

Effect of Steel Microstructure and Corrosion Product Characteristics on Inhibition Performance of Decanethiol Against Top of the Line Corrosion

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ABSTRACT

The use of corrosion inhibitors to control top of the line corrosion (TLC) of steels exposed to CO₂ environments is common in the oil and gas industry. The performance of such chemicals depends on the physical nature of the steel surface and the stability of corrosion product layers. The objective of this work was to investigate and understand the role of steel microstructure (pearlitic-ferritic and tempered martensitic) and the state of a pre-corroded surface, specifically the effect of FeCO₃ and Fe₃C corrosion product layers on the inhibition performance of decanethiol at TLC conditions. Weight loss measurements and Fe²⁺ concentration in condensed water were used to measure the corrosion rate in the absence and presence of decanethiol. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) were used to characterize the morphology and chemical composition of the surface. After the removal of the corrosion products, profilometry was performed to assess the occurrence of localized attack. The acquired data showed that the steel microstructure and the nature of the corrosion product layer affect the inhibition performance of decanethiol in a CO₂ environment. The presence of a FeCO₃ layer decreased the inhibition efficacy of decanethiol (95 to 82%). In contrast, the presence of a Fe₃C layer did not affect the inhibition efficacy of the tested chemical. An inhibition mechanism was also proposed based on the physical properties and the nature of the surface.

Keywords: CO₂ corrosion, iron carbonate, top of the line corrosion, decanethiol, cementite, scale

INTRODUCTION

Chemical composition and microstructure of carbon steel plays an important role in corrosion processes. In 1963, Staicopolus¹ studied the behavior of cementite under cathodic polarization. It was found the cementite can act as a cathodic site, which means that while the ferrite phase dissolves (oxidation reaction), reduction of hydrogen ions happens where the cementite phase is present. In carbon steels, the volumetric quantity of Fe_3C increases with carbon content, thereby affecting the corrosion rate. A twofold increase, or more, in the corrosion rate has been measured on steels when the carbon content is increased from 0.2 to 0.8 wt%.²

Deterioration of carbon steels exposed to aggressive environments, such as those containing CO_2 , H_2S and/or organic acids, cannot be avoided. However, it can be mitigated by injection of corrosion inhibitors (CIs). The efficiency of CIs is usually measured by exposing a polished carbon steel specimen to an aggressive environment. By means of electrochemical techniques, the corrosion rate before adding the CI is measured and the efficiency calculated based on the observed corrosion rate after the addition of the CI. However, the presence of corrosion products on the steel surface, such as iron carbonate (FeCO_3), iron sulfide (FeS) and/or iron carbide (Fe_3C) has the potential to affect the efficiency of CIs; Fe_3C is not considered as a corrosion product in the same way as FeCO_3 or FeS , rather it is a residual phase that is exposed after the oxidative dissolution of the ferrite phase). The development of corrosion product layers on carbon steel is known to depend on operating conditions relating to solution pH, temperature, carbon dioxide partial pressure, aqueous speciation, ionic strength, dissolved oxygen level, hydrodynamics and the steel microstructure.³ Therefore, it is important to study the efficiency of corrosion inhibitors on steel specimens that have been pre-corroded in order to investigate the effect of microstructure and corrosion products on inhibitor performance.

Some researchers have reported that the performance of CIs can be impaired by the presence of a carbide layer. Gulbrandsen *et al.*⁴ tested the efficiency of six commercial inhibitors (imidazolines and amines) at different pre-corrosion times. It was found that the inhibitor's efficiency decreased with an increase in the pre-corrosion time due to the presence of a cementite layer. According to the authors, with longer pre-corrosion times, the inhibition kinetics became slower but no further explanation was given. Recently, Xiong *et al.*⁵ studied the impact of pre-corrosion on steel with a pearlitic-ferritic microstructure. Similar to what Gulbrandsen *et al.* found, Xiong *et al.* reported a decrease of the inhibitor efficiency with the pre-corrosion duration, an effect that was possible to counteract with an increase of inhibitor concentration. Kapusta, *et al.*⁶ found that 1 day of pre-corrosion had a negative effect on inhibitor performance. However, Dougherty, *et al.*⁷ found that certain oil soluble inhibitors performed better on pre-corroded surfaces. Liu *et al.*⁸ investigated the inhibition performance of thioglycolic acid (TGA), diethylenetriamine (DETA), and naphthenic acid imidazolines (IM), on the bare surface of N80 steel and its scaled surface pre-corroded in CO_2 -saturated 1 wt.% NaCl solution. It was found that IM and DETA have a positive synergistic effect with the corrosion scale formed on N80 steel. However, TGA shows good inhibition efficiency on bare N80 steel. The author showed that the inhibition performance depends on the size of inhibitor molecule and its interaction with the corrosion product. In another study⁹, the inhibition performance of the amine-based inhibitor on iron carbonate was superior at lower concentration than at higher concentration.

Many studies have discussed the influence of chemical composition and microstructure of carbon steels on inhibitor performance.^{4,10,11} Lopez *et al.*^{12,13} evaluated the effect of the addition of 100 ppm of benzimidazole in the presence of corrosion product layers obtained on ferritic-pearlitic and martensitic microstructures of a J55 carbon steel. The authors concluded that the microstructure of the steel

influences the inhibitor efficiency, as well as the morphology and chemical composition of the corrosion product layers.

However, most of these studies did not give a clear explanation relating microstructure, pre-corrosion and chemical composition of steel to corrosion inhibition mechanisms in CO₂ environments. Heretofore, there is no research reported in the open literature about the effect of pre-corrosion on the efficacy of volatile corrosion inhibitors. The objective of this paper is to evaluate the effect of the steel surface (steel type, microstructure and corrosion product layers (Fe₃C, FeCO₃)) on the efficacy of decanethiol, proven to be an effective volatile inhibitor for TLC on non-pre-corroded mild steel surface exposed to CO₂ environment.¹⁴ Belarbi *et al.*¹⁵ investigated the inhibition mechanism of CO₂ corrosion by decanethiol and discussed the anodic and cathodic reaction inhibition using electrochemical measurements. The author was able to propose a mechanism of adsorption of decanethiol using electrochemical techniques and surface analysis (specifically XPS).

EXPERIMENTAL PROCEDURE

Materials and Chemicals

The specimens used in the corrosion inhibition experiments were made of an API⁽¹⁾ 5L X65 carbon steel with a tempered martensitic microstructure and a 1018 (UNS G10180) steel with a ferritic-pearlitic microstructure. Figure 3 and Figure 4 show SEM images at different magnifications of the etched surface. The 1018 steel microstructure consists of two phases (α -ferrite and cementite) organized between grains of ferrite and colonies of pearlite. The pearlite microconstituent has a lamellar structure with cementite (white) and ferrite (gray) lamellae (Figure 1). However, the API X65 carbon steel microstructure consists of ferrite with cementite precipitates at the grain boundaries (Figure). The chemical compositions of each steel are given in Table 1 and Table 2.

The samples were machined into a cylindrical shape, with a diameter of 3.151 cm and 1.146 cm in height. One of the faces and sides were covered with Xylan® coating, leaving an exposed area of 7.79 cm². Decanethiol used in this research was acquired from Sigma-Aldrich[‡].

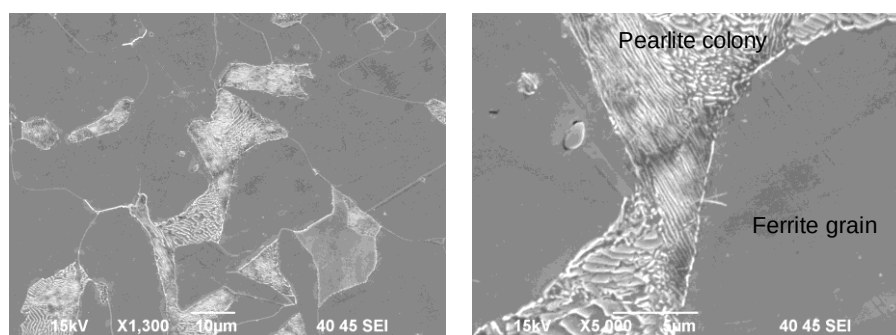


Figure 1. Microstructure of the 1018 carbon steel, 30 second etch in 2% Nital solution

[‡] Trade name

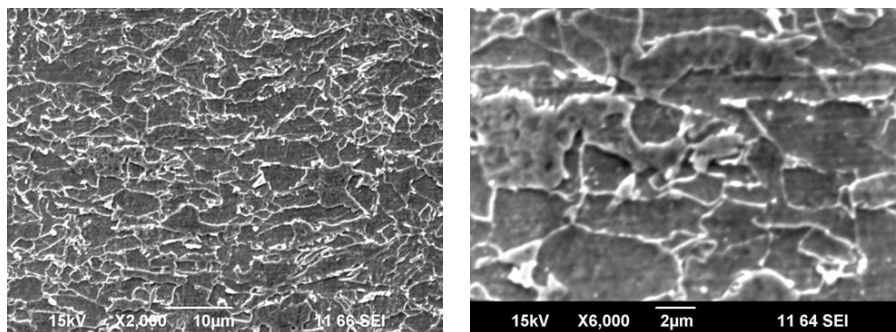


Figure 2. Microstructure of the API 5L X65 carbon steel, 30 second etch in 2% Nital solution

Table 1. Composition (wt.%) of API⁽¹⁾ 5L X65 carbon steel

Element	C	Nb	Mn	P	S	Ti	V	Ni	Fe
X65	0.05	0.03	1.51	0.004	<0.001	0.01	0.04	0.04	balance

Table 2. Composition (wt.%) of 1018 carbon steel

Element	C	Nb	Mn	P	S	Ti	V	Ni	Cr	Cu	Mo	Al	Fe
1018	0.17	0.002	0.66	0.007	0.02	0.001	0.002	0.06	0.073	0.14	0.04	0.04	balance

Weight loss measurements

The experimental setup consisted of a 4 L glass cell that was designed for top of the line corrosion experiments. Figure shows different views of the TLC glass cell. A 1 wt.% NaCl electrolyte (2.5 l) was placed in the glass cell and sparged with CO₂ for 2 hours to deoxygenation and ensure saturation. A hot plate allowed for the heating of the bottom solution to 74°C and the gas temperature to 65°C. In order to facilitate different water condensation rates, the weight loss (WL) specimens were heated or cooled by circulating a glycol solution through specimen heating/cooling systems. A circulating bath was used to control the glycol temperature. On the lid, a WL specimen was flush mounted, allowing their exposure to the wet gas phase. WL specimens were mechanically polished using silicon carbide paper (180, 400 and 600 grit), cleaned with isopropanol in an ultrasonic bath for 5 minutes, and dried at room temperature before introduction into the glass cell. Gas, steel temperature and solution pH were monitored during the experiment. A 45 ml cup was placed just below a WL sample and was used to collect the condensed water every 12 – 24 h, enabling calculation of the water condensation rate. In addition, the iron concentration was measured with a spectrophotometer.

WL Corrosion rate of the specimen at the top (TLC rate) with and without the addition of inhibitors was measured following the ASTM ⁽²⁾ G1 standard. ¹⁶ The detailed TLC experimental matrix for the experimental work is shown in Table 3 and Table 4. In order to investigate the inhibition performance of decanethiol in the presence of corrosion products, carbon steel specimens were pre-corroded in the glass cell at lower temperature (to avoid FeCO₃ precipitation) for 2 days to form cementite or at higher temperature for 7 days to form iron carbonate. The experimental procedure used for investigating the inhibition performance of decanethiol in the presence of corrosion products under TLC conditions is shown in Figure 4.

⁽¹⁾ American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.

⁽²⁾ American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, West Conshohocken, PA, 19428-2959.

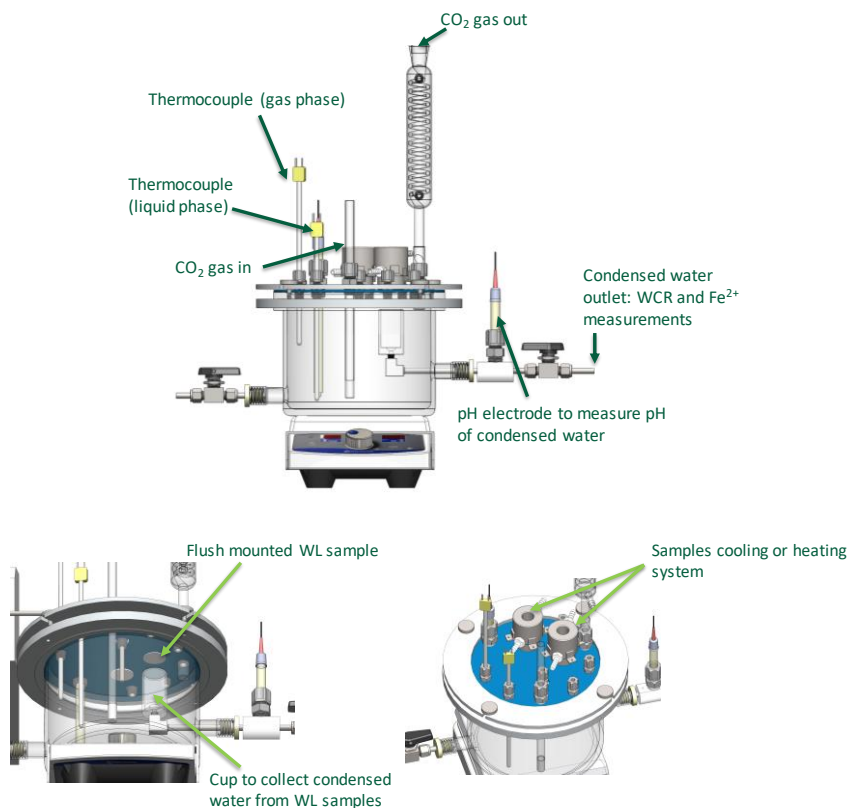


Figure 3. Top of the line corrosion glass cell system

Table 3. Experimental parameters to test the effect of microstructure and carbon content on the inhibition efficiency of decanethiol

Total pressure (bar)	1	
pCO ₂ (bar)	0.66	
Solution	2.5 l of 1 wt.% NaCl	
Solution temperature at the bottom	74 ± 2°C	
Gas temperature	~ 65 ± 1°C	
Sample temperature	~ 56 ± 1°C	
Measured water condensation rate (ml/m ² /s)	~ 0.50	~ 0.28
decanethiol (ppm _v)	0	400
Working electrode	X65 carbon steel 1018 carbon steel	
Acetic acid (ppm _v)	600	
Duration (day)	2, 4	