Effectiveness of Vapor Corrosion Inhibitors Compared with Nitrogen Blanketing

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The corrosion behavior of steel samples used for storage tanks and cross casing pipe applications was investigated using two different protection mechanisms: a vapor phase corrosion inhibitor and a nitrogen blanketing system. The objective of this project was to demonstrate which technique provides more protection in corrosive environments, especially where there are restricted geometries such as crevices, threads, notches, and underdeposits.

The corrosion behavior of steel samples was studied under two different conditions. Two probes were placed in an environment comprised of a 200-ppm chloride solution and 10% corrosion inhibitor. Two additional steel probes were placed in an environment consisting of a 200-ppm chloride solution (without a corrosion inhibitor) and a nitrogen blanketing system at 10 psi (69 kPa) applied pressure. The corrosion rate of the steel samples was monitored for ~4,000 h using linear polarization resistance (LPR) and electrical resistance (ER) probe techniques.

The corrosion data demonstrate that vapor phase corrosion inhibitors (VCIs) provide advantages over nitrogen blanketing in the presence of excessive salt and moisture. On average, for samples immersed in and exposed to the VCI solution, the corrosion rate measured <0.06 mpy with no signs of corrosion. The immersed and nitrogen blanketed samples showed a corrosion rate of 1.78 mpy and were covered with a thick red rust. The ER probes showed a corrosion rate of 0.18 mpy for the VCI-treated samples, while the nitrogen blanketed samples showed a 2.12-mpy corrosion rate and the probes were heavily corroded. When a VCI was injected into the nitrogen blanketed corrosion cell, the corrosion rate of the corroded steel probes dropped to <0.26 mpy in <20 h. This significant reduction in the corrosion rate is mainly due to the VCI's strong physisorption to the steel surface that minimizes surface contact with corrosive species.

Storage tank interiors are susceptible to corrosion when exposed to moisture or an aggressive environment. The costs associated with corrosion go far beyond the $350 billion dollars estimated for the year 2000[1] because of plant shutdowns, leaking containers, loss of products and employment, contamination, and hazards to humans and wildlife.

Common methods of protecting equipment from atmospheric attack include coatings, use of corrosion-resistant alloys, sparging, inerting, and blanketing. Gas blankets have been used on storage tanks downstream of other deoxygenation devices to preserve deoxygenated water, and on boilers during downtime to control corrosion. The mechanism for this type of corrosion attack is electrochemical; the electrolyte derives from a thin layer of humidity on the surface of the metal.[2]

An alternative, less expensive protection method that is effective in controlling vapor corrosion, uses VCIs. A VCI is a volatile compound and must be capable of forming a stable bond at the interface of the metal to prevent the penetration of corrosive species.[3-9] VCIs offer protection for storage tank interiors, cased pipes, or metallic structures in general. VCIs are well suited for protection of internal void spaces and exposed surfaces.[9-12] 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 surface.[13-14]

Compared to other methods of corrosion prevention, such as nitrogen blanketing and dehumidification, VCIs provide better corrosion control at a lower cost and require very low dosage rates. For practical purposes, it is preferable to use fewer VCIs that provide long-lasting and durable protection over periods of two to three years. Components and equipment treated with VCIs will have indoor protection up to 24 months without reapplication and roughly six months for outdoor protection.[3-4] The protection is independent of environmental conditions and is effective even in extreme conditions.

Previous research on ASTM A470[15] steel confirms the benefits of using this technology in gas and steam turbines that are susceptible to stress corrosion cracking and crevice corrosion.[10-11] In this study, the addition of a VCI increased the resistance polarization (Rp) values during electrochemical impedance testing as compared to ASTM A470 steel samples tested without an inhibitor. The higher Rp values were attributed to the progressive adsorption of inhibitor molecules and film formation on the metal surface.[10] The corrosion inhibition mechanism was determined to be the physical adsorption of inhibitor molecules to the metal surfaces. Physical adsorption requires energy between –5 to –20 kJ/mol.[13,16] The analysis of the inhibitor showed an enthalpy of adsorption in the range of –14 to –18 kJ/mol.[11] Generally, chemisorption requires more energy and leads to stronger bonding between the molecules and the surface of the substrate, which forms a more stable protective film.[14]

FIGURE 1 The setup for corrosion tests on steel LPR and ER probes using 10% VCI and nitrogen blanketing at 10 psi applied pressure.

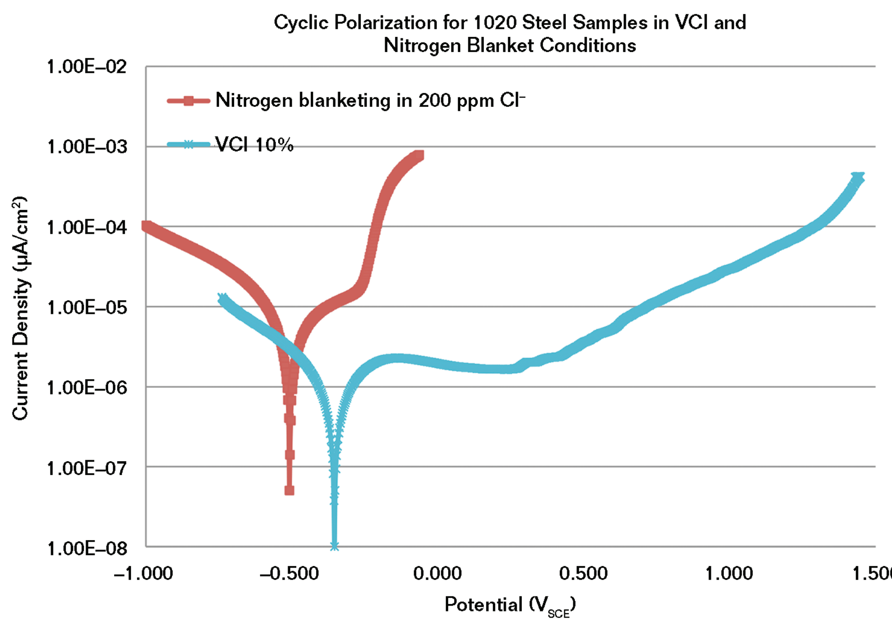


FIGURE 2 Electrochemical polarization behavior of the 1020 steel samples in 10% VCI and nitrogen blanketing in 200-ppm chloride ion solution.

The tank blanketing technique applies an inert gas to the empty space in a storage container. The buffer gas adds pressure and controls the speed of oxidation. Nitrogen is used to either prevent the degradation of food, chemicals, and metallic vessels from atmospheric oxidation and corrosion, or to prevent the possibility of combustion. This is a safe and reliable way to protect food from degrading from oxidation. The presence of nitrogen keeps oxygen levels low. Humid air in the head space is replaced by high-purity, inert, dry nitrogen, which effectively displaces all oxygen from the system and stops corrosion by eliminating the cathodic oxygen reaction.

Experimental Procedure

Corrosion inhibition of a commercially available VCI, VpCI 337,[†] was investigated for 1020 carbon steel (CS) (UNS G10200) commonly used in tank and casing applications. Electrochemical polarization standards per ASTM G61[17] and corrosion rate measurements using LPR and ER techniques were used to evaluate the behavior

[†]Trade name.

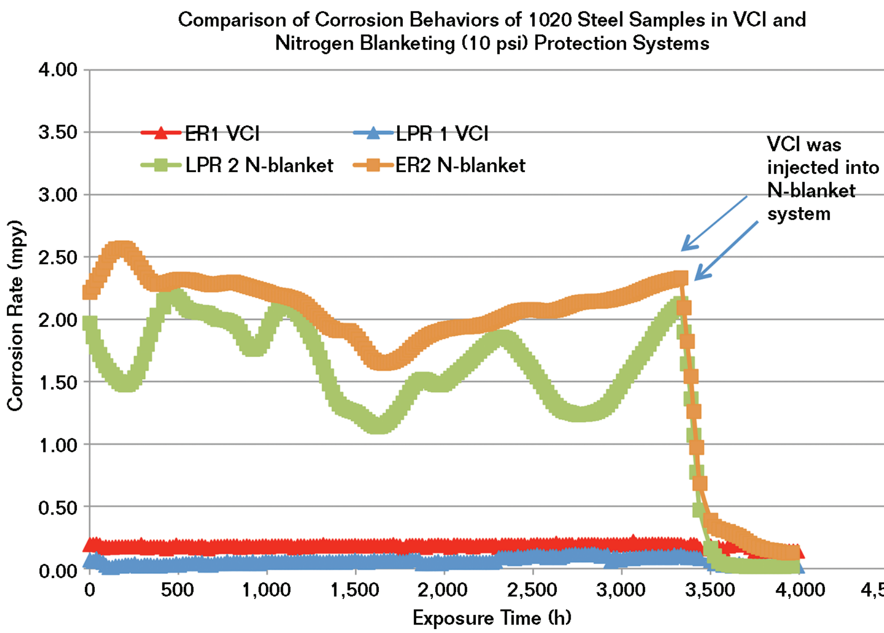


FIGURE 3 Comparison of corrosion on steel probes in a VCI and nitrogen blanketing system.

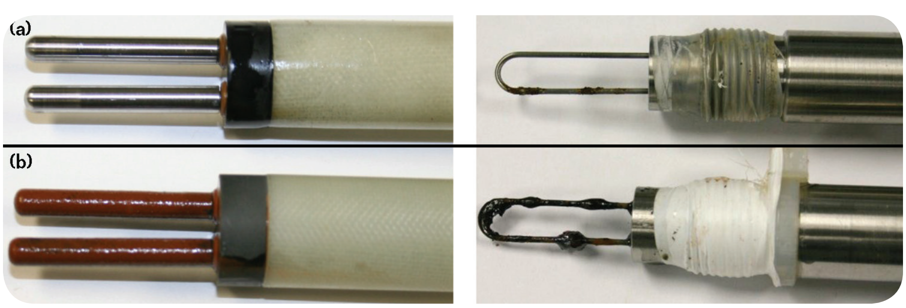


FIGURE 4 Comparison of corrosion damages on both LPR and ER probes (1020 steel) in (a) VCI and (b) nitrogen blanketing system.

of this inhibitor on the steel in a 200-ppm chloride solution and compare it with nitrogen gas blanketing.

A CORRATER 9030 Plus† (corrosion rate measuring instrument) was used to monitor the corrosion rate using LPR techniques, and the Metal Samples MS3500E ER Data Logger† was used to collect corrosion data. Further experiments were conducted using Gamry's PC4/750 Potentiostat/Galvanostat/ZRA† instrumentation and DC105 DC Corrosion Techniques Software†. Samples were polished (600 grit), placed in a flat cell, and tested in deionized water solutions containing 200 ppm Cl^- with 10% VCI. A series of cyclic polarization tests was performed in temperatures ranging from 20 to 60 °C to define the inhibitor surface adsorption mechanism. The Rp value was used to fit the data into adsorption isotherm models.

Figure 1 shows the test setup for steel probes in 10% VCI and a nitrogen blanketing system at 10 psi applied pressure (without a corrosion inhibitor). In each case, one probe was immersed in the solution and the ER probes were suspended above the solution. The corrosion rate measuring instrument was used to monitor the corrosion rate for the 1020 steel LPR Probe #2 with 10% VCI and LPR Probe #1 with the nitrogen blanket. The data logger measured the corrosion rate for one 1020 steel ER probe in 10% VCI and another probe in the nitrogen blanketing system. The corrosion rate for the samples was monitored continuously for roughly 4,000 h (5.5 months). Samples were visually inspected and scanning electron microscopy/energy dispersive x-ray (SEM/EDAX) analysis was conducted using a JEOL JSM-6480LV† and Thermo Scientific NORAN System 7 X-ray Microanalysis System†.

†Trade name.

Experimental Results

Cyclic Polarization Behavior

Figure 2 shows the polarization behavior for 1020 steel in 10% 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, and had beneficial consequences for reducing localized corrosion damages. The extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, yields a more stable passive film, and shifts the critical pitting potential to higher levels.

Adhesion of corrosion inhibitors can be modeled using an adsorption isotherm, which is a mathematical function relating the surface coverage of a chemical to the concentration of the chemical. The corrosion current density is representative of the number of corrosion sites. In recent years, electrochemical and weight loss methods have been used to study adsorption and the corrosion inhibition of various materials.[13-14,16] Each adsorption isotherm explains a different type of relationship between concentration and surface coverage of an inhibitor.[13-14]

Corrosion Rate Results (LPR and ER)

Figure 3 shows the corrosion rate results after monitoring with LPR and ER techniques for nearly six months. It is clear that the steel experienced a higher corrosion rate when using only a nitrogen blanketing system (average of 1.8 mpy) compared to an average corrosion rate of 0.04 mpy for probes protected with 10% VCI. After roughly 4,000 h, 10% VCI was added to the nitrogen blanket environment and the corrosion rate for both LPR and ER probes dropped significantly (Figure 3).

Figure 4 shows the surface of the steel probes. The difference in degree of protection offered by the VCI and a nitrogen blanketing system is evident. The steel probes in the VCI show no rust formation. The nitrogen blanket-protected steel probes were covered with thick red rust.

Figure 5(a) shows the SEM micrographs for the LPR 1020 steel probe from the nitrogen blanketing system, which indicate severe corrosion attack on the sample. Figure 5(b) shows SEM micrographs for the LPR 1020 steel probe protected by the VCI, which has a clean, corrosion-free surface. Figure 6 shows the SEM/EDAX analysis on the LPR nitrogen blanketed probe; its surface chemistry contains multiple corrosive species and severe corrosion. The SEM/EDAX analysis on the LPR probe in 10% VCI and 200 ppm Cl ions, also shown in Figure 6, indicates no corrosion attack on its surfaces after roughly 4,000 h of continuous corrosion testing.

Conclusions

A comprehensive investigation was undertaken to characterize the corrosion behavior of CS in VCIs and in a nitrogen blanketing system. The first contained 200 ppm chloride solution and 10% corrosion inhibitor; the second included 200 ppm chloride solution with a nitrogen blanketing system at 10 psi applied pressure. The corrosion data have demonstrated that the VCI has superior advantages over the nitrogen blanketing system in the presence of excessive salt and moisture. The VCI corrosion rate measured <0.06 mpy and no sign of corrosion was observed. The immersed and nitrogen blanketed samples showed a corrosion rate of 1.78 mpy and the samples were covered with a thick red rust.

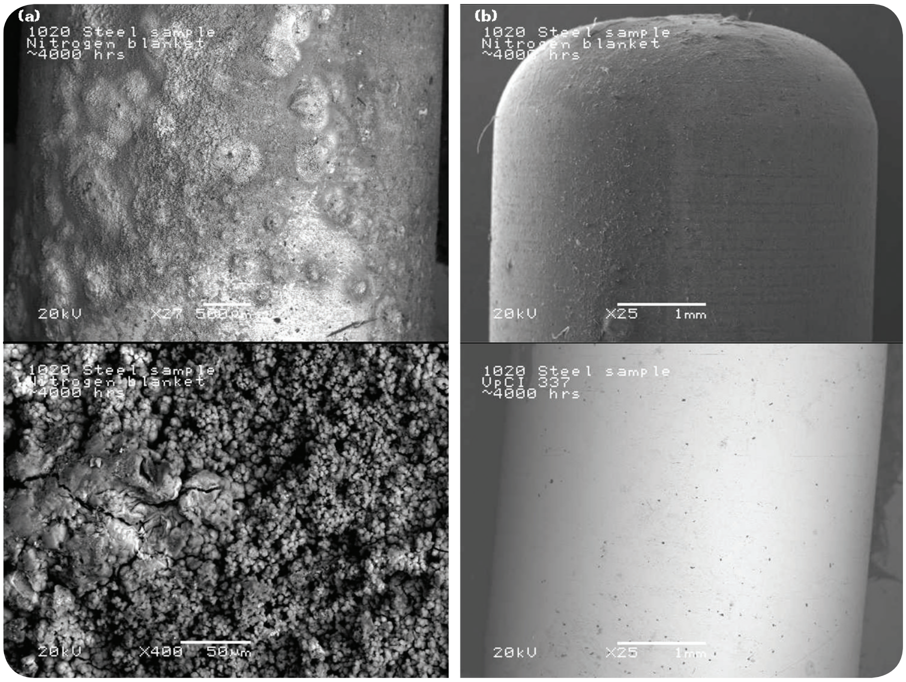
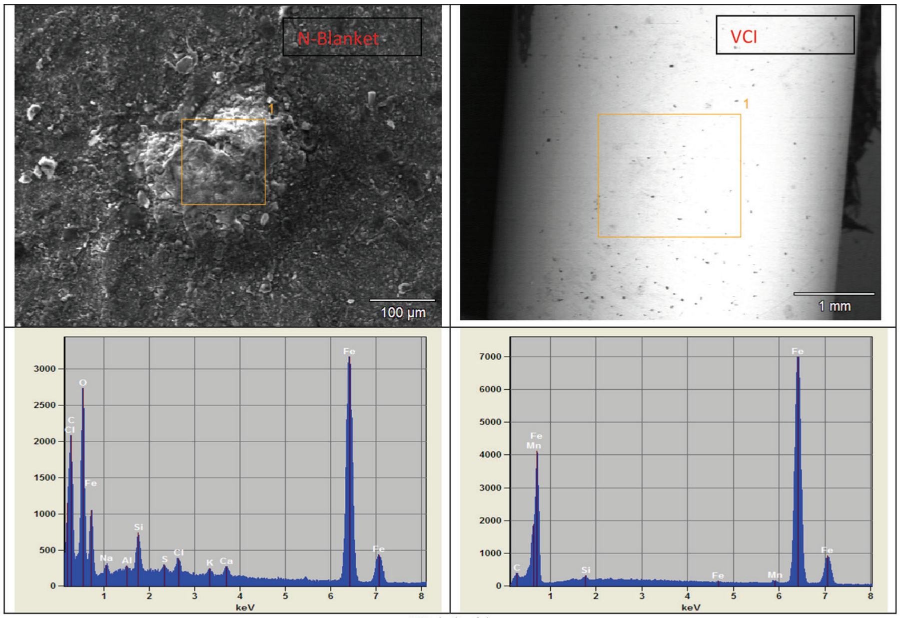


FIGURE 5 SEM micrographs of the LPR probes (1020 steel) (a) in a nitrogen blanketing system and (b) VCI and nitrogen blanket.



Weight %

	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Fe-K
N-steel_pt1	18.62	2.92	0.39	3.29	0.60	1.41	0.66	1.13	70.97

	C-K	Si-K	Mn-K	Fe-K
VCI-steel_pt1	8.38	0.47	0.89	90.26

FIGURE 6 SEM/EDAX analysis on the LPR probe (1020 steel) in a nitrogen blanketing system shows severe corrosion attacks on the sample surfaces. Samples in 10% VCI and 200 ppm Cl ions show no corrosion attack after roughly 4,000 h of continuous corrosion testing.

VCIs provide effective corrosion protection for steel materials used in storage tanks, pipe casings, and similar applications. A nitrogen blanketing system can reduce the moisture level, but it won't prevent corrosion and the steel will aggressively corrode.

Acknowledgment

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