

# Inhibiting Corrosion in Transport Pipelines by VpCI Additives to Crude Oil

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## Abstract

Typical patterns of corrosion and the corrosion growth obtained from the successive intelligent pig runs in ageing pipelines, made obvious that after decades of problem free operation, corrosion may become a serious threat. Application of corrosion inhibitors is a mean of ensuring continuation of pipeline operation without costly repairs, leaks and release of hazardous materials into the environment. This paper investigates protective ability of VCI 629 BIO and VCI 637 HF on carbon steel, in stagnant and flowing electrolytes, in order to take into account the unfavourable conditions at critical points of the pipeline (low points, dead legs) and the intermittent flow regime. Laboratory measurements were done in crude oil and in 3.5% NaCl of pH 7.5. Corrosion coupons and the LPR probe were used to quantify the corrosion rate in the absence and the presence of the inhibitors. FTIR results have shown that the inhibitor adsorbs onto the rusted surface and retains in the rust layer even when the LPR probe transferred back to inhibitor free electrolyte. The role of inhibitors was discussed with respect to the corrosion conditions prevailing at pipeline critical spots, deduced from H<sub>2</sub>S measurements in transported crude oils, SEM/EDX, FTIR, XRD, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> analyses of samples (oil, sludge and paraffin) collected from cleaning pig exits and from a dead leg at which perforation of pipe wall has occurred due to corrosion.

## Keywords

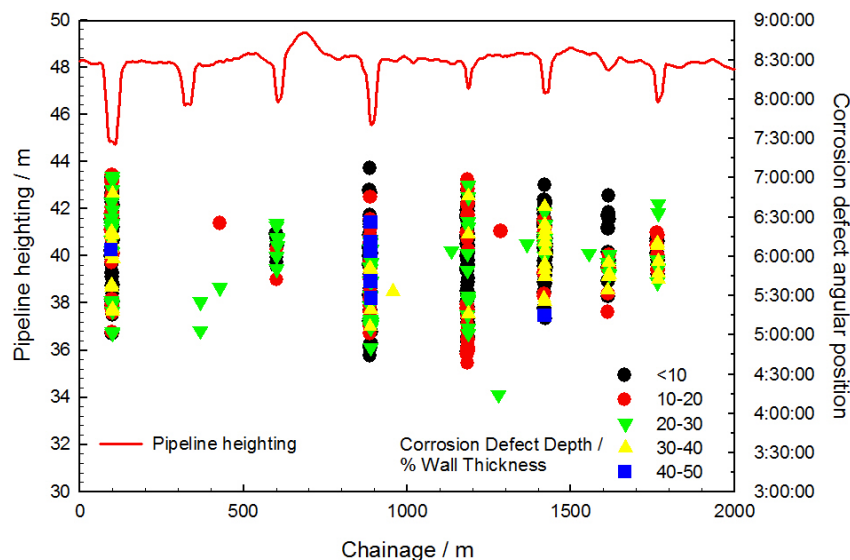
vapour phase corrosion inhibitor; crude oil corrosivity; transport pipeline; linear polarization resistance probe;

## Introduction

Crude oil transmission pipelines, due to the basic sediment and water limit usually set to < 0.5%, have a long history without significant levels of internal corrosion. However, for ageing pipelines, it became obvious after decades of problem free operation, that corrosion may shorten the pipeline's life cycle and can lead to costly repairs, leaks and release of hazardous materials into the environment [1]. At some point in the pipeline's life, operators are bound to initiate various measures to ensure integrity and safe operation for the remaining operation period. For large diameter pipelines carrying heavy oils [2], pipelines with intermittent flow and/or product velocities insufficiently high to keep water entrained in oil [3], balancing the safe operation requirement with the costs of inspection and protective measures aimed to achieve a successful long-time operation, may become an ongoing task. Transmission-quality heavy crude oil is generally expected to be non-corrosive [1,3]. However, not only the oil corrosivity but also the development of local corrosive conditions determines corrosion incidence and severity [2]. In low water cut crude, water is entrained in oil as an emulsion and is also wetting the solid particles suspended in oil [4]. Unfavourable

flow regime may cause accumulation of water at pipeline low spots or, depending on the product type, accumulation of water-wetted solid particles at pipeline bottom, typically downstream of over-bends thereby forming corrosion „hotspots“.

Example of a characteristic pattern of corrosion damage observed in crude oil pipeline suffering from free water accumulation in low spots is shown in Figure 1.



*Figure 1. Characteristic pattern of corrosion damage observed in a crude oil pipeline suffering from free water accumulation at low spots.*

Additives formulated utilizing volatile corrosion inhibitors (VpCIs) were previously proven to provide a very high level of protection for steel subjected to a broad range of flow regimes and corrosive contaminants [5]. This paper investigates protective ability of VCI 629 BIO and VCI 637 HF corrosion inhibitors, on carbon steel, in a set of experiments that take into account unfavourable conditions that prevail at critical points of the pipeline.

## **Experimental**

In mass loss experiments, coupons made of X52 5L steel, of dimensions 3 cm x 4 cm x 3 mm, were cleaned with abrasive paper grit 600, degreased in ethanol in an ultrasonic bath and exposed in and above crude oil collected during tanker load-off operation. 150 ml of crude oil was placed in six bottles. Two of the samples were spiked with 60 ppm of VCI 629 BIO, while the other two were spiked with 60 ppm VCI 637 HF. Three of the samples were left without the inhibitor. In each bottle, a coupon was laid at the bottom, with its upper side exposed to the liquid, and its bottom side isolated with tape. Also, in each bottle, one coupon was suspended above crude oil. Figure 2, shows the experimental setup.



*Figure 2. Experimental setup for the mass loss measurements.*

The coupons were weighted after degreasing in ethanol in an ultrasonic bath and drying, immediately before exposure to the corrosive media. The mass was also recorded after the 90 days of exposure, following retrieving from the bottles and a thorough process of cleaning with detergent and a plastic wire brush.

Corrosion rate was calculated from mass loss, divided by the time of exposure and the surface area exposed to the corrosive media. It was then converted into mpy units. Duplicate experiments have shown insignificant variations. The resulting corrosion rate was calculated as an arithmetic mean.

Identical mass loss experiments were also done in the following media: (i) slurry of a solid sample (collected from a dead leg, at which perforation of pipe wall has occurred due to corrosion) and distilled water mixed in 1:1 ratio, (ii) oil/sludge mixture and (iii) paraffin collected from 2 cleaning pig run exits. These samples were tested for sulphate reducing bacteria (SRB) using BTI SRB Medium test.

The corrosion rate measurements were also done on linear polarization resistance (LPR) probe Model 2000, connected to MS1500L Handheld LPR Corrosion Data Logger, produced by Metal samples. Electrode pins were made of UNS C10100 steel. The testing electrolyte was 3.5 % NaCl, without and with the inhibitors. The probe was placed in a glass jar containing 0.75 litres of 3.5% NaCl. The corrosion rate was measured under stagnant conditions and during mixing the electrolyte with a magnetic stirrer. The mixing rate was successively increased and the corresponding corrosion rates were collected as a function agitation intensity. These experiments were done on an electrode preconditioned in: (i) stagnant 3.5 % NaCl for 0 h, (ii) stagnant 3.5 % NaCl for 72 h, (iii) stagnant 3.5 % NaCl for 24 h and then for 48 hour following a 2000 ppm inhibitor addition.

In the next set of experiments, the experimental regime was chosen to mimic batch inhibitor application. LPR probe was pre-corroded in 3.5% NaCl for 24 hours before the inhibitor was injected. After further 24 h of exposure to inhibitor bearing electrolyte, the probe was transferred to fresh 3.5% NaCl solution. Corrosion rate was recorded for another 24 h. For comparison, the same procedure was done without the inhibitor, but with the same cumulative exposure time. The electrolyte was mixed at 600 RPM.

Fourier transform infrared (FTIR) spectra were recorded using a PerkinElmer spectrometer Spectrum One, USA. Spectra were obtained in the range from 400 to 4000  $\text{cm}^{-1}$ , each spectrum being an average of ten scans with a resolution of 4  $\text{cm}^{-1}$ . 350 mg of KBr was rubbed into the surface of the LPR electrodes after the batch simulation experiments. Samples bearing KBr was then hydraulically pressed into a 13 mm stainless steel die and the resulting pellets further subjected to FTIR measurement.

## Results and discussion

The results of mass loss experiments are shown in Figure 3. A significant decrease in corrosion rate (< 90%) is observed for the inhibitor containing systems with respect to the inhibitor free systems, for both, oil and vapour exposed samples.

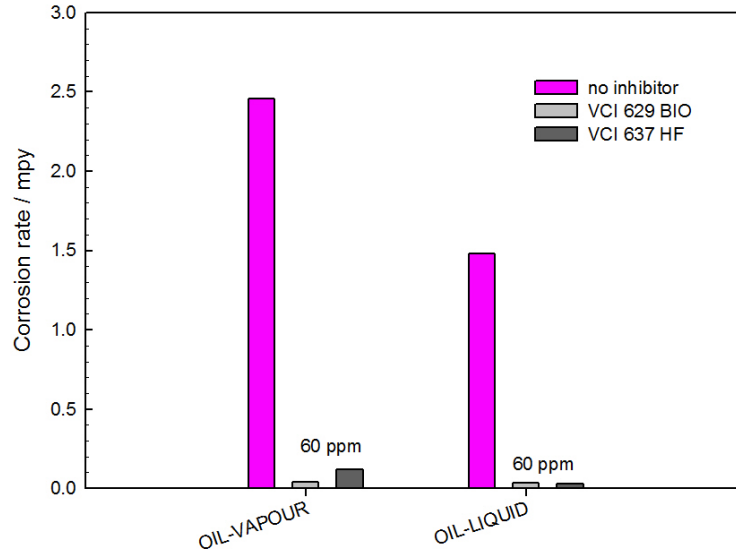


Figure 3. Corrosion rate of X52 5L coupons in liquid crude oil and crude oil vapour, calculated from mass loss experiments.

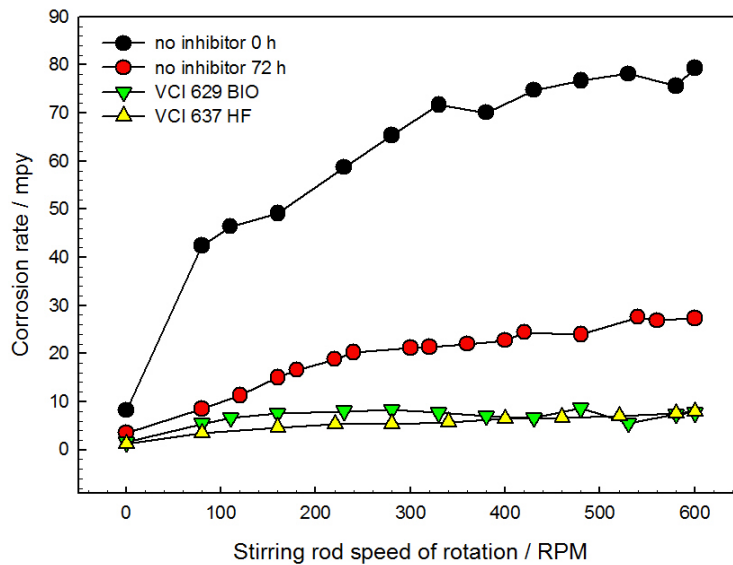


Figure 4. Corrosion rates on electrodes preconditioned in: (i) stagnant 3.5 % NaCl for 0 h, (ii) stagnant 3.5 % NaCl for 72 h, (iii) stagnant 3.5 % NaCl for 24 h and then for further 48 hour after 2000 ppm VCI 629 BIO or VCI 637 HF addition.

The corrosion rates recorded as a function of the stirring rate of the electrolyte are shown in Figure 4. Experiments were done on an electrode preconditioned in: (i) stagnant 3.5 % NaCl for 0 h, (ii) stagnant 3.5 % NaCl for 72 h, (iii) stagnant 3.5 % NaCl for 24 h and then for further 48 hour after 2000 ppm inhibitor addition.

The first measurement shows the effect of electrolyte stirring rate on the corrosion of bare steel surface. The rate increased from approximately 10 to 80 mpy for stirring rod rates ranging from 0 to 600 RPM.

The second measurement shows the effect of the electrolyte stirring rate on the pre-corroded surface. The rate increases from approximately 4 to 25 mpy in the same RPM interval.

The third measurement shows the effect of the electrolyte stirring rate on the surface that was first pre-corroded in 3.5% NaCl, and then exposed to 2000 ppm solution in 3.5% NaCl, of each of the investigated inhibitors, in two separate identical experiments. The corrosion rate increased from below 1 to 4 mpy in the same RPM interval, as in the previous two experiments.

The overall time of specimen exposure to the electrolyte with the aim of pre-corroding them was the same in each experiment i.e. 48 hour. Hence, the beneficial effect observed in the inhibitor containing systems was solely due to inhibitor presence. Moreover, it has been shown that the inhibitor acted at the already pre-corroded specimen. This is particularly important, as in real systems in which the inhibitors are applied, the surface will never be free from corrosion products.

High degree of suppression of corrosion is observed in all systems, and even for very high stirring rates, when the electrolyte directly impacts on the surface of LPR pin electrodes.

Results of the experiments mimicking batch inhibitor application are shown in Figure 5. The probe, immediately after the immersion, is shown in Figure 6 a. During the first 24 hours of exposure to 3.5 % NaCl, the corrosion rate decreases from approximately 66 mpy to 40 mpy. The solution attains intensive orange colour of corrosion of products of steel, shown in Figure 6 b. The appearance of the solution after 48 h, is shown in Figure 6 c. The decrease of the corrosion rate with time is due to the rust layer formed on LPR pin electrodes.

After 48 h, the probe was transferred into the new 3.5% NaCl solution. Minimum corrosion rate reached in after 24 h of exposure is approximately 38 mpy, and the appearance of the solution at the end of the experiment is given in Figure 6 d.

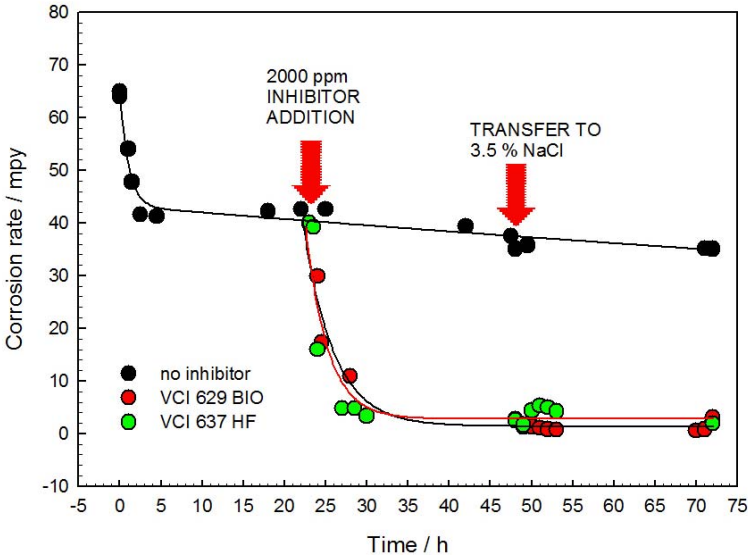
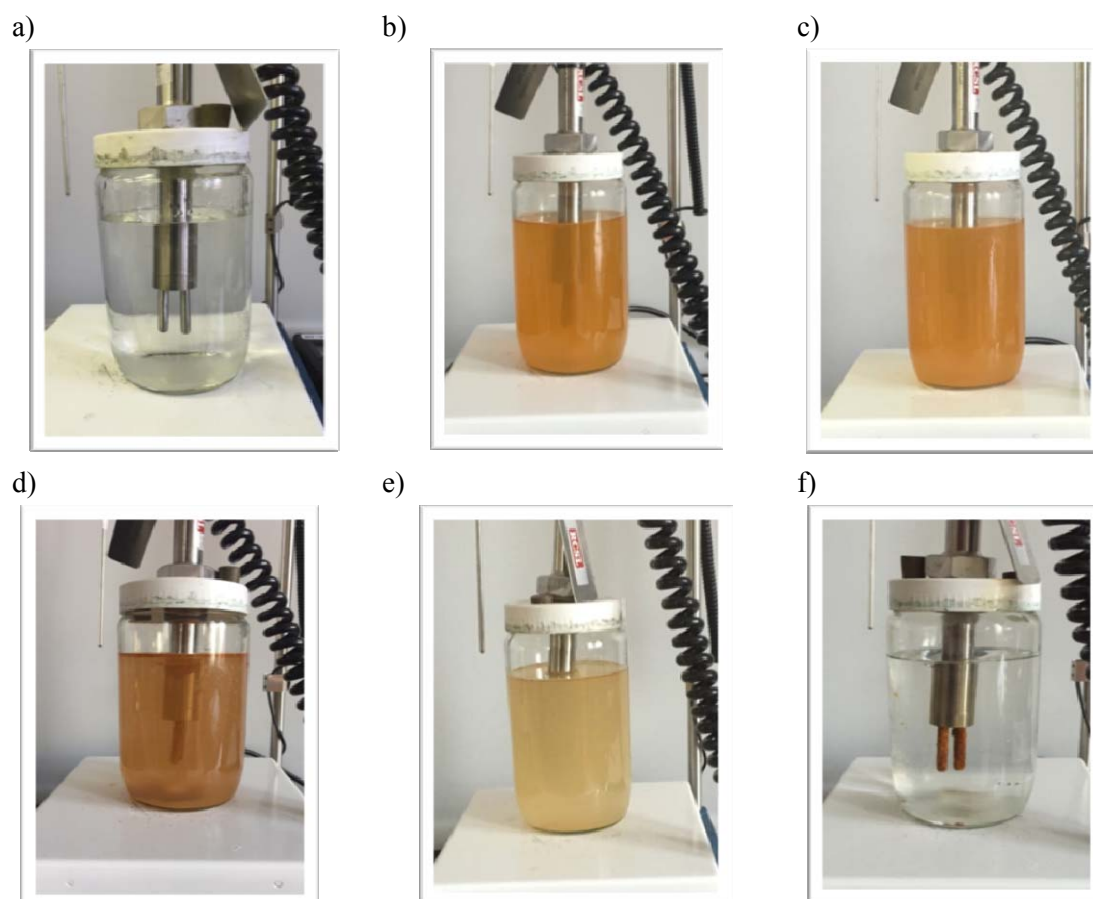


Figure 5. Corrosion rates in batch inhibitor application simulation, measured on LPR probe in stirred 3.5% NaCl, with stirring rod rate equal to 600 RPM.

When the inhibitor is added into the solution after 24 h, the corrosion rate drops to approximately 2 mpy within 10 h. The solution, almost immediately after the inhibitor addition, turns to hazy light orange colour, indicating that interaction between the inhibitor

and the rust in the solution has taken place (Figure 6 e). When the probe is transferred into pure 3.5% NaCl, and left for 24 h, practically no corrosion products are visible in the solution, and the solution remains clear and transparent (Figure 6 f). The corrosion rate is approximately 2 mpy for both inhibitors, which compared to the 38 mpy in the inhibitor free system, yields the efficiency > 90%. The protective characteristics of the rust layer formed in the presence of the inhibitors is much better than in their absence.



*Figure 6. Colouring of the solution, in various phases of the experiments. Experiments without the inhibitor, at 0, 24, 48 and 72 h are shown in figures a to d, and with the inhibitor, at 48 and 72 h are shown in figures, e and f.*

Figure 7 shows characteristic FTIR fingerprint region of the corrosion product layers formed in the inhibitor free solution and the inhibitor bearing solutions. Spectra of the rust layers formed in the presence of inhibitors show multiple overlapping peaks that are not present in the rust formed without inhibitors. Hence, these bands are due to organic compounds presence in the layer. Since the rust was sampled after transference to 3.5% NaCl, and additional 24 h of exposure, this results show that the inhibitor has adsorbed irreversibly, and has retained in the layer.

Lepidocrocite ( $\gamma$ -FeOOH) and magnetite ( $\text{Fe}_3\text{O}_4$ ) bands are present in all samples and are denoted by L and M, respectively [6]. In the inhibitor free solution, magnetite band is more pronounced. This has also been confirmed visually, as the LPR pin electrodes in 3.5% NaCl without inhibitor, were covered by a bottom layer of black rust topped by a layer of orange rust. The same effect is observed on coupons, as shown in Figure 8. Some reports state that

magnetite is favoured in more aggressive environments where the oxidation process is faster [7 and references within].

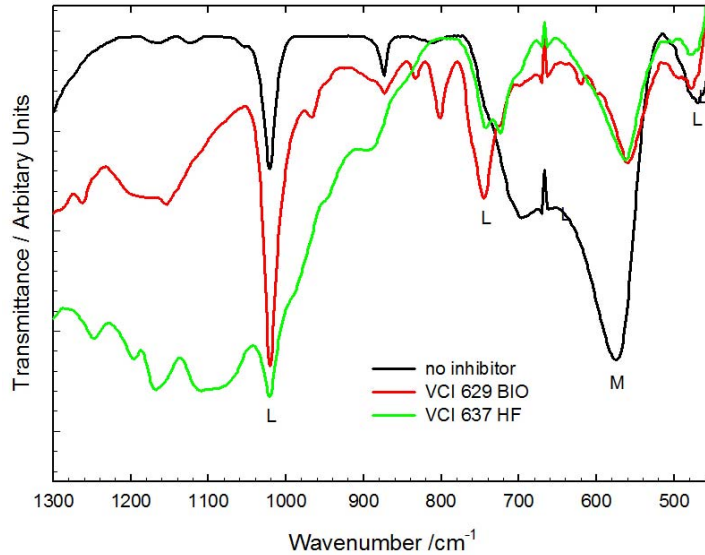


Figure 7. Characteristic FTIR fingerprint region of the corrosion product layers, formed on LPR pin electrodes, in the inhibitor free solution and the inhibitor bearing solutions, after experiments mimicking batch inhibitor application.

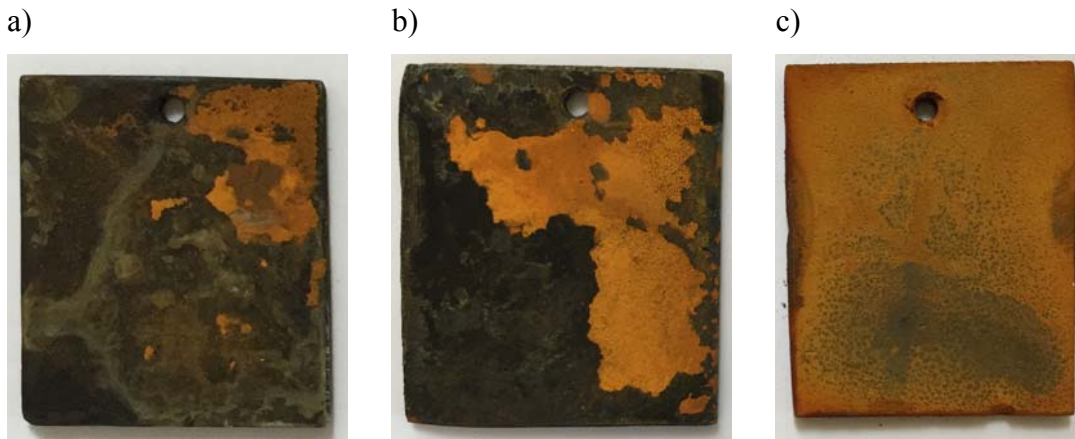


Figure 8. Appearance of the rust layer after 30 days of exposure to: a) inhibitor free solution, b) 60 ppm of VCI 629 BIO in 3.5% NaCl and c) 2000 ppm of VCI 629 BIO in 3.5% NaCl.

Table 1 shows corrosion rates measured in mass loss experiments in samples collected from a crude oil pipeline. The samples were proven to contain  $> 10^6$ ,  $10^3$ - $10^4$  and  $10^4$ - $10^5$  of SRB per ml, respectively.

The high corrosion rate of 7.12 mpy observed in the sample with high SRB content is in line with the practical observations that the SRB are prevalent in low-oxygen environments that may occur locally in pipelines [3], particularly in dead legs. The pH of the slurry equalled 7.4. 800 ppm of  $\text{Cl}^-$ , and 2671 ppm of sulphates have been measured in the solid sample. SEM/EDX, XRD and FTIR analyses of the sample has been given previously [8, 9]. Major

elements determined in the sample by EDX were C, Fe and O and minor elements were Ca and Si. XRD of the sample has shown presence of magnetite, hematite, goethite, siderite, and quartz. FTIR has shown presence of lepidocrocite.

*Table 1. Corrosion rates in samples collected from a crude oil pipeline.*

<b>Sample</b>	<b>Corrosion rate/mpy</b>
Slurry of a solid sample collected from a dead leg and distilled water, mixed in 1:1 ratio.	7,12
Oil/sludge mixture collected from cleaning pig run 1	1.58
Oil/sludge mixture collected from cleaning pig run 2	1.64
Paraffin collected from cleaning pig runs 1 and 2	no corrosion

The corrosion rates obtained in oil/sludge mixtures are comparable to those obtained in crude oil collected in a tanker load-off operation. However, higher corrosion rates may be expected locally, at pipeline low spots where water separates and is capable of wetting the pipe bottom. The sour gases, salts and acids from organic phase may undergo extraction into the aqueous phase at the bottom and may cause a decrease in the pH and increase in the water corrosivity [10]. No corrosion has been observed on samples exposed to paraffin.

## **Conclusions**

Two vapour phase inhibitors have been investigated in the present study. A set of experiments was designed to assess the inhibitor effectiveness at conditions that can be extended to those characteristic for the crude oil transport pipeline. The inhibitors were tested in crude oil and 3.5% NaCl, under stagnant and flowing conditions. They have been applied to clean and pre-rusted steel. Continuous and batch regimes of inhibitor addition have been simulated. Significant improvement of rust layer protectiveness against metal dissolution was observed when the rust layer was exposed to any of the tested inhibitors for 24 h. Under all circumstances, the inhibitors limit the corrosion rate to < 2 mpy. Taken the typical wall thicknesses in oil transport and storage systems of 6-12 mm, the rate of 2 mpy is acceptable and will ensure long-term problem free operation.

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