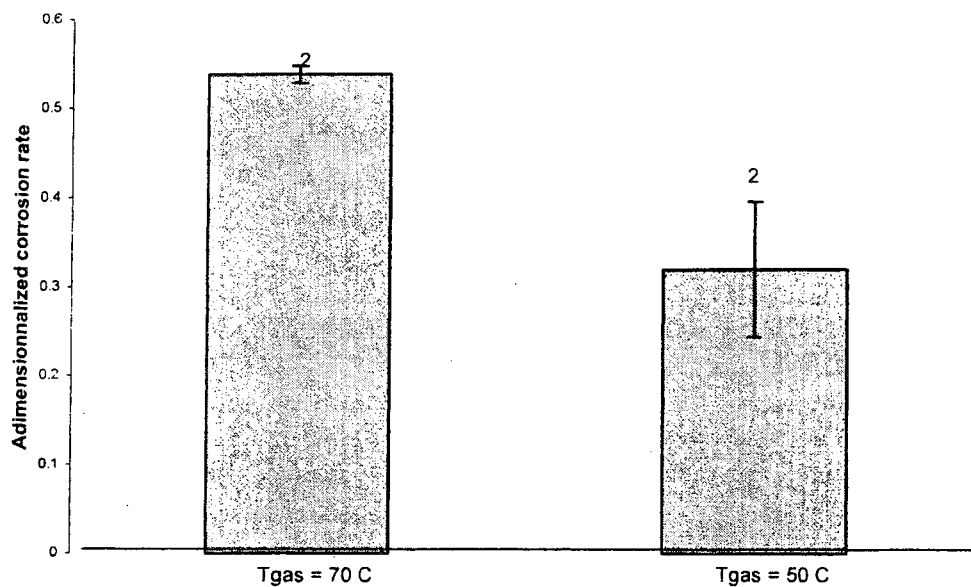


Figure 9: Influence of the condensation rate on the corrosion rate at the **top of the line**
 - Gas velocity = 5 m/s, HAc = 171 ppm, Critical condensation rate, Partial pressure of CO₂ constant -

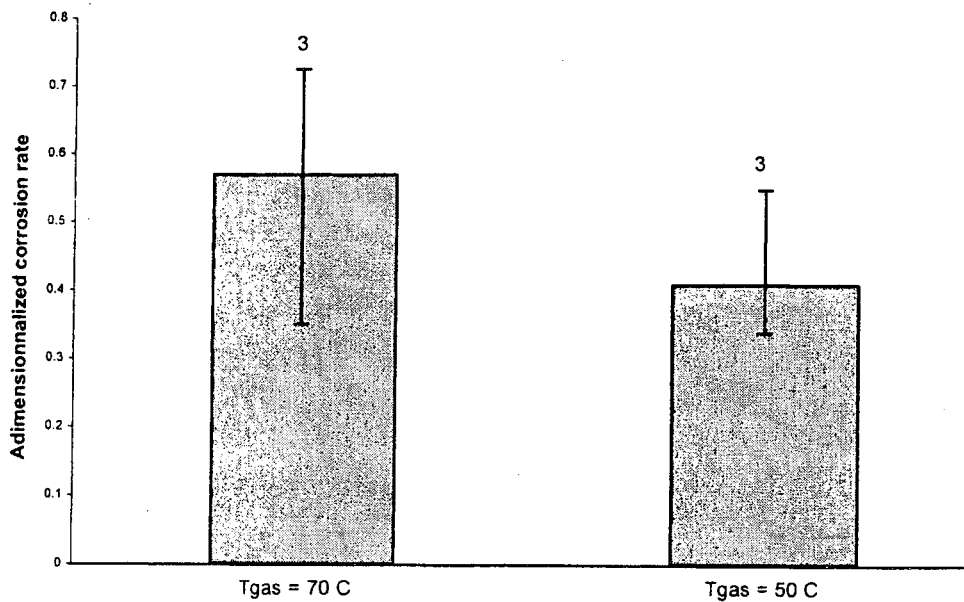


Figure 10: Influence of the condensation rate on the corrosion rate at the **bottom of the line**
 - Gas velocity = 5 m/s, HAc = 171 ppm, Critical condensation rate, Partial pressure of CO₂ constant -

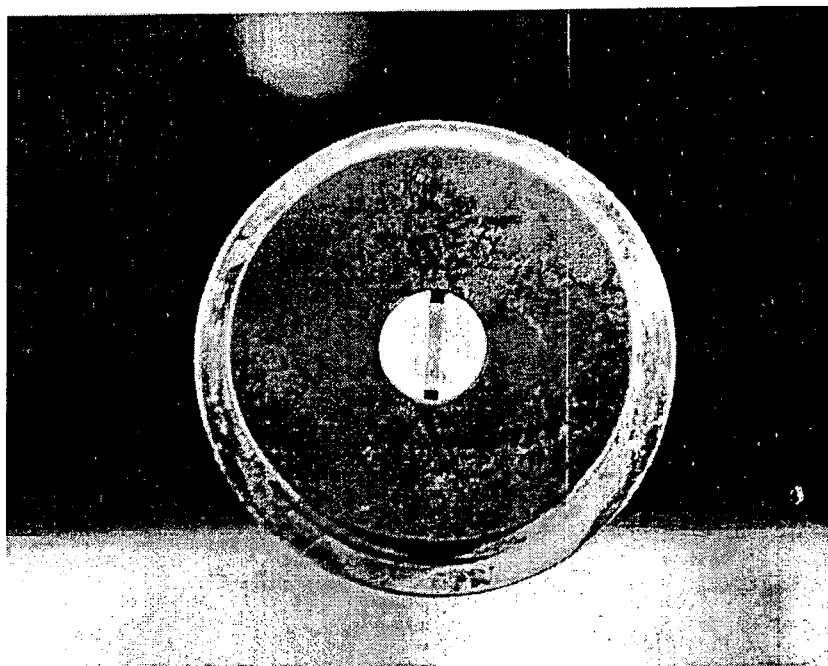


Figure 11: Corrosion product layer – **Top of the line**
T=70 C, Low condensation rate, $V_{\text{gaz}}=5$ m/s, HAc=171ppm

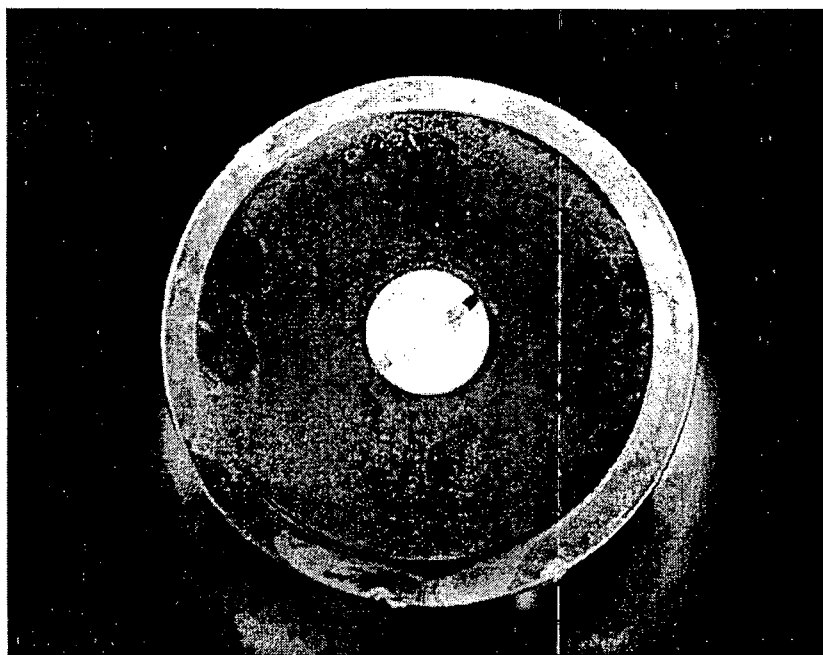


Figure 12: Corrosion product layer – **Top of the line**
T=70 C, Critical condensation rate, $V_{\text{gaz}}=5$ m/s, HAc=114ppm

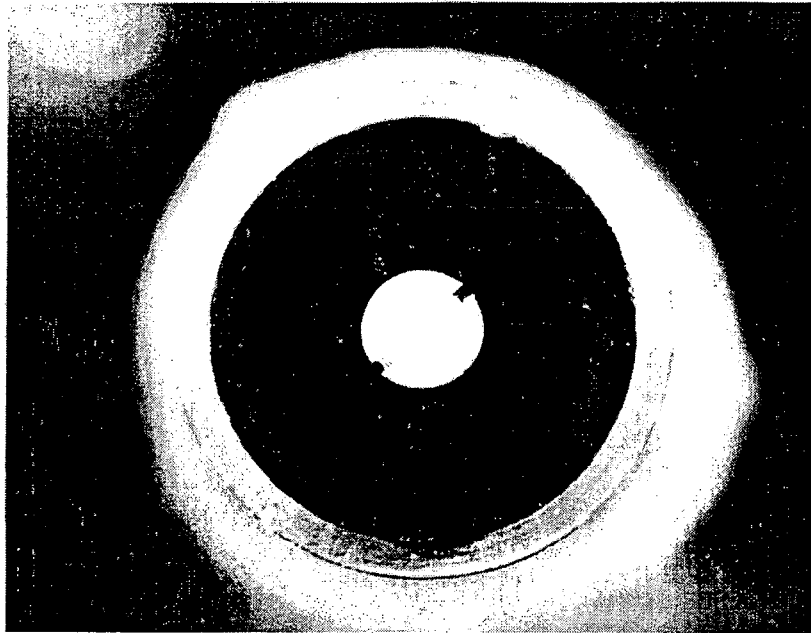


Figure 13: Corrosion product layer – **Bottom of the line**
T=70 C, Critical condensation rate, $V_{\text{gaz}}=5$ m/s, HAc=114ppm

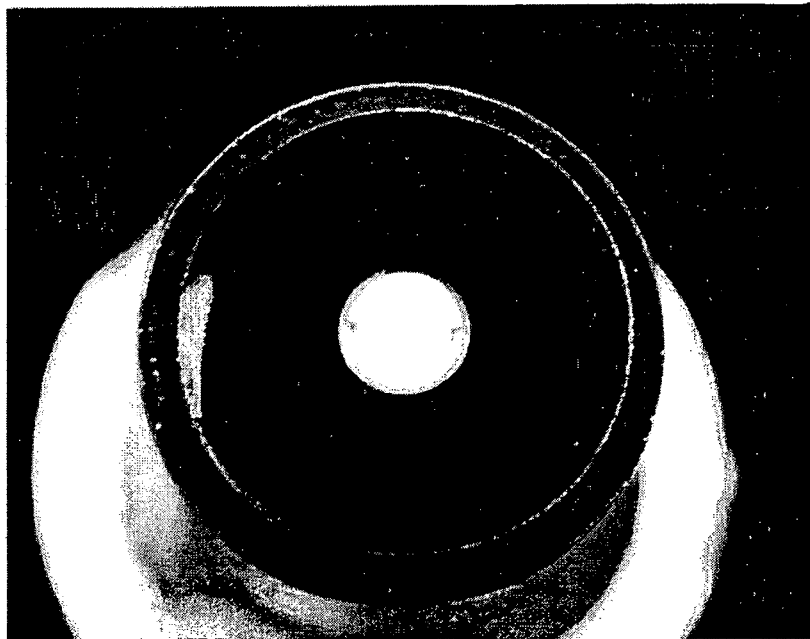


Figure 14: Corrosion product layer – **Bottom of the line**
T=70 C, High condensation rate, $V_{\text{gaz}}=5$ m/s, HAc=171ppm

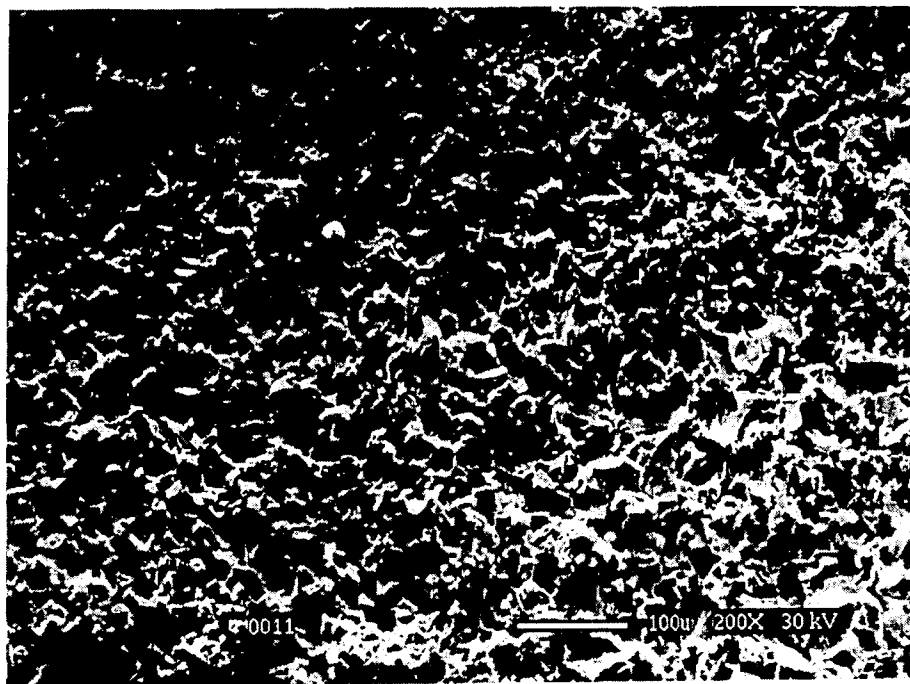


Figure 15: SEM Top of the line after removal of the corrosion product layer
 Tgas= 70C, Vgas= 5m/s, HAc=1014ppm, Critical condensation rate

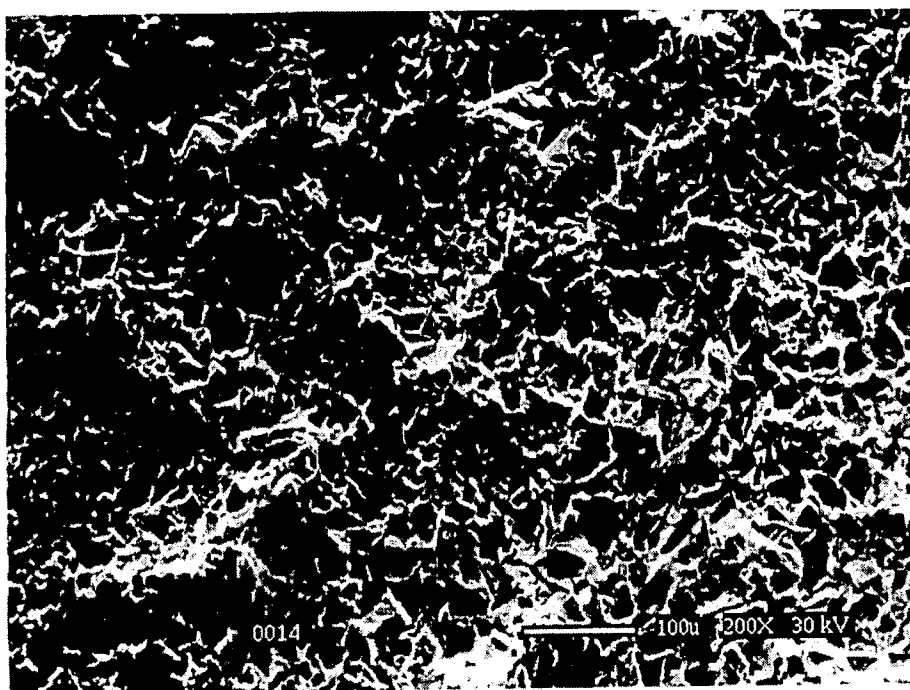


Figure 16: SEM Bottom of the line after removal of the corrosion product layer
 Tgas= 70C, Vgas= 5m/s, HAc=171ppm, Critical condensation rate

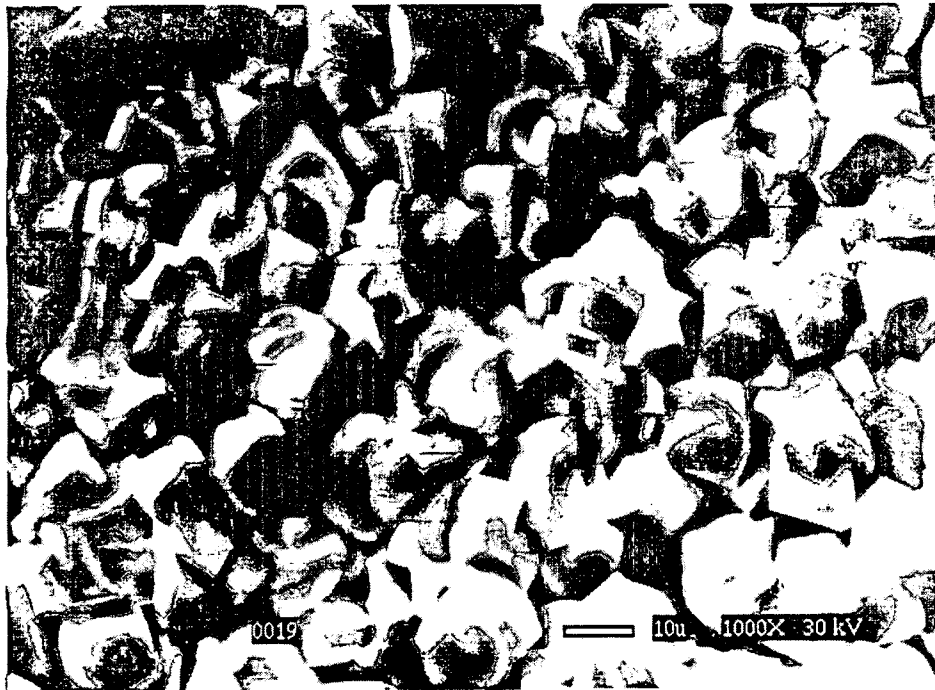


Figure 17: SEM Top of the line – Iron carbonate layer
 Tgas= 70C, Vgas= 5m/s, HAc=114ppm, Low condensation rate

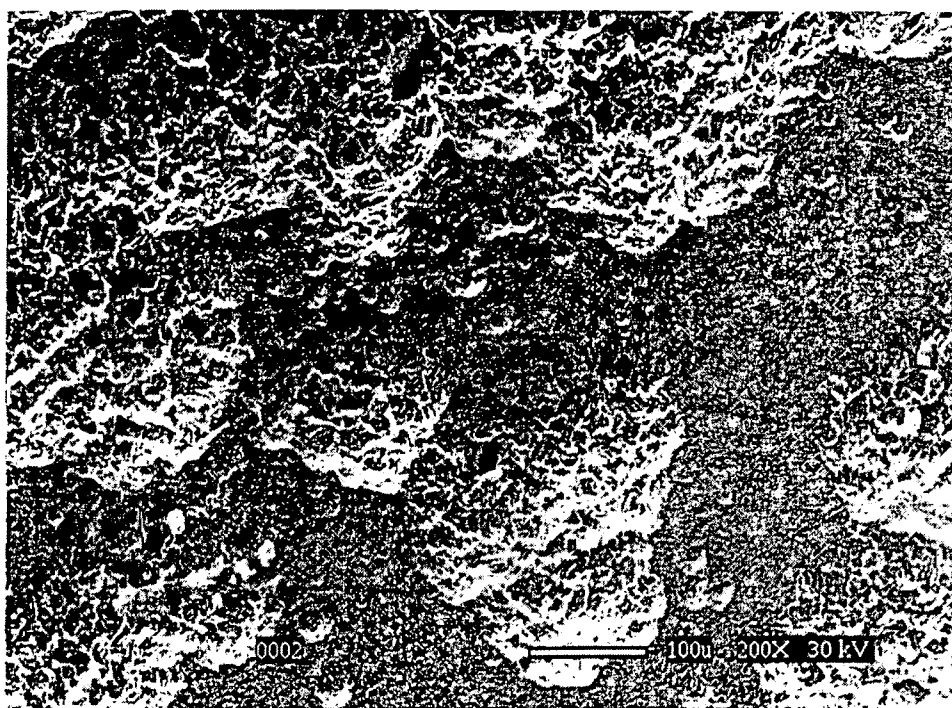


Figure 18: SEM Bottom of the line after removal of the layer – Localized corrosion
 Tgas= 70C, Vgas= 5m/s, HAc=171ppm, Very high condensation rate