ABSTRACT

One of the methods of corrosion protection of metal reinforcement in concrete is cathodic protection. This protection can be achieved by different arrangements including sacrificial coatings. Several companies have made an attempt to create such a product, including NASA, and others. The goal of this study was to evaluate one existing formulation and optimize the corrosion protection by adjusting powders, resins, and installation techniques. A number of electrochemical techniques were utilized for measuring parameters of the galvanic coating. These laboratory and field techniques include electrochemical potential, electric resistance, corrosion current, and others.

Key Words: Corrosion, concrete, rebar, sacrificial cathode, galvanic coating

INTRODUCTION

Corrosion is a problem in the US that costs billions. The latest study by the Federal Highway Administration estimated the direct costs of corrosion to be $276 billion—approximately 3.1% of the nation’s Gross Domestic Product (GDP). Based on the National Bridge Inventory Database, there are 586,000 bridges in the United States. Of this total, 435,000 bridges are made from steel and conventional reinforced concrete, 108,000 bridges are constructed using pre-stressed concrete, and the balance is made using other materials of construction. Approximately 15 percent of the bridges are structurally deficient, primarily due to corrosion of steel and steel reinforcement. The dollar impact of corrosion on highway bridges is considerable. The annual direct cost of corrosion for highway bridges is estimated to be $8.3 billion, consisting of $3.8 billion for the annual cost to replace structurally deficient bridges over the next 10 years, $2.0 billion for maintenance and cost of capital for concrete bridge decks,
$2.0 billion for maintenance and cost of capital for concrete substructures (minus decks), and $0.5 billion for maintenance painting of steel bridges. Life-cycle analysis estimates indirect costs to the user due to traffic delays and lost productivity at more than 10 times the direct cost of corrosion.\(^1\)

Cathodic protection is an electrochemical method of the corrosion control in which the oxidation reaction in a galvanic cell is concentrated at the anode to suppress corrosion of the cathode at the same cell. In cathodic protection the anode is often “sacrificed” to corrosion in order to protect the cathode. In practice, cathodic protection is primarily used for the protection of carbon steel. Commercial sacrificial anodes include magnesium, zinc and aluminum alloys.

Historically several criteria have been used to verify performance of cathodic protection from corrosion:
1. A uniform potential on the structure, which would eliminate galvanic cells between different regions.
2. A shift of the potential, from native or unprotected potential to a more negative, protected potential (-50mV to -300mV).
3. A shift of the structure potential to a potential at which current will flow into the structure instead of away from it.

Later, a -850mV or -950mV vs. Cu/CuSO4 electrode was accepted and widely used for its simplicity and convenience for evaluation. An “instant off” of -850mV and a -100mV shift in potential are also in use as criteria.\(^2\)

Concrete structures normally rely on the concrete cover to provide protection that prevents the corrosion of embedded steel. Over time, this protection can be lost due to moisture and/or chloride ingress. When the corrosion of the embedded steel occurs, cathodic protection can be used to extend the life of the already deteriorated structure.

Corrosion of the reinforcing steel in concrete has gained much attention in recent years because of the decaying infrastructure of highways and bridges. States, federal agencies and other researchers indicate that cathodic protection is a proven method for corrosion control of concrete reinforcing.\(^3\) The latest development in this area is sacrificial cathodic protection systems, including embedded zinc anodes, zinc mesh anodes, sacrificial jackets and metallized sacrificial coatings.\(^3\)

Sacrificial coatings present a barrier between concrete and its surrounding environment, but in addition they protect reinforcement by allowing corrosion to occur on the sacrificial metal. Therefore, the coating prevents corrosion from occurring on the actual structural steel in the concrete.

The development of a Galvanic Liquid Applied Coating System (Galvanic Coating) would be a breakthrough technology having great commercial value for the following industries: Transportation, Infrastructure, Marine Infrastructure, Civil Engineering, and Construction.

The present Galvanic Coating includes a mixture of metallic powders, conducting agents, and moisture attractors in a moisture-cure polyurethane vehicle.
EXPERIMENTAL PROCEDURE

Test Criteria

The experimental effort was directed at solving reinforcing steel corrosion in concrete for bridge structures. The experimental design incorporated the following methods: weight gain in water soak of coating, electrical impedance testing, depolarization testing, and multi-meter checks of millivolt potential and milliamp current to test different formulations and installation techniques. Out in the field, millivolt potential and milliamp output per square foot of anode have been studied at actual bridge structures.

According to the performance criteria for the cathodic protection listed above, the desired qualities of the galvanic coating used for the protection of the imbedded in concrete rebars are:

a) Cathodic potential vs. steel reinforcement potential;
b) Sufficient rate of anodic reaction to provide the level of current necessary for cathodic protection;
c) Electrical conductivity;
d) Good adhesion to the concrete and durability;
e) Sufficient ‘pot life’ for the convenience of application;

To optimize the formulation of the coating many various formulations were prepared and tested in the laboratory. Because the metal components play an essential part in sacrificial cathodic coating performance such factors as total amount of the metal components, ratio between the different metallic components, the metallic particle sizes and shapes were initially evaluated.

Next, the evaporation rate of solvents used in the formulation, the presence and amount of moisture attractors and the presence and amount of corrosion accelerators used in coating design were studied. Table 1 presents the ‘importance’ of the design variables in the final formula of the coating.

Testing Procedures

**Lab Samples.** For the majority of laboratory testing four types of the samples were used:

1. Samples of the coating molded on the inert plastic (‘chips’);
2. Coating applied on the small concrete pucks;
3. Coating applied on ‘lollipop’ shaped concrete samples with one embedded rebar;
4. Coating applied on 1ft x 1ft x 3 inch concrete blocks with two embedded rebars.

The concrete used for lab samples was prepared using a 1:3 Portland Cement Type 1 to dry sand mix and a 3.5% NaCl solution to cement ratio of 0.45. Samples were cured for over 28 days before application of galvanic coating.

**Instruments.**

1. Potentiostat/Galvanostat Versastat with 352.252 SoftCorr11 Corrosion Software, manufactured by EG&G Princeton Applied Research and PCI4 Potentiostat/Galvanostat with EIS 300 Electrochemical Impedance Spectroscopy Software were used for the evaluation of the electrochemical potential and electrical conductivity of the samples.
prepared in the laboratory. During these measurements, standard calomel saturated electrode was used as a reference.

2. Electrochemical potential, the current density, decay level and conductivity in the field were measured with a DM8600 multi-meter manufactured by A.W. Sperry or Fluke 16.

3. Zero resistance Ammeter

**Testing Procedures.**

1. Corrosion rate of the galvanic coating was evaluated using the electrochemical polarization data. Polarization curves in Tafel technique were obtained in a 3.5% Sodium Chloride solution. ‘Chips’ made from the galvanic coating were used as a working electrode, calomel saturated was used as a reference and high density graphite was used as counter electrode.

2. Susceptibility of the galvanic coating to electrochemical anodic reaction was evaluated by weight change. Galvanic coating “chips” were immersed in 3.5% NaCl solution. The containers of solution were closed and placed in oven to further accelerate testing. Oven was set at 40°C and the test was performed during 30 days. The weight change was determined.

3. Galvanic coating was applied onto ‘lollipop’ shaped samples with one embedded rebar. To accelerate the test, some of the samples were placed in a ‘Salt Spray’ cabinet set according to ASTM B 117 at 95°F with a constant salt fog produced from a 5% NaCl solution and some of the samples were immersed in a 3.5% NaCl solution. Electrochemical potential, current flow and ‘instant off’ were evaluated.

![FIGURE 1 – Lollipop Set-up](image)

4. Galvanic coating was applied on a concrete block with two embedded rebars at 28mil wet
film thickness. To accelerate the test, the coated and control blocks were placed in humidity cabinet set at 105°F and with a 100% Relative Humidity. Blocks were monitored for the level of electrochemical potential for 1700 hours.

RESULTS
The results of the laboratory testing of the galvanic coating are presented in tables 1-4 and fig. 4-5. During the formulation work many components were evaluated. Based on laboratory test results, the components in the coating were ranked by importance based on the impact on the coating performance. This data is presented in table one.
Table 1
Affect of the formulation components on the performance of the galvanic coating

<table>
<thead>
<tr>
<th>Component of Formulation</th>
<th>How it Affects Galvanic Coating</th>
<th>Test Method Used</th>
<th>Importance on the scale of 1 - 10 (10 is the most important)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of resin</td>
<td>Provides the mechanical properties and structure of the coating</td>
<td>Visual evaluation</td>
<td>8</td>
</tr>
<tr>
<td>Chemical nature of metal powders incorporated into the resin</td>
<td>Forms the sacrificial cathode</td>
<td>Field and lab testing. Measurement of the electrochemical potential, cathodic and corrosion current, and electrical conductivity</td>
<td>6</td>
</tr>
<tr>
<td>Total amount of metal powder in formulation</td>
<td>Same as above</td>
<td>Same as above</td>
<td>10</td>
</tr>
<tr>
<td>Particle size and the shape of metal fillers</td>
<td>Same as above</td>
<td>Same as above</td>
<td>4</td>
</tr>
<tr>
<td>Type of solvent</td>
<td>Affects pot life. Affects the structure of the coating and possibly the conductivity of the coating.</td>
<td>Same as above, lab and field application experience.</td>
<td>10</td>
</tr>
<tr>
<td>Amount of solvent</td>
<td>Same as above</td>
<td>Same as above</td>
<td>8</td>
</tr>
<tr>
<td>Film thickness of the coating</td>
<td>Affects Conductivity level, durability</td>
<td>Same as above</td>
<td>3</td>
</tr>
</tbody>
</table>

Table two presents data from the electrochemical evaluation of the coating chips. It was found that the level of electrochemical potential of Galvanic Coating is in the range -810 to -890mV. It was also found that this coating undergoes an electrochemical type of corrosion and has relatively low electrical resistance. Considering that the half cell potential of actively corroded steel embedded in concrete would not be lower than – 560mV SCE on its own, the data below suggests that the developed coating can be use it as sacrificial anode for embedded rebars.

Table 2
Electrochemical and Electrical Properties of the Galvanic Coating ‘Chips’

<table>
<thead>
<tr>
<th>Galvanic Coating</th>
<th>Electrochemical potential, mV</th>
<th>Corrosion rate, mpy</th>
<th>Conductivity, Ohms</th>
<th>Weight change, mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimized formula</td>
<td>-810 to -890</td>
<td>1.66</td>
<td>50 to 690</td>
<td>21.1</td>
</tr>
</tbody>
</table>

Data presented in table three shows that when ‘lollipop’ concrete samples are placed into
aggressive environments such as a salt spray cabinet or immersed into a salt solution, electrochemical potential of rebar correspondingly shifts to lower numbers. Nevertheless, the electrochemical potential of the coating remains consistently cathodic vs. rebars; coating does not develop passivity to act as an active anode when connected to the rebar but instead the protective cathodic level of electrochemical potential is maintained.

Table 3
Electrochemical potential of connected and ‘instant off’ galvanic coating applied on ‘lollipops’

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrochemical potential of rebar, mV vs.Cu/CuSO4,mV</th>
<th>Electrochemical potential of the disconnected galvanic coating, mV vs.Cu/CuSO4,mV</th>
<th>Electrochemical potential of rebar connected with galvanic coating, mV vs.Cu/CuSO4,mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial data (kept at 95% relative humidity)</td>
<td>-370</td>
<td>-1012</td>
<td>-684</td>
</tr>
<tr>
<td>After 72 hours in Salt Spray cabinet</td>
<td>-425</td>
<td>-1113</td>
<td>-750</td>
</tr>
<tr>
<td>After 7 days in salt solution</td>
<td>-466</td>
<td>-1133</td>
<td>-770</td>
</tr>
<tr>
<td>Sample w/o galvanic coating</td>
<td>-350</td>
<td></td>
<td>-350</td>
</tr>
</tbody>
</table>

Table four presents the results from the galvanic coating applied on concrete slabs and electrically connected with rebars. Figure four shows the concrete slabs and figure five is a graphically interpretation of the data. The data shows that a cathodic potential was provided for the rebar and was maintained during the testing time, which agrees with the testing done in table three.

Table 4
Study of the slab samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Connected for 7 days</th>
<th>Humidity for 348 hours</th>
<th>Humidity for 1700 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanic Coating</td>
<td>-182 mV</td>
<td>-700 mV</td>
<td>-700mV to -1100 mV</td>
</tr>
<tr>
<td>Control</td>
<td>-149mV to -175 mV</td>
<td>-300mV to -350mV</td>
<td>-300mV to -330 mV</td>
</tr>
</tbody>
</table>
Figure 4 - Concrete Slabs After 1700 Hours in Humidity Chamber

Figure 5 - Half-Cell Potentials of Embedded Rebars in Concrete Slabs
FIELD APPLICATIONS

1. Saint Paul, MN Bridge

Concrete deck patch repairs on a bridge in Saint Paul, MN had been only averaging a life span of three years due to chloride induced corrosion. Chloride amounts are tested to be 3000ppm. The original bridge (now the two east bound lanes) was built in 1954 and it was resurfaced in 1974, when two additional lanes were added. (Now the two west bound lanes.) The galvanic coating was roller applied in September 2003 (after sand blasting) to an area on the underside of the bridge in order to protect two new patches in the six inch concrete overlay on the eastbound lanes.

Before the two areas were patched, a hole was drilled through to the bottom of the bridge in each area. The rebars were welded together to assure conductivity. Then a thick wire was welded to the rebar in each area and fed through to the bottom of the bridge. These wires are the connection to the rebar for current coming from the coating. Plastic tubes were put on the wires where they pass out through the coating to avoid contact at that point. The coating is connected to the rebar wires with a small junction box in between in order for potential readings to be taken and recorded.

Wires were installed overhead on the bottom of the bridge. Then four zinc wires for collecting the coating current were installed. Next, small holes were drilled in the bottom surface of the bridge and anchor nails put into plastic collars at three-foot spacing. Plastic collars were used so these pins would not “leak off” current into the concrete. These anchor ends were 13 feet apart in the other direction. The zinc wires were connected and pulled tight on these pins in the 13-foot direction. Then they were glued every five inches to be sure they were flat against the bottom of the concrete surface so the coating could cover them.

With a two-foot boarder of coating out around the wires, a total area of 340 sq. ft was coated with 2.6 kg of the galvanic coating.

Readings were taken using a Copper/Copper Sulfate Electrode starting after one week to verify that the galvanic coating was “charging” the rebar and stopping their current production. After several months a “disconnect test” to check for rebar potentials was performed. Levels should be less then the –350 mV, to show corrosion is suppressed.

<table>
<thead>
<tr>
<th>Date</th>
<th>Half-Cell Potentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-20-03</td>
<td>-500mV (natural potential before anode application)</td>
</tr>
<tr>
<td>11-18-03</td>
<td>-486mV (closed circuit)</td>
</tr>
<tr>
<td>4-21-04</td>
<td>-662mV (closed circuit)</td>
</tr>
<tr>
<td>5-21-04</td>
<td>-722mV (closed circuit)</td>
</tr>
<tr>
<td>5-25-04</td>
<td>-719mV (closed circuit)</td>
</tr>
<tr>
<td>5-9-07</td>
<td>~-700mV to -900mV (closed circuit)</td>
</tr>
</tbody>
</table>

On May 25, 2004, a depolarization test was performed. The depolarization value is the difference between the instant off and the subsequent readings. The NACE standard for
This test is 100mV of polarization. This is the difference between the first reading on 10-21-03 and the instant off reading of -665mV (see chart below). This gave a polarization shift of 165mV.

Table 6
Depolarization Test of Galvanic Coating on St. Paul Bridge

<table>
<thead>
<tr>
<th>Depolarization period</th>
<th>Inst. Off Potential (mV. CSE)</th>
<th>Decay (mV)</th>
<th>NACE Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instant off</td>
<td>-665</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One minute:</td>
<td>-495</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>One hour:</td>
<td>-445</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>Four hours:</td>
<td>-430</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>24 hours:</td>
<td>-476</td>
<td>185</td>
<td>150</td>
</tr>
</tbody>
</table>

This project has resulted in a professional looking application of the galvanic coating. The outdoor weathering to date indicates that the galvanic coating will have a white oxide form on the surface with time. But it has not had any peeling or sagging. In spite of the damp saline concrete conditions, the coating remains completely intact as it was applied. This suggests that a ten year life could be expected.

The patches were averaging a life span of about 3 years in between repairs before the galvanic coating was applied because of the high chloride environment. After four years, there were no visual signs of ring anode affect or spalling of the patches.

After 4 years, the half cell potentials of the coating remain lower than the half cell potentials of the rebar. The lower potential of the coating, versus the rebars, shows that the coating is acting as an anode for the rebars and when it is connected to the rebars, the coating is sacrificed as it oxidizes before the rebars. Although the coating is connected to the whole bridge deck rebar grid, the protection has been enough to stop ring anode effect corrosion around the two patches.

![Figure 5 - View of Galvanic Coating under deck in 2007](image-url)
2. Jordan, MN Bridge

In July 2005, MN-DOT Bridge #9123 in Jordan, MN had previous repair patches that were falling off due to rebar corrosion underneath them. The most expensive part of a bridge is the pier cross beams and their columns, which include deep pilings to avoid settling. The bridge deck can be replaced in a much shorter time if the piers are intact. The galvanic coating was applied on the two piers to prevent corrosion of embedded rebars and extend the life of repair work; two piers were left uncoated as controls.

The rebar connection leads were installed by contractor. The rebars were checked for continuity using a long wire with an alligator clip and an ohm meter to be sure galvanic current would be provided to all the bars. Steel wires were connected to any rebars that were not electrically connected. Only two rebars on pier cap three and one on cap four were not able to be connected to the system. The steel “H” plates on top of the caps could not be connected to the coating.

Quarter inch aluminum tape and zinc connection wires were put in place before coating was sprayed onto concrete. The zinc wire formed a “U” shape around the bottom of the beam three feet apart from each other and was anchored with pins. The aluminum tapes ran perpendicular to the zinc wire approximately one and one-half feet apart. Five kits (4 gallon each) of the galvanic coating were mixed and applied at approximately 20 mil wet thickness. The temperature range was 71-90°F and the humidity range was 64-84%. A contract electrician connected lines and junction box between the rebar leads and the coating leads.

This project has resulted in a very professional looking application of the galvanic coating. The outdoor weathering to date indicates that the galvanic coating will have white oxide form on the surface with time. It has not had any peeling or sagging. See photos at the end of this report.
An initial reading of -420mV on the deck rebars is well above the NACE value of -350mV for 90% probability of corrosion. However, the pier rebars’ very high reading of -660mV makes it appear that the following situation may take place. First, strong winter salt solution drains down onto the support piers below. Then, rain washes the deck concrete but does not effectively wash the piers. This has resulted in severe active corrosion of the pier rebars. Most likely, the piers would show a very high chloride contamination level.

After winter deicing cycles, and as the concrete loses its alkalinity, it would be expected that the corrosion current would increase. Recent galvapulse measurements of the rebars in the bridge showed a range of 1.7-3.7uA/cm$^2$ (average of 2.7uA/cm$^2$) on the side protected by the galvanic liquid coating versus a range on the control side of 3.5-19.6uA/cm$^2$ (average of 8.3uA/cm$^2$.)

Figure 7 - Bridge piers with Galvanic Coating 4/2007

Figure 8 - Bridge piers without Galvanic Coating 4/2007
CONCLUSIONS
1. Extensive formulation work has resulted in a system that provides the needed polarization for cathodic protection of reinforcing steel embedded in concrete for a variety of structure environments.
2. Laboratory and field measurements show that the formulated galvanic coating conforms to performance criteria of sacrificial cathodes.
3. The observations made of the field applications: the presence of the white powder across the entire surface and no cracks of the concrete on the protected side of the bridge vs. the presence of cracks on the control side, confirm that the coating is providing the necessary cathodic protection for the structure.

REFERENCES
   Gerhardus H. Koch, Ph.D., Michiel P.H. Brongers, Neil G. Thompson, Ph.D., Y. Paul Virmani, Ph.D.
   Joe H. Payer, Ph.D.