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Study of the Effects of Flow Conditions on the Performance of Corrosion inhibitors under CO_2 Environment

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Abstract

Major process safety incidents have been caused by corrosion all over the world. These incidents are usually related to loss of containment of highly flammable liquids or gases, causing severe damages to the environment, impacts on people and monetary losses. Despite the increasing knowledge in corrosion, efforts are still needed to understand different damage mechanisms and their control methods. This work focuses on the study of different flow parameters such as flow velocity in a brine solution saturated with CO_2 in presence of a non-toxic corrosion inhibitor. The tests will be performed using a rotating cylinder electrode which is a well-defined apparatus to study changes in hydrodynamic conditions in a pipe. Electrochemical techniques such as Electrochemical Impedance Spectroscopy (EIS) coupled with surface images will be used to understand the behavior of the inhibitor under different flow velocities. The objective is to enhance the fundamental understanding of the damage mechanisms present in the in downstream processes of oil and gas industry. The experimental results from this work would allow developing a model describing the corrosion behavior.

Keywords: *Pipe corrosion, Flow conditions, CO_2, corrosion inhibitors*

Introduction

Corrosion is an area of continuous interest by different industries due to the economic and safety concerns that it represents. A study by NACE International in 2002 reveals that the direct costs of corrosion in the United States are about $276 billion per year (Koch, Brongers et al. 2002); an extrapolation of this study shows that the estimated direct and indirect costs of corrosion by 2016 are about $1 trillion per year (G2MT Laboratories LLC.).

As mentioned before, one of the major concerns of corrosion is related to the risk of a loss of containment event from pipes transporting flammable and toxic materials that can lead to catastrophic consequences. An example of such incidents is the explosion and fire at the Co-op Refinery in Regina, Canada in 2011. The catastrophic rupture of the pipe in a diesel processing area was caused by pipe thinning (Anderson Associates Consulting Engineers Inc. 2012, Golosky 2016) and as a result, 13 people were injured (CBC News 2011).
Another recent example is the fire in the Chevron Refinery in Richmond, California in 2012, where 6 employees were injured. This incident was caused due to the rupture of a corroded pipe transporting high-temperature light gas oil (U.S. Chemical Safety Board).

According to the U.S. Energy Information Administration, there are 141 operating refineries in the United States as of January 2017 (U.S. Energy Information Administration 2017). A major concern is the aging infrastructure of these refineries, therefore, more studies are required to understand the corrosion problems affecting the oil and gas industry. Corrosion in pipes has been a known and constant issue in the refining industry. Crude and refining products are mainly transported by carbon steel pipes, which are highly susceptible to internal corrosion.

Carbon dioxide corrosion is a common damage mechanism known to be present in crude oil transportation (López, Simison et al. 2003). CO_2 can be dissolved in the aqueous phase causing an accelerated attack on the inner walls. Although extensive research has tried to address this damage mechanism, efforts are still needed to gain more understanding of the fundamental mechanisms affecting it, such as changes in the flow and operating conditions.

The objective of this work is to study the corrosion effects in a carbon steel surface under different flow conditions. The analysis will be done by electrochemical techniques and surface imaging. These efforts are expected to increase the knowledge, which contributes to establishing and maintaining mechanical integrity programs adjusted to the varying field operating conditions.

Materials and Methodology

Test apparatus

The apparatus used for the test was a 12 mm outside diameter rotating cylinder electrode (RCE) by PINE Research Instrumentation. The basic diagram of the setup used is shown in Figure 1.

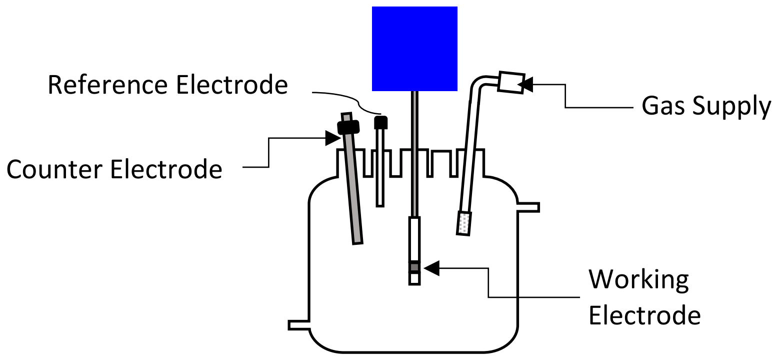

Figure 1. Schematic of a Rotating Cylinder Electrode (RCE)

This instrument is convenient in the study different flow conditions as it allows to move the metal sample respect to the fluid to simulate different turbulent conditions at low velocity (PINE Research 2016). It is possible to adjust the hydrodynamic conditions in the pipe by varying the rotation rate in rpm to mimic Reynolds Number or Wall Shear Stress. The transition from laminar to turbulent flow in an RCE corresponds to a Reynolds Number of 200 approximately (PINE Research 2016).

The corrosion process is then studied using electrochemical tests. Each experiment was performed with a freshly prepared solution and samples were used one time for the experiment.

Material Preparation

All experiments were conducted using a solution containing 3.5% NaCl (99% purity from VWR® Chemicals) and deionized water. The solution was saturated by injection of CO_2 grade 4.0 supplied by Praxair Inc.

The brine solution was added to a 0.7 L glass cell. The CO_2 was bubbled for 1 hour before starting the test to remove dissolved O_2 from the solution. During the experiments, a constant flow of CO_2 was maintained to guarantee saturation. The pH at this conditions is 3.8 ± 0.5. After the initial saturation period of 1 hour, the working electrode was immersed into the solution and the connections to the system were done to perform the electrochemical tests; the rotation system was activated to reach the desired rotation rate. The rotation rates used for this work were 0, 100 and 500 rpm.

For the test in presence of inhibitor, an imidazole-based inhibitor (96% purity supplied by Sigma-Aldrich) was used at a concentration of 500 ppm. The inhibitor was added into the system before immersing the working electrode into the corrosive solution.

The carbon steel specimens for the tests were obtained from Metal Samples®. The chemical analysis performed by Laurel Steel shows that the chemical composition of the C1018 specimens (wt%) is as follows: 0.184% C, 0.75% Mn, 0.011% P, 0.014% S, 0.17% Si, 0.004% Pb, 0.015% Sn, 0.10% Cu, 0.08% Ni, 0.10% Cr, 0.023% Mo, 0.0039% N, 0.04% V, 0.0002% B, 0.001% Nb(Cb), 0.0017% Ca, 0.001 % Ti.

The dimensions of the samples are 1.2 cm outer diameter, 0.6 cm inner diameter, and 0.8 cm height.
The temperature of the solution was maintained at 22 °C ±1. After each experiment the samples were removed from the cell and rinsed with ethanol, dried with nitrogen and stored in a desiccator for posterior analysis.

Electrochemical experiments

A three-electrode cell was used to perform the electrochemical tests with a carbon steel working electrode, an Ag/AgCl (saturated) reference electrode and a graphite rod as the counter electrode. The potentiostat used is a Gamry Instrument reference 1000. All potentials were measured versus the reference electrode. The working electrode had an exposed area of 3 cm^2.

The open circuit potential (OCP) was measured for 60 min until a steady-state was reached. The Electrochemical Impedance Spectroscopy (EIS) was performed in a frequency range of 100 kHz to 10 mHz and an AC amplitude of 10 mV. The EIS data was analyzed using the EC-lab® software.

Optical microscopy analysis

The optical microscope used to analyze the surface after the test was a Nikon Eclipse MA100.

Results and discussion

Open Circuit Potential

In the blank solution, the OCP was about -0.64 V vs. Ag/AgCl immediately after the immersion. This value decreased during the first minutes and reached stability after the first 30 minutes, with a variation of less than 10 mV vs. the reference electrode. The value of OCP remains stable over the range for the rotation rate of 100 rpm. A different value of OCP is obtained for the steady-state condition at a rate of 500 rpm, with an increase of about 40-50 mV compared to the blank solution. These low OCP values are characteristic of the bare metal surface (Yang, Rosas et al. 2014).

The OCP for the test with 500 ppm and rotating at 500 rpm, shows and increased value near -0.6 V vs. the reference electrode immediately after the immersion. The variation of the OCP, in this case, is less than 20 mV.

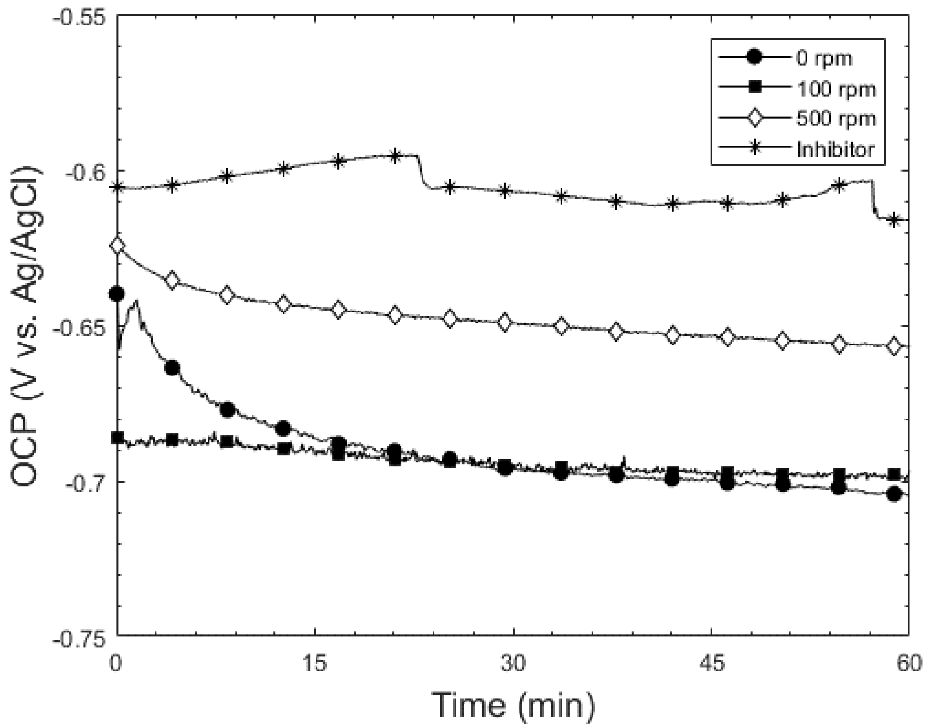

Figure 2. Open Circuit Potential (OCP) curves for carbon steel in 3.5% NaCl solution at different rotation rates: ● no inhibitor and 0 rpm, ■ no inhibitor and 10 rpm, ◊ no inhibitor and 500 rpm, * 500 ppm inhibitor and 500 rpm

Electrochemical Impedance Spectroscopy (EIS)

EIS tests were performed to understand the kinetics and electrochemical reactions taking place on the surface of the metal. The EIS results for the test material at different times of exposure are represented using Nyquist plots shown in Figures 3 a-e.

In general, we can observe that the diameter of the semicircle is significantly reduced when the samples are under rotation. The semi circles are also reduced with time. The diameter of the semicircle is related to the charge transfer resistance (Zhang, Chen et al. 2007), therefore, the reduction of the semicircle indicates a lower resistance with time and rotation speed. This translates into the reduction in the corrosion protection of the surface. An inductive loop is observed in the low-frequency range (approaching 10 mHz) which has been reported to be related to the adsorption of intermediate metal products on the surface (Zhang, Chen et al. 2007, Yang, Rosas et al. 2014).

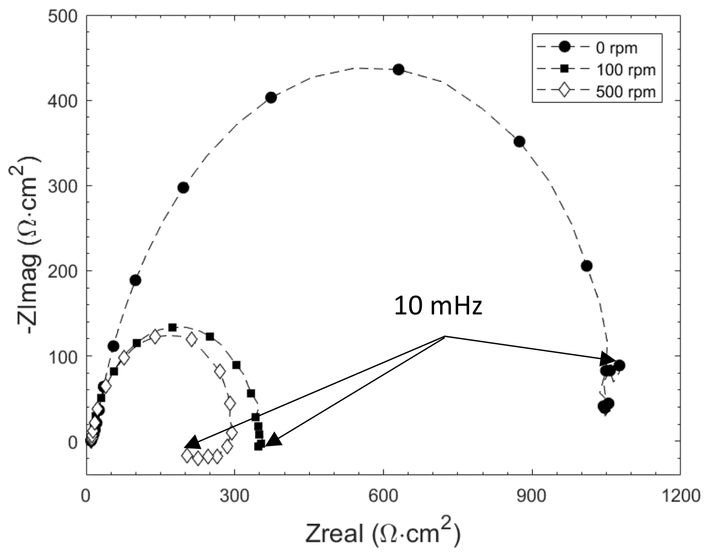

Figure 3a. Nyquist plot for carbon steel C1018 in 3.5% NaCl under CO_2 after 1 h immersion: ● no inhibitor and 0 rpm, ■ no inhibitor and 10 rpm, ◊ no inhibitor and 500 rpm

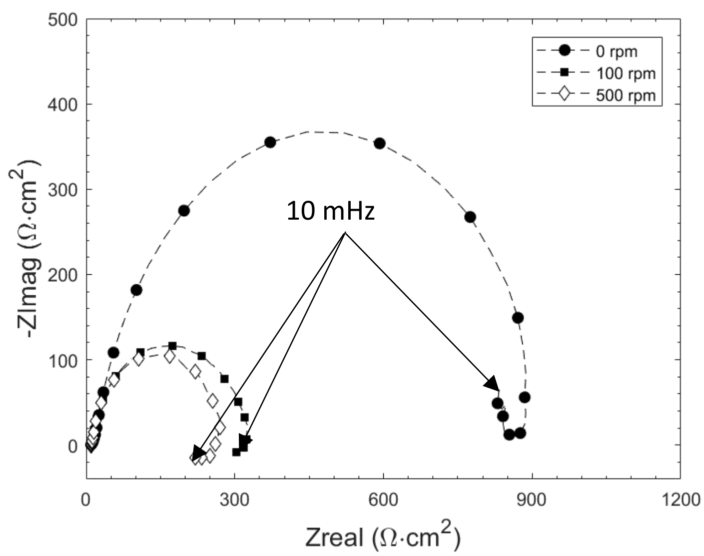

Figure 3b. Nyquist plot for carbon steel C1018 in 3.5% NaCl under CO_2 after 5 h immersion: ● no inhibitor and 0 rpm, ■ no inhibitor and 10 rpm, ◊ no inhibitor and 500 rpm

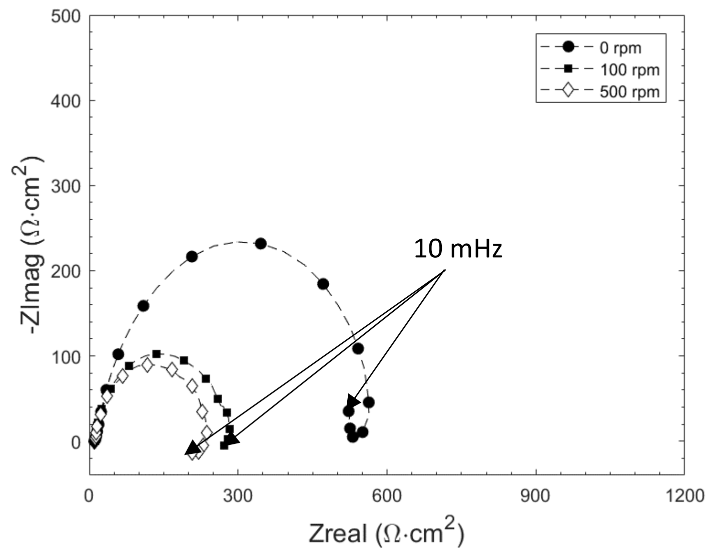

Figure 3c. Nyquist plot for carbon steel C1018 in 3.5% NaCl under CO_2 after 10 h immersion: ● no inhibitor and 0 rpm, ■ no inhibitor and 10 rpm, ◊ no inhibitor and 500 rpm

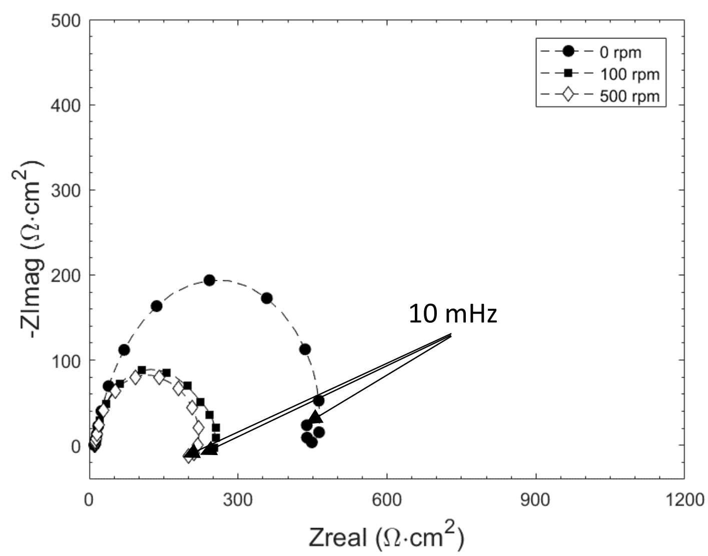

Figure 3d. Nyquist plot for carbon steel C1018 in 3.5% NaCl under CO_2 after 15 h immersion: ● no inhibitor and 0 rpm, ■ no inhibitor and 10 rpm, ◊ no inhibitor and 500 rpm

Figure 3e shows the comparison of the Nyquist plots at a rotation of 500 rpm. We can observe an increase in the diameter of the curve once the inhibitor is added which can indicate higher charge transfer resistance in presence of inhibitor. This hypothesis will be further investigated by using different concentrations of inhibitor and performing surface analysis.

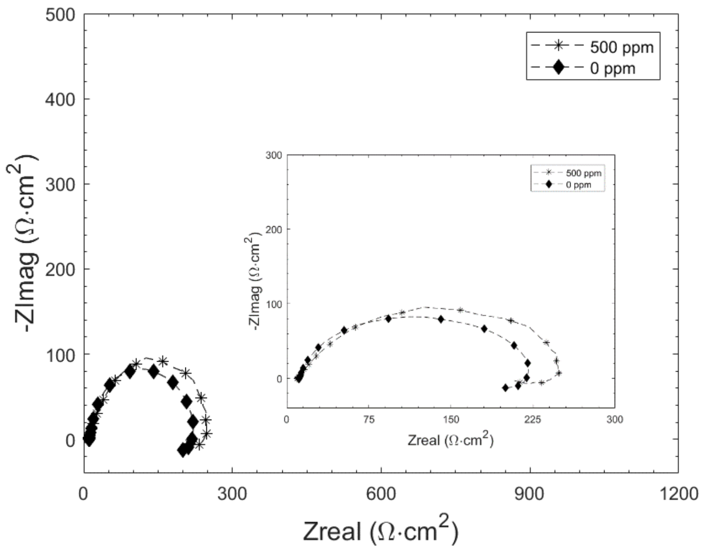

Figure 3e. Comparison of Nyquist plot for carbon steel C1018 in 3.5% NaCl under CO_2 after 1 h immersion: ♦ no inhibitor (0 ppm) and 500 rpm, * 500 ppm inhibitor and 500 rpm

Optical Microscope Images

The optical images from the surface of the metal after the experiments are shown in Figures 7 - 10. It is noted that there is a formation of corrosion products on the surface of the metal, however, it needs further characterization to determine the protective or non-protective nature.

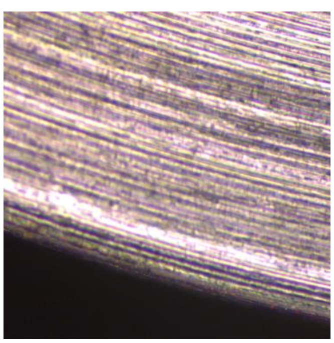

Figure 4a. Optical Microscope of cross-sectional area of the new sample surface before immersion: 10X magnification

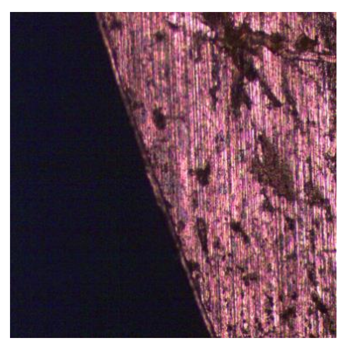

Figure 4b. Optical Microscope of cross-sectional area of corroded surface after EIS test at 0 rpm: 10X magnification

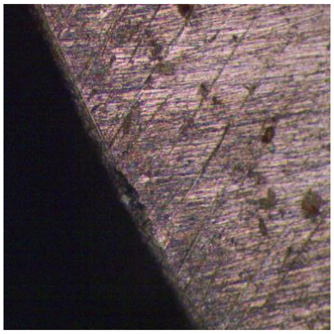

Figure 4c. Optical Microscope of cross-sectional area of corroded surface after EIS test at 100 rpm: 10X magnification

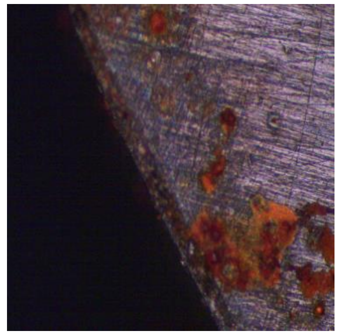

Figure 4d. Optical Microscope of cross-sectional area of corroded surface after EIS test at 500 rpm: 10X magnification

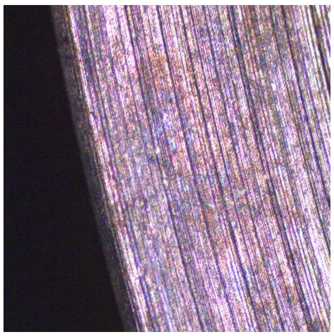

Figure 4e. Optical Microscope of cross-sectional area of corroded surface after EIS test at 500 rpm: 10X magnification

Conclusions

This work presented some experimental results of corrosion under different flow conditions in a CO_2 environment using a Rotating Cylinder Electrode (RCE). As rotation rate is increased, the diameter of the Nyquist plots was reduced.

Also, a layer is observed on the metal surface which may indicate the presence of protective corrosion products.

The ongoing work is focused on studying the corrosion products on the metal surface and the effects of different inhibitor concentration.

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