

Top of Line Corrosion and Water Condensation Rates in Wet Gas Pipelines

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ABSTRACT

Condensation of water in wet gas pipelines can cause top of line corrosion when the water condensation rate is high or acetic acid is present in the gas. 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. Fluid flow model simulations have shown that different approaches for pipeline insulation can give widely different water condensation rates. Application of a top of line corrosion prediction model has demonstrated that such variations in water condensation rates can have a much larger effect on the top of line corrosion rate than variation in the CO₂ partial pressure.

Keywords: CO₂ corrosion, top of line corrosion, condensation, gas pipeline

INTRODUCTION

Water condensation in the upper part of wet gas pipelines can cause top of line corrosion. The condensing water is unbuffered with low pH, but becomes rapidly saturated and supersaturated with corrosion products, leading to increased pH and possibility for iron carbonate film formation. 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}, but it was only after top of line corrosion problems were encountered in wet gas pipelines a few years later that the problem caught the oil and gas industry's attention.

Several cases of top of line corrosion in gas pipelines were reported around 2000^{3,4}. Common factors for these cases were excessive cooling of the gas and high water condensation rates due to high inlet temperatures, little thermal insulation and in one of the cases flowing river water. Based on these cases it was suggested⁴ that top of line corrosion may become a problem when the water condensation rate is above 0.15 to 0.25 g/m²s. Also common for these cases was the presence of organic acid in the gas, with reported values of 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 solubility of iron and top of line corrosion.

Top of line corrosion is primarily a concern in wet gas pipelines with relatively high inlet temperatures, and then primarily in the first few kilometers of the pipeline, as the water condensation rate is rapidly reduced when the temperature decreases.

Water condensing in the top of a wet gas pipeline will form small droplets or a thin film on the steel surface. The condensed water 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 water¹. Most attempts to predict top of line corrosion have this dependence of water condensation rate and iron carbonate supersaturation as the starting point. The presence of acetic acid in the gas may increase the top of line corrosion rate considerably, as it increases the amount of iron which can be dissolved in the condensing water. Top of line corrosion has now been included in the Lipucor and Hydrocor models^{4,5}. Other researchers have developed models for top of the line corrosion from a more detailed mechanistic viewpoint^{6,7}.

The top of line corrosion model discussed in this paper was first presented by Olsen and Dugstad¹ and later by Nyborg et al², and has also been included in the corrosion module in the OLGA multiphase flow model⁸. This paper describes practical application of this model with emphasis on illustrating the effects of variations in water condensation rate, temperature and CO₂ partial pressure.

TOP OF LINE CORROSION MODEL

The top of line corrosion model used here is based on experiments with measurement of corrosion rate and water condensation rate in a loop system where moist gas with CO₂ was led through a carbon steel tube with external cooling^{1,2}. These experiments showed that the CO₂ top of line corrosion rate is limited by the water condensation rate and the amount of iron which can be dissolved in the condensed water. The condensing water has a low pH and high corrosivity, but corrosion products accumulate rapidly in the condensed water, and the pH increases. When the water condensation rate is not excessively high, the water becomes rapidly supersaturated with respect to iron carbonate, and precipitation of protective iron carbonate films can occur. The top of line corrosion then becomes limited by the amount of iron that can be dissolved in the condensed water, and is then proportional to the water condensation rate and the iron concentration in the condensed water phase².

The iron concentration in the condensed water is calculated as the solubility of Fe^{2+} ions multiplied by a supersaturation factor. The solubility of iron in the condensed water is a function of temperature and CO_2 partial pressure. At low temperature, the precipitation of iron carbonate is slow and the condensed water can be strongly supersaturated. The supersaturation decreases with increasing temperature. For systems with no H_2S , low acetic acid ($< 1 \text{ mM}$) and low to medium CO_2 ($< 3 \text{ bar}$) the supersaturation factor is given by:

$$S = 12.5 - 0.09 * T \text{ (}^\circ\text{C)}$$

This supersaturation factor is derived from experiments with measurement of the supersaturation in a bulk water phase in the presence of corroding steel⁹, giving 4 to 10 times supersaturation in the range 20 to 90 $^\circ\text{C}$ and highest at low temperature. Similar degrees of supersaturation have been observed in several corrosion loop experiments for bottom of line corrosion in the authors' laboratories. Measurements of condensation rates and corrosion rates in experiments with corrosion under condensing conditions indicate that the supersaturation factor for top of line corrosion can be somewhat lower². The actual supersaturation factor which should be used for the thin film of condensed water will depend on a large number of factors including the steel properties. The steel composition and microstructure will affect the type of solid products (carbides, alloying elements etc.) that accumulate on the surface and these solids will affect the transport of dissolved corrosion products to the film surface. Due to these uncertainties a conservative approach was used in the equation for the estimation of maximum supersaturation.

With this approach the top of line corrosion rate is calculated as the product of the water condensation rate and the concentration of dissolved iron in the condensed water². When the supersaturation factor above is used, the top of line corrosion rate then becomes:

$$\text{CR} = 0.004 * R_{\text{cond}} * C_{\text{Fe}} * (12.5 - 0.09 * T)$$

where CR is the top of line corrosion rate in mm/y, R_{cond} is the water condensation rate in $\text{g/m}^2\text{s}$, C_{Fe} is the solubility of iron in ppm wt and T is the temperature in $^\circ\text{C}$.

The solubility of iron is calculated as function of temperature, total pressure, CO_2 partial pressure and glycol concentration with an in-house pH and solubility program. The top of line corrosion rate predicted by this model is then dependent on temperature, CO_2 partial pressure and water/glycol condensation rate. The predicted top of line corrosion rate is not directly dependent on the flow velocity of the condensed water film or the gas flow velocity in this simplified model, but the gas flow rate will influence the water condensation rate. It is only for water condensation rates well above those usually found in wet gas pipelines that the water condensation rate is no longer the limiting factor for top of line corrosion.

Acetic acid or other organic acids which can be present in the gas will condense together with the water and thereby lower the pH of the condensed water phase and increase the amount of iron which can be dissolved in the condensing water. This gives an increase in the calculated iron solubility used in the model and hence an increased top of line corrosion rate. The amount of acetic acid in the produced gas can be estimated from a formation water analysis and the reservoir pressure and temperature. The amount of acetic acid condensing together with the water along the pipeline can

then be used to calculate the amount of iron which can be dissolved in the condensing water, which then gives the top of line corrosion rate.

The model only applies for pure sweet CO₂ systems. When even a few mbar of H₂S is present in the gas phase, the corrosion product films may be dominated by iron sulfide instead of iron carbonate, as iron sulfide is formed much more easily than iron carbonate. The mechanisms for iron sulfide formation are very different from a situation dominated by iron carbonate. The model described above is only valid when iron carbonate is the dominating corrosion product, and the validity limit with respect to H₂S is then given by the H₂S content necessary to switch to an iron sulfide dominated corrosion film. Top of line corrosion experiments with small amounts of H₂S present in addition to CO₂ are currently being performed in the authors' laboratories.

Glycol is often used to control hydrate formation in gas condensate pipelines. The vapor pressure of glycol is very low compared to water, and at moderate temperatures very little glycol will be present in the vapor phase. It has been discussed how much glycol will actually be available for condensation together with the water. Three-phase flow loop experiments with measurement of the droplet content in the gas have shown that the amount of droplets containing glycol in the gas phase probably will be high enough to keep the gas phase saturated with glycol². If equilibrium is achieved, the addition of glycol reduces the water vapor pressure and less water will therefore condense at a given cooling rate. However, the total amount of condensing liquid can be higher as glycol is mixed with the water. If glycol equilibrium is achieved, the water phase will contain a large fraction of glycol and this will reduce the iron solubility. Since an increased volume of the condensed aqueous phase is counteracted by reduced iron solubility, the estimated top of line corrosion rate will not be so much affected by the uncertainty in the condensation rate caused by the presence of glycol.

PRACTICAL APPLICATION OF THE TOP OF LINE CORROSION MODEL

Top of line corrosion rates up to 1.5 mm/y were reported in gas flowlines in the Tunu field, where excessive cooling occurred at river crossings³. The present top of line corrosion model has been applied for two different locations in these pipelines:

Zone 1: Temperature 72 °C, total pressure 90 bar,
 CO₂ partial pressure 4.2 bar, water condensation rate 1.3 g/m²s

Zone 2: Temperature 68 °C, total pressure 85 bar,
 CO₂ partial pressure 4.0 bar, water condensation rate 1.0 g/m²s

The iron solubility was calculated to 35 - 40 ppm and the supersaturation factor is 6.0 to 6.4 for these conditions. The top of line corrosion model then gives a predicted top of line corrosion rate of 1.2 mm/y for the Zone 1 conditions and 1.0 mm/y for Zone 2. This is close to the measured top of line corrosion rate in the field, which was 1.3 mm/y in Zone 1 and 1.5 mm/y in Zone 2³. The calculations were done without effect of acetic acid, as the amount of acetic acid in the gas was not known in detail. It was later reported that this field has 300 - 2100 ppm acetic acid in the produced water⁴, and this will increase the predicted top of line corrosion rate, probably with a factor 2 or more in this case.

The top of line corrosion model described by Pots has also been used for this field case, and resulted in a top of line corrosion rate of 1.5 mm/y⁵. This top of line corrosion model and the one described in this paper have given similar results also for other cases where they have been used in the design stage.

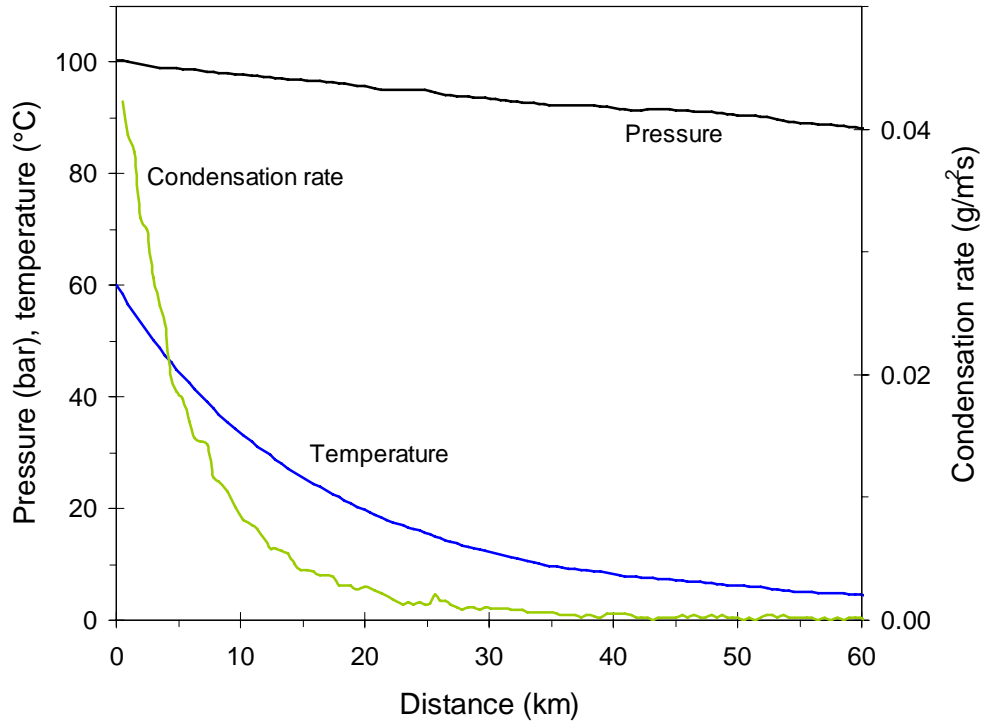


FIGURE 1. Pressure, temperature and condensation rate in a wet gas pipeline.

Figure 1 shows an example of profiles for pressure, temperature of the gas and water condensation rate calculated with a multiphase fluid flow simulator for a wet gas pipeline with 60 °C inlet temperature and 7 % CO₂ in the gas. The gas temperature profile is calculated by computing the heat flux from the fluid through the different layers in the pipe wall along the pipeline, and the water condensation rate is then calculated by assuming that the gas is always saturated with water vapor.

Figure 2 shows the iron solubility and the top of line corrosion rate for this case calculated by the present top of line corrosion model. The figure illustrates that the top of line corrosion rate is highest at the pipeline inlet where the water condensation rate is highest. The top of line corrosion rate decreases rapidly along the pipeline as a result of the rapid decrease in the water condensation rate, but the top of line corrosion rate does not decrease as fast as the water condensation rate, since both the iron solubility and the supersaturation factor increases when the temperature is decreased. For this case the predicted top of line corrosion rate is below 0.1 mm/y already at the pipeline inlet. Other cases with higher water condensation rates resulting from higher pipeline inlet temperatures or less insulation of the pipeline could result in higher top of line corrosion rates.

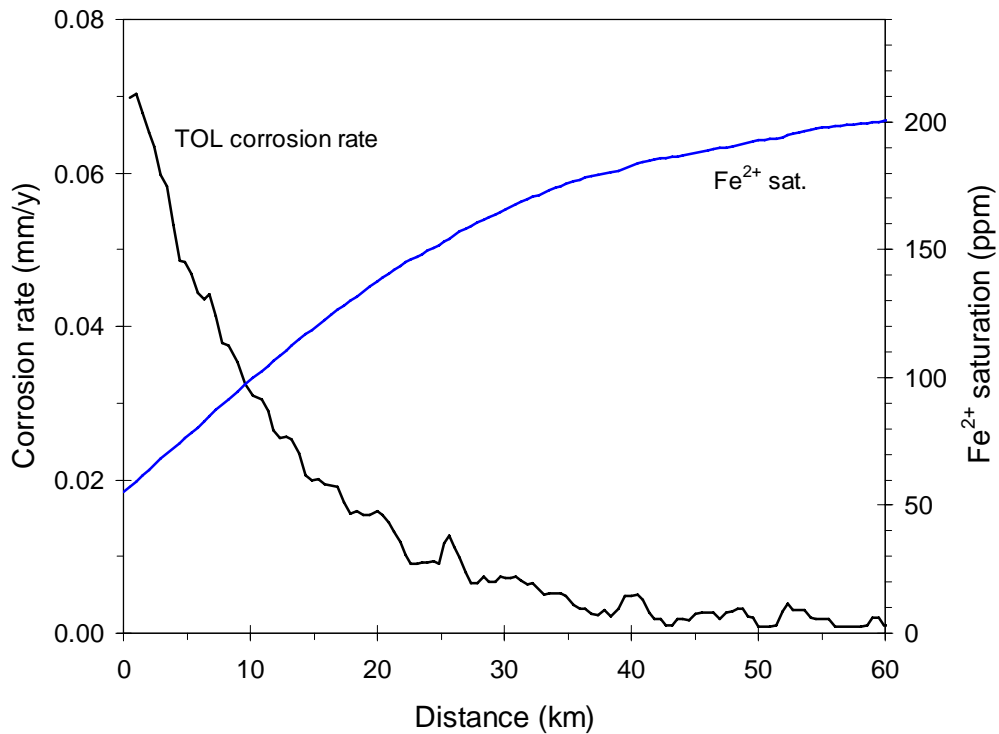


FIGURE 2. Iron solubility and predicted top of corrosion rate for the conditions in Figure 1.

The presence of moderate amounts of acetic acid in the gas can increase the calculated top of line corrosion rate by a factor of two to three for some cases. Solubility model calculations show that the presence of acetic acid corresponding to 400 mg/l acetate in the formation water could more than double the iron solubility and hence the top of line corrosion rate in a situation with 1 bar CO₂ partial pressure, while the same acetic acid concentration results in 40 % increase in iron solubility when the CO₂ partial pressure is 10 bar. This illustrates that the effect of acetic acid is most pronounced for cases with low CO₂ partial pressure, where the effect of acetic acid on the iron solubility is highest. Top of line corrosion experiments performed at 1 bar CO₂ for the Ormen Lange development showed that presence of 300 to 350 mg/l acetic acid in the condensed water increased the top of line corrosion rate with a factor around 3 compared to experiments without acetic acid¹⁰.

EFFECT OF VARIATIONS IN MODEL INPUT PARAMETERS

Variation in water condensation rate

The water condensation rate and thereby the top of line corrosion rate will vary not only with the temperature and the gas production rate, but also with the type of pipeline insulation. Different types of pipeline coating with different thermal insulation properties can give large differences in the water condensation rate for otherwise similar cases.

Temperature profiles and values for overall heat transfer coefficient and water condensation rates were calculated for different types of pipeline coating with a commonly used multiphase fluid flow simulator. The calculated water condensation rates were then used as input in the present top of line corrosion model. The calculated water condensation rates and predicted top of line corrosion rates are shown in Table 1. Four different commonly used pipeline coatings were used for a 28" wet gas pipeline case with inlet temperature 80 °C, inlet pressure 100 bar, 2 % CO₂ in the gas, and gas flowrate 20 MSm³/d. Organic acid was not considered in this exercise.

TABLE 1. Different pipeline coatings, 80 °C, 2 bar CO₂ partial pressure.

Coating	Overall heat transfer coefficient W/m ² K	Water condensation rate g/m ² s	Top of line corrosion rate mm/y
0.5 mm fusion bonded epoxy	283	1.26	0.74
6 mm coal tar enamel	100	0.46	0.25
4 mm 3-layer polypropylene	53	0.24	0.13
8 mm polypropylene	28	0.13	0.07
4 mm PP + 40 mm concrete	21	0.10	0.05

Hot gas pipelines are often coated with a three layer polypropylene coating, giving an overall heat transfer coefficient around 50 W/m²K for the example case used here with 4 mm coating. Increasing the coating thickness to 8 mm decreases the heat transfer coefficient to below 30 W/m²K in this particular case. The heat transfer coefficient is dependent on the geometry of the pipeline and the actual thermal conductivity of the different materials, so the actual values for the overall heat transfer coefficient may be somewhat different for other cases. The purpose here is to demonstrate that different pipeline coating options can give large differences in water condensation rates and hence a large variation in predicted top of line corrosion rates.

Another commonly used coating type for moderate temperatures is coal tar enamel, giving higher overall heat transfer coefficient since this material has higher thermal conductivity. For some deep water pipelines a thin 0.5 mm fusion bonded epoxy coating only has been specified. This gives a much higher heat transfer coefficient, 280 W/m²K in this case. On the other hand, a thick concrete coating which is often used can give a very low heat transfer coefficient, down to 20 W/m²K for the case shown here. These different coating types will give very different thermal characteristics, with large variation in water condensation rate and hence in top of line corrosion rate. In the example used here, the calculated top of line corrosion rate varies from 0.05 to 0.74 mm/y, or with a factor 15, only by varying the pipeline coating for otherwise identical conditions. Areas with damage in the coating can give cold spots with higher water condensation rates locally.

The water condensation rate and the top of line corrosion rate can be reduced in the design stage by either using better thermal insulation in the first part of the pipeline where most of the cooling takes place or by cooling the fluid before the inlet of the carbon steel pipeline. An example of a field where choice of pipeline coating was used actively to control top of line corrosion is the Ormen Lange

field, where a maximum overall heat transfer coefficient of $40 \text{ W/m}^2\text{K}$ was specified in order to limit the top of line corrosion rate to 0.1 mm/y . This was achieved by applying an 8 mm polypropylene coating and was based on detailed modeling of water condensation rates and an extensive experimental program¹⁰ to study top of line corrosion under conditions representative for this pipeline where acetic acid is expected to be present in addition to CO_2 .

Variation in temperature

When the temperature of the gas decreases, the water condensation rate decreases sharply because both the cooling rate and the water vapor content of the gas decreases. However, both the iron solubility and the supersaturation factor in the top of line corrosion model increases when the temperature is decreased. This means that the predicted top of line corrosion rate does not fall as sharply as the water condensation rate. This is illustrated in Figure 1 and 2. Table 2 shows the case with 4 mm polypropylene coating above for different temperatures.

TABLE 2. Different temperatures, 2 bar CO_2 , 4 mm polypropylene coating.

Temperature °C	Water condensation rate $\text{g/m}^2\text{s}$	Iron solubility ppm	Supersaturation factor	Top of line corrosion rate mm/y
90	0.37	20	4.4	0.14
80	0.24	25	5.3	0.13
60	0.10	37	7.1	0.11
40	0.03	57	8.9	0.05
30	0.01	72	9.8	0.03

For this case the top of line corrosion rate drops to very low values below $40 \text{ }^\circ\text{C}$ because the water condensation rate becomes very low. However, it should be remembered that the pipeline coating is important also at these low temperatures. When only a 0.5 mm thick fusion bonded epoxy coating is used in the example above, the predicted top of line corrosion rate increases to 0.17 mm/y at $30 \text{ }^\circ\text{C}$ since the cooling rate and hence the water condensation rate is much higher with this thin coating. This illustrates that lack of pipeline insulation can give significant top of line corrosion even at this low temperature.

Variation in CO_2 partial pressure

In the top of line corrosion model the corrosion rate is proportional to the water condensation rate and the iron solubility. When the CO_2 partial pressure increases the iron solubility increases and thereby also the top of line corrosion rate. Table 3 shows the variation in iron solubility and predicted top of line corrosion rate for the case described above. The table shows that an increase in CO_2 partial pressure by a factor 20 gives an increase in the predicted top of line corrosion by a factor around 3. This illustrates that variations in CO_2 content has a less pronounced effect on the top of line corrosion rate than variations in water condensation rate.

TABLE 3. Different CO₂ partial pressures, 80 °C, 4 mm polypropylene coating.

CO ₂ partial pressure bar	Water condensation rate g/m ² s	Iron solubility ppm	Top of line corrosion rate mm/y
0.5	0.24	16	0.08
2	0.24	25	0.13
5	0.24	33	0.18
10	0.24	42	0.22

CONCLUSIONS

The top of line corrosion in wet gas pipelines is limited by the amount of iron which can be dissolved in the thin film of water condensing in the top of the pipeline. The top of line corrosion rate can then be modeled as proportional to the water condensation rate, the iron carbonate solubility and a supersaturation factor. When acetic acid is present in the gas the solubility of iron in the condensed water phase is increased, and this increases the top of line corrosion. The model is not valid when H₂S is present in the gas, as iron sulfide then is formed instead of iron carbonate. Model calculations have shown that different approaches for pipeline insulation can give widely different water condensation rates and thereby large differences in the top of line corrosion rate. This has a much more pronounced effect on the top of line corrosion rate than variations in the CO₂ partial pressure.

REFERENCES

1. Stein Olsen, Arne Dugstad: "Corrosion under Dewing Conditions", CORROSION/91, Paper No. 472, (Houston, TX: NACE, 1991).
2. Rolf Nyborg, Arne Dugstad, Liv Lunde: "Top-of-the-Line Corrosion and Distribution of Glycol in a Large Wet Gas Pipeline", CORROSION/93, Paper No. 77, (Houston, TX: NACE, 1993).
3. Yves Gunaltun, D. Supriyam, J. Achmad: "Top of Line Corrosion in Multiphase Gas Lines. A Case History", CORROSION/99, Paper No. 99036, (Houston, TX: NACE International, 1999).
4. Yves Gunaltun, Dominique Larrey, "Correlation of Cases of Top of Line Corrosion with Calculated Water Condensation Rates", CORROSION/2000, Paper No. 00071, (Houston, TX: NACE International, 2000).
5. Bert Pots, Edwin Hendriksen, "CO₂ Corrosion under Scaling Conditions - The Special Case of Top-of-Line Corrosion in Wet Gas Pipelines", CORROSION/2000, Paper No. 00031, (Houston, TX: NACE International, 2000).

6. Frédéric Vitse, Srdjan Nestic, Yves Gunaltun, Dominique Larrey de Torreben, Pierre Duchet-Suchaux, "Mechanistic Model for the Prediction of Top-of-the-Line Corrosion Risk", CORROSION/2003, Paper No. 03633, (Houston, TX: NACE International, 2003).
7. Ziru Zhang, Dezra Hinkson, Marc Singer, Srdjan Nestic, "A Mechanistic Model of Top of the Line Corrosion", CORROSION/2007, Paper No. 07556, (Houston, TX: NACE International, 2007).
8. Rolf Nyborg, Peter Andersson and Magnus Nordsveen: "Implementation of CO₂ Corrosion Models in a Three-Phase Fluid Flow Model", CORROSION/2000, Paper No. 48 (Houston, TX: NACE International, 2000).
9. Arne Dugstad: "The Importance of FeCO₃ Supersaturation on the CO₂ Corrosion of Carbon Steels", CORROSION/92, Paper No. 14, (Houston, TX: NACE International, 1992).
10. Tore Roberg Andersen, Anne Marie K. Halvorsen, Arne Valle, Gry Pedersen Kojen, Arne Dugstad: "The Influence of Condensation Rate and Acetic Acid Concentration on TOL Corrosion in Multiphase Pipelines", CORROSION/2007, Paper No. 07312, (Houston, TX: NACE International, 2007).