



## Role of Migratory Corrosion Inhibitors for Protecting Embedded and Exposed Steel

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### ABSTRACT

Steel corrosion is an electrochemical process that can be both accelerated and inhibited by the conditions at the steel surface. Corrosion can be prevented on new steel by a surface barrier, but can only be inhibited on corrosion active steel by use of a chemical corrosion inhibitor.

There are two types of migratory corrosion inhibitors. Inorganic chemicals that function at the anodic corrosion site and migrate in the ionic phase; and organic types that function at both the anodic and cathodic sites and migrate in the vapor phase (VCI).

The degree of corrosion protection is determined by measuring corrosion current and half-cell potential and by observing the formation of rust on the steel surface or through a surface coating

Both types of migratory corrosion inhibitors can be applied to the surface of hard concrete or added to a concrete mix to inhibit reinforcing steel corrosion. The application and performance of migratory corrosion inhibitors used on a U. S. Army Corps of Engineers (COE) sponsored project in Okinawa will be presented and discussed. Corrosion current measurements made over several years showed that the rebar corrosion rates were significantly reduced. Original work performed at the Kennedy Space Center (KSC) on the performance of the two types of migratory corrosion inhibitors is also presented. The corrosion rate change measured after application of the two types of inhibitors on a parking garage deck are used to calculate the change in expected time for sufficient rebar corrosion to occur to cause structural damage.

A vapor phase migratory corrosion inhibitor (VCI) was formulated into a two part polyamide epoxy primer on another COE contract; and the improvement in corrosion resistance was measured by exposure in a salt fog chamber. Performance on both white and corroded rust cover steel was measured with and without the VCI added. Corrosion was reduced to the same degree on both types of steel surfaces showing that the VCI penetrates the rust layer and inhibits further corrosion of the white steel sub layer.

Key Word: Concrete, Steel corrosion, Corrosion inhibitor, Anti-corrosion coating

## INTRODUCTION

Concrete typically contains 15 wt. % cement and at a 0.5 water cement ratio is about 20% porous. The porous component or gel pores are where most of the chemical processes occur in hard concrete. The cement in fresh concrete has a pH of 12 to 13 signifying a high level of alkalinity and hydroxyl ion content. The hydroxyl ions act to inhibit corrosion on the surface of embedded reinforcing steel or rebar by stabilizing the ferrous oxide film or passivating film. Air containing carbon dioxide and water containing chlorides penetrate the cement over time and will reduce the pH through the process of carbonation and raise the cement chloride ion content. A drop in pH below 11 results in loss of the natural rebar corrosion inhibiting affect and as the chloride content increases the passive film is attacked and the rate of corrosion accelerates.

Steel corrosion has two basic electrochemical mechanistic sites. The anodic site where the steel is oxidizing and producing a flow of electrons or current, and the cathodic site where oxygen and water combine to form hydroxyl ions which completes the formation of ferrous hydroxide. The rate of corrosion can be determined by measuring directly or indirectly the corrosion current, and corrosion can be inhibited by reducing the potential of either the anodic or cathodic reaction processes. Macro cell corrosion current can be measured directly as it flows from concrete embedded rebar in the corrosion active anodic state to rebar in the corrosion passive cathodic state. Micro cell corrosion current can be determined by measuring the polarization resistance of a known area of near surface rebar as described in ASTM G59. There are instruments available, such as the Galvapulse which measures polarization resistance using galvanostatic polarization and present corrosion current as micro amps per centimeter square ( $\mu A/cm^2$ ).

Anodic and cathodic mechanism type corrosion inhibitors can be added to the concrete mix or be applied to the surface of hard concrete. It is necessary for the inhibitors to migrate through the cement to the rebar surface in order to affect a change in the rebar corrosion rate. There are two paths through which an inhibitor can migrate through the cement gel pore structure. An inorganic inhibitor can migrate in the ionic phase along the water film on the gel pore surface, and an organic vapor phase type inhibitor can migrate in the void space of the gel pores. These two types of migratory inhibitors are available and being used on commercial projects. The inorganic, ionic phase migratory type inhibitors function at the anodic corrosion mechanism site. The organic vapor phase migratory types function at both the anodic and cathodic sites.

## EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSIONS

The performance of migratory inhibitors are illustrated by four experiments where the degree of corrosion is measured before and after application and changes in steel corrosion reported and analyzed. The first three are examples of application on cured reinforced concrete and the fourth the addition of a vapor phase migratory inhibitor to a steel surface coating.

### **NASA Kennedy Space Center Evaluation of Inorganic and Organic Migratory Corrosion Inhibitors**

#### **Experimental Procedure**

A joint R&D project between the National Space and Aeronautics Administration (NASA) and Surtreat involved the construction of corrosion inhibitor test cells similar to those described in ASTM G109. The

cell were manufactured by Surtreat and delivered to the NASA/KSC Corrosion Laboratory along with samples of an inorganic ionic phase and organic vapor phase migratory inhibitors in liquid formulations. The cells had rebar embedded at 1, 2 and 5 inches from the surface. This allowed for measurement of corrosion current flowing from rebar at 1 and 2 inches in an anodic condition to the rebar in a cathodic condition at 5 inches. The initial flow of current was measured and a 10 % solution of sodium chloride placed in a reservoir on the surface of two test blocks. Fourteen days after application of the salt solution the average corrosion current had increased from 5 micro amps ( $\mu\text{A}$ ) to  $70\mu\text{A}$  for rebar at 1 and 2 inches for both blocks. The salt solution was removed, and a quantity of the two inhibitor solutions equal to  $100\text{ft}^2/\text{gallon}$  ( $2.4\text{M}^2/\text{l}$ ) were separately placed on the surface of the two test blocks.

### **Results and Discussion**

Sixty days after application of the two corrosion inhibitors the average corrosion current from rebar at 1 and 2 inches had dropped from  $70\mu\text{A}$  down to  $10\mu\text{A}$  for both types of corrosion inhibitors. This experiment demonstrated that both types of inhibitors can migrate from a concrete surface to rebar at 1 to 2 inches below the surface and inhibit chloride ion induce corrosion.

## **Corps of Engineers Okinawa Application of Migratory Corrosion Inhibitors on Bridges and Ring Girders**

### **Experimental Procedure**

The Corps of Engineers in 2007 commissioned a project with Surtreat for the application of inorganic ionic phase and organic vapor phase migratory corrosion inhibitors containing formulations on bridge structures at the Kadeana Air Force Base fuel depot and on ring girders in a warehouse at Port Naha, Okinawa. The contract specified measurement of initial corrosion rates, performance of necessary concrete repairs, application of the two types of corrosion inhibitors together on all concrete surfaces and then the follow up measurement of the degree to which rebar corrosion had been decreased. Corrosion current was measured using the Galvapulse instrument and the result converted into corrosion rate in terms of micrometers of steel being lost from the rebar surface per year ( $\mu\text{M}/\text{Yr}$ ).

Chemical analysis of the concrete cement on the bridges and warehouse girders, which were built in the 1950 time frame, showed that the primary cause of the observed rebar corrosion was due to the carbonation front reaching the rebar level and dropping pH to 11.

An organic vapor phase migratory inhibitor was applied first to both structures at rate of  $100\text{ft}^2/\text{gallon}$  ( $2.3\text{M}^2/\text{l}$ ) follow by an application of water to drive all active ingredients into the cement pores. Twenty four hours later a formulation containing an inorganic ionic phase migratory inhibitor was applied at the rate of  $100\text{ft}^2/\text{gallon}$  ( $2.3\text{M}^2/\text{l}$ ) to both types of structures, and as soon as the surface was dry, water was applied to the surface.

### **Results and Discussion**

The average corrosion rate on the warehouse structural beams in January 2007 was  $61\mu\text{M}/\text{Yr}$ . The rate had decreased to  $23\mu\text{M}/\text{Yr}$ . in July 2007 and down to  $14\mu\text{M}/\text{Yr}$ . on July 2010. The average corrosion rate on the bridge structures in January 2007 was  $37\mu\text{M}/\text{Yr}$ . and decreased to  $13\mu\text{M}/\text{Yr}$ . on July 2007 and down to  $7\mu\text{M}/\text{Yr}$ . by July 2010. These measurement show that application of the two types of migratory corrosion inhibitors has decreased the average rebar corrosion rate on both structures, three years after application, by a factor of three times.

# Application of Migratory Corrosion Inhibitors to Parking Garage Deck with Measurement of Expected Structure Life Extension

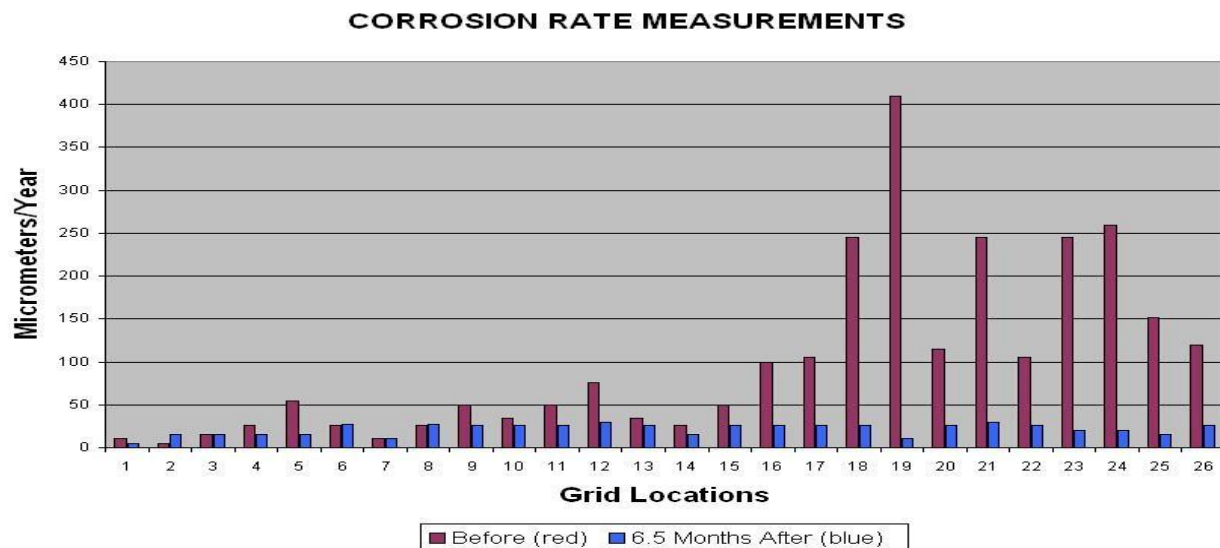
## Experimental Procedure

The decks of a parking garage were experiencing corrosion of reinforcing steel as observed by concrete spalling and exposed rusted rebar due to invasion of deicing salt increasing the chloride content to the corrosion activity level. A 200ft<sup>2</sup> (18.6M<sup>2</sup>) area on a deck section was selected for measuring the rate of rebar corrosion before and after application of two migratory corrosion inhibitors. The corrosion current was measured at 26 points on the rebar mat and on an adjacent 9 point area using the Galvapulse instrument and recorded as micro amps per cm<sup>2</sup> (μA/cm<sup>2</sup>).

Two types of migratory corrosion inhibitors were applied on the 26 measurement point area; and the 9 point area was not treated to be used as a control point to correct for changes over time in the base corrosion rate. An organic vapor phase migratory corrosion inhibitor was applied at the rate of 150ft<sup>2</sup>/gallon (3.7M/l) followed by application of water. Twenty four hours later a formulation containing an inorganic ionic phase migratory inhibitor was applied at the rate of 150ft<sup>2</sup>/gallon (3.7M<sup>2</sup>/l) followed by application of water.

## Results and Discussion

Six and one half months after inhibitor application the corrosion current on the 26 and 9 point areas was measured and recorded. The after application measurements are corrected by plus 0.5μA/cm<sup>2</sup> for the change in base corrosion rate. The corrosion current measurements from both time periods were converted to corrosion rate by multiplying current in μA/cm<sup>2</sup> by 11.6, a conversion factor determined by the Faraday Law of current to atomic equivalency, and are displayed on Figure 1.



**Figure 1: Corrosion rate measurements made before and after application of migratory corrosion inhibitors**

Examination of Figure1 shows a significant decrease in rebar corrosion rate especially at measurement points 16 through 26 where there was a rate much higher than the average. This can be identified as a corrosion hot spot with high anodic potential. The fact that the corrosion rate at these points has been reduced to a greater degree than the average indicates that the corrosion inhibitors have a high degree of anodic site inhibiting function. The numerical corrosion rates show a decrease in the average rate from 100µM/Yr. to 28µM/Yr. and that the average rate before inhibitor application for the 5 highest rate points is 250µM/Y. Equation1 can be written for the time it will take at a specific corrosion rate for an amount of rebar steel to be lost to cause structural concern.

$$T = D/2 \times 10^{-3} \times R(t) \times K \quad (1)$$

T = Years to reach structural deficiency

D = Rebar diameter loss in mm

R(t) = The average corrosion rate at time zero

K = A factor to account for the impact of corrosion rates above the average

The expected time to reach deficiency can be calculated on basis of time zero rebar diameter of 20mm and a 20% loss being the critical point or 4mm, and that the 250µM/Yr. average rate for the corrosion hot spots justifies using a K factor of 2.5.

Before inhibitor application  $T = 4/2 \times 10^{-3} \times 100 \times 2.5 = 8$  Years

After inhibitor application  $T = 4/2 \times 10^{-3} \times 28 \times 1.0 = 72$  Years

A sixty year life extension is calculated. There are degrees of uncertainty and factors that could decrease the time, but it is certain that application of the corrosion inhibitors has resulted in a significant degree of life extension.

## **Addition of Vapor Phase Migratory Corrosion Inhibitor to Steel Coating Epoxy Primer**

### **Experimental Procedure**

Steel exposed to the environment is covered with paint to protect it from corrosion. A primer is applied as the first barrier to corrosion followed by a finish top coat. Zinc pigments and compounds are added to primers to act as a cathodic type corrosion inhibitor. Direct contact with the steel surface is needed for the zinc to fully function. The most common type of primers are two- part polyamide epoxy's.

The Corps of Engineers gave a contract to Surtreat to investigate the addition of vapor phase migratory corrosion inhibitors to a primer used by the military as was specified in the contract.

A process was developed for addition of an organic amine carboxylate type of vapor phase inhibitor to Part A to a two part epoxy- polyamide paint primer, MIL-DTL 24441 Formula 150 Type III, in an amount, such that the dry film formed when Parts A and B are combined will contain 2.5 wt. % of the inhibitor. The primer with and without inhibitor was applied to abraded ASTM A1008 steel panels in both the white and corroded states at an average dry film thickness of 2.5 mils. One side of the coated panels are cross scribed to measure the degree of creep per ASTM D1654. The coated panels were place in a salt fog chamber, ASTM B117, for 500 hours and then removed and graded with respect to the degree of rust formation on scale of 0 to 10 in accordance with ASTM D610 and the degree of creep.

### **Results and Discussion**

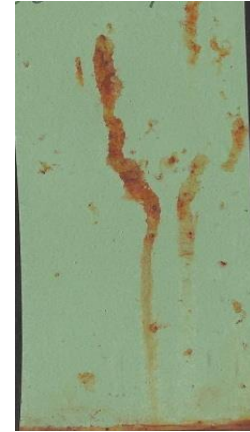
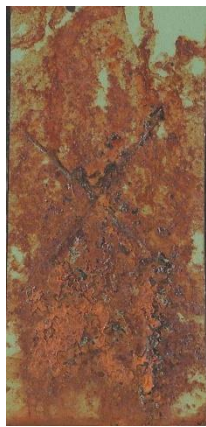
Appearance of the panels after exposure are shown on Figures 2 and 3. The 2 panels on left side are scribed and the 2 on the right are the un-scribed reversed sides.

VCI ADDED AT 2.5%

WITHOUT VCI

VCI ADDED AT 2.5%

WITHOUT VCI



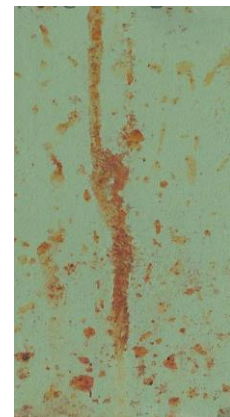
**Figure 2: Polyamide epoxy primer on abraded white steel with and without vapor phase corrosion inhibitor added after 500 hours in salt fog chamber**

VCI ADDED AT 2.5%

WITHOUT VCI

VCI ADDED AT 2.5%

WITHOUT VCI



**Figure 3; Polyamide epoxy primer on abraded corroded steel with and without vapor phase corrosion inhibitor added after 500 hours in salt fog chamber**

Table 1 presents the numerical rating of the panels with and without inhibitor added

**TABLE 1**

**Performance Rating For Degree of Creep and Rust on Coated Panels With And Without Migratory Inhibitor Added**

TEST PANEL CONDITION	WITHOUT INHIBITOR			WITH INHIBITOR		
	Creep	Degree of Rust X Scored Flat Side		Creep	Degree of Rust X Scored Flat Side	
Abraded White Steel	5	1	4	7	7	9
Abraded Corroded Steel	3	1	3	6	6	9

It is apparent from both the pictures and numerical rating of the panels that addition of the migratory inhibitor to the primer has made a significant improvement in resistance to corrosion. The fact that the degree of corrosion protection is almost equal on white and corroded steel is an indication that the inhibitor has migrated through the layer of rust and inhibited further corrosion on the white steel surface.

**CONCLUSIONS**

Three examples have been given of the application of two types of migratory corrosion inhibitors on reinforced concrete with measurement of corrosion rate before and after application using two types of corrosion current measurement. The average corrosion rates were decreased by a factor of three due to application of the inhibitors, and continue to decrease with time. There are two primary classes of migratory corrosion inhibitor active ingredients, inorganic anodic and organic dual function. Two of the organic types are amine carboxylates and amine alcohols. Two of the inorganic type are silicates and nitrites. These can take several forms and be formulated to optimize penetration and performance and can be used alone or in combination. Two types of the inorganic and organic inhibitors were tested alone and gave similar results as shown in the NASA experiment. It is critical that the inhibitor formulation active ingredients are penetrated into the concrete cement where they can migrate in the gel pore structure and reach rebar level. This is why in the examples water is applied to the surface to drive all ingredients into the surface. Calculation of the loss of rebar steel over time with respect to the corrosion rate shows that reduction of rebar corrosion rate by application of migratory corrosion inhibitors can significantly extend the life of a reinforced concrete structure

A vapor phase migratory inhibitor was formulated into a steel surface coating primer. The primer coating was applied to steel panels with and without the inhibitor and exposed in an accelerated corrosion environment. Reduction in the degree of corrosion by inhibitor addition was visually observed and supported by measurement procedures. The reduction in corrosion on rusty steel panels is do the ability of the corrosion inhibitor to migrate through the rust layer and inhibit further corrosion on the white steel substrate.

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