

Use of UV Spectroscopy for Detecting Migrating Corrosion Inhibitor Depth in Concrete

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Migrating corrosion inhibitors (MCIs) are organic inhibitors based on amino-carboxylate chemistry that have been effectively used for the protection of embedded steel rebar in concrete. This work discusses MCI detection using ultraviolet spectrophotometric methods. We found that five weeks after a surface was impregnated with a MCI, the inhibitor migrated to a depth of more than 3 in (76 mm).

Migrating corrosion inhibitor (MCI) technology was developed to protect embedded steel reinforcement and the concrete structure. MCIs are organic compounds that protect by forming a monomolecular barrier film on the metal surface to prevent attack by harsh elements.¹⁻²

In new and well-constructed concrete, cement paste provides an alkaline environment. Steel forms a protective ferric oxide (Fe_2O_3) film in this alkaline environment and is protected. With time, however, carbonation occurs in concrete that reduces the pH of pore water and destroys the Fe_2O_3 film. Ingression of chloride ions also destroys the Fe_2O_3 film. When the protective Fe_2O_3 film is compromised, corrosion of rebar starts, which leads to subsequent spalling and cracking of a concrete structure. Thus, corrosion inhibition measures are necessary to ensure a safer concrete structure with a longer life. This is particularly true in corrosive environments such as coastal areas, locations where deicing salts are commonly used, acid rain-affected regions, and locales where high humidity is common. According to a recent report, the estimated annual costs of repairing and protecting concrete structures is between \$18 to \$21 billion in the United States alone.³

MCIs have been used effectively for the protection of rebar in concrete.^{1,3-5} MCIs can be incorporated as concrete admixtures or as topical treatments on existing concrete structures through surface impregnation or MCI repair mortar application. MCIs have been shown, with x-ray photoelectron spectroscopy (XPS) analysis,⁶ to migrate through concrete capillary networks and form a protective layer on rebar that provides protection in the presence of chlorides.^{4,7}

When a MCI is topically applied, there is interest in understanding its migration profile in the concrete at a given time. There is also interest in verifying the dosage when a MCI is used as an admixture. Both call for a detection method for the MCI. There are several challenges associated with developing a reliable MCI

detection method—the method needs to be able to detect a minute amount of MCI, which is typically dosed at very low rates in concrete. In addition, concrete mix designs vary considerably and concrete itself is highly alkaline.

Currently, the following methods exist for detecting MCI in concrete:

- Alkalinity test by titration
- Quaternary ammonium compound test kit
- Detection of tracer
- Detection using ultraviolet (UV) spectroscopy
- XPS

This work focuses on detecting MCI using UV spectroscopy because this spectroscopy is routinely used in analytical chemistry and is easily accessible. It also provides the ability to detect low concentrations of a MCI. Using UV spectroscopy, the inhibitor was detected at 3 in (76 mm) below a concrete surface treated with a topical MCI after five weeks. This method also can be easily applied to verify the admixture dosage rate of a MCI.

Experimental Procedures

Concrete Specimens

Concrete specimens were prepared using Portland Type I cement, playground sand, and tap water. The water/cement/sand ratio is 0.45/1/3 by weight and the cylinder dimensions were ~2.75 in (70 mm) (D) by 4 in (100 mm) (H). The concrete was cured for 28 days.

Topical Migrating Corrosion Inhibitor Application

The top face of a cured concrete cylinder was coated with a surface-applied MCI product, MCI-2020[†] (Figure 1). The coverage was 0.026 g/cm². The MCI coating was allowed to stay on the concrete surface for four or five weeks.

Migrating Corrosion Inhibitor Migration Depth Profile Analysis

The MCI-impregnated specimens were cross-cut into 0.5-in (13-mm) thick discs (Figure 1), four and five weeks after MCI

FIGURE 1

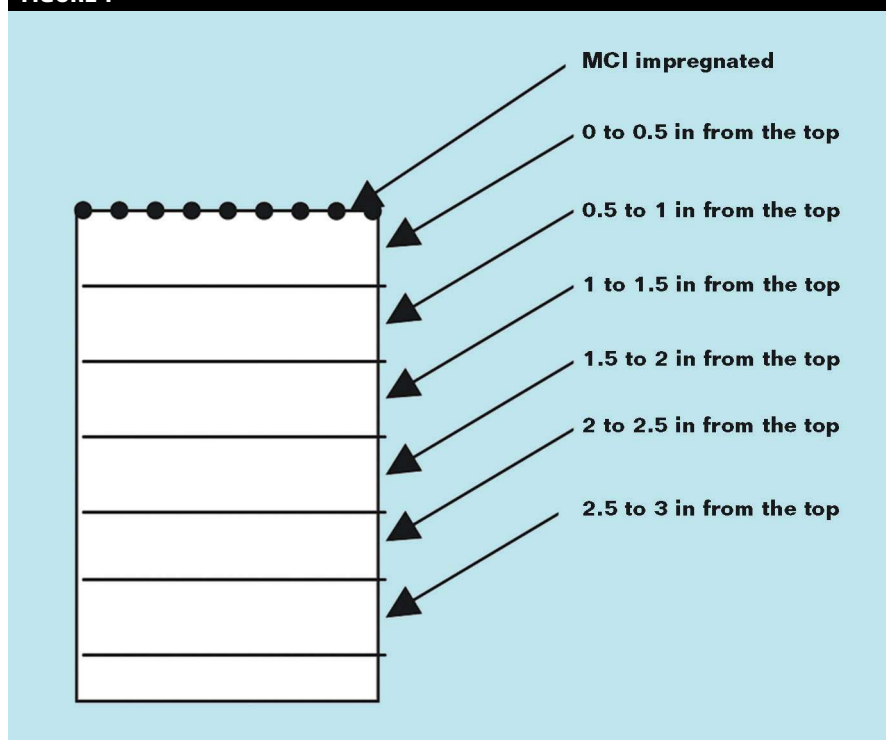
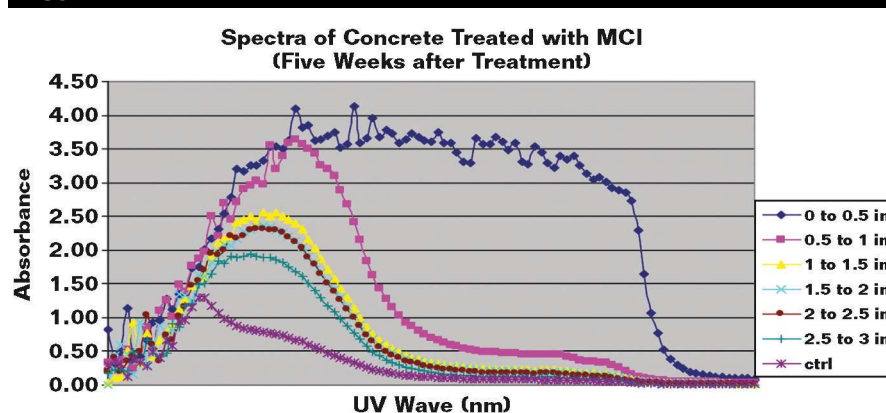


Illustration of MCI migration depth analysis in concrete.

FIGURE 2



Spectra of concrete extract at different depths five weeks after treatment.

treatment, respectively. Each disc was labeled with its distance from the MCI-treated top. The concrete discs were pulverized and the powders that passed through a #20 sieve were saved for analysis.

Extraction of Migrating Corrosion Inhibitor

Equal weights of the concrete powder and deionized (DI) water were mixed thoroughly in a capped jar, and allowed

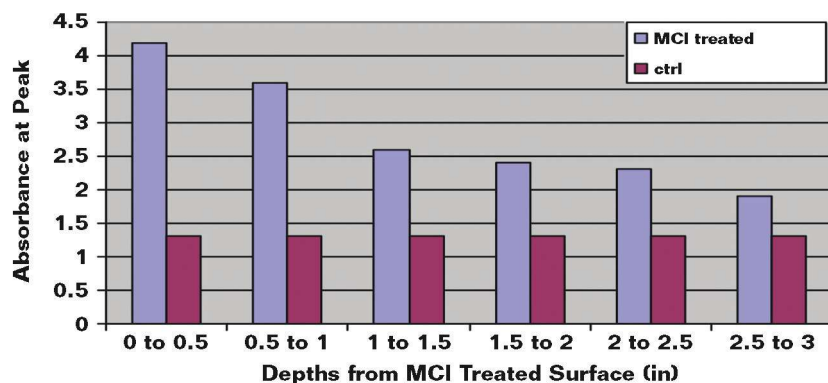
to stand at least 4 h. The extracted liquid was filtered (0.45 µm) and used for UV analysis.

Ultraviolet Detection

Water extracts of the concrete samples were analyzed using a UV-Vis spectrophotometer (Thermo Scientific Evolution 201[†]) with a 10-mm light path disposable UV cuvette (Brand Tech[†]).

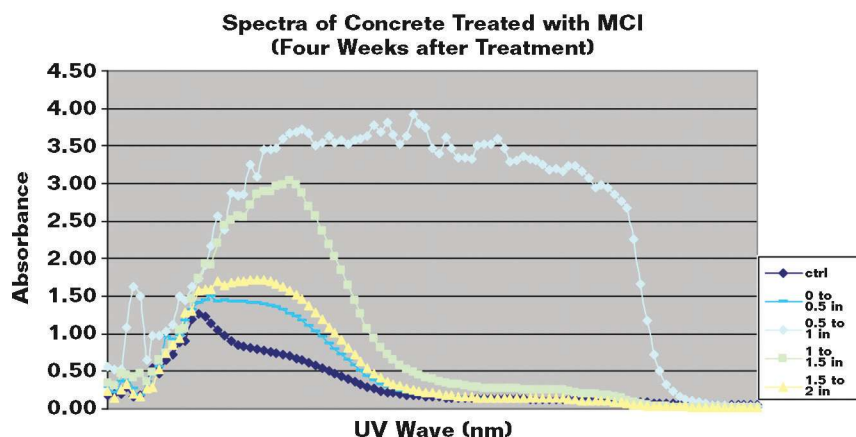
[†]Trade name.

FIGURE 3



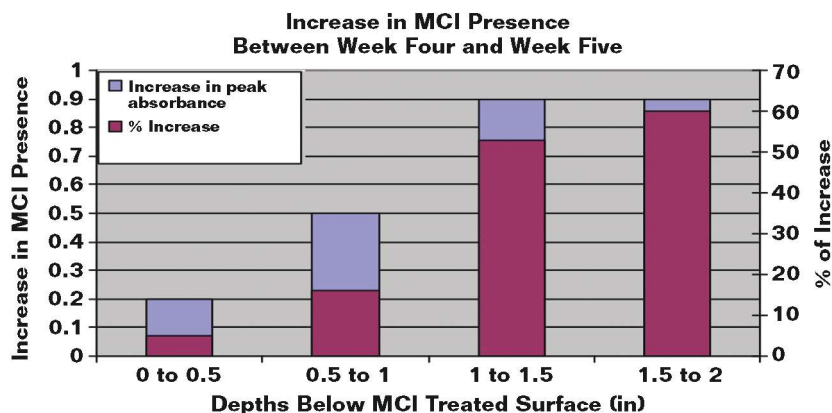
Progression of MCI migration five weeks after treatment.

FIGURE 4



Spectra of concrete extract at different depths four weeks after treatment.

FIGURE 5



Increase in MCI abundance in concrete interior between week four and week five.

DI water was used to obtain a machine background. Scans were performed in the UV range. The spectrum of each sample was compared with that of a control sample (a concrete of the same mix design but without MCI treatment) to derive the MCI presence in the sample.

Results

The inhibitor is detected as a distinctive peak in UV spectroscopy and the height of the peak represents the abundance of the inhibitor. The water extracts of the MCI-treated concrete slices all exhibited this distinctive peak in their spectra. When compared to the spectrum of the control, MCI was shown at 3 in below the treated surface (Figure 2). The spectra also showed that five weeks after the application, the inhibitor abundance in concrete at 0.5 in below the treated surface was similar to that at the surface. In addition, there was a logical progression of MCI migration in the concrete cylinder, as demonstrated in Figure 3.

By examining the spectra of concrete slices cut at four weeks (Figure 4) and five weeks (Figure 2) after the topical treatment with a MCI, it was found that there was considerable progression of MCI moving deeper into the concrete interior and becoming available for rebar protection. Between week four and week five, the increase in MCI abundance was ~60% at the depths of 1 to 2 in (25 to 51 mm) below the treated surface, the area where the steel reinforcement is typically located (Figure 5). It would be reasonable to anticipate that this migration of MCI from the surface into the interior of concrete continues with time.

Conclusions

UV spectroscopy showed that the inhibitor was detectable in the UV range. Using UV spectroscopy, the MCI was found at 3 in below a treated surface. Furthermore, it was found that the inhibitor migrated at a considerable rate from a treated surface into the concrete interior. The abundance of MCI at

depths of 1 to 2 in below the treated surface increased ~60% between week four and week five following a surface treatment.

References

- 1 D. Stark, *Influence of Design and Materials on Corrosion Resistance of Steel in Concrete* (Skokie, IL: Portland Cement Association, 1989).
- 2 D. Bjegovic, B. Miksic, "Migrating Corrosion Inhibitor Protection of Concrete," *MP* 38, 11 (1999).
- 3 P. Emmons, D. Sordyl, "The State of the Concrete Repair Industry, and a Vision for its Future," *Concrete Repair Bulletin*, July/August 2006.
- 4 D. Rosignoli, L. Gelner, D. Bjegovic, "Anticorrosion Systems in the Maintenance, Repair and Restoration of Structures in Reinforced Concrete," International Conf. Corrosion in Natural and Industrial Environments; Problems and Solutions, held May 23-25, 1995 (Houston, TX: NACE International).
- 5 B. Bavarian, L. Reiner, "Corrosion Inhibition of Steel Rebar in Concrete by Migrating Corrosion Inhibitors," Eurocorr 2000 (Bedfordshire, U.K.: The Institute of Corrosion).
- 6 B. Baravian, L. Reiner, "Corrosion Protection of Steel Rebar in Concrete using Migrating Corrosion Inhibitors," BAM 2001 (London, U.K.: BAM, 2001).
- 7 A. Phanaganokar, B. Cherry, M. Forsyth, "Organic Corrosion Inhibitors: How Do They Inhibit and Can They Really Migrate Through Concrete?" Proc. Corrosion and Prevention 97, held November 9-12, 1997 (Kerrimuir, VIC, Australia: Australasian Corrosion Association).

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