

SAUDI ARAMCO ENGINEERING REPORT: SAER 5579

CSD TECHNOLOGY ITEM 05/95-J

CAPCIS: THE FLOW TEST PROJECT FINAL REPORT

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EXECUTIVE SUMMARY

CSD frequently becomes involved in recommendations to evaluate corrosion inhibitors for flowing oil field systems or to predict corrosion rates in such systems. We initiate corrosion inhibitor tests programs to select the most appropriate inhibitor for a specific field application. Presently, many common test methods do not consider the effects of flow on the performance of inhibitors and the evaluation of corrosion rates.

This report analyzes the results⁽¹⁴⁾ from a Joint Industry Project (JIP) performed at CAPCIS, Manchester, England, on the correlation between three test techniques that simulate flowing systems, namely: rotating cylinder, flowloop, and jet impingement. We also correlate the findings of the JIP to progress reported in literature sources.

The present work is important to Saudi Aramco because it demonstrates the need to include flow effects in inhibitor selection and also validates various test methods that can be used. This will help in selecting the most cost effective products in future field applications.

The objectives of the JIP were completed successfully. Major conclusions from the JIP and literature analysis are as follows:

- Inhibitors are sensitive to flow. Some inhibitors perform significantly better in flowing environments than do others. Therefore, where velocity might be a major consideration in a field environment, we recommend the use of velocity controlled tests in the selection of corrosion inhibitors.

⁽¹⁴⁾ J. L. Dawson, G. Dicken, J. W. Palmer, S. Turgoose, "The Flow Test Project - Final Report," CAPCIS reference CGDGZQ-R.

- Data between the flow test methods can be directly correlated when compared on an equivalent basis. For uninhibited systems, the JIP finds that the results can be compared on the basis of mass transport. For inhibited systems, the JIP proposes that shear stress is the critical factor.
- When comparing data on the basis of mass transfer, it is essential that entry length effects be adequately considered in flowloops and jet impingement rigs. In this type of equipment, data are best described by equations for developing mass transfer rather than by equations for fully developed mass transfer.
- The CAPCIS report includes equations used to analyze each specimen geometry. An Excel spread sheet is available for calculating shear stress and mass transfer.
- Field and laboratory tests indicate that inhibitor film life is limited. Batch applied film life was found to be of the order of 20 days, depending on the product being tested and the exact field conditions.
- Our results clearly demonstrate the need for advanced flow testing equipment in-Kingdom. We concur with Lab R&D Center's recent proposal⁽¹³⁾ to develop these facilities.
- We propose that further work be considered. While most laboratory research programs concentrate on the CO₂ reaction process, many of Saudi Aramco's fields also produce hydrogen sulfide. Only limited work has been performed on the transition from a predominantly sweet (CO₂) corrosion mechanism to a predominantly sour (H₂S) mechanism. We propose the development of a new Technology Item on this subject to give improved information to assist in the prediction of corrosion in new fields.

⁽¹³⁾ J. K. Boah, P. Frazer, and A. S. Khuraidah, "A Study into the Effects of Flow on Corrosion rates of Materials," ARI 220-04/93-F, July 1997.

PRACTICAL SIGNIFICANCE

CSD frequently becomes involved in the selection of corrosion inhibitors for operating environments, especially pipelines. Velocity of the fluids in the pipeline plays an important part in the distribution of inhibitors inside the pipe and therefore on performance of inhibitors.

Inhibitors are either applied continuously or in a batch process such as a well squeeze. Distribution of the inhibitor is dependent on the hydrodynamics of the system. Under some circumstances, too low a velocity may provide insufficient momentum to carry inhibitor along the pipe, while too high a velocity may result in large shear forces that remove the inhibitor from the pipe wall.

In order to select inhibitors for a field application, CSD often commissions laboratory tests to compare performance of several products. Usually these tests do not involve a systematic evaluation of hydrodynamic effects. There are benefits from considering the inclusion of a velocity factor in the evaluation matrix.

The situation has been complicated in recent years by research workers in different parts of the world favoring different types of tests to simulate velocity effects. It is often difficult to correlate results from one test to another. The results of this JIP in combination with our analysis of literature now make correlation of the different test methods possible.

OBJECTIVES

- To establish, through a joint industry program, the relationship between various hydrodynamic corrosion test methods and understand any differences in the resulting data. The methods examined were rotating cylinder electrode (RCE), impinging jet, and a single phase flowloop.
- To define test procedures so that a more consistent approach to flow testing and inhibitor testing could be established.
- To increase awareness of the concepts of testing under controlled hydrodynamic conditions and their relevance to field performance.

CONCLUSIONS

- For the experimental conditions encompassed by the joint industry program, data from rotating cylinders and flow loops can be directly correlated when compared on an equivalent basis. CAPCIS data from the jet impingement rig were more widely scattered and need additional clarification of empirical equations.

- For the conditions studied, mass transfer was found to be the critical factor in the effect of flow on the uninhibited corrosion rate of steel in sweet systems. In the flowloop and jet impingement test systems, mass transfer conditions are best described by equations for developing mass transfer, recognizing the effect of entry length on the specimens' results.
- For inhibited conditions, the JIP authors propose that the controlling factor is shear stress physically removing inhibitor from the pipe wall.
- Inhibitors are sensitive to flow. Some inhibitors perform significantly better in flowing environments than do others. Therefore, where velocity might be a major consideration in a field environment, velocity controlled tests are recommended.
- The rotating cylinder test method provides a good inhibitor screening test for known hydrodynamic conditions. However, the range of shear stress that can be obtained with a rotating cylinder is limited.
- In the CAPCIS experimental work, flowloop tests and jet impingement tests were found to be inherently more severe in inhibitor tests. It is speculated that this is because of local turbulence effects in the design of the flowloop and jet resulting in higher shear stresses. Flowloop and jet impingement tests do provide the opportunity to study higher shear stresses.
- CAPCIS reports the equations considered to be most appropriate to define the hydrodynamics of each flow test method that has been investigated. These are available from CSD in the form of a Excel 7.0 file for application in future work, as needed.
- For high temperature, high pressure work, the use of a rotating cylinder weight loss coupon for inhibitor studies provides the benefits of hydrodynamic modeling without the disadvantages of difficult cleaning and rotating, pressurized electrical feed throughs.
- The CAPCIS work identifies some aspects of test procedure that lead to variability in results between different laboratories. The use of either wide range potentiodynamic scans or cathodic charging results in the deposition of impurities on the test specimen and possible reduction in the corrosion rate.
- Corrosion prediction in sweet environments remains difficult. After 21 years research, there is considerable controversy over the corrosion reaction process and therefore the factors to be included in modeling and interpretation. Any data interpretation that relies on equivalence of mass transport relies on an understanding of the corrosion

mechanism and the availability of mass transport coefficients for the species in question.

- The development of advanced flow testing facilities in Saudi Aramco is recommended. This recommendation concurs with the conclusions of ARI 220-04/93-F, "A Study Into the Effects of Flow on Corrosion Rates of Materials."⁽¹³⁾

SCOPE: FLOW ENHANCED CORROSION

This project studies flow enhanced corrosion in sweet oil-field systems where the effect of flow is to enhance mass transport of corrodents to the metal surface and the removal of corrosion products from the surface. Film formation and stability may be affected. CO₂ corrosion has been found to be dependent upon the hydrogen ion mass transfer coefficient, and this provides the basis for the current work.

It does not include true "erosion-corrosion" where solid particles remove corrosion films or passive layers.⁽¹⁾ It does not include "erosion" where metal loss is due solely to mechanical erosion mechanisms such as cutting and fatigue from repetitive impacts of solid particles, and no electrochemical dissolution occurs.*

Applied research over the last several years has used a variety of test methods, with each worker favoring their own approach. Controversy was increased by a technical committee meeting at Corrosion 94 when data were presented that showed apparent differences between the three single phase test methods, rotating cylinder, flow loop, and impinging jet. This JIP was initiated to investigate these differences.

For the equations reported below, it must be appreciated that many of them are derived from empirical rather than theoretical sources. For the jet impingement rig, where adequate equations are not available in literature, a relationship for mass transfer has been derived from flow loop equations.

This JIP does not include any work on multiphase test loops or simulated slug flow. While these techniques are extremely important to the understanding of corrosion in flowing systems, the cost and availability of such systems makes them unattractive for most work.

* While erosion caused by liquid droplets is possible without any corrosion dissolution reaction, research has found this will not occur at speeds less than those typical of aircraft, i.e., about 300 m/s or 1000 ft/s. Such velocities are not of interest to normal oil and gas operations.

RESULTS: UNINHIBITED CORROSION

Rotating Cylinder

The rotating cylinder is described by the following equations[†]:

Mass Transfer

$$\frac{kd}{D} = 0.079 \text{ Re}^{0.7} \text{ Sc}^{0.357}$$

Wall Shear Stress

$$\frac{\tau}{\rho \mu^2} = 0.079 \text{ Re}^{-0.30}$$

Corrosion in a flowing system is dependent on mass transport of reactants to and from the metal surface and momentum transferred from the bulk fluid to the wall. There are two boundary layers. An outer, hydrodynamic, boundary layer and an inner, mass transport, boundary layer. These are shown schematically in Figure 1.⁽²⁾ Both these layers may be affected by eddies in the flow that effectively increase the diffusivity or mass transfer and increase the momentum transfer, measured as shear stress, to the wall.

For a rotating cylinder (with no exposed top or bottom surfaces), the hydrodynamic and mass transport boundary layers are well established much as would exist in a perfectly uniform, very long pipeline.

The rotating cylinder is a valid test method which is relatively simple to perform at atmospheric pressure and can be easily cleaned. This makes it well suited for inhibitor studies in medium flow environments, within the hydrodynamic conditions achievable by the test. It is very cost effective. At atmospheric pressure, electrochemical experiments can be used to track the progress of a test. Wide range potentiodynamic scans or cathodic charging are not recommended, however, due to the problem observed during the JIP of deposition of trace contaminants in the test system.

At pressures higher than atmospheric pressure, the performance of rotating cylinder electrochemical tests is achievable as shown in Figure 2.⁽³⁾ The data indicate an apparent velocity threshold to remove protective carbonate scales. However, the classical rotating cylinder design requires a noise free electrical connection to a pressure sealed, electrically isolated shaft. A complex multi-component shaft seal/bearing is required. High speed rotation results in wear on the pressure seal and, eventually, pressure integrity is lost. Rotating cylinder electrochemical measurements at elevated temperature and pressure are extremely difficult.

[†] For a definition of terms, please see the Glossary at the end of this report.

Flow loop**Fully Developed Mass Transfer**

$$k = 0.057 \left(\frac{\tau}{\rho} \right)^{1/3} Sc^{-2/3}$$

Developing Mass Transfer ("Short Electrode")

$$k_{av} = 0.081 \left(\frac{\tau}{\rho} \right)^{1/3} \left(\frac{v}{L} \right)^{1/3} Sc^{-2/3}$$

Wall Shear Stress

$$\frac{\tau}{\rho \mu^2} = 0.0395 Re^{-0.25}$$

While the hydrodynamic boundary layer is well established in a flowloop with flush specimens, the mass transfer boundary is not established at the leading edge of a test specimen. Therefore, mass transfer rates at the front edge of a flowloop specimen can be much larger. This is shown schematically in Figure 3.⁽²⁾ This makes the description of mass transfer more complex and results in the appearance of higher corrosion rates in a test. Figure 4 shows the variation of mass transfer rates depending on test specimen (electrode) length, compared to that for an long specimen. Figure 5 shows the calculated effect on the ferrous iron concentration at various shear stresses. The critical point is that at any particular constant value of shear stress, the long test specimen results in the highest concentration of ferrous ions and therefore, the lowest corrosion rate.

In the real world, pipe systems are effectively infinitely long and therefore, everything else being equal, the mass transfer boundary layer will be a consistent thickness. The conclusion is that for a normally corroding system, the data generated from a flow loop must be compared on the basis of the same mass transfer rate and not the same shear stress.

The JIP investigated three different flow loop test specimen lengths: 1 mm, 5 mm, and 10 mm. The internal bore diameter in the test section was 10 mm. For the 1 mm long specimen, it was concluded that leading edge effects predominate. In the opinion of the researchers, the 5 mm electrode results correlated best with the calculations for short electrodes, whereas, the longer 10 mm electrodes did not correlate as well with the "short electrode equations." An example of the data is shown in Figure 6. For different diameter flow loops, it is possible that different test specimen lengths would provide the optimum

correlation. Accordingly, each flow loop must be carefully calibrated to define mass transfer conditions and appropriate test specimen length.

Jet Impingement

Mass Transfer

$$k = 0.13 \left(\frac{\tau}{\rho} \right)^{1/2} Sc^{-0.75}$$

Wall Shear Stress

$$\frac{\tau}{\rho \mu^2} = 0.0447 Re^{-0.182} \left(\frac{x}{d} \right)^{-2}$$

where, x is the radial distance. Valid for "wall-jet" region only where $x/d > 3$.

The jet electrode was found to function in a similar manner to short flow loop electrodes, and on several occasions provided the highest corrosion rates. An example of data is provided in Figure 7. Results with the jet were found to be more variable than with the flow loop or with the rotating cylinder. This maybe partly due to crevice effects between the ring elements. However, it is also probable that there is considerable opportunity for improvement in the empirical equations. This is confirmed by the data presented in Figure 8. For very high shear stress experiments, the jet may be the only practical answer.

RESULTS: INHIBITOR DATA

For the most part, rotating cylinder experiments showed the highest efficiencies and jet impingement the lowest, as shown in Figures 9 and 10. CAPCIS concludes from its analysis of the data that for inhibitor studies, shear stress is expected to be the most important flow parameter for correlation with service. It is proposed that the corrosion rate is not limited by delivery of reactants to the surface but rather by physical adsorption/desorption of the inhibitor. With corrosion inhibitor present, the corrosion rates are significantly reduced. Unfortunately, CAPCIS did not present sufficient graphical data in the final report to allow independent derivation of the same conclusions.

Round Robin testing with some of the sponsors of the JIP showed generally consistent results, though occasional unusual results were obtained, as shown in Figure 11.

The variation in inhibitor performance with test method may be indicative of inadequacies in the equations that define mass transfer and shear stress for each of the geometries. It may also be due to leading edge effects that are more pronounced in the jet.

CAPCIS investigated two inhibitors in this program: a water soluble inhibitor and an oil soluble inhibitor. Both were applied in the same way being added to give a certain ppm dispersion in the water phase. While this maybe satisfactory for water soluble/dispersible products, it is not usually an appropriate way to test oil soluble products, because the inhibitor tends not to reach the active metal surface. As would be expected, the results for the oil soluble inhibitor were far more scattered.

LITERATURE DATA—INHIBITORS

Inhibitor selection methods for sweet systems vary between oil companies. While some have considered flow effects for some time⁽⁴⁾ others hold fast to conventional static tests.⁽⁵⁾ Data from multiple sources show that inhibitor performance is dependent on flow and varies from one inhibitor to another. Figure 12⁽³⁾ shows the breakdown of an inhibitor film in a film-persistency test with increasing rotation speed on a rotating cylinder electrode. Figure 13 shows a different inhibitor with far more effective film persistency. Figure 14 similarly shows the effect of velocity on an inhibitor tested in a flowloop.⁽⁶⁾ Farquhar⁽⁷⁾ reports data that shows some corrosion inhibitors are markedly less efficient in flowing rather than static tests. Olsen⁽⁸⁾ reports field data where an inhibitor that was effective at 1.5 m/s was ineffective at 4.4 m/s (~ shear stresses of 5.4 and 40 N/m²). The conclusion is that velocity has a significant effect on corrosion inhibitor performance and therefore should be considered in the design of experiments.

One test method for inhibitor studies at elevated temperatures and pressures is the rotating cylinder as a weight loss coupon in an autoclave. This approach has been adopted by Chesnut et al.⁽⁹⁾ Electrical connection is not required and conventional magna-drive autoclaves can be employed. Also, because an electrochemical measurement is not used, multi-component systems including hydrocarbon can be evaluated. The technique proved useful in an integrated program that included flowloop testing and field evaluations.

Chesnut et al.⁽⁹⁾ found that the candidate inhibitor that performed best in atmospheric pressure rotating cylinder experiments also performed best in autoclave rotating cylinder, flowloop, and field tests. The field tests with five candidate inhibitors revealed that inhibitor film life for field conditions of 80% water cut, 180°F, up to 170 Pa shear stress is approximately 20 days. Once inhibition began to fail, the corrosion rate rose rapidly.

The design of the inhibitor test is critical in the interpretation of the results. Performance in laboratory tests is highly dependent on the method of inhibitor application in the test compared with the method of inhibitor application in the field. For example, inhibitors with poor water dispersibility may perform poorly in tests that do not allow the inhibitor to effectively contact the metal surface. Figure 15 demonstrates the effect of addition of an insoluble inhibitor in a poorly mixed situation. An increase in rotation speed to 6000 RPM eventually results in dispersion of the inhibitor through the test environment and some inhibition. Conversely, Figure 16 shows the effect of a highly water soluble inhibitor

which appears to be far more effective because of its ability to reach the specimen surface.⁽³⁾

The intensity of the flow effects that are designed into laboratory experiments is also important. Too severe a test may eliminate inhibitors that might be cost-effective. In the design of autoclave test procedures, it has been concluded that discontinuous coupon designs can result in extremely high shear stresses on the leading edges and possibly bubble impingement in low pressure areas.⁽¹⁰⁾

LITERATURE DATA—FLOW TEST METHODS AND CO₂ CORROSION MECHANISM

Efird's comparison between shear stress data for flowloop, jet impingement, and rotating cylinder test methods is summarized in Figure 17. Jordan and Rhodes,⁽²⁾ parallel to the efforts of CAPCIS, took Efird's original data and recalculated it, based on mass transfer coefficient, as shown in Figure 18. The disparity between the data sets vanishes, confirming the validity of the concept used in the CAPCIS work.

Along the same lines, Nesic et al.⁽¹¹⁾⁽¹²⁾ found excellent correlation between data generated in a flowloop and data generated with a rotating cylinder electrode. The corrosion rate at pH<4 was largely dependent on the transport of the hydrogen ion. As the pH increased, the hydrogen ion contribution to the corrosion reaction reduced, while another mass transport controlled reaction became more significant.

The challenge clearly remains that for any analysis based on mass transfer coefficient, there must be a clear understanding of the reaction mechanisms under the conditions of interest.

FUTURE WORK

- 1 The need for advanced flow testing equipment in-Kingdom is clearly demonstrated above. We concur with Lab R&D Center's recent proposal⁽¹³⁾ to develop these facilities.
- 2 The great majority of laboratory research programs concentrate on the CO₂ reaction process. While an understanding of this process is critical to accurate corrosion prediction, most of Saudi Aramco's fields also produce hydrogen sulfide. Only limited work has been performed on the transition from a predominantly sweet corrosion mechanism to a predominantly sour mechanism. We propose the development of a new Technology Item on transitional environments. The new technology item will:
 - Perform a detailed analysis of any available literature and models on the corrosion process and field experience.

- Generate low pressure laboratory data on the corrosion process over a range of hydrogen sulfide concentrations and carbon dioxide concentrations.
- Give improved information to assist in the prediction of corrosion in new fields.

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GLOSSARY

k	Mass transfer coefficient, m/s
D	Diffusivity, m^2/s
Re	Reynolds number, $\mu d/v$
Sc	Schmidt number, v/D
τ	Shear stress N/m^2
ρ	density, kg/m^3
μ	velocity, m/s
ν	kinematic viscosity, m^2/s
p	cylinder diameter or pipe diameter
L	length of pipe electrode, m
d	jet diameter for jet impingement
x	distance from center of jet to test ring

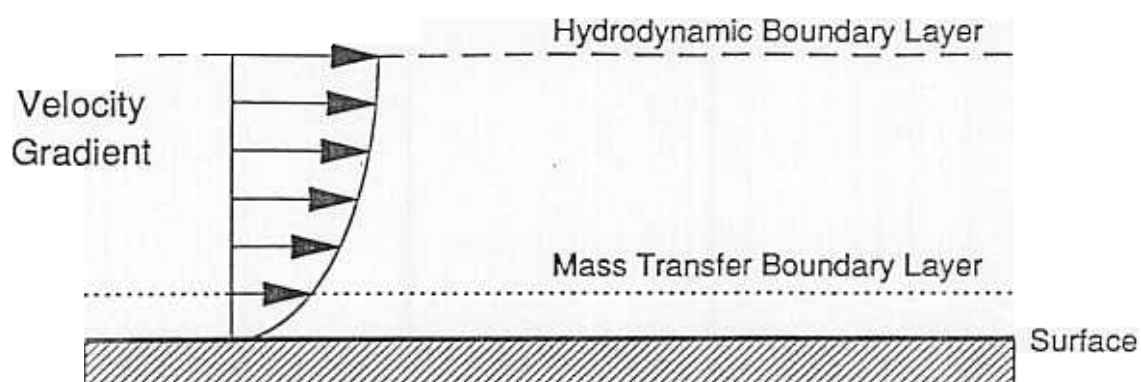


Figure Fully developed momentum and mass transfer ⁽²⁾

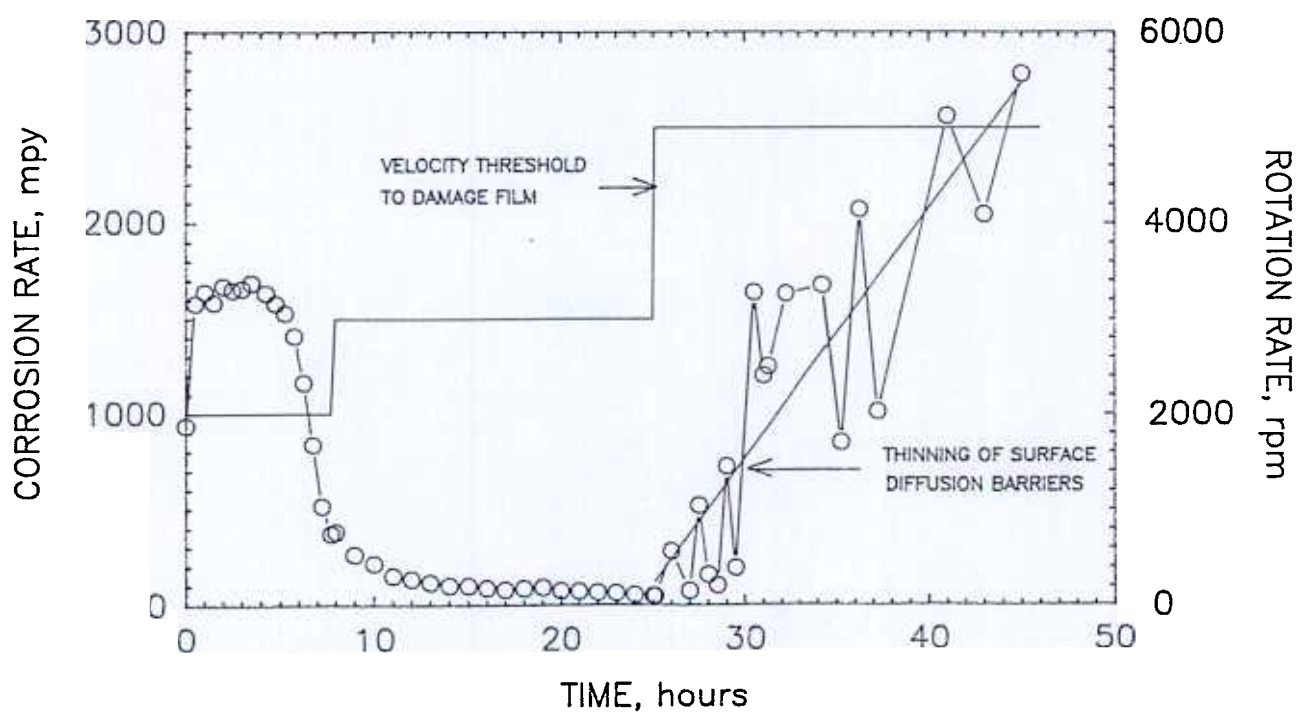


Figure 2: Film removal generated in a high pressure rotating cylinder electrode ⁽³⁾

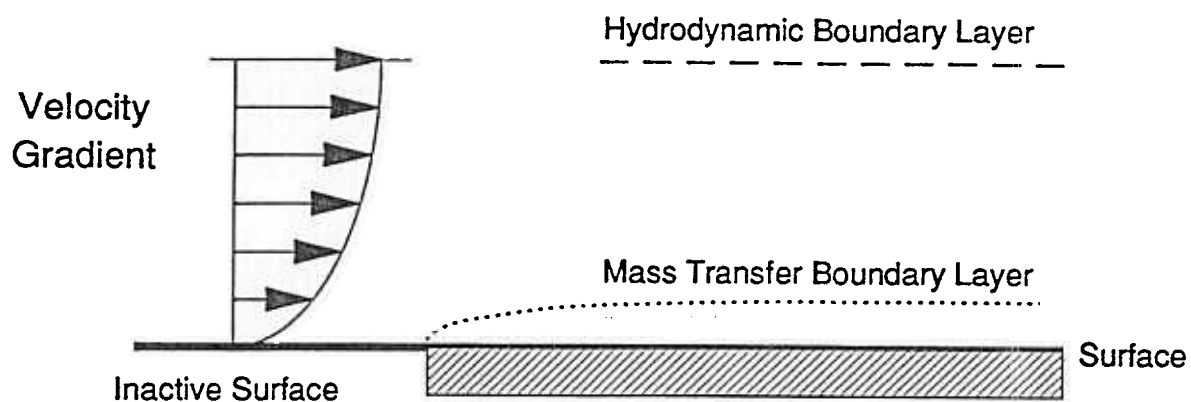


Figure 3: Fully developed momentum and developing mass transfer ⁽²⁾

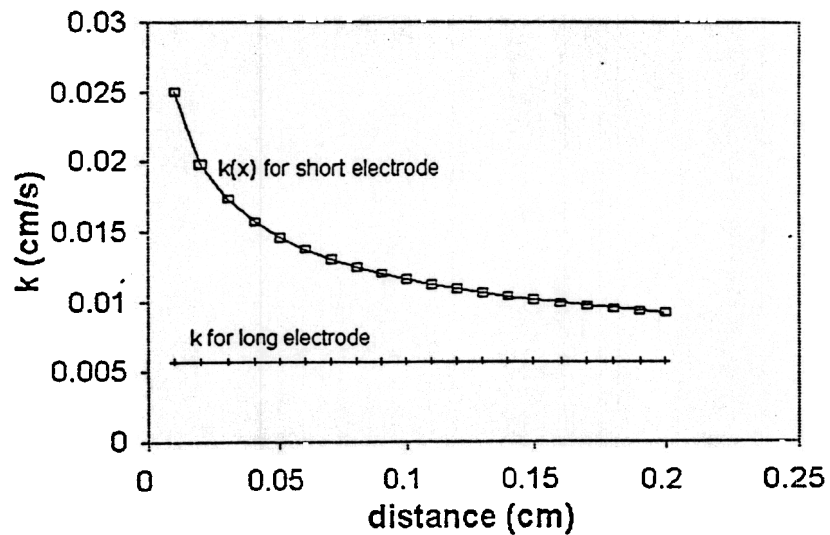


Figure 4: Variation of k with distance from leading edge of electrode compared to k for fully developed mass transfer

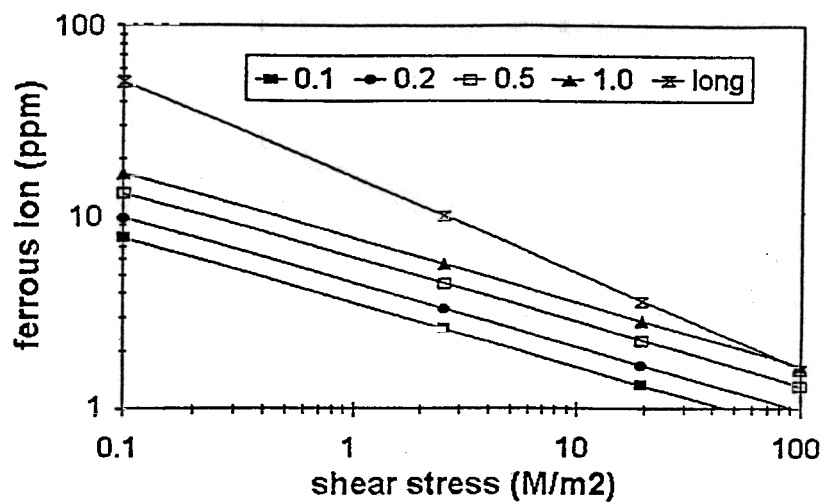


Figure 5: Average ferrous ion concentration for various length short pipe electrodes compared to long electrode, calculated for dissolution current of 1 A/m^2 .

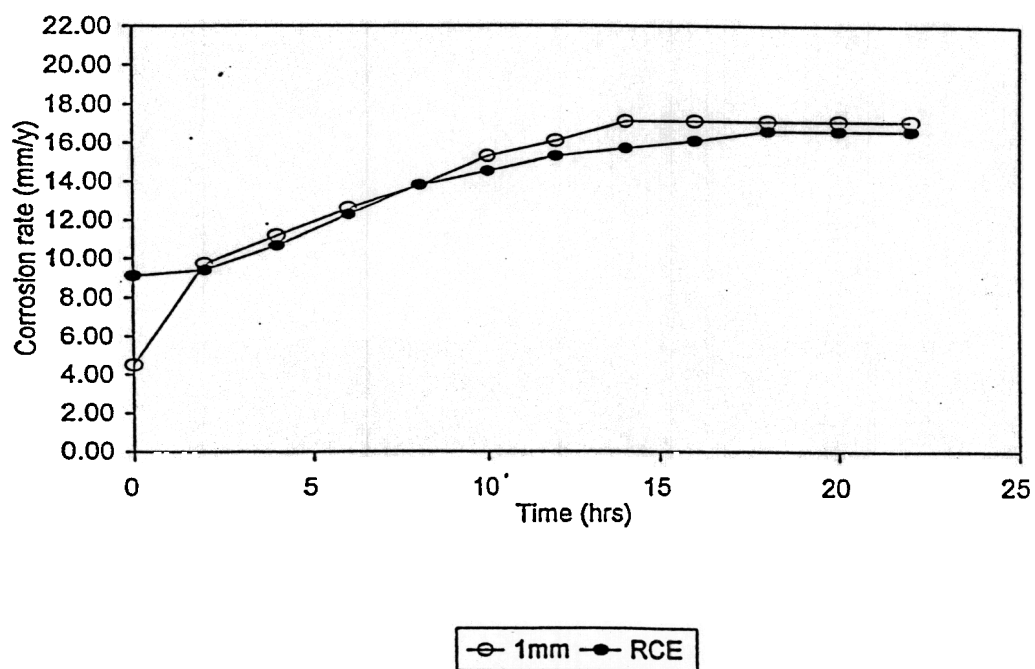


Figure 6: Corrosion rates of 5 mm loop electrode and RCE under mass transfer correlation in 3% NaCl at 70°C

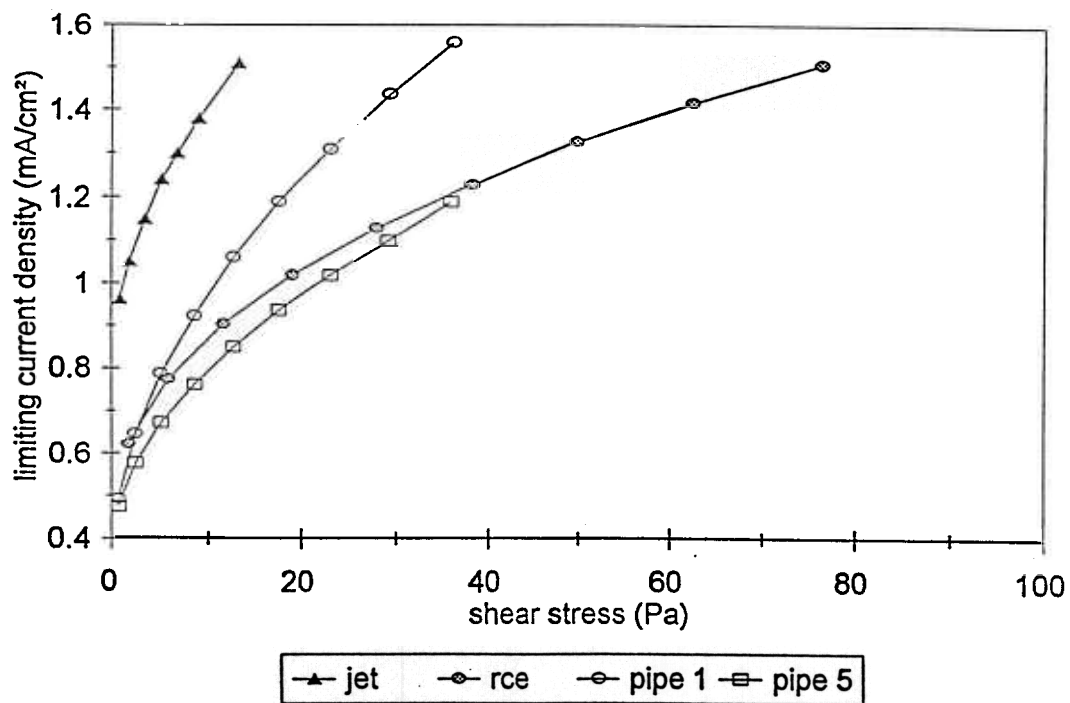


Figure 7. Limiting current versus shear stress for the four electrode geometries.

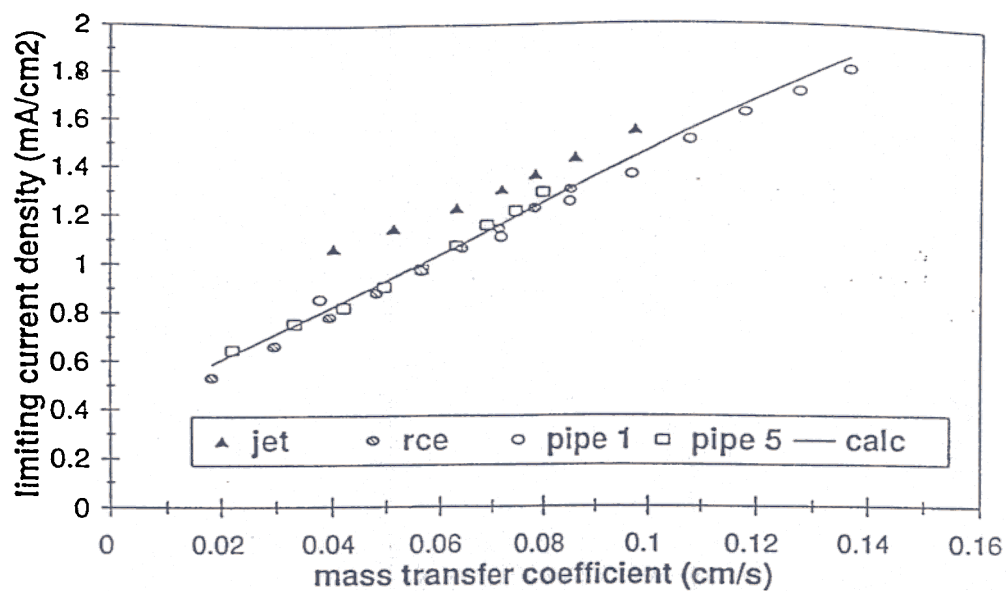


Figure 8: Limiting current versus mass transfer coefficient for ferri-ferrocyanide studies.

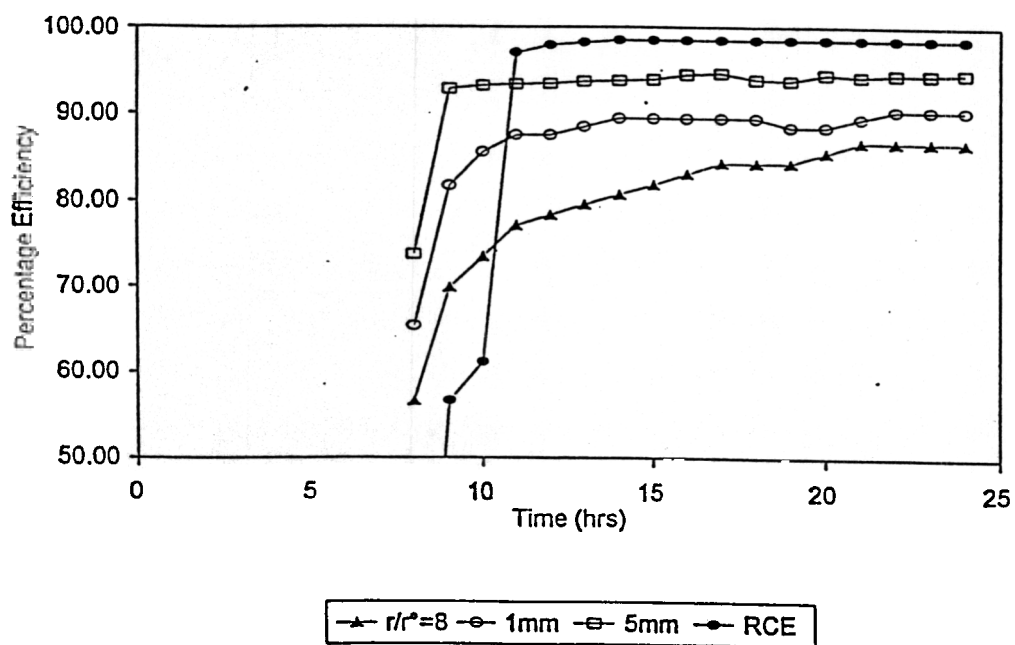


Figure 9: Efficiency versus time of 50 ppm quaternary amine in NaCl at 50°C, 30 N/m²

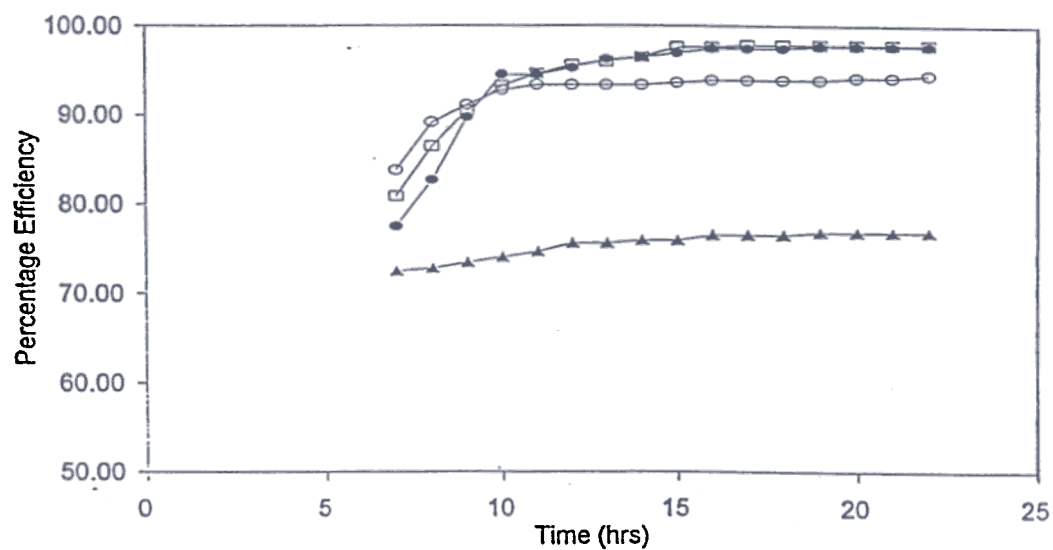


Figure 10: Efficiency versus time of 50 ppm quaternary amine in Forties brine at 50°C, 30 N/m²

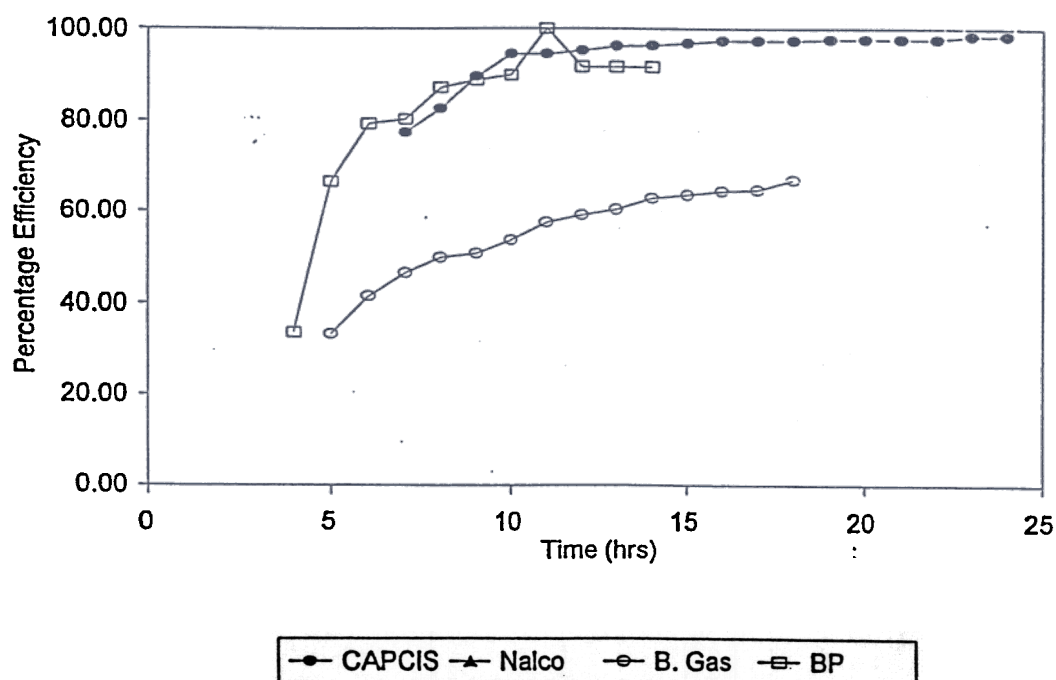


Figure 11: Round robin RCE inhibitor data for 50 ppm quaternary amine in Forties brine at 50°C, 30 N/m².

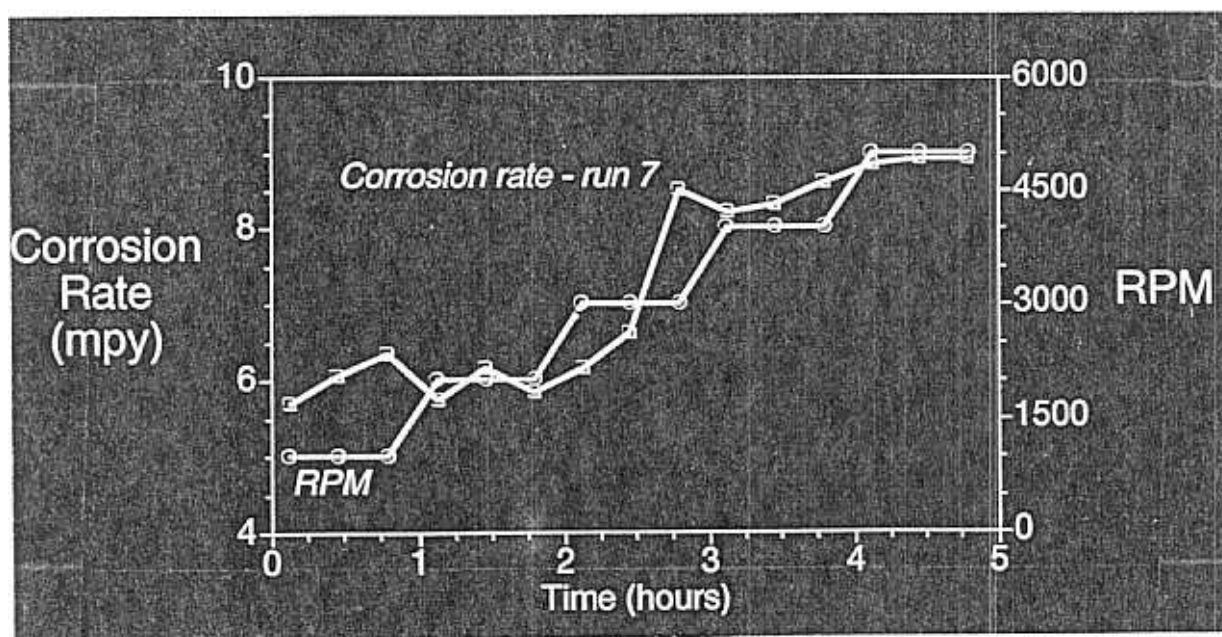


Figure 12: Film persistency of water soluble corrosion inhibitor⁽³⁾.

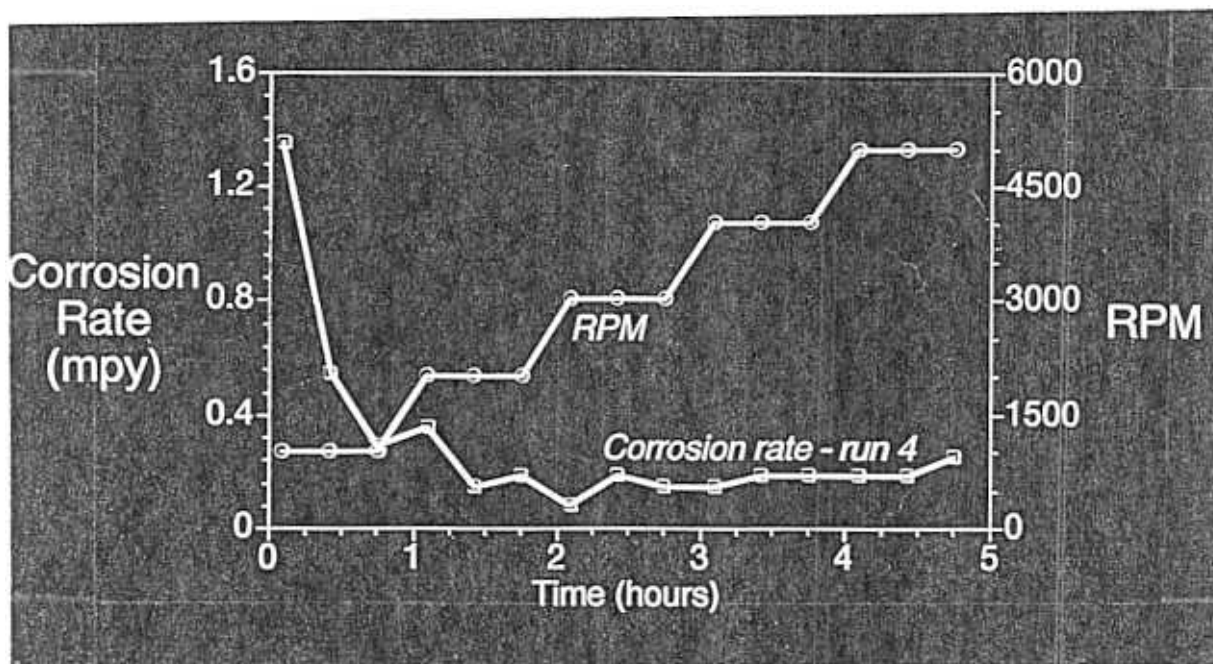


Figure 13: Film persistency of effective film former.⁽³⁾

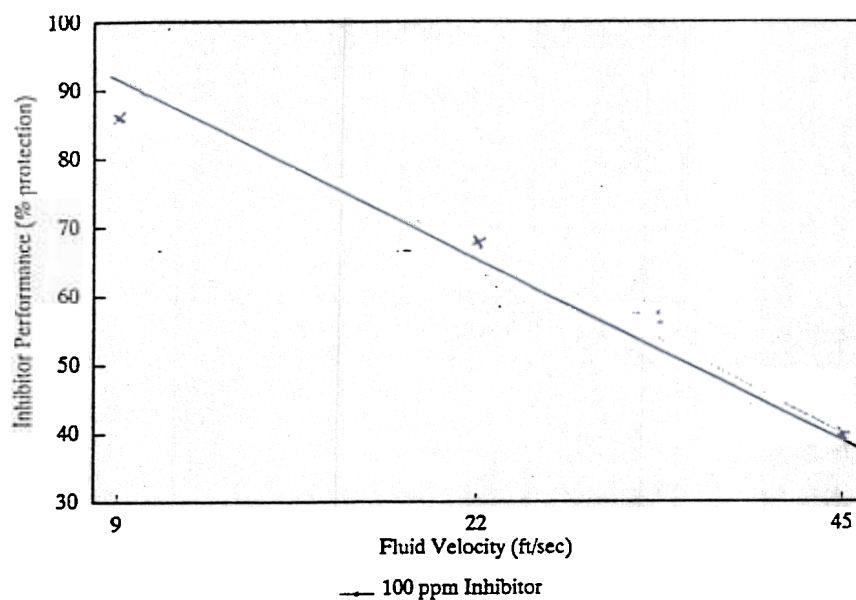


Figure 14: Inhibitor performance versus velocity, 20% oil-80% brine, 30 psi CO₂, 72°C⁽⁶⁾

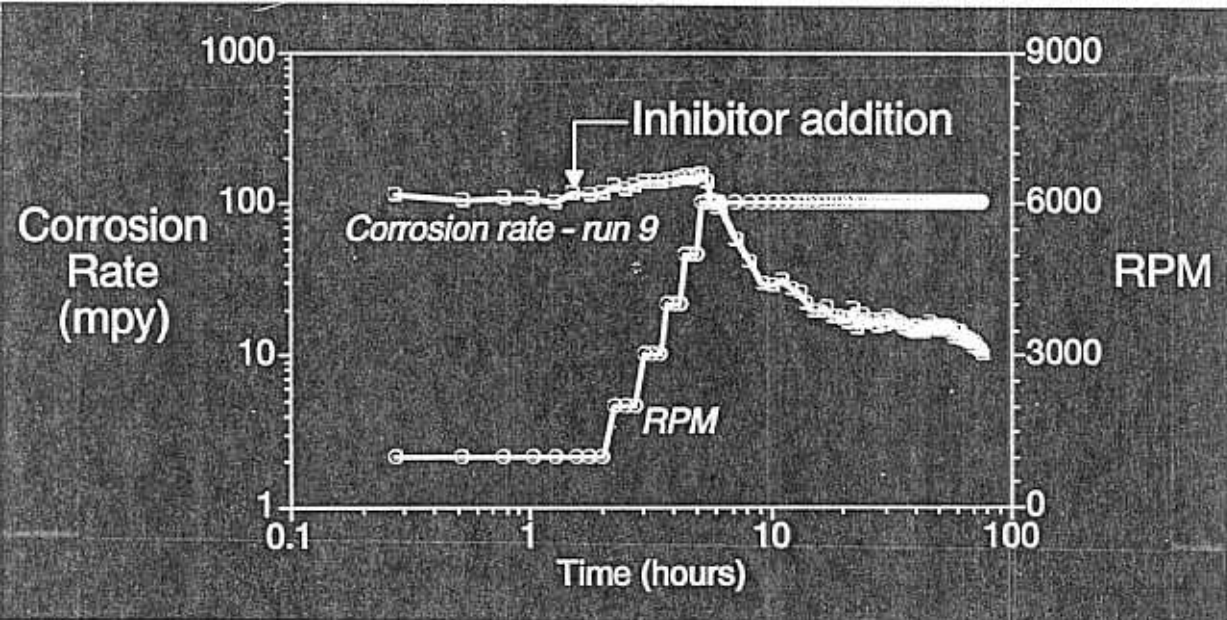


Figure Oil soluble inhibitor applied brine test solution

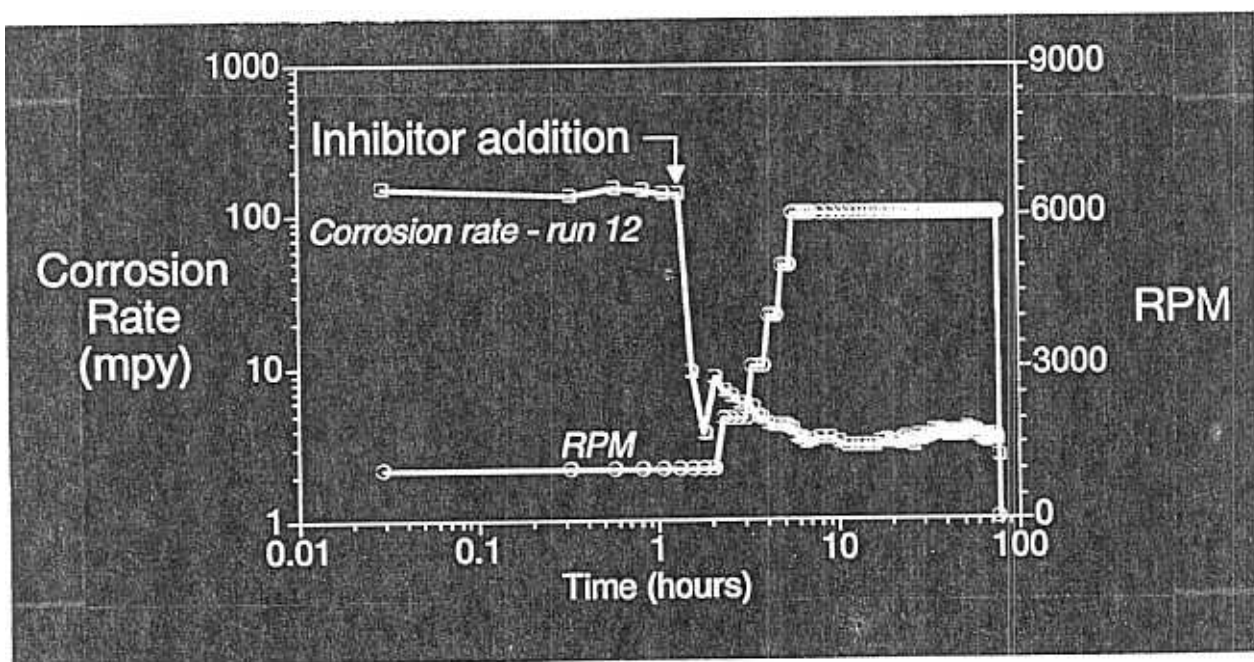


Figure 16 Water soluble inhibitor applied brine test solution

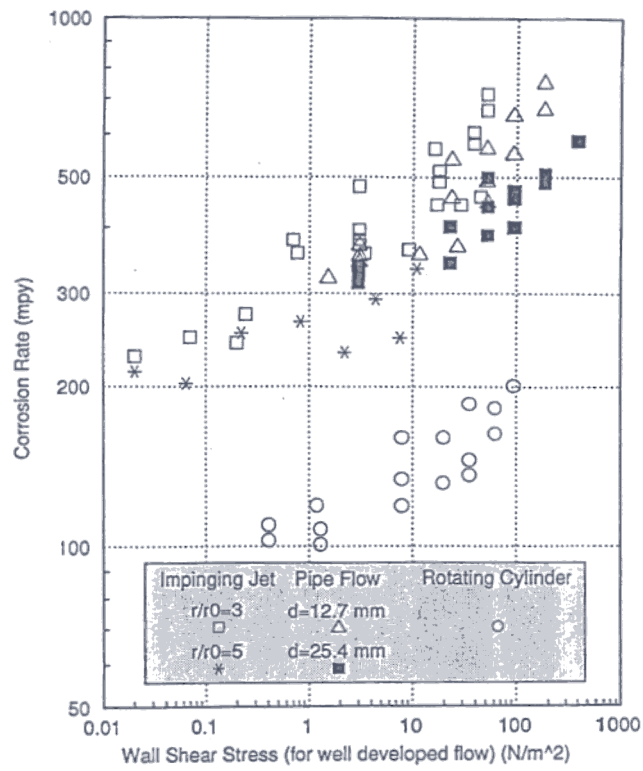


Figure 17: Corrosion rate data of Efird et al plotted against wall shear stress.⁽²⁾

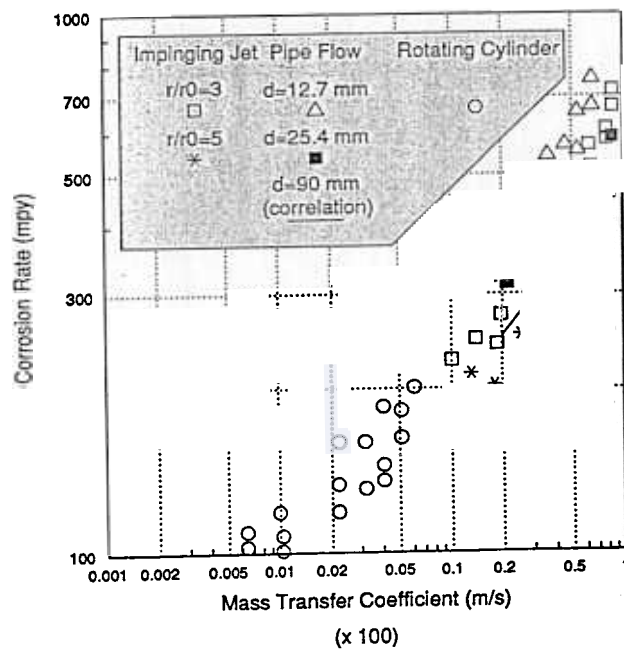


Figure 18 Corrosion rate data of Efird et al plotted against mass transfer coefficient including entry length effects.⁽²⁾