

INHIBITION OF MULTIPHASE WET GAS CORROSION

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ABSTRACT

Corrosion rates at the top and bottom of the pipe have been measured in wet gas multiphase flow at carbon dioxide partial pressures of 0.46 MPa and 0.79 MPa and temperatures of 40 C and 60 C in a high pressure 10-cm diameter system. Gas velocities up to 30 m/s and liquid velocities up to 0.5 m/s were used. The liquid consisted of a mixture of de-ionized water and low viscosity oil at two water cuts of 80% and 40%, and carbon dioxide was used in the gas phase. Corrosion inhibition studies were carried out at 50 ppm and 100 ppm dosage levels. The inhibitor used was an oleic imidazoline active compound dissolved in isopropyl alcohol and water.

The corrosion rate was found to increase with increase in gas velocity, liquid velocity, temperature and CO₂ partial pressure. The corrosion rate at the top of the pipe is negligible up to a gas velocity of 20 m/s. However, at a gas velocity of 30 m/s, there is substantial and measurable corrosion at the top of the pipe. This was attributed to wave spreading.

Addition of inhibitors reduced the corrosion rate at the top and bottom of the pipe significantly. However, the corrosion rates are not negligible.

INTRODUCTION

The forecast for the consumption of natural gas shows an upward trend. The Gas Research Institute estimates that a significant portion of the demand will be met by deep water systems by 2005. A typical natural gas is composed of several hydrocarbon compounds, water vapor, carbon dioxide, nitrogen and sometimes compounds such as hydrogen sulfide. In natural gas pipelines, reduction in

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temperature and pressure results in condensation of moisture and hydrocarbons along the length of the pipeline. Conventional production involves removal of liquid and transportation of dry gas. Economic considerations require reduction in capital costs and this involves development of low cost, technically advanced, equipment and hardware to replace conventional production facilities (Jones et al., 1996)¹. The development cost of gas/condensate fields can be significantly reduced if multiphase transportation of gas-liquid mixtures is employed. As more reserves are discovered offshore in deeper waters, long distance multiphase flow lines are becoming increasingly common. These are expected to be in excess of hundreds of miles in the near future.

There is also an extensive use of carbon steels as materials of construction for pipes in the oil and gas industries. These steels are cheap materials of construction for many applications and therefore involve lesser capital investment, but they usually exhibit poor corrosion resistance properties. Corrosion in wet natural gas pipelines is a major problem facing the oil and natural gas industry. During the later years of gas production, water break-in occurs as a result of reduction in pressure of the reservoir itself, causing increased corrosion.

King (1981)² proposed corrosion mechanisms for the cause of internal corrosion of hydrocarbon pipelines. These include carbon dioxide corrosion, sulfide corrosion, microbiological corrosion, acid corrosion and erosion corrosion. Since corrosion is an electrochemical reaction with an aqueous phase as the conducting medium, the quantity of water present in the system is a common factor in all the corrosion mechanisms.

The term 'flow related corrosion' was first introduced by Sydberger (1987)³. Three corrosion mechanisms were described: convective mass transfer controlled corrosion, phase transport controlled corrosion and erosion corrosion.

Investigation into the mechanism of carbon dioxide corrosion on carbon steel under different conditions of pH, temperature, pressure and oil-water fractions have been carried out in the past. Some relevant works are those by de Waard and Milliams (1975)⁴, Ikeda et al. (1985)⁵, de Waard, Lotz and Milliams (1991)⁶, de Waard and Lotz (1993)⁷ and de Waard, Lotz and Dugstad (1995)⁸. They have proposed various models to predict carbon dioxide corrosion of carbon steel. Most of these studies were however conducted in stirred beakers, autoclaves or single phase pipe flow.

Bockris et al. (1962)⁹ showed that the rate-controlling step depended upon the pH. The overall reaction is given by:



For $pH < 4$, which is typical of gas wells, Nesic (1995)¹⁰ proposed that the surface reduction of hydrogen ions to hydrogen is dominant.

Studies on corrosion under dewing conditions were carried out by Olsen and Dugstad (1991)¹¹. An autoclave was used for stagnant conditions and for flowing conditions a 16 mm gas loop was used. Higher condensation rates resulted in higher corrosion rates and traditional inhibitors were found not to reduce the corrosion in the vapor phase significantly.

A risk analysis model was developed to detect unacceptable down hole corrosion in gas-condensate wells by Riekels et al. (1997)¹² based on field data. The corrosion rates were found to be a strong function of water to hydrocarbon ratio. Maximum pit penetration rates up to 225 mpy (5.71 mm/y) were observed.

The University of Southern Louisiana (USL) corrosion model for gas-condensate wells has been designed to estimate the tubing life of a gas condensate well containing CO_2 (Perkins et al., 1996)¹³. Field data from 12 gas condensate wells in the Gulf of Mexico was used to develop this model and an attempt has been made to extrapolate this model to other systems. The final equation was:

$$T(\text{months}) = 1.78 \left(\frac{r_1^{1.2}}{U_0^{0.8} \delta_{l+b}} \right) + 13.8 \quad (2)$$

where, $T(\text{months})$ = predicted life of tubing in months
 r_1 = thickness of the tube (cm)
 δ_{l+b} = thickness of the laminar and buffer sub-layers (cm)
 U_0 = bulk average velocity of the liquid film (m/s)

This correlation holds only when the corrosion process is mass transfer controlled and overpredicts the corrosion rate for reaction controlled mechanisms and underpredicts if there is erosion corrosion.

Gopal and Jepson (1995)¹⁴ described the effect of multiphase flow on corrosion. In highly turbulent flows, enhanced corrosion rates were observed due to erosion of corrosion product layers.

The flow patterns that are encountered in wet gas systems are mist flow, annular-mist flow, and stratified flow. Figure 1 shows the various flow patterns observed. At very high gas velocities and low liquid contents, a mist flow can be achieved. However, it is usual for liquid droplets to coalesce and drain to the bottom to form a thin liquid layer. In annular-mist flow the liquid flows in the form of an annular ring and the gas flows through the core. A true annular liquid film may be difficult to achieve and a crescent shaped film is observed at the bottom half of the pipe with liquid flowing as streaks at the top. Stratified flow is observed at lower gas.

Corrosion studies have not been carried out in flow conditions similar to those observed in wet gas systems. This paper discusses the corrosion results at the top and bottom of a high pressure, wet gas flowline at different liquid and gas velocities, for different pressures, temperatures and water cuts. The effect of inhibition on corrosion rates at the top and bottom are also discussed.

EXPERIMENTAL SETUP AND PROCEDURE

The flow loop is a unique 18-m long, 10-cm diameter, high pressure, high temperature, inclinable system. A schematic diagram of this system is shown in Figure 2. The entire flow loop is manufactured from 316 stainless steel. A predetermined oil-water mixture is stored in a 1.4 m³ tank which serves as a storage tank as well as a separation unit for the multiphase gas-oil-water mixture. The tank has a heating jacket around it. Heater oil is heated in a separate heating tank using four 15KW heaters and pumped to the heating jacket, to heat the contents of the storage tank. Liquid is moved through this system by a 3-15 kW variable speed centrifugal pump. The flow is then controlled within a range of 0 to 100m³/hr with the variable speed pump in conjunction with a recycle stream. Flow rate is metered with an inline turbine meter.

A fresh gas feed line at 2 MPa pressure supplies carbon dioxide gas from a 20,000 kg storage tank. This line is used initially to pressurize the system and for calibration purposes when the system is run with once through gas. In normal operation, gas is continuously circulated through the system at desired speeds by a Moyno-“Tri Phaze system”, multiphase progressing cavity pump, driven by a variable speed motor through a reduction gear system. The actual velocity of the gas is measured using a pitot tube mounted along the test section. An exhaust line with a knock out drum is used to vent gas from the system when required.

At the start of the experiments, the system is pressurized to the required level. The liquid pump is turned on and a required flow rate is set. The recirculating gas pump is then turned on and the required flow rate is set. The gas-liquid mixture enters the test section where corrosion measurements are made and is then returned to the storage tank where the mixture is separated. After separation, the gas is then fed to the recirculating pump.

Description of the Test Section

The test section is a 0.10 m diameter, 2 m long schedule 80 stainless steel pipe. A schematic of the section is given in Figure 3. The two pairs of ports at the top and at the bottom are used to insert flush-mountable electrical resistance probes for corrosion rate measurements. ER probes from Metal samples Inc. are used with an automatic data logging system from Cortest Inc. for accurate corrosion data logging. The pressure tappings are connected to a pressure transducer, and are used to measure the pressure drop across the pitot tube. There are ports for inserting the pH probe, the pitot tube and the thermocouple.

TEST MATRIX

De-mineralized water and a 2 cP oil (specific gravity = 0.8) are used as the liquid phase and CO₂ is used as the gas phase. Table 1 shows the test matrix. The oil used was a refined oil with no paraffin or asphaltene and is comparable to hydrocarbons found in condensate lines. The inhibitor used consists of 25% imidazoline, 70% isopropyl alcohol and 5% de-ionized water.

RESULTS AND DISCUSSION

The effects of gas velocity, liquid velocity, pressure, temperature and water cut on the corrosion rate at the top and bottom of the pipe are first discussed. Then, the effect of adding inhibitor to the multiphase mixture is analyzed.

Effect of Superficial Gas Velocity

Figure 4 shows the effect of superficial gas velocity on the corrosion rate at the bottom and top of the pipe for a superficial liquid velocity of 0.2 m/s, a carbon dioxide partial pressure of 0.46 MPa and a temperature of 40 C for 80% water cut. It is seen that the corrosion rate increases slightly at the bottom of the pipe from 101 mpy (2.56 mm/y) to 112 mpy (2.84 mm/y) and then to 117 mpy (2.97 mm/y) as the gas velocity is increased from 10 to 20 and then 30 m/s. The corrosion rate at the top of the pipe is 2 mpy (0.05 mm/y) at a gas velocity of 10 m/s. It then increases slightly to 6 mpy (0.15 mm/y) at 20 m/s and then increases dramatically to 95 mpy (2.41 mm/y) at 30 m/s. A similar trend was observed for higher liquid velocities and higher gas pressure.

From the results obtained, it is seen that gas velocity has a slight effect on the corrosion rate at the bottom of the pipe. This is because the liquid film velocity increases due to the enhanced turbulence generated by the increased gas velocity. The increase in corrosion rate at the top of the pipe is due to spreading of the liquid film around the circumference. Video images clearly show the effect of increasing gas velocity on film spreading around the pipe. There is not enough turbulence and secondary flow up to a gas velocity of 20 m/s to spread the film completely around the pipe. A gas velocity of about 30 m/s is needed to achieve this and cause measurable and substantial corrosion.

Effect of Superficial Liquid Velocity

The effect of superficial liquid velocity on the corrosion rate at the top and bottom of the pipe at a temperature of 40 C, 80% water cut and a carbon dioxide partial pressure of 0.46 is shown in Figures 5. It is seen from Figure 5 that there is a slight effect of liquid velocity on the corrosion rate at the bottom of the pipe. For example, at 30 m/s, increasing the liquid velocity from 0.2 m/s to 0.5 m/s, results in an increase in corrosion rate from 117 mpy (2.97 mm/y) to 136 mpy (3.45 mm/y). When the pressure is increased to 0.79 MPa, a slightly higher effect of liquid velocity is observed. The increase at lower gas velocities is similar. Increasing the liquid flow rate causes more water to be present in the pipe at higher velocities. This results in a higher turbulence-enhanced mass transfer rate.

It is seen that liquid velocity has negligible effect on the corrosion rate at the top of the pipe. For example, it is seen from Figure 5 that the corrosion rate values at the top of the pipe are negligible and 2 mpy (0.05 mm/y) for liquid velocities of 0.2 and 0.5 m/s at a gas velocity of 10 m/s. At a higher gas velocity of 30 m/s, the corrosion rate increases from 100 mpy (2.54 mm/y) to 110 mpy (2.79 mm/y). The liquid velocity has negligible effect on the corrosion at the top of the pipe over the velocities studied, since the film spreading is primarily controlled by the gas flow rate. Once the gas flow rate is set, increasing the liquid flow rate does not seem to affect the corrosion at the top.

Effect of Water Cut

The effect of water cut on corrosion rate at the top and bottom of the pipe is shown in Figure 6 for a liquid velocity of 0.2 m/s at 0.46 MPa and 40 C. It is seen that water cut has a significant effect on corrosion rate at the bottom of the pipe. For example, at a superficial gas velocity of 20 m/s, the corrosion rate at the bottom decreases from 112 mpy (2.84 mm/y) to 61 mpy (1.54 mm/y) when the water cut decreases from 80 to 40%. The results at the other gas velocities are similar.

When the corrosion rates at the top of the pipe are compared, it is seen that the effect of water cut is negligible for gas velocity up to 20 m/s. The measured corrosion rate is itself negligible up to this gas velocity. As mentioned previously, there is not enough turbulence to spread the liquid film completely around the pipe and negligible corrosion occurs at the top. At a gas velocity of 30 m/s, there is now enough turbulence to spread the liquid completely around the pipe and cause measurable corrosion to occur. However, when there is more oil in the liquid, the amount of oil in the film also increases. Hence, substantial reduction in corrosion rate from 95 mpy (2.41 mm/y) to 11 mpy (0.28 mm/y) is seen for a change in water cut from 40% to 80%. Similar results are observed at a higher liquid velocity and higher pressure at both the top and bottom of the pipe.

Effect of Pressure

The effects of increasing carbon dioxide partial pressure on the corrosion rate at the bottom of the pipe is shown in Figure 7 for a liquid velocity of 0.5 m/s at a temperature of 40 C and 80% water cut. It is seen that the corrosion rate increases with increase in carbon dioxide partial pressure. For example, at a gas velocity of 10 m/s, the corrosion rate increases from 110 mpy (2.79 mm/y) to 155 mpy (3.93 mm/y) as the pressure is increased from 0.46 MPa to 0.79 MPa. Similar results are observed at other conditions. The increase in corrosion rate with pressure is due to lowered pH associated with greater dissolution of carbon dioxide. The variation of corrosion rate with carbon dioxide partial pressure is similar to the variation of pH with pressure.

Effect of Temperature

The effect of temperature on corrosion rate at the bottom of the pipe is shown in Figure 8 for a liquid velocity of 0.2 m/s at 0.79 MPa and 80% water cut. A significant increase in corrosion rate with increasing temperature can be seen. For example, at a gas velocity of 20 m/s, the corrosion rate increases from 140 mpy (3.55 mm/y) to 306 mpy (7.77 mm/y) when the temperature increases from 40 C to 60 C. The corrosion rate increases with temperature due to increased reaction rate. The pH decreases due to increase in temperature but the kinetic effect is seen to be stronger than the thermodynamic effect. The kinetic effect increases with increasing temperature.

Effect of Corrosion Inhibition

There is a substantial reduction in corrosion rate with addition of inhibitor, both at the top and bottom of the pipe. Figures 9 through 11 depict the reduction in corrosion rate at different gas velocities upon addition of inhibitor at 40 C, 80% water cut.

Figure 9 shows the reduction in corrosion rate with the addition of 50 and 100 ppm of corrosion inhibitor for a liquid velocity of 0.2 m/s and carbon dioxide partial pressure of 0.46 MPa. It is seen that there is a substantial reduction in corrosion rate upon addition of 50 ppm of inhibitor. For example, at 30 m/s, the corrosion rate decreases from the blank value of 117 mpy (2.97 mm/y) to 32 mpy (0.81 mm/y). Further addition of another 50 ppm of inhibitor results in a negligible decrease in corrosion rate to 24 mpy (0.60 mm/y). Similar results are seen from for liquid velocity of 0.5 m/s.

The inhibitor is seen to be effective at the top of the pipe as well. As can be seen from Figure 10, for a liquid velocity of 0.2 m/s and a gas velocity of 30 m/s, at a pressure of 0.46 MPa, the corrosion rate decreases from a blank value of 95 mpy (2.56 mm/y) to 24 mpy (0.60 mm/y) and then to 20 mpy (0.50 mm/y) with addition of 50 and 100 ppm of inhibitor respectively. A similar decrease is observed for a liquid velocity of 0.5 m/s.

From these results, it is seen that the addition of 50 ppm inhibitor lowers the corrosion rate to the maximum possible value. The corrosion rate, however, is not negligible. Further addition of inhibitor has negligible effect.

The reduction of corrosion rate at the bottom of the pipe with the addition of inhibitor at a carbon dioxide partial pressure of 0.79 MPa and a liquid velocity of 0.2 m/s is shown in Figures 11. Substantial reduction in corrosion rate is seen with the addition of 50 ppm of inhibitor. For example, at a gas velocity of 30 m/s, the corrosion rate decreases from 150 mpy (3.81 mm/y) to 71 mpy (1.80 mm/y). In this case, a further addition of 50 ppm of inhibitor further decreases the corrosion rate to 44 mpy (1.11 mm/y). It appears that there is potential for more inhibition at the higher pressures and this reduces the corrosion rate even further.

The reduction of corrosion rate at the bottom of the pipe for 40% water cut, at a liquid velocity of 0.5 m/s, a carbon dioxide partial pressures of 0.46 MPa and a temperature of 40 C is shown in Figure 12. Again, the same trend as before is seen, with substantial corrosion rate reduction. For example, the corrosion rate at a gas velocity of 30 m/s, is reduced from 117.6 mpy (2.98 mm/y) to 38.8 mpy (0.98 mm/y) upon addition of 50 ppm inhibitor.

CONCLUSIONS

The following conclusions are made:

- Corrosion rate increases with gas velocity at the bottom of the pipe due to increased turbulence. The corrosion at the top of the pipe is negligible until enough liquid is spread around the pipe at a gas velocity of 30 m/s and then it becomes substantial.
- Increase in liquid velocity causes more corrosion at the bottom of the pipe. This is probably due to higher liquid film velocity. The corrosion at the top is not affected by the liquid velocity.
- Water cut has a significant effect on corrosion rate at the bottom of the pipe. At lower water cuts, there is more oil wetting the pipe wall resulting in reduced corrosion rates.
- Corrosion rate increases with carbon dioxide partial pressure due to decreasing pH.
- Temperature increases the corrosion rate due to enhanced reaction rate.
- At a carbon dioxide partial pressure of 0.46 MPa, addition of 50 ppm inhibitor reduced the corrosion rate significantly, but not to negligible values. Further addition of inhibitor had no significant effect on corrosion. At a higher pressure of 0.79 MPa, increasing the inhibitor concentration to 100 ppm reduced the corrosion rate further, but the rates were still not negligible.

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TABLE 1

TEST MATRIX

<u>PARAMETER</u>	<u>CONDITIONS</u>
Water cut	40%, 80 %
Temperature	40, 60 C
Pressure	0.27 and 0.79 MPa
Liquid velocity	0.2 and 0.5 m/s
Gas velocity	10, 20, 30 m/s
Inhibitor concentration	0ppm, 50ppm , 100ppm

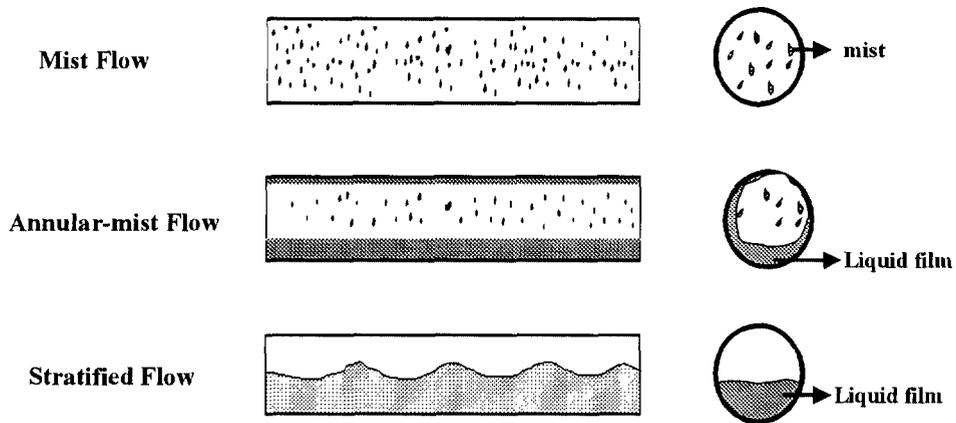


Figure 1. Flow patterns observed in wet gas flowlines

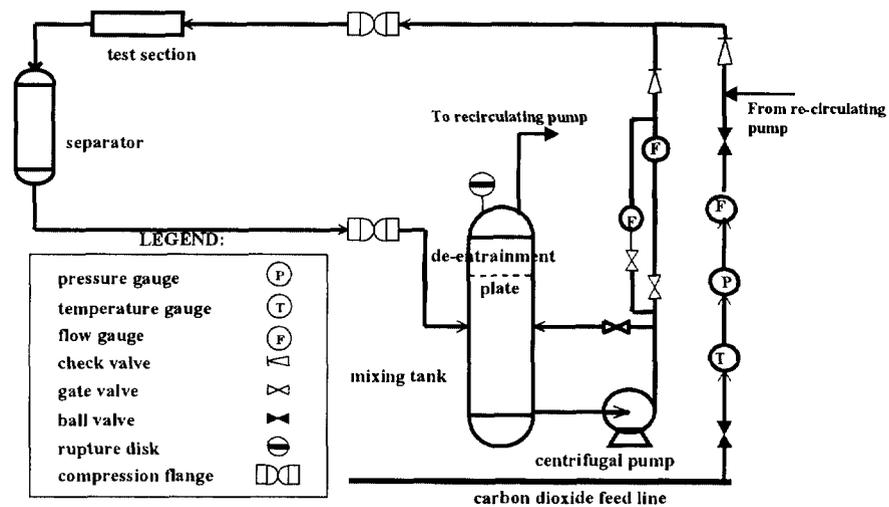


Figure 2: Schematic of the high-pressure inclinable flow loop system

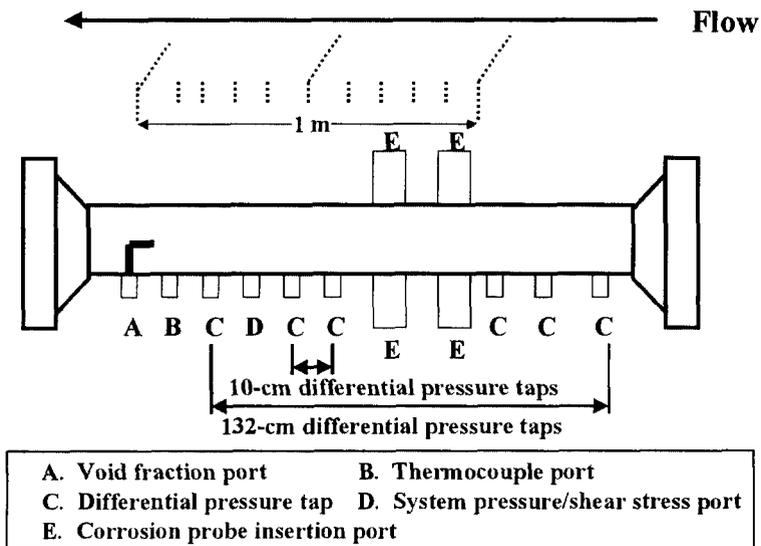


Figure 3: Schematic of the test section

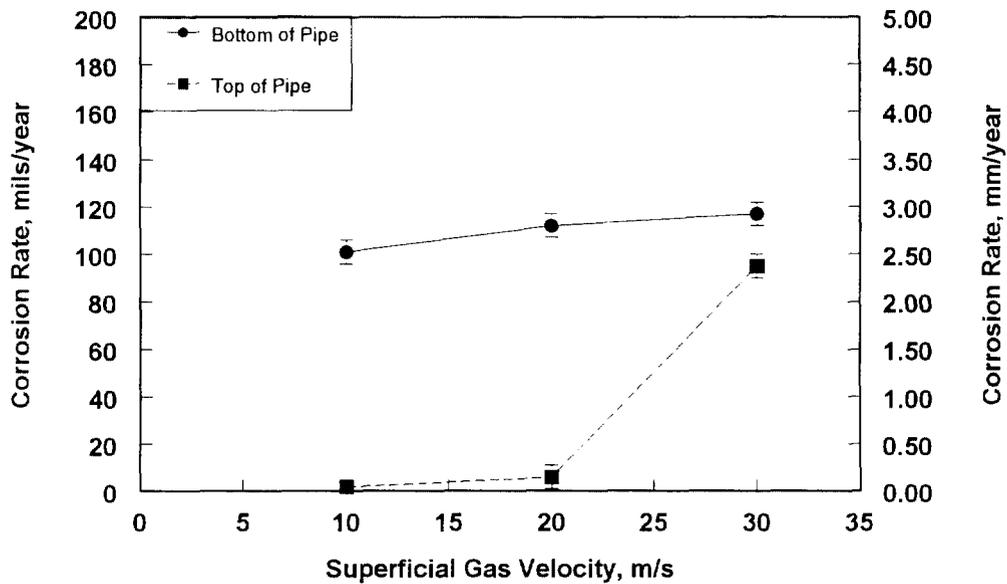


Figure 4. The effect of gas velocity on the corrosion rate at the top and bottom of the pipe for a superficial liquid velocity of 0.2 m/s at 0.46 MPa, 40 C and 80% water cut

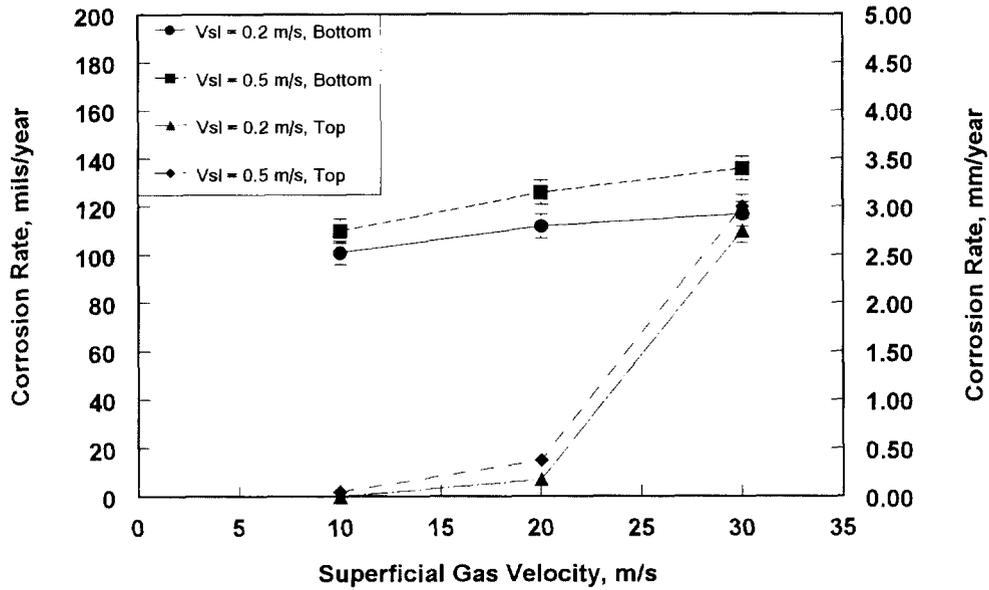


Figure 5. The effect of superficial liquid velocity on the corrosion rate at the top and bottom of the pipe at 0.46 MPa, 40 C and 80% water cut

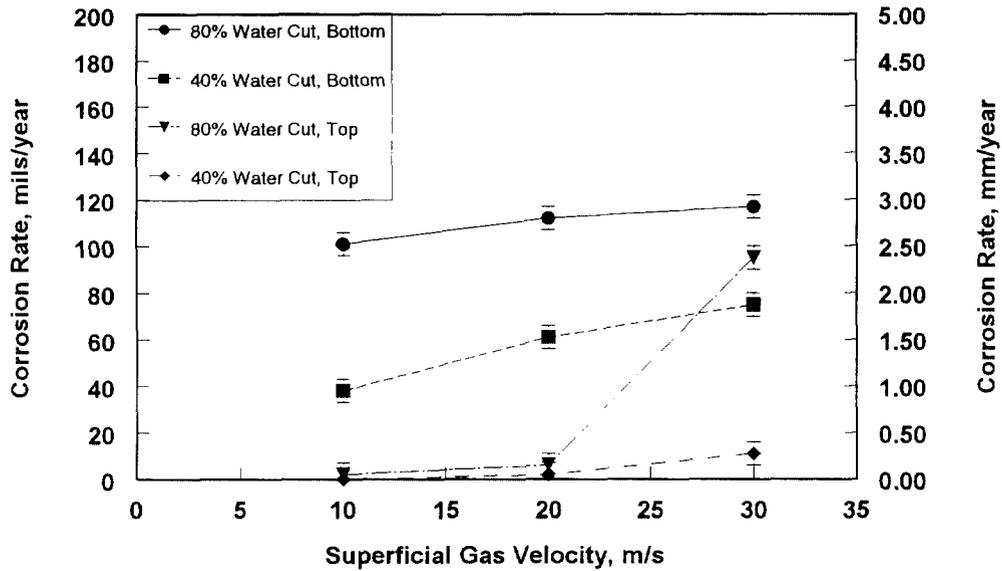


Figure 6. The effect of water cut on corrosion rates at the top and bottom of the pipe for a superficial liquid velocity of 0.2 m/s, a gas pressure of 0.46 MPa and 40 C

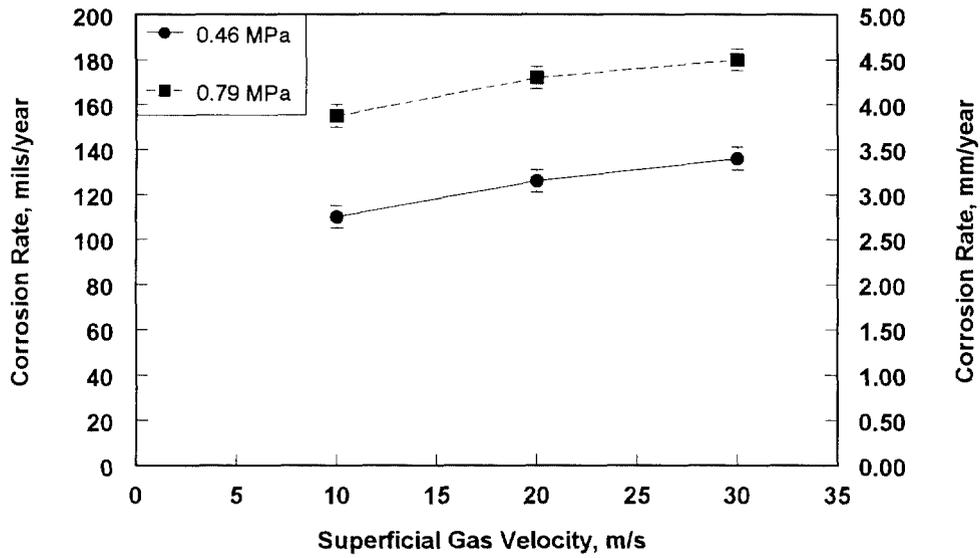


Figure 7. Effect of pressure on corrosion rate at the bottom of the pipe for a superficial liquid velocity of 0.5 m/s at 40 C and 80% water cut

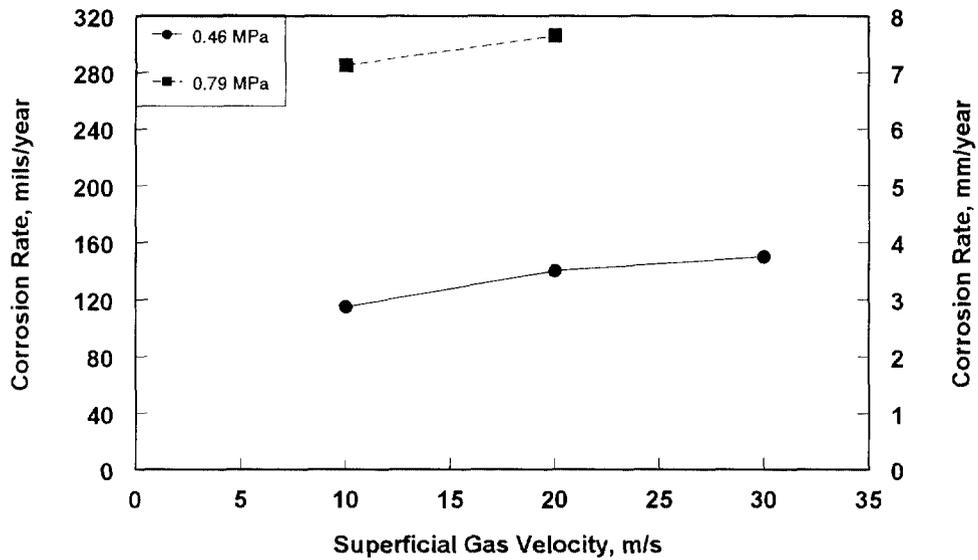


Figure 8. The effect of temperature on the corrosion rate at the bottom of the pipe for a superficial liquid velocity of 0.2 m/s at 0.79 MPa and 80% water cut

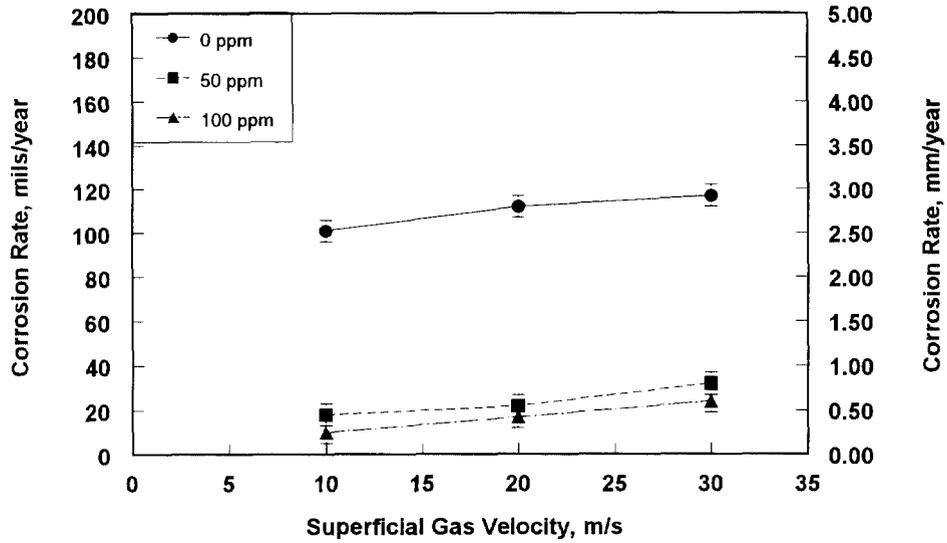


Figure 9. The effect of inhibitor on corrosion rate at the bottom of the pipe for a superficial liquid velocity of 0.2 m/s at 0.46 MPa, 40 C and 80% water cut

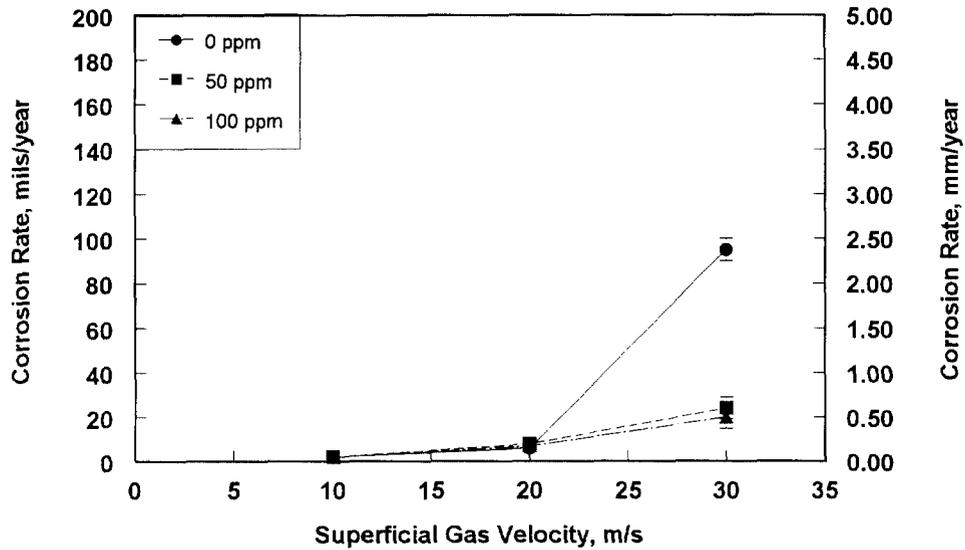


Figure 10. The effect of inhibitor on the corrosion rate at the top of the pipe for a superficial liquid velocity of 0.2 m/s at 0.46 MPa, 40 C and 80% water cut

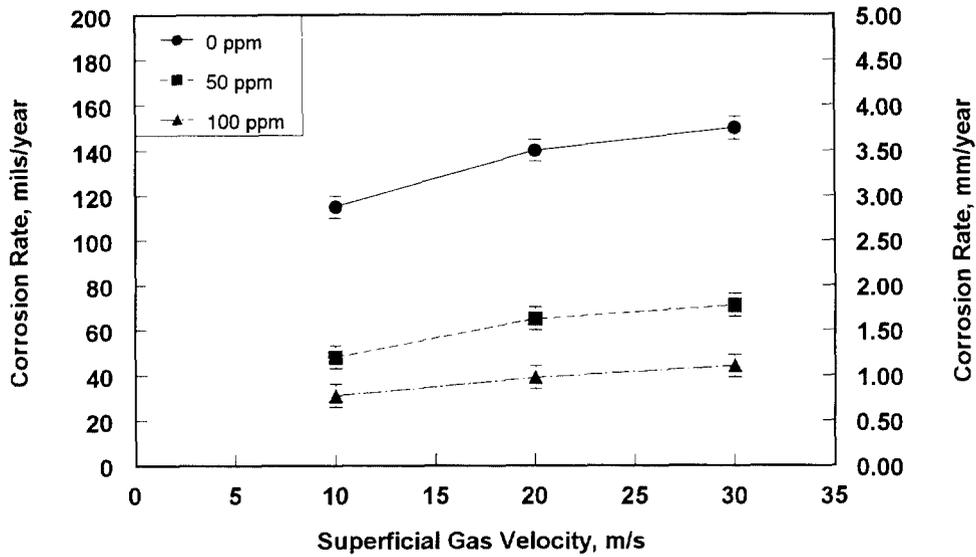


Figure 11. Effect of inhibitor on the corrosion rate at the bottom of the pipe for a superficial liquid velocity of 0.2 m/s at 0.79 MPa, 40 C and 80% water cut

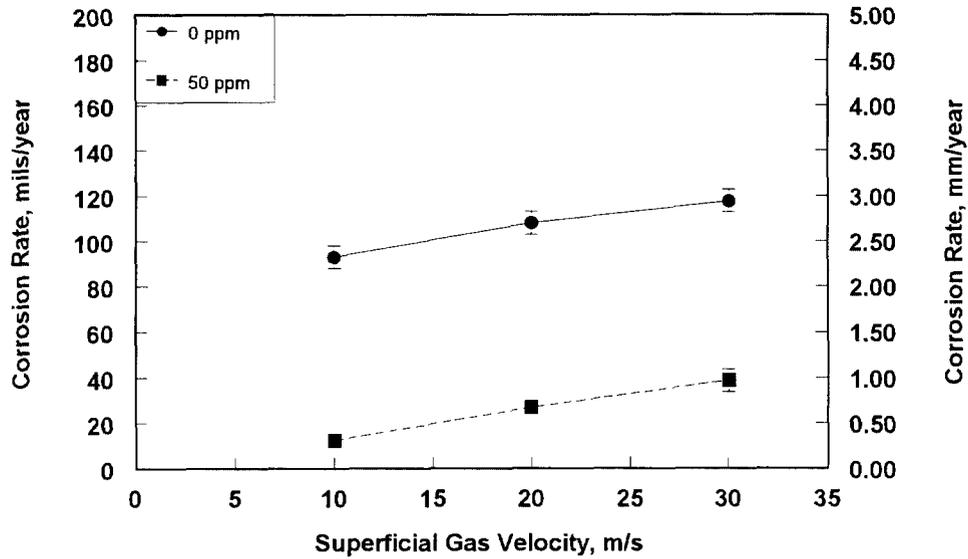


Figure 12. Effect of inhibitor on the corrosion rate at the bottom of the pipe for a superficial liquid velocity of 0.5 m/s at 0.46 MPa, 40 C and 40% water cut