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CORROSION PREVENTION AND CONTROL WORLDWIDE

Restoration of Reinforced Concrete Structures Using Migrating Corrosion Inhibitors

Corrosion Inhibitor Solutions for Cased Pipeline Crossings

Protective Systems Derived from Agricultural Byproducts

NACE
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About the Cover

Tim Suess of American Engineering and Testing uses ground-penetrating radar technology to locate steel rebar in the concrete deck of the Randolph Avenue Bridge located in St. Paul, Minnesota. Built in 1963, the bridge experienced severe cracking and spalling caused by chloride-induced corrosion of the reinforcing steel. The article beginning on p. 8 describes the use of migrating corrosion inhibitors to restore and repair the bridge, as well as how the technology worked for the rehabilitation of a parking garage located in Dayton, Ohio.

Innovative Technologies for Protecting People, Assets, and the Environment

Vapor phase corrosion inhibitors (VCIs) and migrating corrosion inhibitors (MCIs) have been used for many years to protect structures, equipment, and the environment from the adverse effects of corrosion. These proven technologies offer a variety of benefits, including easy, economical application and earth-friendly qualities.

This special supplement to *Materials Performance* magazine describes a variety of projects where VCIs and MCIs have been effectively used, including applications for protecting cased pipeline crossings and steel-reinforced concrete structures. In addition, one article describes a nonhazardous corrosion inhibitor derived from agricultural byproducts and how it is being used to prevent corrosion on steel in such highly corrosive environments as acids and saltwater.

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Corrosion Inhibitor Solutions for Proactive Control of Corrosion Inside Cased Pipeline Crossings

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

Pipeline integrity management programs are being expanded to include assessment and control of carrier pipe corrosion within cased pipeline crossings. 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 annular space of cased pipeline sections.

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

External corrosion on the carrier pipe can occur due to a variety of factors:

- If condensation accumulates at coating holidays on the carrier pipe coating, a high concentration of diffused oxygen can lead to an accelerated rate of corrosion.
- General atmospheric corrosion can occur at coating holidays on the carrier pipe.
- Accelerated corrosion can happen at coating holidays in direct contact with an electrolyte such as water or other debris.
- Localized corrosion can develop because of concentration cells or the presence of bacteria.
- For casings located near a compressor station, elevated temperature may accelerate any existing corrosion problem. Elevated temperatures may also cause coating damage and expose the carrier pipe surface.

An example of a significant pipeline safety incident attributed to carrier pipe corrosion inside a cased crossing is described in a National Transportation Safety Board (NTSB) report issued on February 18, 1987.[2] It was reported that the incident occurred on April 27, 1985 in Beaumont, Kentucky, when a natural gas pipeline leaked under a state highway. The escaping gas ignited and burned an area about 700 ft (213 m) long and 500 ft (152 m) wide. Five persons in one house were killed and three others burned as they ran from their mobile home. There was extensive damage to buildings, construction equipment, and other property.

The corrosion was attributed to several factors. The NTSB report stated the probable cause of the accident to be "… unsuspected and undetected atmospheric corrosion." Atmospheric corrosion occurs on a pipeline where moisture from the air, along with contaminates, comes into contact with exposed metal.

This casing was located about two miles (3.2 km) downstream of a compressor station with the line temperatures in the range of 140 to 160 °F (60 to 71 °C). With high heat, the coating was badly damaged. With the presence of vents and the consis-

FIGURE 1

VCI molecular layer on both steel surfaces

Casing

Inhibits corrosion in vapor, liquid, and air/water interface phases
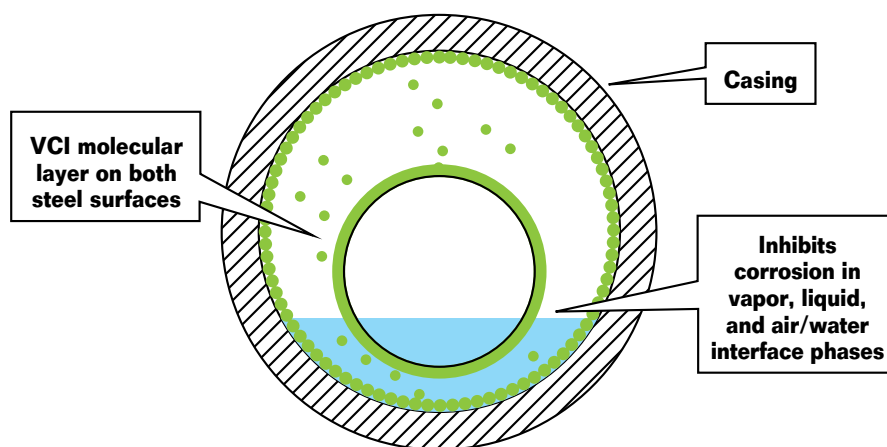
Multiphase corrosion control within casing annular space.

FIGURE 2

Custom ER probe for casings.

tently higher line temperatures than the local temperature, cyclic water condensation occurred on the carrier pipe, which provided the electrolyte necessary for the atmospheric corrosion.

Annular Space Corrosion Mitigation Solutions

As pipeline integrity assessment programs and processes generate improved information on external corrosion of carrier pipe inside casings, new external corrosion threats are being discovered within those environments. Options for mitigation of the external corrosion on the annular space metals of a cased crossing include the following:

1. Apply vapor phase corrosion inhibitor (VCI) products inside the annular space and monitor effectiveness with electrical resistance corrosion rate probes.
2. Fill the casing annular space with a newly developed gel that contains a significant dosage of multiphase corrosion inhibitor chemistry.
3. Fill the annular space with cold petroleum blend filler or a hot-applied petrolatum wax.

This article addresses only the first and second options, utilizing corrosion inhibitors for proactive corrosion mitigation.

VCI Basics

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

It is important to utilize VCIs that provide corrosion control in all three potential phases that may exist inside a cased crossing (Figure 1):

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

An effective VCI product forms a protective mono-molecular layer on the metal's surface throughout all three phases described above. This molecular layer inhibits the electrochemical reaction on the metal surface. Mitigation of corrosion with VCI chemistry is mature and well proven. VCI products have been in existence for more than 30 years and there are multitudes of successful applications within numerous environments similar to the annular space of a pipeline casing.

An early documented example of VCI application for cased crossings was written by Klechka.[3] Among other VCI projects, this article describes the successful application of VCIs to mitigate corrosion inside numerous cased sections along the Trans-Alaska Pipeline.

Evaluating the Corrosiveness of the Annular Space Environment

Measuring the corrosiveness of the environment inside cased crossings in real time is a valuable integrity management program component. Mature and reliable technology is available to assess the corrosiveness of the annular space in real time. This is accomplished through the use of custom-designed electrical resistance (ER) corrosion rate probes. Figure 2 shows an example of such a probe. The probe is designed to be lowered down to the carrier pipe surface and has a shield that prevents contact of the probe sensing element with the carrier pipe

ER probes are commonly used on a daily basis to understand the corrosiveness of many types of environments inside a variety of structures. ER probes can be installed as part of a casing integrity program before inhibitor is applied to identify casings with corrosive environments. They are also very useful after a VCI is applied to evaluate the inhibitor effectiveness over the long term.

Casing vent pipes normally located on each end of a cased crossing provide the only readily available access for installation of ER probes into the annular space (Figure 3). From a corrosion evaluation perspective, and per industry studies, the casing ends are found to normally experience the most ag-

gressive corrosion. This is due to potential infiltration of water and soil debris through the casing ends plus the introduction of fresh air through the vents. Therefore, if the corrosion rate is acceptable near the ends, there's a reasonable chance the rate will be acceptable throughout the rest of the casing.

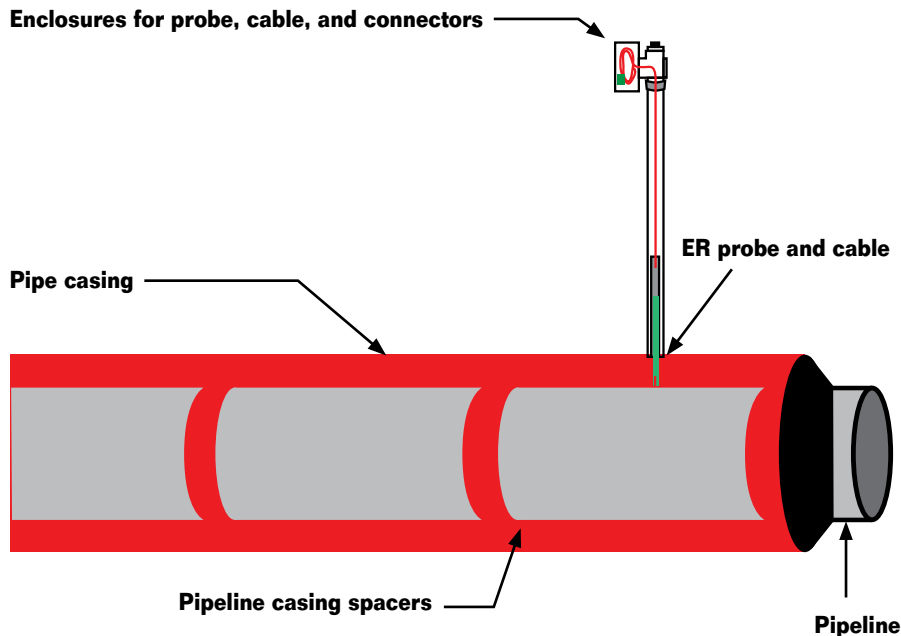### Using a VCI System Inside Casing Annular Space

If the casing system is well sealed and the operator determines that the casing does not need to be filled in order to prevent future migration of water and other debris into the annular space, a liquid VCI product can be used to mitigate annular space corrosion. This is accomplished by inserting a special tool down one or both vent pipes and spraying atomized liquid VCI into the annular space (Figure 4). Many factors are considered and engineered into this approach to be sure that sufficient quantities of the inhibitor are effectively applied. If the correct multiphase VCI products are utilized, the inhibitor molecules will mix with, and migrate through, any water, soil debris, and vapor space that might exist inside the casing. Therefore, corrosion control is produced on all annular space metal surfaces. These products are environmentally friendly—their release into the environment around the casing is not a hazard.

The VCI system should include insertion of ER probes into the casing vents at each end in order for the operator to monitor the annular space environment for a future change in the corrosion rate. The system should also include modifications to the casing vents to prevent infiltration of fresh air into the annular space. Caps and special two-way check valves are used to control the air infiltration while allowing the casing to breathe if needed.

Filling the Casing Annular Space with a VCI Filler Gel

This option was developed for the pipeline operator who determines the annular space should be filled with a product that mitigates annular space corrosion, while also preventing future infiltration of water and air into the casing. In 2011, chemists and other experts in corrosion

FIGURE 3

Enclosures for probe, cable, and connectors

ER probe and cable

Pipe casing

Pipeline casing spacers

Pipeline

Typical ER probe installation.

FIGURE 4

Injection pump

VCI liquid

If needed, repeat VCI spray process through second vent

Atomized liquid VCI sprayed into casing

Sealed at both ends

Casing spacer

Pipeline casing
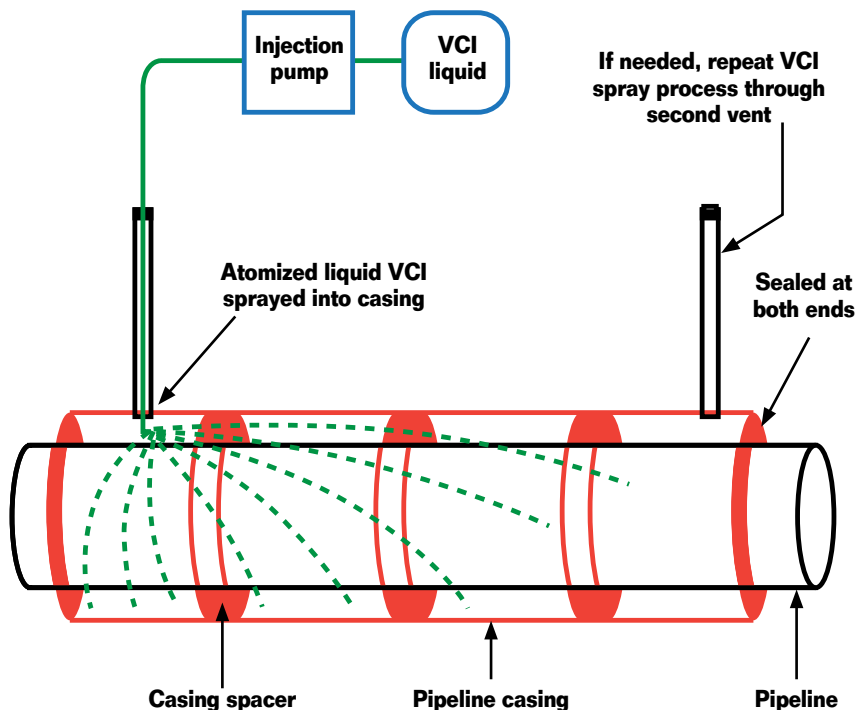
Pipeline

Application of atomized VCI into the annular space.

control within the author's company developed the CorroLogic[†] VpCI[†] Filler for Pipeline Casings (patent pending). Development was at the request of a North American pipeline corrosion engineering group. This new product is designed to totally fill the annular space of cased pipe-

line crossings with a water viscosity product that transforms into a gel within a short period of time. This product is engineered to proactively control corrosion on the carrier pipe surface while also preventing the intrusion of fresh air and water inside the casing. Initial applications of this innovation were completed in late 2011. Many more are scheduled for 2012.

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[†]Trade name.

FIGURE 5
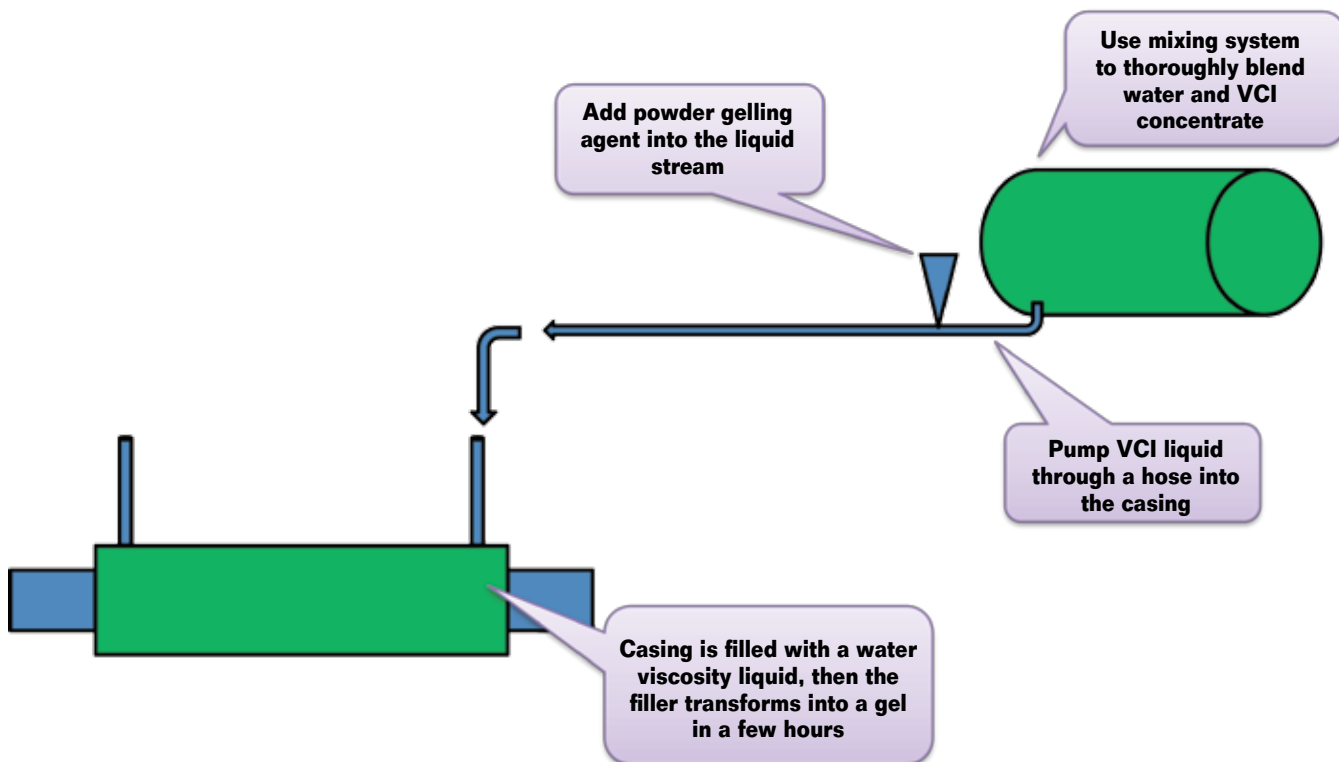
Filler gel installation schematic.

This product is produced in two parts. Part A is a high dosage of a specially designed liquid VCI concentrate that is mixed with water in the field. Part B is a superabsorbent polymer powder. These are nonhazardous, environmentally friendly products.

Installation is accomplished by pumping the liquid mixture into the annular space of a cased pipeline crossing (Figure 5). The superabsorbent powder is added into the liquid discharge stream as it flows to the casing. The powder absorbs the liquid over a short time period and converts it into a gel after it is delivered inside the casing. The gel bathes the carrier pipe with a corrosion inhibitor that has been proven to provide effective multiphase inhibition of corrosion for many years. It is applied at ambient temperature. An incomplete fill of the casing due to air pockets, etc. is not a concern because the inhibitor has a vapor phase component that will also provide corrosion control on the carrier pipe surface within any void space. Again, the system should also

include modifications to the casing vents to prevent infiltration of fresh air.

Mitigation of annular space corrosion is accomplished through multiple processes:

- The filler is electrically conductive and allows migration of cathodic protection current to the carrier pipe surface.
- It contains a high dosage of proven corrosion inhibitors for long-term corrosion control at coating holidays and on the interior surface of the casing.
- The inhibitor migrates on a molecular level to mitigate corrosion under disbonded carrier pipe coating.
- The filler prevents the migration of oxygen and fresh water to the pipeline.

Conclusions

Pipeline operators are increasingly adding components to their integrity management programs that address mitigation of carrier pipe corrosion inside

cased crossings. VCIs and VCI products provide an effective and economical way to evaluate, monitor, and mitigate corrosion inside casings. The environment inside a casing system is ideal for application of multiphase corrosion inhibitors.

References

1 Southwest Research Institute, "Statistical Analysis of External Corrosion Anomaly Data of Cased Pipe Segments," INGAA Foundation, Report No. F-2007-10, December 2007.

2 National Transportation Safety Board, "Pipeline Accident Report," Report No. NTSB PB87-916501, April 1987.

3 Ernest W. Kletchka, "Use of Corrosion Inhibitors on the Alaska Pipeline," Cortec Supplement to *MP* 40, 1 (2001).

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Evaluation of Migrating Corrosion Inhibitors Used in the Restoration and Repair of Reinforced Concrete Structures

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Corrosion inhibitors used in reinforced concrete structures can greatly increase service life and reduce long-term maintenance costs. In this work, migrating corrosion inhibitors were utilized in the repairs of two concrete structures that were deteriorating due to corrosion of embedded reinforcement. These two projects show that migrating inhibitors have a direct and significant impact on the reduction of corrosion.

The two projects covered in this article are the Randolph Avenue Bridge in St. Paul, Minnesota, and the Apple Street Parking Garage in Dayton, Ohio. The bridge was built in 1963 and chloride-induced corrosion of the reinforcing steel eventually caused major spalling and cracking of the concrete decks. In 1986 the top deck was repaired with a concrete overlay that incorporated a migrating corrosion inhibitor in one side, while the other was left untreated as the control. The garage is of pre-topped precast double tee construction. The lower two levels were built in 1986 and upper levels in 1989. In the early 2000s, the double tees exhibited advanced corrosion. Repairs were completed in 2006 using a ready-mixed concrete containing a migrating corrosion inhibitor.

Experimental Procedures

Randolph Avenue Bridge

Background

Constructed in 1963, the Randolph Avenue Bridge spans Interstate 35E in Saint Paul, Minnesota (Figure 1). Due to chloride-induced corrosion, embedded reinforcement deteriorated to the point of causing major cracking and spalling on the concrete bridge decks. In 1986, the top deck of the bridge was repaired in a project sponsored by the Minnesota Department of Transportation (DOT). Both sides of the deck were repaired using a low-slump, dense concrete overlay that incorporated a migrating corrosion inhibiting admixture in one side while the other was left untreated as the control. The treated westbound lanes have served as a real-world comparison of corrosion current reduction vs. the untreated "control" eastbound lanes (Figure 2).

The rehabilitation of this bridge was part of a Federal Highway Administration (FHWA) project from 1986 to 1990 and a Virginia Tech study in 1991 and 1992. Updated readings were performed by the Minnesota DOT in 2003 and by Cortec Corp. in 2000, 2007, and 2011.

TABLE 1

MIX DESIGN PARAMETERS OF THE RANDOLPH AVENUE BRIDGE REPAIR

Component	Control (lb/yd³)	Treated (lb/yd³)
Type I cement	836	836
Water	270	270
w/c ratio	0.32	0.32
Coarse aggregate	1,385	1,385
Fine aggregate	1,374	1,374
Water-reducing admixture	0.25	0.25
Air-entraining agent	0.073	0.073
Corrosion inhibitor	—	0.95

The rehabilitation process included the application of a low-slump dense concrete that varied in depth from 2.3 to 4.2 in (58.4 to 106.7 mm). Table 1 shows the mix design of the overlay. An amino alcohol-based migrating corrosion inhibiting admixture was added to the concrete overlay at 1 pint/yd³ (0.62 L/m³) for the two westbound traffic lanes. The eastbound lanes were repaired with the same type of concrete, which did not contain the corrosion inhibitor to act as the control. Prior to application of the overlay, the deck was milled to a depth of 0.5 in (13 mm) and the areas of unsound concrete were removed. The cavities from the removal of the unsound concrete were filled with the overlay concrete. The general slope of the bridge for water runoff appears to be toward the northeast.

Corrosion assessments were conducted on the eastbound (control) and westbound (amino alcohol) travel lanes of the structure by Virginia Tech researchers on two occasions that took place in June 1991 and August 1992. The assessments included visual inspection, delamination survey, cover-depth survey, chloride contents as a function of depth, corrosion potentials, and estimates of corrosion current densities (i_{corr}), using a 3LP† Meter (Linear Polarization Device 1). Prior to the assessments completed by Virginia Tech, the repair was part of a FHWA Project until 1990.

FIGURE 1

Constructed in the early 1960s, the Randolph Avenue Bridge in St. Paul, Minnesota, required extensive repairs from the results of chloride-induced corrosion of the reinforcing steel.

FIGURE 2

The westbound lanes of the Randolph Avenue Bridge were treated with a migrating corrosion inhibiting admixture and compared to the eastbound lanes that were refurbished with an untreated concrete overlay.

†Trade name.

TABLE 2

CORROSION INTENSITY VS. CORROSION CURRENT AND RATE OF CORROSION FOUND BY LINEAR POLARIZATION DEVICE 1

Corrosion Current ($\mu A/cm^2$)	Corrosion Rate ($\mu m/year$)	Intensity of Corrosion
<0.5	<5.8	Passive condition
0.5–2.7	5.8–31.8	Low corrosion (damage possible in 1–15 years)
2.7–27	31.3–313.2	Moderate corrosion (damage possible in 2–10 years)
>27	>313.2	HIgh corrosion (damage expected in 2 years or less)

TABLE 3

CORROSION INTENSITY VS. CORROSION CURRENT AND RATE OF CORROSION FOUND BY LINEAR POLARIZATION DEVICE 2

Corrosion Current ($\mu A/cm^2$)	Corrosion Rate ($\mu m/year$)	Intensity of Corrosion
<0.5	<1.2	Negligible corrosion
0.5–2.7	1.2–5.8	Low corrosion
2.7–27	5.8–11.6	Moderate corrosion
>27	>11.6	HIgh corrosion

TABLE 4

CORROSION INTENSITY VS. CORROSION CURRENT AND RATE OF CORROSION FOUND BY LINEAR POLARIZATION DEVICE 3

Corrosion Current ($\mu A/cm^2$)	Corrosion Rate ($\mu m/year$)	Intensity of Corrosion
<0.5	<1.2	Passive condition
0.5–5	5.8–58	Low corrosion
5–15	58–174	Moderate corrosion
>15	>174	HIgh corrosion

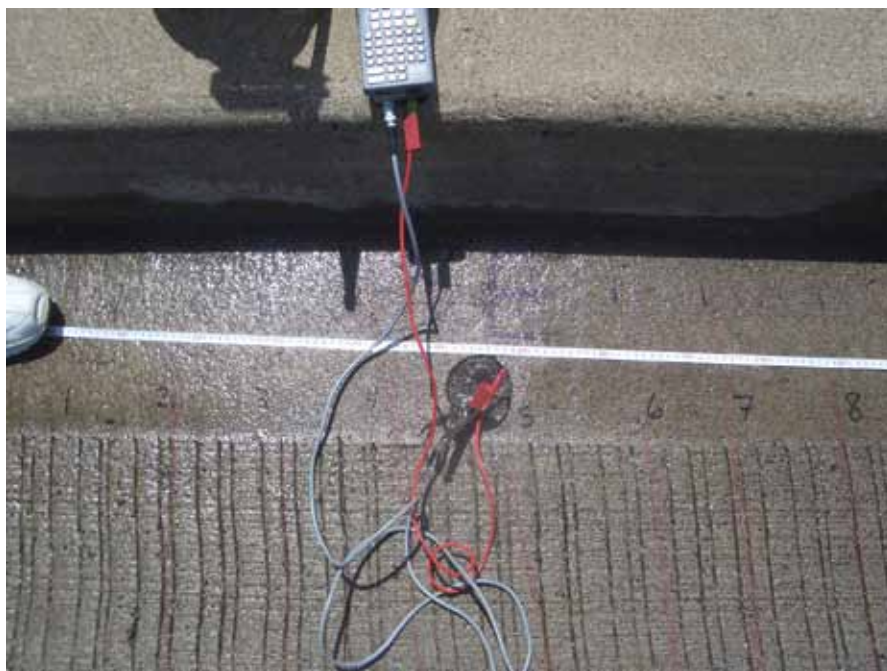In November 2000, technicians returned to the bridge and took new measurements. These included linear polarization readings obtained by a Gecor 6[†] (Linear Polarization Device 2) instrument, and copper/copper sulfate ($Cu/CuSO_4$) half-cell potentials. A new chloride analysis was also taken at various depths.

In June 2007 and July 2011, chloride analysis, alkalinity testing, and half-cell potential readings were performed. Linear polarization readings using Linear Polarization Device 2 and a Galvapulse[†] (Linear Polarization Device 3) instrument (Figure 3) were also taken to determine corrosion current, corrosion rate, and concrete resistivity.

Chloride Contamination Levels

Powdered concrete samples for chloride analysis were taken at mean depths of 0 to 1, 1 to 2, and 2 to 3 in (0 to 25, 25 to 51, and 51 to 76 mm) from six locations, three on each side of the bridge. Samples were taken using a rotary impact type drill with a 0.5-in size bit. Three-gram samples that passed through a #20 sieve were obtained from each depth. The powder was then mixed with 20 mL of digestion solution for a total of 3 min and then 80 mL of stabilizing solution was added. A calibrated electrode coupled to an Orion[†] Model 720-pH/ISE meter was then immersed in the solution, and the chloride-ion concentration was recorded. This method was consistent with the AASHTO T260[1] Procedure C. The standard deviation for this chloride test was determined by testing the six pulverized concrete quality assurance (QA) samples of

[†]Trade name.

FIGURE 3

Linear Polarization Device 3 was used to help determine corrosion current, corrosion rate, and concrete resistivity on the concrete bridge decks.

known chloride content. Each QA sample was tested five times.

Corrosion Current Measurements

Corrosion current density (i_{corr}) estimates were taken at the Randolph Avenue Bridge in June 1991 and August 1992 using Linear Polarization Device 1. Readings were also performed in November 2000, July 2007, and July 2011 using both Linear Polarization Device 2 and Linear Polarization Device 3.

The i_{corr} measurement is proportional to the corrosion rate through Faraday's Law. The instruments used measure the corrosion rate of steel in concrete by "polarization resistance" or "linear polarization" techniques. This is a nondestructive technique that works by locating the rebar (Figure 4), applying a small current to it, and measuring the change in the potential. Then the polarization resistance, R_p (the change in potential measured) is divided by the applied current. The corrosion rate, i_{corr}, is obtained from the polarization resistance, R_p, by means of the "Stearn and Geary" relationship:

$$i_{corr} = B/R_p, \text{ where } B = 26 \text{ mV} \qquad (1)$$

Each device used on the bridge has different criteria for evaluating the corrosion rates (Tables 2-4[2-4]).

Concrete Resistivity Measurements

Linear Polarization Device 2 also calculates the concrete resistivity by means of Equation (2):

$$\text{Resistivity} = 2 \times R \times D \qquad (2)$$

where R = resistance by the "IR drop" from a pulse between the sensor counter-electrode and the rebar network and D = the counter-electrode diameter of the sensor.

The value of the concrete's resistance is used as an additional parameter for the interpretation of the rate of corrosion. Table 5 shows the interpretation of the results.[3]

TABLE 5

CORRELATION OF RESISTIVITY MEASUREMENTS TO CORROSION RATE USING LINEAR POLARIZATION DEVICE 2

Resistivity	Corrosion Rate
>100–200 kΩ·cm	Very low, even with high chloride and carbonation
50–100 kΩ·cm	Low
10–50 kΩ·cm	Moderate to high where steel is active
<10 kΩ·cm	Resistivity is not the parameter controlling the corrosion rate

TABLE 6

CORROSION POTENTIAL OF HALF-CELL POTENTIAL READINGS USING A CSE

Potential	Probability of Corrosion
>–200 mV	Less than 10%
–200 mV to –350 mV	Indeterminate corrosion risk
<–350 mV	Greater than 90%

FIGURE 4

Ground-penetrating radar was used to locate reinforcing steel in the bridge.

Half-Cell Potentials

ASTM C876[5] corrosion half-cell potentials were measured for both the eastbound and westbound travel lanes with a Cu/CuSO$_4$ electrode (CSE) in June 1991, August 1992, November 2000, June 2007, and July 2011 and with Linear Polarization Device 2 in November 2000, June 2007, and July 2011. According to ASTM C876, the results can be interpreted in Table 6.[6]

Carbonation

Carbonation of concrete is a process by which carbon dioxide (CO_2) from the air penetrates the concrete and reacts with the hydroxides, such as calcium hydroxide [$Ca(OH)_2$], to form carbonates. This process increases shrinkage on drying (promoting crack development) and reduces the alkalinity of the concrete. High alkalinity is needed to protect embedded rebar from

TABLE 7

AVERAGE CHLORIDE LEVELS OF RANDOLPH AVENUE BRIDGE

Year	Treated Side (lb/yd³)			Control Side (lb/yd³)		
	0–1 in	1–2 in	2–3 in	0–1 in	1–2 in	2–3 in
1991	3.5	0	0.7	7.7	2.5	1.9
1992	6.5	1.1	1.9	9.5	3.5	2.5
2000	11.7	1.6	1.3	17.2	6.2	2.4
2007	11.7	1	2.6	20	7.4	2.3
2011	12.3	4.9	1.8	14.7	6.6	3.5

TABLE 8

AVERAGE CHLORIDE LEVELS OF RANDOLPH AVENUE BRIDGE

Year	Treated Lanes			Control Lanes		
	Northwest (µA/cm²)	North Central (µA/cm²)	Northeast (µA/cm²)	Southwest (µA/cm²)	South Central (µA/cm²)	Southeast (µA/cm²)
2000	0.0081	0.0006	0.0077	0.093	0.175	0.145
2007	0.1258	0.2522	0.4231	0.2982	0.1878	0.368
2011	0.2659	0.4202	0.3196	0.6254	1.2755	0.8607

FIGURE 5
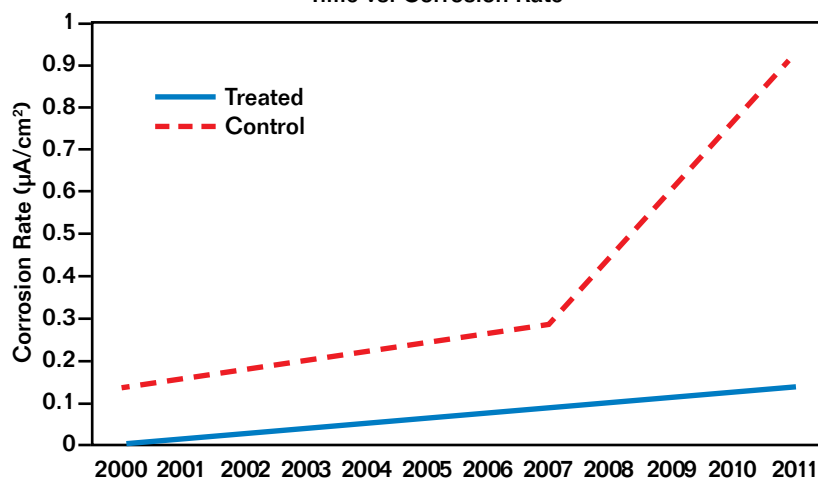
Average corrosion rates of the Randolph Avenue Bridge.

corrosion; consequently, concrete should be resistant to carbonation to prevent steel corrosion.[7] The carbonation of powdered concrete samples taken from the Randolph Avenue Bridge was determined by using phenolphthalein (alkalinity) measurements.

Apple Street Parking Garage
Background

The Apple Street Parking Garage in Dayton, Ohio is a pre-topped, precast, double tee garage. The lower two levels were constructed in 1986 and the upper levels were added in 1989. During an inspection in the early 2000s, the precast double tees were found to have advanced corrosion that led to necessary full depth repairs of the concrete. In 2006, repairs were completed using ready-mixed concrete that included a migrating corrosion inhibiting admixture. Surface treatments were also made to existing concrete outside of the patchwork using a penetrating corrosion inhibitor.

The highest rate of corrosion was measured in the center section of the control side, which was 1.2755 µA/cm² compared to the treated center section of 0.4202 µA/cm², a reduction of 67%.

The concrete reinforcement is a steel mesh that is located 1.75 to 2 in (44.5 to 50.8 mm) deep. The mesh was laid out in a 4 ft by 8 ft (1.22 m by 2.44 m) grid. In November 2006, patchwork was completed using ready-mixed concrete that incorporated an amine carboxylate-based migrating corrosion inhibiting admixture dosed at 1.5 pints/yd³ (1 L/m³).

Also in 2006, a water-based penetrating corrosion inhibitor was applied to both the deck and the underside at a coverage rate of 150 ft²/gal (3.68 m²/L). The substrate was allowed to dry for a

week and was then shot-blasted prior to application of a 40% silane water repellant to the deck surfaces.

On July 1, 2009, linear polarization readings were obtained using Linear Polarization Device 3. Ten corrosion current readings were taken at five different locations within the garage. Table 4 shows the interpretation of these readings.

Results and Discussion

Randolph Avenue Bridge

Chloride Threshold

Chloride threshold refers to the concentration of chlorides at which corrosion in the steel is initiated. Based on the service life prediction model, Life 365[†], the chloride threshold of the concrete used in the Randolph Avenue Bridge is 0.05% of the concrete.[8] This converts to 0.4% by weight of the cement and 3.35 lb/yd³ (1.98 kg/m³).

Chloride content readings were taken at 0 to 1, 1 to 2, and 2 to 3 in (0 to 25, 25 to 51, and 51 to 76 mm) from three different locations on each side of the bridge. These readings indicated that the overall chloride levels in the control side were slightly higher than in the treated side. The chloride levels have continued to rise at the level of the steel (Table 7).

Corrosion Current Readings

Corrosion currents of the rebar have increased on both sides of the bridge since the year 2000, when the treated side had very low corrosion currents, an average of 0.0081 μA/cm², approximately 42% below readings taken on the control side (average of 0.014 μA/cm²).

The corrosion current readings taken in July of 2011 are substantially higher at almost all points on the bridge. As shown in

TABLE 9

ALKALINITY RESULTS ORGANIZED BY SECTION OF THE RANDOLPH AVENUE BRIDGE

Treated			Control		
Sample (in)	Alkalinity (mg/L)	Average (mg/L)	Sample (in)	Alkalinity (mg/L)	Average (mg/L)
NW 0-1	1,680		SW 0-1	1,800	
NW 1-2	1,800	1,800	SW 1-2	1,920	1,800
NW 2-3	1,920		SW 2-3	1,680	
NC 0-1	1,800		SC 0-1	1,920	
NC 1-2	1,800	1,840	SC 1-2	1,800	1,800
NC 2-3	1,920		SC 2-3	1,680	
NE 0-1	1,920		SE 0-1	1,560	
NE 1-2	1,800	1,760	SE 1-2	1,680	1,640
NE 2-3	1,560		SE 2-3	1,680	

TABLE 10

HALF-CELL POTENTIAL VALUES FROM EACH SEGMENT OF THE RANDOLPH AVENUE BRIDGE

Rebar	Treated Side (lb/yd³)			Control Side (lb/yd³)		
	NW (mV)	NC (mV)	NE (mV)	SW (mV)	SC (mV)	SE (mV)
1	−378	−130	−130.3	−84	−332	−231
2	−331.3	−128.7	−93.3	−91.5	−397.5	−248.5
3	−294.3	−98.3	−59.7	−88.5	−381.5	−187
4	−239.7	−83.3	−68.3	−104	−400	−150
5	−227.3	−72.3	−82.7	−97.5	−392	−125.5
6	−183.7	−79	−37	−99	−400	−117.5
7	−185	−69.3	−36.7	−122	−404.5	−140
8	−170.3	−72	−46.3	−163.5	−381.5	−147
9	−156	−78	−79.3	−231	−397.5	−181
10	−172	−76.3	−167	—	—	−206.5
11	−190.7	−74.3	−192	—	—	−270.5
12	—	−97.3	−189.7	—	—	—
13	—	−96.3	−191.7	—	—	—
14	—	—	−218.7	—	—	—
Average	−229.8	−88.9	−113.8	−120.1	−387.4	−182.2

TABLE 11

CORROSION CURRENT READINGS FOR TREATED AREAS OF THE APPLE STREET PARKING GARAGE

Reading	Location 1 (µA/cm²)	Location 2 (µA/cm²)	Location 3 (µA/cm²)	Location 4 (µA/cm²)	Location 5 (µA/cm²)
1	2.97	1.75	0.51	1.62	3.12
2	1.76	1.35	0.57	0.65	0.89
3	3.01	1.08	0.47	0.81	0.36
4	1.22	1.37	0.26	1.17	0.38
5	1.59	6.76	0.32	0.96	0.25
6	3.48	1.38	0.41	0.24	0.24
7	1.55	0.96	0.60	0.26	0.52
8	2.15	8.22	0.40	0.92	0.22
9	6.43	9.71	0.45	0.62	6.63
10	5.28	3.37	0.38	1.20	2.86
Average	2.94	3.60	0.43	0.84	1.55

Table 7, the control side has reached the chloride threshold at the depth of the reinforcing steel. Table 8 indicates the average corrosion rate of the treated side is 35% of the level on the control side. The highest rate of corrosion was measured in the center section of the control side, which was 1.2755 µA/cm² compared to the treated center section of 0.4202 µA/cm², a reduction of 67%. This reduction is confirmed by the half-cell potentials, which show a high probability of corrosion in the control South Central section (Table 10).

Table 8 shows the average corrosion current data and compared segments of the bridge using Linear Polarization Device 2. In 2011, all readings taken on the treated areas of the bridge were much lower than the readings taken on the control side. Additionally, all three control locations had average corrosion rate readings that would be considered active, whereas the treated side readings were all in the passive range. This indicates the corrosion inhibiting admixture is functioning as expected.

Figure 5 shows the comparison of corrosion rate readings on the control side vs. the treated side using Linear Polarization Device 2. Prior to 2007, both sides of the bridge showed average corrosion rates in the passive range, but the treated side exhibited 40% lower readings. Now that the control side has entered active corrosion, the treated side is exhibiting corrosion rates that are approximately 85% less.

All readings taken on the treated areas of the bridge were much lower than the readings taken on the control side. Additionally, all three control locations had average corrosion rate readings that would be considered active, whereas the treated side readings were all in the passive range.

Weather can be a factor that affects readings. Of particular importance is the humidity level as the moisture in the concrete affects the conductivity and readings that are taken. To mitigate the effects of the weather, the surface was prepared using ASTM C876. This method requires a specific pattern of adding moisture to the concrete so a consistent environment is achieved across all areas.

Alkalinity Levels

The core samples from 2011 were tested and exhibited average alkalinity levels between 1,640 and 1,840 mg/L. The samples that were taken from the treated side of the bridge show results of higher alkalinity levels, which can signify the presence of corrosion inhibitor and resistance to carbonation. Table 9 shows the results from the 2011 samples.

Half-Cell Potentials

Table 10 shows the half-cell potential readings taken in 2011. The average reading for each side of the bridge shows that the potential for corrosion is higher on the control side than that of the treated side according to Table 6.

The time vs. average half-cell potential results, shown in Figure 6, shows that the potential for corrosion within the bridge is higher on the control side and has been for 20 years. These data along with the rest of the supporting information suggest that levels of corrosion in the treated side are lower than in the control.

Apple Street Parking Garage
Corrosion Rate Readings

All readings at the Apple Street Parking Garage were performed using Linear Polarization Device 3. All locations had average readings in the passive to low levels (Table 4). Fifty readings were taken

in total; 10 readings at five different locations throughout the garage. Table 11 presents all readings taken in 2009.

Conclusions

Amino alcohol and amine carboxylate-based corrosion inhibitors have proven beneficial when used in repair of concrete that has cracked and spalled due to chloride-induced corrosion of the embedded reinforcing steel. In the Randolph Avenue Bridge, corrosion was significantly decreased compared to the control due to the presence of the amino alcohol corrosion inhibiting admixture. The Apple Street Parking Garage is showing very low corrosion currents due to the high affinity of the amine carboxylate corrosion inhibiting admixture and the penetrating corrosion inhibitor. The lower corrosion currents are due to the adsorption of the amino alcohol and amine carboxylate molecules on the embedded reinforcing steel, showing that these molecules can displace existing chloride and water molecules. Thus, corrosion rates can be decreased significantly.
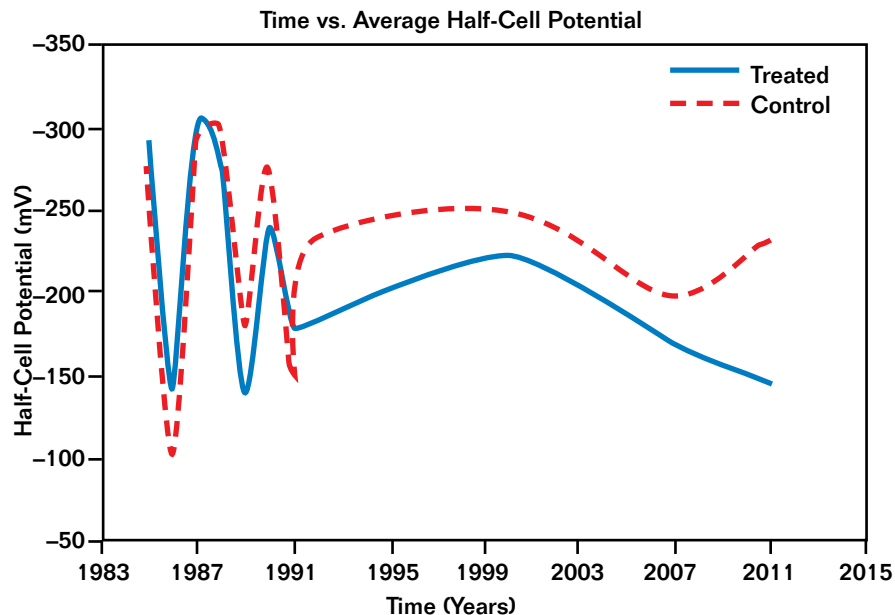
Aknowledgments

The authors thank American Engineering and Testing, Inc. for their assistance in obtaining readings on the Randolph Avenue Bridge. They would also like to thank Chris Przywara, structural engineer with THP, Ltd., and Rae Jean Nicholl of S.M.A.R.T. Distribution for their assistance with the Apple Street Parking Garage readings.

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This article is based on CORROSION 2012 paper no. C2012-0001420, presented in Salt Lake City, Utah.

FIGURE 6

Average half-cell potentials of the Randolph Avenue Bridge.

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Novel Corrosion Inhibitors Derived from Agricultural Byproducts

Margarita Kharshan, Alla Furman, Ming Shen, Robert Kean, Kristy Gillette, and Liz Austin, *Cortec Corp., St. Paul, Minnesota*

I n an effort to prepare corrosion inhibitors using renewable, nonhazardous and biodegradable materials, a number of agriculture byproducts have been evaluated for protection in vapor phase, in acidic solutions, and in salt solutions.

Molasses and raffinate (de-sugared molasses) have been reported to be multimetal corrosion inhibitors in water-based electrolytes,[1] but their vapor phase protection has not been reported. This article investigates the ability of molasses and raffinate to provide vapor phase protection. Distillation, cation exchange, ultra-filtration, and reactions with common volatile nitrogen-containing components were evaluated as means to concentrate and enhance molasses for use as a volatile corrosion inhibitor (VCI).

A variety of corn-derived byproducts from ethanol production were also studied (Figure 1). They included thin stillage, thick stillage, and distillers dried grains with solubles (DDGS). Stillage is the material left behind in still bottoms after fermentation and ethanol removal. DDGS are dried residue remaining after the starch fraction of grain is fermented. Containing proteins, fibers, and oils, DDGS represent one-third of the weight of the starting material in ethanol production.[2] Each of these corn ethanol byproducts is solid or semi-solid. Liquid extracts of these materials were prepared for inhibitor evaluation. DDGS were chosen as the main focus as they contain all the basic components in stillage.

A solvent extract of DDGS demonstrated up to 97% protection for steel in acidic environments and in salt water. A variety of plant extracts have been shown to inhibit corrosion of steel in acidic conditions,[3-9] but such activity has not previously been reported with corn extracts. Aqueous corn extracts provided corrosion protection as an inhibitor in de-icing compounds.

Agriculture byproducts were evaluated to determine their potentials as nonhazardous corrosion inhibitors. Sugar beet molasses showed vapor phase protection. A solvent extract of distillers dried grains with solubles (DDGS), a byproduct from corn ethanol, demonstrated protection for steel in acidic and salt solutions. Aqueous extracts of corn ethanol byproducts provided inhibition in de-icers. Tests, enhancements, and applications are presented.

TABLE 1

VAPOR-INHIBITING TEST RESULTS ON MOLASSES AND VARIOUS TYPES OF TREATED MOLASSES

Component	Sample	Sample	Sample
Molasses/raffinate as received	**Plug #1**	**Plug #2**	**Plug #3**
5 g sugar beet raffinate	Grade 2	Grade 3	Grade 3
5 g sugar beet molasses	Grade 1/0	Grade 3	Grade 3
5 g (Sample 1 food grade molasses)	Grade 1/0	Grade 2	Grade 2
5 g (Sample 2 food grade molasses)	Grade 2	Grade 0	Grade 0
2.5 g sugar beet raffinate	Grade 2	Grade 2	Grade 3
2.5 g sugar beet molasses	Grade 2	Grade 2	Grade 3
Control	Grade 0	—	—
Raffinate after distillation	**Plug #1**	**Plug #2**	**Plug #3**
2.5 g of distillate	Grade 3	Grade 3	Grade 3
2.5 g of pot residue	Grade 3	Grade 3	Grade 3
Raffinate treated with cation ex resin	**Plug #1**	**Plug #2**	**Plug #3**
Equivalent 0.3 g raffinate (pH 1.94 adjusted to 9.8)	Grade 2	Grade 2	Grade 2
Molasses after ultrafiltration			
MW range of fraction (equivalent to 0.5 g solids)	**Plug #1**	**Plug #2**	**Plug #3**
<1,000	Grade 0	Grade 0	Grade 0
1,000–3,000	Grade 3	Grade 2	Grade 2
3,000–10,000	Grade 0	Grade 0	Grade 0
10,000–30,000	Grade 0	Grade 0	Grade 1
>30,000	Grade 2	Grade 2	Grade 2
Control	Grade 0	—	—
Molasses after ammonium blending	**Plug #1**	**Plug #2**	**Plug #3**
1 g of sugar beet molasses with 1.5% NH$_4$OH	Grade 3	Grade 3	Grade 3
1 g of Sample 1 food grade molasses with 1.5 NH$_4$OH	Grade 3	Grade 3	Grade 3
0.25 g of aqueous NH$_4$OH	Grade 0	Grade 0	Grade 0

FIGURE 1

A variety of corn-derived byproducts were analyzed for use as corrosion inhibitors.

Experimental Procedures

Molasses as a Vapor Phase Corrosion Inhibitor

Sugar beet molasses and raffinate (feedstock grade) and sugar cane molasses (food grade) were evaluated for their VCI ability. Efforts were made to concentrate and enhance the vapor-inhibiting ability (VIA) of the sugar beet molasses. The data showed no discernable difference between molasses and raffinate in terms of their VIA capability so the terms are used interchangeably for the discussion of VCI in this article.

Distillation

Distillation was carried out on sugar beet raffinate. Typically, up to 30% of the

starting material was collected as distillate with an apparent boiling point of 100 °C. The temperature of the pot residue (70% of starting material) was about 127 °C when distillation was terminated.

Cation Exchange

Cation exchange was performed using Dowex® HCR-W2 H† cation exchange resin (J.T. Baker). The resin was first washed with de-ionized water, and added to a 50% raffinate solution. After decanting the resin, the pH of the solutions was adjusted to 9.8 with aqueous ammonia (NH³).

Ultrafiltration

Ultrafiltration was performed with a Stirred Ultrafiltration Cell Model 8400† (Millipore). Fifty percent of the diluted raffinate was subjected to sequential size fractionation using cellulose membranes with cutoffs in nominal molecular weight of 30,000, 10,000, 3,000, and 1,000.

Chemical Treatment with Ammonia

Combinations of molasses or raffinate with 5% of ammonium hydroxide (NH$_4$OH) solution were obtained.

Evaluation of Vapor-Inhibiting Ability

A VIA test evaluates a product's ability to protect metal from corrosion without being in direct contact. A sample of vapor inhibitor was placed in a capped quart jar with a freshly polished and cleaned carbon steel (CS) (SAE 1010 [UNS G10100]) plug for 20 h at ambient temperature. A relative humidity of nearly 100% was then created in the jar by the addition of 3% glycerol in water for 2 h at ambient temperature, followed by another 2 h at 40 °C. After that 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.

Chemical Identification by Solid Phase Micro Extraction

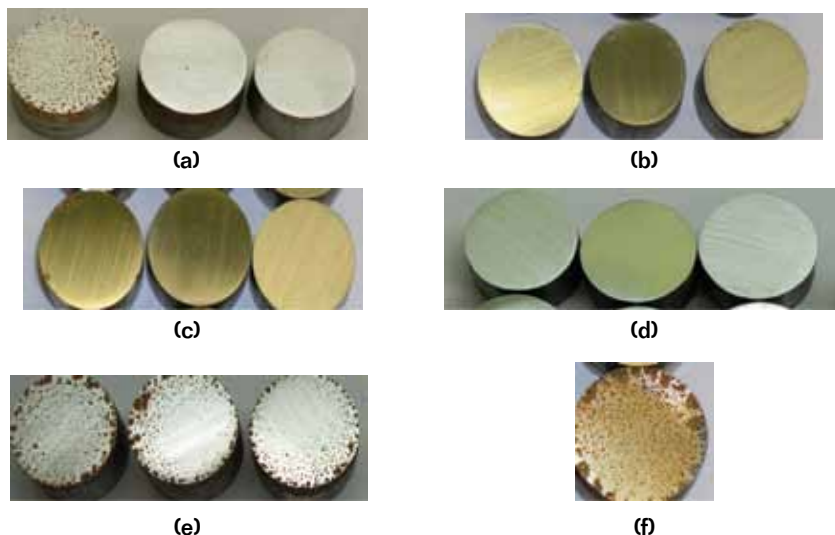A solid phase micro extraction (SPME) fiber (polydimethylsiloxane/divinylbenzene) was inserted into the headspace of a jar containing molasses for 30 min at ambient temperature, then placed into the injection port of a gas chromatography column (Hewlett Packard 6890 GC with 5975 MSD†); column DB5MS† 30 m x 0.25 mm x 1.0 μm; carrier: Helium Gas†. The injection temperature was 250 °C, the interface temperature was 290 °C, and the temperature ramp was 10 °C/3 min, 10 °C/min to 200 °C/0 min, and 40 °C/min to 280 °C/5 min.

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†Trade name.

TABLE 2

PROTECTION OF STEEL FROM ACID CORROSION BY 2% DDGS SOLVENT EXTRACT

Acid	Acid Concentration	Z (% Corrosion Protection)
Hydrochloric	10%	97%
Sulfuric	10%	95%
Phosphoric	10%	90.9%
Citric	20%	87.7%

FIGURE 2

VIA test results of 5 g of sugar beet molasses: (a) as received, (b) raffinate distillate, (c) raffinate pot residue, (d) NH$_3$-treated molasses, (e) NH$_3$ only, and (f) control.

FIGURE 3
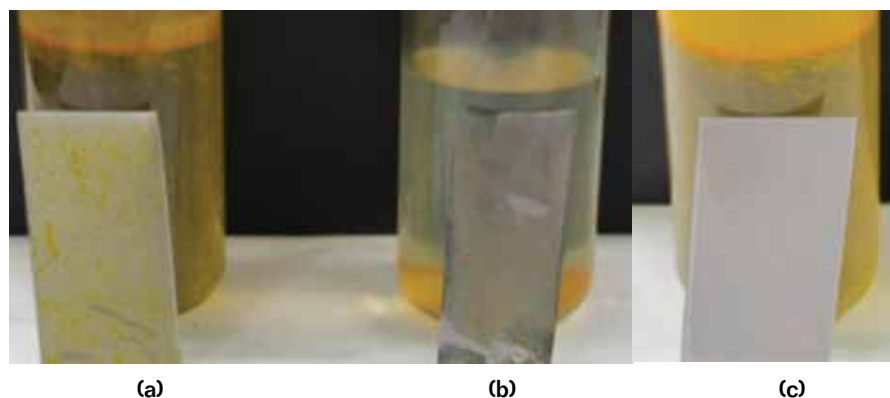
Steel coupons after removal from saltwater immersion test: (a) 0.5% DDGS extract, (b) control, and (c) cleaned coupon from (a).

TABLE 3

DE-ICER TEST RESULTS (3% FORMULA IN 3% NaCl SOLUTION)

Sample No.	Formula Composition	Pass/Fail (PNS Test)	Corrosion Rate (mpy) (PNS Test)	% NaCl Corrosion Rate	Freezing Point (°C)
1	50% propylene glycol + 25% aqueous extract of DDGS + 25% water	Pass	1.73	3.3	−35
2	50% propylene glycol + 25% extract of thick stillage + 25% water	Pass	0.07	0.13	−35
3	24% calcium chloride ($CaCl_2$) + 20% aqueous extract of DDGS + 56% water	Pass	18.56	29.6	−35
4	3% NaCl (control 1)		62.62		
5	De-ionized water (control 2)		0.42		

Solvent Extract and Aqueous Extract of DDGS as Corrosion Inhibitors

Solvent Extraction

DDGS were extracted with ethyl acetate at 4 g/25 mL ratio overnight. Removal of the solvent yielded an amber-colored viscous oil in low yield (20%). Being immiscible, the extract/test solutions were agitated throughout the following tests to achieve an even distribution. The extracted oil was evaluated in acidic solutions according to a modified ASTM G31[10] immersion test. Two percent of the amber oil was added to 10% solution of hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and 20% citric acid ($C_6H_8O_7$), respectively. Steel coupons (SAE 1010) were immersed in the above acidic solutions at room temperature for 24 h. After cleaning, the mass loss of each coupon was determined and the corrosion rate was calculated. The extracted oil, at 0.5% w/w, was also evaluated in synthetic seawater. Synthetic seawater by itself was a control. CS coupons (SAE 1010) were immersed in the two test solutions for 48 h, cleaned, and visually inspected for corrosion.

Aqueous Extraction

For aqueous extractions, a ratio of one part DDGS, four parts water, and one part NH_4OH (30%) or 40 h at 80 °C, and a ratio of two parts thick stillage, two parts water, and one part NH_4OH were used. The nonvolatile content of the aqueous extract was 11%. To determine the effectiveness of the aqueous extracts as

FIGURE 4
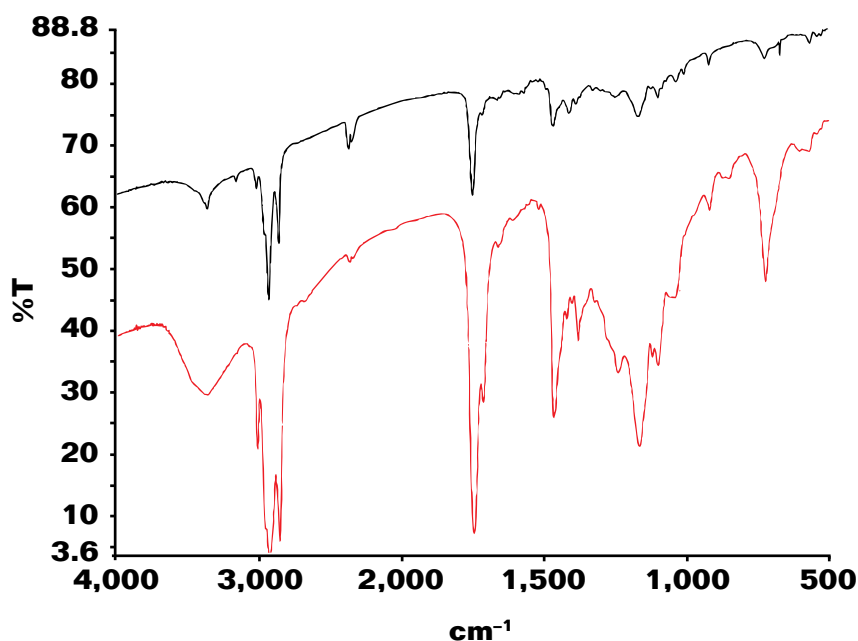
FTIR spectrum of solvent extract (red) and aqueous extract (black).

de-icers, freezing point and corrosion inhibition through Pacific Northwest Snowfighter (PNS)[11-14] testing were performed. Formulas of freezing points below −35 °C were subjected to PNS testing. Test solutions were 3% formula in a 3% sodium chloride (NaCl) solution. Two controls, 3% NaCl and de-ionized water, were used. Metal coupons, hung from an automatic PNS testing apparatus, were dipped into the test solutions at a rate of 10 min/h for 72 h. The coupons were cleaned according ASTM G1[15] after the test, and their mass losses and corrosion

rates were calculated according to PNS protocol. The effectiveness of the de-icer was reported as a percentage of the corrosion rate in a 3% NaCl solution. PNS requires that a de-icer must be at least 70% less corrosive than the 3% NaCl control solution.

Compound Identification

The extracts were analyzed using gas chromatography mass spectroscopy (GCMS), liquid chromatography mass spectroscopy (LCMS), and Fourier transform infrared (FTIR) spectroscopy.

Results

Molasses as a Vapor Phase Corrosion Inhibitor

Molasses and raffinate from sugar beet and sugar cane showed significant VCI ability (VIA grades 2-3) in as-received forms (Figure 2[a] and Table 1). Interestingly, less processed molasses showed better VCI property than the more processed molasses. For instance, feedstock sugar beet molasses showed better VCI than the Sample 1 food grade molasses; less processed Sample 1 food grade molasses showed better VCI property than the more processed Sample 2 food grade molasses.

Effect of Distillation

Surprisingly, both distillate and pot residue from the distillation of raffinate showed strong VCI property (Figures 2[b] and [c], Table 1). Also, 2.5 g of either distillate or pot residue showed better VCI property than 5g of as-received raffinate.

Effect of Ion Exchanging

Ion exchange using a strong cation exchange resin showed that when potassium ions were removed and replaced with ammonium, the resulting organic salts demonstrated VCI property. It is likely that VCI components in molasses and raffinate existed as potassium salts of a number of organic acids.

Ultrafiltration

Ultrafiltration showed that those raffinate fractions of molecular weight (MW) between 1,000 to 3,000 and of MW above 30,000 demonstrated VCI properties (Table 1).

Chemical Treatment with Ammonia

The addition of 5% NH_4OH solution (~1.5% NH_4OH) enhanced the vapor corrosion inhibiting ability of the molasses. It was noted that 1 g of enhanced molasses (blended with NH_4OH) (Figure 2[d]) showed better VCI protection than 5 g of as-received molasses (Figure 2[a]). NH_4OH by itself showed almost no VCI effect (Figure 2[e]).

Chemical Identification

SPME GCMS of the volatile portion of molasses showed a number of organic acids, ketones, aldehydes, pyrazines, alcohols, alkenes, pyrrolidinones, lactones, and furanones. Some of the identified components match those found in the aroma analysis of molasses.[16] Due to the complexity of molasses, no inhibiting compound was identified.

Solvent Extract and Aqueous Extract of DDGS as Corrosion Inhibitors

Acid Immersion Test

Two percent DDGS solvent extract showed significant protection of steel from acid corrosion (Table 2).

Saltwater Immersion Test

The solvent extract, 0.5 wt%, provided excellent protection for steel in synthetic seawater. Figure 3(a) displays the film-forming properties of the solvent extract. This viscous yellow film acts as an air, moisture, and salt barrier protecting the coupon from saltwater attack. This film, however, was easily removed using conventional detergent. Figure 3(c) illustrates the coupon that has been cleaned, showing no corrosion on the surface. The control (Figure 3[b]) was found to have a lot of corrosion on the surface.

De-icer Testing

Aqueous extracts of both DDGS and thick stillage showed good potential as a de-icer component (Table 3).

Gas and Liquid Chromatography

Gas and liquid chromatography results showed that the chemical makeup of the solvent and aqueous extracts are similar. Due to the complexity in the GCMS and LCMS data, the specific molecular basis of corrosion inhibition could not be established for the DDGS extracts. Some of the major components detected were long chain fatty acids, C-16 and C-18 specifically; ethyl esters; butanediol; tocopherol; ergost-5-en-ol; sig-mast-5-en-3-ol; methoxy propanol; and ethoxy ethanol, among a large number of minor peaks.

FTIR Spectroscopy

Figure 3 shows the FTIR spectra. The spectra are dominated by peaks characteristic of corn oil. However, the peak at 1,711 cm^{-1} is indicative of a carboxylic acid, possibly fatty acid. The broad peak at 3,359 cm^{-1} is indicative of a small amount of hydrogen-bonded water or possibly polyols (e.g., glycerol or budantediol).

Conclusions

Feedstock sugar beet molasses and raffinate are compelling raw materials as VCIs. It is known that vapor corrosion inhibition is mostly provided by the salts of weak volatile acids and weak volatile bases.[17-18] Molasses and raffinate appear to be good sources of such materials. The easy addition of a small amount of NH_4OH greatly enhanced the VCI property of molasses and raffinate.

A solvent extract of DDGS demonstrated good corrosion prevention in acidic and/or saltwater solutions. The extract forms a tenacious film on metal surfaces and lends itself very well as a float coat with applications in holding tanks, ballast tanks, and offshore structures. This float coat has the advantage of not drying out and not cracking after prolonged use. It can be easily removed using conventional detergents and is very economical. Being bio-based and biodegradable, it doesn't pose a problem when discharging into ground or surface water; however, the maximum discharge amount should be verified through testing by the EPA laboratory.

Aqueous extracts of DDGS and thick corn stillage revealed several de-icer formulations that met the freezing point requirements. Moreover, the extracts yielded increased corrosion protection. Commercially available propylene-glycol-based deicing fluids report corrosion rates of 2 to 20 mpy on CS,[6] whereas the aqueous extracts of DDGS and thick corn stillage offer protection rates as low as 0.07 mpy.

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