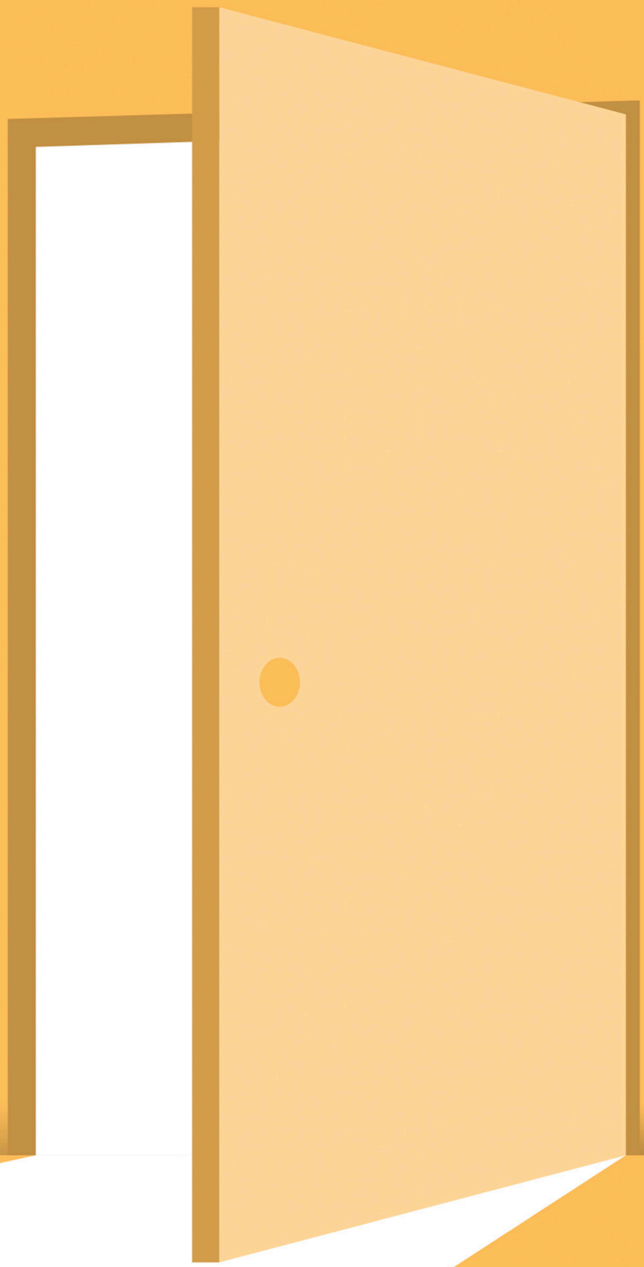
Opening the door

Julie Holmquist, Jessi Meyer, and Dr Sen Kang, Cortec Corp., explain how migrating corrosion inhibitor technology can help extend the service life of new and existing concrete structures in the fertilizer industry.



More than 25 years ago, the rail beams and floors of train sheds at a site in Northern Ontario, Canada, were deteriorating from the unloading of potash. This mineral, a common fertilizer component, was penetrating the concrete and causing corrosion on the structural reinforcement. True to nature, the force of expansion from the corrosion products was causing the concrete to delaminate. Galvanic corrosion was detected at the outside wall and even 10 ft (3 m) away at the railroad.

In early December 1994, a surface treatment containing migrating corrosion inhibitors (MCIs) was applied to a 10 ft^2 (0.9 m^2) test area to see if it could mitigate corrosion. An engineering firm took cores for analysation 5 months later in April 1995. Results indicated that the treatment had been successful, and a contractor was commissioned to apply the MCIs to the train shed beams and floor in conjunction with repair work that involved patching, sandblasting, and application of an epoxy coating.[1]

This story is just one example of why facilities in the fertilizer industry can be at greater risk for deterioration from corrosion. Structures and equipment used in the fertilizer industry are more vulnerable to corrosive attack because of exposure to various chemicals such as ammonium nitrate, dihydrogen ammonium phosphate, potassium or ammonium chloride, or compounds that react or break down into ammonia or hydrogen sulfide.[2] Corrosion can also be increased because dry fertilizers are usually hygroscopic and they tend to absorb moisture,[3] some at lower levels of humidity than others.[2] Usage of MCIs is an effective solution to counteract corrosion of embedded reinforcement and structural steel, extending the service life of concrete structures such as bins and railway beams involved in the storage or transport of fertilizers.

Figure 1. Illustration of MCI molecules adsorbing on and protecting rebar against corrosive elements that make their way through the concrete pore structure.

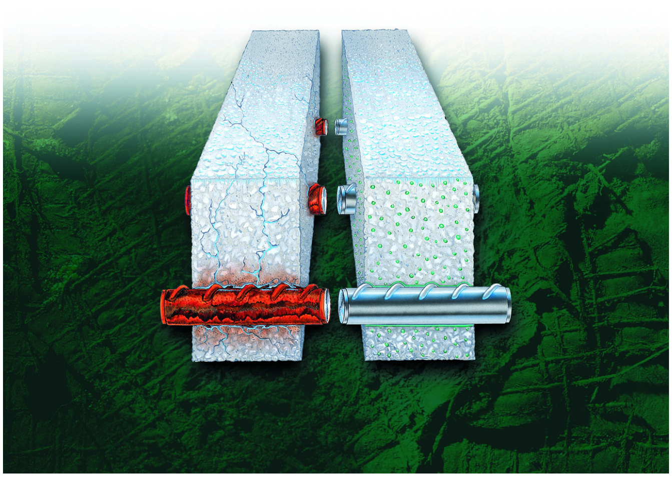


Figure 2. Illustration of untreated, corroded rebar (left) and treated, protected rebar (right).

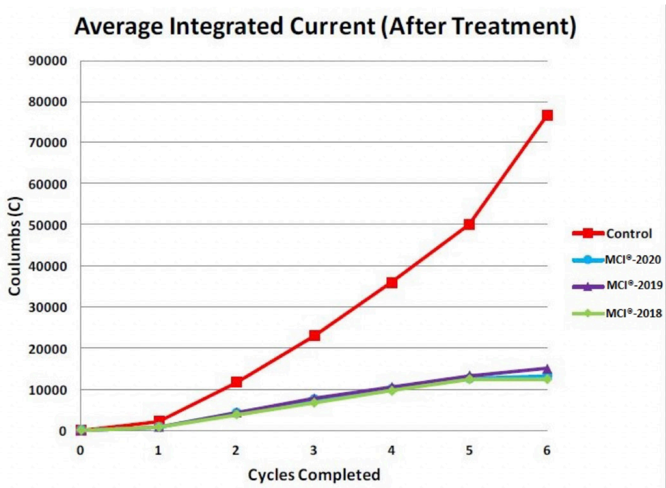


Figure 3. Results of USBR M-82 testing showing lower average integrated current on samples protected with MCI surface treatments.

The technology

MCIs can be used in the construction, repair, and maintenance of structures. Developed by Cortec Corp. in the 1980s, the basic technology involves organic amine-based corrosion inhibitors that 'migrate' through a concrete pore structure by liquid and/or vapour diffusion. They adsorb onto the rebar surface as a protective molecular layer that serves as a 'mixed' inhibitor to disrupt both anodic and cathodic reactions involved in corrosion. The molecular film also helps to hold the pH at the rebar surface at a good level for corrosion-resistance. In the case of amine-carboxylate-based inhibitors, MCIs can delay corrosion initiation by two to three times and reduce corrosion rates once started by five to 15 times. MCIs have been incorporated into concrete admixtures, repair mortars, surface treatments, and gels that can be injected to reach the level of the rebar.[4] Because of the vulnerability of cement paste to fertilizer chemicals, it is recommended that MCI be used in combination with a chemical resistant coating on the concrete surface for best results in fertilizer applications. The MCI admixture/topical treatments work to protect embedded metals, while the chemically resistant coating protects the concrete surfaces from disintegrating over time.

Constructing a new fertilizer plant for long-term durability

In the construction of new facilities that will be used to make, store, or transfer fertilizer, there are a variety of ways to build for greater durability. These include the use of epoxy-coated, galvanised, or stainless rebar, increasing concrete cover, and/or using protective concrete coatings. Each additional durability enhancement technique adds cost to the structure, which must be weighed against future replacement costs. MCI admixtures tend to be more cost-effective than using specialty reinforcing steel, significantly extending projected service life often at a small fraction of the structure's total cost.[5] A good example of this is the use of an MCI admixture in the podium structure of the Princess Tower in the UAE. Use of MCI more than doubled the estimated service life while only adding 0.07% to the total construction costs.[6] If the choice is made to include an MCI admixture in a concrete structure, it can be easily added into the concrete mix at the batching plant or onsite. MCI admixtures meet all parameters of 'ASTM C1582 – Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Reinforcing Steel in Concrete.'[7] They have also been tested to EN 904 standards for effects on the physical properties of concrete. Furthermore, ready-mixers typically find them easy to work with.

Repairing an existing fertilizer structure to extend its service life

It has been established that MCI admixtures provide a cost-effective approach for the construction of new structures. The next question is, what can be done for existing structures in need of repair now or in the future? MCI technology is also available in the form of repair mortars and surface treatments. Pre-blended repair mortars are characterised as full depth, trowel grade, or vertical/overhead products for use according to the location and degree of repair needed. Alternatively, an MCI admixture can be added to standard repair mortar for enhanced corrosion protection. These are often supplemented with surface applied corrosion inhibitors (SACIs) to enhance the durability of the repair.

The new International Concrete Repair Institute's (ICRI) 'Guideline for Use of Penetrating Surface Applied Corrosion Inhibitors for Corrosion Mitigation of Reinforced Concrete

Structures' outlines various types of topical treatments, including several MCI formulations. These include the following SACI types that cover MCI technologies:

- 5.4.1: Amino-based materials. This encompasses both amino alcohol and amine carboxylate technology. These inhibitors penetrate the concrete pores by capillary action and later migrate as vapours to form a film on the rebar surface to protect anodic and cathodic sites. While amino alcohols have a hydrophilic tail, amine carboxylates have a carboxylate (COOH) functional group that can anchor onto the metal surface and a hydrophobic tail that allows the molecular film to be more resistant to water and chlorides.
- 5.4.2.1: Silane type. Amino alcohol MCIs combined with silane yields the characteristics outlined by ICRI's definition of organo-functional silane SACIs. MCIs in this category also migrate through the concrete by capillary and vapour action to adsorb on the rebar surface. They can also react with the concrete matrix to decrease water and chloride ingress.
- 5.4.2.2: Silane/siloxane blend with amine inhibitor. These are similar to the silane type and have better coverage on lower density (more porous) concrete.

Amine-based materials have the highest concentration of MCI, whereas silane and silane/siloxane types have less MCI but serve a dual function in that the silane or silane/siloxane in the material also seals the surface to prevent ingress of moisture and other contaminants.

Before applying any of these MCI based SACIs to mitigate corrosion and increase the durability of a concrete repair, the ICRI guidelines recommend basic surface prep procedures such as removing delaminated concrete, cleaning the surface, and performing wet or dry blasting to help open up the pore structure.[8]

Testing of MCI based SACIs for efficacy

Various tests have been performed to confirm the efficacy of MCI SACIs, both on fresh surfaces and on repair surfaces. In one study, Dr Bavarian, et al., coated concrete samples with surface applied MCI (plus sealer to prevent sloughing off in liquid) and immersed them in a saltwater solution (3.5% sodium chloride [NaCl]) for 500 days. XPS depth profiling indicated that the inhibitor had migrated deeper than the chlorides and was present at depths as much as 75 or 85 nm below the unetched rebar surface, whereas the untreated samples had localised corrosion on the rebar. Polarisation resistance and current density were generally better in treated specimens versus untreated specimens. Based on the test results, it was estimated that the treatments could extend service life by over 15 – 20 years.[9]

The benefit of MCI surface treatments specifically for concrete repairs is demonstrated in a report on three MCIs that were evaluated according to the US Bureau of Reclamation M-82 (M0820000.714) 'Standard Protocol to Evaluate the Performance of Corrosion Mitigation Technologies in Concrete Repairs'. This testing involves multiple rounds of saltwater ponding prior to treatment until enough corrosion has occurred for repair materials to be applied.

The MCI treatments were not applied until average corrosion had reached upwards of 10 000 Coulombs, twice as much as the protocol requires (treatment can occur at 5000 Coulombs). This route can be taken if the treatment is independent of chloride levels or if there is a desire to show protection at a higher chloride content.

Three different MCI based SACIs were applied. One was a 100% silane sealer containing amine alcohol. Another was a solvent-based silane (40%) and amine alcohol mixture. The third was a combination amine alcohol/amine carboxylate MCI (the same used in the railway repair at the beginning of this article). Since this third treatment did not contain a water repellent, a standard water repellent (40% silane) was applied over it for the test.

By the end of the test, the slabs treated with three MCI based SACIs showed a decrease in corrosion with less cracking compared to the controls, reducing the corrosion rates by a statistically significant 'order of magnitude' at a 95% confidence level. This led the testing firm to conclude that these three treatments were useful in mitigating corrosion that has already started.[10,11]

Conclusion

Structures and equipment used in the fertilizer industry have a greater risk of corrosion from exposure to various chemical compounds that can be harsh in themselves or absorb water to hold in contact with the concrete. MCI is an excellent technology that can be used to prolong the reinforced concrete durability by application either at the outset as a concrete admixture or later as a topical treatment or repair mortar for existing structures. Multiple external tests have shown MCI to be effective in delaying corrosion and reducing existing corrosion rates, thus opening the door to extending the service life of basic structures in the fertilizer industry. **WF**

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