

Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitor and Nitrogen Blanketing System

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ABSTRACT

Vapor phase corrosion (VCI) inhibitors have superior protection performance compared to nitrogen blanketing systems. Proof of this was seen after monitoring the corrosion rate of steel samples for more than five months (roughly 4,000 hours). Corrosion behavior was evaluated in two different conditions; the first contained 200 ppm chloride solution + 10% corrosion inhibitor addition, the second included 200 ppm chloride solution with a nitrogen blanketing system at 10 psi applied pressure. The exposed samples typical of those found in storage tanks and cross casing pipes were tested using linear polarization resistance (LPR) and electrical resistance (ER) probe techniques in the presence of excessive salt and moisture. Vapor phase corrosion inhibitors demonstrated excellent protection in corrosive environments, even where restricted geometries such as crevices, threads, notches and under-deposits exist. The LPR corrosion rate measured less than 0.06 mpy for samples immersed in VCI solution with no observable corrosion. The immersed and nitrogen blanketed samples, in contrast, showed a 1.68 mpy corrosion rate and samples were covered with a thick red rust. ER probes showed a corrosion rate of 0.18 mpy for VCI treated while the nitrogen blanketed samples showed a 2.12 mpy corrosion rate and probes were heavily corroded.

Key words: nitrogen blanketing, vapor phase corrosion inhibitors, linear polarization resistance, electrical resistance probe techniques

INTRODUCTION

Steel storage tanks are susceptible to corrosion when exposed to moisture or an aggressive environment. Storage tanks, however, both above ground and below, are abundant throughout the world given their use in multiple industries such as power generation, municipal water, biodiesel, mining, waste, oil and gas. Their prevalence is not surprising considering the variety of storage tank contents: grain, water, oil, chemicals, and fuel. The atmosphere on earth contains moisture, and when water is present as well as oxygen, the combination can cause metal structures, parts, equipment, tanks and pipes to corrode, sometimes with catastrophic consequences. In the absence of oxygen, water is still corrosive but at a much slower rate. The costs associated with corrosion go far beyond the 350 billion US dollars estimated for the year 2000¹ in financial considerations and include plant shutdowns, leaking containers, loss of products and employment, contamination and hazards to human and wildlife.

Classical methods of protecting equipment from atmospheric attack include the use of coatings or paints and alloying the metal to increase its resistance to corrosion. Other commonly used mitigation techniques include sparging, inerting and blanketing. A technique referred to as tank blanketing applies a gas cover to prevent combustion and degradation. Gas blankets have been used on storage tanks downstream of other deoxygenation devices, such as vacuum degasifiers and oxygen stripping columns, to preserve deoxygenated water. Nitrogen gas blankets have been used on utility boilers during downtime corrosion control. The mechanism for this type of corrosion attack is electrochemical in nature; its electrolyte derives from a thin layer of humidity on the surface of the metal². An alternative protection method that is both effective in controlling vapor phase corrosion and inexpensive, uses vapor phase corrosion inhibitors (VCI). A vapor phase corrosion inhibitor is a volatile compound and must be capable of forming a stable bond at the interface of the metal, preventing penetration of corrosive species³⁻⁹. VCIs offer an alternative way to protect storage tanks and their contents, cross casing pipes, or metallic structures in general. These inhibitors are easy to apply, versatile and can be used to protect multiple metal types in a variety of industries. Casings, mentioned previously, are commonly used to surround and protect pipelines where the lines cross highways, railroads and similar locations. If isolation is impractical, other measures must be taken to minimize corrosion of the pipeline inside the casing. The vapor phase corrosion inhibitors are well suited for this application and for protection of internal void spaces and exposed surfaces⁹⁻¹². These materials have stable passivating properties, strong tendencies toward surface adsorption, and the ability to form a comparatively strong and stable bond with the metal surface¹⁴⁻¹⁵. Compared to other methods of corrosion prevention such as nitrogen blanketing and dehumidification, vapor phase corrosion inhibitors (VCI) provide substantially better corrosion control at lower cost and require very low dosage rate. For practical purposes, it is preferable to use less volatile inhibitors that provide long-lasting and durable protection over periods of 2 to 3 years. Components and equipment treated with VCI will have indoor protection up to twenty-four months without reapplication and roughly six months for outdoor protection³⁻⁴. The protection is independent of environmental conditions and is effective even in extreme conditions. Previous research on ASTM A470¹⁶ steel confirms the benefits of using this technology in gas and steam turbines that are susceptible to stress corrosion cracking and crevice corrosion¹⁰⁻¹¹. In this study, the addition of VCI increased the resistance polarization (R_p) values during electrochemical impedance testing as compared to ASTM A470 steel samples tested without inhibitor. The higher R_p values were attributed to the progressive adsorption of inhibitor molecules and film formation on the metal surface¹⁰. The corrosion

inhibition mechanism was determined to be the physical adsorption of inhibitor molecules to the metal surfaces²⁻³. Physical adsorption requires energy between -5 to -20 kJ/mol¹³⁻¹⁴. The analysis of the inhibitor showed an enthalpy of adsorption in the range of -14 to -18 kJ/mol¹¹. Generally, chemisorption requires more energy and results in stronger bonding between the molecules and the surface of the substrate, forms a more stable protective film¹⁵. The majority of corrosion damage to turbo-machinery systems, however, occurs during the shutdown period due to chemistry changes and stagnant condition in localized areas. Therefore, a corrosion inhibitor with strong physical adsorption to the metal surface will provide satisfactory protection and does not require strong chemical bonding.

The vapor phase corrosion inhibitors are water-based and ideal for equipment with complex geometries such as boilers, heat recovery steam generators and pressure vessels. VCI forms a solution in water and when applied by spraying or dipping, will protect ferrous and nonferrous metals, including castings, tubular parts, finished parts, gears, pumps, housings, structural steel, sintered metals, bars and roll stock. VCI has excellent wetting properties and forms a clear, dry, hydrophobic film of roughly 0.25 mils thick (6.35 micron) on the surface that is stable up to 350°F (176°C)³. Adsorption of the inhibitor on to the metal surface provides a protective inhibitor layer. As well, the vapor phase action protects surfaces that have not been directly coated and are difficult to reach. This type of corrosion inhibitor is useful when oil, grease or other adherent films are not practical. The inhibitor is transmitted by vapor and the vapor phase is controlled by the crystal lattice structure and the atomic bond characteristics of the molecule². The protective vapor expands within the enclosed space until the equilibrium determined by its partial pressure is reached; the higher the vapor pressure, the sooner the saturation of protected space. The VCI organic chemistry is free of hazardous amines, nitrites and phosphate ester. There are no hazardous decomposition by-products. Furthermore, the product is biodegradable and non-flammable unlike some of the earlier chemicals tested in the 1940s and 1950s: dicyclohexyl ammonium nitrite, ammonium nitrite, urea, and acetamide².

Tank blanketing or tank padding is a commonly used corrosion mitigation technique. This process applies an inert, relatively inexpensive gas to the empty space in a storage container. Though tank blanketing is used for a variety of reasons, it typically involves an inert buffer gas to protect the storage container and its contents. The buffer gas adds pressure to a system and controls the speed of combustion with existing oxygen. A few of the benefits of blanketing include a longer product life, reduced hazards, and longer equipment life cycles. When storing highly volatile substances or substances likely to oxidize, safety and product preservation are important goals. The list of products blanketed is extensive and includes adhesives, catalyst, chemicals, fats and oils, foods, coffee, fuels, inks, pharmaceuticals, photographic chemicals, soaps, and water.

Nitrogen is used in a wide range of industries to either prevent degradation of food, chemicals and metallic vessels due to atmospheric oxidation and corrosion, or to enhance safety by preventing the possibility of combustion. This is a safe and reliable way to protect food from degrading as a result of oxidation. Oxidation is a chemical reaction where atmospheric oxygen attacks the food surface or metal. The presence of nitrogen keeps oxygen levels in and around the product low. Humid air in the head space is replaced by high purity, inert, dry nitrogen. Nitrogen is an inert gas that does not support the corrosion reaction. Nitrogen effectively displaces all oxygen from the system and stops the corrosion reaction by eliminating the cathodic oxygen reaction. The dew point of 95% nitrogen is approximately -40°F, which

enables it to absorb significantly more moisture than compressed air. From a corrosion point of view, air is roughly 20% oxygen, 80% nitrogen. Since fuels require oxygen to combust, reduced oxygen content in the vapor space lowers the risk of unwanted combustion.

EXPERIMENTAL PROCEDURE

Corrosion inhibition of commercially available inhibitor (VCI) was investigated for 1020 carbon steel commonly used in tank and casing applications. Electrochemical polarization standards per ASTM-G61¹⁷ and corrosion rate measurements using linear polarization resistance (LPR) and electrical resistance (ER) techniques to evaluate the behavior of this inhibitor on the steel alloy in 200 ppm chloride solution and to compare with nitrogen gas blanketing. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate and localized corrosion susceptibility of a material in a given environment.

RCS CORRATER® 9030 Plus[†] was used to monitor the corrosion rate using LPR techniques, and the Metal Samples MS3500E[†] electrical resistance probes which is a remote data-logger capable of measuring and storing data were used to collect corrosion data. Further experiments were conducted using Gamry[†] Potentiostat/Galvanostat/ZRA instrumentation and corrosion test software. Samples were polished, placed in a flat cell and tested in deionized water solutions containing 200 ppm chloride with 10% VCI inhibitor. A series of cyclic polarization (CP) tests were performed in temperatures ranging from 20°C to 60°C to define the inhibitor surface adsorption mechanism. The R_p , polarization resistance value was used to fit the data into adsorption isotherm models.



Figure 1: Test setup for corrosion test on steel LPR and ER probes using 10% VCI or nitrogen blanketing at 10 psi applied pressure.

The test setup for steel probes in 10% VCI and a nitrogen blanketing system at 10 psi applied pressure (with no inhibitor) are shown in Figure 1. In each case, one probe was immersed in solution and the ER probes were suspended above the solution. Linear polarization resistance was used to monitor the corrosion rate for the 1020 steel LPR probe #2 with 10% VCI and LPR probe #1 with nitrogen blanket. Electrical resistance equipment measured the corrosion rate for a 1020 steel ER probe using 10% VCI and another probe for the nitrogen blanket. The corrosion rate for the samples was monitored continuously for roughly 4,000 hours (5.5

[†] Trade name

months). Samples were visually inspected and SEM/EDAX analysis was conducted using a JEOL[†] JSM-6480LV and Thermo[†] System Seven detector.

RESULTS

Cyclic Polarization Behavior

Figure 2 shows the polarization behavior for 1020 steel in 10% inhibitor (VCI) with 200 ppm chloride ions. The most noticeable changes are the positive shift in the breakdown potential and expansion of the passive range for these alloys in the VCI. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and had beneficial consequences for 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 shift of the critical pitting potential to higher levels.

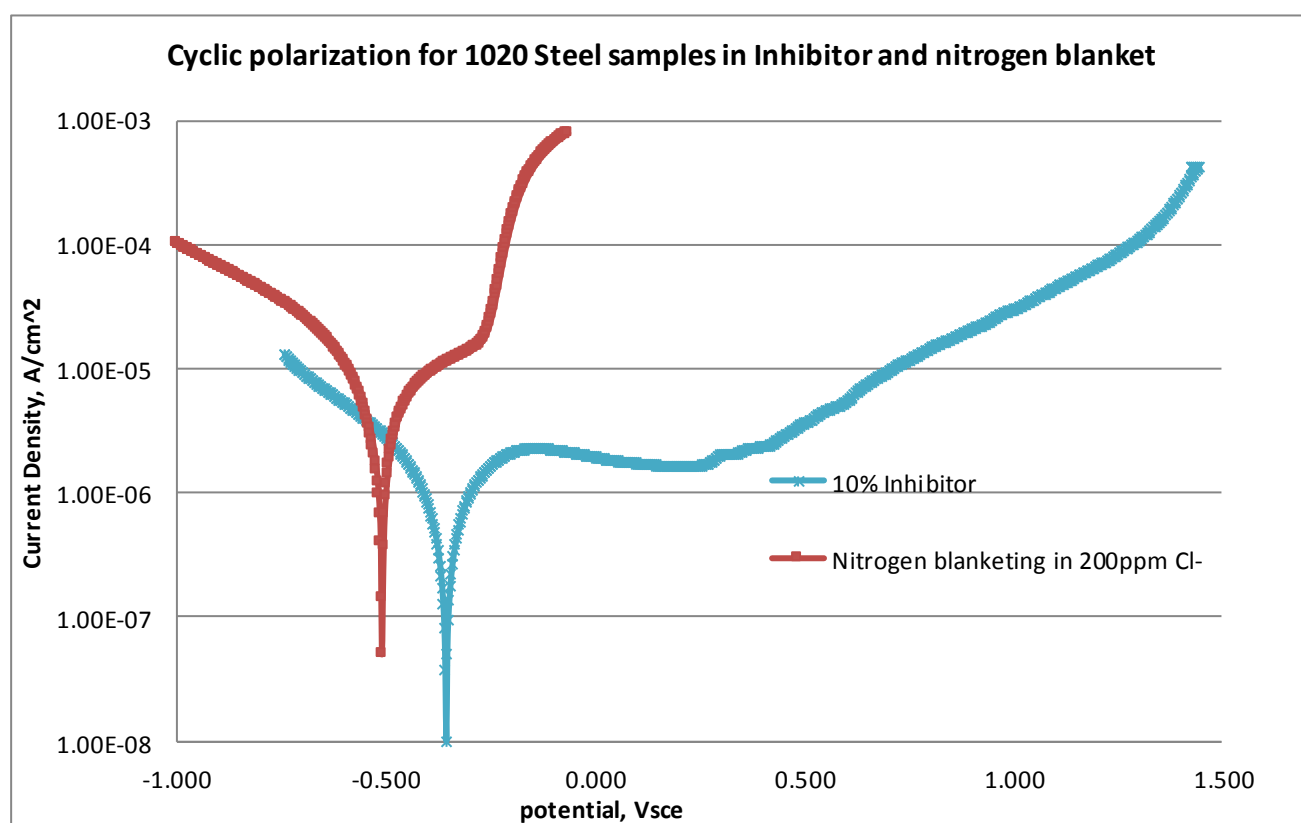


Figure 2: Electrochemical polarization behavior of the 1020 steel samples in 10% VCI and nitrogen blanket in 200 ppm chloride ion solution.

The adhesion of corrosion inhibitors to a metal surface can be modeled using an adsorption isotherm. An adsorption isotherm is a mathematical function that relates the surface coverage of a chemical on a surface to the concentration of the chemical. Identification of the surface adsorption isotherm can lead to the determination of a mechanism. It is assumed that the corrosion current density, which is directly related to the corrosion rate, is representative of the

[†] Trade name

number of corrosion sites. Therefore, adding inhibitor to the environment should diminish the number of corrosion initiation sites by displacing water molecules on the surface with inhibitor molecules, thereby decreasing the corrosion rate. In recent years, electrochemical and weight loss methods that relate the corrosion current density or the amount of weight loss with the inhibitor coverage have been used to study adsorption and the corrosion inhibition of various materials on a metallic surface¹³⁻¹⁵. Many models for adsorption isotherms have been defined (Temkin, Freundlich, Langmuir and Frumkin). Each of these adsorption isotherms explains a different type of relationship between concentration and surface coverage of an inhibitor on a metal or alloy surface¹⁴⁻¹⁵. Based on the adsorption isotherm graph, the adsorption equilibrium constant, K_{ad} can be calculated. Identifying the adsorption equilibrium constant, can lead to the calculation of the free standard energy of adsorption, $\Delta G_{ad} = -RT \ln (K_{ad})$. By repeating the same experiment at different temperatures, the enthalpy of the adsorption, ΔH_{ad} can be calculated. The corrosion inhibition mechanism of VCI inhibitor best fit the Langmuir adsorption isotherm (Figure 3) and was determined to provide physical adsorption to the metal surface¹⁰⁻¹¹. The enthalpy of adsorption for the VCI inhibitor was roughly -10 to -14 kJ/mol, indicative of an inhibitor with strong physical adsorption to the metal surface.

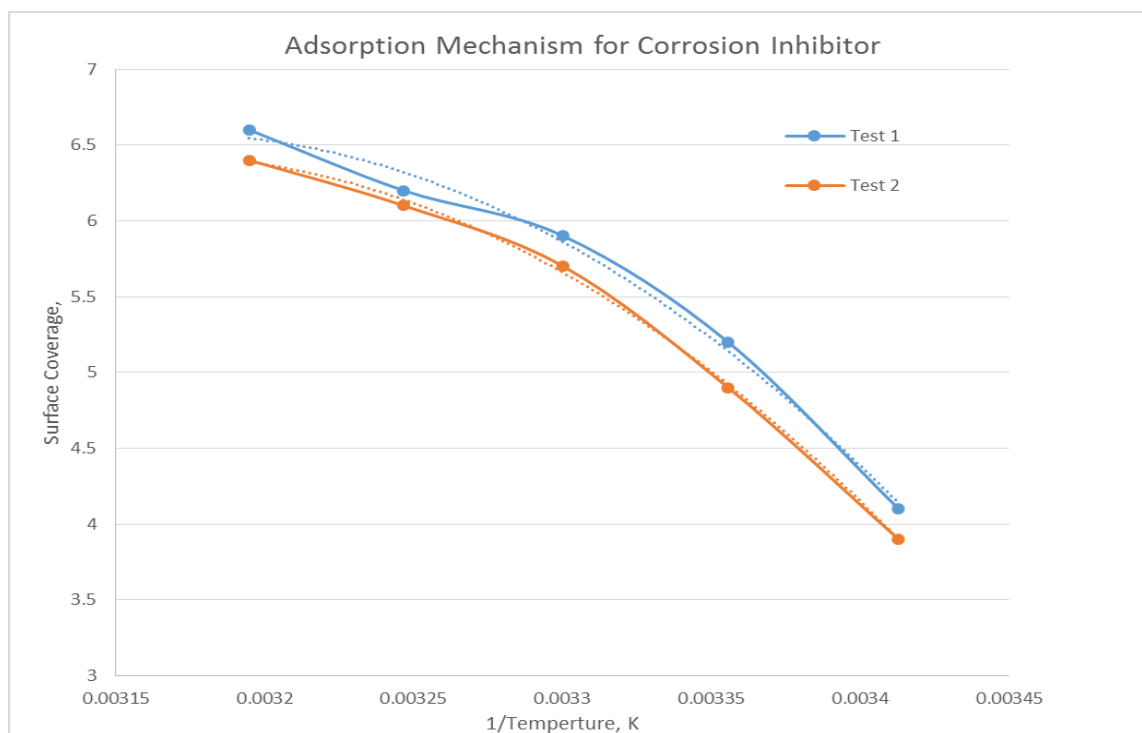


Figure 3: Langmuir adsorption isotherm showing the relationship between surface coverage and temperature for VCI Inhibitor on the surface of steel.

Corrosion Rate results (LPR and ER)

Figure 4 shows the corrosion rate results monitored using LPR and ER techniques for nearly six months. It is clear from the data that the steel probes suffered a higher corrosion rate when using only a nitrogen blanket system (average corrosion rate of 1.8 mpy compared to an average corrosion rate of 0.04 mpy for 10% VCI protected probes). After roughly 4,000 hours of testing, 10% VCI was added to the nitrogen blanket environment where the corroded samples were exposed. Notice in Figure 3 (roughly 4,000 hours of testing) when 10% VCI was added to the nitrogen blanket system, the corrosion rate for both LPR and ER probes dropped significantly.

VCI clearly offered better corrosion protection for these steel samples. VCI addition stopped any further corrosion of these steel samples. Figure 5 shows the surface of the steel probes. The difference in degree of protection offered by VCI and a nitrogen blanket system is starkly contrasted. The steel probes in VCI show no rust formation. The nitrogen blanket protected steel probes were covered with thick red rust. Though nitrogen blanketing may lower the overall corrosion rate, the data showed that it cannot adequately protect steel samples in a corrosive environment. These results for VCI protection are very promising as the following SEM micrographs demonstrate. Figure 6 shows the SEM micrographs for the LPR 1020 steel probe from the nitrogen blanket protection system. This figure shows severe corrosion attack on the sample surfaces. In several areas, the thick red rust was removed to show the severity of the corrosion attack. Figures 7 and 8 show the SEM/EDAX analysis on the LPR nitrogen blanketed probe and its surface chemistry containing multiple corrosive species and severe corrosion attacks. Figure 9 shows the SEM/EDAX analysis on the LPR probe (1020 steel) in 10% VCI + 200 ppm Cl ions with no corrosion attack on its surfaces after roughly 4,000 hours of continuous corrosion testing.

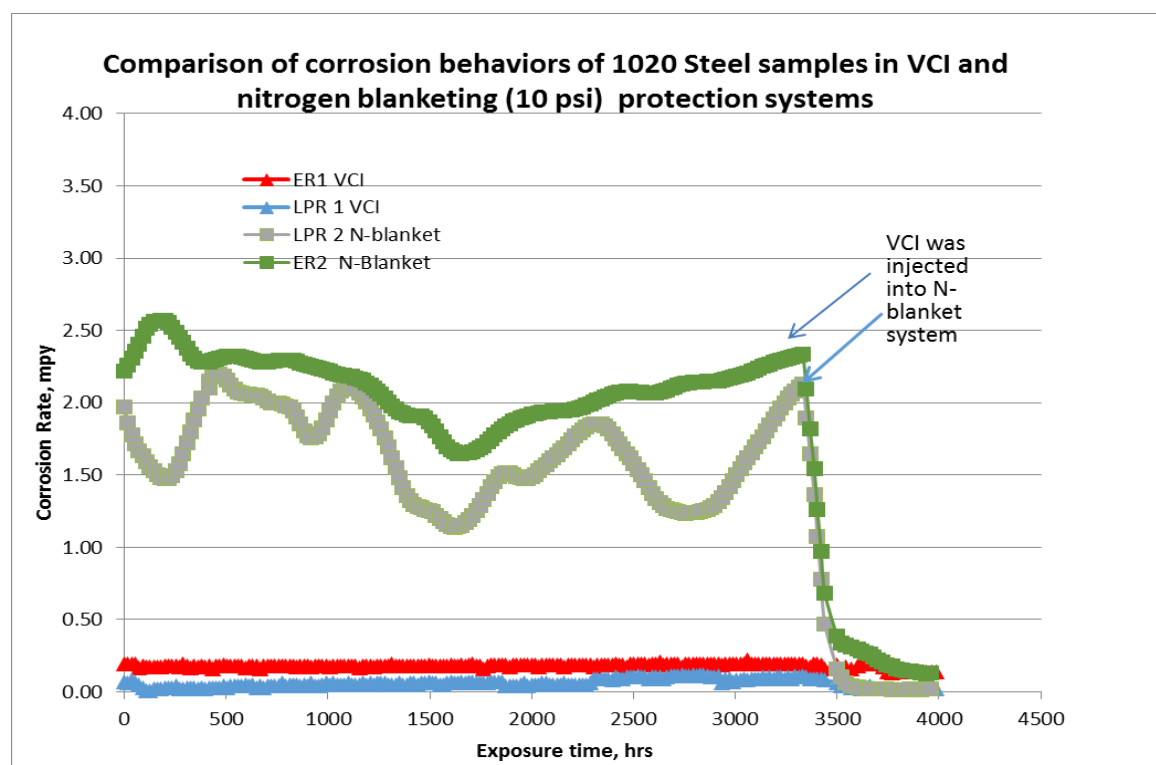


Figure 4: Comparison of corrosion on steel probes in VCI and nitrogen blanket protection system. There is a much lower corrosion rate for steel samples protected by VCI (average corrosion rate of 0.04 mpy), while nitrogen blanket coverage resulted in higher corrosion rate, regardless of technique used to monitor (average corrosion rate of ~2.0 mpy).

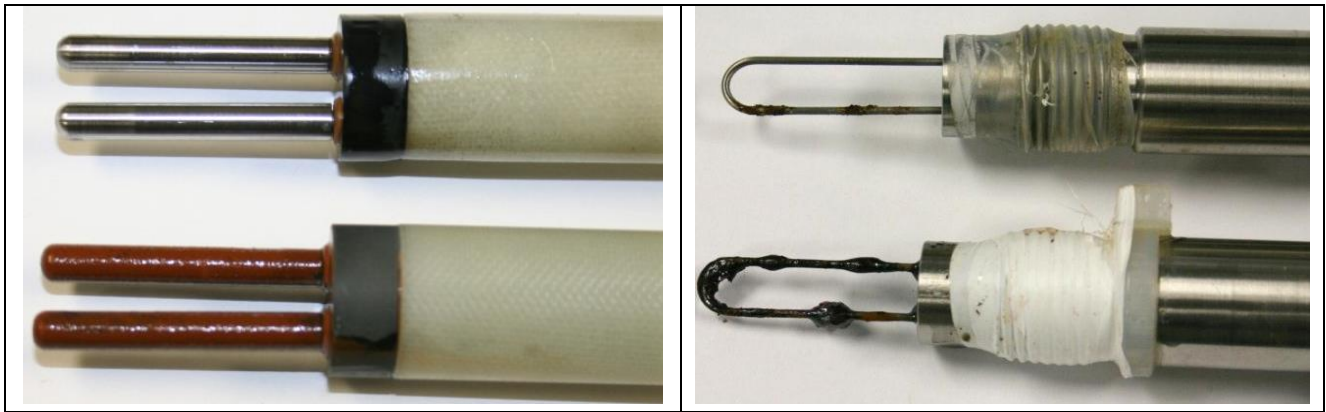


Figure 5: Comparison of corrosion damages on both LPR and ER Probes (1020 steel) in inhibitor and nitrogen blanket protection system. There is no rust formation on inhibitor protected steel samples while nitrogen blanket protected steel samples are covered with a thick red rust.

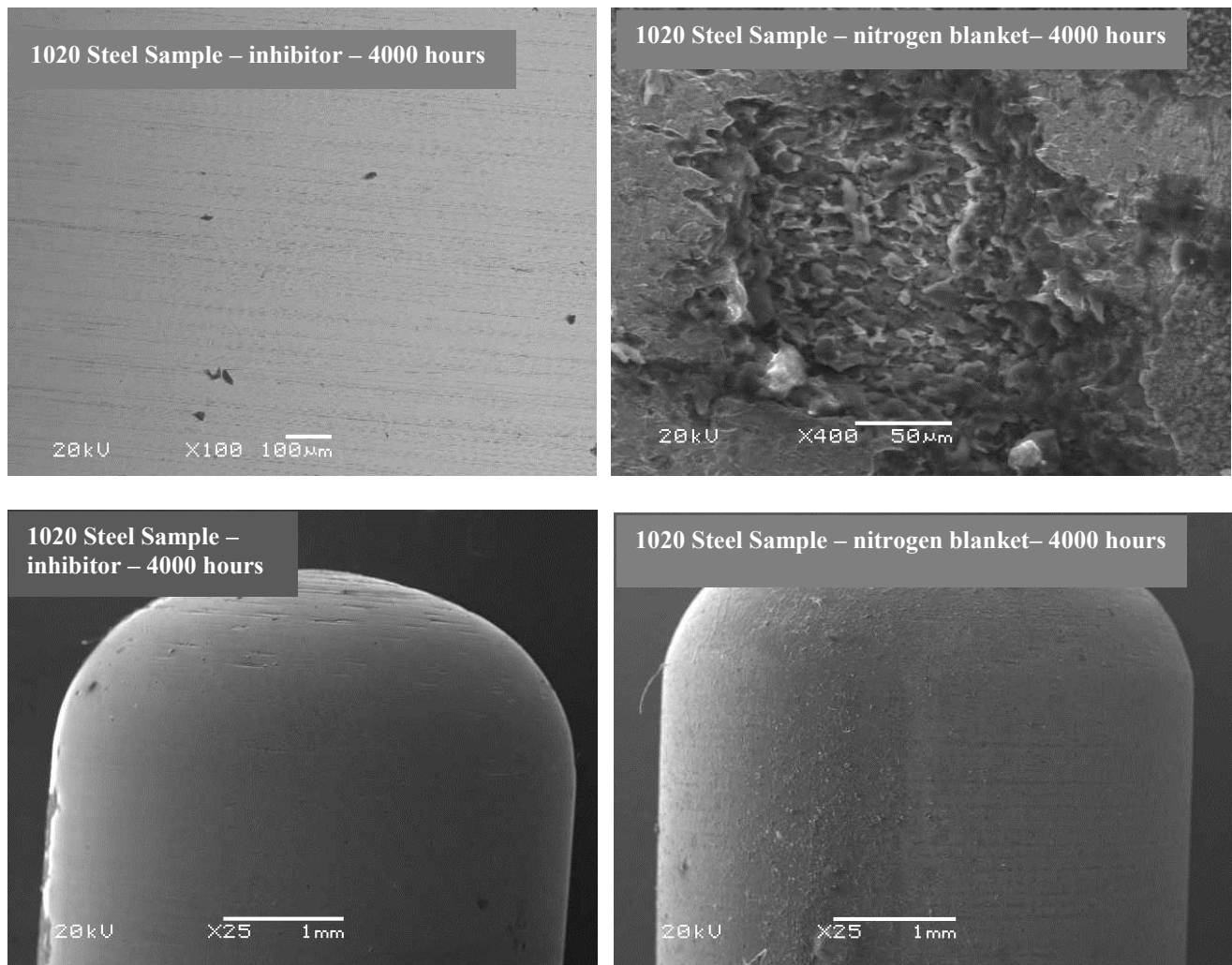
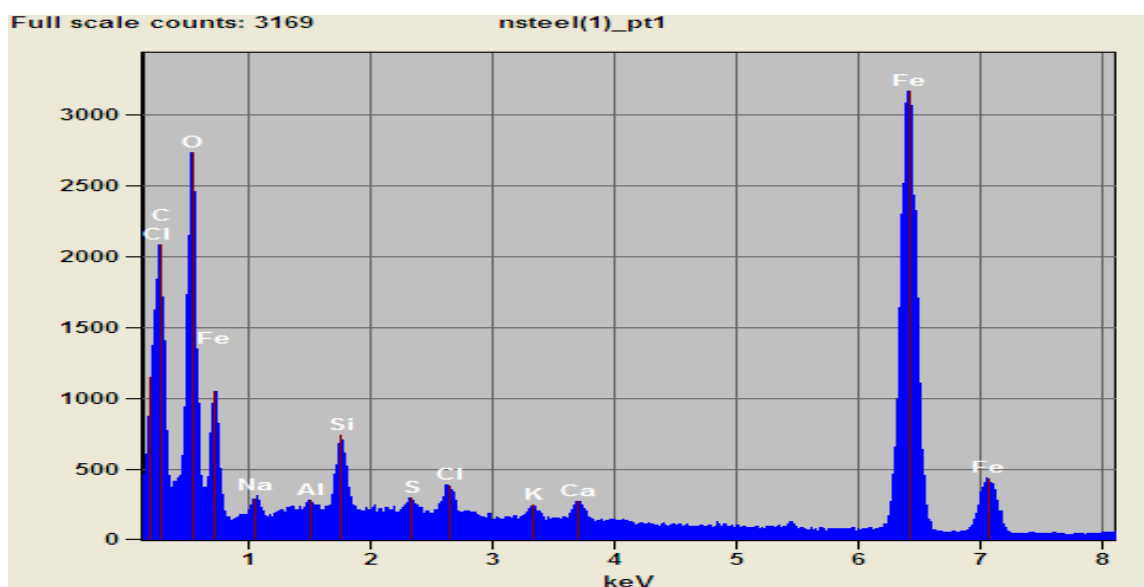
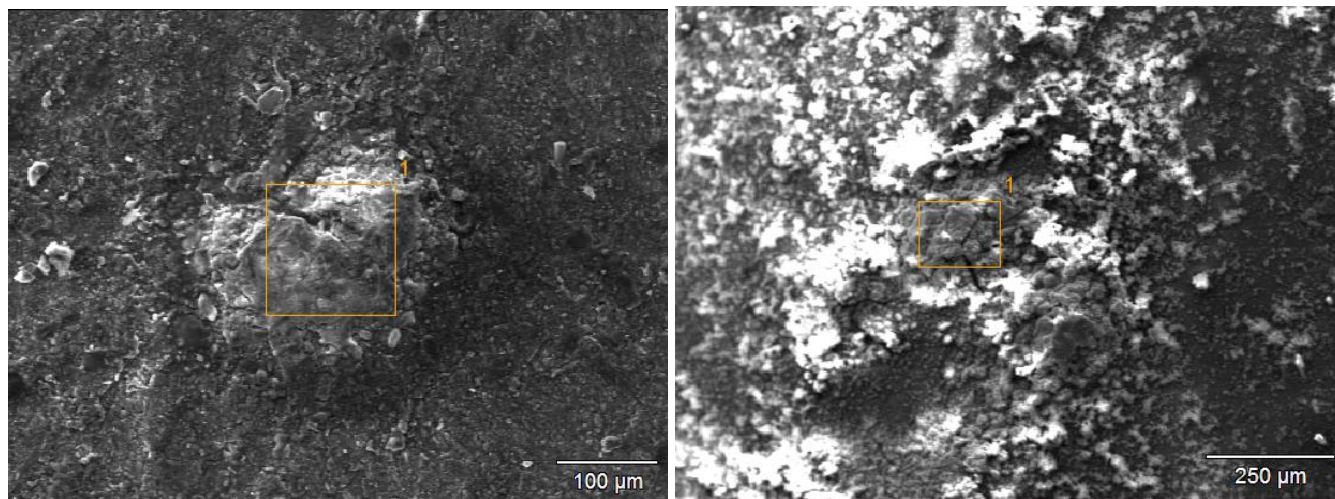
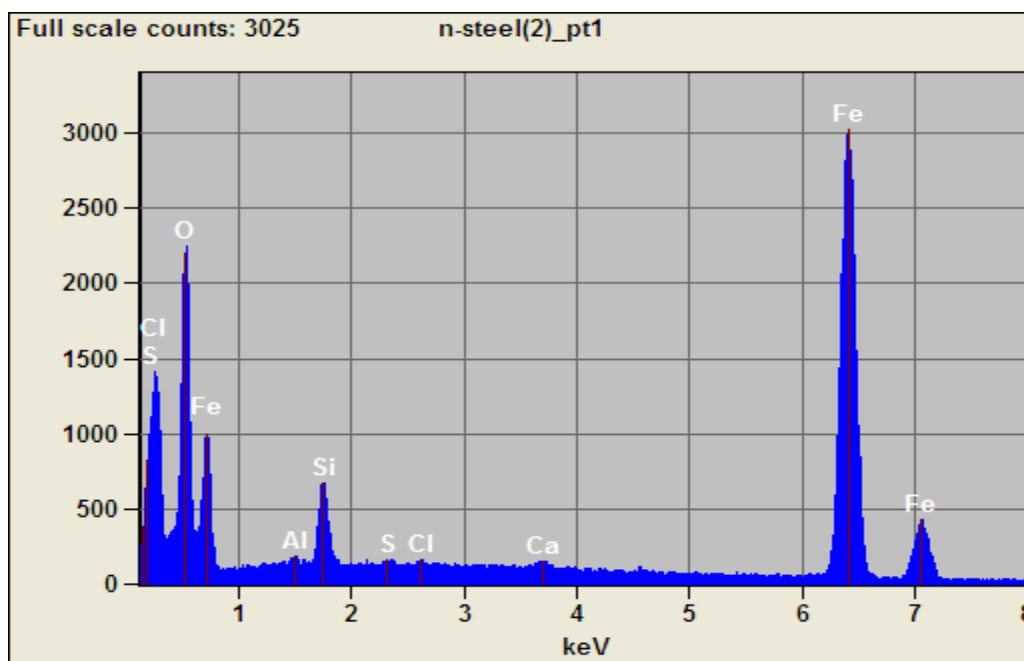
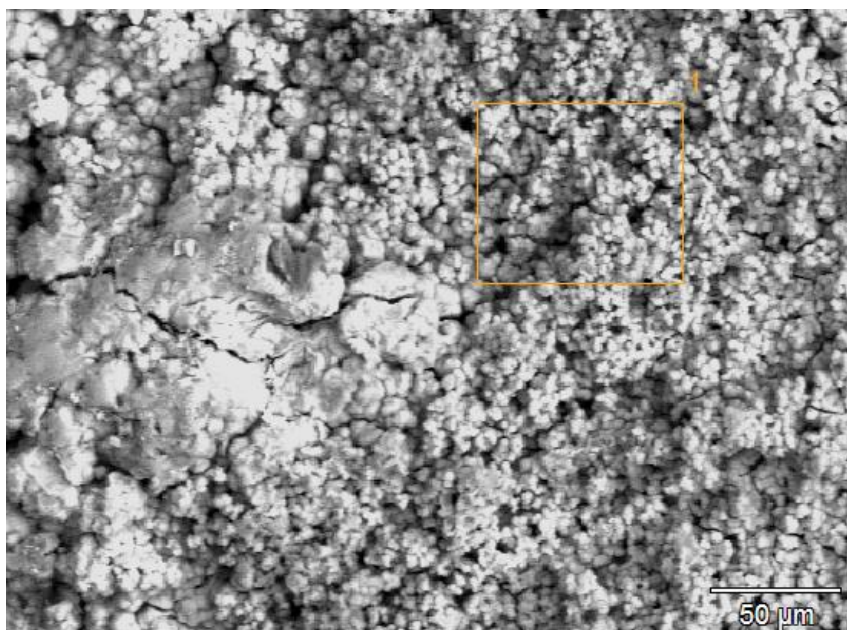


Figure 6: SEM micrographs of corrosion on 1020 steel LPR probe in inhibitor (left) and nitrogen blanket protection system (right). Image shows a clean corrosion free surface for the inhibitor protected steel sample while nitrogen blanket protected steel sample is covered with a thick red rust corrosion products.



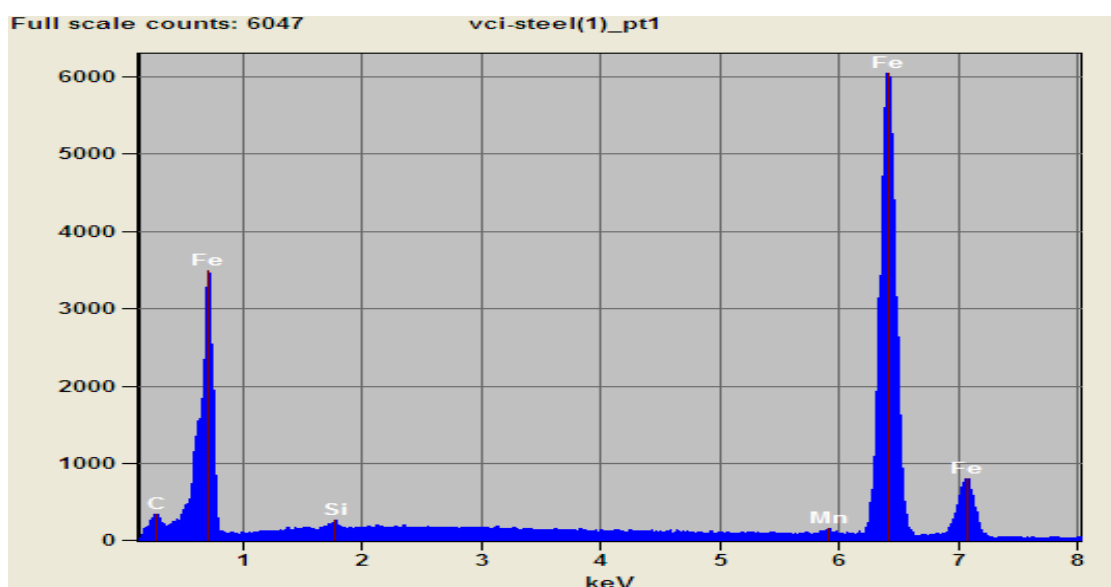
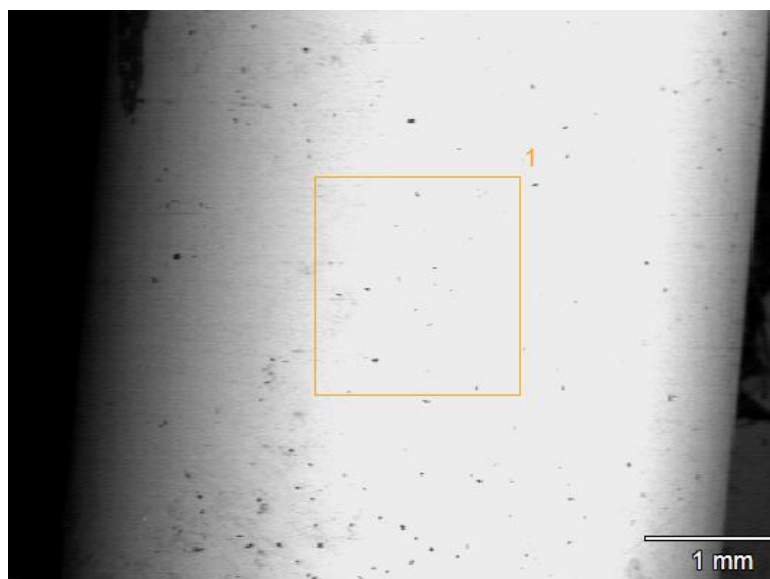
Weight %									
	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Fe-K
N-steel(1)_pt1	18.62	2.92	0.39	3.29	0.60	1.41	0.66	1.13	70.97

Figure 7: SEM/EDAX analysis on the LPR probe (1020 steel) in nitrogen blanket protection system shows severe corrosion attacks on the sample surfaces.



Weight %						
	O-K	Al-K	Si-K	S-K	Cl-K	Ca-K
N-steel(2)_pt1	16.61	0.24	4.10	0.27	0.17	0.45
	Fe-K					
N-steel(2)_pt1	78.17					

Figure 8: SEM/EDAX analysis on the LPR probe (1020 steel) in nitrogen blanket protection system shows severe corrosion attacks on the sample surfaces.



Weight %			
	Si-K	Mn-K	Fe-K
Vci-steel(1)_pt1	0.52	0.89	98.59

Figure 9: SEM/EDAX analysis on the LPR probe (1020 steel) in 10% inhibitor + 200 ppm Cl ions show no corrosion attack on its surfaces after roughly 4,000 hours of continuous corrosion testing.

CONCLUSIONS

A comprehensive investigation was undertaken to characterize the corrosion behavior of carbon steel using corrosion inhibitors and a nitrogen blanket protection system. Corrosion behavior of steel samples were studied in two different conditions; the first contained 200 ppm chloride solution + 10% corrosion inhibitor addition, the second included 200 ppm chloride solution with a nitrogen blanketing system at 10 psi applied pressure. The corrosion data have demonstrated that corrosion inhibitors have superior advantages over the nitrogen blanketing system in the presence of excessive salt and moisture. On average, the LPR corrosion rate measured less than 0.06 mpy for samples immersed in VCI solution and no sign of corrosion was observed. The immersed and nitrogen blanketed samples, in contrast, showed a corrosion rate of 1.78 mpy and the samples were covered with a thick red rust. ER probes showed a corrosion rate of 0.18 mpy for VCI treated while the nitrogen blanketing samples showed a 2.12 mpy corrosion rate and probes were heavily corroded. It is interesting to report that when VCI was added to the nitrogen blanketing corrosion cell at roughly 3,500 hours of testing, the corrosion rate of the corroded steel probes dropped to less than 0.26 mpy in less than 20 hours. Indicating that the nitrogen blanketing is not able to stop corrosion reaction while, VCI shows a significant reduction in the corrosion rate by more than eight times.

The electrochemical data acquired from corrosion tests showed that VCI inhibitor adsorption to the steel surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption was approximately -10 to -14 kJ/mol that suggests a physical adsorption compound. Cyclic polarization behavior for samples in the vapor phase inhibitors showed a significant shift in the passive film breakdown potential. This increase in the passive film range will improve localized corrosion resistance. While the nitrogen blanketing samples did not show passive film formation.

In summary, the corrosion inhibitors can provide a very effective corrosion protection for steel materials used in storage tanks, both above ground and below, pipe casings, and similar applications. Although, nitrogen blanket protection system in theory can suppress the cathodic reaction and lower the corrosion rate, in reality the amount of moisture and oxygen that is required to initiate the corrosion reaction for steel is extremely low. A nitrogen blanket system can reduce the moisture level, but it won't be enough to prevent corrosion and the steel sample will aggressively corrode. The advantage of the VCI inhibitor is the creation of a strong physisorption to the steel surface that minimizes any surface contact with corrosive species due to its hydrophobic film. Therefore, corrosion inhibitors have superior advantages over the nitrogen blanketing system in the presence of aggressive environments that contain excessive salt, oxygen and moisture.

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