

Improving the Controlled Humidity Protection Systems by Addition of Vapor Phase Corrosion Inhibitors

Behzad Bavarian
Dept. of MSEM
California State University,
Northridge, USA 91330

Yashar Ikder
Dept. of MSEM
California State University,
Northridge, USA 91330

Babak Samimi
Dept. of MSEM
California State University,
Northridge, USA 91330

Lisa Reiner
Dept. of MSEM
California State University,
Northridge, USA 91330

Boris Miksic
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

ABSTRACT

Controlled Humidity Protection (CHP) reduces corrosion created by exposing items to high relative humidity (exceeding 40%). 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 in presence of corrosive species like chloride that is required to initiate the corrosion reaction for steel is extremely low, and once corrosion reaction starts there is no defense mechanism to stop it. Addition of the vapor phase corrosion inhibitors to the CHP provide a more effective corrosion protection for materials exposed to the environment during short term storage. A dry air controlled humidity system can reduce the moisture level, but it will not be able to prevent corrosion. The advantage of the vapor phase corrosion inhibitor addition to CHP system is the creation of a strong physisorption to the material surface that minimizes any surface contact with corrosive species or water due to its hydrophobic film. Therefore, vapor phase corrosion inhibitors addition can provide superior advantages over the controlled humidity protection system in the presence of aggressive environments that contain excessive salt, oxygen and moisture.

Key words: atmospheric corrosion, corrosion inhibitor, Controlled humidity protection, Vapor phase corrosion inhibitors, adsorption model

INTRODUCTION

Trillions of dollars are lost to corrosion each decade¹. The vast majority of natural degradation to materials is classified as uniform corrosion with atmospheric corrosion being the most prevalent type². In atmospheric corrosion, a material that is subjected to air moisture and pollutants is at serious risk³. The U.S. Government reports that corrosion damage for military defense exceeds \$20 billion per year⁴. Preservation and mothballing equipment during storage is extremely important in maintaining military preparedness. The Department of Defense has an enormous amount of equipment and facilities that are susceptible to corrosion. Military forces operate worldwide where corrosion related effects including humidity, fluctuating temperature, salt spray and harsh desert environments can attack the surface of materials reducing availability and deteriorating performance. DoD corrosion related maintenance costs are estimated at \$23 billion each year⁵.

Atmospheric corrosion is an electrochemical process initiated by a thin layer of moisture on the metal surface. The electrolyte composition depends on the deposition rates of the air pollutants and varies with the wetting conditions⁶. Corrosion severity is affected by humidity, pollutants and temperature². 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. Reducing the temperature does not always help and reducing the pollutant concentration is not always achievable. Salts (chlorides) and acids (sulfurs) promote condensation by affecting vapor pressure, which leads to an increased corrosion. Similarly, the nitrogen and sulfur compounds discharged by some industries can form acids, accelerating the corrosion process. Sulfur dioxide (SO₂), a gaseous pollutant in the atmosphere resulting predominantly from the combustion of most fossil fuels, contributes to atmospheric corrosion of most metals. Clean iron in pure air does not corrode until the air is nearly saturated. Relative humidity seems to be less significant than the air quality. The corrosion rate will increase if the pollutants react with the surface water to create a low pH environment and compromise the protective oxide film on the metal surface³. They 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.

Common techniques used to reduce humidity or isolate the metal from moisture include physical barriers, such as paints and lubricants. System modification and new barrier coatings have been developed out of concern for the environment and desire to avoid hazardous chemicals. An alternative approach, controlled humidity protection, focuses on the air moisture, specifically relative humidity (RH). RH is the amount of moisture in the air, as compared to the amount of moisture it can hold at a given temperature. 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 form⁷.

Dry air is recirculated around the equipment to prevent oxidation. It has been determined that steel is much less likely to corrode in environments with less than 40% humidity^{3,6,8}.

Controlled Humidity Protection (CHP) has been extensively evaluated and is applied by many nations as a maintenance technology for operational weapon systems. Independent studies and analyses performed by DoD Inspector General and Army Cost and Economic Analysis Center validated the significant benefits achieved with controlled humidity protection⁷. Many foreign defense forces (Royal Netherlands Air Force and Royal Air Force) currently use CHP as a maintenance technology for their operational weapon systems. An industry analysis of eleven European defense forces^{8, 9} showed that the majority have instituted CHP technology in both operational and longer term applications.

The U.S. Army relies on dehumidification systems, special covers, composite materials and galvanizing techniques to combat the damaging effects. Dehumidification systems are used inside military vehicles and aircraft to reduce damage to electronics engines, radar and avionics, at the naval base in Kuwait for the protection of Army watercraft and inside storage facilities. Typically the dehumidification units are used in conjunction with other preventative measures and require portable systems with hoses and fittings that can be connected and disconnected quickly. Despite positive data for dehumidification systems, localized corrosion attacks have been reported. When a system is breached and pollutants or contamination enter the dry air system, localized corrosion can occur.

For several decades, various corrosion protection systems have been implemented to improve structural longevity. Japan (with the Innoshima, Ohnaruto and Akashi-Kaikyo Bridges)¹⁰, Denmark (the Danish Faroe, Great Belt and Little Belt Bridges), Sweden (Högakusten Bridge)^{8,10} and South Wales (Severn Bridge)¹¹ have been studied to assess these corrosion concerns. Several of the bridges in Japan with high strength cables (typically steel that has been hot dip galvanized in zinc) suffered advanced states of corrosion (cracking and swelling) due to inadequate paint coatings and high levels of humidity¹⁰. Subsequent bridge construction required the use of a dehumidification system to force dry air in and limit moisture. Two countries, Norway (Hálogaland and Hardanger Bridges) and Japan have required dehumidification systems in all bridge construction since 2009⁸.

Vapor phase corrosion inhibitors (VCIs) offer an alternative way to protect stored equipment, facilities and their contents. A vapor phase corrosion inhibitor is a volatile compound and forms a stable bond at the interface of the metal, preventing penetration of corrosive species¹²⁻¹⁷. These inhibitors are easy to apply, effective at controlling corrosion and can be used to protect multiple metal types in a variety of industries. The VCI substance (whether applied to paper, film or foam supports, in a powder, spray or oil formulation) transforms to a gas phase and deposits a film onto the metal surfaces. This transformation is independent of temperature or humidity levels. These materials have stable passivating properties, strong tendencies toward surface adsorption (stronger than the water molecules), and the ability to form a comparatively strong and stable bond with the metal surface¹⁸⁻¹⁹. Compared to other methods of corrosion prevention such as nitrogen gas blanketing and dehumidification systems, inhibitors (VCI) provide substantially better corrosion control at lower cost and require 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 protect¹¹. 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 attacks where there are restricted geometries, notches, crevices, under deposits and laps. VCI forms a solution in water and when applied by spraying or dipping, will protect

ferrous and nonferrous metals, including castings and structural steel. VCI has excellent wetting properties and forms a clear, dry, hydrophobic film of roughly 6.35 micron thick on the surface that is stable up to 176°C¹². 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. 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. The VCI organic chemistry is free of hazardous amines, nitrites and phosphate ester. There are no hazardous decomposition products. Furthermore, it is biodegradable and non-flammable²⁰.

The corrosion inhibition mechanism for VCI was determined to be the physical adsorption of inhibitor molecules to the metal surfaces^{18, 21-22}. Physical adsorption requires energy between -5 and -20 kJ/mol¹⁴⁻¹⁵. The analysis of the inhibitor showed an enthalpy of adsorption in the range of -14 to -18 kJ/mol²⁰⁻²¹. 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.

EXPERIMENTAL PROCEDURE

Corrosion behavior of carbon steel and galvanized steel samples were studied in two different controlled humidity protection conditions; the first environment contained 200 ppm chloride solution + 10% inhibitor (VCI, commercially available vapor phase corrosion inhibitor), the second test environment included 200 ppm chloride solution (injected into the environment every 48 hours) with a constant flow of dry air at less than 40% RH and 20 psi applied pressure. The corrosion rate of the exposed samples were monitored for more than six months (roughly 4,464 hours) using electrical resistance (ER) probe techniques. Relative humidity and the temperature of each test chamber were monitored by (Sensirion)[†] sensors and data logging software. The temperature sensor and the humidity sensor form a single unit that 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^{23†} and corrosion rate measurements from electrical resistance (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. A Metal Samples MS3500E electrical resistance probe system[†] with a remote data logger was used to collect and store corrosion data. Further experiments were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA[†] instrumentation and DC105 corrosion test software. Samples

[†] Trade name

[†] ASTM G61, ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

were polished (600 grit), placed in a flat cell and tested in deionized water solutions containing 200 ppm Cl⁻ and 10% VCI inhibitor.

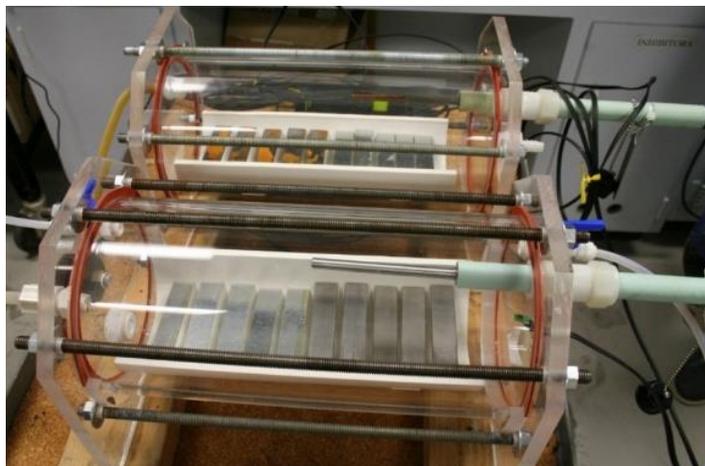


Figure 1: Test chambers for the controlled humidity evaluation of UNS G10200 carbon steel and galvanized steel samples. Both chambers were controlled with dry air at 20 psi applied pressure.

The corrosion test setup for the metal samples is shown in Figure 1. 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 rate for the samples was monitored continuously for 4,464 hours (roughly 6 months). Samples were visually inspected on a daily basis, and their surface conditions were documented on a monthly basis. SEM/EDAX analysis was conducted using a JEOL JSM-6480LV and Thermo System Seven detector[†].

RESULTS

Figure 2 shows the ER probes after 4,464 hours exposure in both environments. The ER probe protected by 10% inhibitor (bottom probe) shows no corrosion damage. The results show that the dry air system is unable to protect the steel against corrosion. Figures 3-4 show the progression of corrosion damage to the metal surface over time. Corrosion rate for the probes can be seen in Figure 5. The morphology of the corrosion products are identical to atmospheric corrosion of carbon steel and galvanized steel. The adsorption isotherm relationship between surface coverage and temperature for VCI Inhibitor on the surface of steel is shown in Figure 6. Adsorption Energy is roughly -14 kJ/mol, indicative of a strong physical adsorption to the metal surface. XPS depth profiling analysis showed ~ 90-100 nm of adsorbed inhibitor on the exposed samples, indicating that multi-layer Brunauer Emmett Teller Model (BET Model) is more realistic adsorption model than the monolayer Langmuir model for this case. These observations reinforce that the addition of inhibitor that forms multi-layer molecules is more capable for protecting the steel structures.

[†] Trade name

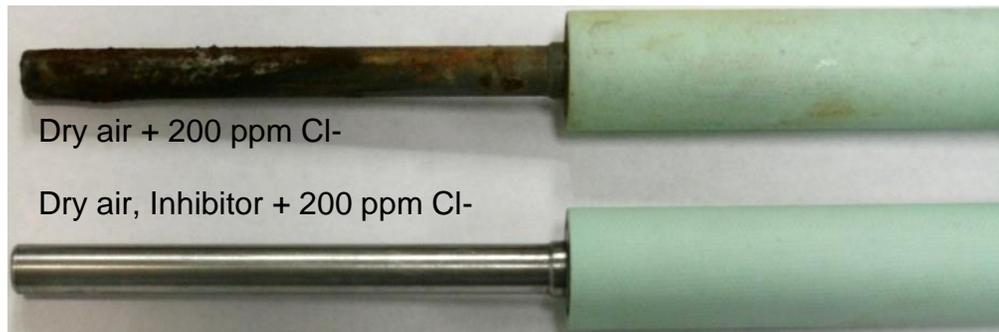


Figure 2: ER probes after six months exposure; top probe placed in dry air system, lower probe protected with inhibitor.



Figure 3: Comparison of UNS G10200 steel samples after 186 days (4,464 hours): (left) inhibitor still protects metal surface; (right) samples have significant corrosion when using dry air protection method.

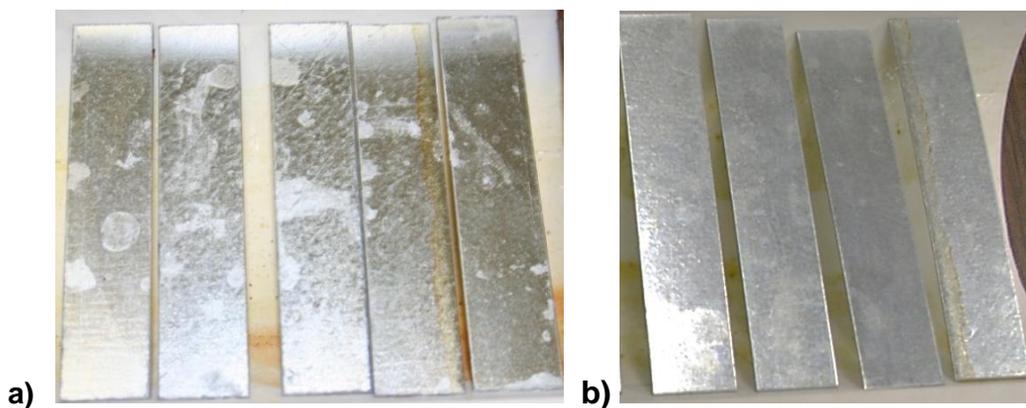


Figure 4: Comparison of galvanized steel samples in dry air and VCI after 155 days; **a)** white rust formation is seen on dry air samples, while **b)** VCI exposed samples were corrosion free.

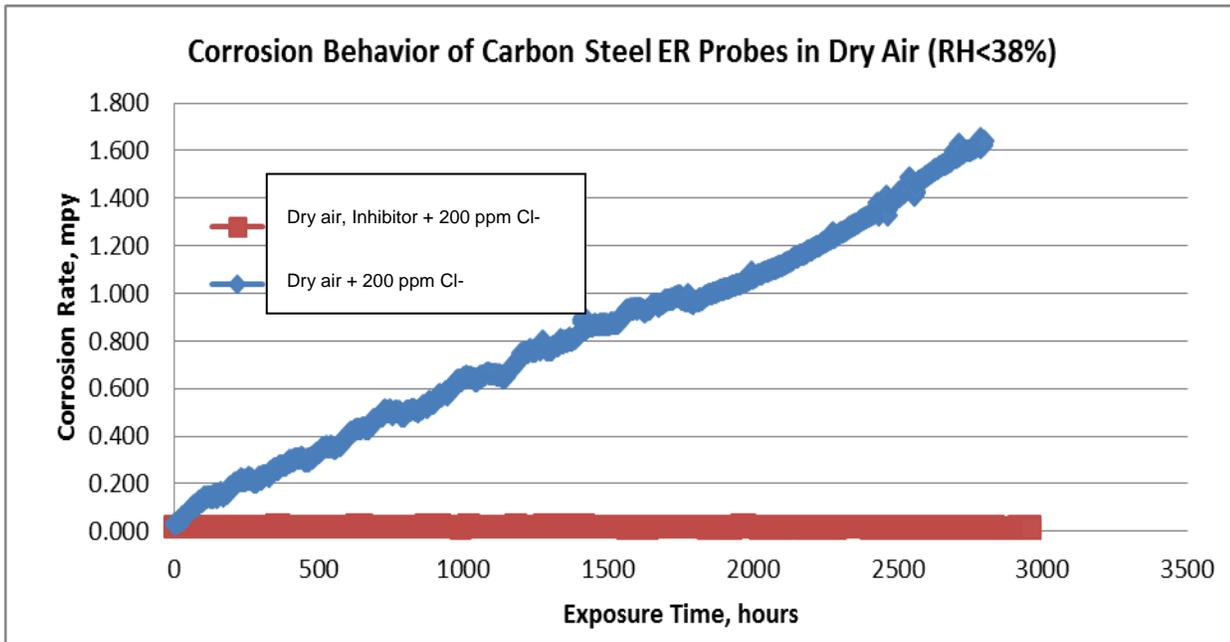


Figure 5: Comparison of corrosion on steel probes in VCI and dry air protection system. There is a much lower corrosion rate for steel samples protected by VCI (average corrosion rate of 0.04 - 0.08 mpy), while the dry air system resulted in increasing attack with corrosion rate as high as 1.7 mpy.

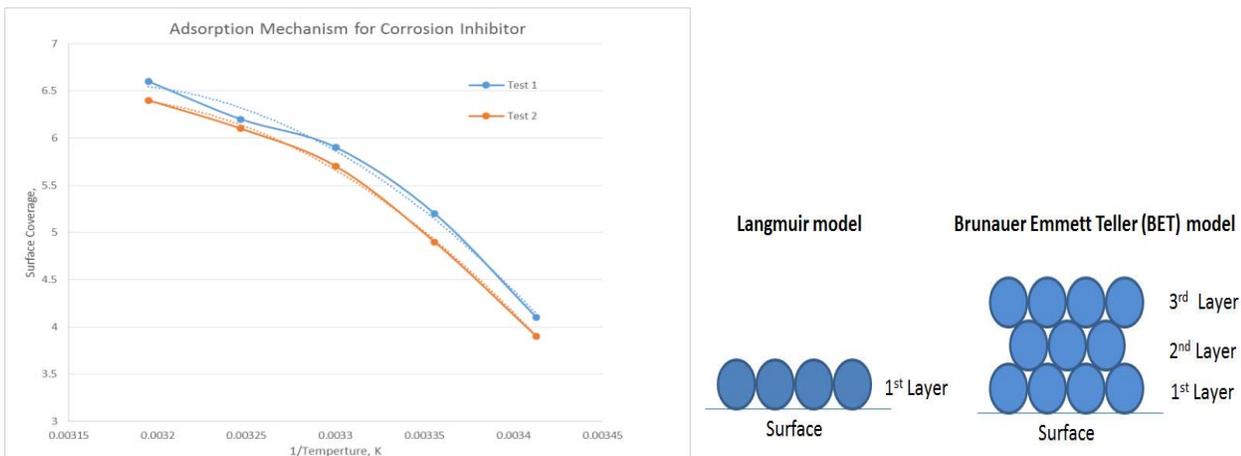


Figure 6: BET adsorption isotherm relationship between surface coverage and temperature for VCI Inhibitor on the surface of steel. Adsorption Energy is roughly -14 kJ/mol, indicative of a strong physical adsorption to the metal surface.

CONCLUSIONS

The corrosion test results have demonstrated that corrosion inhibitors have superior advantages over the dry air system. Samples that were placed in dry air only showed corrosion attack and red rust formation after 21 days of exposure. ER probes showed a corrosion rate of 0.04-0.08 mpy for VCI treatment, while the dry air samples showed a 1.3-1.6 mpy corrosion rate and ER probes were heavily corroded. The samples in dry air showed an increasing

corrosion trend, indicating inability of controlled humidity protection to slow corrosion once the reaction had begun. Test results showed that a dry air system is not an effective method to mitigate corrosion.

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

Brunauer Emmett Teller Model (BET Model) and Langmuir model showed adsorption energy of -14 kJ/mol, indicative of a strong physical adsorption to the metal surface for this inhibitor.

In summary, the vapor phase corrosion inhibitors provide effective corrosion protection for steel materials exposed to the environment during 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 extremely low. A dry air controlled humidity system can reduce the moisture level, but it will not be able to prevent corrosion and the steel will corrode. Furthermore, once corrosion begins, the dry air system cannot impede the accelerating corrosion reaction. 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, vapor phase corrosion inhibitors have superior advantages 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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