



Review: The Effect of Methanol on the Corrosion of Carbon Steel in Sweet or Sour Environments

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Review: The Effect of Methanol on the Corrosion of Carbon Steel in Sweet or Sour Environments

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ABSTRACT

In world regions with extended winter seasons, significant amounts of methanol are injected into wells and pipelines in order to inhibit the formation of natural gas hydrates. However, this application creates an avenue for the intrusion of dissolved oxygen into a pipeline system, since oxygen is more soluble in methanol than in aqueous fluids. In both sweet and sour systems, the presence of oxygen has a negative impact on the corrosion rate of carbon steel.

This paper is a review of multiple studies carried out in our laboratory over the past five years; the effect of anaerobic and aerobic methanol on the corrosion rate of carbon steel in both sweet and sour environments will be presented.

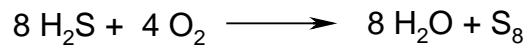
KEYWORDS

Sweet, sour, H₂S, CO₂, corrosion, methanol, oxygen, corrosion inhibitor

INTRODUCTION

Methanol is injected in large quantities into pipelines within Canada and other cold climate locations in order to alleviate or prevent hydrate formation in extremely low temperatures. Previous literature suggests that methanol and glycol injection in sweet systems actually reduces corrosion rates.¹ While this is true for general corrosion rates, it does not take into account the effect of dissolved oxygen or other secondary concerns. The injection of methanol into pipelines is known to increase the risk of corrosion due to a number of factors:

1. Oxygen (O₂) is more soluble in methanol than it is in water.²
 - o In a sour system, a large amount of methanol has the potential to carry a large amount of dissolved oxygen. The reaction of H₂S with O₂ can produce elemental sulfur, which increases the risk of under-deposit, localized corrosion³



- o In a sweet system, oxygen diffuses to the metal surface and increases the corrosion rate. The resulting iron oxides and iron hydroxides act as initiator sites for localized corrosion.
2. Oxygen introduction into a sour system can also lead to a change in composition and morphology of the iron sulfide (FeS) layer, leading to the formation of an FeS scale that is less protective. This scale is more easily removed, which increases the risk of localized corrosion.^{4,5}
 3. Under sour gas conditions, the presence of methanol can increase the risk of sulfide stress cracking (SSC) and stress-oriented hydrogen induced cracking (SOHIC)⁶
 4. Methanol can increase the rate of vapor phase corrosion, which directly increases the risk of a top-of-the-line corrosion failure⁷
 5. Large quantities of methanol may reduce the success of a corrosion inhibitor treatment program by diluting the inhibitor concentration or, when large slugs are used, by eroding an existing batch inhibitor film.⁸

The Canadian Association of Petroleum Producers (CAPP) Guidelines reference the risks associated with methanol in their guidelines as oxygen ingress into the production system.^{9, 10} The solubility of oxygen in seawater at 20 °C is 7.2 ppm as compared to 79 ppm in alcohol,² which is a significant amount of O₂ when methanol is injected on a continuous basis.

Conventional oil and gas corrosion inhibitors are organic in nature and primarily nitrogen-based. Although extremely effective against acid gas corrosion, they provide minimal protection against oxygen related corrosion. The rate of the oxygen corrosion is defined by its rate of diffusion to the steel surface and nitrogen-based corrosion inhibitors do not hinder the oxygen from contacting the steel. A passivating type of corrosion inhibitor, such as phosphate-based

inhibitors, provides the best protection against oxygen corrosion. These phosphate chemistries are the basis of methanol corrosion inhibitors.

The intent of this paper is to present a condensed summary of previous work conducted in our laboratory on methanol related corrosion. The effect of methanol on the corrosion of carbon steel in anaerobic⁴ and aerobic⁵ sour environments, as well as anaerobic and aerobic sweet¹¹ environments will be reviewed. A phosphate ester-based corrosion inhibitor, designed for oxygenated systems, was also examined for its efficacy at different dosages and in different methanol/brine fluid ratios.¹¹

EXPERIMENTAL PROCEDURES

Corrosion tests were conducted using Rotating Cylinder Electrode (RCE) and Static Autoclave (SA) equipment.

All coupons (AISI C1018 carbon steel coupons) were machined by Stellar Manufacturing (Cochrane, AB, Canada) and polished to a 600-grit finish. Prior to testing, all coupons were ultrasonically cleaned by consecutive immersion in xylene/toluene, isopropyl alcohol (IPA) and acetone or methanol for a minimum of 15 minutes in each solution. Coupons were wiped dry with a tissue and mounted on the equipment. Coupons for the SA test were also oven dried and weighed to 0.0001 g using an analytical balance prior to use.

Conditions for both, RCE and SA, tests were based on a field in Western Canada where large amounts of methanol are injected into the pipeline. The brine was prepared by dissolving appropriate amounts of analytical grade NaCl, MgCl₂·6H₂O, Na₂SO₄, and CaCl₂·2H₂O in de-ionized water. Parameters for each type of test are summarized in Table 1.

Rotating Cylinder Electrode Test Procedure

The Rotating Cylinder Electrode (RCE) apparatus consists of glass vessels with a volume capacity of 1000 mL and Pine MSR type instruments (Figure 1). All electrochemical experiments were performed using a Gamry PC4/300 with ECM8 multplexer. The corrosion rate of the coupons was monitored using Linear Polarization Resistance (LPR): ± 10 mV applied to the open current potential (OCP) with a sweep rate of 0.1 mV/s. Electrochemical Impedance Spectroscopy (EIS) studies were performed using a frequency range of 0.005 Hz to 100000 Hz with ± 10 mV applied to the OCP. Potentiodynamic sweep studies were performed with ± 200 mV applied to the OCP with a sweep rate of 0.2 mV/s. LPR data was collected for a total of 20 hours, followed by EIS and Potentiodynamic scans. The reference electrode was a Saturated Calomel Electrode (SCE) immersed in a Luggin capillary tube containing a 3% NaCl solution and fitted with a Vycor frit on the tip. The auxiliary electrode was a carbon rod.

The test fluid was a brine and methanol mixture consisting of 0%, 10%, 25%, and 50% by volume of methanol, to give a total volume of 1000 mL. Analytical grade

methanol was used in all solutions. The mixture was purged with bone dry CO₂ gas for 2 hours at 22°C, followed by the addition of a 10% solution of NaHCO₃ to adjust the pH to 4.00 ± 0.05. The test fluids were then purged for the duration of the test (20 hours) under ambient conditions with either a) bone dry CO₂ gas or b) a 3% O₂ and 97% CO₂ gas mixture. Bone dry CO₂ and the prepared mixture of O₂ with CO₂ were supplied by Air Liquide.

Coupons were immersed in the fluid and rotated at a rate of 1000 rpm prior to the collection of LPR data. After 3 hours, a phosphate ester-based corrosion inhibitor, Inhibitor A, was added to the solution. The amount of Inhibitor A added to the test fluid may be represented as a percentage with respect to the volume of methanol or as a dosage in ppm with respect to the total volume of fluid (Table 2). For example, one litre of test fluids with 10% methanol content has 100 mL of methanol; treating 100 mL of methanol with 1% Inhibitor A requires 1000 µL of the corrosion inhibitor. With respect to the total fluid volume, 1000 mL, a treatment dosage of 1000 µL corresponds to 1000 ppm.

Static Autoclave Test Procedures

All corrosion tests were conducted in Hastelloy C276 static autoclaves with a volume capacity of 300 mL. Flat surface, “mushroom cap”, coupons were mounted in a PEEK holder prior to being inserted into the test fluid (Figure 2). The autoclaves each have the capacity for one mushroom cap coupon, where the flat exposed surface is horizontal and upward facing.

The fluid for testing was a brine and methanol mixture consisting of 0, 10, 25, 50, 75, 90 and 99% by volume of methanol. The mixture was purged with bone dry CO₂ gas for 20 minutes, followed by the addition of NaHCO₃ to adjust the pH to 6. For anaerobic tests, the brine was purged with CO₂ for an additional 2 hours following pH adjustment. For aerobic tests, the mixture was agitated for 1 minute to ensure the presence of O₂. The pH was measured after the introduction of O₂ and again when the test was completed; the pH of the fluids could not be monitored for the entire duration of the SA test. All of the solutions had a pH of 6 prior to pressurization with CO₂, H₂S and N₂ gases. Once the autoclaves were sealed, the fluids were heated to a temperature of 60 °C, which was followed by the introduction of CO₂, H₂S and N₂ gases. Where indicated, a 3% O₂ and 97% CO₂ gas mixture was used in the final pressurization step in order to simulate a highly oxygenated environment. A summary of test conditions is given in Table 1.

For the one week SA test, clean coupons were inserted into the brine prior to pressurization. For a two week test, an FeS film was formed on the coupon surface under anaerobic conditions (pre-corrode step) for one week and then exposed to an oxygenated or deoxygenated methanol solution for the following week (corrode step). The pre-corrode step consisted of immersing a clean mushroom cap coupon into a buffered and de-oxygenated brine solution, followed by a CO₂ purge of the autoclave headspace for an additional 2.5 hours prior to pressurization with CO₂, H₂S and N₂ gases. Over a period of a week, an

iron sulfide scale formed in the anaerobic brine. In the second week, for the corrode step, the fluids in the autoclave were replaced with fresh fluids: a brine solution with varying ratios of methanol. For the aerobic corrode condition, the methanol/brine solution was buffered and agitated to incorporate O₂, as described above for the one-week tests. For anaerobic corrode tests, the methanol/brine solution was buffered in the usual manner; however, the solution and headspace of the autoclave was purged with CO₂ for an additional 2.5 hours prior to pressurization. Care was taken to preserve the FeS film on the coupon (during the fluid-exchange step in the procedure) by minimizing agitation of the coupon as it was moved in and out of the autoclave. The introduction of O₂ into the 'anaerobic corrode' step was minimized by keeping the coupon immersed in the 'pre-corrode' fluids until it could be transferred into an autoclave with fresh fluids. The total duration of these tests was 13 days, or ~312 hours.

Where indicated, Inhibitor A was injected into the fluid prior to inserting the coupons. An explanation of the inhibitor dosage is shown in Table 2.

At the end of a given test period, the gas was released from the autoclaves and the coupons were carefully removed to preserve the scale on the metal surface. Coupons selected for weight-loss measurement were cleaned by immersion in a hydrochloric acid solution of 1,3-dibutyl-2-thiourea and then rinsed thoroughly with de-ionized water and methanol. The coupons were wiped with a tissue and oven dried (60°C) for a minimum of 15 minutes. The coupons were photographed and a ZEISS Stemi SV6 Microscope was used to examine and record the appearance of the metal surface at 16x magnification.

Coupons chosen for scale analysis (by Scanning Electron Microscopy or X-ray Diffraction) were lightly rinsed with methanol, dried under a stream of CO₂ gas and stored in an N₂-purged desiccator. A low viscosity epoxy was used to coat selected coupons without disrupting the surface layer of scale. The epoxy-coated coupons were cross-sectioned and polished using wet sandpaper of increasing grit (600, 1000, 2000), where IPA was the lubricating solvent. The cross-sectioned coupons were then dried under CO₂ and stored in a desiccator until SEM analysis. Coupons for front-face SEM and XRD analysis were also stored in the desiccator.

XRD analysis was provided by DNX Inc. in Calgary, AB, Canada. SEM images and EDX analysis (Energy Dispersive X-ray Spectroscopy) were obtained in accordance with the practices outlined by the Microscopy Imaging Facility at the University of Calgary. XRD analysis and EDX spectroscopy was used to identify the composition of the scale on the coupon surface.

RESULTS AND DISCUSSION

Methanol has shown inhibitive effects on the corrosion of carbon steel in anaerobic, sweet environments.¹¹ However, in sour environments the effect of methanol on corrosion is more complicated; the risk of localized corrosion increases with methanol content even though the general corrosion rate appears unaffected. An associated risk with the use of methanol is that oxygen is more soluble in methanol than in water. This allows for the intrusion of oxygen into pipelines when methanol is injected for the purpose of hydrate inhibition.

The purpose of this extended study was to determine the effect of dissolved oxygen in methanol/brine mixtures on the corrosion of carbon steel in a sweet or sour environment. In order to do this, the corrosion of carbon steel was studied in aerobic and anaerobic solutions with various concentrations of methanol. The results of the anaerobic studies^{4,11} are presented first, followed by the effect of oxygen in sweet or sour environments.^{5,11} The final section describes the efficacy of a phosphate ester-based inhibitor, referred to as Inhibitor A, on the corrosion of carbon steel in aerobic methanol in both sweet and sour environments.¹¹

Effect of ANAEROBIC Methanol on Corrosion of Carbon Steel

In sweet systems, the corrosion rate of carbon steel immersed in a methanol/brine mixture was found to be lower than the corrosion rate measured in a brine-only solution, where all the fluids were anaerobic. The LPR data (RCE test) for the corrosion of carbon steel in four different solutions is shown in Figure 3.¹¹ As expected, the highest initial corrosion rate (~75 mpy) is observed in the brine-only solution and the lowest rate (~10 mpy) is found in the 50% methanol solution. This trend can be attributed to the increased solution resistance with the increase of methanol content: approximate values of 18 ohm, 24 ohm and 50 ohm for 10%, 25% and 50% methanol in solution, respectively. Over time, the corrosion rate decreased in each of the solutions. For the brine-only condition, the decrease in corrosion rate is likely due to the formation of a protective iron carbonate film on the surface of the coupon. The low corrosion rates (<5 mpy) observed after 20 hours in the 25% and 50% methanol solutions are an indication of the surface activity of methanol; it is presumed that methanol inhibits corrosion through adsorption onto the metal surface. As further evidence of this assumption, EIS data has shown that the adsorbed layer in the 50% methanol solution has the largest impedance, which is consistent with a low corrosion rate.¹¹ A potentiodynamic sweep of each solution also showed that the inhibitive effect of methanol in an anaerobic environment increases as the methanol content increases.¹¹

In sour systems, the general corrosion rate of carbon steel appears to be unaffected by increasing the methanol content in the solution (Table 3).⁴ However, localized corrosion is more prominent as the methanol content is increased. One theory suggests that H₂S and methanol compete for adsorption

sites on the metal surface, which limits the amount of H₂S that can reach the surface to form iron sulfide.¹² As a result, a protective iron sulfide film may not form consistently over the surface of the metal, causing an increase in the risk of localized corrosion. The thickness of the iron sulfide scale was also found to be dependent on the amount of methanol in the solution: the greater the methanol content, the thinner the scale layer on the metal surface (Table 3).⁴

Effect of AEROBIC Methanol on Corrosion of Carbon Steel in a Sour Environment

The intent of this portion of the study was to examine the effect of oxygen on the general corrosion rate and on the formation of iron sulfide (FeS) scale in a methanol solution.⁵ Two methods were chosen for introducing oxygen into the methanol/brine solutions. In the first, the test fluid was oxygenated by agitation in air; this was done in order to mimic the amount of dissolved oxygen that would naturally be found in a solution under ambient temperature and pressure. However, in a closed static autoclave test the oxygen cannot be replenished and may be consumed by H₂S rather than the corrosion process. As a result, a second method was used to ensure that the solution would be saturated with oxygen for the duration of the test: mixed gas containing 3% O₂ in CO₂ was used in the final pressurization step in place of bone dry CO₂. For simplicity, solutions aerated by agitation will be referred to as the Low-O₂ condition and solutions pressurized with 3% O₂ in CO₂ will be referred to as the High-O₂ condition.

In a one week static autoclave test, the corrosion rates from the aerobic conditions (Low-O₂) were consistently higher than the anaerobic corrosion rates (comparison of Table 4 and 3, respectively). This trend is most evident in solutions where the methanol content was high (75% methanol or more). For example, the corrosion rate in an aerobic, 90% methanol solution was over *three times* larger than the corrosion rate of a coupon in the anaerobic counterpart. Two trends were consistent for both the aerobic and anaerobic conditions: 1. localized corrosion was observed when the methanol content was 50% or greater and 2. FeS scale thickness decreased with increasing methanol content. The corrosion product that formed at higher methanol concentrations was loosely adhered to the metal surface, which suggests that this scale is more susceptible to erosion and does not act as a good protective film. Mackinawite was identified as the most abundant form of iron sulfide scale formed in either aerobic or anaerobic conditions, irrespective of the methanol content (Table 5). However, greigite was identified as a significant component of the corrosion product when large concentrations of methanol were present (>90% MeOH).

A two week test was devised to determine the effect of methanol on an existing scale layer, which is known to be predominantly mackinawite, on the metal surface. The scale layer, which was formed under anaerobic conditions, provided protection when the coupons were exposed to oxygenated methanol (Table 6). The corrosion rate values were lower in the 2-week tests compared to the 1-

week tests, but the actual beneficial effects of the scale layer are only evident when the total weight-loss is examined. The total weight-loss of coupons with the pre-existing iron sulfide film was *less than* that of coupons without the protective scale, even though the former coupons were exposed to corrosive fluids for a longer period of time. However, even with the protective FeS film, the corrosion rate of coupons exposed to oxygenated methanol was higher than that of coupons exposed to anaerobic methanol. Analysis of the scale showed that the introduction of methanol does alter the composition of the FeS film: with higher methanol concentrations, the amount of mackinawite decreases and greigite increases in either aerobic or anaerobic conditions (Table 7).

The effect of oxygen rich solutions (High-O₂) on the corrosion of carbon steel in a sour environment was also examined. The most notable difference between these tests and those described above is the large increase in the corrosion rate. For example, a one-week test at 75% MeOH gives a corrosion rate of 0.558 mm/y (21.97 mpy), where O₂ was introduced into the system by agitation of the testing fluids (Table 4). When 3% O₂ was used for the same test (Table 8), the corrosion rate is 1.616 mm/y (63.62 mpy). With a high methanol concentration, the effect of O₂ on the corrosion rate is even more pronounced: at 90% MeOH and with 3% O₂ the corrosion rate is 5.895 mm/y (232.09 mpy), compared to 0.867 mm/y (34.13 mpy) from previous tests.

The amount of iron sulfide scale formed during the tests with 3% O₂ was large compared to the previously described one-week tests (Table 8). Although the scale was loosely adhered to the coupon, a large amount of iron sulfide remained on the surface and was successfully preserved for cross-sectioning of the sample. The 90% methanol solution gave the largest film thickness, which was 10x larger than that of the 75% methanol solution under the same conditions. In the oxygen rich environment, the iron sulfide scale consisted primarily of mackinawite. The sulfur content in the scale formed in the high-O₂, 90% methanol solution is a product of the side reaction of H₂S with oxygen. With increasing methanol content, the metal surface was exposed to larger amounts of oxygen, resulting in significantly larger corrosion rates and increased scale formation.

Effect of AEROBIC Methanol on Corrosion of Carbon Steel in a Sweet Environment

Oxygen contamination of a sweet environment was found to adversely affect the corrosion rate of carbon steel in methanol solutions.¹¹ This effect can be readily seen through the comparison of corrosion rates derived from LPR data for coupons immersed in fluids purged with bone dry CO₂ (Figure 3) or a 3% O₂ in CO₂ mixed gas (Figure 4). Figure 5 shows a direct comparison of the initial and final corrosion rate for each type of solution. The initial corrosion rate observed for coupons in an O₂/CO₂ environment is higher than that of coupons in a purely sweet environment in each of the methanol solutions. As discussed previously,

the corrosion rate of carbon steel in methanol solutions decreased significantly after 20 hours in bone dry CO₂, whereas the corrosion rate in the O₂/CO₂ systems remained constant or increased over time. Both of these observations indicate that the corrosion protection offered by the presence of methanol is insufficient for counteracting the corrosion caused by oxygen in the system.

Mitigation of Corrosion Caused by Oxygenated Methanol in Sweet or Sour Environments

A recommended practice in industry is to treat methanol with a corrosion inhibitor (1% by volume of methanol) prior to injecting methanol into a pipeline. Part of one study was to investigate the quantity of corrosion inhibitor required to mitigate corrosion caused by oxygen. The effectiveness of a phosphate ester-based corrosion inhibitor (Inhibitor A) was investigated in different dosages for various methanol solutions (10%, 25%, 50%, 90%). Since methanol is treated prior to injection into a pipeline, the dosage of Inhibitor A was calculated with respect to the volume of methanol in the test fluids. Three concentrations of Inhibitor A were tested using the RCE test under *sweet*, oxygen-rich conditions: 0.01%, 0.1% and 1% by volume of inhibitor to volume of methanol. The SA test was used to measure the effectiveness of Inhibitor A (1% dosage) under conditions conducive localized corrosion: an oxygenated 90% methanol solution in a *sour* environment. A description of the calculations is in the Experimental Procedure and in Table 2.

The addition of Inhibitor A to a *sweet*, anaerobic, 10% methanol solution caused an immediate drop in the corrosion rate of carbon steel (Figure 6). A dosage of 1% and 0.1% of Inhibitor A were both effective in lowering the corrosion rate to values less than 1 mpy; 0.01% of Inhibitor A lowered the corrosion rate, but to a lesser extent (<10 mpy). EIS data showed that the solution with 0.1% or 1% of Inhibitor A resulted in an adsorbed layer with large impedance.¹¹

In the presence of oxygen, the addition of 1% or 0.1% of Inhibitor A caused an immediate reduction in the corrosion rate of carbon steel in a *sweet*, 10% methanol solution (Figure 7). However, the addition of only 0.01% of Inhibitor A had an insignificant effect on lowering the corrosion rate. Potentiodynamic sweeps for the untreated fluids and those treated with 0.01% of Inhibitor A were nearly identical, indicating that 0.01% of Inhibitor A did not have an effect on the corrosion mechanism.¹¹ A Nyquist plot of the EIS data showed that the solution treated with 1% of Inhibitor A resulted in an adsorbed film with the largest impedance, indicating that this concentration of Inhibitor A (1% or 1000 ppm) was the most effective under these conditions.¹¹

Tests were also conducted with variable concentrations of Inhibitor A in 25% and 50% methanol solutions in both aerobic and anaerobic, *sweet* conditions.¹¹ Under anaerobic conditions, chemical treatment of the 25% and 50% methanol solution showed trends that are similar to those observed in the 10% methanol solution (Figure 6); the corrosion rate was reduced to <1 mpy with the addition of

Inhibitor A and a 0.1% or 1% dosage of inhibitor gave the largest impedance values. In the presence of oxygen, the corrosion of carbon steel in the 25% and 50% solutions was effectively inhibited with 1% of Inhibitor A, whereas a low dosage of 0.01% did not reduce the corrosion rate.

Under sour conditions, the effect of Inhibitor A (1% in methanol) on the corrosion of carbon steel in a 90% methanol solution was studied (Table 9). In both the Low-O₂ and High-O₂ conditions, the presence of Inhibitor A reduced the corrosion rate dramatically, providing 97% protection. More importantly, coupons in the inhibited solution did not have any evidence of localized corrosion; no pits or etching was observed.

CONCLUSIONS

The results of this study provide evidence for the inhibitive properties of methanol in an anaerobic environment, where methanol is likely a surface active reagent that inhibits the anodic reaction. Large quantities of methanol (25%-50% by volume) were found to be the most effective for inhibiting the general corrosion of carbon steel under anaerobic, sweet conditions. However, in an anaerobic H₂S environment the risk of localized corrosion increased with methanol content, since pitting corrosion was observed when the methanol content was 50% or more. When present in large quantities, methanol may compete with H₂S for adsorption sites on the metal surface and block the passage of H₂S, resulting in the formation of an uneven iron sulfide film.¹² A metal surface with an inconsistent protective film is more prone to localized corrosion.

In real systems, the practice of using methanol for hydrate inhibition provides an avenue for the intrusion of dissolved oxygen into a pipeline system, since oxygen gas is more soluble in methanol than in aqueous fluids.² For solutions with a methanol content of 50% or more, the corrosion rate of carbon steel was significantly higher in the *aerobic* environment than the *anaerobic* environment in either sweet or sour conditions. For this reason, the results of the aerobic studies are believed to be more representative of the corrosion that is occurring in pipelines when methanol is present; it is highly unlikely that methanol introduced into a pipeline system would be anaerobic.

A phosphate ester-based corrosion inhibitor was found to be effective in reducing corrosion under either aerobic CO₂ or H₂S conditions. Inhibitor A was most effective in lowering the corrosion rate when the concentration of inhibitor was high with respect to the volume of methanol. Specifically, a dosage of 1% of corrosion inhibitor (with respect to methanol volume) performed exceptionally well in each of the methanol/brine fluid ratios where an excess of O₂ was present. Inhibitor dosages of 0.1% and 0.01% were also tested under sweet conditions. Based on these tests, the performance of a 0.1% of Inhibitor A was only comparable to the performance of 1% of Inhibitor A when the methanol content was high and 0.01% of Inhibitor A was not effective in any of the test fluids.

The methanol content in pipeline fluids is variable and often unknown. The results of this study support the industry recommended practice to treat methanol with 1% of inhibitor; this dosage of inhibitor in methanol provides effective corrosion inhibition whether the methanol content is high or low in the corrosive environment. The reduction of oxygen is a diffusion controlled process, which is dependent on the amount of oxygen in the system and the fluid velocity. Based on the efficacy of Inhibitor A under an oxygen contaminated environment, the phosphate ester likely adsorbs on the metal surface and hinders the diffusion of oxygen, whereas methanol alone is ineffective in slowing down this process.

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Table 1: Conditions for RCE and SA Tests

Condition	Static Autoclave	Rotating Cylinder Electrode
Temperature, °C	60	22
Gas composition [‡]	150 psi H ₂ S 50 psi CO ₂ (total pressure = 500 psi, balance with N ₂)	CO ₂ (continuous purge)
Brine Composition	3330 ppm Cl ⁻ ; 83 ppm Mg ²⁺ ; 217 ppm Ca ²⁺ ; 197 ppm SO ₄ ²⁻ ; 1848 ppm Na ⁺	
Coupon Material	AISI C1018	
Total Exposure Time	144 or 312 hours	20
Methanol Concentration (% v/v)	0, 10, 25, 50, 75, 90, 99	0, 10, 25, 50
pH	6	4

[‡]Where CO₂ is indicated, either bone dry CO₂ (anaerobic conditions) or a gas mixture consisting of 3%O₂ in CO₂ (aerobic, high-O₂) was used

Table 2: Dosage of Inhibitor A for each Test Fluid Mixture. Corrosion inhibitor dosage was determined with respect to the volume of methanol (MeOH) in the solution and represented as a ppm value with respect to the total fluid volume.

% of MeOH in Fluids for each type of Test	Rotating Cylinder Electrode									Static Autoclave
	10% MeOH			25% MeOH			50% MeOH			90% MeOH
Inhibitor A (% in MeOH)	1%	0.1%	0.01%	1%	0.1%	0.01%	1%	0.1%	0.01%	1%
MeOH Volume (mL)	100			250			500			225
Total Fluid (mL)	1000			1000			1000			250
Volume Inhibitor in Brine (µL)	1000	100	10	2500	250	25	5000	500	50	2250
Dosage of Inhibitor in Total Fluid Volume (ppm)	1000	100	10	2500	250	25	5000	500	50	9000

Table 3: Corrosion Rates and Iron Sulfide Film Thickness for Mushroom Cap Coupons in a Sour Anaerobic Environment after a One Week Test

% Methanol	Flat Test Specimens			
	Corrosion Rate (mm/yr)	Corrosion Rate (mpy)	Observations (after cleaning)	[‡] FeS Film Thickness (μm)
0	0.204	8.03	No localized corrosion	4.8-8.6
10	0.264	10.39	No localized corrosion	6.2-9.0
25	0.186	7.32	No localized corrosion	3.1-5.9
50	0.486	19.13	Low density, small size pits	0.4-24.0
75	0.192	7.56	Low density, small size pits	1.9 - 4.8
90	0.244	9.61	Medium density, medium size pits	0.5-1.3
99	0.137	5.39	Medium density, medium size pits	0.7-1.7

[‡]FeS film thickness determined from SEM images of the cross-sectioned samples, where the scale was preserved in an epoxy coating

Table 4: Corrosion Rates and Iron Sulfide Film Thickness for Mushroom Cap Coupons in a Sour Aerobic (Low-O₂)* Environment after a One Week Test

% Methanol	Flat Test Specimens			
	Corrosion Rate (mm/yr)	Corrosion Rate (mpy)	Observations (after cleaning)	[‡] FeS Film Thickness (μm)
0	0.225	8.86	General corrosion, etching	4.4-8.9
10	0.282	11.10	General corrosion, etching	6.7-14.7
25	0.222	8.74	Localized corrosion: pits	3.4-27.1
50	0.632	24.88	General corrosion, etching	8.0-16.5
75	0.558	21.97	General corrosion, etching	4.9-11.6
90	0.867	34.13	Small to medium size pits	2.2-5.8
99	0.484	19.06	High density, small size pits	0.9-4.0

*Indicates that O₂ was introduced by agitation of the solution in air prior to pressurization

[‡]FeS film thickness determined from SEM images of the cross-sectioned samples, where the scale was preserved in an epoxy coating

Table 5: Comparison of XRD Analysis of Iron Sulfide Scale Formed in an Anaerobic or Aerobic (Low-O₂)* Sour Environment after a One Week Test

% Methanol	Anaerobic		Aerobic	
	Compound	Abundance	Compound	Abundance
0	Mackinawite Magnetite	95-99% 1-5%	Mackinawite Cubic FeS	50-60% 40-50%
10	N/A	N/A	Mackinawite Cubic FeS	85-95% 5-15%
25	Mackinawite	100%	Mackinawite Greigite Magnetite Unidentified	90-99% 1-10% Trace Trace
50	N/A	N/A	Mackinawite Magnetite	98-100% Trace
75	Mackinawite Cubic FeS	75-85% 15-25%	Mackinawite Cubic FeS	85-95% 5-15%
90	N/A	N/A	Mackinawite (1) Magnetite (1) Mackinawite (2) Greigite (2) Fe _{0.91} S (2) Unidentified (2)	95-99% 1-5% 85-95% 1-5% 1-5% 1-5%
99	Mackinawite (1) Cubic FeS (1) Mackinawite (2) Greigite (2)	85-95% 5-15% 85-95% 5-15%	Mackinawite Greigite	75-85% 15-25%

*Indicates that O₂ was introduced by agitation of the solution in air prior to pressurization

Table 6: Corrosion Rates for Mushroom Cap Coupons with a Pre-existing FeS Film under Anaerobic and Aerobic (Low-O₂)* Conditions after a Two Week Test

% Methanol	Corrosion Rate (mm/y)		Corrosion Rate (mpy)	
	Anaerobic	Aerobic	Anaerobic	Aerobic
0	0.128	0.111	5.04	4.37
50	0.068	0.186	2.68	7.32
90	0.195	0.340	7.68	13.39

*Indicates that O₂ was introduced by agitation of the solution in air prior to pressurization, only in the second week of the test

Table 7: Comparison of XRD Analysis of Iron Scale: The Effect of Oxygenated Methanol (Low-O₂)* on a Pre-existing FeS Film in a Sour Environment

% Methanol	Anaerobic		Aerobic	
	Compound	Abundance	Compound	Abundance
0	Mackinawite Magnetite	98-100% Trace	Mackinawite Magnetite	95-99% 1-5%
50	Mackinawite Greigite Unidentified	85-95% 5-15% 1-5%	Mackinawite Greigite Iron Sulfide Unidentified	85-95% 1-5% 1-5% 1-5%
90	Mackinawite Greigite Unidentified	35-45% 50-60% 5-10%	Mackinawite Greigite Unidentified	55-65% 30-40% Trace

*Indicates that O₂ was introduced by agitation of the solution in air prior to pressurization

Table 8: Corrosion Rates, Iron Sulfide Composition and Film Thickness for Mushroom Cap Coupons in a Sour Aerobic (High-O₂)* Environment after a One Week Test

% Methanol	Flat Test Specimens			
	Corrosion Rate (mm/yr)	Corrosion Rate (mpy)	[§] Scale Composition (Abundance %)	[‡] FeS Film Thickness (μm)
25	0.313	12.32	Mackinawite (80-90%) Cubic Iron Sulfide (10-20%) Unidentified (trace)	10.6-12.5
75	1.616	63.62	Mackinawite (98-100%) Magnetite (trace)	23.5-25.5
90	5.895	232.09	Mackinawite (95-100%) Magnetite (1-3%) Sulfur (1-3%)	290.2-296.1

*Indicates that O₂ was introduced into the solutions during pressurization with a 3%O₂ in CO₂ gas

[§]Determined by XRD analysis

[‡]FeS film thickness determined from SEM images of the cross-sectioned samples, where the scale was preserved in an epoxy coating

Table 9: Effect of 1% Inhibitor A on the Corrosion Rates for Carbon Steel in an Aerobic 90% Methanol Solution in a Sour Environment

Corrosion Rate		*Aerobic, Low-O ₂			**Aerobic, High-O ₂		
		No Inhibitor	1% Inhibitor A	% Protection	No Inhibitor	1% Inhibitor A	% Protection
Units	mm/y	0.867	0.025	97%	5.895	0.176	97%
	mpy	34.13	0.98		232.09	6.93	

*Indicates that O₂ was introduced by agitation of the solution in air prior to pressurization

**Indicates that O₂ was introduced into the solutions during pressurization with a 3% O₂ in CO₂ gas



Figure 1: Rotating Cylinder Electrode Apparatus



Figure 2: Static Autoclave Apparatus with Mushroom Cap Coupon

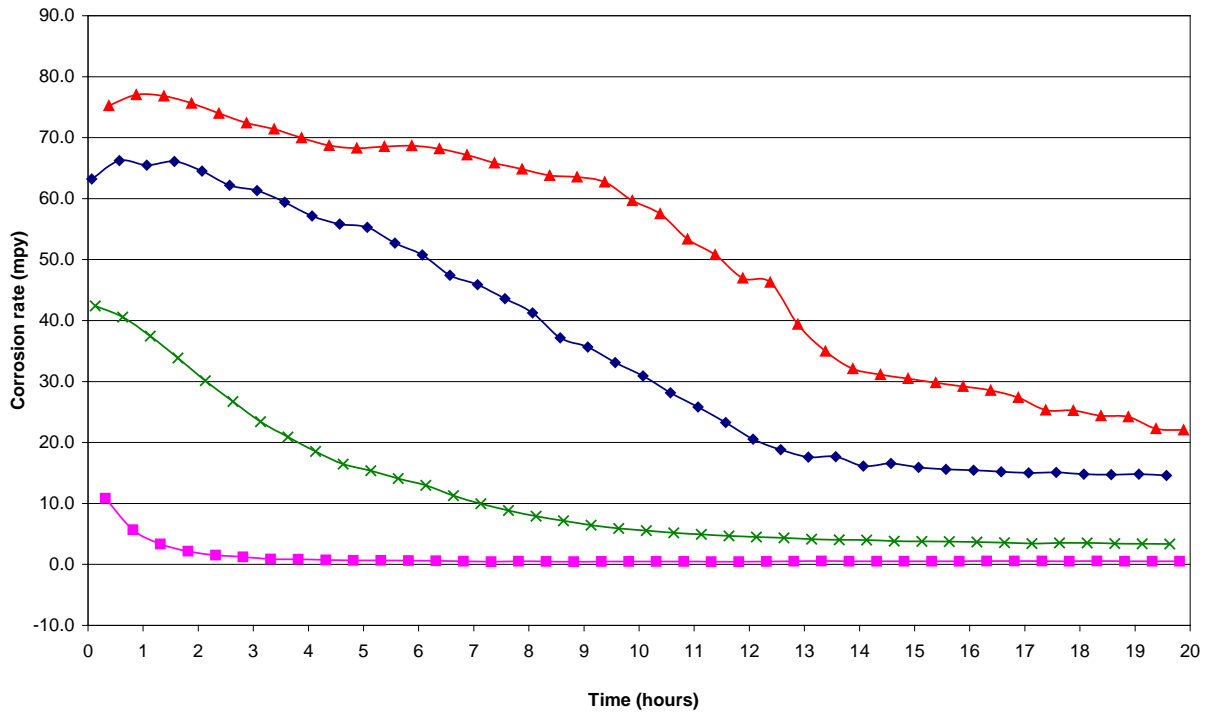


Figure 3: Corrosion rate (mpy) of carbon steel immersed in brine only (▲), 10% methanol in brine (◆), 25% methanol in brine (×) and 50% methanol in brine (■) over a period of 20 hours while purged with bone dry CO₂.

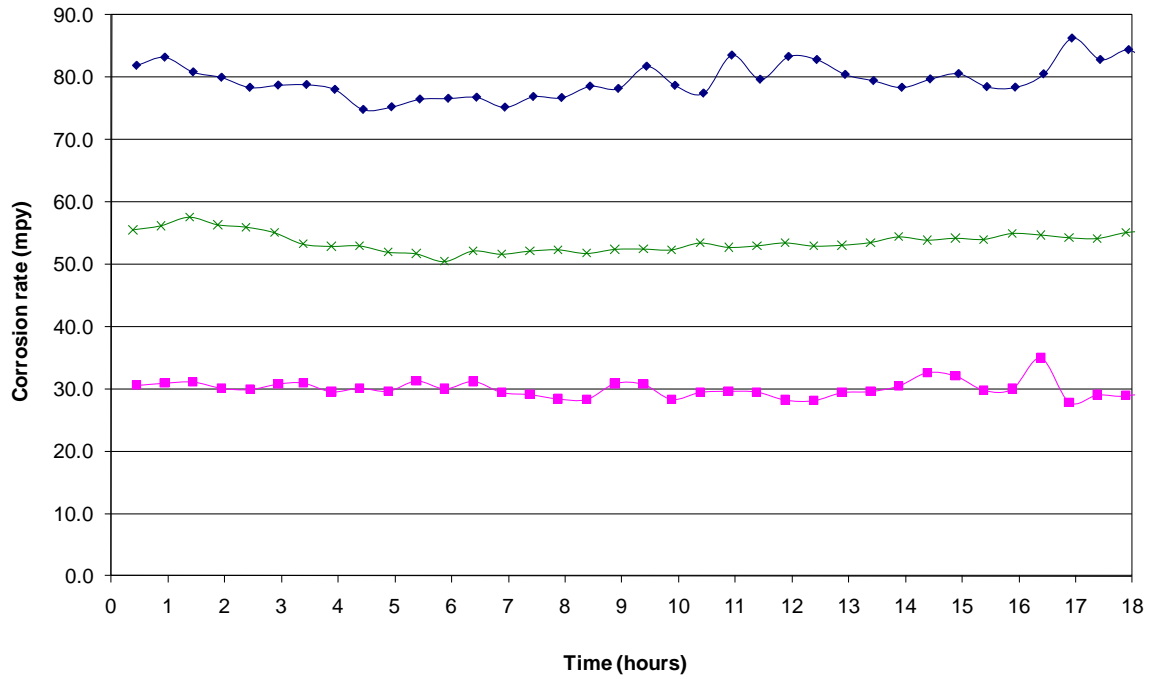


Figure 4: Corrosion rate (mpy) of carbon steel immersed in brine only (▲), 10% methanol in brine (◆), 25% methanol in brine (×) and 50% methanol in brine (■) over a period of 20 hours while purged with 3% O₂ in CO₂ mixed gas.

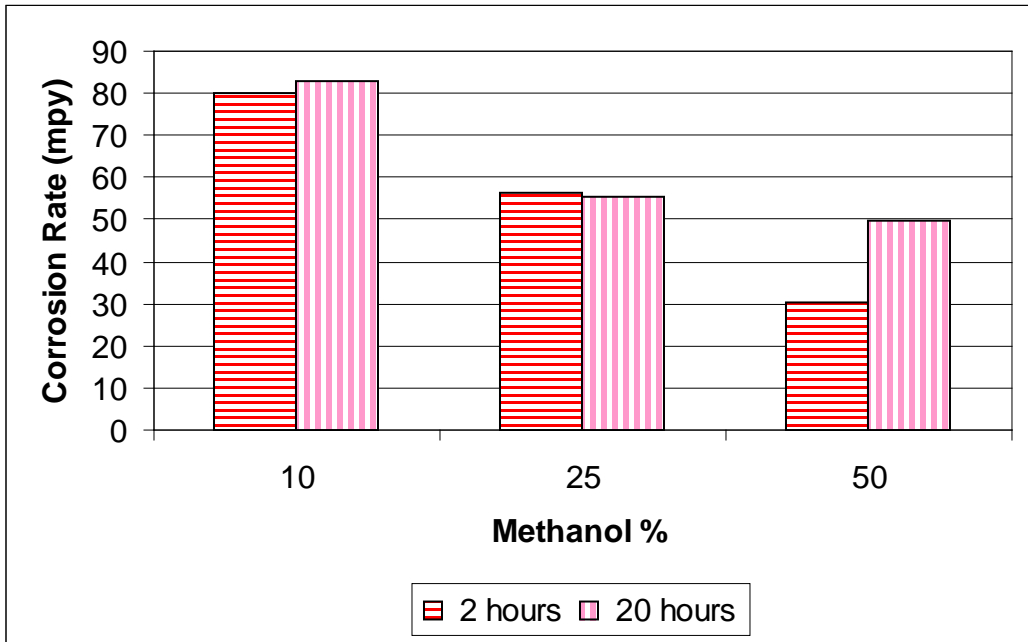
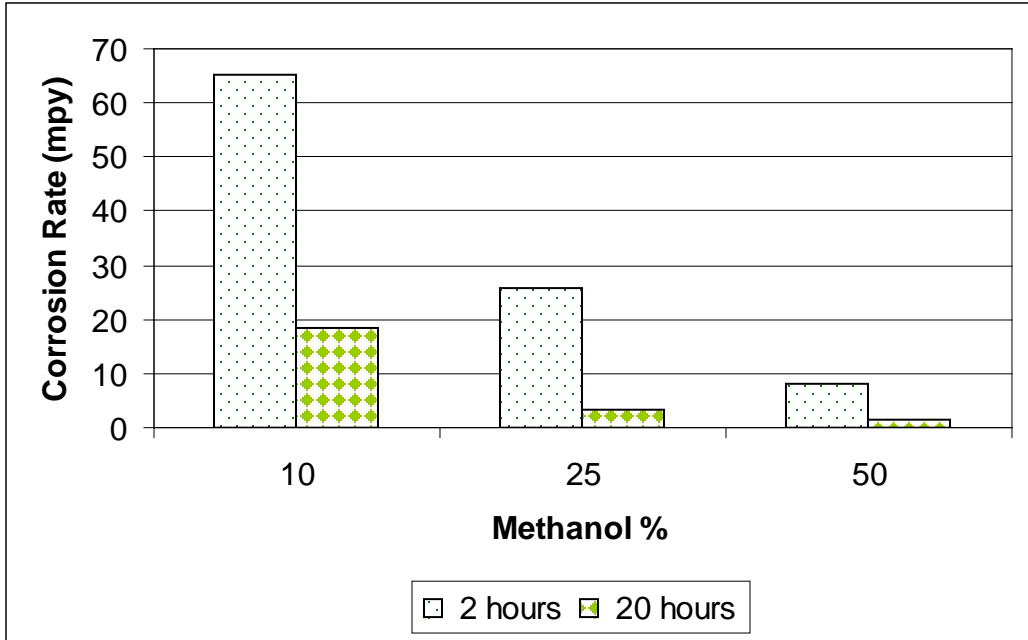


Figure 5: Corrosion rates derived from LPR data for environments purged with i) (top) bone dry CO₂ gas and ii) (bottom) 3% O₂ in CO₂ gas mixture

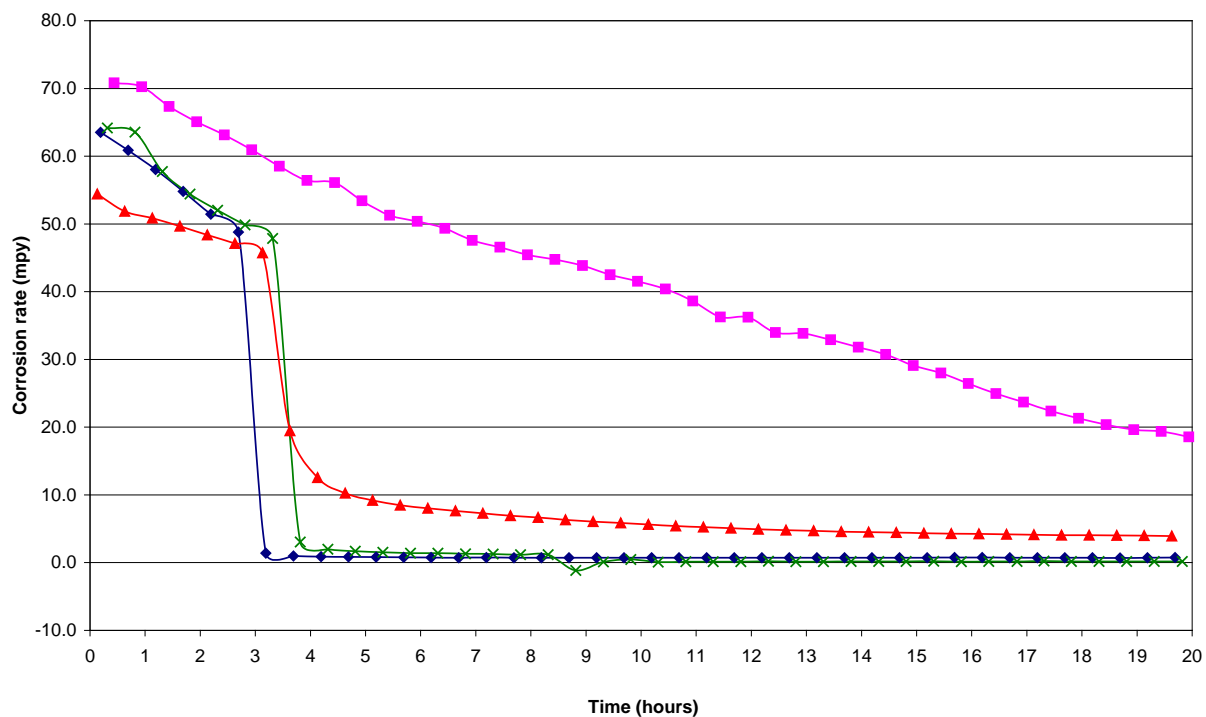


Figure 6: Corrosion rates derived from LPR data for carbon steel in a 10% methanol solution purged continuously with bone dry CO₂ gas. After a minimum of 2 hours each solution was treated with Inhibitor A as follows: 1% Inhibitor A (1000 ppm) (◆), 0.1 % Inhibitor A (100 ppm) (×), 0.01% Inhibitor A (10 ppm) (▲), and no inhibitor (■).

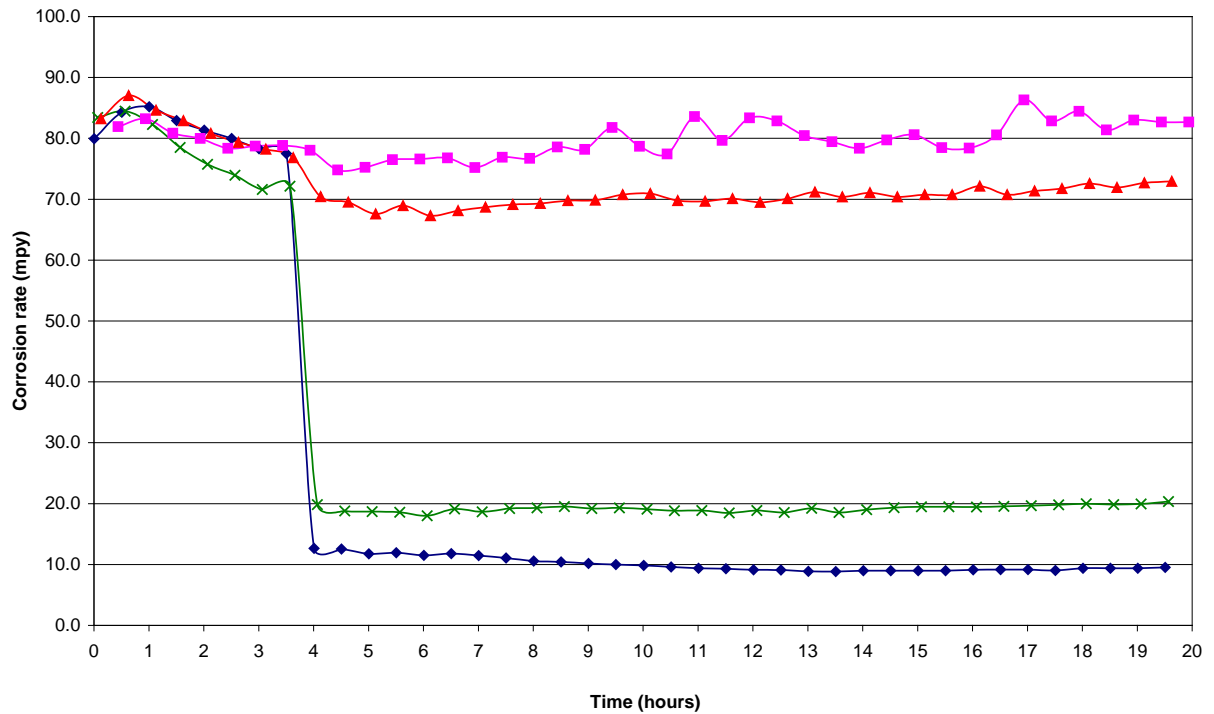


Figure 7: Corrosion rates derived from LPR data for carbon steel in a 10% methanol solution purged continuously with 3% O₂ in CO₂ mixed gas. After a minimum of 2 hours each solution was treated with Inhibitor A as follows: 1% Inhibitor A (1000 ppm) (♦), 0.1 % Inhibitor A (100 ppm) (×), 0.01% Inhibitor A (10 ppm) (▲), and no inhibitor (■).