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Detecting MCI in Concrete Using UV-Spectroscopy -Migration Depth and Dosage Detections

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Abstract

Migrating Corrosion Inhibitors (MCI) are organic inhibitors based on amino-carboxylate chemistry. MCIs have been effectively used for the protection of embedded steel rebar in concrete. They can be incorporated as admixture, as topical treatment on existing concrete structures through surface impregnating, or as MCI repair mortar. Detection of the presence of MCI in treated concrete is important for the purpose of verifying MCI admixture dosage rate, and understanding MCI migration depth after topical treatment. A reliable and accessible detection method has been very much sought after. This work discusses the methods of MCI detection through simple physical-chemical means. Using a UV spectrophotometric detection method, it was found that the inhibitor migrates to a depth of more than 7.62cm (3”) below a treated surface 5 weeks after the surface was impregnated with MCI. Study on the inhibitor amount at 5.08cm (2”) depth showed that between week 4 and week 5 the inhibitor migrated to the interior of the concrete at a considerable rate to avail itself for rebar protection. The UV method was also used to verify MCI dosage rates in various concrete mix designs.

Keywords: migrating corrosion inhibitors, reinforced concrete, detection of MCI, migration depth of MCI in concrete, MCI admixture dosage verification, UV-spectroscopy

Introduction

Migrating Corrosion Inhibitors (MCIs) are organic compounds that can migrate through concrete and form a barrier film on metal surface to prevent attack of harsh elements (1, 2).

In new and well-constructed concrete, cement paste provides an alkaline environment that fosters a protective ferric oxide film on steel rebar. However, concrete settlement cracking is common, causing intrusion of corrosive species that destroy the ferric oxide film. With time carbonation also occurs, reducing the pH and destroying the ferric oxide film. Both factors initiate corrosion of rebar that causes subsequent spalling and further cracking of a concrete structure. Thus, corrosion inhibition measures are necessary. This is particularly true in corrosive environments. The estimated annual costs of repairing and protecting concrete structures is $18 to $21 billion in the U.S. alone (3).

MCIs have been used effectively for the protection of rebar in concrete (1,2,4,5). MCI can be incorporated as concrete admixtures, as topical treatment or repair mortar on existing concrete structures. MCIs have been shown, with XPS analysis (6), to migrate through concrete and form a protective layer on rebar, providing protection in the presence of chlorides (4,5,6,7).

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When MCI is topically applied, there is interest in understanding its migration profile in the concrete at a given time. When MCI is used as an admixture there is interest in verifying the dosage. Both call for a detection method of MCI in concrete. The challenges in developing a reliable MCI detection method are that the method needs to be able to detect minute amount of MCI which is typically dosed at very low rates, that concrete mix designs vary considerably, and that concrete itself is highly alkaline. Currently the following detection methods of MCI in concrete exist: alkalinity test by titration, quaternary ammonium compound test kit, detection of tracer, detection using UV spectroscopy, and X-ray photoelectron spectroscopy (XPS).

This work focuses on detecting MCI using UV spectroscopy, a tool routinely used in analytical chemistry and is easily accessible. UV spectroscopy also provides the ability to detect low concentrations. Using UV spectroscopy, the inhibitor was detected at 7.62cm (3”) below a concrete surface treated with a topical MCI (MCI-2020) after 5 weeks. This method also can be applied to verify admixture dosage rate of MCI-2005.

Methodology

Concrete specimens 2 kinds of concrete specimens were prepared:
Concrete specimens without admixture were made as blank to receive MCI topical treatment. They were prepared using Portland Type I cement, playground sand and tap water. The water/cement/sand ratio is 0.45/1/3 by weight. They were molded in cylinder with the approximate dimension of 7cm (D) x10cm (H). The concrete was cured for 28 days.

Concrete specimens with MCI admixture were made with various doses of an admixture (MCI2005). The portioning and curing of the specimens were similar to that of the blank specimens

Topical MCI application A surface-applied MCI product, MCI-2020, was coated to the top face of a cured concrete cylinder (Figure 1). The coverage was $0.026 g/cm^2$. The MCI coating was allowed to stay on the concrete surface for 4 or 5 weeks.

MCI migration depth profile analysis The above MCI impregnated specimens were cross-cut into 1.3cm (0.5”) thick discs (Figure 1), 4 and 5 weeks after MCI treatment, respectively. Each disc was labeled with its distance to the MCI treated top. The concrete discs were pulverized and the powders that passed a #20 sieve were saved for analysis.

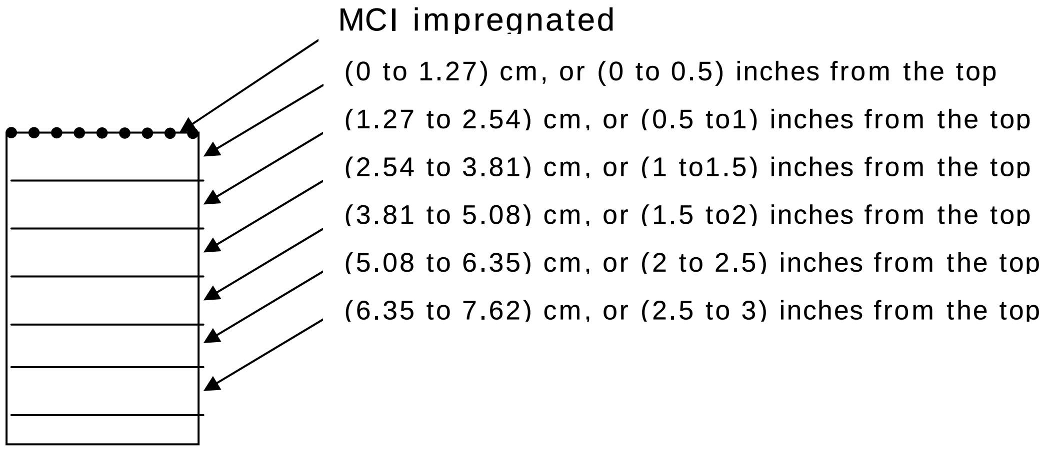

Figure 1 - Illustration of MCI migration depth analysis in concrete

Admixture dosage verification Concrete specimens containing 0.5X, 1X, 1.7X dose of an admixture, MCI-2005, were made. These specimens, and a blank of the corresponding mix design, were pulverized after curing and the powders that passed a #20 sieve were saved for analysis. A correlation of the dosage vs. peak height from the resulting UV spectra was established and used to verify the dosage of the admixture in an unknown sample of the same mix design.

Extraction of MCI Equal weight of the concrete powder and de-ionized water were mixed thoroughly in a capped jar, and allowed to stand at least 4 h. The extracted liquid was filtered (0.45µm PTFE) and used for UV analysis.

UV detection Water extracts of the concrete samples were analyzed using a UV-Vis spectrophotometer (Thermo Scientific Evolution 201) with a 1cm light path disposable UV cuvette (Brand Tech). De-ionized water was used to obtain a machine background. Scans were performed in UV range. The spectrum of each sample was compared with that of a blank (control), a concrete of the same mix design but without MCI treatment, to derive at MCI presence in the sample.

Results and discussion

Topically Applied Inhibitor Migration Depth Study

The MCI 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 7.62cm (3”) below the treated surface, Figure 2. The spectra also showed that 5 weeks after the application, the inhibitor abundance in concrete at 1.27cm (0.5”) below the treated surface was similar to that at the surface. In addition, a logical progression of MCI migration in the concrete cylinder is demonstrated in Figure 3.

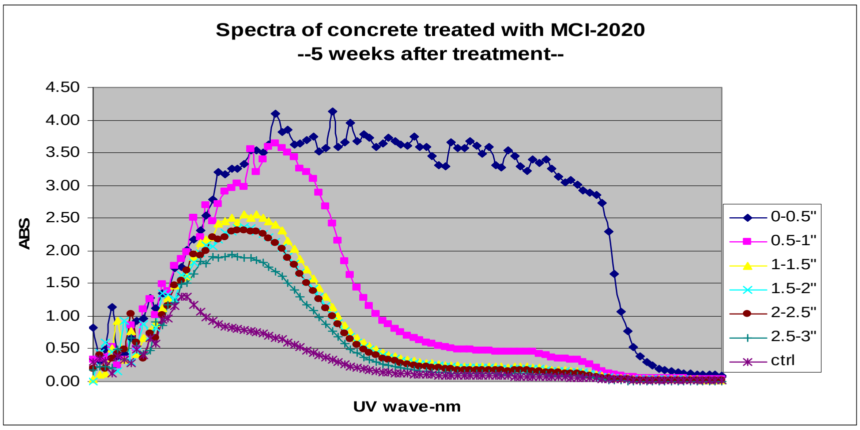

Figure 2 - Spectra of Concrete Extract at Different Depths 5 Weeks after Treatment

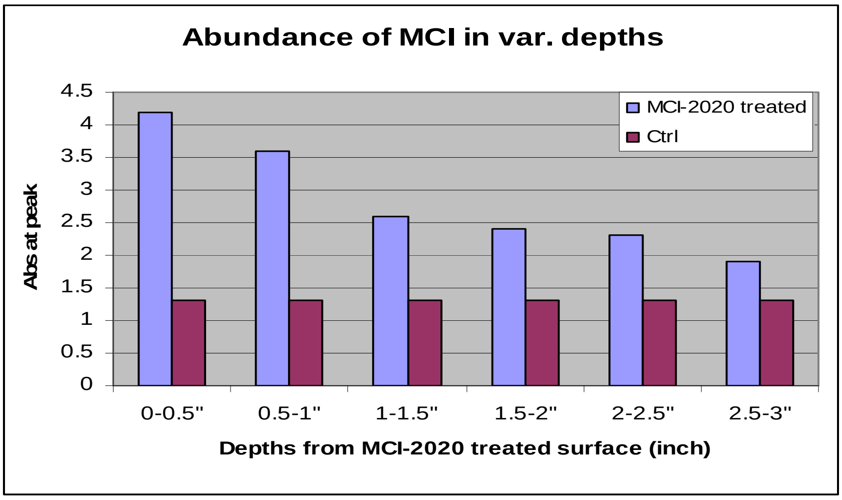

Figure 3 - Progression of MCI Migration 5 Weeks after Treatment

By examining the spectra of concrete slices cut at 4 weeks (Figure 4) and 5 weeks (Figure 2) after the topical treatment of MCI-2020, it was found that there was considerable progression of MCI moving deeper into the concrete interior and become available for rebar protection. Between week 5 and week 4, the increase in MCI abundance was about 60% at the depths 2.54cm (1 inch) to 5.08cm (2 inches) below the treated surface, the area where the steel reinforcement is typically located. It would be reasonable to anticipate this migration of MCI from surface into the interior of concrete continues with time.

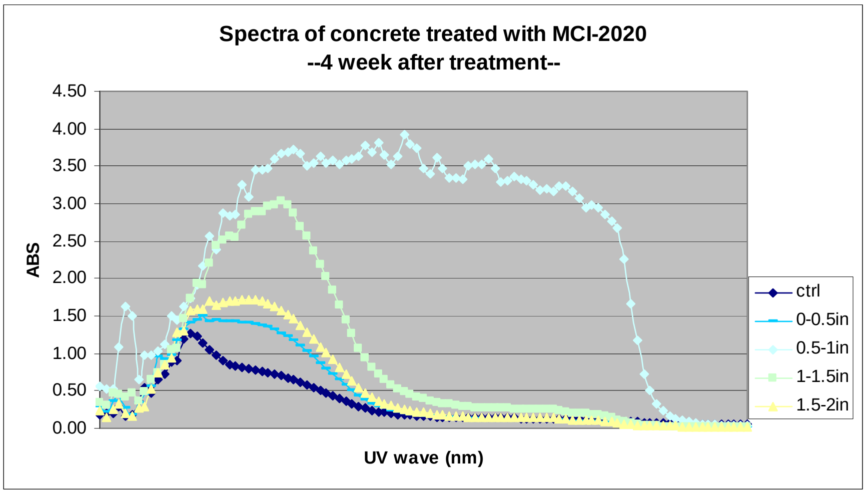

Figure 4 - Spectra of Concrete Extract at Different Depths 4 Weeks after Treatment

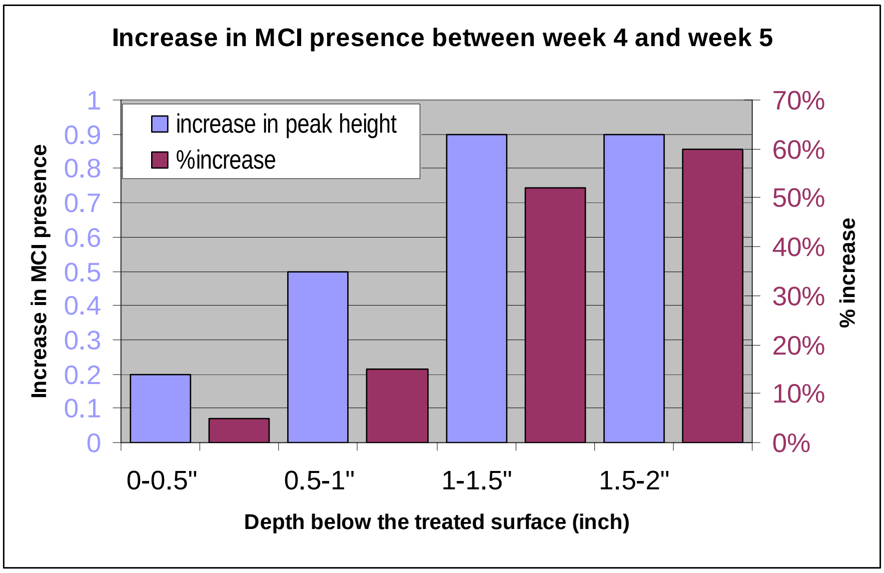

Figure 5 - Increase in MCI Abundance in Concrete Interior

Between Week 4 and Week 5

Admixture Dosage Verification

To verify dosage of an admixture in a particular concrete, it is necessary to have specimens of known dosages and a blank of the corresponding mix design. Their powders will be extracted with water and their spectrum will be obtained, Figure 6. A correlation of the known dosages and their absorbance peaks shows a linear relationship, Figure 7. Using this correlation, the dosage of the admixture in an unknown sample can be detected.

With certain mix designs, the correlation can be established after an additional separation step. Analysis of the relevant blank will dictate if the separation is necessary.

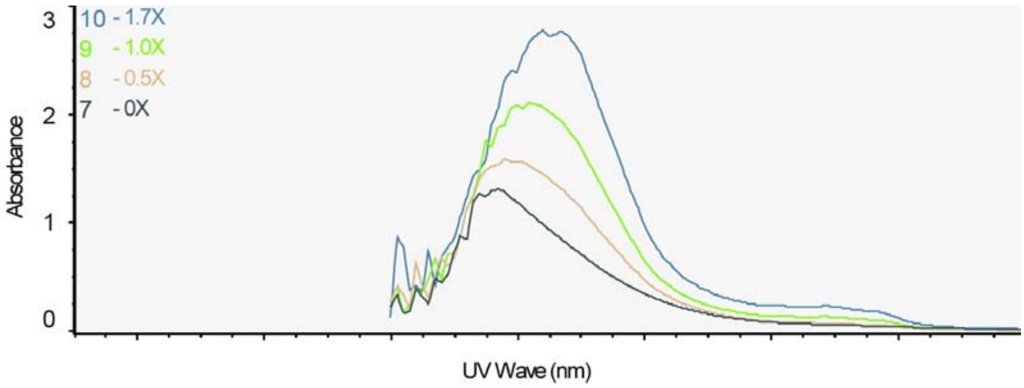

Figure 6 - Spectra of Concrete of Known Dosages of an Admixture

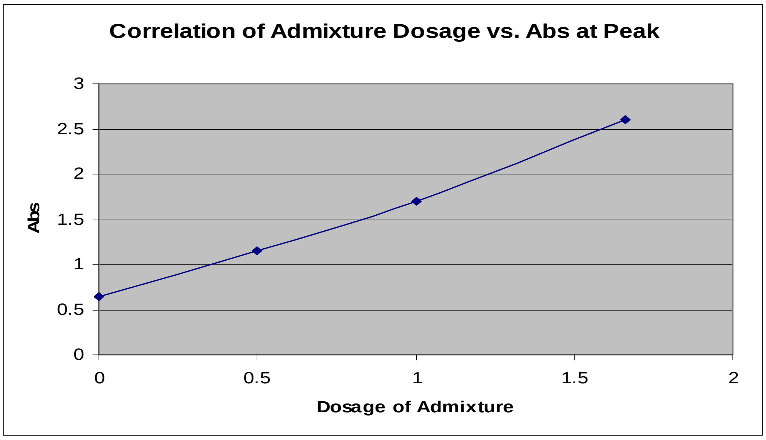

Figure 7 - Correlation of Dosage and Abs Peak

Conclusions

UV spectroscopy showed that the inhibitor in MCI was detectable in UV range. Using UV spectroscopy, the MCI was found at 7.62cm (3”) below a treated surface (Figures 2, 3). Furthermore, it was found that the inhibitor migrated at considerable rate from a treated surface into concrete interior. The abundance of MCI at 1 to 2 inches below the treated surface increased about 60% between week 5 and week 4 following a surface treatment (Figure 5).

UV spectroscopy was also used to verify the dosage of admixture in concrete. A linear correlation of dosage vs. absorbance peak should be established for each mix design and referred to find the admixture dosage in unknown specimen for the corresponding concrete (Figures 6, 7).

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