Mitigating Soil-Side Corrosion on the Underside of Crude Oil Tanks

Preventing Stress Corrosion Cracking in Multi-Alloy Systems

Analysis of a Slow-Release Corrosion-Inhibiting Block for Water Treatment Programs

Brochure Enclosed:
CorroLogic Innovative Corrosion Inhibitor Systems
Cortec® Receives the Materials Performance Readers’ Choice Corrosion Innovation of the Year Award!

Cortec® is the recipient of a 2013 MP Readers’ Choice Corrosion Innovation of the Year Award for our PTC Emitters. The award recognizes Cortec’s development of this innovative, environmentally friendly, corrosion-inhibiting product. Boris Miksic, President/CEO of Cortec®, was presented the trophy during the NACE CORROSION 2013 Conference and Exhibition in Orlando, Florida on March 18th. This recognition will also be announced in the June issue of Materials Performance magazine. MP Readers’ Choice Corrosion Innovation of the Year Award winners are determined by the number of votes received from readers of MP magazine who vote online for their favorite innovation. Cortec® wishes to thank everyone who voted for our invention.

Beautiful Severn Bridge in Wales, England is a cable stay bridge maintained by the UK Highways Agency. The suspension cables on this type of bridge are known to corrode over a long period of time. World-renowned bridge design engineering firm Mott MacDonald has specified PTC Emitters for this project because of their effectiveness, ease of application, and low overall cost of corrosion protection.

Cortec® has been engaged in the development of corrosion control products and systems since 1977. PTC Emitters are one of over four hundred effective rust prevention products that Cortec® makes to serve the Construction, Packaging, Petrochemical, Electronic/Electrical, Metal Working, Automotive, Marine, and many more industries.
About the Cover

Providing effective corrosion protection to the bottoms of aboveground storage tanks can be challenging, particularly when the tank floors are constructed on oily sand and intermittent gaps exist between the tank pad and bottom plates. When these conditions exist, the effectiveness of cathodic protection (CP) is reduced and corrosion can result. The article beginning on p. 3 describes severe corrosion problems that occurred at a crude oil tank farm in the Arabian Peninsula that had been under the protection of an impressed current CP system. The oily sand plus intermittent gaps below the carbon steel bottom plates reduced the CP effectiveness and led to corrosion. A volatile corrosion inhibitor was applied under the floor plates and mitigated the problem, as shown by test data taken during the first year after application.

Cost-Effective Corrosion Inhibitor Technologies Offer Earth-Friendly Benefits

Corrosion control technologies have long been recognized as critical to preserving the world’s infrastructure, thereby protecting people, assets, and the environment and minimizing costly repair and replacement work. As much of the world’s aging infrastructure reaches the end of its design life, corrosion prevention methods are constantly being developed and improved to ensure reliable performance of everything from pipelines and tanks to buildings and processing plants.

Volatile corrosion inhibitors (VCIs) and vapor-phase corrosion inhibitors are examples of an economical class of products that have been refined over the years to offer high versatility and cost-effective performance while maintaining a low impact on the environment. The performance of these inhibitors is driven by the ability to alter the environment where corrosion occurs. They can be designed to form protective barriers on internal or external surfaces or alter the corrosion properties of an enclosed vapor space.

The articles that follow describe VCI and vapor phase inhibitor performance in applications that include aboveground storage tank bottoms, steam turbine equipment, and water and wastewater treatment facilities.

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 wide range of applications.

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Mitigating Soil-Side Corrosion on Crude Oil Tank Bottoms Using Volatile Corrosion Inhibitors

This article describes a pilot project that followed the initial investigations described in a previous paper. The pilot project was conducted in 2011 on an aboveground storage tank (AST) at a crude oil tank farm in the Arabian Peninsula. This project was designed to evaluate the procedures for application of a volatile corrosion inhibitor (VCI) beneath select areas of the tank floor and then evaluate the effectiveness of the VCI in reducing the corrosiveness of the environment under the tank floor.

For many years throughout the entire Middle East region, it has been a common practice for most operators to construct AST floors on tank pads consisting of thick layers of bituminous (oily) sand. The formula for the mixture and the thickness of the oily sand varies throughout the region. Research indicates that the sand contains varying levels of chlorides and moisture. The research also indicates frequent challenges in controlling corrosion on the soil side of the tank floors.

The Yu paper concluded that many corrosion issues are likely related to the inability of cathodic protection (CP) current to flow through the oily sand and effectively distribute throughout the tank floor plate surface. The oily sand presents a high resistance barrier to the flow of CP current to the tank floor. Numerous air gaps between the oily sand surface and the tank floor surfaces also negate CP effectiveness (Figure 1). The paper recommended that vapor phase corrosion inhibitors be injected into the gaps under tank bottoms to mitigate the severe soil-side corrosion as a supplement to the existing CP system.

VCI Application Pilot Project

The VCI application pilot project went through a significant design and engineering phase with a specific Saudi Aramco terminal facility targeted for the project. The floor plates of all tanks at the facility are constructed directly on a tank pad that consists of a 0.2-m thick oily sand layer. Data from past tank floor inspection reports at this facility indicated a predominance of soil-side corrosion was occurring on floor plates within approximately 6 m of the tank shell. This phenomenon was attributed to a combination of warm, moist salt air migration under the floor plates, along with the predominance of significant intermittent air gaps between the floor plates and the oily sand pad. Therefore, this pilot project was developed to evaluate the use of VCIs as a means to mitigate soil-side corrosion of AST floor plates. The initial decision was to only apply VCI under the floor plates within a distance of 6 m from the tank shell. Corrosion rate monitoring was incorporated into the project design, along with a system to seal the gap between the annular plate and the concrete ringwall to prevent migration of fresh air under the floor.
nation of two methods for delivery of both a liquid and a powder VCI were originally specified.

3. Install a tape seal to prevent intrusion of outside air between the annular plate and the concrete ringwall. A special sealant material was to be applied into the gap between the chime plate and the ringwall, then a tape was applied spanning the chime plate and ringwall surface.

4. Seal the gaps around the nozzle penetrations. The gaps around the two fill, one clean out, and three water drain nozzles were sealed in the areas where they penetrated the concrete ringwall.

5. Obtain ER corrosion rate probe data after VCI application. Data from all corrosion rate probes were then to be obtained after VCI application to monitor the effectiveness of the VCI.

Description of the Selected Corrosion Inhibitor

Criteria for the VCI necessary to successfully complete this complex project included the following:

- The VCI should control corrosion through the formation of a monomolecular layer throughout the soil-side surface of the tank floor.
- The VCI should have a proven capability of effective molecular migration through the headspace between the floor plates and the tank pad, plus a proven capability of molecular migration through the tank pad soil materials.
- The VCI should be environmentally friendly.
- Molecular adsorption onto the metal surfaces should be accomplished without the need for direct contact of the VCI chemical on the steel floor plates.
- The VCI should have the physical characteristics necessary to emit VCI molecules long-term and be effective during a 10-year period between T&I maintenance intervals.

An amine carboxylate-based VCI was selected for the project. This product has been in existence for many years and has a long history of successful laboratory monitoring.

The pilot project was to be performed on an AST that was out of service for testing and inspection (T&I). Once the design was completed, it was necessary to identify a tank candidate that was scheduled for T&I, then conform the pilot project phases to the T&I project schedule. A very large 107.4-m diameter crude oil storage AST located at a tank farm in the eastern Arabian Peninsula on the edge of the Arabian Gulf was selected for the pilot project. The field portion of the project was completed in the second half of 2011.

Original Pilot Project Scope of Work

The original design scope of work included the following steps:

1. Install a real-time corrosion rate monitoring system. This included the installation of six electrical resistance (ER) corrosion rate monitoring probes at numerous locations under the tank floor a minimum of two months prior to the installation of the VCI. A total of four probes were to be located 2 m from the tank shell; and two probes were to be 4 m from the tank shell. All probes were to be installed inside of 25-mm schedule 80 polyvinyl chloride (PVC) pipe so that they could be removed and inspected or replaced in the future if necessary. The pipe was to be located immediately under the tank floor so that the probes would be in the air-gap environment.

2. Deliver VCI under all floor plates within 6 m of the tank shell. A combination of two methods for delivery of both a liquid and a powder VCI were originally specified.

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evaluations, plus an extensive field application history of effective corrosion mitigation in ASTs and many other complex environments. The formation of a monomolecular layer that is adsorbed onto a metal surface to mitigate corrosion was well understood and documented for this product. The strong propensity of the product to achieve equilibrium when released into an environment and produce molecular distribution through soils and vapor spaces was also well understood and documented. The product was also well researched and tested to verify that it is no threat to the environment.

**Revised Pilot Project Scope of Work**

Once the tank to be used for the pilot project had been cleaned and the magnetic flux leakage (MFL)/ultrasonic inspections of the floor were completed, the VCI project team personnel entered the tank to begin the first phase. At that time it was discovered that cement grout had been pumped under the floor plates near the shell during the previous T&I 10 years ago. The grout had been injected through holes in the floor plates and was approximately 100 mm thick. The grout layer extended at least 6 m past the shell around the entire circumference of the tank.

Unlike some of the past floor inspection records at this facility, the report from the floor inspection identified corrosion in the 6-m area but also significant random corrosion under many plates throughout the entire floor. Figure 2 provides an example of severe soil-side corrosion on this tank. Figure 3 identifies the different degrees of corrosion from the tank floor inspection report. The inspection results coupled with the existence of the grout under the floor plates caused the project to be revised. The scope of work was modified to include application of VCI chemistry under all plates that had experienced corrosion—not just the plates in the 6-m perimeter area.

The revised pilot project scope of work included the following steps:

1. Install a real-time corrosion rate monitoring system. The corrosion rate monitoring system was installed per the original design. The system was installed two months prior to the application of the VCI. The locations of the ER probes were chosen by using the MFL scan drawing to identify the area where severe corrosion was noted and the floor plates were not going to be replaced. The first element of the corrosion rate monitoring system was the installation of the 25-mm PVC piping under the tank floors. A pilot hole was accomplished at the interface of the grout layer and the oily sand. (The pilot hole could not be accomplished above the grout layer.) Then the PVC pipe was pushed into the hole. The leading pipe section was perforated with four rows of 0.5-mm slots and the end was left uncapped. This ensured each ER probe was exposed to the undertank environment. The floor plate was cut out above the end of four PVC pipes and the cement grout was removed. Sweet sand was backfilled over the PVC pipe in the ER probe locations (Figure 4). Two of the probes were installed inside slotted PVC pipe located beneath the grout. The floor plate was not removed above these installations (Figure 5). The ER probe chosen for the project is depicted in Figure 6. This probe configuration was chosen for compatibility with the PVC access pipes installed immediately under the floor plates. Data from the probes were obtained by connecting to a meter supplied by the probe manufacturer.
2. Deliver VCI under all floor plates within 6 m of the tank shell, plus all plates that had experienced severe corrosion. A combination of two methods for delivery of both a liquid and a powder VCI were originally specified. The revised plan included injection of VCI powder only through 50 by 20-mm temporary injection ports in the floor plates. The design addressed the 6-m perimeter floor plate area, and also includes the interior floor plates where corrosion was identified on the MFL report (Figure 7). Pneumatic equipment was used to effectively distribute 9.5 kg of VCI powder through the temporary injection ports under the floor plates a minimum of 10 m in all directions. Steel plate patches were welded over each port after the VCI applications were completed.

3. Install a tape seal to prevent intrusion of outside air between the annular plate and the concrete ringwall. After proper surface preparation, a special visco-elastic sealant paste was to be applied into the gap between the annular plate and the ringwall. Next, an adhesive visco-elastic tape was applied spanning the annular plate and ringwall surface (Figure 8).

4. Seal the gaps around the nozzle penetrations. A total of six large-diameter pipes (two fill, one clean out, and three water drain) transitioned through into the bottom of the tank floor at various locations. The gaps around the nozzles were sealed in the areas where they penetrated the concrete foundation to prevent intrusion of air and moisture to the tank floor.

5. Obtain ER corrosion rate probe data after VCI application. Data from the ER corrosion rate probes were then to be obtained weekly after application of the VCI to monitor the effectiveness of the corrosion inhibitor at each probe location.

**Pilot Project Results**

This pilot project provided excellent information related to the following:

- Procedures for installation of ER probe corrosion rate monitoring systems
- Procedures for application of VCI chemistry under the floor of an above-ground storage tank
- Evaluation of VCI physical distribution under the floor plates
- Evaluation of VCI effectiveness

**Installation of the Corrosion Rate Monitoring System**

The use of ER probes to evaluate the corrosiveness of the undertank environment is very common in the United States and was effective for this project. There were challenges in achieving the undertank installations due to the existence of the cement grout around the tank perimeter. Different processes may be considered for future projects.

**Application of VCI Chemistry Under the Floor Plates**

The T&I tank repair contractor was employed to install the temporary injection ports, assist with application of the VCI, then remove the fittings and patch the holes. The process of transferring the port design and configuration from the drawings to the correct locations inside the tank was well planned and executed by the VCI pilot project team. The pneumatic equipment used to inject the VCI powder through the temporary ports and
under the floor enabled the specific dosages to be effectively delivered. The entire process resulted in a coordinated effort that was implemented and completed with a focus on minimal disruption to the overall T&I schedule. The process is now well understood for future projects.

**Evaluation of VCI Physical Distribution**

Experience has proven that the floor plates inside an empty tank do not typically lay flat against the tank pad. The floor plates are subjected to significant stresses from the weight of the products when the tank is in service. Therefore, the plates beyond the annular plates inside an empty tank normally undulate and are not tight against the tank pad. This provides sufficient air gap for distribution of the VCI powder into a wide radius area beyond the injection ports.

The floor in the pilot project tank conformed to this expectation. Monitoring of adjacent injection ports was conducted intermittently during the application of the VCI powder. The VCI was visually observed in the adjacent injection ports to easily migrate distances of 10 m and greater beyond the injection ports in all directions.

**Evaluation of VCI Effectiveness**

The corrosion rate monitoring system was used as the primary tool to evaluate VCI effectiveness in the near term. It is important to understand that the corrosion rate monitoring system does not measure the rate of floor plate corrosion directly. It measures the corrosiveness of the environment in the vicinity of each ER probe. Since the probes are positioned extremely close (<100 mm) to the tank floor and exposed to the same environmental conditions as the tank floor, there is a direct relationship between the corrosion rate of the ER probe and the tank floor corrosion rate.

The ER probes were located 2 to 4 m inside the tank perimeter because that was the historical location of the most severe corrosion on ASTs at this facility. Note the proximity of the VCI injection ports to the ER probe locations in Figure 7. The VCI injection ports were not close to the probes. The ports were 6 to 10 m away from the probes and outside of the concrete grout layer. This design enabled the project team to evaluate the VCI overall effectiveness and molecular distribution through the very dense oily sand and the cement grout applied under the perimeter floor plates (Figure 9).

ER probe measurements were obtained weekly over the two months prior to the VCI application, and on a weekly basis for seven months after the VCI was applied. The ER probe data prior to application of the VCI was then compared to the probe data after the VCI was applied.

There are different methods for interpreting ER probe data. For this project, linear trend analysis was applied to the spreadsheet data for each probe to calculate the liner trend “average” rates of corrosion over the two-month period before and the seven-month period after VCI application. Table 1 provides the results of this analysis.
TABLE 1: CORROSION RATE DATA RESULTS

<table>
<thead>
<tr>
<th>Probe Inner Diameter</th>
<th>Distance Inside Tank Shell (m)</th>
<th>Linear Trend Average Corrosion Rate Before VCI Application (mils/y)</th>
<th>Linear Trend Average Corrosion Rate After VCI Application (mils/y)</th>
<th>Percentage of Corrosion Rate Reduction After VCI Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>4</td>
<td>1.26</td>
<td>0.69</td>
<td>45%</td>
</tr>
<tr>
<td>P2</td>
<td>2</td>
<td>1.52</td>
<td>0.21</td>
<td>86%</td>
</tr>
<tr>
<td>P3</td>
<td>2 (A)</td>
<td>0.69</td>
<td>0.0</td>
<td>100%</td>
</tr>
<tr>
<td>P4</td>
<td>2</td>
<td>0.49</td>
<td>0.0</td>
<td>100%</td>
</tr>
<tr>
<td>P5</td>
<td>2 (A)</td>
<td>2.06</td>
<td>0.40</td>
<td>81%</td>
</tr>
</tbody>
</table>

(A) Probe was installed under the 50-mm grout layer. VCI molecules had to penetrate the grout and/or oily sand to reach the probe.

Figure 9

Molecular distribution of the VCI through the undertank environment.

This data clearly define the effectiveness of VCI chemistry in mitigating corrosion within the very difficult environment under ASTs. It is significant to observe Figure 9 and note the challenges for effective molecular distribution through the oily sand and cement grout. The project team considers the project a success based upon the initial data.

Conclusions

From a corrosion perspective, aboveground storage tanks constructed in the Middle East, and especially tanks constructed in locations near the Arabian Gulf, present corrosion control challenges that are unique in comparison to ASTs constructed in other parts of the world. Given the predominant regional practice of constructing the tanks on oily sand tank pads, typical CP corrosion control solutions are not always found to be reliably effective.

This pilot project was designed to evaluate the effectiveness of VCIs within the undertank environment below a large-diameter AST. The tank was constructed on an oily sand pad and the floor plates had experienced severe soil-side corrosion. An amine carboxylate VCI powder product was selected based upon specific criteria. The results of the pilot test indicate that:

- Electrical resistance corrosion rate probes can be used to evaluate the corrosiveness of the environment under ASTs.
- VCI chemistry can be efficiently applied and distributed under AST floors.
- VCI molecules will migrate well beyond the physical product through oily sand and cement grout.
- The amine carboxylate-based VCI products effectively applied beneath AST floors, in combination with other practices designed to seal the undertank environment from infiltration of outside air and moisture, were demonstrated to produce an effective corrosion mitigation solution for ASTs.

Acknowledgments

The authors would like to thank the terminal management of Saudi Aramco for their support of this pilot project.

References

Corrosion Inhibitor Releasing Block (IRB) is formulated using renewable soybean-based wax and proven vapor-phase corrosion inhibitor technology. Bench tests and pilot cooling tower tests show that when immersed in water, IRB slowly dissolves and releases a calculated amount of inhibitors required for corrosion protection of a system. IRB can be used as a corrosion inhibitor additive in most water treatment programs, including open, recirculating cooling systems and wastewater systems. It is also compatible with the majority of commercially available biocides and anti-scalants. IRB can be placed in makeup water, cooling tower basins, return water circuits, or wastewater systems.

Water treatment systems contain environments that are vulnerable to destructive corrosion attack on metals. Slow-release corrosion-inhibiting products provide an easy way to combat corrosion in water treatment systems and avoid expensive repairs and disruptions. Products that slowly release their active ingredients are used by many industries, including the water treatment industry. Generally a slow-release product incorporates relatively large amounts of active ingredients with an appropriate delivery system to provide a steady concentration of the active components over a specified period of time.

This study includes:
- Selecting the corrosion inhibitors
- Selecting a biodegradable inactive carrier that is based on a renewable source
- Evaluating the compatibility of the inhibitors and carrier
- Determining the weight ratio of the inhibitor/carrier and the size of the block
- Adjusting the manufacturing technology
- Evaluating the product in a bench test
- Evaluating the product in a pilot cooling tower

**Experimental Work**

**Corrosion Inhibitor Selection**
The corrosion inhibitor selected as the active ingredient for the Corrosion Inhibitor Releasing Block (IRB) is the Cortec Building Block™ (BB). BB is a blend of contact and vapor corrosion inhibitors and alkalinity builders. Previous studies and field experience show that BB provides effective protection in water treatment at a low dosage level (starting dosage is 7 ppm) when continuously added to makeup water. In addition, BB is very low in toxicity; Table 1 shows its toxicity test results conducted by a test lab.

The results showed that BB had very low impact on the freshwater aquatic life, and the discharge of BB would not be a concern for environment regulations. All these data make BB an ideal candidate as the active ingredient in a slow-release format. The IRB provides easy application of a field-proven water treatment protection.

**Inactive Carrier Selection**
Several samples of slow-release carriers were prepared and evaluated. For the preliminary evaluation, a blend of sodium sulfonates and cocoamides was used as the carrier for the corrosion inhibitor, and the blocks were manufactured by extrusion. Laboratory and pilot cooling tower tests confirmed that the selected corrosion inhibitors can be incorporated in, and later released from, the blocks. Tests in a pilot cooling tower, however, showed that such a carrier was very foamy and dissolved faster than the desired rate for a slow-release product.

In the second round of the tests, soybean-based waxes were utilized as the carrier. In addition to being bio-based and biodegradable, soybean-based waxes were chosen because of their melting point.

**Table 1: Acute 48-h Static-Renewal Toxicity Test in Selected Inhibitor BB**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NOEC/LOEC (ppm)</th>
<th>NOEC/LOEC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB (test #E-17766-01)</td>
<td>10,000/&gt;10,000</td>
<td>10,000/&gt;10,000</td>
</tr>
</tbody>
</table>

\(^{\text{1}}\)NOEC: no observable effect concentration.

\(^{\text{2}}\)LOEC: lowest observable effect concentration.
The main objectives of evaluations in the stagnant condition were to obtain the following:
- Average time for complete dissolution of the IRB
- Effect of the IRB on bio-growth
- Effectiveness of the corrosion inhibitors released from the IRB vs. the BB

The main objectives of evaluations in the open recirculating cooling tower were to obtain these data:
- Lifespan of an IRB in an open recirculating cooling tower
- Bio-growth impact
- Effectiveness in corrosion prevention

**Instruments and Materials Used**

The following materials and items were used to conduct the tests:
- Metal coupons: Carbon steel (CS) coupons (SAE 1010) were used in the stagnant water testing and pilot cooling tower testing. A galvanized steel coupon (hot dip, ASTM A525 [G90]³), and a copper coupon (CA110, QQ-C576) were used in the pilot cooling tower testing. The corrosion rate was determined by coupon weight loss. Coupons were cleaned with laboratory-grade methanol prior to testing. Corrosion products after testing were removed according to the ASTM G14 cleaning procedure.
- Molybdate test kit: A MO-2 test kit (HACH) was used to measure the amount of a molybdenum-based tracer to determine the inhibitor concentration released from the IRB.
- Total dissolved solids (TDS) meter (OakTon, EC/TDA/Salt Testr³)
- pH meter (IQ Scientific Instruments³)
- Duo bio dip slides: BTM-2™ (WET International, Inc.) were used to check bio growth in the water.
- Pilot cooling tower (RSD–005) with a 0.5-hp pump and flow rate of ~30 gpm. The water velocity inside the circulating pipe was ~298 m/min (Figure 1).
- VIA test kit

**Notes**
1. Dimension in inches
2. All parts of the assembled test lid shall be in contact with adjacent part

**Evaluating IRB Performance**

IRB was evaluated in stagnant water conditions in a bench test, and in fast-flowing water conditions in a pilot open recirculating cooling water system. Vapor phase protection of IRB was evaluated using the Vapor Inhibiting Ability (VIA) test.

**Test Procedures**

The VIA test evaluates a product’s abil-
Cortec Supplement to MP

Slow Release Corrosion Inhibiting Block

FiguRE 3

Grade 0 Blind test
No corrosion inhibiting effect

Grade 1 Blind test
Minute corrosion inhibiting effect

Grade 2 Blind test
Medium corrosion inhibiting effect

Grade 3 Blind test
Good corrosion inhibiting effect

VIA test grading chart (Grades 2 or 3 are passing).

FiguRE 4

CS plug after VIA test in IRB.

FiguRE 5

Immersion of carbon steel in IRB treated water (L) vs. untreated water (R).

Results

The IRB showed protection in the vapor phase in the VIA test (Table 2 and Figure 4).

Corrosion tests were performed by inserting coupons of galvanized steel, steel, and copper into circulating pipe to study the protection during the life-span of an IRB. The control was circulating water from a cooling tower operated without IRB.

Corrosion rate and percent of corrosion protection were calculated according to Equations (1) and (2):

\[
\text{Corrosion rate (mpy)} = \frac{(3.45 \times 10^6 \times W)}{(A \times T \times D)} \quad (1)
\]

where \( T \) = time exposure in hours to the nearest 0.1 h, \( A \) = surface area of the coupon in cm² to the nearest 0.1 cm², \( W \) = mass change in g, to the nearest 1 mg, and \( D \) = density of metal in g/cm³ (steel = 7.85 g/cm³; copper = 8.94 g/cm³).

\[
\text{Corrosion Protection %} = \frac{(C_c - C_i) \times 100}{C_c} \quad (2)
\]

where \( C_c \) = the corrosion rate without inhibitor and \( C_i \) = corrosion rate with inhibitor.

For tests in stagnant water (bench results), it took approximately four months for one IRB to be mostly dissolved in 1 L of stagnant tap water (several small pieces remained). After an IRB had been immersed in 1 L of tap water for 10 days, the concentration of the corrosion inhibitor to protect metal from corrosion without being in direct contact. The method used is based on the Federal Standard MIL-STD 3010B, Method 4031. An illustration of the VIA test assembly is shown in Figure 2. A sample of IRB material was placed in a dish inside a capped quart-sized jar with a freshly polished and cleaned CS plug (SAE 1010) for 20 h at ambient temperature. A relative humidity of nearly 100% was then created in the jar (via the addition of 3% glycerol in water) for 2 h at ambient temperature, followed by another 2 h at 40 °C. After being removed from the oven, the plugs were inspected and rated on a scale of 0 to 3, where 0 is heavily corroded (no corrosion inhibition), and 3 means no visible corrosion and good inhibiting effects (Figure 3). The test was run in triplicate. The control was a plug exposed in a jar without inhibitor.

The test in stagnant conditions was performed as follows:

1. An IRB was weighed, and immersed in 1 L of tap water. After 10 days the concentration of inhibitor was determined using the molybdenum test kit; a CS immersion test was set up in this water.
2. The time lapsed before the IRB was dissolved (fell apart) was recorded.
3. A solution of 1,200 ppm calcium carbonate (CaCO₃) in water was made and used as a blank. Solutions of 0.7% IRB and 0.28% BB were made in this water. Immersion of CS was carried out again in the above three solutions.
4. Based on a control run (without the IRB in the tower basin), the blowdown schedule was set at every seven days using the measured cycle of concentration data (within the range of 4 to 6). The bacterial count and weight of IRB were measured at each blowdown.
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where \( C_c \) = the corrosion rate without inhibitor and \( C_i \) = corrosion rate with inhibitor.

For tests in stagnant water (bench results), it took approximately four months for one IRB to be mostly dissolved in 1 L of stagnant tap water (several small pieces remained). After an IRB had been immersed in 1 L of tap water for 10 days, the concentration of the corrosion inhibit-
TDS increased when IRB was added to the cooling tower basin, as expected. Furthermore, IRB released inhibitor slowly into the circulating water. During the lifespan of an IRB in one pilot test, the inhibitor concentrations in the circulating water were in the range of 150 to 440 ppm (Figure 8).

The circulating water treated with IRB provided 70% protection for galvanized steel (Table 5). It also provided 45% protection for CS and 6.38% protection for copper. In addition, it showed a slightly reduced bio-growth (Table 6).

### Summary and Discussion

- **IRB protected in the vapor phase.**
- **IRB released corrosion inhibitors from the carrier.** The steel panel was corrosion-free after 90+ days in the IRB-treated water.
- **Immersion corrosion test showed that the manufacturing process of IRB did not affect the protection effectiveness of the corrosion inhibitors.**

Based on pilot cooling tower experiments:

- **IRB dissolved slowly and evenly in a linear fashion.** The lifespan of an IRB was about five weeks in a cooling tower basin. To maintain an effective inhibitor concentration level, the useful life of an IRB is probably four weeks.
- **IRB released corrosion inhibitor.**
- **One IRB treated ~4,200 L (1,904 gal) of water.**
- **IRB provided good protection to CS and galvanized steel.**
- **IRB doesn’t promote bio-growth in a cooling tower.**
- **IRB can be easily placed in makeup water, cooling tower basins, return water circuits, or wastewater systems to provide time release of corrosion inhibitors.**

### References


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Weight change of IRB in pilot test.

Comparison of pH and TDS in circulating water—with or without IRB.

Release of inhibitor BB.
Electrochemical and SCC Inhibition of Multi-Alloy Systems Using Vapor Corrosion Inhibitors

Behzad Bavarian, Jia Zhang, and Lisa Reiner, Dept. of Manufacturing Systems Engineering & Management, College of Engineering and Computer Science, California State University, Northridge, California

Commercially available inhibitors were successfully investigated for their effectiveness in reducing the corrosion susceptibility of turbo expander and steam/gas turbine industry alloys. However, because the power-generating system is complex and consists of a multi-alloy system, the investigation was expanded to study the corrosion behavior and stress corrosion susceptibility of other alloys such as copper and brass alloys including C36000 (38% Zn), eco-brass C69300 (21% Zn), red brass C83600 (8% Zn), and nickel-plated copper in the presence of these inhibitors. The objective was to verify performance in terms of effectiveness or adverse effects on auxiliary components such as valves, strainer, and heat exchanger caused by the corrosion inhibitors.

The most costly yet best method for eliminating SCC is to replace the material with an alloy specifically designed to resist this form of corrosion. The inhibitors investigated in this program are biodegradable compounds that blend amine salts, carboxylic acid, and a wetting agent (surfactant) in a water solution. Improved corrosion prevention compounds and coating systems can protect the sensitive alloys from the environment. These coatings, combined with improved repair and maintenance procedures, will ensure adequate performance of equipment manufactured from a SCC-sensitive alloy.

Turbo-Machinery Maintenance

Turbo-machinery systems have regular service maintenance and unexpected shut-downs. During scheduled service maintenance, components are frequently washed to dilute or remove any in-service contaminants (salt, dirt, grease, and oil). There are three main types of cleaning: aqueous, organic solvent, and abrasive. Aqueous cleaning covers a wide variety of cleaning methods (detergents, acids, and alkaline compounds) to displace soil. Improved corrosion prevention compounds and coating systems can protect the sensitive alloys from the environment. These coatings, combined with improved repair and maintenance procedures, will ensure adequate performance of equipment manufactured from a SCC-sensitive alloy.

The compounds alter hydrocarbons (grease) so that the deposits can be removed with water. Any conventional cleaning equipment (power washers, steam cleaners, dip tanks) can be used for multi-metal corrosion protection.

Corrosion Inhibitors

Several groups of organic compounds have shown corrosion inhibition properties. Most of the effective organic compounds contain oxygen, sulfur, phosphorus, or nitrogen atoms, and in terms of structure, have triple bonds and aromatic rings to improve the inhibitor’s adsorption to the metal surface. Organic inhibitors can protect by adsorbing to the metal surfaces—molecules attach directly to the surface in a very thin layer (monomolecular), and do not penetrate into the bulk of the metal. The extent of adsorption of an inhibitor depends on many factors:
acid salts as a vapor inhibitor for metal surfaces not sufficiently coated. The thin polar layer of surfactants is tightly bound to the metal surface through chemisorption or physisorption. Between this thin polar layer and the corrosive environment is the thicker barrier layer of hydrocarbons. The sulfonate part of the inhibitor displaces water from the metal surface and promotes adsorption of inhibitor to the surface. Active sites with complementary energy levels to the polar group energy levels form a tighter, more uniform layer over the metal surface. The barrier layer has three important characteristics:

1. Low permeability by moisture
2. Compatibility with the oleophillic ends of the polar layer molecules so that the barrier is held firmly in place
3. Good solubility in the carrier to attach the polar and barrier layers to the metal surface

The VCI film barrier replenishes through further evaporation and condensation of the inhibitor on the metal surface. VpCI-337† (Inhibitor A) is a ready-to-use waterborne corrosion inhibitor for indoor use. The vapor phase corrosion inhibitors in Inhibitor A migrate over time and protect metal surfaces, resulting in time and cost savings.

An adsorption isotherm is a mathematical function that relates the surface coverage of a chemical on a surface (usually a metal) to the concentration of the chemical. Identification of the surface adsorption isotherm is important and can lead to the determination of a mechanism. It is assumed that the corrosion current density (CD), which is directly related to the corrosion rate, is representative of the number of corrosion sites. Therefore, adding inhibitor to the environment should diminish the number of corrosion initiation sites by displacing water molecules on the surface with inhibitor molecules, thereby decreasing the corrosion rate.

In recent years, electrochemical and weight loss methods that relate to the corrosion CD or amount of weight loss with the inhibitor coverage have been used to study adsorption and the corrosion inhibition of various materials on a metallic surface.\(^4\)\(^5\) Many models for adsorption

\[\text{Electrochemical polarization behavior of Ni-plated copper in 10% Inhibitor A with 200 ppm chloride ions at different temperatures, showing no significant changes.}\]

\[\text{Electrochemical polarization behavior of brass C36000 in 10% Inhibitor A with 200 ppm chloride ions at different temperatures.}\]

\[\text{TABLE 1: EFFECTS OF TEMPERATURE ON ELECTROCHEMICAL BEHAVIOR OF BRASS C36000 IN SOLUTION WITH 200 PPM Cl\textsuperscript{–} AND 10.0% INHIBITOR A}\]

<table>
<thead>
<tr>
<th>Solutions in Combination with 200 ppm Cl\textsuperscript{–}</th>
<th>Temperature (°C)</th>
<th>Ec (mV\textsubscript{SCE})</th>
<th>Eb (mV\textsubscript{SCE})</th>
<th>CR (µA/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0% Inhibitor A</td>
<td>20</td>
<td>−250</td>
<td>−37</td>
<td>4.05</td>
</tr>
<tr>
<td>10.0% Inhibitor A</td>
<td>20</td>
<td>−279</td>
<td>+1,280</td>
<td>0.30</td>
</tr>
<tr>
<td>0.0% Inhibitor A</td>
<td>30</td>
<td>−285</td>
<td>Active</td>
<td>13.40</td>
</tr>
<tr>
<td>10.0% Inhibitor A</td>
<td>30</td>
<td>−279</td>
<td>+1,150</td>
<td>0.34</td>
</tr>
<tr>
<td>0.0% Inhibitor A</td>
<td>40</td>
<td>−250</td>
<td>Active</td>
<td>13.80</td>
</tr>
<tr>
<td>10.0% Inhibitor A</td>
<td>40</td>
<td>−279</td>
<td>+1,090</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0% Inhibitor A</td>
<td>50</td>
<td>−233</td>
<td>Active</td>
<td>8.50</td>
</tr>
<tr>
<td>10.0% Inhibitor A</td>
<td>50</td>
<td>−280</td>
<td>+1,060</td>
<td>0.62</td>
</tr>
</tbody>
</table>
isotherms have been defined (i.e., Temkin, Freundlich, Langmuir, and Frumkin). Each of these adsorption isotherms explains a different type of relationship between the concentration and surface coverage of an inhibitor on a metal or alloy surface. Based on the adsorption isotherm graph, the adsorption equilibrium constant, \( K_{ads} \), can be calculated. Identifying the adsorption equilibrium constant can lead to the calculation of the free standard energy of adsorption:

\[
\Delta G_{ad} = -RT \ln (K_{ads})
\]

By repeating the same experiment at different temperatures, the enthalpy of adsorption, \( \Delta H_{ad} \), can be calculated.

**Experimental Procedure**

Corrosion inhibition of Inhibitor A was investigated for Cu alloys such as UNS C36000, C60300, and C83600, and Ni-plated copper commonly used in turbo-expander and steam/gas turbine applications. Electrochemical and polarization standards per ASTM G61 and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical behavior of this inhibitor on these alloys. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate, and localized corrosion susceptibility of a material in a given environment.

The studies were conducted using Gamry PC4750™ potentiostat/galvanostat/ZRA instrumentation and DC105™ corrosion test software. Samples were polished (600 grit), placed in a flat cell, and tested in different inhibitor concentrations with deionized water and 200 ppm Cl– solutions. A series of cyclic polarization tests were performed in temperatures ranging from 20 to 60 °C. Gamry’s electrochemical impedance spectroscopy (EIS300™) software was used to investigate the inhibitor effectiveness on these alloys and gather data for adsorption isotherms in different inhibitor concentrations of deionized water solutions containing 200 ppm Cl–. The \( R_p \) polarization resistance value (determined from the Bode plot) was used to fit the data into adsorption isotherm models.

**Stress Corrosion Investigation**

C-ring samples (ASTM G38™) of these alloys were tested in an eight-station alternate immersion system (ASTM G44™). The samples were immersed in 10% VCI A corrosion inhibitor, sodium chloride (NaCl), and tap water. The applied stress on these C-rings ranges from 60 to 90% of the alloy yield strength. Alternate immersion, an aggressive procedure, was performed to evaluate the inhibitor’s ability to retard SCC. The testing cycle for the samples consisted of 10 min immersion and 50 min exposure to air per ASTM G44 and G38. After 200 cycles of testing, the samples were disassembled, examined, and photographed to document corrosion resistance.

**Results**

**Cyclic Polarization Behavior**

Figure 1 and Table 1 show the polarization behavior for brass C36000 in varying concentrations (0 and 10%) of Inhibitor A with 200 ppm Cl– at temperatures ranging between 20 to 50 °C. The most noticeable changes are the positive shift in the breakdown potentials and expansion of the passive range for these alloys in Inhibitor A. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and had beneficial consequences for reducing localized corrosion damages. As demonstrated in these polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film, and shift of the critical pitting potential to higher levels.

Figure 2 shows the polarization behavior for Ni-plated copper in solution with 10% Inhibitor A and 200 ppm Cl– at different
temperatures (20 to 50 °C). These graphs show that the inhibitor has no adverse effect on this material. Table 2 shows the electrochemical behavior of different alloys in different concentrations of inhibitor. EIS (per ASTM G10610) test results are summarized in Table 3 and Figures 3 and 4. Inhibitor A increased the resistance polarization. The increased polarization resistance can be attributed to the film formation on the metal surfaces and its ability to neutralize the corrosive species.

**Stress Corrosion Cracking**

Susceptibility to SCC was determined for these alloys using ASTM G38 C-ring samples at an applied stress of 60 to 90% of their yield strength using the ASTM G44 alternate immersion technique. None of the alloys showed any susceptibility to SCC in different concentrations of inhibitor. The only sample that showed crack initiation was brass C36000 at 90% applied stress level in salt solution. However, when the inhibitor was added, no sign of any cracking was found. Figure 5 shows fracture surfaces for the C36000 C-ring samples after 200 cycles in ASTM G44. Figure 5 demonstrates the ductile dimple-type overload failure morphology for the samples tested in corrosive environments (chloride ions) with inhibitor as compared to the intergranular failure surfaces seen for samples with no inhibitor.

### Verification of the Inhibition Mechanism

The corrosion inhibition mechanism of Inhibitor A was investigated using the polarization resistance data acquired from the cyclic polarization and EIS tests. The increased polarization resistance can be attributed to the adsorption of inhibitor molecules to the metal surfaces. The addition of inhibitor has increased the $R_p$ value for all alloys (Tables 1 and 2). The high $R_p$ value is due to the progressive adsorption of inhibitor molecules and film formation on the metal surface. The data obtained from the electrochemical experiments best fit the Langmuir adsorption isotherm.

The important thermodynamic values (changes in enthalpy of adsorption and changes in free standard energy of adsorption) were obtained with adsorption isotherms and classical thermodynamics. The value of $\Delta G_{ads}$ could be used to identify the adsorption mechanism. In chemical adsorption, $\Delta G_{ads}$ is usually much higher than physical adsorption. The criterion for chemical adsorption varies depending on the paper referenced; the range is stated to be between $–40$ kJ/mol and $–100$ kJ/mol energy. Physical adsorption requires energy between $–5$ to $–20$ kJ/mol. The analysis of Inhibitor A showed the enthalpy of adsorption to be roughly $–10$ to $–14$ kJ/mol (Figure 6); this would indicate that the inhibitor has strong physical adsorption to the metal surface. The majority of corrosion damage to turbo-machinery systems, however, occurs during the shutdown period due to chemistry changes and stagnant conditions in localized areas. Therefore, a corrosion inhibitor with strong physical adsorption to the metal surface is preferred.

### Conclusions

Corrosion behavior of turbo-machinery system auxiliary component alloys in the presence of a vapor corrosion inhibitor was investigated. EIS and cyclic polarization at room temperature and elevated temperature showed no adverse effects on any alloys; in fact, in most cases corrosion was inhibited. Cyclic polarization behavior for samples in the vapor inhibitors showed a significant positive shift in the passive film breakdown potential for copper alloys. The increase in the passive film range will improve localized corrosion resistance.

The data acquired from electrochemical tests showed that inhibitor adsorption to these alloy surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is approximately $–10$ to $–12$ for Cu alloys and about $–14$ to $–16$ (for Ni-plated) kJ/mol, which suggests the inhibitor function is based on a physisorption mechanism.

The tests showed less SCC susceptibility in environments with Inhibitor A for all alloys including active alloys such as C36000. Almost no crack initiation was observed for the alloys tested in the chloride solution with 10% Inhibitor A. In the presence of inhibitor only, C36000 showed crack initiation when the applied stress was 90% of its yield strength.
In summary, Inhibitor A can be deduced to provide effective corrosion protection for steel, copper alloys, nickel-plated parts, and all other auxiliary components used in low-pressure steam turbines during the shutdown period.

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References


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CorroLogic™ System for Above Ground Storage Tanks (AST)

Is a system of filling the interstitial spaces of double bottom above ground storage tanks. A growing number of Oil & Gas companies are embracing the CorroLogic™ System approach for their ASTs. Data from the real-time corrosion rate monitoring equipment that is installed in each tank along with the VpCI®, proves the long term effectiveness of this solution. Cortec® completed a pilot project for the Saudi Arabian Oil Company, Saudi Aramco, on an AST with an oil-sand tank pad at one of their critical Arabian Gulf oil export terminals. Product is used as a powder or string of EcoPouch.

Corrologic™ VpCI®-609 is 100 percent biodegradable in marine environment per OECD***306, BOD 28 Marine Test.

Typical Tanks for Corrosion Inhibitor Systems

Double Bottom Tanks
- Retrofit on existing tanks.
- Easy to install on new tanks.

Single Bottom with Liner
- Retrofit on existing tanks.
- Easy to install on new tanks.

Monitoring for Double Bottom ASTs
- Use magnetic base drill and pipe tap to create threaded ports in the dead shell at specified locations.
- Insert ER probe and adapt secure with pipe fittings.
- Read probes on specified intervals.

Monitoring for Single Bottom ASTs with Liner
- Use a concrete core drill to core the ring wall at specified locations.
- Install PVC sleeve through the corehole.
- Insert a long ER probe so that probe tip extends into the sand.

CorroLogic™ System for Insulated Pipe Corrosion Under Insulation (CUI)

VpCI® products processes and equipment are used to mitigate CUI in a wide variety of environments. The equipment is capable of producing real-time measurements at the surfaces of insulated pipe and the processes are for application of VpCI® chemistry. In the very near future, Cortec® will be well prepared to make a huge impact on mitigation of CUI with no service disruption, no recoating, and no insulation removal.

Conclusion:
- Cortec’s CorroLogic™ program provides a comprehensive, 4-phase, turnkey solution for resolution of CUI issues.
- The program does not require removal and replacement of the existing pipe insulation.
- The system incorporates the application of Cortec’s proven multi-phase VpCI® chemistry on in-service piping systems to mitigate external surface corrosion.
- The system includes real-time corrosion rate monitoring to evaluate the corrosiveness of the insulated pipe environment and to evaluate the effectiveness of the corrosion inhibitor.
- Long-term control of CUI is engineered into the program through easy and economical replenishment of VpCI® as needed at any time in the future.
CorroLogic™ System for Control of Corrosion Under Insulation (CUI)

- Install permanent Cortec® Vapor phase Corrosion Inhibitor (VpCI®) liquid injection ports along the length of each insulated piping section.
- Install Electrical Resistance (ER) probes intermittently between liquid injection points.
- Spacing & configuration of VpCI® injection ports & ER probes vary according to pipe diameter and a variety of factors.

- Apply Cortec® VpCI®-658 per specified dosage.
- Intermittently obtain real-time corrosion rate data from the ER probes and evaluate effectiveness of corrosion inhibitor.
- Replenish VpCI®-658 in the future as indicated by ER probe data.

CorroLogic™ System for Pipeline Casings (CPC)

Head VpCI® corrosion control product that is applied as a liquid into the annular space between the carrier pipe and the casing which quickly sets into a gel. Options for corrosion rate monitoring are also available. Cortec® is providing the Oil and Gas industry with unique choices for carrier pipe corrosion control.

Corrosion Control Options for Cased Pipelines

Option 1: Install atomized liquid VpCI® system.

Option 2: Fill the casing with a gel containing corrosion inhibitor chemistry.

VpCI® Effectiveness Factors

- Vapor Pressure
  - The pressure exerted when a solid or liquid is in equilibrium with its own vapor.
  - VpCI® vapor pressure is lower than water.

- Diffusion
  - Natural process by which VpCI® molecules travel from an area of high concentration an area of low concentration until equilibrium is reached.
    (e.g. scent of an air freshener traveling through a room)

VpCI®-649

- Effective combination of vapor phase and film forming corrosion inhibitors
  - Protects in liquid, vapor, and inter phase
  - Contains an anti-scalant
  - Protects ferrous and non-ferrous metals
  - Vapor phase and film forming protection for drained systems
  - Contact protection for wet pipe system

VpCI®-649 Compatibility

- Compatibility with common elastomers
  - Natural rubber
  - Synthetic rubber (EPDM, Neoprene, Buna)
  - Silicone
  - Polypropylene
  - Fluoroelastomers (Teflon, Viton, Fluorosilicone, Dyneon Fluoroelastomer)
- Tested in the lab and field to ensure no negative effects
- ASTM D 471
  - Standard test for determining fluid effects on rubber properties
  - Determine the change in mass and shape after 7 days of immersion.

VpCI® in Suppression Systems

- Does not cause skin sensitization
  - 72 hour exposure test
- Compatible with many biocides
- Effective in low dosages
- Best performing inhibitors ever tested by Cortec® Laboratories.
CorroLogic™ Systems

Deluge System

• Corrosion leads to leaks in piping and blockages in nozzles.
• Field testing with 5% solution of VpCI®-649 led to 98% decrease in blocked sprinkler nozzles in the first year after and 99% decrease after 2 years.

Conclusions

• VpCI® products reduces corrosion in fire suppression systems thereby reducing the risk of pipe leaks and nozzle blockage.
• Protects from corrosion in stagnant water and drained systems.
• VpCI®-649 is environmentally friendly and non-hazardous
• It is safe and effective for use in most sprinkler systems.

CorroLogic™ System for Top of the Line (TOL) Corrosion Protection of Pipelines

CorroLogic™ VpCI®-637 (TOL) conforms to MIL-I-22110C VIA Test (Vapor Inhibiting Ability)

CorroLogic™ VpCI® is a synergistic blend of the best performing inhibitors ever tested by Cortec® Laboratories. The results from the VIA tests above show very positive performance which indicates CorroLogic™ VpCI® will provide excellent protection in TOL.

Pipeline section shows active VpCI® protection at the liquid phase, vapor phase, and the interface: partition and emulsion barriers.


+ Wheel Test, NACE test method ID 182 (Film persistency-90+% protection, Continuous Treatment-90+% protection)
+ Corrosion Loop Test, method of Continental products of Texas, "Specialty Oilfield and Water Chemical Solutions"
+ Rotating Cylinder Electrode Test, ASTM G-170-01, “Standard guide for evaluating Qualifying Oilfield and refinery Corrosion Inhibitors in the Laboratory”, 95+% of protection


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Corrologic™ VpCI® conforms to MIL-I-22110C VIA Test (Vapor Inhibiting Ability)

CorroLogic™ VpCI®-637 (TOL) for Top of the Line Corrosion Protection of Pipelines

X65 Pipe Steel: Control

X65 Pipe Steel: Protected with CorroLogic™ VpCI®
Being a World Leader in Environmentally-Safe Corrosion Protection/Solutions has its Responsibilities

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Environmentally Safe VpCI®/MCI® Technologies

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