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CORROSION 99

Development of a Corrosion Inhibition Model
I: Laboratory Studies

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ABSTRACT

The production of a CO_2 flood in the Oklahoma panhandle led to severe corrosion of the carbon steel production tubing and casing. Traditional approaches to chemical corrosion inhibition were unsuccessful. A laboratory study was initiated to determine first the best corrosion inhibitor, and second the optimum effective inhibitor concentration in the produced fluids as a function of the production rate, CO_2 partial pressure, and water to oil ratio. The tool used was the high speed autoclave test (HSACT) discussed in earlier publications. Statistical experimental designs were used to study the three major parameters. The results were expressed in terms of the inhibitor concentration necessary to achieve a desired corrosion rate (for example 1 mpy), and presented either in the form of response surfaces or linear multiple regression equations. While it was generally known that higher fluid velocities require a higher inhibitor concentration for equal target corrosion rates, it was less well appreciated that the CO_2 partial pressure also has a significant effect on the effective inhibitor concentration. The model as represented either by the response surface or the predictive equations is both inhibitor and field specific.

Keywords: carbon dioxide, fluid velocity, partial pressure, corrosion inhibitor, modeling, statistical design, response surface, effective inhibitor concentration, target corrosion rate,

BACKGROUND

1. Introduction

Mobil E & P US, Inc. operate a CO_2 flood in Texas County, Oklahoma which is known as the Postle Field. The Field produces from the Morrow Sand formation at a depth of 6000 ft., The field was discovered in 1958 and has been in continuous production since that time. CO_2 flooding began in November 1995 and severe corrosion was experienced on select wells in this field shortly after CO_2 breakthrough. The corrosion was extremely rapid, new tubing strings would be severely damaged, both internally and externally and a number of casing failures occurred. The corrosion took the form of typical flow induced corrosion, with a MESA pattern and penetration rates in excess of 300mpy. The corrosion was reported, by field personnel, to be associated with CO_2 breakthrough corrosion pattern throughout the field was irregular, however. Although the CO_2 was moving through the formation exactly as planned, and CO_2 breakthrough was predictable some wells would experience severe corrosion and others would not.

Typically, sandstone formations, when flooded with CO_2, generate a more corrosive environment on the production side than limestone (carbonaceous) formations (Ref 1). Not only is corrosion more severe, but it is also more difficult to chemically inhibit with traditional corrosion inhibitors (Ref 2, 3). There are many reasons for this. The lower bicarbonate concentrations often found in brines from sandstone formations result in lower pH's, particularly when CO_2 is produced back at increased partial pressure. CO_2 breakthrough also leads to increased liquid volumes produced through the production tubing, or the casing space in the case of packerless completions.

It has been demonstrated in numerous generic studies (Ref 4) that the effective corrosion inhibitor concentration i.e. the concentration required to achieve a specified (low) corrosion rate depends, amongst other things, upon in situ pH, the relative liquid velocity 1) and the oil/water ratio. When formulating a corrosion inhibition program for a field, these 3 variables must be taken into account but are sometimes overlooked. This paper describes the work undertaken to develop a corrosion inhibition model for the Postle Field which takes account of all the important production variables.

2. Previous Experience

Extensive laboratory and field studies had been undertaken in the mid 1980's in an effort to bring corrosion in Shell's Little Creek (Mississippi) CO_2 flood under control (Ref. 5, 6). This is also a sandstone flood, albeit from greater depths (14,000 to 15,000 ft) and therefore with higher shut-in bottomhole pressures (6000 psi). Upon CO_2 breakthrough, bare tubing had been observed to corrode uniformly and with pronounced mesa type attack to less than half of its original thickness in 3 to 4 months with the most severe damage occurring at the upstream pinends. The effectiveness of the chemical corrosion inhibition program was monitored with coupons installed at either the well head, or the high and low pressure manifolds to the plant inlet where the flowlines from different wells came

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1) The linear liquid velocity relative to the metal surface.

together. Along with the corrosion, production rates and CO_2 partial pressures were monitored and associated with the individual coupon corrosion rates for the period of exposure. After over 240 corrosion rate data points had been accumulated, a least squares multiple linear regression analysis was attempted over the following parameter space:

Table 1

Parameters Monitored	**Significant Parameters**	**Natural log of Effect**
Superficial Gas Velocity	yes	0.252302
Superficial Liquid Velocity	yes	0.674294
Type of Inhibitor (A, B,)	yes	A +0.539158 B − 0.539158
Inhibitor Concentration	no	-
Water Prod. Bbl/MMscf	no	-
CO_2 Partial Pressure, P	yes	- 0.228016
Water/Oil Ratio	yes	- 0.199186
Natural log of Identity (intercept)		1.065763

The resulting correlation equation for Inhibitor A has the following form:

$$\ln\text{(corr. rate)} = 1.066 + 0.5392 + \ln(U_{SG})*0.2532 + \ln(U_{SL})*0.6743 + \ln(\text{Water/Oil})*(-0.1992) + \ln(P)*(-0.2280)\ (^{*}) \qquad (1)$$

The factors were significant at the 95^{+}% level except for the pressure (93 %). In interpreting these results one must remember, that all corrosion rates were obtained under inhibited conditions and at the low temperatures prevailing on the surface. The effects therefore are relatively small, but nevertheless indicate that inhibitor B was about 3 times as effective as inhibitor A, a result that had been predicted from laboratory studies. The inhibitor concentration did not seem to affect the corrosion rate, because essentially all results had been obtained at near-constant inhibitor concentrations. The superficial gas and liquid velocity effects were both positive as expected. However, the negative effects of the water/oil ratio and the pressure were surprises.

Since the inhibitors were both oil soluble and had very little water solubility and/or dispersibility, and since furthermore the dosage was based on total fluid production, it was argued that a higher water/oil ratio would increase the inhibitor concentration in the oil, and thereby increasing inhibition (lowering the corrosion rate) under turbulent conditions in the production tubing and flowlines. The thought was that an increased inhibitor concentration in the oil would lead to more effective adsorption on the metal surface, even though with the increased water cut the frequency of oil droplets in turbulent flow contacting the metal surface might be diminished. It should be added that such an effect is probably inhibitor specific and might be observed only with oil soluble poorly dispersible compounds. Figures 1

(*) for Inhibitor B the second number in equation 1 would have a negative sign indicating superior activity.

and 2 show calculated corrosion rates for Inhibitor A first as a function of the superficial gas and liquid flow rates (Fig. 1) and then as a function of the water/oil ratio and the CO_2 partial pressure (Fig. 2).

The pressure effect was clearly unexpected and contrary to everything that had been known previously. For this reason it was studied more extensively in the laboratory.

3. Laboratory Studies of Pressure Effect

The high-speed autoclave rotating cage methodology (Ref. 7, 8) was chosen for this investigation. The test conditions are summarized in Table 2:

Table 2

Parameter	Value
Brine	100,000 ppm Cl^- 10,000 ppm Ca^{++} 1,000 ppm Mg^{++}
Autoclave	3.75 L
Brine Vol.	1800 ml
Hydrocarbon	Isopar M
Hydrocarbon Vol.	200 ml
Inhibitor (concentration in active ingredients)	B
Corrosion Coupons	L-80
Coupon size (4 per test)	30 cm^3
Temperature	125 F
Gas	CO_2
Pressure	Variable
Speed of rotation of cage	1500 rpm
Test duration	100 hrs

The iron in solution was measured at intervals during the test, and the total iron in solution at the end of the test was compared to the weight loss. Generally in excess of 95% of the weight loss iron was found in solution. It was felt, therefore, that corrosion kinetics could be estimated from the iron counts. The test protocol was essentially identical to the one listed in Appendix I. Typically the corrosion rates were observed to drop within the first two or three hours to a steady state level which was very close to the average weight loss corrosion rate. Quoting the average corrosion rates for the 100 hour test period will therefore represent a realistic picture of the degree of inhibition which could be achieved at each pressure level with each inhibitor concentration.

The results are shown in Figure 3. The concentrations for Inhibitor B are given in active ingredients which are generally 50% by weight of the formulation.

Below 450 psi CO_2 partial pressure the corrosion rate increases with pressure at constant inhibitor concentration as expected. This is equivalent to saying the effective inhibitor concentration increases with CO_2 pressure. Above 450 psi the corrosion rate decreases with pressure, which mirrors the field experience. Whether the observed maximum is indeed at 450 psi is open to question since the test pressures were chosen arbitrarily and spaced fairly widely, but there is no doubt that a maximum exists. The range of pressures recorded along with the corrosion rates in the field varied from 250 psi to about 1800 psi with, however, only few data points below 450 psi. The multiple linear regression analysis did therefore show a negative pressure effect, with reduced significance (93%), because it could not account for the inherent non-linearity of the corrosion rate – pressure relationship.

INHIBITOR DEVELOPMENT FOR THE POSTLE AREA

1. Background

In view of the facts, as known from the above and discussed in earlier studies, it was not immediately obvious whether the corrosion inhibitor used at the time across the Postle field was a) the best product available, b) used at the appropriate concentration and c) used in such a manner as to be transported to those areas in the production system where it was needed most.

The wells at Postle are to a large extent equipped with electrical submersible pumps in packerless completions (Fig. 4). The miscible pressure in the reservoir is about 3600 psi. Flowing bottom hole pressures are of the order of 2500 psi. However, the pressure at the pump intake depends on the fluid level maintained in the casing space for optimum pump efficiency and the flowline pressure (150 to 200 psi). The fluid level can vary from 500 to 2000 feet resulting in pump intake pressures from about 450 to 1100 psi[2]. The pressure inside the production tubing above the pump is always of the order of 2000 to 2500 psi (corresponding approximately to the static pressure of the fluid column in the production tubing), and therefore higher than the pressure on the annular side. All gas not separated out in the gas separator upstream of the pump, will therefore most likely be in solution in the fluids in the tubing, at a concentration corresponding to the partial pressure prevailing on the casing side, or slightly higher[3]. The flow regime in the tubing will be full liquid flow up to the point where the static pressure is lower than the bubble point pressure of CO_2. At that point gas will break out of solution and a three phase flow (gas, oil, water) will develop. As a consequence of this the mixture velocity will increase and can easily reach 3 fold the velocity of the liquid alone depending on the pump intake pressure; (the higher the fluid level the greater the pump intake pressure and the more gas dissolves in the liquids). The flow conditions in the tubing therefore change from the bottom to the top along with the chemical conditions in the liquid. Lower flow rates, higher temperatures and higher CO_2 concentrations prevail at the bottom while higher up in the production tubing the temperature and CO_2 partial pressure will be lower while the flow rate can be considerably higher. It is, under these conditions not a priori possible to predict the minimum effective inhibitor concentration.

A similar situation exists on the annular side and is even less accessible to prediction. The flow condition here will always be gas churning up the annulus through the fluid level forming a frothing liquid until the gas velocity is high enough to gas lift liquids from the casing space. At this time some

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[2] these numbers are approximate because they also depend on the mixture density of the fluids in the annulus.

[3] It appears that the downhole gas separators placed ahead of the pump intake have an efficiency of 80% and perhaps even higher.

sort of slug flow or eventually annular flow will develop. The flow intensity (shear stress) will depend on the gas flow rate up the annulus, which in turn depends on the pressure, hence the fluid level. In general one would expect again that the higher the pressure (fluid level) the lower the "flow intensity, but the greater the CO_2 partial pressure. Even though all these parameters can be calculated, their relationship to corrosion and corrosion inhibition has never been established and it is impossible in a situation of this kind to guess at the effective inhibitor concentration for those areas experiencing most severe corrosion conditions.

The chemical treatment of these wells consisted originally of weekly batch treatments into the annulus with an over-flush of produced fluids. As the CO_2 breakthrough occurred, continuous treatment facilities were installed. The corrosion inhibitor was injected continuously into the annulus with an over-flush of produced fluids. Because the turbulence at the well head could potentially carry some or all of the inhibited fluids into the gas flowline at surface, 40 ft injection capillaries were installed with the expectation that the injected fluids would bypass this turbulent zone and still fall to bottom. Later, some full length capillaries were installed in selected wells (Fig. 4) in order to mix the inhibitor into the produced fluids at the perforations and thereby protect the casing and liner below the pump intake. The estimate of the effective inhibitor concentration, which had been shown to be dependent on pressure and flow rate remained elusive however, and became the subject of the subsequent study.

2. Laboratory Evaluation of the Effective Inhibitor Concentration.

Test Methodology and Preliminary Inhibitor Selection

For the purpose of determining optimum use concentrations for inhibitors in a situation where the CO_2 partial pressure, the flow rate and the water cut of the produced fluids can all change in wide limits, high speed autoclave rotating cage methodology (HSAT)was again chosen. This methodology has been described in numerous prior publications (Ref. 7. 8, 9, 10). The generalized test protocol is detailed in Appendix I. Since at Postle the concern was both with preventing corrosion of the production tubing as well as the casings, all representative metallurgies (J-55, N-80, L-80 and AISI-1018) were included. The rotating cage contained in general two J-55 coupons and one each of N-80 and L-80 cut from tubing sections received from the field. In order to assess the corrosion kinetics and to establish steady state corrosion rates continuous PAIR (LPR) measurements were made along with iron count studies. The build-up of iron in the test solution during the 120 hr test was monitored often enough to establish an adequate corrosion rate – time trend which could be compared with the PAIR – time trend and from which the steady state (final corrosion rate) could be extracted. The PAIR corrosion rate readings, however, were more difficult to interpret. The weight-loss corrosion rates of the AISI-1018 electrodes were many times (2 to 10 times) greater than the corrosion rates obtained by averaging the PAIR measurements over time[4] [5]. It was therefore necessary to rely almost exclusively on the iron count kinetics. It was found that the steady state corrosion rate was generally established within a few hours of the start of the test and differed little from the average weight-loss corrosion rate, particularly in those situations where good inhibition was achieved.

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[4] Averages were obtained by integrating the area under the corrosion rate-time curve and dividing the integral by the total time.

[5] This effect was later also observed in the field and will be discussed in the following publication

Initially a fair number of inhibitors, selected for the purpose by experienced personnel in two supplier companies, were tested under the most severe conditions anticipated in the field (6) at 100 ppm each. The results ranged from zero protection all the way to about 90 or 95% protection.

Table 3

Screening of Inhibitors at 100 ppm in the HSAT at
750 psi CO_2, 1500 rpm, 160 °F, Averages of all Metals

Inhibitor	General Weight-loss mpy	Local Corrosion Rate mpy
C	66.8	700
D (7)	243	1620
E	284	3000
F	73	2700
G	775	4400

On this basis Inhibitor C was selected for a detailed parametric study in an effort to determine the optimum effective concentration over a producing parameter range expected to prevail in the field.

Test Matrix

The test matrix for inhibitor C is shown in Fig. 5. The choice in rotational speed (500, 1000, and 1500 rpm) was somewhat arbitrary in that the most severe flow conditions had to be represented as well as milder ones, but not so low that the oil and water phases in the autoclave would not be properly mixed. It was verified that at 500 rpm good mixing still prevailed in the autoclave with, however, much lower shear stresses. The test pressures varied over a range which can be expected to prevail in the Postle wells. The water to oil ratio initially was chosen at 1.8 to be varied later. The test matrix was planned as a 2^2 factorial design with a center point to facilitate assessment of non linearity in the resulting correlations.

The objective of the series was to evaluate the inhibitor concentration necessary to achieve a target corrosion rate, rather than determining the corrosion rate at a given inhibitor concentration. In order to do this it was necessary to perform several tests with different inhibitor concentrations at each of the five test conditions. It was hoped that the resulting performance curves (corrosion rate vs. inhibitor concentration) could be reasonably extrapolated to the desired target corrosion rates.

Evaluation of the Results

Figures 6 and 7 show typical performance curves for J-55 and L-80 steels. In a double logarithmic plot the relationship between performance (inhibited average weight loss corrosion rate and/or final corrosion rate from iron counts) and inhibitor concentration turned out to be linear. Within experimental error this was also true for the steady-state corrosion rates. Within experimental error the steady-state corrosion rates (from iron counts) varied only little from the average weight loss rates as one would expect in

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(6) At this stage the judgement whether the most severe laboratory conditions also represented the most severe field conditions was obviously intuitive and solely based on qualitative prior experience.

(7) Inhibitor previously used in field at concentration of less than 100 ppm

inhibited systems. The correlation equations, which are only shown for the average weight loss in Fig. 6 and 7, are a tool to calculate the corrosion rate for any inhibitor concentration. For the purpose of developing the model, however, the inhibitor concentrations for the target corrosion rates of 1, 2, and 4 mpy were extrapolated manually from the graphs for the steady-state corrosion rate curves. The results are summarized in Table 4.

Interpretation or the Results

An overview of Table 4 quickly shows that not all metals are inhibited equally. In particular the L-80 metallurgy proved less susceptible to corrosion inhibition, a fact which had also been observed consistently during the screening tests for all compounds tested. It is further observed that the differences in inhibition efficiency on different metals becomes more pronounced as the corrosion conditions become more severe.

In order to obtain a better overview of the relationship between the severity of corrosion (combination of CO_2 partial pressure and velocity) response surface methodology[8] was used. Specifically, as shown in Fig. 8 and 9, "iso-corrosion-inhibitor-concentration" lines were generated in a grid of CO_2 partial pressure vs. rotating velocity of the cage. From Figure 8 one can conclude that for J-55 the major effect which controls the effective inhibitor concentration is the velocity (rpm) or by implication the shear stress. Only at higher shear stress does pressure begin to play a role in increasing the effective concentration. In comparison, L-80 (Fig. 9) is clearly more difficult to inhibit and pressure appears to have a more pronounced effect. The contours for N-80 are between those of J-55 and L-80. The mild steel, AISI-1018, performed in almost the same manner to the J-55, even though the PAIR electrodes were stationary. It is assumed that the rotating agitation of the liquid in the autoclave generates similar shear stress as experienced by the rotating cage. This point is important later when laboratory data will be compared to field data.

3. Localized Corrosion

As is well known, high fluid velocities in CO_2 environments cause flow induced localized corrosion, and it is also known that inhibition of FILC requires high inhibitor concentrations. As indicated in Appendix I, the maximum local penetration rates were routinely measured using a standard microscopic technique. Figures 10 and 11 show the pitting rates as a function of the general weight loss corrosion rates for J-55 and L-80. The trend-lines for both metals are similar in that the pitting rate is not proportional to the general corrosion rate (in inhibited solutions). Of greater importance, however, is the fact that pitting inhibition on J-55 occurs below 2 mpy general corrosion rate, while for L-80 much lower corrosion rates (< 1mpy) are required for reliable inhibition of pitting. N-80, while more easily inhibited than L-80, has shown a greater tendency toward localized corrosion. This reversal in behavior may need further study relative to metallurgy and compositional parameters, but seems to be in general agreement with earlier studies.

An alternate way of evaluating the above data consists of a multiple linear regression analysis. For J-55, the following equation was obtained:

$$(\text{Inhib. Conc.})_{1\ \text{mpy}} = -117.1 + 0.105\text{x}(CO_2\ \text{partial pressure}) + 0.228\text{x}(\text{rpm}) \qquad (2)$$

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[8] Software: JMP 3.2 Prof. Ed. 1997, SAS Institute, Inc., Cary, NC, USA

This equation, which does not account for any non-linearity in the system, holds only within the experimental parameter range and can obviously not be extrapolated to milder corrosive conditions since negative inhibitor concentrations would result. Never the less, if the problem of the relationship of shear stress on the rotating cage and shear stress in the production tubing can be resolved, the above equation begins to offer a first approximation prediction of the inhibitor concentration which may have to be used under prevailing conditions in the field.

4. The Effect of the Water/Oil ratio on Corrosion Inhibition

In addition to flowrate and CO_2 partial pressure, the water to oil ratio in the produced fluids was expected to be a major parameter in influencing the effective concentration. Table 5 summarizes the results. The general trend in the data indicates that an increasing water/oil ratio increases the corrosion rate at both velocity conditions with the exception of the two data points at 225 ppm inhibitor where the trend is reversed. The discrepancy is small and possibly, at the low corrosion rates, within experimental error. A linear regression analysis resulted in the following equation:

$$(\text{corr. rate})_{750\text{psi}, \text{J-55}} = 1.4 + 0.00815\text{x(rpm)} + 0.480\text{x(Water/Oil)} - 0.0616\text{x(Inhibitor)} \quad (3)$$

which allows one to evaluate qualitatively the trends of the water/oil ratio and the effectiveness of the inhibitor as a function of velocity. Figure 12 shows how the corrosion rate increases with water/oil ratio. At the 100 ppm level of inhibitor, for example, increasing the water/oil ratio from 2 to 8 can move the corrosion of J-55 from non- pitting to a pitting situation, particularly at high rpm levels.

Similarly, one can see from Figure 13 how the inhibitor concentration may have to be increased at a given water/oil ratio in order to move from a pitting situation (corr. rate >2 mpy) to one where no pitting occurs.

Inhibitor C in these studies behaved differently from Inhibitor B discussed earlier on the basis of field data for this inhibitor. The differences in the two inhibitors is seen in their respective dispersibilities. Inhibitor B was essentially totally oil soluble and formulated only with a wetting agent to facilitate "filming" from the oil phase without resulting in water dispersibility. Inhibitor C on the other hand was formulated with the aid of dispersants. Since inhibitor dosage is always assessed on the basis of total produced fluids, high water dispersibility causes a reduction of the inhibitor concentration in the water as the water cut increases. Hence the observed effect for inhibitor C was not unexpected.

DISCUSSION AND SUMMARY

The purpose of a corrosion inhibitor program is to reduce failures, and the effective inhibitor concentration to do this must be capable of inhibiting corrosion under the most aggressive conditions. In order to achieve those objectives one must have 2 models. The first model must describe quantitatively the environmental and the flow conditions (including those pertaining in annular spaces and across upsets such as tubing collars), and the second model must relate the effective inhibitor concentration to the parameter values obtained from the first model (local shear stress, temperature, partial pressure and water/oil ratio).

This study, an early attempt to quantify such relationships, has demonstrated a complex interplay between the effective inhibitor concentration (concentration to achieve a target corrosion rate) and the systems parameters. Helpful in this endeavor was the fact that the inhibitor performance curve could easily be linearized in a log (corr. rate) vs. log (inhib. conc.) plot. Correlations were attempted between the effective inhibitor concentration and flow rate (rpm), CO_2 partial pressure, and the water/oil ratio. The correlations were expressed either by means of surface response methodology or regression equations. The latter have predictive value within the experimental parameter range.

It was found that both increasing flow rate and pressure call for increased inhibitor concentration if target corrosion rates are to be achieved. In the case of inhibitor C, increased water/oil ratio also calls for increased inhibitor concentration.

However, it was also shown, in agreement with earlier studies, that the pressure relationship may be very complex and that the water/oil ratio effect depends on the nature of the inhibitor. The oil soluble inhibitors A and B showed the opposite behavior from inhibitor C with respect to the oil/water ratio. The fact that it is possible to formulate inhibitors such that they become more effective as the water/oil ratio increases, an effect not heretofore recognized as such, should open up new avenues of both inhibitor synthesis as well as formulation.

The missing links between modeling corrosion inhibition in the lab and application in the field are twofold:

- verification of the lab results in the field
- translation of the shear stress from the cage to the tubulars.

Both these issues will be dealt with in the follow up publication. (Ref.11)

The above correlations were expressed in terms of steady state corrosion. Of greater interest, however, is localized corrosion, particular in CO_2 environments at high flow rates (FILC). Detailed and extensive pitting measurements indicated that under test conditions general corrosion rates have to be reduced to below a certain level to prevent localized corrosion as well. In the case of J-55, this level is about 2 mpy. In the case of L-80 and N-80 it is below 1 mpy. How this correlation will hold up in the field is yet to be shown, however, there has long been a feeling in the industry that general corrosion rates should be inhibited below 1 mpy (preferably 0.5 mpy) to prevent local attack.

A final word about economics. From the above it becomes clear that corrosion inhibition in high pressure, high flow rate, high water cut systems becomes very expensive in terms of ¢/bbl of oil produced unless either improved inhibitors are developed, or producers make an effort to combat corrosion in those areas most difficult to inhibit by other means, an effort which is well underway in many instances.

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APPENDIX I

Test Protocol for Laboratory Testing in the HSACT Postle Diagnostic Inhibitor Evaluations

I. Test Conditions

• Autoclave:	4 L		
• Liquid Charge			
Brine	1.83 L		
Hydrocarbon [1]	1.00 L		
• Temperature	160 °F		
• Pressure	variable from 100, 425, 750, and1500 psi (at test temperature)		
• Gas Composition			
CO_2	100 %		
H_2S	500 ppm H_2S in CO_2[2]		
• Stirring Rate	variable (500, 1000, and 1500rpm)		
• Test Duration	5 days		
• Synthetic Brine [3]			
NaCl	93.1 g/L	CL^-	70,000 mg/L
$CaCl_2.2H_2O$	22.0 g/L	Ca^{2++}	6,000 mg/L
$MgCl_2.6H_2O$	8.4 g/L	Mg^{2++}	1,000 mg/L
TDS	113,900 mg/L		
• Coupons	4 PAIR electrodes		
Cage	2 x J-55, N-80, L-80, (Coupon area 30 cm^2 per coupon)		
Electrodes	4 std PAIR electrodes (Electrode are 9 cm^2 per electrode)		

II. Coupon Preparation

- Sandblast coupons with 80 grit silicon carbide
- Degrease coupons by
  1. Using an ultrasonic bath: wash coupons in 50/50 xylene/isopropanol mixture for 5 minutes
  2. Rinse in isopropanol
  3. Rinse in acetone
  4. Dry with nitrogen
- Weigh to 0.1 mg

III. Test Procedure

- Install coupons in rotating cage on stirring shaft
- Install PAIR electrodes on autoclave head
- Add 1000 ml Isopar M to autoclave
- Add 1830 ml of brine to autoclave
- Sparge fluids in autoclave with nitrogen for 30 minutes (prior to closing autoclave)
- Inject inhibitor as needed
- Add 200 ppm of bicarbonate based on brine volume (0.504 gm $NaHCO_3$)
- Assemble and close-up autoclave

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[1] Isopar M™ (a paraffinic hydrocarbon available from EXXON Corp.)

[2] the H_2S concentration in the CO_2 charge gas was designed to result in about 150 ppm H_2S in the gas under test conditions. This level was the maximum encountered in the field. The concentration in the gas under test conditions is only slightly dependent on total pressure with constant temperature.

[3] Note: bicarbonate is added directly to the autoclave in order to avoid precipitation of $CaCO_3$

- Begin data logging of PAIR corrosion data and other test parameters
- Deoxygenate fluids be repeating the following steps 5 times:
  1. Turn stirrer on at 1500 rpm
  2. Charge nitrogen to 1000 psi
  3. Mix fluids and gases for 3 minutes
  4. Turn stirrer to 200 rpm
  5. Slowly vent nitrogen to atmosphere
- Set stirring rate to 1500 rpm
- Charge test gas to charging pressure[4] and verify equilibration (> 1 psi loss in 10 minutes)
- Heat to test temperature (160 °F)
- Sample test solution and stabilize with HCl for iron count measurements
  1. When autoclave reaches test temperature
  2. 2 hours after sample #1
  3. every 24 hours (Note: these will be skipped over weekends)
  4. 24 hrs before end of test
  5. at end of test.
- Run test for total of 120 hrs
- Turn of heat
- Vent gases
- Turn off stirrer
- Open autoclave
- Remove and dry coupons
- Disassemble and clean autoclave. The cleaning procedure will include the dissambly and cleaning of the inside of the magnetic stirrer. All residual iron carbonate is to be removed completely.

IV. Coupon Cleaning Procedure

- Clean coupons in inhibited acid solution (standard procedure)
- Rinse and dry coupons
- Weigh to 0.1 mg
- Calculate weight loss and corrosion rate

V. Evaluation of Results

- **PAIR Probes**
  1. Determine weight loss as above
  2. Print out PAIR data
  3. Integrate under PAIR/time curve
  4. Compare PAIR corrosion rate to weight loss

- **Rotating Cage Coupons**
  1. Determine weight loss as above
  2. Determine pit depth using microscope
  3. Coupons will be photographed to maintain visual record of the corrosion damage

- **Iron Counts**
  1. Measure ppm iron using HACH Ferrover method
  2. Calculate corrosion rates based on differential iron concentrations to obtain corrosion kinetics
  3. Compare corrosion rate from total iron count to weight loss corrosion rate

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[4] The charge pressure is lower than the target pressure at test temperature. A special model was used to determine the exact charge pressure (Ref. 9)

Table 4

I. Inhibitor Concentrations for 1 mpy Target Corrosion Rate

Pressure	Rpm	J-55	N-80	L-80	AISI-1018
750	500	40	50	55	25
425	1000	160	150	180	120
100	500	42	60	52	37
100	1500	200	200	200	150
750	1500	339	400	841	400

II. Inhibitor Concentrations for 2 mpy Target Corrosion Rate

Pressure	Rpm	J-55	N-80	L-80	AISI-1018
750	500	34	40	46	28
425	1000	140	130	170	80
100	500	30	54	46	30
100	1500	150	170	170	100
750	1500	248	309	646	251

III. Inhibitor Concentrations for 4 mpy Target Corrosion Rate

Pressure	Rpm	J-55	N-80	L-80	AISI-1018
750	500	24	28	32	20
425	1000	110	105	140	52
100	500	20	48	42	20
100	1500	100	150	150	75
750	1500	180	240	487	160

Table 5

Final [Fe] Corrosion Rate Data for Different Metals as a Function of the **Water/Oil Ratio**, the **Rotational Velocity** of the Cage and the **Inhibitor Concentration** for Inhibitor C at 750 psi CO_2 Partial Pressure

Run #	**Water/Oil Ratio**	**Inhibitor Conc. ppm**	**General Corrosion Rates for different Metals**			
			J-55	**N-80**	**L-80**	**AISI-1018**
A. Low Velocity (500 rpm)						
21	-	50	*0.99*	*0.99*	*1.7*	*0.66*
22	+	50	*8.8*	*8.6*	*11.5*	*1.25*
15	-	100	*0.28*	*1.69*	*0.44*	*0.36*
24	+	100	*3.75*			*1.2*
B. High Velocity (1500 rpm)						
12	-	150	*4.9*	*11.67*	*51.4*	*2.1*
25	+	150	*9.2*			*11..3*
13	-	225	*3.2*	*5*	*33*	*5.64*
23	+	225	*1.4*	*1*	*1.1*	*1.1*

<u>Oil/Water Ratio:</u> - equals **1.83** + equals **9**

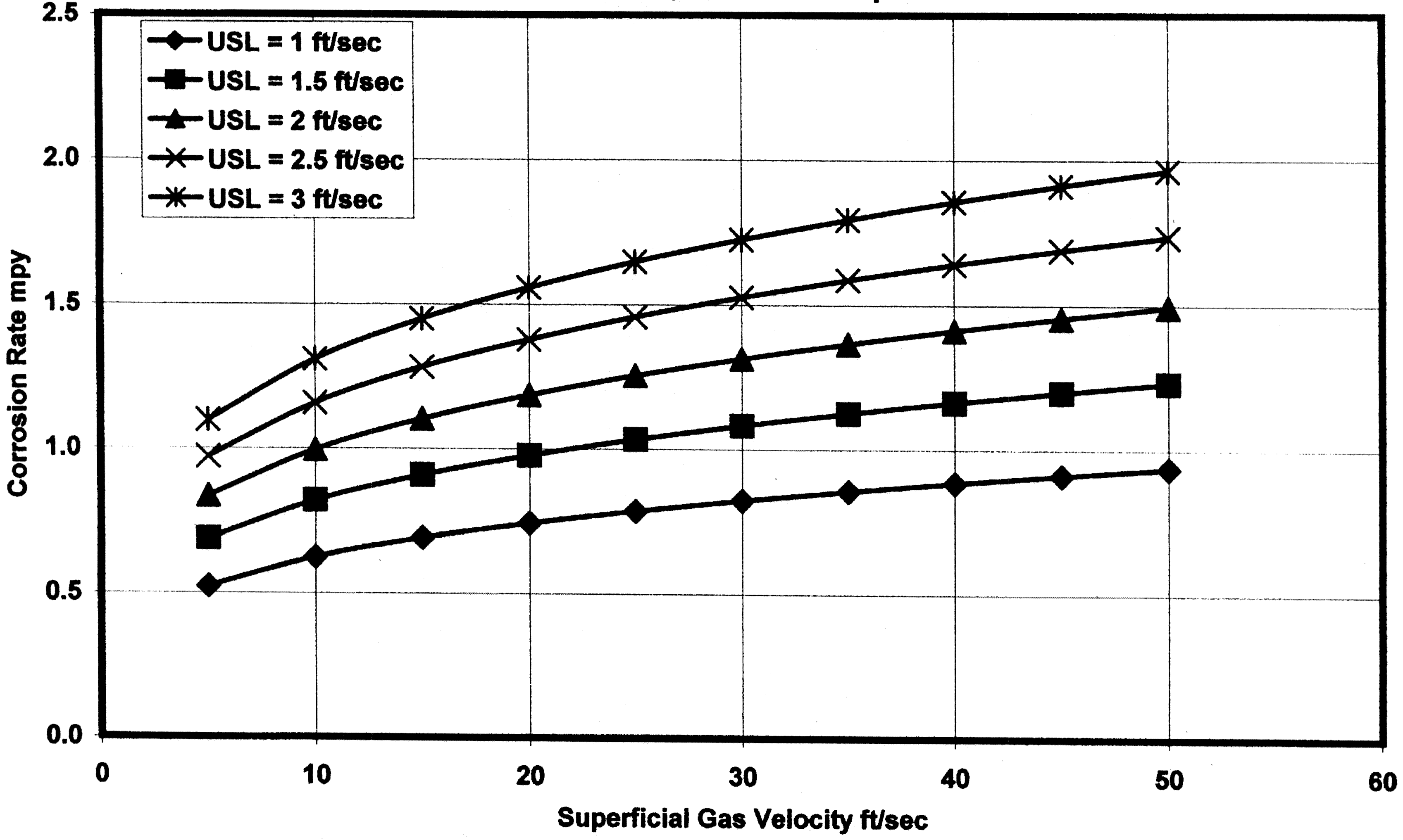


Figure 1: Inhibited Corrosion Rates as Function of Superficial Gas and Liquid Velocities from Little Creek Correlation of Coupon Data

Inhibitor A, Water/Oil = 117, Pressure 1800 psi

Figure 2: Corrosion Rate as Function of Pressure and Water/Oil Ratio based on Little Creek Correlation of Coupon Data

Inhibitor A, U_{SL} = 2 ft/sec, U_{SG} = 2 ft/sec

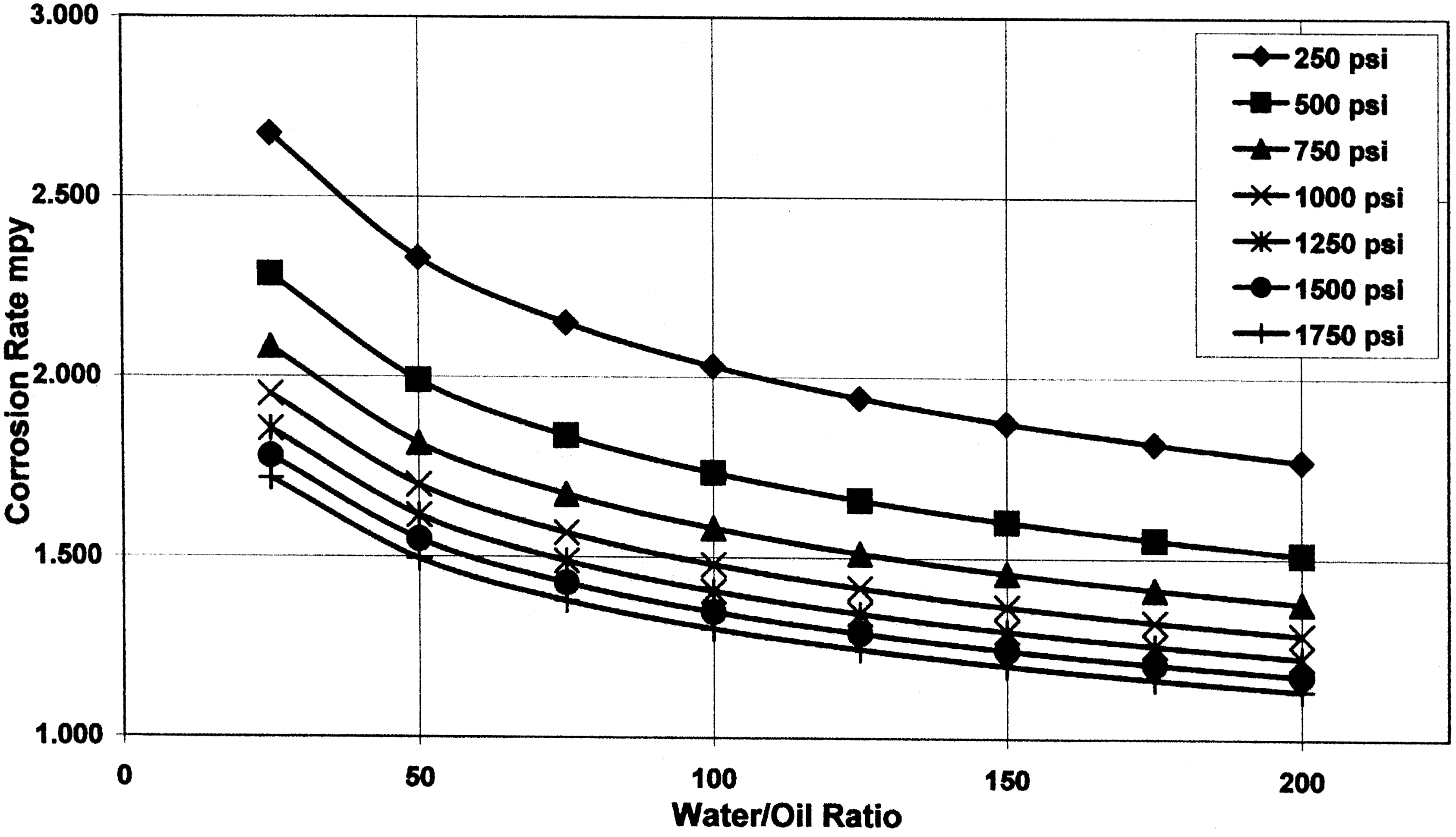


Figure 3: Inhibited Corrosion Rate as Function of CO2 Pressure
(High Speed Autoclave Test)

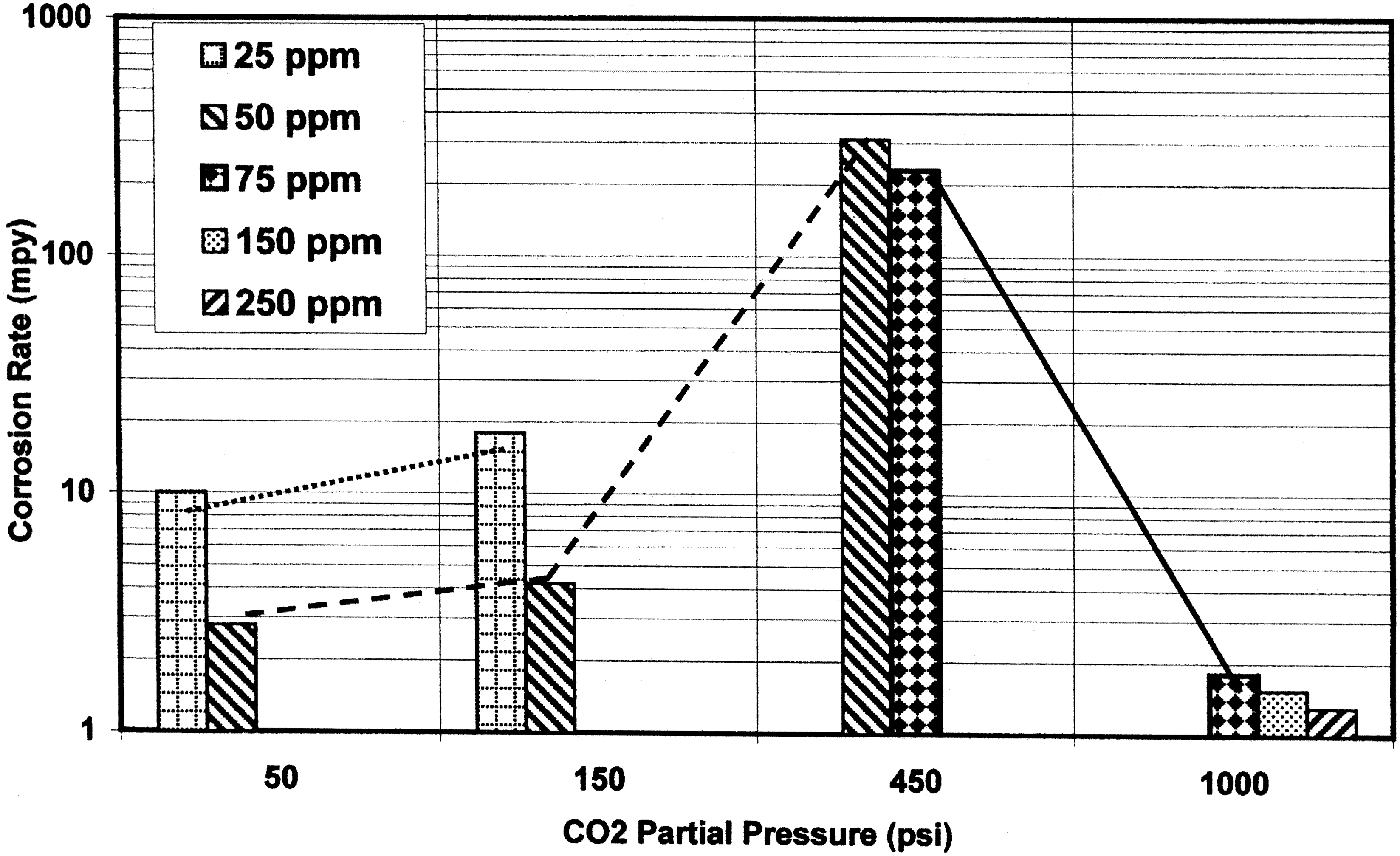
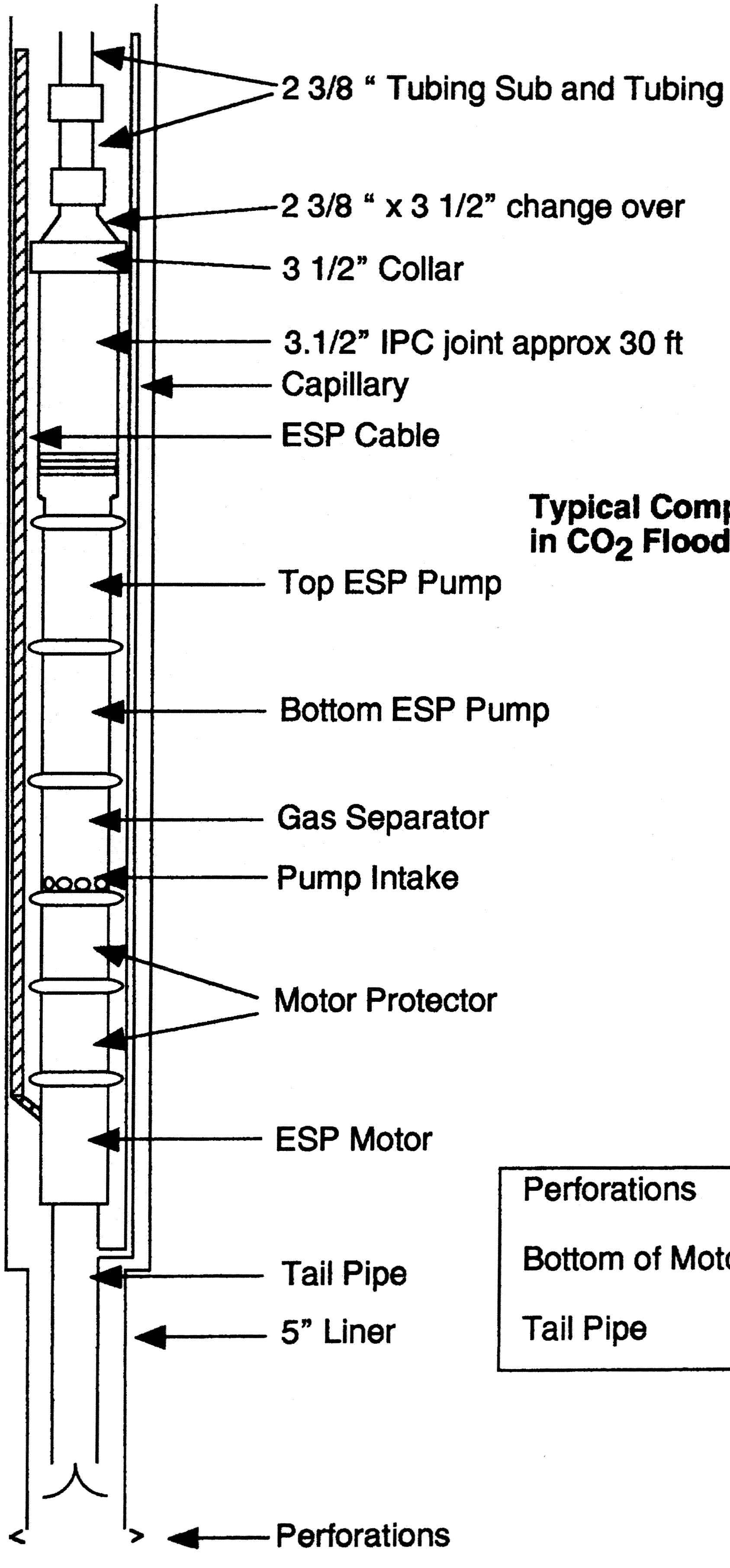


Figure 4

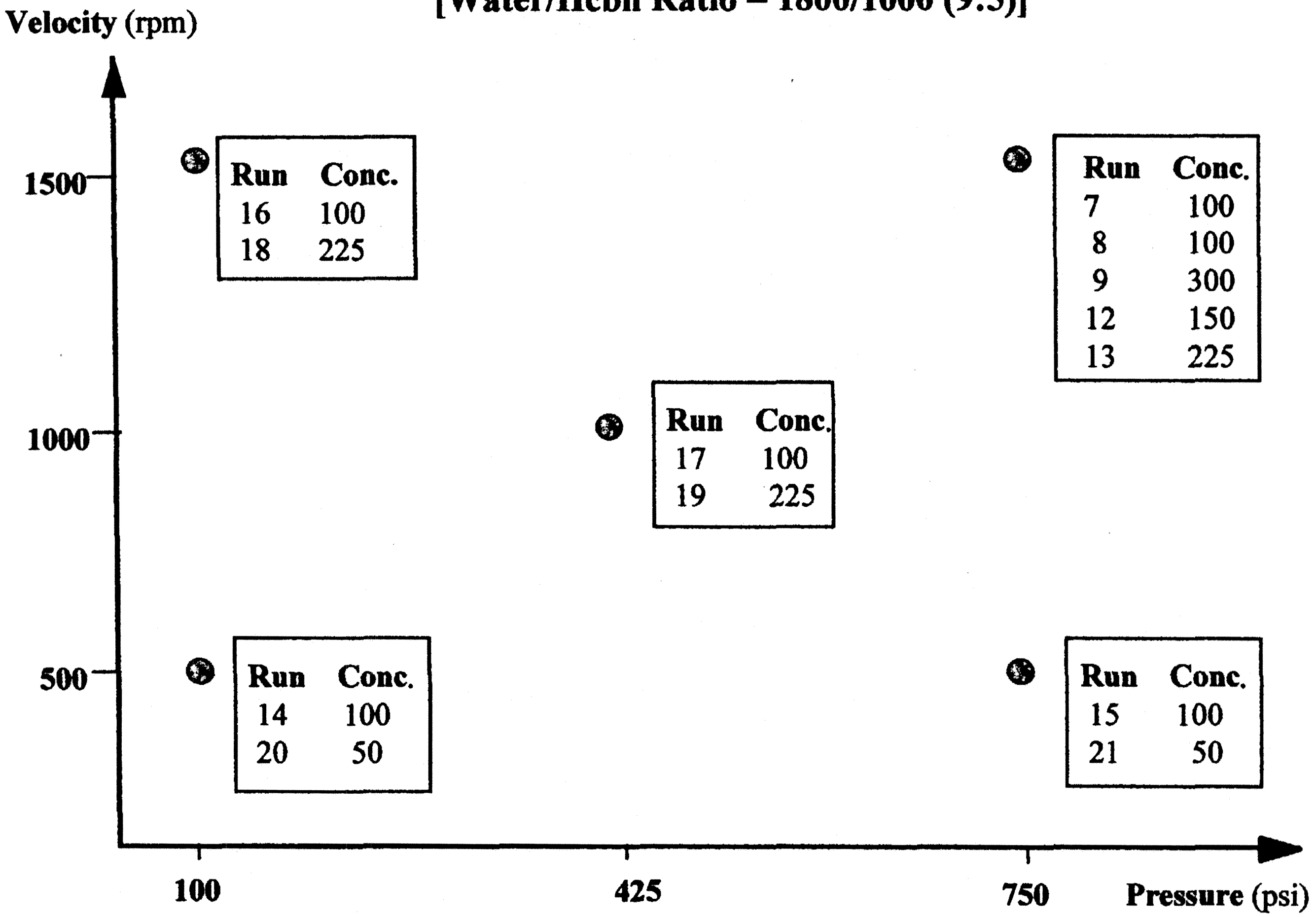
Typical Completion of Producing Well in CO_2 Flood with full length Capillary



Perforations	approx 6150 ft
Bottom of Motor	approx. 6000 ft
Tail Pipe	approx. 100 ft

Figure 5

Evaluation of Inhibitor C at Different Concentrations and Test Conditions in the HSAT
[Water/Hcbn Ratio = 1800/1000 (9:5)]



Run	Conc.
16	100
18	225

Run	Conc.
7	100
8	100
9	300
12	150
13	225

Run	Conc.
17	100
19	225

Run	Conc.
14	100
20	50

Run	Conc.
15	100
21	50

Figure 6: Inhibited Corrosion Rates of J-55 at 750 psi and 1500 rpm

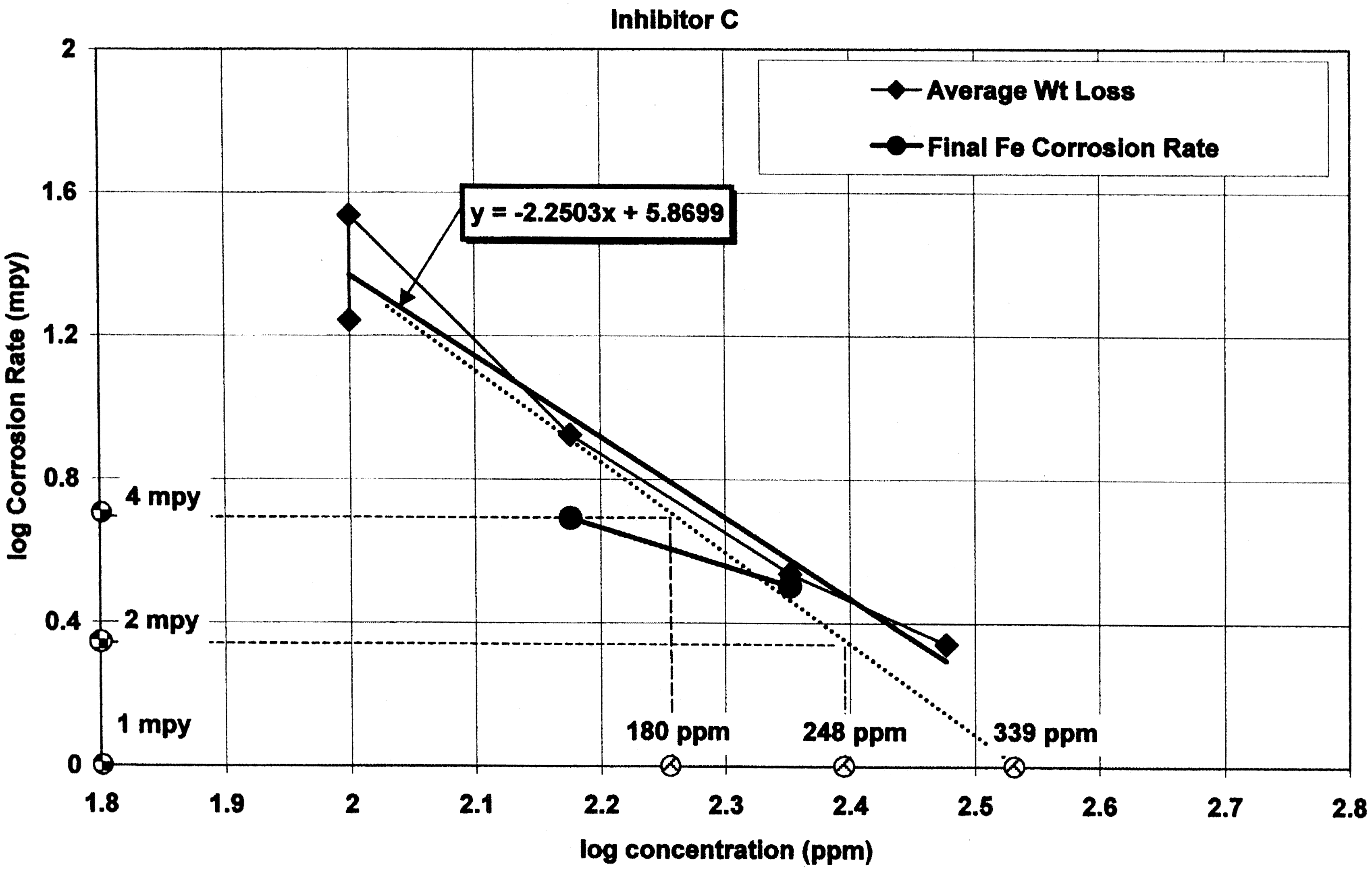


Figure 7: Inhibited Corrosion Rates of L-80 at 750 psi 1500 rpm

Inhibitor C

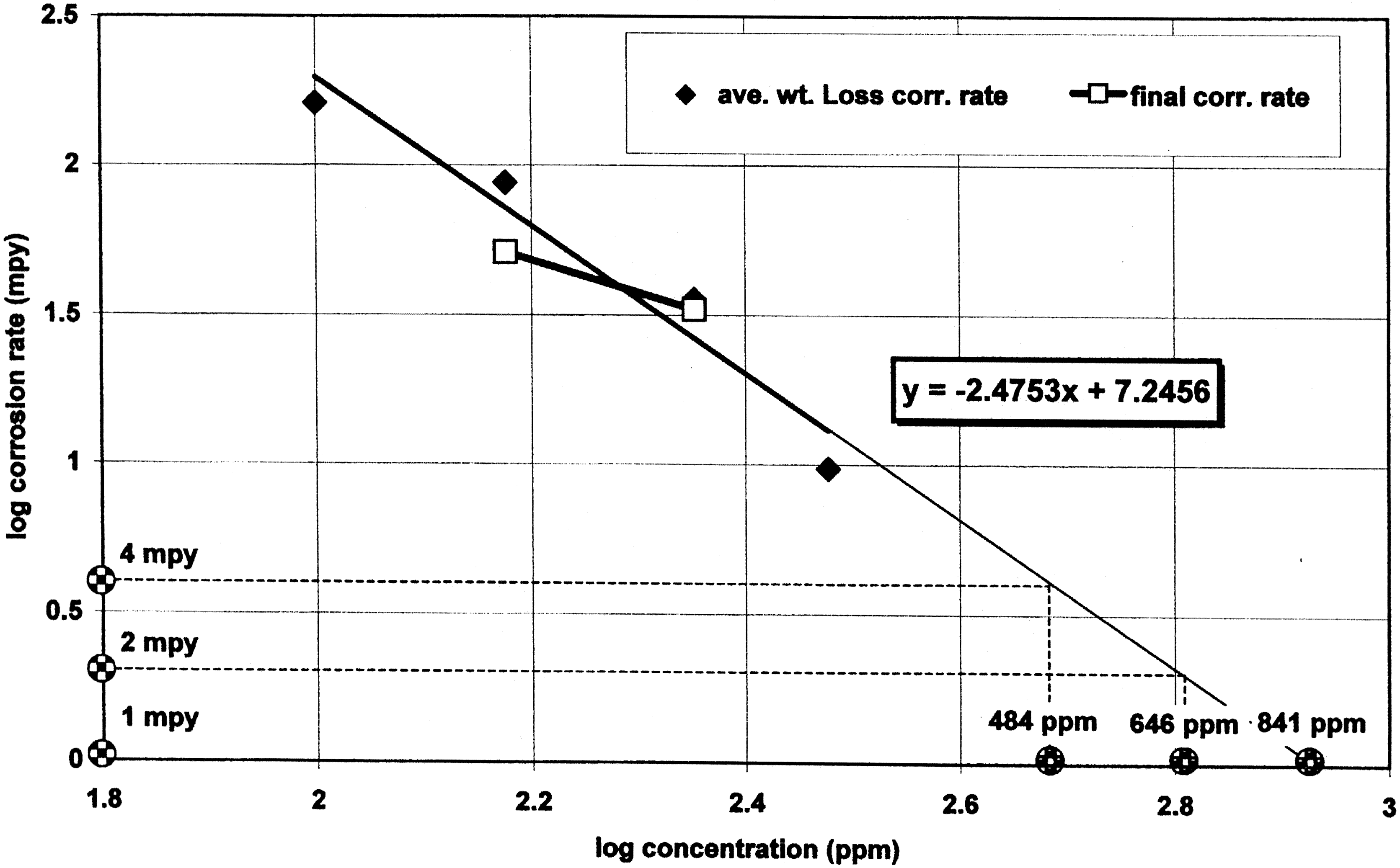


Figure 8: Contour Plot for J-55
Inhibitor Concentrations Necessary to Achieve 1 mpy Based on Final Corrosion Rates from Differential Iron Counts

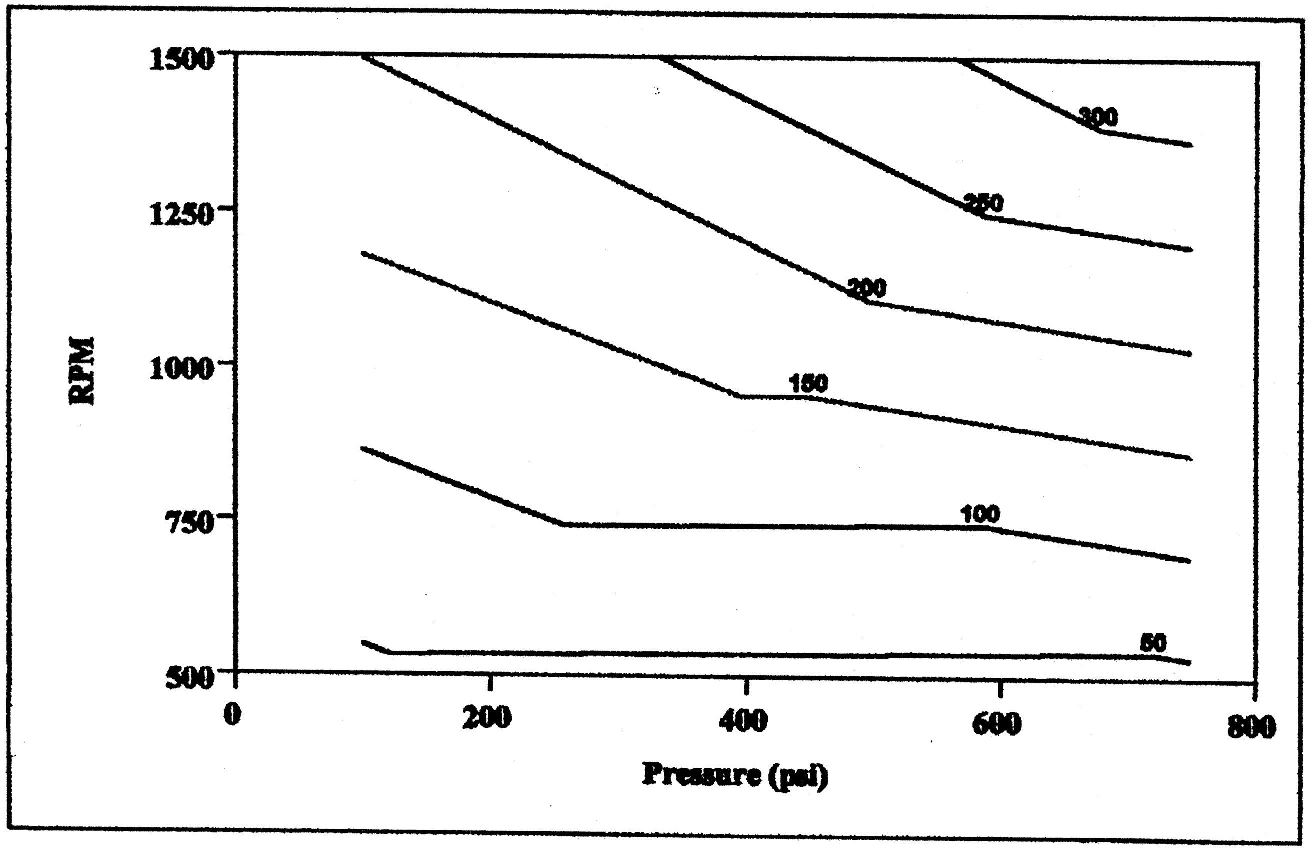


Figure 9: Contour Plot for L-80
Inhibitor Concentrations Necessary to Achieve 1 mpy based on
Final Corrosion Rates from Differential Iron Counts

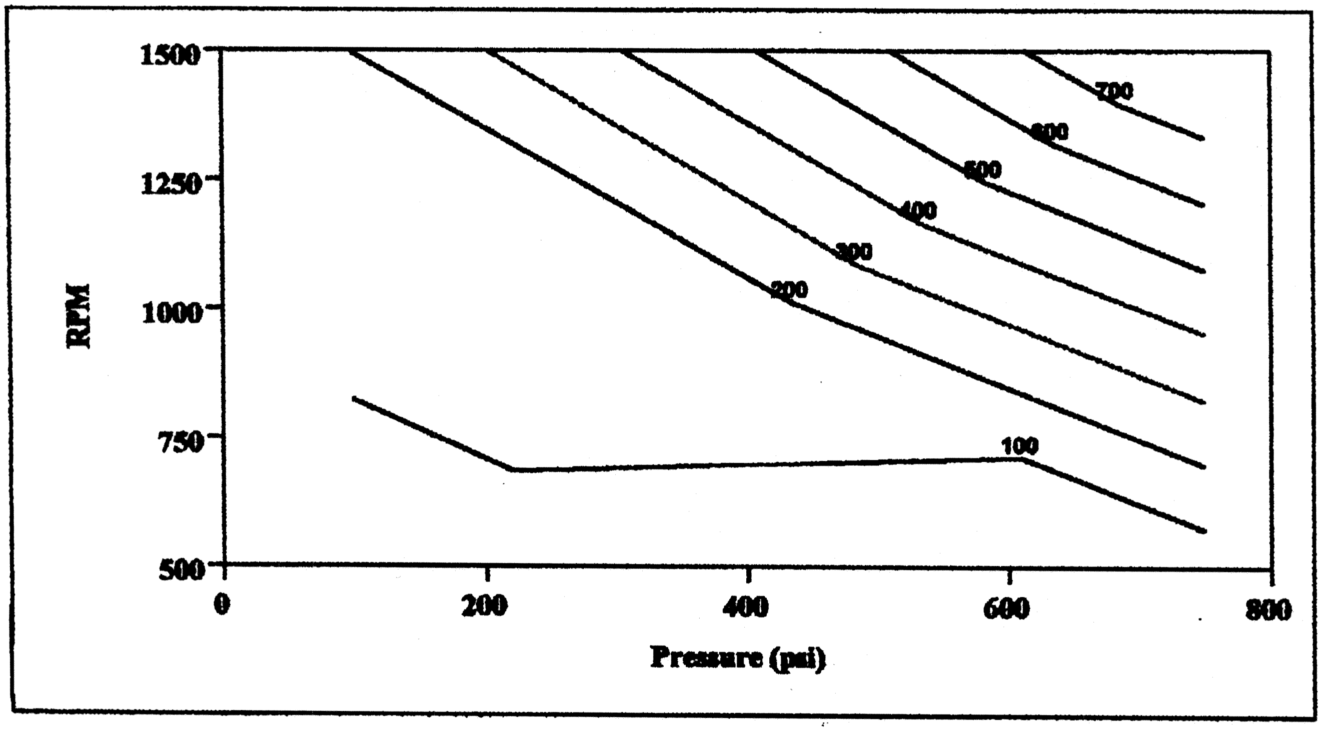


Figure 10: J-55 Pitting rate vs. Corrosion Rate

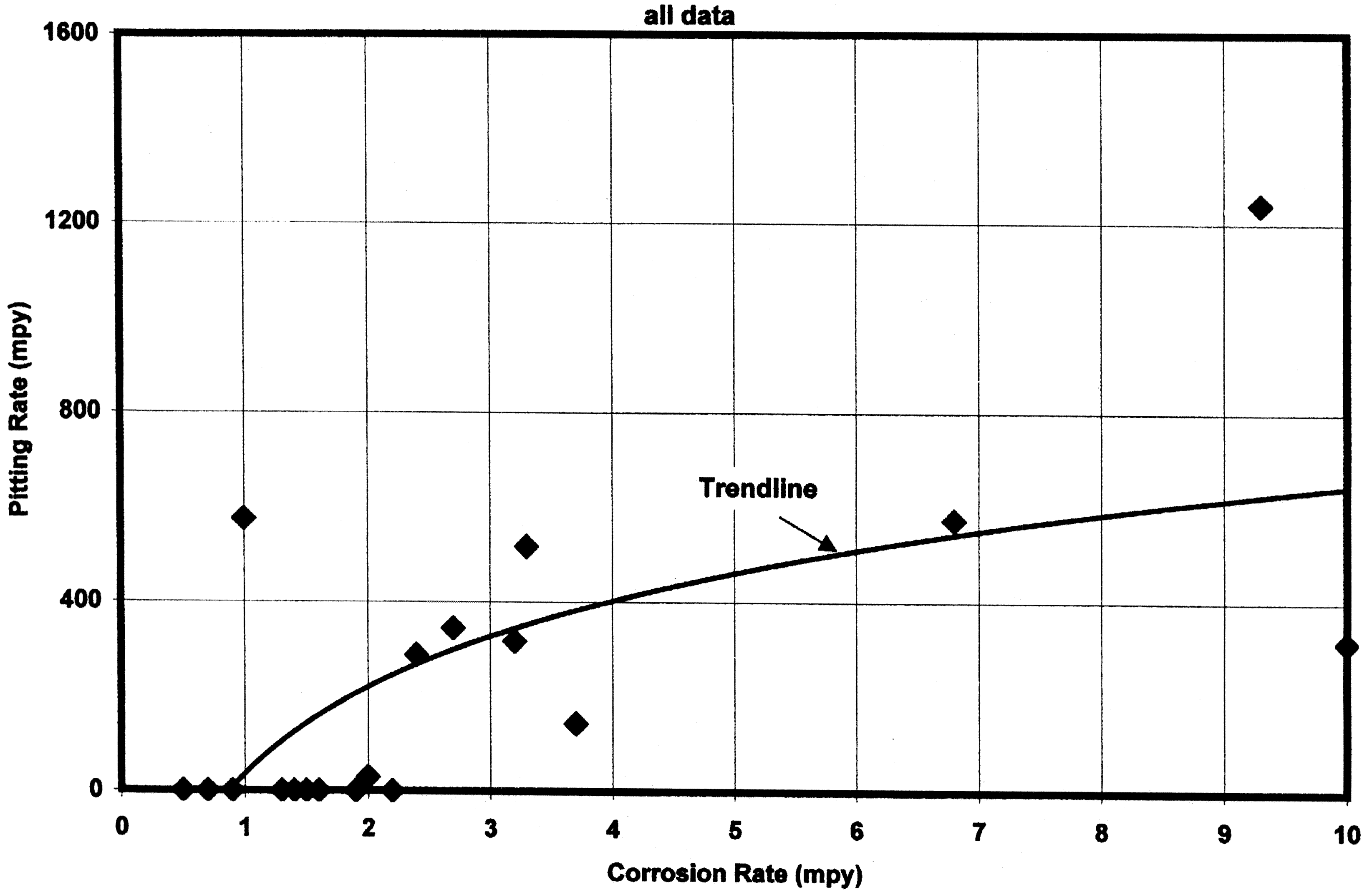


Figure 11: L-80 Pitting Rates vs. Corrosion Rates

all data

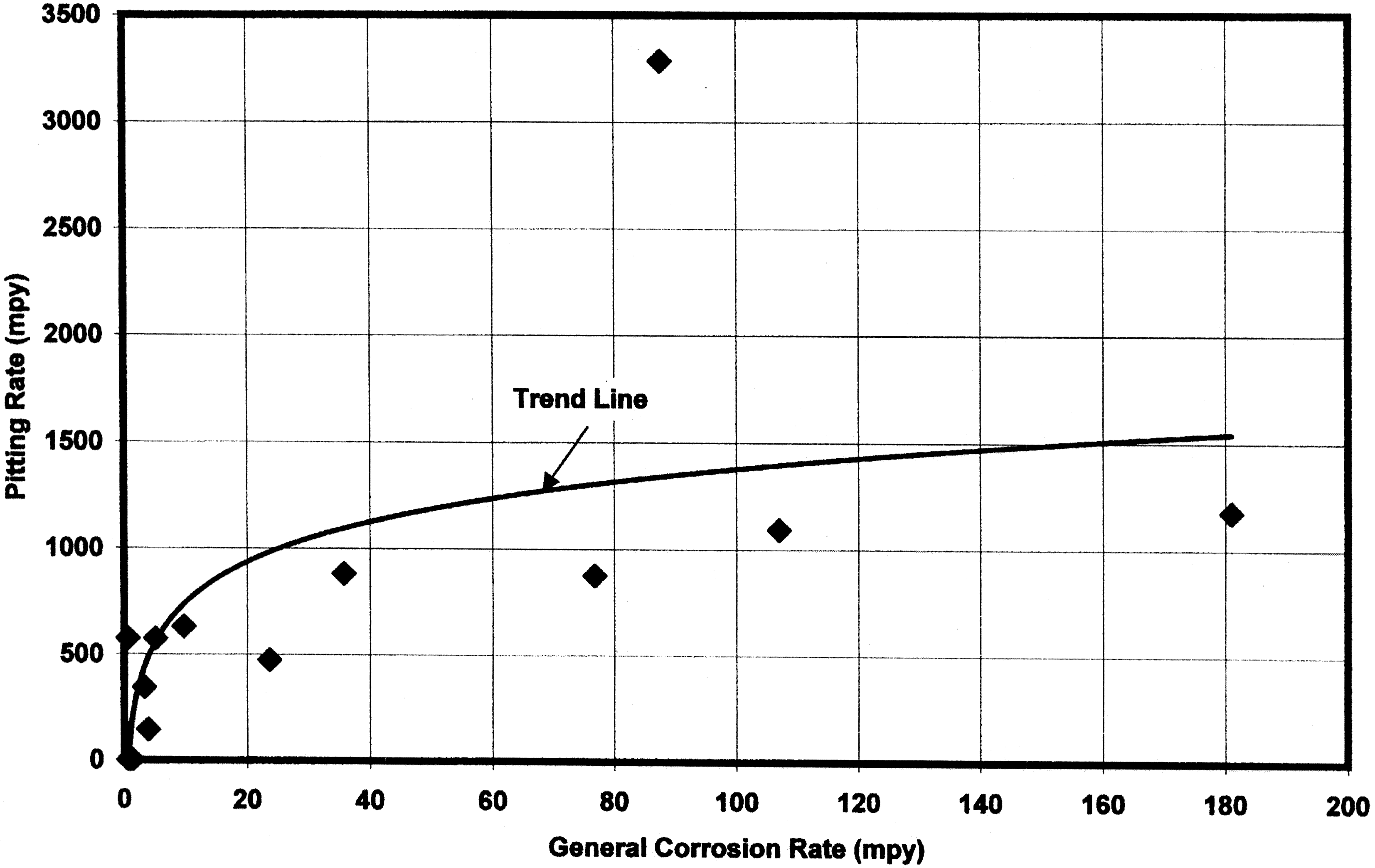


Figure 12: Corrosion Rate vs. Velocity at 750 psi CO_2 Pressure

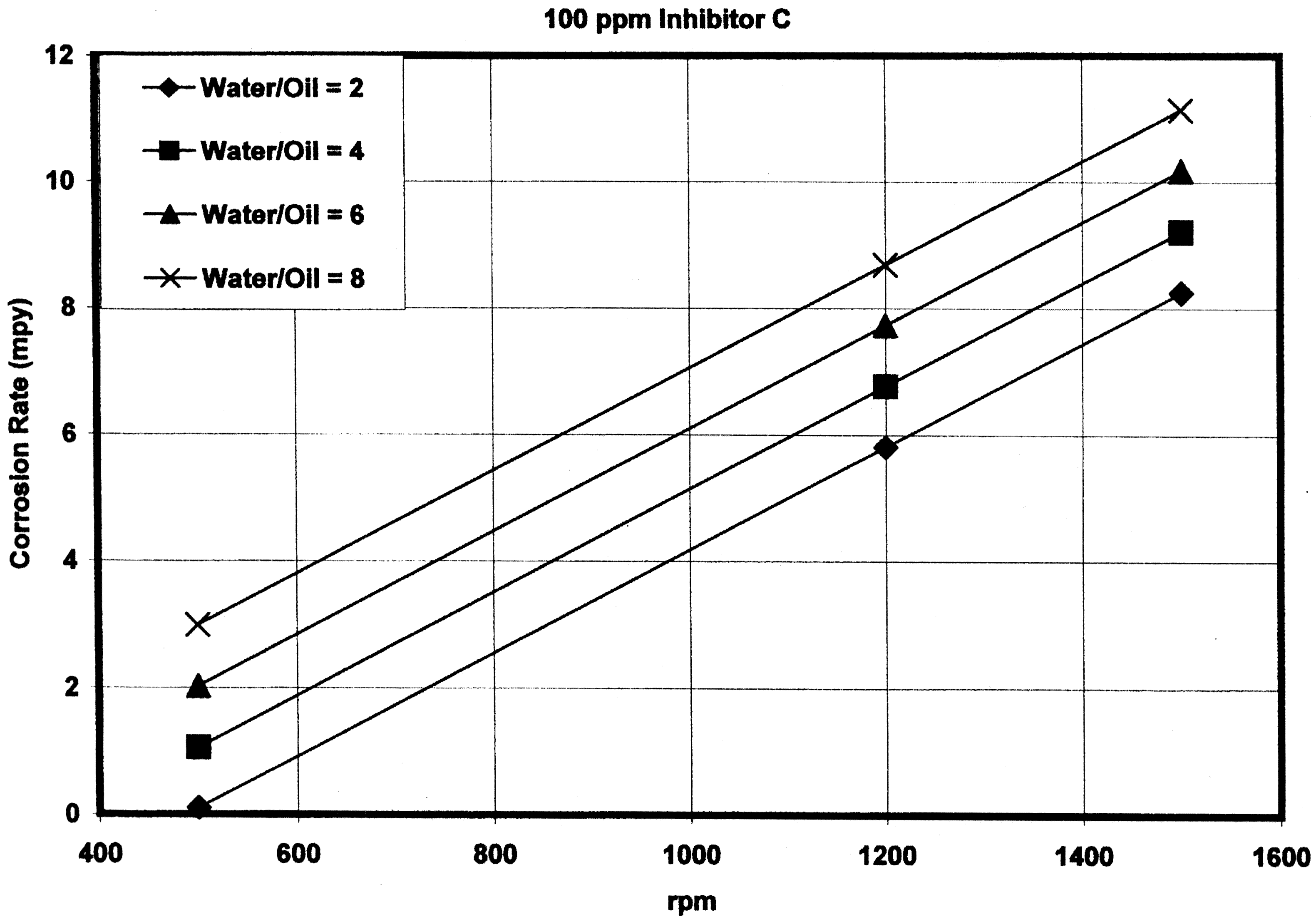


Figure 13: Effect of Inhibitor Concentration

Inhibitor C, 750 psi CO2, Water/Oil Ratio = 2