

IMPROVING DURABILITY OF REINFORCED CONCRETE STRUCTURES USING MIGRATING CORROSION INHIBITORS

Behzad Bavarian and Lisa Reiner
Dept. of Manufacturing Systems Engineering & Management
College of Engineering and Computer Science
California State University, Northridge, USA

ABSTRACT

Steel corrosion poses formidable concerns for long term reliability of reinforced concrete structures. In the United States, with its vast infrastructure of concrete and steel bridges, superhighways, and reinforced concrete buildings, billions of dollars have been spent on corrosion protection. Among the commercial technologies available today, migrating corrosion inhibitors (MCIs) show versatility in their use as admixtures, surface treatments, and in rehabilitation programs. The effectiveness of two commercial inhibitors applied to the reinforced concrete surface was evaluated. The corrosion behavior of the steel rebar was monitored using AC electrochemical impedance spectroscopy (EIS). Corrosion potentials and polarization resistance values corroborated the inhibiting effects of the amine carboxylate and amino alcohol chemistry in an aggressive environment. The MCI products have successfully inhibited corrosion of the rebar in a 3.5% NaCl solution for duration of testing. MCI protected samples showed an average corrosion rate of $0.34 \mu\text{A}/\text{cm}^2$ compared to untreated samples that were $1.50 \mu\text{A}/\text{cm}^2$. This will increase the life expectancy by more than 15 years. XPS analysis demonstrated the presence of inhibitor on the steel rebar surface indicating MCI migration through the concrete.

Keywords: steel rebar, migrating corrosion inhibitors, electrochemical monitoring techniques

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]. 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].

EXPERIMENTAL PROCEDURES

The main objective of this investigation was to study the corrosion inhibiting properties and to determine whether these inhibitors protect the steel rebar in concrete. 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 was 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 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.

Prior to investigating the performance of two inhibitors, MCI 2020 and MCI 2020M, their potentiodynamic behavior was assessed. Studies were conducted in a saturated Ca(OH)_2 solution with

and without chloride ions using EG&G M352 DC corrosion test software. Comparisons of the polarization behavior were made for the steel rebar in solution with varying concentrations of inhibitor and the introduction of a corrosive species (2000 ppm NaCl). The effects of the mixed inhibitor in an alkaline environment similar to the concrete medium were observed.

In this investigation, the steel rebar/concrete combination is treated as a porous solution and modeled by a Randies electrical circuit [8]. 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.

Concrete samples with dimensions 20cm x 10cm x 10cm were prepared using a 20 cm steel rebar (class 60, 1.27 cm diameter) and a 20 cm 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 27.2 Kg (60-lb) bag in a mechanical mixer. The water to cement ratio was varied to achieve the two densities and the coverage layer was maintained at 2.5 cm (1 inch) concrete for all samples. Compressive strengths were roughly 27.6 MPa (4000 psi) for the low density and 41.4 MPa (6000 psi) for the high density concrete cured for 28 days per ASTM C387 [9], All samples were sandblasted to remove loose particles and provide surface uniformity. 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.

As outlined in Table 1, there were six (6) concrete samples in total, two were surface impregnated with several coats of MCI 2020 and two were coated with MCI 2020M. The inhibitor was applied to the surface of the concrete with a paint brush while partially immersed in a shallow container of inhibitor. The remaining two samples were left untreated and used as standards for comparison. An additional coat of MCI 2022 sealer was used to prevent the inhibitor from washing off in solution. 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) of each sample continuously immersed for 360 days. A Cu/CuSO₄ electrode was used as the reference and each sample was tested once every two weeks.

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 360 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 [10], 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 1 shows that the corrosion potentials for the samples (except the untreated low density sample) were between the range of 0 mV to -100 mV after 360 days of immersion in NaCl. Given an open circuit potential of -270 mV and declining, the untreated (low density) sample appears to suffer corrosion.

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 the following Stern-Geary equation: $I_{\text{corr}} = B/(R_p \cdot A)$. 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. Figure 2 shows increasing trends for the samples with polarization resistance values between 60 $k\Omega$ and 70 $k\Omega$. The R_p value for the untreated low density sample reached 40 $k\Omega$ before rapidly declining to 4 $k\Omega$ at 350 days of partial immersion in the aggressive solution.

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 3 shows a comparison of bode plots for the first day of testing and after 360 days of immersion. There is not much variation in the curves, except for the low density untreated sample which sharply contrasts with the rest.

Potentiodynamic Behavior

Figure 4 shows a comparison of the polarization behavior from a potentiodynamic test of steel rebar in a saturated $\text{Ca}(\text{OH})_2$ solution. This graph shows the effects of a mixed inhibitor in an alkaline environment similar to the concrete medium with minor reduction in the corrosion current upon addition of MCI. Figure 5 shows the polarization results from the steel rebar tested in a saturated $\text{Ca}(\text{OH})_2$ solution with 2000 ppm NaCl. The effects of the inhibitor are far more noticeable in the presence of a corrosive species. The breakdown potential for the rebar tested with no inhibitor was around 350 mV SCE as compared to 600 mV for the rebar tested with 2000 ppm MCI. Figure 6 shows the corresponding current density for the various additions of MCI in column format. Consistent with the graph in Figure 5, the rebar tested in a saturated $\text{Ca}(\text{OH})_2$ solution with 2000 ppm NaCl and 2000 ppm MCI had the lowest corrosion rate. According to the data in Table 2, where a level of corrosion severity has been associated with a given i_{corr} value, the sample tested with 2000 ppm MCI and having a corrosion rate of less than $0.34 \mu\text{A}/\text{cm}^2$ will have "no expected corrosion damage."

X-ray photoelectron spectroscopy (XPS)

The XPS analysis verified the inhibitor's ability to penetrate through the concrete pores by vapor phase diffusion, permeation along the microcracks, and capillary effects. Figure 7 shows the XPS analysis and spectrum for the rebar removed from the MCI treated sample after 320 days. The analyses show an organic compound carboxylate chemistry similar to the migrating corrosion inhibitor compound (nitrogen content, carbon and oxygen ratio is attributed to MCI compound). Depth profiling (using 4 kV Argon ions) measured a 100 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 demonstrate that both MCI and corrosive species had migrated in through the concrete capillary system, however, MCI had managed to coat the surface and neutralize the corrosive species (chloride ions and carbon dioxide) to protect the steel rebar.

CONCLUSIONS

At 360 days of immersion, all samples but one (low density-untreated), seem to have maintained a stable passivation layer that has protected the steel reinforcement from the corrosive environment. The MCI products have successfully inhibited corrosion of the rebar in a 3.5% NaCl solution for duration of testing. MCI protected samples showed an average corrosion rate of $0.34 \mu\text{A}/\text{cm}^2$ compared to untreated samples that were $1.50 \mu\text{A}/\text{cm}^2$. This will increase the life expectancy by more than 10-15 years. 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; however the neutralizing effects of the inhibitor assured satisfactory corrosion resistance.

ACKNOWLEDGEMENT

Thanks go to the National Aeronautics and Space Administration (NASA-IRA program) and CORTEC Corp. for their sponsorship of this project.

REFERENCES

1. <http://www.corrosioncost.com/home.html>
2. D. Bjegovic and B. Miksic, "Migrating Corrosion Inhibitor Protection of Concrete," *MP*, NACE International, Nov. 1999.
3. D. Stark "Influence of Design and Materials on Corrosion Resistance of Steel in Concrete." *R & D Bulletin*, RD098.01T. Skokie, Illinois: Portland Cement Association, 1989.
4. B. Bavarian and L. Reiner, "Migrating Corrosion Inhibitor Protection of Steel Rebar in Concrete," *Materials Performance*, 2003.
5. B. Bavarian and L. Reiner, "Corrosion Protection of Steel Rebar in Concrete using Migrating Corrosion Inhibitors," BAM2001.
6. J. P. Broomfield et al, "Corrosion of Metals in Concrete," ACI 222R-96.
7. R. Dagani, "*Chemists Explore Potential of Dendritic Macromolecules As Functional Materials*," Chemical & Engineering News, American Chemical Society, June 3, 1996.
8. D. Jones, Principles and Prevention of Corrosion, 2nd Edition, Prentice Hall, NJ, 1996.
9. ASTM C387 Standard Specification for Packaged, Dry, Combined Materials for Mortar and Concrete, Vol. 04.02.
10. ASTM C876 Standard Test Method for Half Cell Potentials of Reinforcing Steel in Concrete, Annual Book of ASTM Standards, Vol. 04.02, 1983.

Table 1. Sample specifications.

Number of samples	Concrete Surface Coating	Density	Water to cement ratio
1	No treatment-control sample	Low = 2.08 g/cm ³	0.65
1	No treatment-control sample	High = 2.40 g/cm ³	0.35
1	MCI2020	Low = 2.08 g/cm ³	0.65
1	MCI 2020	High = 2.40 g/cm ³	0.35
1	MCI 2020M	Low = 2.08 g/cm ³	0.65
1	MCI 2020M	High = 2.40 g/cm ³	0.35

Figure 1: Corrosion Potential vs Time: Various Density Concrete (MCI 2020M, MCI 2020, untreated).

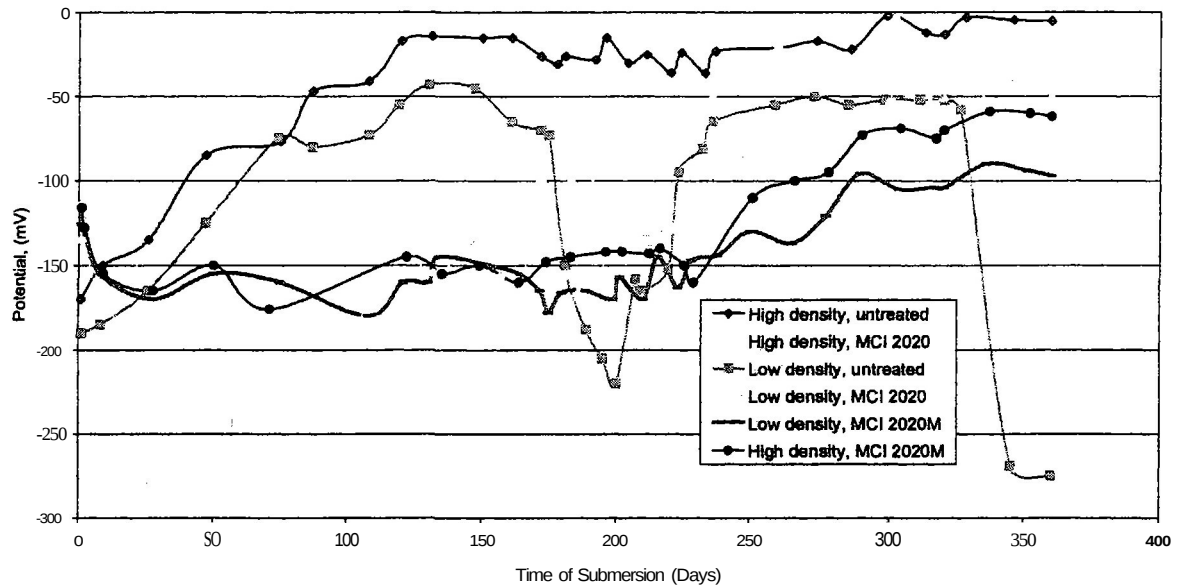


Figure 2: Polarization Resistance (R_p) Versus Time; Comparison of treated (MCI 2020 & Md 2020M) low & high density concrete with untreated concrete.

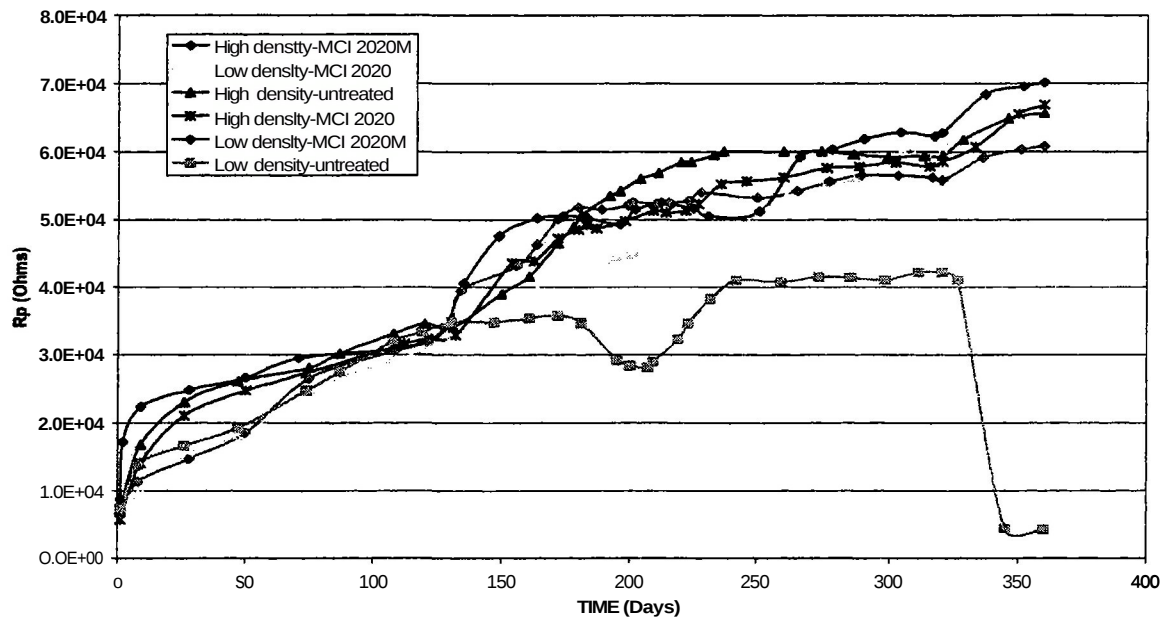


Figure 3: AC Impedance Spectroscopy Results (Concrete density H = 2.40 g/cm³, L = 2.08 g/cm³)
Bode Plot Comparison of MCI 2020 & 2020M with Untreated Concrete

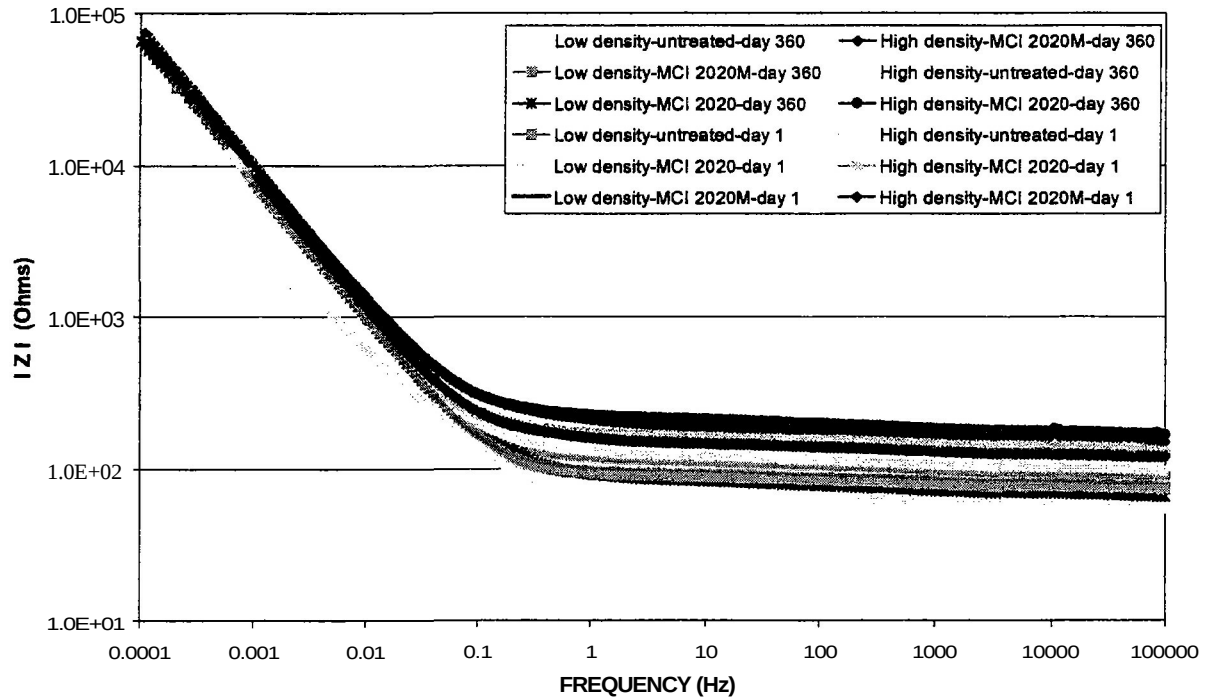


Figure 4: Polarization Behavior of Steel Rabor In a saturated Ca(OH)₂ solution
+various ppm MCI additions, pH 12.5, 23 C

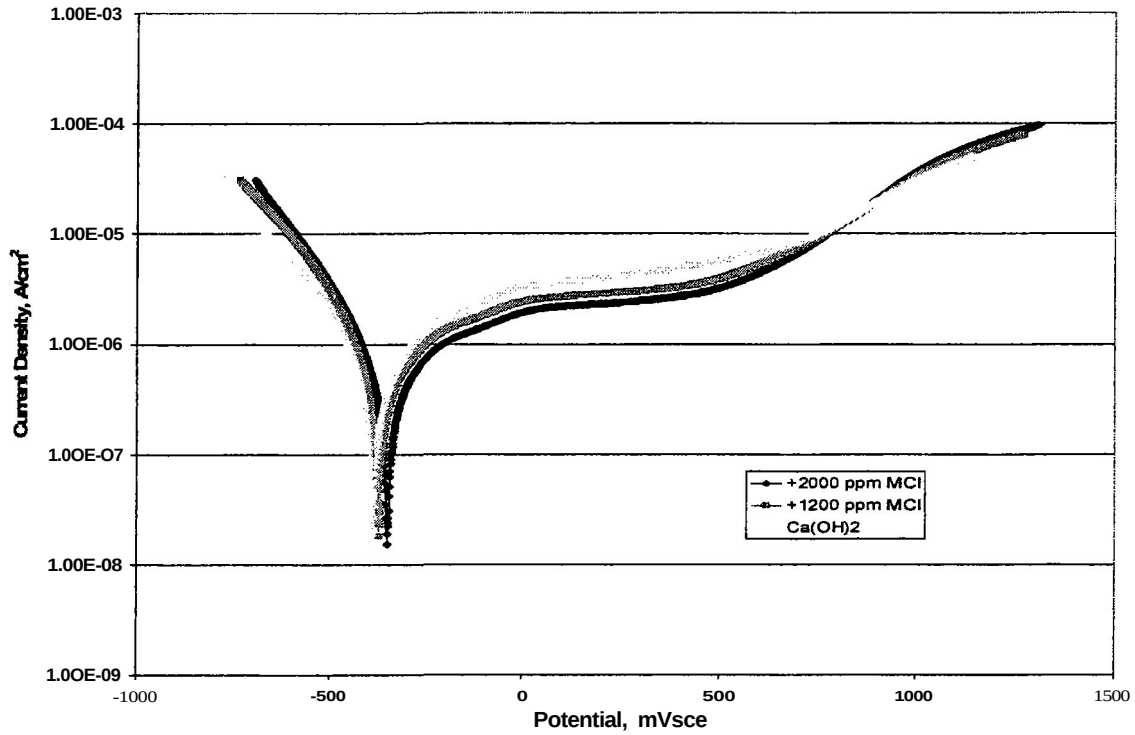


Figure 5: Polarization Behavior of Steel Rebar In a saturated $\text{Ca}(\text{OH})_2$ solution+2000 ppm NaCl and various ppm MCl additions, pH 12.4, 23 C

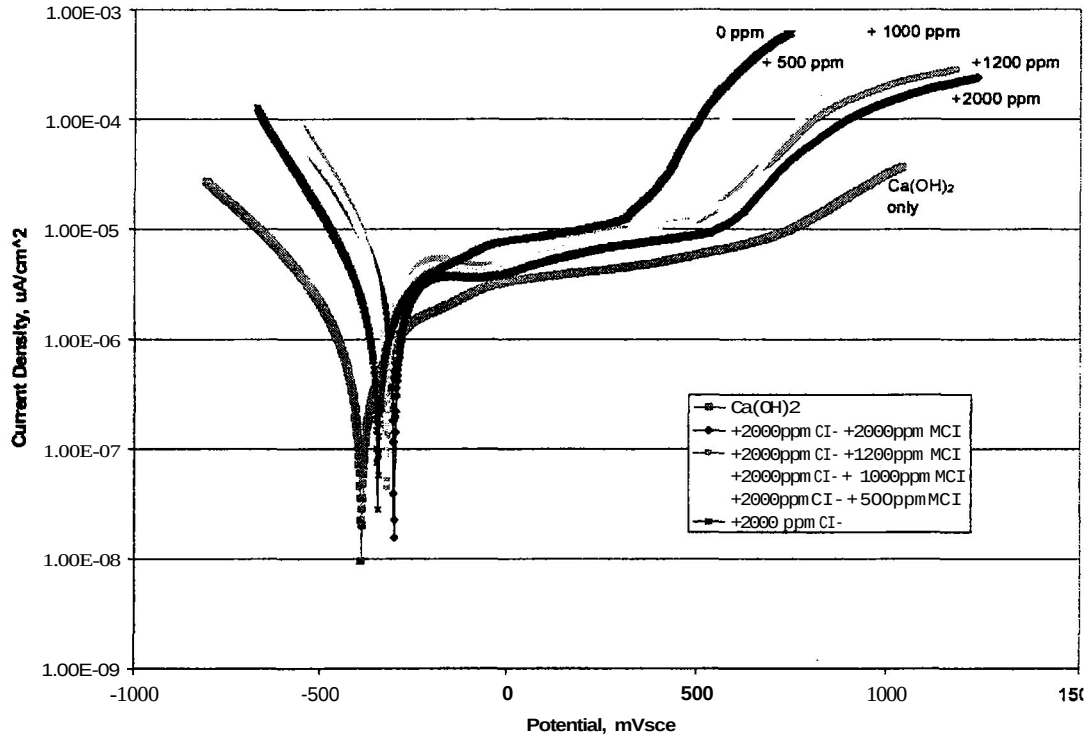


Figure 6: Polarization Behavior of Steel Rebar In a saturated $\text{Ca}(\text{OH})_2$ solution +2000 ppm NaCl and various ppm MCl additions, pH 12.4, 23 C

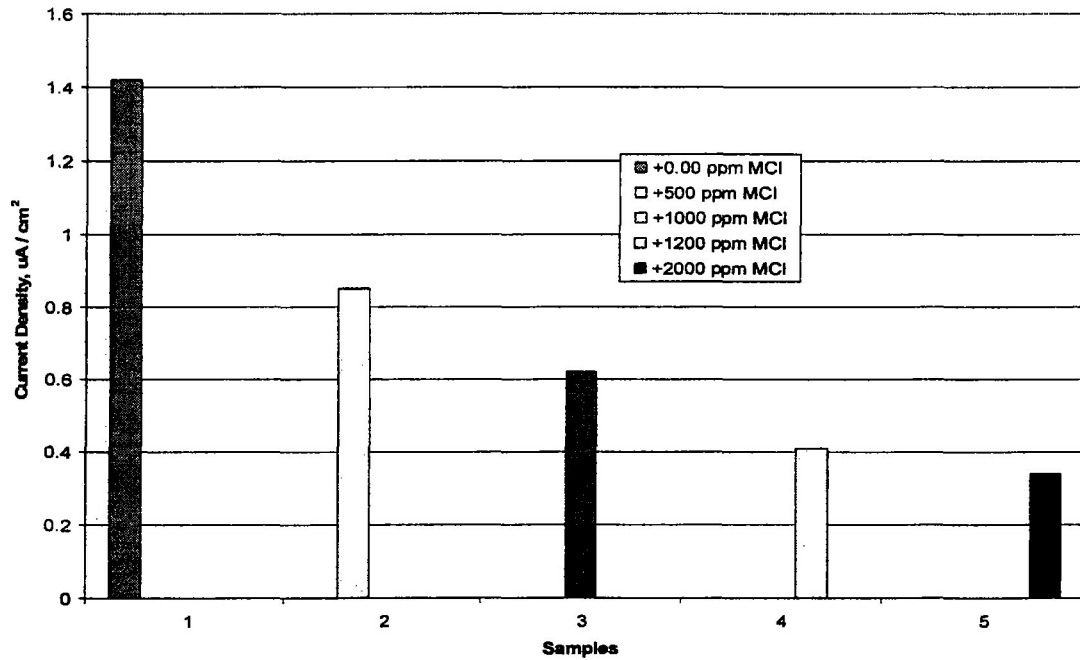


Table 2. Proposed Relationship between Corrosion rate and Remaining Service Life(6).

i_{corr} ($\mu\text{A}/\text{cm}^2$)	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

Figure 7. XPS analysis and spectrum of the rebar surface, MCI coated concrete after 320 days in 3.5% NaCl.

Peak	Position BE (eV)	FWHM (eV)	Raw Height (CPS)	RSF	Atomic Mass	Atomic Conc%	Mass Conc%
O 1s	530.000	2.920	117775.0	0.736	15.999	31.40	35.95
N 1s	397.000	3.373	14932.8	0.505	14.007	5.69	5.71
C 1s	283.500	3.003	101090.9	0.318	12.011	60.63	52.12
Cl 2p	190.000	2.507	5635.4	0.964	35.460	1.11	2.81
Ca 2p	344.500	3.079	11044.8	1.950	40.078	1.08	3.11
Fe 2p	686.000	0.236	1082.4	2.947	55.646	0.08	0.30

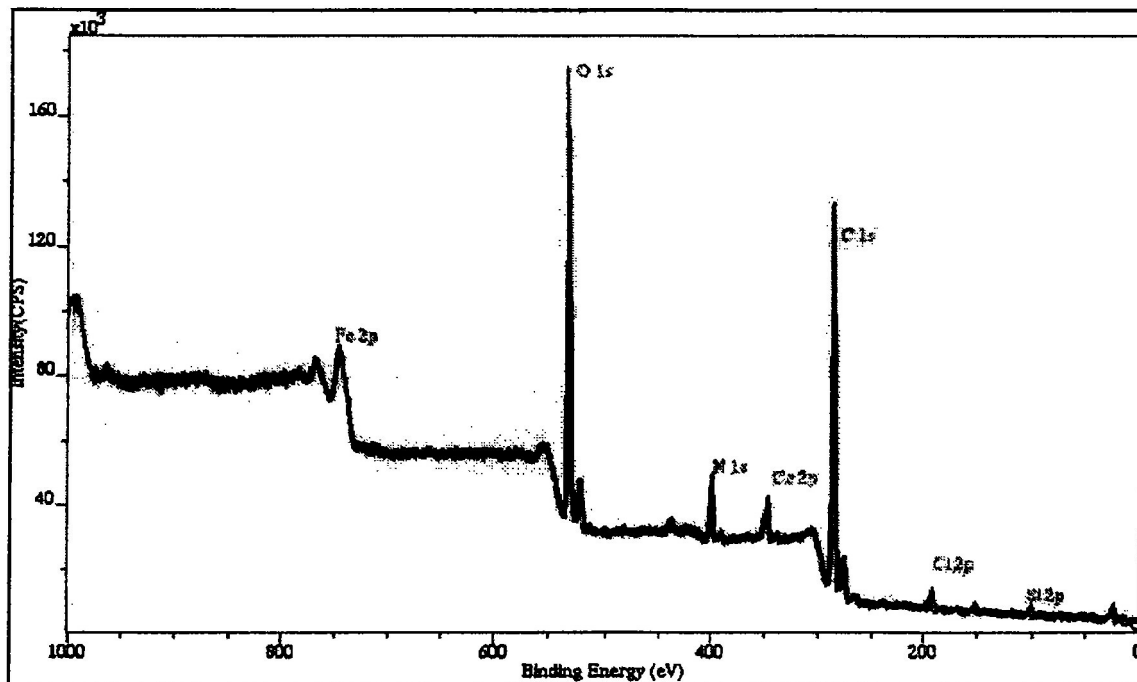


Figure 8. XPS analysis and spectrum of the rebar surface, untreated concrete after 320 days in 3.5% NaCl.

Peak	Position BE (eV)	FWHM (eV)	Raw Height (CPS)	RSF	Atomic Mass	Atomic Conc%	Mass Conc%
Fe 2p	745.000	6.989	17227.9	2.947	55.846	0.87	3.32
O 1s	533.000	1.920	144771.6	0.736	15.999	30.19	33.06
C 1s	286.500	2.991	122769.6	0.318	12.011	62.48	51.37
Ca 2p	344.500	2.529	1849.0	1.950	40.078	0.15	0.42
Si 2p	103.000	2.043	10424.1	0.371	28.086	4.72	9.08
Cl 2p	198.000	3.108	4892.7	0.964	35.460	0.84	2.04
N 1s	403.000	2.234	2372.8	0.505	14.007	0.74	0.71

