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Removable Coatings in the Oil and Gas Industry

Migrating Corrosion Inhibitors for Reinforced Concrete

Extending the Life of Aboveground Storage Tank Floors

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Economic, Environmentally Friendly Solutions for Corrosion Prevention and Control

Vapor phase corrosion inhibitors (VCIs) and migrating corrosion inhibitors (MCIs) have been used for many years to protect structures, equipment, and the environment from the adverse effects of corrosion. These technologies offer a variety of benefits, including easy, economical application and earth-friendly qualities. This special supplement to *Materials Performance* describes several projects where VCIs and MCIs have been effectively used, including applications for protecting steam-generating systems and steel-reinforced concrete structures. In addition, there are articles on how VCIs are used in the formulation of protective coatings, how they prevent corrosion under insulation, and their use to extend the life of aboveground storage tank floors. Whether asset preservation is a matter of product containment or keeping structures safe and intact, environmentally friendly VCIs are proven to control corrosion in a multitude of applications.

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NACE International Contact Information

Tel: +1 281-228-6200 Fax: +1 281-228-6300
Email: Firstservice@nace.org Web site: www.nace.org

Online Injection of Vapor Phase Corrosion Inhibitors to Extend Storage Tank Floor Life

Asad Al Ghafri, Jayant R Nair, Naif Al Abri, and Latifa Al Shibli,
Oman Oil Refineries & Petroleum Industries Co. (ORPIC), Suhar, Oman

The API 650 oil storage tanks in a refinery have experienced accelerated corrosion from the soil side at the rate of 1 to 2 mm/year, primarily due to inefficiency of the impressed current cathodic protection system and underdeposit corrosion caused by the presence of corrosive bacteria in the soil. This caused failure of several tank bottom plates within eight years of commissioning, resulting in loss of primary containment. With no other means of corrosion control from the soil side, the priority was to apply a short-term stratagy by which the corrosion rate is substantially slowed and enable the refinery to distribute these tank turnarounds across as many years as possible. If this is not achieved, a large number of tanks might be expected to perforate in any given year, overwhelming refinery maintenance and disrupting operations. The short-term strategy adopted with best likelihood of success and minimal disruption to maintenance and operations was to drill under the tanks and inject vapor phase corrosion inhibitors. The primary objective was to increase the reliability by extending the floor life and meeting the agreed tank out-of-service schedule.

The soil-side corrosion of aboveground storage tanks (ASTs) is a chronic problem in the oil and gas industry, not only in the Middle East but also in the world at large.[1] Corrosion of the underside of the tank bottom plates leads to metal loss and perforations, resulting in loss of primary containment. The results of such failures are dramatic on multiple fronts: loss of product, costly repairs, and environmental impact and safety concerns in the case of flammable fluids.

Traditionally, impressed current cathodic protection (ICCP) has been used for corrosion management of tank bottoms. However, experience has shown that CP fails to provide adequate protection in some types of AST construction.

Suhar Refinery is part of Oman Oil Refineries and Petroleum Industries Co. (ORPIC). It was commissioned in 2006 and has 48 ASTs for various refinery products. The refinery tanks have experienced severe corrosion at a very high rate from the underside (soil) side of the bottom plates and resulted in failures of more than six tanks within 10 years of commissioning (2006), with the first failure in 2013. Tanks floors are expected to provide service life of over 30 years.

From a root cause analysis study, it was concluded that the tanks were corroding at an unacceptably high rate and the corrosion was specifically related to the inadequate strategy of CP design, which completely failed in its objective of corrosion control combined with a corrosive soil.

The priority was to apply a short-term strategy by which the corrosion rate is substantially slowed and enable the refinery to distribute these tank turnarounds across as many years as possible. Otherwise, a large number of tanks might be expected to perforate in any given year, overwhelming maintenance and disrupting operations.

The immediate strategy with the best likelihood of success and minimal disruption to maintenance and operations was to drill under the tanks and inject vapor phase corrosion inhibitors (VCIs). These inhibitors have been increasingly used in this particular application for the last 15 years with proven results. The inhibitors can help control the corrosion and prevent any further corrosion by forming a layer on the metal surface and restricting the corrosion reactions.

This article demonstrates the concept of using an amine carboxylate-based VCI slurry, as an online soil-side corrosion control method for in-service refinery storage tanks coupled with electrical resistance (ER) corrosion probe monitoring, and exemplify the difference in cost by using a VCI and other maintenance options such as patch plate repair or jacking up and rebottoming the ASTs.

Fundamentals of VCI Technology in ASTs

Amine carboxylate-based VCIs are used beneath ASTs. They are effective for prevention of metal corrosion when a VCI product is released within the interstitial space between the bottom plate and sand pad. The mechanism for corrosion control is the formation of a monomolecular layer throughout the soil-side surface of the tank floor. VCI molecules adsorb on the steel surface to suppress both metal dissolution and the reduction reaction (both the anodic and cathodic processes). This adsorption is accomplished without the need for direct contact of the VCI chemical on the metal surface.

The effectiveness of any corrosion inhibitor can be evaluated using ER probes and the same is valid for VCI used for soil-side corrosion in ASTs. Since the sensing element of the ER probe is usually made of an alloy with the same grade as the tank bottom plate, it is believed that the data obtained from these probes are more representative of AST bottom plate corrosion.[2]

The probe sensing tip is mild steel and will corrode at a rate similar to the tank floor in that area. Readings of metal loss in mils are obtained from the ER probes with a special meter, which is incorporated into a formula that produces a rate of corrosion in mils per year (mpy).

VCI Application Project

The refinery experienced its first tank failure in July 2013 when a sour water tank experienced bottom plate perforations due to soil-side corrosion after seven years in service. A magnetic flux leakage (MFL) survey was carried out for the floor and it revealed more than 40% reduction in a majority of the plates. The most severe corrosion (80 to 100%) with perforations was observed only in the peripheral sketch plates adjacent to the annular plates (Figure 1). This gives a corrosion rate of almost 1 mm/year in the corner plates and 0.4 mm/year at the other bottom plates.

The tank was patch-plate repaired and VCI was injected for soil-side protection along with ER probes that were installed to monitor the efficiency of the chemical and corrosion rates. The injection of VCI was from inside the tank during an off-stream period. There were seven injection ports in different locations of the tank floor to fog VCI powder, and four points in the ring wall were cored to introduce sleeves for installing ER probes to monitor the effectiveness of the VCI slurry (Figure 2).

Subsequently, multiple tank failures were observed with another five tanks experiencing severe bottom plate underside corrosion. Similar MFL results as the sour water tanks were revealed. The patch plate repair method was adopted for three tanks, whereas for two tanks rebottoming

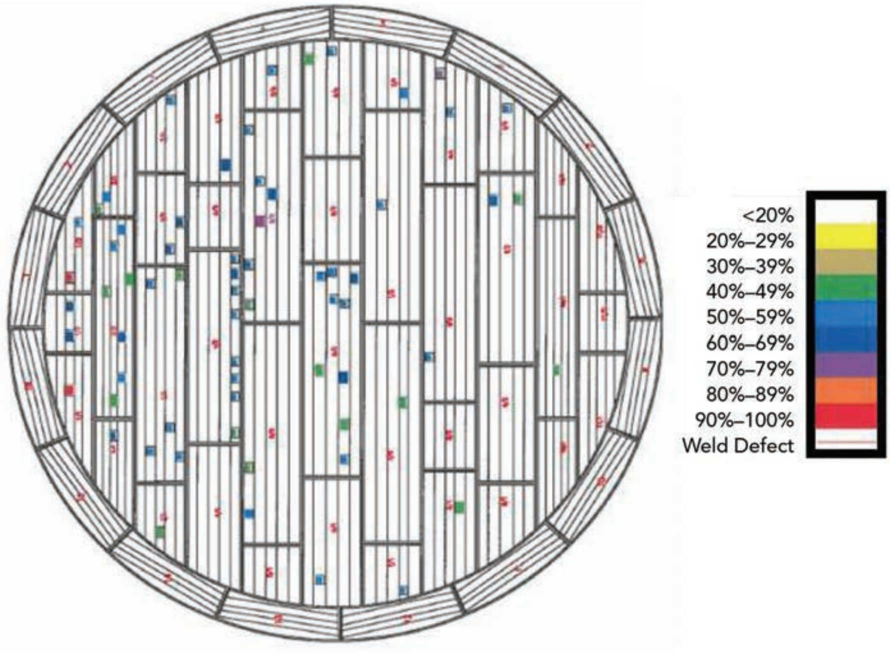

FIGURE 1 MFL floor scan results for sour water tank.

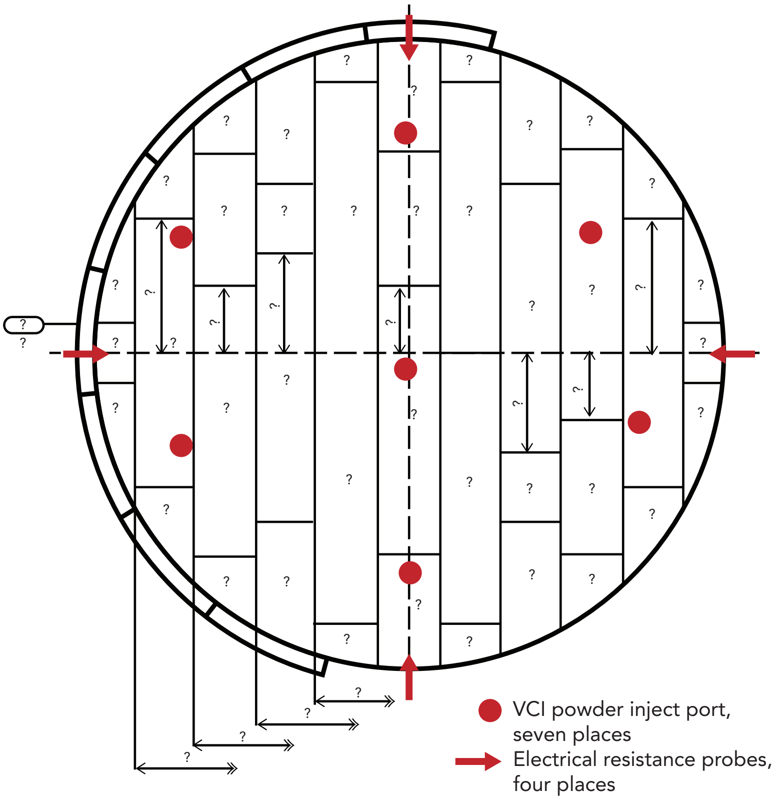

FIGURE 2 Plan view with ER probes and VCI injection port locations.

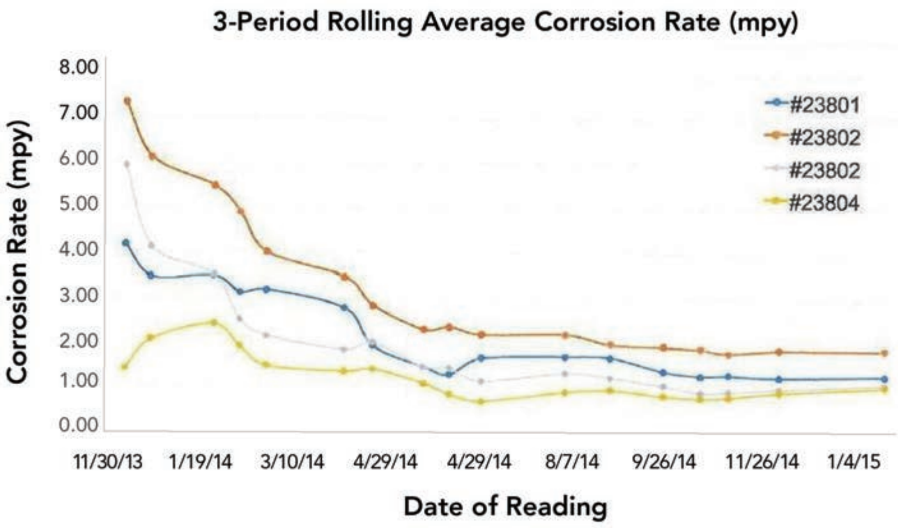

FIGURE 3 Three-period rolling average corrosion rate (mpy) for sour water tank.

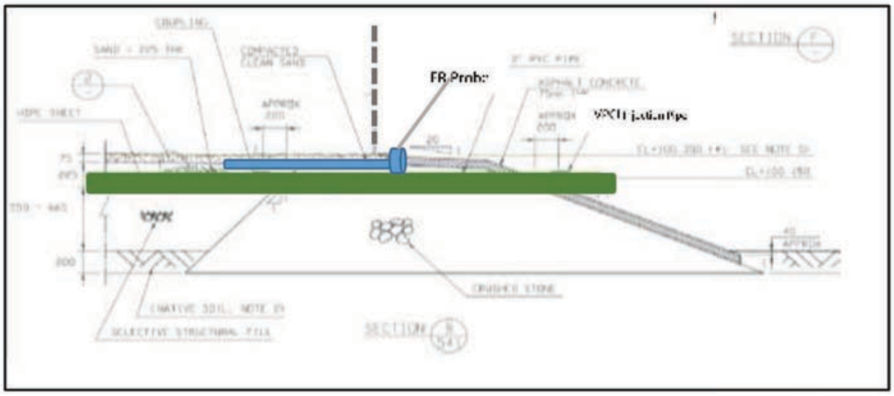

FIGURE 4 Typical ER probe installation with grout removed above probe location.

TABLE 1. CORROSION RATES AND CALCULATED INHIBITOR EFFECTIVENESS

Tank	Probe No.	Pre-Injection Corrosion Rate (mpy)	Post Injection Corrosion Rate (mpy)	% Efficiency
TK-02	2731	1.09	0.25	77
	2732	1.17	0.25	79
	2733	1.96	0.27	86
TK-03	2829	1.67	0.28	83
	2830	1.60	0.36	78
	2831	3.44	0.65	81
	2832	2.21	0.28	87
	2834	10.29	0.74	93
	2835	2.82	0.28	90
	2836	1.46	0.28	81

was carried out by jacking up the tank. The rebottomed tanks were replaced with bitumen foundations as the corrosion protection barrier. Consequent to the failures, a detailed CP survey was carried out for the storage tanks in 2016. The previous CP survey was done in 2008. Both surveys showed very low "instant off" potentials for all the tanks, with an average of –450 mV vs. a copper/copper sulfate ($Cu/CuSO_4$) electrode (CSE). This highlighted that the CP system had failed in its design purpose and there was inadequate protection to the AST bottom plates.[3]

As it was not practical to inspect all the tanks, an out-of-service schedule (OOS) was agreed upon by all stakeholders of the plant, with the intention of implementing an online corrosion protection strategy to extend the service life of the tanks and meet the OOS. The refinery evaluated all possible options, with its feasibility based on a cost/time and success factor. As the ICCP system is placed between the tank bottom and a high-density polyethylene (HDPE) liner, there is no possibility of providing any additional external anodes due to the shielding effect of the plastic sheet. Hence, as there is no direct access to the CP system, any rectification would mean to jack up the tank and have access to the soil. Secondly, it would require a complete redesign of the CP system with hardware changes. In spite of all this, the bottom plate replacement would be required and there is uncertainty on achieving protection potentials. Therefore, the refinery identified other possible short-term options that would extend the tank life to meet the OOS. The immediate solution adopted was to inject corrosion inhibitors without any disruption to the operations and seal the chime area of the tanks to avoid any further air or moisture ingress.

Instantly, the number of tanks was identified based on a consequence-based risk ranking for the implementation of online injection of the VCI and installation of ER probes to evaluate the effectiveness of this technology. The main objective of the project was to extend the service life of the tanks floors, eliminate unplanned shutdowns or emergency incidents, and avoid corporate maintenance and repair costs.

The promising results of the first injection in a sour water tank (Figure 3), along with positive feedback from tank operators (Middle East and the United States) and technical papers, the company management gave the go-ahead for the project. For the first phase, 21 tanks were selected.

The exact location of chemical injection and the number of ER probes were determined during the engineering study. The ER probes were installed in a polyvinyl chloride (PVC) pipe under the tank floor with a sensing element completely embedded in the sand pad (Figure 4). Data were regularly collected for all tanks before and after corrosion inhibitor application.

The design scope of work included the following general steps:

1. Installation of monitoring device: This included installation of a number of ER monitoring probes at numerous locations under the tank floor. A minimum of two months prior to VCI injection, ER probe readings were collected. The number of monitoring probes depended on the size of the tank. The ER probe readings revealed the corrosiveness level of the under tank environment without VCI.
2. Installation of VCI injection pipes: The VCI was applied into the interstitial space for effective distribution. Injection tubes were installed by core drilling into the bitumen/concrete ring foundation. VCI slurry was injected through distributed perforated injection pipes. The pipes were embedded within the sand pad to ensure effective and even distribution of the slurry, such that once applied and migrated, the entire bottom plate was controlled (Figure 4). The application system was configured for future online replenishment. The annular plate was sealed to avoid escaping of the VCI or air and moisture ingress into the tank bottom during breathing out.
3. Collection of ER probe data: ER probe readings were collected and the efficacy of VCI was evaluated by differentiating results between ER probe readings prior to VCI injection and after.

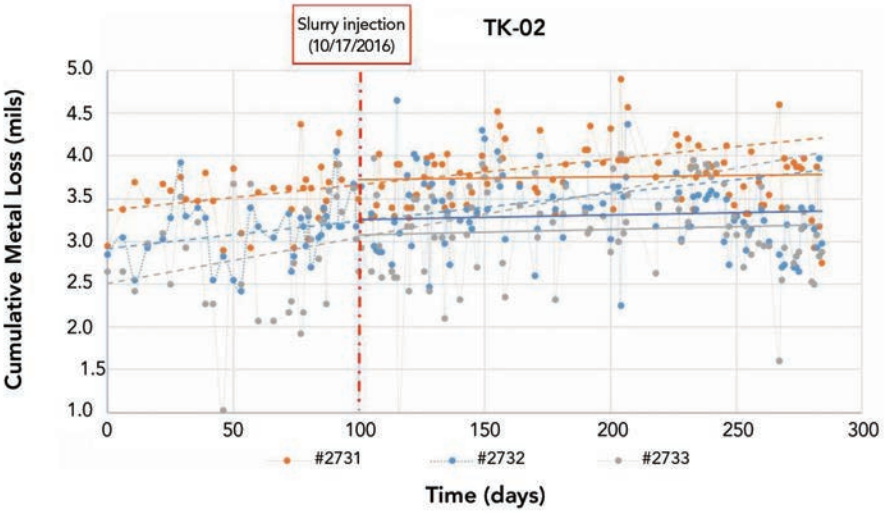

FIGURE 5 Metal loss monitoring graph for ER probes in TK-02.

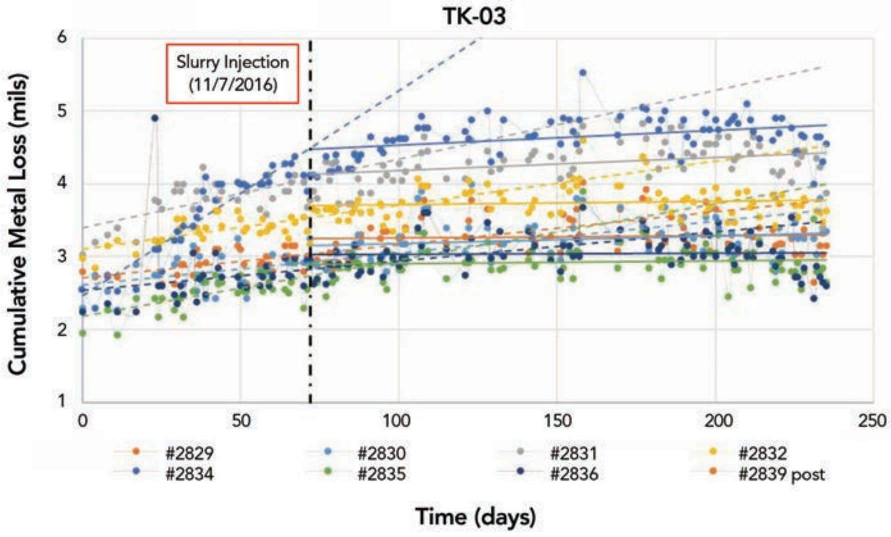

FIGURE 6 Metal loss monitoring graph for ER probes in TK-03.

Results

Significant reduction in corrosion rate is now clearly identifiable across the majority of ER probes. It is expected that as time progresses the outliers shall also reinforce the success of the project. ER probe data showed a significant reduction in corrosion rate after injection of the VCI slurry, with the average percentage reduction for all probes to be 70%.

Sample ER probe metal loss charts and three-period rolling average corrosion rate charts for two tanks are displayed in Figures 5 and 6. The pre-and-post injection trend lines are clearly separated with a vertical dotted line.

The decline in corrosion rate trends confirms the functionality of the ER probes. The corrosion rate data were treated by using a three-day moving average as shown in Figures 7 and 8. Data after injection of VCI illustrate a reduction in the corrosion rate and ended up to a common corrosion rate.

Table 1 clearly defines the efficacy of the

VCI slurry in protecting two tanks by evaluating 10 ER probes before and after injection. The achieved data declare a satisfactory success of VCI in minimizing soil-side corrosion by reducing the corrosion rate prior and after injection. It is important to mention that diffusion of VCI to reach the metal surface to be protected is a time process and is dependent on the aeration degree of the under-tank soil. That is the reason why VCI action is not instantaneous and takes some time to be visible through ER readings.[4]

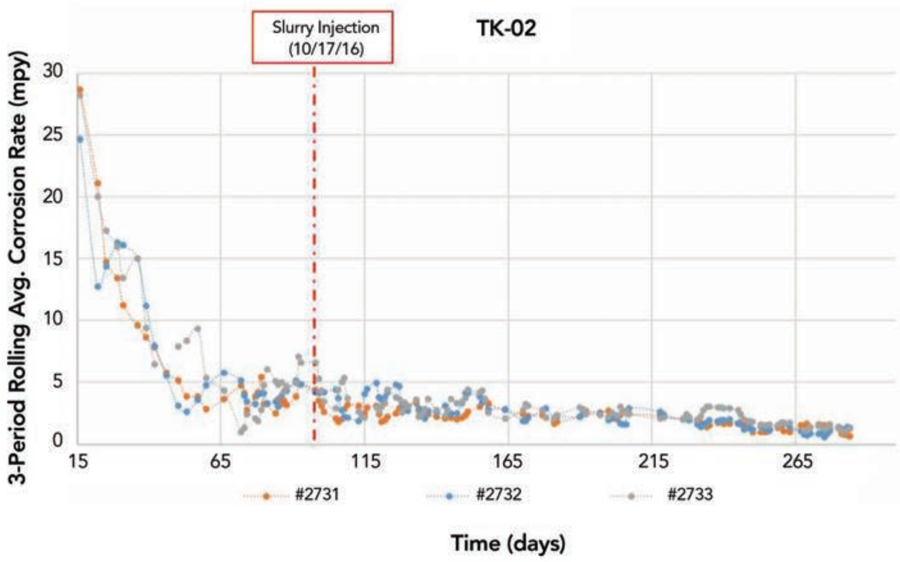

FIGURE 7 Three-period rolling average corrosion rate of ER probes in TK-02.

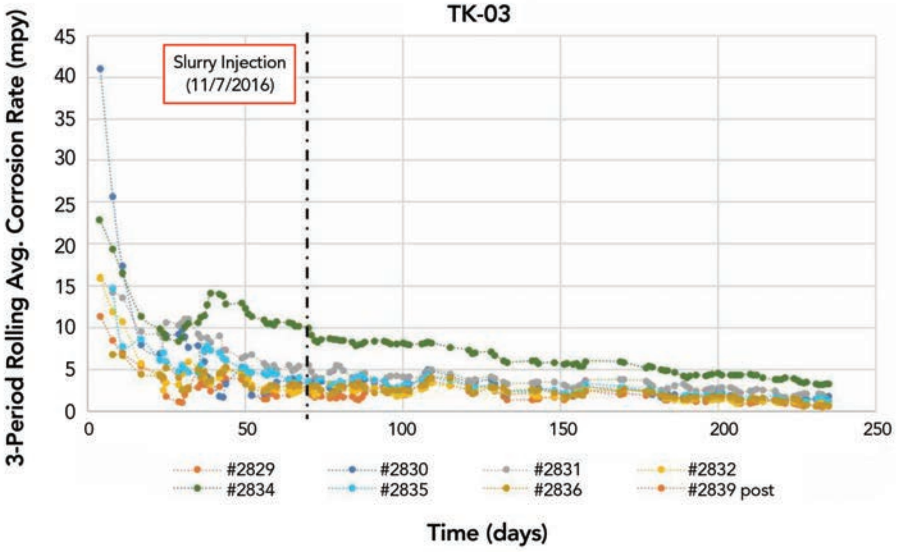

FIGURE 8 Three-period rolling average corrosion rate of ER probes in TK-03.

Cost Savings

A business case was presented to the refinery management for 40 tanks that were identified for the project.

The business case presented was based on the following assumptions:

- Tank bottom plate condition is not known as no inspection had been done.
- The chemical injection is to extend the life of the tank bottom plates. Hence, some plates may have already corroded to an extent of complete replacement.
- Bottom plate repair strategy is either by jack up and complete rebottoming or inspection and patch repair.
- The cost of both of these methods varies upon the size (diameter) of the tank to be repaired/replaced, with rebottoming cost almost 4 to 5 times patch repair cost.

Therefore, even after chemical injection, some repair is anticipated and the following assumptions are used for the cost savings calculation:

- Eight tanks (20% of total tanks) may require rebottoming and jack up.
- Thirty-two tanks may require patch up, but not to an extent as required without any chemical injection.

Table 2 shows the difference in repair cost either by replacing the bottom floor or by patch repair and injecting VCI underneath 40 tanks.

TABLE 2. COST SAVING FOR VCI VS. FLOOR REPLACEMENT/PATCH REPAIR OF 40 ASTS

Cost Description	Cost (USD)
Typical cost of rebottoming eight tanks (A)	10,400,000
Typical cost of patch repair of 32 tanks (B)	6,240,000
Typical cost of chemicals for 40 tanks (C)	2,808,000
Typical saving for 40 tanks [(A+B)-C]	13,832,000

The benefits of using VCI rather than a repair route are in the following:

- Technical/operations: The project has reduced the risk of plant slow down or shutdown as the reliability of the tanks has increased.

- Integration focus: Implementation of lessons learned from existing plants to growth projects
- Financials: Savings by avoiding major replacements that include specialized services, and revenue when plant reliability and availability increase
- Human resources: Savings by reducing the manpower requirements for jacking up and replacing the bottom plate
- Corporate responsibility: Prevent the unexpected leakage of hydrocarbons to the groundbed and the surrounding environment, which can be a safety and environment hazard.

Conclusions

Engineered systems utilizing VCI technology offer an important supplement for mitigation of AST floor corrosion. These systems are economical, effective, and can be installed on a retrofit basis without disrupting tank service. The reading of corrosion rate data provides confidence that if the VCI chemistry is effectively delivered under the tank bottoms, and if the intrusion of fresh air and water under the tanks are eliminated, soil-side floor plate corrosion will be mitigated. The results of the VCI project in Suhar conclude the following realities:

- VCI can be effectively injected underneath ASTs during on-stream service without any disturbance to operation and corporate business.
- VCIs can extend the serviceable life of ASTs in case of absent protection such as insufficient protection from CP.
- ER probes can be used to evaluate the effectiveness of VCI in reducing soil-side corrosion by exploring the corrosive rate of the soil environment.
- VCI accomplishment is time-dependent and related to the soil properties in order to reach complete protection with enough concentration.

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References

1. A. Meraufel, M. Al-Hajri, K. Abed, “Mitigation of Soil-Side Corrosion on Storage Tank Bottoms in the Absence or Deficient of CP System,” paper no. MECCFEB16-7795, 16th Middle East Corrosion Conference, Bahrain (2010).
2. P.R. Roberge, *Corrosion Inspection and Monitoring* (Hoboken, NJ: John Wiley & Sons, 2007).
3. N. Al Abri, J.R. Nair, A. Al Ghafri, F. Al Mawali, “Premature Failure of API 650 Oil Storage Tank Bottom Plates Due to Soil Side Corrosion,” CORROSION 2017, paper no. 9025 (Houston, TX: NACE International, 2017).
4. T. Whited, X. Yu, R. Tems, “Mitigating Soil-Side Corrosion on Crude Oil Tank Bottoms Using Volatile Corrosion Inhibitors,” CORROSION 2013, paper no. 2242 (Houston, TX: NACE, 2013).

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ASAD R. AL GHAFRI is a senior material and corrosion engineer at Oman Oil Refineries & Petroleum Industries Co. (ORPIC), Sohar Industrial Port, PO Box 282 PC 322, Sohar, Oman, email: asad.alghafri@orpic.com. He has seven years of experience in this position, with five years of previous experience in refinery operations. He is a member of NACE International.

JAYANT R. NAIR is a senior material and corrosion engineer at ORPIC, email: jayant.nair@orpic.com. Nair has extensive experience in material selection, risk-based inspection/integrity operating windows implementation, and corrosion control and monitoring of hydrocarbon, water, and steam systems, and is a member of NACE.

NAIF AL ABRI is a senior material and corrosion engineer at ORPIC, and is involved in developing corrosion control documents, corrosion loops, and mechanical integrity-related critical operating envelopes. Abri analyzes and checks the addition of chemical inhibitors and investigates incidents and failures related to integrity and system failures, and is a member of NACE.

LATIFA AL SHIBLI is a material and corrosion engineer at ORPIC, email: latifa.alshibli@orpic.com. Al Shibli has four years of experience in this position, and is the leader of a VCI phase two project. *MP*

Amine-Based Vapor Phase Corrosion Inhibitor Alternatives to Hydrazine for Steam-Generating Systems and Power Plants

Behzad Bavarian and Lisa Reiner, *California State University, Northridge, California, USA*
James Holden and Boris A. Miksic, FNACE, *Cortec Corp., St. Paul, Minnesota, USA*

Hydrazine is used as an oxygen scavenger to control corrosion in steam-generating systems, despite being a genotoxic carcinogen. Alternative chemicals, nontoxic corrosion inhibitors, or new oxygen scavenger-free water treatment technologies are preferred. A newly developed amine-based vapor phase corrosion inhibitor (VCI) was investigated. Electrochemical tests were conducted and showed a significantly lower corrosion rate in steam-generating boilers and boiling water. Short-term (720-h) corrosion tests in boiling water showed a decreased corrosion rate from 5.3 mpy to 1.93 mpy for 50 mg/L VCI and 1.32 mpy (0.001 metal loss per year) for 100 mg/L VCI addition. Long-term (2,200-h) corrosion tests in the hot steam-generating closed loop system showed a decreased corrosion rate from 8.2 to 8.9 mpy for the control sample to 0.72 to 0.74 mpy when washed with 500 mg/L VCI solution. The closed loop system was subsequently maintained at 100 mg/L inhibitor for the test remainder. Inhibitor added at the beginning of the test resulted in a corrosion rate of 1.09 to 1.24 mpy (with 100 mg/L VCI). X-ray photoelectron spectroscopy analysis showed that the amine-based inhibitor promoted and stabilized a protective magnetite oxide (Fe_3O_4) on the pipe internals. This investigation confirmed the inhibitor can be an effective replacement for toxic hydrazine.

The presence of dissolved oxygen in metal boiler feedwater and steam-generating systems can present serious problems in a steam-generating plant by promoting corrosion and thick scale formation in the feedwater system, the boiler, and the steam condensate system. Therefore, it is important to remove oxygen from the feedwater and also from the condensate where in-leakage can occur. The first step in the elimination of oxygen from the boiler feedwater is mechanical deaeration. The second step involves chemical oxygen scavenging to remove the residual oxygen. For many years, sodium sulfite and hydrazine were the preferred chemical oxygen scavengers. However, sodium sulfite contributes solids to the boiler water and hydrazine was found to be extremely toxic.

Hydrazine has been used as an oxygen scavenger and corrosion inhibitor for corrosion control in steam-generating systems. Although hydrazine is very effective, it is a genotoxic pollutant. The use of alternative chemicals such as nontoxic corrosion inhibitors, oxygen scavengers, or new oxygen scavenger-free water treatment technologies is highly recommended and in most countries required by law. Prohibiting the use of hydrazine requires the availability of nontoxic alternatives for water treatment technology without oxygen scavengers.[1-9] Hydrazine-free water treatment provides the following advantages: reduction in environmental impact and improvement of the work environment; reduction in deposition, which in turn reduces the frequency of chemical cleaning for through-flow boilers; reduction in pipe wall thinning due to flow-accelerated corrosion; and reduction in startup time and water consumption in the drum boilers and heat recovery steam generator boilers.

Restrictions on the Use of Hydrazine

In recent years, an international framework for the control of chemical substances has been created. In 1992, the United Nations Conference on Environment and Development adopted the Earth Summit Agenda 21,[3] a global action plan for sustainable development in the 21st century. In 2002, the World Summit on Sustainable Development adopted the Johannesburg Plan of Implementation containing guidelines on the management of chemical substances to minimize major adverse effects on human health and the environment by 2020. The International Conference on Chemicals Management in 2006 adopted the Strategic Approach to International Chemicals Management designed to implement the Johannesburg Plan.[1] In 2007, the European Union implemented the Regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals to achieve the World Summit on Sustainable Development goals by 2020.

These factors led to the introduction of alternative oxygen scavengers including amine-compounds, diethylhydroxylamine,[10-14] helamine (amine-based compounds),[15-18] surface-active fatty alkyl polyamines, and amines of different volatility (cyclohexylamine + aminoethanol + (Z)-N-9-octadecenylpropane-1, 3-diamine), and cyclohexylamine-based corrosion inhibitors.[8-9, 19-24] These amine-based compounds were introduced as an alternative oxygen scavenger to hydrazine, offering the advantages of very low toxicity and the volatility of a neutralizing amine. Like hydrazine, amine-based compounds also promote the formation of a passive magnetite film on low carbon steel (CS) surfaces, minimizing corrosion in the system.[11] Amine-based water treatment has numerous beneficial properties as an oxygen scavenger in boiler feedwater systems: protects by forming a thin magnetite oxide (Fe_3O_4) layer; prevents lime scale or minerals on surface installations; removes old deposits without causing damage; disperses impurities, inorganic salts, and oxides of iron; alkalinizes vapor networks, including the return of condensate and hot water systems; and provides effective heat transfer and energy savings.

The operating parameters of the boiler systems (pressure, temperature) are very important in determining how much inhibitor is required to maintain an acceptable corrosion rate level (<1.0 mpy). In low to moderate pressure industrial boiler systems, an initial feedwater inhibitor dosage of 100-500 mg/L is recommended.[17] However, during operation an adjusted product feed rate is used until a consistent inhibitor residual of 80-120 mg/L can be established in the condensate.

Volatile Corrosion Inhibitors

Volatile corrosion inhibitors (VCIs) are compounds transported in a closed loop environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide (CO_2) or by shifting surface pH toward less acidic and corrosive values.[15-18, 20-25] In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine, and hexamethylene-amine are generally used. When these inhibitors come in contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility and complex compound formation.

In addition to oxygen scavenging and metal passivating capabilities, another key advantage of amine-based inhibitors is their volatility. Not only do they scavenge oxygen and passivate metal in the feedwater and boiler portions of a steam boiler cycle, they also cause evaporation or dispersion by vapor phase (volatilize) with the steam to provide complete system protection. The fact that the amine-based compounds are volatile represents an enormous advantage in condensate system treatment because most of it is transported and absorbed into the condensate system, allowing it to passivate condensate system metallurgy, preventing corrosion; scavenge oxygen if it enters the condensate system, preventing corrosion; reduce corrosion byproduct transport to the boiler, minimizing the potential for boiler deposition and underdeposit corrosion; improve equipment reliability and efficiency; and minimize overall condensate system corrosion, reducing the related maintenance costs.

Research Objectives

Corrosion of the steam/waterside interiors during the various stages of the steam cycle is a major problem for steam-generating and power plant operators. The industry standard for corrosion protection in operating systems is the use of hydrazine required to be limited per the European Union. Amine-based compounds are considered an alternative to hydrazine. These amines are normally injected into the steam line but may be injected into the boiler water or the condensate system. The purpose of this investigation was to compare the performance of the new amine-based VCI vs. the hydrazine capabilities to provide corrosion protection for the boiler steam/water system internal surfaces through the phases of the steam system (water, transition, steam). Prior to investigating this new VCI in a closed loop system, some preliminary testing was conducted at high temperature (roughly 182 °C [357 °F) to determine when it would start to boil; the hydrazine boiling point is 114 °C (238 °F). The assumption was that if hydrazine can survive the steam cycle, then this new VCI

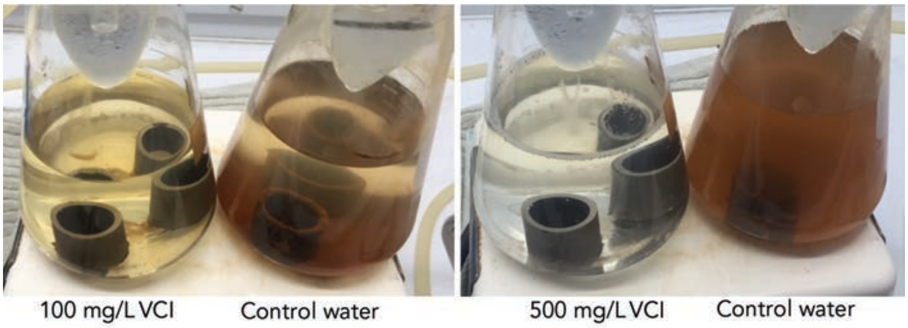


FIGURE 1 Corrosion behavior of the steel pipe samples in boiling water. Corrosion rate decreased to 1.36 mpy with 100 and 500 mg/L VCI addition (700 h).

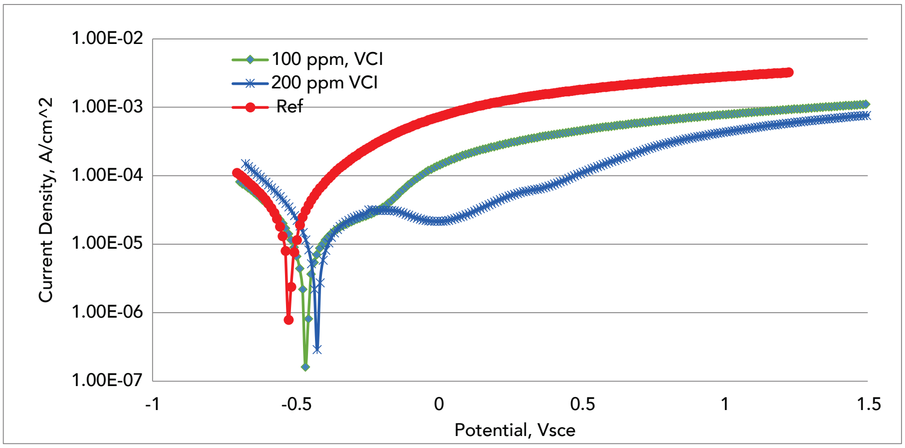


FIGURE 2 Comparison of cyclic polarization behavior of steel pipe in hot water solution in 100 °C when exposed to control solution, 100, and 200 mg/L VCI.

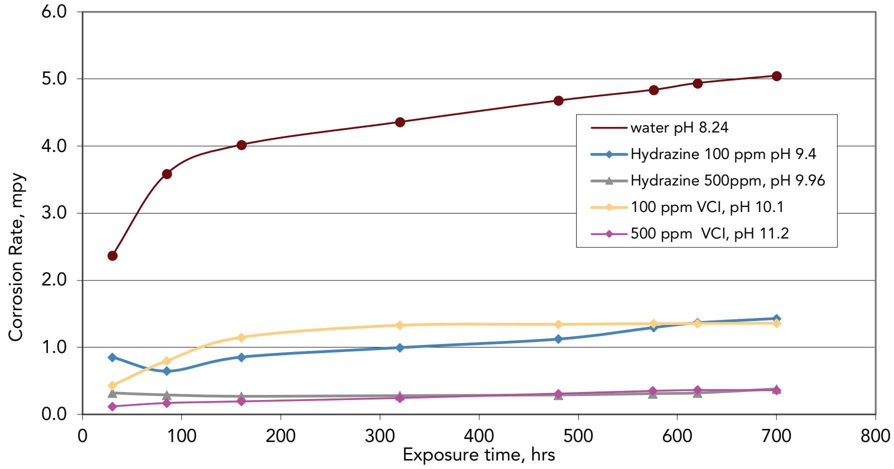


FIGURE 3 Corrosion behavior of steel pipes in hot water solution in 100 °C when exposed to control solution, 100, and 500 mg/L VCI and hydrazine.

should provide effectiveness and good functionality in those conditions. The auto-ignition temperature for both hydrazine and new VCI is around 288 to 293 °C (553 to 555 °F). However, when the molecules are attached to surface oxides, they are more stable and this temperature is not critical.

The research program implemented a closed loop with water/steam circulating through at 90 psi and 118 °C (245 °F). The objectives were to investigate electrochemical behavior of CS pipe samples (ASME B31.1 pipes)[26] under the following conditions: 1) exposed to the new VCI and a control solution; 2) total immersion in boiling water with new VCI and without inhibitor (control-reference); and 3) in steam/water closed loop system with VCI and without inhibitor (control-reference). Post-test evaluation was conducted by scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analysis and x-ray photoelectron spectroscopy (XPS) analysis of surface conditions for samples with inhibitor.

Experimental Procedure

Corrosion behavior of steel pipe samples in the new amine-based VCI in steam/water loops at elevated temperature was investigated to explore its inhibiting effectiveness as an alternative for hydrazine. Electrochemical polarization behavior was conducted in 50 to 500 mg/L inhibitor solutions. Samples were polished (1.0 μm surface finish), placed in a flat cell, and tested in deionized water solutions containing 50 to 500 mg/L VCI at elevated temperatures. Corrosion behavior of CS pipe samples was assessed during complete immersion in boiling water while exposed to the new VCI and without inhibitor (control sample). Apparatus for testing was similar to that recommended in ASTM G123[27] (Erlenmeyer flask and condenser, hot plate to maintain solution at its boiling point, Figure 1). These tests were conducted in control solution (filtered water, no inhibitor), with 50, 100, 200, and 500 mg/L VCI addition. Test duration was ~700 h.

The steam/water loop system included a Chromalox[†] electric boiler and steel pipe loop. The system is a safe and versatile heat source to produce low- or high-pressure steam (~100 psi). A closed loop system was assembled that can circulate and maintain steam at 118 °C and 90 psi. Tests were conducted on the control (no inhibitor was used) for a duration of 1,100 h. Test duration for the 100 mg/L VCI was 2,200 h. During these tests, corrosion rate measurements were monitored using electrical resistance (ER) techniques, and the Metal Samples MS3500E[†] electrical resistance probe system with a data-logger was used for measuring and storing corrosion data.

Light microscopy, SEM/EDS analysis, and XPS analysis were performed after corrosion tests to verify the extent of corrosion damage on the exposed surfaces after each test, using image analysis and SEM/EDS, followed by surface chemistry post-corrosion tests using high-resolution XPS analysis.

Results and Discussion

Electrochemical polarization behavior of the steel pipes in different concentrations of corrosion inhibitors at different temperatures are shown in Figure 2. Results indicated that the new VCI is an anodic corrosion inhibitor capable of lowering corrosion rate and expanding the passivation range for steel pipe in the working condition of hot steam/water systems. The corrosion rate based on the cyclic polarization test results were as follows: for the control, 17.2 μA/cm^2 (7.91 mpy); in the presence of 100 mg/L VCI, 4.73 μA/cm^2 (2.18 mpy); and when a 200 mg/L VCI was added to solution, the corrosion rate decreased to 2.86 μA/cm^2 (1.24 mpy). In general, the boiler industry assumes approximately 1.0 mpy corrosion rate to be an acceptable range for the open circulating system.

Corrosion behavior of the steel pipe sam-

[†] Trade name.

ples in boiling water are shown in Figures 1 and 3. Corrosion rates were monitored for 700 h of continuous immersion at boiling temperature. The corrosion rate was 5.3 mpy (determined from weight loss measurement) for the steam environment with no inhibitor. When 50 mg/L of VCI was added, the corrosion rate decreased to 1.94 mpy and for 100 mg/L VCI addition, corrosion rate dropped to 1.36 mpy. The addition of 200 mg/L VCI decreased the corrosion rate to 0.97 mpy, while the addition of 500 mg/L resulted in a very low corrosion rate of 0.37 mpy. The corrosion rates for the solutions with different amounts of VCI had become steady at roughly 120 h (corrosion rate showed a logarithmic rate) while the nonprotected steel samples showed an increasing trend for the corrosion rate. From observation, the nonprotected steel samples (control-reference) showed heavy corrosion attack with hematite (Fe_2O_3) (brown color solution, an indication of heavy rust formation). To the contrary, the presence of VCI in low dosages (50 to 100 mg/L addition) resulted in an oxide formation of magnetite (Fe_3O_4) and no significant change in solution color was observed. At higher dosages (200 to 500 mg/L), no color change was observed on the steel samples or their solutions, which correlates with the (measured) low corrosion rates.

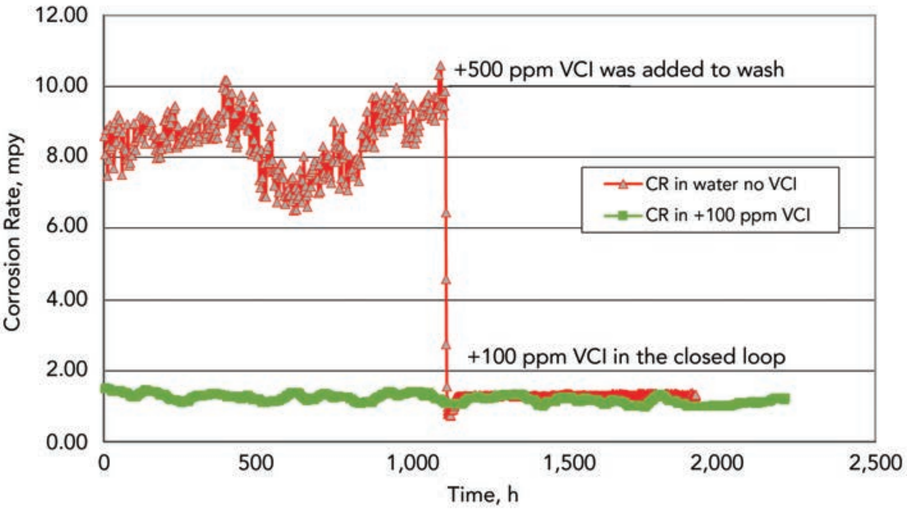


FIGURE 4 Comparison of corrosion rate measurements of the inhibitor treated loop and control test after 2,200 h corrosion test in hot steam/water closed loop.

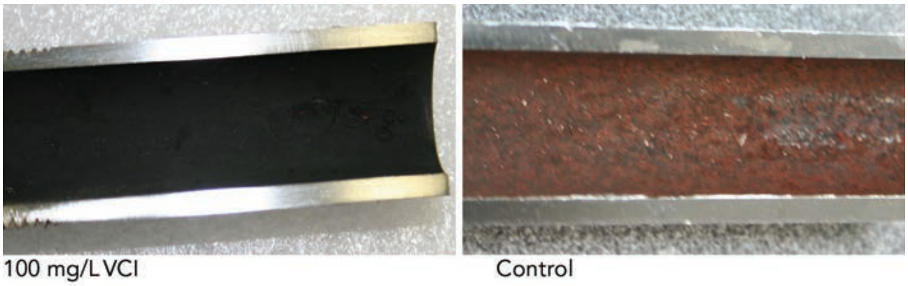
FIGURE 5 Comparison of corrosion ER probe surface condition of the inhibitor treated loop and control test after 2,200 h corrosion test in hot steam/water closed loop.

Elevated temperature corrosion tests on CS pipe samples in the steam/water loop with VCI and without inhibitor (control reference) were conducted using the electric boiler steam/water in a closed loop system that could circulate and maintain hot steam at 90 psi and 118 °C. The control reference test (without inhibitor addition) was conducted for 1,100 h and the corrosion rate was monitored using ER techniques. Figure 4 shows the corrosion rate over time for the reference sample without using any water treatment or inhibitor. The average corrosion rate was measured to be 8.2 to 8.9 mpy.

After 1,100 h, 500 mg/L of VCI was injected into the closed loop system. This addition resulted in a significant drop in the corrosion rate to 0.72 mpy. This indicates that the VCI had successfully retarded the corrosion reaction and managed to stabilize formation of protective magnetite on the internal surfaces. The corrosion test in the steam/water closed loop was continued for 1,900 h in total (800 h beyond introduction of inhibitor to the closed loop system) and the dosage of inhibitor was maintained at 100 mg/L. The ER probe showed a steady corrosion rate of 1.30 mpy. This is a very impressive result, indicating that a corroding closed loop steam/water system can be successfully recovered by introduction of inhibitor treatment to lower its corrosion rate to an acceptable level. Figure 5 also shows the corrosion rate over time for the corrosion test in the steam/water closed loop with 100 mg/L VCI addition for 2,200 h. The average corrosion rate was measured at 1.09 to 1.24 mpy. During the boiler drainage (blowout), no sign of any rust formation in the discharged water was observed.

Figure 5 shows the comparison of the ER probes that were used to monitor corrosion rate during these investigations. Figure 6 shows the comparison of corrosion rate measurements for the inhibitor treated loop and control reference after 2,200 h corrosion in the hot steam/water closed loop. The control probe showed heavy rust formation on its surface, while the 100 mg/L VCI ER probe showed a thin layer of black magnetite and relatively clean surfaces. Figure 6 shows the section of the closed loop steel pipe after corrosion tests. Comparison of these internal surfaces show that the control pipes internal surfaces are covered by hematite (rust formation due to their high corrosion rate) while the test conducted with corrosion inhibitor VCI is mainly covered by a thin magnetite oxide.

XPS analyses were conducted on the internal surfaces of both the control sample and inhibitor-treated steel pipe. Results are shown in Figure 7. High-resolution XPS analysis was also conducted on both the control and inhibitor-treated steel pipes (Figure 8). The nature of the surface oxide was compared after 2.0 nm of the top surface deposits were etched to remove ambient changes or accidental surface contamination. XPS data showed that the oxide on the internal surface of the control sample (no inhibitor) is hematite, Fe 2p, with binding energy 710.4 eV, while the oxide on the inhibitor-treated pipes is magnetite oxide, Fe 2p with a binding energy of 708.2 eV (Figure 8). These observations reaffirmed that VCI presence in water promotes formation of a protective thin layer of black magnetite, adheres very well to steel pipe surfaces due to its magnetic properties, and provides very suitable corrosion performance.


100 mg/L VCI

Control

FIGURE 6 Comparison of steel pipe inner surface conditions of the inhibitor treated loop and control test after 2,200 h corrosion test in hot steam/water closed loop.

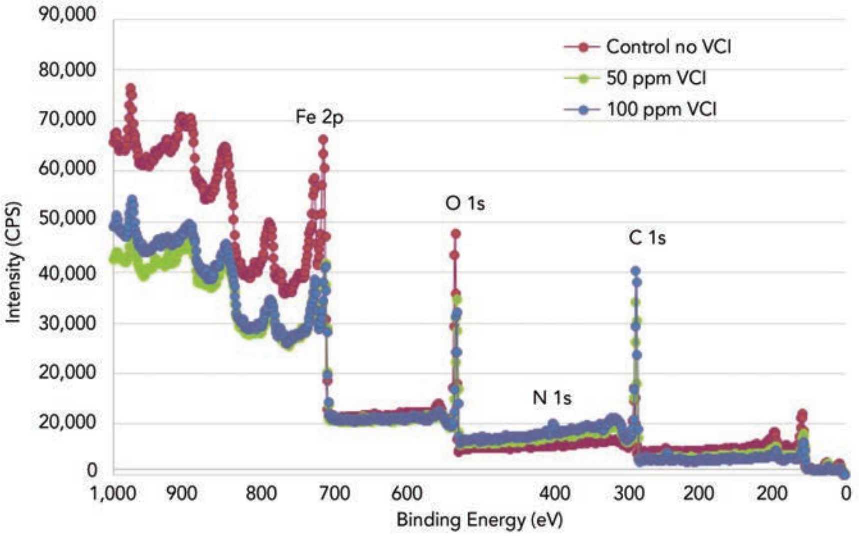


FIGURE 7 XPS analyses on the inner pipe surfaces after corrosion test in the hot steam loop shows more corrosion product on the control test.

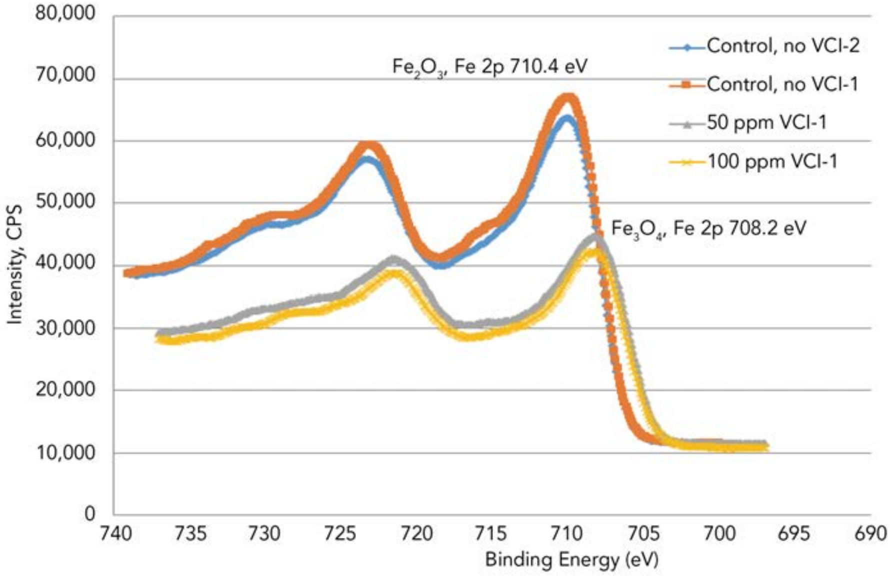


FIGURE 8 Comparison high-resolution XPS analyses on the inner pipe surface after corrosion test in the hot steam loop. Primary oxide seen on inner diameter (ID) surface of non-treated pipes (control) is hematite, while magnetite is predominant oxide on ID surface of VCI-treated pipes.

Conclusions

Corrosion behavior of CS pipe material samples in a steam/water loop with and without VCI was investigated. Electrochemical polarization behavior showed the VCI is an anodic corrosion inhibitor and when present in the environment, expands the region of stability of a magnetite Fe_3O_4 passive film. The passive range and film breakdown potential increased and shifted to more anodic voltage, indicating less susceptibility to localized corrosion. Corrosion behavior of the steel pipe samples in boiling water showed corrosion rates for the control sample to be roughly 5.3 mpy; when 50 mg/L VCI was added, it decreased to 1.94 mpy; and for 100 mg/L addition, the corrosion rate dropped to 1.36 mpy. The addition of 200 mg/L reduced the corrosion rate to 0.97 mpy, while the addition of 500 mg/L resulted in a very low corrosion rate of 0.37 mpy. In boiling water, corrosion rates for the reference steel sample was ~5.3 mpy; for 100 mg/L hydrazine addition, the corrosion rate was 1.46 mpy; and for 500 mg/L hydrazine addition, a 0.38 mpy rate was achieved.

Corrosion behavior of CS pipe material samples in a steam/water loop with VCI and without inhibitor in a closed loop system of 90 psi at 118 °C showed a corrosion rate of 8.2 to 8.9 mpy, while the corrosion rate in the steam/water closed loop with 100 mg/L VCI addition decreased to 1.09 to 1.24 mpy. In a corroding system (control sample condition) when 500 mg/L VCI was injected into the closed loop system after 1,100 h, the corrosion rate dropped to 0.72 mpy. This indicates that the VCI successfully retarded corrosion reactions and managed to form stable protective oxide of magnetite on the pipe interior surfaces. This is a very impressive result; a corroding closed loop steam/water system can be recovered with the inhibitor treatment and its corrosion rate lowered to an acceptable level.

High-resolution XPS analysis confirmed that the dominant oxide on the internal surfaces of the control (no inhibitor) pipe was hematite, while the oxide on the inhibitor-treated pipes was magnetite oxide. These observations reaffirmed that the VCI presence in water promotes formation of a protective thin layer of black magnetite that adheres well to the steel pipe surface due to its magnetic properties and provides very satisfactory corrosion control performance.

In summary, this investigation confirmed that the new VCI ican be an effective replacement for the toxic hydrazine for steel materials exposed to hot steam/hot environments. The major advantage of the new VCI is its very low toxicity, making it safe and easy to handle in typical application systems. The oral toxicity test measure of the LD50 "Lethal Dose" of the new VCI is 2,190 mg/L for rats. Hydrazine has an LD50 of only ~15-22 mg/L, indicating a very high toxicity.

The new amine-based VCI corrosion inhibitor is very promising and can reduce environmental impact, improve the work environment, reduce deposition that minimizes the frequency of chemical cleaning for through-flow boilers, and reduce pipe wall thinning due to flow-accelerated corrosion.

References

1. G. Choudhary, H. Hansen, "Human Health Perspective of Environmental Exposure to Hydrazines: A Review," Web (05-Jan. 2017).
2. A.A. Berk, "Observations on the Use of Cyclohexylamine in Steam-heating Systems" (Washington, D.C.: U.S. Dept. of the Interior, Bureau of Mines, 1944).
3. Water Purification Handbook, Chapter 19, "Condensate System Corrosion," Web (09 Mar. 2017).
4. E.W. Schmidt, *Hydrazine and Its Derivatives: Preparation, Properties, Application,* Vol. 2. (New York, NY: J. Wiley, 1984).
5. "Cyclohexylamine," Chemical Book—Chemical Search Engine, Web (24 Aug. 2016), http://www.chemicalbook.com/ChemicalProductProperty_EN_CB8139274.
6. "CYCLOHEXYLAMINE," *Chemical Market Reporter* (16 Nov. 1998): 41, General OneFile, Web (23 Aug. 2016).
7. "Cyclohexylamine (Hexahydroaniline)," Web (24 Aug. 2016).
8. L. Estevão, and R. Nascimento, "Modifications in the Volatilization Rate of Volatile Corrosion Inhibitors by Means of Host–Guest Systems," *Corrosion Science* 43, 6 (2001).
9. L.L. Schneider, D.C. Hutchins, "Alternative Chemical Treatment for Cyclically Operated Unit-DEHA," *International Water Conference J.* (1986): p. 21.
10. D.I. Bain, G.G. Engstrom, M.T. Fryer, "Recent Advances in Volatile Oxygen Scavenger Technology," *CORROSION* (1994): p. 201.
11. D.M. Ellis, D.G. Cuisia, H.W. Thompson, "The Oxidation and Degradation Products of Volatile Oxygen Scavengers and their Relevance in Plant Applications," *CORROSION* (1987): p. 432.
12. K.L. Rossel, J.A. Kelly, J. Richardson, "Steam Cycle Protection for Pulp and Paper Systems," *CORROSION* (1991): p. 184.
13. H.W. Thompson, "Use of Oxygen Scavengers in Wet Lay-up of Boilers and Auxiliaries," *CORROSION* (1986): p. 174.
14. D.G. Cuisia, J.W. Rudolph, C.M. Hwa, T.E. Tehle, Jr., "New Oxygen Scavenger for Boiler Systems," *CORROSION* (1983), p. 83.
15. "HELAMIN-How It Works," Web (08 Jan. 2017).
16. "Amine Proves Effective Alternative to Hydrazine," Web (08 Jan. 2017).
17. "HELAMIN® BRW 150H," Web (09 Jan. 2017).
18. "Fulmer Technical Services," *Physics Bulletin* 21.4 (1970): pp. 147-48.
19. B.A. Miksic, *Preservation, Lay-Up and Mothballing Handbook*, 3rd ed. (2014).
20. B.A. Miksic, "Use of Vapor phase Inhibitors for Corrosion Protection of Metal Products," CORROSION/83, paper no. 308 (Houston, TX: NACE International, 1983).
21. B.A. Miksic, R.H. Miller, "Fundamental Principles of Corrosion Protection with Vapor Phase Inhibitors," 5th European Symp. on Corrosion Inhibitors, EFC (1980).
22. B.A. Miksic, *VpCI Technology Handbook* (St. Paul, MN: Cortec Corp., 2014).
23. B. Bavarian, "Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitor and Dry Air Systems," Eurocorr/2014.
24. M.H. Taylor, "Corrosion Inhibitor," Patent US2060138.
25. C.D. Kuhfeldt, J.M. Bryson, Ashland, Inc., "Process for Retarding the Formation of Corrosion on Metal Surfaces," Patent US650344 (Jan. 2017).
26. ASME B31.1, "Power Piping" (New York, NY: ASME, 2016).
27. ASTM G123-2015, "Standard Test Method for Evaluating Stress-Corrosion Cracking of Stainless Alloys with Different Nickel Content in Boiling Acidified Sodium Chloride Solution" (West Conshohocken, PA: ASTM International, 2015).

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BEHZAD BAVARIAN is a professor in the Department of Manufacturing Systems Engineering and Management and director of the W.M. Keck Advanced Materials Laboratory at California State University Northridge (CSUN), Northridge, California, USA, email: Bavarian@csun.edu. He received his Ph.D. in metallurgical engineering at The Ohio State University in 1980. He has been a member of NACE International for 35 years and received a 2012 NACE Technical Achievement Award for contributions to corrosion and corrosion engineering.

LISA REINER is a professor in the Department of Manufacturing Systems Engineering and Management and manager of the W.M. Keck Advanced Materials Laboratory at CSUN.

JAMES HOLDEN James E. Holden is the director of Energy and Engineered Services at Cortec Corp. He has more than 40 years of experience in the design and manufacture of rotating equipment such as jet engines, gas and steam turbines, and gearboxes. He is a Professional Engineer, has an M.B.A., and has a Master Black Belt in Six Sigma. He is a member of NACE..

BORIS A. MIKSIC, FNACE, is president and chief executive of Cortec Corp., St. Paul, Minnesota, USA. He has served in this capacity for 40 years. Cortec is a world leader in the manufacture of corrosion inhibitors in several industries, including modern plastic products. Miksic holds more than 43 U.S. and foreign patents and patent applications and has presented papers throughout the world. He received the NACE International F.N. Speller Award for longtime contributions to corrosion engineering. A NACE Fellow, he has been a NACE member for more than 40 years. MP

Removable Coatings for Up to One Year Service Life in the Oil and Gas Market

Markus Bieber, *Cortec Corp., St. Paul, Minnesota, USA*

The oil and gas industry has a tremendous need for the protection of assets during shipment and storage. Newer advances have allowed the use of the vapor phase corrosion inhibitor (VCI) technology to be incorporated into temporary coatings that are designed to provide corrosion protection in extreme environments, yet still be easily removable compared to the older traditional wax-type coatings made from hydrocarbons. By incorporating the VCI technology into these temporary coatings, it allows the use of thinner film thicknesses and less reliance on a thick barrier to keep contaminants away from the surface.

Vapor phase corrosion inhibitors (VCIs) are a corrosion inhibitor technology that is comprised of very small particles that are attracted to a metal substrate. They come in various formulations that are dependent on the type of system they will be used in; for example, films, oils, coatings, cleaners, etc. There are also a variety of formulations that provide protection in ferrous, nonferrous, or multi-metal applications. Other variables include the amount of vapor phase compared to contact phase inhibitors.

How VCIs Work in a Coating

VCIs are formulated into a coating through a complex development process that involves determining chemical compatibility of the VCIs with the other components of the coating, such as the resin, solvents, pigments, and other additives used for a variety of reasons. VCIs work by adsorbing onto the metal surface in a nonreactive attractive capacity; in other words, they are attracted to the metal through the particle charge.[1]

How VCIs Compare to Traditional Inhibitors

Traditional inhibitor systems use inorganic metal particles such as zincs, chromates, aluminum, and others. Additionally, traditional inhibitor systems often rely on thick barriers to prevent moisture and oxygen from getting to the substrate. VCIs compare with traditional inhibitor systems by using smaller particles as well as relying not only on contact inhibition but also vapor phase inhibition, providing more complete coverage and protection of the surface.[2-3] This is illustrated in Figures 1 and 2.

Types of Coating Systems That Can Use VCIs

VCIs can be used with most coating systems. There are many variations of VCIs and the key is to choose the correct VCI for the corresponding coating system by checking compatibility, effectiveness, and processability. Compatibility is determined using bench ladder tests that use various concentrations of VCIs and various versions of VCIs to determine if there is phase separation, gelling, or particle generation. Typically this is done visually and the formulating chemist will determine if the results are acceptable.

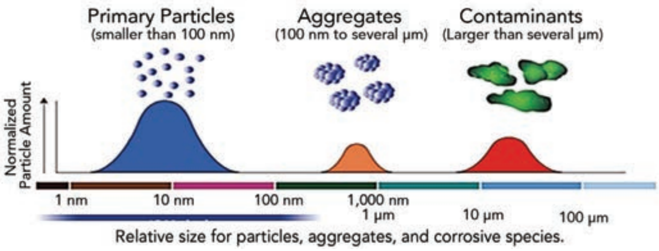


FIGURE 1 VCIs provide more complete coverage and protection of a surface than traditional inhibitor systems.[4]

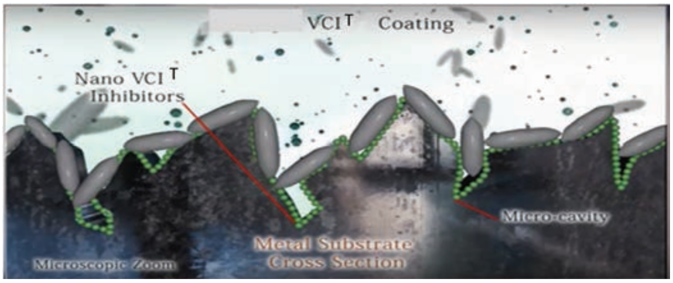


FIGURE 2 The larger platelets are representative of traditional inhibitors that are unable to fill the micro-crevices, leaving gaps where corrosion can start and/or grow.[5]

Environmental Advantages of VCIs Over Traditional Inhibitors

Traditional inhibitors containing heavy metals, nitrites, or secondary amines or banned materials such as dicyclohexylammonium nitrite are becoming increasingly more regulated and often are no longer allowed to be used due to the negative impact they have on the environment and carcinogenic effects on workers exposed to them. The environmental advantages of using VCIs are that they are nontoxic, do not contain heavy metals, and have no adverse effect due to their low usage concentrations. VCIs have long been used in other products such as polyethylene films, foams, powders, and liquids to provide a vapor phase of corrosion protection without impacting the environment.

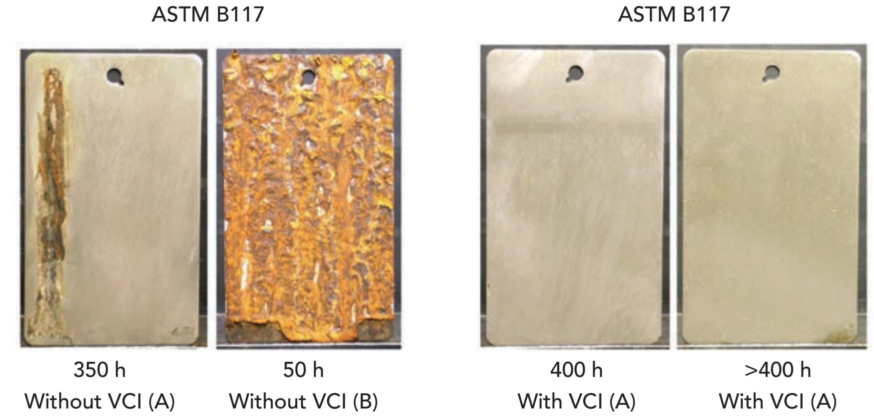
Removal of Temporary Coatings

Removal of temporary coatings can be done using environmentally friendly alkaline cleaners. These cleaners are typically diluted in water at a relatively low concentration (2 to 20%), sprayed or brushed onto the coated surface, and allowed to dwell for a period of 5 to 15 minutes. The coating is then removed using a hot water wash (120 to 180 °F [49 to 82 °C]).

Experiments

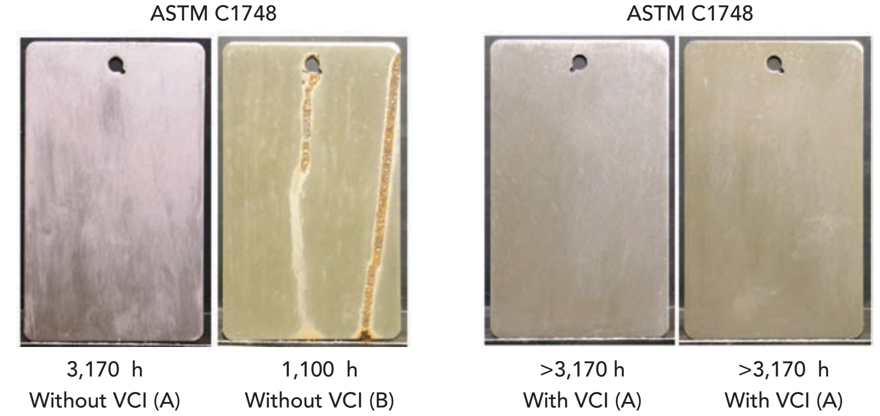
These studies examine the effectiveness of various types of corrosion inhibitors in solvent and waterborne removable coatings, based on salt fog results (ASTM B117[6]) and humidity results (ASTM D1748[7]). ASTM B117 tests products in a 5% sodium chloride (NaCl) salt fog chamber with continuous exposure. ASTM D1748 tests products in a 120 °F, 95% relative humidity chamber with continuous exposure.

Each coating was applied on cold rolled steel panels (SAE 1010) obtained from an industry supplier of test panels. The panels provided are pre-cleaned test panels that are ready to use without any additional surface preparation required. In some cases, coatings were applied to actual parts provided by customers. Dry film thicknesses (DFTs) were according to the manufacturer's recommendations (Figure 3, 4, 5, and 6).


ASTM B117 ASTM B117

350 h Without VCI (A) | 50 h Without VCI (B) | 400 h With VCI (A) | >400 h With VCI (A)

FIGURE 3 Salt spray testing for solvent-borne wax coating without and with VCIs.


ASTM C1748 ASTM C1748

3,170 h Without VCI (A) | 1,100 h Without VCI (B) | >3,170 h With VCI (A) | >3,170 h With VCI (A)

FIGURE 4 Humidity testing for solvent-borne wax coating without and with VCIs.

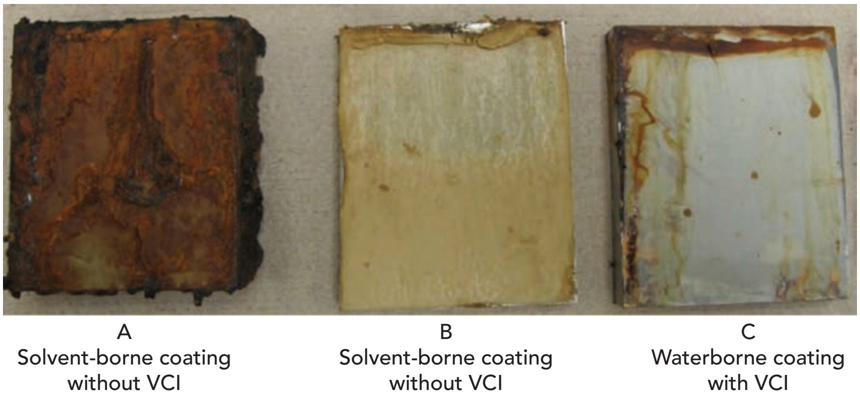

A Solvent-borne coating without VCI | B Solvent-borne coating without VCI | C Waterborne coating with VCI

FIGURE 5 Salt spray (ASTM B117) testing for various systems (600 h).

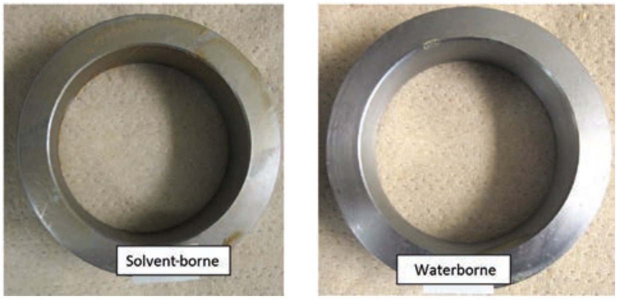


FIGURE 6 Humidity testing for solvent-borne wax coating and waterborne wax coating with VCIs (768 h).

FIGURE 7 Construction grader.

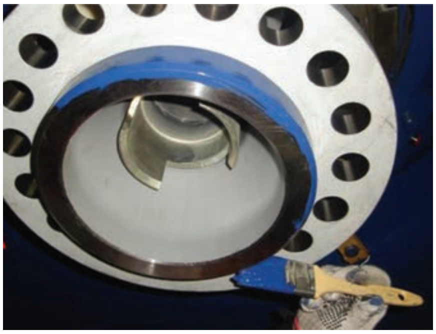


FIGURE 8 Industrial equipment.

This testing shows that waterborne systems can compete with solvent-borne systems through the use of VCIs (Figure 5 and 6). However, there are some distinct advantages for using a waterborne system, which include:

- More environmentally friendly
- Lower volatile organic compounds (VOCs)
- Easier cleanup

Case History 1

Problem

A manufacturer of large construction graders (Figure 7) needed an effective alternative to prevent corrosion on its products. There were several disadvantages to the heavy wax-type product it was using. First, it did not always work if the equipment was stored outdoors for extended periods of time before shipping. Second, it left a greasy and slippery film on the graders, which made it difficult to climb into them for moving and shipping. Finally, the product was hard to remove and had to be disposed of as hazardous waste.

Application

The manufacturer sprayed the VCI-containing coating and solvent in a 3:1 ratio on the equipment, which resulted in DFTs between 0.8 and 1 mil (20 to 25 µm). Then the machines were transported by rail to the seaports. A few of the graders were placed in containers, but the majority were left uncovered.

The VCI-containing coating at 1 mil outperformed the traditional wax-type coating at 3 mils (75 µm). The manufacturer also found the VCI-containing coating easier to spray, free of offensive odors, and much easier to remove. After two years of export shipments, it had experienced no corrosion problems when using the thinner film VCI-containing coating.

Case History 2

Problem

A manufacturer of industrial equipment (Figure 8) was struggling with protecting critically machined surfaces from corrosion and damage during transport. Due to the nature of the equipment, it was not able to deal with a spray application of a coating nor washing it down for removal.

Application

The manufacturer brush-applied the waterborne VCI-containing coating onto the equipment, which resulted in DFTs between 2 to 10 mils (50 to 250 µm). The equipment was transported to the final destination where the coating was removed by simply peeling it off.

Conclusions

There is a need in the marketplace for environmentally friendly, low VOC, removable coatings that can be applied at a thin film thickness (1 mil) that provide adequate corrosion protection and yet can still be easily removed. Compared to permanent coatings where removal requires blasting or the use of heavy-duty solvents, or thick heavy barrier-type wax coatings that are difficult to remove and dispose of, many removable thin film coatings with VCI technology can be easily removed using an alkaline solution and high-pressure water.

In offshore oil and gas applications where the preservation of critical spare parts, or structures in a very severe environment is critical, these coatings can save customers from costly downtime of their equipment.

This article shows, through research, that systems enhanced with VCIs can greatly improve the corrosion resistance of both solvent and waterborne coatings. In addition, waterborne coatings with VCI inhibitors can compete from a performance aspect with solvent-borne systems, while at the same time being more environmentally friendly, easier to clean up, and lower in VOCs.

References

1. Y.I. Kuznetsov, et al., "Inhibiting Action and Absorption of Beta-Aminoketones on Metals," *Zasshchita Metallov* 32, 5 (1996): pp. 528-533.
2. C.W.Lea, FUCHS Lubricants, 2003 National Corrosion Service.
3. S. Prabhu, "Temporary Corrosion Protection during Storage, Transportation and Handling" (2016).
4. B. Bavarian, B.A. Miksic, "Influence of Crystalline Structure and Particle Size of Vapor Corrosion Inhibitor Powders on Their Inhibiting Effectiveness," CORROSION 2016 Research Symposium, Vancouver, BC, Canada.
5. B.A. Miksic, "Use of Vapor Phase Inhibitors for Corrosion Protection of Metal Products," CORROSION/83, paper no. 308 (Houston, TX: NACE International,1983)
6. ASTM B117-16, "Standard Practice for Operating Salt Spray (Fog) Apparatus" (West Conshohocken, PA: ASTM International, 2010).
7. ASTM D1748-10, "Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet" (West Conshohocken, PA: ASTM, 2010).

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MARKUS BIEBER is the director of sales—High Performance Coatings & Additives at Cortec Corp., St. Paul, Minnesota, USA, email: mbieber@cortecvci.com. He has spent more than 20 years in product and sales management in the coatings industry, with a focus on providing customers with value-added coating solutions. He is a member of NACE International. MP

Preventing Corrosion Under Insulation

Corrosion under insulation (CUI) is a serious concern both in terms of monetary loss and danger to personnel safety. It is a top culprit for piping leaks and near misses and results in significant maintenance costs. It can mean the difference between a safely operating refinery or the depressurization of an entire hydrocarbon system at a gas plant.[1]

CUI is caused by water trapped between insulation and a metal surface. It may be due to leakage, condensation, rain, or other causes. CUI occurs mainly on carbon steel (CS), but it also affects stainless steel (such as 18-8 grades and 300 series). CUI tends to be the most severe on equipment operating at temperatures of 120 to 200 °F (49 to 93 °C), but it can affect both carbon and stainless equipment operating at temperatures anywhere from 25 to 302 °F (–4 to 150 °C).[1-2]

Based on Exxon data,[1] 84% of CUI leaks happen on piping, 81% of which is less than 4 in (100 mm) in Nominal Pipe Size (NPS). Pipe wall thickness appears to be a key factor in CUI failure, with failures of piping in the 16 to 20-year range occurring mainly on <4-in NPS low Wall Thickness (WT) >Sch 40 wall piping, and failure in the over 25-year range occurring mainly on piping with >6-in (150-mm) heavy WT >Sch 40 wall thickness.[1]

Temperature and containment sources influence the CUI rate, with wet insulation being the root cause of the problem. Maintenance costs are significant both in terms of materials and resources. Approximately $0.35 of every general maintenance dollar goes to costs for fixed equipment, such as vessels and piping. Of fixed equipment costs, about 54% is spent on piping (about $0.20 of every maintenance dollar), with CUI making up 40 to 60% of piping cost (or $0.10 of every maintenance dollar).[1]

One example of the cost impact of CUI occurred in 2006 when a leak in a 4-in hydrocarbon line caused a massive fire at an aging Gulf Coast petrochemical facility. Half the unit was destroyed, and resulting costs reached $50 million.[2] This demonstrates how dangerous and expensive a leak from CUI can be. Another example occurred in 2008 at a Dow Chemical Plant. Despite excellent maintenance, inspection, and safety records, aging materials suffered from CUI in a high condensation area. An 8-in (200-mm) CS hydrocarbon line sprang a pinhole leak that caused the piping to fail drastically as the operators worked on isolating and de-pressurizing the area. The force of the explosion buckled the pipe, fortunately causing it to seal itself and offset what could have been a terrible disaster.[3]

Use of Volatile Corrosion Inhibitors to Prevent CUI

Testing performed at California State University, Northridge,[4] demonstrated that Cortec® VpCI®-619†, a volatile corrosion inhibitor (VCI), is an effective means of controlling CUI in the temperature range of 170 to 350 °F (77 to 177 °C).

In this investigation, four API 5L X65 steel pipes were insulated with a thermal insulator (fiberglass system) to determine the effective protection of a VCI corrosion inhibitor against CUI. The specimens underwent isothermal and cyclic wet/dry test conditions at 170 °F and 350 °F. Results demonstrated that this VCI could successfully reduce corrosion attack under insulation even in a chronic wet environment. After corrosion testing, chemical analysis of insulated samples exhibited the presence of a protective Mo-rich inhibition compound on pipe surfaces. In a companion test, the corrosion rate dropped by a factor of 15 when the VCI was added to a 200-ppm salt solution during the testing of bare pipe segments at boiling temperature. The report states, "These results showed that an effective protective coating system under the insulation is critical and requires the inclusion of VCI to prolong the pipe integrity and lower inspection and maintenance cost."[4]

The test was performed in two parts. In the portion of the test that involved boiling a steel pipe segment in a 200-ppm chloride solution, one sample included VCI and one did not. The corrosion rate of the control pipe was ~5.3 mpy, while the corrosion rate of the pipe boiled in the VCI/chloride solution was 0.36 mpy, 15 times less than the control.

The other part of the test involved insulated piping that was subjected to cyclic corrosion testing for 240 h. The purpose was to see if VCI impregnated into the thermal insulation would protect the pipe. The insulation of the control pipe remained untreated. Both the control and treated sample were injected with a 200-ppm sodium chloride (NaCl) solution every 48 h, and the samples were inspected every five days. After 240 h, the untreated pipe showed localized corrosion, but the surface of the VCI-treated pipe remained well-protected. Consistent with inhibitor chemistry, a molybdenum-rich protective film was detected on the surface of the VCI-protected pipe.

References

1. H. Ahluwalia, "The Hidden Enemy: Corrosion Under Insulation." Material Selection Resources Inc. presentation on 14 Nov. 2014, https://rbi1.gatech.edu/2014-corrosion-symposium-presentations.
2. S.A. Anderson, "Out of Sight, Out of Mind?" *Hydrocarbon Engineering*. August 2010, http://www.intertek.com/articles/2010-08-corrosion-under-insulation/.
3. R. Sampaio, A.L.M.V. Leite. "More Lesson Re-Learned from Corrosion Under Insulation," 13 Mar. 2018. http://www.penderlo.com/doc/Dow_CUI.pdf.
4. B. Bavarian, "Protection Effectiveness of Vapor Corrosion Inhibitor VpCI 619 for Corrosion Under Insulation at Elevated Temperatures." California State University, Northridge, and Cortec Corp., Feb. 2018, https://www.cortecvci.com/Publications/Papers/CUI-report-on-VCI-619.pdf. MP

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†Trade name.

Migrating Corrosion Inhibitors to Protect Steel Reinforced Concrete Structures

Behzad Bavarian, Akinbosede Oluwaseye Alaba, and Lisa Reiner, *California State University, Northridge, California, USA*
Jessica Meyer, *Cortec Corp., St. Paul, Minnesota, USA*

Most transportation infrastructure is built from steel and concrete. The steel may be in structural sections, such as girders, piles, or rails, or embedded in concrete to form reinforced or prestressed concrete. Concrete provides excellent protection for embedded steel because Portland cement is very alkaline, forming a passive, protective layer on the steel surface. Concrete is also permeable, and even good-quality concrete can be penetrated by aggressive chemical ions that may initiate steel corrosion. Migrating corrosion inhibitors (MCIs), a blend of amine carboxylates and amino alcohols, show versatility as admixtures, surface treatments (coatings), and in rehabilitation programs. Examination of the embedded steel rebar after corrosion tests showed no corrosion attack for the MCI-treated concrete samples, while non-treated concrete showed localized corrosion. X-ray photoelectron spectroscopy and depth profiling confirmed that the inhibitor had reached the rebar surface in about 150 days. The amine-rich compound on the rebar surface improved corrosion protection for the MCI-treated steel rebar even in the presence of chloride ions and prevented red rust formation.

Corrosion is one of the primary concerns in the durability of materials and structures. Research efforts have been made to find a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damage in new structures.[1-3] Outside the laboratory environment, infrastructure may suffer from attack by carbonation, and chloride ions dissolved in water can permeate through the concrete pores, then penetrate the protective oxide film on the steel surface. Carbonation of concrete can lower the amount of chloride ions needed to promote corrosion. In new concrete with a pH of 12 to 13, about 7,000 to 8,000 ppm by weight of cement chloride is required to initiate steel corrosion. If, however, the pH is lowered to a range of 10 to 11, the chloride threshold for corrosion is significantly lowered to roughly 100 ppm.[4]

Chlorides in the concrete can come from several sources. They can be cast into the structure by the use of deliberate admixtures (calcium chloride [$CaCl_2$]), or the chloride ions can appear in the mix (mixing water, aggregates) unknowingly. However, the major cause of chloride-induced corrosion in most structures is the diffusion of chlorides from the environment due to direct exposure with a marine environment or the use of deicing salts and chemicals. There are four different mechanisms of chloride transport into crack-free concrete. They include capillary action, diffusion due to the high concentration on the surface, permeation under pressure, and migration due to electrical potential gradients.[4-5] Similar to carbonation, the chloride attack process does not directly corrode steel reinforcement; however, it does break down the protective iron oxide film and promote corrosion. Chlorides do play a role as catalysts to corrosion. However, the mechanism of chloride diffusion into concrete is different for carbonation in that it attacks the passive layer without the requirement of pH reduction.

Corrosion inhibitor technology was developed to protect the embedded steel rebar/concrete structure. These inhibitors use compounds that work by forming a monomolecular film between the metal and the water. In the case of film-forming amines, one end of the molecule is hydrophilic and the other hydrophobic. Most current migrating inhibitor admixtures are based on amino carboxylate chemistry and the most effective types of inhibitor interact at the anode and cathode simultaneously.[2] These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement, forming a barrier.[3,6-11] Migrating corrosion inhibitors (MCIs) are able to penetrate into existing concrete to protect steel from chloride attack. The inhibitor migrates through the concrete capillary structure, first by liquid diffusion via the moisture that is normally present in concrete, then by its high vapor pressure, and finally by following hairlines and microcracks. The diffusion process requires time to reach the rebar surface and to form a protective layer. These corrosion inhibitors can be incorporated as an admixture or can be surface impregnated on existing concrete structures. Laboratory tests have proven that these corrosion inhibitors migrate through the concrete to protect the rebar against corrosion even in the presence of up to 2.20% chlorides.[9]

Experimental Procedure

This study focused on the usefulness of inhibitors based on amino carboxylate chemistry and their means of application. Six concrete samples were cast (dimensions 280 by 110 by 150 mm) per ASTM G109[12-13] using commercial-grade silica sand, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate). The reinforced concrete samples included one control, one with soda ash, and four with corrosion inhibitor admixtures. Two inhibitors, A and B (both amine carboxylate-based), were added to the concrete mix per the ASTM G109 sample preparation method, with reinforcement rebar placed at 20-mm concrete coverage. These samples were prepared with a 0.55 water/cement ratio. All samples contained three electrodes (class 60 steel rebar with dimensions of 300 mm length, 12.5 mm diameter). Concrete compressive strengths were roughly 26 MPa after 28 days of curing.

The ASTM G180[14] test method involving steel and concrete admixtures was used to verify effectiveness of the corrosion inhibitors. The concrete samples were immersed in 3.5% sodium chloride (NaCl) at ambient temperatures and tested for a period of 150 days. The corrosion behavior of the steel rebar was monitored using electrochemical impedance spectroscopy (EIS). The experiments were conducted using commercially available systems for EIS and direct current corrosion tests. Bode plots were created from the data obtained using the potentiostatic technique. By comparing the Bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the resistance polarization (Rp) value over time. To verify this analysis, the Rp values were also estimated by using a curve-fitting algorithm on the Nyquist and Bode plots. In these plots, the Rp and RΩ combined values are displayed in the low frequency range of the Bode plot and the RΩ value can be seen in the high frequency

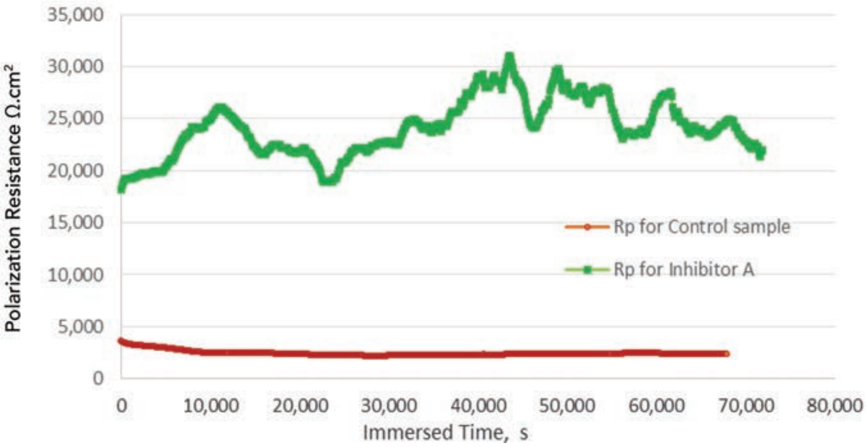

FIGURE 1 Polarization resistance measurements of steel rebar in 3.5% NaCl solution.

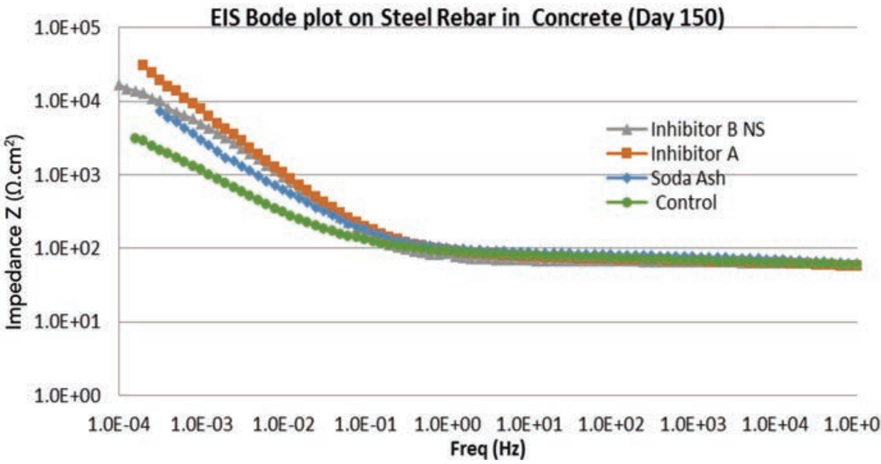

FIGURE 2 Comparison of the EIS Bode plots of steel rebar in different concrete mixes after 150 days of immersion testing.

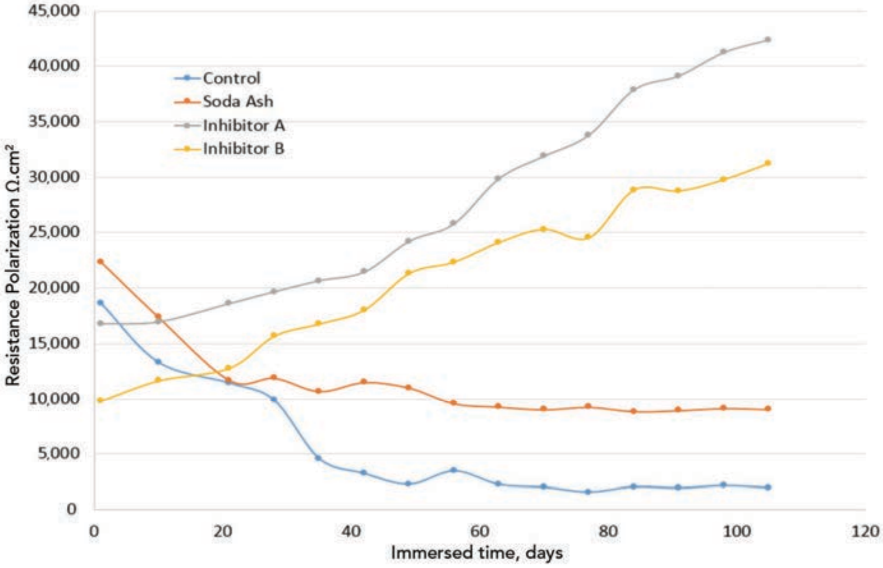

FIGURE 3 Polarization resistance measurements of steel rebar in concrete using EIS show an increasing trend (lowered corrosion rate) for the inhibitor, while control and soda ash samples have a decreasing trend (increased corrosion rate).

TABLE 1. LIFE EXPECTANCY PREDICTION BASED ON THE CORROSION OF THE STEEL REBAR IN CONCRETE

Sample	Rp ($\Omega.cm^2$)	Corrosion Rate (uA/cm^2)	Life Expectancy (Years)
Inhibitor A	39,400	0.28	>50
Inhibitor B	28,800	0.39	>50
Soda Ash	7,180	1.56	~10-12
Control	2,030	5.51	~5-6

Inhibitor A after 150 days

Control after 150 days

Inhibitor B after 150 days

Soda Ash after 150 days

FIGURE 4 Comparison of corrosion behavior for the steel rebar from different concrete samples after 150 days immersed in 3.5% NaCl solution shows localized corrosion attack and red rust formation on the control and soda ash samples.

range of the Bode plot. The diameter of the Nyquist plot is a measure of the Rp value. During this investigation, changes in the Rp and the corrosion potential of the rebar were monitored to ascertain the degree of effectiveness for these admixture products. The samples were tested on a weekly basis and the data were collected for analysis.

Post experiment, visual observation scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analyses were conducted on the steel rebars. A large area surface x-ray photoelectron spectroscopy (XPS) analysis was performed on several steel rebars removed from different concrete samples using XPS in electrostatic lens mode with a resolution pass energy of 80 eV and an aluminum monochromator anode. The depth profiles were conducted using argon ions at 4.0 kV.

Results and Discussion

Polarization resistance measurements of steel rebar in a 3.5% NaCl solution are shown in Figure 1. The amine carboxylate-based MCIs increased the Rp from 2,300 $\Omega.cm^2$ to 31,000 $\Omega.cm^2$. There was successful corrosion inhibition of the steel rebar even in the presence of chloride when the admixtures were added to the concrete. The control sample and the sample with soda ash had decreasing polarization resistance. The steel rebars were not protected from corrosion attack. EIS Bode plots for the steel rebar from the different concrete samples after 150 days immersion in 3.5% NaCl are shown in Figures 2 and 3.

Polarization resistance measurements show an increasing trend (reduced corrosion rate) for the samples with inhibitor, while the control and soda ash samples have an increasing corrosion rate. Inhibitor-protected samples showed an average corrosion rate of 0.28 $\mu A/cm^2$ (with a decreasing trend) compared to the EIS Bode plot results for untreated samples showing a rate of 5.5 $\mu A/cm^2$. This reduction of the corrosion rate translates to an increase in the life expectancy by more than 50 to 60 years (Table 1). The steel rebar surface conditions after 150 days of testing are shown in Figure 4.

XPS analysis confirmed the presence of the amine carboxylate-based inhibitor on the steel rebar surface. Depth profiling showed a 50-nm layer of amine-rich compounds and chloride ions on the rebar surface. Neutralizing effects of the inhibitor assured satisfactory corrosion resistance and the ability to passivate the steel rebar even in the presence of corrosive chloride ions. The XPS results established that both the admixtures and corrosive species (chloride 1.60-2.20%) were present on the rebar surfaces (Figures 5 and 6). The corrosion inhibitors managed to coat the surface and neutralize the corrosive species (chloride ions) to protect the steel rebar.

Conclusions

Amino carboxylate-based corrosion inhibitors (admixtures) successfully demonstrated corrosion inhibition of rebar and can prolong the life of reinforced concrete structures. Rp increased from 2,300 $\Omega.cm^2$ to 31,000 $\Omega.cm^2$ when admixtures were added to concrete. The addition of soda ash to the concrete mixture showed better corrosion protection than for the untreated concrete sample; however, inferior results occurred to those of the concrete samples with corrosion inhibitors. Inhibitor-protected samples showed an average corrosion rate of 0.28 $\mu A/cm^2$ (with a reduced trend) compared to untreated samples that measured 5.5 $\mu A/cm^2$ (based on EIS test results). This reduction in the corrosion rate will increase life expectancy by more than 50 to 60 years. Depth profiling showed a 50-nm layer of amine-rich compound and chloride ions on the rebar surface. XPS analysis confirmed the presence of the amino carboxylate-based inhibitor on the steel rebar surface. Neutralizing effects of the inhibitor assured satisfactory corrosion resistance even in the presence of 1.6-2.2% chloride ions.

References

1. http://www.infrastructurereportcard.org/.
2. D. Bjegovic, B. Miksic, "Migrating Corrosion Inhibitor Protection of Concrete," *MP* 38, 11 (1999).
3. D. Stark, "Influence of Design and Materials on Corrosion Resistance of Steel in Concrete," R & D Bulletin, RD098.01T (Skokie, Illinois: Portland Cement Association, 1989).
4. Portland Cement Association, "Types and Causes of Concrete Deterioration," IS536.01, R&D Serial No. 2617, © 2002 PCA.
5. D.A. Koleva, K. van Breuge, J.H.W. de Wit, E. van Westing, N. Boshkov, A.L.A. Fraaij, "Electrochemical Behavior, Microstructural Analysis, and Morphological Observations in Reinforced Mortar Subjected to Chloride Ingress," *J. of the Electrochemical Society,* 154 (2007): pp. E45–E56.
6. M. Shen, A. Furman, A. Hansen, "Protecting Concrete Reinforcement Using Admixture with Migrating Corrosion Inhibitor and Water Repellent Component," CORROSION 2014, paper no. 4250 (Houston, TX: NACE International, 2014).
7. J.P. Broomfield et al., *Corrosion of Metals in Concrete,* ACI 222R-96.
8. R. Dagani, "Chemists Explore Potential of Dendritic Macromolecules as Functional Materials," *Chemical & Engineering News,* American Chemical Society (June 3, 1996).
9. B. Bavarian, L. Reiner, "Migrating Corrosion Inhibitor Protection of Steel Rebar in Concrete," *MP* (2003).
10. H. Saricimen, M. Mohammad, A. Quddus, M. Shameem, M.S. Barry, "Effectiveness of Concrete Inhibitors in Retarding Rebar Corrosion," *Cement and Concrete Composites,* 24 (2002): pp. 89–100.
11. S. Sawada, J. Kubo, C.L. Page, M.M. Page, "Electrochemical Injection of Organic Corrosion Inhibitors into Carbonated Cementitious Materials," *Corro. Sci.* 49 (2007): pp. 1186-1204.
12. ASTM G109, "Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments" (West Conshohocken, PA: ASTM).
13. G. Qiao, J. Ou, "Corrosion Monitoring of Reinforcing Steel in Cement Mortar by EIS and ENA," *Electrochimica Acta,* 52 (2007).
14. ASTM G180, "Standard Test Method for Corrosion Inhibiting Admixtures for Steel in Concrete by Polarization Resistance in Cementitious Slurries" (West Conshohocken, PA: ASTM).

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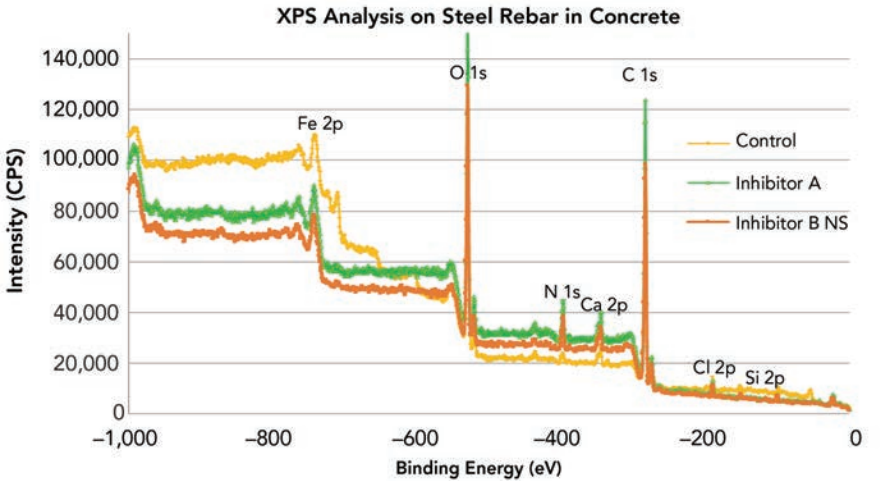

FIGURE 5 Comparison of XPS analysis on steel rebar from different concrete samples after 150 days immersed in 3.5% NaCl solution.

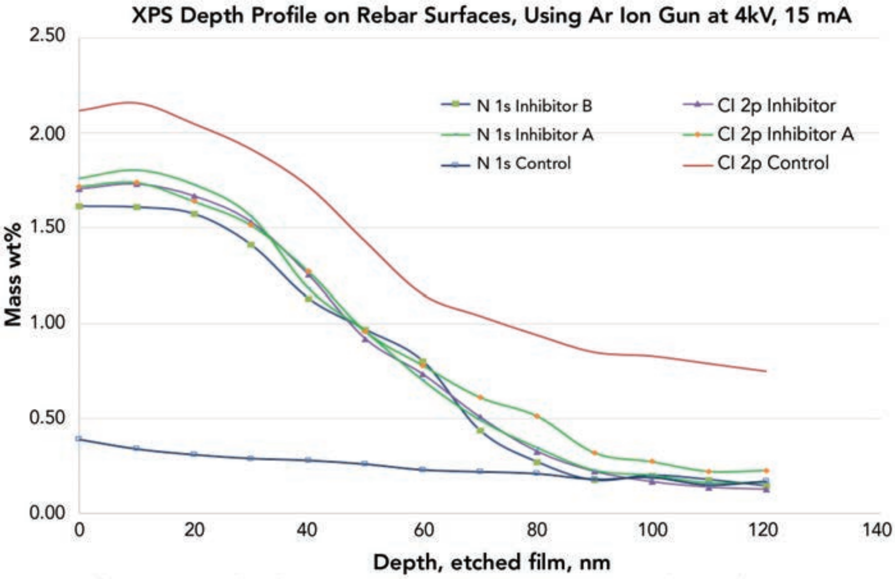

FIGURE 6 Comparison of XPS depth profiling analysis on steel rebar from different concrete samples after 150 days immersion.

BEHZAD BAVARIAN is a professor in the Department of Manufacturing Systems Engineering and Management and director of the W.M. Keck Advanced Materials Laboratory at California State University Northridge (CSUN), Northridge, California, USA, email: Bavarian@csun.edu. He received his Ph.D. in metallurgical engineering at The Ohio State University in 1980. He has been a member of NACE International for 35 years and received a 2012 NACE Technical Achievement Award for contributions to corrosion and corrosion engineering.

AKINBOSEDE OLUWASEYE ALABA is a materials and corrosion research assistant analyst with CSUN, email: seye.akin@yahoo.com. On this project, which was a master's degree thesis, Alaba was a research assistant analyst to Dr. Behzad Bavarian. Alaba holds a Master of Science degree in materials engineering, and is a member of The American Society for Nondestructive Testing and the World Safety Organization.

LISA REINER is a professor in the Department of Manufacturing Systems Engineering and Management and manager of the W.M. Keck Advanced Materials Laboratory at CSUN.

JESSICA MEYER is the vice president of sales—Asia/MCI/Additives at Cortec Corp., St. Paul, Minnesota, USA, email: jessij@cortecvci.com. She holds a B.S. degree in chemistry and business from the University of Wisconsin and has more than 18 years of experience in the construction and corrosion industries. During that time she has held positions in technical service and sales. Meyer is an active member of the American Concrete Institute (ACI) and the International Concrete Repair Institute (ICRI), where she serves on the Board of Directors both locally and nationally. She also serves on a number of technical committees for both ACI and ICRI related to corrosion inhibitors, service life, and sustainability as well as the marketing and chapter committees. *MP*

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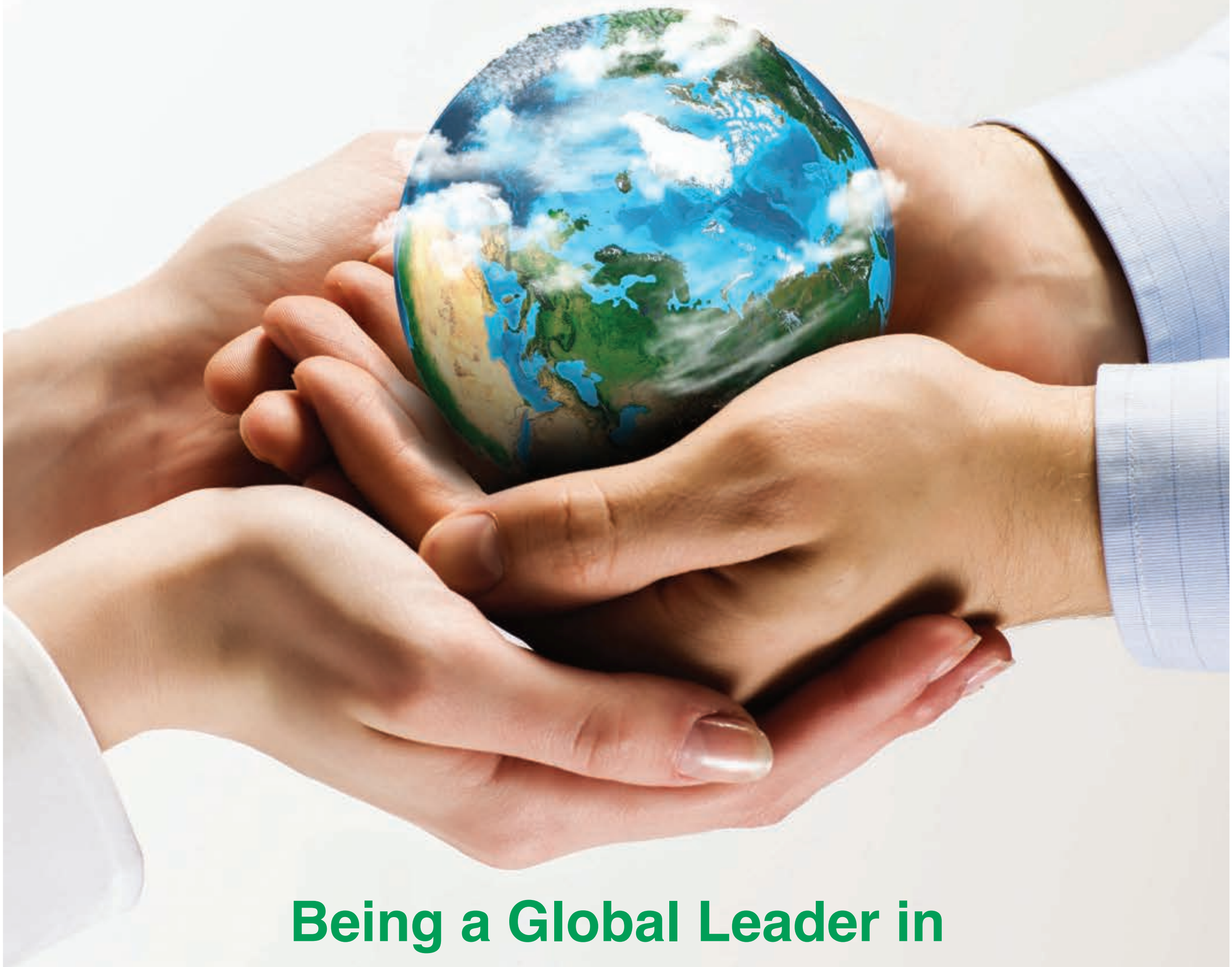

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