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CORROSION INHIBITION STUDIES IN MULTIPHASE FLOW AT HIGH PARTIAL PRESSURE OF CO_2

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ABSTRACT

Laboratory testing of chemicals is considered effective when the conditions tested resemble the operating conditions where the chemical will be used. Six inhibitors were tested under a CO_2 partial pressure of 2.5 MPa, three different flow regimes, and two water/oil/methanol compositions at 40°C to show their effectiveness in limiting the corrosion rate. Turbulence under slug flow conditions produced the highest corrosion rates and one inhibitor was less effective when methanol was added to the system. Therefore, testing of inhibitors under multiphase flow conditions is recommended for pipeline inhibitor selection studies.

INTRODUCTION

Choosing the appropriate inhibitor for a multiphase pipeline is an arduous task requiring information from various sources to select the one that best fits the overall conditions. Multiphase flow at high partial pressure CO_2 in conjunction with a 2 cp oil produces different facets to look at with respect to the corrosion rate. First, with the increase in the CO_2 partial pressure, an increase in the corrosion rate is expected (Videm and Dugstad, 1989)[1]. Second, the increase in the oil/water fraction, up to 60%, has the effect of increasing the corrosion rate (Vuppu, 1994)[2]. And third, an increase in the turbulence of the flow, ie. slug flow, associated with the multiphase system will also produce a higher corrosion rate.

Two important parameters that help define the effect that slug flow has on corrosion are slug frequency and Froude number. The relationship between superficial gas velocity (V_{sg}), superficial liquid velocity (V_{sl}), and slug flow for this experiment is seen in Figure 1 (Cai, 1999)[3]. Sun and Jepson (1992)[4] show that the Froude number gives a measure of turbulence and associated wall sheer in the mixing zone at the front of the slug. Froude number is defined as:

$$Fr = \frac{v_t - v_{LF}}{\sqrt{g h_{eff}}}$$

where v_t = translational velocity

v_{LF} = average velocity of the liquid film

g = acceleration due to gravity

and h_{eff} = effective height of the liquid film

Bhongale and Jepson (1996)[5] and Menezes and Jepson (1995)[6] experimented with slug flow in 10 cm diameter, horizontal flow loops at 0.27, 0.45, & 0.79 MPa partial pressure CO_2 and indicated that corrosion rate increased with an increase in Froude number, carbon dioxide partial pressure, and/or temperature.

In this set of experiments, six inhibitors were tested under 2.5 MPa CO_2 partial pressure and multiphase flow conditions for two different flow regimes, full pipe oil/water flow and three phase oil/water/gas slug flow. The liquids used in this study are 0.5% NaCl solution, laboratory grade methanol, and oil. At 40°C, the oil has a density of 800kg/m^3, a viscosity of 2 cp, and is similar to light condensate oil. Oil-water mixtures at 50% water cut were used for the liquid phase. All inhibitors were added to the system at 150 ppm concentration based upon the aqueous phase volume.

The objectives of this work are to measure corrosion rates under multiphase conditions with a high partial pressure of CO_2, to compare the effectiveness of 6 different inhibitors under similar conditions of high partial pressure of CO_2 and in different multiphase flow regimes, and to compare the emulsion tendencies of the 6 inhibitors in the study.

EXPERIMENTAL

Description of the Flow Loop

The flow loop is a unique 18-m long, 10-cm diameter, high pressure, high temperature, 316 SS pipe system which can be raised to various levels of inclination. A schematic diagram of this system is shown in Figure 2. A predetermined oil-water mixture is stored in a 1.4 m^3 tank that serves as a storage tank as well as a separation unit for the multiphase gas-liquid mixture. Temperature is controlled by heat transfer oil circulated through a dimpled jacket around the tank. The oil is heated in a separate heating unit using four 15 kW heaters and temperature controlled by monitoring the temperature of the system tank. Liquid is moved through this system by a 3-15 kW variable speed centrifugal pump. The flow is controlled within a range of 0 to 100 m^3/hr with the variable speed pump in conjunction with a recycle stream. Liquid flow rate is continuously measured 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. For pressure in excess of 2 MPa, a manifold connecting six 150-lb (68 kg) bottles of CO_2 through two pressure regulators provides constant CO_2 pressure. In normal operation, gas is continuously circulated through the system at desired speeds by a progressive cavity pump, driven by a variable speed motor through a reduction gear system. Use of progressive cavity pumps for pumping wet gas is a new application for a well-known pump. One to five percent of the ideal calculated volumetric flow rate from the pump must be added as liquid to the pump from the system to provide lubrication. The gas velocity is measured using a pitot tube mounted along the test section with the pressure taps connected to a 0 to 35 kPa heavy duty differential pressure transducer. A 12-bit data acquisition board is used in conjunction with these transducers to measure pressure drop over the pitot tube. The transducers transmit a current of 4 to 20 mA to the data acquisition board related to pressure drop. Computerized data acquisition acquires 500 data values over a user provided time frame. All data for this report was collected at 500 data points in 30 seconds. All stored data is imported to a spreadsheet program where the gas flow rate can be calculated.

Description of the Test Section

The test section is a 2 meter spool piece, with a 10.16 cm I.D. and a 0.95 cm wall thickness. A schematic of this section is given in Figure 3. Two pairs of ports at the top and at the bottom are used to insert flush-mountable electrical resistance (ER) probes for corrosion rate measurements. An electrical resistance probe monitoring system was used to record the ER probe resistance at one-minute intervals. Pressure taps on this section are connected to two transducers that measure the pressure drop across a 1.3-meter interval and a 0.1-meter interval of pipe. Data collected from the transducers during operation of the flowloop is used to determine the flow regime within the enclosed system.

Procedure

Test 1. The specified amount of oil/water mixture was added to the system to provide a 50/50 mixture of oil and water at the test section during operation. A low-pressure purge of oxygen was carried out with carbon dioxide until the dissolved oxygen level decreased to values below 10 ppb. When the purging process was complete, the ER probes were wet-sanded with 400-grit sandpaper and then again with 600-grit to ensure a clean probe surface. The probe surface is rinsed with distilled water, rinsed with acetone, and cool-dried before being inserted into the system. Care was taken to ensure that the surface of the probe was flush with the bottom of the pipe. The system pressure was then raised to 350 psig (2.5 MPa) and the liquid and gas velocities set for a baseline corrosion test in the slug flow regime. Temperature was maintained at 40°C.

The two different multiphase flow regimes used in this procedure are slug flow and full pipe flow. Slug flow at Froude number 6 was achieved in this system at 1 m/s superficial liquid velocity and 2.5 m/s superficial gas velocity. Full pipe flow for this work was carried out at 1 m/s liquid flow velocity. The test matrix for Test 1 is Table 1.

The corrosion monitoring software was started and ER probe readings taken every minute. The baseline test ensures that the system has no residual inhibitor from previous testing and also acts as a pre-corrosion step. For the system to be considered clean, the baseline corrosion rate had to be above 200 mpy (5.08 mm/yr). Each test run was carried out long enough to ensure an equilibrium corrosion rate was obtained. Typically the duration of each experiment was 8 to 10 hours for full pipe flow and 3 to 4 hours for slug flow.

Figure 4 shows the ER probe data acquired and used for corrosion rate analysis of inhibitor #2. It must be realized that analysis during experimentation is an ongoing process looking back at previous raw data to determine steady state values. Data collection began with pressure and temperature stabilization occurring within the first hour of testing. The baseline steady state corrosion rate of 5.08 mm/yr was established after 2 hours under slug flow conditions. In the figure at point "a," inhibitor was slowly injected into the system and the corrosion rate decreased as perceived by the change in slope. After 3 hours of monitoring, a corrosion rate of 1.7 mm/yr was determined between point "a" and point "b" in Figure 4. At the end of the slug flow experiment, the system was set for the full pipe flow experiment. Figure 4, points "c" & "d," show the corrosion rate for full pipe flow calculated at 0.5 mm/yr.

With the first half of the test complete, the system pressure was dropped to 25 psig (0.27 MPa) and the probes were removed. The system was shut down and depressurized for the purpose of adding methanol. Corrosion probes were removed and cleaned for more testing while methanol was pumped into the storage tank. The system was purged again until the oxygen level decreased below 10 ppb. While purging, additional inhibitor was added to the system to bring the aqueous phase inhibitor concentration to 150 ppm. The ER probes were then re-inserted before system pressurization to 2.5 MPa. The liquid and gas velocities were set as before, and the entire procedure was repeated for both slug flow and full pipe flow. Data collected for inhibitor #2 in a 15% MeOH mixture is given in Table 2.

The system was then cleaned and the entire experimental procedure repeated for each inhibitor.

Since inhibitor packages usually contain surfactants, possible oil/water emulsions may exist which effect the corrosion rate. The amount of time necessary for complete separation of the phases within a sample is indicative of the emulsion tendency caused by the inhibitor. For each inhibited test, emulsion tendencies taken are reported in Table 3. The level of the oil/water interface was visually observed in a 200ml graduated cylinder and time of observance recorded. The time and volume measurements were compared until no emulsified or cloudy layer existed between the phases and there was no apparent change in the interface location. This was considered 100% separation and all previous values compared by volume for their respective % separation values. Those inhibitors with less emulsion tendency are listed first in Table 3, but no direct relation to corrosion rate was observed.

Test 2. The second test was conducted using one specific inhibitor at three different concentrations and two different flow regimes. The slug flow regimes, defined for test two, use a 1 m/s superficial liquid velocity with different gas velocities. Froude 6 flow characteristics were defined as before and Froude 4 flow characteristics were achieved using a 1.5 m/s superficial gas velocity. Full pipe flow tests were carried out at 1 m/s full pipe liquid flow.

System set up and baseline test procedures were conducted in a manner similar to that previously done in Test 1. With the increase in inhibitor and decrease in flow turbulence as compared to Test 1, the ER probe exposure to each condition was increased to 4 hours minimum for equilibrium corrosion rate to be attained. It was also decided that the more turbulent Froude 6 test would follow the Froude 4 tests, so that the effect of turbulence on corrosion rate could be measured and not just considered an effect of time exposure to the inhibitor. Flow adjustment and inhibitor injection times were always just under 15 minutes.

After the baseline test, the flow regime was changed to slug flow at a Froude number of 4 and inhibitor was injected for a 200 ppm concentration in the aqueous phase. After equilibrium corrosion conditions were attained, the conditions were adjusted for Froude 6 and monitoring continued.

After attaining a stabilized corrosion rate for Froude number 6, more inhibitor was injected for a 300 ppm concentration and the experiment continued in slug flow. Gas flow rates were adjusted to produce slug flow at Froude numbers of 4 and 6. Again, 8 hours later, more inhibitor was injected for a 400 ppm concentration and the same two conditions repeated. The results are given in Table 4.

Full pipe flow corrosion rate testing with higher concentrations of inhibitor was completed next. Baseline test procedures were repeated for a steady state corrosion rate proving the system was cleaned properly. After the baseline experiment, the flow was reduced to 1 m/s full liquid flow and inhibitor was injected for a 200 ppm concentration in the aqueous phase. Equilibrium corrosion conditions were attained after 8 hours of exposure. Additional inhibitor was added to set a 300 ppm concentration and steady state conditions maintained to measure corrosion rates over a 16-hour time span. After addition of inhibitor necessary for a 400 ppm concentration, equilibrium corrosion conditions were measured over a 21-hour time period. The results are shown in Table 5.

RESULTS & DISCUSSION

The corrosion rate results for Test 1 are shown in Table 2.

For the first set of experiments, inhibitor #1 was used as a reference inhibitor to determine the inhibitor concentrations to be used for subsequent experiments. It is seen that with inhibitor #1 the corrosion rate dropped to 1.09 mm/yr from the 5.08 mm/yr baseline corrosion rate after addition of the inhibitor at 150 ppm into the 0.5% NaCl aqueous phase. After methanol was added and the system purged, additional inhibitor was not added and testing proceeded with full pipe flow. This resulted in a new inhibitor concentration of 112 ppm in the aqueous phase and 1.04 mm/yr was measured. To check this inhibitor concentration with methanol in an emulsified state, the system was set for slug flow conditions and 3.05 mm/yr was measured. Noting the unacceptable increase in corrosion rate, inhibitor was added to increase the concentration to 150 ppm in the aqueous phase and the corrosion rate dropped to 1.85 mm/yr. Maintaining the slug flow test conditions, another 50 ppm of Inhibitor #1 was added and the corrosion rate dropped only slightly to 1.80 mm/yr. From this, it was determined that all inhibitors were to be studied at 150 ppm in the aqueous phase, with or without methanol.

The addition of inhibitor #2 dropped the corrosion rate to 1.73 mm/yr from the baseline corrosion rate of 5.08 mm/yr during slug flow. This is close to the median corrosion rate in slug flow for all the inhibitors used. For full pipe flow at 1 m/s, the corrosion rate stabilized at 0.46 mm/yr. After methanol was added to the system, the corrosion rate remained moderate at 0.30 mm/yr for the slug flow testing and dropped slightly to 0.25 mm/yr during the full pipe test. Overall, this inhibitor dropped corrosion rates to their median values for each experiment as compared to the other inhibitors tested.

The third inhibitor had the best overall performance with an initial decrease in corrosion rate to 1.45 mm/yr, lower than the mean value for the slug flow conditions with other inhibitors. With 15% MeOH present, inhibitor #3 also decreased the corrosion rate 0.36 mm/yr, the mean corrosion rate for slug flow conditions with methanol. And for both full pipe flow tests, inhibitor #3 dropped the corrosion rate well below the median rates to 0.20 mm/yr for full pipe flow without methanol and 0.08 mm/yr for full pipe flow with methanol.

Inhibitor #4 had a corrosion rate similar to other inhibitors during the slug flow regime, but improved 5% over the other inhibitors during full pipe flow with a corrosion rate of 0.25 mm/yr. With the addition of methanol, this inhibitor had a 3% lower corrosion rate than the other inhibitors in slug flow (0.20 mm/yr) and full pipe flow (0.10 mm/yr). Inhibitor #4 had the second best overall performance, with corrosion rate measurements below the median for all but the initial slug flow test.

Inhibitor #5 decreased the corrosion rate from the baseline test 17% better than the mean corrosion rate for slug flow with 1.17 mm/yr, but overall performance was not exceptional. The corrosion rate for inhibitor #5 was 0.58 mm/yr for full pipe flow without methanol and 0.53 mm/yr for slug flow with methanol, both rates greater than the mean corrosion rate measured for other inhibitors.

The sixth inhibitor dropped the corrosion rate to 1.88 mm/yr in slug flow from the baseline corrosion rate. When the flow regime was changed to 1 m/s full pipe flow, the corrosion rate stabilized at 0.48 mm/yr. After methanol was added to the system by procedure, the corrosion rate was measured at 0.38 mm/yr for a stabilized rate during slug flow and 0.36 mm/yr during full pipe flow. For each test, the corrosion rate for inhibitor #6 was above the median measured value for all inhibitors tested.

Figure 5 provides a comparison of corrosion rates for three of the six inhibitor packages. As was expected, the corrosion rate was reduced when the flow regime was changed from a turbulent slug flow condition to a full pipe laminar flow condition. With the addition of methanol to the system, the overall corrosion rate was lowered for most of the inhibitor packages. Figure 6 shows the comparison of the corrosion rates for the changes in flow conditions with 15% MeOH present in the system. For each inhibitor that would be considered for future testing, the corrosion rate was reduced by more than a factor of two. Inhibitor #3 was chosen as the better than average rated inhibitor for the second test because of the lower corrosion rates in full pipe flow with and without methanol.

The second set of experiments, a full pipe flow test for 200, 300, & 400 ppm of inhibitor #3, show lower corrosion rates in stratified flow which should be comparable for all of the inhibitors tested. At an inhibitor concentration of 200 ppm, the corrosion rate was measured at 0.20 mm/yr. With the addition of more inhibitor for the 300 ppm and 400 ppm concentrations, the corrosion rate decreased and a longer amount of time was necessary to measure metal loss on an ER probe. Through observation of fluctuations in the data, the resolution of the ER probes used was determined to be ± 0.05 mm/yr. The corrosion rate results for Test 2 are shown in Tables 4 and 5.

Figure 7 gives a visual examination of the effects of reducing the system turbulence on the corrosion rate along with the examination of the effects of increasing the inhibitor concentration. As expected, the increase in inhibitor concentration lowered the corrosion rate. The assumption could also be made from this graph that inhibitor efficiency decreases at concentrations greater than 300 ppm due to the large decrease in slope between 300 and 400 ppm.

CONCLUSION

Since some selection process must exist, the decision for use of the proper inhibitor is an overall consideration of economic and reservoir compatible choices that must be considered. Experimental comparison testing provides the insight as to which inhibitor would be the most effective under similar pipeline conditions. This experiment was used to review six prospective inhibitors at a 150 ppm concentration for economic reasons and to expand on the inhibitor which produced the lowest corrosion rates to examine expected results in the field. Expected field conditions will be the overall deciding factor on which inhibitor would be most effective. Through the use of the proper equipment and testing parameters, experimental results should be close to actual field results.

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TABLES

Table 1. Test Matrix for Test 1.

Inhibitor amount	0.5% NaCl (ltr)*	Oil (ltr)	MeOH (ltr)	Total vol. (ltr)	Vsl (m/s)	Vsg (m/s)	Flow Regime
None	625	587	0	1212	1	4	Slug
150 ppm	625	587	0	1212	1	4	Slug
150 ppm	625	587	0	1212	1	0	Full pipe
150 ppm	625	587	208	1420	1	4	Slug
150 ppm	625	587	208	1420	1	0	Full pipe

* 38 liters more than exact 50/50 mix because of "dead space" in tank.

Table 2: Corrosion Rates (mm/yr)
Inhibitors vs. Flow Conditions

Inhibitor at 150ppm	Slug flow	Full pipe flow	Slug flow 15% MeOH	Full pipe flow 15% MeOH
1	1.09	0.43	1.85	1.04$^{\Delta}$
2	1.73	0.46	0.30	0.25
3	1.45	0.20	0.36	0.08
4	1.80	0.25	0.20	0.10
5	1.17	0.58	0.53	0.23
6	1.88	0.48	0.38	0.36

Blank slug flow: 5.08 ± 0.51 mm/yr

$^{\Delta}$ - inhibitor concentration 112ppm in the aqueous phase

Table 3: Emulsion Tendency based upon oil separation.

Inhibitor Number	0.5% NaCl and oil		0.5% NaCl / MeOH and oil	
	time (min)	% separation	time (min)	% separation
2	1	80	1	92
	2	100	2	100
6	1	88	1	74
	2	100	40	100
3	1	92	1	89
	3	93	2	98
	5	99	5	99
	15	100	10	100
5	1	44	1	100
	3	52	7	100
	40	89	120	100
	123	100		
4	1	58	1	66
	60	60	30	64
	99	92	75	91
	1200	100	1020	100

Table 4: Corrosion Rates (mm/yr)
Inhibitor Concentration vs. Flow Regime

Inhibitor #3 concentration	Slug flow Froude 4	Slug flow Froude 6
200 ppm	0.94	1.02
300 ppm	0.56	0.69
400ppm	0.53	*

* - pressure loss during test, invalid data.

Table 5: Corrosion Rates at 1 m/s full pipe flow

Inhibitor #3 concentration	Corrosion Rate (mm/yr ± 0.05 mm/yr)
200 ppm	0.20
300 ppm	0.10
400 ppm	0.05

FIGURES

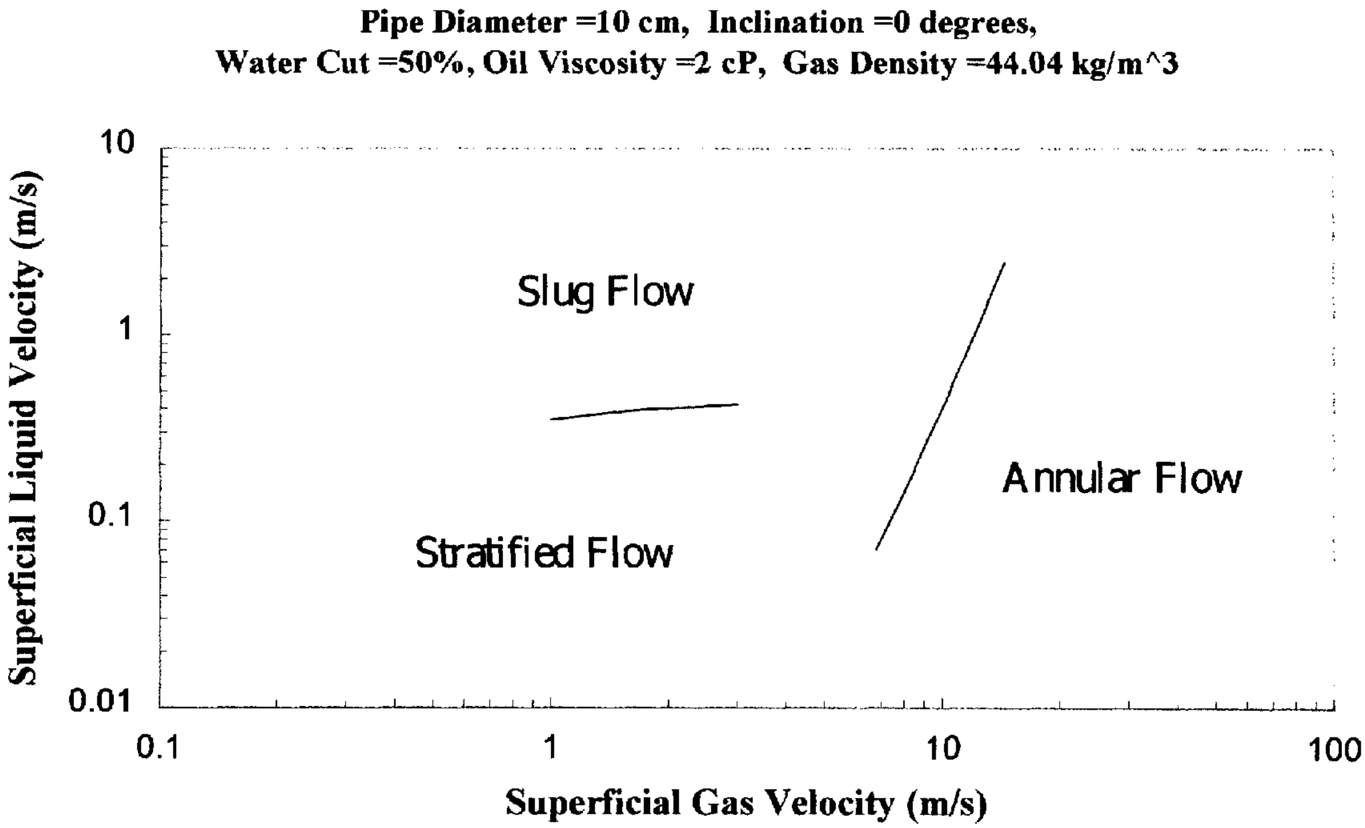

Figure 1. Flow regime map for 2.5 MPa CO_2.

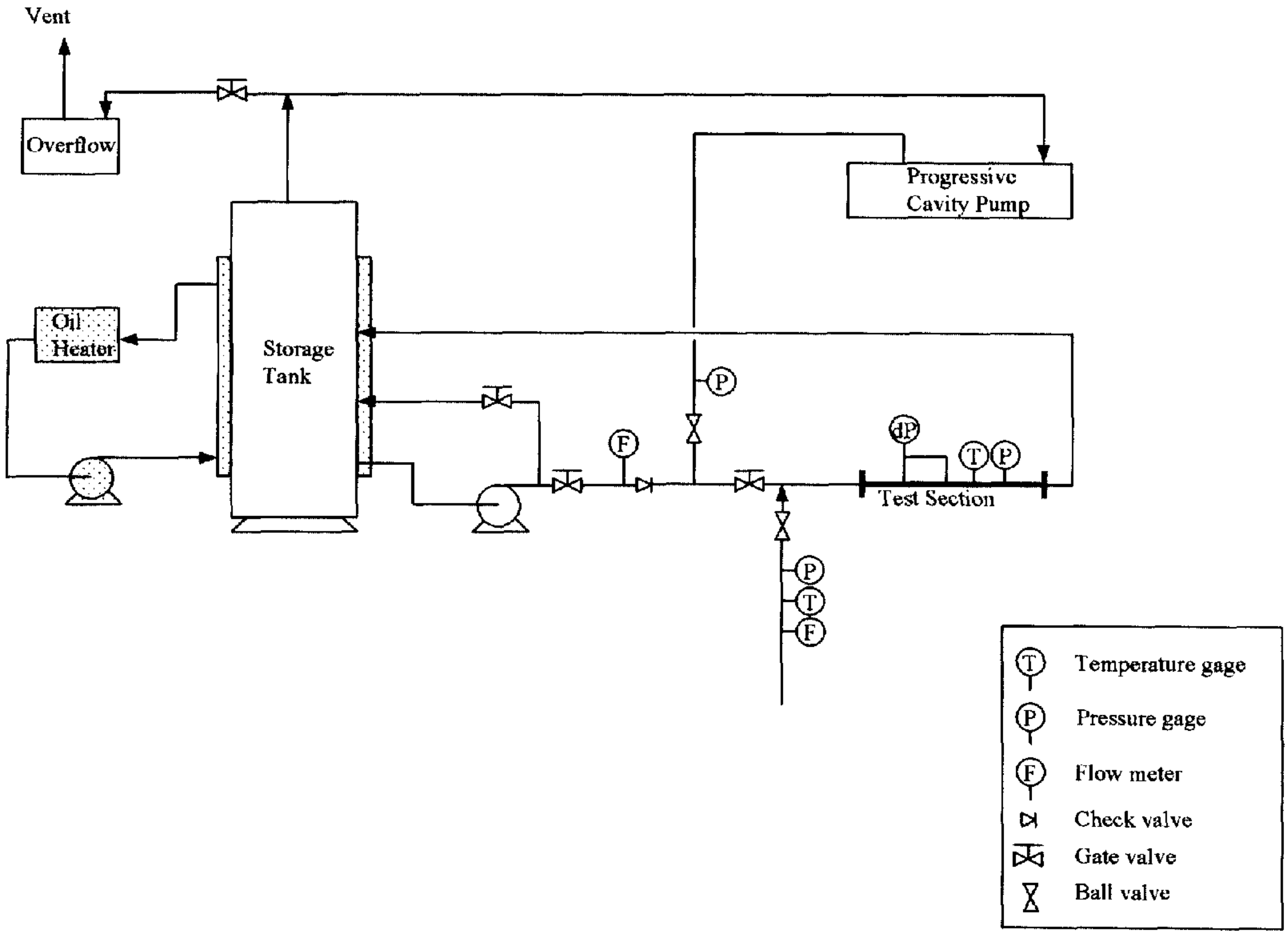

Figure 2. High pressure flow system schematic diagram.

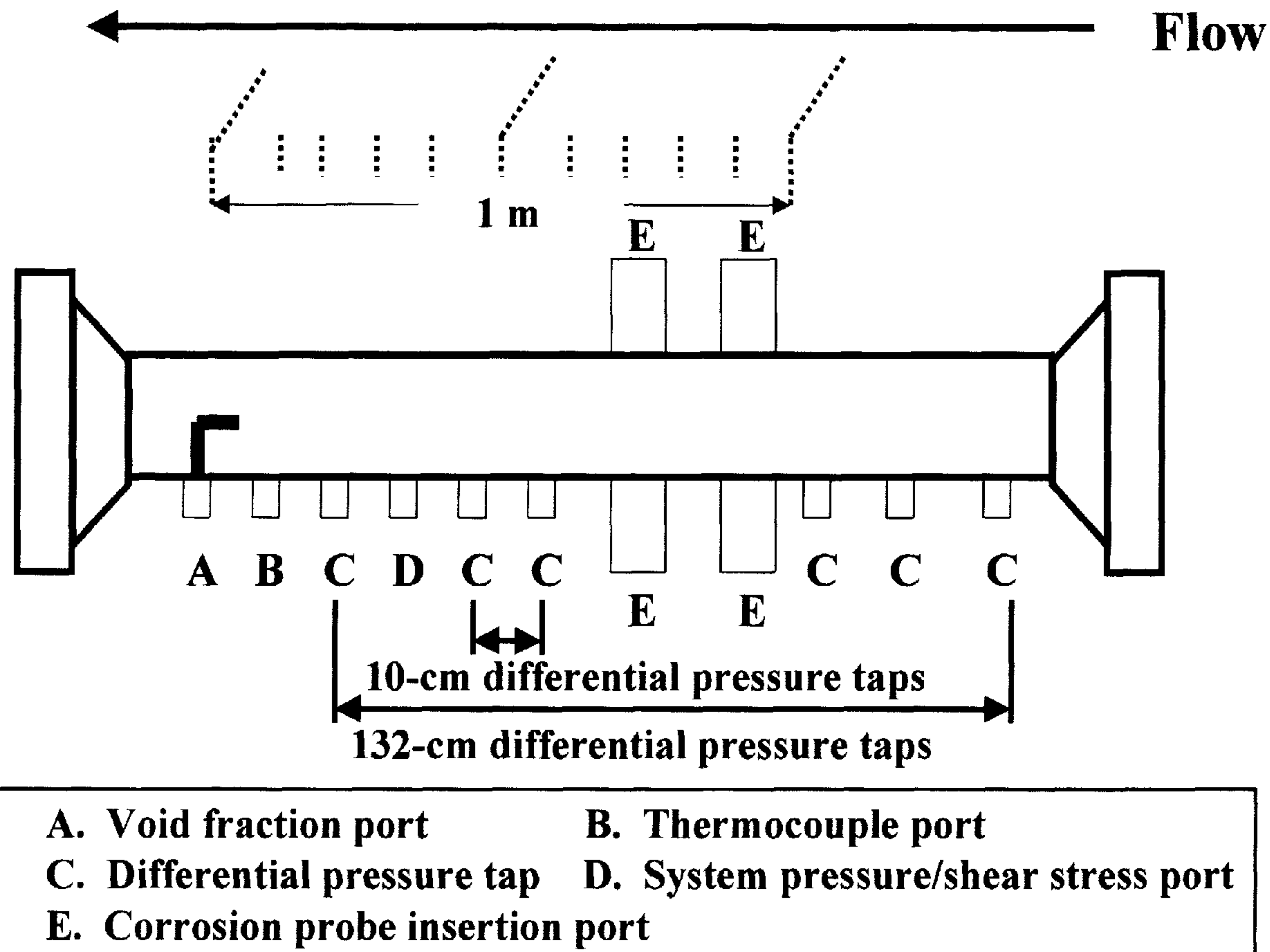

Figure 3: High pressure test section diagram

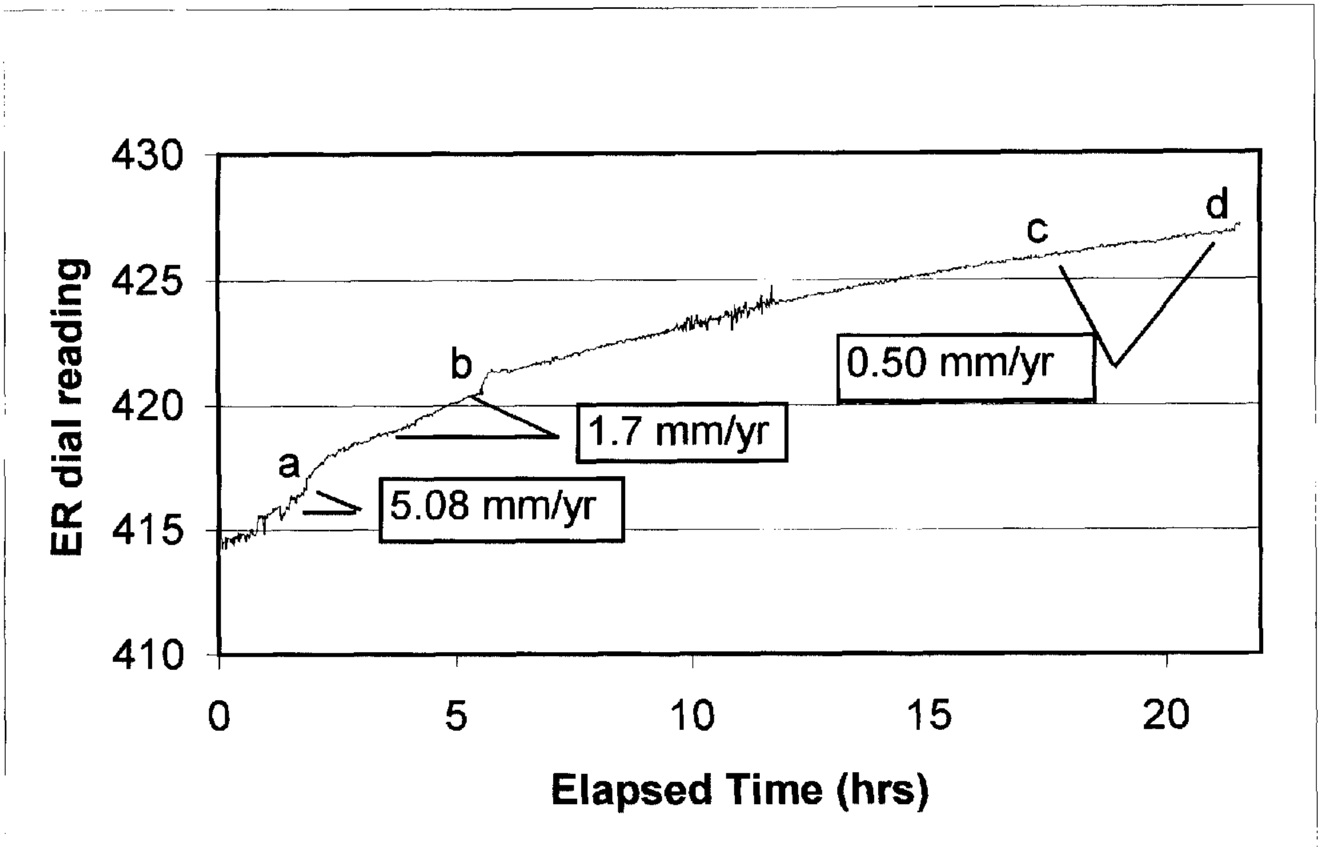

Figure 4. Data analysis, corrosion rates for inhibitor package #2.

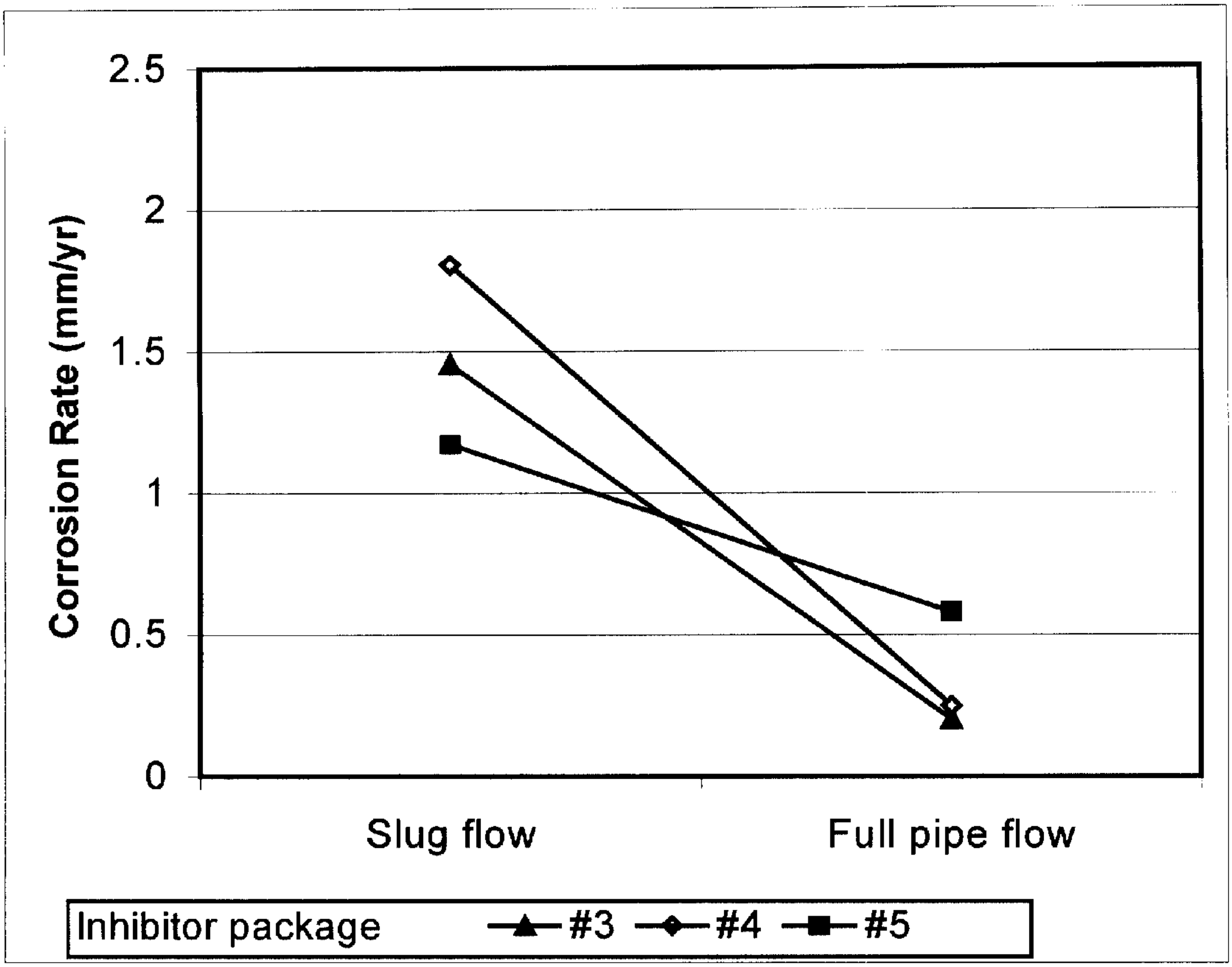

Figure 5. Corrosion rate comparison, 2.5MPa, 50/50 oil/water, 150 ppm inhibitor

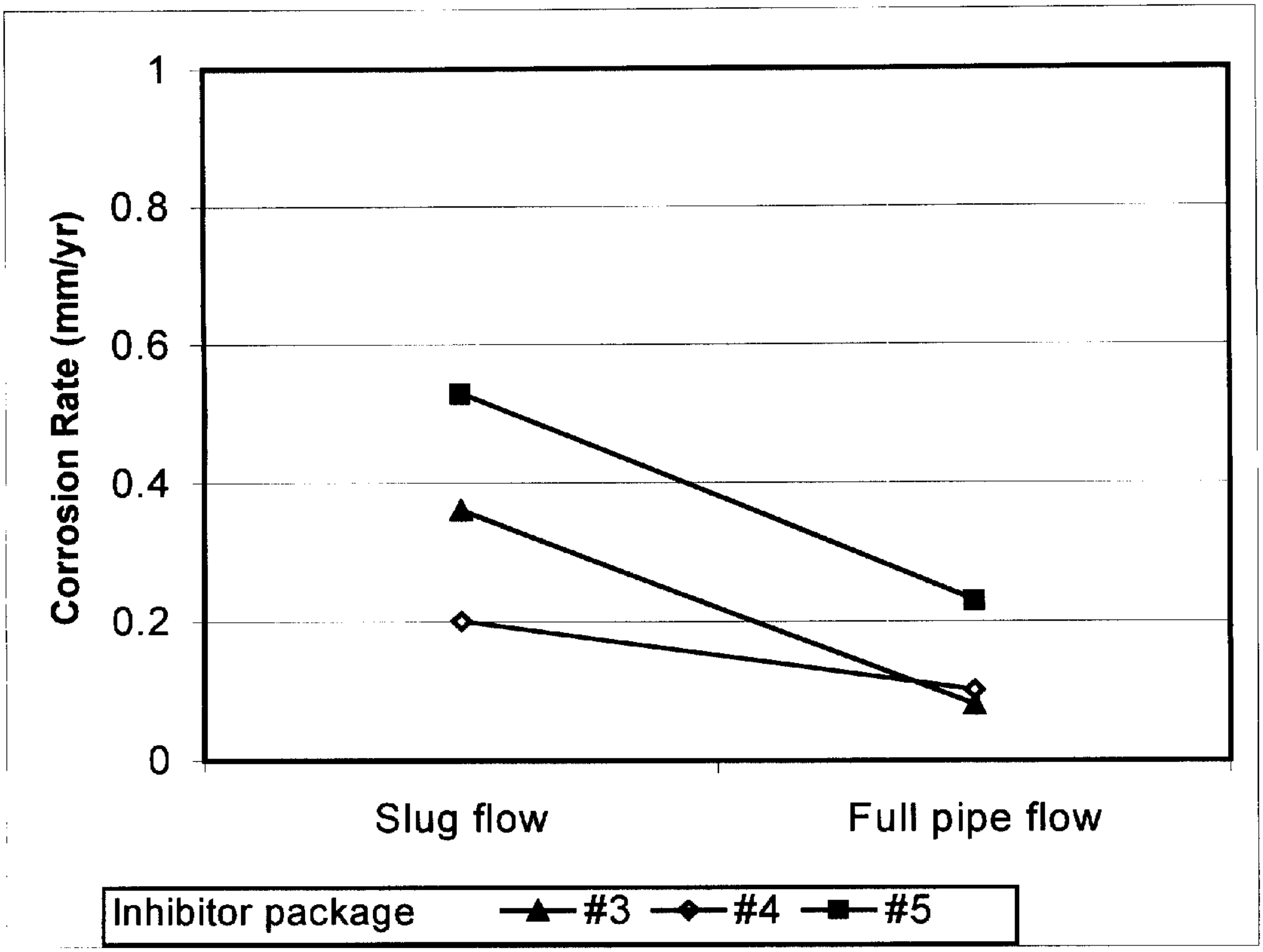

Figure 6. Corrosion rate comparison, 2.5MPa, 50/50 oil/water, , 15% MeOH, 150 ppm inhibitor

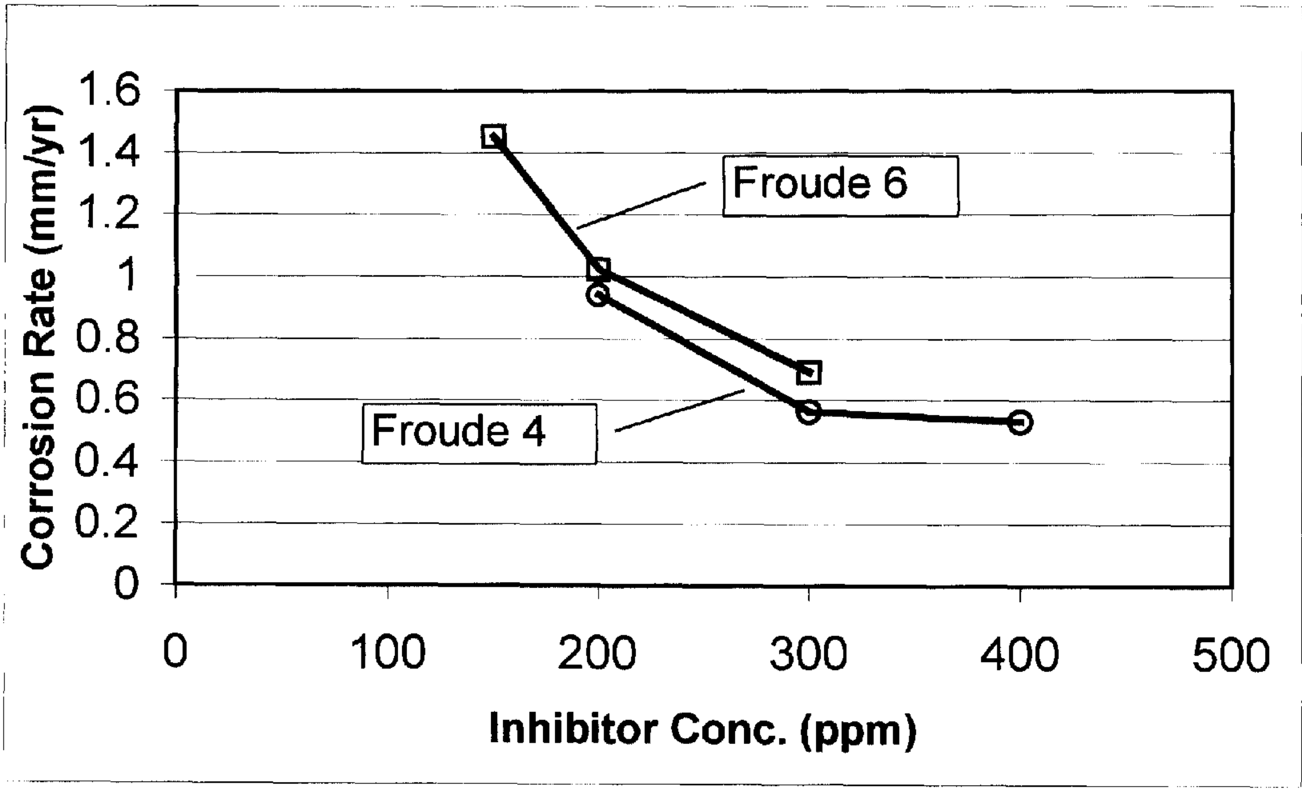

Figure 7. System turbulence effects an increasing inhibitor concentration on corrosion rate, 2.5MPa, 50/50 oil/water.