NACE® INTERNATIONAL

CORROSION 2015
CONFERENCE & EXPO

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

Behzad Bavarian[1], Yashar Ikder[1], Babak Samimi[1], Lisa Reiner[1] and Boris Miksic, FNACE[2]
Dept. of Manufacturing Systems Engineering & Management
College of Engineering and Computer Science
California State University, Northridge, USA 91330[1]

Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110[2]

ABSTRACT

Corrosion behavior of carbon and galvanized steel samples were 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% RH at 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. 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 corrosion rate and ER probes were heavily corroded.

Key words: atmospheric corrosion, corrosion inhibitor, controlled humidity protection, vapor phase corrosion inhibitors

INTRODUCTION

Over the past 20 years, various corrosion protection systems have been implemented to improve structural longevity. These implementations have been worldwide, as corrosion concerns affect all industrialized countries from Japan (with the Innoshima, Ohnaruto and

Akashi-Kaikyo Bridges) [1], to Denmark (the Danish Faroe, Great Belt and Little Belt Bridges) and Sweden (Högakusten Bridge) [1, 2] to South Wales (Severn Bridge) [3] and France (Aquitane Bridge) to China (Rung Yang Bridge) and the Middle East (Qatar Lusail Bridges) [2]. In the United States there are numerous complications regarding infrastructure, military equipment and aging aircraft due to atmospheric corrosion. To examine more closely, several of the bridges in Japan, these 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 [1]. 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 (Hálogaland and Hardanger Bridges) and Japan have required dehumidification systems in all bridge construction since 2009 [2].

It has been estimated that between $2 trillion and $4 trillion are lost to corrosion each decade [4]. In atmospheric corrosion, a material is subjected to air moisture and corrosive species (pollutants) [5]. 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 [6]. 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 [7]. 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 [8]. 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 [2, 5]. 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 department od Defense (DoD), the Army National Guard is a proponent for applying CHP to its 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 protection [8]. Many foreign defense forces currently use CHP as a maintenance technology for their operational weapon systems. An industry analysis of eleven European defense forces [2, 9] 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 [8]. 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 [10]. Corrosion severity is affected by humidity, pollutants and temperature [6]. 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. SO_2, CO_2, NO_2, Cl^- and F^- 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 [5]. Other causes are formation of hygroscopic films (water absorption without formation of bonds) as a result of corrosive by-products and precipitation of salt particles. 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. In Figure 1a, the effect of 0.01% SO_2 on the corrosion rate (weight loss of steel) as compared to pure air can be seen. Relative humidity 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 [10]. Figure 1b, shows road salt usage for the United States in millions of tons; point being there is no shortage of atmospheric pollutants to exacerbate corrosion.
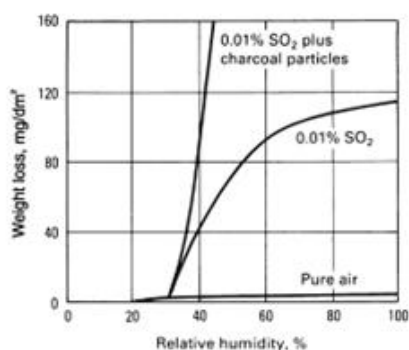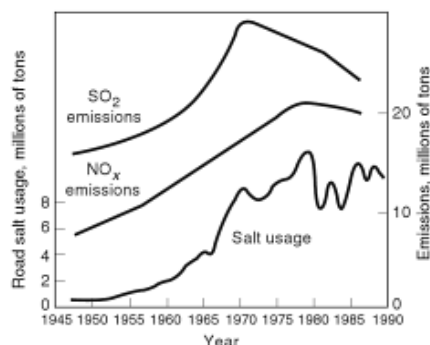
a.   b.

Figure 1a: A comparison for iron weight loss over a 55 day period. Air without contaminants shows no significant weight loss up to 100% RH, while accelerated corrosion rate can be seen for the 0.01% SO_2 contaminants even at RH below 40%. Figure 1b: large source of corrosive species are used in road salts [10].

Vapor phase corrosion inhibitors (VCI) are an alternative protection method that is both effective at controlling corrosion and inexpensive. A vapor phase corrosion inhibitor is a volatile compound and must form a stable bond at the interface of the metal, preventing penetration of corrosive species [11-16]. 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 [17-18]. Compared to other methods of corrosion prevention such as inert gas blanketing and dehumidification, 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 protect [3].

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, 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) [11].

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 that is controlled by the crystal lattice structure and atomic bond characteristics of the molecule [14-15]. 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 like dicyclohexyl ammonium nitrite, ammonium nitrite, urea, and acetamide [19].

The corrosion inhibition mechanism was determined to be the physical adsorption of inhibitor molecules to the metal surfaces [20-21]. Physical adsorption requires energy between -5 to -20 kJ/mol [13-14]. The analysis of the inhibitor showed an enthalpy of adsorption in the range of -14 to -18 kJ/mol [20-21]. 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 [18]. 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), 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 temperature of each test chamber was monitored by the Sensirion sensors[†] and data logging software. The temperature sensor and the humidity

---

[†] Trade name

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 devices is only a few square millimeters in size.

Electrochemical polarization standards per ASTM-G61 [22] and corrosion rate measurements using 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 dry air system. The Metal Samples MS3500E[†] electrical resistance probe system is a remote data-logger capable of measuring and storing data that was used to collect corrosion data. Further experiments were conducted using Gamry PC4/750 Potentiostat /Galvanostat/ZRA[†] instrumentation and DC105[†] corrosion test software. Samples were polished (600 grit), placed in a flat cell and tested in deionized water solutions containing 200 ppm Cl^{-} with 10% VCI inhibitor.
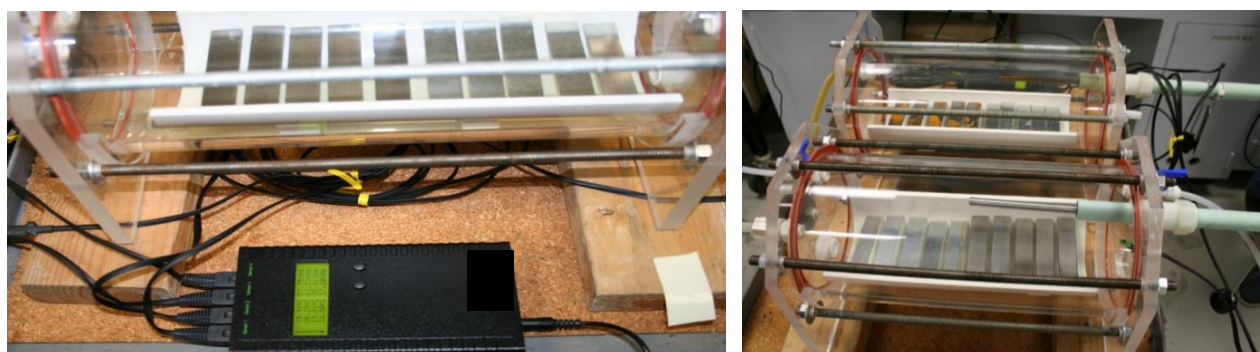

Figure 2: Test setup for the controlled humidity corrosion tests on UNS GUNS G102000 steel and galvanized steel samples. ER probes were in environments with 10% VCI or nitrogen blanketing at 10 psi applied pressure.

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 rate for the samples was monitored continuously for roughly 4,464 hours (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 SEM/EDAX analysis was conducted using a JEOL JSM-6480LV[†] and Thermo System Seven detector[†].

RESULTS

Cyclic Polarization Behavior

Figure 3 shows the polarization behavior for UNS G10200 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

---

[†] Trade name
UNS: Unified Numbering System for Metals and Alloys

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.
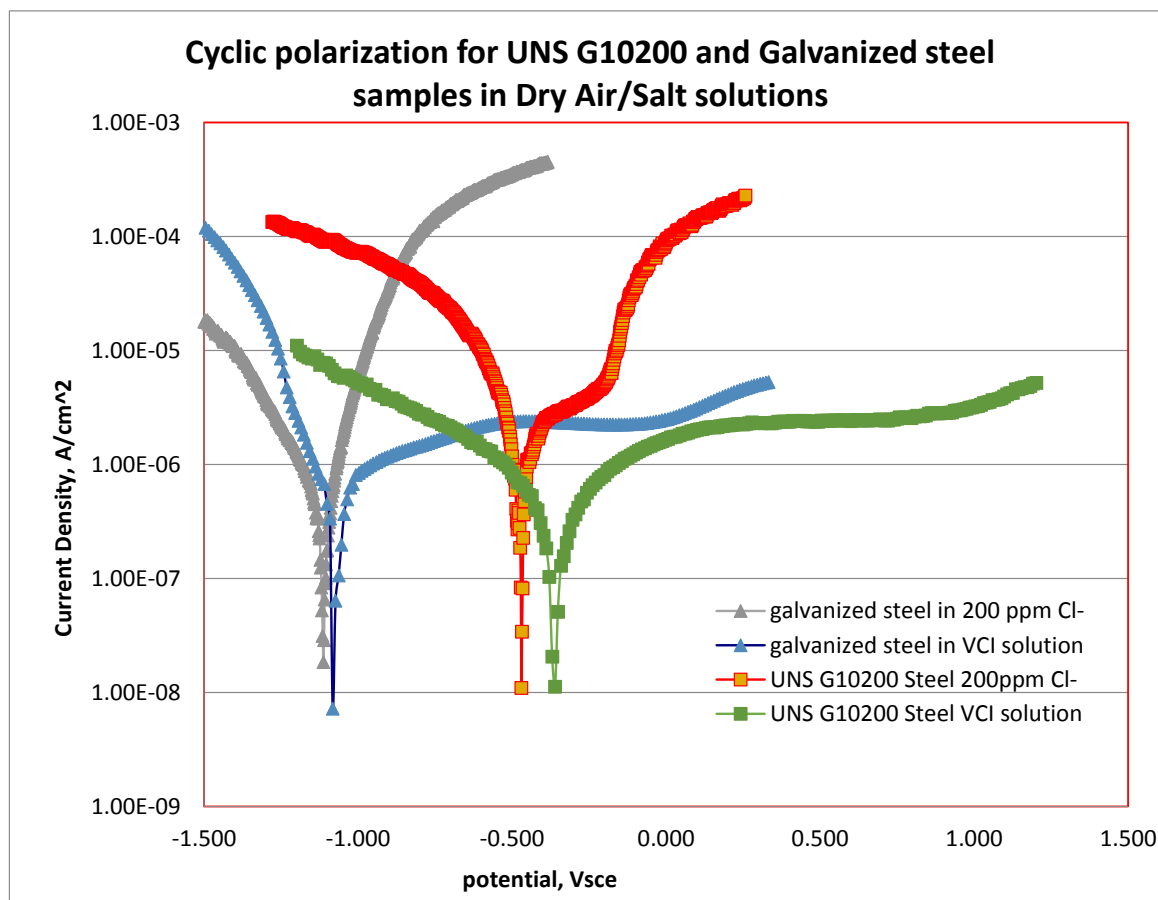

Figure 3: Electrochemical polarization behavior of the UNS G10200 steel samples in 10% VCI and dry air in 200 ppm chloride ion solution.
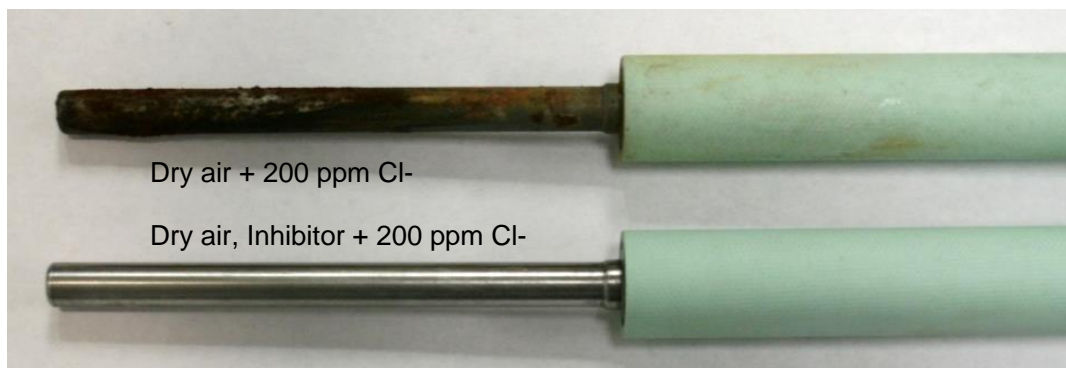

Figure 4: ER probes after 4,464 hours exposure, top probe exposed to dry air, lower probe protected with inhibitor.

Figure 4 shows the ER probes after 4,464 hours exposure in both environments. ER probe protected by 10% inhibitor (bottom probe) shows no corrosion damage. Corrosion rate for probe can be seen in Figure 5. The results show that the dry air system is unable to protect the steel against corrosion. Figures 6-8 show the progression of corrosion damage to the metal surface over time.
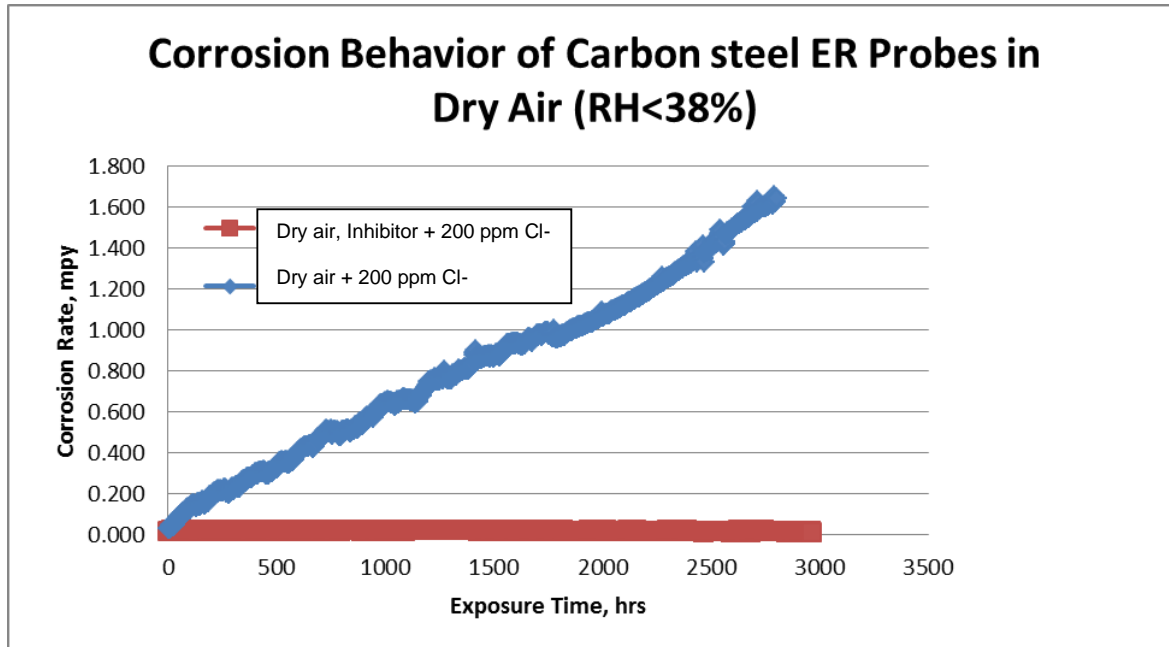

Figure 5: Comparison of corrosion on steel probes in VCI and dry air protection system. There is a much lower corrosion rate for steel samples protected by VCI (average corrosion rate of 0.04 -0.08 mpy), while dry air system resulted in increasing attack with corrosion rate as high as 1.6 mpy.
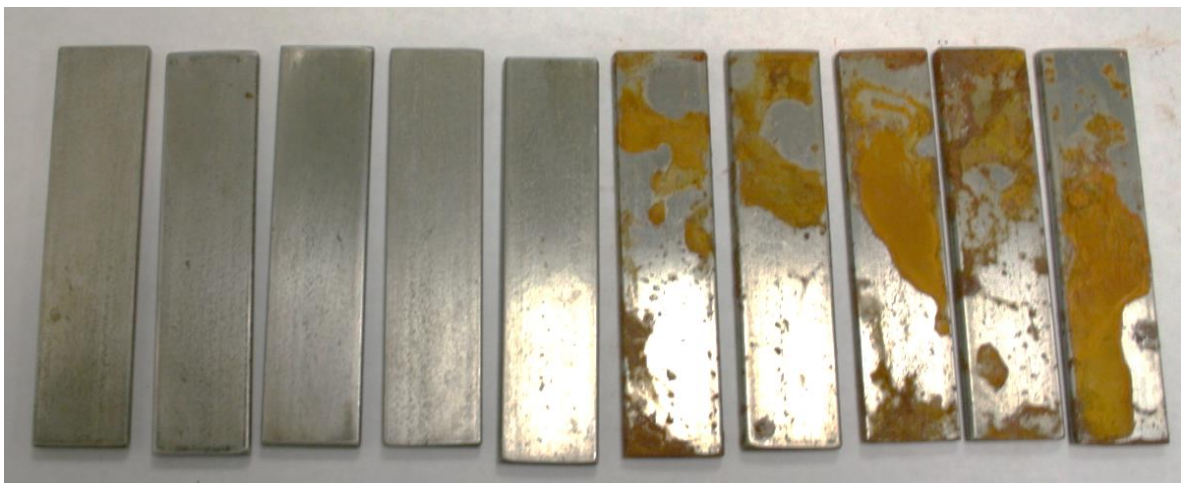

Figure 6: Comparison of UNS G10200 steel samples protected with inhibitor (left) and exposed to dry air (right) for 96 days.
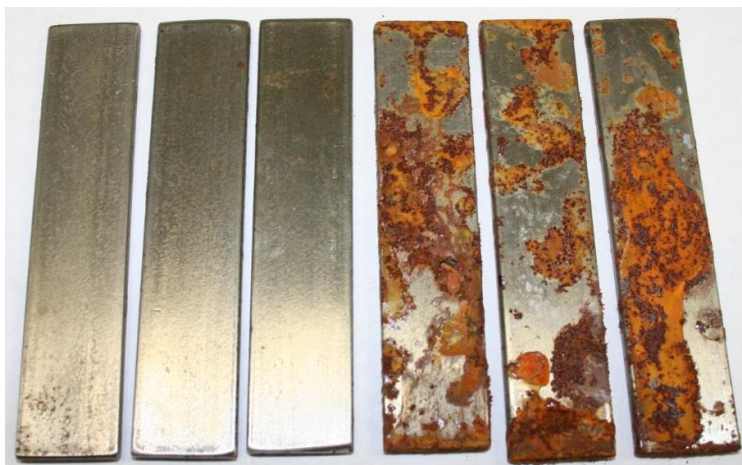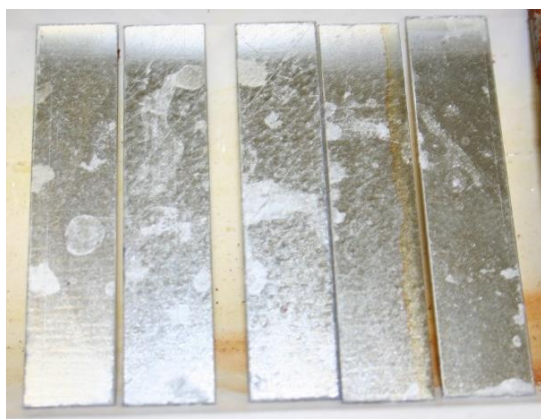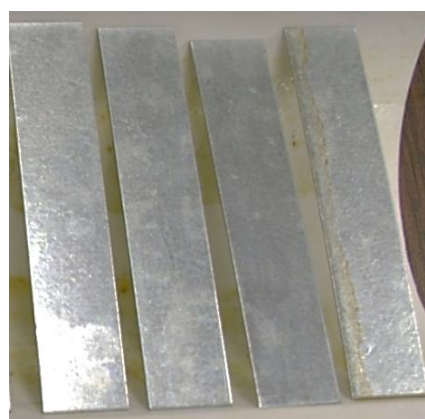
Figure 7: Comparison of UNS G10200 steel samples after 155 days: (left) inhibitor still providing protection, (right) samples exposed to dry air in test chamber.


a)   b)

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.

Figures 9-11 show the SEM/EDAX analysis 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 carbon steel and galvanized steel. These observations demonstrate that the addition of inhibitor is critical for protecting the steel structures.
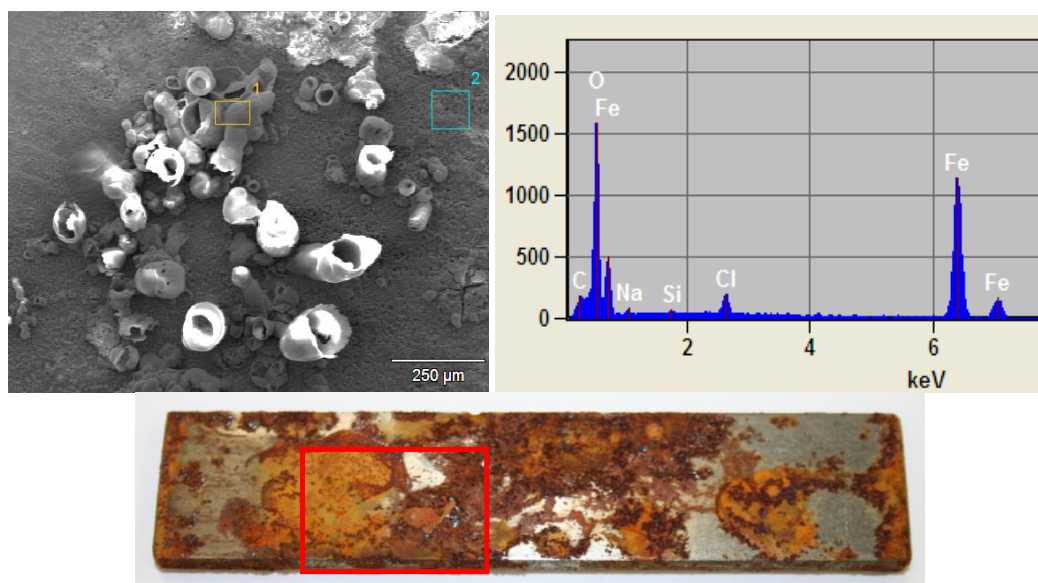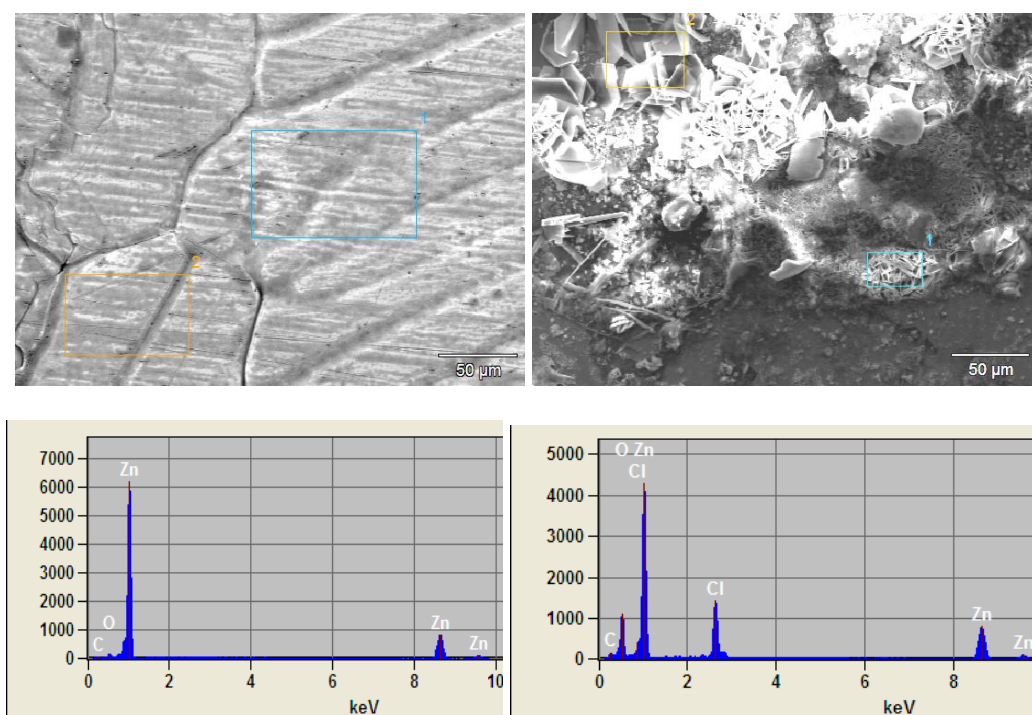
Weight %					
	C-K	*O-K*	*Na-K*	*Cl-K*	*Fe-K*
steel dry air (1)_pt1	5.35	30.01	1.77	0.24	62.63
steel dry air (1)_pt2	6.04	26.35	1.69	0.43	65.50

Figure 9: SEM/EDAX analysis on the steel sample in dry air test chamber after 186 days, showing severe rust formation.
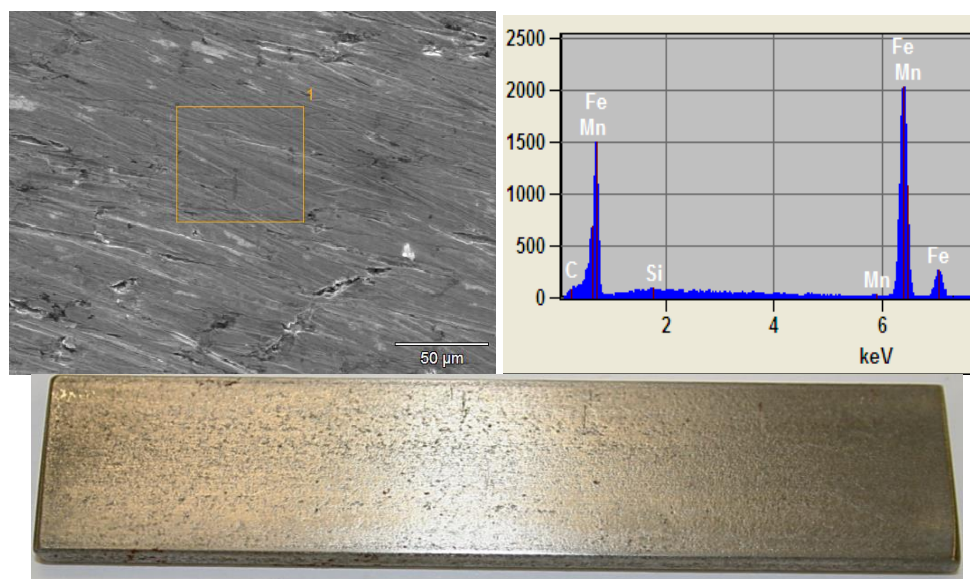
Weight %			
	C-K	*Si-K*	*Mn-K*	*Fe-K*
steel dry vci(1)_pt1	4.40	0.40	0.57	94.63

Figure 10: SEM/EDAX analysis on the steel sample in dry air + VCI test chamber after 186 days, showing a corrosion free surface.

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/EDAX analysis 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.

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 0.04-0.08 mpy for VCI treated while the dry air samples showed a 1.3-1.6 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 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 passive film. The passive film breakdown potential for VCI treated steel samples increased by nearly 1.0 volt, indicating less susceptibility to localized corrosion.

In summary, the vapor phase corrosion inhibitors 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 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**.**

REFERENCES

[1] Tatsuya Eguchi and Tetsuro Matusoka, Development of Corrosion Protection, Methods Using S-Shaped Wire Wrapping System, Nippon[†] Steel Technical Report No. 82, July 2000.

[2] Matthew L. Bloomstine, Ove Sørensen, Prevention of Main Cable Corrosion by Dehumidification, Modern Techniques in Bridge Engineering: Proceedings of 6th New York City, edited by Khaled Mahmoud, CRC Press.

[3] Jeffrey Fisher and Paul Lambert, Severn Bridge Cables Corrosion Models, Use of Inhibitors and their Impact on the Cable Assessment, 8th International Cable Supported Bridge Operators Conference, Edinburgh, June 2013.

[4] Research Opportunities in Corrosion Science and Engineering, Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council, 2011, National Academies Press (US).

[5] M. Tullmin and P.R. Roberge, Chapter 18: Atmospheric Corrosion, Uhlig's Corrosion Handbook, 2nd Ed., John Wiley & Sons, March 2000, pp. 305-321.

[6] D. Jones, Principles and Prevention of Corrosion (2nd Edition), Prentice Hall, Inc, 1996.

[7] Gerhard Koch, Michiel Brongers, Neil Thompson, Paul Virmani, Joe Payer, Corrosion Costs and Preventive Strategies in the United States, CC Technologies Laboratories, Inc, Federal Highway Administration (2001). Publication No. FHWA-RD-01-156

[8] Andrew Timko, Owen R. Thompson, Controlled Humidity Protection, Modifying the Environment to Fight Corrosion, AMPTIAC Quarterly, Vol 7, No 4, 2003.

[9] Luka Miskovic and Tadija Madzar, Environmentally Friendly Protection Methods Used by the Armed Forces of the Republic of Croatia, Corrosion 2002, NACE paper 02324.

[10] Joseph R. Davis, editor, Corrosion: Understanding the Basics, Chapter 5, Atmospheric Corrosion, ASM International, 2000.

[11] J. Holden, A. Hansen, A. Furman, R. Kharshan and E. Austin, Vapor Corrosion inhibitors in Hydro-testing and Long Term Storage Applications, CORROSION/2010, paper # 10405, NACE International, Houston, TX., 2010.

[12] M. Kharshan, and C. Cracauer, Applications for Biodegradable Vapor Phase Corrosion Inhibitors, MP, NACE International March 2011.

[†] Trade name

[13] A. Furman, M. Kharshan, Methodology of VCIs for Water Treatment, CORROSION/97, paper no. 182, NACE International, Houston, TX, 1997.

[14] B.A. Miksic, R.H. Miller, Fundamental Principals of Corrosion Protection with Vapor Phase Inhibitors, 5th European Symposium on Corrosion Inhibitors, Italy, 1980.

[15] C.G. Moore, B.A. Miksic, Vapor Corrosion Inhibitors, CORROSION/95, paper no. 490, NACE International, Houston, TX, 1995.

[16] C. Kraemer, A Procedure for Testing the Effect of Vapor Phase Corrosion Inhibitors on Combined Multi Metals, paper no. 178, NACE International, Houston, TX, 1997.

[17] M. Lagrenée, B. Mernari, M. Bouanis, M. Traisnel and F. Bentiss, Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on mild steel corrosion in acidic media, Corrosion Science, Vol 44, Issue 3, March 2002.

[18] F. Bentiss, B. Mernari, M. Traisnel, H. Vezin and M. Lagrenée, On the relationship between corrosion inhibiting effect and molecular structure of 2,5-bis(n-pyridyl)-1,3,4-thiadiazole derivatives in acidic media: AC Impedance and DFT studies, Corrosion Science 53 (2011).

[19] G. E. Fodor, The Inhibition of Vapor-Phase Corrosion: A Review, Interim Report BFLRF No. 209, Belvoir Fuels and Lubricants Research Facility, SWRI 1985.

[20] B. Bavarian, L. Reiner and H. Youssefpour, Vapor Phase Inhibitors to Extend the Life of Aging Aircraft, NACE Corrosion 2005, paper # 05329.

[21] B. Bavarian, J. Zhang and L. Reiner, SCC and Crevice Corrosion Inhibition of Steam Turbines ASTM A470 and AA7050 Al-alloys using VCI, NACE Corrosion 2012 Conference, March 2012.

[22] ASTM G61, "Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys" (West Conshohocken, PA: ASTM).