Improving Durability of Reinforced Concrete Structures using Migrating Corrosion Inhibitors

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Abstract

Corrosion creates long term reliability issues for reinforced concrete structures. Billions of dollars have been spent on corrosion protection of concrete and steel bridges, highways, and reinforced concrete buildings. Among the commercial technologies available today, migrating corrosion inhibitors (MCIs) show versatility as admixtures, surface treatments, and in rehabilitation programs. The effectiveness of the MCIs (mixture of amine carboxylates and amino alcohols) on reinforced concrete was evaluated throughout this project. Corrosion test results conducted over 1500 days, 200 cycles per ASTM G109) using immersion and ponding in 3.5% NaCl solution indicated that polarization resistance (R_p) for the MCI coated concrete was higher (60-80 kohms-cm^2 with increasing trends) than non-coated concrete. The untreated not only had lower R_p values, but also decreasing trends. Examination of the embedded steel rebar after corrosion tests showed no corrosion attack for the MCI treated concrete samples, while non-treated concrete showed corrosion. X-ray photoelectron spectroscopy (XPS) and depth profiling confirmed that the inhibitor had reached the rebar surface in less than 150 days. Depth profiling showed an amine-rich compound on the rebar surface that corresponded with the increase in R_p and improved corrosion protection for the MCI treated steel rebar even in the presence of chloride ions. Based on measured corrosion rate the life expectancy of a concrete reinforced structure can be improved by more than 40 years.

1. Introduction

Corrosion is one of the main concerns in the durability of materials and structures. Much work has been done to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages in new structures. Carbon steel is one of the most widely used engineering materials despite its relatively limited corrosion resistance. Iron in the presence of oxygen and water is thermodynamically unstable, causing its oxide layers to break down. Corrosion undermines the physical integrity of structures, endangers people and the environment, and is very costly. Because carbon steel represents the largest single class of alloys used [1], corrosion is a huge concern. The billions of dollars committed to providing protective systems for iron and steel have provided new ways of combating corrosion. Migrating corrosion inhibitors (MCIs) are one means of protection for reinforced concrete structures. Previous studies have established the benefits of using migrating corrosion inhibitors, the importance of good concrete, and the significance of the ingredients used to make the concrete [2-6]. Reinforcing steel embedded in concrete shows a high amount of resistance to corrosion. The cement paste in the concrete provides an alkaline environment that protects the steel from corrosion by forming a protective ferric oxide film. The corrosion rate of steel in this state is negligible. Factors influencing the ability of the rebar to remain passivated are the water to cement ratio, permeability and electrical resistance of concrete. These factors determine whether corrosive species can penetrate through the concrete pores to the rebar oxide layer. In highly corrosive environments (coastal beaches and areas where deicing salts are common), the passive layer will deteriorate, leaving the rebar vulnerable to chloride attack, thereby requiring a corrosion prevention system.

Migrating Corrosion Inhibitor (MCI) technology was developed to protect the embedded steel rebar/concrete structure. Recent MCIs are based on amino carboxylate chemistry and the most effective types of inhibitor interact at the anode and cathode simultaneously [2]. Organic inhibitors use compounds that work by forming a monomolecular film between the metal and the water. In the case of film forming amines, one end of the molecule is hydrophilic and the other hydrophobic. These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement forming a barrier [3, 7, 14]. Migrating corrosion inhibitors are able to penetrate into existing concrete to protect steel from chloride attack. The inhibitor migrates through the concrete capillary structure, first by liquid diffusion via the moisture that is normally present in concrete, then by its high vapor pressure and finally by following hairlines and microcracks. The diffusion process requires time to reach the rebar's surface and to form a protective layer. MCIs can be incorporated as an admixture or can be surface impregnated on existing concrete structures. With surface impregnation, diffusion transports the MCIs into the deeper concrete layers, where they will inhibit the onset of steel rebar corrosion. Laboratory tests have proven that MCI corrosion inhibitors migrate through the concrete pores to protect the rebar against corrosion even in the presence of chlorides [4, 5].

2. EXPERIMENTAL PROCEDURES

This study focused on the usefulness of inhibitors and their means of application. Concrete samples were cast (dimensions 280 mm x 110 mm x 150 mm per ASTM G109 and 100 mm x 100 mm x 250mm for immersion tests) using commercial grade silica, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate). Five samples (low density concrete at 2.08 g/cm^3) were prepared with a 0.65 water/cement ratio and five samples (high density concrete at 2.40 g/cm^3) were prepared using a 0.35 water/cement ratio. All samples had three class 60 steel rebar (with dimensions of 381 mm length, 12.5 mm diameter) and were referenced to a $Cu/CuSO_4$ electrode (Figure 1a). The rebar coverage layer was maintained at 25.4 mm of concrete. Concrete compressive strengths ranged about 21 MPa after 28 days of curing for the low density samples and 26 MPa for the high density. Migrating corrosion inhibitors, MCI 2020, MCI 2020M, and MCI 2022 (sealer) were applied to the concrete surface. The objective was to study the corrosion inhibiting properties and to determine whether these inhibitors protect the steel rebar. Due to the low conductivity of concrete, the corrosion behavior of steel rebar was monitored using electrochemical impedance spectroscopy

(EIS) was applied while samples were immersed in 3.5% NaCl at ambient temperatures. Effectiveness of this MCI product was based on changes in the polarization resistance and the corrosion potential of the rebar, measurements that can be performed without destroying the sample. This data can provide early warning of structural distress and evaluate the effectiveness of corrosion control strategies that have been implemented. Once rebar corrosion has proceeded to an advanced state, where its effects are visually apparent on the concrete surface, it is too late for minor patchwork. The key to fighting corrosion is in preventative measures.

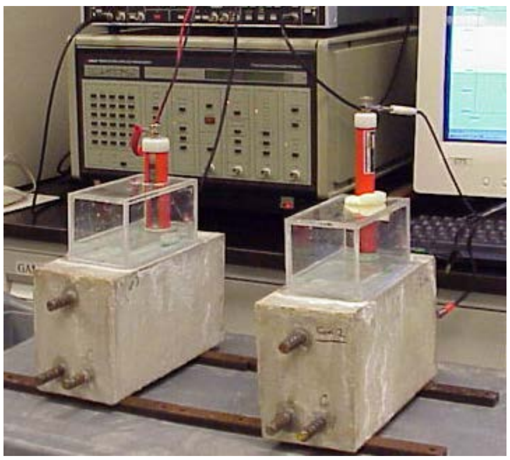
a)  b) 

Figure 1: **a)** Concrete samples prepared per ASTM G109; **b)** concrete samples modified for continuous immersion [8].

The experiments were conducted using Gamry EIS300 software and Echem Analyst. Bode and Nyquist plots were created from the data obtained using the single sine technique. Potential values were recorded and plotted with respect to time. By comparing the bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the R_p value over time. To verify this analysis, the R_p values were also estimated by using a curve fit algorithm on the Nyquist plots (available in the software). In these plots, the R_p and R_Ω combined values are displayed in the low frequency range of the bode plot and the R_Ω value can be seen in the high frequency range of the bode plot. The diameter of the Nyquist plot is a measure of the R_p value.

In this investigation, the steel rebar/concrete combination is treated as a porous solution and modeled by a Randles electrical circuit [9]. EIS tests performed on a circuit containing a capacitor and two resistors indicate that this model provides an accurate representation of a corroding specimen. Electrochemical impedance technique has been widely used as a corrosion measurement tool. A number of publications have reviewed both the theory and many areas of application [10-12]. EIS tests, by means of a small amplitude signal of varying frequency, give fundamental parameters relating to the electrochemical kinetics of the corroding system. The values of concern in this study are R_p and R_Ω. The R_p value is a measure of the polarization resistance or the resistance of the surface of the material to corrosion. R_Ω is a measure of the solution resistance to the flow of the corrosion current. By monitoring the R_p value over time, the relative effectiveness of the sample against corrosion can be determined. If the specimen maintains a high R_p value in the presence of chloride, it is considered to be passivated or immune to the effects of corrosion. If the specimen displays a decreasing R_p value over time, it is corroding and the inhibitor is not providing corrosion resistance.

During this investigation, changes in the polarization resistance (R_p) and the corrosion potential of the rebar were monitored to ascertain the degree of effectiveness for these MCI products. The samples were tested on a weekly basis and the data was collected for analysis for the first 500 days of exposures tests followed by monthly data collection. After 1,500 days of testing, four concrete samples (One reference sample and three MCI treated concrete samples) were cut open to remove the rebar for examination. A large area surface analysis was performed on several MCI treated concrete samples using a Kratos Axis Ultra XPS in electrostatic lens mode with resolution pass energy of 160 and an aluminum monochromator anode. The depth profiles were conducted using Argon ions at 4 kV.

There were ten concrete samples in total, eight were surface impregnated with several coats of MCI 2020 and MCI 2020M. The remaining two samples were left untreated and used as control for comparison. Clear silicon was applied to the concrete/metal interface to prevent easy access for ions. The testing environment was a solution of 3.5% NaCl and water with roughly 175 mm (7 inches) (Figure 1b) of each sample continuously immersed during testing, while the ASTM G109 [8] was subjected to 3.5% NaCl salt solution ponding for every other two weeks for roughly 210 cycles.

RESULTS

Many procedures have been developed for monitoring the corrosion of rebar in concrete, each method attempts to improve a shortcoming of an existing technique. Measuring the open circuit potential is very easy and inexpensive, but is not considered very reliable since the potential provides no information about the kinetics of the corrosion process. Linear polarization resistance (LPR) measurements are influenced by IR effects from the concrete. A significant potential drop in the concrete makes an accurate determination of the potential of the rebar surface very difficult. Electrochemical impedance spectroscopy (EIS) is able to overcome the difficulties of the concrete resistance, yet requires more testing time. The different analytical methods of electrochemical impedance spectroscopy are capable of giving more detailed information than LPR. The rebar potential, polarization resistance and current density data can provide information as to whether the rebar is in the active or passive corrosion state. Estimates made from these parameters for Tafel constants can be input into LPR analysis or can be used for corrosion rate measurement and cathodic protection criteria. Evaluation of the effectiveness of corrosion inhibitors and the effects of concrete composition is often based on these variables. For a more comprehensive approach to the corrosion process, several tests methods have been implemented in this investigation.

Corrosion Potentials

The corrosion inhibition for the inhibitor identified as MCI 2020 has been investigated over a period of 1500 days using EIS techniques. Throughout this investigation, changes in the corrosion potential of the rebar were monitored to determine the effects of this commercially available inhibitor. According to the ASTM (C876) standard [13], if the open circuit potential (corrosion potential) is -200 mV or higher, this indicates a 90% probability that no reinforcing steel has corroded. Corrosion potentials more negative than -350 mV are assumed to have a greater than 90% likelihood of corrosion. Figure 2 shows the corrosion potentials for the high and low density samples. The MCI treated samples showed a potential of roughly -100 mV after 1500 days of immersion in a salt solution. Given an open circuit potential of -570 mV for the untreated (low density) sample, it is highly probable that corrosion initiation has occurred. Figure 3a confirmed these findings. The untreated high density concrete maintained a potential of -240 mV, but had a high resistance polarization and did not suffer any corrosion.

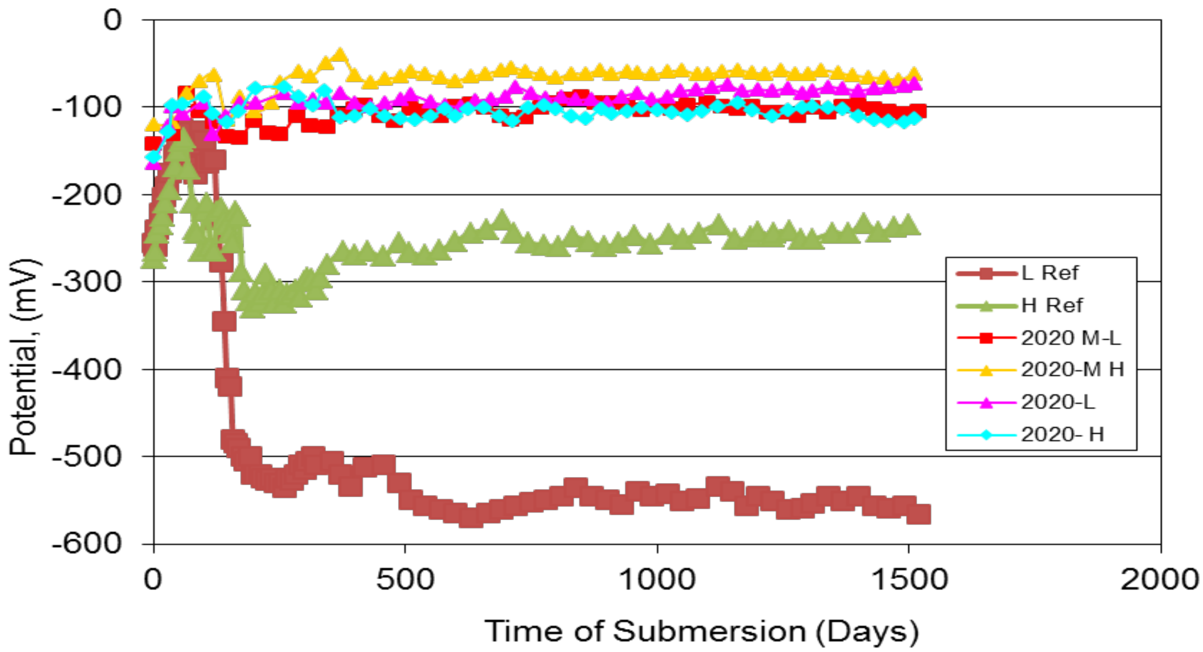


Figure 2: Comparison of Corrosion Potentials for MCI Treated Concrete with Untreated Samples per ASTM G109 [8].

a) b)

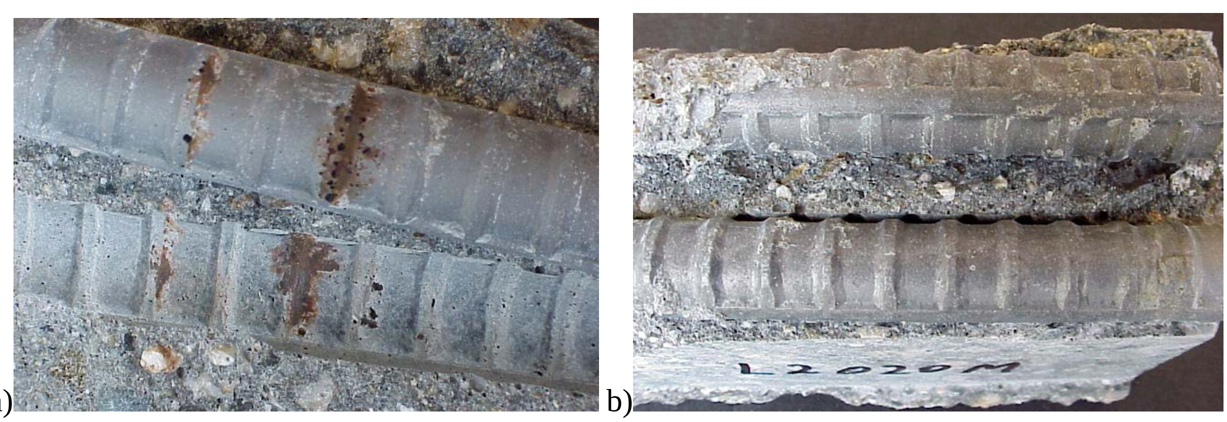


Figure 3: **a)** Non-treated concrete, rebar showed localized corrosion attacks. **b)** MCI-treated concrete, rebar did not show any corrosion attacks.

Polarization Resistance

This electrochemical technique enables the measurement of the instantaneous corrosion rate. This R_p value is related to the corrosion current I_{corr} by the following Stern-Geary equation [9]:

$$I_{corr} = B/(R_p A) \qquad (1)$$

where A is the area of the metal surface evenly polarized and B is a constant that may vary from 13 to 52 mV for the case of steel embedded in concrete. Figure 4 shows EIS data for polarization resistance that demonstrated an increasing trend for the MCI coated samples with polarization resistance values between 88 kΩ-cm^2 and 94 kΩ-cm^2. The R_p value for the untreated low density sample showed a declining trend of 9.8 kΩ-cm^2 at 350 days of partial immersion in the aggressive solution. The calculated corrosion rate of the steel rebar in concrete based on the measured polarization resistance values indicated a 1.6-2.2 mpy for the non-treated samples while MCI treated samples were in the range of 0.18-0.22 mpy. This can result in an additional 30-40 years of service life for protected concrete structures compared with non-protected concrete structures.

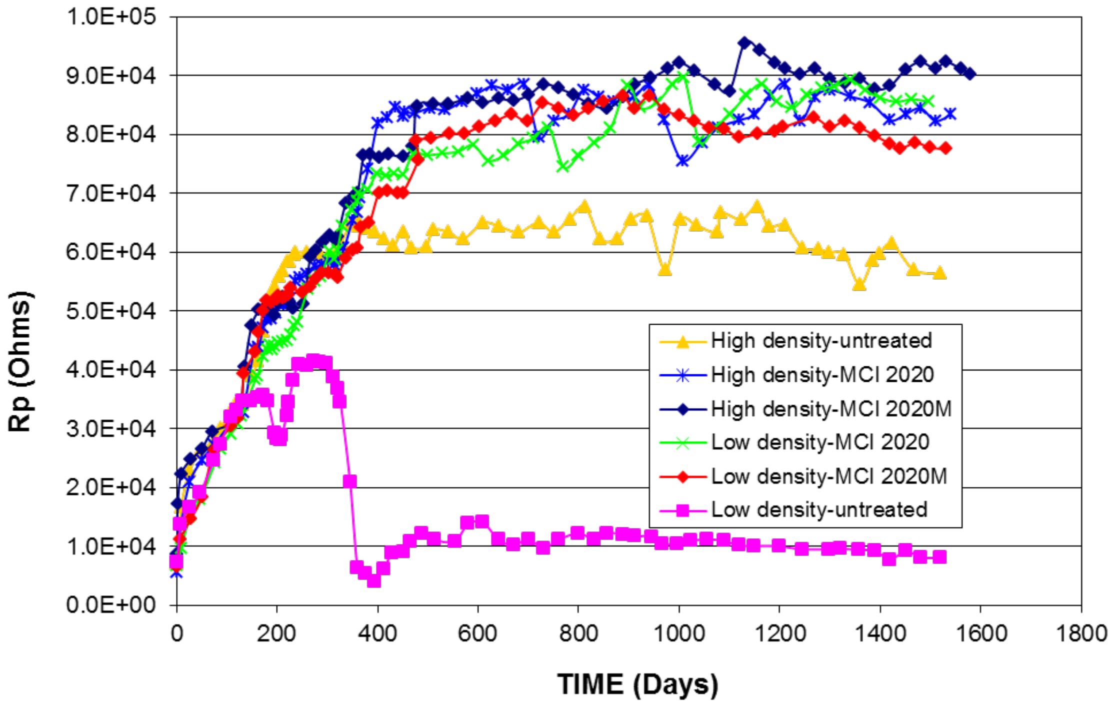


Figure 4: Polarization Resistance (R_p) Versus Time; Comparison of treated (MCI 2020 & MCI 2020M) low & high density concrete with untreated concrete.

X-ray photoelectron spectroscopy (XPS)

The XPS analysis of the rebar surface verified the inhibitor's ability to penetrate through the concrete pores by vapor phase diffusion and capillary effects. The data analyzed was consistent with an organic compound carboxylate chemistry similar to the migrating corrosion inhibitor compound (nitrogen, carbon and oxygen presence was attributed to MCI compound). Depth profiling (using 4 kV Argon ions) measured an approximate 120 nm layer of amine compounds on the rebar surface, confirming surface adherence after migration. Chloride was also found on the surface of the rebar. The XPS results demonstrated that both the MCI and corrosive species had migrated in through the concrete capillary system. Table 1, however, shows that MCI managed to coat the surface and neutralize the corrosive species (chloride ions and carbon dioxide) to protect the steel rebar.

Table 1: XPS analysis and spectrum of the rebar surface, untreated and MCI 2020M treated concrete after 1500 days in 3.5% NaCl.

Peak	Atomic Conc%	Mass Conc%	Atomic Conc%	Mass Conc%
	Untreated	**Untreated**	**MCI**	**MCI**
Fe 2p	0.87	3.32	0.08	0.3
O 1s	30.19	33.06	31.4	35.91
C 1s	62.48	51.37	59.43	48.12
Ca 2p	0.15	0.42	1.08	3.01
Si 2p	4.72	9.08	1.26	4.14
Cl 2p	0.84	2.04	1.11	2.81
N 1s	0.74	0.71	5.64	5.71

CONCLUSIONS

Migrating corrosion inhibitors effectiveness were studied in continuous long duration corrosion tests, all samples but one (low density-untreated) have maintained a stable protective layer that has improved the steel reinforcement performance in the corrosive environment. The MCI products have successfully inhibited corrosion of the rebar in a 3.5% NaCl solution for the duration of testing. MCI protected samples showed an average corrosion rate of 0.4 $\mu A/cm^2$ (less than 0.17 mpy) compared to untreated samples that were 5.10 $\mu A/cm^2$ (2.2 mpy). This will increase the life expectancy of a concrete reinforced structure by more than 40 years. XPS analysis demonstrated the presence of inhibitor on the steel rebar surface indicating MCI migration through the concrete. XPS depth profiling showed a layer of amine-rich compounds and chloride ions on the rebar surface; however the neutralizing effects and film forming ability of the inhibitor assured satisfactory corrosion resistance.

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