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# Top of line corrosion in gas-condensate pipelines

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**Abstract.** Low alloyed carbon steel is the only viable material of construction for long pipelines transporting unprocessed gas-condensate. The water that condenses is highly corrosive because it contains dissolved acid gases, i.e., CO<sub>2</sub>, H<sub>2</sub>S and organic acids like acetic and formic acid. The high velocity gas also contains droplets of water and condensate, and these will deposit if they hit the steel surface. Monoethylene glycol (MEG) injected to prevent ice and hydrates must be considered when predicting the composition and corrosivity of the aqueous phases in the pipeline. The liquids gathering at the bottom of the pipe have a higher heat capacity than the gas, and the temperature at the top of the pipe will be slightly lower than at the bottom. As the produced fluids cool during the transport from the hot wells to the process plant, water will condense on the cold pipe surface and more at the top than at the bottom. The literature on Top-of-line corrosion (ToLC) has grown steadily since the first reported case in 1960. There are also several prediction models for ToLC. This review is an overview of the main factors that cause ToLC and how these are modelled. Mass transfer from the aqueous phase at the bottom to the top contribute to the condensation. Despite the low MEG to water ratio in the gas due to the difference in vapour pressure, the fraction of MEG in the condensing water may be considerable. The concentration of MEG in the aqueous phase at the top depends on the mass transfer from bottom. The same is the case for organic acids. Liquid droplets entrained in the gas may deposit top of line and contribute to the chemistry of the aqueous phase. Models for ToLC must thus not only predict the composition of the condensing phases but also the mass transfer to be able to estimate the corrosion rate.

## 1. Introduction

There are ca. 8 800 km pipelines on the Norwegian continental shelf [1]. Although the major part is made in carbon steel, few encounter corrosion at the inside. The reason is that most of them carry dry gas or condensate. Corrosion on the hydrocarbon side is an issue for multiphase pipelines which transport unprocessed well fluids or water saturated fluids. These are not only infield pipelines, but also long-distance flowlines, as the Troll pipeline to Kollsnes, the Ormen Lange pipeline to Nyhamna and the Snøhvit pipeline to Melkøya. The Troll pipeline was a major step for the Norwegian oil and gas industry as one of the first long distance pipelines transporting water saturated natural gas. The later multiphase pipelines Ormen Lange and Snøhvit are carrying unprocessed well fluids from subsea templates to onshore terminals.

The water that condenses from unprocessed gas is corrosive to carbon steel as the gas contains CO<sub>2</sub> that dissolves in the water. Other components in the gas that contribute to the corrosion are H<sub>2</sub>S and organic acids. The fluids are normally cooled to seabed temperature within a few kilometres from the pipeline inlet. The cooling rate depends on the insulation and exposure to seawater. Water will condense on the pipeline wall if the gas is not dried to a sufficiently low dew point.



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The water condenses on the whole circumference of the pipe, but if the fluid flow is stratified, the aqueous phase that condenses at the upper part of the pipe can differ considerably in composition compared to the aqueous phase flowing at the bottom. If the heat transfer at the top of the pipe is higher than at the bottom, the major condensation will take place at the upper part. Mass transfer from the aqueous phase bottom of line to the gas and from the gas to the liquid top of line plays a role, too. The effect becomes apparent when the bulk liquid is not water only but contains glycol or other cosolvents.

Corrosion takes place both at the bottom (BoL) and top of line (ToL), but the characteristics are different [2]. The ability of the water to take up (dissolve) corrosion products is a key parameter. At the bottom it is controlled by the temperature and the composition of the aqueous phase in contact with the steel. At the top, the water condensation rate is the factor that determines the corrosion rate. A recent review lists the following processes that controls top of line corrosion (ToLC) [3]:

- Fluid mechanics – The ToLC risk is largest for stratified flow
- Heat and mass transfer – condensation on cold wall and transport of corrosive species to the condensed liquid
- Chemistry (electrochemistry) – the composition of the aqueous phase determines the rate of the corrosion reactions

The ToLC rate is controlled by the build-up of  $\text{Fe}^{2+}$  in the condensing aqueous phase. Some models are based on a  $\text{Fe}^{2+}$  flux balance which consider the precipitation of  $\text{FeCO}_3$  (iron carbonate) as well as  $\text{Fe}^{2+}$  transportation in the water film such as in [4]. Other older models base the ToLC rate on the  $\text{FeCO}_3$  solubility and supersaturation factor that must be exceeded to form protective  $\text{FeCO}_3$  [5, 6].

When thermodynamic hydrate inhibitors as MEG are employed, it will have large effects on the condensation rate and the corrosion mechanism. MEG at the BoL dilutes the water and reduces the water vapour pressure, but at the same time, MEG will evaporate and be present in the gas phase. It has a lower vapour pressure than water, and while the MEG:water ratio in the aqueous phase at BoL is about 1:1, it is typically 1:50 in the gas phase. If the condensation rate calculation is based on condensing the water and MEG in the gas phase without resupply, the condensing phase will be water with a few percent MEG. If chemical equilibrium is maintained, the MEG concentration in the condensing aqueous phase will be nearly the same as at the BoL [7].

Another key parameter for ToLC is presence of volatile fatty acids (VFAs) sometimes denoted organic acids. The most common is acetic, formic and propanoic acid. As they are volatile, they will be produced with the gas when they are present in the formation water. Hence even if there is no formation water break through, there may be VFAs in the produced fluids. Another source of VFAs is back production of salts used as completion fluids. Although the concentration of VFAs in the gas is low, in the ppb level, they can reach ppm levels in the condensing aqueous phase and have major impact on the ToLC [8]. The chemistry of the BoL aqueous phase and the mass transfer to the gas are the main factors that determine the dissolution rate of VFAs and thereby the corrosion rate ToL. In fields using MEG, it is important to consider that VFAs can be recycled to the pipelines via the recycled MEG.

Another known factor for ToLC that has been little implemented in models so far is droplet transport. Both droplets precipitating in the gas phase and teared off from the liquids BoL can be transported to the top. The aqueous phase BoL normally contains corrosion inhibitor, and it may also have a relatively high alkalinity. So, even a small number of droplets from the BoL aqueous phase will have large impact on the volume and chemistry of the ToL aqueous phase. Hydrocarbon liquid on the pipe wall may prevent water wetting and thereby reduce the corrosion rate considerably. Hence, oil droplets carried with the gas that hit and adhere to the wall at the upper part will limit the corrosion.

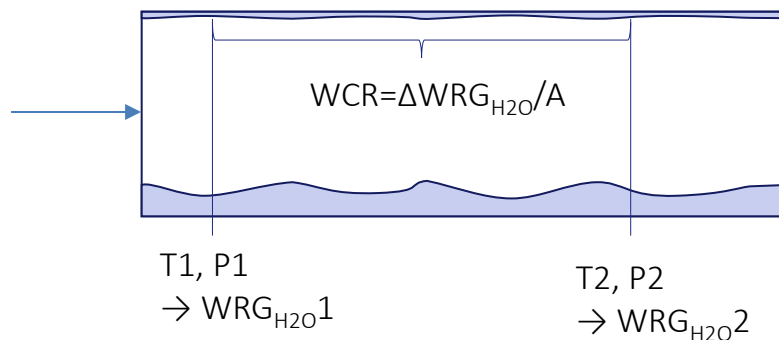
This article presents a summary of the principles that ToLC prediction models build on, and with particular focus on the kinetics of the mass transfer. The objective for improving the prediction models is to avoid over conservatism that may lead to costly facilities like cooling spools, CRA clad sections and/or insulation with low U-values.

## 2. Modelling ToLC

Recent literature reviews of ToLC give overview of the development of models for ToLC over the years and discuss the main equations and algorithms they included [4, 9]. For water condensation Singer distinguishes between “Water dropout approach” and “Local water condensation approach” [9]. The difference is that the first approach uses the reduction in water vapour pressure along the pipeline to calculate the condensation rate while the second approach links it to dropwise condensation and has the heat flux as basis for calculating the condensation rate. The second method is more accurate as it considers evaporation from the aqueous phase at the bottom and gives a better prediction of local water condensation at the top of the pipe. The worst case of ToLC is cold spot corrosion [10]. Evaporation from the bulk aqueous phase at the bottom becomes even more important when species as MEG and VFAs with relatively low vapour pressure take part in the condensation and corrosion reactions.

### 2.1. Co-condensation of MEG/water

The net condensation in a pipeline can easily be calculated based on the temperature and pressure profile along the pipeline as illustrated in Figure 1. It is the same as the “Water dropout approach”.

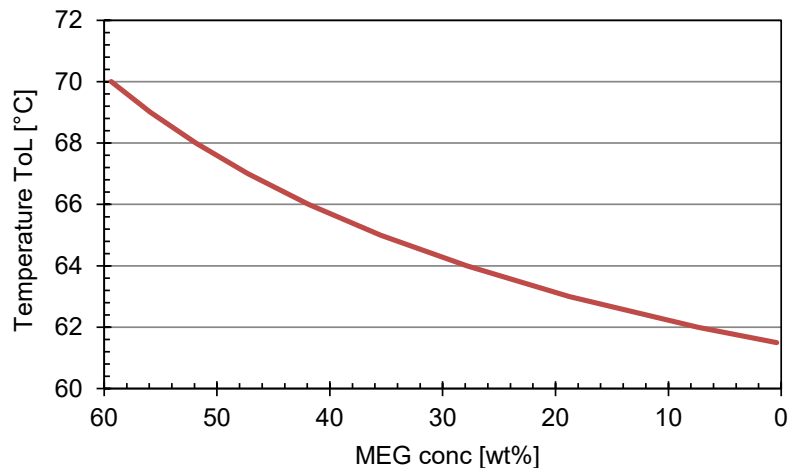


**Figure 1.** Calculation of net water condensation rate (WCR) between two points with temperature  $T1$  and  $T2$  and pressure  $P1$  and  $P1$ .  $WRG_{H_2O}$  is the mass rate of water in the gas phase, and  $A$  is the pipeline surface area between the points.

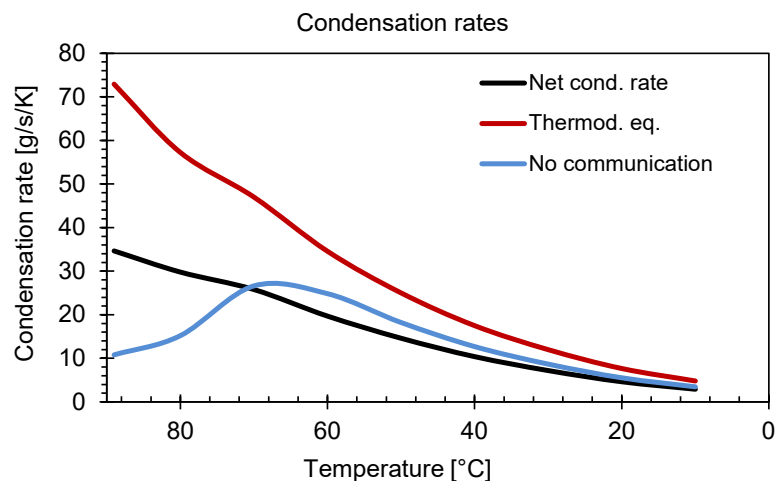
When MEG is a major constituent in the aqueous phase BoL, it has a major effect on the aqueous condensation. It lowers the activity of water in the aqueous phase BoL and thereby reduces the partial pressure of water in the gas. Unless the temperature at the top is lower than the water dew point, there will only be condensation if both water and MEG deposit at the top. If the temperature difference between ToL and the bulk gas is small and the gas phase is in thermodynamic equilibrium with the aqueous phase, it implies that the MEG concentration in the condensing phase must be nearly the same as in the aqueous phase BoL. The example in Figure 2 shows the dew temperature as function of the MEG concentration in the condensing aqueous phase. It illustrates that the mass transfer from the aqueous phase BoL to the gas must be considerable to maintain the condensation if the temperature difference between the bulk gas and wall surface is small.

The local condensation rate will be considerably higher than the net condensation rate between two points if mass transfer can be maintained, and the temperature difference between the bulk gas and the upper wall is small. Figure 3 gives the net condensation (cond.) rate and the actual condensation rate for two different scenarios in a pipeline with MEG. The calculation is for a pipeline where the temperature at the inlet is 90 °C. The thermodynamic equilibrium (Thermodynamic equation) curve is calculated assuming that the mass transfer of MEG from bottom to gas is sufficiently high to maintain thermodynamic equilibrium. The No communication curve is calculated based in thermodynamic equilibrium at the pipeline inlet and then no mass transfer of MEG from the bottom to the gas. That situation can occur in a gas-condensate pipeline if the condensate layer covers the rich MEG at the bottom and prevents evaporation of MEG from that layer. The difference is considerable. The actual

condensation rate is more than the double of the net condensation near the inlet if thermodynamic equilibrium is achieved while the net condensation cannot be obtained for a distance downstream of the inlet if there is no mass transfer from the rich MEG to the gas phase. The difference in corrosion rate will be the same as most ToLC models set the corrosion rate proportional to the condensation rate.



**Figure 2.** Dew temperature as function of MEG concentration in a condensing aqueous phase. The bulk gas is saturated at 70 °C in contact with an aqueous phase with 60 wt% MEG. Software used for the calculation: MultiScale 8.1.



**Figure 3.** Condensation rate along a pipeline. Net condensation rate is calculated as illustrated in Figure 1. The two scenarios, thermodynamic equilibrium (Thermod. eq.) and no communication are discussed in the text. Calculation for pipeline with inlet temperature and pressure 90 °C and 100 bar and outlet temperature and pressure 10 °C and 70 bar. The gas (pure CH<sub>4</sub>) is water saturated at 200 bar and 110 °C and 90 wt% MEG is injected at a rate that gives 40 wt% MEG at the outlet. The gas rate is 20 MSm<sup>3</sup>/d.

There are experimental studies of co-condensation of water and MEG, but the parameter range that has been covered is limited. Islam et al. performed experiments in a glass cell with condensation on a cold finger [11]. They found that the MEG concentration in the condensing phase was much lower than in the bulk aqueous phase, especially when the MEG concentration in the bulk was more than 50 wt%. The experimental conditions in that study gave a relative high temperature difference, 10 – 25 °C, between the cold surface and the bulk gas. The article does not state the gas flow rate, but the set-up implies that it was low. It is noted that the high temperature difference between the bulk gas and the surface with condensation implies that the MEG concentration will be low in the condensing aqueous phase according to Figure 2.

Guo et al. studied MEG/water co-condensation in a flow loop with controlled gas flow rate [12]. The condensation took place in a cooled section of the loop and there was no condensation upstream of the cooled part. The gas velocity was 1 and 3 m/s, the gas temperature was 42 to 67 °C and the pipe wall temperature was 32 to 65 °C. They also found that the MEG concentration in the condensing MEG/water was much lower than the MEG content in the bulk liquid in the tank where the gas was saturated with MEG and water. The conditions in the tests were close to the “No communication” case in Figure 3. The results confirm that the MEG concentration in the condensing MEG/water was much lower than in the aqueous phase the gas was equilibrated with.

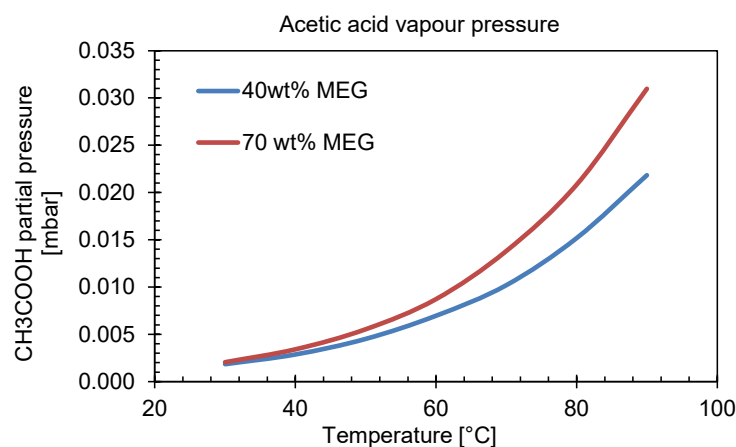
## 2.2. Mass transfer of volatile species to ToL aqueous phase

Volatile VFAs and corrosion inhibitor components can be transferred to the ToL aqueous phase and affect the corrosion rate. Only VFAs will be discussed here, but similar mechanisms apply for other components that speciate between gas and aqueous phase. Formation water may contain VFAs that partly speciate to the produced gas. They are thus produced even though there is no formation water break through. The most common acid is acetic acid, but formic, propionic, butyric, and heavier acids can also be present. Another source of VFAs can be completion fluids used to stabilise the wells before production start-up. Formate salts are highly soluble and have been used as high-density brines for this purpose. VFAs is always a concern, but especially in pipelines which use recycled MEG. Depending on the MEG regeneration process considerable amounts of VFAs can be injected with the MEG. In such cases, completion brine that is back produced for a short time may reside in the MEG loop for years if the salt removal capacity of the MEG regeneration system is low.

Dugstad studied the impact of formic and acetic acid in the gas phase on ToLC [8]. By an indirect method he showed that a corroding surface could consume all acid that was supplied. Results from loop experiments with formic acid showed that mass transfer of acid increased with flow velocity and the presence of MEG seemed to increase the uptake of acid. Furthermore, the experiments indicated that acids were consumed until the aqueous phase was saturated with iron carbonate. That implies that the formic acid can be more corrosive than acetic acid as its dissociation constant is 10 times higher.

Singer et al. made a parametric study of ToLC in presence of acetic acid [13]. They found that high concentration of acetic acid led to high localised corrosion rates even at low water condensation rates. Svenningsen et al. reported that ToLC rate increased strongly with amount of acetic acid in the condensed water [14]. They concluded that the amount of iron that can dissolve in the condensed water limits the corrosion rate and acetic acid increases the solubility of iron in the condensing water. It also plays a role that the corrosion reactions with formic and acetic acid are much faster than the reactions with CO<sub>2</sub> and carbonic acid [15].

Even though the term volatile is used for these acids, their vapour pressures are relatively low, and there is a linear relationship between the concentration of acid in the gas and an aqueous phase (Henry's law). As shown in Figure 4, the partial pressure of acetic acid in a gas phase in equilibrium with an aqueous phase with 40 to 70 wt% MEG that contains 120 mg/kg acetic acid typically is in the range 0.002 to 0.03 mbar at 30 to 90 °C. It implies that the volume fraction in a gas phase at 100 bar is less than 1 ppmv when the concentration in the aqueous phase at the BoL is around 100 ppmw. It can thus be anticipated that the gas can become depleted in organic acids when they dissolve in the aqueous phase ToL unless the mass transfer of acids from the BoL to the gas is fast.



**Figure 4.** Acetic acid ( $\text{CH}_3\text{COOH}$ ) vapour pressure as function of temperature and MEG concentration when the concentration in the aqueous phase is 120 mg/kg.

The VFAs will be partially dissociated in the aqueous phase, and as it is acid that is volatile, it is possible to control the partial pressure of acid in the gas by adding an alkali e.g., NaOH or an organic base to the MEG before injection. To keep a constant low concentration of acid, the alkalinity in the recycled MEG must increase if the total concentration of acid and carboxylate, e.g., acetic acid and acetate, increases. According to the dissociation reaction (acetic acid as an example):



The equilibrium concentrations are given by

$$\frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = K_a \quad (2)$$

where the  $[\ ]$  denotes concentration of the bracketed specie and  $K_a$  is the dissociation constant.

The dissociation of VFAs decreases with increasing MEG concentration, and this must be taken into account in order to estimate the amount of VFAs that may dissolve in the aqueous phase and take part in the corrosion ToL. There is software available which can do that. The mass transfer coefficient is connected to the flow conditions in the pipeline and can be estimated from Sherwood, Schmidt and Reynolds numbers.

### 2.3. The effect of droplets

It is largely agreed that ToLC only occurs if the flow is stratified. However, there may be droplets of the liquid phases carried in the gas, and they can impact the ToLC considerably. From the discussion above, it follows that mass transfer of MEG and VFAs to the gas may control the condensation rate and concentration of corrosive species in the aqueous phase ToL. Droplets of the BoL phase in the gas can increase the area for mass transfer considerably and thus maintain the concentration of MEG and VFAs in the gas phase during deposition / dissolution ToL.

Droplets that are carried to the ToL and deposited will increase the actual condensation rate. The aqueous droplets will carry dissolved salts and chemicals and thus the chemistry of the phase ToL may change considerably. It is envisaged that increased alkalinity and transfer of corrosion inhibitor may decrease the ToLC rate despite the increase in aqueous volume.

### 3. Conclusions

There is an extensive number of publications that describe experiments and models for ToLC in pipelines carrying unprocessed or partly processed gas and condensate. The emphasis has been on corrosion mechanisms, and it is unclear how the models consider mass transfer of species that are important for the condensation rate and corrosivity of the aqueous phase that deposits ToL.

The net condensation calculated from thermodynamic flash calculation at points along a pipeline does not give the actual condensation rate. When MEG is applied as a hydrate inhibitor, it will affect the condensation. The condensation rate can be considerably higher than the net condensation if the mass transfer of MEG from the aqueous phase at the bottom is fast. On the other hand, the net condensation rate cannot be reached if the mass transfer of MEG is slow, if it, e.g., is hindered by a layer of hydrocarbon condensate.

The mass transfer to the gas phase is also the key factor to maintain the concentration when non-dissociated VFAs dissolve in the aqueous phase ToL. These dependencies imply that to take ToLC prediction a step further one must include flow models which make it possible to calculate mass transfer between liquid and gas phases.

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