

Top of Line Corrosion (TLC) Mitigation using Volatile Corrosion Inhibitor (VCI) via Batch and Continuous Injection in Sweet Environment System

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Volatile corrosion inhibitor (VCI) was developed to inhibit Top of Line Corrosion (TLC) in wet gas pipelines and its injection methods can significantly affect the required dosage and consequently, its efficiency. In this study, a VCI's efficiency was compared using batch and continuous injection methods. A series of TLC tests, including a 5-day control test, a 7-day continuous injection test (200 ppm of VCI every 3 days), and a 5-day batch injection test (1000 ppm of VCI) were conducted using API 5L X65 carbon steel grade samples. The uniform corrosion rates (UCR) were determined using the Weight Loss method (ASTM G1-03). The pitting rates (ASTM G1 46-21) were assessed with an Infinite Focus Microscope (IFM), and surface morphology characterisation was analysed using Scanning Electron Microscopy (SEM). Overall, both tests were unable to efficiently inhibit corrosion, due to under dosage of VCI concentration. However, the batch injection test performed better than the continuous injection test (UCR: 0.40 mm/y vs. 0.69 mm/y; pitting rate: 0.70 mm/y vs. 3.28 mm/y) as it only caused uniform corrosion. The severity of the corroded sample from continuous injection test was due to partial coverage of VCI film on top coupon surfaces, that led to the local breakdown of VCI and consequently, resulted in a high pitting rate. In conclusion, in this testing environment, both methods require a higher concentration of VCI to reduce the corrosion rate efficiently.

1. Introduction

Pipelines as the medium of transportation of hydrocarbon in the oil and gas field are preferable over other methods of transportation due to their well-proven continuous reliability in operation and economic feasibility (Molnar, 2022). However, they are susceptible to corrosion. For instance, about 3% of 267 pipeline incidents reported in the US from 2014 to 2023 were caused by corrosion (Pipeline Incident 20 Year Trends, 2022). Another report stated that internal pipeline corrosion caused more incidents than external pipeline corrosion. In Canada, for example, the Alberta Energy Regulator reported that 42% of 354 pipeline incidents were caused by internal pipeline corrosion (Pipeline Performance, 2023). One type of internal corrosion is Top of Line Corrosion which refers to corrosion occurring on the upper part of the internal pipeline, typically between ten to two o'clock positions (Figure 1). TLC was only first recognised in the 1960s (R. Pailassa et al., 1963) and usually poses a risk for wet gas pipelines in Southeast East Asia (SEA) and parts of the North Sea and the Middle East (Gunaltun Yves et al., 2010). It tends to occur within a large diameter of wet gas pipelines because of its low fluid velocity, which favours stratified flow conditions (Pessu, 2015). The high-temperature inlet of wet gas slowly decreases as it flows further from the inlet because of the heat loss due to the low temperature of the environment. The decline in temperature initiates the condensation process of wet gas on the upper surface of the pipeline due to the side effect of a stratified flow regime which eventually leads to corrosion of the pipeline. The lower part of the pipeline, however, is not affected as a conventional corrosion inhibitor is being injected to protect the pipeline from corrosion. Unfortunately, the stratified flow conditions and the unavailability of the conventional corrosion inhibitor to reach the upper part of the pipeline failed to protect it from corrosion. Hence, a corrosion inhibitor

that can vapourise and protect the top of the internal pipeline was introduced, named as a Volatile Corrosion Inhibitor (VCI).

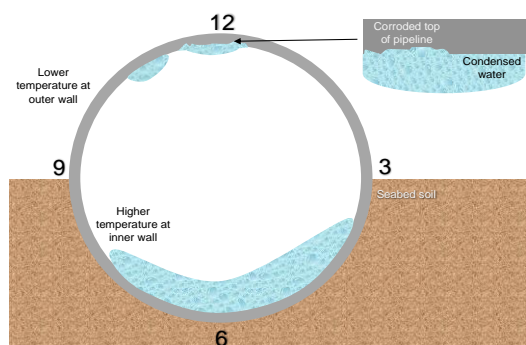


Figure 1: Location of Top of Line Corrosion

VCI is a corrosion inhibitor known for its high volatility despite its appearance of being solid or liquid (Al-Moubaraki & Obot, 2021). It can be characterised by its vapour pressure (Andreev & Kuznetsov, 1998) as it needs to be able to reach the upper part of the pipeline where the TLC occurs. Another important characteristic for the commercialisation of the VCI is its ability to inhibit corrosion on different metals simultaneously and possesses strong adsorption on metal surfaces, thus providing a long-sustainable layer of protection (Kuznetsov et al., 2020). These characteristics are needed as the mechanism of VCI requires it to vapourise, co-condense with water vapour, condensate, and adsorb onto the metal surface, while creating a layer of film that protects the surface of the pipeline, making it less susceptible to corrosion (Miksic et al., 2004). For a VCI to be considered successful, several conditions must be met such as it must be fully effective in the presence of organic acids, have sufficient tolerance to saturated vapour pressure, and be less likely to undergo chemical reactions in an acidic environment (Shen et al., 2013).

On top of that, the effectiveness of VCI can vary depending on the method of application to the pipeline. Two common VCI deployment methods are batch injection and continuous injection. Batch injection involves injecting a higher dosage of VCI at set time intervals, while the continuous injection method is employed within short time intervals but with a low concentration of VCI (Moloney et al., 2022). Although batch injection via pigs is a common industry practice, its efficiency is limited as it depends on the movement of the pigs in the pipeline (Punpruk, 2010). In terms of operation, the continuous injection method is preferable for existing operating pipelines, but it requires continuous monitoring of produced water samples to ensure the optimal dosage of VCI (Guan Ong et al., 2020). The selection of VCI and its injection method are closely related, as both selections are unique to each field (McMahon & Groves, 1995) and require laboratory testing as a pre-screening selection to fulfill the requirement of reducing the corrosion rate to 0.1 mm/y (Hinds & Turnbull, 2010). Therefore, the objective of this research is to compare the performance of a VCI using batch injection and continuous injection methods by evaluating the efficiency of VCI through corrosion rate analysis via Weight Loss Method (ASTM G1-03) and pitting rate analysis via Infinite Focus Microscope (ASTM G1-46), followed by surface morphology characterisation via Scanning Electron Microscopy.

2. Methodology

2.1 Materials

The VCI used in this work is a commercialised Thiols-based VCI. The top coupons were made of API 5L X-65 carbon steel. The same type and amount of gas condensate (1.25% v/v) was injected into every test conducted. The bottom solution consisted of 1000 ppm of sodium chloride and 500 ppm of acetic acid. A Clarke solution consisting of 93% concentrated hydrochloric acid (HCl), 2% antimony trioxide (Sb_2O_3), and 5% stannous chloride (SnCl_2) was used for the post-experiment procedure.

2.2 Methods

The method for this study was divided into three stages which are pre-experiment, during the experiment, and post-experiment. The procedure and testing setup were based on previous research (Singer et al., 2019). The procedure and parameters of all tests conducted were similar with variations only in VCI concentration and test duration. The control test used 0 ppm of VCI, the continuous injection test used 200 ppm (every 3 days), and the batch injection test used 1000 ppm. The durations for these tests were 5 days, 7 days, and 5 days, respectively, as listed in the test matrix in Table 1. Replenishment of the bottom solution, gas condensate, and

200 ppm of VCI was conducted on the 4th day of the continuous injection test. The overall setup of the TLC Testing Unit is illustrated in Figure 2.

Table 1: Test matrix of Control Test, Continuous Injection Test, and Batch Injection Test

Parameters	Control	Continuous Injection	Batch Injection
VCI concentration (ppm)	N/A	200	1000
Test material		API 5L X65 Carbon Steel	
CO ₂ partial pressure (bar)		0.8	
Total pressure (bar)		1	
Testing solution	1000 ppm NaCl, 500 ppm acetic acid, and 1.25% (v/v) gas condensate		
Liquid temp. (°C)		60	
Gas temp. (°C)		45 ± 2	
Steel temp. (°C)		30 ± 2	
Water condensation rate (mL/m ² .s)		0.68 ± 2	

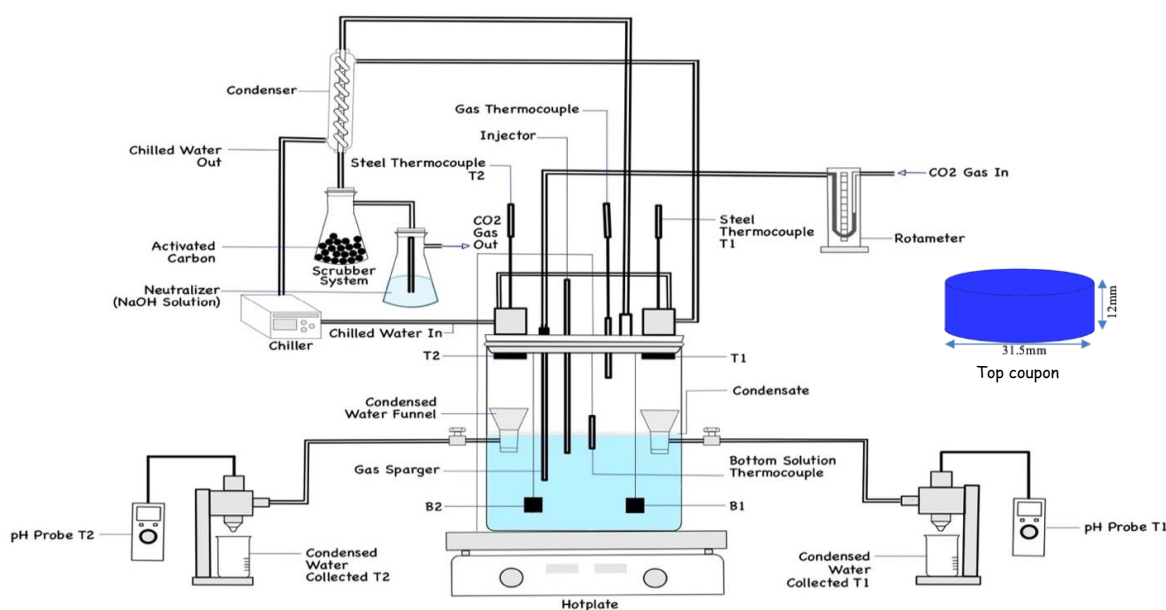


Figure 2: TLC glass-cell testing unit and top coupon

Pre-experiment

Two top coupons made from API 5L X-65 carbon steel were xylan-coated with one exposed side. The preparation of the coupons started with a polishing process on the uncoated sides using Silica Carbide abrasive paper with different grits ranging from 80 to 800, followed by rinsing with distilled water and acetone. These coupons were then attached to coupon holders that were mounted onto the lid of the glass cell unit, with the uncoated sides exposed to the corrosive environment inside the glass cell. A 1.58L bottom solution containing 1000 ppm sodium chloride and 500 ppm of acetic acid was purged with N₂ for deoxygenation purposes for at least 30 minutes before the tests began. Afterward, 20 mL of gas condensate was injected into the glass cell. A 200 ppm and 1000 ppm of VCI were injected for continuous and batch injection testing sets, respectively. To create a condensation environment, the coupons were cooled using cooling water that flowed around the top coupons (Gunaltun Yves et al., 2010), while the liquid in the glass cell was heated using a hot plate with a magnetic stirrer, whilst maintaining a desired temperature of 60 °C. A sweet environment was established in the glass-cell unit by purging 1 bar of CO₂ gas continuously into the system, which then passed through a scrubber system consisting of a series of flasks containing activated carbon and concentrated sodium hydroxide to neutralise the corrosive gas before discharge into the environment. Only for continuous injection, the bottom solution was replenished on the 4th day. The current bottom solution inside the glass cell unit was fully pumped out before pumping in a new set of a bottom solution, along with the gas condensate and 200 ppm of VCI.

During experiment

Similar procedures were applied to all tests to ensure the operating system remained constant throughout the experiment. This includes monitoring of gas and coupon temperatures, determining the water condensation rate, and measuring the in-situ pH value using the collected condensed water.

Post experiment

Once the corrosion product layers were removed from the coupons using a Clarke solution, the determination of uniform corrosion rate (Eq.1) based on the Weight Loss Method “ASTM G1-03 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, 2017” was conducted. This was followed by pitting rate analysis (Eq. 2) using an Infinite Focus Microscope (IFM), in accordance with the “ASTM G46-21 Standard Guide for Examination and Evaluation of Pitting Corrosion, 2021”. The pit ratio was calculated using Eq.3 to define the severity of the pits. If the pit ratio is less than 3, it is considered uniform corrosion, while if the pit ratio ranges between 3 and 5, it is considered possible localised, and if it is above 5, it is considered localised corrosion (Zhang et al., 2021).

$$\text{Corrosion rate} \left(\frac{\text{mm}}{\text{year}} \right) = \frac{87600 \times W}{A \times t \times \rho} \quad (1)$$

Where,

- W = The difference in mass of coupon before testing and after cleaning using Clarke, in gram
- K = Corrosion rate constant, $K = 8.76 \times 10^4$
- A = Surface area of coupon, in cm^2
- t = Duration of the test, in hour
- ρ = The density of metal coupon, in $\frac{\text{g}}{\text{cm}^3}$

$$\text{Pitting rate} \left(\frac{\text{mm}}{\text{yr}} \right) = \frac{\text{Pit depth}}{t} \quad (2)$$

Where,

- Pit rate = Penetration rate, in $\frac{\text{mm}}{\text{year}}$
- Pit depth = Penetration depth, in mm.

$$\text{Pit ratio} = \frac{\text{Piting rate}}{\text{Corrosion rate}} \quad (3)$$

3. Results and discussion

Figure 3 depicts the uniform corrosion rate (UCR) and pitting rate (PR) for all tests. UCR of the control test was the highest at 0.83 mm/y, followed by the continuous injection test at 0.69 m/y, and batch injection test at 0.40 mm/y.

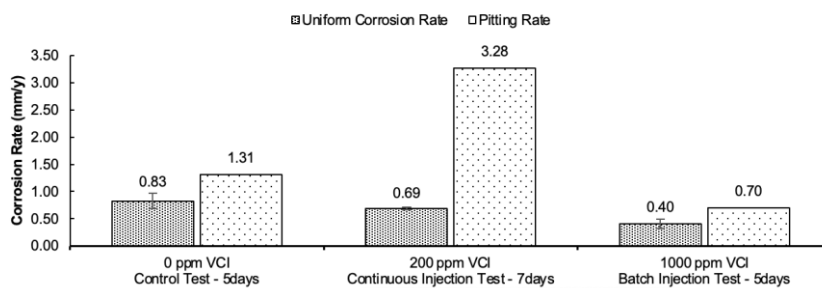


Figure 3: Comparison of TLC rate for Control Test, Continuous Injection Test, and Batch Injection Test

As for the pitting rate analysis (Figures 3 and 4), the continuous injection test showed the highest pitting rate at 3.28 mm/y which consequently contributed to the highest pit ratio of 4.77, thereby indicating possible localised corrosion due to under-dosage of VCI (Guan Ong et al., 2020). A possible explanation of localised corrosion occurrence is due to the VCI's under dosage, which caused partial coverage protection of the VCI film on the metal surface. This phenomenon is further proven via SEM images shown in Table 2a. Pits were observed on the coupon surface during continuous injection tests, even before the coupon was cleaned using Clarke solution, and the number of pits became more apparent after the corrosion product layers were removed.

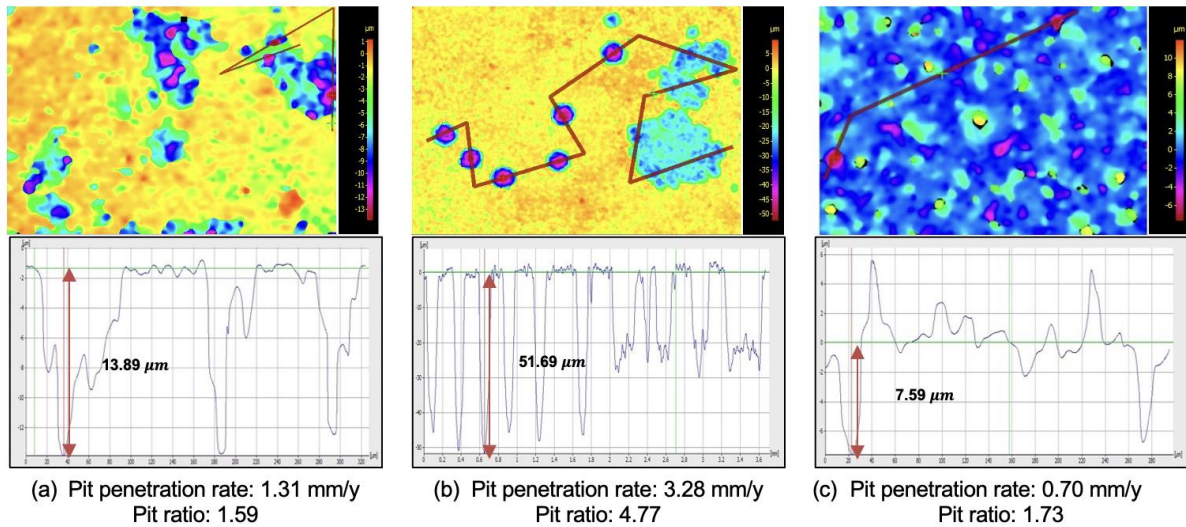
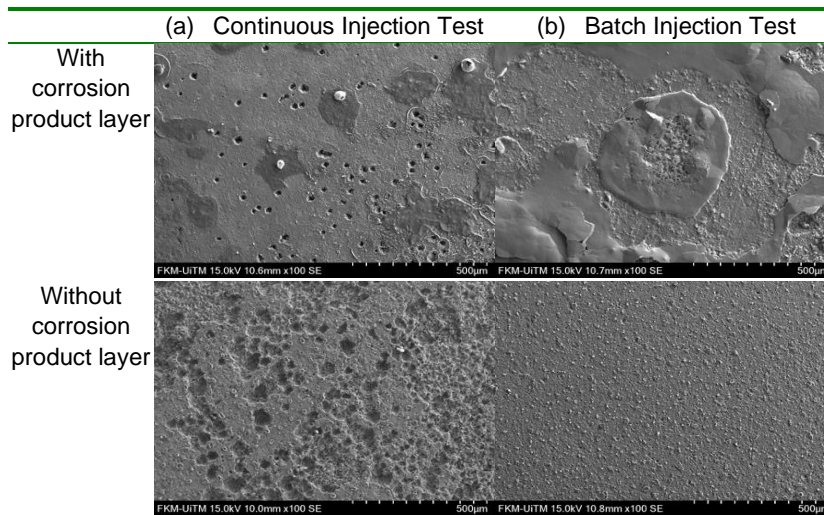


Figure 4: IFM data (surface and depth profile along the line) for the top coupon of tests a) Control Test, b) Continuous Injection Test, and c) Batch Injection Test

Despite the reduction in UCR values compared to the control test, the batch injection test was still unable to fulfill the ideal requirement of 0.1 mm/y, with the inhibition efficiency of this VCI being only 51%. However, the low pitting rate of 0.70 mm/y and the pit ratio of 1.73 showed that VCI at 1000 ppm delivered via the batch injection method still managed to provide a protective layer on the top coupon surface against localised corrosion. This is supported by SEM images that showed no obvious localised pitting, both with and without corrosion product (Table 2(b)).

Table 2: SEM data for top coupons with corrosion product layer of Continuous Injection Test, and Batch Injection Test



4. Conclusions

Overall, both continuous and batch injection test methods were unable to inhibit corrosion efficiently. The continuous injection test, which used only 200 ppm of VCI concentration, resulted in both a UCR and possible localised corrosion. While the batch injection test (using 1000 ppm of VCI) improved the efficiency of VCI by 34% compared to the continuous injection test, it still demonstrated an unsatisfactory performance with only 51% efficiency. Hence, it can be concluded that, in this type of environment, 200 ppm of VCI using the continuous injection method and 1000 ppm of VCI using the batch injection method are insufficient dosages. Therefore, a higher concentration of VCI is needed, or both methods should be used simultaneously for this type of environment to increase the inhibition efficiency.

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