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MIP **MATERIALS PERFORMANCE**

CORROSION PREVENTION AND CONTROL WORLDWIDE

Protecting the World's Tallest Building from Corrosion

**Testing and Utilization of Next-Generation
Migrating Corrosion Inhibitors**

**Volatile Corrosion Inhibition of
Stress Corrosion Cracking in a Steam Turbine**

**Mitigation of Soil-Side Corrosion on
Double-Contained Aboveground
Storage Tank Floors**

**Case Study: Bioremediation of
Petroleum Hydrocarbon-Contaminated
Soil under a Residential Building**



NACE



About the Cover

The Burj Khalifa Building in Dubai, U.A.E.—the tallest building in the world—is exposed to the harsh, highly corrosive gulf environment. The building's foundation and piles are constructed of concrete containing migrating corrosion inhibitors (MCIs) as one of the measures to achieve a 100+ year design life. See the article beginning on p. 3 for a description of an MCI testing program as well as examples of their use in protecting reinforced concrete structures from corrosion.

Cost-Effective Vapor Phase 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.

Vapor-phase corrosion inhibitors (VCIs) are one example 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.

VCI performance 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. A related technology, migrating corrosion inhibitors (MCIs), can even diffuse into concrete to help protect embedded reinforcing steel.

The articles that follow describe VCI and MCI performance in applications that include reinforced concrete buildings, aboveground storage tank floors, steam turbine equipment, and remediation of soil contaminated with petroleum hydrocarbons.

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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Bionetix International

The latest generation of migrating corrosion inhibitors (MCIs) contains a blend of amine-based inhibitors, but is based mostly on amine carboxylates. These organic compounds are derived from sugar beets, a renewable source, and are called “mixed” corrosion inhibitors, meaning they affect both anodic and cathodic portions of a corrosion cell. Their use adds to the durability of structures by reducing corrosion. Many of these MCIs have NSF/ANSI Standard 61¹ certification, meaning they are safe for use in structures holding potable water.

MCIs have the ability to move as a vapor through the pores of concrete. When they come into contact with embedded metals, they form a protective, molecular layer on the surface of the metal. The blend of amines used in each product is tailored to the expected application, i.e., admixtures are less volatile (much slower to go into vapor phase) because they are mixed in and evenly dispersed through the concrete from the beginning, whereas surface treatments are more volatile to ensure that they can penetrate to the depth of the embedded reinforcement in a timely manner. Loss of inhibitor from air exchange near the surface of the concrete is accounted for in the dosage rate of the inhibitor. The oldest case histories for MCIs are now more than 25 years old.

MCI materials have been thoroughly tested to show corrosion protection and that they do not affect physical properties of the concrete mix. One of these tests is ASTM C1582.² There are two aspects of ASTM C1582; one relates to corrosion inhibiting performance (ASTM G109³) and the other relates to the physical properties of the concrete containing additives.

Inhibitor Tests

ASTM C1582

MCI products have little effect on most

Testing and Utilization of Next-Generation Migrating Corrosion Inhibitors

JESSI MEYER, *Cortec Corp., St. Paul, Minnesota*

Migrating corrosion inhibitors have been utilized in the construction industry over the past 25 years. Lab and field testing have confirmed their benefit in extending the durability of concrete exposed to corrosive environments. This article describes the tests done and gives examples of their use.

concrete mix properties. The latest generation of MCI admixtures performs within the acceptable ranges given in ASTM C1582. Figure 1 shows typical results for compressive strength.

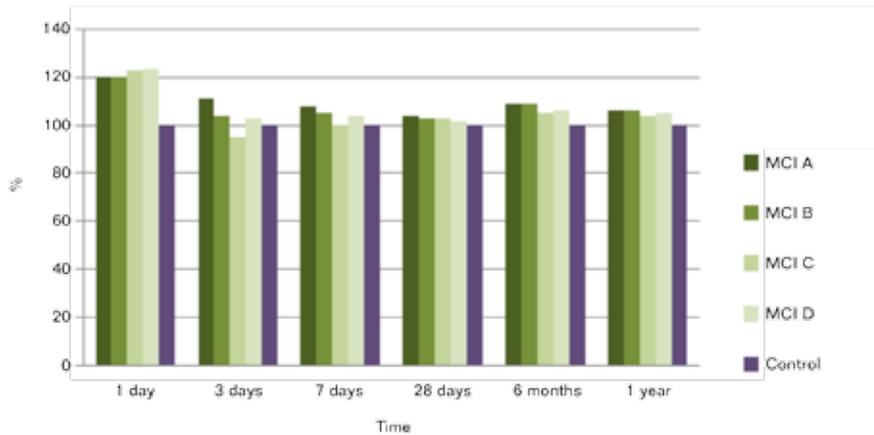
ASTM G109

ASTM G109 measures the ability of an admixture to reduce corrosion in concrete exposed to chlorides. Concrete slabs

are cast with a triangular array of rebar inside. The top bar is 1.0 in (25 mm) \pm 0.1 in (2.5 mm) from the top of the slab. Salt solution (3.5%) is ponded on the surface for two weeks and then drained. The samples are then allowed to dry for two weeks, so each test cycle is a total of four weeks.

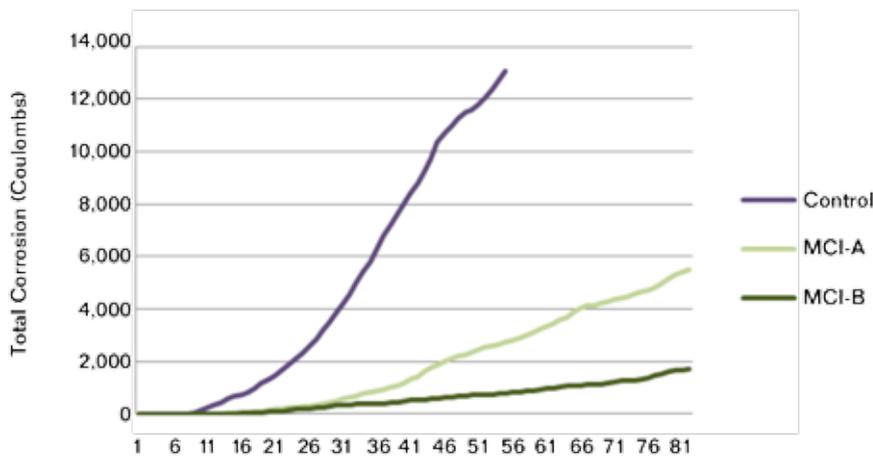
MCI admixtures provide a dual benefit. They extend the time to corrosion

FIGURE 1



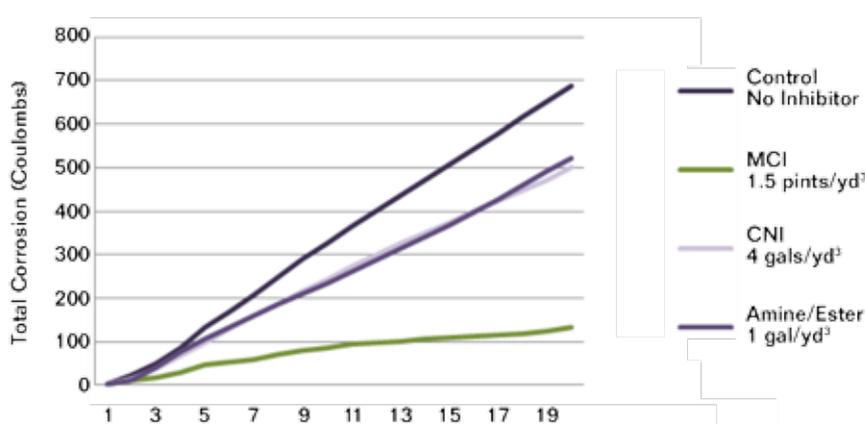
Compressive strength of concrete—MCI compared to control sample.

FIGURE 2



ASTM G109: MCI total compared to control.

FIGURE 3



Cracked beam admixture testing: MCI compared to control, other inhibitors.

initiation compared to a control (double to triple the time to initiation depending on the product), and once corrosion starts, the rates are five to 13 times slower (Figure 2).

Modified G109

A modified G109 test is set up similarly to the standard ASTM G109 test; in this case, however, a small cut is made on the surface of the slab and a load is applied to the ends of the sample to form a crack that goes to the depth of the top bar. This allows the salt solution to reach embedded reinforcement immediately, making the test more aggressive. The test involves one-week cycles (four days wet with a 6% salt solution, three days drying), and a comparison of MCI to two other corrosion inhibiting admixtures. This test highlights MCI’s advantages over other corrosion inhibitor products in a situation where a crack forms after construction. The MCI acts on the metal as a protective layer, and its vapor phase ability enables it to replenish itself on the surface of the rebar at the crack, keeping the corrosion rate lower over time. Figure 3 shows that MCI outperforms other admixtures in reducing corrosion in cracked beam structures.

Cracked beam testing was also completed on MCI surface treatment products for existing structures. This test was modified differently from the admixture test. Samples were cast, cured, and cracked. MCI was surface-applied to the top of the slab. Test cycles were one week wet, one week dry for the first month, followed by two weeks wet, two weeks dry for the next 19 months, and a 3% salt solution was used for ponding.

ASTM C157

When designing durable concrete structures that will have a long service life, it is necessary to minimize shrinkage that could lead to cracking. While some corrosion inhibitors are known to increase contraction (shrinkage) of concrete, MCI does not. ASTM C157⁴ tests length change (expansion or contraction) of concrete or mortars from various causes other than applied force or temperature change.

MCI-treated mix designs perform similarly to a control (Figure 4). Calcium nitrite (a different type of corrosion inhibitor) increases the amount of shrinkage. Shrinkage can lead to cracking during curing, thus allowing easier ingress of contaminants and can lead to a decreased service life of the structure.

Global MCI Use

Burj Khalifa Building

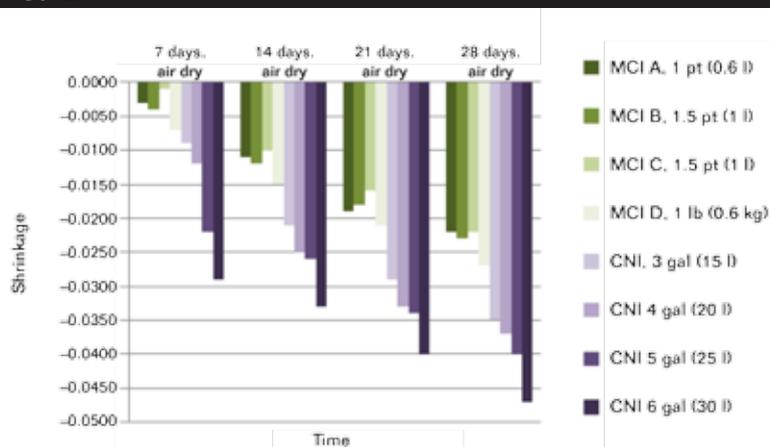
Because MCIs are compatible with most mix designs, as well as with other types of corrosion protection, they have some interesting case histories. The Burj Khalifa, currently the tallest building in the world, is located in Dubai, United Arab Emirates (Figure 5). The structure was designed to have a 100+ year service life, and is exposed to the harsh gulf environment, one of the most corrosive in the world. This means that durability of critical elements (such as foundations, raft slabs, and piles), which are exposed to the environment and cannot be easily repaired, is of utmost importance. To achieve the desired service life, durable concrete containing MCI, and cathodic protection were used in the foundations and piles of the Burj Khalifa as well as many other structures in this region.

Hospital Parking Structure

MCI products also extend the service life of existing structures when used in repair, such as in a hospital parking garage. This structure was built in the late 1980s and was exposed to heavy applications of deicing salts through the years. In 1996, a traffic membrane was applied to the drive surfaces. Moisture in the deck could move out of the concrete only through the bottom of the slab, carrying chlorides with it.

In 2007, an evaluation showed the deck was heavily contaminated with chlorides. Some areas of the deck required full depth replacement (Figure 6[a]). In these areas, ready mix concrete containing an MCI admixture was used. The remaining areas were treated with a surface-applied MCI—both on the drive surface and the underside (Figure 6[b]) to protect both layers of reinforcing steel in

FIGURE 4



Comparison of MCIs with calcium nitrate per ASTM C157.

FIGURE 5



The Burj Khalifa Building in Dubai, U.A.E.

FIGURE 6



(a)



(b)

Hospital parking garage during repair: (a) deck level and (b) underside of deck.

TABLE 1

Location	Average Reading ($\mu\text{A}/\text{cm}^2$)
1	2.94
2	3.60
3	0.43
4	0.84
5	1.55

Galvanostatic pulse instrument readings on hospital parking garage taken 2.5 years after application of MCI.

TABLE 2

Corrosion Current, $\mu\text{A}/\text{cm}^2$	Corrosion Rate, $\mu\text{m}/\text{year}$	Corrosion Level	Time to Visible Deterioration
<0.5	<5.8	Passive	N/A
0.5 to 5	5.8 to 58	Low	>10 years
5 to 15	58 to 174	Moderate	3 to 10 years
>15	>174	High	<2 years

Interpretation of corrosion rates of reinforcing steel in hospital concrete parking deck before repair by Thomas Frolund, 2002, using a galvanostatic pulse instrument.

the deck. A 40% silane water repellent was applied to the deck, preventing intrusion of water, but allowing vapor transmission of moisture out of the concrete. Followup corrosion testing showed the repaired deck remains in a state of low corrosion (Table 1). Table 2 shows interpretation of the corrosion rates.

Conclusions

The latest generation of MCI products have been thoroughly tested and used in corrosive applications worldwide. Lab and field test results confirm that MCIs reduce corrosion rates and extend the useful life of concrete and masonry structures, with minimal effect on the concrete properties.

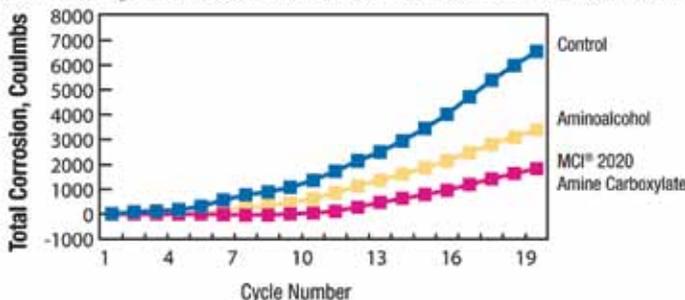
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Cortec® MCI® used on Pentagon Repair Project as featured in Concrete Repair Bulletin Sept./Oct. 2010 Issue.

Cracked Beam Testing of Surface Treatments. Details: www.CortecMCI.com



Cortec’s Migrating Corrosion Inhibitors (MCI®) offer superior corrosion protection for new and existing structures. Proven to penetrate to embedded reinforcement, MCI® can reduce corrosion rates as much as 80%. This offers an economical solution to more expensive cathodic protection systems used for concrete. For more information, including testing and case histories, please visit our newly updated website:

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Double-bottom tank installations and tanks with high-density polyethylene (HDPE) liner containment often create difficult corrosion control challenges. Current from external cathodic protection (CP) systems will not flow through the lower floor of a double-bottom tank or a HDPE containment liner. CP can be applied only by installing anodes between the upper floor and lower floor, or containment liner.

Many tanks have been upgraded with double bottoms, or under-tank liners (Figure 1), and a variety of CP systems have been installed on these tanks. Some interstitial space CP systems have become ineffective, however. Replacement without taking the tanks out of service and removing the floors is not practical or economical. Operating the tanks without soil-side corrosion control on the fluid containment floor is not an acceptable option for many tank owners and regulatory authorities.

Corrosion Control with VCIs

Engineered systems utilizing vapor phase corrosion inhibitor (VCI) technology offer an important alternative for mitigation of tank floor corrosion. These systems are economical, effective, and can be installed on a retrofit basis without disrupting tank service.

A developing history of corrosion rate data provides confidence that if the VCI chemistry is effectively delivered under the tank bottoms, and if the intrusion of fresh air and water under the tanks is eliminated, soil-side floor plate corrosion will be mitigated. VCIs are effective alone, or in combination with CP.

Fundamentals of VCI Operation

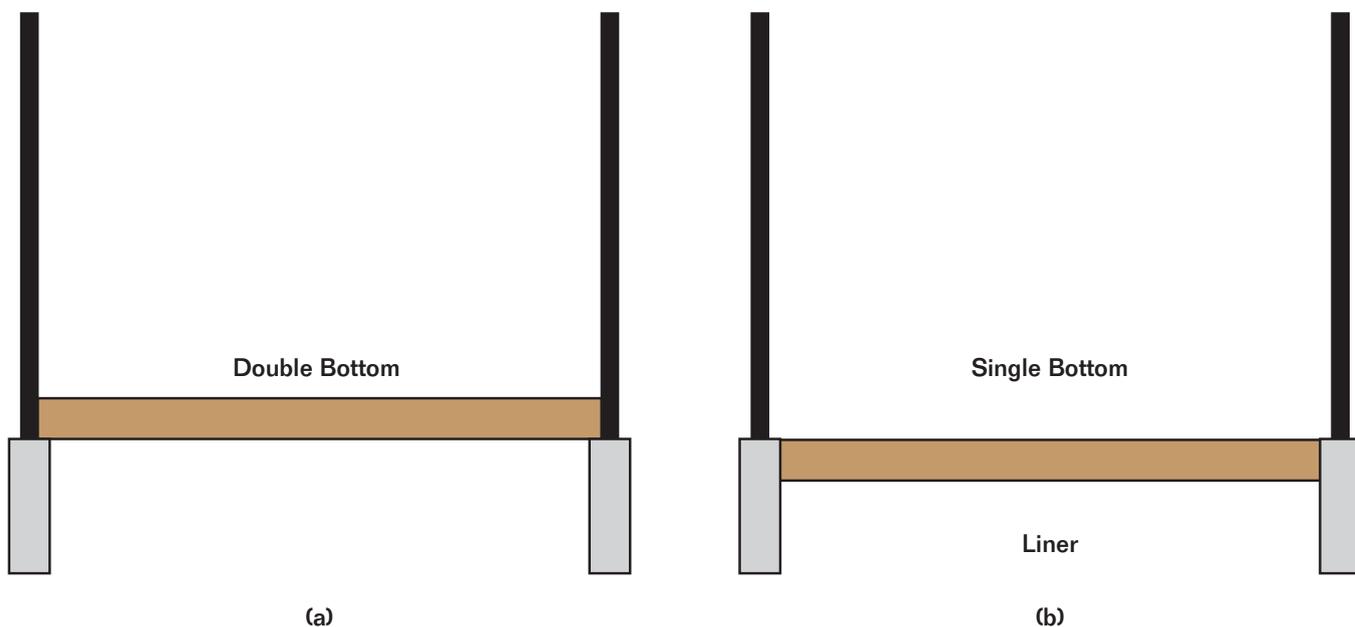
It is important to recognize that VCI chemistry/technology is very mature and well proven. The author's company has researched, invented, innovated, manufactured, and applied environmentally friendly VCI chemistry for over 30 years to solve

Mitigation of Soil-Side Corrosion on Double-Contained Aboveground Storage Tank Floors

TIM WHITED, *Cortec Corp., St. Paul, Minnesota*

The application of vapor phase corrosion inhibitor (VCI) chemistry, combined with a corrosion rate monitoring system, provides an excellent method to mitigate and monitor corrosion within the interstitial spaces of aboveground storage tank bottoms. This article describes VCI chemistry and presents several case histories of VCI usage in these spaces.

FIGURE 1



Tank configurations having interstitial spaces: double bottom and (b) HDPE liner under a single bottom.

many basic corrosion control challenges on metallic surfaces. VCI solutions for corrosion mitigation are utilized by many major corporations in most regions of the world for a wide variety of applications.

Amine carboxylate-based VCIs are used beneath aboveground storage tanks (ASTs). These environmentally friendly products are effective for prevention of metal corrosion in three phases: on the surface of the steel in contact with the sand tank pad materials, at the air/sand interface, and in the vapor space above the sand. When a VCI output is released within an AST interstitial space, protective vapors disseminate until equilibrium, determined by the partial vapor pressure, is reached. The mechanism for corrosion control is the formation of a monomolecular layer throughout the soil-side surface of the tank floor. VCI molecules adsorb on the steel surface to suppress both metal dissolution and the reduction reaction (both the anodic and cathodic processes). This adsorption is accomplished without the need for direct contact of the VCI chemical on the metal surface.

FIGURE 2



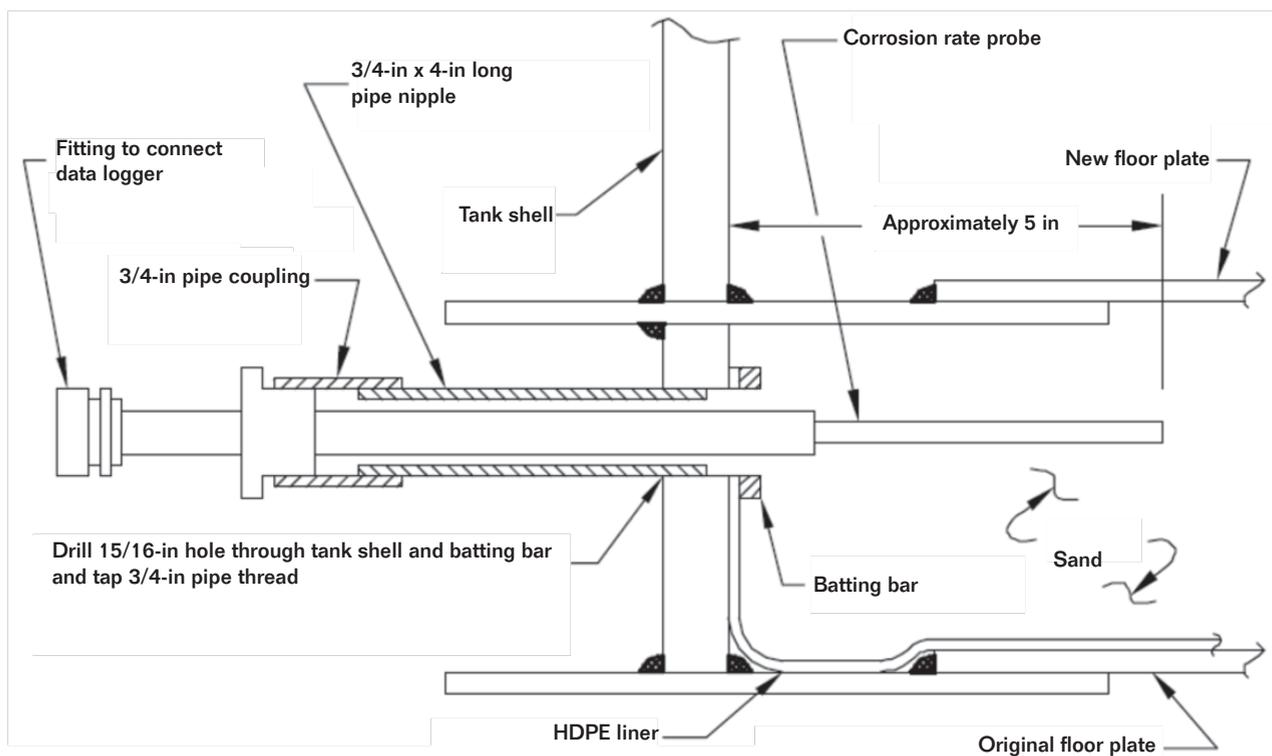
Corrosion rate monitoring probe: (a) delivering VCI slurry under the tank floor and (b) completed ER probe assembly through the ringwall.

U.S. History with VCIs in ASTs

In 1993, Rials & Kiefer¹ published a technical paper presenting results from testing a variety of corrosion control options for double-bottom tanks. One of the corrosion prevention methods tested included a VCI mixed with a typical tank pad material. Corrosion was monitored and measured over an extended time period. Almost no corrosion developed in the presence of the VCI.

One of the first known AST applications of the VCI technology in the United States was in Florida. A VCI was installed in a water slurry mixture under 17 ASTs in Florida between the years of 2000 and 2001. Electrical resistance (ER) corrosion rate probes were installed under each tank to monitor the inhibitor effectiveness. Approximately five years after VCI application, the corrosion rate probe data were evaluated. The corrosion rates were still very low, ranging

FIGURE 3



ER corrosion rate probe installation through the tank wall in a double-bottom tank.

from 0.150 to 0.720 mils (3.8 to 18 μm) metal loss per year.²

The author spent about 10 years engineering and developing systems and processes for delivery of VCI chemistry under ASTs. He applied this solution to well over 100 tanks in the United States.

Today it is estimated that more than 10 major oil and gas companies operating ASTs in the United States utilize VCI chemistry to control corrosion on tank floors. VCIs are also soon to be used in the Middle East for mitigation of AST corrosion challenges that are unique to the Persian Gulf region.

Monitoring and Mitigation of Corrosion in the Interstitial Space

The Cortec VCI system for ASTs is named CorroLogic[†]. A typical system includes:

1. Sealing any gaps between the tank floor and dead shell on double-bottom

[†]Trade name.

tanks, or gaps between the tank floor and concrete ringwall on single-bottom tanks to prevent intrusion of fresh water and air into the interstitial spaces of these tank systems.

2. Engineered application of the VCI into the interstitial space in such a way that effective distribution of the chemistry is ensured.
3. A corrosion rate monitoring system utilizing electrical resistance probe technology to measure the real-time rate of corrosion within the interstitial space and near the tank floor.

Sealing the Interstitial Space

Significant mitigation of interstitial space corrosion can be accomplished by preventing intrusion of fresh water and fresh air into the space. On double-bottom tanks there are gaps between the underside of the upper floor and the dead shell. Those gaps can be welded or sealed with a caulk/tape system. On single-bottom tanks with liners, consideration should be given to sealing the chime plate

to ringwall interface with a caulk and tape system.

Application of the VCI

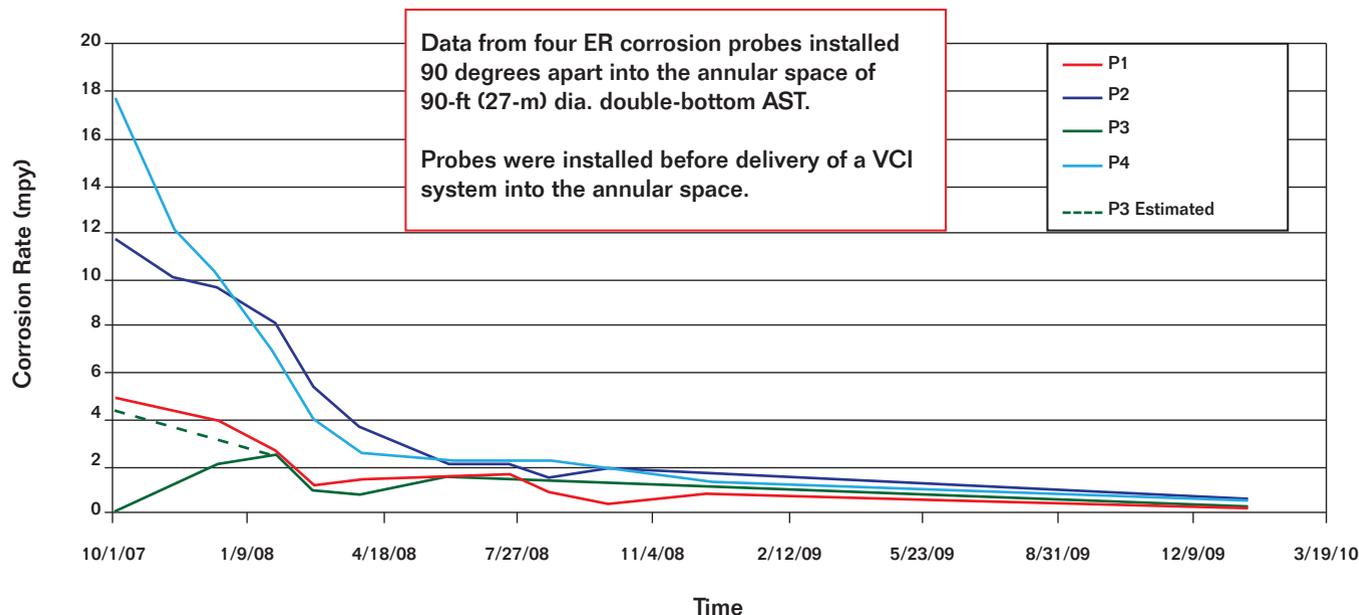
For new construction tanks, the inhibitor is applied in a powder form on top of the liner before the sand is installed. The powder is contained in long strips of breathable EcoPouches[†]. This system is easily installed by the tank-erecting contractor.

For in-service double-contained tanks, the VCI is applied into the interstitial space by delivery of concentrated inhibitor slurry beneath the liquid bearing floor. The slurry injection is accomplished through a network of perforated pipes that is installed into the space with vacuum equipment. Special mixing equipment and delivery systems are used to apply the slurry through the injection pipes.

Corrosion Rate Monitoring System

ER corrosion rate probes (Figure 3) are installed to obtain real-time corro-

FIGURE 4



ER probe data from an AST over a period of about 2½ years.

sion rate measurements of the interstitial space environment. The data obtained from the probes are the calculated mils per year metal loss. The ER probes are installed at numerous locations under a tank floor. In double-floor tanks they are installed directly through the dead shell and into the sand a few inches beyond the shell. In single-bottom tanks with liners they are installed through the ringwall and into the sand. In either case, if ER probe data are desired further under the tank, the probes can be installed through access pipes retrofitted into the space.

Some operators choose to install the corrosion rate monitoring systems before any inhibitor is applied in order to assess the corrosiveness of each AST interstitial space. Once a VCI system is installed, the corrosion rate monitoring system provides continuous evaluation of the corrosion inhibitor effectiveness for the life of the tank.

Figure 4 shows typical ER probe tank

data that illustrate the performance of VCI systems over nearly 2½ years.

System Maintenance

A significant advantage associated with this type of corrosion mitigation system is reduced maintenance costs. There are no ongoing maintenance requirements, other than collecting the corrosion monitoring system data on a predetermined schedule. There are no power costs, no wiring to repair, and no equipment to maintain. If the corrosion rates increase sometime in the future to higher than desired levels, the inhibitor can be replenished.

Conclusions

When steel is exposed to properly applied VCI chemistry, the corrosion is reliably mitigated. This has been proven in a wide variety of applications for many years throughout the world. The use of environmentally friendly VCI chemistry and engineered systems for aboveground tanks is maturing and expanding. Ap-

plication of VCI chemistry, combined with real-time corrosion rate monitoring, provides AST owner/operators with an effective and economical solution to the challenge of soil-side corrosion mitigation on double-contained ASTs.

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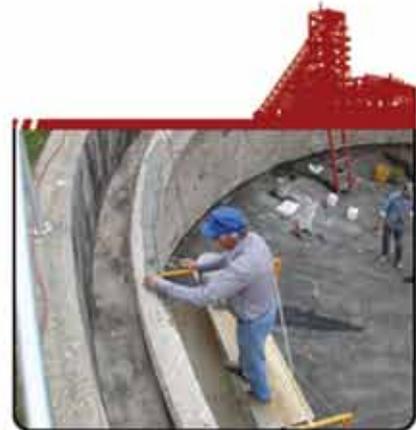
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2. T. Whited, "Inhibiting Tank Corrosion," *Hydrocarbon Engineering* 8 (2005).

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TURNKEYAPPLICATIONS

Volatile Corrosion Inhibition of Stress Corrosion Cracking in a Steam Turbine

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The accumulation of damage caused by localized corrosion, pitting, stress corrosion cracking, and corrosion fatigue in low-pressure steam turbine components such as blades, discs, and rotors has been consistently identified as the main cause of turbine failure. The development of effective localized corrosion inhibitors is essential for the successful avoidance of unscheduled downtime in steam turbines or other complex industrial and infrastructure systems. Commercially available inhibitors were investigated for their effectiveness in reducing and controlling the steel equipment's susceptibility to corrosion.

Steam turbines and other complex industrial systems are susceptible to stress corrosion cracking (SCC) and other forms of corrosion because of the hostile environments in which they operate. The majority of damage occurs during shutdown periods because of chemistry changes and stagnant conditions in localized areas. The environmental changes during the shutdown period are the primary contributing factors that determine the probability of blade and disc failures in low-pressure steam turbines. Oxygen, chlorides, temperature, pH, and time spent under aerated conditions during the shutdown period increase the likelihood of localized corrosion attack. Increases in Cl^- concentration and pH changes affect the stability of protective oxides, and eventually pitting, SCC, and corrosion fatigue (CF) can occur.

In general, it is believed that by lowering Cl^- below 35 ppm, the susceptibility to localized corrosion decreases significantly. If chloride concentration on the surfaces is reduced immediately upon shutdown, this will provide a corrective strategy for minimizing or even eliminating the failure of discs and blades. This is most easily accomplished by washing the blade and disc surfaces with chloride-free water immediately upon shutdown of the turbine. In fact, an even more effective strategy would be to combine turbine surface washing with dehumidification or nitrogen blanketing.

For the accessible surfaces, this strategy can work, but for the restricted geometries such as crevices, notches, and cavities, reaching these surfaces is very difficult and it is dangerous to assume that those areas have been washed effectively. Accumulation of corrosive species and pH changes inside these restricted geometries can alter the electrochemical reactions to initiate pitting or crevice corrosion that eventually leads to SCC and CF.

Low-pressure rotors are typically constructed of forgings conforming to ASTM A470,¹ 3.5NiCrMoV (Class 2 to 7). Shrink-on discs are made of ASTM A471² (Class 1 to 3). The strength and hardness of turbine components must be

limited because the stronger and harder materials become very susceptible to SCC and CF, particularly turbine rotors, discs, and blades. The crack propagation rate increases with yield strength and hydrogen embrittlement (HE) can occur. This susceptibility limits the use of high-strength materials for turbine discs in power plants (a yield strength <140 ksi [965 MPa] is recommended). However, in turbo machinery, the common impeller and turbine are 7xxx series high-strength aluminum alloys, mainly 7050 (UNS A97050) forged aluminum alloy. Some of the main reasons for selecting this alloy for turbine applications are light weight, toughness, and corrosion resistance. However, residual stresses induced by the heat treatment in conjunction with those from the machining process make these materials sensitive to SCC. To improve SCC and CF resistance, this alloy is used in T74 tempered condition. Corrosion protection is critical to maintain the functionality of these systems.

Vapor Phase Corrosion Inhibitors

Several groups of organic compounds have corrosion inhibiting effects for different alloys. The extent of adsorption of an inhibitor depends on many factors: the nature and surface charge of the metal, the inhibitor adsorption mode, and the inhibitor's chemical structure. The presence of heteroatoms (oxygen, nitrogen, sulfur, phosphorus), triple bonds, and aromatic rings in the inhibitor's chemical structure enhance the adsorption process. Coating-to-substrate adhesion and the diffusion of water and other species from an external environment to the coating/substrate interface are critical factors for the corrosion inhibition of organic protective coatings.

One possibility for turbine materials protection is a volatile corrosion inhibitor (VCI), where protective vapors deposit on the exposed surfaces, including cracks and crevices, and condense to form a thin barrier of tiny crystals. The crystals dissolve when in contact with water, causing the adsorption of a monomolecular coat-

FIGURE 1



Turbine machinery blades.

ing to the metal surface that helps repel water. A VCI can also neutralize the pH and other corrosive species, which is an effective way to adjust the localized chemistry inside a crevice, pit, or crack.

VCIs are often a complex mixture of amine salts and aromatic sulfonic acids that provide direct contact inhibition and incorporate volatile carboxylic acid salts as a vapor phase inhibitor for metal surfaces not sufficiently coated. The thin polar layer of surfactants is tightly bound to the metal surface through chemisorption. Between this thin polar layer and the corrosive environment is the thicker barrier layer of hydrocarbons. The sul-

fonate part of the inhibitor displaces water from the metal surface and promotes chemisorbed inhibitor to the surface. A surface-active inhibitor component will be strongly chemisorbed or adsorbed to the surface.³ Active sites having energy levels complementary to the energy levels of the polar group form a tighter, more uniform layer over the metal surface.

The barrier layer has three important characteristics: 1) low permeability by moisture and other corrosives, 2) compatibility with the oleophilic ends of the polar layer molecules so that the barrier is held firmly in place, and 3) good solubility in

FIGURE 2



Steam turbine system.

the carrier to attach the polar and barrier layers to the metal surface.⁴The VCI film barrier replenishes through further evaporation and condensation of the inhibitor on the metal surface.

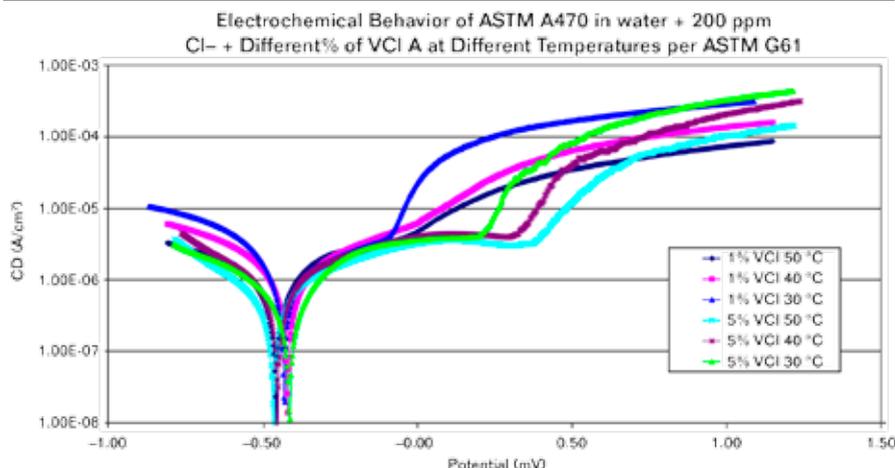
Turbo Machinery Maintenance

Turbo machinery systems (Figures 1 and 2) have regular service maintenance and unexpected shutdowns. During scheduled maintenance, components are frequently washed to dilute or remove any surface contaminants, such as salt, dirt, grease, and oil. There are three main types of cleaning: aqueous, organic solvent, and abrasive. Aqueous cleaning covers a wide variety of methods, including the use of detergents, acids, and alkaline compounds. The proposed inhibitors investigated in this program are heavy-duty, biodegradable, water-based alkaline cleansers and degreasers. The compounds function by altering hydrocarbons (grease) so that the deposits can be removed with water. Any conventional equipment (power washers, steam cleaners, dip tanks) can be used for multi-metal corrosion protection. Ethoxylated alcohols, the active ingredient in the inhibitors, are based on short-chain alcohols giving fast penetration of soil and improved performance on hard surfaces.

Adsorption Isotherm Models

An adsorption isotherm is a mathematical function that relates to the coverage of a chemical on a surface (usually a metal) to the concentration of the chemical. Identification of the surface adsorption isotherm is important in that it and classical thermodynamics 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

FIGURE 3



Electrochemical polarization behavior of A470 steel in different percentages of VCI A solutions.

surface with inhibitor molecules, thereby decreasing the corrosion rate. By measuring the CD of a solution with no inhibitor (blank) and an inhibited solution (or by measuring the polarization resistance), the surface coverage, θ , can be defined by the following formula:

$$\theta = \frac{I_{\text{corr}}(\text{B}) - I_{\text{corr}}(\text{I})}{I_{\text{corr}}(\text{B})} \quad \text{or} \quad \theta = \frac{\frac{1}{R_p(\text{B})} - \frac{1}{R_p(\text{I})}}{\frac{1}{R_p(\text{B})}} \Rightarrow$$

$$\theta = \frac{R_p(\text{I}) - R_p(\text{B})}{R_p(\text{I})} \quad (1)$$

where $I_{\text{corr}}(\text{B})$ and $R_p(\text{B})$ are the corrosion current and polarization resistance of the blank solution, respectively. $I_{\text{corr}}(\text{I})$ and $R_p(\text{I})$ are the corrosion current and polarization resistance for the inhibited solution, respectively.

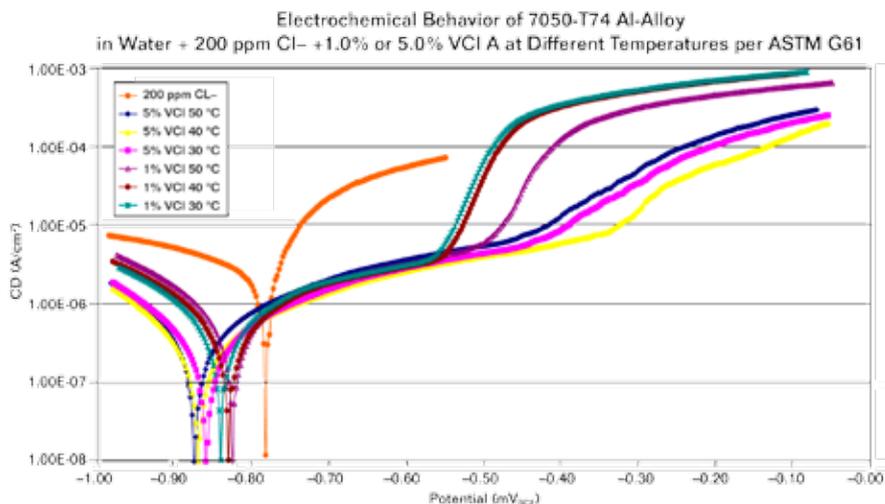
Experimental Procedures

Corrosion inhibition of VCI 337[†] (VCI A) and Ecoline 3690[†] (VCI B) were investigated for 7050 aluminum alloy and ASTM A470 steel in the turbo expander and steam/gas turbines industry. The A470 steel is common for constructing low-pressure steam turbine discs and rotors. Its chemical composition contains 3.5% Ni, 1.5% Cr, 0.8% Mo, and 0.25% V. The samples for investigation were annealed for 24 h and air-cooled. A Rockwell C hardness of 32 was achieved after heat treatment. The 7050 alloy contains 6.5% Zn, 2% Mg, and 2% Cu that was used in T74 tempered condition. Rockwell B hardness was 82 to 84, while electrical conductivity was 38% IACS (International Annealed Copper Standard).

Electrochemical polarization per ASTM G61⁵ was used to evaluate the electrochemical behavior of these inhibitors on the A470 steel and 7050 alloy. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate, and localized corrosion susceptibility of the material for a given environment. The studies were conducted using a Gamry PC4/750[†] potentiostat/galvanostat/zero resistance

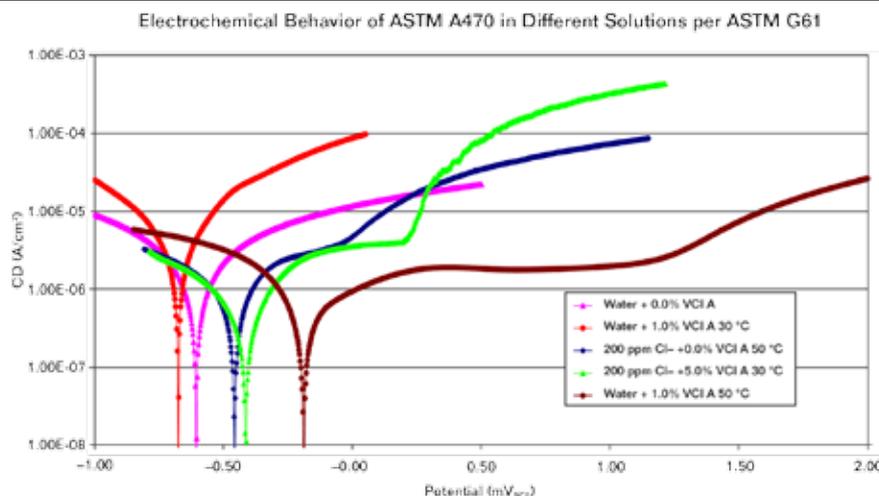
[†]Trade name.

FIGURE 4



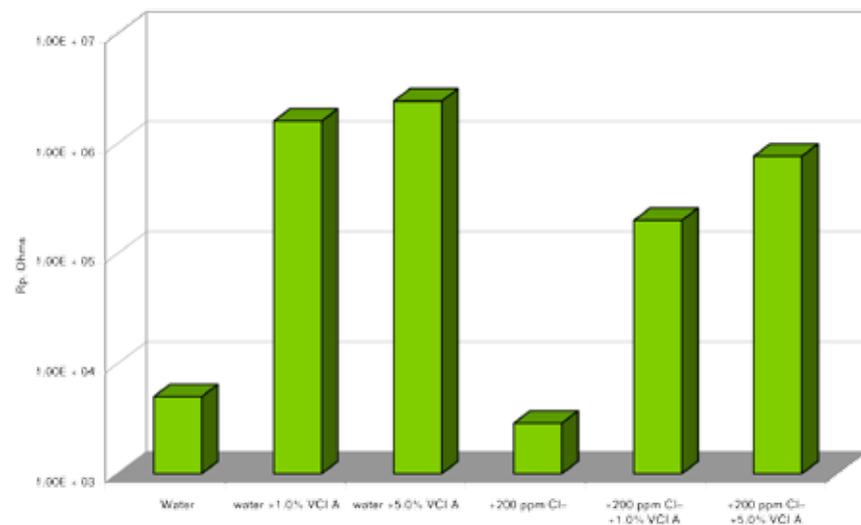
Effects of temperature on the electrochemical polarization behavior of 7050-T74 alloy in different percentages of VCI A solutions.

FIGURE 5



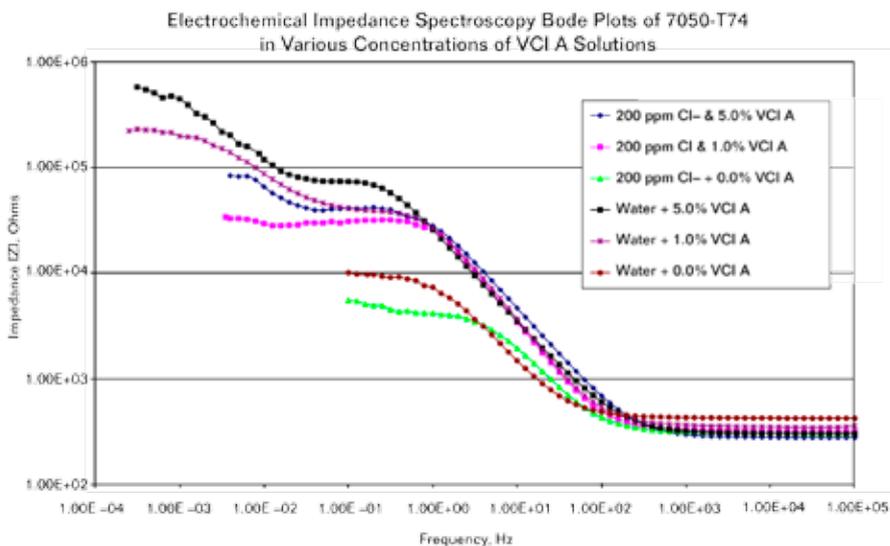
Electrochemical polarization behavior of A470 steel in different percentages of VCI A solutions.

FIGURE 6



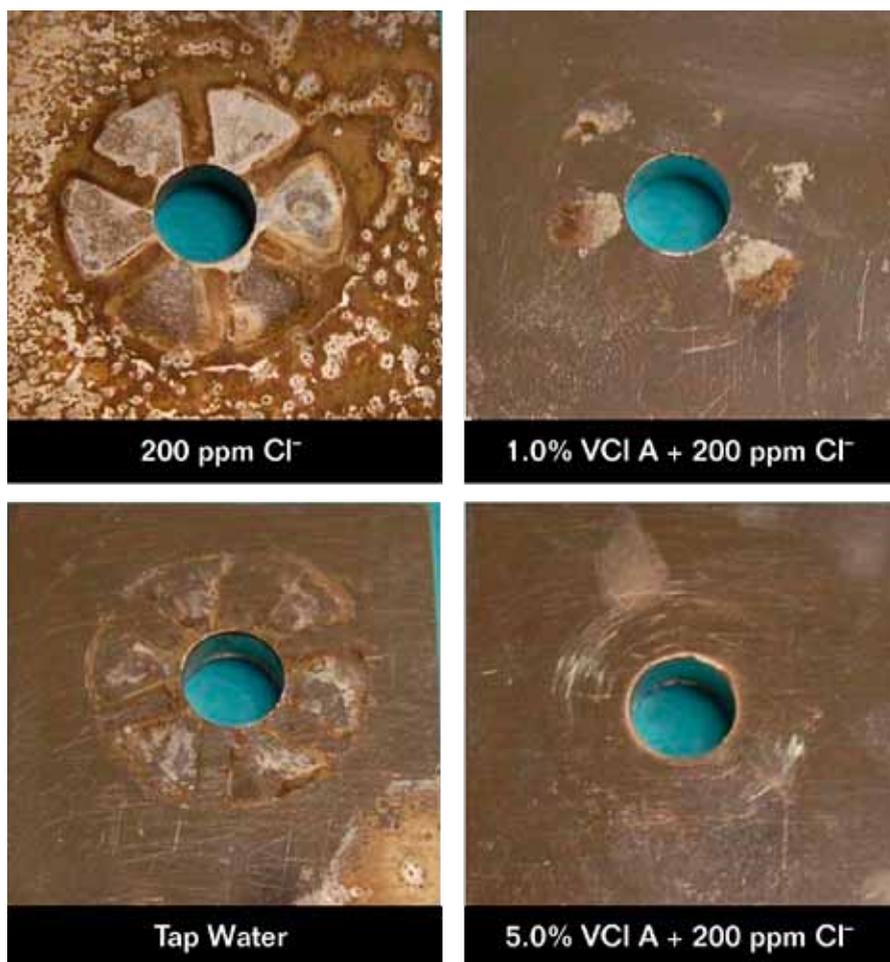
Effects of VCI A on the resistance polarization of ASTM A470 in different solutions.

FIGURE 7



EIS Bode plots of 7050-T74 alloy in various concentrations of inhibitor VCI A.

FIGURE 8



Crevice corrosion tests on 7050-T74 alloy in alternate immersion for 200 h.

ammeter and DC105[†] corrosion test software. These alloys were tested in a solution of 1.0% and 5.0% inhibitor with 200 ppm Cl⁻. A series of cyclic polarization tests was performed to investigate the effect of temperature on the VCI/metal behavior. For the cyclic polarization tests, samples were polished with 600 grit sandpaper, placed in a flat cell, and tested in different inhibitor concentrations of deionized water and 200 ppm Cl⁻ solutions.

The potentiostat with electrochemical impedance spectroscopy (EIS) software (EIS300[†]) was used to further investigate the inhibitor effectiveness on these alloys and gather data for adsorption isotherms in different inhibitor concentrations of deionized water plus 200 ppm Cl⁻. Electrochemical impedance was measured by applying a sinusoidal signal to an electrochemical cell and measuring the current. The Rp value (determined from the Bode plot) was used to fit the data into adsorption isotherm models.

Crevice Corrosion Investigation

Both the A470 and 7050 alloys were tested in an eight-station alternate immersion system. The samples were immersed in various concentrations of corrosion inhibitor, sodium chloride (NaCl), and tap water. Alternate immersion, an aggressive procedure, was performed to evaluate the inhibitors' ability to resist crevice corrosion. The testing cycle immersed the samples for 10 min, then exposed them to air for 50 min per ASTM G44⁶ and G47.⁷ After 200 cycles of testing, the samples were disassembled, examined, and photographed to document crevice corrosion resistance.

SCC Investigation

The slow strain rate tests were conducted on cylindrical samples under controlled electrochemical conditions using a strain rate of $5 \times 10^{-7} \text{ sec}^{-1}$. To evaluate an inhibitor's effectiveness, these alloys were tested in a 1.0 and 5.0% VCI solution (a typical concentration

[†]Trade name.

recommended to retard corrosion attack) and the reference samples were tested in tap water and +200 ppm Cl⁻ solutions without inhibitor. To determine the degree of inhibitor effectiveness, anodic potentials of -400 mV vs. saturated calomel electrode (SCE) (for the 7050 alloy) and -200 mV vs. SCE were applied to the samples during the test. These potentials are close to the passive film breakdown potentials for these alloys, and are the most critical range of potential to initiate localized corrosion. Twenty-four tests per alloy were completed to assess the degree of SCC susceptibility of each alloy in different solutions.

Results

Cyclic Polarization Behavior

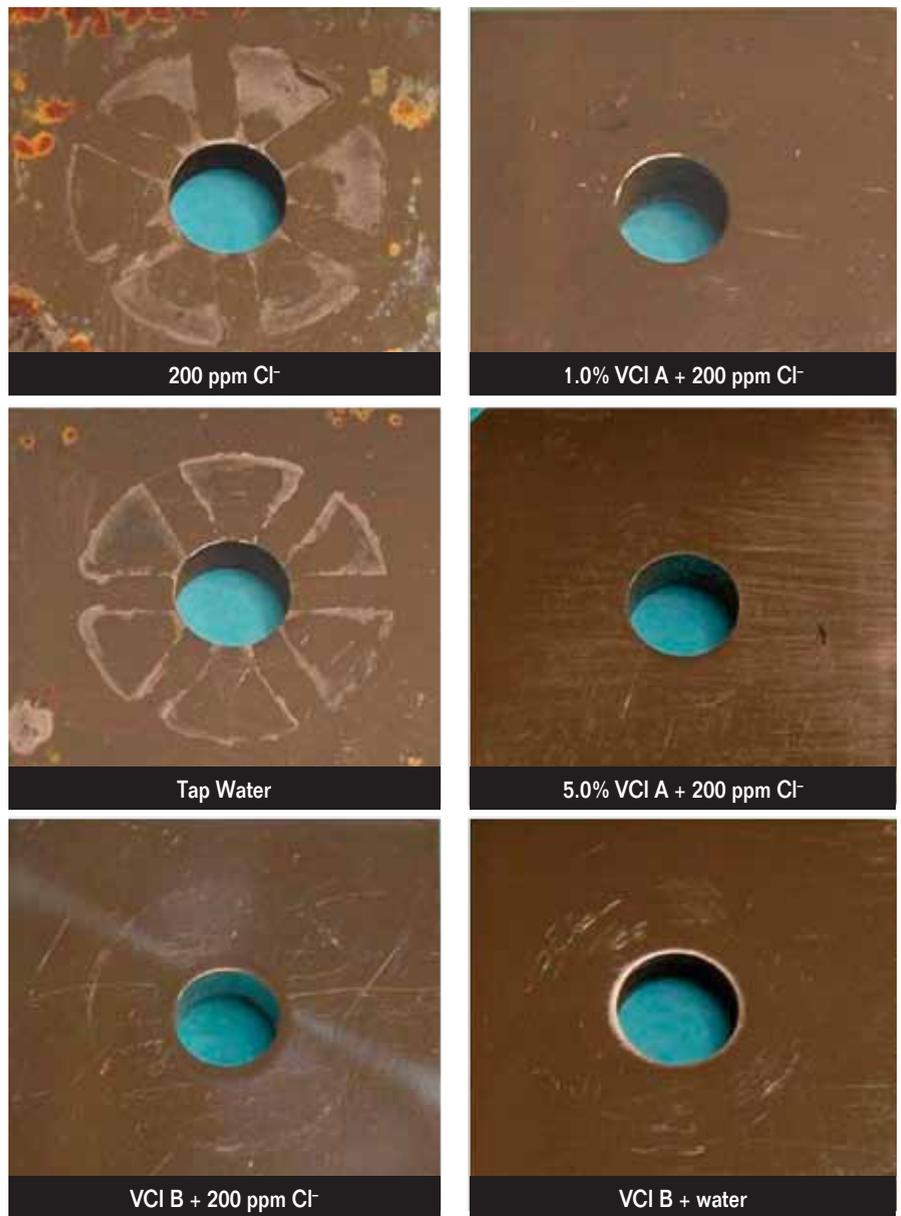
Figures 3 to 6 and Tables 1 to 3 show the polarization behavior of both alloys in different solutions. Most noticeable changes are the positive shift in the breakdown potentials by more than +500 mV for alloys in the VCI A inhibitor solutions. The inhibitor altered the electrochemistry, increased the passivation rate significantly, and had beneficial consequences for reducing localized corrosion. As demonstrated in the 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.

Figure 7 shows EIS test results of the 7050 alloy in different solutions and inhibitor concentrations. VCI B increased the resistance polarization. The increased polarization resistance can be attributed to the film formation on the metal surfaces and neutralizing of corrosive species. However, it appears that VCI A is more protective on A470 steel. Similar inhibition effectiveness was observed for VCI B.

Crevice Corrosion

Figures 8 and 9 show photos of 7050-T74 aluminum alloy and A470 samples, respectively, after 200 h of alternate immersion in various solutions. The samples immersed in tap water and +200 ppm Cl⁻ show severe corrosion damage. The corrosion damage was reduced with the addition of inhibitor to the environments

FIGURE 9



Crevice corrosion tests on A470 in alternate immersion for 200 h.

TABLE 1

CYCLIC POLARIZATION (ASTM G61) AND EIS (ASTM G106⁸) CORROSION TESTS ON ASTM A470 (3.5 NI-1CR-1MO-0.25V) AND 7050 AL-ALLOYS IN DIFFERENT SOLUTIONS OF VCI A AND VCI B.

Environment	Inhibitor Concentration, %	# of Tests Each Alloy
Water	0.0	4
Water + ppm Cl ⁻	0.0	4
Water	1.0	4
Water + 200 ppm Cl ⁻	1.0	4
Water	5.0	4
Water + 200 ppm Cl ⁻	5.0	4

TABLE 2

CREVICE CORROSION TESTS ON ASTM A470 (3.5Ni-1Cr-1Mo-0.25V) AND 7050 Al-ALLOYS USING ARTIFICIAL CREVICE SAMPLES IN DIFFERENT SOLUTIONS, ALTERNATE IMMERSION TEST ASTM G48⁹ AND ASTM G44

Environment	VCI A Concentration, %	# of Tests Each Alloy
Water	0.0	2
Water + ppm Cl ⁻	0.0	2
Water	1.0	2
Water + 200 ppm Cl ⁻	1.0	2
Water	5.0	2
Water + 200 ppm Cl ⁻	5.0	2

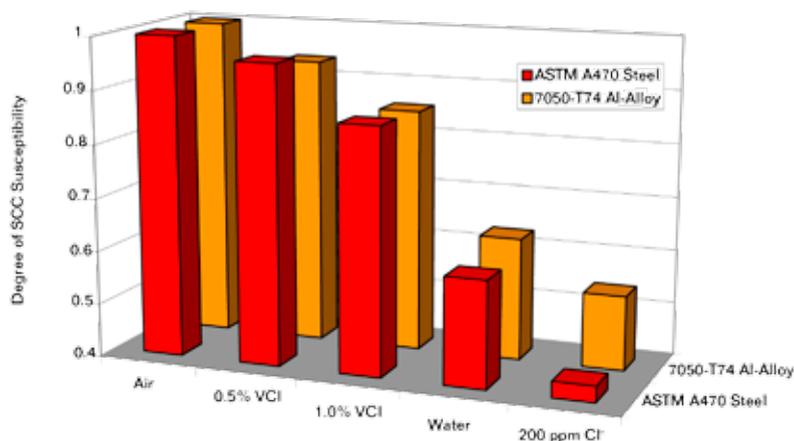
TABLE 3

CREVICE CORROSION TESTS ON ASTM A470 (3.5Ni-1Cr-1Mo-0.25V) AND 7050 Al-ALLOYS USING ARTIFICIAL CREVICE SAMPLES IN DIFFERENT SOLUTIONS, ALTERNATE IMMERSION TEST ASTM G48 AND ASTM G44

Environment	VCI A Concentration, %	# of Tests Each Alloy
Water	0.0	2
Water + ppm Cl ⁻	0.0	2
Water	coated	2
Water + 200 ppm Cl ⁻	coated	2

FIGURE 10

Slow Strain Rate Tests on 7050-T74 Al-Alloy ($-400\text{ mV}_{\text{SCE}}$) and ASTM A470 ($-200\text{ mV}_{\text{SCE}}$), ASTM G128, in Different Solutions at 5×10^{-7}



Comparison of SCC susceptibility of ASTM A470 and 7050 in different solutions.

(solutions). The passive film stability improved the corrosion resistance for the inhibitor-treated samples. Coated samples with VCI B did not show any corrosion attacks. Due to the hydrophobic nature of this inhibitor, aggressive species could wet the surface and still have corrosion protection.

Stress Corrosion Cracking

Susceptibility to SCC was determined for these two alloys using the slow strain rate test per ASTM G128.¹⁰ At applied potentials close to the passive film breakdown potential, a noticeable increase in susceptibility was seen for the samples tested without inhibitor. The greatest reduction in the degree of susceptibility is seen around -200 mV vs. SCE for the A470 steel and around -400 mV vs. SCE for the 7050-T74 alloy. Figure 10 shows a comparison of the SCC susceptibility of the A470 steel and 7050 alloy in different solutions.

Verification of the Inhibition Mechanism

The corrosion inhibition mechanism of VCI A was investigated using the data acquired from the EIS tests. EIS, when modeled correctly, is a powerful tool for the analysis of complex electrochemical systems. A modified Randles model was used to obtain the polarization resistance (R_p) values. The Bode plots showed that VCI increases the polarization resistance of both alloys, with higher concentrations resulting in higher R_p values. The increased polarization resistance can be attributed to the adsorption of inhibitor molecules on the metal surfaces. The addition of inhibitor increased the R_p value from $2.8\text{ k}\Omega$ for A470 in the blank solution (0 ppm concentration) to $220\text{ k}\Omega$ for 1.0% VCI, and $766\text{ k}\Omega$ for 5.0% VCI in solution. 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 EIS experiment best fit the Lang-

muir adsorption isotherm, where $\ln(\theta)$ (concentration) vs. $[\ln \theta - \ln(1 - \theta)]$ resulted in good linearity.

The analysis on VCI A showed the enthalpy of adsorption to be about -14 to -18 kJ/mol; this suggests that this product is borderline between a strong physisorption and a weak chemical adsorption to the metal surface. Generally, chemisorption makes strong bonding between the inhibitor and the surface of the substrate, resulting in a more stable protective film. But, the majority of corrosion damage to turbo-machinery systems occurs during shutdown periods due to chemistry changes and stagnant conditions in localized areas; therefore, a strong physisorption corrosion inhibitor will provide satisfactory protection.

Conclusions

A comprehensive investigation was undertaken to characterize the corrosion behavior of turbo-machinery systems in VCIs. Effectiveness of the inhibitor was confirmed with electrochemical impedance spectroscopy and cyclic polarization in room temperature and elevated temperature studies. As well, identification of the adsorption mechanism and corrosion activation energy was explored. The data acquired from EIS tests showed that inhibitor adsorption to these alloy surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is about -14 to -18 kJ/mol, suggesting that this product is a strong physisorption or at least a relatively weak chemisorption compound.

Cyclic polarization behavior for samples in the VCI showed a shift in the passive film breakdown potential by roughly $+500$ mV. This increase in the passive film range will improve localized corrosion resistance. Crevice corrosion test results showed improved corrosion inhibition behavior compared to unprotected samples. The SCC studies revealed significant reduction in SCC susceptibility in environments with added VCI. Furthermore, ductile overload

failure mode was observed for the alloys tested in 5% VCI A and VCI B inhibitor solution. In summary, both VCI A and VCI B provide effective corrosion protection for both A470 and 7050 alloys during the shutdown period for blades and discs in low-pressure steam turbines.

Acknowledgements

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CASE STUDY

In June 2009, a series of soil samples taken under a residential building in Montreal, Quebec, Canada, revealed the existence of petroleum hydrocarbon concentrations exceeding the applicable provincial environmental criteria.

The results indicated petroleum hydrocarbon concentrations in the center of the contaminated area—the “hotspot”—were 1,200 mg/kg.

Since the contamination was under the concrete slab of an underground parking garage, close to the footing of the exterior wall of the building, and the excavation of the soil posed significant technical difficulties, it was decided to use in situ remediation as a means to rehabilitate the site.

Enutech, Inc. (Saint-Laurent, Quebec, Canada), an environmental company that specializes in in situ remediation of contaminated sites, was selected to rehabilitate the site.

Treatment

The project consisted of installing seven injection wells in and around the contaminated area and injecting a solution of biosurfactants and the appropriate type of bacteria in the affected soil (Figure 1).

The biosurfactant that was used, called Stimulus[†], is a liquid plant extract produced by Bionetix International. The biosurfactant has the ability to desorb and emulsify the petroleum hydrocarbon adsorbed onto soil particles, making it vulnerable to bacterial biodegradation. The bacterial culture, called BCP35S[†], was injected at the same time as the biosurfactant. The culture contains different naturally occurring bacteria that are well adapted to petroleum hydrocarbon contaminated environments and are used to treat such contaminants.

After two series of injections in the contaminated soil using a solution of the

Bioremediation of Petroleum Hydrocarbon-Contaminated Soil under a Residential Building

BIONETIX INTERNATIONAL, *Sainte-Anne-de-Bellevue, Quebec, Canada*

The soil beneath a residential parking area had become contaminated with petroleum hydrocarbons. The remediation program involved the injection of a solution comprising a biosurfactant, bacterial culture, and other additives. After two series of injections of the solution over a 10-month period, results indicated that petroleum hydrocarbon concentrations were virtually undetectable.

[†]Trade name.

biosurfactant, bacterial culture, and other additives, samples were taken from the hotspot and analyzed in a certified laboratory.

The results showed that petroleum hydrocarbon concentrations in the soil were undetectable (<100 mg/kg) where concentrations were 1,200 mg/kg approximately 10 months before (Figure 2). Since petroleum hydrocarbons were undetectable in the once-contaminated soil, the biodegradation of the sum total of those hydrocarbons most likely occurred in fewer than 10 months.

However, because biodegradation of 1,200 mg/kg of petroleum hydrocarbons occurred within 10 months, it can be extrapolated that the environmental goal (700 mg/kg in this case) was achieved in approximately four or five months, assuming the degradation rate was constant.

Conclusions

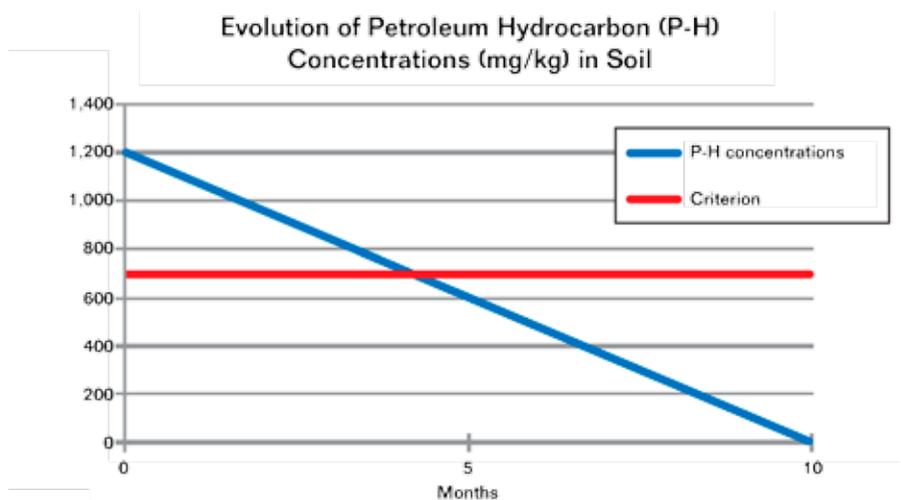
Overall, the results show that sites contaminated with petroleum hydrocarbons can be rehabilitated with the in situ remediation method used in this case, achieved with repeated injections of a solution of biosurfactants and specialized bacterial cultures. In situ remediation using this method proves to be a practical and economical way of achieving compliance with environmental criteria. *MP*

FIGURE 1



Injection of a remedial solution to decontaminate the soil.

FIGURE 2



Remediation of petroleum hydrocarbon concentrations in the hotspot.



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