

Inhibitor tests achieve 97% corrosion-protection level

Part 2: Research opens up possibilities for design of high-velocity, multiphase pipe line systems

Michael Swidzinski, Phillips Petroleum, Woking, Surrey, UK; **Bob Fu**, Nalco/Exxon Energy Chemicals, L.P., Sugar Land, Texas; **Audrey Kelly**, Nalco/Exxon Energy Chemicals, Aberdeen, Scotland; and **W. Paul Jepson**, Ohio University, Athens, Ohio

Laboratory tests suggest that inhibitor injection can help operators of multiphase, high-velocity pipe lines achieve corrosion-protection levels of 97% or better.

The tests were to determine design parameters for a new wet gas line to be installed in the North Sea. The goal was to develop material selection guidelines that would optimize throughput while maintaining integrity. To these ends, imidazoline and polyamidoamine-based inhibitor fluids were specially developed for high-shear applications.

To simulate the pipe line's working conditions, tests were carried out in two high-pressure flow loops, one single-phase and the other multiphase.

As described in Part 1, the single-phase flow loop was used to study high liquid velocity and its effects. Both inhibitors were injected in these tests. Here, corrosion-protection levels better than 97% were achieved by injecting 200 ppm of either inhibitor.

Tests were next carried out in a multiphase flow loop to study high gas velocities, and their flow regime effects (Figs. 1 and 2). These tests confirmed the single-phase test findings that corrosion-protection levels greater than 96% can be achieved with inhibitor injection.

Overall, the experiments suggested that carbon steel line pipe and corrosion inhibition can be used together to offer a viable and cost-

effective option for transporting wet, corrosive multiphase hydrocarbon fluids at high velocities.

multiphase study. For the multiphase flow loop study, tests were run

with both a synthetic brine/oil mixture, as well as a de-ionized water/oil mixture.

Synthetic brine/oil tests. As shown in Table 1, the initial experimental design was to include gas velocities of 7, 15, and 25 m/sec. and test temperatures of 95° and 130°C in the matrix, using a synthetic brine/oil mixture. These values were

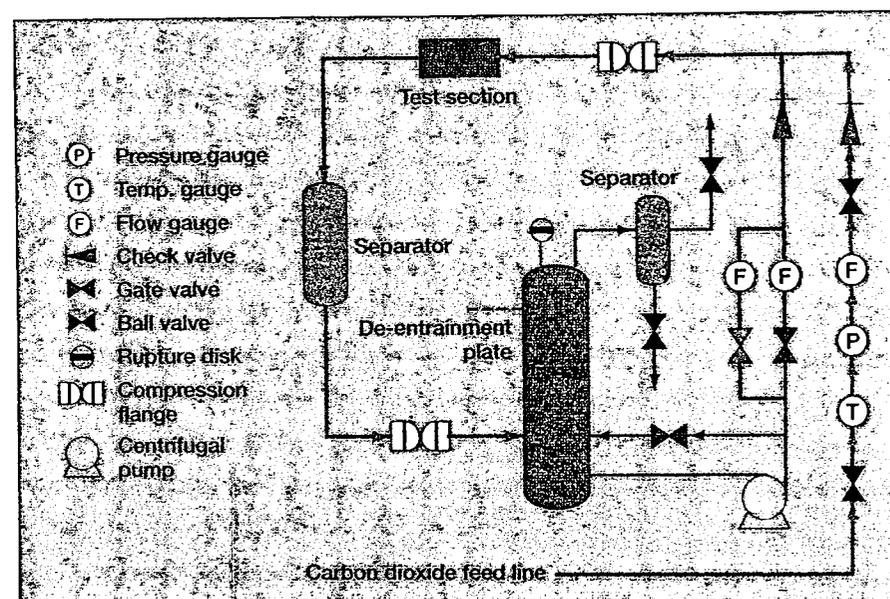


Fig. 1. Schematic of high-pressure multiphase flow loop.

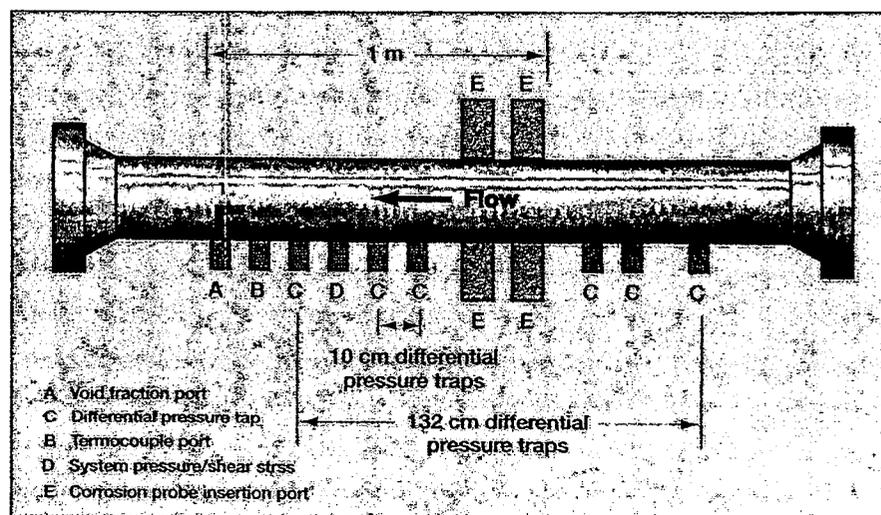


Fig. 2. Test section in the high-pressure multiphase flow loop.

Table 1. The test matrix used in the multiphase studies

Test parameters	Condition
Partial pressure of carbon dioxide	0.8 MPa
Temperatures	95° and 130°C
Gas velocities	7.5, 15, and 25 m/sec.
GOR (gas-to-liquid ratio)	1,780 sm ³ /sm ³
Liquid 1	90% synthetic brine and 10% oil
Liquid 2	100% de-ionized water
Liquid 3	90% de-ionized water and 10% oil
Oil	hydrotreated, light-paraffinic distillate, 2 cP @40°C
Inhibitor	A and B
Concentration	50, 100, 150, 200 ppm

Table 2. Baseline and inhibited corrosion rates, at 95°C and 0.8 MPa CO₂, in multiphase flow containing 90% synthetic brine and 10% oil as liquid phase

Gas velocity, m/sec.	Baseline corrosion rate, mpy	Inhibitor dosage, ppm	Corrosion rate after 1 hr, mpy	Corrosion rate after 2 hr, mpy	Final corrosion rate, mpy	Percent protection
7.5	105	50	skipped*	skipped*	skipped*	N/A
7.5	105	100	23	17	16	85
7.5	105	150	16	12	11	90
7.5	105	200	10	10	10	91
15	67	50	skipped*	skipped*	skipped*	N/A
15	67	100	6	3	<2	97
15	67	150	skipped*	skipped*	skipped*	N/A
23	45	50	19	14	14	69
23	45	100	3	<2	<2	96
23	45	150	skipped*	skipped*	skipped*	N/A

* The test was unnecessary judging from the low corrosion protection at 23-m/sec. gas velocity and 50-ppm inhibitor.
 * The test was unnecessary because corrosion was successfully inhibited at the lower velocity.

chosen to simulate expected field conditions. However, slight variations were made during the tests, to adjust for difficulties encountered.

One difficulty was experienced with the new multiphase pump when the temperature was raised to 90°C. The test temperature was too high for the pump rotor. The high temperature caused significant thermal expansion of the rubber in the stator.

As a consequence, the stator became too tight for the rotor to fit. The rubber began to be stripped from the stator after a period of 24 hours. This led to high levels of vibration and contamination in the system, especially at higher gas velocities.

Further, pump efficiency decreased with time, and eventually the pump failed. The baseline tests were completed before the pump failure. After a new stator was installed, tests were repeated to confirm the earlier results.

The new pump assembly limited the test temperature to 95°C, in order to achieve the high gas velocity of 23 m/sec. These test results are summarized in Table 2.

It was noted that flow regime depended heavily on gas velocity. The predominant flow regime was slug flow at gas velocity of 7.5 m/sec. Flow

changed to annular at gas velocities of 15 m/sec. and higher. Since slug flow generated the highest flow turbulence, measured corrosion rate was the highest at 7.5 m/sec. gas velocity.

It also was noted that corrosion rate was higher at 15 m/sec. gas velocity (67 mpy) than at 23 m/sec. (45 mpy). This phenomenon was not unusual, and has been observed in other studies. It can be explained by a combination of two effects.

In annular flow, increasing gas velocity can result in more liquid entrainment in the gas phase, and more spreading of the remaining liquid around the pipe. Both effects lead to thinning of the liquid film created by the inhibitors. Consequently, average velocity in the boundary layer in the remaining liquid film can be lower, resulting in a lower corrosion rate.

Corrosion-rate measurements were taken using both types of ER probes. An inductance-type probe is more sensitive than the conventional type. Therefore, data were taken every 5 min. from the former, and every 15 min. from the latter.

Corrosion rates obtained from both probes were comparable, typically within 10–15 mpy in difference. If the difference was larger than this aver-

age, the experiment was repeated. Some later experiments were performed using two inductance ER probes to improve response time. Each test was not terminated until a steady state corrosion rate had been recorded for at least an hour.

Although the multiphase flow loop was constructed of 316L stainless steel, the multiphase pump did produce a small amount of ferrous iron, Fe⁺⁺. Iron concentrations ranged from 20 ppm (in the baseline experiments) to 50 ppm (in the inhibitor experiments).

Since the Fe⁺⁺ saturation level in the solution is expected at much higher value (greater than 130 ppm Fe⁺⁺), this small iron amount did not appear to interfere with the experiments. In fact, pH was found to be stable at approximately 4.8. An excess amount of iron in the solution would readily raise pH to above 5.0.

Baseline corrosion rate increased with decreasing gas velocity. The increase was marginal when gas velocity was decreased from 23 to 15 m/sec. (from 45 to 67 mpy). However, a nearly two-fold increase was observed when gas velocity was further reduced to 7.5 m/sec. (from 67 to 105 mpy). The pronounced effect was attributed to change in flow regime from annular to slug, which resulted in a more severe flowing condition.

Only inhibitor B was evaluated in the multiphase study. Its effect was dramatic, immediately reducing corrosion rate upon injection. The same effect was observed in the single-phase flow loop study. The first inhibitor test was carried out at gas velocity of 23 m/sec. in the annular flow regime.

Addition of 50 ppm of inhibitor B decreased corrosion rate rapidly, from 45 to 19 mpy within an hour. Corrosion rate was further decreased and stabilized at 14 mpy as time progressed. Calculated corrosion protection at 50 ppm was equivalent to 69%. The low corrosion protection at this concentration did not favor good corrosion protection at lower velocities, where flow-accelerated corrosion was more severe. Therefore, no further inhibitor testing was performed at 50-ppm concentration.

As inhibitor concentration was increased to 100 ppm, the corrosion rate at 23 m/sec. gas velocity decreased quickly to 3 mpy after an hour. Corrosion rate decreased further to less than 2 mpy, the measurement system's detection threshold. This level was

equivalent to 96% corrosion protection.

It was deemed unnecessary to conduct further inhibitor evaluation at higher concentrations, such as 150 and 200 ppm, since corrosion was successfully inhibited at 100 ppm.

The results obtained at 15-m/sec. gas velocity were similar to those recorded at 23 m/sec. This was likely due to the fact that both were in the annular flow regime.

Addition of 100 ppm inhibitor B decreased corrosion rate from 67 to 6 mpy within an hour. Corrosion rate continued to decrease with time to below 2 mpy. Ultimately, a corrosion-protection level of better than 97% was obtained. For the same reason as in the high gas velocity study (23 m/sec.), further inhibitor tests at 150 and 200 ppm were deemed unnecessary.

As the gas velocity was further decreased to 7.5 m/sec., flow regime changed to slug, with a frequency of 4 to 6 slugs per min. It is well known that slug flow gives the highest corrosion rate, due to the high level of turbulence and localized shear forces at the front of each slug. As a consequence, pitting corrosion is quite typical for corrosion in slug flow. Presence of slug also increased baseline corrosion rate to 105 mpy.

Injection of 100 ppm of inhibitor B reduced corrosion rate from 105 to 23 mpy after an hour. Corrosion rate continued to decrease and eventually stabilized at 16 mpy. This amounted to 85% corrosion protection.

As the concentration was further increased to 150 ppm, corrosion rate fell to a final rate of 11 mpy, equivalent to 90% protection. No further decrease in corrosion rate was noted upon raising the inhibitor concentration to 200 ppm.

De-ionized water/oil tests. Since corrosion protection provided by inhibitor B was acceptable, it was decided to change the water composition from synthetic brine to de-ionized water.

The goal here was to simulate the condition where water would be mainly coming from condensation. The lack of buffering ions in the de-ionized water made the fluid more corrosive.

In these tests, the pump was assembled with an undersized rotor to eliminate the rubber interior abrasion problems experienced during the high-temperature operations. The change allowed tests to be conducted at 130°C.

The same flow conditions used in the previous tests (with synthetic

Table 3. Baseline and inhibited corrosion rates, at 95°C and 0.8 MPa CO₂, in multiphase flow containing 90% synthetic brine and 10% oil as liquid phase

Gas velocity, m/sec.	Corrosion rate at 95°C, mpy	Corrosion rate at 130°C, mpy
7.5	120	124
15	78	80
18	72	N/A
25	N/A ¹	60

¹ Test was not performed due to high liquid slippage as a result of undersized rotor.

Table 4. Baseline and inhibited corrosion rates at 95°C and 0.8 MPa CO₂, in multiphase flow containing 90% de-ionized water, and 10% oil as liquid phase

Gas velocity, m/sec.	Baseline corrosion rate, mpy	Corrosion rate, mpy @100 ppm	Protection @100 ppm	Corrosion rate, mpy @150 ppm	Protection @150 ppm
7.5	120	6	95%	6	95%
15	76	3	96%	<2	>97%

brine) were used again. Tests were carried out at both 95° and 130°C. Baseline corrosion rates are given in Table 3. The iron content for these tests was approximately 30 ppm.

The undersized rotor did cause some problems in experiments at 95°C. Since the rotor's diameter was smaller, the seal between the rotor and the stator was not perfectly tight. This led to significant gas slippage through the pump. As a consequence, the highest gas velocity of 25 m/sec. could not be achieved. Maximum gas velocity for experiments at 95°C had to be limited to 18 m/sec.

Gas slippage, however, was not a problem for the experiments at 130°C. The seal was good, and gas velocity of 25 m/sec. was attained. As shown in Table 4, increasing the temperature from 95° to 130°C did not change baseline corrosion rate substantially. The pH values for these runs were approximately 4.0.

Inhibitor B was added at various concentrations to study its effectiveness. The results from the 95° and 130°C experiments are listed in Tables 4 and 5, respectively.

The experiment with 50 ppm inhibitor B at 130°C was carried out first. It was found that 50 ppm was insufficient to provide adequate corrosion protection. This result also agreed with previous tests at 95°C using the synthetic brine. Because of the low corrosion protection at 50 ppm from these previous experiments, it was decided to bypass the 50-ppm tests at 95°C and to jump directly to 100 ppm.

The results shown in Table 4 are comparable with those in Table 2.

Tests in Table 2 were conducted using synthetic brine, whereas de-ionized water was used in the Table 4 tests. The percent protection looks slightly better in Table 4 than in Table 2. The slight difference was attributed to the high baseline corrosion rates, in which de-ionized water was used.

The inhibitor proved effective under all test conditions. Even in the most severe slug flow condition (at 7.5 m/sec. gas velocity), corrosion rate could be reduced to 6 mpy at 100 ppm of inhibitor.

However, further increasing the dosage did not significantly reduce corrosion rate. With respect to annular flow (at 15 m/sec. gas velocity), the corrosion rate was reduced to less than 2 mpy at 150 ppm inhibitor.

As previously noted, inhibitor B's performance at 50 ppm was marginal at 130°C. The corrosion protection was in the 80% range, regardless of gas velocity or flow regime.

However, increasing inhibitor concentration to 100 ppm boosted performance significantly. Corrosion rate at 7.5-m/sec. gas velocity decreased from 125 to 8 mpy, equivalent to 94% protection. Corrosion rates at 15 and 25-m/sec. gas velocities also decreased to 10 and 8 mpy, respectively.

Further increasing inhibitor concentration to 150 ppm only slightly improved efficiency at 7.5-m/sec. gas velocity. It did, however, considerably reduce the corrosion rate at 15 and 25-m/sec. velocities to less than 2 mpy.

Overall effectiveness was 95% for the 7.5-m/sec. gas velocity in slug flow, and greater than 96% for higher velocities in annular flow. Since over 95%

Table 5: Baseline and inhibited corrosion rates at 130°C and 0.8 MPa CO₂, in multiphase flow containing 90% de-ionized water and 10% oil as liquid phase

Gas velocity, m/sec.	Baseline corrosion rate, mpy	Corrosion rate, mpy	*Percent protection						
Inhibitor, ppm	0	50		100		150		200	
7.5	125	18	86	8	94	6	95	5	96
15	80	11	86	10	88	<2	>97	N/A	N/A
25	60	12	80	8	87	<2	>96	N/A	N/A

* Percent protection = percentage of corrosion protection.

corrosion protection was achieved at 150 ppm inhibitor, little improvement was seen upon further increasing the dosage to 200 ppm.

It should be pointed out that the reported corrosion rates were those measured using conventional probes, and give only an indication of general or uniform corrosion. In slug flow, and in the presence of high chloride concentrations, pitting is the main corrosion mechanism. Therefore, localized corrosion rates are likely to be higher than those reported here.

Conclusions. Flow loop experiments were carried out under single-phase and multiphase conditions at a partial pressure of 0.7–0.8 MPa carbon dioxide, and temperatures of 93° and 130°C.

The highest liquid velocity considered in the single-phase flow loop was 14 m/sec. Gas velocity in the multiphase flow loop was up to 25 m/sec. with the gas/oil ratio maintained at 1,780 sm³/sm³. Two flow regimes, annular and slug, were established in the multiphase flow loop under the conditions of interest.

Baseline corrosion rates were measured to determine corrosion severity. Two corrosion inhibitors, specially formulated for high-shear applications, were injected into the test loops. They were evaluated at concentrations in the range of 50–200 ppm to assess their performance under varying flow conditions.

Measured baseline corrosion rates were higher in the single-phase flow loop than in the multiphase flow loop. The difference was attributed to the probe's geometrical location in the single-phase loop. A baseline corrosion rate of around 1,500 mpy was measured in the high-velocity section of this test assembly.

In comparison, the highest corrosion rate measured in the multiphase loop was 125 mpy, more than an order of magnitude lower than that

observed in the single-phase flow loop.

The two specially-formulated corrosion inhibitors evaluated were effective over the range of flow conditions considered. A protective film formed almost instantaneously, as indicated by the immediate decrease in corrosion rate upon inhibitor injection. Effective protection was demonstrated at a corrosion inhibitor concentration of around 100 ppm.

This study indicates that corrosion inhibitors can satisfactorily mitigate corrosion in pipe lines carrying wet, corrosive multiphase hydrocarbon product at high velocities. The results support the premise that inhibitor and carbon steel are a viable combination for pipe lines designed for a high production throughput. The combination can reduce front-end

capital cost considerably, and offers an attractive option for fields that have a short life or uncertain recoverable reserves.

UNIT GLOSSARY

ppb.....part per billion	m/sec.....meter per second
mpy.....mils per year	ppm.....part per million
L/s.....liter per second	Pa.....Pascal
sm ³standard cubic meter	cP.....centipoise
MPa.....million Pascal	

ACKNOWLEDGMENT

The authors would like to thank Antoine Griffin (Nalco/Exxon), Bruce Brown and Cheloh Kang (Ohio Univ.) for conducting the experiments reported herein. The authors also would like to thank their organizations for permission to publish this work. Based on the paper "Corrosion inhibition of wet gas pipelines under high gas and liquid velocities" (No. 70, Copyright 2000 by NACE International, The Corrosion Society), presented at CORROSION/2000, Mar. 26–31, 2000, Orlando, Florida.

The authors



Michael Swidzinski is principal engineer—materials & corrosion at Phillips Petroleum Company (UK) Ltd, Woking. He is a chartered engineer with over 22 years experience in materials and corrosion engineering in the petroleum and petrochemicals industries. In his current position with Phillips, he is responsible for the definition, implementation, and direction of all materials selection and corrosion control requirements associated with the company's UK operations and projects. Swidzinski holds a PhD degree in metallurgy and materials science from Imperial College, London.

Bob Fu is staff scientist, Nalco/Exxon Energy Chemicals, L.P., Sugar Land, Texas. He is currently working on the flow assurance and corrosion teams. Fu has 10 years experience in oilfield production chemical technologies with Nalco and Nalco/Exxon. A member of SPE and NACE International, he has published more than 20 technical publications and has two patents. Fu holds a BS degree in chemical engineering from National Tsing Hua University, Taiwan, and a PhD in chemistry from Texas A&M University.



Audrey Kelly is district sales representative, Nalco/Exxon Energy Chemicals, Aberdeen, Scotland. In that role, she provides total chemical management services to North Sea operators, and is currently working with BP Amoco West's Shetland business unit.

Prior to that she served as senior research chemist to Nalco/Exxon Energy Chemicals. Kelly holds BS and PhD degrees in chemistry from the University of Strathclyde, Glasgow, Scotland.

W. Paul Jepson is F. J. Russ professor of chemical engineering and director of the National Science Foundation, Industry/University Cooperative Research Center, corrosion in multiphase systems center, Ohio University, Athens, Ohio. Prior to that, he served as visiting professor at the University of Illinois at Urbana/Champaign, and as section leader of multiphase flow and heat transfer at the Atomic Energy Research Establishment, Harwell, UK. Jepson holds a PhD in chemical engineering from Heriot-Watt University, Edinburgh, Scotland.

