

Migrating Corrosion Inhibitors to Protect Steel Reinforced Concrete Structures

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Most transportation infrastructure is built from steel and concrete. The steel may be in structural sections, such as girders, piles, or rails, or embedded in concrete to form reinforced or prestressed concrete. Concrete provides excellent protection for embedded steel because Portland cement is very alkaline, forming a passive, protective layer on the steel surface. Concrete is also permeable, and even good-quality concrete can be penetrated by aggressive chemical ions that may initiate steel corrosion. Migrating corrosion inhibitors (MCIs), a blend of amine carboxylates and amino alcohols, show versatility as admixtures, surface treatments (coatings), and in rehabilitation programs. Examination of the embedded steel rebar after corrosion tests showed no corrosion attack for the MCI-treated concrete samples, while non-treated concrete showed localized corrosion. X-ray photoelectron spectroscopy and depth profiling confirmed that the inhibitor had reached the rebar surface in about 150 days. The amine-rich compound on the rebar surface improved corrosion protection for the MCI-treated steel rebar even in the presence of chloride ions and prevented red rust formation.

Corrosion is one of the primary concerns in the durability of materials and structures. Research efforts have been made to find a corrosion inhibition process to prolong the

life of existing structures and minimize corrosion damage in new structures.¹⁻³ Outside the laboratory environment, infrastructure may suffer from attack by carbonation, and chloride ions dissolved in water can permeate through the concrete pores, then penetrate the protective oxide film on the steel surface. Carbonation of concrete can lower the amount of chloride ions needed to promote corrosion. In new concrete with a pH of 12 to 13, about 7,000 to 8,000 ppm by weight of cement chloride is required to initiate steel corrosion. If, however, the pH is lowered to a range of 10 to 11, the chloride threshold for corrosion is significantly lowered to roughly 100 ppm.⁴

Chlorides in the concrete can come from several sources. They can be cast into the structure by the use of deliberate admixtures (calcium chloride [CaCl₂]), or the chloride ions can appear in the mix (mixing water, aggregates) unknowingly. However, the major cause of chloride-induced corrosion in most structures is the diffusion of chlorides from the environment due to direct exposure with a marine environment or the use of deicing salts and chemicals. There are four different mechanisms of chloride transport into crack-free concrete. They include capillary action, diffusion due to the high concentration on the surface, permeation under pressure, and migration due to electrical potential gradients.⁴⁻⁵ Similar to carbonation, the chloride attack process does not directly corrode steel reinforcement; how-

ever, it does break down the protective iron oxide film and promote corrosion. Chlorides do play a role as catalysts to corrosion. However, the mechanism of chloride diffusion into concrete is different for carbonation in that it attacks the passive layer without the requirement of pH reduction.

Corrosion inhibitor technology was developed to protect the embedded steel rebar/concrete structure. These 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. Most current migrating inhibitor admixtures are based on amino carboxylate chemistry and the most effective types of inhibitor interact at the anode and cathode simultaneously.² These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement, forming a barrier.^{3,6-11} Migrating corrosion inhibitors (MCIs) 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 surface and to form a protective layer. These corrosion inhibitors can be incorporated as an admixture or can be surface impregnated on existing concrete

structures. Laboratory tests have proven that these corrosion inhibitors migrate through the concrete to protect the rebar against corrosion even in the presence of up to 2.20% chlorides.⁹

Experimental Procedure

This study focused on the usefulness of inhibitors based on amino carboxylate chemistry and their means of application. Six concrete samples were cast (dimensions 280 by 110 by 150 mm) per ASTM G109¹²⁻¹³ using commercial-grade silica sand, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate). The reinforced concrete samples included one control, one with soda ash, and four with corrosion inhibitor admixtures. Two inhibitors, A and B (both amine carboxylate-based), were added to the concrete mix per the ASTM G109 sample preparation method, with reinforcement rebar placed at 20-mm concrete coverage. These samples were prepared with a 0.55 water/cement ratio. All samples contained three electrodes (class 60 steel rebar with dimensions of 300 mm length, 12.5 mm diameter). Concrete compressive strengths were roughly 26 MPa after 28 days of curing.

The ASTM G180¹⁴ test method involving steel and concrete admixtures was used to verify effectiveness of the corrosion inhibitors. The concrete samples were immersed in 3.5% sodium chloride (NaCl) at ambient temperatures and tested for a period of 150 days. The corrosion behavior of the steel rebar was monitored using electrochemical impedance spectroscopy (EIS). The experiments were conducted using commercially available systems for EIS and direct current corrosion tests. Bode plots were created from the data obtained using the potentiostatic technique. By comparing the Bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the resistance polarization (Rp) value over time. To verify this analysis, the Rp values were also estimated by using a curve-fitting algorithm on the Nyquist and Bode plots. In these plots, the Rp and RΩ combined values are displayed in the low frequency range of the Bode plot and the RΩ value can be seen in the high frequency

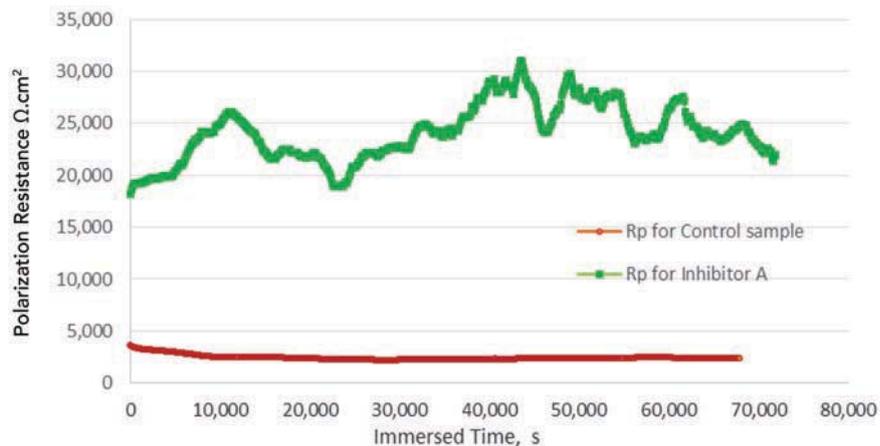


FIGURE 1 Polarization resistance measurements of steel rebar in 3.5% NaCl solution.

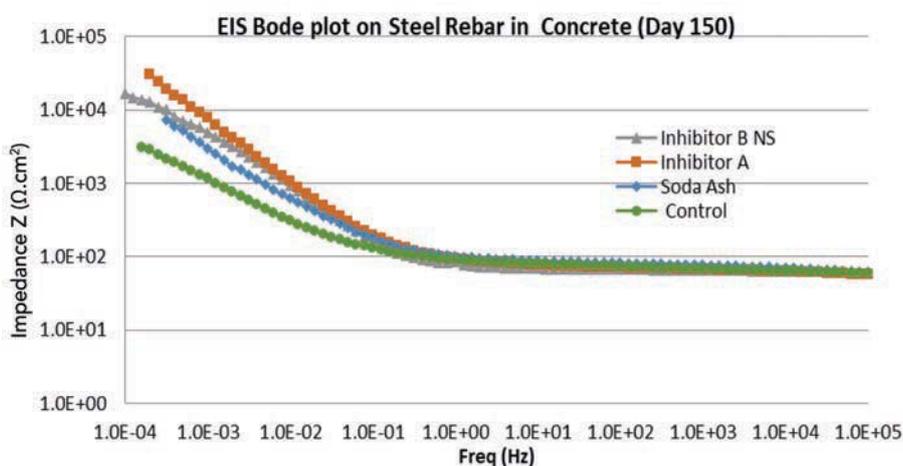


FIGURE 2 Comparison of the EIS Bode plots of steel rebar in different concrete mixes after 150 days of immersion testing.

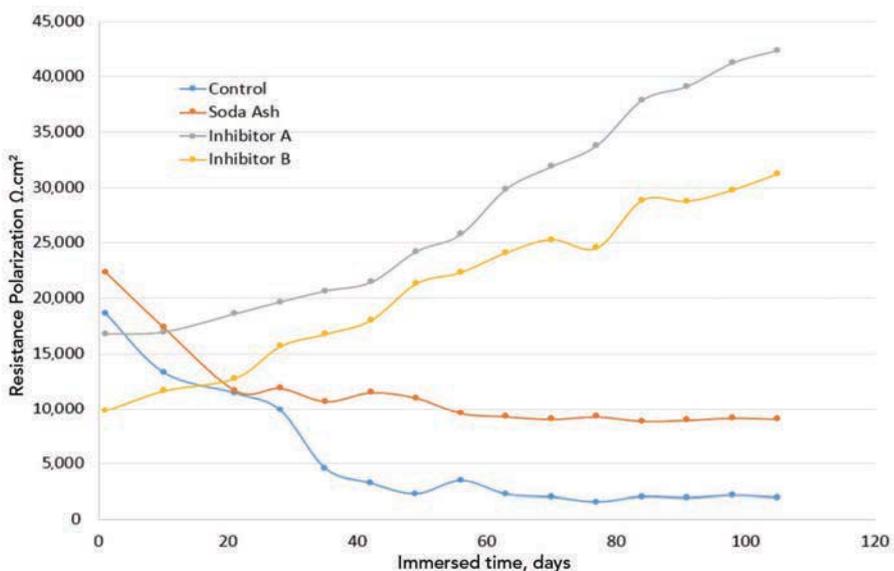


FIGURE 3 Polarization resistance measurements of steel rebar in concrete using EIS show an increasing trend (lowered corrosion rate) for the inhibitor, while control and soda ash samples have a decreasing trend (increased corrosion rate).

TABLE 1. LIFE EXPECTANCY PREDICTION BASED ON THE CORROSION OF THE STEEL REBAR IN CONCRETE

Sample	Rp ($\Omega \cdot \text{cm}^2$)	Corrosion Rate ($\mu\text{A}/\text{cm}^2$)	Life Expectancy (Years)
Inhibitor A	39,400	0.28	>50
Inhibitor B	28,800	0.39	>50
Soda Ash	7,180	1.56	~10-12
Control	2,030	5.51	~5-6

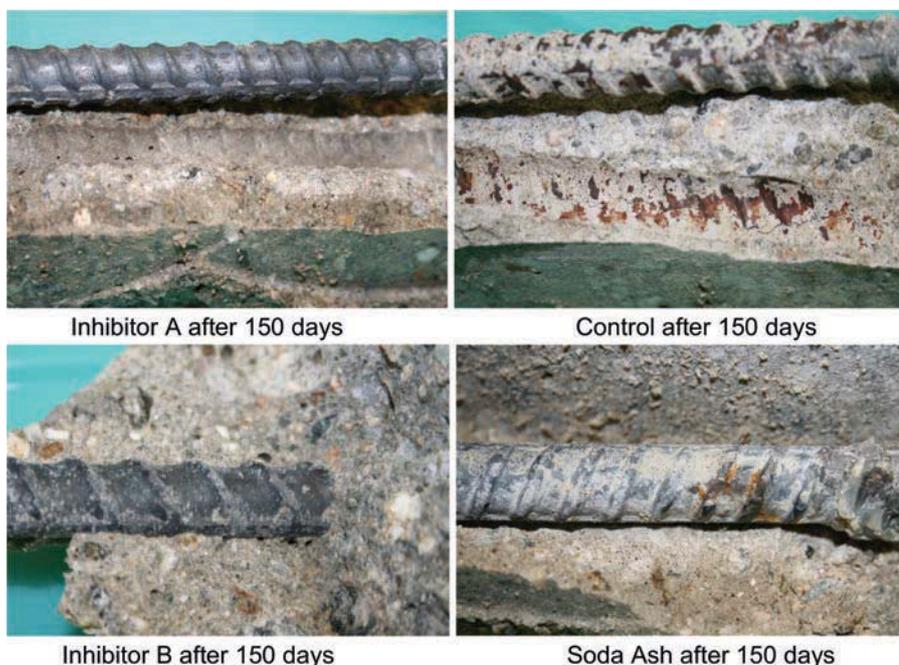


FIGURE 4 Comparison of corrosion behavior for the steel rebar from different concrete samples after 150 days immersed in 3.5% NaCl solution shows localized corrosion attack and red rust formation on the control and soda ash samples.

range of the Bode plot. The diameter of the Nyquist plot is a measure of the Rp value. During this investigation, changes in the Rp and the corrosion potential of the rebar were monitored to ascertain the degree of effectiveness for these admixture products. The samples were tested on a weekly basis and the data were collected for analysis.

Post experiment, visual observation scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analyses were conducted on the steel rebars. A large area surface x-ray photoelectron spectroscopy (XPS) analysis was performed on several steel rebars removed from different concrete samples using XPS in electrostatic lens mode with a resolution pass energy of 80 eV and an aluminum monochromator anode. The depth profiles were conducted using argon ions at 4.0 kV.

Results and Discussion

Polarization resistance measurements of steel rebar in a 3.5% NaCl solution are shown in Figure 1. The amine carboxylate-based MCIs increased the Rp from 2,300 $\Omega \cdot \text{cm}^2$ to 31,000 $\Omega \cdot \text{cm}^2$. There was successful corrosion inhibition of the steel rebar even in the presence of chloride when the admixtures were added to the concrete. The control sample and the sample with soda ash had decreasing polarization resistance. The steel rebars were not protected from corrosion attack. EIS Bode plots for the steel rebar from the different concrete samples after 150 days immersion in 3.5% NaCl are shown in Figures 2 and 3.

Polarization resistance measurements show an increasing trend (reduced corrosion rate) for the samples with inhibitor, while the control and soda ash samples

have an increasing corrosion rate. Inhibitor-protected samples showed an average corrosion rate of 0.28 $\mu\text{A}/\text{cm}^2$ (with a decreasing trend) compared to the EIS Bode plot results for untreated samples showing a rate of 5.5 $\mu\text{A}/\text{cm}^2$. This reduction of the corrosion rate translates to an increase in the life expectancy by more than 50 to 60 years (Table 1). The steel rebar surface conditions after 150 days of testing are shown in Figure 4.

XPS analysis confirmed the presence of the amine carboxylate-based inhibitor on the steel rebar surface. Depth profiling showed a 50-nm layer of amine-rich compounds and chloride ions on the rebar surface. Neutralizing effects of the inhibitor assured satisfactory corrosion resistance and the ability to passivate the steel rebar even in the presence of corrosive chloride ions. The XPS results established that both the admixtures and corrosive species (chloride 1.60-2.20%) were present on the rebar surfaces (Figures 5 and 6). The corrosion inhibitors managed to coat the surface and neutralize the corrosive species (chloride ions) to protect the steel rebar.

Conclusions

Amino carboxylate-based corrosion inhibitors (admixtures) successfully demonstrated corrosion inhibition of rebar and can prolong the life of reinforced concrete structures. Rp increased from 2,300 $\Omega \cdot \text{cm}^2$ to 31,000 $\Omega \cdot \text{cm}^2$ when admixtures were added to concrete. The addition of soda ash to the concrete mixture showed better corrosion protection than for the untreated concrete sample; however, inferior results occurred to those of the concrete samples with corrosion inhibitors. Inhibitor-protected samples showed an average corrosion rate of 0.28 $\mu\text{A}/\text{cm}^2$ (with a reduced trend) compared to untreated samples that measured 5.5 $\mu\text{A}/\text{cm}^2$ (based on EIS test results). This reduction in the corrosion rate will increase life expectancy by more than 50 to 60 years. Depth profiling showed a 50-nm layer of amine-rich compound and chloride ions on the rebar surface. XPS analysis confirmed the presence of the amino carboxylate-based inhibitor on the steel rebar surface. Neutralizing effects of the inhibitor assured satisfactory corrosion resistance even in the presence of 1.6-2.2% chloride ions.

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This article is based on *CORROSION* 2018 paper no. 11011, presented in Phoenix, Arizona, USA.

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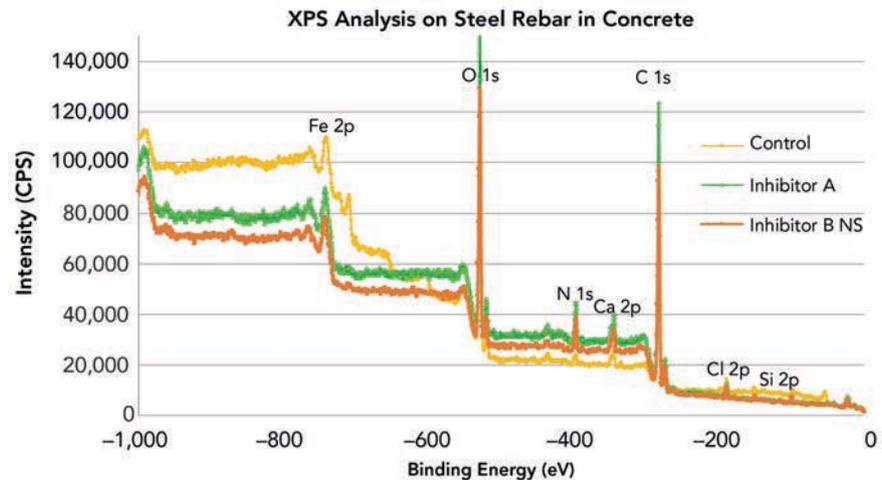


FIGURE 5 Comparison of XPS analysis on steel rebar from different concrete samples after 150 days immersed in 3.5% NaCl solution.

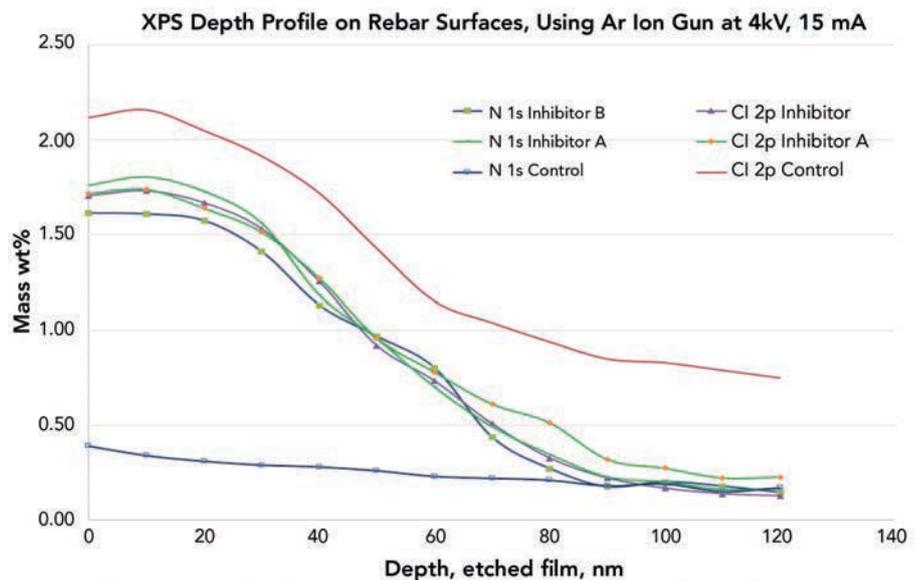


FIGURE 6 Comparison of XPS depth profiling analysis on steel rebar from different concrete samples after 150 days immersion.

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