Migrating Corrosion Inhibitor Protection of Steel Rebar in Concrete

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Laboratory analysis determined the effectiveness of migrating corrosion inhibitors (MCIs) for reinforced concrete. Nyquist plots showed high polarization values for concrete treated with inhibitor. X-ray photoelectron spectroscopy (XPS) analysis confirmed that MCI migrated through the concrete. XPS depth profiling indicated that the inhibitor was able to suppress corrosion even in the presence of chloride. The effects of applying MCI directly to the rebar into the concrete were not apparent. Additional data are required to make any conclusion about the effectiveness of an application method.

According to the final report of a 2-year nationwide study released to the U.S. Congress in March of 2002,[1] the U.S. incurs billions of dollars in corrosion costs each year for reinforced concrete structures (e.g., highway bridges, waterways, ports, and drinking water and sewer systems). The annual direct cost of corrosion for highway bridges alone is estimated to be $8.3 billion (Figure 1). Indirect costs related to traffic delays and lost productivity are estimated to exceed 10 times the direct cost of corrosion maintenance, repair, and rehabilitation.

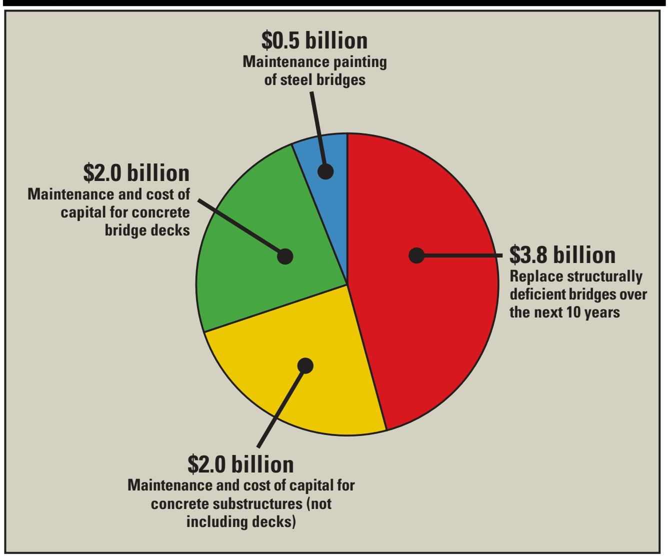
Previous studies have verified the benefits of using migrating corrosion inhibitors (MCIs), the importance of good concrete, and the significance of ingredients used to make the concrete for protection of reinforced concrete structures from corrosion.[2-10] Steel reinforcing bars (rebar) embedded in concrete show high resistance to corrosion because the alkaline environment provided by the cement paste in the concrete promotes the formation of a protective ferrous oxide (FeO) film. The rebar's ability to remain passivated and protected from corrosive species, such as carbonation and chloride ions that can penetrate through the concrete pores to the rebar oxide layer, is influenced by the water-to-cement ratio, permeability, and electrical conductivity of concrete. In highly corrosive environments, the passive layer will break down, leaving the rebar vulnerable to carbonation and chloride attack. In these environments, corrosion prevention is necessary.

Advancing MCI Technology

MCI technology was developed to protect the embedded steel rebar and the concrete structure. Recent MCIs are based on amino-carboxylate chemistry, with the most effective types of inhibitor interacting at the anode and cathode simultaneously.[2-4] MCIs penetrate into the existing concrete to protect steel from chloride attack.[6] The inhibitor migrates through the concrete capillary structure, first by liquid diffusion via the moisture normally present in concrete, then by its high vapor pressure, and finally by following hairlines and microcracks. The diffusion process requires time for the MCI to reach the rebar and form a protective layer.

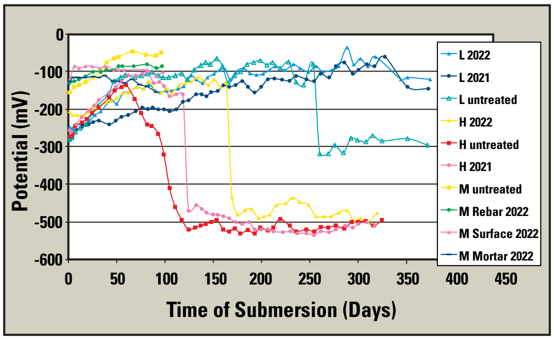
MCIs can be incorporated into concrete batches as an admixture or can be used by surface impregnation of existing concrete structures. With surface impregnation, MCIs diffuse into the deeper concrete layers to inhibit the onset of steel rebar corrosion. Bjegovic and Miksic demonstrated the effectiveness of MCIs over 5 years of continuous testing.[2-4] They also showed that the MCI admixture is effective in repairing concrete structures.[2] Laboratory tests have also proven that MCIs migrate through the concrete pores to provide rebar with protection from corrosion even in the presence of chlorides.[4,5]

FIGURE 1



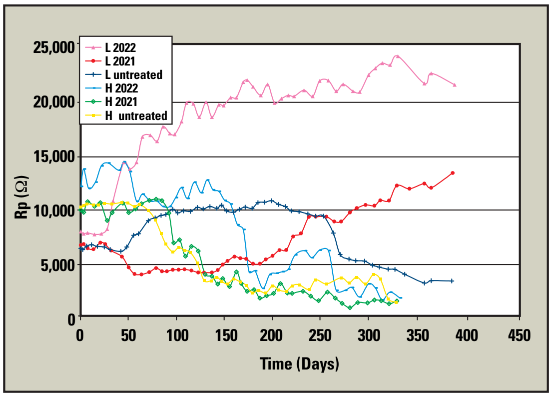
Distribution of the estimated $8.3 billion annual direct cost of corrosion for highway bridges.[1]

FIGURE 2



Corrosion potential vs time, ASTM C876-91, MCI 2022 and 2021 compared with unprotected concrete (various concrete densities).

FIGURE 3



Comparison of R_p for MCI-treated concrete (various densities) with untreated samples.

Concrete Density and MCI Application Method

The rate of MCI migration in part depends on the density and permeability of the concrete. A high-density concrete that impedes the movement of corrosive species to the surface of the rebar may also prevent the inhibitor from reaching the rebar surface. To determine the effects of concrete density and application method when using MCIs, 10 specimens comprising three concrete densities were compared for corrosion inhibition properties. Six concrete samples were prepared with corrosion inhibitors using different application methods (Table 1). Two concrete samples were left untreated as references.

Concrete samples were cast (dimensions 20 x 10 x 10 cm) using commercial-grade silica, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate). Low-density concrete at 2.09 g/cm^3 (130 lb/ft^3) was prepared with a 0.5 water/cement ratio with a concrete mixture for 2.5 ft^3 (20.4 kg cement, 40.8 kg fine aggregate, 81.7 kg coarse aggregate, and 10 kg water). Medium-density concrete at 2.24 g/cm^3 (140 lb/ft^3) was batched using a 0.50 water/cement ratio, with a concrete mixture for 2.5 ft^3 (21.8 kg cement, 43.6 kg fine aggregate, 78 kg coarse aggregate, and 10.9 kg water). High-density concrete at 2.40 g/cm^3 (150 lb/ft^3) was batched using a 0.50 water/cement ratio with a concrete mixture for 2.5 ft^3 (24 kg cement, 47 kg fine aggregate, 94.4 kg coarse aggregate, and 11.8 kg water).

TABLE 1

TEST SAMPLES

Concrete Sample (0.5 water/cement ratio)	Concrete Density	MCI	Application Method
A (2 samples)	Low (L) (2.08 g/cm^3)	2022	MCI-treated concrete surface
B (2 samples)	Low (L) (2.08 g/cm^3)	2021	MCI-treated concrete surface
C (1 samples)	Low (L) (2.08 g/cm^3)	Untreated	No MCI application
D (2 samples)	High (H) (2.40 g/cm^3)	2022	MCI-treated concrete surface
E (2 samples)	High (H) (2.40 g/cm^3)	2021	MCI-treated concrete surface
F (1 samples)	High (H) (2.40 g/cm^3)	Untreated	No MCI application
G (2 samples)	2.24 g/cm^3	Untreated	No MCI application
H (2 samples)	2.24 g/cm^3	2022	MCI-treated concrete surface
I (2 samples)	2.24 g/cm^3	2022	MCI-coated rebar cast in concrete
J (2 samples)	2.24 g/cm^3	2022	MCI-mortar mixture applied to concrete surface

The maximum aggregate size was ~1/2 to 5/8 in. (12 to 15 mm). Gradation was uniform. Coarse aggregate was crushed stone, natural gravel (river gravel), quartzite, quartz, and sandstone. Fine aggregate primarily comprised sand, quartz, and some clay. The water/cement ratio was moderately low at ~0.50. Paste content was moderate and unhydrated cement grains rarely were found in pastes. The degree of consolidation was good, the contacts of matrix with aggregates were relatively close, and some minor openings were visible on the polished or broken surfaces. The degree of air entrainment was measured to ~1.2 to 1.5% (28 to 30 mm^2/mm^3 or 700 $in.^2/in.^3$). Compressive strengths were ~3,100 to 3,950 psi (21 to 27 MPa).

Prior to being placed in the concrete sample, the steel rebar (class 60) was exposed to 100% relative humidity to initiate corrosion. The rebar was covered with a 1-in. (2.5-cm) layer of concrete. On all samples, a copper/copper sulfate ($Cu/CuSO_4$) reference electrode was used, with an Inconel 800[†] metal strip serving as the counter electrode. The concrete samples were partially immersed (87.5% of the height) in a 3.5% sodium chloride (NaCl) solution. The top portion of the concrete sample was exposed to air.

Changes in the resistance polarization (R_p) and the corrosion potential of the rebar were monitored weekly using direct current (DC) electrochemical and alternating current (AC) electrochemical impedance spectroscopy over a 450-day period to determine the effectiveness of the MCI products. After 450 days of immersion in NaCl solution, several concrete samples were cut open and the rebar removed for x-ray photoelectron spectroscopy (XPS) analysis to verify inhibitor migration through the concrete and its adherence to the rebar structure.

Investigation Results

The assessment of the corrosion inhibitors for the three concrete densities was based on open circuit potential (corrosion potential) values, R_p values, and XPS analysis.

OPEN-CIRCUIT POTENTIALS

According to ASTM C876,[11] if the open-circuit potential is –200 mV or less negative, a 90% probability exists that

[†]Trade name.

no reinforcing steel has corroded. Corrosion potentials more negative than –350 mV are assumed to have >90% likelihood of corrosion. Corrosion potentials for the high-density samples (H2021, H2022, H untreated) were between –400 mV and –600 mV after 128 days of immersion in NaCl (Figure 2). The untreated control sample (L untreated) had a corrosion potential of –295 mV at the end of testing. MCI-treated, low-density samples (L2022, L2021) had corrosion potentials ranging from –120 mV to –145 mV. The inhibited samples with a density of 2.24 g/cm^3 showed corrosion potentials between –48 mV to –175 mV during the first 130 days of testing, regardless of the application method. The low-density samples had significantly less negative corrosion potentials, indicating good passivation.

POLARIZATION RESISTANCE

Figure 3 shows the R_p values at the end of testing to be from 13,000 to 22,000 Ω for the low-density samples treated with MCI. The high-density concrete showed significantly less corrosion inhibition, with R_p values ranging from 1,000 to 2,000 Ω. R_p values for non-treated samples ended at 3,170 Ω for low-density samples and 1,200 Ω for high-density concrete. Changes in R_p value were not immediately observed, indicating that diffusion of corrosive species or MCIs into the concrete requires an induction period (~120 days). Figure 4 illustrates the substantial difference between low-density and high-density concrete samples.

XPS ANALYSIS

Figure 5 shows the XPS spectra for two rebar removed from the MCI-treated samples after 450 days. The inhibitors had penetrated the concrete layer, reaching the rebar and slowing down corrosion. Figure 6 illustrates the depth profiling of steel rebar removed from MCI-treated concrete samples, indicating that a 140-nm layer of amine-rich compound (amine-based MCI) was detected on the rebar's surface. Chloride was also found on the rebar surface, with deposits varying from 0.99 and 0.84 wt% concentration for MCI 2022 and MCI 2021, respectively. The XPS results showed that MCI and corrosive species (chloride ions) had migrated through the concrete, but the MCI had neutralized the corrosive species and protected the steel rebar.

Conclusions

Lower-density concrete samples provided an easier path for the inward diffusion of MCI, resulting in faster corrosion retardation. The MCI products were found to offer protection for the steel rebar by suppressing the chloride ions. They are capable of inhibiting corrosion in aggressive environments, such as seawater. MCIs continue to demonstrate their effectiveness in protecting reinforced concrete structures.

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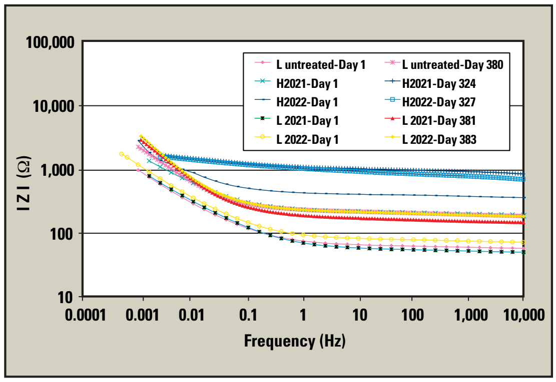
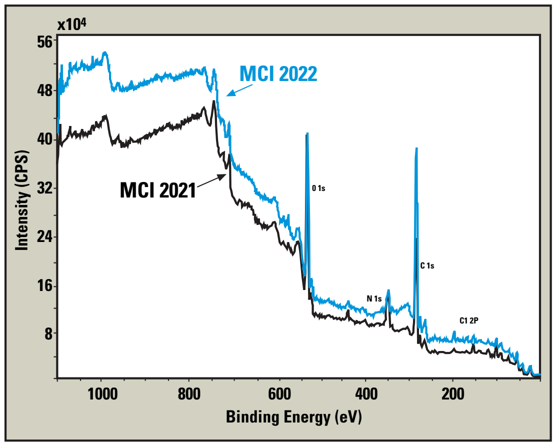
FIGURE 4



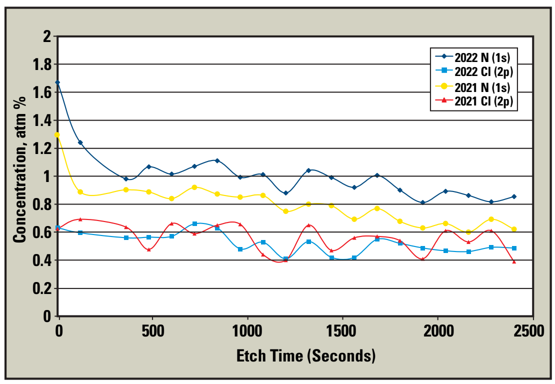
Comparison of AC impedance spectroscopy bode plot results for low (L)- and high (H)-density concrete.

FIGURE 5



XPS spectrum of steel rebar removed from MCI-treated concrete after 450 days of submersion. Large area (1,000 by 800 mm) survey scan. Lens mode electrostatic; resolution pass energy –160; anode: Mg (150 W).

FIGURE 6



XPS depth profiles of steel rebar removed from MCI-treated concrete samples after 450 days of submersion (etched using 2kV argon ions).

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