Top-of-the-line corrosion

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16.1 Overview of the current understanding/knowledge

Although it was first identified in the 1990s, top of the line corrosion (TLC) has only recently been recognized as an issue for the oil and gas industry. Initially regarded as a laboratory curiosity, it is now considered a major concern for pipeline integrity and is taken into account in the design of any new gas field development. Significant effort has been invested toward elucidating its governing mechanism and developing prediction and mitigation tools.

TLC is a phenomenon encountered in the transportation of wet gas, where temperature differences between the pipelines and the surroundings lead to corrosion issues. Condensation of saturated vapors present in the unprocessed gas stream collects on the internal surface of the cold pipe wall. The condensed phase is made not only of hydrocarbons but also water, which forms a thin film and/or droplets of liquid. The condensed water phase can be, at least initially, very corrosive to typical pipeline steel, because it contains dissolved acid gases (e.g., carbon dioxide and hydrogen sulfide) and organic acids. The corrosion mechanism encountered in this scenario is not different from what can be expected in the bulk liquid phase, but it holds important specificities that make its mitigation difficult and the occurrence of localized corrosion likely.

TLC mechanisms involve four main engineering processes, which can interact in a complex way:

- **Fluid mechanics**: TLC can only occur in a specific flow regime where the liquid and gas phases are clearly stratified.
- **Heat and mass transfer**: The condensation of water vapor on cold pipe wall and the transport of corrosive species to the liquid film are controlling the extent of corrosion.
- **Chemistry**: As for most corrosion phenomena, the chemical composition of the electrolyte is key in determining both the corrosion kinetics and the likelihood of corrosion product formation.
- **Electrochemistry**: The corrosion process is inherently driven by well-known electrochemical reactions.

16.1.1 TLC mechanisms

16.1.1.1 Flow regime

Flow regime determination is an important clue as to whether or not TLC may become an issue. Three major three-phase flow regimes are commonly encountered in horizontal oil and gas pipelines:

- **Stratified flow**: Segregation of the gas and liquid phases, usually at low gas and liquid flow rates

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- **Intermittent flow**: Formation of slugs or plugs at high liquid flow rates as the crests of the waves intermittently reach the top of the pipe
- **Annular flow**: The bulk liquid phase is partly atomized at high gas flow rate, leading to transport and deposition of droplets to the whole circumference of the pipe

The flow regime transition lines between stratified and intermittent or annular flow are obtained following the well-known wave-mixing mechanism developed by Milne—Thomson [1] and, later, Taitel [2]. Only one of these flow regimes, stratified flow, will lead strictly to TLC, as annular and intermittent flow implies wetting of entire pipe surface with bulk liquid phase.

If the flow regime is not stratified, the bulk liquid phase is likely to wet all parts of the pipe surface, even intermittently. Coupled with the use of corrosion inhibitor, effective protection against corrosion is needed. However, TLC is encountered exclusively when noncondensable gas (light hydrocarbons, CO_2, etc.) and saturated water vapor are produced together with little or no liquid hydrocarbons. In this condition, the three-phase flow is stratified, meaning that standard corrosion inhibitors dissolved in the bulk liquid phase will not be effective in mitigating corrosion at locations where the pipe surface is not wetted, i.e., on the sides and top of the pipe.

16.1.1.2 Condensation process

Once the flow regime is established to be stratified, the next step is to determine the extent of water vapor condensation. Water vapor comes from the presence of liquid water, together with hydrocarbons, in the reservoir. It can be assumed that the water vapor, along with most of the hydrocarbon vapors (except the lighter end), is saturated in the gas phase. The fluid's pressure inevitably decreases as the fluids are produced through the tubing and flow lines. The temperature also decreases along the pipe due to heat exchange with the outside environment and to a lesser degree due to Joule—Thomson effects.

The rate of water condensation is mainly dependent on the gradient of temperature between the transported fluid and the outside environment. It is also very sensitive to any pipeline characteristics that may affect the rate of heat transfer, such as thermal insulation, concrete coating or pipe burial ratio, as well as the nature of the outside environment (soil, air, sea, or river).

Once formed, the droplets can behave differently depending on the magnitude of drag force caused by the gas flow and the nature of the steel surface. The droplets, initially small, grow to reach a critical size and either fall to the bottom of the line due to gravity forces, which is typical of low gas velocity, or slide along the pipe at higher gas velocity. A thin, liquid film typically remains on the surface, and the renewal of the droplets is governed by the rate of condensation.

16.1.1.3 Condensed water chemistry

The condensed water chemistry logically determines the corrosivity of the environment and the eventual formation of corrosion product layer. It is, therefore, essential

to have a good understanding of the basic principles of the $H_2O/CO_2/H_2S$ system as they pertain to condensed water.

The water phase present in any given oil and gas pipeline can come from either the well formation itself (formation water) or the condensation of water vapor. On the one hand, formation water typically contains elevated amounts of salts such as chloride, sodium, and calcium ions. Acid gases dissolve in the formation water and determine its pH, which is usually higher than 5.5−6.5 due to the buffering effect of high content of bicarbonate. On the other hand, there is no salt in the condensed water. This makes the pH of freshly condensed water very acidic, as will be discussed further.

The different chemical reactions involved in the H_2O/CO_2 system are well established and can be found summarized in Chapter 7. Among the organic acids often present in produced fluids, the most common and abundant are acetic acid, propionic, and formic acids [3,4], which are all weak acids.

The presence of H_2S in a growing number of fields considerably complicates the situation, especially in terms of corrosion product and electrochemical reactions [5]. Both CO_2 and H_2S dissolve in water and decrease the pH to a comparable extent at similar partial pressure. This is because compared to CO_2 gas, H_2S gas is about three times more soluble in water but has a constant acidity of about four times lower than for carbonic acid. Depending on the field, contents of CO_2, H_2S, and organic acid range from 0.1 to 10 mol%, 5 to 5000 ppm, and 0 to 5000 ppm, respectively. Typical operating pressure and temperature also range from 30 to 200 bars (435−2900 psi) and from 5 to 100°C (41 to 212°F), respectively. Under these conditions, the pH of any droplets of freshly condensed water can be expected to vary between 3 and 4.5 [6]. However, this is only the starting value of the pH, as it will rapidly change due to the release of iron ions in solution through the corrosion process occurring on the steel surface. This process will eventually lead to conditions that are favorable for the precipitation of corrosion products, a process also dependent on the rate of renewal of the condensation rate.

Two main types of corrosion products can form in $CO_2/H_2S/H_2O/Fe^{2+}$ systems, namely iron carbonate ($FeCO_3$) and iron sulfides (Fe_xS_y). Because no oxygen is present in the produced fluids, iron oxides are ignored.

The iron carbonate precipitation reaction is written as follows:

$$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons FeCO_{3(s)}$$

Thermodynamically, precipitation occurs once the saturation level $S_{FeCO_3} = \frac{[Fe^{2+}]\left[CO_3^{2-}\right]}{K_{sp,FeCO_3}}$ is above one. However, the rate of precipitation is strongly dependent on temperature and the degree of supersaturation. Sun [7] suggested expressions for the equilibrium constant $K_{sp,FeCO3}$ and the $FeCO_3$ precipitation rates. Organic acids have also been reported to affect the corrosion product layer characteristics [8−10]. In general, iron carbonate layers provide effective protection against CO_2 corrosion, especially at high temperature, as long as their integrity is not challenged by sudden changes in chemistry, mechanical damage, or changes in operating conditions.

For iron sulfide formation, although the chemical reactions describing sulfide chemistry are well known [7], the pathways for iron sulfide layer formation are still debated [11–13]. The latest developments in the mechanism of FeS (mackinawite) formation involve a rapid formation of a thin layer by "direct" reaction, where the Fe atom does not leave the metal microstructure and reacts directly with the adsorbed H_2S, followed by a more standard precipitation reaction. As for $FeCO_3$, precipitation of iron sulfides only occurs if the saturation level is above unity.

By direct reaction	$Fe_{(s)} + H_2S_{(ad)} \rightarrow FeS_{(s)} + H_{2(g)}$
By precipitation	$Fe^{2+}_{(aq)} + HS^{-}_{(aq)} \overset{K_{sp,mck}}{\longleftrightarrow} FeS_{(s)} + H^{+}_{(aq)}$

The uncertainty related to the expressions for the equilibrium constants involved in H_2S aqueous chemistry is much more acute than with CO_2 aqueous chemistry [7]. In addition, several types and polymorphs of iron sulfides can be encountered, presenting different characteristics and providing varying levels of resistance to corrosion. The work by Smith [14] presents the most common forms of iron sulfides reported in the industry: mackinawite, pyrrhotite, cubic FeS, and pyrite. They are described briefly below:

- Mackinawite is a metastable form of FeS that forms quickly and is always present on the metal surface.
- Pyrrhotite ($Fe_{1-x}S$) is a more thermodynamically stable form of iron sulfide but suffers from relatively slower kinetics of formation. It has also been reported to form from the transformation of mackinawite.
- Cubic FeS is a metastable form of iron sulfide. Its formation is mitigated by the presence of foreign ions such as chloride ions. Condensed water environments are, therefore, more favorable.
- The most stable form of iron sulfide is pyrite, which is often associated with high H_2S partial pressure.

16.1.1.4 Corrosion process

The main corrosion mechanisms of mild steel in sour and sweet environments are reasonably well understood [15–25] and can naturally be applied directly to condensing environments. This is presented in detail in Chapters 6 and 7, respectively. However, the TLC environment holds some degree of specificity, especially as it pertains to corrosion product formation. The next sections present a comprehensive review of the current state of understanding related to CO_2 and H_2S systems, which are treated separately due to their fundamental differences.

CO_2 top of the line corrosion mechanisms

Research work related to TLC mechanisms in CO_2 environments started in the early nineties with the first systematic studies performed in small-scale setups [26,27] and large-scale flow loops [28–32].

The first stage of TLC involves the wetting of the steel surface by freshly condensed, and consequently quite "aggressive", water. Initially, the uniform corrosion rate is high but decreases with time to relatively low average values due to the release of ferrous ions in solution and the consequent increase in pH. At a certain point, depending on the system temperature, saturation of $FeCO_3$ is reached and precipitation of the corrosion product layer occurs. $FeCO_3$ layers can initially reach a relatively high level of protectiveness leading to a decrease of the rate of release of ferrous ions. However, as this process takes place, the concentration of ferrous ions diminishes as new, freshly condensed water, free of iron ions, continues to dilute the existing electrolyte. The $FeCO_3$ saturation level decreases and eventually leads to the dissolution of the existing corrosion product layer and the exposition of bare steel surface. A steady state eventually occurs when the concentration of ferrous ions and the pH reach a stable value corresponding to a saturation level of $FeCO_3$ approaching unity (or higher, depending on the temperature). The addition of ferrous ions due to steel dissolution is balanced by their dilution in the electrolyte through condensed water renewal. This also means that the rate of top of the line corrosion cannot be zero as long as the rate of water condensation is not zero. As the continuous source of fresh and acidic condensed water affects the chemistry of the solution (pH, $FeCO_3$ saturation level), the protectiveness of the $FeCO_3$ layer is constantly challenged. Very high water condensation rates can theoretically prevent the formation of corrosion products altogether and lead to high uniform corrosion. Very low condensation rates favor the formation of a relatively protective $FeCO_3$ layer, leading to a low, but nonnull, corrosion rate.

The acidity of the environment naturally affects this phenomenon. The higher the partial pressure of CO_2 or organic acid concentrations is, the higher the initial corrosion rate will be. Weak acids also act as pH buffers and require higher content of ferrous ions in solution to reach $FeCO_3$ saturation. The kinetics of $FeCO_3$ precipitation also depend strongly on temperature. Lower gas temperatures ($<40°C$, $104°F$) typically do not favor $FeCO_3$ precipitation, and the corrosion remains uniform with time with a low rate. TLC issues, especially localized corrosion, are often experienced at higher temperatures (above $70°C$, $158°F$) with a more rapid formation of the $FeCO_3$ layer.

The constant undermining of the integrity and protectiveness of the corrosion product layer leads to the initiation and propagation of localized corrosion at the top of the line. As mentioned earlier, the first few days of exposure to dewing conditions do not often yield representative corrosion rates, as the corrosion product layer needs time to form. Once this initial stage has passed, small breakdowns generally form on the surface of the $FeCO_3$ layer. They often display specific characteristics, with a top layer comprised of tightly packed crystals of $FeCO_3$ and a macroscopically amorphous phase, identified as Fe_3C, present inside these breakdowns (Fig. 16.1).

A cross-section analysis of the specimen reveals that the location of the breakdown relates clearly to the occurrence of localized attack and that the localized features involve a much wider area than the size of the layer breakdown implies. A thick $FeCO_3$ layer covers the sides of the "pit," whereas the bottom of the feature is flat-bottomed and partially covered with iron carbide. The feature is, in general, relatively empty, which is typical of a mesa-type localized attack. The localized features grow in depth but also laterally, underneath the already formed surface $FeCO_3$ layer (Figs. 16.2 and 16.3).

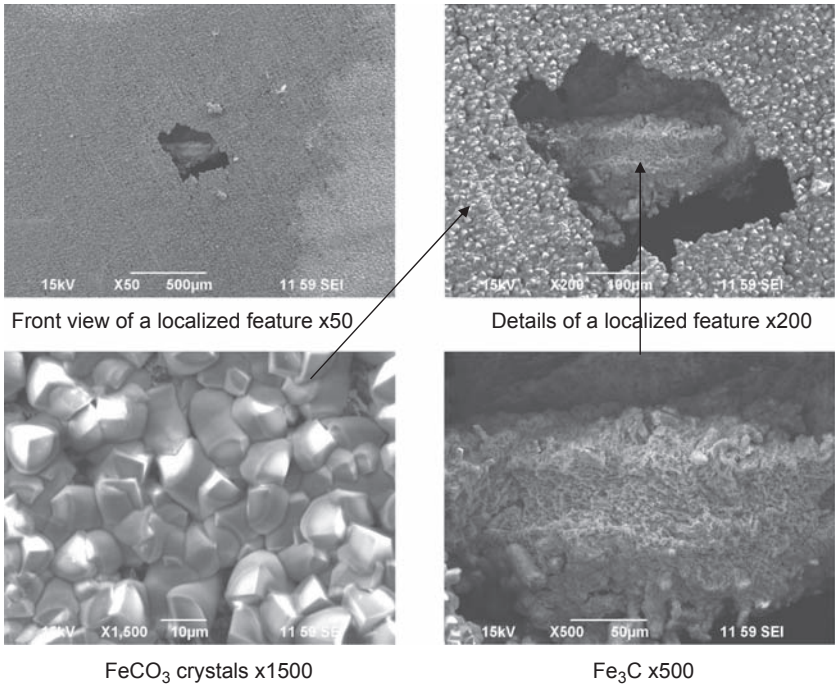

Figure 16.1 Corrosion product layer and associated breakdowns [45].

Undermining and consequent collapse of large portions of the $FeCO_3$ layer can clearly be seen. However, the localized features do not remain "active" throughout the exposure to the corrosive environment. If they become deep enough, the local chemistry within narrow localized features may favor the formation of a protective corrosion product layer. Because the flux of iron dissolution needs to be sustained, another location on the steel surface would become active and experience localized corrosion.

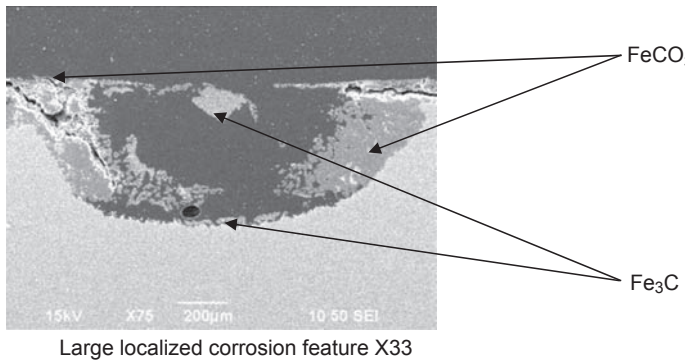

Figure 16.2 Cross section analysis − Morphology of large localized features [45].

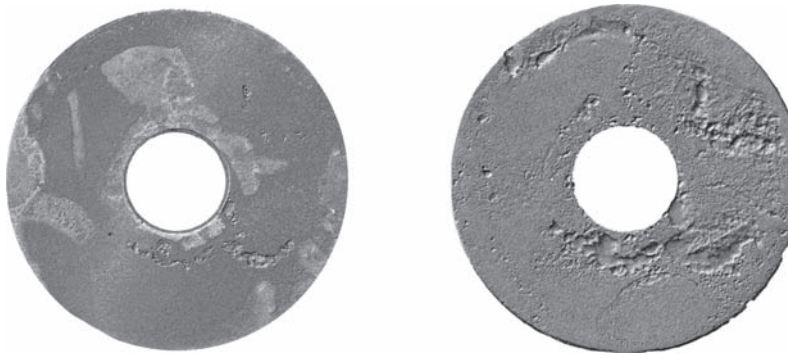

Figure 16.3 Localized corrosion features growth underneath $FeCO_3$ layer. T = 70°C (158°F), WL X65, WCR = 1 mL/m^2 s, exposure time = 21 days [45].

Depending on the water condensation rate and the corrosivity of the environment, the localized corrosion rates can be very high, often reaching 5−10 mm/year (Fig. 16.4). It is important to stress that this high rate is not driven by galvanic coupling between the corrosion product covered surface and the exposed localized corrosion features. It is rather driven by the specific chemistry of the condensed water and the effort to maintain the level of $FeCO_3$ saturation. Nevertheless, galvanic corrosion cannot be completely ruled out, especially in the early stages of pit formation. However, the localized corrosion rates at the top of the line are very similar to bare metal corrosion rates and do not require the use of galvanic coupling argument. The extent of the localized corrosion rate is consequently dependent on the concentration of organic acid specifically, and on the overall corrosivity of the electrolyte in general. The complex interaction of environmental parameters should preclude the use of restrictive threshold values, often utilized throughout the industry as engineering guidelines. Instead, a solid understanding of the mechanisms should always go hand in hand with practical field experience.

A fairly large amount of experimental work has been done on sweet TLC using a number of test setups especially designed for dewing conditions simulation [34]. A parametric study was performed by Zhang [31] and Singer [32] in 4″ID flow loops, looking at the effect of the most influencing parameters on which the severity of the corrosion attack, namely the condensation rate, the gas temperature, the gas flow rate, the CO_2 partial pressure, and the presence of organic acid. These sets of experiments, as well as other studies done through a wide array of experimental setups [27−30,33,34], have helped greatly in building the current state of understanding on TLC mechanisms in CO_2 dominated environments. Here the term "CO_2 dominated" is used to describe an environment that leads to the formation of metal carbonate corrosion products, as opposed to metal sulfide.

The influence of mono-ethylene-glycol (MEG) or pH control was also investigated [35−42]. MEG is typically used to prevent hydrate formation, mainly by decreasing

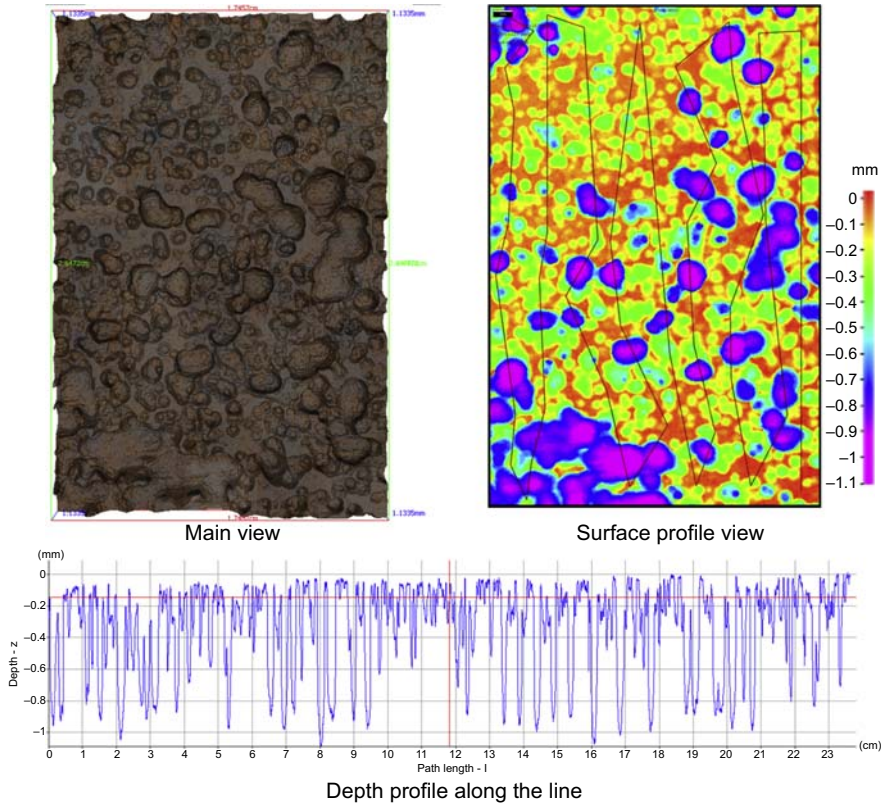

Figure 16.4 Surface profile analysis. T = 65°C (149°F), API 5L X65, WCR = 0.8−1 mL/m^2 s, pCO_2 = 2 bars (29 psi), exposure time = 21 days [45].

the water vapor pressure. MEG consequently has a direct effect on TLC by decreasing the water condensation rate. The effect is only significant when large concentrations of MEG are used (above 50 wt%). The presence of MEG also decreases the CO_2 corrosion rate, but it is debated how much can actually condense together with water because the MEG vapor pressure is much lower. pH control is also a very common method used to control the bottom of the line corrosion rate by injecting a base in the bulk aqueous phase. The bulk pH, however, has little influence on the acidity of the condensed water because it is mainly defined by the CO_2 content. Nevertheless, this method can be used to limit the concentration of undissociated acetic acid present in the bulk liquid phase, as it is pH dependent. This, in turn, limits the concentration of organic acids available for evaporation and, consequently, in the condensed water.

The possible role of hydrocarbon condensate [43] was also investigated in small-scale setup. This topic is an important aspect of TLC mechanism since it is expected that, in the field, light hydrocarbons (heptane, hexane, etc.) can co-condense at a rate 5−10 times higher than water. The experimental study showed that the presence of hydrocarbon influences the surface wetting characteristics and

segregated water droplets. However, the hydrophilicity of the steel surface seemed to guarantee water wetting on some parts of the exposed steel, and the resulting corrosion rates were similar to hydrocarbon-free systems.

The occurrence and characterization of localized corrosion have been somewhat less investigated, mostly due to the inherent complexity of the experimental procedure [44–46]. Amri [47,48] completed a comprehensive study looking at the influence of organic acid on localized corrosion propagation and developed a conceptual model of pit growth and annihilation. The authors mentioned that their findings could be applied to TLC and explain corrosion stabilization often observed in field environments [49].

H_2S top of the line corrosion mechanisms

The mechanisms of H_2S TLC are not as well investigated as their CO_2 counterparts. This is also true as it pertains to "standard" sweet or sour corrosion [50]. The controlling parameters appear to be different, but these differences are mostly due to the inherent characteristics of each type of corrosion, especially with regard to the types of corrosion products that can form.

In general, sour TLC is not as severe in terms of corrosion rate as sweet TLC. The presence of H_2S, even small amounts [51–55], often leads to a rapid and significant reduction of the CO_2 corrosion rate due to the prompt formation of a very thin mackinawite layer in the steel surface [54–56]. Depending on the conditions, different types of FeS can be formed (mackinawite, cubic FeS, and troilite) some being more thermodynamically stable or more protective than others. Experimental studies often showed the presence of two distinct layers: a thin and dense inner layer and a porous and thick outer layer [57]. As in sweet environments, the severity of TLC is directly linked to the properties of the corrosion product layers. Determining whether FeS or $FeCO_3$ precipitates is, therefore, of prime importance for TLC predictions. This is, however, quite difficult to predict [53,58,59].

Overall, sour TLC is still caused by the condensation of water vapor, but the effect of common controlling parameters is different compared to sweet systems. Only uniform corrosion is experienced in most cases, and higher rates are expected at lower gas temperatures [60,61], although these rates remain fairly low and relatively constant over time. As a result, the water condensation rate generally has little effect on the corrosion attack. The gas temperature thus becomes the key factor, as it directly affects the type and protectiveness of the formed iron sulfide. Being much less soluble than $FeCO_3$, the different types of FeS that can be encountered are stable at a pH typically encountered in condensing conditions. Therefore, the constant renewal of the condensed water does not undermine the protectiveness of the formed layer, whereas the presence of acetic acid seems to trigger the occurrence of localized corrosion in the form of small pits [55,61,62], though the penetration rate is similar to the general corrosion rate.

Even if the partial pressure reaches several bars [57], the H_2S content does not seem to have a strong effect on TLC rates as long as the integrity of the FeS layer is not challenged and that the surface is fully covered. However, more recent work investigating the presence of trace amounts of H_2S shows that even these trace amounts seem to trigger the occurrence of localized corrosion with rates approaching several mm/year [63].

16.2 Review of field experience in sweet and sour environments

Valuable information has also been published related to actual TLC field cases. Most of the well-documented cases are related to sweet fields. The first report of a CO_2-dominated TLC case was made by Gunaltun [64] regarding an onshore pipeline in Indonesia (CO_2 content of 4.7 mol%, total pressure of 90 bars (1305 psi), inlet temperature of 80°C (176°F)). This case is of particular importance because it underlines the effect of water condensation and identifies this as the main controlling parameter. In-line inspection (ILI) indicated that three locations along the flowline experienced extensive internal corrosion on the upper side of the pipe. These locations correlated strongly with zones where the pipe was crossing a river delta, being alternately buried and in contact with the flowing water. The resulting change in local heat transfer, and consequently water condensation rate, was identified as the main driving force of corrosion. The data collected enabled the identification of a critical condensation rate, below which TLC was considered to be manageable. This threshold value was set initially at 0.25 mL/m^2/s but was later reduced to 0.025 mL/m^2/s in case organic acid was present in the brine in large concentrations (above 2500 ppm) [65]. This threshold value was presented as a helpful design tool [66], but care should be taken when using it under different field conditions.

A large network of offshore pipelines off the coast of Thailand [67–72] has offered a new and very well-documented set of information containing both operating conditions and inspection data. Considering that the inlet fluid temperature could reach 90°C (194°F), very high water condensation rates occurred at the beginning of the lines, which were only partially buried. Severe TLC, with features as deep as 30%–60% of the original wall thickness, was detected in the first 500 m of the line, leading to potential derating of the pipe or replacement of entire sections. The severity of the corrosion attack decreased as the fluid temperature and the water condensation slowly decreased.

The notion of "cold spot" corrosion was introduced [71] to describe a case where the thermal insulation or coating is locally damaged, leading to a high rate of condensation. This was defined as the "worst case" TLC scenario, difficult to predict and ultimately leading to pipeline failure.

Consecutive ILI results showing no progress in localized corrosion features over time [43] seem to indicate that TLC stabilized after an initial high rate of metal loss. However, the same decrease in the severity of the corrosion attack could also be related in some cases to the overall decrease of the aggressiveness of the environment as the field ages. This point remains quite important as it could impact the design of the pipeline.

Sour TLC does not appear to be a common issue [73,74]. Only a few well-documented sour TLC field failures have been described in the literature [57,75–79]. In all cases, the flow regime was stratified with relatively low fluid velocities, and the temperature was always below 50°C. Under these conditions, the water condensation rate is not expected to be very high. Nevertheless, TLC features and pipe leakage were identified. It is, however, important to mention that methanol injection

was often used in these cases and that possible associated ingress of oxygen could have been determined to be a contributing factor with the formation of elemental sulfur.

16.3 Knowledge gaps

Although many significant improvements have been made in the understanding of corrosion mechanisms, especially in sweet TLC, some crucial aspects are still not well defined, especially in terms of corrosion assessment and management. This section aims at highlighting these concerns.

16.3.1 Gaps in the understanding

16.3.1.1 Localized corrosion and TLC stabilization

Sweet TLC is thought to be a "uniform" localized corrosion phenomenon instead of a purely pitting-dominated process. The localized aspect is explained by the fact that the corrosion attack is restricted to the top of the pipe, whereas the "uniform" qualification of the attack is supported by the large size of the features and the extent of the corrosion rate, which never surpasses the "layer free" rate.

In this sense, the penetration rate is driven by the corrosivity of the environment and the water condensation rate and is not particularly affected by any galvanic coupling between bare steel and layer-covered areas of the steel surface. Consequently, if a given pipeline is subject to TLC, metal loss is expected to occur continuously over the production life, assuming that the operating conditions do not change dramatically and that no successful mitigation method is implemented.

However, some evidence collected through multiple, consecutive in-line inspections seem to indicate that the TLC rate, although initially high, decreases with time and eventually stabilizes a fairly low value. This is indicated by the observation that TLC features do not appear to progress in depth after a certain time. If correct, this behavior would have strong implications for the design of new pipelines because added corrosion allowance would represent a relatively simple and efficient TLC management method. As mentioned earlier, some experimental work has been performed to explain how the conditions at the bottom of a pit become less corrosive as localized corrosion progresses [47,48]. This could explain why some TLC localized features may cease to progress in depth after a period of time.

However, the constant renewal of the condensed water dictates that a corresponding Fe^{2+} release must be maintained at the same time. Existing TLC features may then grow in width rather than in depth, and new features may be initiated. This would explain the wide and open characteristics of typical TLC features. However, once these pits become wide enough, the mass transfer limitations associated with TLC stabilization do not hold anymore.

Consequently, actual stabilization of TLC features, i.e., significant slowing of the wall thickness loss rate over time, cannot be fully explained theoretically. Validation of this phenomenon with actual field data is also challenging, as the lack of accuracy of

most ILI results leaves a lot of room for interpretation [43,65,67], especially when the variation of production conditions is taken into account. The experimental validation of TLC stabilization is also problematic, as it would require a very long testing time.

16.3.1.2 Hydrocarbon/water co-condensation

In real field conditions, the rate of hydrocarbon condensation is expected to be at least an order of magnitude higher than the rate of water condensation. In this environment, issues related to water wetting of the pipe become extremely relevant.

Most of the experimental work performed so far completely ignores the presence of light hydrocarbons, and only one study has been performed looking at the effect of hexane and decane [80,81]. The results of this study confirmed the tendency of liquid water to wet the steel surface in the presence of light liquid hydrocarbons. This is also validated by field experience showing that corrosion actually occurs in co-condensation environments.

However, the experimental data also highlighted that, although areas of the steel wetted by water did corrode at expected rates, areas wetted by hydrocarbon did not. The alternation of wetting conditions over time and their effect on overall corrosion severity has not been well characterized until now. Again, pipelines do corrode due to TLC, so there is no doubt liquid water eventually finds a way to wet the steel surface. The extent of the corrosion attack may not be fully understood, and therefore corrosion prediction by existing TLC models that do not take the presence of hydrocarbons into account may lack accuracy [70].

16.3.1.3 Sour TLC

The underlying mechanisms of sour corrosion and sour TLC are obviously identical. Beyond the specificity of a condensing scenario, both types of corrosion share the same fundamental chemical and electrochemical reactions and the same overall corrosion product characteristics. They also suffer from the same uncertainties related to the overall corrosion mechanisms and, more specifically, to the kinetics of corrosion reactions, the kinetics of corrosion products formation and transformation, and initiation and propagation of localized corrosion. In this sense, sour TLC inevitably lags behind the slow progress of sour corrosion understanding [82–85]. It also suffers from a relative lack of interest when compared to its sweet counterpart as actual field cases of sour TLC are relatively rare and not usually well documented.

In general, sour TLC seems to occur at low temperature, when the corrosion product layer is less protective. However, field experience is neither coherent nor conclusive on this aspect, as sour TLC does not systematically happen whenever the fluid temperature falls below a certain critical value. Also, no strong correlation could be found between the water condensation rate and the extent of corrosion. The influence of operating parameters on the characteristics and protectiveness of formed corrosion products is definitely key in determining the extent of uniform corrosion and the occurrence of localized corrosion. By itself, this topic is vast and complex.

As it pertains to TLC, most of the reported cases involve the injection of hydrate preventers such as methanol and monoethylene glycol (MEG) [75–77]. The chemistry of $H_2O/H_2S/CO_2$/MeOH or MEG systems and the associated formation thiols or dithiols [86] deserves further investigation. In addition, the effect of potential ingress of oxygen and the formation of elemental sulfur could also be key in understanding the underlying mechanism behind reported sour TLC pipe failure.

Overall, severe sour TLC is a rare event compared to sweet TLC [74]. The reasons behind this have not been fully elucidated. The low solubility of FeS corrosion product layers in water and their high protectiveness against corrosion must play a key role in the understanding of sour TLC.

16.3.2 Uncertainty related to mitigation principles and applications

Effective mitigation of TLC is a difficult process, as most commonly used methods, such as continuous injection of inhibitors, do not guarantee any protection at the top of the line, especially if the flow regime is stratified. To be successful, TLC inhibition requires that the inhibitor contact the steel surface on the entire inner pipe circumference.

Periodic batch treatment can ensure proper TLC mitigation but the selection of the correct application frequency is quite a challenge as well. The key to address this issue is to determine the inhibitor persistency. This can be done by performing laboratory testing in simulated field conditions or by conducting frequent ILI runs. However, the implementation of this method is costly in terms of both direct cost and production loss.

16.3.2.1 Volatile inhibition

Continuous injection of inhibitor is often the preferred solution for operators due to the low cost and relative ease of application. Typical surfactants included in inhibitor packages are long chain molecules that are effective in developing strong bonds with the metal surface and insulating it from the surrounding bulk water phase. However, these molecules are not typically volatile and are not present at the top part of the pipe unless they are physically transported there via droplet transport or nonstratified flow.

The search for inhibitors that retain sufficient inhibitive properties (usually held by long chain molecules) and present superior volatility (more common for smaller molecules) is of strong interest for the industry. However, this search has so far proven elusive, and only limited success has been achieved in the development and use of volatile corrosion inhibitor (VCI) in the field [87]. VCI is not a new concept. It is commonly used in the packaging industry, and attempts have been made, although only recently, to expand its domain of validity to multiphase flow systems [88–91]. Most current VCIs are made of complex mixtures of imidazoline salts and light amines. Their inhibition effectiveness obviously depends on their chemical structure,

the characteristics of the metal surface, the operating conditions, and the environments they are exposed too.

In order to select effective molecules, a "trial and error" approach is still much more common than a systematic theoretical approach. Fundamental investigations of the type of adsorption (either physical or chemical) and of the adsorption/desorption kinetics are not often performed, which greatly limits the validity domain of this type of mitigation method and, more importantly, the confidence that operators may have in the VCIs effectiveness in specific environments.

As pertains to TLC, recent efforts have been made in this direction [92], looking at the adsorption mechanism of amines (used as single components rather than part of a package). The low TLC inhibition reported and the lack of filming properties of the molecules tested highlight the gap in understanding between fundamental mechanism and field application. In addition, the influence of the steel surface characteristics (roughness, scale, presence of oxide or other corrosion product layers) on the efficiency of the volatile inhibitors has not been studied at all.

16.3.2.2 Foam matrix

The use of a foam matrix as an alternative to batch treatment has been proposed to physically transport the inhibitor to all parts of a pipeline potentially suffering from TLC. The main advantage of this method is that its application would not require any significant reduction in production rates, as is the case for batch treatment. The foam matrix concept relies on injected inhibitor liquids being carried with the foam slug along the line with the gas flow. The foam carrier would provide homogeneous delivery of the inhibitor through the pipe, which would then form a protective film all over the internal pipeline surface.

A "proof of concept" validation of this novel TLC mitigation method was successfully conducted in a small-scale laboratory setup consisting of a foaming cell and a corrosion cell used to simulate intermittent contact between the foam and the steel surface [93]. The TLC rate was reduced effectively by periodic treatment using the foam containing a tall oil fatty acid (TOFA)/diethylenetriamine (DETA) imidazoline corrosion inhibitor. Further validation was performed in a large scale flow loop to enable a more realistic simulation of the corrosive environments as well as the flow conditions typically encountered in the field [94]. Similar results were obtained, but the inhibition persistency was estimated between 3 and 20 h, depending on the inhibitor selected.

Although the use of a foam matrix to transport corrosion inhibitor to the top of the line appears to be a very promising technique, several challenges still need to be overcome before considering deployment in the field environment. Chemical compatibility with liquid hydrocarbons needs to be investigated, as the integrity of the foam matrix is likely to be strongly affected. Optimization of the type and concentration of corrosion inhibitor also needs to be addressed. Finally, considering an application in the field, the properties of the selected foaming agent need to be carefully studied in order to ensure that the foam matrix forms and remains as a plug for the first few hundred meters of line but disintegrates further along the line, thus avoiding issues with processing facilities.

16.3.2.3 Droplet transport

The atomization of liquid droplets can represent an effective means of transporting inhibitor through the vapor phase and combat TLC. Ensuring that droplets of inhibited fluids do reach the top of the pipe requires the correct sets of gas and liquid velocities, fluids density, and pipe geometry. Droplet deposition by itself may also not be enough to inhibit TLC, as it will have to "compete" against the water and hydrocarbon condensation rate, which would dilute the inhibitor concentration. Defining the onset of droplet deposition depending on operating parameters would constitute a useful tool that could help in the design and operation of wet gas pipelines. Recent efforts have been made to improve prediction of droplet transport in pipelines [95] and to link it to TLC mitigation applications [96].

16.3.3 TLC prediction

Compared to other types of corrosion, efforts to model and predict TLC have been relatively successful, especially in sweet environments. This is due to the simpler chemistry of condensed water, which leaves less room for assumptions both in terms of modeling and field data collection. An extensive effort to develop methodology for comparison between field data and model prediction has been undertaken, raising the operator confidence in using TLC prediction software for failure analysis and design. However, a number of uncertainties still remain, as models are just a representation of the current state in the understanding of mechanisms. The description of the modeling approaches developed for TLC is presented in Chapter 29.

16.4 Discussion on the corrosion trends to close gaps

Since much progress in the understanding of mechanisms has been achieved, the focus of new developments in the area of TLC is driven mostly by the need to improve and validate methods to predict and effectively mitigate corrosion. TLC prediction is covered in Chapter 29, and this section focuses on mitigation methods. On the laboratory side, there is a strong interest and need in developing standard methodology for corrosion testing and inhibitor evaluation in condensing conditions. On the field operation side, a number of TLC mitigation options that have been proposed to ensure that pipeline integrity still requires optimization.

16.4.1 Development of testing methodology for TLC assessment

16.4.1.1 Laboratory testing setups

Over the past 20 years or so, many experimental setups have been proposed to study corrosion under dewing conditions [97]. Typical CO_2 TLC setups involve low-pressure glassware under stagnant or low flow conditions [6,27,80], high pressure

autoclave systems [26,34,98], and large scale flow loops [30,32,99]. Sour TLC has also been investigated using similar setups, although the use of cracking resistant alloys is often required [57,61,100].

Each system holds its own set of advantages and drawbacks, but it is recognized that the proper simulation of the condensing conditions (i.e., condensation rate and surface wetting) is key in developing accurate and representative experimental system. It is also important to recognize that specific field conditions cannot entirely be reproduced in any laboratory setup. However, the desired outcome of most experimental study does not require exact reproduction of field conditions. If the study focuses on mechanisms, a simplified setup is often pursued where single operating parameters can be investigated separately. High-pressure and flow loop setups tend to reproduce field operating conditions more accurately but are also far more difficult to control. Proper interpretation of the results is always necessary in order to understand how experimental data and trends can be extended to field conditions. Consequently, the multitude of laboratory systems used to characterize TLC can become cumbersome in terms of interpretation of results obtained using different methods. This is especially true when it comes to validation of VCIs.

16.4.1.2 Toward a standard for volatile inhibition evaluation

Several experimental setups have been developed with the sole objective of evaluating the performance of VCIs [88,91,92,101,102]. The measured inhibition efficiency has enormous importance on the selection of inhibitors for field application and on the management of inhibition programs. It is important, therefore, that the experimental method influences the outcome of the test as little as possible. Standardization is an effective method to ensure that all tests are run following the same methodology and that the results can be compared. However, the adopted standard must be relevant and represent accurately the problem at hand. The only existing standard for VCI testing was developed for the packaging industry [103] and is not practical when it comes to TLC studies.

16.4.2 Design of multiphase pipelines

Most of the underlying mechanisms related to CO_2-dominated TLC have been elucidated in laboratory environment and are backed to some degree by extensive field experience. However, design of new pipelines still relies on the operator's in-house knowledge and on a set of guidelines specific to each company. Gunaltun presented a comprehensive review of the best TLC management practices [49] and stated that "there are still questions about the availability of sufficient know how, adequate specification and standards, and reliable prediction, corrosion control and monitoring systems." This section presents a summary of these technical "best practices". It is also important to stress that this summary applies to sweet environments, as sour TLC remains a rare event.

16.4.2.1 CRA, cladded pipe, and internal coating

The most obvious way to combat internal corrosion in general and TLC in particular is by using corrosion resistant alloy (CRA), cladded pipe, or internal coating. If applied to the entire length of the pipe, this option can also be the most expensive and is, therefore, seldom applicable. However, cladded pipe would be used along the first few hundred meters of pipe where the fluid is the hottest and when high water condensation rate and TLC rates are expected. The cladded section is purposely not thermally insulated in order to ensure maximum heat exchange and rapid decrease in the fluid temperature. The length of the cladded section is determined using flow assurance and TLC prediction models to ascertain the temperature, water condensation rate, and TLC rate profiles. Several corrosion concerns exist at the CRA/CS (carbon steel) transition. First, care must be taken to avoid galvanic coupling. Second, issues related to the so-called "hungry water" could also appear as rivulets of condensed water, coming from the cladded section and transitioning to the CS section, and are free of corrosion products and so very corrosive [104]. This condition is not TLC per se but is a direct consequence of the condensation of water in the cladded section. It is also difficult to mitigate without clever design of the CRA/CS.

16.4.2.2 Corrosion allowance

If the use of CRA is not an option, enough corrosion allowance needs to be considered during the design phase. Gunaltun proposed a minimum corrosion allowance of 10−12 mm for the warmest sections of the pipeline (above 50°C, 122°F), which can be reduced to 6−8 mm for colder sections [49]. The use of proper heat insulation could also reduce these values accordingly. These specifications are made based on field experience and also counting on TLC stabilization, which is "also the most controversial aspect in the TLC mechanism" [49]. Rather than using fixed corrosion allowance derived from a limited number of field cases, another approach is to use available TLC prediction models in order to calculate the expected metal loss during the operating life of the field.

16.4.2.3 Thermal insulation and pipe burial

The application of thermal insulation (typically polyurethane elastomers or polypropylene) can be used to reduce the water condensation rate. Full pipe burial is even more effective in ensuring low heat exchange with the outside environment. These methods, if applied well, can reduce the TLC rate considerably, but the fluids flowing inside the pipe can remain hot all along the insulated section, prohibiting any interruption in thermal insulation or pipe burial that could lead to cold spots. It is important to stress that partial pipe burial yields no benefit in terms of TLC. In addition, antiexternal corrosion coating such as three layer polypropylene (3LPP) and concrete weight coating cannot be considered effective thermal insulation as they are either too thin (3LPP) or have too high a thermal conductivity (concrete). The proper U-value of thermal insulation can be determined using fluid flow and TLC simulations.

16.4.2.4 Corrosion inhibition via chemical means

Chemical inhibition of TLC can be achieved, at least partially, with pH control, MEG injection, or volatile corrosion inhibition.

pH control involves the use of a nonvolatile base, most often methyl diethanolamine (MDEA), to neutralize organic acids present in the bulk aqueous phase. These acids dissociate into their ionic conjugate base and cannot evaporate anymore. However, this has no effect on standard CO_2 TLC as the acid gas content in the condensed water is not affected by the pH of the bulk liquid solution. Care must be taken to select the proper base dosage for this method, which only has practical applications at low produced water flow rate because scaling issues must also be avoided.

Similarly, the use of MEG can be used in wet gas lines to decrease the water condensation rate. As mentioned earlier, the presence of MEG in the condensed water in any substantial amount is doubtful in typical operating conditions. A significant effect is seen at MEG content above 70 wt% which, again, limits its application to systems with low water flow rates. The proper MEG injection flow rates are selected using flow assurance tools and TLC prediction models.

The use of VCI is probably the inhibition technique generating the most interest today due to its ease of application and its relatively low cost compared to other traditional techniques. However, evaluation of the efficiency of VCIs in laboratory and field environments has rarely exceeded 70%. The key challenge is to develop the right molecules or package of molecules "light" enough to evaporate and capable of high corrosion inhibition efficiency. Other requirements must also be taken into account, such as solubility in the hydrocarbon and water phases, compatibility with other chemicals used in oil and gas production, environmental friendliness, and health and safety. Once these challenges are overcome, VCI continuous injection could become the most practical and cost-effective TLC control system.

Finally, most current gas fields with high TLC risk operate with periodic batch treatment: a plug of fluid containing high inhibitor content is periodically pushed through the pipeline system between two pigs. A similar method involves the use of a specially designed spraying device [43]. This technique does not require the use of VCI, as it directly provides a means for the inhibitor to reach the top of the line. The line obviously has to be pig-able and the batch treatment must be carefully calibrated by evaluating the inhibitor persistency, because the inhibitor film will tend to desorb from the metal surface between two batch treatments, as pure condensed water continuously condenses.

16.4.2.5 Monitoring (corrosion probe and intelligent pigging)

Monitoring is a very important aspect of any corrosion management plan. As pertains to TLC, a number of tools exist to monitor corrosion in the field but the search for an accurate and practical tool has proven to be elusive. Common ILIs involve monitoring devices mounted on "smart" inspection pigs. Although pigging does not require a complete halt in production, it still involves slow down and consequent loss of revenue. Magnetic flux leakage (MFL) and ultrasonic testing (UT) are the two main

techniques currently used [43,65,69]. MFL detects pipeline defects through magnetization of the ferrous metal, and UT is based on measuring the ultrasonic signal propagated through the pipe wall.

Newer and possibly more appropriate monitoring methods are also available. Among them, field signature method (FSM) is very promising for TLC applications. FSM is a stationary and current-based method of internal corrosion monitoring. If positioned optimally, it could prove quite useful for TLC.

Other, much less expensive methods involve the use of electrical resistance or weight loss probes installed at specific locations in order to monitor the corrosion. The probes are cooled artificially to simulate condensing conditions. As with FSM, the relevance of the results is highly dependent on the location of the measurements [87]. Comparatively, the use of electric-chemical probes such as linear polarization resistance can be problematic in condensing environments due to the low conductivity of the electrolyte.

16.5 Conclusions

More than 40 years after it was first encountered, TLC remains a serious asset integrity concern for many oil and gas producers. The understanding of the mechanisms involved in TLC has improved tremendously, especially in CO_2-dominated conditions, and operators now have access to a set of tools and methods to effectively manage TLC risks in wet gas pipelines. However, the effects of several factors, such as the presence of H_2S, on TLC are still not fully understood. More importantly, more work is needed to develop a cost-effective technique to mitigate TLC using corrosion inhibitors. Sharing of field experience and strong collaboration between research and operation remain critical to any progress in this area.

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