MEASURING THE EFFECTIVENESS OF MIGRATING CORROSION INHIBITORS (MCIs) BY ELECTROCHEMICAL TECHNIQUES

By

Paul Vrkljan
Alla Furman
Christophe Chandler
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

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ABSTRACT

Metal reinforcing bars for concrete structures are susceptible to corrosion due to contamination from factors such as chloride presence and carbonation effects. Several ways to provide protection to the steel have been devised: cathodic protection, protective coatings, and corrosion inhibitor admixtures added to the concrete. This paper is aimed at studying a type of admixtures, namely migrating corrosion inhibitors (MCI).

Vapor and migrating corrosion inhibitors can make use of the porosity of concrete. Conventional inorganic contact inhibitors need a liquid carrier to reach the metal. MCIs reach the surface of reinforcing steel while moving through the porous structure of concrete.

Electrochemistry and other methods were used to evaluate the effectiveness of the corrosion inhibiting ability of MCIs. Their usefulness and limitations are discussed. The results of laboratory and independent tests for a new generation of MCIs combined with field experience of their applications is also presented.

Keywords: migrating corrosion inhibitors, vapor corrosion inhibitors, concrete, rebar, corrosion test, electrochemical test, polarization curves, impedance spectroscopy, ASTM test methods, aminocarboxylates, salts of oxycarbonic acids.

INTRODUCTION

The use of reinforcing steel to improve the physical properties of concrete has been an accepted practice for many years. With this technique follows the technique of protecting the reinforcing steel in the concrete matrix from corrosive media and deterioration of the concrete covering. A breakdown in the concrete cover can be in the form of cracks which provides a direct route for chlorides, sulfates and carbonates to the reinforcing steel. This becomes more common as the age of the structure increases. Cracks can quickly change the environment surrounding the steel from protective to corrosive in a relatively short time. The rate of change is related to but is not limited to the external environment (industrial, marine, etc.). Wide variations in the temperature would make a significant impact on the destruction of the concrete and an increase in the corrosion rate of the reinforcing steel. The traditional methods of protection range from cathodic protection, coating the reinforcing steel, adding inhibitors to the concrete or a combination of these methods.

This paper is devoted to the study of Cortec's MCIs (Migrating Corrosion Inhibitor) [1-4] through their effectiveness as a corrosion inhibitor. This paper also looks at the effects of this corrosion inhibitor on the plastic properties of concrete.

The goal of this study is to suggest an additive to concrete which has the ability to provide corrosion protection to reinforcing steel.

EXPERIMENTS

A sufficient complex of the test methods was used to evaluate the effectiveness of the corrosion inhibiting admix. All of the tests were divided into:

1. Screening tests
2. Testing in concrete

1. Screening test methods:

An immersion test was performed at room temperature using an electrolyte solution of 3.5% NaCl(pH 10.5, adjusted by adding NaOH). Panels (carbon steel SAE 1010) and sections of rebar were used as specimens. The results were evaluated by recording the time before corrosion was visible on the specimens in solution and these results were compared to the control without inhibitors (Table 1.).

Polarization curves were obtained using the Potentiastat/Galvanostat "Versastat" from EG&G Company with corrosion software SoftCorr™ 252/352 in a 3.5% NaCl/pH 10.5 solution with the following electrodes:

Working:	Carbon steel SAE 1010
Reference:	Calomel saturated
Counter:	High density graphite

Polarization curves were obtained using two techniques: Tefel plots and cyclic polarization [5] . Tafel plots were obtained for the evaluation of the corrosion rates. Cyclic polarization curves show the characteristics of the tendency to pitting corrosion.

Also used as a screening test was "Test Method of Salt Water Immersion Test for Reinforced Steel" (JIS-A6205) [6]. According to this test, sanded, degreased, and cleaned rebars are half-immersed in a solution containing:

Material	**% Weight**
Sodium chloride: NaCl	0.500
Magnesium chloride: $MgCl_2 \times 6H_2O$	0.200
Sodium sulfate: Na_2SO_4	0.080
Calcium chloride: $CaCl_2$	0.030
Potassium chloride: KCl	0.015
Calcium hydroxide: $Ca(OH)_2$	0.600

Duration of the test was 8 days. The corrosion potential was measured using a silver chloride saturated electrode as a reference. The condition of the surface of the rebars was visually evaluated after 8 days.

2. Testing in concrete:

After the screening tests of the inhibitor in solution it was studied in concrete by electrochemical impedance measurement [7,8]. The concrete specimens were prepared:

Material	**MCI-2005 (parts)**	**Control (parts)**
Portland cement	1	1
Sand	2	2
Water	0.45	0.45
MCI-2005	0.0036	-

The geometry of the samples is shown in Figure 1. The impedance measurements were carried out after 2, 8, and 12 weeks after soaking the specimens in a 3% NaCl solution the samples using the EIS900 system from Gamry Instruments. The impedance plots were obtained in a potentiostatic regime in a 3% sodium chloride solution using the imbedded rebar as working electrode. Saturated Colomel electrode as reference and high density graphite as a counter electrode. Results are presented in the form of Bode plots/absolute value of impedance $|Z|$. vs. frequency.

The effect of MCI-2005 on the corrosion of embedded steel reinforcement according to ASTM G109 were studied by an independent laboratory.

The physical properties of concrete treated with MCIs were examined. An independent laboratory tested for slump, air content, set times and compressive strength.

MCI-2005 was added to the concrete mix at a dosage of 1.5 pints per cubic yard or l liter per cubic meter. Table 4 shows the plastic properties of concrete with this corrosion inhibiting admixture compared to a control concrete mix with no inhibitor. While table 5 compares the compressive strength of concrete with MCI-2005 and concrete with no inhibitor after 7 and 28 days of curing.

RESULTS

1. Screening tests:

Immersion test data is presented in Table 1.

Table 1
Immersion Test Data, Visual Inspection

Product, % Weight in 3.5% NaCl(pH 10.5	**Time Before Corrosion (Days)**	
	Carbon steel panel	Reinforcing steel bars
0.8% MCI-2005	>60	>15
Control	<1	<1

MCI-2005 stopped corrosion from occurring on the carbon steel panels for more than 60 days compared to the control's steel panel that corroded in less than one day. The reinforcing steel bars corroded more quickly with the MCI-2005 treated bar corroding after 15 days and the control bar corroding in less than one day.

The polarization curves (Tafel and cyclic polarization plots) are presented in Figures 2 and 3, and the corrosion rates calculated from Tafel plots are presented in Table 2.

Table 2.
Electrochemical evaluation data, calculated using Tafel plots

Product, % in 3.5% NaCl (pH 10.5)	Corrosion Rate (mpy 10^3)	Coef. of Inhibitor	Z, %, Protective Ability
0.8% MCI-2005	**0.64**	**120**	**99.2**
Control	**76.31**	**-**	**-**

Coefficient of inhibition $\gamma = \frac{\delta c}{\delta i}$

Protection Ability $Z = \frac{\delta c - \delta i}{\delta c} \times 100\%$, where

δc = Corrosion rate in control solution
δI = Corrosion rate in inhibited solution

The data presented in Figure 2, which corresponds to that of Table 2, shows that adding MCI-2005 affects both anodic and cathodic electrochemical reactions and reduces the corrosion rate ($\gamma = 120$, $Z = 99.2\%$).

The data presented in Figure 3, are curves obtained using the cyclic polarization technique. The smaller size of the hysteresise loop of the MCI-2005 polarization curve in comparison with the control curve signifies the lower pitting tendency [9]. This is confirmed by the corrosion testing in which no pitting was visually observed on the MCI-2005 treated metal.

Table 3.
Corrosion potential measurements and
visual evaluation according to JIS-A6205

	Natural Electrode Potential, mv (-) Each Day								
Product, % Weight in 3.5% NaCl (pH 10.5)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Presence of Corrosion after 8 Days**
0.8 % MCI-2005	467	497	500	500	500	500	500	500	No Corrosion
Control	695	710	710	715	715	720	720	720	Corrosion

MCI-2005 meets the Japanese standard that specifies no corrosion after eight days in their accelerated conditions. One could notice that the level of corrosion potential of the treated sample is relatively neutral. It does not mean that the sample corroded, but the nature of MCI-2005 is to affect anodic and cathodic electrochemical reactions, which makes the corrosion potential stay negative, however the corresponding corrosion current (icorr) is significantly reduced.

2. Testing in concrete:

Concrete specimens, because of their high electrical resistivity, are studied using AC, and DC. The data of the electrochemical impedance which is presented in Figure 4 was obtained after 2 weeks, but they did not change after 8 or 12 weeks after soaking the specimens in a 3% NaCl solution. This data (Bode plots) shows that the MCI-2005 treated specimen has a higher absolute value of impedance /Z/ vs. frequency than the control. Because the measured electrochemical impedance /Z/ includes the resistance to the electrochemical reaction, a higher level of impedance /Z/ confirms the lower rate of electrochemical corrosion on the specimen treated with MCI-2005.

The results of the testing for the plastic properties of both concrete with and without corrosion inhibitors are as follows. The concrete was of a standard mix design with a water-to-cement ratio of 0.5.

Table 4.
Plastic properties of concrete study

Plastic Properties		
Inhibitor	none	MCI-2005
Set time initial	4:15	9:05
final	5:45	12:00
Slump, in	3¾	3¾
Air %	5.7	8.2

The set time of the MCI-2005 treated concrete was twice that of the control taking 12 hours for the final set. The air content of the concrete treated with MCI-2005 showed a 40% increase compared to the control sample while the slump values were the same. Adjustments could be made to the mix design to compensate for the changes found in Table 4. by adding a chloride free accelerator and by reducing or completely removing the air entraining agent.

Table 5.
Compressive strength of concrete study

Compressive Strength		
Inhibitor	none	MCI-2005
7 days, psi	5997.3	3916.1
28 days, psi	7658.0	7803.1

The early strength of the MCI-2005 treated concrete was about 2,000 psi lower than the control after 7 days. At 28 days there was a 2,145 psi swing in strength value where the MCI-2005 treated concrete posted a value of 145 psi higher than the control.

CONCLUSION

Results presented in this paper confirm the idea of using migratory and vapor corrosion inhibitors to protect reinforcing steel concrete from corrosion. MCI-2005 has been proven to provide corrosion protection to carbon steel reinforcement that was embedded in concrete and together was immersed in a salt contaminated environment. These results were confirmed through the use of corrosion and electrochemical techniques.

However a side effect of providing corrosion protection is a change in the plastic properties of the concrete mix and the strength. These changes include; an increase of the setting time, more than doubling it, an early reduction of the compressive strength but an increase of the final strength values and an increase in the air content. Adjustments can be made by adding a commercial accelerator and by removing the air entraining agent from the mix design.

CAPTIONS

Figure 1: Concrete specimen

Figure 2: Polarization curves, Tafel technique
1. MCI-2005
2. Control

Figure 3: Polarization curves, cyclic polarization technique
A. MCI-2005
B. Control

Figure 4: Electrochemical impedance, Bode plots

Table 1: Immersion test data, visual evaluation

Table 2: Electrochemical evaluation data, calculated using Tafel plots

Table 3: Corrosion potential measurements and visual evaluation according to JIS-A6205

Table 4: Plastic properties of concrete study

Table 5: Compressive strength of concrete study

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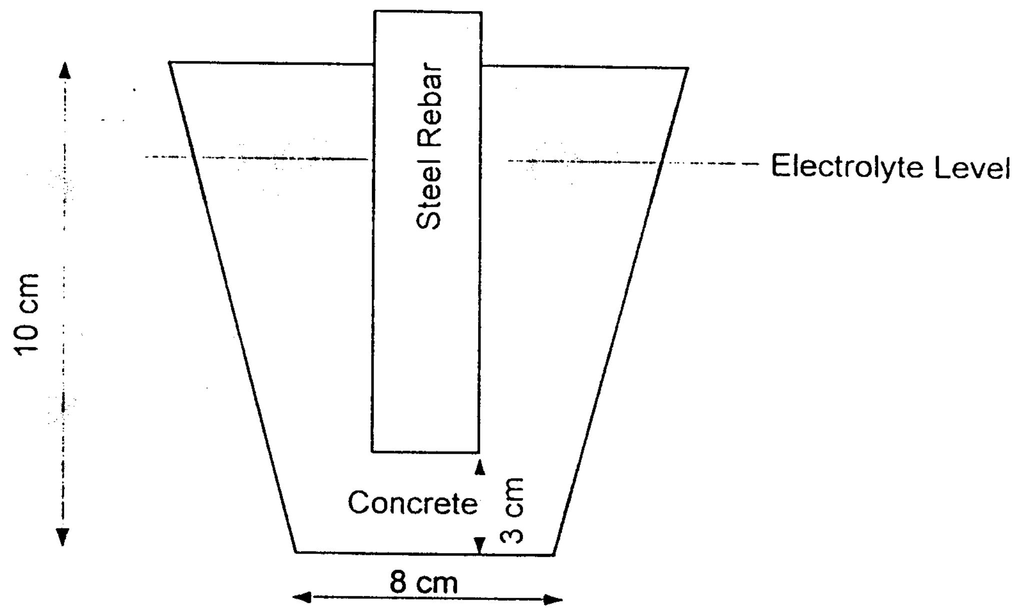

Figure 1. Concrete specimen used in this study.

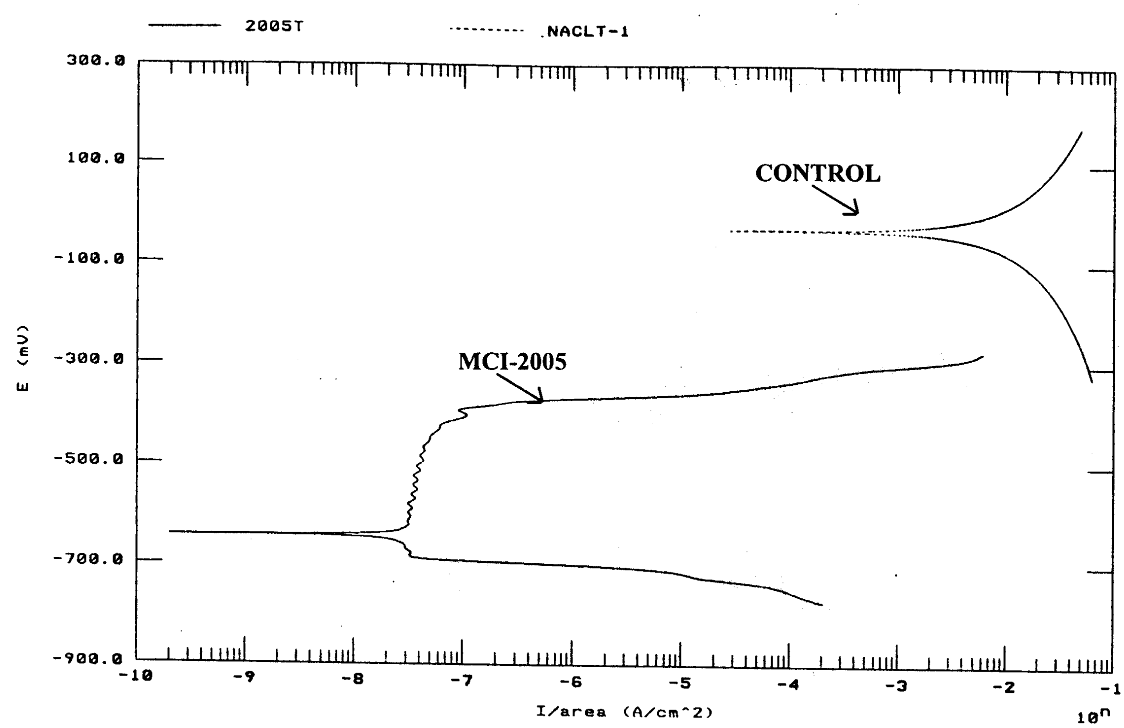

Figure 2. Tafel plots of solutions with and without MCI-2005.

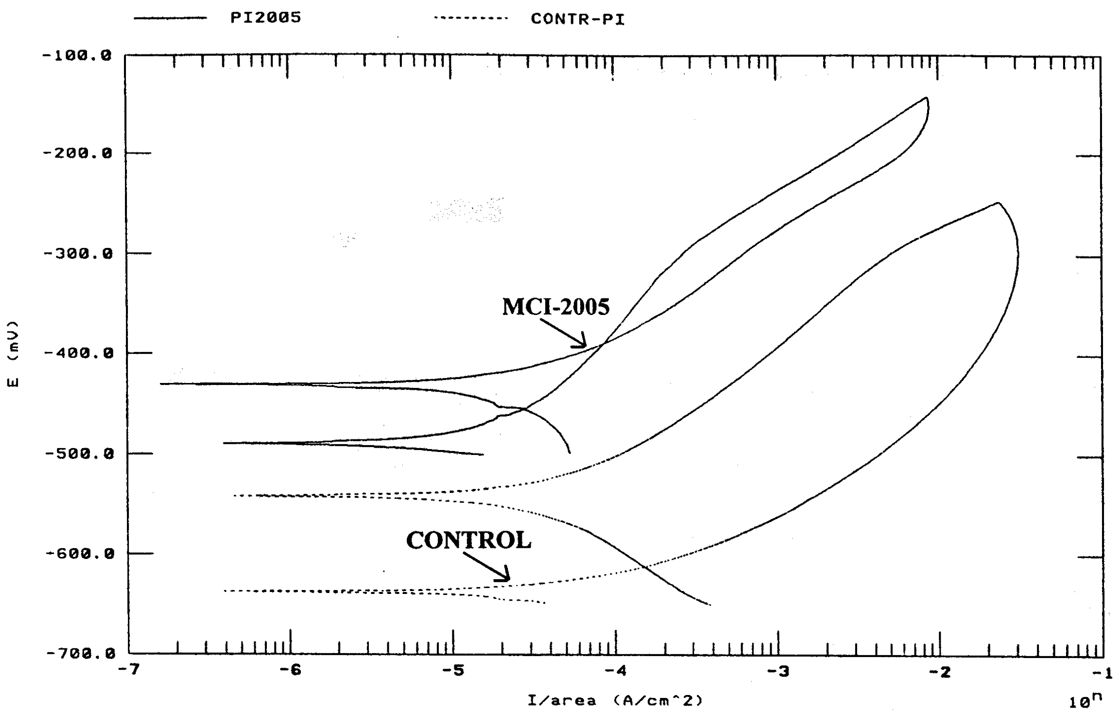

Figure 3. Cyclic polarization plots of solutions with and without MCI-2005.

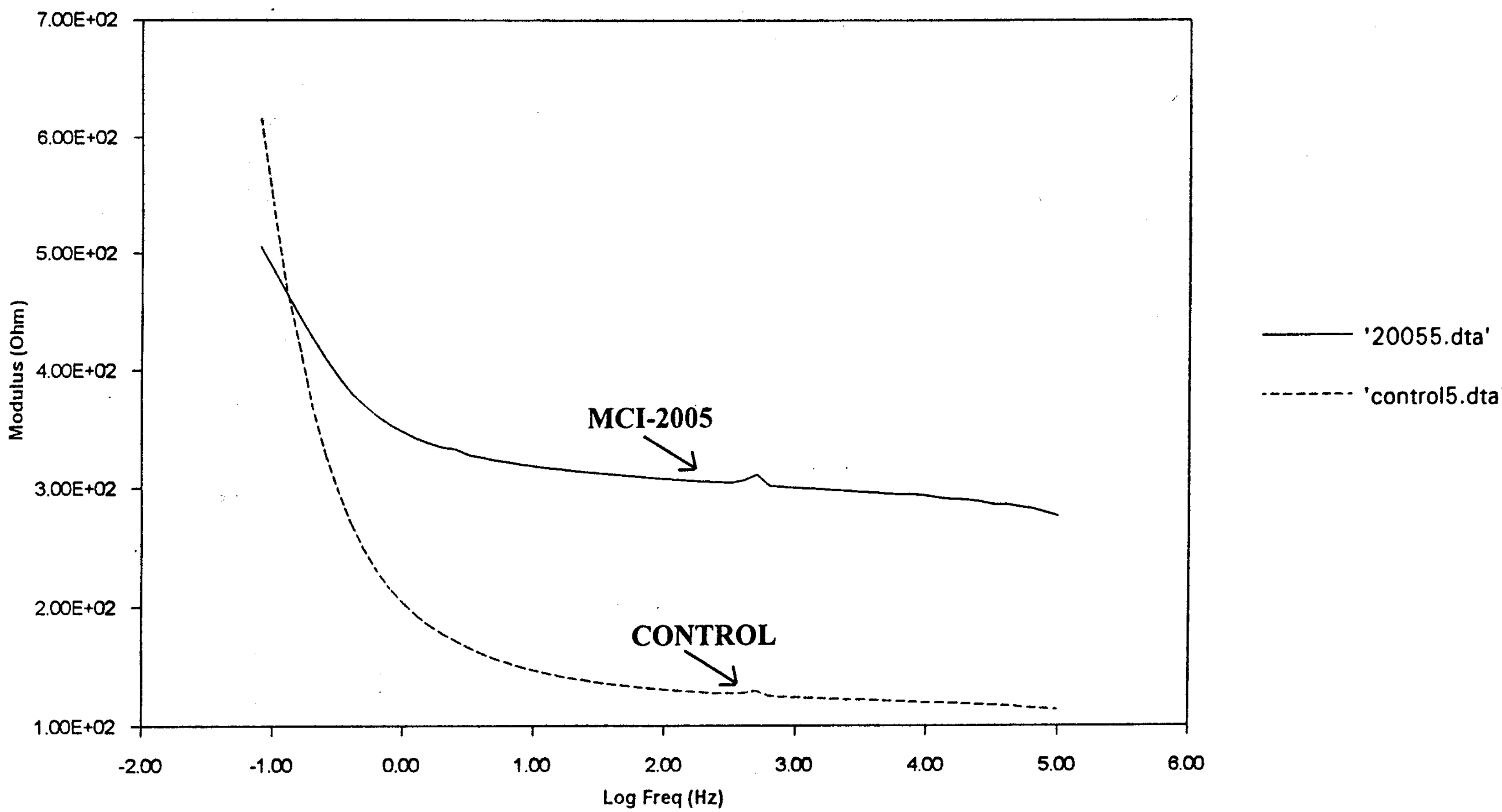

Figure 4. Electrochemical impedance measurements of reinforced cement with and without MCI-2005.