

## Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitors and Dry Air System

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*The corrosion behavior of carbon and galvanized steel samples was investigated in two test environments containing 200 ppm chloride solution. The first set up used 10% inhibitor, while the second used dry air to maintain moisture levels below 40% relative humidity at 20 psi (0.14 MPa) applied pressure. The corrosion rates of the exposed samples were monitored for more than six months (roughly 4,464 h) using electrical resistance (ER) probe techniques. The data demonstrated that the inhibitor provided superior corrosion protection for the steel samples. The samples in the dry air system suffered corrosion attack and red rust formation after 21 days. The ER probes showed a corrosion rate of less than 0.08 mpy with inhibitor, while the dry air samples showed, worst case, a 1.6 mpy (2.03  $\mu\text{m}/\text{y}$ ) corrosion rate and ER probes were heavily corroded.*

**Over the past 20 years, various corrosion protection systems have been implemented to improve structural longevity. These implementations have been worldwide, as corro-**

sion concerns affect all industrialized countries, including Japan (with the Innoshima, Ohnaruto, and Akashi-Kaikyo Bridges),<sup>1</sup> Denmark (the Danish Faroe, Great Belt, and Little Belt Bridges), Sweden (Högakusten Bridge),<sup>1,2</sup> South Wales (Severn Bridge),<sup>3</sup> France (Aquitane Bridge), China (Rung Yang Bridge), and the Middle East (Qatar Lusail Bridges).<sup>2</sup> In the United States, there are numerous complications regarding infrastructure, military equipment and aging aircraft due to atmospheric corrosion.

On several of the bridges in Japan, high-strength cables (typically steel that has been hot dip galvanized in zinc) were suffering from advanced states of corrosion (cracking and swelling) due to inadequate paint coatings and high levels of humidity.<sup>1</sup> The common element in all of the “fixes” or improvements made to subsequent bridge construction was the addition of dry air; that is, the use of a dehumidification system. This was either a retrofit or part of the new construction. Two countries, Norway (Halogaland and Hardanger Bridges) and Japan, have required dehumidification systems in all bridge construction since 2009.<sup>2</sup>

It has been estimated that between \$2 trillion and \$4 trillion are lost to corrosion each decade.<sup>4</sup> In atmospheric corrosion, a material is subjected to air moisture and corrosive species (pollutants).<sup>5</sup> Corrosion, the natural degradation of materials due to interactions with the environment, can be uniform or localized. The vast majority of natural degradation, however, is uniform, and atmospheric corrosion is probably the

most prevalent type.<sup>6</sup> Atmospheric corrosion is generally a serious risk to metals that are exposed to the environment. The U.S. Government reports that corrosion damage for military defense exceeds \$20 billion per year.<sup>7</sup> Preservation and mothballing equipment during short-term or long-term storage is extremely important to maintain access and military preparedness.

Common techniques used to reduce humidity or isolate the metal from moisture, including physical barriers such as paints and lubricants, will lessen the corrosion rate significantly. Concern for the environment and desire to minimize use of hazardous chemicals has led to system modernization and the development of new technologies for barrier coatings. An alternative approach, controlled humidity protection, focuses on the air moisture, specifically relative humidity (RH). Elimination of moisture is critical for suppressing the corrosion rate in atmospheric corrosion. By extracting moisture from the air, RH can be reduced to a level where surface wetness cannot form.<sup>8</sup> The processed dry air is then recirculated around the equipment. Dehumidification is effective—it has been determined that steel is much less likely to corrode in environments with less than 40% humidity.<sup>2,5</sup> Reducing the temperature does not always help and reducing the pollutant concentration is not always achievable.

Controlled humidity protection (CHP) has been extensively evaluated and is applied by many nations as a maintenance technology for operational weapon systems. Within the Department of Defense

(DoD), the Army National Guard is a proponent of applying CHP to its weapon systems. Independent studies and analyses performed by the DoD Inspector General and Army Cost and Economic Analysis Center validated the significant benefits achieved with controlled humidity protection.<sup>8</sup> Many foreign defense forces currently use CHP as a maintenance technology for their operational weapon systems.

An industry analysis of 11 European defense forces<sup>2,9</sup> revealed that the majority have instituted CHP technology in both operational and longer-term applications. The tangible benefits of CHP as a maintenance technology can include reduced ownership costs for weapon systems and equipment, and increased readiness and sustainability.<sup>8</sup> Despite positive data, localized corrosion attacks have been reported for this method of corrosion protection. When a system is breached and pollutants or contamination enter the dry air system, localized corrosion can occur.

Atmospheric corrosion is an electrochemical process initiated by a thin layer of moisture on the metal surface. The composition of the electrolyte depends on the deposition rates of the air pollutants and varies with the wetting conditions.<sup>10</sup> Corrosion severity is affected by humidity, pollutants, and temperature.<sup>6</sup> Humidity is a necessary component for corrosion to occur, but it is not the only factor. Even in very humid environments, corrosion of uncontaminated surfaces is often relatively low.

Pollutants or other atmospheric contaminants increase atmospheric corrosion by enhancing the electrolytic properties and stability of water films that condense from the atmosphere. Sulfur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), Cl<sup>-</sup>, and F<sup>-</sup> are common industrial pollutants. The corrosion rate will increase if the pollutants react with the surface water to create a low pH environment (acidification) and compromise the protective oxide film on the metal surface.<sup>5</sup> Other causes are formation of hygroscopic films (water absorption without formation of bonds) as a result of corrosive byproducts and precipitation of salt particles. They

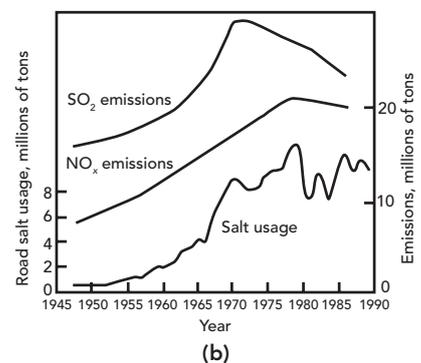
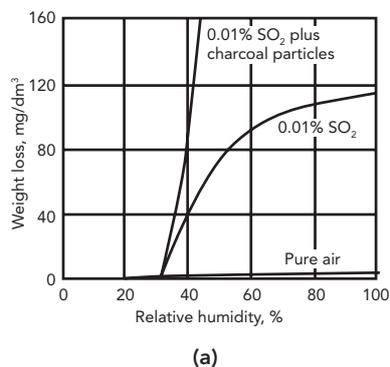


FIGURE 1. Custom ER probe for casings.



FIGURE 2. Test setup for the controlled humidity corrosion tests on UNS G102000 steel and galvanized steel samples. ER probes were in environments with 10% VCI or nitrogen blanketing at 10 psi applied pressure.

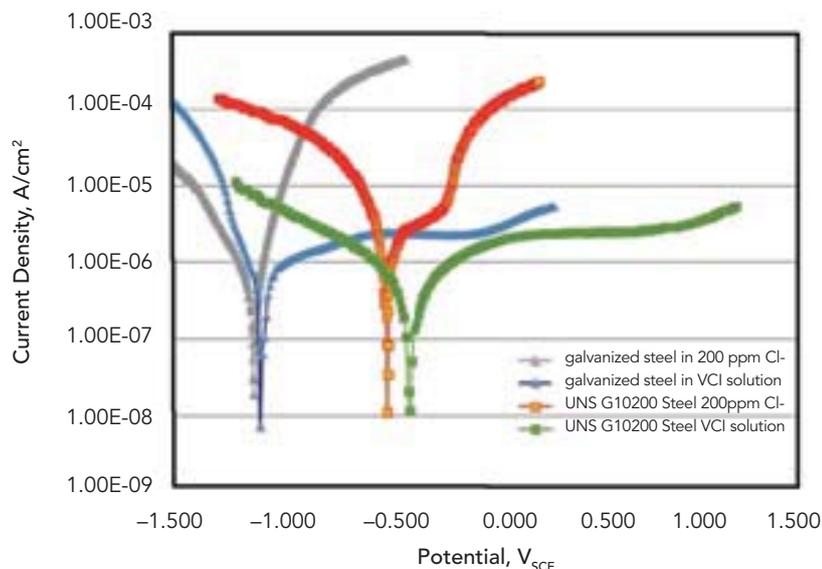
reduce the relative humidity necessary to cause water condensation and enhance the presence of a water film that increases the time of wetness and the consequent extent of corrosion. Only when the relative humidity is below a critical value for existing contaminants, will the film formation be suppressed and corrosion minimized.

In Figure 1(a), the effect of 0.01% SO<sub>2</sub> on the corrosion rate (weight loss of steel) as compared to pure air can be seen. RH seems to be less significant than the air quality. Despite 100% RH, the graph shows no increase in weight loss (rusting of iron) if pollutants are not present.<sup>10</sup> Figure 1(b) shows road salt usage for the United States in millions of tons, the point being there is no shortage of atmospheric pollutants to exacerbate corrosion.

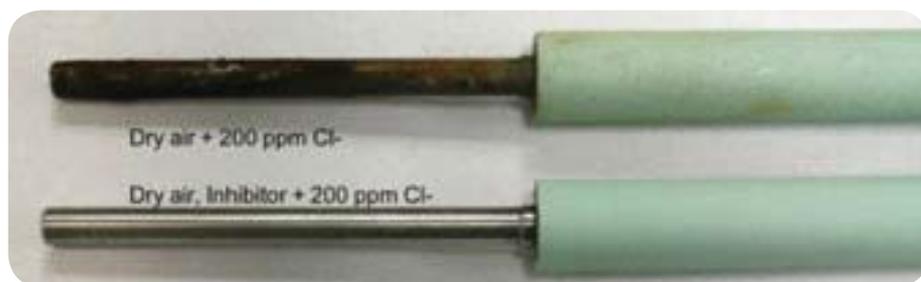
Vapor phase corrosion inhibitors (VCIs) are an alternative protection method that is both effective at controlling corrosion and inexpensive. A VCI is a volatile compound and must form a stable bond at the interface of the metal, preventing penetration of corrosive species.<sup>11-16</sup> VCIs offer an alternative way to protect stored equipment, facilities, and their contents. These inhibitors are

easy to apply, versatile, and can be used to protect multiple metal types in a variety of industries. 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.<sup>17-18</sup> Compared to other methods of corrosion prevention such as inert gas blanketing and dehumidification, VCIs provide substantially better corrosion control at lower cost and require a very low dosage rate. Controlled humidity protection in combination with VCI injection has recently been used to control the corrosion in main cables on suspension bridges, where traditional methods have been unable to adequately protect them.<sup>3</sup>

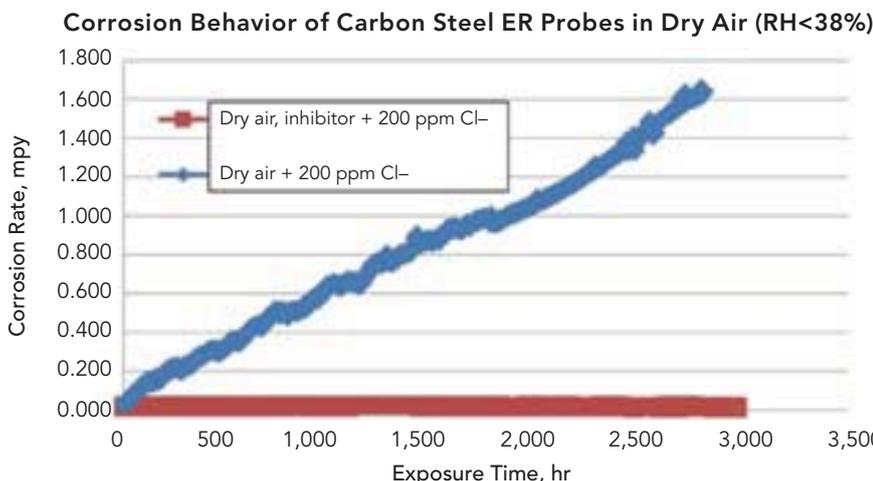
The inhibitors are water-based and ideal for equipment with complex geometries such as boilers, heat recovery steam generators, and pressure vessels, for mothballing, and short-term storage applications. This method can also minimize corrosion attack where there are restricted geometries, notches, crevices, underdeposits, and laps. VCI forms a solution in water and when applied by spraying or dipping, will protect ferrous and nonferrous



**FIGURE 3.** Electrochemical polarization behavior of the UNS G10200 steel samples in 10% VCI and dry air in 200 ppm chloride ion solution.



**FIGURE 4.** ER probes after 4,464 h exposure; top probe exposed to dry air, lower probe protected with inhibitor.



**FIGURE 5.** Comparison of corrosion on steel probes in VCI and dry air protection system. There is a much lower corrosion rate for steel samples protected by VCI (average corrosion rate of 0.04 to 0.08 mpy), while dry air system resulted in increasing attack with corrosion rate as high as 1.6 mpy.

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 (6.35  $\mu\text{m}$ ) thick on the surface that is stable up to 350 °F (176 °C).<sup>11</sup>

Adsorption of the inhibitor onto 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 prac-

tical. The inhibitor is transmitted by vapor that is controlled by the crystal lattice structure and atomic bond characteristics of the molecule.<sup>14-15</sup> 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 byproducts. Furthermore, the product is biodegradable and non-flammable unlike some of the earlier chemicals tested in the 1940s and 1950s like dicyclohexyl ammonium nitrite, ammonium nitrite, urea, and acetamide.<sup>19</sup>

The corrosion inhibition mechanism was determined to be the physical adsorption of inhibitor molecules to the metal surfaces.<sup>20-21</sup> Physical adsorption requires energy between -5 to -20 kJ/mol.<sup>13-14</sup> The analysis of the inhibitor showed an enthalpy of adsorption in the range of -14 to -18 kJ/mol.<sup>20-21</sup> Generally, chemisorption requires more energy and results in stronger bonding between the molecules and the surface of the substrate, which forms a more stable protective film.<sup>18</sup> The majority of corrosion damage to turbo-machinery systems, however, occurs during the shutdown period due to chemistry changes and stagnant conditions 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.

## Experimental Procedure

Corrosion behavior of carbon steel (CS) and galvanized steel samples were studied in two different controlled humidity protection conditions; the first environment contained 200 ppm chloride solution plus 10% inhibitor (VCI), and the second test environment included 200 ppm chloride solution (injected into the environment every 48 h) with a constant flow of dry air at less than 40% RH and 20 psi (0.14 MPa) applied pressure. The corrosion rates of the exposed samples were monitored for more than six months (roughly 4,464 h) using electrical resistance (ER) probe techniques. RH and temperature of each test chamber were monitored by the Sensirion<sup>†</sup> sensors

and data logging software. The temperature sensor and the humidity sensor form a single unit. This enables an accurate and precise determination of the dew point, without incurring errors due to temperature gradients between the humidity and the temperature sensors. The sensor elements are integrated with a signal amplifier unit, an analog-to-digital converter, and a calibration data memory, yet the device is only a few square millimeters in size.

Electrochemical polarization standards per ASTM G61<sup>22</sup> and corrosion rate measurements using ER techniques were used to evaluate the behavior of this inhibitor on the steel alloy in 200 ppm chloride solution and to compare with a dry air system. Corrosion data were collected using the Metal Samples MS3500E<sup>†</sup> electrical resistance probe system, a remote data logger capable of measuring and storing data. Further experiments were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA<sup>†</sup> instrumentation and DC105<sup>†</sup> corrosion test software. Samples were polished (600 grit), placed in a flat cell, and tested in deionized water solutions containing 200 ppm Cl<sup>-</sup> with 10% VCI.

The corrosion test setup for the metal samples is shown in Figure 2. In each case, the ER probes were installed in the chamber. The electrical resistance probe equipment measured the corrosion rate for a UNS G10200 steel probe using 10% VCI and another probe for the dry air system. The corrosion rates for the samples were monitored continuously for roughly 4,464 h (6 months). Samples were visually inspected on a daily basis, and their surface conditions were documented on a monthly basis. Samples were visually inspected and scanning electron microscopy (SEM)/energy dispersive x-ray analysis (EDXA) were conducted using a JEOL JSM-6480LV<sup>†</sup> and Thermo System Seven detector<sup>†</sup>.

## Results

### Cyclic Polarization Behavior

Figure 3 shows the polarization behavior for UNS G10200 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 pas-

<sup>†</sup>Trade name.



**FIGURE 6.** Comparison of UNS G10200 steel samples protected with inhibitor (left) and exposed to dry air (right) for 96 days.



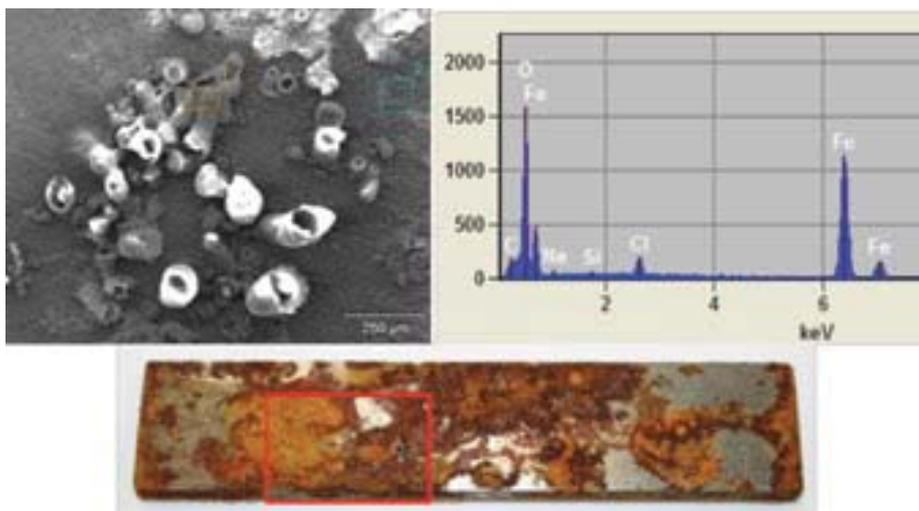
**FIGURE 7.** Comparison of UNS G10200 steel samples after 155 days: (left) inhibitor still providing protection, (right) samples exposed to dry air in test chamber.



**FIGURE 8.** Comparison of exposed galvanized steel samples for dry air and VCI test chamber after 155 days; (a) white rust formation is seen on dry air samples, while (b) VCI exposed samples were corrosion-free.

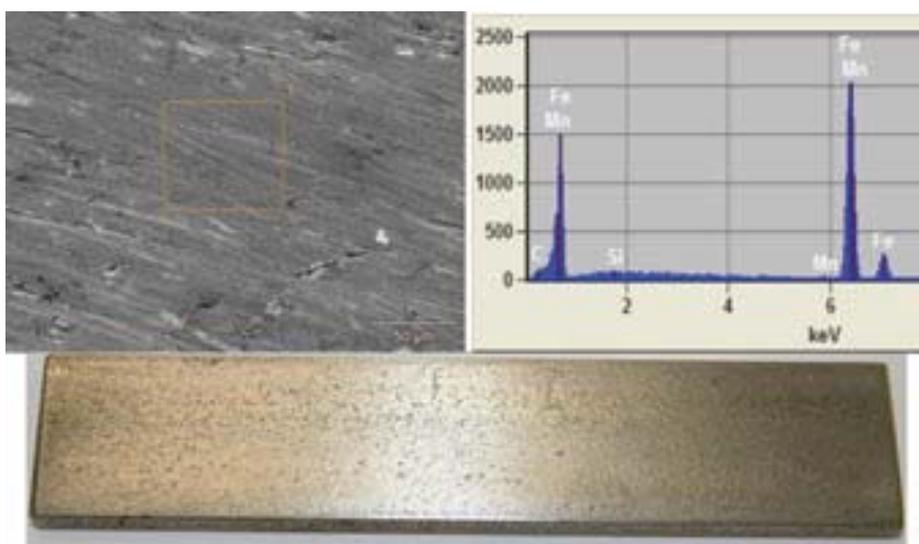
sive range for these alloys in the VCI. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and had beneficial consequences for reducing localized corrosion

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



	Weight%				
	C-K	O-K	Na-K	Cl-K	Fe-K
Steel dry air (1)_pt1	5.35	30.01	1.77	0.24	62.63
Steel dry air (1)_pt2	6.04	26.35	1.69	0.43	65.50

**FIGURE 9.** SEM/EDXA on the steel sample in dry air test chamber after 186 days, showing severe rust formation.



	Weight%			
	C-K	Si-K	Mn-K	Fe-K
Steel dry vci(1)_pt1	4.40	0.40	0.57	94.63

**FIGURE 10.** SEM/EDXA on the steel sample in dry air plus VCI test chamber after 186 days, showing a corrosion-free surface.

film, and shift of the critical pitting potential to higher levels.

Figure 4 shows the ER probes after 4,464 h exposure in both environments. The ER probe protected by 10% inhibitor (bottom probe) shows no corrosion damage. Corrosion rates for the probes can be seen in Figure 5. The results show that the dry air

system is unable to protect the steel against corrosion. Figures 6 through 8 show the progression of corrosion damage to the metal surface over time.

Figures 9 through 11 show the SEM/EDXA results for the steel and galvanized steel samples. The dry air system showed severe corrosion products (chloride rich)

while the presence of inhibitor suppressed the formation of corrosion products on the steel surface. Similar results were observed for the galvanized steel sample exposed to dry air only and dry air with inhibitor. The morphology of the corrosion products are identical to atmospheric corrosion of CS and galvanized steel. These observations demonstrate that the addition of inhibitor is critical for protecting the steel structures.

## Conclusions

The corrosion test results have demonstrated that corrosion inhibitors have superior advantages over the dry air system. Samples that were exposed to dry air showed corrosion attack and red rust formation after 21 days of exposure. ER probes showed a corrosion rate of 0.04 to 0.08 mpy for VCI-treated samples while the dry air samples showed a 1.3 to 1.6 mpy corrosion rate and ER probes were heavily corroded. The dry air exposed samples showed an increasing trend, indicating inability of controlled humidity protection to retard corrosion once the corrosion reaction had started. Test results showed that a dry air system is not an effective method to retard corrosion.

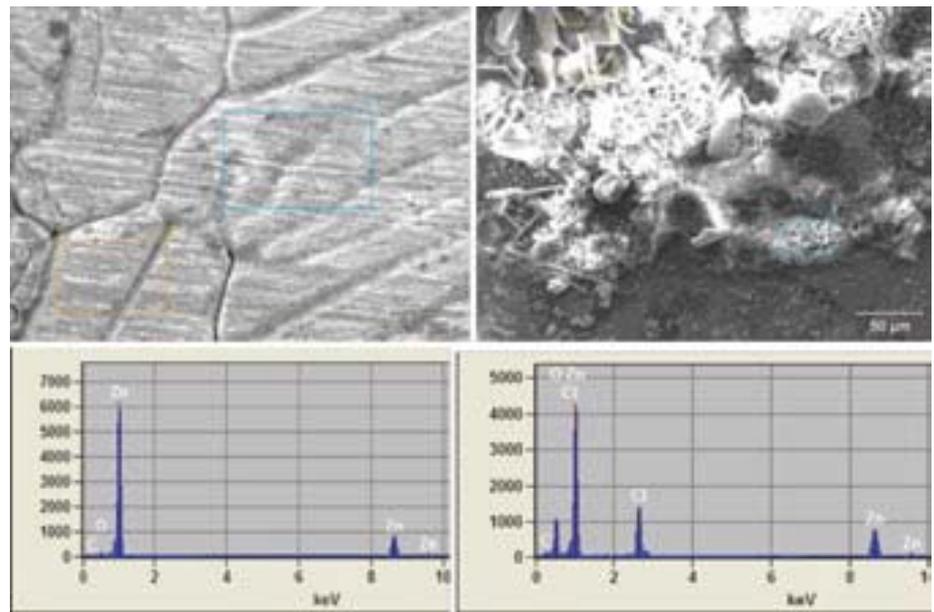
Electrochemical polarization behavior showed the addition of VCI to the environment expands the region of stability of the passive film. The passive film breakdown potential for VCI-treated steel samples increased by nearly 1.0 V, indicating less susceptibility to localized corrosion.

In summary, the VCIs provide effective corrosion protection for steel materials exposed to the environment for short-term storage. Although controlled humidity protection systems, 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 still extremely low. A dry air-controlled humidity system can reduce the moisture level, but it won't be enough to prevent corrosion and the steel sample will corrode. Furthermore, once corrosion begins, the dry air system cannot retard the accelerating corrosion reaction. The advantage of the VCI 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, VCIs have superior advan-

tages over the dry air or gas blanketing system in the presence of aggressive environments that contain excessive salt, oxygen, and moisture.

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	Weight%			
	C-K	O-K	Cl-K	Zn-K
gal dry(2)_pt1	4.05	20.07	13.61	62.27
gal vci(2)_pt2	10.28	3.12		86.59

**FIGURE 11.** SEM/EDXA on the galvanized steel samples in dry air with and without VCI addition after 186 days, showing only white rust formation on dry air without VCI addition.

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