Application of Vapor Phase Corrosion Inhibitors for Contaminated Environments

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Availability and accessibility to clean water for industrial applications such as hydrostatic pressure testing of pipelines, vessels, and plumbing distribution systems have been a challenging task, especially when the job sites are in remote locations. These circumstances have forced the use of contaminated water containing, for example, large amounts of chloride. Hydrostatic testing of metallic equipment is an important method for quality control of parts, after production and during use. When contaminated water is used in these tests, corrosion of the metallic components of the system during and after testing become a major concern; therefore, application of an inhibiting system is required. Vapor-phase corrosion inhibitors (VCIs) can be added to water in small concentrations to prevent corrosion during testing, or wet storage and after testing. These inhibitors are to prevent corrosion of metallic components in three phases: within the solution, at the water line, and above the water line.

Three commercially available corrosion inhibitors were evaluated in this study to optimize the best combination of inhibitors to minimize the corrosion of these multi-metallic component systems. Laboratory studies presented in this article show the effectiveness of VCI products in both fresh and salt water applications. Results confirmed the effectiveness of VCI products in various water chemistries including fresh and salt water. The average corrosion rate dropped from ~10 mpy for salt solution to less than 1 to 1.6 mpy when various inhibitors were added. However, the effectiveness of these inhibitors is remarkable in the fresh water (less than 0.4 mpy). Exposure of the steel samples to these inhibitors did not show any loss in mechanical properties. Both strength and ductility of the low carbon steel samples were maintained. Adsorption energy for these inhibitors was about –21,520 to –24,970 J/mol, indicating a strong physisorption mechanism.

The application of an inhibitor in any water system requires compliance with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES). The three corrosion inhibitors investigated were water-based, bio-based, environmentally friendly, and can be effective replacements for toxic nitrite, chromate or hydrazine-based inhibitors and satisfy all the required environmental compliance regulations.

Hydrostatic pressure testing of metallic equipment such as pipes, vessels, and valves is an important method for quality control of parts, after production and during use in order to demonstrate the strength and integrity of the systems.[1] This test is a key part of ensuring that they are fit for purpose depending on factors such as contact time, chemicals used, oxygen, and bacteria. Water is the most common media to be used in this test; however, corrosion of the metal during and after testing is a concern because the water is typically left in pipelines from a couple of days to months. The challenge is that hydrostatic test water is corrosive, and disposal of the water is costly. Hydrostatic test water contains micro-organisms, oxygen, and sediment that are known to accelerate corrosion progression. Also, because of the large volume of water used, treatment can be very expensive. In some cases, equipment that has gone through a hydrostatic test will also be stored for future use or shipped long distances. This storage may take place while water is still inside the equipment (wet storage) or even after draining.[2-4] Therefore, a pipeline undergoing a hydrostatic test may become quite vulnerable to general corrosion, crevice and pitting corrosion, stress corrosion cracking, differential aeration corrosion, or microbially induced corrosion.[2] Corrosion caused by any one or a combination of these mechanisms may reduce pipeline service life and in extreme cases make it unfit for purpose.

With the growing shortage of fresh water resources, it is often preferrable to utilize seawater as supplement water of recirculating cooling water systems.[2-3] But seawater is an electrolyte solution with multiple salts, mainly 3.0 to 5.0% sodium chloride (NaCl); a pH value of ~8; and dissolves a certain amount of oxygen.[1] Due to its chemistry, seawater easily corrodes pipelines. So the key to seawater utilization is to solve piping and equipment corrosion problems in the seawater environment by modifying its chemistry with the addition of corrosion inhibitors.

Corrosion and corrosion inhibition of steel have received enormous attention for recirculating cooling water systems.[5-7] The common methods to control and prevent metal equipment corrosion are using resistant material, using a cooling water anticorrosion coating, increasing the pH value of the cooling water operation, and adding corrosion inhibitor.[6-9] Among these methods, using resistant material can protect metal equipment effectively, but the expense is too high. The technology of an anticorrosion coating method is complex and applies to local anticorrosion in the system. Increasing water pH makes mild steel deactivate easily. Adding corrosion inhibitor can protect the system and it is economical and practical.[7] After the completion of a hydrostatic test, the water must be discharged, often with environmental considerations due to toxicity or excessive chemicals when inhibitors are added.[8]

The development of seawater corrosion inhibitor goes from inorganic to organic, from single to compound, from single inhibition type, to mixed inhibition type and other electrochemical method combination processes.[8] Many organic molecules exhibit high anticorrosion potential, but they pollute the environment during their synthesis and applications.[7-9] The effect of a single seawater corrosion inhibitor is unsatisfactory in general, so two or several types used in conjunction improve inhibition efficiency.

Therefore, to control corrosion and bacterial growth in the pipeline during hydrostatic pressure tests and future storage, the test water may be treated with corrosion inhibitors and other chemical compounds to manage and control corrosion activities. Commonly used chemicals are biocides that kill the micro-organisms and prevent the formation and growth of bacteria and other organisms in the seawater. Corrosion inhibitors are used to retard general corrosion when residual oxygen is available, and oxygen scavengers are used to reduce the amount of oxygen available for corrosion and bacterial growth. Different classes of corrosion inhibitors may be used to protect systems from corrosion, including inorganic or organic. Inorganic inhibitors include nitrites, phosphorous-based compounds, and others. Organic inhibitors are the products formulated from molecules constructed from of carbon, hydrogen, oxygen, and nitrogen atoms. Vapor-phase corrosion inhibitors (VCIs) described in this article are organic-based blends. The mechanism of the corrosion protection of organic inhibitors includes the formation of a thin, sometimes monomolecular layer on the metal, which is a protective barrier to aggressive ions.[4-5] In the majority of cases,

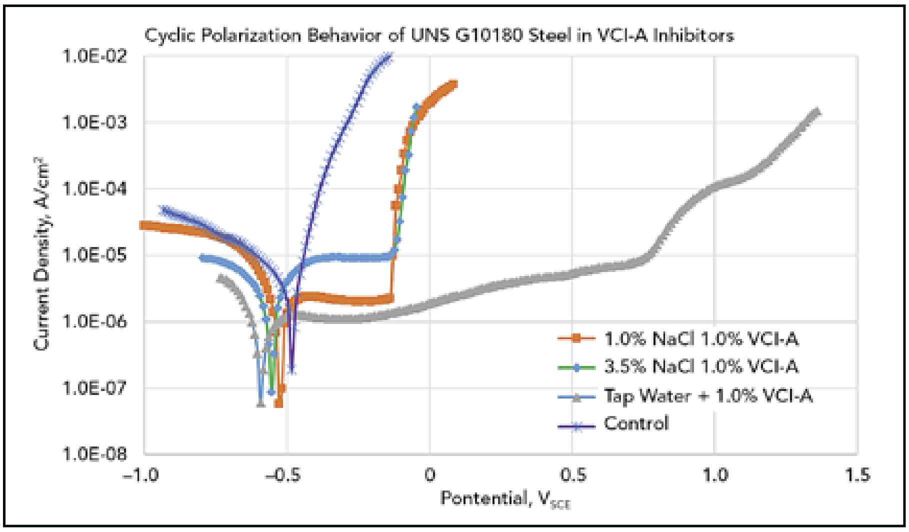

FIGURE 1 Cyclic polarization behavior of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

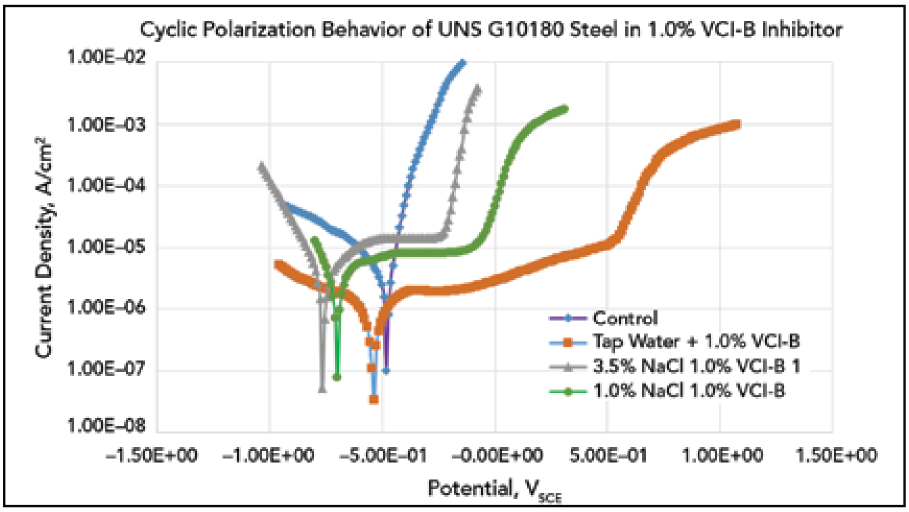

FIGURE 2 Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

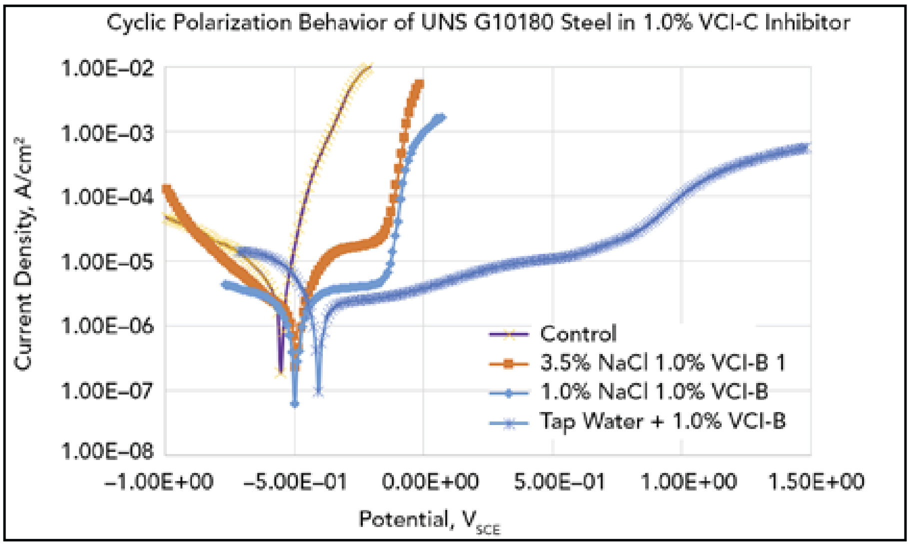

FIGURE 3 Cyclic polarization behavior of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

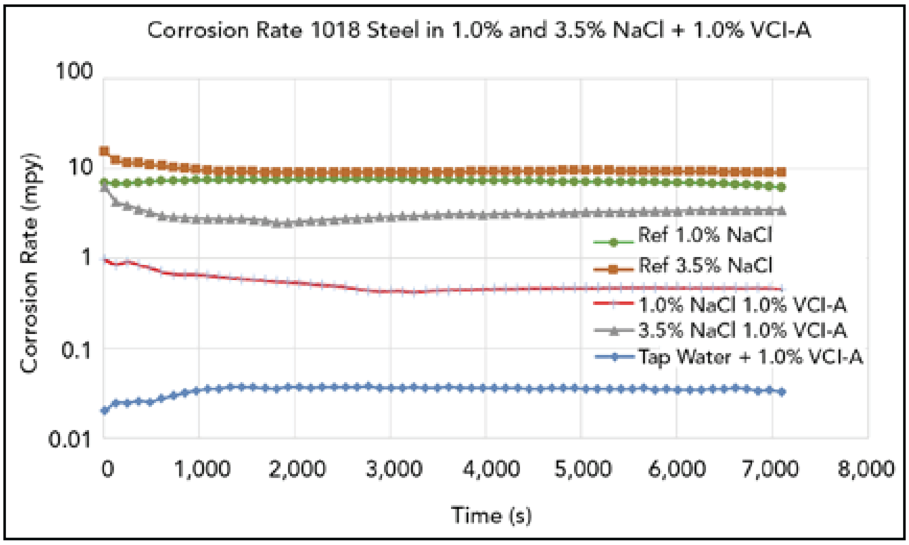

FIGURE 4 Corrosion rate measurement (based on linear polarization resistance [LPR]) of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

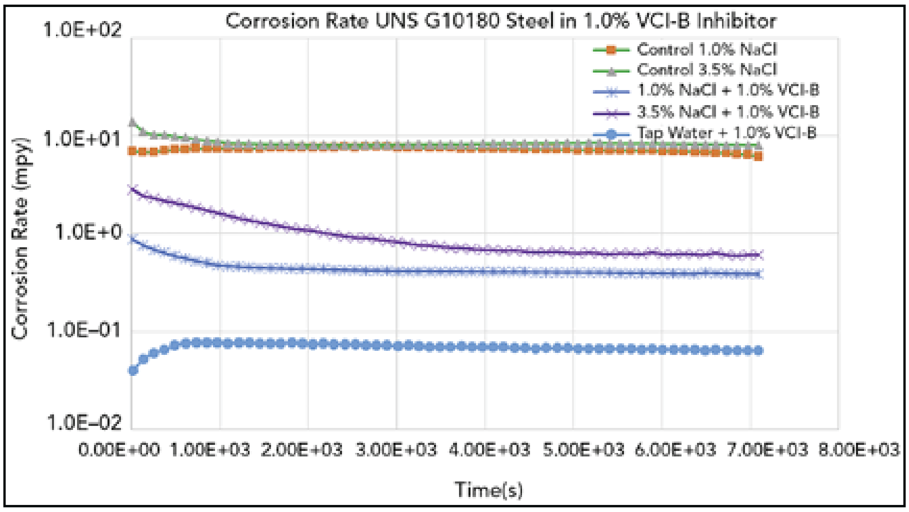

FIGURE 5 Corrosion rate measurement (based on LPR) of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

organic components form a physical bond with the metal substrate. Formulations can include components with other functionalities for added protective capabilities. The main difference of the VCI products vs. non-VCI products is the presence in the formulation of an ingredient with moderately high vapor pressure that can prevent corrosion in the vapor space without applying the VCI directly to the metal surface.[9-10] The typical examples of this class are organic amines and their salts with carboxylic acids (amino-carboxylates). The advantage of VCIs are that the volatilized molecules can penetrate hard to-reach spaces. When they reach the metal, the VCI attaches to it by the active group, creating a strong physisorption mechanism. After the completion of a hydrostatic test, the water must be discharged and be in compliance with environmental restrictions. It is required to comply with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES).[8]

Experimental Procedure

The main objective of this investigation was to study corrosion behavior of steel samples used as base material for pipelines to demonstrate effective corrosion protection of different VCIs. The choice of corrosion inhibitors for this study was made based on their functions and effectiveness in different aqueous solutions. VCI-A, VCI-B, and VCI-C are water-soluble products that have been demonstrated to inhibit corrosion of low carbon steel (CS) during hydrotests using fresh water. These inhibitors are a combination of film formers and VCIs. The main ingredients are salts of amines, organic acids of different chemical structures, and triazole. The main function of these products is to form a protective film with some VCI action. All these inhibitors are biodegradable and are surface modifiers.

The steel used in this study was a low CS with a chemical composition (wt%) of 0.14 to 0.22% C, 0.3 to 0.65% Mn, ≤0.3% Si, ≤0.05% S, ≤0.045% P, and the remainder Fe. The CS samples were pretreated prior to the experiments by polishing with silicon carbide paper (240, 320, 400, 600, and fine polishing with 1.0 µm almina powder), degreased in acetone for 5 min in an ultrasonic bath, then rinsed with ethyl alcohol and dried in a desiccator at room temperature. The three different USDA bio-based inhibitors labeled VCI-A, VCI-B, and VCI-C were remixed with different dosages (0.5% or 1.0%) in order to find out the optimum proportional relation for effective protection. The salt solutions were prepared based on 1.0% NaCl or 3.5% NaCl solutions. The corrosion behavior of the low CS was investigated when exposed to three different corrosion inhibitors in salt solutions using electrochemical techniques, total immersion tests, and vapor-inhibiting ability (VIA) (NACE TM0208-201811). Electrochemical polarization standards per ASTM G61[12] (cyclic polarization), polarization resistance and corrosion rate measurements, and electrochemical impedance spectroscopic (EIS) techniques were used to evaluate the behavior of these inhibitors on the different alloys in different chloride solutions.

The corrosion behavior of low CS was investigated using EIS in different salt concentrations. The experiments were conducted using commercially available systems for EIS and direct current corrosion tests. Bode plots were created from the data obtained using the potentiostatic technique. By comparing the Bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the R_p value over time. To verify this analysis, the R_p values were also estimated by using a curve fitting algorithm on the Nyquist and Bode plots. In these plots, the R_p and RΩ combined values are displayed in the low frequency range of the Bode plot and the RΩ value can be seen in the high frequency range of the Bode plot. The diameter of the Nyquist plot is a measure of the R_p value. During this investigation, changes in the polarization resistance (R_p) of these alloys were monitored to ascertain the degree of effectiveness for these inhibitors to lower the corrosion rate.

The NACE TM0208-2018 Standard Test Method was also used to evaluate the VIA of various forms of VCI.[11] This laboratory test method evaluates the VIA of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces. The VIA corrosion test method represents standard conditions in a test jar of water-saturated warm air without the presence of accelerating contaminants. The combination of (1) vapor transport across a gap containing

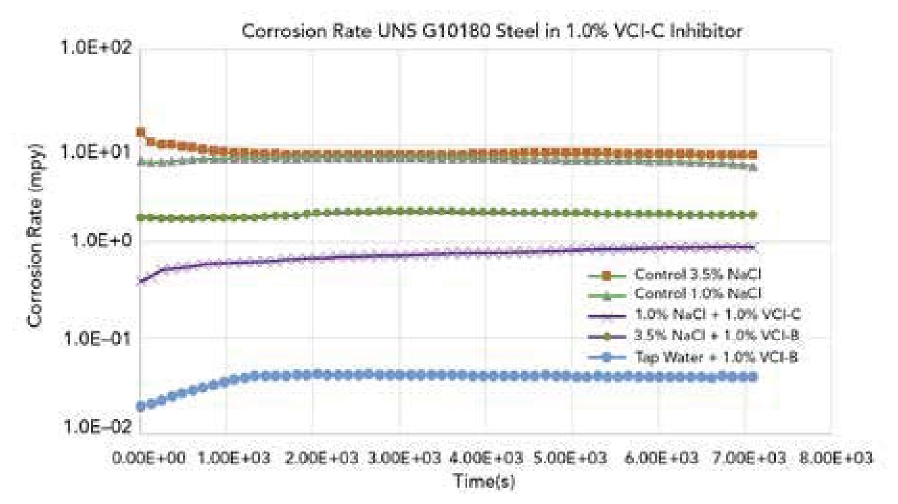

FIGURE 6 Corrosion rate measurement (based on LPR) of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

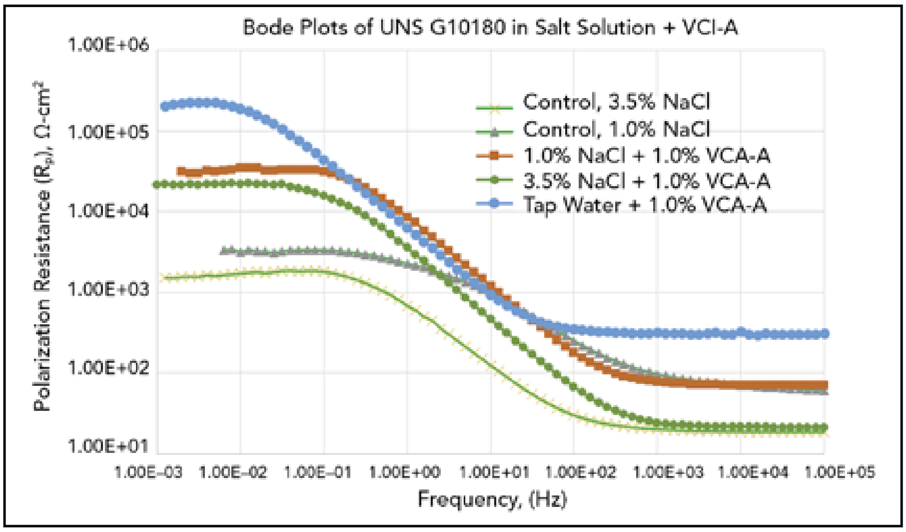

FIGURE 7 EIS Bode plot of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

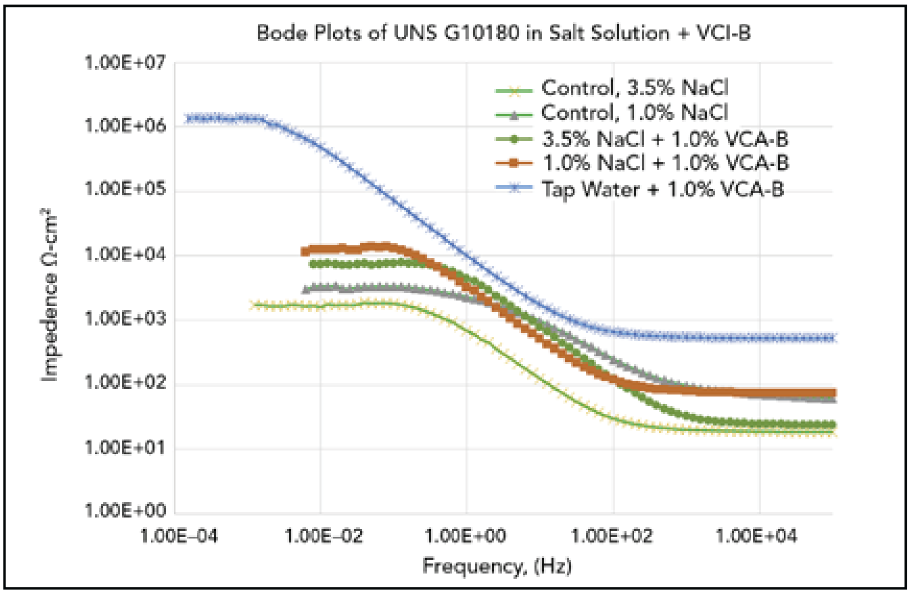

FIGURE 8 EIS Bode plot of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

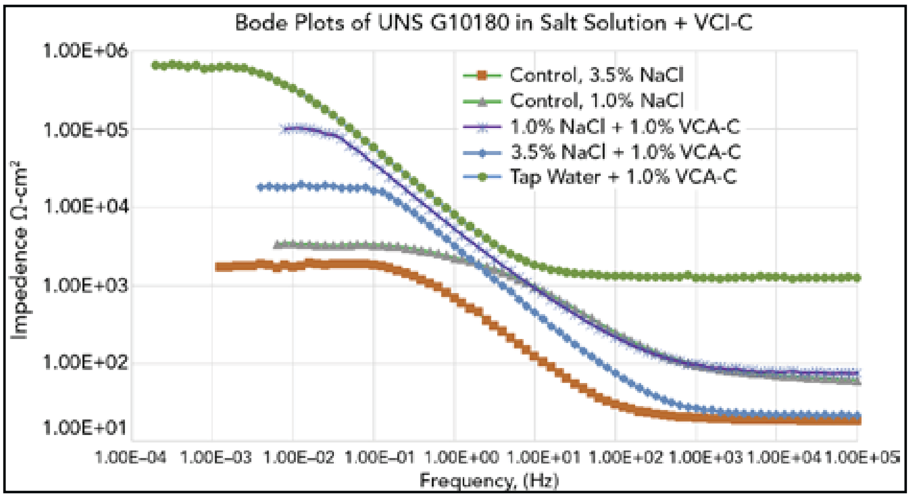

FIGURE 9 EIS Bode plot of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

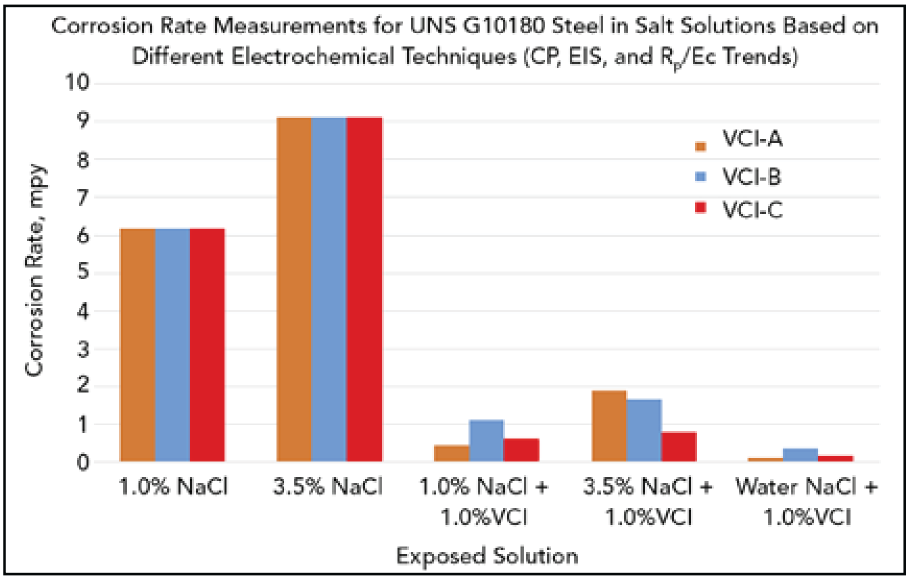

FIGURE 10 Corrosion rate measurements of UNS G10180 steel using different electrochemical techniques (cathodic protection, EIS, and Rp/Ec trends) at different aqueous solutions.

air, water vapor, and VCI, and (2) corrosion protection are evaluated in this test method. The VIA tests consist of four steps of sample conditioning or saturation for 20 h at 22 °C, a cooling cycle at 2 °C, and prewarming at 50 °C, followed by 3 h at 22 °C for specimen conditioning. After the last conditioning period, the steel samples were inspected for visible water condensation. Following verification of water condensation on each sample, visual examination of the surface was done and microscopic observation was conducted to determine the corrosion rating for each sample. The corrosion criteria for rating steel specimens consist of Grade 0 through Grade 4. To have a valid test, the control sample must have Grade 0; samples with no inhibitor received the worst grade. The control samples consistently rated a Grade 0 for all VIA tests, therefore validating the test method. Relative humidity and the temperature of each test jar were monitored by inserted sensors and data logging software. Post-test evaluation of the surface condition of exposed samples involved digital light microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy, and x-ray photoelectron spectroscopy.

Results and Discussion

Figures 1 to 3 show the polarization behavior for UNS G10180 steel in 1.0% inhibitor (different VCI products) in different salt solutions. The most noticeable changes are the positive shift in the breakdown potential and expansion of the passive range for these alloys when inhibitors were added. These inhibitors acted as effective cathodic inhibitors. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and was beneficial in reducing localized corrosion damages. As demonstrated in these polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film, and shifts the critical pitting potential to higher levels.

Corrosion rate measurements based on the linear polarization rate are shown in Figures 4 to 6. The effectiveness of these VCI products is confirmed in various water chemistries including fresh and salt water. The corrosion rate dropped from ~10 mpy for the salt solution to less than 1 to 2 mpy when various inhibitors were added. The effectiveness of these inhibitors was remarkable in the fresh water (less than 0.4 mpy).

The corrosion behavior of low CS was investigated using EIS in different salt concentrations. Various Bode plots are shown in Figures 7 to 9. These results showed a significant increase in polarization resistance when inhibitors were added. Measured polarization resistance jumped from 2,000 to 3,000 Ω-cm² to more than 30,000 to 110,000 Ω-cm². These increases in polarization resistance are equivalent to a significant decrease in the corrosion rate.

Figure 10 summarizes the average measured corrosion rate by different electrochemical techniques. These results reaffirmed the necessity to add these inhibitors to testing media during hydrotesting.

The laboratory test method evaluations of the VIA of these VCI products are shown in Figures 11 to 12. Samples were visually inspected and their surface conditions were documented after VIA tests were completed using optical digital microscopy and SEM. Based on three sets of VIA tests, the observation showed that the control had a Grade 0 (severe pitting corrosion), while the addition of VCI-A, VCI-B, and VCI-C resulted in a significant improvement to Grade 3 (almost no corrosion attacks). These results showed that these inhibitors have a very strong VIA. Additionally, any leftover residue of hydrotesting solution in pipes will be beneficial and provide extra protection during a storage period, contrary to the stagnant wet condition that testing without an inhibitor might cause.

The VIA visual observations are shown in Figure 11. Figure 12 shows SEM micrographs of the steel sample after VIA tests. The high-resolution SEM images show a significant improvement for VCI-A, VCI-B, and VCI-C with no sign of any pitting corrosion.

Figure 13 shows the effects of different corrosion inhibitors on the mechanical behavior of low CS. Tensile tests on the exposed samples after four-week immersion tests indicated that the level of corrosion attacks were minimized, and no sign of any deterioration in ductility of the exposed samples was detected.

Inhibitor Adsorption Mechanism

The adsorption isotherm relationship between surface coverage and temperature for the VCI-A, VCI-B, and VCI-C inhibitors on the surface of steel is shown in Figure 14. Adsorption energy was –21,520 J/mol for VCI-A, –22,950 J/mol for VCI-B, and roughly –24,970 J/mol for VCI-C. This energy range is indicative of a good physical adsorption to the metal surface. Generally a multilayer adsorption energy between –5,000 to –50,000 J/mol is defined as a physisorption mechanism, a weak, long-range bonding. However, it can be seen that the interaction of VCI-C with the steel surface is higher than the other inhibitors, leading to better corrosion protection. XPS depth profiling analysis showed ~60 to 65 nm of adsorbed inhibitor on the exposed samples, indicating multilayer adsorption of inhibitor molecules to the steel surfaces. Therefore, the Brunauer Emmett Teller Model (BET Model) is a more realistic adsorption model than the monolayer Langmuir model for this case.[13-15] But for the adhesion energy calculation between inhibitor molecules and the metal surface, it is appropriate to use the monolayer Langmuir model.[16]

Conclusions

This investigation demonstrated that VCI additives can prevent corrosion of CS during and after hydrotesting. When necessary, other VCI products can complement hydrotest additives for long-term storage. Electrochemical cyclic polarization showed formation of a stale passive range when these inhibitors were added to the environments.

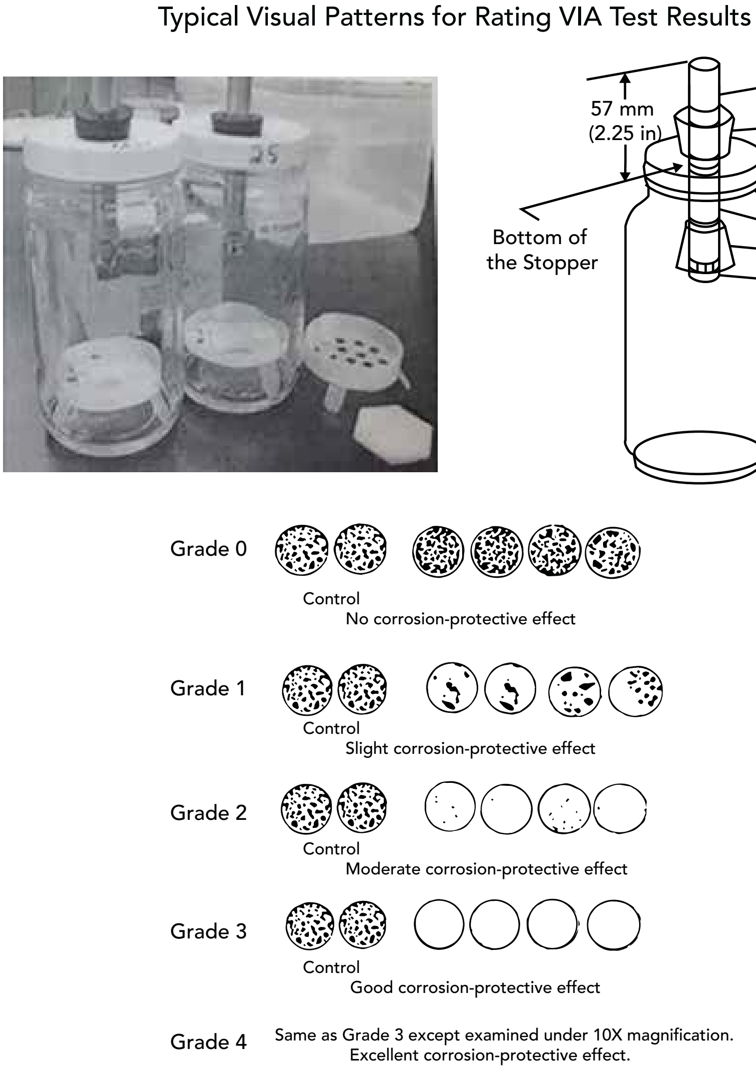

FIGURE 11 **Test setup and rating criteria for the NACE TM0208-2018 Standard Test Method.**

The effectiveness of VCI products is confirmed in various water chemistries including fresh and salt water. The corrosion rate dropped from ~10 mpy for the salt solution to less than 1 to 2 mpy when various inhibitors were added. The effectiveness of these inhibitors was remarkable in fresh water (less than 0.4 mpy).

Tensile post-immersion tests did not show any loss in mechanical properties of the exposed samples. Both strength and ductility of the low CS samples were maintained. Adsorption energy was about –21,520 J/mol for VCI-A, –22,950 J/mol for VCI-B, and roughly –24,970 J/mol for VCI-C, indicating a strong physisorption mechanism (Figure 15).

Results indicated that these bio-based, environmentally friendly VCI additives have low toxicity levels and waters containing these VCI products remain safe for many species, allowing discharge according to local specifications.

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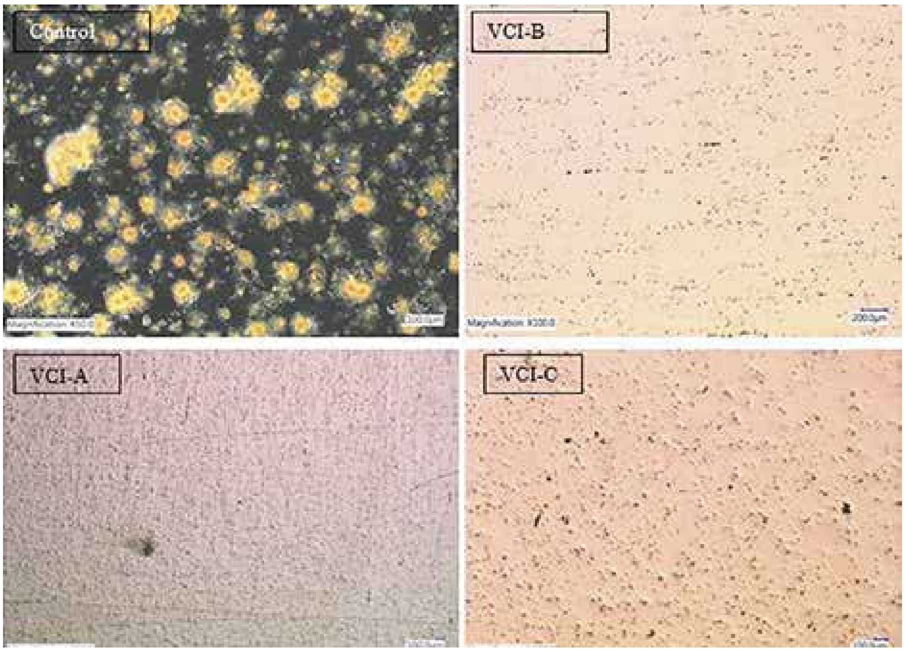

FIGURE 12 Optical micrographs of the steel sample after VIA tests. These tests showed a significant improvement for VCI A, VCI-B, and VCI-C compared with the control sample. VIA rating: Control Grade 0; VCI-A, VCI-B, and VCI-C Grade 3.

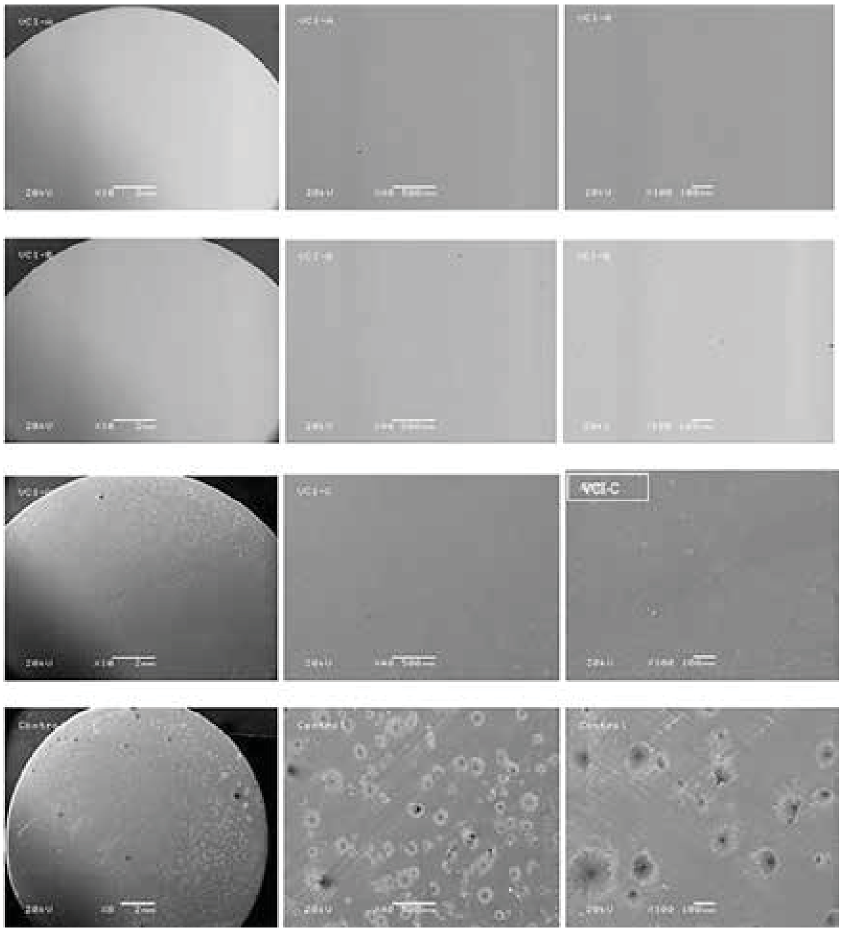

FIGURE 13 SEM micrographs of steel samples after VIA tests. Superior performance for VCI-A, VCI-B, and VCI-C were observed compared with the control sample. VIA Rating: Control Grade 0; VCI-A, VCI-B, and VCI-C Grade 3.

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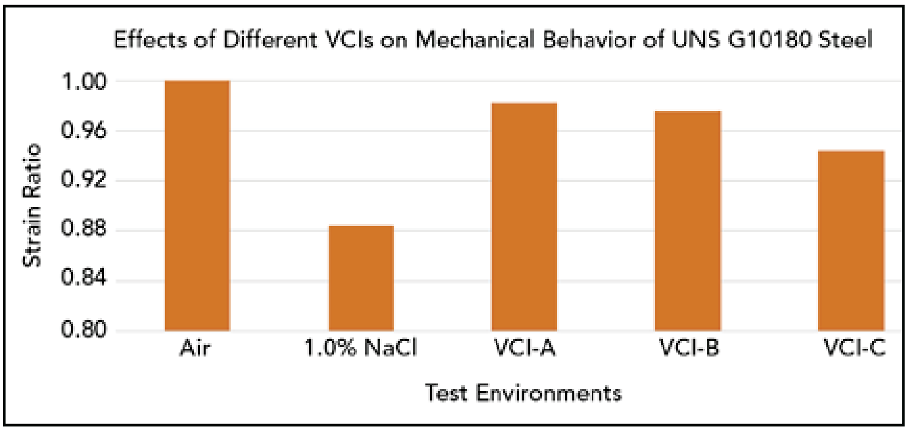

FIGURE 14 Effects of different inhibitors on tensile ductility of UNS G10180 steel.

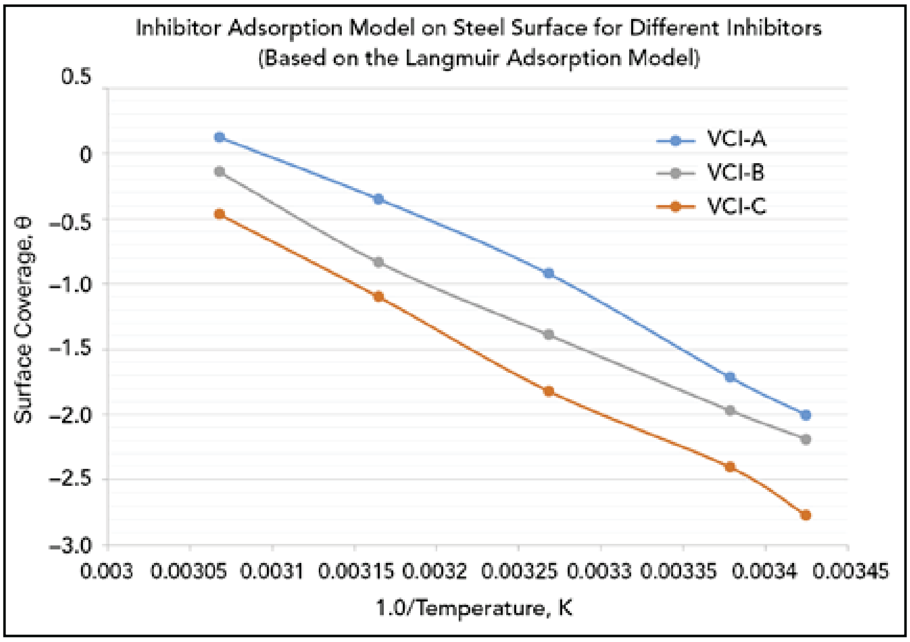

FIGURE 15 The adsorption isotherm relationship between surface coverage and temperature for different VCIs on the surface of steel. Adsorption energy was roughly –21,500 to –24,970 J/mol for these inhibitors.


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