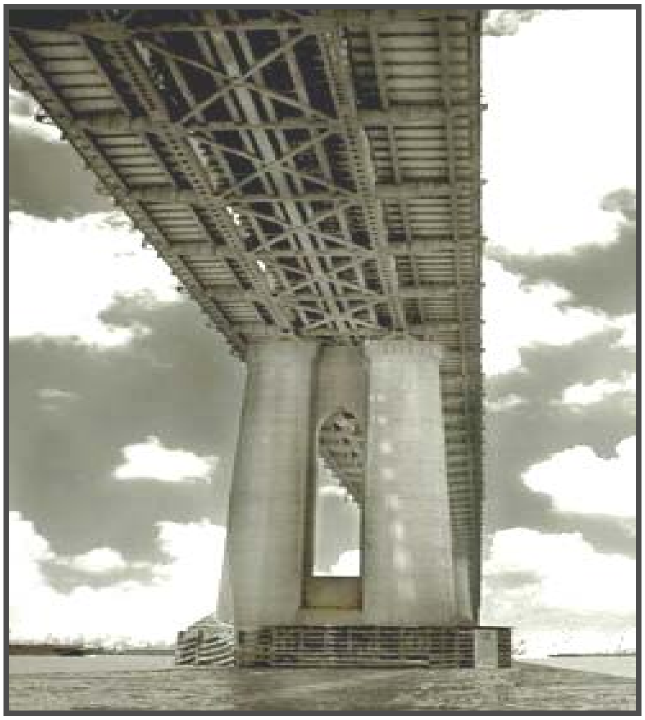
Corrosion Protection of Steel Rebar in Concrete with Optimal Application of Migrating Corrosion Inhibitors, MCI 2022



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Steel corrosion is a major concern for any society with reinforced concrete structures. More specifically, the United States, with its vast infrastructure of concrete and steel bridges, superhighways, and reinforced concrete buildings has spent billions of dollars for corrosion protection. Among the commercial technologies available today, migrating corrosion inhibitors (MCIs) show versatility in that they can be incorporated as admixtures, surface treatment, or used in rehabilitation programs. The effectiveness of Cortec's MCI 2022, a mixture of amine carboxylates, amino alcohols and siloxane, on reinforced concrete using various application methods was evaluated. Bode and Nyquist plots showed high polarization resistance values for inhibitor treated concrete. XPS analysis verified the presence of inhibitor chemistry and chloride molecules on the steel rebar surfaces. Depth profiling revealed a 100 nm amine-rich layer of inhibitor along with chloride ions on the rebar, confirming that MCI had migrated through the concrete coverage to suppress chloride ion corrosiveness. Eight concrete specimens were prepared with reinforcement placed at 1 inch (2.5 cm) concrete coverage and tested for a period of 400 days. MCI 2022 was applied directly to the rebar, by surface impregnation and combined in a mortar coating. Electrochemical monitoring techniques were applied to samples immersed in 3.5% NaCl at ambient temperatures. The corrosion behavior of the steel rebar was monitored using AC electrochemical impedance spectroscopy (EIS). The changes in the polarization resistance and the corrosion potential of the rebar were compared with previous investigations conducted on several admixtures and stainless steel rebar.

Introduction

Corrosion is one of the main concerns in the durability of materials and structures. Much effort has been made 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.[2-7] 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 like carbonation and chloride ions 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 additional help to prevent corrosion damage.

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.[2,3] Organic inhibitors utilize 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.[5] 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. Bjegovic and Miksic recently demonstrated the effectiveness of MCIs over five years of continuous testing.[2,3] They also showed that the migrating amine-based corrosion-inhibiting admixture can be effective when incorporated in the repair process of concrete structures.[2] Furthermore, 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.[6,7]

Purpose

The objective of this investigation was to further study migrating corrosion inhibitors, focusing on their usefulness and means of application. In many cases, there is thought to be an induction period, where time is required for the inhibitor to migrate through the concrete pores. A high density concrete may impede corrosive species from reaching the surface of the rebar and could also prevent inhibitor from reaching the surface of the concrete. Direct application of the inhibitor to the rebar surface would eliminate this concern. Also, a thicker coating of inhibitor and mortar was investigated; this combination may be necessary to protect steel rebar in extremely aggressive environments. Electrochemical monitoring techniques were applied while samples were immersed in 3.5% NaCl at ambient temperatures. Due to the low conductivity of concrete, the corrosion behavior of steel rebar had to be monitored using AC electrochemical impedance spectroscopy (EIS). 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 destruction to the reinforcing steel. 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 to introduce preventative measures.

Experimental Procedures

For purposes of this study, the steel rebar/concrete combination is treated as a porous solution and modeled by a Randles electrical circuit. EIS tests performed on a circuit containing a capacitor and two resistors indicate that this model provides an accurate representation of a corroding specimen. 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.

The experiments were conducted using an EG&G Potentiostat/Galvanostat (Model 273A with a 5210 Lock-in amplifier), EG&G M398 and Power Suite Electrochemical Impedance Software and a Gamry PC4-750 Potentiostat with 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.

Number of samples	Application method
2	No treatment-control samples
2	MCI 2022 coated rebar
2	MCI 2022 treated concrete surface
2	2/8 to 3/8 inch mortar/MCI 2022 coating

Table 1. Shows the application method used for each sample.

As seen in Table 1, several methods were used to treat the concrete samples. The objective was to determine whether the location of the inhibitor had any impact on its ability to protect the steel rebar. Prior to the concrete batching, two rebars were immersed for 20 minutes in MCI 2022 to ensure thorough coverage, then set to dry for several days. Concrete samples with dimensions 8” x 4” x 4” were prepared using an 8 inch steel rebar (class 60, 1/2” diameter) and one 8-inch Inconel 800 metal strip (for the counter electrode). A concrete mixture containing commercial grade-silica, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate) were combined with one-half gallon water per 60-lb (27.22 Kg) bag in a mechanical mixer. The mix resulted in a 0.5 cement to water ratio and the coverage layer was maintained at one inch concrete for all samples. Compressive strengths were roughly 3750 psi for this medium density concrete cured for 28 days per ASTM C387. After curing, samples were set to dry, then sandblasted to remove loose particles and provide surface uniformity.

Two of the concrete blocks were surface impregnated with several coats of MCI 2022 and set to dry. The inhibitor was applied to the surface of the concrete with a paint brush while partially immersed in a shallow container of inhibitor. Mortar samples were prepared using a 10 lb (4.5 kg) bag of Quikrete mortar mix, 100 ml MCI 2022 and 800 ml water. The remaining two samples were left untreated and used as standards for comparison. Clear silicon was applied to the concrete/metal interface to prevent easy access for ions. Figure 1 shows the samples partially immersed in a solution of 3.5% NaCl and water; roughly 7 inches of each sample was continuously immersed in the solution for the entire testing period. A $Cu/CuS0_4$ electrode was used as the reference and each sample was tested approximately every two weeks. The results were compared with previous investigations conducted on several admixtures and stainless steel rebar.

Figure 1. This photo shows four of the concrete samples partially immersed in a 3.5% NaCl solution.

Results & Discussion

Many procedures have been developed for monitoring the corrosion of rebar in concrete, each method attempts to improve a shortcoming of an alternate 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 Cortec MCI 2022 was investigated over a period of 400 days using AC electrochemical impedance spectroscopy (EIS). 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, 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 that the corrosion potentials for all the samples were between the range of -25 mV to -150 mV after 100 days of immersion in NaCl.

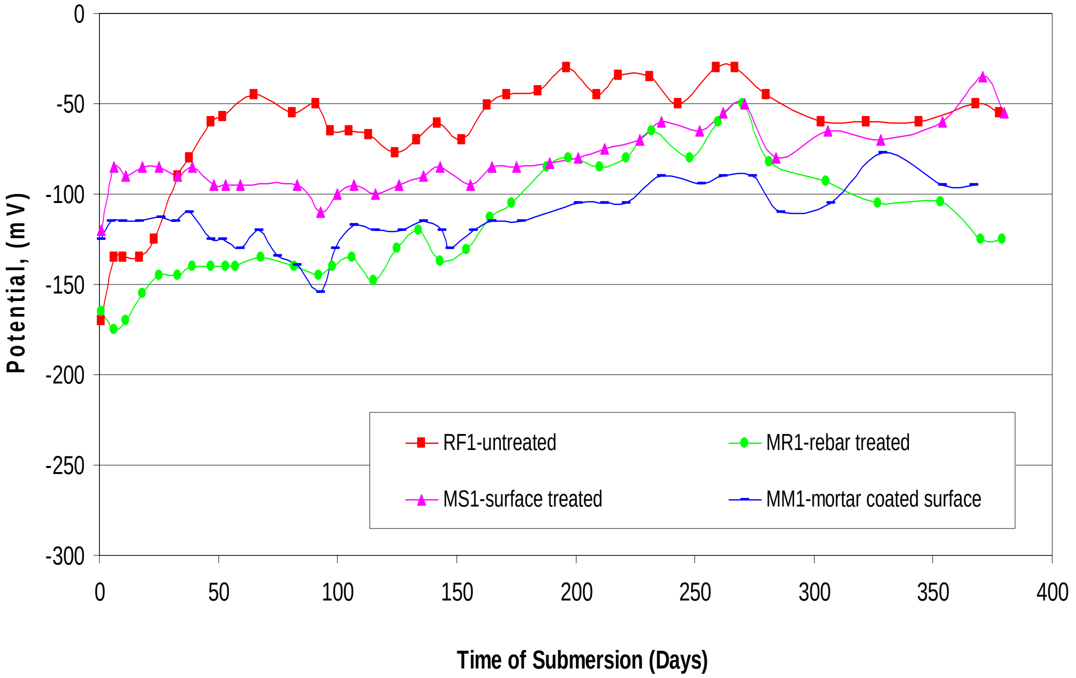


Figure 2. Comparison of corrosion potential vs time for MCI treated and untreated samples.

Polarization Resistance

This electrochemical technique enables the measurement of the instantaneous corrosion rate. It quantifies the amount of metal per unit of area being corroded in a particular instant. The method is based on the observation of the linearity of the polarization curves near the potential E_{corr}. The slope expresses the value of the polarization resistance (R_p) if the increment diminishes to zero. This R_p value is related to the corrosion current I_{corr} by means of the expression:

$$R_p = \left(\frac{\Delta E}{\Delta I} \right)_{\Delta E \to 0} \qquad\qquad I_{corr} = \frac{B}{R_p \cdot A}$$

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, the best fit with parallel gravimetric losses, results in B= 26 mV for actively corroding steel, and B= 52 mV for passivated steel. Figures 3 & 4 show that MCI treated concrete samples have higher R_p values compared with the control sample. Figure 3 shows a declining trend for the untreated concrete sample and stable polarization resistance values after 400 days of testing for the treated concrete. Figure 4 shows R_p values obtained during linear polarization consistent with Figure 3. The inhibitor treated rebar had the highest polarization resistance, the next highest R_p values were for the concrete with mortar treatment, then surface treated concrete and finally the untreated concrete with somewhat lower values around 27000 (ohm) (cm^2). The corrosion rate in $\mu A/cm^2$ is shown in Figure 5 and the relative value is specified in Table 2. For example, at the present rate of corrosion, it is estimated that the untreated sample will suffer corrosion damage in 10-15 years.

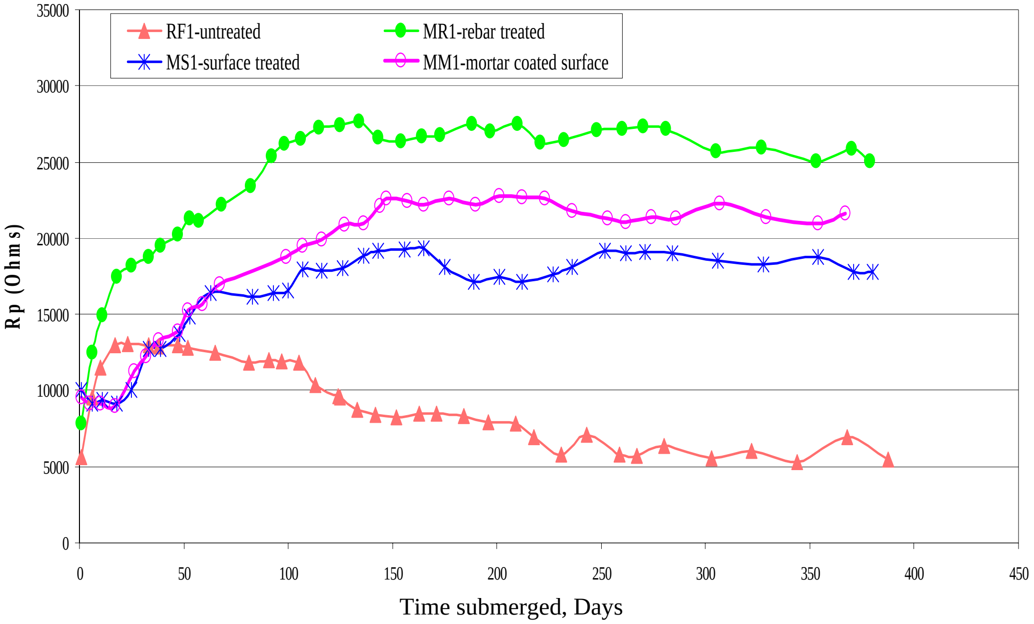


Figure 3. Comparison of polarization resistance (R_P) for MCI treated & untreated concrete samples.

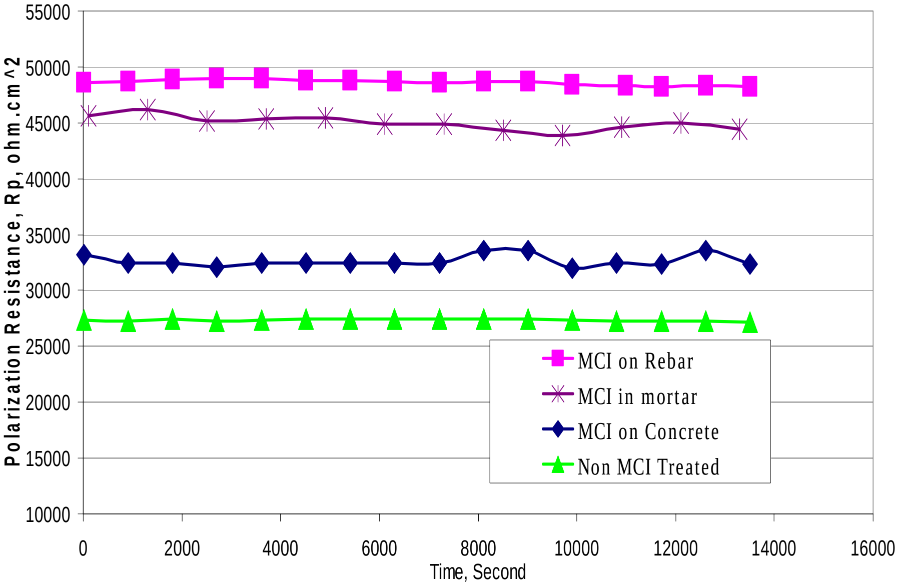


Figure 4. Linear polarization resistance tests on concrete samples partially immersed in 3.5% NaCl solution, day 365.

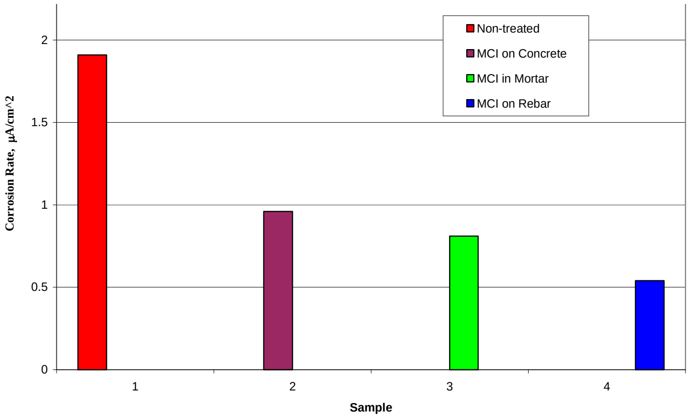


Figure 5. Bar chart obtained from LPR data quantifying the corrosion rate (µA/cm^2) for concrete samples on day 365.

Corrosion rate (uA/cm^2)	**Severity of Damage**
< 0.5	no corrosion damage expected
0.5-2.7	corrosion damage possible in 10 to 15 years
2.7-27	corrosion damage expected in 2 to 10 years
> 27	corrosion damage expected in 2 years or less

Table 2. Proposed relationship between corrosion rate and remaining service life.

Bode Plots

Bode plots are not dependent on modeling the corroding system as are polarization resistance values. The electrochemical impedance spectroscopy data are obtained by applying a single sine wave over a range of frequencies while measuring the corresponding impedance. Since the results are independent of an assumed model, the technique is highly reliable. Figure 6 shows a comparison of the bode plots for the first day of testing. The similar results for day 1 are a good indication that the concrete samples were consistently cast. Figure 7, the bode plot results from day 400, shows an obvious decline in the impedance values measured for the control sample. The passivating layer for this sample appears to have been breached, indicating a high likelihood of corrosion. The MCI treated samples still have corrosion protection after 400 days in an aggressive environment.

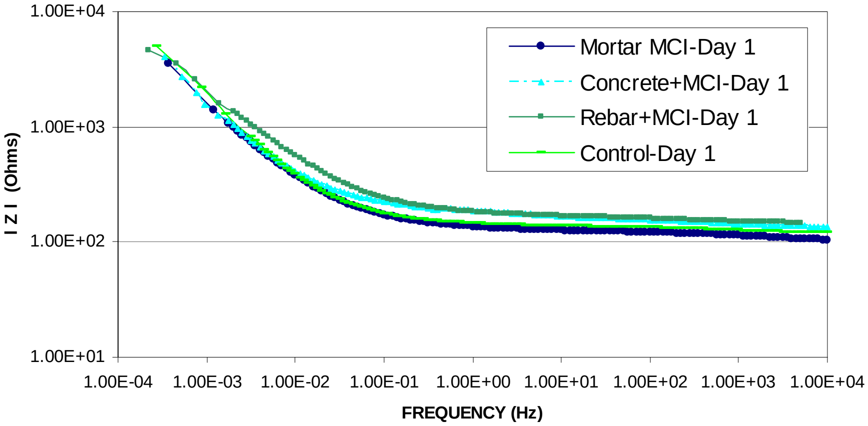


Figure 6. EIS Bode plot for MCI 2022 treated & untreated concrete on day 1 of testing.

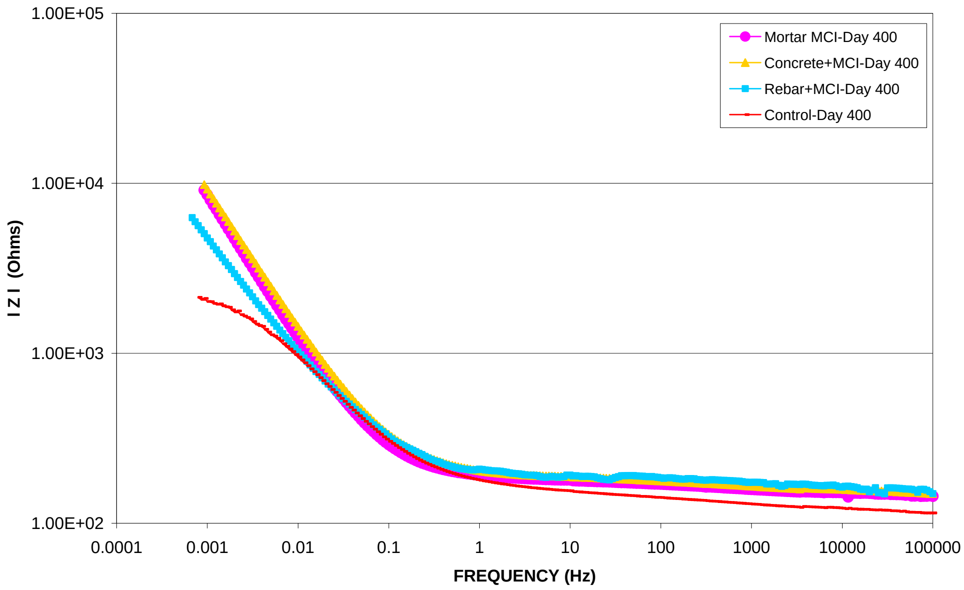


Figure 7. EIS Bode plot for MCI 2022 treated & untreated concrete after 400 days of testing.

XPS Analysis

After 415 days of immersion in a NaCl solution, several samples were removed from testing for XPS analysis and depth profiling. The rebar was removed from the concrete (Figures 8 & 9) and its surface chemistry was assessed. Figure 10 shows the XPS spectrum from untreated rebar sample after 450 days. It is similar to the spectrum shown in Figure 11 for the rebar removed from an MCI treated sample after 415 days.

Figure 8. This photo shows the treated rebar still embedded in the concrete and the portion of the rebar that was exposed to the corrosive environment.

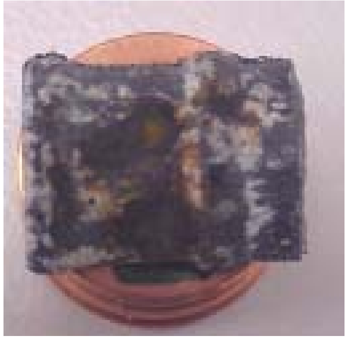


Figure 9. Untreated rebar sample used for XPS analysis. Sample shows obvious indications of corrosion.

The major difference in the spectrums is the N 1s peak for nitrogen not seen on the untreated rebar. The amine-rich compounds found on the rebar surface are associated with the MCI 2022 chemistry (75% water, 20 % silane/siloxane based sealer, 1-2% amino alcohols, 3-4% amine carboxylate), derivatives of nitrogen. Figure 12 shows a narrow spectrum for the N 1s energy band region verifying the presence of nitrogen. XPS chemical quantification results (Figure 11) revealed organic compounds with carboxylate chemistry. Chloride was also detected at depths up to 50 nm from the analysis surface on the rebar and at a concentration of approximately 0.52 atomic %. The XPS results demonstrate that both MCI and corrosive species had migrated in through the concrete pores, but MCI had formed a protective film on the steel rebar surface. These results are promising for the MCI product in its ability to protect steel rebar in concrete in aggressive environments. Figure 13 shows several SEM micrographs of the rebar surface and the EDAX analysis.

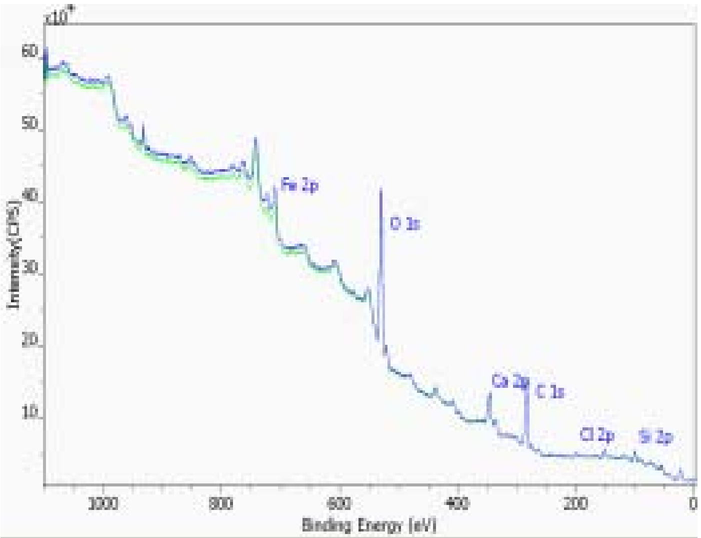
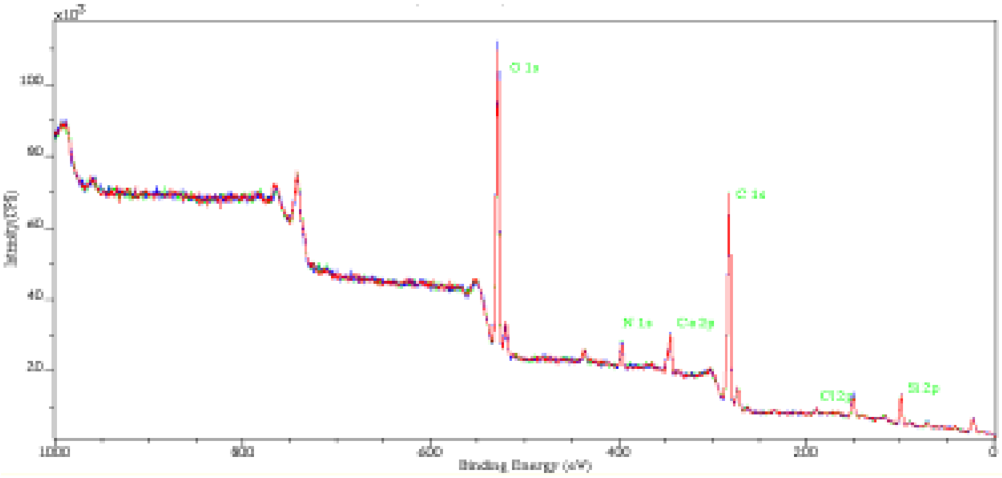
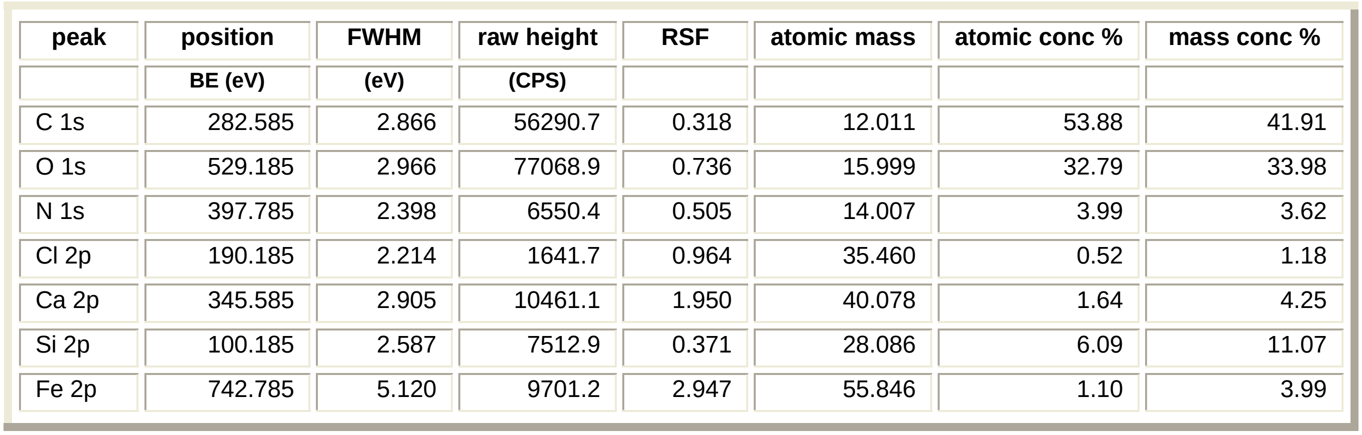


Figure 10. XPS spectrum of steel rebar removed from untreated concrete after 450 days of immersion. Large area (1000 x 800 mm). Lens mode electrostatic; Resolution pass energy 160; anode: Mg (150 W).





peak	position	FWHM	raw height	RSF	atomic mass	atomic conc %	mass conc %
	BE (eV)	(eV)	(CPS)				
C 1s	282.585	2.866	56290.7	0.318	12.011	53.88	41.91
O 1s	529.185	2.966	77068.9	0.736	15.999	32.79	33.98
N 1s	397.785	2.398	6550.4	0.505	14.007	3.99	3.62
Cl 2p	190.185	2.214	1641.7	0.964	35.460	0.52	1.18
Ca 2p	345.585	2.905	10461.1	1.950	40.078	1.64	4.25
Si 2p	100.185	2.587	7512.9	0.371	28.086	6.09	11.07
Fe 2p	742.785	5.120	9701.2	2.947	55.846	1.10	3.99

Figure 11. XPS spectrum analysis of steel rebar removed from MCI 2022 treated concrete after 400 days immersion and chemical quantification.

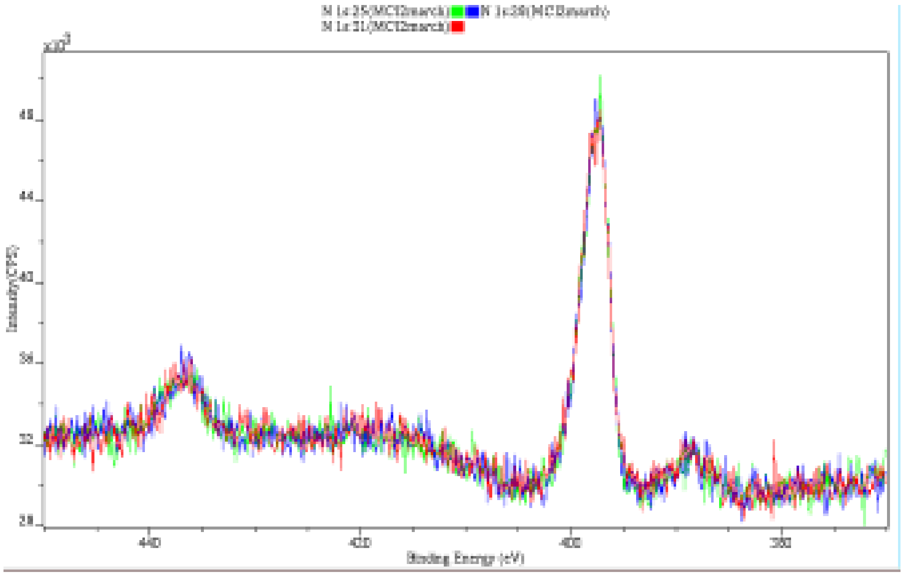
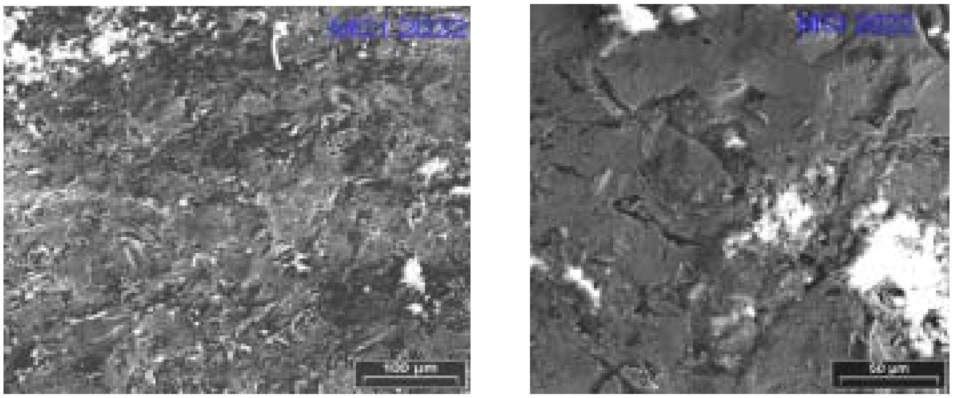
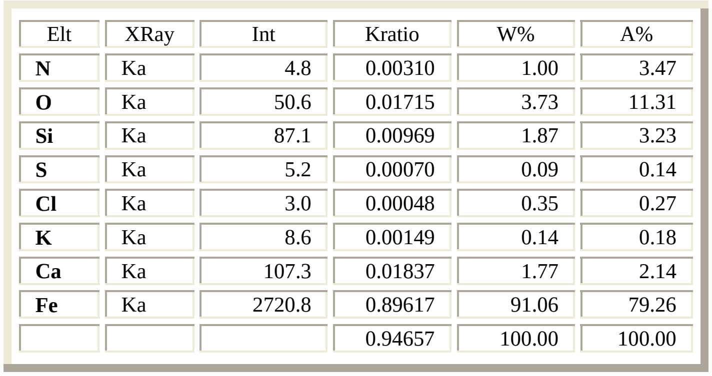


Figure 12. High resolution XPS spectrum for nitrogen peak (N 1s region) on surface of steel rebar removed from MCI 2022 treated concrete after 400 days immersion.





Elt	XRay	Int	Kratio	W%	A%
N	Ka	4.8	0.00310	1.00	3.47
O	Ka	50.6	0.01715	3.73	11.31
Si	Ka	87.1	0.00969	1.87	3.23
S	Ka	5.2	0.00070	0.09	0.14
Cl	Ka	3.0	0.00048	0.35	0.27
K	Ka	8.6	0.00149	0.14	0.18
Ca	Ka	107.3	0.01837	1.77	2.14
Fe	Ka	2720.8	0.89617	91.06	79.26
			0.94657	100.00	100.00

Figure 13. SEM photos (magnification: 100, 50 μm) showing the surface of an MCI treated rebar after 400 days in a 3.5% NaCl solution and the EDAX analysis.

Conclusion

The MCI products have successfully inhibited corrosion of the rebar in a 3.5% NaCl solution for 415 days. Steel rebar corrosion potentials were maintained at approximately -150 mV, and rebar polarization resistance showed a gradual increase reaching as high as 27,000 ohms. MCI coated rebar and MCI added to mortar showed significant reduction in the corrosion rate. XPS analysis demonstrated the presence of inhibitor on the steel rebar surface indicating MCI migration through the concrete. Depth profiling showed a layer of amine-rich compounds and chloride ions on the rebar surface; neutralizing effects of the inhibitor assured satisfactory corrosion resistance in the presence of corrosive chloride ions.

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