

Top of the line corrosion – Part 1: Review of the mechanism and laboratory experience

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ABSTRACT

Top of the Line Corrosion (TLC) is now known to be the main mode of failure in incidents associated with a number of wet gas pipelines operated all over the world. TLC is nevertheless a relatively recent phenomenon in a sense that its existence was only acknowledged about 10 to 15 years ago. A number of research activities have been carried out since then and although there are still a number of uncertainties, the main aspects of the mechanism involved in TLC have been identified. This paper presents a review of the laboratory work performed on the topic with a detailed list and analysis of the different experimental setups proposed for its study. The latest findings in the specific influence of each controlling parameter (water condensation rate, organic acids, hydrogen sulfide, flow regime, etc) are also laid out. A number of TLC predicting tools (some empirical, some mechanistic) have also been developed based on the current understanding and their value and limitations are discussed as well.

INTRODUCTION

Since the drilling and completion of the first oil well, the oil and gas industry has had to battle many types of corrosion, some more serious than others. Top of the line corrosion (TLC) is one of these types and probably one of the most recent to be discovered, as it was first identified only in the 1990s. At that time, it was regarded as a curiosity more than a real problem. However, TLC has been progressively recognized as a major cause of pipeline failure all over the world and has become the focus of intense research relating to its mechanism, prevention and prediction.

The transportation of fluid is critical in the oil and gas industry. When the fluid comes directly from the oil well, it is usually unprocessed and consists of multiple phases, *i.e.*, a mixture of oil, solids, gas and water (as brine). The presence of water can lead to considerable corrosion problems on the internal walls of the pipelines, though the use of corrosion inhibitors dissolved in the oil or water phase can usually provide some protection if these are applied effectively.

The phenomena of interest in this study are related to the transportation of gas containing condensable liquids (“wet gas”) and, more precisely, the corrosion issues that occur when significant heat exchange is present between the pipelines and the surroundings (frozen land, deep-sea water, etc.). The unprocessed water and hydrocarbon vapor flowing through the pipe have the potential to condense particular components on the cold walls, one of them being water, forming a thin film and/or droplets of liquid. The condensed water can contain corrosive species such as organic acids and dissolved corrosive gases (e.g. carbon dioxide or hydrogen sulfide). Typical carbon steels can corrode rapidly under these conditions, which could lead to a loss of pipeline integrity and potential failure. The use of standard corrosion inhibitors to combat TLC is usually inefficient since the inhibitors themselves are non-volatile and typically do not provide any protection to the top of the pipeline, at least in stratified flow regime.

The objective of the paper is to draw a comprehensive review of the current understanding of TLC mechanisms obtained through laboratory experience. The advantages/drawbacks of a number of experimental “TLC” setups are reviewed together with the main conclusions of the related studies.

MECHANISM

TLC is a complex phenomenon in which several processes interact:

- Fluid mechanics: Knowing the location and velocity of the gas and liquid phases on the cross section of the pipe is the first step in determining whether TLC is an issue.
- Heat and mass transfer: TLC is the consequence of water vapor condensation on the pipe wall which is driven by a gradient of temperature across the pipe wall.
- Chemistry: Corrosive gases dissolve in the condensed water and generate a number of species, some of them acidic, which can react to form corrosion products.
- Electrochemistry: The acidity of the condensed water drives the corrosion process.

Flow regime

The issue of TLC occurs only when specific flow conditions are met. Probably the most important one is the flow regime. The transportation of fluids coming from the well involves a mixture of gas (containing water vapor, hydrocarbon vapors, carbon dioxide, and hydrogen sulfide), liquid hydrocarbon and water. At the temperatures and pressures encountered in flowline conditions, the presence of liquid water in contact with the pipe steel is responsible for corrosion. As mentioned earlier, the injection of corrosion inhibitor, often water soluble, does provide effective protection against metal loss. Consequently, any parts of the pipe surface wetted - even intermittently - by the inhibited water, should benefit from some level of protection. Some flow conditions lead to this kind of scenario while some others do not. The most common type of flow encountered in the transport of unprocessed hydrocarbon fluids is gas-oil-water three-phase flow (oil here meaning liquid hydrocarbons). Some fields may generate little or no liquid hydrocarbons but they all produce non-condensable gas (light hydrocarbons, CO₂, etc.) and water vapor (saturated water vapor in most cases). Three major flow regimes may be encountered and their characteristics and corresponding flow conditions are described below:

- Stratified flow (wavy or smooth): At low gas and liquid flow rates, the gas and liquid phases are clearly segregated and the gas-liquid interface is smooth. With increased liquid and gas velocity, waves can be initiated at the gas-liquid interface.

- Intermittent flow (slug or plug): At higher liquid velocity, the crests of the waves can reach the top of the pipe, and a liquid connection (slug) between the top and the bottom of the line is formed.
- Annular flow: When gas velocity increases but liquid velocity is kept low, droplets of liquid are atomized and transported to the upper pipe wall surface, forming a liquid film covering the whole circumference of the pipe, with the gas flowing in the core and the majority of liquid flowing at the bottom.

Only one of these flow regimes (stratified flow) leads to TLC issues. In the case of slug or annular flow, the liquid phase (water or oil), which can be inhibited, is at least intermittently in contact with the pipe surface. In terms of TLC, the area of risk is below the “stratified” line, where the gas and liquid flow rates are low enough that the water vapor can condense freely on the upper pipe steel surface, while the bulk liquid phase, which can be inhibited, stays at the bottom of the line (Figure 1).

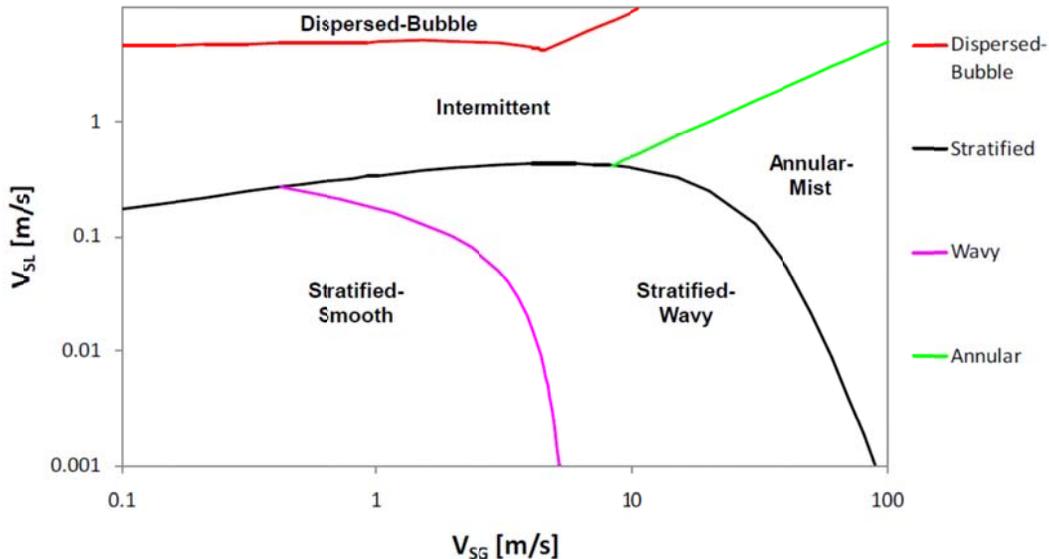


Figure 1: Flow regime map generated for a mixture for air / water system
 V_{SL} : Superficial liquid velocity and V_{SG} : Superficial gas velocity
 $P=1.013\text{bar}$, $T=25^\circ\text{C}$, Internal diameter=6", Inclination=0° (Reproduced from ¹⁾)

Condensation process

Liquid water, as brine, is always present in the well together with a variety of hydrocarbons. Considering the many thousands of years it took for the fluids to accumulate, water vapor can be assumed to be in equilibrium with the liquid water. This is also true for a number of hydrocarbons, although the lighter ones (methane, ethane, etc.) are always in a superheated state. As the fluids are extracted from the well through production tubing and flowlines, the pressure and temperature decrease. A decrease in pressure tends to move the equilibrium towards the super-heated zone (leading to more evaporation of the liquid water) while a decrease in temperature leads to the formation of water by condensation of the vapor phase. These two changes in conditions “work” in opposite directions but, practically speaking, the drop in temperature always has a much greater effect. Consequently, the water vapor should always remain at saturation as long as the produced fluids are not artificially separated. Gas and liquid treatment will effectively remove the water from the produced fluids but this complex process is only typically done at the production facilities.

In a typical off-shore oil and gas transport system, particular segments of the transmission infrastructure involve vertical tubing (from the reservoir to the subsea wells) where the flow regime is never stratified and no TLC should be expected. However, once the fluid enters the flowlines, *i.e.*, the sections of pipe between the wells, the platform and the onshore facilities, stratified flow can be expected, depending on the line topography and the flow rates. Under these conditions, there is no

reason to believe that any inhibited water present at the bottom of the line could reach the top of the pipe, and TLC can therefore occur in an un-mitigated environment.

The top part of the pipeline will corrode if liquid water comes into contact with the steel surface. This is why a significant amount of water vapor condensation is required for there to be any significant amount of corrosion. In practical terms, the main factor affecting the amount of water that can condense is the gas temperature; the hotter the fluid is, the higher is the saturated water vapor pressure. However, other parameters do influence the process. The rate of water condensation is dependent on not just the amount of water vapor carried in the gas phase but also on the gradient of temperature with respect to the outside environment. Thermal insulation or burial of the pipeline is particularly important, as it will limit the heat transfer between the pipeline and the outside environment and consequently limit the rate of water condensation. Finally, the nature of the outside environment also plays a role, as more heat can be “extracted” from the produced fluid if the pipe is in contact with flowing water (river or maritime current) as opposed to air or soil.

In summary, several key factors can be identified in assessing whether a pipeline will suffer from significant water condensation:

- The water vapor pressure of the produced fluid
- The gradient of temperature between the produced fluid and the outside environment
- The nature of the outside environment (air, sea or river)
- The extent of thermal insulation or pipeline burial

Water chemistry of H₂O/CO₂/H₂S system

Understanding the water chemistry is a necessary step in assessing the severity of a corrosion attack. The basic principles of the H₂O/CO₂/H₂S system have been presented elsewhere² and are not specific to TLC. Organic acids are also often present in produced fluids and the most common and abundant among them is acetic acid³. In addition, the presence of large concentrations of H₂S in a growing number of fields is becoming one of the most pressing matters in term of corrosion prediction in the oil and gas industry⁴. The understanding of H₂S corrosion mechanisms is clearly not as advanced as that of CO₂, even though much effort has already been made in this direction⁵. Although H₂S gas is about three times more soluble in water than CO₂ gas (at 25°C, $K_{sol}^{H_2S} = 0.1$ mol/L/bar and $K_{sol}^{CO_2} = 0.03$ mol/L/bar), the acidity constant for H₂S is about four times lower than for carbonic acid (at 25°C, $K_a^{H_2S} = 9.3 \cdot 10^{-8}$ mol/L and $K_a^{H_2CO_3} = 4.6 \cdot 10^{-7}$ mol/L). Consequently, CO₂ and H₂S gases do approximately affect the solution pH to the same extent.

In the field, typical CO₂ contents range from 0.1 to 10 mol% (although much higher concentrations have been reported). In terms of H₂S, gas contents ranging from 5 to 5000 ppm are also common. Considering that the production pressures and temperatures in flowlines typically range from 30 to 200 bars and from 5 to 100°C, respectively, the pH of condensed water should vary between 3 and 4.5.⁶ However the presence of formation water and the injection of a strong base (a common corrosion mitigation method) result in significantly higher in-situ pH of the bulk aqueous phase at the bottom of the line (practically between 6 and 8).⁷

The only difference between the chemical composition of the water at the bottom of the line (brine) and the water at the top is the mineral content, which is nil in freshly condensed water. In addition, any base injected in-line as part of a corrosion mitigation method would typically have no effect at the top of the line. Determining the pH of the condensed water requires knowing the partial pressure of acetic acid, in addition to the CO₂ and H₂S content. The typical pH value of freshly condensed water is consequently quite low and varies between 3 and 4.5. However, as the corrosion process takes place, iron ions are released in solution as acidity is consumed, which rapidly increases the pH; especially when the rate of condensed water renewal is low.

Corrosion process

CO₂ corrosion has been extensively studied by many different investigators.⁸⁻¹⁵ Consequently, the main corrosion mechanisms for this system are now well defined and have been incorporated into prediction models.^{16,17}

It should be noted that the acetic acid and, to some degree, the carbonic acid direct reduction reactions are currently subject to debate regarding whether or not they actually occur to any significant degree in the environment considered. Following the pathway of direct reduction, the concentration of acetic acid is directly linked to the corrosion rate, as more acid leads to a higher steel dissolution rate. Considering the buffering effect, the acetic acid only acts as a provider of hydrogen ions and the corrosion rate will increase until it eventually falls under charge transfer control. Distinguishing between the two pathways is not an easy task, but recent work seems to favor the buffering effect over the direct reduction.^{12,13} It is understood that the presence of acetic acid leads to a considerable increase in the corrosion rate.^{3,11}

Corrosion product layer

As a direct product of the dissolution of steel, the concentration of Fe²⁺ ions can increase in solution depending on the flow conditions. In a top of the line scenario, the Fe²⁺ concentration can quickly reach a relatively high level, especially if the rate of water condensation is slow. In CO₂/H₂S/H₂O systems, two main families of corrosion product can form: iron carbonate (FeCO₃) and iron sulfide (Fe_xS_y).

Precipitation reactions have been proposed to describe FeS formation and dissolution.¹⁸ Other authors¹⁹⁻²¹ have suggested different pathway: a so called “direct” reaction where it is assumed that iron dissolution does not occur; rather, a fast oxidation of solid iron transforms it directly into solid iron sulfide attached to the steel surface. The mechanism of this reaction is still under investigation, including the role of various species in the formation of the different types of iron sulfide compounds.

LABORATORY EXPERIENCE

The present section presents a review of the main laboratory studies related to TLC published over the years. It is divided into three main parts, whether the study focuses on CO₂ dominated TLC, H₂S dominated TLC or chemical inhibition of TLC.

Experimental work on CO₂ TLC

In the past twenty years, TLC has been the subject of intensive research. As early as in 1991, Olsen proposed the first high-pressure autoclave especially designed for the study of TLC.²² The lid of the autoclave was cooled with water and clamped with weight loss (WL) flushed samples (Figure 2). The partial pressure of CO₂ could be raised up to 5 bars. The author conducted a systematic experimental study on parameters influencing TLC in sweet conditions. The formation of a protective FeCO₃ corrosion product layer was suggested to play a key role. The precipitation of FeCO₃ only occurred when the saturation level was above the value of one. High levels of super-saturation in FeCO₃ could lead to very dense and protective FeCO₃, as was the case at a high temperature (70°C) and a low condensation rate. The authors also found that the competition between the rate of iron dissolution (*i.e.*, the increase of Fe²⁺ ions in the aqueous phase) and the water condensation rate controlled the extent of FeCO₃ film formation. At a high condensation rate, the saturation in FeCO₃ is more difficult to obtain due to the rate of fresh water renewal.

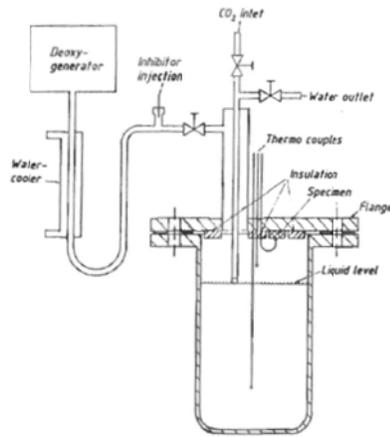


Figure 2: Autoclave setup designed by Olsen
(Reproduced from ²² - © NACE international 1991)

In 2000, Pots et al.²³ developed an apparatus comprised of a carbon steel tube mounted on a heat exchanger and inserted inside an atmospheric chamber containing wet CO₂ (saturated water vapor and CO₂ gas). The water vapor would condense on the cooled steel tube at a rate controlled by the cooling water flow rate (Figure 3). The condensed water was also collected in a container underneath, enabling the measurement of the condensation rate and the sampling of the condensed water for chemical analysis. Although the pressure rating of the device was atmospheric, a wide range of gas temperatures and water condensation rates could be achieved (30-70°C and 0.1 to 1.5 mL/m²/s, respectively). Rates of corrosion were measured by evaluating the difference in mass of the tube before and after the test (weight loss method) and by visual observation of the steel surface. The main disadvantage of this system is that the corrosion process occurred on the outside diameter of the relatively small tube (only a few mm internal diameter), affecting the retention time of the condensed water and creating areas of non-homogeneous corrosion. Nevertheless, this setup enabled the collection of condensed water for pH and iron ion concentration analysis (although it can be argued that the composition of the condensed water may have been altered by re-evaporation). Using this system, the author conducted a series of experiments aimed at highlighting the competition between the scale formation rate linked to the iron dissolution and the condensation rate. Pots developed a corrosion prediction model for TLC based on the calculation of the concentration of iron at saturation under film-forming conditions. The author emphasized the importance of correctly evaluating the condensation rate in order to accurately predict the corrosion rate.

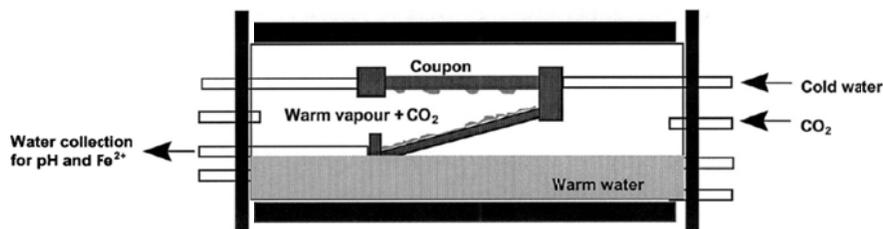


Figure 3: TLC experimental device involving a cooled steel tube
(Reproduced from ²³ - © NACE international 2000)

In 2002, Vitse et al.²⁴⁻²⁵ published a series of experimental results on condensation and corrosion in sweet environment performed in a large-scale flow loop. This flow loop was comprised of the three main components: a large tank (1000L) holding the bulk liquid phase, a gas blower, and a system of 4"ID (0.1 m internal diameter) stainless steel pipes forming a loop about 30 meters in total length. Several test sections, where the actual corrosion measurements were performed, were located along the pipe system. These test sections were externally cooled by tap water circulating through a set of cooling coils wrapped around the pipe. The corrosion probes, either Electrical Resistance (ER) or

weight loss (WL) probes, were used flushed to the internal wall of the pipes (Figure 4). Vitse was able to link high gas temperatures to larger condensation rates and consequently to corrosion rates at the top of the line. However, Vitse observed that the formation of FeCO_3 was favored by high fluid temperature and could lead to a decrease in the corrosion rate. The experiments also explored the effect of the gas velocity and partial pressure of CO_2 on TLC, which play an important role in the water condensation rate and corrosion rate, respectively. However, the experiments conducted by Vitse were all of relatively short duration (2-4 days) and consequently could not capture the full extent of the corrosion, especially in terms of localized corrosion, which often requires weeks of exposure.

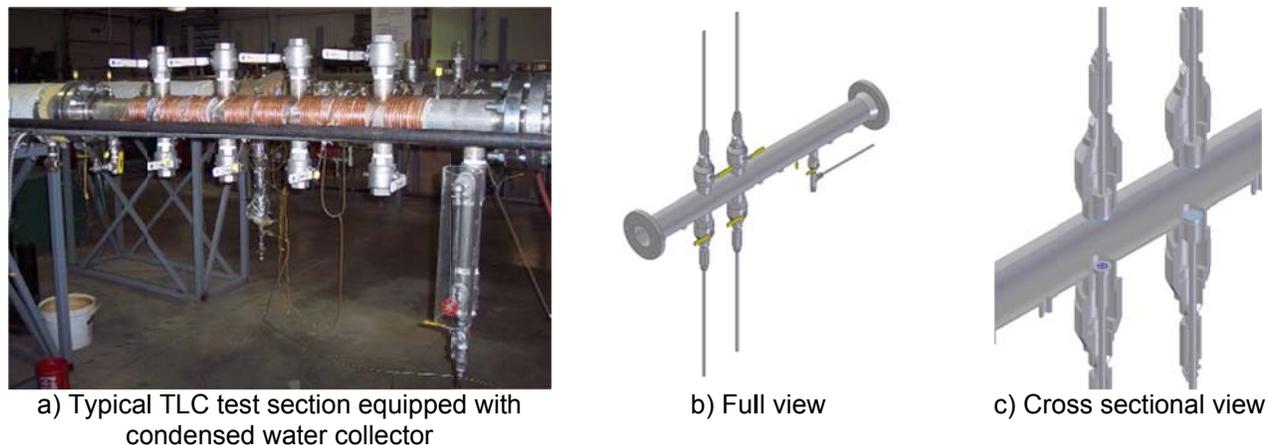


Figure 4: Test section proposed by Vitse and Singer

Several new experimental studies²⁶⁻³¹ were published on the effect of different parameters such as acetic acid, Mono-Ethylene-Glycol (MEG) or pH control. However, these experiments also had a relatively short exposure time and offered only limited data in terms of localized corrosion. MEG is commonly used in gas fields in order to prevent the formation of methane gas hydrate (a solid ice structure which can obstruct the flow). The presence of a large quantity of MEG (typically 50 to 70 wt%) decreases the water vapor pressure, which effectively inhibits hydrate formation. It also decreases the water condensation since the amount of water vapor is lower. The concentration of MEG present in the condensed water at the top of the line is key to understating its effect on TLC.^{10,28} pH control (a method consisting of injecting a base in order to control the bulk aqueous pH) was shown to have the effect of limiting the concentration of undissociated acetic acid in the bulk liquid phase available for evaporation, which in turn would help mitigate TLC. The presence of acetic acid was found to greatly affect TLC and mild steel corrosion in general.³²

In 2007, Andersen et al.³¹ and later Nyborg et al.³³ proposed a system enabling the circulation of the gas phase from a high-pressure reservoir to a low-pressure reservoir, containing the bulk liquid phase. A liquid pump/ejector setup ensured proper mixing between the phases, such that the vapor phase was always in equilibrium with the bulk liquid phase. Only the gas phase circulated through the 55 mm ID piping. Several carbon steel pipes, from 1.8 to 5m in length, could be inserted in the flow loop and exposed to the moist gas (Figure 5). The bottom inner area of the pipes (about 20% of the entire surface area) was painted with corrosion resistance coating in order to differentiate between top and bottom of the line corrosion. Water condensation was achieved by circulating water through cooling coils mounted on the outside of the pipe. The rate of condensation was controlled by the flow rate of cooling water. A condensed water collector placed downstream of the test section enabled the measurement of the condensation rate as well as important chemical parameters (pH, iron, acetic acid concentration). Visual inspection of the test pipes before and after the experiment as well as continuous iron content monitoring were used for corrosion measurement. The authors mentioned the balance between FeCO_3 growth and the transport rate of Fe^{2+} ions away from the surface as a central parameter controlling the corrosion rate. The presence of acetic acid in the condensed water was also found to increase the solubility of Fe^{2+} ions.

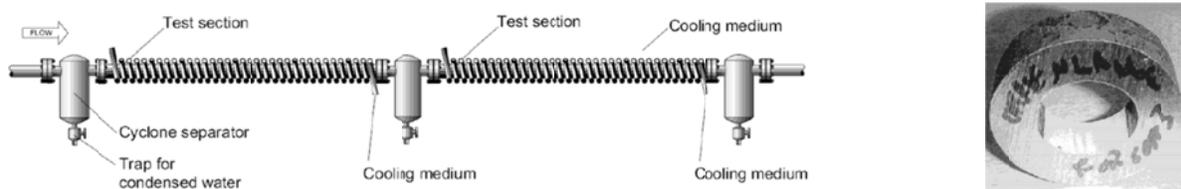


Figure 5: Test section proposed by Andersen and Nyborg (reproduced from ^{33,31} - © NACE international 2007 & 2009)

Singer et al.²⁷ published the results of this experimental parametric study of sweet TLC (CO₂ dominated) performed in the same 4"ID flow loops originally proposed by Vitse et al.²⁴⁻²⁵. This study summarized the effect of the most influencing parameters on which the severity of the corrosion attack depends: the condensation rate, the gas temperature, the gas flow rate, the CO₂ partial pressure and the presence of organic acid. Information about both uniform and localized corrosion was collected through this series of long-term experiments (3 weeks long). It was found that a long exposure time was essential in capturing the extent of TLC and especially of localized corrosion. Strong pitting and mesa attack was observed in sweet environment in the presence of acetic acid and under high water condensation rate.

In 2008, Hinkson et al.⁶ published the results of a study focused on the composition of the condensed water. A glass cell setup was constructed utilizing a heated container that would generate water vapor, which would then condense when passing through a heat exchanger (Figure 6). Using this sort of configuration, samples could be collected in vials for subsequent chemical analysis, such as their pH and Fe²⁺ ion concentration. This system was later upgraded by inserting a carbon tube (coated on its outside) inside the heat exchanger in order to perform TLC experiments. The focus of the study was on determining the chemistry in the freshly condensed water (low initial pH) and its evolution with time due to the corrosion process. The concentration of total acetate species in the condensed water was found to be of the same order of magnitude compared to the concentration of undissociated acetic acid in the bulk liquid phase, depending on the temperature.

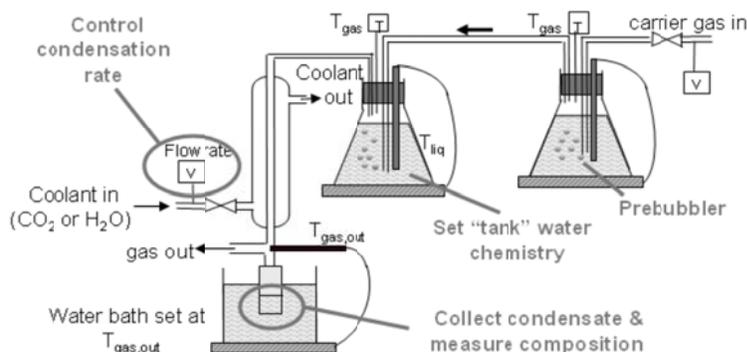


Figure 6: TLC experimental device focused on the composition of the condensate (Reproduced from ⁶ - © NACE international 2008)

Since then, Pojtanabuntoeng et al.³⁴ published an experimental study on the characteristics of the water condensation at the top of the line and on the possible role of hydrocarbon condensate. The authors proposed a setup similar to Hinkson et al.⁶ equipped with a borescope and a weight loss (WL) sample for corrosion measurement. However, the cooling setup involved the innovative use of a thermoelectric "Peltier" device, enabling better control of the local condensation rate on the steel sample (Figure 7). Using this setup, the temperature of the corroding sample could be closely monitored. It was found that the condensation of light hydrocarbons could not prevent liquid water from reaching the hydrophilic steel surface.

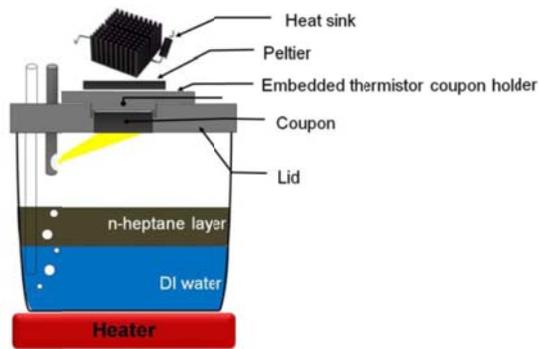


Figure 7: Experimental setup designed for the observation of condensation
(Reproduced from ³⁴ - © NACE international 2011)

In 2011, Rotimi³⁵ conducted a series of long-term experiments (up to 6 weeks of exposure) in an autoclave especially designed for TLC study. The effect of water condensation and temperature was evaluated under different partial pressures of CO₂. The author reported that the uniform corrosion decreased as the temperature increased, due to the formation of a more protective FeCO₃ layer. However, no information was reported on localized corrosion although this type of corrosion was expected to play a big role in these conditions.

Zhang et al.³⁶ and Qin et al.³⁷ presented in two separate studies an original setup which combined external cooling as well as rotation of the specimen. The samples were “arc shaped” (108 mm diameter and 14 mm width) and mounted around the rotating shaft (Figure 8). Consequently, vapor condensation occurred on the sides of the specimen with a thin film or with droplets of condensed water sliding to the bottom of the autoclave. The study confirmed observations made previously on the effect of the fluid temperature and water condensation rate on the extent of TLC.

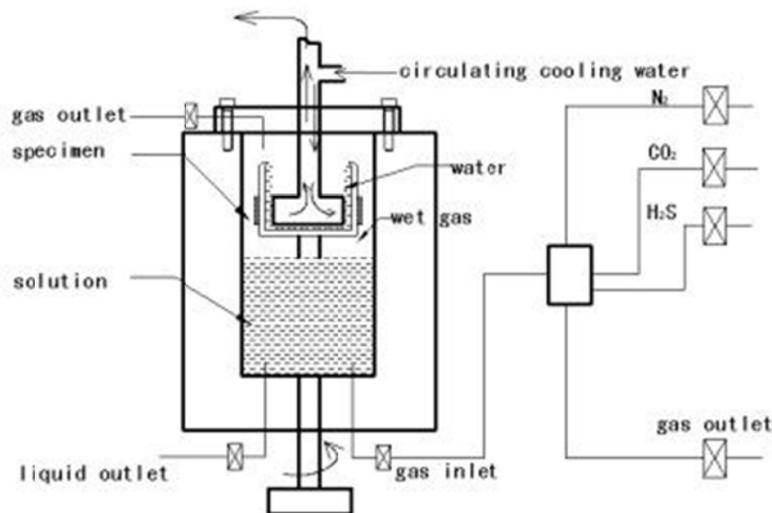


Figure 8: Wet gas autoclave design proposed by Zhang
(Reproduced from ³⁶ - © NACE international 2009)

Experimental work on H₂S TLC

Although sour corrosion in general is one of the most important issues for the oil & gas industry, very little experimental work has been dedicated to sour TLC. It is fair to say that even “standard” (bottom of the line) sour corrosion is not very well understood⁵, making any attempt to understand sour TLC rather unclear. However, most of the findings valid for bottom of the line corrosion are also true in a TLC scenario.

Camacho³⁸ presented a series of short-term (2 to 4 days long) experiments carried out in a 4"ID flow loop. The tests were performed at 3 bars total pressure, at 70°C and at a gas velocity of 5m/s ensuring stratified flow. The condensation rate was kept constant at 0.25 mL/m²/s. The presence of small quantities of H₂S (up to 0.13 bar) led to a strong decrease in the general corrosion rate compared to its pure CO₂ counterpart. The corrosion was strictly uniform and did not seem to be greatly affected by the range of CO₂/H₂S ratio tested. An FeS layer was always found to be the predominant corrosion product present on the carbon steel surface. As is customary in TLC testing, the short duration of the experiment made it difficult to extrapolate laboratory corrosion rates to field reality.

Nyborg³³ presented a series of experiments in a 2"ID flow loop using carbon steel tubes as corrosion samples. The tests were conducted at 25°C, with 0.02 bar of H₂S and 10 bars of CO₂ with 300 ppm of acetic acid. The experiments lasted for more than 30 days at very low condensation rates (lower than 0.006 mL/m²/s). The corrosion rate was very stable during the entire test duration. A porous and fluffy FeS film was found on top of a more protective FeCO₃ layer covering the metal surface. It was proposed that dissolved H₂S acted as a "sink for ferrous ions" by promptly forming an un-protective FeS layer and enabling the corrosion to continue, albeit at a low rate (0.1 mm/year).

Pugh³⁹ performed experiments in an autoclave equipped with TLC capabilities. The aim was to simulate specific field conditions where TLC was observed. The tests were conducted at 25 and 55°C and at condensation rates of 0.002 and 0.1 ml/m²/s respectively. The gas phase consisted of 2.4% CO₂ and 1.0% H₂S and the tests were performed over a 6 to 10 weeks period. The results showed that the corrosion rate was higher at a lower temperature and lower condensation rate (25°C and 0.002 ml/m²/s) than at a higher temperature and higher condensation rate (55°C and 0.1 ml/m²/s). In both cases, a mackinawite film formed on the metal surface but had different characteristics depending on the temperature; at 25°C, the film was fluffy, porous, crystalline with 500 nm grains and un-protective; at 55°C, the film was denser, crystalline with 10 microns grains and protective. The presence of organic acid increased the general corrosion rate and promoted localized corrosion, especially where the FeS film was protective.

Singer⁴⁰ continued Camacho's work³⁸ and conducted a parametric study in a 4" ID flow loop. The partial pressure of H₂S (up to 0.13 bar) and the acid acetic concentration (up to 1000 ppm) were studied in a series of 21-day experiments. In the presence of H₂S, the presence of acetic acid seemed to affect the integrity of the FeS film and trigger the occurrence of localized corrosion initiation.

In 2011, Singer et al. conducted an experimental study performed in an innovative high pressure autoclave⁴¹. The 20L autoclave made of alloy C-276 (UNS^a N10276) was specially manufactured to equipped with an internal cooling system and a sample holder plate. The design of the sample holder enabled the study of the effect of the condensation rate in one single test. This was done by "hanging" some of the steel samples in the gas phase but a distance (15 cm) away from the cooled plate. Experiments were conducted under high H₂S and CO₂ partial pressures (4 and 10 bars, respectively) and for an exposure time of 3 weeks. Mackinawite, cubic FeS and troilite were identified as components of the corrosion product layer, which seemed to be comprised of two distinct layers: a thin and dense inner layer and a porous and thick outer layer. It was also shown that higher uniform corrosion rates could be expected at lower gas temperatures and that the water condensation rate had little effect on the corrosion results.

Although no firm conclusion can be made at this stage, some important characteristics of sour TLC have been proposed:

- Sour TLC does not seem to be as serious or as common as sweet,
- The condensation rate may not be the main controlling parameter, as it is in sweet TLC,

^a Unified Numbering System for Metals and Alloys (UNS)

- The severity of the attack seems to depend on the type and protectiveness of the iron sulfide film formed at the condensed water/steel interface,
- Gas temperature could consequently be a key factor, as it directly affects the phase identity and characteristics of the formed iron sulfide.

Chemical inhibition of TLC

Several studies were performed for the sole objectives of evaluating the performances of volatile inhibitors.

Cough et al.⁴² and Oehler et al.⁴³ developed an experimental design involving a sample holder mounted with carbon steel pins exposed to the corrosive vapor phase. The sample holder was externally cooled in order to force water condensation onto the pins, which dripped and was collected in a condensed liquid container. The pins could also be used for Linear Polarization Resistance (LPR) measurements (Figure 9). However, readings could not be made unless the electrodes (working, reference and counter) were fully immersed in the electrolyte, which is not the case in the vapor phase (as only a thin and poorly conductive liquid film covers the metal surface). Consequently, they were intermittently lowered into the condensed water reservoir for direct corrosion readings. It is important to mention that accurate LPR readings require a strong electrolyte in order to minimize the solution resistance, which is not the case for condensed water. Although this setup presented many advantages (notably, two methods for corrosion measurements), the specific design of the metal samples (vertical pins) and the intermittent reading of corrosion in the condensed water reservoir cannot accurately represent the influence of environmental parameters such as condensation rate and temperature. This setup has been used primarily for the evaluation of the efficiency of inhibitors. It was well-adapted for this type of work because it only required a black and white answer -- either full protection or active corrosion.

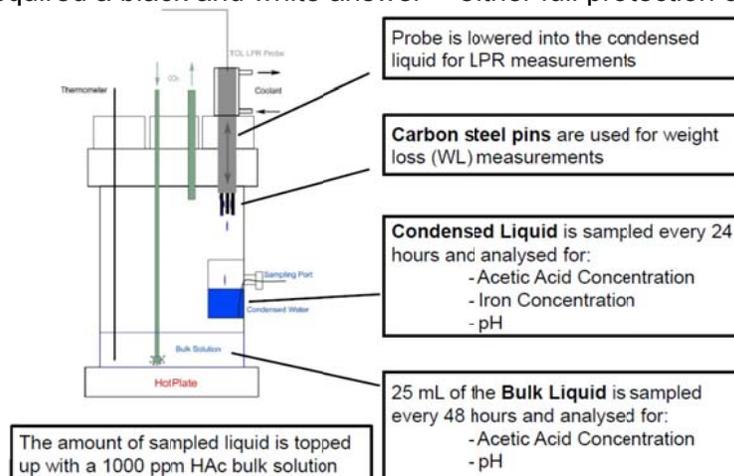


Figure 9: Cooled finger probe concept
(Reproduced from ⁴³ - © NACE international 2012)

Gunaltun et al.⁴⁴ published another comprehensive effort at evaluating the efficiency of volatile inhibitors using a variety of experimental setups. One of these innovative setups consists of a heated reactor generating the water vapor and a “condensation cell”, where electrochemical measurements are performed (Figure 10). These two main elements were connected in a loop enabling control of condensation rate, temperature and water chemistry as well as online corrosion measurements using an LPR setup. This rather complex setup obviously presented many advantages, especially since the chemistry of the condensed water in contact with the sensing element (LPR probe) could be measured (pH and Fe^{2+} concentration). However, the condensed water accumulated on top of the electrodes, which were facing up instead of down. The true effect of condensed water renewal was altered by this specific setup. In addition, LPR measurements are not believed to give very accurate results in condensed water due to the poor quality of the electrolyte.

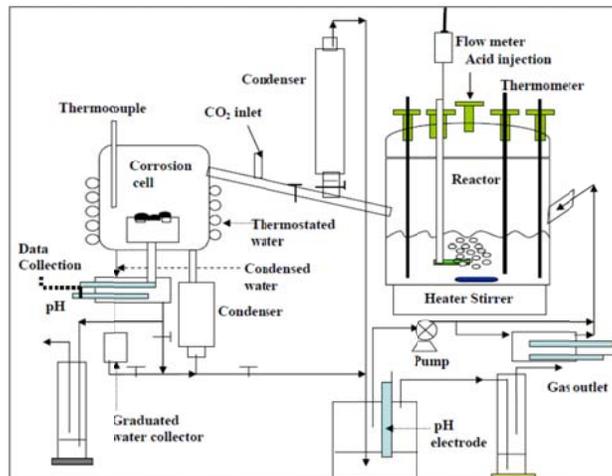


Figure 10: Volatile inhibitor testing equipment (Reproduced from ⁴⁴ - © NACE international 2010)

Another experimental glass cell design proposed by Gunaltun et al.⁴⁴ involved a unique glass cell used for vapor generation and online corrosion measurement with a weight loss steel sample and Electrical Resistance (ER) probe (Figure 11). The ER technique is more appropriate for the study of TLC since it does not require a good electrolyte and a reference/counter electrode setup. However, full coverage of the sensing element is still essential for accurate measurement of the corrosion rate. The ER and WL probes were flush mounted to the bottom side of the lid facing down and the condensation process was observed using a borescope. This specific setup was quite representative of a real case of TLC. However, the condensed water accumulating on the surface of the corrosion sample could not be collected for analysis, which represents a drawback.

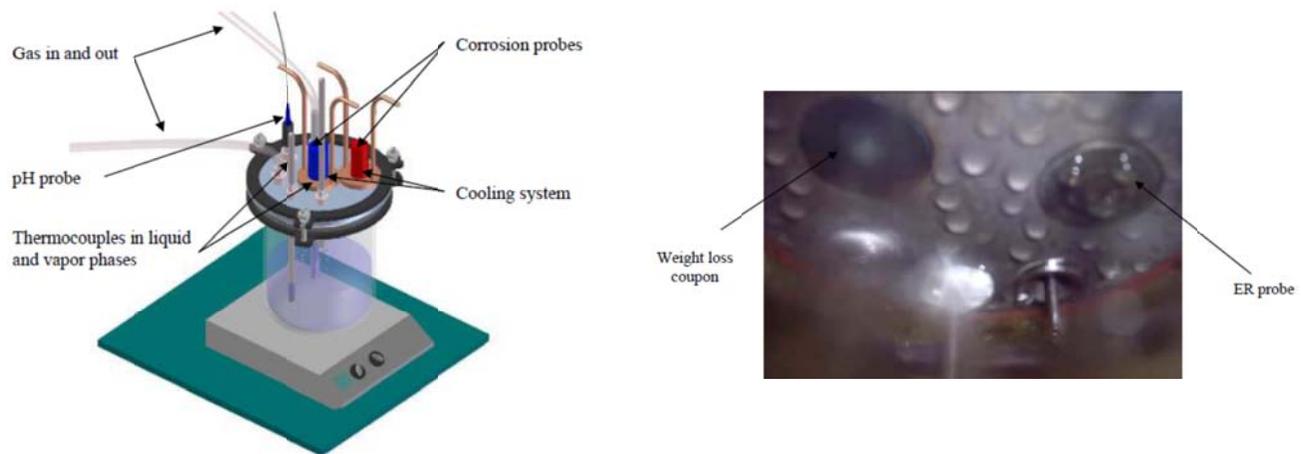


Figure 11: Experimental setup using Electrical Resistance (ER) probe (left) and water condensation process on the lid (right) - (Reproduced from ⁴⁴ - © NACE international 2010)

A rather innovative setup was proposed by Jovancicevic et al.⁴⁵. It involved the use of a Quartz Crystal Microbalance (QCM), a device in which the change in mass of a thin film deposited on a quartz crystal resonator is determined by measuring its change in frequency. The QCM can accurately measure very small rates of iron dissolution (if the deposited film is made of iron) and can, in theory, be adapted to measure the rate of water evaporation on the surface of the sensing element. A small autoclave was adapted to include a QCM for evaluation of the efficiency of corrosion (Figure 12). Although the results are promising, many technical challenges still exist in adapting this very specialized device to simulate representative conditions.

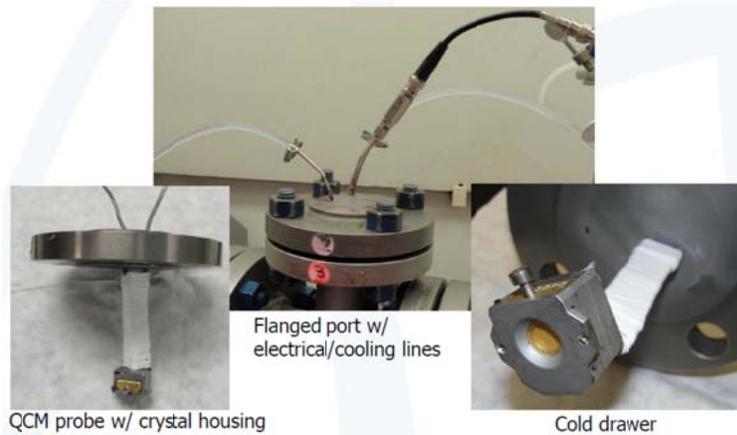


Figure 12: Quartz crystal microbalance design proposed by Jovancicevic (Reproduced from ⁴⁵ - © NACE international 2012)

MODELING APPROACHES

Water condensation rate (WCR) modeling

- Average WCR calculations considering water dropout

The way most commercial flow assurance software predicts a WCR is by calculating the overall heat loss over a small section of pipe, creating a temperature gradient profile, and then calculating how much water drops out from the vapor over this section of pipe. The saturation level of water carried in the gas phase is specifically modeled; any reduction in its vapor pressure is presumed to be due to water condensing out of the system on the upper pipe wall.

Only the upper half of the pipe area is considered for the water condensation rate calculations. The equation below is only valid for small sections of pipes:

$$WCR = m_{gas} \frac{M_{water}}{M_{gas}} \frac{2}{AL} \left(\frac{P_{vap}^{in} - P_{vap}^{out}}{P_{Total}} \right) \quad \text{Eq (1)}$$

With WCR: Water condensation rate [kg/m²/s]

m_{gas} : Gas mass flow rate [kg/s]

M_{gas} and M_{water} : Molecular weight of gas phase and of water [kg/mol]

P_{vap}^{in} and P_{vap}^{out} : Vapor pressure at the inlet and outlet of the pipe section [bar]

$A/2$: Half of pipe perimeter [m]

L : Pipe length of the section considered [m]

The water that drops out is assumed to be the total amount of condensed water, but the pipeline is a dynamic system and the gas phase cools more rapidly than the bulk liquid. Therefore, while some water vapor condenses at the cold steel surface, some liquid water should also evaporate at the warmer bulk liquid interface. The overall rate of water accumulation that the above method calculates is actually the water condensed from the vapor minus the water that evaporates from the bulk liquid. This approach does not separate the two, and, consequently, can under-predict the actual water condensation rate happening locally at the top of the pipe.

- Local WCR calculations considering dropwise condensation theory

The phenomenon of dropwise condensation (as opposed to filmwise condensation) has been studied extensively over the past sixty years. It can be described in terms of a four-stage scenario⁴⁶: nucleation, growth, coalescence and removal. It is now commonly accepted that nucleation is an essential feature of dropwise condensation and that the existence of a thin film of liquid between the droplets is not

necessary⁴⁷. The commonly accepted approach developed to evaluate the total heat flux through a number of randomly sized droplets is to consider a distribution function⁴⁸. Phase change and the presence of non-condensable gases are also important parameters to take into account.

In 2007, Zhang⁴⁹ adapted the dropwise condensation theory to a pipeline situation in which the presence of droplets of condensed water was clearly identified. It is important to mention that dropwise condensation is believed to happen at the 11 to 1 o'clock position in the pipeline while the remainder of the surface is more likely to be subject to filmwise condensation. Zhang added a mass balance of the water in order to calculate the condensation rate:

$$WCR = \rho_g \beta_g \times (x_b^g - x_i^g) = \rho_g \beta_g \times \frac{M_w}{P_T M_g} (P_{sat}(T_b^g) - P_{sat}(T_i^g)) \quad \text{Eq (2)}$$

With: WCR: Water condensation rate (kg/m²/s)

β_g : Mass transfer coefficient in the gas boundary layer (m/s)

x_b^g : Mass fraction of water vapor in the bulk gas flow (kg_v/kg_g)

x_i^g : Mass fraction of water vapor at the gas-liquid interface (kg_v/kg_g)

ρ_g : Density of gas (kg_g/m³)

M_w and M_g : Molecular weight of the water and the gas mixture (g/mol)

P_T : Total pressure (Pa)

P_{sat} : Saturation pressure as a function of temperature (Pa)

Zhang could then calculate the condensation rate by solving the equations above using an iterative method. This new approach is also able to take into account the effect of non-condensable gas.

In summary, the dropwise condensation approach calculates a local WCR, while the water dropout approach calculates an overall water accumulation rate (or a net water condensation rate). The dropwise condensation approach likewise only considers the water that condenses from the vapor phase. Since the calculations are made locally at the surface of the pipe, the evaporation of water from the bulk is not taken into account. This is why dropwise condensation can calculate greater WCRs than the water dropout approach.

A significant difference between the two approaches should only exist when there is a considerable amount of produced water in the pipe. The heat carried in the water is much larger than in the gas and it will prevent the fluid from rapidly cooling, acting as a constant source of water vapor. If there is little liquid water produced in the line, the fluid will cool down rapidly and the influence of evaporation will be reduced.

Corrosion modeling in dewing conditions

- Empirical and semi empirical modeling of TLC

The first attempt to model TLC was made twenty years ago by Olsen et al.²² The author stated that the extent of the corrosion attack was ultimately controlled by the competition between the corrosion and the condensation rates which in turn controlled the FeCO₃ saturation level.

DeWaard et al.⁵⁰ modified his widely used full pipe flow empirical equation in order to introduce a correcting TLC factor: $F_{cond}=0.1$. This factor was to be multiplied to the original corrosion rate for condensation rates below an experimentally determined critical rate of 0.25 mL/m²/s. The correlation proposed by DeWaard gives an extremely conservative prediction. It is listed below:

$$CR = F_{Cond} \times 10^{\left(\frac{5.8 - 1710}{T_K} + 0.67 \times \log(p_{CO_2})\right)} \quad \text{Eq (3)}$$

With p_{CO_2} : Partial pressure of CO_2 (bar)
 T_K : Temperature (K)
 F_{cond} : 0.1
 CR: Corrosion rate (mm/year)

This competition between scale formation and the condensation rate was developed further by Pots et al.²³ in 2000. The so called “supersaturation model” was based on the calculation of the concentration of iron at saturation under film-forming conditions. The accurate prediction of the chemistry in the condensed water and especially of the WCR was underlined by the author. The concentration of Fe^{2+} was determined so that the corrosion rate and the precipitation rate would balance each other. The expression of the corrosion rate CR is shown in equation Eq (4):

$$CR = \frac{M_{Fe} \times 10^6 \times 24 \times 3600 \times 365}{\rho_{Carbonsteel}} \times [Fe^{2+}]_{supersat} \times \frac{WCR}{\rho_w} \quad \text{Eq (4)}$$

With CR: Corrosion rate (mm/y)
 WCR: Water condensation rate ($g/m^2/s$)
 ρ_w : Water density (g/m^3)
 $[Fe^{2+}]_{supersat}$: Iron concentration at $FeCO_3$ saturation (mol/L)
 M_{Fe} : Iron molecular weight (55.847 g/mol)
 $\rho_{carbonsteel}$: Density of a typical carbon steel (7860000 g/m^3)

Nyborg et al.⁵² developed a new empirical equation for TLC prediction which takes into account the iron carbonate solubility, the water condensation rate and a temperature dependent supersaturation factor, developed experimentally. The empirical equation is displayed below and is valid only for low acetic acid content (<0.001 Mol/L), low to medium carbon dioxide partial pressure (<3 bars) and no H_2S :

$$CR = 0.004 \times WCR \times [Fe^{2+}] \times (12.5 - 0.09 \times T) \quad \text{Eq (5)}$$

With CR: Corrosion rate (mm/y)
 WCR: Water condensation rate ($g/m^2/s$),
 $[Fe^{2+}]$: Concentration of iron ions at $FeCO_3$ saturation (ppm_w)
 T: Temperature ($^{\circ}C$)

Nyborg notes that the solubility of iron ion is a function of temperature, total pressure, CO_2 partial pressure and glycol concentration, and calculates this with an in-house pH and solubility program. Although no detail is provided on how the condensation rate is calculated, Nyborg stresses the importance of predicting an accurate condensation rate, as it will have a much more pronounced effect on TLC than, for example, the CO_2 partial pressure

- Mechanistic modeling of top of the line corrosion

As detailed below, a fair amount of research and modeling work has been done on TLC. It should be noted that these works pertain almost exclusively to sweet (CO_2 dominated) TLC and that no serious attempt to model sour (H_2S dominated) TLC has been performed to date.

In 2002, Vitse et al.²⁴⁻²⁵ developed a semi-empirical corrosion model adapted to a TLC scenario. This corrosion model constituted a considerable breakthrough in the understanding of the mechanisms involved in TLC. A baseline “film free” corrosion rate was determined using the electrochemical model

developed by Nesic et al. in 1996¹⁶. However, once the value of the condensation rate was obtained (through a filmwise condensation model also described by the author), Vitse conducted a Fe^{2+} flux balance in a controlled volume, taking into account the fluxes of Fe^{2+} created by corrosion, removed by $FeCO_3$ precipitation and transported by condensed water film convection. Vitse modified his corrosion equation in order to include the influence of corrosion product film on the corrosion rate once the saturation in $FeCO_3$ is reached. It was done by introducing an empirical correcting factor K which would represent the covering effect of the $FeCO_3$ film, underneath which no corrosion would occur. This factor was determined experimentally but was correlated with the scaling tendency (ratio of corrosion and precipitation rate). The equation used in the Fe^{2+} flux balance is displayed:

$$\frac{d[Fe^{2+}]}{dt} = \frac{1}{\delta} \times [K \times CR - (1 - K) \times PR - WCR \times [Fe^{2+}]] \quad \text{Eq (6)}$$

With Fe^{2+} : Concentration of iron ion (mol/m^3)
 t: Time (s)
 CR: Corrosion rate ($mol/m^3/s$)
 PR: Precipitation rate ($mol/m^3/s$)
 WCR: Water condensation rate ($m^3/m^2/s$)
 δ : Liquid film thickness (m)
 K: Covering factor

Okafor et al.⁵³ proposed through his experimental study a mechanism for corrosion under liquid droplets containing acetic acid. Okafor linked the initiation of localized corrosion with the presence of protected and non-protected regions under drop-wise condensation. He assumed the formation of a galvanic cell between the film-free regions, with those regions covered by a $FeCO_3$ film. It was the first attempt to differentiate general and localized corrosion at the top of the line.

In 2007, Zhang et al.⁴⁹ published the first fully mechanistic approach on TLC modeling. The model covers the three main processes involved in TLC phenomena: dropwise condensation, chemistry in the condensed water and corrosion at the steel surface. Since the condensation approach is drop-wise, the model is valid only for the 11-1 o'clock position in a pipeline. The chemistry of the condensed liquid is established through standard chemical and thermodynamic equations⁶. The corrosion model is adapted from the mechanistic CO_2 corrosion approach developed by Nordsveen et al.¹⁷ and Nesic et al.⁵⁴⁻⁵⁵. Zhang stated that, from a statistical point of view, every point on the metal surface has the same probability of being covered by liquid droplets and, consequently, the entire surface is subject to uniform corrosion. This simplifies the mathematical approach from a three-dimensional situation (semi-hemispherical droplet) to a one-dimensional situation (liquid layer). The droplet growth is simulated by an increase in the liquid film with time until it reaches a calculated maximum size where the droplet disappears (falls or slides). The calculation then restarts with a minimum film thickness (corresponding to the minimum droplet size), and the cycle is carried out until the corrosion process reaches a steady state. The corrosion module includes chemical reactions, transport of species to and away from the metal surface, and the electrochemical reactions at the metal surface. The main equations used are described in details in the original publication⁴⁹.

Remita et al.⁵⁶ also extended the work proposed by Vitse et al.²⁵ and developed a model for CO_2 corrosion under a thin liquid film. It follows a mechanistic approach for the chemical and electrochemical side of the phenomena but assumes a homogeneous composition within the film. Like Vitse, Remita introduces a covering factor θ in order to take into account the effect of $FeCO_3$ film formation, this factor being difficult to obtain.

Overall guidelines on sweet and sour TLC prediction were proposed by Asher et al. in 2011.⁵⁷ The importance of modeling the chemistry and the physics of the corrosion process was stressed. The corrosion model is based on the concept that, at steady state, the corrosion flux (flux of iron ions away

from the surface) is equal to the FeCO_3 precipitation flux (*i.e.*, flux of iron ions required to form the corrosion product layer). No specifics were given on the algorithm or equations used.

Modeling of localized corrosion

Even though much progress has been made over the years in the understanding of TLC mechanisms, none of the models proposed thus far tackles the occurrence and prediction of localized corrosion. In 2008, Amri⁵⁸ performed experiments in an effort to relate pit growth and environmental conditions, especially in the presence of acetic acid. It was found that the growth of the pit was related to the depletion of the acetic acid concentration inside the pit. It was also stated that the growth should stop once the pit reaches a certain depth. Many of the observations made by the author were typical of a TLC scenario and were put forward to explain TLC stabilization. Consequently, this study constituted the first attempt to adapt the localized corrosion process to TLC.

CONCLUSIONS

A great deal of research has been performed in the past twenty years to gain a better understanding of TLC. However, compared to other corrosion mechanisms commonly found in oil and gas production, this research is in its infancy and further work is required in a number of specific areas. Sweet TLC is much better understood than sour TLC; however in both cases the prediction of localized corrosion and the ability to accurately reflect field reality experimentally are the main gaps to be able to accurately model TLC.

As described in this paper, corrosion inhibitors are commonly deployed in gas pipelines to mitigate TLC. These corrosion inhibitors are routinely selected based on laboratory evaluations. However, in these tests the corrosion inhibitor only has to travel a small distance from the bulk fluid to the test sample (probe or weight loss coupon) to provide protection. In reality, TLC inhibitors are required to be transported many kilometers in the gas phase in a pipeline and be present at the location where the water condenses. A pipeline will also pass through areas of varying topography and will also consist of several bends that will impact inhibitor transport. Therefore, further research is needed to determine if inhibitors can be transported long distances in a gas pipeline and establish if they are present in a pipeline at the point where condensation occurs.

Many laboratory techniques are available for assessing the efficacy of corrosion inhibitors in preventing TLC. However, at present there is no industry standard (ASTM^b recommended practice or NACE Standard) that provides guidelines for TLC inhibitor testing. In order to standardize inhibitor testing for TLC, it is recommended that an approved recommended practice document is prepared and approved by a relevant professional body.

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