Chapter 1
Introduction

Improving Durability of Infrastructure with Migratory Corrosion Inhibitors (MCI) and Vapor Phase Corrosion Inhibitors

Introduction

Failing Infrastructure

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, increasing the cost of repairs and decreasing the useful service life. There is a need for modernization and creating long term funding for proper maintenance and improvement of existing structures.

The American Society of Civil Engineers (ASCE) releases a report card on the American infrastructure every four years. Since 1998, the grades have been near failing, averaging only Ds, due to delayed maintenance and underinvestment across most categories. The average grade for the 2013 report is a D+, and they estimate that an investment of $3.6 trillion dollars is needed by the year 2020 to improve the infrastructure to a grade of B (infrastructurereportcard.org).

Between 2003 and 2007, the United States overall spending on infrastructure declined by $23 billion, or 6%. Today the United States spends about 2.4 percent of GDP on infrastructure. Peak spending was 3.1 percent and occurred in the early 1960's. In comparison, China's goal is to invest 9 percent of their GDP on infrastructure between 2012 and 2017, and Mexico's is to increase their percentage to about 5.5 percent of GDP in 2012 (businessinsider.com/infrastructure-urban-land-institute-2011-10?op=1).

Recognizing a need for improvement in design of new structures and maintenance of existing, the American Concrete Institute (ACI) and the International Concrete Repair Institute (ICRI) have committees dedicated to life cycle performance and evaluation. Durability models such as LIFE-365 have been developed in an effort to better evaluate design of structures and to show how changes in design can increase useful service life and decrease lifetime cost.

Historic Use of Corrosion Inhibitors in Concrete

Corrosion of reinforcing steel is one of the most serious and costly problems facing concrete structures. Through the years, many methods have been used to prevent corrosion of embedded steel including increasing the concrete cover, reducing the concrete porosity, use of more corrosion resistant reinforcement (galvanized, epoxy coated, stainless steel), cathodic protection, use of membranes/coatings/sealers, and use of corrosion inhibiting materials.

Corrosion inhibitors are a desirable option because they can significantly increase useful design life of structures at a very low cost. Corrosion inhibitors have been used in concrete since the mid-1970's. Amine alcohol based migrating inhibitors were introduced in the mid-1980's.

Several other types of inhibitors were introduced in the early 1990's including morpholine derivatives, phosphates, benzoate, a fatty ester of oleic acid amine, as well as amine carboxylate based migrating inhibitors. Today, the following corrosion-inhibiting admixtures are supported commercially: amine alcohol, amine carboxylate, amine-ester organic emulsion, calcium nitrite, and an organic alkenyl dicarboxylic acid salt. Commercially available surface treatments include amine alcohols, amine carboxylates, organofunctional silanes, as well as silane/siloxane blends and silicates.

The first corrosion inhibiting admixture used in concrete construction was calcium nitrite. Originally used to offset admixed chlorides from sea sand used in a structure in Japan [1], it was discovered that calcium nitrite also had an effect on the chloride threshold. Calcium nitrite is generally available as a 30% solution, and some versions contain a retarder to reduce its set accelerating effect. It works by enhancing the formation of passivating layer on the rebar surface. Nitrite ions compete with any chloride ions present to react with free iron ions. If the ratio of nitrite to chloride ions is high enough, the nitrite and iron ions form an oxide layer on the rebar that helps prevent corrosion. The required dosage rate of calcium nitrite is based on the anticipated chloride loading of a structure over its expected design life. If the chloride loading prediction is incorrect, the structure will be left vulnerable. Dosage rate recommendations are shown in Table 1 [2].

Table 1: Calcium Nitrite Dosage Rate for expected Chloride Levels [3]

Chloride ion, lb/yd^3 (kg/m^3)	Calcium Nitrite (30% sol'n), gal/yd^3 (L/m^3)
6 (3.6)	2 (10)
9.9 (5.9)	3 (15)
13 (7.7)	4 (20) 13 lb/yd^3
15 (8.9)	5 (25) 15 lb/yd^3
16 (9.5)	6 (30) 16 lb/yd^3

While effective in increasing chloride thresholds, calcium nitrite can cause problems with concrete mix properties such as accelerated setting time and an increase in shrinkage. These problems become more dramatic as the dosage rate increases. Once the chloride threshold of the calcium nitrite dose has been exceeded, corrosion will begin – and the rate of corrosion is the same or faster than that of a control concrete. A study done on sodium nitrite (similar to calcium nitrite), showed that while this product can prevent rebar corrosion caused by carbonation in non-chloride contaminated concrete, it is not effective when chlorides and carbonation are present, even at dosage rates up to 4%. (Xu Yongmo, She Hailong, Miksic B. Comparison of Inhibitors MCI and $NaNO_2$ in Carbonation Induced Corrosion, *Materials Performance*, January 2004). The polarization diagram study showed that if insufficient amounts of anodic inhibitor are used, corrosion will proceed at a higher rate and passivity is unstable ususally resulting in pitting of the metal (Corrosion: An Introduction, an official NACE publication, 1984, p.128).

Additionally, because calcium nitrite does not have a vapor phase at ambient temperatures, it cannot migrate as such through the concrete. Therefore, it is typically used as an admixture i new construction. Past attempts to use it in restoration applications require a very low concrete cover (generally less than 0.5 inches (1 cm) over the reinforcing steel) and a floodin application to drive the inhibitor in as a liquid.

Cortec Corporation was the first to introduce migrating corrosion inhibitors (MCI) in the ea 1980's. MCI were initially added as an admixture to help protect compromised epoxy coatec reinforcing steel, but it was soon discovered that they provided excellent corrosion protectic to uncoated reinforcing steel as well. The first recorded use of MCI was as an admixture in Minnesota bridge deck repair to protect against damage from deicing salts.

Migrating corrosion inhibitors fill gaps in corrosion inhibition left by other inhibitors – they provide direct protection to the metallic reinforcing steel, reducing corrosion rates in all kind of corrosive environments. Their migrating capability means they can be used effectively in both new construction and restoration applications. MCI are environmentally friendly and safe to use. Many of the latest generation products are certified to meet NSF/ANSI Standard 61 for use in potable water structures and components.

MCI Technology

High performance mix designs have significantly improved the quality of today's concrete. Unfortunately, cracking, whether due to shrinkage, settlement or other forces, is a reality tha is never completely eliminated no matter how good your concrete is. The need for a corrosion inhibitor that can provide protection in the presence of minor cracks is very real. addition, with aging infrastructure, preserving integrity of the structure and extending useful service life is of paramount importance. Topical treatments must be capable of penetrating tc the depth of embedded reinforcing steel.

Migrating corrosion inhibitors meet these challenges in a cost effective manner. They are available in many different forms for all types of construction – admixtures for new concrete, repair mortars and grouts; topical treatments, injectable products, and many specialty format

MCI are organic, amine based chemicals that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor transport of the inhibitive substance (Miks B.A., 1983). Concrete and other cementitious materials have pore structures that allow for liquid and vapor diffusion of MCI throughout the substrate. When MCI encounter embeddec reinforcing, they have an attraction to it, forming a protective molecular layer.

MCI are a mixed (anodic/cathodic) inhibitor system. The inhibition of the cathodic process is achieved by the incorporation of one or more oxidizing radicals in an organic molecule. Inhibitor molecules are hydrolyzed in the electrolyte and then adsorbed on the metal surface. The nitrogen of the amine group is capable of entering into a coordinate bond with metal thus enhancing the adsorption process. Adsorption of cations increases the over potential of metal ionization and slows down corrosion. The molecular layer serves as a buffer to hold the pH at the interface in the optimum range for corrosion resistance.

MCI migrate or transport through the concrete depending on the MCI type and application method. MCI admixtures are readily dispersed in the mixing process and can also migrate to reinforcement by diffusion as both a liquid and a vapor. Topical treatments of MCI penetrate first as a liquid through capillary suction and then by diffusion (Bjegovic, D., Sipos, L., et al,1994). All types of MCI are effective against chloride induced corrosion, as well as carbonation and other corrosive elements.

Whereas calcium nitrite has varying dosage rates, MCI have set dosage rates that are significantly lower and independent of expected chloride loading. Typical dosages for admixtures range from 1-1.5 pints/yd^3 (0.6-1 L/m^3) and from 125-175 ft^2/gallon (3-4.3 m^2/Liter) for surface treatments. They are compatible with pozzolans such as fly ash, silica fume and slag as well as most other admixtures. Laboratory and field tests show that MCI are compatible with cathodic protection (Cortec case history #310, Burj Khalifa).

The first generation of migrating inhibitors was based on amine alcohol technology. The latest generation is based on amine carboxylates and was first introduced in the early 1990's. The amine carboxylate technology includes fermentation products of sugar beets – a renewable resource.

Amine carboxylate based MCI can delay setting time of concrete 3-4 hours at 70°F (20°C). This delay is less pronounced at warmer temperatures. Set delay is a desired side effect in warm weather as less retarder will need to be added to the concrete mix when using MCI. Combining amine carboxylate based MCI with some set retarding materials may create increased setting times, but generally no other concrete properties are affected. In cases where set delay is not desired, normal set (NS) versions of MCI or a non-chloride accelerator can be used.

MCI Chemistry

MCI are classified as mixed inhibitors, meaning they affect both anodic and cathodic portions of the corrosion cell. These inhibitors adsorb onto metal, forming a protective molecular layer on steel surfaces. This film prevents corrosive elements from further reacting with embedded reinforcement, and also reduces existing corrosion rates. Adsorption of the inhibitor takes place via its polar functional group anchored to the metal while the non-polar or hydrophobic chain is oriented perpendicularly to the metal surface. The hydrophobic chains not only repel aqueous corrosive fluids, but interact with each other to form aggregates thereby forming a tight film on the metal surface.

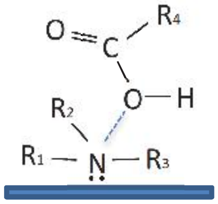


Illustration of Molecular Interactions – Amine Carboxylate Inhibitor

Where $R_{1,2,3}$ is H or alkyl group, and R_4 is hydrophobic tail

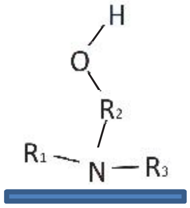


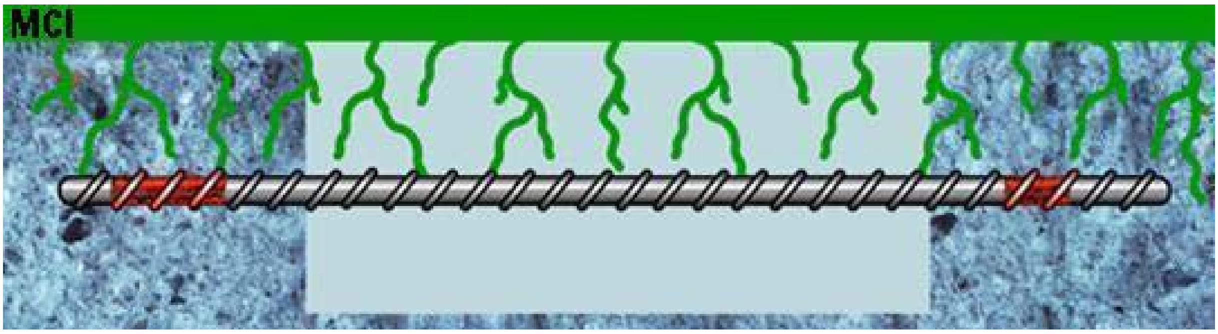
Illustration of Molecular Interactions – Amine Alcohol Inhibitor

Where $R_{1,2,3}$ is H or alkyl group, OH tail end group

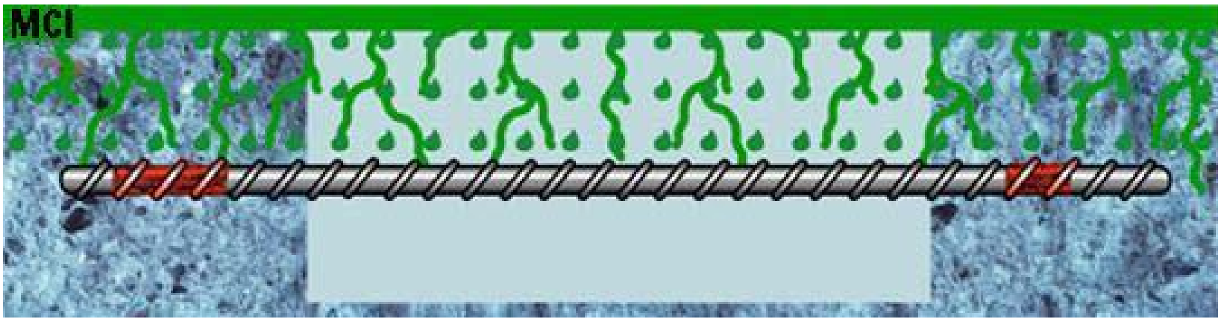
Migrating corrosion inhibitors reach embedded reinforcement in several ways. First, the inhibitor is dispersed through the concrete with adequate mixing. The transportation of MCI within concrete then occurs via infiltration through concrete pore capillary networks. Thirdly, due to their relatively high vapor pressures, MCI move via diffusion in a gaseous state through the pore network and minor cracks. Finally, when the molecules come into contact with embedded metals, they have a specific attraction to it. This process is illustrated in Figure 2.

The molecules move randomly from areas of high concentration to areas of low concentration until equilibrium is reached (Fick's 2nd Law). Because of the final adsorption of MCI on embedded metal, the concentration gradient drives MCI to move towards the metal. X-Ray Photoelectron Spectroscopy (XPS) analysis has demonstrated the nitrogen rich layer (from amine moiety in MCI molecules) formed on rebar surfaces embedded in concrete that received a topical treatment of MCI. This protective, monomolecular layer also reduces the corrosion rate (Dr. Bavarian; Radioactive Isotope Tagging).

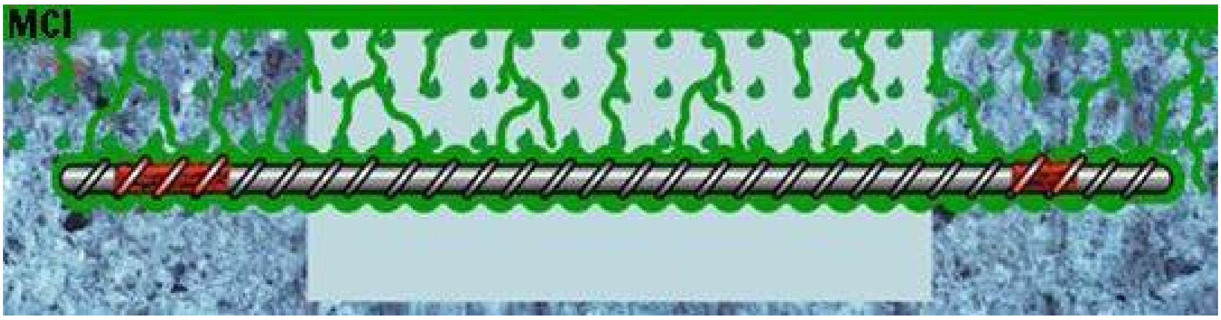
Figure 2 – Illustration of MCI Migration Mechanisms



Infiltration through concrete capillary network



Vapor phase diffusion through concrete pores and minor cracks



Final adsorption on the metal to form protective layer

Amine alcohols differ from amine carboxylates in their tail end group. As can be seen in the diagram above, the amine alcohols contain an OH terminal group at the tail end, whereas amine carboxylates have no such hydrophilic terminal group. The exposed OH group on amine alcohols makes it available to interact with water based electrolyte near the rebar. This means that the amine alcohol film could more easily desorb from the metal surface compared to the amine carboxylate film, and allow corrosive species (such as chlorides) to attack the metal. As a result the amine carboxylate based MCI by nature have a more tenacious bond to the metal surface.

The bond strength of the MCI molecule is what delays the onset of corrosion and reduces corrosion rates compared to a control once initiated. With amine alcohols, we typically see a slight extension in time to corrosion initiation, and corrosion currents cut in half compared to a control. With amine carboxylates, we typically see a double to tripling in time to corrosion initiation, and once corrosion starts, rates are reduced by 5-15 times compared to a control.

Another small effect amine carboxylates have is that as they migrate through the concrete, some of them will react with calcium hydroxide to form $Ca(COO)_2$, and insoluble salt, which effectively blocks some of the pores, making future ingress of chlorides and other contaminants more tortuous (Tourney Consulting Group, ASTM E96 Testing, 2010).

MCI can be added with the mix water to concrete at a ready mix plant, or added on the jobsite to the ready mix truck prior to pouring. As previously mentioned, their dosage is independent of the expected chloride levels. The recommended dosage rate is a sufficient concentration of inhibitor to form a monomolecular film on embedded metals and that dosage rate is not dependent on chloride concentrations. Unlike anodic inhibitors such as calcium nitrite, MCI do not have a “dangerous” concentration level—situations where a lower than required dosage rate relative to chloride content concentration would promote pitting corrosion (Nathan, p.259).

Efficacy of MCI in Construction:

There are many test methods used to assess the efficacy of migrating corrosion inhibitors in concrete. It is important to note that are described by category – corrosion protection, migrating ability, film forming ability, and compatibility with other materials.

Assessment of Corrosion Protection

The most widely used test method for evaluating concrete corrosion inhibiting admixtures is ASTM C1582 / C1582M – Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Reinforcing Steel in Concrete. This standard consists of two components. The first is an evaluation of how the corrosion inhibitor affects concrete properties such as setting time, air entrainment, compressive and flexural strengths, freeze thaw resistance, and length change.

The second component involves corrosion testing according to ASTM G109 – Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments or ASTM G180 – 13, Standard Test Method for Corrosion Inhibiting Admixtures for Steel in Concrete by Polarization Resistance in Cementitious Slurries.

ASTM G109 test samples can be seen in Figures 3 and 4 below. The test consists of casting concrete blocks containing a triangular arrangement of rebar embedded within them – one bar on top and two on the bottom. These samples are then exposed to cyclic wetting and drying cycles with salt water, and the integrated macrocell current in the beams is monitored and recorded every 4 weeks (4 weeks = one cycle).

Figure 3

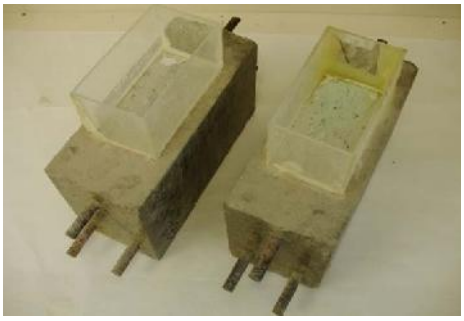


Figure 4

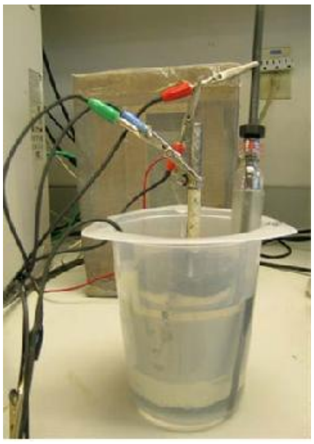
When the average integrated macrocell current reaches 150 Coulombs or greater in the control, and in at least half of all test samples, the test stops. The test admixture must show corrosion-inhibiting performance by taking longer to reach an average macrocell current of 150 Coulombs than the control, while having a mean chloride ion content of greater than or equal to the control samples. This process could take several years to show results.

ASTM G180 – 13 can be seen in Figure 5. This test method that provides a means for assessing corrosion-inhibiting concrete admixtures in a filtered cementitious liquid. Compared with a testing period of up to a few years required by ASTM G 109, this test method provides results within a few days. It is not suitable for emulsion types of admixture. A reduction in corrosion rate versus chloride alone by at least one order of magnitude in this test, is a strong indication that an admixture is a corrosion inhibitor (and a passing result). However, poor performance in G180 requires completion of ASTM G109 testing to determine if the admixture improves corrosion resistance.

Figure 5 – Test setup of ASTM G180

Electrochemical Impedance Spectroscopy (EIS) is a powerful, rapid and accurate non-destructive method for the evaluation of a wide range of materials including coatings, anodized films and migrating corrosion inhibitors. During EIS experiments, a small amplitude AC signal is applied to the system being studied. Data from EIS can provide detailed information on corrosion rate, electrochemical mechanisms, reaction kinetics, and detection of localized corrosion in a system.

Figure 6 – EIS Test setup



In addition to the above standard tests, ASTM G109 is frequently modified to make it more aggressive so results can be seen faster. These tests are generally referred to as Modified ASTM G109 or a Cracked Beam Test. In a Cracked Beam Test, test samples are created in the same manner as the ASTM G109 standard shown above, but the beams are cracked in a controlled way prior to salt water cycling to make the test more aggressive. Other modifications include changing the NaCl (salt) concentration as well as the cycle times (adjusting from 4 weeks down to as little as 1 week cycles). Another variation on ASTM G109 is immersion of concrete beams in salt water instead of using ponding cycles.

Assessment of Migrating Ability

Migration of MCI materials into concrete can be evaluated using UV Spectroscopy. This method allows us to detect MCI presence at various depths of concrete by analyzing sliced core samples. MCIs are visible in the UV range. By extracting powdered concrete in deionized water, and measuring the extract using UV spectroscopy, the presence of MCI in concrete can be detected.

Assessment of Film Forming Ability

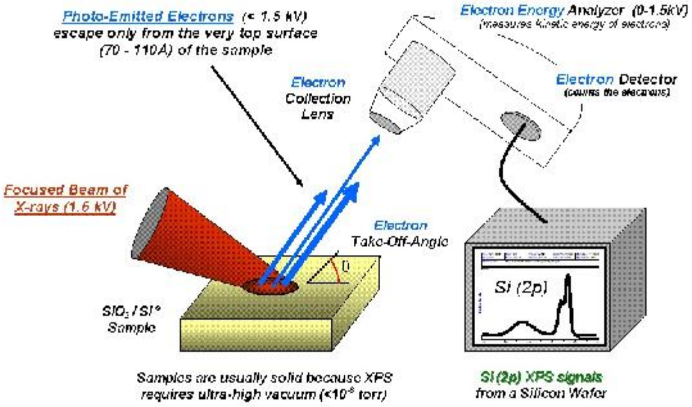
Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) is an electron microscopy that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface composition and topology. Presence of MCI, or the lack of it, on metal surface can be detected using SEM.

X-ray Photoelectron Spectroscopy (XPS)

XPS is a spectroscopic technique in which a beam of x-rays is focused onto the surface of a material and as the beam bounces off of the surface it received by an electron collection device. The data received is then analyzed to determine the elemental composition of the material which reflected the x-ray beam. A diagram showing how XPS works can be seen in Figure 7 below.

Figure 7 - XPS



In terms of migrating corrosion inhibitors XPS detection can be used to analyze a sample of rebar to determine if there is inhibitor on the surface. Being an amine carboxylate the corrosion inhibitor is a nitrogen containing compound which is not found in abundance in the concrete matrix. Therefore, nitrogen levels recorded on the XPS spectrogram can be used to determine if corrosion inhibitor has migrated to the depth of the rebar. XPS also has the capability to look at the depth at which an element is from the surface of the steel so the spectrogram can be used to determine depth at which the corrosion inhibitor is on the rebar in comparison to other elements like chloride.

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