

Effect of Elevated Temperatures (30-80 °C) on CO₂ Corrosion after Intermittent Oil/Water Wetting

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ABSTRACT

The main goal of this research is to electrochemically determine the influence of temperature elevation (30 °C - 80 °C) on the wetting state and corrosion behavior of mild steel during intermittent oil/water wetting. The results obtained in separate experiments demonstrated that the corrosion mitigation effect of an oil phase (LVT-200 model oil) containing myristic acid (surface-active compound representing naturally occurring oxygen-containing compounds in crude oils) on CO₂ corrosion decreased with temperature after intermittent wetting. The influence of the same temperature range on interfacial properties during intermittent oil/water wetting such as oil/water interfacial tension (IFT) and oil-in-water contact angle were also investigated. For model oil containing myristic acid, the IFT value was unchanged with temperature and could not be correlated to the corrosion rate. In the presence of the oil phase, the surface became more hydrophilic at 55 °C, which diminished the adsorption and persistency of the oil layer and decreased the corrosion mitigation effect. The effect of temperature on IFT and contact angle can depend on the nature of oil and surface-active compound.

Key words: CO₂ corrosion, carbon steel, oil/water intermittent wetting, naturally occurring surface-active compound, elevated temperatures.

INTRODUCTION

Carbon steel pipelines are the most efficient and economical method for transporting oil and natural gas, especially for their large-scale transfer across long distances^{1,2}. However, these pipelines are prone to corrosion due to the presence of corrosive gases such as carbon dioxide (CO₂) and/or hydrogen sulfide (H₂S) dissolved in any present aqueous phase derived from reservoir brine. The oil phase itself does not lead to corrosion and can even be preventive^{3,4,5,6}. In oil-water flow through a horizontal pipeline at low flow rates, the aqueous phase is present as a separate layer flowing at the bottom of the pipe. This corresponds to a stratified flow regime because gravity dominates over turbulent forces. By increasing the flow rate inside the pipeline, the turbulent energy increases, as a result the water phase can become gradually dispersed as droplets in the oil phase^{7,8,9}. When considering pipelines operated at low water cut, the water phase is typically entrained by the hydrocarbon phase and the oil phase wets the internal surface of the pipe, minimizing the risk of corrosion. By increasing the water content, water breakout may occur, consequently water may wet more easily the surface of the pipe, and corrosion can become possible^{10,11,12}. Considering that production flow rates can vary significantly during the life of a pipeline

system, different flow patterns can be expected in which oil and water can alternately wet the pipe internal surface. This phenomenon is identified as “intermittent wetting”¹³, flow rate and water cut playing governing factors thereon¹². This influences the mechanism of the corrosion of the metal surface which may differ from those commonly accepted for aqueous corrosion (i.e., full water wetting)^{3,7,14,15}. The wetting condition of the metal surface is consequently a key parameter to predict corrosion behavior^{16,17,18,19}, and it is important to know the relation between surface wetting and corrosion processes^{20,21,22}. This knowledge can help decrease economic costs and mitigate the potential for adverse environmental impacts caused by corroding tubular steels. Although the corrosion behavior of carbon steel during intermittent wetting conditions at low temperature has been investigated in our previous studies²³, little has been reported on the mitigation effect of oil/water intermittent wetting at elevated temperatures.

Crude oils can be defined as naturally occurring liquid mixtures of hydrocarbons (83 wt.%–87 wt.% of carbon, 10 wt.%–14 wt.% of hydrogen) containing derivatives of nitrogen (0.1 wt.%–2.0 wt.%), oxygen (0.05 wt.%–1.5 wt.%), sulfur (0.05 wt.%–6.0 wt.%), metals (less than 1000 ppm), and other elements^{24,25}. Some chemical compounds native to crude oils identified as surface-active compounds have an ability to preferentially adsorb at steel-water, steel-oil, and oil-water interfaces, which can alter the wetting and corrosion properties of steel surfaces⁷. Surface-active compounds such as oxygen compounds, sulfur compounds, and nitrogen compounds were identified as factors influencing the wettability preference of a crude oil²⁶. The corrosion inhibition and wettability effect of oxygen containing compounds has been studied^{20,22}. In this study, the effect of a select carboxylic acid surface-active compound (myristic acid) on corrosion inhibition, interfacial tension, steel/oil contact angle, and oil/water interface structure is described for elevated temperatures.

EXPERIMENTAL PROCEDURE

Corrosion rate measurements

Chemicals and Materials

In this study, LVT-200[‡] model oil, which is a hydrotreated light distillate petroleum fraction²⁷, was used with and without the addition of 0.1 wt.% of myristic acid, which is representative of oxygen containing compounds that naturally exist in crude oils. The surfactant concentrations used in this study are in the common range for such a type of naturally occurring compound in crude oils. The molecular structure of myristic acid is shown in Figure 1. Note the amphiphilic character of myristic acid.



Figure 1. Molecular structure of myristic acid

The metal specimens used for electrochemical measurements were machined from a X65 carbon steel, a typical pipeline steel material used upstream in the oil and gas industry. This X65 carbon steel has a uniform, fine structure of cementite in a ferrite matrix and conforms to applicable specifications for API

[‡] Trade Name

5L, Grade X65 seamless or welded pipe with the following chemical analysis (Table 1Error! Reference source not found.).

Table 1. Chemical compositional analysis of X65 pipeline steel

C	Mn	Nb	P	S	Ti	V	Fe
0.05%	1.40%	0.04%	0.003%	<0.001%	0.01%	0.03%	balance

Experimental Apparatus and Procedure

Experiments were performed in a standard three electrode glass cell with an X65 carbon steel rotating cylinder electrode (RCE) working electrode, a platinum-coated titanium mesh counter electrode, and an Ag/AgCl (KCl saturated) reference electrode. Before each experiment, the RCE was sequentially polished with 400 and 600 grit silicon carbide abrasive papers, cleaned with isopropanol in an ultrasonic bath, and air-dried. Both oil and water solutions were deoxygenated and saturated with carbonic species by 1 hour of sparging with CO₂ before the introduction of the working electrode. After the RCE was inserted into the glass cell, a pre-corrosion test was conducted to determine whether the initial corrosion rate was close to the blank experiment corrosion rate to ensure no contamination occurred from the previous test. Linear polarization resistance (LPR) measurements were taken with a scan range from –5 mV to +5 mV vs. OCP, a scan rate of 0.125 mV/s, and a B value of 26 mV using a Gamry[§] Interface 1010B™ potentiostat. The glass cell was sparged with CO₂ throughout the test to prevent air (oxygen) ingress and to maintain saturation of the aqueous electrolyte with CO₂. To minimize the noise in electrochemical measurements caused by CO₂ sparging, the sparge tube was retracted into the headspace during data acquisition. The pH was adjusted by adding deoxygenated hydrochloric acid or sodium bicarbonate solution during each experiment as needed. The experiments were performed using intermittent wetting procedure, where the electrochemical glass cell was connected to another reservoir glass cell to change the level of the water phase in the main glass cell, enabling placement of the specimen in oil and water, alternately. These two glass cells are connected to each other using a pump with two solenoid valves. A simple schematic of the intermittent wetting setup is shown in

Figure 2. Experiments were performed therein in four steps:

1. Pre-corrosion: polished specimen was immersed in the water phase.
2. Partitioning: 300 ml of an oil layer containing surface-active compounds was added to the top of the water phase. The polished specimen was still immersed into the water phase and rotated for one hour at 1000 rpm.
3. Intermittent wetting: The intermittent wetting step includes two sub-steps:
 - a. Oil wetting step: Brine is pumped from the electrochemical cell to the reservoir cell to lower the oil layer, so the oil layer completely envelopes the specimen surface.
 - b. Water wetting step: Brine is pumped from the reservoir cell back to the electrochemical cell to lift the oil layer well above the specimen surface.
4. Persistency: After the intermittent wetting cycles, the specimen was returned to the water phase. The corrosion rate was measured every 20 minutes for at least 10 hours.

A schematic picture of the procedure for these experiments is shown in Figure 3. The test matrix used to study the effect of elevated temperatures on corrosion rate after intermittent contact with oil is presented in Table 2.

[§] Trade Name

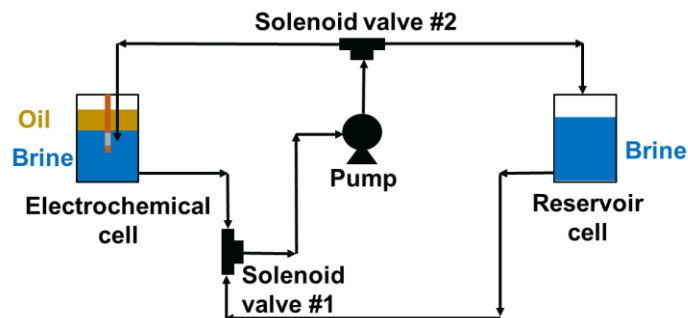


Figure 2. the intermittent wetting setup

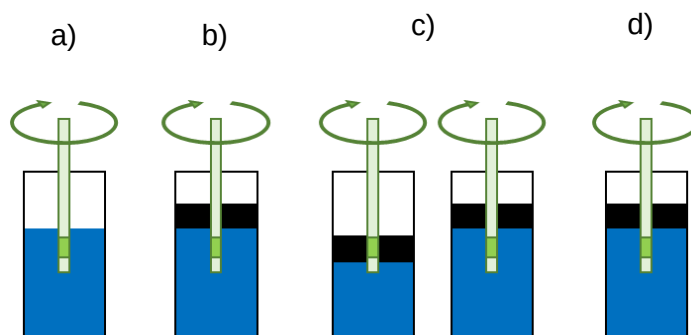


Figure 3. Procedure of intermittent wetting experiments: a) pre-corrosion; b) partitioning; c) oil/water intermittent wetting repeated multiples times over 1 hour; and d) persistency.

Table 2. Test matrix to study the effect of intermittent wetting on corrosion rate

Parameter	Conditions
Material	X65 steel
Electrolyte	1 wt.% NaCl in DI water
Oil phase	100% model oil (15% of total liquid)
Temperature	30,55,80 °C
CO ₂ partial pressure	0.96, 0.84, 0.52 bar
pH	4.0
RCE rotational speed	1000 rpm
Intermittent wetting period	1 minute
Duration of intermittent wetting	1 hour
Surface-active compound	Myristic acid (0.1, 0.5, 1, 2 wt.% of oil phase)
Experimental equipment	RCE, Glass cell
Electrochemical measurements	OCP, LPR, EIS

Interfacial tension measurements

Interfacial tension is the measure of free energy per unit area of interface between two liquid phases, which can help to characterize changes that occur at the oil/water interfaces^{28,29}. Oil-water interfacial tension measurements were performed to evaluate the surface activity of acidic compounds. The measurements were done using the K20 KRÜSS** tensiometer and Wilhelmy plate method. Both 1 wt.%

** Trade Name