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SUPPLEMENT TO JUNE 2014

MMP MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE

CASE STUDY: PROTECTING OFFSHORE PLATFORM CAISSON LEGS WITH A VAPOR CORROSION INHIBITOR

New Solution for Mitigating Corrosion
of Cased Pipelines

Corrosion Control in Dry Fire
Protection Systems

Using Migrating Corrosion Inhibitors
for Concrete Reinforcement



NACE





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About the Cover

Platforms, piping, reinforced concrete, and other components of offshore structures are subject to highly corrosive saltwater and splash zone conditions that require stringent monitoring, maintenance, and corrosion control measures. The article beginning on p. 4 describes a pilot study conducted to evaluate the use of a vapor corrosion inhibitor for structure integrity protection of an offshore platform in Abu Dhabi, United Arab Emirates. The study was undertaken following an explosion caused by gas buildup in the confined compartment around a caisson leg.

EDITORIAL

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ADMINISTRATION

CHIEF EXECUTIVE OFFICER Robert (Bob) H. Chalker
GROUP PUBLISHER William (Bill) Wageneck

ADVERTISING

SALES MANAGER Diane Gross
diane.gross@nace.org,
+1 281-228-6446

ASSISTANT SALES MANAGER Teresa Wright
t.wright@nace.org,
+1 281-228-6472

ACCOUNT EXECUTIVES Erica R. Cortina
erica.cortina@nace.org,
+1 281-228-6473

Brian Daley
brian.daley@nace.org,
+1 281-228-6455

Pam Goliias
pam.goliias@nace.org,
+1 281-228-6456

Jody Lovsness
jody.lovsness@nace.org,
+1 281-228-6257

Leslie Whiteman
leslie.whiteman@nace.org,
+1 281-228-6248

ADVERTISING/BOOKS COORDINATOR Brenda Nitz
brenda.nitz@nace.org,
+1 281-228-6219

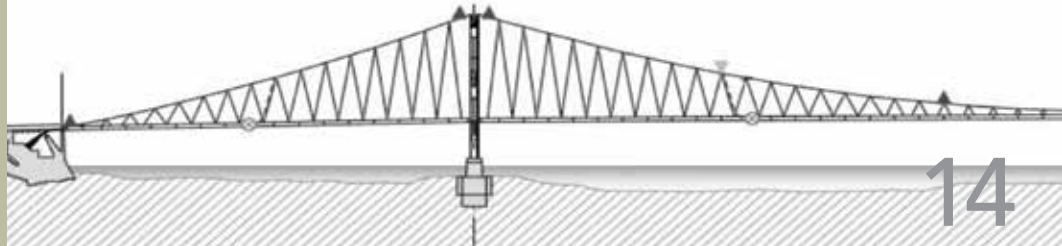
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NACE International Contact Information

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

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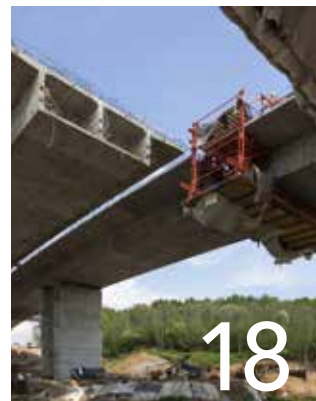


Innovative Technologies for Corrosion Control in a Wide Array of Applications

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* magazine describes several projects where VCIs and MCIs have been effectively used, including applications for protecting cased pipeline crossings and steel-reinforced concrete structures. In addition, there is a case study on how an amine carboxylate VCI is being used to prevent corrosion in the caisson legs of an offshore structure, and a feature that describes a new method for corrosion control in dry fire protection systems.

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.



Protection of Offshore Platform Caisson Legs with a Vapor Corrosion Inhibitor—A Case Study

TALAL A. RAHMAN AL-SAYED, AHMED FATHI EID, AND MAHDI MOHAMED AL-MARZOOQI, Abu Dhabi Marine Operating Co. (ADMA-OPCO), Abu Dhabi, United Arab Emirates

USAMA JACIR, Cortec Middle East, Dubai, United Arab Emirates

In November 2000, gas buildup inside the confined compartment around an offshore platform caisson leg led to an explosion. The gas was found to be hydrogen generated by the depleted anodes inside the caisson leg. An investigation of the fatal explosion made several recommendations, including removal of the anodes, biocide-treated water, and blasting grit that had accumulated inside the caisson legs over two decades. A pilot study was conducted to evaluate the use of a vapor corrosion inhibitor (VCI) for structure integrity protection after removing the blasting grit and biocide-treated water from one of the legs. Treatment commenced with spraying the internal diameter of the leg with a water-based solution containing a VCI with a biocidal treatment. This was followed by fogging the internals with an amine carboxylate VCI. Finally, a string of pouches containing VCI powder was suspended on hangers to assure continuous saturation of inhibitor in the space. Corrosion coupons were installed 6 m below the manhole before closing it. Results after one year and beyond were positive and the system was adopted for rectification of the problem.

ADMA-OPCO is a major producer of oil and gas from the offshore areas of Abu Dhabi in the United Arab Emirates. It is a partnership between ADNOC (60%), BP,

Total S.A., and JODCO. It operates two major fields—Umm Shaif and Zakum—where oil and gas are produced and transferred to Das Island for processing, storing, and exporting. Multiple barge-type offshore platforms are constructed and operated on caisson legs.

Internals of the platform caisson legs are uncoated and filled with biocide-treated water and protected using suspended sacrificial anodes. They also contain debris including blasting grit. After two decades of operation, the anodes had been depleted and gas generation led to a fatal accident in 2000 when an explosion occurred inside the confined compartment around a caisson leg of a platform.

A board of inquiry recommended several actions including the removal of the blasting grit and biocide-treated water. A multidisciplinary team was assigned to investigate a methodology to maintain the integrity of the caisson legs and mitigate internal corrosion. Several options were considered and assessed for their effectiveness, ease of application, and environmental impact. These included a new grouting and sealing procedure, installation of a glass-reinforced plastic (GRP) pipe and filling the annular space with inhibited cement, and others. The final recommendation was corrosion management utilizing a vapor corrosion inhibitor (VCI). To assess the effectiveness of this approach, a pilot project was launched in 2009 whereby one caisson leg was emptied and preserved with VCI. Carbon steel (CS) weight loss corrosion coupons were used to assess the effectiveness of this approach.

Unlike traditional contact corrosion inhibitors, VCIs have a moderately high vapor pressure that allows them to function in the vapor phase without applying VCI directly to the metal surface.¹⁻² Therefore, VCIs provide protection in the liquid phase, vapor phase, and critical interphase. They can access difficult-to-reach spaces and provide effective protection against crevice corrosion.

Several groups of organic compounds have reported corrosion inhibiting effects. The effectiveness of amine carboxylate VCIs is well documented in lab and field assessments over the last 30 years.³ Amine carboxylate VCIs are dipoles where charges are not uniformly distributed, allowing them to be attracted and adsorbed to both cathodic and anodic locations of a corrosion cell. Their adsorption to different alloys has been found to fit with the Langmuir adsorption isotherm [Equation (1)] with an enthalpy of adsorption of about -10 to -16 kJ/mol.⁴ This physical bond on the metal surface creates a monomolecular barrier that protects against aggressive ions. The barrier re-heals and self-replenishes, and can be combined with other functional properties such as binders and biocides for added protective capabilities.

$$\theta = \frac{\alpha \times P}{1 + \alpha \times P} \quad (1)$$

O = Fractional coverage of the surface
 p = Gas pressure
 α = Constant

Unlike hazardous nitrite or secondary amine inhibitors, amine carboxylates are salts with mostly neutral pH and relatively low vapor pressure, making them an environmentally safe option for corrosion protection. They are also nonflammable and safe to handle and use, which is a considerable advantage especially in the offshore work environment.

Amine carboxylate VCIs have been effectively used for over 30 years in multiple applications including the protection and mothballing of equipment, hydrostatic testing, protection of the underside of tank

floors, protection of cased crossings, and other applications. Their use in caisson legs, while theoretically achievable, had not been tried in the past.

Methodology

The integrity team in charge selected caisson leg WIN 4494 0052 in the Umm Shaif Additional Accommodation Platform (USAAP) for the pilot project and recommended protecting the inside of the leg by applying an amine carboxylate VCI. The caisson leg was constructed of CS 1.80 m in diameter and 20.8 m in length. Three products with different delivery systems were chosen to achieve the desired result.

First, a pipe coater was used to apply Inhibitor A (liquid) on the internal diameter of the leg. This was chosen to provide both contact corrosion inhibition and biocidal treatment for the internal surfaces. Then Inhibitor B (pouch containing powder) was suspended on a stainless steel (SS) wire rope down the length of the leg. Inhibitor B is intended to provide a source of VCI to replenish any gaps in the surface protection. This was followed by fogging the leg internals with Inhibitor C (powder), which is intended to settle into the stagnant water and provide inhibition at that level. Application of all three products for a single structure was done within the same day. The adoption of three different products followed the philosophy of incorporating multiple protective methods to mitigate the risk of corrosion.

Inhibitor A

Inhibitor A is a waterborne amine carboxylate corrosion inhibitor for internal use that provides protection against corrosion caused by bio-growth. Having been immersed in treated seawater for two decades, the internal surfaces needed such a surface treatment to mitigate the risk of microbiologically induced corrosion. Inhibitor A provides both contact and vapor phase corrosion inhibition to multiple metal types. Inhibitor A has extensive lab and field history that validates its performance. Its adsorption and effectiveness have been verified using electrochemical



FIGURE 1 Testing apparatus for verifying VCI diffusion with no air movement.

impedance spectroscopy and cyclic polarization. Vapor diffusion capability was also studied at the manufacturer to determine whether Inhibitor A can diffuse through 100 ft (30 m) of 1-in (25-mm) tubing with no air movement. Inhibitor A was introduced into one box, which was linked to another with the tubing (Figure 1). After 24 h the inhibitor was detected in the second box using a VCI detection kit confirming diffusion was achieved. The quantity of inhibitor used in the caisson leg was calculated to cover the surface area of the internal diameter and provide sufficient vapor phase to saturate the volume of the leg.

The original intention was to apply Inhibitor A using a three-lance spray system. However, prior to adoption of this system, the painting section conducted a trial using its pipe coating system hung in the center of the leg. The pipe coater (Figure 1)



FIGURE 2 Application of Inhibitor A using a pipe coater.



FIGURE 3 Steel frame setup for suspending Inhibitor B pouches.



FIGURE 4 Application of Inhibitor C by fogging.

was hung using a single sheave pulley attached to the scaffolding. The trial was successful and this application methodology was adopted. The application was carried out in one run starting from the bottom section going up. The pipe coater was raised slowly as it applied a pre-calculated quantity of product to ensure the entire uncoated surface was well covered. It took approximately 15 minutes to apply all the materials.

Inhibitor B

Inhibitor B is an amine carboxylate in powder form packed in lightweight breathable pouches that allow the diffusion of the VCI while maintaining the powder in a contained area. The pouch material is made of high-density polyethylene fibers manufactured in a flash-spinning process without the use of binders. This provides a durable, rugged sheet structure that maintains properties even in the harshest environmental conditions. The contained inhibitor is suitable for ferrous metals only. Extensive testing had been done primarily using the Vapor Inhibiting Ability (VIA) test method.⁵

Inhibitor B is 100% biodegradable in marine environments and it is classified as a rapidly degradable substance (OECD 306,⁶ BOD 28 Marine Test) as per testing performed in accordance with Oslo-Paris Commission Protocol. It has very low toxicity and has no bioaccumulation potential. The quantity of inhibitor used was calculated to saturate the volume of the leg.

Cross-angle bars were fabricated and bolted to the welded pad eyes inside the

caisson legs (Figure 2). Inhibitor B pouches were attached through their button holes to a 6-mm SS wire rope, which was then lowered down the leg. Three sets of pouches on wire were suspended. The first set of pouches accidentally detached when the buttonholes failed to hold the pouches. The other two sets were suspended successfully.

Inhibitor C

Prior to the application, the painting section tagged the caisson leg and found a dead volume of water at the bottom. It was decided to fog inhibitor C powder in the caisson leg to allow it to settle into that water and provide protection in that critical zone. Inhibitor C is the same powder as Inhibitor B but supplied in loose powder form mixed with silica. The addition of silica improves the free flow properties of the powder through the application equipment.

An air compressor and an after-cooler were used to supply air to the blast pot. Since moisture is detrimental to this operation, all water traps were kept open. The material was loaded in a medium size blasting pot connected with 1-in diameter blast hose and the nozzle was removed to allow better flow. Application started with fogging the powder in the bottom of the caisson leg.

The caisson leg was then covered with a 15-mm steel plate (Figure 4) with an opening for CS weight loss corrosion coupons attached to a small plate cover using a wire rope. Corrosion coupons were introduced to monitor and evaluate the effectiveness of the protection system.

Results and Discussion

The corrosion coupons were retrieved and evaluated at different intervals (Table 1). The first such evaluation was in October 2011, one year after the pilot, when a corrosion rate of 0.29 mpy was recorded. In January 2012, the coupons were again evaluated as per ASTM G4-01⁷ and found to have corroded at a rate of 0.11 mpy.

The results showed clear improvement in the VCI-treated caisson leg where corrosion was maintained at low rates that were deemed acceptable.

Since there was no control against which these results can be benchmarked, similar corrosion coupons were introduced in December 2010 in two control caisson legs that had not been emptied. Being full of water, one coupon was immersed in the treated water while another was installed in the overhead above the water line.

By September 2012, the corrosion rate for the pilot leg was 0.45 mpy while the control leg corroded at an average of 12.90 mpy above the water line and 0.97 mpy under the water line.

In March 2013, the corrosion rate for the pilot leg increased to 3.18 mpy while the control leg corroded at an average of 16.50 mpy above the water line and 1.17 mpy under the water line.



FIGURE 5 Caisson leg sealed cover.



FIGURE 6 Weight loss corrosion coupons.

TABLE 1. CORROSION RATES IN PILOT AND CONTROL CAISSON LEGS

Caisson Leg		Monitoring Location	Corrosion Rate, MPY				
			Oct. 11	Jan. 12	Sept. 12	Mar. 13	Sept. 13
USEAP							
4494-0034	PC-USEAP-4494 0034	Above water			12.63	18.56	11.88
4494-0034	PC-USEAP-4494 0034	Below water			0.88	0.29	0.36
4494-0036	SB-USEAP-4494 0036	Above water			13.23	14.44	10.98
4494-0036	SB-USEAP-4494 0036	Below water			1.05	2.05	0.40
USAAP							
4494-0052	SB-USAAAP-4494 0052	VCI, pilot leg	0.29	0.11	0.45	3.18	0.09

The results showed clear improvement in the VCI-treated caisson leg where corrosion was maintained at low rates that were deemed acceptable. The methodology was adopted for the treatment of all other caisson legs at the complex.

In August 2013, another pilot was launched to qualify a new methodology for treated water disposal. After adopting this methodology, all caisson legs will be emptied and preserved.

Acknowledgments

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TALAL A. RAHMAN AL-SAYED is vice president of integrity at ADMA-OPCO, PO Box 303, Abu Dhabi, U.A.E.

AHMED FATHI EID is the Corrosion and Flow Assurance Section leader at ADMA-OPCO. He is a corrosion engineer with 19 years of experience in the oil and gas production industries. He specializes in corrosion control, cathodic protection, and asset integrity. He has a B.S. degree in chemistry and an M.S. degree in synthesis of corrosion inhibitors. He is a registered Professional Corrosion Engineer in the British Institute of Corrosion, and a NACE-certified Senior Corrosion Technologist. He is a six-year member of NACE International.

MAHDI MOHAMED AL-MARZOOQUI is with ADMA-OPCO.

USAMA JACIR is general manager of Cortec Middle East, PO Box 115133, Dubai, U.A.E., e-mail: ujacir@cortec-me.com. He has 20 years of experience in corrosion mitigation using protective coatings and corrosion inhibitors. He is a five-year member of NACE International. **MP**

Development and Application of a New Solution for Mitigation of Carrier Pipe Corrosion Inside Cased Pipeline Crossings

LEN J. KRISKA, Enbridge Pipelines, Inc.,
Edmonton, Alberta, Canada
JERRY DEWITT, Enbridge Pipelines, Inc.,
Griffith, Indiana
TIM WHITED, MESA, Tulsa, Oklahoma

Increasing emphasis is being placed upon control of carrier pipe corrosion inside cased pipeline crossings from both an operator and regulatory perspective. Inline inspection associated with pipeline integrity management programs has identified external carrier pipe corrosion inside casings. Many factors contribute to this corrosion concern. Systems designed to proactively mitigate corrosion inside cased crossings were not readily available. The desire for a proactive carrier pipe corrosion control system led a pipeline operator and a company expert in the manufacture and application of volatile corrosion inhibitor (VCI) chemistry to consider a new corrosion mitigation solution. This effort resulted in the development of a unique product designed to fill the annular space of a casing with a gelatinous product that proactively controls carrier pipe corrosion and prevents intrusion of water, etc. into the annular space. The gel filler has been applied inside cased crossings since late 2011. Electrical resistance probes have been installed through the casing vents and submerged in the filler to the carrier pipe surface. The probes are monitored remotely with automated technology. The corrosion rate data validates the effectiveness of the VCI filler.

According to a Southwest Research Institute 2007 study,¹ cased pipe segments are generally believed to be very safe since the time-independent threats, including third-party excavation and outside force damage, are largely eliminated. However, external corrosion of carrier pipe inside casings still poses a threat to pipeline safety. Understanding the causes and characteristics of carrier pipe corrosion is an important step forward to better management of corrosion threats within cased crossings.

External corrosion on the carrier pipe is caused by a variety of factors, including:

- A high concentration of diffused oxygen with accumulated condensation at holidays (pinholes and voids) on the carrier pipe coating, which can lead to an accelerated rate of corrosion
- General atmospheric corrosion at coating holidays on the carrier pipe
- Accelerated corrosion at coating holidays in direct contact with an electrolyte such as water or other debris
- Localized corrosion due to concentration cells or the presence of bacteria, etc.
- For casings located near a compressor station, elevated temperature may accelerate an existing corrosion cell. Elevated temperatures may also cause coating damage and expose the carrier pipe surface.

A major pipeline company has an inventory of more than 2,000 cased crossings installed throughout the various regions of Canada and the United States. For many years steel casings were commonly installed over sections of pipelines to provide

mechanical protection for those constructed under roads and railways. They incorporate electrically isolating spacers and end seals that separate the carrier pipe from the casing. Over time the integrity of the end seals can degrade, allowing for the ingress of potentially corrosive groundwater. Pipe movement caused by settling and degradation of the isolating spacers may produce a potential contact of the casing to the carrier pipe, resulting in an electrical short. These factors may present an elevated risk of external corrosion on the section of piping located within the cased crossing.

Historically, casing rehabilitation programs have included projects to fill the annular space with a di-electric wax in an attempt to mitigate carrier pipe corrosion and prevent intrusion of groundwater. In-line inspection (ILI) of cased pipeline crossings has identified the existence of external corrosion anomalies on the carrier pipe within the annular space inside cased crossings. These anomalies have been identified inside casings filled with wax, as well as unfilled cased crossings. Concern for control of corrosion at areas of disbanded coating inside cased crossings was also a focus because of awareness that portions of the pipeline system were subject to disbondment of tape coating.

This data, coupled with other factors and concerns with wax-filled casings, caused the pipeline company's Integrity Management Team to begin investigating alternative solutions in 2010. The goal of this investigation was to identify solutions that would produce proactive control of carrier pipe corrosion inside cased crossings. A company skilled in the manufacture and application of volatile corrosion inhibitor (VCI) chemistry was consulted for consideration of an ideal carrier pipe corrosion mitigation solution.

Experimental Procedures

A team comprising the engineer and research and development specialists from the corrosion inhibitor company, pipeline engineers, and a pipeline integrity expert from a major corrosion service company

began work on this project in late 2010 to early 2011. The goal was to create a product that could be used to fill the annular space of a cased crossing and proactively control carrier pipe corrosion while preventing the intrusion of external water and air into the annular space. The team then initially developed a list of criteria defining the features of an ideal casing filler. The criteria for this casing filler are as follows:

- The filler should contain ample quantities of a VCI product designed to mitigate corrosion on the external surface of the carrier pipe and the internal surface of the casing.
- The filler should contain sufficient dosages of a VCI that will migrate on a molecular level under any disbanded coatings to provide corrosion protection on the carrier pipe surface.
- The VCI in the filler should also have a vapor phase component capable of mitigating corrosion within any portions of the annular space that are not completely filled.
- The VCI in the filler should be proven to diffuse through any soil debris inside the annulus and mitigate carrier pipe corrosion on surfaces in contact with the soils.
- In order to ensure a complete fill, the product should have the viscosity of water and be at ambient temperature while the casing is being filled. Once inside the casing, the product should transform into a high-viscosity gel within a short time.
- Once transformed into a gel, the viscosity should be sufficiently high to prevent the infiltration of water into the annulus and prevent loss of the filler from the annulus.
- The filler should be electrically conductive and allow flow of cathodic protection (CP) current to the carrier pipe.
- The product needed to be non-flammable.
- The product needed to be environmentally friendly, nontoxic, free of nitrites and phosphates, and made of biodegradable materials.
- Application of the filler should not require excessive carrier pipe surface preparation.

- The casing should not need to be dry before filler application. The filler should have the ability to combine with nominal quantities of annular space water during installation. The additional water should not reduce the effectiveness of the filler's ability to mitigate corrosion of the annular space metals.
- The product should produce economical corrosion protection and minimal shipping costs.

This list of product specifications was then provided to the research and development group for the VCI company. After an initial review, a determination was made that this product could be developed with a unique combination of recognized chemistries and technical knowledge. The pipeline team then requested that the filler product be developed. By mid-2011, product development of the gel filler was progressing on schedule. The chemists at the VCI company were on track to provide a VCI gel filler product that met all of the criteria listed above. The pipeline team then designed and engineered a pilot project to test application of the filler and begin monitoring its effectiveness for control of corrosion.

The goal was to create a product that could be used to fill the annular space of a cased crossing and proactively control carrier pipe corrosion while preventing the intrusion of external water and air into the annular space.

VCI Basics for Casings

The annular space of a cased pipeline crossing is an ideal environment for the application of VCI technologies and systems.² With the development of the VCI filler gel, even greater flexibility is available for casings that may not be totally sealed.

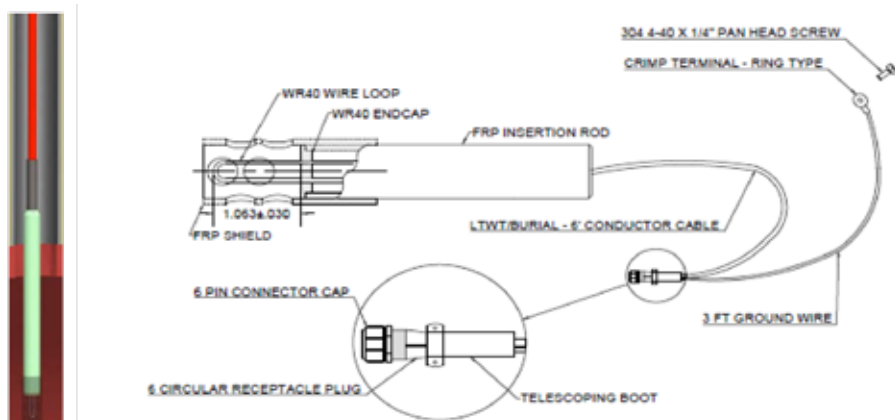


FIGURE 1 Custom ER probe for casings.

It was important to utilize VCIs that provide corrosion control in all three environments that might potentially exist inside a cased crossing. An amine carboxylate-based VCI was selected to meet the following multiphase criteria for corrosion protection.

1. The liquid/solids phase where the metal surfaces are covered with water or soils that have migrated inside the casing or were left inside the casing during the original installation
2. The region along the interface of vapor and liquid/solids where accelerated corrosion may normally exist
3. The vapor space exposed to atmospheric corrosion conditions

The amine carboxylate-based VCI product adsorbs onto the metal surface and forms a protective mono-molecular layer on that surface within all three phases described above. This molecular layer inhibits the electrochemical reaction on the metal surface. Mitigation of corrosion with VCI chemistry is mature and well proven. VCI products have been in existence for over 30 years and there are multitudes of successful applications within numerous environments similar to the annular space of a casing.

An early documented example of VCI application for cased crossings is contained in the NACE article published in 2001 entitled “Use of Corrosion Inhibitors on the Alaska Pipeline.”³ This article describes the successful application of VCIs to mitigate

corrosion inside numerous cased sections along this pipeline.

The new gel filler product is designed to totally fill the annular space of cased pipeline crossings with a water viscosity VCI product that transforms into a gel within a short time. This product is produced in two parts, with Part A being a high dosage of a specially designed liquid VCI concentrate that is mixed with water in the field. Part B is a unique superabsorbent polymer powder that is added to the liquid stream flowing to the casing, transforming the water viscosity liquid into a high-viscosity gel. These are nonhazardous, environmentally friendly products.

Corrosion Rate Monitoring Inside the Annular Space

The pipeline team decided it would be important to evaluate the effectiveness of the gel filler and its ability to maintain a noncorrosive environment over long periods of time. Team members were familiar with electrical resistance (ER) corrosion rate probe technology and decided to employ this equipment inside the casing annulus.

ER probes are commonly used on a daily basis to evaluate the corrosiveness of many types of environments inside flowing pipelines and other structures. ER probes can be installed as part of a casing integrity program before inhibitor is applied in order to identify casings with corrosive environments. They are also very useful after a VCI

is applied to evaluate the inhibitor effectiveness over the long term.

An ER probe had already been custom developed by a leading U.S. company for application inside casings. The probe is designed to be lowered down through a casing vent to the carrier pipe surface. It has a shield that prevents contact of the probe sensing element with the carrier pipe (Figure 1).

The pipeline team decided it would be important to evaluate the effectiveness of the gel filler and its ability to maintain a noncorrosive environment over long periods of time.

Multi-function Corrosion Control Monitoring System

A new and unique automated monitoring system was custom designed for use on the pilot project and also future casing applications. (Refer to CORROSION 2013 paper no. 2741,⁴ “Corrosion Rate Monitoring in Pipeline Casings,” for additional information.) The system is multi-purpose and capable of monitoring CP pipe-to-soil (P/S) potentials on the pipeline 1 ft (0.3 m) from the casing, the casing potential, and corrosion rates from the ER probe installed inside the casing annulus. The system incorporates remote monitoring technology designed to capture P/S variances in real time with immediate notification transmission of readings outside of acceptable, pre-set parameters. This method of benchmarking and verification of CP and corrosion rate inhibitor performance provides a comprehensive, proactive data set through the transmission of actionable alarm data and increased frequency of logged data accessibility. The system produces a permanent, ongoing verification of VCI and CP system effectiveness as external influences vary.

The monitoring systems are equipped with the capacity to measure CP applied and polarized P/S “off” potentials and if

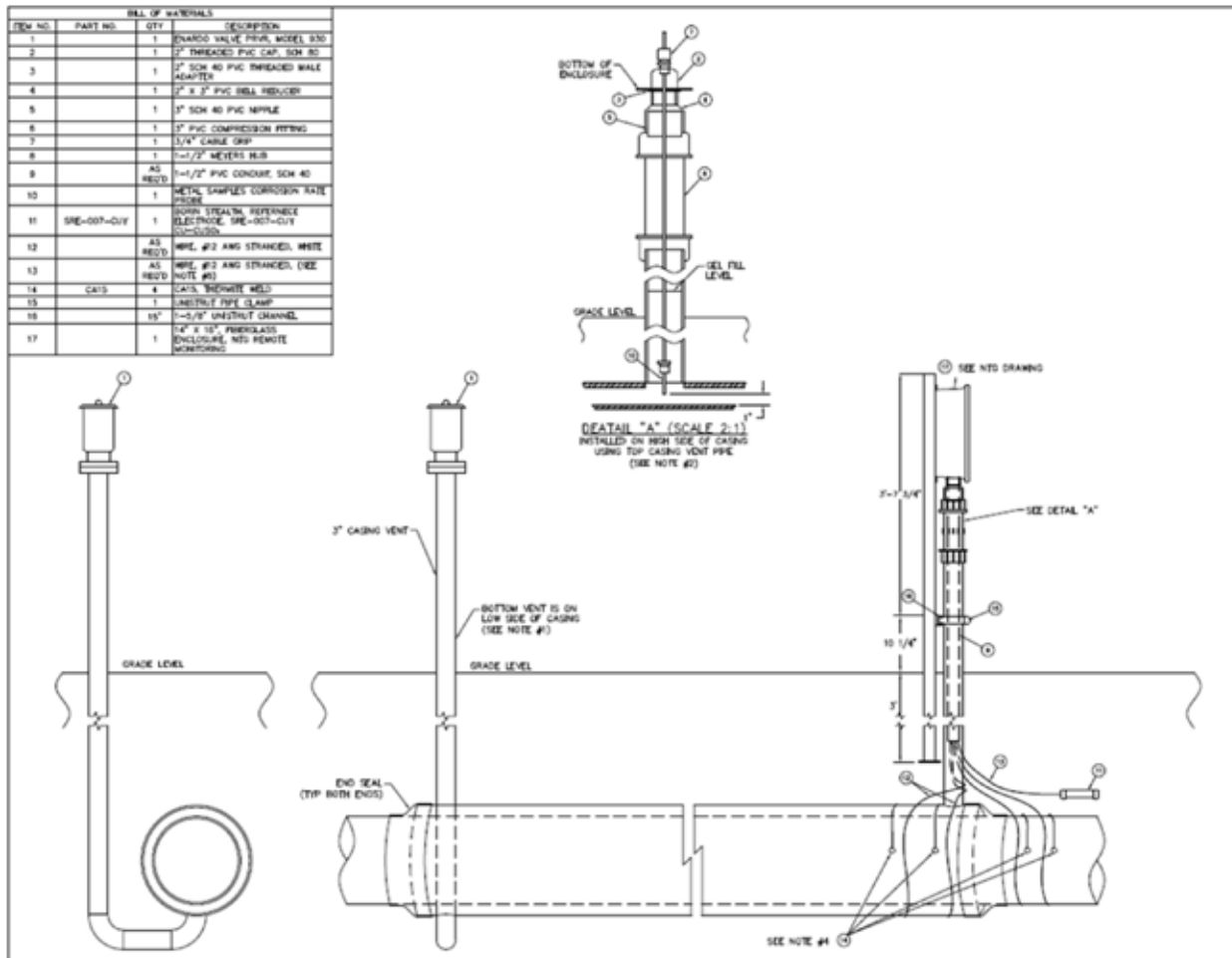


FIGURE 2 Remote monitoring system schematic.

applicable, induced alternating current potential and corrosion current by utilizing a dual-coupon test station design. Values are measured at predetermined time intervals and stored SD memory cards located on board the device. The monitoring systems are equipped with either satellite or cellular communication capability and readings are transmitted to the Web-based interface at a user-defined time interval. Interrogation, monitoring, reconfiguration, or system troubleshooting can also be accomplished through an Internet connection. Figure 2 shows the schematic.

Initial Casing Field Study

The pipeline company performed integrated data analysis on its Chicago Region

TABLE 1. REPAIR PRIORITY MATRIX

ILI Data Results	CP Survey Results	Priority	Proposed Action	
Ext. ML Indicated	Metallic short		End-seal refurbishment w/ VCI gel injection and RMU installation ^(A)	
Ext. ML Indicated	Electrolytic coupling		End-seal refurbishment w/ VCI gel injection and RMU installation ^(A)	
Ext. ML Indicated	Clear (no short)			
No Ext. ML	Metallic short			Monitor through ILI for indications of ongoing corrosion (growth), and CP for changing status of isolation
No Ext. ML	Electrolytic coupling			
No Ext. ML	Clear (no short)			
Wax-filled casing (any ILI condition)	Wax filled casing (any CP condition)			Wax-filled casings continue to be monitored for ongoing external corrosion

^(A)Priority for remediation or ultimate casing removal and pipeline repair is established by severity of corrosion damage.

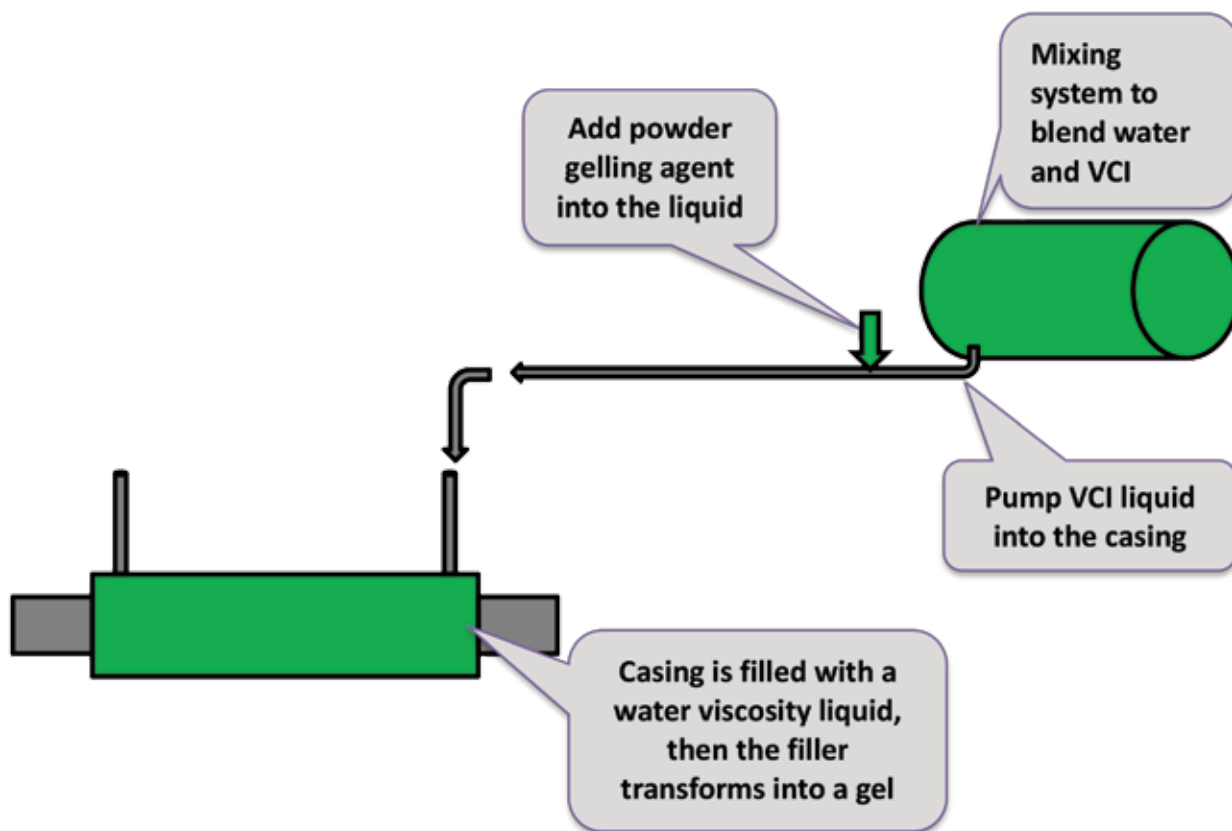


FIGURE 3 Graphic depiction of casing VCI gel filler system.

pipeline system. Data from inline inspection (ILI) and CP surveillance were correlated and utilized to identify and improve prioritization of vulnerable cased crossing locations. This approach enabled more comprehensive monitoring and remediation programs to be established.

CP survey information was evaluated and locations were prioritized based upon electrical isolation status and level of protection. ILI data were prioritized accordingly on locations of high corrosion density that were approaching repair criteria. Priority for repair is summarized by the matrix presented in Table 1.

The results from the Chicago Region's analysis were leveraged and applied for long-term planning of repair on the entire system. The short-term program objectives (2011-2012) were to:

- Develop and refine conceptual end-seal refurbishment and VCI filler delivery processes at four pilot locations (2011 Q4).
- Demonstrate and prove feasibility of the

process at six to 10 locations within the Chicago Region and establish a system-wide prioritized list of locations for rehabilitation (2012 Q1-4).

The long-term program objectives (2013 to 2018+) were to:

- Reduce or eliminate extremely costly reactionary integrity or regulatory-driven repairs on pipelines at cased crossings. These repairs had historically cost \$1.5 to \$3.0+ million.
- Mitigate and monitor corrosion activity at all prioritized cased crossing locations.

2011 Casing Remediation Project

A comprehensive pilot project was initiated in late 2011 for cased crossing corrosion management at four locations. ILI data had demonstrated limited success with conventional di-electric wax fill and the operator suspected the wax fill may have sometimes compounded the problem due to incomplete fill of the void space, the non-

compatibility of the wax with water in the casing, and a lack of corrosion control under disbanded coating. Therefore, the pilot program comprised the following components:

- Modifications to vents and improved end-seal refurbishment process/materials as needed
- Sealing of the annular space inside each casing with the VCI gel filler
- Installation of automated monitoring systems designed to measure the real-time rate of corrosion inside the annulus and provide measurement of CP data

Application of VCI Gel Filler

After inspection/repair of end seals and vents, the VCI gel filler was applied into the casing annulus. Installation was accomplished with a unique set of equipment that was custom constructed for application of the VCI gel filler product. The equipment package was designed by the engineering department of the VCI manufacturer and a

major corrosion control service company already experienced with installation of VCI systems in other applications.

Once the installation and support equipment is staged near a casing, the necessary connections are made to the casing vents. Next the VCI concentrate Part A is mixed with water. The ambient temperature liquid mixture is then pumped into a hose connected to a casing vent. The Part B superabsorbent powder is added into the liquid discharge stream as it flows to the casing. After the casing is filled, the powder absorbs the liquid over a short time period and converts it into a gel. The gel surrounds the carrier pipe with a high dosage of VCI that has been proven to provide effective multi-phase inhibition of corrosion for many years. An incomplete fill of the casing due to air pockets, bends, etc. is not a concern because the inhibitor has a vapor phase component that will also provide corrosion control on the carrier pipe surface within any void space. See Figure 3 for a graphic depiction of the process.

Results

At this time seven cased crossings are monitored. The automated corrosion control monitoring systems have been collecting ER probe and CP potential data every three days for 1 to 1.5 years. All data is reported to a Web site via the remote communication capability of the systems. The corrosion rate at each ER probe is less than 1 mpy. The CP potentials do not indicate electrical shorts. Additional cased crossings will be addressed in 2013. Future ILI analysis of the carrier pipe inside the cased crossings will produce additional evaluation of corrosion control systems effectiveness.

Conclusions

ILI data make it readily apparent that corrosion does sometimes occur on the carrier pipe inside of wax filled and unfilled cased pipeline crossings. When integrity programs discover carrier pipe corrosion that is coupled with disbanded tape coating concerns inside the annular space, it becomes important to proactively mitigate this corrosion. The Pipe-

line Integrity Team has developed a well-engineered program to mitigate the corrosion through a multi-step process described in this article. The development of the amine carboxylate-based VCI gel filler designed to satisfy a number of stringent criteria is an integral component of the casing integrity program. The automated multi-function monitoring system developed for cased crossing applications keeps a close watch on the integrity of the corrosion control systems at each cased crossing. As a result of the collaborative processes described in this paper, a number of innovations have resulted to provide a solid foundation for methodically addressing carrier pipe integrity inside cased crossings.

The Pipeline Integrity Team has developed a well-engineered program to mitigate the corrosion through a multi-step process.

Acknowledgments

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LEN J. KRISKA is an engineering specialist at Enbridge Pipelines, Inc., 10201 Jasper Ave., Edmonton, AB T5J 3N7, Canada. He has gained extensive international experience on pipeline evaluation projects, applying modern survey techniques to CP and coating field evaluations. He has been associated with various pipeline management programs and assisted in the design and development of new survey equipment and procedures. He is currently a pipeline integrity engineering specialist at Enbridge, where his role involves the integration of ILI and metal loss data with CP survey results along with managing alternating current and casing corrosion prevention. Kriska is a professional engineer, registered through Apega, and has been involved with the pipeline corrosion industry for more than 20 years. He is a NACE-certified Cathodic Protection Specialist (CP4) in conjunction with having NACE Level 2 Coating Inspector certification. He has been a member of NACE since 2000.

JERRY DEWITT is the senior cathodic protection specialist at Enbridge Energy, 222 U.S. Hwy. 41, Schererville, IN 46375. He is involved in the design, operation, and maintenance of CP systems for pipelines and aboveground storage tanks. He is a NACE-certified Cathodic Protection Specialist (CP-4), Level 3 Coating Inspector, and Internal Corrosion Technologist. He has been a member of NACE for 28 years.

TIM WHITED is the corrosion solutions director of business development at MESA, 4445 S. 74th E. Ave., Tulsa, OK 74145, e-mail: tim.whited@mesaproducts.com. He has 35 years of experience in the field of corrosion control and extensive experience with both CP and VCIs. He has a B.S. degree in mathematics and has been a NACE-certified Cathodic Protection Specialist (#3245) since 1992. He has co-authored six NACE annual conference technical papers and has been a member of NACE for 33 years. **MP**

A New Method for Corrosion Control in Dry Fire Protection Systems

CLIFF CRACAUER AND JOSH HICKS,
Cortec Corp., St Paul, Minnesota

There are currently two accepted methods for managing corrosion in fire protection systems. These methods include controlling the environment or treating the system with a chemical corrosion inhibitor. One method of controlling the environment is to use a nitrogen blanket and dehumidification, which can be costly. Chemical corrosion inhibitors are appropriate for wet and dry systems, but can be difficult to apply in a dry system. A new method is being developed to apply vapor-phase corrosion inhibitors to dry systems, which can address the concerns with existing methods. This entails saturating the system with vapor phase inhibitor using airflow to carry the inhibitor throughout the system. Lab evaluation and analogous field studies are presented that can identify this new application method as viable for managing corrosion potential in dry fire protection systems.

Current methods for corrosion control in dry fire protection systems include nitrogen blanketing, dehumidification using compressed air, and the use of chemical corrosion inhibitors. In addition, systems are often designed using galvanized steel in place of black steel to increase the useful service life of a system.

Correct use of each method can reduce the corrosion rate in a dry system with different degrees of success. The method gen-

erally considered to be the most effective is the use of nitrogen generator with a drying system (>98% nitrogen). Compared to compressed air, it has been shown that using nitrogen can reduce the corrosion rate in a dry system 70 to 90% for black and galvanized steel.¹

The downside of such methodology is that the capital investment required can be quite high. Nitrogen generation systems typically cost upwards of \$20,000 depending on the size of the sprinkler systems, and whether there is a need for ancillary equipment such as air compressors or dryers.

For systems designed using galvanized steel rather than black steel, there is also a rather substantial capital investment. This choice is made primarily based on the desired service life, when corrosion potential is significant. The incremental increase of material cost is generally between 35 to 50% additional costs for galvanized over black steel.²

When compressed air is used alone, the potential for corrosion can still be quite high in a dry system. This is because water pooling and moisture content can still be quite high in such a system. This can occur at low points in the system, or if there is a lack of a good system to remove all of the moisture, especially in systems that have been hydrotested.

A new method is under development to utilize vapor-phase corrosion inhibitors (VCIs) in combination with compressed air in order to provide corrosion protection in a dry sprinkler system. This would alleviate the need for a nitrogen generator or blanketing system. Based on analogous applica-

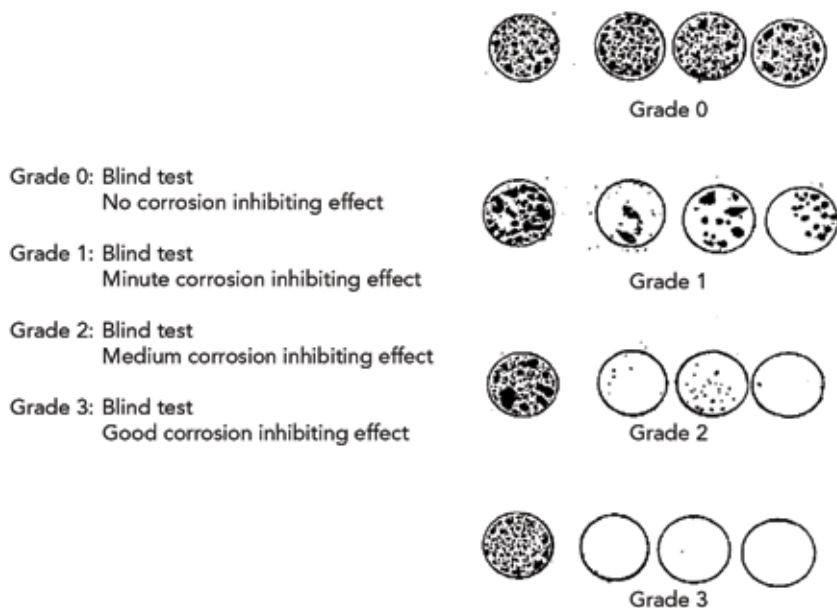


FIGURE 1 The VIA grading scheme.

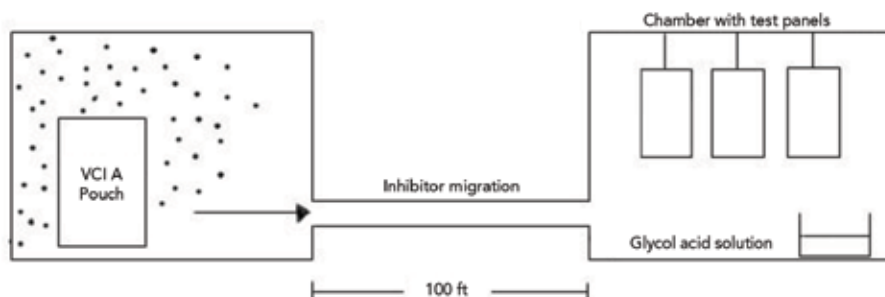


FIGURE 2 Diagram of the migration test.

tions, it is believed that such a system can yield similar results to the use of nitrogen with a lower capital investment required.

Experimental Procedures

Vapor Corrosion Testing

To illustrate the efficacy of a corrosion inhibitor, the test most commonly used is a Vapor Inhibiting Ability (VIA) test. The test used polished carbon steel (CS) samples placed in 1-L glass jars that contained either 0.05 grams of inhibitor VCI A or remained empty for the conditioning period. The jars are sealed to allow for the plugs to condition in the environment that contains corrosion inhibitor. After the conditioning period, 300 mL of a 3% glycerin solution were added to the container. The container was sealed and

placed in an oven at 38 °C for 4 h. The plugs were then removed and inspected for corrosion. The corrosion level was rated on a scale of 0 to 3 according to standards seen in Figure 1. A rating of 2 or 3 is considered passing while 0 and 1 are failing.

When the treated plugs were evaluated, they all showed good corrosion inhibition. Three of the plugs had ratings of 3 and one displayed some slight corrosion so it was graded a 2. These samples all compared favorably to the control plug, which had a grade of 0, showing convincingly that VCI A provides corrosion protection. Table 1 summarizes the data.

Inhibitor Migration Test

To determine how effective VCI A pouches would be diffusing in a static sys-

TABLE 1. VIA RESULTS FOR VCI A

Sample	Grade	Result
Control	0	Fail
1	2	Pass
2	3	Pass
3	3	Pass
4	3	Pass

tem, the migration properties over long distance were tested. The test apparatus included two 5-gal (19-L) containers connected by a tube 100 ft (30.5 m) in length. The first container contained the material to be tested, either a VCI A pouch or no inhibitor as the control (Figure 2). The second container contained three steel test panels and a solution of 3% glycerol and 0.1% hydrochloric acid (HCl) in deionized water. The solution is similar to that used in the VIA test to initiate corrosion.

The test apparatus shown in Figure 2 was set up with inhibitor pouches added to the first container while the steel test panels were placed into the second container, which was sealed. The inhibitor was given three days to migrate through the tube from the first container to the second container. The second container contained steel test panels to evaluate the level of corrosion. After the conditioning period, 300 mL of corrosive solution were added to the container with the steel panels and the panels were allowed to stand for two additional days. This test was performed with and without inhibitor pouches in the first container to determine if the inhibitor will migrate 100 ft and effectively reduce corrosion.

The result, which is illustrated in Figures 3 and 4, was that the control panels displayed corrosion while the panels treated with VCI A were clean. This comparison shows that the inhibitor is volatile enough to migrate at least 100 ft in distance even when it is unassisted by forced air.

Field Testing of VCI A

The Severn Bridge in the United Kingdom was built in 1966 using a suspension cable design in which cables run within ducts along the entire 1,598-m length of the

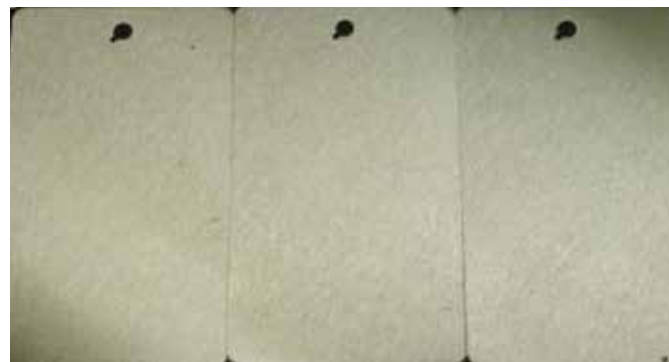
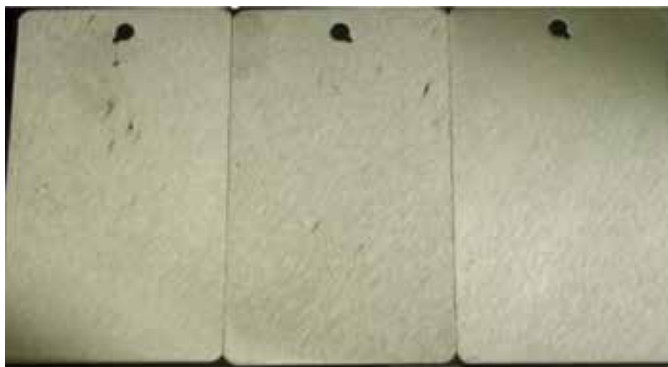


FIGURE 3 Control panels.

FIGURE 4 Panels treated with an inhibitor.

TABLE 2. COMPARISON OF STRAND STRENGTH BEFORE AND AFTER TREATMENT

Wire Group	2006 Data		2007 Data	
	Tensile Strength (N/mm ²)		Tensile Strength (N/mm ²)	
	Mean	Standard Deviation	Mean	Standard Deviation
2	1,604	33	1,650	28
3	1,574	67	1,606	42
4	1,546	67	1,587	41
5	1,487	87	1,534	111

bridge. After concern was raised about deterioration and breaking of cables in these types of bridges, a study was initiated to look into methods for reducing corrosion. In 2006 a dehumidification system was installed on Severn Bridge that was designed to reduce moisture buildup around the cables. The system included the use of VCI A emitters that would be installed to allow the dehumidification system to force inhibitor through the cables.

The heated air of the dehumidification system is forced through a plenum, which contains the inhibitor emitter. The inhibitor moves through the system with the forced air and there are sensors throughout the length of the duct used to measure the inhibitor content in the air (sensor locations are shown in Figure 5). The inspection points are used to monitor and ensure that the VCI A molecules are present.

The strength of the cables was evaluated when the VCI A system was installed in 2006 and again in 2010 after it was operational for 4 years. The data in Table 2 show that the strength of the cables in all segments is improved after the corrosion inhibitor was

added to the system. Since the implementation of the corrosion inhibiting system, there have not been any cable wire failures, which is down from a rate of 5%.

Both the corrosion rate and the monitoring system show that VCI A has the capability to migrate long distances and effectively reduce corrosion.³

Environmentally Friendly Qualities

Biodegradation is a measure of the length of time over which a substance will remain in the environment. The OECD 306 test guideline⁴ is primarily used for biodegradation in marine environments. Chemical compounds are subjected to a 28-day Biochemical Oxygen Demand (BOD-28) test. The start of degradation occurs when 10% of the substance has been degraded. In order to be rapidly degradable, at least 60% degradation of the substance must be attained within 10 days of the start of degradation.

VCI A degraded 10% in less than two days. At Day 7, it was 76% degraded and after 27 days was completely decomposed. Ten days after the start of the degradation, the level of biodegradation was above 60%,

indicating that VCI A could be classified as a rapidly degradable substance. The results can be seen in Figure 6.

Acute oral toxicity is a measure of the dosage of a substance that is required to reduce mortality in half of the subject animal population. This measurement is referred to as the lethal concentration 50 (LC50). Typically the test is performed with rats over a 14-day period and that data can be used to compare the toxicity level between different substances. A lower toxicity value indicates that a substance is more lethal.

VCI A was tested and determined to have an LC50 in rats of 5,000 mg/kg. For comparison, the LC50 of common table salt in rats is 3,000 mg/kg.

VCI A is a less significant health concern than sodium chloride (NaCl). Also, when discharged with water it will rapidly degrade and not pose an environmental concern.

Results

Based on the corrosion data that we have, VCI A would be an ideal inhibitor for a dry sprinkler system. In VIA testing, VCI A has proven that it significantly decreases corrosion levels on CS. The migration studies show that the inhibitor migrates long distances, particularly under forced air, which allows it to be used in long runs of pipe.

In a dry sprinkler system VCI A would be implemented in Tyvek[†] pouches that contain the corrosion-inhibiting powder. In the

[†]Trade name.

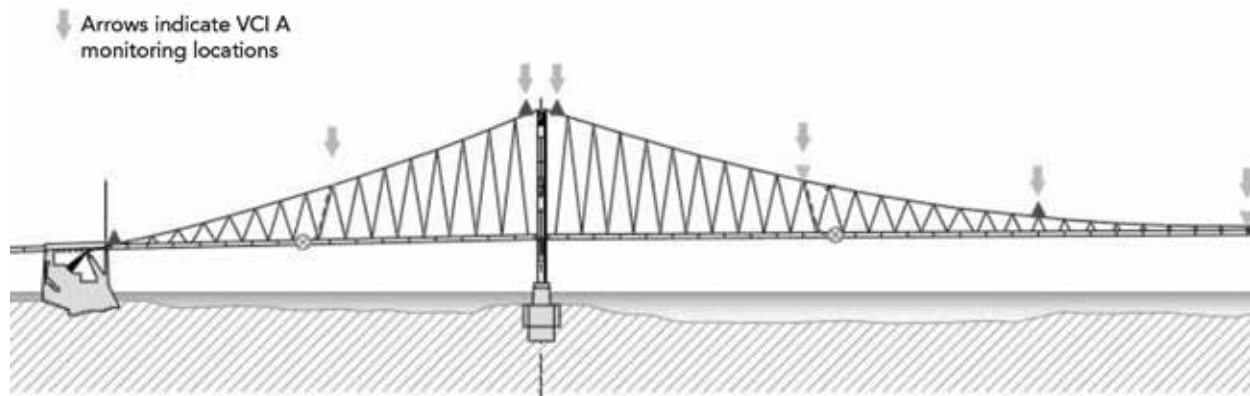


FIGURE 5 Each arrow in the diagram represents a monitoring site for the inhibitor, which is forced through the ducts by the dehumidification system located at the anchor point on the left side.

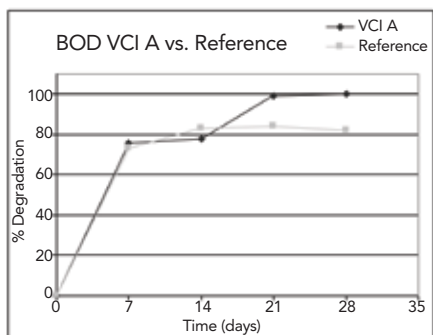


FIGURE 6 The biodegradability of VCI A compared to a reference sample.



FIGURE 7 An example of a plenum that could be installed to introduce VCI A to a sprinkler system.

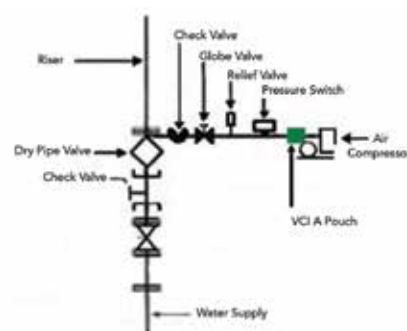


FIGURE 8 A diagram of the dry system with the inclusion of a VCI A delivery system.

sprinkler system, a plenum containing the VCI A pouches would be added downstream from the air compressor used to maintain a positive pressure in the sprinkler system. Figure 7 shows an example of the type of plenum that would be added in the air compressor line. The diagram in Figure 8 shows where the inhibitor would be implemented within the sprinkler system.

Conclusions

VCI inhibitors have been proven to significantly reduce corrosion rates in steel systems and they have the ability to migrate long distances. The VIA testing indicates the dramatic difference in corrosion protection between untreated metal surfaces and those treated with VCI A. The migration testing demonstrates the ability of the

inhibitor to travel long distances both unassisted and when it is under pressure. Use of VCI A will be a good alternative for corrosion prevention by reducing costs as well as limiting additional equipment needed to maintain the corrosion inhibitor.

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CLIFF CRACAUER is vice president of Sales at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110, e-mail cliff@cortecvci.com. He has 15 years of experience at the company and previously held the positions of technical service engineer and technical sales manager. He has a B.S. degree in chemistry from the University of Minnesota's Institute of Technology, holds two patents, and has published eight papers. He is a five-year member of NACE International.

JOSH HICKS is a technical service engineer at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110, e-mail: jhicks@cortecvci.com. He has worked at the company for the last four years with a focus on water treatment and construction industry projects. **MP**

Protecting Concrete Reinforcement Using Admixture with Migrating Corrosion Inhibitor and Water-Repellent Component

MING SHEN, ALLA FURMAN, AND ANDREA HANSEN, Cortec Corp., St. Paul, Minnesota

Corrosion of embedded rebar in concrete can lead to ultimate deterioration of a concrete structure. Corrosive electrolytes and species can penetrate concrete due to its porous nature. An admixture was developed employing a synergistic blend of migrating corrosion inhibitors and waterproofing ingredients. The admixture enhances the protection by forming a protective film on rebar. In addition, it reduces ingress of water-soluble corrosive species. Electrochemical tests show that this admixture provides superior corrosion protection to the rebar. Additional test results demonstrate that the admixture reduces water permeability with no negative effects on workability, set time, and mechanical properties of concrete.

The corrosion of steel reinforcement in concrete structures is one of the most common reasons for infrastructure failure. The corrosion-caused premature deterioration of a concrete structure is particularly pronounced in coastal areas, in cold climates where winter deicing chemicals have to be used, and in high-humidity locations. Corrosion initiates due to the ingress of moisture, chloride ions, and carbon dioxide (CO₂) through the concrete to the steel surface. After initiation, the corrosion products, iron oxides, and hydroxides develop expansive stresses that crack and spall the

concrete cover. This further exposes the reinforcement to direct environmental attack and accelerates deterioration of the structure.

The monetary cost in maintaining safe concrete structures is estimated to be between \$18 billion to \$21 billion annually in the United States alone.¹ Failed structures also have grave consequences to human lives and to the environment.

A well-designed concrete mix can prolong the life of reinforced concrete structures. There are various waterproofing admixtures on today's market aimed at reducing the intrusion of chloride-containing water into the concrete. The majority are based on polymeric compounds, silicon chemistry, metallic stearates, or hydrophilic crystalline materials such as silicates.²⁻⁶ The protection mechanism of these types of products is to block water or to reduce corrosive species. The products do not directly protect the steel rebar—the entity that plays the most important role in determining the longevity of a concrete structure. Inevitably, some electrolyte ingress will occur, setting the stage for the initiation of rebar corrosion and eventual deterioration of a concrete structure. Incorporating a second protection mechanism to the steel rebar itself is much desired in a well-considered admixture for the long-term integrity of a concrete structure.

Reported here is an admixture developed employing a synergistic blend of migrating corrosion inhibitors (MCIs) and

PROTECTING CONCRETE REINFORCEMENT USING ADMIXTURE WITH MIGRATING CORROSION INHIBITOR AND WATER-REPELLENT COMPONENT

waterproofing ingredients. The new Admixture A enhances the protection by forming a protective film on steel rebar while simultaneously reducing ingress of water-soluble corrosive species through the concrete cover.

The MCIs have been used effectively for the protection of rebar in concrete.⁷⁻¹⁰ MCIs form a self-replenishing monomolecular protective layer on steel. They migrate through concrete by capillary infiltration and vapor diffusion to reach the surface of the rebar, and deposit on the steel surface by polar attractions.^{7,10}

The inhibitor chosen for Admixture A delays the onset of corrosion by 100%, demonstrated through a ponded-salt solution test¹¹ according to ASTM G109.¹² In addition, a cracked-beam test (based on ASTM G109) showed that it reduced the average corrosion currents by 50% vs. the control, protecting the embedded rebar even when the concrete developed minor cracks.¹¹

Trials were run to find compatibility of the corrosion inhibitor and waterproofing component. Various waterproofing materials were screened to meet the following three criteria: reducing water ingress while not negatively impacting concrete workability and mechanical properties; not requiring a special mixing procedure for its effectiveness; and being a nonrestrictive material during transportation. A blend of silane/siloxane emulsion demonstrated the best performance.

Experimental Procedures

Concrete blocks for water repellency tests were made per ASTM C1582.¹³ The dose rate of the Admixture A was 0.5 wt%. A water/cement ratio of 0.5:1 was used. The set time was noted. The concrete blocks were cured for 28 days prior to the water repellency testing.

Water permeation testing was performed according to RILEM Test No. 11.4.¹⁴ The change of water level inside the aforementioned test tube was compared for concrete with the Admixture A or without (control).

Water absorption testing was conducted using the Alberta Sealer Immersion

TABLE 1. CONCRETE SET TIME

Sample	Set time
With Admixture A	~4 h
Control (without Admixture A)	~4 h

TABLE 2. WATER PERMEATION TEST

Sample	0 min (in)	30 min (in)	1 h (in)	18 h (in)	5 days (in)	% Improvement
With Admixture A	0	0	0	0	0	100
Control (Without Admixture A)	0	0.1	0.2	0.8	2.5	—

TABLE 3. WATER ABSORPTION TEST (ALBERTA TECHNICAL STANDARD BT001)

Sample	Initial Weight (g)	End Weight (g)	ΔW (g)	Water Absorption (%)	% Improvement
With Admixture A	936.8	948.8	12.0	1.3	55
Control	893.0	920.0	27.0	3.0	—



TABLE 4. WATER ABSORPTION TEST (BS1881 PART 122)

Sample	Water Absorption (%)	% Improvement
With Admixture A	1.5	57
Control	3.5	—

TABLE 5. CONCRETE PROPERTY TESTS

	Test 1		Test 2	
	Control	With Admixture	Control	With Admixture
Slump (mm)	95.3	177.8	55.0	55.0
Air Content (%)	2.8	4.5	1.1	1.3
Compressive Strength (psi)				
7 days	4,040	3,850	5,070	4,713
28 days	5,410	4,780	6,743	5,583

TABLE 6. LINEAR POLARIZATION RESISTANCE

	Corrosion Rate: Control (mpy)	Corrosion Rate: Admixture A (mpy)	% Improvement
After 4 h conditioning	1.07	0.34	68
After 24 h conditioning	4.22	0.45	89

TABLE 7. EIS MEASUREMENT (12-DAY IMMERSION IN 3% NaCl SOLUTION)

Sample	Rp (Kohm)	% Improvement
With Admixture A	59.60	354
Control	13.25	—



Test (Alberta Transportation Technical Standard BT001¹⁵), and BS 1881 Part 122.¹⁶ In the BT001 test, the weight changes of the

concrete blocks, before and after being immersed in tap water for 120 h with 25-mm headspace, were measured for

those with the Admixture A or without (control). The BS 1881 Part 122 test on Admixture A was conducted by the Infrastructure Sustainability and Assessment Center, School of Engineering, American University in Dubai.

The concrete properties of slump (ASTM C143¹⁷), air content (ASTM C231¹⁸), and compression strength (ASTM C39¹⁹), were tested at the American Engineering Testing facility (St. Paul, Minnesota) and at the School of Engineering, American University in Dubai.

A linear polarization resistance (LPR) Test was carried out in a 1-L electrolyte of 3.5% sodium chloride (NaCl) and 4 g of calcium hydroxide [Ca(OH)₂] in deionized water. Admixture A was added at 1.42 wt%. A working electrode of C1215 carbon steel (UNS G12150) was conditioned in the above electrolyte for 4 h and 24 h and its corrosion rates were measured with or without the addition of the Admixture A.

An electrochemical impedance spectroscopy (EIS) test was carried out on concrete specimens with or without Admixture A (0.5% of the cementitious material). The rebar-inserted concrete blocks (“lolly-pops”) were made per ASTM C192²⁰ and ASTM C1582 using ordinary basic rebars. After being cured for 28 days, the blocks were immersed in 3% NaCl solution for 12 days and their polarization resistances (Rp) were measured.

Results

The set time was not affected by the addition of Admixture A (Table 1).

Water repellency tests consisted of a water permeation test and water adsorption test. The permeation test showed that concrete treated with Admixture A provided 100% improvement vs. the untreated control (Table 2). The adsorption test per Alberta Technical Standard BT001 showed that concrete treated with Admixture A absorbed 55% less water vs. the untreated control (Table 3). Another water absorption test, BS 1881 Part 122, showed a similar improvement of 57% (Table 4). All water repellency tests indicated that Admixture A produced a concrete of less water permeability and thus of fewer electro-

lyte ingress when placed in service in harsh environments.

Concrete property tests on slump, air content, and compression strength showed that the addition of Admixture A resulted a more workable concrete with some slight changes in mechanical properties (Table 5).

LPR and EIS tests were carried out. LPR tests showed that when 1.42% (wt) Admixture A was added to an electrolyte of 3% NaCl and 0.4% Ca(OH)₂, the corrosion rate was reduced 68% vs. the control after a 4-h contact period; the corrosion rate was reduced 89% after 24 h (Table 6). The LPR results illustrated good corrosion protection power of Admixture A in electrolyte. The EIS test showed that after being immersed in 3% NaCl solution for 12 days, the rebar embedded in concrete containing Admixture A exhibited a 354% increase in polarization resistance vs. the control (Table 7). The EIS result indicated that the embedded rebar would be 3.5 times less likely to corrode in a concrete containing Admixture A than in one without. The result confirmed the corrosion protection capability of Admixture A in concrete.

These two sets of corrosion tests demonstrated that the corrosion inhibitors in Admixture A provided synergistic protection to rebar.

Conclusions

After a substantial amount of screening, a new Admixture A containing both MCI and a waterproofing component was formulated. The new Admixture A protects by increasing the Rp experienced by the embedded rebar to 3.5 times than that of a concrete without the admixture while maintaining a favorable concrete property profile in compression strength and workability. At the same time, Admixture A increases concrete water repellency. The data showed approximately 55% reduction in the water adsorption test and approximately 100% reduction in the permeation test.

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MING SHEN is a research and development engineer at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. She has worked for the company for four years, conducting research and development on corrosion inhibitors in water treatment, concrete reinforcement protection, and gas line protection. She has a Ph.D. in chemical engineering from the University of Virginia.

ALLA FURMAN is a senior corrosion engineer at Cortec Corp. She works primarily in the area of formulating and testing corrosion preventive products using various corrosion and electrochemical techniques. The products include water treatment, process additives, metalworking, and concrete admixtures. She has a Ph.D. in engineering.

ANDREA HANSEN is a technical service engineer at Cortec Corp. She has worked at the company for eight years. She is the also the Environmental Management System coordinator. She has a B.S. in chemical engineering from Michigan Technological University. **MP**

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Electrochemical Impedance Measurements	ASTM G106 CC-022	Concrete samples with rebars
Cyclical Testing	GMW 14872	Coatings, RP
Color Matching	CC-033	Coatings
Adhesion (Tape)	ASTM D2399	Coatings
Adhesion (Testers)	ASTM D 4641 (Test Method B); ASTM D7534 CC-034 CC-036	Coatings

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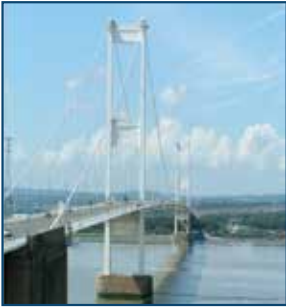


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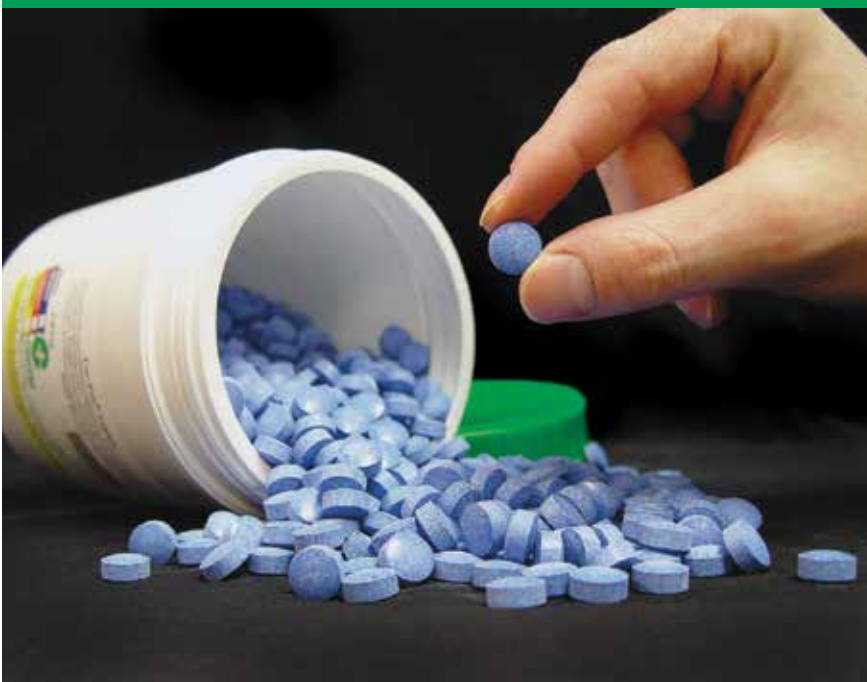
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