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SUGAR BEETS AGAINST CORROSION

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ABSTRACT

Every year several billion dollars are spent to repair and maintain reinforced concrete structures. Over time, the metal reinforcing bars used to improve the physical properties of concrete become susceptible to corrosion due to factors such as the presence of chloride and carbonation. There are several methods to mitigate corrosion of the steel rebars. These techniques include the use of sealants, cathodic protection and inhibitors. Organic corrosion inhibitors have been developed from the fermentation products of sugar beets. One of the main features of these new products is their ability to migrate through concrete and reach the corroding metals. A reduction of the corrosion rate is obtained once the inhibitors access the surface of the metal. This work presents test results from studies of the effectiveness of these environmentally friendly corrosion inhibitors. Field applications are also reviewed.

INTRODUCTION

Reinforcing steel corrosion

Reinforcing steel has been used to improve the physical properties of concrete for many years. However, a breakdown in the concrete cover in the form of cracks can lead to the rapid deterioration of the structure. Cracks can quickly change the environment surrounding the steel from protective to corrosive in a relatively short time by providing a direct route for corrosive agents such as chlorides, sulfates and carbonates. Another problem is carbonation. Due its alkaline nature, concrete reacts with carbonic acid formed by the dissolution of atmospheric carbon dioxide in water found in the concrete mass. The reaction eventually leads to a lower pH where the reinforcing steel rebar is susceptible to corrosion.

Corrosion prevention

The prevalent protection methods are cathodic protection, using pore blockers, applying a coating on the reinforcing steel, adding inhibitors to the concrete or a combination of these methods.

Migrating corrosion inhibitor

Migrating corrosion inhibitors (MCIs) use the porosity of concrete to diffuse through the structure. Admixtures based on 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.

This diffusion process requires a period of time to migrate through the concrete's pores. Most MCIs are based on amino-carboxylate chemistry. They act as cathodic and anodic corrosion inhibitors. Once the MCIs migrate to the rebar's surface, a protective layer is formed. This suggests that the migratory inhibitors are physically adsorbed onto the metal surfaces *I1I*.

Chemical admixtures have been combined with concrete as a possible means of preventing chloride ions from reaching the steel's surface. Inhibitors have the effect of promoting a passive layer at the steel's surface, which prevents its reaction with the chloride ions.

Furthermore, laboratory tests have proven that MCI corrosion inhibitors migrate through the concrete pores and protect internal steel bars against corrosion even in the presence of chlorides /3,4/.

Derivatives from beets

Corrosion inhibitors vary in their chemical nature and mechanism of protection. The basic component of MCI is the organic compound obtained from the derivatives of beets.

Corrosion testing

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 are also presented.

EXPERIMENTAL

Migrating corrosion inhibitors (MCIs) were studied. Several test methods were used to evaluate the effectiveness of the corrosion inhibiting admixture:

- **Immersion test:**

An immersion test was performed at room temperature using a solution of 3.5% NaCl (pH 12-13, adjusted by adding $Ca(OH)_2$). Panels (carbon steel SAE 1010) and sections of rebar were used as test samples. The corrosion protection was evaluated by recording at what time corrosion was visible on the samples in solution, and these results were compared to the control without inhibitors (Table 1).

- **Electrochemistry:**

Polarization curves were obtained using the potentiostat/galvanostat "Versastat" (from EG&G Company) controlled with the corrosion software SoftCorr™ 252/352 (from EG&G Company) in a 3.5% NaCl with a pH 12-13 adjusted by addition of Ca(OH)2 solution. The working electrode was made of carbon steel SAE 1010. A Standard Saturated Calomel served as the reference electrode while high density graphite was used as the counter electrode.

Corrosion rates were determined from Tafel, while pitting corrosion tendencies were analyzed using cyclic polarization curves.

- **'Test Method of Salt Water Immersion Test for Reinforced Steel'**

(JIS-A6205) /6/ was utilized. According to this test method, 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 . 0 8 0
Calcium chloride: $CaCl_2$	0 . 0 3 0
Potassium chloride: KC1	0 . 0 1 5
Calcium hydroxide: Ca(OH)2	0.60 for
Water	100%

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

• **Electrochemical Impedance Spectroscopy.**

MCI performance in concrete was studied by electrochemical impedance measurement /7,8/. The specimens were prepared using the following mix design:

Material	**Sample with MCI**	**Sample w/o MCI**
Portland cement	**1**	**1**
Sand	**2**	**2**
Water	**0.45**	**0.45**
MCI	**0.0036**	**-**

The geometry of the samples is shown in Figure 1. The sample was immersed in 3% NaCl solution for 20 hours and then the impedance measurements were carried out in a potentiostatic regime using the imbedded rebar as working electrode. Saturated calomel electrode was used 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).

• **ASTM G 109 Standard Test Method** for Determining the Effect of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environment

MCI was added to the concrete mix at a dosage of 1.5 pints per cubic yard, or 0.85 liter per cubic meter. Table 4 shows the plastic properties of concrete with this corrosion inhibiting admixture compared to 'control' concrete mix with no inhibitor. Table 5 compares the compressive strength of concrete with MCI-A and concrete with no inhibitor after 7, 28 days and 6 months of curing.

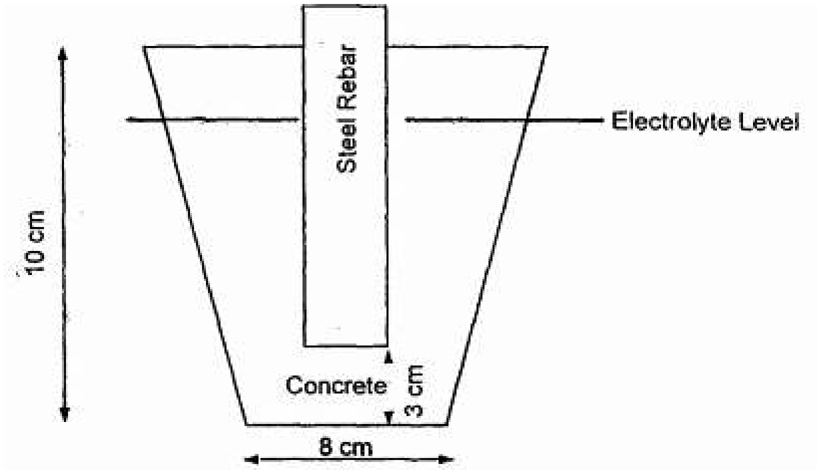

Fig. 1: Concrete specimen used for EIM measurements.

RESULTS

Immersion test data is presented in Table 1. According to this test MCI 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 in 15 days in the MCI treated solution and the 'control' bar started to corrode in less than one day.

Table 1
Protective properties of MCI according to immersion test data.

	Time Before Corrosion (Days)	
Material	**Carbon steel panel**	**Reinforcing steel bars**
0.8% MCI-A	**>60**	**>15**
'Control'*	**<1**	**<1**

* No inhibitor in the testing solution

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

Protective properties of MCI according electrochemical evaluation data (calculated using Tafel plots)

Material	Corrosion Rate	Coef. of	Z, % Protective
0.8% MCI-A	0.64	120	99.2
'Control'*	76.31	-	-

*No inhibitor in the testing solution

Coefficient of inhibition

$$\gamma = \frac{\delta c}{\delta i}$$

Protection Power

$$Z = \frac{\Delta c - \Delta i}{\Delta c} X100\%$$

, where

Δc = Corrosion rate in control solution

ΔI = Corrosion rate in inhibited solution

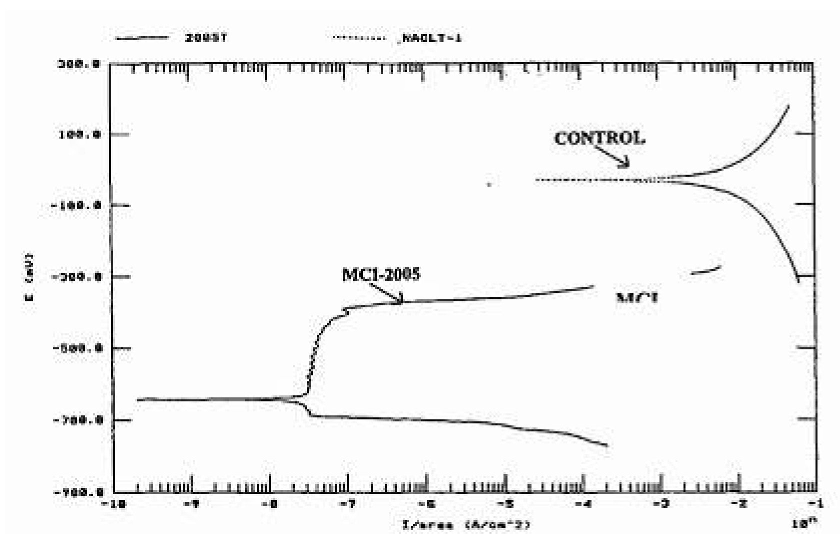

Fig. 2: Tafel plots obtained in 3.5%NaCL, pH 12-13 solutions with and without MCI

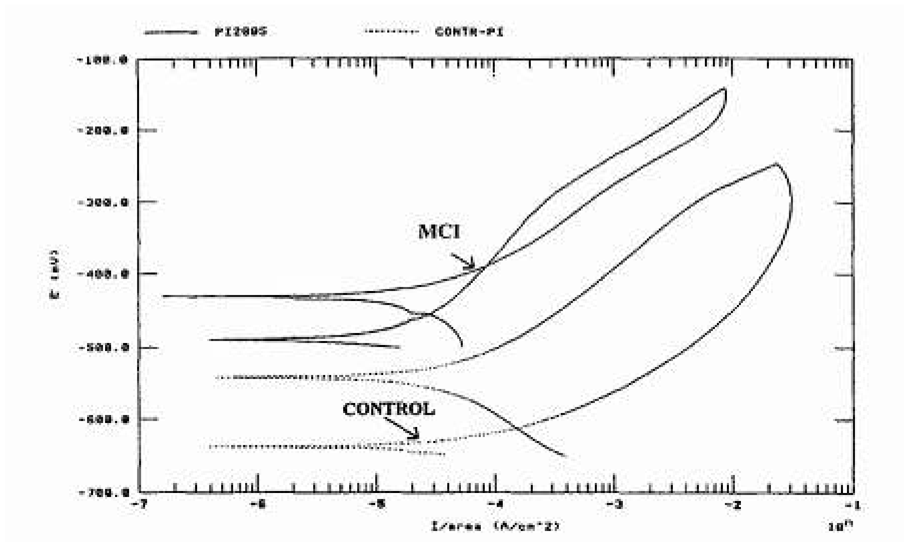

Fig. 3: Cyclic polarization plots obtained in 3.5%NaCl, pH 12-13 solutions with and without MCI

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

The data presented in Figure 3 are curves obtained using the cyclic polarization technique. The smaller size of the hysteresis loop of the MCI polarization curve in comparison with the control curve signifies the lower pitting tendency *191*. This is confirmed by corrosion testing in which no pitting was visually observed on the MCI treated metal.

MCI meets the requirements of the Japanese industrial standard (JIS-A6205) that specifies no corrosion after eight days in their accelerated conditions. One could notice that the level of corrosion potential of the MCI-treated sample is relatively steady for 8 days, while the corrosion potential of 'control' sample becomes more negative. Consequently, no visible corrosion was found on the MCI-treated sample, but the 'control' sample had pitting corrosion.

Testing in Concrete

Concrete specimens, because of their high electrical resistivity, are studied using AC and DC. This data (Bode plots) shows that the MCI treated

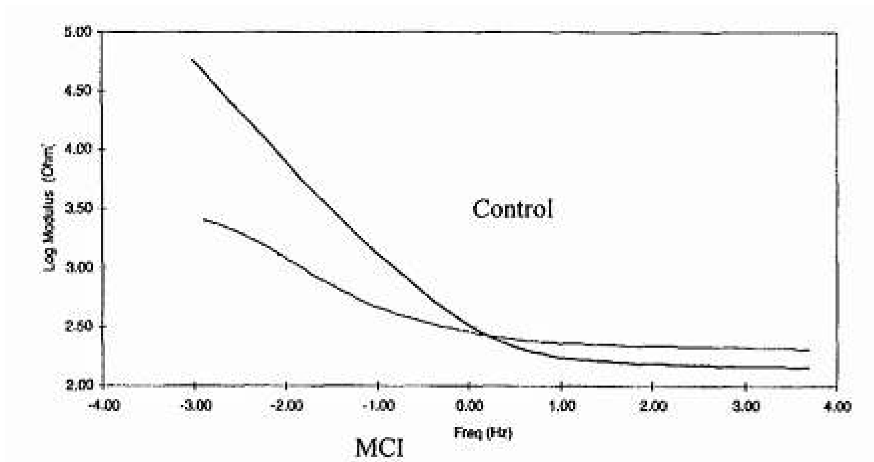

Fig. 4: Electrochemical impedance specters (EIS) with and without MCI

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.

The results of the testing for the plastic properties of both concrete with and without corrosion inhibitors are shown in Table 4. The concrete was of a standard mix design with a water-to-cement ratio of 0.5.

The set time of the MCI treated concrete was twice that of the control taking 12 hours for the final set. The air content of the concrete treated with MCI 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).

Table 3

Corrosion potential measurements and visual evaluation according to JIS-A6205

	Corrosion Potential (-Ecorr), mV, Daily								
Material	1	2	3	4	5	6	7	8	Presence of Corrosion after
0.8 % MCI-A	467	497	500	500	500	500	500	500	No Corrosion
Control	695	710	710	715	715	720	720	720	Corrosion

Table 4

Plastic Properties of Concrete.

Properties	Without MCI	With MCI
Set time initial	4:15	9:05
Set time final	5:45	12:00
Slump, in	*3 ¾*	*3 ¾*
Ai,r %	5.7	8.2

Table 5

Compressive Strength of Concrete

Compressive Strength	Without MCI	With MCI
After 7 days, psi	5997.3	3916.1
After 28 days, psi	7658.0	7803.1

The early strength of the MCI 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 treated concrete posted a value of 145 psi higher than the control.

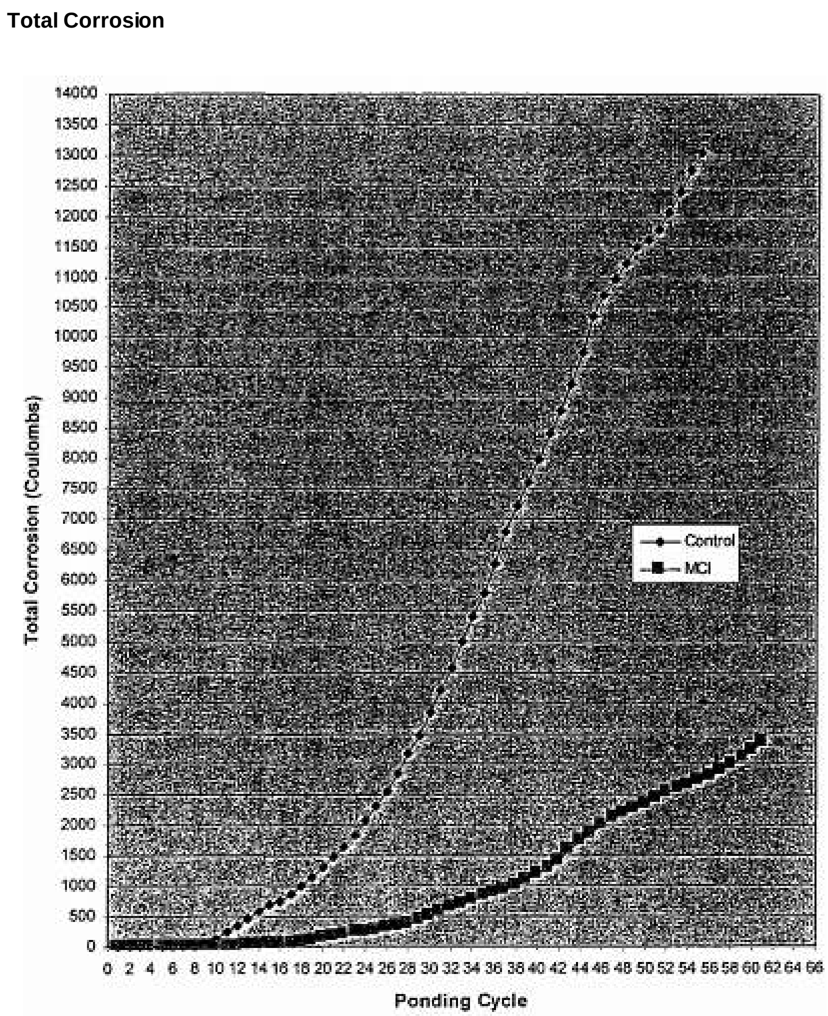

Fig. 5: Evaluation of MCI performance according to ASTM G-109

APPLICATION

MCI manufactured from the derivatives of beets is in compliance with ANSI/NSF Standard 61: Drinking Water System Components - Health Effects.

CONCLUSION

Results presented in this paper confirm the idea of using the derivatives of beets as the components of migratory corrosion inhibitors to protect reinforcing steel concrete from corrosion. MCIs have been proven to provide corrosion protection to carbon steel reinforcement that was embedded in concrete and 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.

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