Top of line corrosion in pipelines with high CO₂ and low H₂S

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Summary

Top of line corrosion can occur in wet gas pipelines when water condenses in the upper part of the pipeline. For CO₂ dominated systems the top of line corrosion is limited by the amount of iron which can be dissolved in the water condensing in the top of the pipeline. When acetic acid is present in the gas in addition to CO₂ the solubility of iron in the condensed water is increased, and this increases the top of line corrosion.

Top of line corrosion has been studied in a flow loop where moist gas is circulated and water is condensed in 1.8 m long carbon steel pipes with external cooling. The condensed water is collected at the end of each test section. This setup enables measurement of top of line corrosion on large surfaces with low water condensation rates. Experiments with high CO₂ partial pressure and traces of H₂S in the gas showed that the corrosion products were predominantly iron carbonate at high temperature and iron sulphide at low temperature.

1 Introduction

Water condensing in the upper part of wet gas pipelines can cause top of line corrosion under stratified flow conditions, where the water chemistry in the thin film of condensed water in the top of the pipeline can be very different from the bulk water phase in the bottom of the line. Laboratory studies of top of line corrosion were performed already around 1990 [1], [2]. Field cases of top of line corrosion in gas pipelines have been reported mainly in the Far East [3], [4]. Common factors for these cases were excessive cooling of the gas, high water condensation rates and presence of organic acid in the gas, with 300 to 2000 ppm acetic acid in the produced water. The acetic acid is transported in the gas phase and will condense together with the water and increase the solubility of iron in the condensed water.

The water condensing in the top of a wet gas pipeline will have a low pH and high corrosivity, but can become rapidly supersaturated with corrosion products, resulting in increased pH and iron carbonate film formation. The top of line corrosion rate then becomes dependent on the water condensation rate and the amount of iron which can be dissolved in the condensing water [1], [5]. Several top of line corrosion models have been developed based on this dependence of water condensation rate and iron carbonate solubility [5], [6]. Top of the line corrosion models have also been developed from a more detailed mechanistic viewpoint [7], [8]. The presence of organic acids in the gas may increase the top of line corrosion rate, as it increases the amount of iron which can be dissolved in the condensing water [9], [10], [11].

This paper summarizes results from two experimental projects where top of line corrosion was studied under conditions typical for planned gas pipelines with 10 bar CO₂, 1 - 2 mbar H₂S and varying amounts of organic acids [12], [13].
2 Top of line corrosion model

The top of line corrosion rates measured in the experiments presented here are compared with a model where the top of line corrosion rate is predicted to be proportional to the water condensation rate, the solubility of iron carbonate in the condensed water and a supersaturation factor [5]:

\[
CR = k \cdot R_{\text{Cond}} \cdot C_{\text{Fe}} \cdot S
\]

where \( k \) is a constant, \( R_{\text{Cond}} \) is the condensation rate, \( C_{\text{Fe}} \) is iron solubility in the condensed water and \( S \) is the supersaturation factor.

\[
S = 12.5 - 0.09 \cdot T
\]

where \( T \) is temperature in °C.

Since the formation of iron carbonate is slow, a high supersaturation of iron carbonate is normally required to start the precipitation reaction. The required supersaturation varies strongly with temperature, as shown in the empirical equation for the supersaturation factor above.

When organic acids are present in the produced gas, they will condense together with the condensing water. This will lower the pH of the condensing water and increase the iron carbonate solubility in the condensing water, and thereby increase the top of line corrosion rate. The effects of organic acids on top of line corrosion have been discussed in detail in a recent paper [11].

For systems with even small amounts of \( H_2S \) the top of line corrosion models are not directly applicable, as corrosion product films will be dominated by iron sulphide instead of iron carbonate. The mechanisms for supersaturation and protective film formation are very different from a situation dominated by iron carbonate. The applicability of the model for situations with traces of \( H_2S \) will then depend on whether iron carbonate or iron sulphide is the dominating corrosion product.

3 Top of line corrosion loop experiments

A flow loop designed for top of line corrosion studies was used to study the effect of acetic acid and small amounts of \( H_2S \) on top of line corrosion. A schematic drawing of the top of line corrosion loop system is shown in Figure 1. A photograph of the loop is shown in Figure 2. Moist gas is circulated from tank 2 (high pressure reservoir), through the test sections and into tank 1 (low pressure reservoir) where a water/gas ejector system pumps the gas back to the high-pressure reservoir, tank 2. Both tanks are half filled with a water phase, but only the gas phase is circulated in the loop. The gas is thoroughly mixed with the liquid in the ejector, ensuring that the gas which is fed into the test sections is saturated with water vapour.

Three 1.8 m long thick walled carbon steel pipes with 55 mm inner diameter are exposed to the moist gas. This gives a large carbon steel surface where condensation can occur. The pipes are sand blasted before the exposure to remove mill scale and ensure a clean steel surface prior to the experiment. The test pipes are cooled with cooling coils mounted on the outside of the test sections, and the condensation rate can be controlled by varying the flow through the cooling coils. The corrosive condensed water collects in the bottom of the test pipe. In order to avoid
corrosion in the bottom of the pipe, the bottom segment of the test pipe is painted. The paint covers about 20% of the surface. Different condensation rates can be achieved in each of the three test sections.

Small amounts of H$_2$S are added as a sodium sulphide solution to the tanks in the loop, and the H$_2$S content in the loop is measured by sulphide analyses of the water in the tanks in the loop or by gas chromatography of the gas phase. Sulphide is added periodically to replace H$_2$S consumption, based on frequent measurements of the sulphide content in the loop water. Acetic acid is added to the tanks in the loop, and the total acetate/acetic acid content is measured by titration.

The condensed water is taken out at the inlet and outlet of each test pipe, and the amount of water collected in a given time is used to calculate the water condensation rate in each test section. The iron concentration in the condensed water samples is measured with a photometric technique.

The test pipes are inspected visually before and after exposure and the corrosion films are analyzed by SEM (Scanning Electron Microscopy). The corrosion rate is calculated from the total amount of dissolved iron, based on SEM measurement of corrosion film thickness and composition and the measured condensation rate and concentration of Fe$^{2+}$ in the condensed water.

![Figure 1](image.png)

**Figure 1:** The test loop used for top of line corrosion experiments
4 Experiments with 10 bar CO2 and traces of H2S

Top of line corrosion experiments with 10 bar CO2, presence of acetic acid and small amounts of H2S have been performed in two different projects. Details from these experiments have been published previously [12], [13]. Experimental conditions and main results are summarized in Table 1.

The first experiment was performed at 25 °C with 10 bar CO2 and 2 mbar H2S partial pressure. Acetic acid was added to the system in order to obtain 300 ppm free acetic acid in the condensing water. These conditions are representative for the inlet of the carbon steel part of the pipeline system which was the basis for this study. Because of the low temperature very low water condensation rates were expected from multiphase flow simulations, and a water condensation rate of 0.006 g/m²s was used in the experiment.

The second and third experiment was performed at 85 °C, also with 10 bar CO2 partial pressure. The H2S partial pressure and acetic acid content was lower in Experiment 2 (respectively 0.1 mbar and 430 mg/l) than in Experiment 3 (1 mbar and 3400 mg/l). The condensation rate was 0.06 g/m²s in both experiments. This higher condensation rate was expected from multiphase flow simulations for the pipeline in question due to the higher temperature compared to Experiment 1.

As the test specimens are the whole 1.8 m long test pipes it is not possible to obtain direct weight loss measurements to calculate the corrosion rate. The average corrosion rate in each specimen is instead calculated from the sum of accumulated dissolved iron measured in the condensed water and the amount of iron remaining in the corrosion films, as shown in Table 1. The corrosion film weight was measured by cutting small pieces of the test pipes and measuring the weight difference when the corrosion films were stripped off chemically. The SEM examination showed that the corrosion film consisted almost entirely of iron sulphide for Experiment 1 and of iron carbonate in Experiment 2 and 3. This makes it possible to calculate the amount of iron in the corrosion film.
Table 1. Results from top of line corrosion experiments

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>25</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>CO₂ partial pressure bar</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>H₂S partial pressure mbar</td>
<td>2</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Acetic acid in condensed water mg/l</td>
<td>300</td>
<td>430</td>
<td>3400</td>
</tr>
<tr>
<td>Condensation rate g/m² s⁻¹</td>
<td>0.006</td>
<td>0.058</td>
<td>0.062</td>
</tr>
<tr>
<td>Average iron content in condensed water mg/l</td>
<td>410</td>
<td>159</td>
<td>690</td>
</tr>
<tr>
<td>Corrosion rate from iron in condensed water mm/y</td>
<td>0.01</td>
<td>0.04</td>
<td>0.23</td>
</tr>
<tr>
<td>Corrosion rate from iron in corrosion film mm/y</td>
<td>0.16</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Total corrosion rate mm/y</td>
<td>0.17</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>Modelled corrosion rate mm/y</td>
<td>0.06</td>
<td>0.13</td>
<td>0.50</td>
</tr>
<tr>
<td>Dominating corrosion product</td>
<td>FeS</td>
<td>FeCO₃</td>
<td>FeCO₃</td>
</tr>
</tbody>
</table>

In Experiment 1 performed at 25 °C with 10 bar CO₂ and 2 mbar H₂S more than 90 % of the iron dissolved by corrosion remained in the corrosion film. This is much higher than in previous top of line corrosion experiments in pure sweet systems, where the corrosion films consist of iron carbonate [9]. In Experiment 1 the corrosion films consist primarily of iron sulphide, which precipitates much more easily than iron carbonate, and less dissolved iron is transported away with the condensed water. In Experiment 2 and 3 the corrosion films consisted mainly of iron carbonate, and less than half of the iron dissolved by corrosion remained in the corrosion film.

In Experiment 1 the corrosion film on the test pipes spalled and cracked when the specimens dried after being removed from the loop. In some areas most of the film fell off the specimens, while other pieces were kept with the film intact for further examination. Figure 3 shows the appearance of the corrosion film as seen by SEM examination on cross sections of the specimens. The left picture shows a detail of an area where the thick film is intact, while the right picture shows an area where the thick film has fallen off. In the areas where the thick film remained the film thickness was typically in the range 50 - 100 µm.

Element analysis in the SEM showed that the corrosion film in Experiment 1 consisted almost entirely of iron sulphide with an Fe:S ratio very close to 1:1. This applies for the whole film in the left picture in Figure 3, except for the very thin (5 - 10 µm) inner part of the film closest to the steel surface, which appears darker and more compact. This inner part of the film was identified as primarily iron carbonate. It is likely that this iron carbonate film has formed as a result of sulphide depletion in the condensed water close to the steel surface, as the small amounts of H₂S in the condensed water can be consumed by precipitation of iron sulphide in the outer part of the corrosion film.

Element analysis of the corrosion films in Experiment 2 and 3 showed that they consisted almost entirely of iron carbonate. Some iron sulphide was also present as small particles or a layer of small particles, in particular in Experiment 3, as seen as the light grey layer in the centre of the corrosion film in the right picture in Figure 3.
5  Effect of acetic acid and small amounts of H₂S

The results from Experiment 2 and 3 show clearly that the top of line corrosion rate increases with the concentration of acetic acid in the condensed water. Acetic acid affected top of line corrosion by increasing the solubility of iron in the condensed water. The observed effect of acetic acid on the top of line corrosion rate in the experiments fitted well with the calculated increase in iron solubility in the condensed water due the increase in acetic acid content.

In Experiment 1 at 25 °C iron sulphide was the dominating corrosion product, while the corrosion product was almost entirely iron carbonate in Experiment 2 and 3 at 80 °C. Calculation of the iron carbonate and iron sulphide solubility at the conditions for the three experiments show that the degree of supersaturation for iron carbonate and iron sulphide are almost equal for experiment 1, while the supersaturation of iron carbonate is about 10 times higher than for iron sulphide in Experiment 3 and 100 times higher for Experiment 2 with lower H₂S content. The presence of iron sulphide as the dominating corrosion product in the low temperature experiment is most likely related to the slow kinetics of iron carbonate formation at low temperatures, favouring precipitation of iron sulphide, which is rapid also at low temperatures. At high
temperature iron carbonate forms more rapidly and becomes the dominating corrosion product.

Predictions with the iron carbonate based top of line corrosion model [5] for the conditions in Experiment 1 at 25 °C, 10 bar CO₂, and 2 mbar H₂S gave a corrosion rate of 0.06 mm/y. The corrosion rate measured in the experiment was 0.17 mm/y, or about three times higher than the predicted top of line corrosion rate for pure sweet conditions. The principles of the sweet top of line corrosion model may still be applied since the protection seems to be governed by the thin iron carbonate film close to the steel surface. The top of line corrosion rate might be increased by the presence of small amounts of H₂S due to the effect of H₂S on removing Fe²⁺ ions from the solution and enabling faster iron dissolution. The main effect of H₂S in this system is then to precipitate iron dissolved by corrosion as a porous, non-protective iron sulphide film, and thereby act as a sink for Fe²⁺ ions. This can make it possible to dissolve more iron in the condensed water, resulting in a higher top of line corrosion rate than under pure sweet conditions.

For Experiment 2 and 3 at 85 °C the predicted top of line corrosion rates were higher than the experimental rates. This may be connected to the formation of partly protective surface films that reduced the corrosion rate further, as the model is based on the maximum amount of iron that can be dissolved in the condensing water, without taking further reduction by protective films into account.

It should be pointed out that the iron carbonate based top of line corrosion model can only be used for very small H₂S contents. At higher H₂S partial pressures the situation is totally dominated by iron sulphide, with entirely different mechanisms for top of line corrosion where the sweet top of line corrosion model does not apply.

5 Conclusions

The presence of acetic acid increases top of line corrosion by increasing the solubility of iron in the condensed water. The observed effect of acetic acid on the top of line corrosion rate in the experiments fitted well with the calculated increase in iron solubility in the condensed water due the increase in acetic acid content.

Experiments at 10 bar CO₂ and 1 - 2 mbar H₂S showed that iron sulphide was the dominating corrosion product at 25 °C despite the very low H₂S content, while iron carbonate dominated at 85 °C. The presence of iron sulphide as the dominating corrosion product at low temperature is related to the slow kinetics of iron carbonate formation at low temperatures. At high temperature iron carbonate forms more rapidly and becomes the dominating corrosion product.

The principles of the sweet top of line corrosion model may still be applied with this low H₂S content. At 25 °C the protection seems to be governed by a thin iron carbonate film close to the steel surface, but the corrosion rate was higher than predicted by the model since iron sulphide precipitation reduced the amount of dissolved iron in the condensed water. At 85 °C the corrosion rate was lower than predicted by the model. This may be an effect of partly protective iron carbonate corrosion films.
6 References


