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Volatile Corrosion Inhibitor for Prevention of Black Powder in Sales Gas Pipelines

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ABSTRACT

Black powder is a generic term used to describe entrained corrosion products that can accumulate in sales gas pipelines, potentially damaging process equipment. Black powder mitigation is a challenge in the gas industry. Many factors govern the formation of black powder, including gas composition (particularly CO_2, H_2S, and O_2 impurities), condensation rate, relative humidity, and the existence of hygroscopic salts on the steel surface. The use of volatile corrosion inhibitors (VCIs) could constitute an economic and effective black powder mitigation method. However, little is known about the applicability of VCIs in sales gas environments. Therefore, it is important to study the effect of the key operating parameters on the efficiency of VCIs. The main goal of this study was to evaluate the efficiency of model inhibitor compounds with different functional groups (amine, thiol) and commercial inhibitors as candidates for black powder mitigation. The inhibition efficiencies of these VCIs were determined in dewing and hygroscopic conditions in both sweet (CO_2) and sour (CO_2/H_2S) environments. Weight loss methods were employed to evaluate each VCI. Steel specimens were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and high resolution optical profilometry. Based on the results of laboratory tests, it is found that volatile corrosion inhibitors can be used to prevent corrosion in a sales gas system with carbon dioxide and hydrogen sulfide. The tested amine (morpholine) seemed to affect the pH of the condensed water but did not have “filming” properties. The obtained data show that VCIs reduced the mass of corrosion product and, therefore, the amount of black powder that potentially could be formed in CO_2/H_2S environments. Based on the measured corrosion rates and surface analysis of specimens, commercial inhibitor CI1 was shown to be most effective in inhibiting formation of black powder.

Keywords***:*** Black powder, volatile corrosion inhibitor, carbon steel, sales gas.

INTRODUCTION

Black powder causes problems in the gas industry by, for example, clogging and eroding valves and contaminating the customer's sales gas. As described in the surveyed literature, "black powder" consists of various forms of iron sulfide, iron oxide and iron carbonate, mechanically mixed or chemically combined with any number of contaminants such as salts, sand, hydrocarbons, and metal debris.[1-4] Black powder can form due to the simultaneous presence of corrosive gases (CO_2 and H_2S) and condensable moisture (H_2O) in pipelines; the presence of oxygen (O_2) can also lead to its formation.[5-8] If dew point temperatures are reached, water vapor would condense on the inner walls of pipelines. Water can also enter the pipeline through periodic upsets that causes moisture carryover into the line.[1] The main strategies for controlling black powder formation in sales gas lines are gas dehydration and mechanical removal (*i.e.*, pigging) of any solids formed.[10] In addition, the use of chemical inhibitors, which are common practice in multiphase oil and gas transport pipelines, could constitute an additional mitigation technique.

There are only limited published studies pertaining to the efficiency of standard corrosion inhibitors, applied in the form of batch treatment, for reducing corrosion rates in conditions leading to the formation of black powder.[10,11] The use of volatile corrosion inhibitors (VCIs) seems to be a more promising black powder mitigation technique, especially considering the formation of black powder under dewing conditions. In fact, volatile inhibitors have been used by many industries (automotive, aviation, oil and gas) for several decades to protect metallic items, especially during storage, transportation and preservation.[12]

In previous research, mitigation of dewing corrosion has been studied in top-of-the-line corrosion (TLC) environments.[13,14] Lessons learned there are relevant to the mitigation of corrosion product formation responsible for black powder related damage. Two different types of volatile corrosion inhibitors were examined previously: amines and thiols. Based on the results of these studies, morpholine and diethylamine showed poor inhibition properties. The amines solely increased the pH of the condensed water and did not significantly decrease the corrosion rate.[13] In contrast, thiols, especially decanethiol and 11-mercaptoundecanoic acid, showed superior mitigation of TLC.[14] The authors mentioned that the level of adsorption of VCI candidates depends on the physicochemical characteristics of the inhibitor, environment, metal surface condition, and electrochemical potential at the interface. To understand how VCIs interact with the steel surface, the authors stressed that it is important to define the steel surface charge as it will determine the types of bonding that can occur between the steel surface and the functional groups of the inhibitor molecule. Belarbi, *et al.*,[13] looked at the potential of zero charge (PZC), and found that the corroding steel surface is positively charged with respect to the PZC in acidic environments; therefore, the adsorption of anions (in this case Cl^-) or of inhibitor molecules with a negative site due to the presence of any permanent dipole is favored.

Black powder can also form through hygroscopic corrosion. In this situation, liquid water can still condense within salt deposits that exhibit hydrophilicity even at relative humidity (RH) values well below 100%. These conditions can be achieved if the gas is partially dehydrated to avoid condensation. There is typically a critical RH level below which no corrosion will occur. The critical value depends on the nature of the deposited salts. However, if the RH level is above this critical level, corrosion can be expected.[15,16] The salt particles tend to absorb moisture and form saline droplets, in a process known as deliquescence, which can in turn accelerate corrosion due to the presence of corrosive ions.[17-20] An effective strategy to protect metals from hygroscopic corrosion is *via* surface coatings. Wang, *et al.*,[21] demonstrated the advantage of using super-hydrophobic surfaces (self-assembled monolayers of dodecanethiol) as a barrier against atmospheric corrosion induced by salt deliquescence.

Many factors govern formation of black powder, including gas composition (particularly the presence of CO_2, H_2S, and O_2 impurities), condensation rate, relative humidity, and the existence of hygroscopic salts on the steel surface. Therefore, it is important to study the effect of these different parameters on the efficiency of VCI candidates. The main goal of the present study is to evaluate model compounds with functional groups (amine, thiol) and commercial inhibitors as candidates for black powder mitigation in dewing and hygroscopic corrosion conditions. The inhibition efficiencies of the selected VCIs are determined in both sweet (CO_2) and sour (CO_2 & H_2S) environments using parameters representative of actual sales gas pipeline conditions.

EXPERIMENTAL PROCEDURE

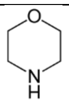
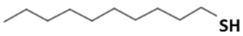
Materials and Chemicals

Specimens, machined from an API(1) 5L X65 carbon steel with a tempered martensitic microstructure, were used for weight loss measurement as well as surface analyses; its chemical composition is given in Table 1. One of the objectives of this study was to investigate the inhibition properties associated with different functional groups and molecular structures under dewing and hygroscopic conditions. The inhibitor efficiency is gauged by its ability to decrease corrosion rate and decrease corrosion product (black powder) formation rate. For this purpose, a secondary amine (morpholine) and a thiol (decanethiol) were chosen due to their widespread use in the oil and gas industry. In addition, three commercials inhibitors (CI1, CI2 and CI3) were also tested for comparison purposes, although little is known about their composition and associated molecular structures. Table 2 lists the selected VCI candidates. The morpholine and decanethiol used in this research were acquired from Sigma-Aldrich(2).

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

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

Table 2
Physical proprieties of the VCIs candidates

VCIs		Chemical structure	P_{vapor} (bar at 25°C)	$T_{boiling}$ (°C)	Solubility (ppm at 25°C)
Secondary amines	Morpholine		1.45×10^{-2}	129	soluble
Thiols	Decanethiol		8.2×10^{-5}	188	2.58
Commercial inhibitors	CI1	blend of imidazolines and amines	-	>= 57	-
	CI2	mixture of Fatty acids and amines	-	-	Insoluble in water
	CI3	-	8×10^{-3}	131	dispersible

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

Experimental Procedure

Experiments were done by exposing carbon steel specimens to CO_2 or CO_2/H_2S mixtures in dewing or hygroscopic conditions. The apparatus and procedures for testing in dewing and hygroscopic conditions are based largely on those used by Colahan, *et al*.[22]

Experiments were performed in a glass cell, as shown in Figure 1a. Weight loss samples were used to measure the dewing corrosion rate. The bulk aqueous phase comprised of 1 L deionized water, sparged with CO_2 for 2 hours prior to the start of the test to facilitate deoxygenation and ensure equilibrium. After specimen insertion, the glass cell was allowed to purge for an additional 30 minutes with CO_2 before H_2S was then added into the system, when required. The CO_2 or H_2S/CO_2 was sparged continuously in order to avoid O_2 contamination and to maintain saturation of the test solution with CO_2 or H_2S/CO_2. The H_2S concentration was set by mixing a CO_2 and a premixed CO_2/H_2S stream metered by a rotameters upstream of the glass cell. The H_2S concentration was measured with colorimetric gas detector tubes and adjusted as necessary. Before introduction into the glass cell, carbon steel specimens (exposed area = 7.9 cm^2) were mechanically polished using silicon carbide paper (600 grit), cleaned with isopropanol in an ultrasonic bath, and dried at room temperature. A pH probe was used to measure the pH of the bottom solution before and after adding the VCI. In order to have a gas temperature of 30^oC, the bottom solution was heated to 38^oC. A weight loss specimen was flush-mounted at the top of the experimental setup, controlling its temperature at 25^oC using a Peltier system and cooling water. Peltier coolers held in thermal contact with the specimen facilitates cooling by thermoelectric effect. This effect occurs whenever electrical current flows through two dissimilar conductors; depending on the direction of current flow, the junction of the two conductors will either absorb or release heat. By controlling the amount of power supplied to the Peltier cooler, the amount of heat transferred can be controlled. Power to the Peltier cooler is supplied by an external AC to 12 V DC power supply controlled with pulse width modulation to the duty cycle determined with the PID algorithm. During operation, a significant amount of heat is generated, so a water-cooled heatsink is placed over the Peltier to prevent overheating

The hygroscopic corrosion tests were conducted in a H_2S/CO_2 environment with the glass cell setup shown in Figure 1b. In this setup, the glass cell contained 100 ml of deionized (DI) water, which was initially sparged with CO_2 in order to facilitate deoxygenation. After this step, 45 g NaCl was added to the DI water to achieve the saturation condition which, in turn, conferred autogenous relative humidity (RH) values of 75% within the glass cell. The specimens were sequentially polished with silicon carbide abrasive paper up to 600 grit and with diamond powder suspensions of decreasing grain size (9µm, 3µm and 0.25 µm), cleaned with isopropanol in an ultrasonic bath, and air dried. The hygroscopic salt on the steel surface was generated by rinsing the specimen with a 3.5 wt.% NaCl solution followed by a drying step, passing nitrogen over its surface. Once the salt crystallized, the specimen mass with salt was measured. The specimen was then placed in the purged glass cell on the platform, salt-side up. The glass cell was allowed to purge with CO_2 for another 20 minutes before replacement with the H_2S gas, which was continuously sparged into the system throughout each experiment.

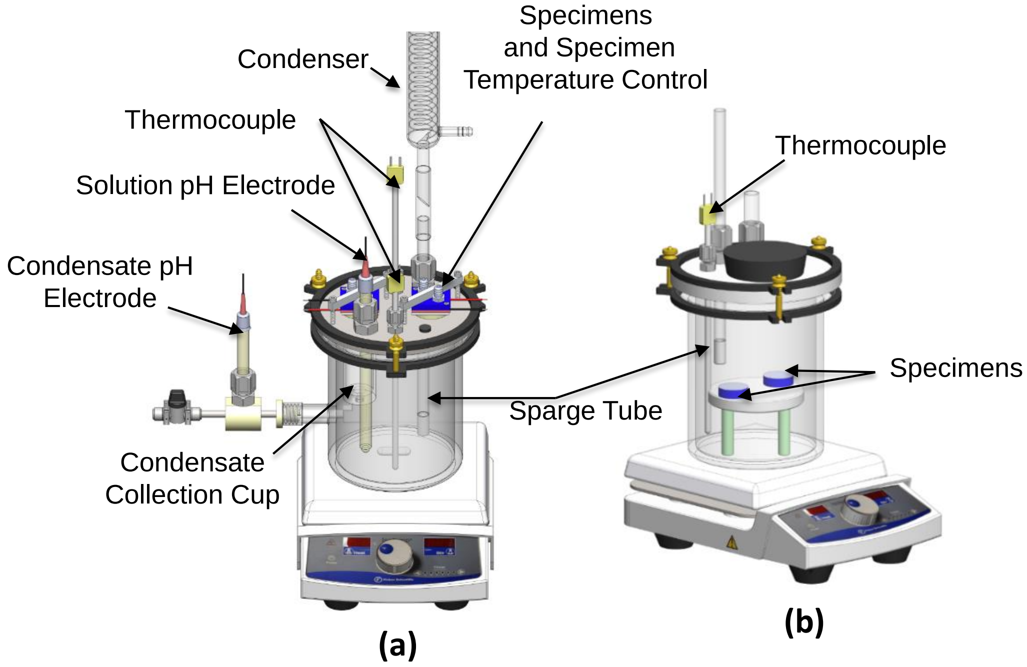

Figure 1: Experimental setup for evaluating efficacy of VCI candidates under: a) dewing conditions. b) hygroscopic conditions.

Corrosion rate of the specimen with and without the addition of inhibitors was measured following the ASTM(3) G1 standard.[23] Experimental conditions for the dewing and hygroscopic corrosion tests are summarized, in test matrix form, in Table and Table 4, respectively, at a typical sales gas temperature.

The time and space averaged corrosion rate is determined by:

$$CR = (K * W)/(A * t * \rho) \qquad (1)$$

where:

CR: corrosion rate in mm/y
K: conversion factor 8.76×10^4 = 24 h/d$*$ 365 d/y$*$ 10 mm/cm
W: weight loss in g
A: area in cm^2
t: time of exposure in h
ρ: density of steel, 7.87 g/cm^3

The corrosion product mass was determined by measuring the actual mass of corrosion product layer removed after exposure. The theoretical corrosion product mass was determined by assuming that all the iron lost due to corrosion ended up in the corrosion product layer. Corrosion product was assumed to be $FeCO_3$ in H_2S-free conditions and FeS mackinawite in H_2S-containing conditions.[22]

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

Table 3
Test matrix for dewing corrosion tests for evaluation of the efficiency of VCI candidates

Parameter	Value
Total pressure (bar)	1
pCO_2 (bar)	0.96
pH_2S (mbar)	0; 0.1
Solution temperature at the bottom (^oC)	35 ± 2
Gas temperature (^oC)	30 ± 1
Sample temperature (^oC)	25 ± 1
Calculated water condensation rate ($mL/m^2/s$)	0.015
VCI concentration (ppm_v)	0; 1000
Test duration (days)	3

Table 4
Test matrix for hygroscopic corrosion tests for evaluation of the efficiency of VCI candidates

Parameter	Value
Type of salt deposited on WL sample	NaCl
Total Pressure (bar)	1
VCI concentration (ppm_v)	0; 1000
pH_2S (mbar)	0.1
pCO_2 (bar)	0.97
Steel Temperature (°C)	25 ± 1
Saturated salt solution composition	Water saturated with NaCl
Test Duration (days)	7
Relative Humidities (%)	75

Surface analysis

Surface analysis of the exposed specimens was performed with a JEOL JSM-6090 LV scanning electron microscope (SEM) and a Bruker energy dispersive X-ray spectroscopy (EDS) system. Imaging was performed at an accelerating voltage of 15 kV using a secondary electron detector (SEI).

RESULTS AND DISCUSSION

Effect of VCI on Mitigation of Formation of Black Powder Components

Dewing Corrosion

Comparison of dewing corrosion rates, measured and theoretical corrosion product mass, with and without VCI under sweet and sour environment are shown in Figure 2, Figure 3 and Figure 4, respectively. The error bars represent the maximum and minimum values obtained on two weight loss samples. The measured corrosion product mass is the actual mass of corrosion product removed with the inhibited hydrochloric acid (Clarke solution) in the procedure described by ASTM G1.[23] Knowing the theoretically expected corrosion product mass is useful as a comparison with the measured corrosion product mass. It provides us with some insight into what fraction of the ferrous ions, dissolved from steel by the corrosion process, end up either forming the corrosion product on the surface or are being "lost", i.e. swept away by the detaching condensed water droplets or through spallation of the corrosion product. As evidenced by the large difference between the measured and theoretical corrosion product mass, most of the ferrous ions generated by corrosion did not end up in the corrosion product layer (Figure 3).

In the absence of an inhibitor, the carbon steel specimens corroded at a corrosion rate of 0.12 mm/y under CO_2 and H_2S/CO_2; the steel surfaces were fully covered by a corrosion product layer. The addition of 0.1 mbar H_2S did not significantly affect the corrosion rate although generally the FeS corrosion product is expected to offer more protection (Figure 2, Figure 3). The SEM images and EDS analysis of this specimen surface are shown in Figure 5. In CO_2 conditions, minimal amount of corrosion product is found, other than residual iron carbide. Although iron carbonate, which is not kinetically favored at the low temperatures used in these experiments, was also detected as a minor phase. The surface was uniformly corroded. At 0.1 mbar H_2S, a friable corrosion product identified as FeS was present and buckling was observed in regions presumed to be the edges of condensed water droplets. The same behavior was observed by Colahan *et al*.[22]

In the presence of morpholine, CI2 and CI3, under CO_2 and H_2S/CO_2 conditions, dewing corrosion rates are similar to the blank. The same is true for the measured and theoretical corrosion product mass. Since most of the amines were protonated in the solution at the bottom of the cell, the expected concentration of amine in the condensed water should be small. It can be also postulated that when the evaporated amine dissolved in the condensed water at the top, it increased the pH, thereby favoring precipitation of iron carbonates. It has been explained in the literature[14] that amines do not form an adsorbed layer due to the positively charged steel surface, unless chloride ions are present. The same behavior should be expected for dewing corrosion. As there are no chloride ions in the condensed water, no adsorption of protonated amine on the steel surface was expected. The results show that morpholine, CI2 and CI3 did not protect the steel specimen exposed to the dewing conditions.

The SEM images and EDS analysis of this specimen surface (Figure 6, Figure 7 and Figure 8) confirmed this conclusion, showing the formation of corrosion product on the steel surface. In the presence of decanethiol and CI1 under sweet and sour conditions (Figure 2 and Figure 3), dewing corrosion rate decreased and decanethiol and CI1 showed an efficacy of 58 and 25 %, under sweet environment, 28 and 75 %, under sour environment, respectively. The SEM micrographs show the mechanical polishing lines on the substrate surface as an indication that the corrosion was minimal in the decanethiol under a sweet environment (Figure 9). However, under a sour environment and in the presence of decanethiol or CI1, some level of corrosion occurred since the morphology of the corrosion product changed, showing signs of possible FeS formation. It is hypothesized that the inhibitor and H_2S molecules competitively adsorb on the metal surface, affecting the kinetics of formation and the morphology of corrosion products. Generally, the FeS corrosion product consists of two distinct layers attached to the steel. A two-step mechanism involving the rapid initial formation of a thin FeS layer, identified as mackinawite, which can be overlaid by different phases of iron sulfide has been described by Smith.[24] Corrosion inhibitor CI1 showed a better efficacy than decanethiol, morpholine, CI2 and CI3; theoretical corrosion product mass decreased from 12 g/m^2 to 3.4 g/m^2 and less corrosion product was observed on the surface (Figure 10).

The maximum black powder production rate shown in Figure 4 is calculated by extrapolating the theoretical corrosion product formation rate averaged over the experimental duration to a hypothetical 100 km length of a 42 inch (106.7 cm) ID pipeline. The maximum black powder production rates decreased from 1340 to 340 kg/day for this hypothetical 100 km, 42- inch ID pipeline. The commercial inhibitor CI1 showed an inhibition efficiency of 75% in the sour environment. These numbers are still relatively high, but they represent a worst-case scenario where the entire hypothetical pipeline surface is experiencing water condensation. Tsochatzidis *et al.* reported a case study of Greek Public Gas Corporation (DEPA) gas transmission line that was badly attacked by black powder. The authors reported to use different types of pigs to remove 11,620 kg of black powder between the years 2000-2003.[25]

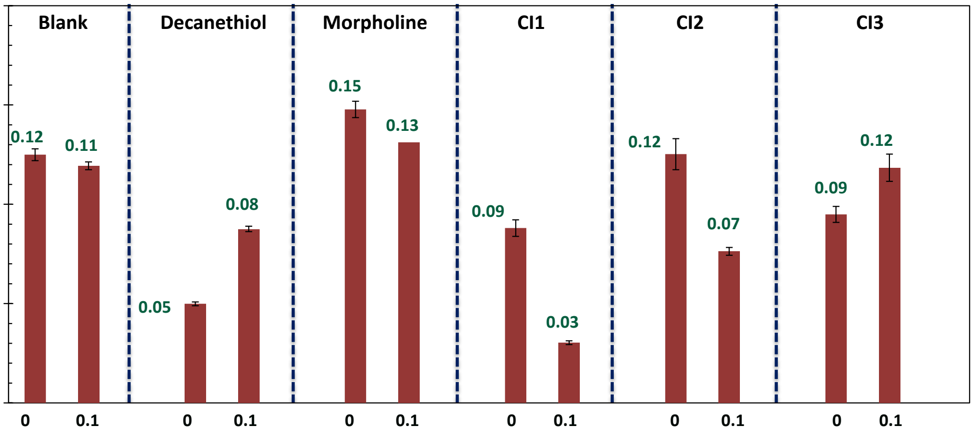

Figure 2: Corrosion rate by weight loss measurement of specimens in the presence and absence of 1000 ppm$_v$ VCI.

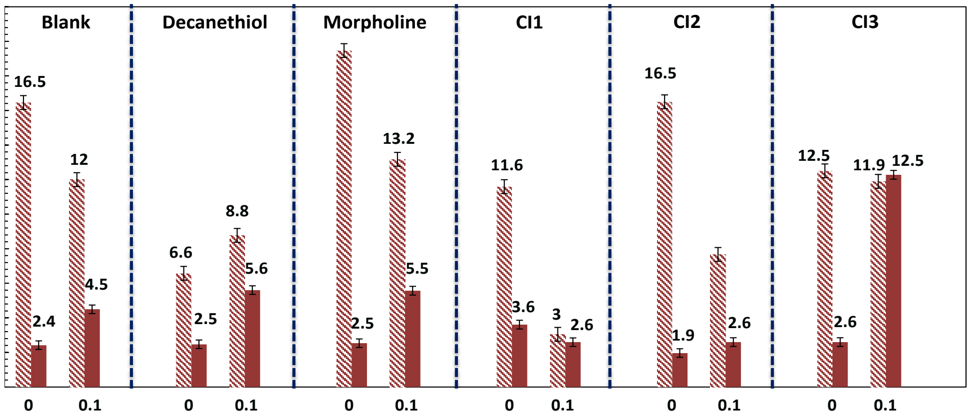

Figure 3: Measured (🟥) and theoretical (▨) corrosion product mass of specimens in the presence and absence of 1000 ppmv VCI.

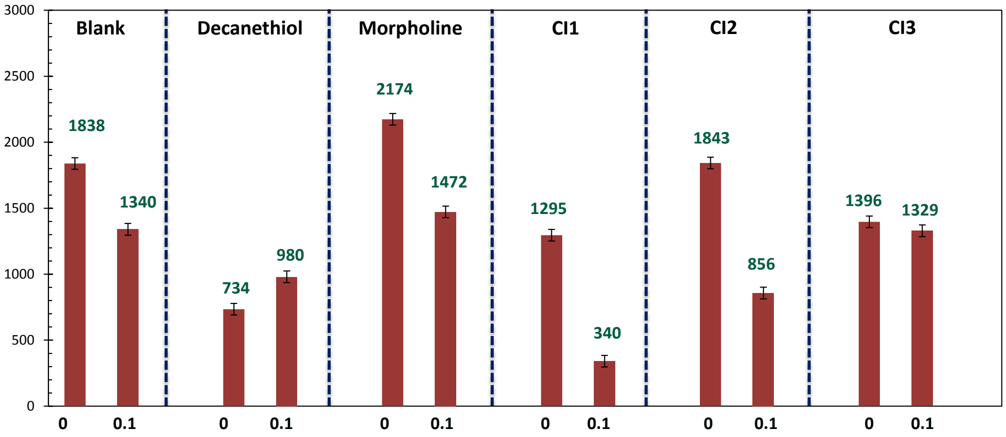

Figure 4: Maximum possible black powder production rate in a pipeline section with 42-inch diameter and 100 km length in the presence and absence of 1000 ppm$_v$ VCI.

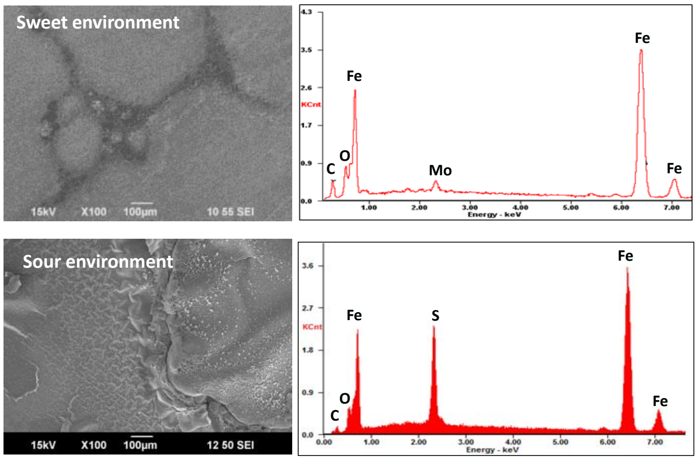

Figure 5: SEM images and EDS analysis of the steel specimen exposed to corrosion with the condensation of water in the absence of VCI after 3 days.

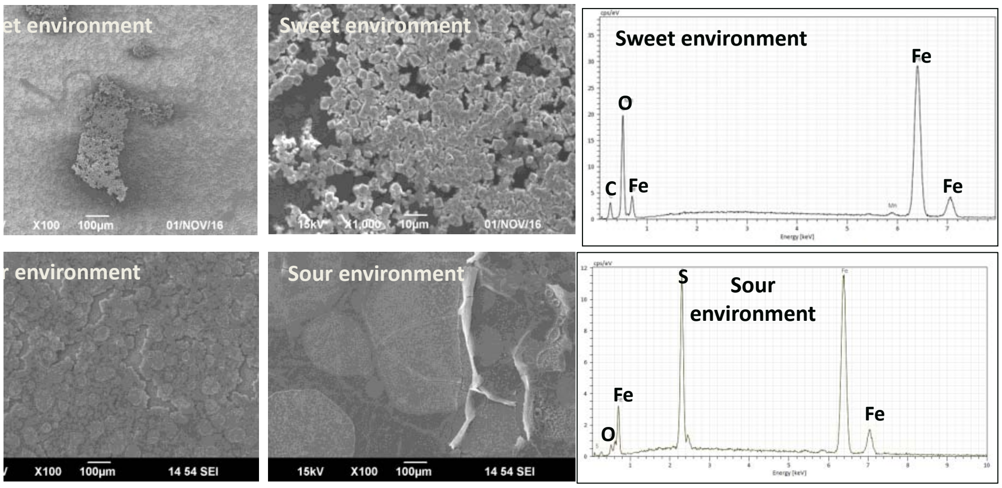

Figure 6: SEM images and EDS analysis of the specimen in the presence of morpholine after 3 days.

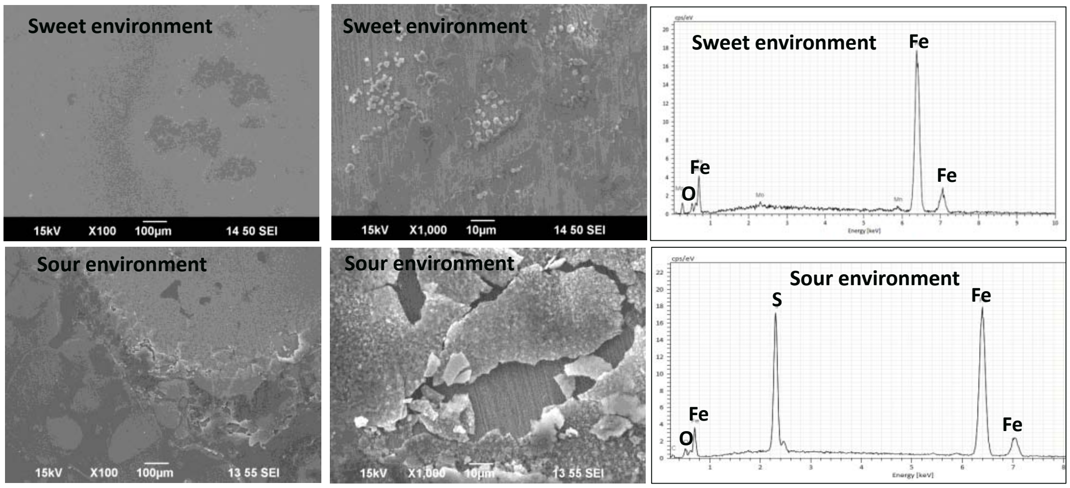

Figure 7: SEM images and EDS analysis of the specimen in the presence of CI2 after 3 days.

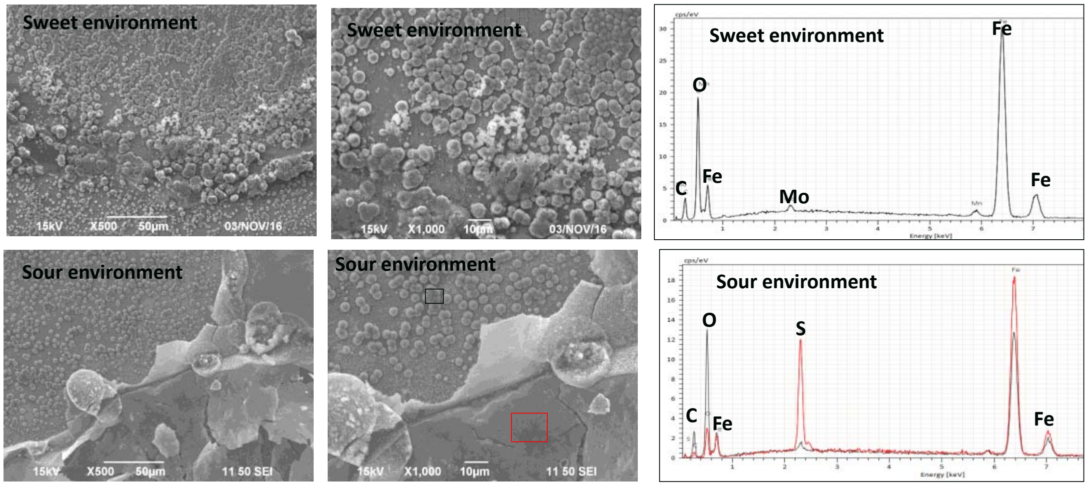

Figure 8: SEM images and EDS analysis of the specimen in the presence of CI3 after 3 days.

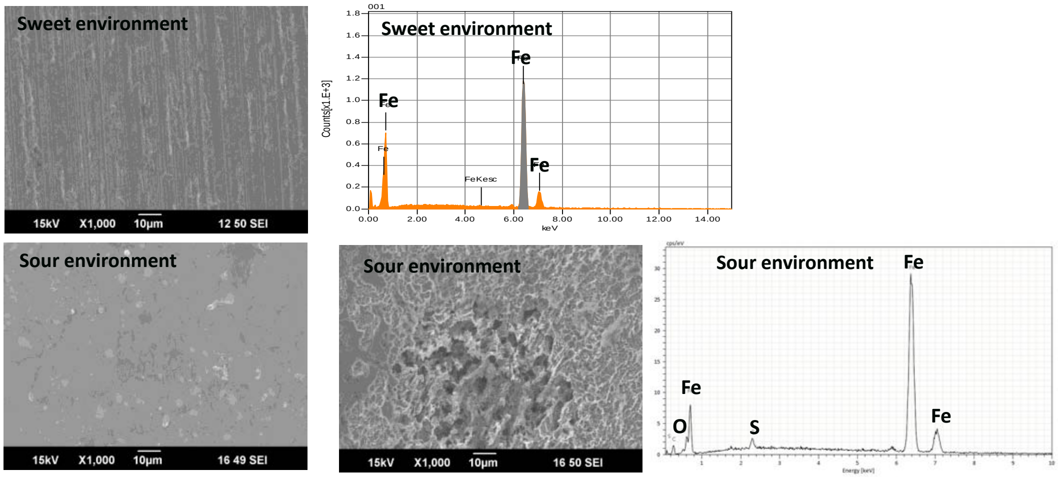

Figure 9: SEM images and EDS analysis of the specimen in the presence of decanethiol after 3 days.

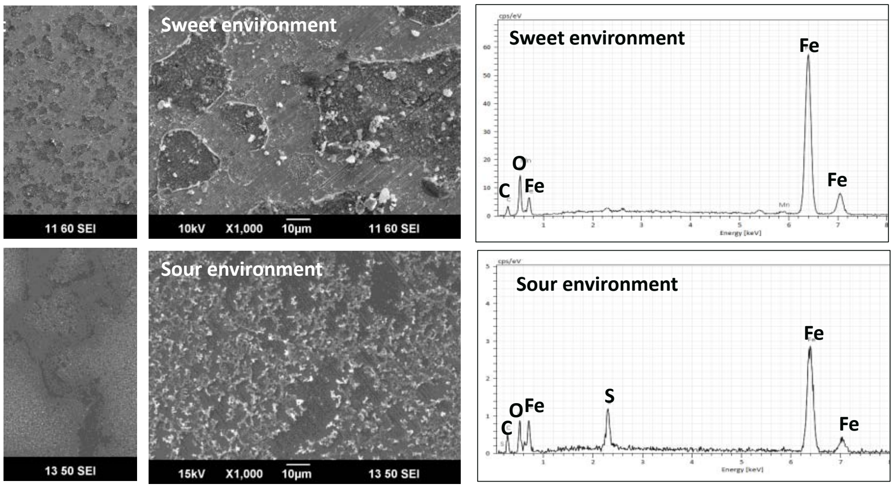

Figure 10: SEM images and EDS analysis of the specimen in the presence of CI1 after 3 days.

Colahan, *et al.*,[22] have examined the effect of relative humidity associated with hygroscopicity on corrosion, corrosion product mass and potential for black powder formation. Based on the obtained results, it is apparent that corrosion occurred below the deliquescence relative humidity (DRH), but corrosion products were most readily observed if deliquescence occurred. Soluble materials with a high affinity toward water can dissolve if the availability of water is sufficiently high through a process called deliquescence. The RH at which a material deliquesces is known as DRH. Corrosion below the DRH was attributed to adsorbed water on the salt and the steel, deliquescence-efflorescence hysteresis, and changing chemistries. The initiation of corrosion due to the hygroscopic salt particles was attributed to the presence of adsorbed water molecules on both the salt and the steel surface and due to capillary condensation at the gas/salt/metal interface. The presence of NaCl deposits on the steel surface was found to lead to corrosion and corrosion product formation at RH as low as 33%, however, corrosion products that can potentially lead to black powder were only found after 3 days of exposure if the salt was able to deliquesce. In hygroscopic corrosion tests, specimen surfaces were covered with salt (NaCl) crystals and exposed to 75% relative humidity, which is the deliquescence point of the NaCl. The temperature of the samples was the same as the bulk environment.

Irrespective of the presence of VCI, the hygroscopic corrosion rates were almost the same, as shown in Figure 11. Since the corrosion rates in the absence of inhibitor, even in dewing conditions, are very low anyway, the results are not conclusive. In all calculations, the exposed area is equal to the area covered by the salt. The effect of VCI on the corrosion product mass is shown in Figure 12. In the presence of the commercial inhibitors (CI1, CI2 and CI3), the measured corrosion product mass increased from 8 g/m^2 to 14 g/m^2. This is difficult to explain as it appears that the commercial inhibitors favored the formation of black powder. However, the presence of decanethiol and morpholine did not affect the amount of the black powder formed during the test, showing neither positive nor negative effect. In the absence and presence of VCI (decanethiol, morpholine and CI2), the measured corrosion product mass was consistently higher than the theoretical mass, but this is likely due to the presence of NaCl in the measured corrosion product that was not quantifiable. Deposited NaCl could not be selectively rinsed off before the corrosion product is removed.

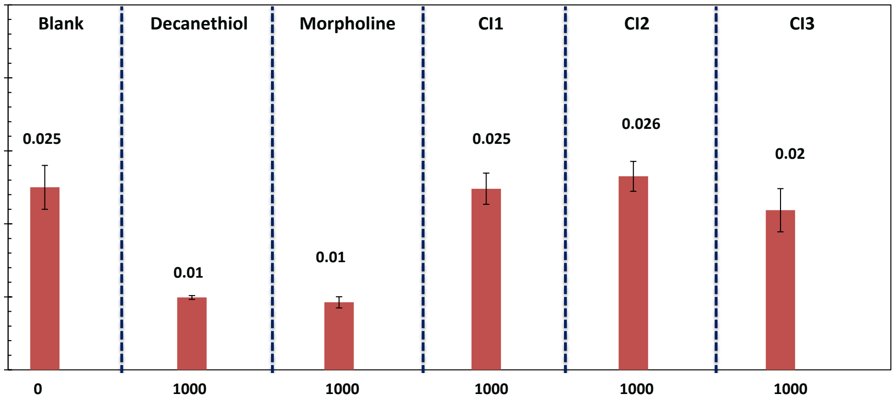

Figure 11: Corrosion rate by weight loss measurement of the specimens exposed to hygroscopic corrosion in a sour environment in the presence and absence of 1000 ppm$_v$ VCI.

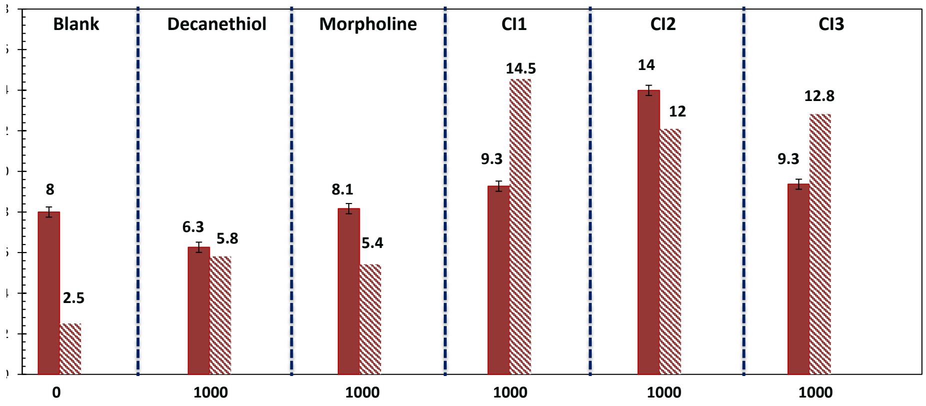

Figure 12: Measured (🟥) and theoretical (▨) corrosion product mass of the specimens exposed to hygroscopic corrosion in a sour environment in the presence and absence of 1000 ppm$_v$ VCI.

Surface analysis by SEM was performed on the specimens retrieved in the absence and presence of VCI after 7 days of experiment duration (Figure 13). Corrosion product formation at the top of the salt crystals is postulated to be due to ferrous ion diffusion through the water layer surrounding the deliquescing salt crystal. The shell of this corrosion product would then be all that remains once the salt crystal fully deliquesces. The SEM images show that the corrosion products were essentially the same with and without inhibitors and that no evidence of a friable corrosion product could be found. The surfaces of specimens were corroded non-uniformly. The specimen surfaces were analyzed by high resolution profilometry after removing corrosion product with a Clarke solution. No localized corrosion was detected in the presence of VCI, except in the presence of decanethiol where pitting was observed with a maximum depth of 30 µm. The pit penetration rate, 1.56 mm/y, was calculated from the depth of the deepest pit. This behavior can potentially be attributed to competition between HS^- (formed from H_2S) and thiol adsorption on the steel surface.

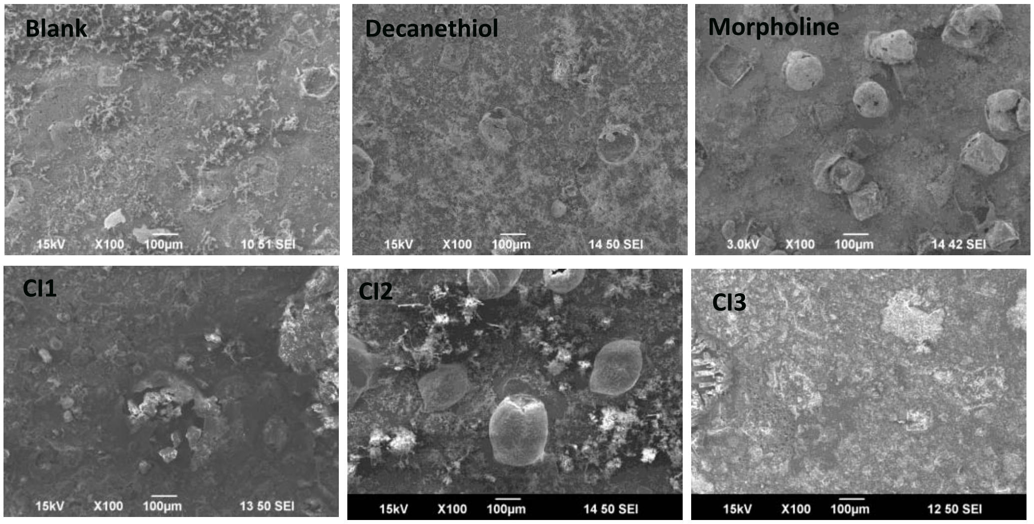

Figure 13: SEM images of the specimen exposed to hygroscopic corrosion in a sour environment in the presence and absence of 1000 ppm$_v$ of each VCI.

Effect of cyclic water condensation on corrosion inhibitor efficiency

Pipeline conditions can vary considerably during operations. Temperatures are expected to change throughout the year, and even throughout the day, due to meteorological conditions. Day/night cycles can have a significant effect on dewing conditions inside a pipeline. To examine the effect of temperature fluctuations on corrosion inhibitor efficiency, the temperature of the specimens was changed every 12 hours between 25°C and 15°C. These temperature changes are supposed to mimic temperature changes that occur due to the day/night cycle. Experiments were conducted in the same conditions as for the dewing experiments in a sour environment (Table 4). The commercial inhibitor CI1 was chosen for these experiments. An optimum concentration of 1000 ppm_v was used, according to weight loss measurement and surface analysis (results are not shown in this paper due to space limitations).

In the absence of inhibitor, the corrosion rates and the measured and theoretical corrosion product masses (Figure 14) of the cycled specimens were almost the same as those from the constant water condensation rate experiment. The surfaces of specimens that experienced cyclic water condensation are compared to their constant condensation rate counterparts in Figure 15. In the absence of VCI, a friable corrosion product was present and buckling was present in regions presumed to be the edges of water droplets for the condensed water. Overall, FeS spalling was more apparent in the constant water condensation rate experiments than the cycling experiments. The sheet-like characteristics of the cycled corrosion product layers were less apparent as compared to the layers formed under constant water condensation rates. This is likely a result of high saturation levels as water evaporated from the steel surface. It is postulated that precipitated corrosion product would have settled on layers similar to those observed from the constant water condensation rate experiments, thereby reinforcing the structural integrity of the layer making spalling less pronounced. Colahan, *et al*.[23] reported that mackinawite was the primary corrosion product detected on the steel surface after three days under cycling conditions. However, in the presence of VCI, the corrosion rate from the cycled experiments was about twice as high and the measured corrosion product masses was five times lower than its constant water condensation counterpart. This suggests that the solid corrosion product produced under constant water condensation rates was more protective than the layers produced during the cycling/drying phase. The large difference in the measured and theoretical corrosion product mass is due to the significant amount of iron that was lost due to condensed water droplet detachment or the spalling of corrosion products. Mechanical polishing line marks are visible on the substrate surface (Figure 15) and less corrosion product was detected, confirming inhibitor protection of the steel surface. This means that CI1 was able to decrease the amount of black powder and change the corrosion product’s proprieties. Less buckling was observed in the cycled conditions than the constant temperature tests.

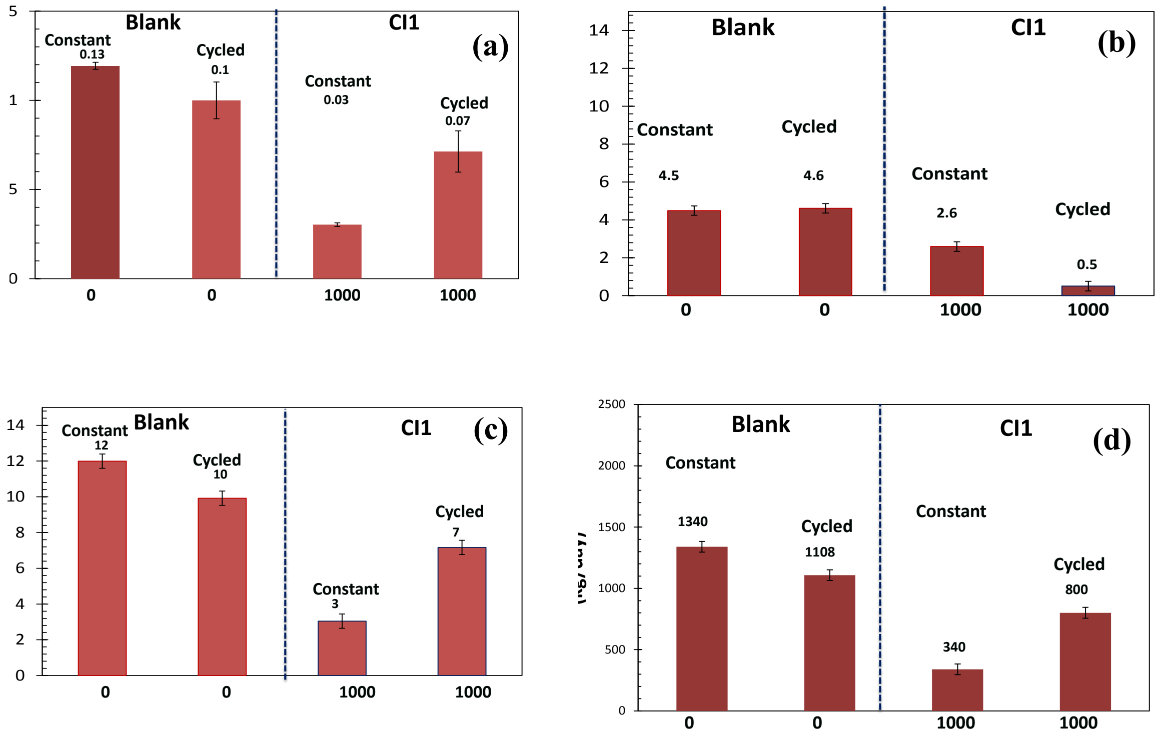

Figure 14: Effect of temperature cycling on corrosion inhibitor efficiency: (a) corrosion rate, (b) measured corrosion product mass (c) theoretical corrosion product, and (d) mass maximum possible black powder production rate in a hypothetical 100 km, 42 in. ID pipeline.

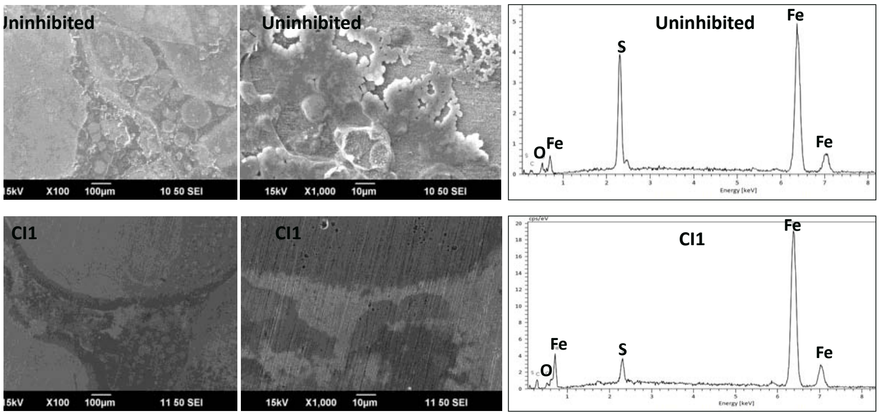

Figure 15: SEM images and EDS surface analysis of the sample exposed to corrosion in the co-condensation of water in the presence and absence of CI1 after 3 days.

CONCLUSIONS

The objective of this paper was to investigate the inhibition properties of several VCIs on black powder formation. Several functional groups and molecular structures were investigated. A cyclic secondary amine (morpoline), an n-alkyl thiol (decanethiol) and three commercial inhibitors were chosen for testing under dewing and hygroscopic corrosion. Tests simulating dewing and hygroscopic corrosion in CO_2/H_2S environments were performed in a glass cell. As a result of this study, the following conclusions were drawn:

- Morpholine showed poor inhibition properties in acidic environment because it was quickly protonated after being injected into the acidic solution. The tested amine seemed to affect the pH of the condensed water but did not have a significant effect on filming properties.

- The commercial inhibitor CI1 provided superior inhibition efficiency while decanethiol and commercial inhibitors (CI2 and CI3) showed poor inhibition relating to formation of black powder components. The commercial inhibitor CI1 showed an inhibition efficiency of 75%, consequently it is the best candidate for field evaluation.

- The effect of hygroscopic salts and condensing/evaporating cycling conditions on inhibitor efficiency was evaluated. The results showed that the tested VCIs have no significant effect on corrosion rate in hygroscopic corrosion conditions. Commercial inhibitor CI1 decreased the amount of black powder that could potentially form and change the corrosion product's properties. Less buckling was observed in the cycled conditions than the constant temperature tests.

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