Detecting Corrosion Inhibitor Migration Depth in Topically Treated Concrete Using Mass Spectrometry

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Direct analysis in real-time mass spectrometry (DART-MS) is an ambient atmosphere mass spectrometry technique. It allows quick analysis with minimum sample preparation. DART-MS was used to detect inhibitor penetration depths into a concrete interior when its surface received topical migrating inhibitor treatment. Two different concrete topical treatments were studied. One is a penetrating silane sealer. The other is a pure migrating inhibitor topical product. Concrete chips at various depths were taken at different times after the concrete surface was given a topical treatment. The analysis showed that five weeks after receiving the silane sealer, the corrosion inhibitor in the sealer was present at 1.2 in (30 mm) below the treated surface. Testing on concrete cores taken 12 weeks after the pure inhibitor topical treatment indicated that one inhibitor was detected as deep as 3 in (76 mm) below the treated surface. Both results indicate that migrating topical inhibitors penetrate into the concrete interior and become available for protection of embedded steel reinforcement.

Across America and the world, structures are being used longer than their original design life. Maintenance is often significantly delayed, leading to even more damage and increasing the cost of repairs while decreasing the useful service life.

The American Society of Civil Engineers (ASCE) releases a report card on the American infrastructure every four years, using a simple A to F school report card format. Since 1998, the grades have been near failing, averaging only Ds, due to delayed maintenance and underinvestment across most categories.[1] The average grade for the 2013 report is a D+, and an estimated investment of \$3.6 trillion dollars is needed by the year 2020 to improve the infrastructure to a grade of B.[1]

Spearheaded by the American Concrete Institute (ACI) and the International Concrete Repair Institute (ICRI), durability models such as LIFE-365† have been developed in an effort to better evaluate life cycle performance of infrastructures and to reward practices that enhance durability and include eco-friendly designs.[2]

To meet the challenge of safely extending the existing infrastructure service life, migrating corrosion inhibitor (MCI) topical treatments have been developed since the mid-1980s.[3] The inhibitors are mostly in the family of vapor phase corrosion inhibitors (VCIs), or a blend of volatile corrosion inhibitors and contact corrosion inhibitors.[3] One of the advantages of topical treatment is its ease of use on existing structures. It is also economical compared to other remedial procedures.

Studies on efficacy of topical corrosion inhibitor treatments have shown that this type of mitigation technique reduced corrosion rates by 93%,[4] or extended the life expectancy by more than 15 to 20 years.[5] Furthermore, x-ray photoelectron spectroscopy (XPS) analysis of the rebar embedded in concrete topically treated with corrosion inhibitors showed that the inhibitor penetrated into rebar surfaces and formed a protective layer.[5]

Construction engineers or contractors, however, often like to know how deep or how soon the corrosion inhibitors in topical treatment would migrate from a treated surface into the concrete interior and avail themselves for the protection of embedded rebar. A simple, straightforward detection method is desired.

Direct analysis in real time-mass spectroscopy (DART-MS) is a mass spectroscopy technique that uses an atmospheric pressure ion source to instantaneously ionize gases, liquids, and solids in open air under ambient conditions.[6] It allows analyzing samples in their native state with little or no preparation, and can produce rapid results. The ionized samples can be analyzed directly by mass spectrometer.[7] DART-MS has been used for analyses in the fragrance, pharmaceutical, foods and spices, forensic science, and health industries.

DART-MS was selected as a detection tool for MCIs in concrete due to its simple sample preparation requirements. The

†Trade name.

added advantage of analyzing samples in ambient atmosphere vs. the high vacuum required in XPS makes DART-MS particularly suitable for analyzing VCIs.

Reported here are the results of DART-MS analysis on concrete specimens at various depths from concretes that received topical corrosion inhibitor treatments. Two topical treatments were studied. Treatment A is a silane sealer containing corrosion inhibitor. Treatment B is a water-based surface treatment product of corrosion inhibitors. Results of DART-MS analysis demonstrated that inhibitors from the surface treatment migrate into the concrete interior and can be detected as deep as 3 in (76 mm) below a treated surface, and avail them to the embedded steel reinforcement for their corrosion protection.

Experimental Procedures

Two corrosion inhibitor topical treatments were studied. Treatment A is a silane sealer containing MCI. Treatment B is a water-based surface treatment product of MCIs.

Table 1 describes concretes and the surface treatment they received prior to DART-MS analysis.

Treatment A was applied to a surface of a newly made concrete block (100 by 100 by 100 mm). Five weeks after the treatment, the block was cut lengthwise. Concrete chips at the surface, at 0.6 in (15 mm) and 1.2 in (30 mm) below the treated surface, were chiseled out for analysis.

Treatment B was applied to an existing concrete structure, circa 1920. The treated surfaces were the underside of an outdoor plaza floor and its supporting beams in a crawl space below grade. Cores were taken 12 weeks after the treatment. The analysis of two cores taken from the supporting beams (B1 and B2) and one core taken from the plaza floor underside (U) are presented here. Again, concrete chips at various depths were chiseled out of the cores for analysis. Table 2 illustrates the labeling of each concrete chip for Treatment B. Blanks—concrete that received no topical treatment—were also analyzed with DART-MS as controls.

TABLE 1. CONCRETE SPECIMENS AND CORROSION INHIBITOR SURFACE TREATMENT RECEIVED

Topical Treatment	A	B
Concrete Description	Type 1 Portland cement; water/cement ratio 0.45. Cured 28 days prior to receiving topical treatment.	Existing concrete structure, circa 1920.
Topical Treatment Dosage	125 ft² /gal (3 m²/L)	150 ft²/gal (3.68 m²/L)
Time Lapse Between Topical Treatment and Concrete Sampling	5 weeks	12 weeks
Depths Analyzed	Surface, 0.6 in, 1.2 in below surface	Surface, 0.6 in, 1.2 in, 1.8 in (48 mm), 2.4 in (61 mm), 3 in below surface.

TABLE 2. LABELING OF CONCRETE SPECIMENS (TOPICAL TREATMENT B)

Specimens	Depth (in)	Note
B1-1	Surface	Beam
B1-2	0.6	Beam
B1-3	1.2	Beam
B1-4	1.8	Beam
B2-1	Surface	Beam 2
B2-2	0.6	Beam 2
B2-3	1.2	Beam 2
B2-4	1.8	Beam 2
U-1	Surface	Floor underside
U-2	0.6	Floor underside
U-3	1.2	Floor underside
U-4	1.8	Floor underside
U-5	2.4	Floor underside
U-6	3	Floor underside

An Accutof[†] time-of-flight (TOF) mass spectrometer operated in positive ion mode was employed for mass measurements. The mass spectrometer resolving power was ~6,000 as measured for protonated reserpine (m/z 609.2812). A mass spectrum of poly (ethylene glycol) with average molecular weight 600 (50 µL in 10 mL methanol [MeOH]) was obtained with each data acquisition as a reference standard for exact mass measurements. The atmospheric pressure interface was typically operated at the following potentials: orifice 1 = 30 V, orifice 2 = 5 V, ring lens = 10 V. The RF ion guide voltage was set to 300 V to allow detection of ions greater than m/z 30. The DART ion source was operated with helium gas at 400 °C. The mass range was m/z 30 to 600.

Concert samples were held in the gas stream for a few seconds, using a pair of forceps, taking care not to block the mass spectrometer sample cone entrance.

Results

Treatment A

Treatment A contained one inhibitor. Its manifestation in DART-MS was a peak at m/z 90.1. This peak was detected at the surface, at 0.6 in and at 1.2 in below the treated surface when the concrete was analyzed five

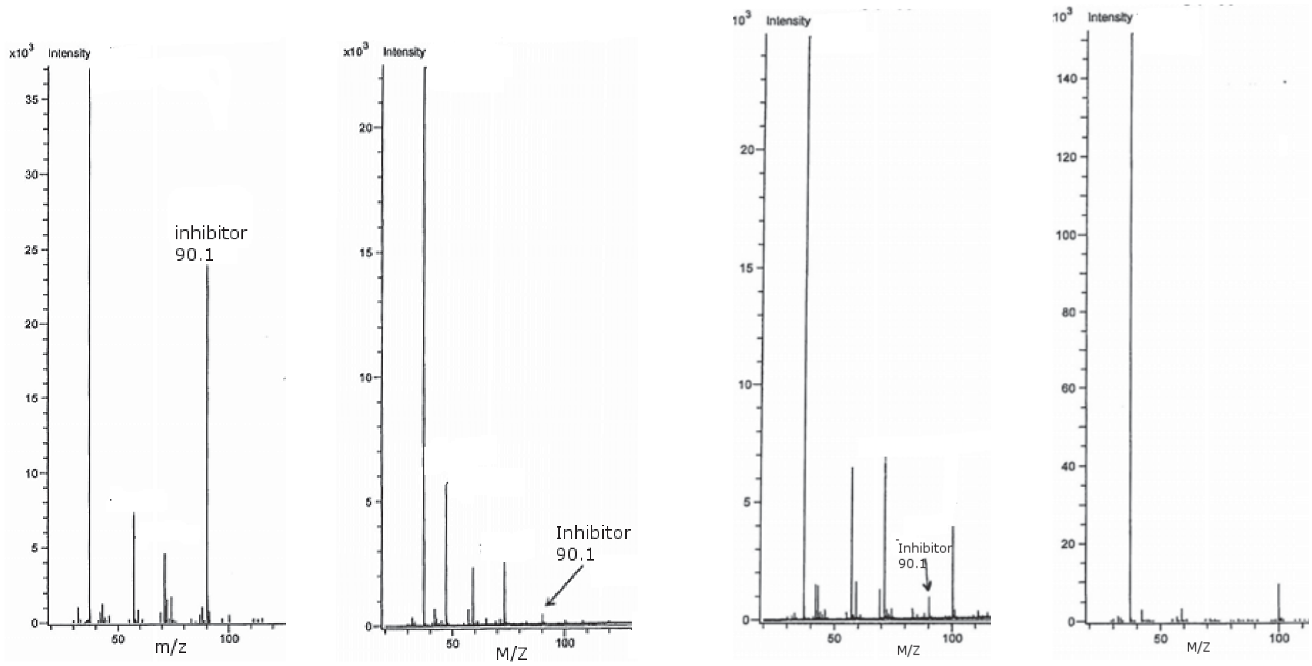


FIGURE 1. Mass spectra of Treatment A coated concrete at various depths casings.

TABLE 3. INHIBITOR DETECTION AT VARIOUS DEPTHS (TREATMENT B)

Specimens	Inhibitor I	Inhibitor II	Inhibitor III
B1-1	Yes	Yes	Yes
B1-2	Yes	Yes	Yes
B1-3	Yes	Yes	No
B1-4	Yes	Yes	No
B2-1	Yes	Yes	Yes
B2-2	Yes	Yes	No
B2-3	Yes	No	No
B2-4	Yes	Yes	Yes
U-1	Yes	Yes	Yes
U-2	Yes	Yes	No
U-3	Yes	Yes	No
U-4	Yes	Yes	No
U-5	Yes	Yes	No
U-6	Yes	Yes	Yes
Control	No	No	No

weeks after the topical treatment. This peak was not detected in untreated concrete (control) (Figure 1).

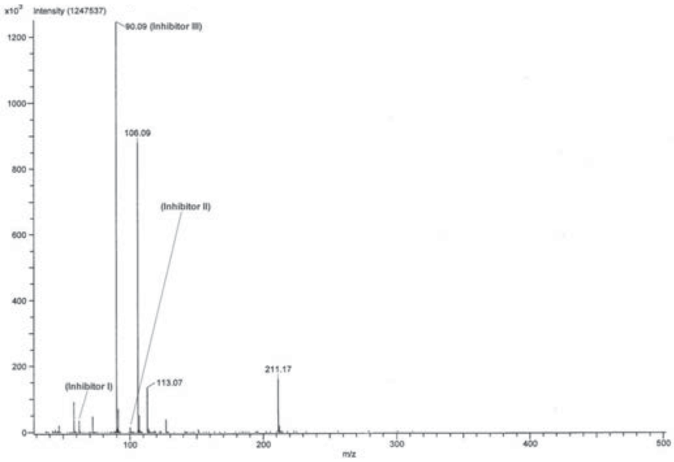
Treatment B

Treatment B contained a number of inhibitors. Inhibitor I manifested as a peak at m/z 62, Inhibitor II at 100.1, and Inhibitor III at 90.1. Table 3 shows a summary of inhibitor detection at various concrete chips.

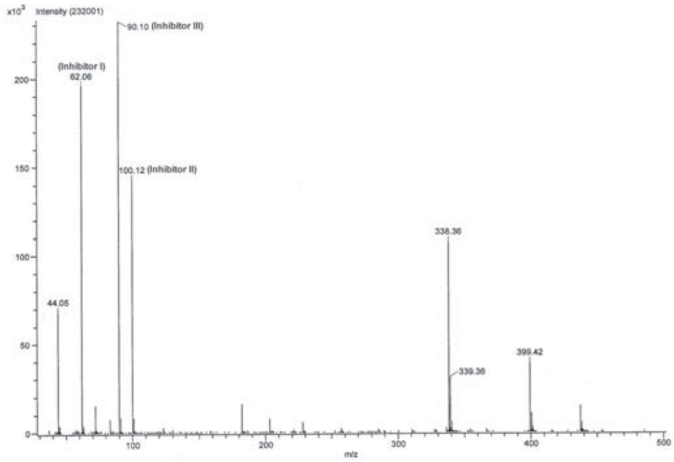
DART-MS data in Table 3 shows that Inhibitor I and Inhibitor II were detected at all depths, as deep down as 3 in below the surface that received Treatment A. The only exception is Inhibitor II in specimen B2-3. One possible explanation for the absence of Inhibitor II in this analysis of B2-3 could be that the ion beam hit at not the cement paste but at the interior of an aggregate, since inhibitors mostly migrate within the cementitious material, but not aggregates. Inhibitors I and II were detected in all the treated concrete samples—two cores from the treated beams and one core from the treated underside of the plaza floor. Inhibitor III was detected less consistently at various depths. It was shown in all the surface specimens, and at 1.8 in depth in specimen B2-4 and at 3 in depth in U-6, but was absent in other specimens.

Penetration depth data of Inhibitor I and Inhibitor II in concrete indicate that these inhibitors are present at the depth of embedded rebar; they are available to be adsorbed onto the rebar surface to form a protective layer. This data corresponds to the XPS analysis of embedded rebar in topically treated concrete.[5]

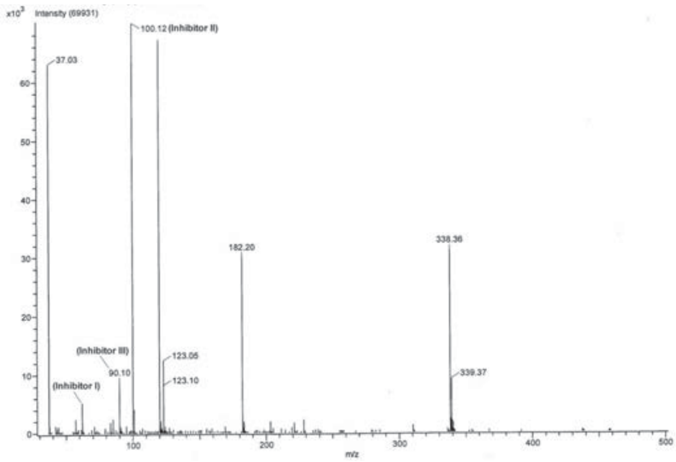
Representative mass spectra of Treatment B, of four concrete chips at different depths from core B1 (taken from the treated beam), and of a concrete chip taken from



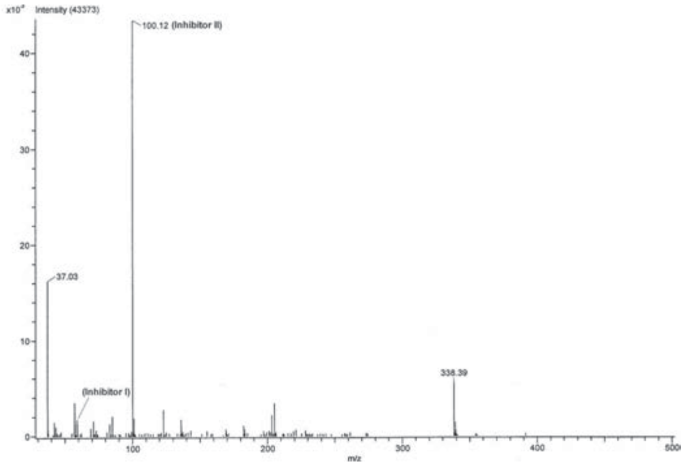
(a) Mass spectrum of Treatment B.



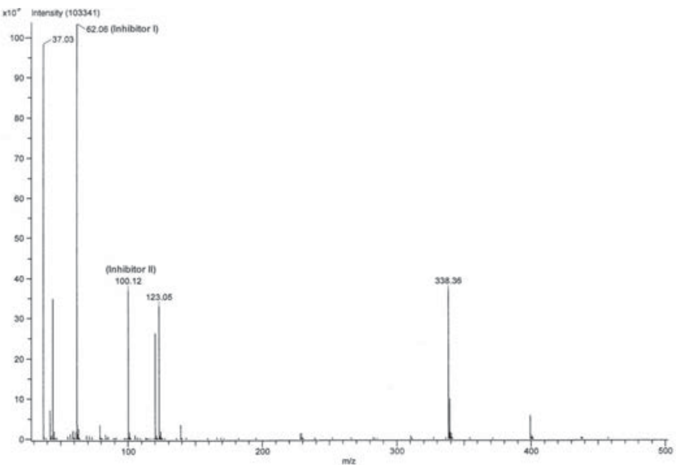
(b) Mass spectrum of concrete surface of treated beam.



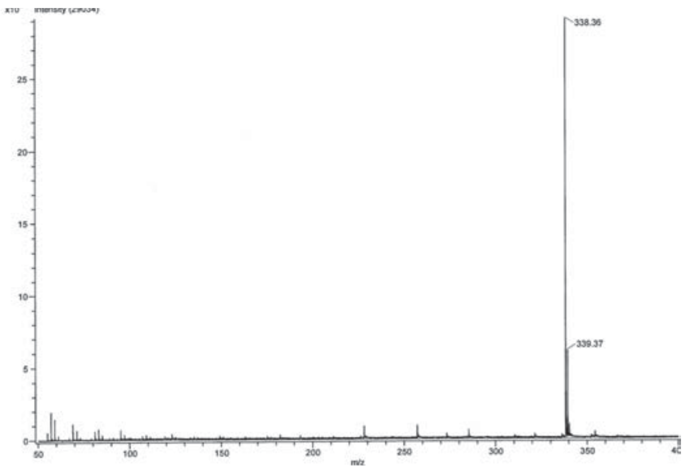
(c) Mass spectrum of concrete at 0.6 in below treated surface.



(d) Mass spectrum of concrete at 1.2 in below treated surface.



(e) Mass spectrum of concrete at 1.8 in below treated surface.



(a) Mass spectrum of untreated concrete (control).

FIGURE 2. Mass spectra of Treatment B coated concrete.

an untreated area of the beam (control), are shown in Figure 2.

Conclusions

DART-MS analysis of concrete chips, taken at various depths of concrete, shows that the inhibitors migrated to the concrete interior from the treated surface, to as deep as 3 in. The surface treatment could be in the form of a sealer containing corrosion inhibitor such as Treatment A; or in the form of a water-based corrosion inhibitor product such as Treatment B. Inhibitor migration occurs in newly made concrete and also in existing concrete structures, making the migrating inhibitor treatment a valuable tool in rehabilitating our aging infrastructure.

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