

Pitting in the Water/Hydrocarbon Boundary Region of Pipelines - Effect of Corrosion Inhibitors -

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ABSTRACT

The boundary conditions leading to pitting in pipelines in the water/hydrocarbon (HC) interface region of the bottom-of-the-line (BOL) liquid were studied using electrochemical noise (ECN) with specially developed evaluation software. It was proved that intermittent surface wetting with HC and brine can increase the likelihood of pitting in the HC/brine boundary region of the pipeline steel. The frequency of the phase boundary movement affects the pitting intensity. Corrosive effects were strongly dependent on the presence of inhibitors, its concentration and phase behaviour influenced by isopropanol. Increasing the inhibitor concentration mitigates pit formation in all surface regions. ECN measurements in combination with the in-house developed evaluation software proved to be a sensitive tool to quantify parameter effects in short exposure times.

Keywords: Pipelines, steel, pitting, CO₂, water/hydrocarbon, inhibitors, electrochemical noise

INTRODUCTION

In some wet sweet and sour gas pipelines with a two-phase bottom-of-the-line (BOL) liquid, pitting is observed in the water/hydrocarbon interface region, preferentially in the 4-5 and 7-8 o'clock positions (Figure 1 and 2). Literature data and field results indicate that inhibitors and their phase behaviour play significant roles ¹. In oil and gas production and transportation, specifically in multiphase flow pipelines, the injection of commercial corrosion inhibitors is most widely applied, because it is economical, highly effective and easily implemented ². Pitting in 4-5 and 7-8 o'clock positions on the inner pipeline surface appears to be the consequence of a vertical movement of the HC/brine phase boundary due to wavy flow of the BOL. This is caused by entrainment of the BOL by the flowing gas. It

as assumed that such vertical phase boundary movements can deplete the inhibitor concentration in the HC/brine phase boundary region and, thus cause pitting preferentially in this region^{1,2}.

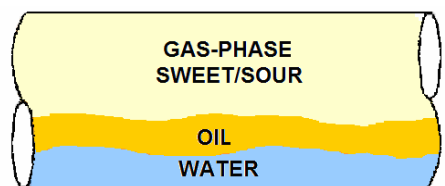


Figure 1: Schematic sketch of flow profiles along a sweet/sour gas pipe section with two-phase BOL liquid

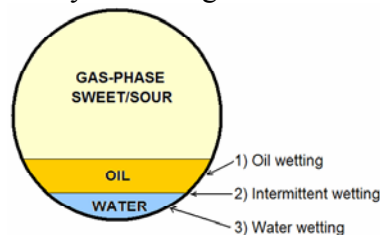


Figure 2: Surface wetting in a horizontal pipeline with two-phase BOL liquid (cross-section view)

The aim of this work was to investigate in more detail the boundary conditions that lead to pitting in pipelines with two-phase BOL. Electrochemical noise (ECN) was used as an experimental tool.

EXPERIMENTAL

Experimental Approach

The simulation of intermittent oil/water wetting of a steel surface was experimentally accomplished by a two electrode arrangement consisting of two flat coupons immersed in a stagnant liquid consisting of a water phase in equilibrium with 1 bar CO₂ topped by a hydrocarbon (HC) phase (Figure 3). One of the coupons was moved up and down with defined frequency and amplitude to simulate intermittent HC/water wetting, while the other electrode was held quiescent.

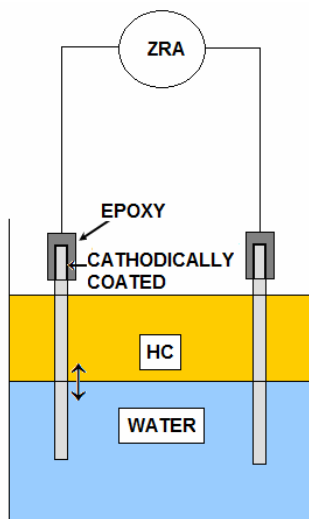


Figure 3: Schematic sketch of the experimental setup.



Figure 4: X65 test electrode

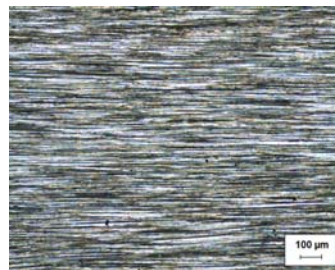


Figure 5: Surface finish of test electrode

The real-time corrosion intensity at the electrodes was indicated by electrochemical noise (ECN) measurements using a Zero Resistance Ammeter (ZRA) (Figure 3) with specially developed current noise diagnosis software, developed in the lab of the correspondence author³⁻⁷ and called CoulCount in the laboratory slang.

Corrosion System

Carbon steel electrodes. X65 steel coupons (70 x 10 x 3 mm; chemical composition see Table 1) were partially inserted in a glass tube, embedded in an epoxy resin leaving a free electrode length of about 55 mm (Figure 4). To effectively avoid crevice corrosion the embedding area of the coupon had been cathodically coated prior to embedding into the glass tube. The coupon surface was finely ground yielding a surface finish as shown in Figure 5.

Table 1
Chemical Compositions of Steel X65

Steel	Chemical Composition (mass- %)									
	C	Si	Mn	P	S	N	Cr	Mo	Ni	Cu
X 65 (API 5L, PSL2)	0.13	0.31	1.37	0.005	0.0005	0.004	<0.01	<0.01	<0.01	<0.01

Media. The aqueous phase consisted of a brine with 200 g/L salt containing 182 g/L NaCl and 18.2 g/L CaCl₂ (molar ratio Na : Ca = 18.9 : 1). The hydrocarbon phase was composed of 80 vol-% model oil represented by a paraffin based oil extracted from a diesel oil fraction (Type LVT 200 from Shell), 10 vol-% of an isomeric mixture of xylenes (to account for aromatic compounds usually contained in the oil) and 10 vol- % isopropanol to improve the partitioning properties between the oil and the water phase. In order to investigate the effect of isopropanol in the hydrocarbon mixture on the likelihood of pitting in the differently wetted metal surfaces, experiments were run with different composition of the organic liquids: i) 100 vol-% isooctane, ii) 90 vol-% isooctane + 10 vol-% xylenes (isomers), iii) 90 vol-% isooctane + 10 vol-% isopropanol, iv) 80 vol-% isooctane + 10 vol-% xylenes + 10 vol-% isopropanol.

All fluids (including the HC phases) were deoxygenated separately prior to use by purging with purified nitrogen gas until the concentration of oxygen in the off-gas dropped below 5 ppb. The oxygen concentration was measured by an oxygen meter (Orbisphere/HACH ULTRA) in the off-gas. The final test solution consisted of 50 vol-% aqueous phase and 50 vol-% HC phase. The liquid medium was in equilibrium with 1 bar CO₂. As corrosion inhibitor a 1 : 1 mixture (mass/mass) of inhibitor K1 and inhibitor K2 (Table 2) was applied in concentrations of 20, 50 and 100 ppm_m (related to the water phase). These concentrations range in the order of inhibitor concentrations technically applied in gas pipelines (most likely 20 to 50 ppm).

Table 2
Corrosion Inhibitors Applied

Short Form	Product name	Composition
K1	TOFA/DETA imidazoline	Tall-oil diethylenetriamine imidazoline (TOFA) [95-100 %] Diethylenetriamine (DETA) [1-5 %]
K2	Coco quaternary amonium salt	C12-C16 alkylbenzyl dimethyl ammonium chloride [50 %] Ethylene glycol [2 %], Water [48 %]

Further Experimental Conditions. The experiments were conducted at room temperature at pH values between 4.0 and 5.5. The medium was kept quiescent while one of the electrodes was used either without any movement or with an up-and-down movement at constant frequencies of 0.2, 0.5, 1.0 and 2 Hz and a constant amplitude of 10 mm. Each of the tests was performed with and without corrosion inhibitors.

Experimental protocol. The experimental procedure is explained by using the more detailed sketch of the experimental setup in Figure 6. In the conditioning (glass) vessel (Figure 6, right) the test liquid was purged first with nitrogen to deoxygenate for approx. 20 h and then with purified CO₂ for about 4 hours, prior to transferring the test liquid from the conditioning vessel via a system of tubes and valves into the test (glass) vessel (Figure 6, left) containing the electrode setup for ECN measurements. The test vessel was positioned in a Faraday cage. To avoid any ingress of oxygen no plastic tubes but stainless steel tubes were used for introducing gases (N₂, CO₂) or transferring the CO₂ saturated test liquid from the conditioning vessel into the ECN test vessel. A column filled with activated carbon was used to adsorb any gaseous hydrocarbons emitted from the test cell.

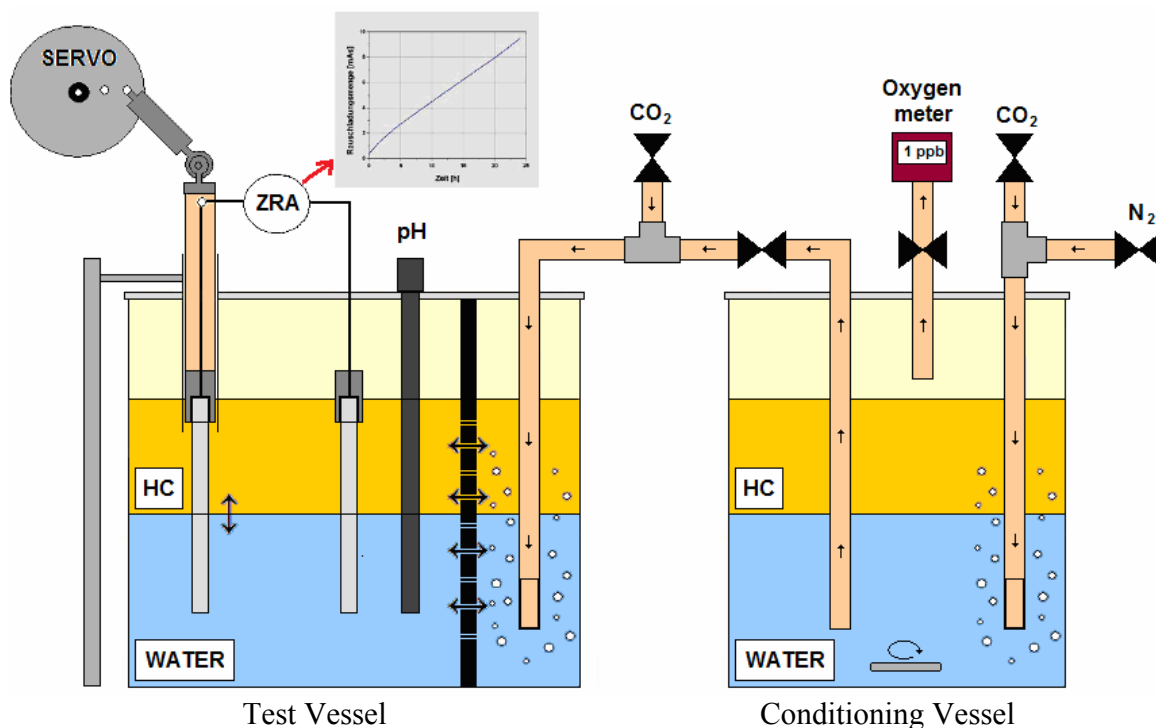


Figure 6: Schematic sketch of the experimental setup.

Prior to transferring the test liquid into the ECN vessel two flat coupons (70 x 10 x 2-3 mm) were positioned vertically in a way that - after introducing the two-phase test liquid into the ECN vessel - the water/HC phase boundary was found close to the middle of the medium-contacted coupon surface. The two coupons were electrically connected via a ZRA, and the electrochemical current noise was recorded and analyzed with the house-made specific diagnostic software which generates “noise charge vs. time” curves with always positive slope. During the coupon exposure (1 to 7 days) the liquid in the ECN cell was continuously purged with purified CO₂. The pH of the aqueous phase was monitored continuously.

After the ECN glass cell was filled with test liquids and the test electrodes were positioned, one of the electrodes was started to move up and down. This was accomplished by connecting the electrode shaft excentrically with a rotating disc which was rotated by a DC motor (outside the Faraday cage) with constant adjustable speed (Figures 6 and 7). By rotation of the disc the electrode made a vertical oscillation with defined constant frequency.

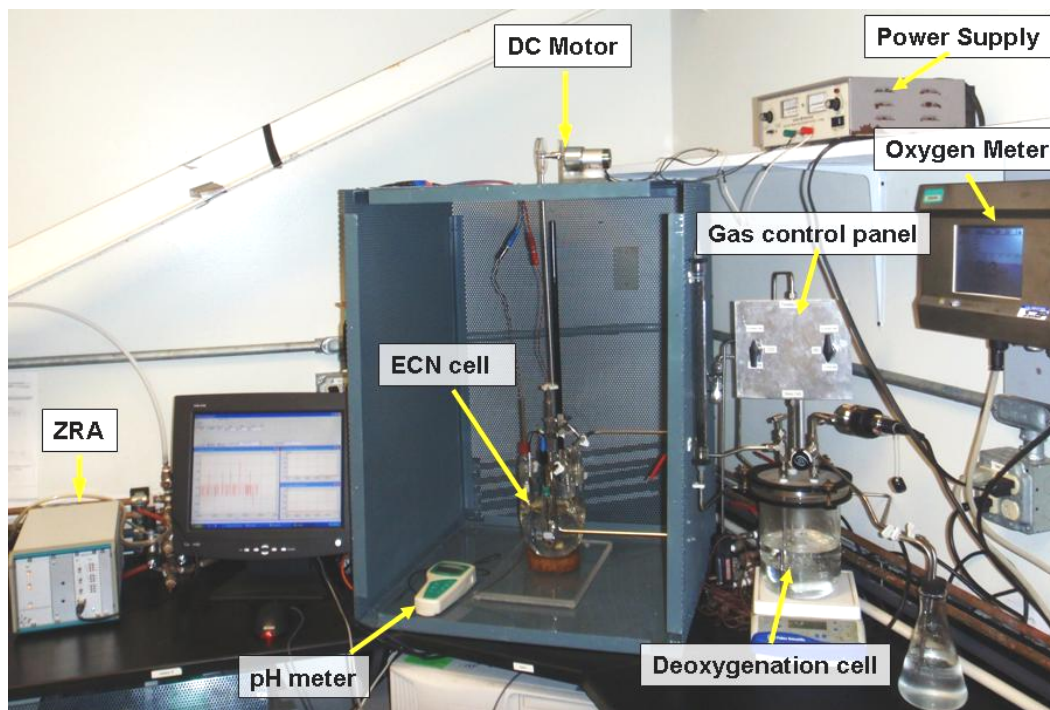


Figure 7: Overall view of the experimental setup

After the test run the coupons were removed from the glass cell, rinsed with DI-water and methanol, dried with air, and photographically documented. Finally the coupons were visually inspected and analyzed using the IFM (INFINITEFOCUS Alicona Optical 3D Measuring Device). The surface appearance and special observations (general corrosion, pitting, pit distribution and density, pit depth, phase related effects) were recorded and analyzed. The IFM was used both to take pictures of the coupon surface and for the topographic profiling of the surface structure (Figures 8 and 9). Thus, it was possible to identify the three surface regions: oil wetted surface, intermittent oil-water region, and water wetted surface. The topographic profile was then generated for each of these surface regions.

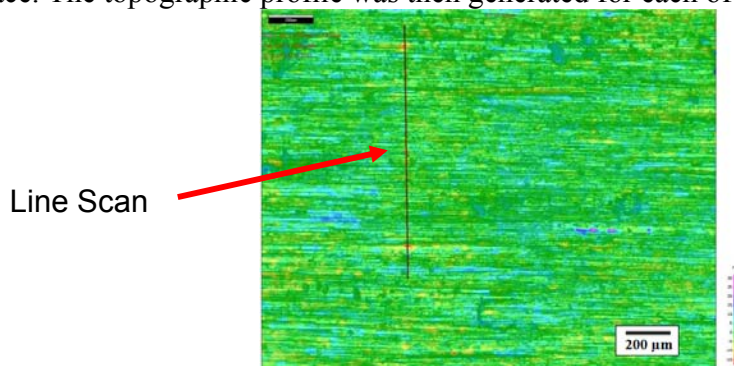


Figure 8: Image of the oil-wetted coupon surface

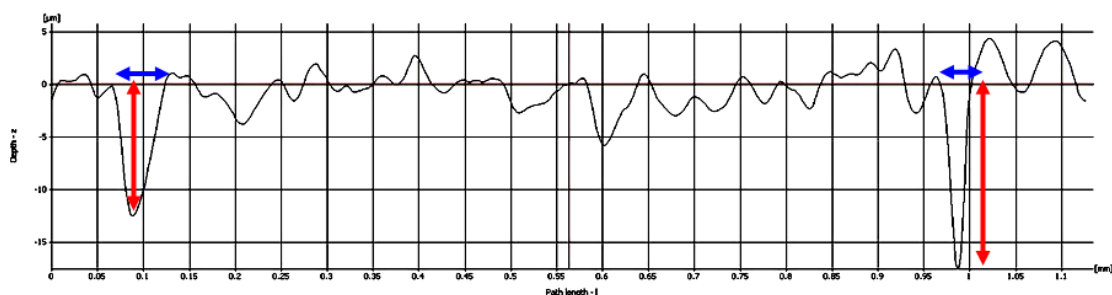


Figure 9: Topographic line scan of the oil-wetted coupon surface, as shown in Figure 8.

Electrochemical Noise and Data Evaluation

Electrochemical noise (ECN) can be taken as a corrosion-related conversation between freely corroding pairs of metal electrodes. This conversation contains information on the actual, real-time corrosion activity, the corrosion rate and even, whether the corrosion activity stems from uniform or localized corrosion^{7, 8}. A novel diagnostic tool has been recently developed which listens to this conversation and translates the message in real-time into easy-to-interpret, technically relevant information³⁻⁷. The ECN diagnosis system includes an ECN sensor, a data acquisition and data evaluation system which has been called CoulCount (“Coulombs Counting”) in the laboratory slang, because the algorithm is based on calculating and summarizing noise charges (given in [Coulombs] or [A·s]) exchanged between a pair of sensor electrodes in a given time interval.

The basics of this ECN diagnosis system have been already explained in earlier publications^{3,4}. In this paper only a short outline shall be given on the general feature of the method. Fluctuations of the element (coupling) currents between a pair of electrodes are measured with a sampling rate of 20 Hz. After elimination of the DC part (fluctuations <0.1 Hz) the absolute values of the currents measured at each sampling time are added yielding the total amount of noise charges $Q(t)$ at the time t (Equation 1)^{3,4}:

$$Q(t) = \sum_{i=0}^{t/\Delta t} |I_{Ri}| \cdot \Delta t \quad (1)$$

This method converts difficult-to-evaluate current noise fluctuations into easy-to-interpret curves with a positive slope which correlates with the actual corrosion activity on one or both of the sensor electrodes (Figure 8). Changes of the noisiness of the noise part of the element current change the slope of the time-related noise charge curve and indicate a change in the corrosion activity. There is basically no limitation as to the nature and specific properties of the sensor electrodes. They need not to be “identical” in nature. The choice of type and properties depends only on the measuring problem. Sensor electrodes can consist of resin-embedded metal coupons with equal or different surface size^{4, 5}, and equal or different types of material^{4, 5} or can consist of rings of pipe sections arranged in pipe ring columns^{4, 5}. Furthermore, each of the two sensor electrodes can be part of an appropriate crevice arrangement the geometry of which can be chosen according to service conditions or to the needs of the measuring problem. This setup was, for example, applied to investigate under-deposit corrosion^{4, 5, 9}. The sensor electrodes can also consist of a pair of coated panels with unscratched or scratched coating⁴.

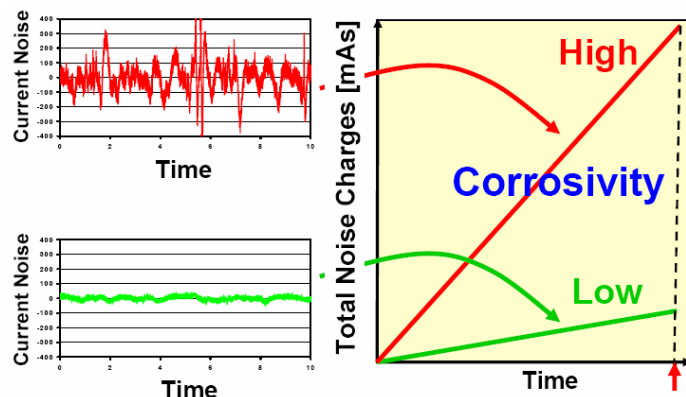


Figure 8: High and low current noise levels translated into information about actual corrosiveness

This versatility allows a multitude of applications of this special ECN diagnosis method and was, therefore, applied to investigate the effect of the fluctuating water/HC boundary region on internal pitting of pipelines in the region of BOL liquids. It was verified in a great number of experiments with different corrosion systems that it is possible to correlate the value of the slopes in noise charge vs. time curves with corrosion intensities and relative corrosion rates in the sense of traffic light phases⁷. The same was observed with the value of wavelet amplitudes^{7, 10}. Table 3 summarizes the threshold values suggested for the green phase (marginal corrosion rates $<< 0.1$ mm/y) and the red phase (considerable corrosion rates $>> 0.1$ mm/y), respectively.

TABLE 3
Threshold Values for Slopes of Noise Charge Curves and Wavelet Amplitudes
Evaluated from ECN data^{7,10}

Phase	Slope of noise charge curve [$\mu\text{As}/\text{cm}^2\text{h}$]	Wavelet amplitudes during 3 minutes observation time [$\mu\text{A}/\text{cm}^2$]
Green	< 20	< 0.1
Yellow	20-50	0.1-0.3
Red	> 50	> 0.3

Linear Polarisation Resistance. In a number of experiments linear polarisation resistance (LPR) measurements were used to get information on corrosion rates and to compare these results with information from corrosiveness measurements via ECN data evaluation. At the start of a test run the LPR method was applied 1 hr after coupon immersion with a two electrodes setup - LPR(2E) - using one of the two steel electrodes both as counter and reference electrode. Then the ECN measurements were started and kept on for 20 h (in some cases up to 70 h). At the end of a test run a reference electrode was added to the system to give a three electrodes setup - LPR(3E). The potentiostat ICTM-Gamry 1 was used to evaluate general corrosion rates.

RESULTS

Effect of Electrode Oscillation

In order to simulate the intermittent HC/brine wetting of the pipeline wall caused by the wavy flow of the BOL, the working electrode of the two electrode arrangement was periodically moved up

and down in the two-phase liquid with frequencies of 0.2, 0.5, 1.0 and 2.0 Hz, respectively. In the stagnant case, the phase boundary between the HC and the brine phase was approx. in the middle of the vertically positioned coupons. The second electrode was always kept quiescent.

Between the pair of measuring electrodes the ECN was measured and the data evaluated with the specially developed software yielding time accumulated noise charge vs. time curves, the slope of which indicates the actual corrosion activity in the corrosion system. For orientation it should be kept in mind that slopes below ca. $20 \mu\text{As}/\text{cm}^2\text{h}$ indicate insignificant corrosion rates while slopes above $50 \mu\text{As}/\text{cm}^2\text{h}$ indicate significant corrosion rates. These threshold values have been evaluated in one-phase aqueous media. They might be not exactly valid in these two-phase systems under oscillation, however, they will correlate in the same order of magnitude. This has been shown also in this work with the results from LPR measurements.

It appeared that the slopes of the time related noise charge curves increased significantly by orders of magnitude with increasing oscillation frequency. Figure 10 gives the results measured in the uninhibited two-phase system.

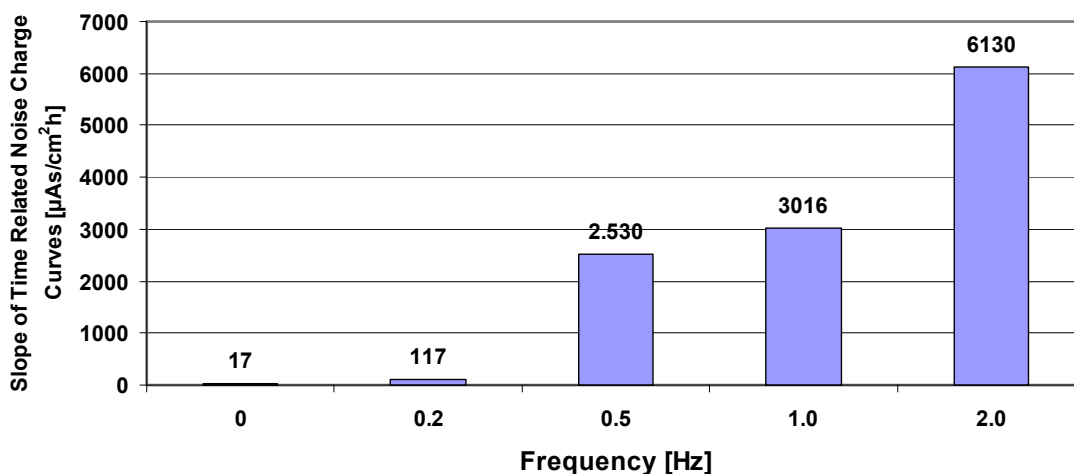


Figure 10: Effect of the coupon oscillation frequency on the slopes of the Noise Charges vs. Time curves from uninhibited systems

Also the inhibited system responded to the electrode movement (Figure 11). With increasing inhibitor concentration the high corrosion activities decreased dramatically to reach below the target line of $20 \mu\text{As}/\text{cm}^2\text{h}$ at about 50 ppm inhibitor. The moving effect of the electrode is clearly visible already at oscillation frequencies as low as 0.2 Hz. From 0.5 Hz onwards the inhibitor efficiency is independent on the oscillation frequency, however, still remarkably lower than in quiescent media.

These data correlate with the results of LPR measurements (Figure 12) which show insignificant general corrosion rates already at 50 ppm inhibitor even at an oscillation frequency of 1 Hz. In the uninhibited system the general corrosion rates ranged between 0.4 to 0.9 mm/a (including effects from pitting).

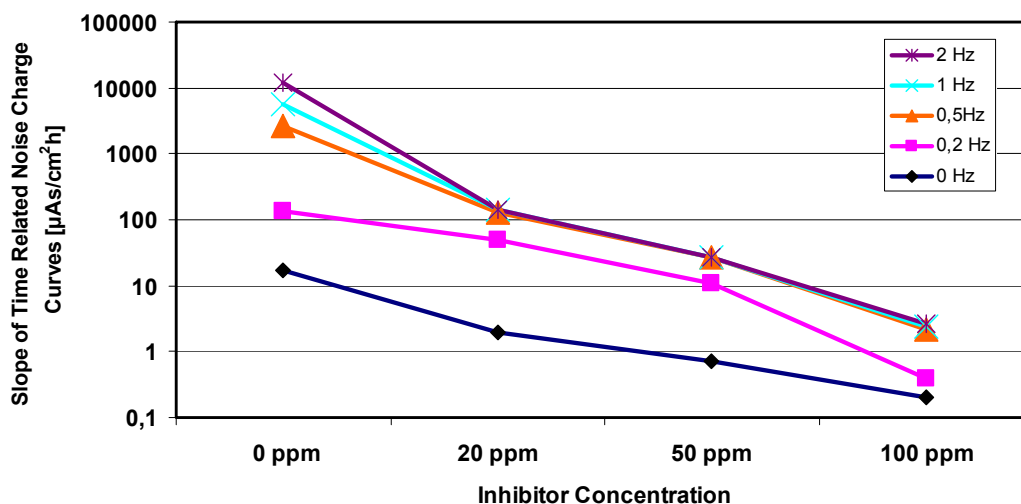


Figure 11: Inhibitor efficiency at different oscillating frequencies

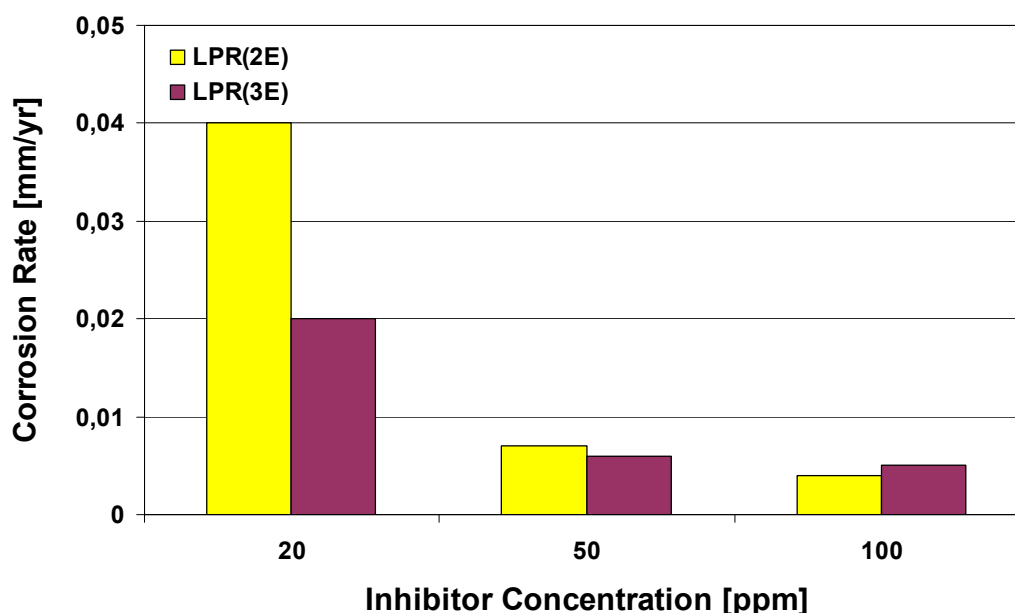
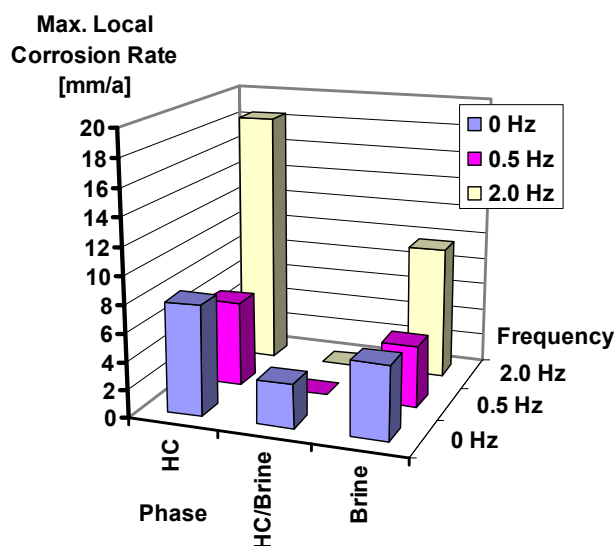


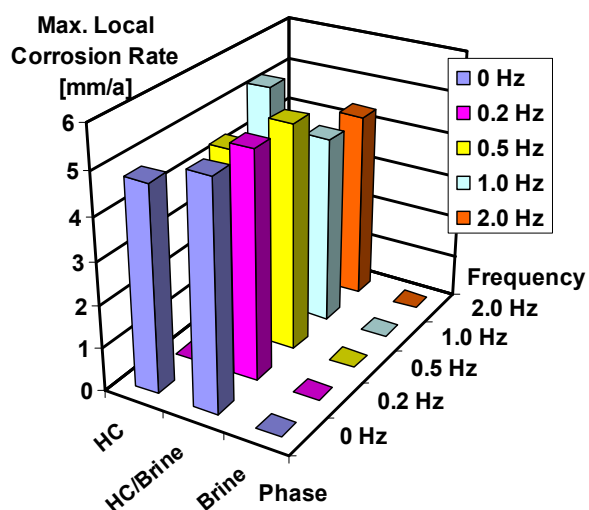
Figure 12: Reduction of corrosion rate by inhibitor addition at 1 Hz electrode oscillation

Phase Effects on Pitting

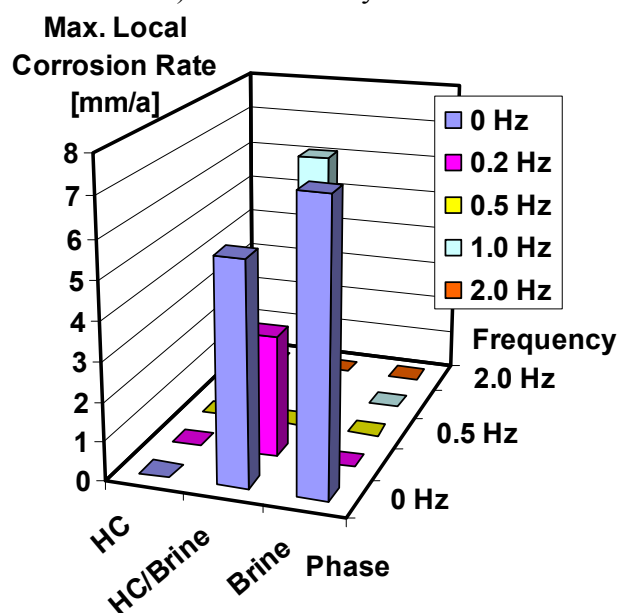
The corrosion effects on the coupons were evaluated with respect to the three surface regions: i) the hydrocarbon (HC) wetted surface, ii) the HC/Brine boundary region and iii) the brine wetted surface. These surface regions were inspected with the IFM, and the maximum depth of pits was measured by topographic scanning. From the maximum pit depth the maximum local corrosion rate was calculated. In view of the short exposure time these calculated values shall only be used for evaluation of general trends. Figure 13 summarizes the results.



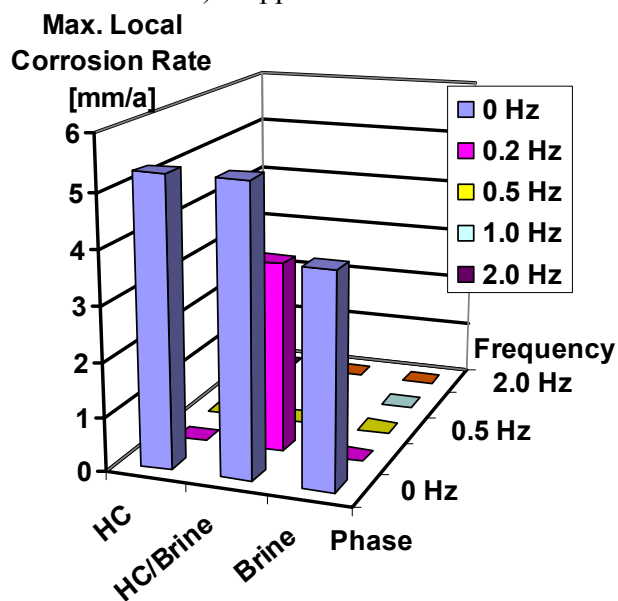
a) uninhibited System



b) 20 ppm inhibitor



c) 50 ppm inhibitor



d) 100 ppm inhibitor

Figure 13: Effect of inhibitor concentration on phase related maximum local corrosion rates at different oscillation frequencies

It appeared that in the uninhibited system pitting was observed in both the HC and the brine wetted surface with deeper pits in the HC wetted surface, specifically at 2 Hz oscillation frequency (Figure 13a). In quiescent medium pits were also found in the HC/brine region which showed no pitting on oscillated coupons (Figure 13a). In the presence of 20 ppm inhibitor (related to the water phase) no pitting occurred on the brine wetted surface regardless of the intensity of coupon movements. However, pitting was found in the HC and HC/brine region (Figure 13b). At higher inhibitor concentrations (50 and 100 ppm) no pitting occurred on any part of the coupons oscillated at 0.5 Hz and higher. Only at low oscillation frequency (0.2 Hz) or in the stagnant system pits were observed in the HC/brine and brine region (50 ppm inhibitor, Figure 13c) or in the HC, HC/brine and brine region (100 ppm inhibitor, Figure 13d). Even when no pitting occurred on the HC and brine wetted surface areas, it could happen

that pitting developed in the HC/brine region. Thus, the HC/brine boundary region proved to be specifically susceptible to pitting in the CO₂ corrosion system.

Effect of Isopropanol as Partitioning Additive

Pitting in the HC and HC/Brine region means insufficient inhibitor concentration in these phase areas. This is supported by the findings with low inhibitor concentrations (Figure 13b). In order to investigate the role of isopropanol in the organic phase, ECN measurements were performed with organic phases of different compositions. The results in terms of steady-state slopes of the noise charge vs. time curves from ECN measurements (20 h) at quiescent or oscillated (1 Hz, 10 mm amplitude) steel electrodes in uninhibited 1 : 1 (vol /vol) HC/brine mixtures at 25°C in equilibrium with 1 bar CO₂ are summarized in Figure 14. Isooctane has been chosen as a model oil with defined chemical composition and high hydrophobicity. Xylenes were added to account for the presence of aromates in oils. Xylenes exhibit some hydrophilic properties (which is the reason for the formation of azeotropes with water). The role of isopropanol as hydrophilic compound which is soluble in both water and hydrocarbon, was to influence the mixing properties of the two phases and the partitioning of the inhibitor compounds in the two phases.

It appeared that at quiescent electrodes (0 Hz) the corrosion intensity was independent of the hydrocarbon composition. However, the steel corrosion activity was influenced dramatically by the hydrocarbon composition when the electrode was oscillated with a frequency of 1 Hz. The corrosion intensity increased with increasing hydrophilicity of the organic phase which increases in the order of the columns in Figure 14 from left to right. The highest effect was achieved when isopropanol was added.

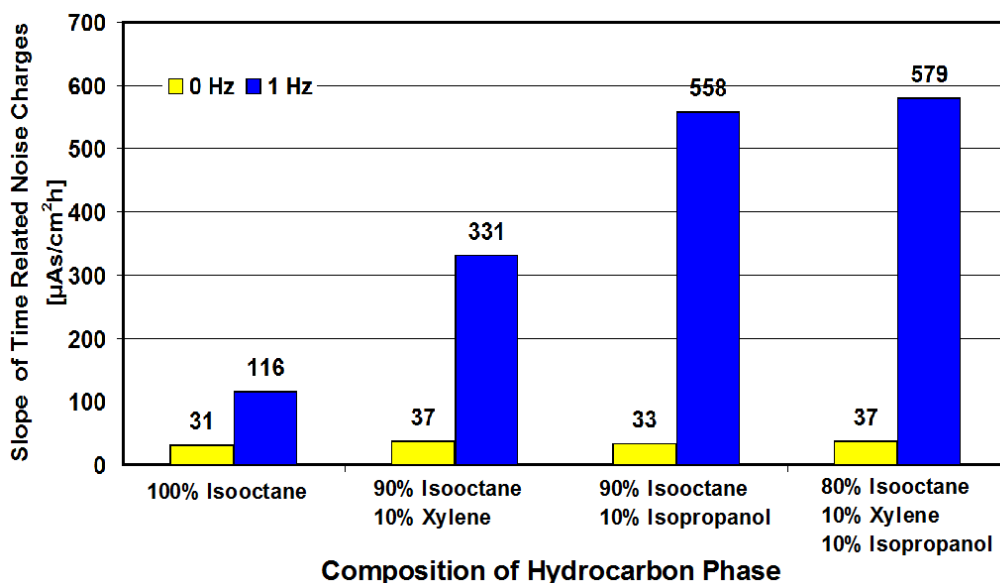


Figure 14: Effect of hydrocarbon composition on the corrosiveness of quiescent and oscillating steel electrodes in HC/brine mixtures at 25°C under 1 bar CO₂

In case of low inhibitor dosage in the aqueous phase, the effective inhibitor concentration in the hydrocarbon phase is low as well, however is influenced by its hydrophilicity. In case of intermittent HC/water wetting at the HC/brine phase boundary region the inhibitor concentration on the steel surface becomes even smaller in this region, because intermittent wetting with the HC phase can wash the inhibitor molecules from the surface depending on its specific solvating properties. Furthermore, re-adsorption of the inhibitor molecules is negatively influenced, as well. All these conditions favor the formation of pitting preferentially in the intermittently wetted HC/brine boundary region. Increasing the inhibitor concentration will decrease the likelihood of pit formation in the aqueous and the HC phase, as well as in the intermittently wetted HC/brine boundary region.

CONCLUSIONS

In wet sweet or sour gas pipelines with inhibited two-phase (HC/brine) bottom-of-the-line (BOL) liquids pitting in the 4-5 and 7-8 o'clock position appears to be related to wavy flow of the BOL liquid caused by entrainment of the BOL by the gas stream. This wavy flow results in intermittent wetting of the HC/brine boundary region of the pipeline wall with the HC and the aqueous phase of the BOL.

ECN studies of CO₂ corrosion at X65 electrodes, oscillated with low-frequency, revealed that the intermittent surface wetting increases local CO₂ corrosion activities with increasing frequency of the wetting cycles, specifically in uninhibited systems. With increasing concentration of a mixed imidazolin/quat inhibitor (20, 50, 100 ppm, related to the aqueous phase) the pronounced effect of the wetting frequency decreased, but was still visible at 100 ppm and 2 Hz wetting frequency. These results were supported by LPR measurements.

Evaluation of the local pit intensity in exposed coupon surfaces showed that the HC/brine boundary region is more susceptible to pit development than the HC and brine wetted surface areas, specifically at low inhibitor concentrations. Under such conditions preferential pitting was observed on the HC wetted surface and the HC/brine boundary region. This effect vanished with increasing inhibitor concentrations (≥ 50 ppm).

Intermittent wetting of the HC/brine boundary region of the pipeline wall with the HC phase can wash inhibitor molecules from the surface depending on the solvating properties of the HC which is greatly influenced by partitioning additives like isopropanol. Under such conditions re-adsorption of the inhibitor molecules is negatively influenced. All these conditions favor the formation of pitting preferentially in the intermittently wetted HC/brine boundary region of the BOL. Increasing the inhibitor concentration will decrease the likelihood of pit formation in the aqueous and the HC phase, as well as in the HC/brine boundary region.

ECN measurements using an in-house developed data diagnosis software proved to be a valuable tool to evaluate the major influencing system parameters within short experimental times.

ACKNOWLEDGEMENTS

This work was part of the Master Thesis of Gilda Karbasi, the experimental part of which was conducted in the Institute of Corrosion and Multiphase Technology of the Ohio University in Athens, Ohio/USA. The generous support by the Director of the Institute, Prof. Dr. Srdjan Nesic, is gratefully acknowledged.

REFERENCES

1. D.F. Ho-Chung-Qui, A.I. Williamson, "Corrosion Experience and Inhibition Practices in Wet Sour Gas Gathering Systems", CORROSION'87, NACE National Association of Corrosion Engineers, Houston/Texas, 1987, Paper 46.
2. N. N. Bich, K.E. Szklarz: "Crossfield Corrosion Experience", CORROSION'88, NACE National Association of Corrosion Engineers, Houston/Texas, 1988, Paper 196.
3. G. Schmitt, K. Moeller, P. Plagemann, "A new service oriented method for evaluation of electrochemical noise data for online monitoring of crevice corrosion", CORROSION'2004, NACE International, Houston/Texas, Paper 04-454.
4. G. Schmitt, R. Buschmann, Ch. Olry, B. Motko, P. Schrems, "Measuring Corrosivity as Simple as Temperature?", CORROSION'2007, NACE International, Houston/Texas, 2007, Paper 07-379.
5. G. Schmitt, R. Buschmann, Ch. Olry, B. Motko, P. Schrems, "Corrosivity Monitoring via Electrochemical Noise: With a New Diagnostic Tool as Easy as Monitoring Temperatures", Int. Conf. Corrosion and Materials Protection, (EFC Event no. 294), October 01-04, 2007, Prague, Czech Republic, Paper 045.
6. B. Motko, G. Schmitt, "Wavelet Diagnosis of Electrochemical Current Noise for Real-Time Indication of Localized Corrosion", 17th Intern. Corrosion Congress, Oct. 06-10, 2008, Las Vegas/ Nevada, USA, organized by NACE International, Houston/Texas, Proceedings CD, Paper 2418.
7. G. Schmitt, B. Motko, "New Tools to Evaluate Electrochemical Noise Data", EUROCORR'2009, Sept. 7.-10, 2009, Nizza, France, Paper 8257.
8. B. Cottis, S. Turgoose, "Electrochemical Impedance and Electrochemical Noise", B.C. Syrett, Editor, Series: "Corrosion Testing Made Easy", NACE International, Houston, Texas, 1999; ISBN: 157590-093-9.
9. Ch. Olry, "Investigations on the Corrosion Conditions under Deposits in Sweet and Lean Wet Gas Transport Pipelines", (in German), MSc Thesis, Iserlohn University of Applied Sciences, Iserlohn, Germany, August 2006.
10. B. Motko, "Evaluation of the Information Contained in Electrochemical Noise Signals for Sensing of Corrosion Processes"(in German), PhD Thesis, Aachen University of Technology, 2010.