CONCRETE HERITAGE CONSERVATION AND THE VIABILITY OF MIGRATING CORROSION INHIBITORS

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# TABLE OF CONTENTS

I. INTRODUCTION | 1

II. CONCRETE | 4
   A. HISTORIC VS. MODERN CONCRETE | 5
   B. ROLE OF CORROSION IN CONCRETE DETERIORATION | 10

III. TREATING CORROSION IN CONCRETE HERITAGE | 16
   A. VALUES-BASED PRESERVATION THEORY | 16
   B. EXISTING TREATMENT OPTIONS | 21

IV. MIGRATING CORROSION INHIBITORS | 33
   A. CLASSIFICATIONS | 33
   B. COMPOSITIONS & MECHANISMS | 34
   C. PRODUCTS & MANUFACTURER CLAIMS | 36
   D. MONITORING & TESTING METHODOLOGIES | 38

V. EXPLORING NEW METHODOLOGIES | 47
   A. INHIBITION | 47
      i. JAR TEST | 48
         a. TEST A: FILINGS | 48
         b. TEST B: COUPONS | 49
         c. CONCLUSIONS | 50
      ii. CELL TEST | 50
         a. TEST A: PROOF OF CONCEPT | 50
         b. TEST B: COLUMBIA UNIVERSITY | 52
         c. TEST C: ECHEM’S LABORATORY | 52
         d. TEST D: HIGHER DOSAGE | 53
   B. MIGRATION | 56

VI. SUMMARY & AREAS FOR FURTHER STUDY | 58

BIBLIOGRAPHY | 63
TABLES | 74
FIGURES | 76
I. INTRODUCTION

Steel has been and continues to be embedded within concrete to create a composite material that combines the compressive strength of the concrete with the tensile strength of the steel.\(^1\) Despite this material’s stress-strain benefits and wide range of applications – including structural engineering, foundations, bridges, and architecture – corrosion of the steel within the concrete presents a serious problem. As the numerous books published, and conferences held each year on this topic prove, corrosion of embedded steel reinforcement in concrete is a huge unresolved issue that so many professionals are grappling with today.\(^2\)

One can narrow the focus even further to look specifically at the issue of corrosion of reinforced concrete buildings. Again, intellectual activity on the subject suggests that corrosion is a problem in buildings that warrants attention from anyone involved in construction, such as contractors, engineers, architects, and asset managers.\(^3\) Not only does the issue pose aesthetic concerns, but perhaps even more importantly, it poses public safety concerns, as corroding reinforcement can result in falling concrete or entire structural failures.

Finally, there is the more specific issue of corrosion of reinforced concrete in historic architecture. The National Park Service identifies corrosion of embedded steel as one of the primary causes of concrete deterioration in their “Preservation of Historic Concrete” brief.\(^4\) Since

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\(^1\) Luca Bertolini et al., *Corrosion of Steel in Concrete: Prevention, Diagnosis, and Repair*, 2nd ed. (Wiley, 2014).


its original appearance in the mid 1800’s, reinforced concrete has become one of the most widely used construction materials in the world.\(^5\) Now, with the passage of over 160 years, the number of concrete structures in need of conservation is very significant. Buildings included in this category have become even more numerous in the last 20 years or so, as an influx of modern architecture, which often employed reinforced concrete as an expressive material, is being considered historic and thus worthy of preservation.\(^6\) With an enormous demand for conservation of historic concrete heritage, an expansion of treatment options for embedded steel corrosion is imperative.

Unfortunately, there is no single solution to the problem of corrosion in reinforced concrete heritage. Rather, conservation treatments must be evaluated through the lens of preservation theory in order to choose a path that best fits the values of the structure and the elements in which those values are instilled. This type of values-based assessment of treatment options illuminates the fact that each treatment poses its own upsides and downsides for the specific values and needs of a structure. These pros and cons may then be considered in conjunction with factors such as efficacy of the treatment, parameters set by the site’s programming, and cost, to decide on the best path forward. But not all treatments for corrosion in reinforced concrete structures are fully proven through monitoring and testing evaluations at this point in time.

One such treatment, migrating corrosion inhibitors (MCIs), despite having been on the market since the 1980’s, still has a number of questions surrounding it. MCIs are products that


are designed to diffuse through concrete and slow the corrosion of embedded reinforcement by forming a protective layer around it. Because of their ability to be applied easily on to the surface, and the claim that they can prevent or retard corrosion without change to appearance or texture, MCIs present an appealing option for corrosion treatment in concrete heritage, allowing for an “invisible hand” to the conservator. This represents a particular advantage for structures in which significance lies in the original appearance of the concrete. Unfortunately, the analysis of MCIs, and of their risks and their benefits seem incomplete today due to unreliable evaluation methodologies, leading practitioners to question their risks and efficacy.

This thesis begins with a discussion of the composition of concrete and the implications of the differences between historic and modern concrete for conservators. It then moves to offer an explanation of the process of corrosion in reinforced concrete, its causes and effects, to inform an understanding of conservation options. Next, the care of concrete heritage structures will be contextualized in a values-based preservation theory, to aid in the subsequent discussion of treatment options as they relate to the values imbued in them. This discussion leads to one treatment in question, MCIs, in which a description of their classifications and their compositions guides an evaluation of the theoretical benefits of this treatment for concrete heritage, a discussion of the limitations of existing evaluation methods its efficacy and risks, and an exploration of how to improve these methods.

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II. CONCRETE

On the most basic level, concrete is a material composed of aggregates and a binder. The aggregate can be crushed stone, gravel, and sand of varying size and shape, while the binder is generally water and cement, which cures through a chemical reaction with water into hardened concrete. Concrete is a complex material as there are many variations on this basic composition, and its conservation is therefore a multifaceted topic.

Aggregates can be classified as coarse or fine depending on their sizes. A range in aggregate size is desirable to ensure efficient use of space within the binder of concrete. The quality of a given concrete depends strongly on the quality of both aggregates and binder, and the way in which they interact. The best concrete will have binder completely surrounding each aggregate particle, and the spaces between aggregate particles filled. The paste is a mixture of cementitious materials and water, and usually constitutes somewhere between 25% and 40% of the total volume of a given concrete. The type of cementitious material used as the binder of concrete has changed throughout the material’s history and has included lime, pozzolana, Portland Cement, fly ash, limestone fines, and silica fume, among others. A combination of these materials creates a cement to be mixed with water. An understanding of the variability of a concrete mix is essential to a conservator working with the material. Conservators also need to

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8 Kosmatka, Kerkhoff, and Panarese, Design and Control of Concrete, 14th ed., 1.
9 Ibid., 1.
10 Ibid., 1.
11 Ibid., 1.
understand how concrete has changed over time in order to analyze the historic concrete they are dealing with. A basic overview of the history of concrete, an analysis of these differences, and how they factor into conservators’ work is what follows.

A. HISTORIC VS. MODERN CONCRETE

The origins of concrete construction can be traced back to the Romans who found that mixing lime and pozzolana (a volcanic ash) caused a chemical reaction which led the material to harden under water. With the addition of aggregates, this material was, in essence, what we today know as a hydraulic concrete\(^\text{13}\) and the Romans employed it all over the empire’s architecture and engineering. The Pantheon is perhaps one of the most widely celebrated concrete structures from this time period (figure 1).\(^\text{14}\) Since then, concrete has been a widely used construction material, undergoing changes and taking a number of different forms.\(^\text{15}\)

The technological history of concrete is far from linear. Local discoveries and advancements occurred across the world and sometimes took ages to reach more distant areas. Therefore, it is difficult to trace the history of concrete from the Romans as a straight line to today. For example, it is known that a form of concrete was employed in Spain and Africa in the middle ages and then brought to the New World by the Spanish in the early 16\(^{th}\) century. In the

\(^{13}\) ACI Committee 225, “225R-16 Guide to the Selection and Use of Hydraulic Cements” (American Concrete Institute, 2016).


New World, a form of concrete called “tapia,” or “tabby,” a mixture of lime and water and an aggregate composed of sand, shells, gravel or stone, was employed mostly on the coasts.\textsuperscript{16}

It was in the mid-19\textsuperscript{th} century that concrete became a very popular material in the United States with the introduction of reinforced concrete. The use of reinforcement in concrete architecture began in the conjunction with the emergence of precast concrete. French industrialist François Coignet is often associated with the first use of precast structural concrete in 1852.\textsuperscript{17} On the other hand, the first patent issued for the technology of a reinforced concrete wall in the United States was to S.T. Fowler in 1860.\textsuperscript{18} This is an example of the non-linearity of the history of concrete technology.

Reinforced concrete remained a specialty material until the early 1900’s when the introduction of the horizontal rotary kiln spurred the production of more consistent cement at a lower price. Well-known architects began to praise the material and employ it in their buildings, starting mostly with industrial structures. Eventually, reinforced concrete began making its way into more complex and expressive designs. French architects Auguste Perret and Gustave Perret are often credited for turning concrete into a “modern” material through their work.\textsuperscript{19} Specifically, their Notre-Dame du Rainey (1922-23) showcased concrete as simultaneously a structural and aesthetically pleasing material when this was still a new concept (figure 2).\textsuperscript{20} In America, this concept was then picked up by architects such as Frank Lloyd Wright in his

\textsuperscript{16} Coney, “Preservation Brief 15: Preservation of Historic Concrete: Problems and General Approaches,” 2.


\textsuperscript{18} Coney, “Preservation Brief 15: Preservation of Historic Concrete: Problems and General Approaches,” 2.

\textsuperscript{19} Adrian Forty, \textit{Concrete and Culture: A Material History} (Reaktion Books, 2013), 23.

\textsuperscript{20} Ibid., 27.
Fallingwater (1937) or his Solomon R. Guggenheim Museum (1959) and Eero Saarinen in his TWA Flight Center (1962) (figure 3). 

Today, these types of buildings have provided reinforced concrete an aesthetic appreciation within the architecture and historic preservation communities and well beyond. With the National Park Service’s definition of “historic buildings” as those that are 50 years or older, these mid-century modern concrete buildings are now being considered historic, and in some cases, warranting preservation. With this, there has been a surge in the publication of books on the subject of the preservation of these mid-century buildings, such as Theodore H.M. Prudon’s *Preservation of Modern Architecture*. Even more specifically, books are being published on historic concrete such as Mark Pasnik, Chris Grimley, and Michael Kubo’s *Heroic: Concrete Architecture and the New Boston* on the topic of Boston’s collection of Brutalist concrete architecture. In approaching the conservation of these buildings, it is important to understand the ways in which historic concrete is a different material than the modern concrete we see today and how it presents its own set of issues when it comes to treatments.

The modern concrete that is used in construction today looks and acts very differently from the historic concrete that architectural conservators work with. A major difference is the use of admixtures. Admixtures are chemicals, natural or manufactured, that are mixed into the concrete before or during the addition of water to give the material certain modified properties. Admixtures are often used to change setting or hardening time, reduce the need for water in the mix, increase the workability of plastic concrete, entrain air in the concrete, or alter other

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characteristics of the fresh or hardened concrete. Some of the most commonly used admixtures include air-entrainers, water reducers, superplasticizers, retarders, and accelerators. Today, most pre-packaged concrete mixes already have one or more admixtures mixed in.

A compilation of when specific admixtures for concrete appeared on the market has yet to be undertaken, but a study like this would be extremely valuable for conservators treating historic concrete structures. A review of the editions of the Portland Cement Association’s *Design and Control of Concrete Mixtures* indicates that calcium chloride was introduced as an accelerating admixture as early as the 1930’s, while magazines have advertised it as early as the 1920’s. The 9th edition of *Design and Control of Concrete Mixtures* published in 1948 has the first mention of air-entrainment. A patent was granted to Aaron C. Horn in 1913 for aluminum stearate in a hydrocarbon solvent, an admixture used to reduce the water absorption of concrete. These particular admixtures and their dates are simply meant to provide an idea of how the components of concrete mixes have evolved over time. Conservators working with a concrete from any date after World War I, for example, would need to be cautious of using a chemical treatment that could react poorly with stearate waterproofing admixtures.

Equally important for conservators is a knowledge of what admixtures the concrete in question lacks based on its date. The absence of one type of admixture in particular,

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27 Ibid.

superplasticizers, earlier known as high range water reducers, has implications that are important for conservators to understand. The addition of superplasticizers effectively reduces the water content necessary for a concrete mixture by 12-15%. A lower water content is referred to as a lower water-cement ratio. The water-cement ratio describes the gravimetric relationship between the amount of water and the amount of cement in the concrete. This ratio, as part of the mix design, affects a number of different factors in hardened concrete. In general, the less water used in a concrete mix (in other words, a lower water-cement ratio) is more ideal for the concrete’s durability. A lower water-cement ratio leads to increased strength, both flexural and compressive, lower permeability (and thereby lower absorption rate), and less shrinkage during curing. A lower water-cement ratio also contributes to better adhesion between the binder and the aggregate and reinforcement. Water-cement ratio’s influence on durability, strength, and porosity makes superplasticizers an appealing admixture for the construction industry. Superplasticizers did not appear on the market until around 1980 (alongside silica fume), making “modern” concrete essential synonymous with them. This is one reason why historic concrete is porous and typically more susceptible to deterioration. Water-cement ratio is therefore one of the most important factors that differentiate historic concrete for conservators to understand.

In general, without the added benefits of many of today’s admixtures, historic concrete is more vulnerable to weathering, shrinkage, cracking, and steel corrosion. Furthermore, these characteristics also have implications for the way in which historic concretes will receive and


31 Kosmatka, Kerkhoff, and Panarese, Design and Control of Concrete, 14th ed., 2.

react to treatments. Superplasticizers are just one of the ways in which modern concrete is vastly different from historic concrete and more of these differences will be considered in the following discussion of deterioration.

**B. ROLE OF CORROSION IN CONCRETE DETERIORATION**

Cracks and spalls are the most common type of deterioration in concrete and can have significant impact on the service life of a structure.\(^3\) Cracking can be caused by various factors including shrinkage during curing, freeze-thaw cycles, or tensile forces from inside or outside the concrete.\(^4\) One of these stresses from within the concrete comes from the increase in volume of reinforcing steel by the addition of the rust created by corrosion. An understanding of the science behind corrosion will aid in the comprehension of its causes in reinforced concrete.

Corrosion is an electrochemical reaction in which ion movement involves positively and negatively charged areas on the metal’s surface and causes a change in both chemistry and structure to occur. Four components must be present for corrosion to occur:

1. **An anode**: location where electrons are generated, negative ions are discharged, positive ions are formed, and where corrosion will occur.

2. **A cathode**: location that will receive the discharged negative ions from the anodic area, discharge positive ones, and where no corrosion will occur.

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33 Paul Gaudette and Deborah Slaton, “Preservation Brief 15: Preservation of Historic Concrete.”

34 ACI Committee 222, “ACI 222R-01: Protection of Metals in Concrete Against Corrosion” (American Concrete Institute, 2002), 6.
3. **An electrical pathway**: the connection between the anodic and cathodic area, which is the metal reinforcement in the case of reinforced concrete.

4. **And an electrolyte**: an electrically conducting solution through which the current flows, e.g., water or moist concrete.

It is worth noting that water and oxygen are essential components in initiating corrosion. The ability of concrete to conduct current depends on the moisture content, relative humidity, and porosity of the material. Oxygen’s ability to increase conductivity is especially pertinent to historic concrete in light of its higher porosity.

With all of these components present and connected, two different reactions occur simultaneously and continuously at the anode and the cathode. At the anode, iron atoms lose their electrons in a reaction called oxidation:

\[
2 \text{Fe} \rightarrow 2 \text{Fe}^{2+} + 4 \text{e}^{-}
\]

The electrons subsequently move from the anodic areas through the electrical pathway of steel to the cathodic areas, while the newly formed ferrous ions enter the concrete. When the electrons have reached the cathode, they will combine with water and oxygen in the concrete to form hydroxyl ions through a reaction called reduction:

\[
2 \text{H}_2\text{O} + \text{O}_2 + 4 \text{e}^{-} \rightarrow 4 \text{OH}
\]

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Subsequently, the hydroxyl ions will combine with the ferrous ions at the cathodic areas to form iron hydroxides, i.e. rust, while the metal at the anodic areas disintegrates:

\[ 2 \text{Fe}^{2+} + 4 \text{OH}^- \rightarrow 2 \text{Fe(OH)}_2 \]

Although Fe is lost at the anodic areas, the rust formed at the cathodic areas causes an increase in volume to occur. The increase in volume causes cracking and spalling in the concrete.\(^{36}\)

As an alkaline material with a pH above 12.6, fresh concrete protects reinforcing steel within it by producing a passive oxide film on the steel. When the concrete maintains this high pH, the very thin oxide layer prevents metal from loss and keeps the corrosion rate to an insignificant level, around 0.1 µm per year as opposed to at least 3 times more than that without it.\(^{37}\) It is when this passive layer is compromised, which can happen in a number of different ways, that active corrosion of the steel can occur.\(^{38}\) This can happen across the entire surface of the steel due to a change in thermodynamic conditions (i.e. a decrease in pH), or in a localized fashion due to chemical attack from chlorides or mechanical failure allowing acidic rainwater to reach the steel.\(^{39}\)

Carbonation is one way in which the passive layer on the metal’s surface can be compromised due to a change in thermodynamic conditions. Carbonation occurs when carbon dioxide from the atmosphere (either as gas or in solution) penetrates the concrete surface.


\(^{38}\) Kosmatka, Kerkhoff, and Panarese, Design and Control of Concrete, 14th ed., 14.

\(^{39}\) ACI Committee 222, “ACI 222R-01: Protection of Metals in Concrete Against Corrosion,” 5.
Through a reaction between the carbon dioxide and the calcium hydroxide created in concrete during curing, calcium carbonate is formed, and lowers the pH of the concrete’s internal environment. The carbonation reaction acts as a front, which moves through the concrete until it reaches the steel, having eliminated the alkalinity necessary for the protective layer to remain on the embedded reinforcement. The water-cement ratio has a significant impact on the carbonation of concrete because of its bearing on porosity. Duff Abrams was the first to comment on this relationship and its implications. Concretes with a high water-cement ratio have very porous, and therefore permeable, microstructures, making them more susceptible to the atmospheric gases and gas-derived solutions, and as previously discussed, historic concretes are often amongst those with high water-cement ratios.

Chlorides, which may be introduced to concrete from seawater, deicing salts, or admixtures, are common initiators of corrosion. Chlorides, which migrate through the concrete, act as film disrupters, attacking the passive layer on the embedded steel and thereby causing or fueling corrosion. While the specifics on how chlorides achieve this on the atomic level are still not fully understood, it is known that in areas where chlorides ions attack the passive layer, active corrosion occurs and continues in a self-feeding manner, meaning the chlorides are not consumed in the reaction. This can happen even when concrete’s alkaline environment still remains intact. If the chloride concentration hits a threshold of about 0.15% water-soluble

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40 Ibid., 14.
41 Duff A. Abrams, *Design of Concrete Mixtures*, (Chicago: Structural Materials Laboratory, 1919).
42 ACI Committee 222, “ACI 222R-01: Protection of Metals in Concrete Against Corrosion,” 14.
43 ACI Committee 222, “ACI 222R-01: Protection of Metals in Concrete Against Corrosion,” 5.
44 Ibid., 5.
chloride by mass of concrete, corrosion will commence. Chlorides also increase corrosion by enhancing the electrolytic behavior of the pore water. Certain treatments for corrosion, which will be discussed later on, specifically address the issue of chlorides by aiming to prevent the ingress of chlorides by blocking surface pores or by protecting the reinforcement from their attack.

While it has been mentioned that corrosion is very often a cause of cracking in concrete, cracking also plays a major role in the causation of corrosion. Cracking may be caused by various factors, including shrinkage during curing, freeze-thaw cycles, or tensile forces. Cracking is problematic for corrosion of embedded reinforcement as it allows the ingress of corrosive species including atmospheric gases and chlorides. Cracks can be most deleterious when they allow the direct ingress of acidic rainwater to the steel. Cracking and corrosion thereby have a “chicken and egg” causality dilemma, making treatment even more complex.

While cracks, chlorides, and carbonation are all threats to concrete, most steel is protected by the high-alkaline environment if concrete has been well designed and executed by mix and reinforcement placement. With suitable concrete coverage, defined by the American Concrete Institute (ACI) 318 Building Code as somewhere between 1.5 to 3 inches depending on the type and location of the concrete, reinforcement will be further from the carbonation front as well as less quick to produce cracks and spalls at the surface of concrete. Additionally,

46 Ibid., 5.
47 Paul Gaudette and Deborah Slaton, “Preservation Brief 15: Preservation of Historic Concrete.”
48 ACI Committee 318, “ACI 318: Building Code Portal” (American Concrete Institute, 2014), 335-337.
finished concrete surfaces have been known to experience less carbonation.\textsuperscript{49} Low water-cement ratio and good curing practices also lower the risk of cracking.

Unfortunately, historic concrete structures were not often built according to modern standards or with these concerns in mind, making many of them highly susceptible to corrosive forces. Certain material choices in historic concrete, before the knowledge we have today of their effects, can make concrete predisposed to corrosion. Seawater used in the paste or beach sand used as an aggregate can accelerate corrosion because of chlorides. Workmanship can also be a contributing factor to historic concrete’s vulnerability. Before the introduction and improvement of vibration technology in the early to mid 20\textsuperscript{th} century, for example, historic concrete was more loosely placed in formwork, leading to higher porosities.\textsuperscript{50}

How to treat these historic reinforced concrete structures experiencing reinforcement corrosion is often the responsibility of architectural conservators. The answer is not “one size fits all,” but rather involves an assessment of the building’s critical values and needs and a choice of treatment or treatments that best achieves or accommodates those.

\textsuperscript{49} ACI Committee 222, “ACI 222R-01: Protection of Metals in Concrete Against Corrosion,” 14.

III. TREATING CORROSION IN CONCRETE HERITAGE

A. VALUES-BASED PRESERVATION THEORY

There are a number of existing treatment options for corrosion in reinforced concrete, all of which have pros and cons. When it comes to choosing a specific treatment for a historic concrete structure, architectural conservators must weigh these pros and cons in relation to the building’s needs. Those needs are determined through a values-based assessment.

This preservation theory was established by the seminal 2002 work published by the Getty Institute titled, “Values and Heritage Conservation,” and written by Erica Avrami, Randall Mason, and Marta de la Torre. The theory pushes back against the schism that exists between what to conserve from how to conserve it. The authors attribute this disconnect to the segregation of different groups in the preservation field, most notably preservation advocates and architectural conservators. The theory thereby stipulates that values are the critical deciding factor on what to conserve within a site and how to conserve it. Values that humans associate with and imbue into sites are extremely complex, ranging from aesthetic to historical to economic. The authors make a convincing argument for letting those values guide the preservation decision-making process. This theory was further solidified in a 2002 research


52 Erica Avrami, Randall Mason, and Marta de la Torre, “Values and Heritage Conservation” (The Getty Conservation Institute, Los Angeles, 2002), 1.

53 Ibid., 3.

54 Ibid., 3.
report from the Getty, titled “Assessing the Values of Cultural Heritage,” and edited by Marta de La Torre, in which the authors offer a toolbox of methodologies for assessing and analyzing the critical values of a site.\(^55\)

The values associated with heritage are wide-ranging and still developing as the number of structures old enough to be considered historic and worthy of preservation increases. The question then becomes why is this structure worthy of preservation and how can a conservator choose a viable treatment for it based on those reasons. Once the values of a certain site have been determined through a variety of different methodologies – such as stakeholder analysis, archival research, mapping, and surveying – those values can often be pinpointed to specific characteristics or elements of the site which can help to drive decisions of what to preserve and how to conserve it.\(^56\) Of course, the decision-making process must also take into consideration the physical condition, management context, programming, and the budget of the site. Furthermore, the efficacy of the treatment, its reversibility, and the ability of the staff, including conservators and contractors, are important considerations in the decision. It is through an integration of these three factors, the authors argue, that a values-based treatment can be achieved.\(^57\)

In an earlier article by Mason and Avrami published in 2000, the authors break down some of the categories of values associated with heritage sites, explaining that these categories are not all encompassing, but instead are meant to offer a “typology as a reference point.” Additionally, the authors emphasize that the categories are far from mutually exclusive and that

\(^{55}\) “Assessing the Values of Cultural Heritage” (Los Angeles: The Getty Conservation Institute, 2002).

\(^{56}\) “Assessing the Values of Cultural Heritage,” 18-23.

\(^{57}\) Avrami, Mason, and de la Torre, “Values and Heritage Conservation,” 4.
most sites have some combination of several of them. Mason and Avrami’s typologies are as follows:

- Historical and artistic values
- Social or civic values
- Spiritual or religious values
- Symbolic or identity values
- Research values
- Natural values
- Economic values 58

These categories are constantly shifting and changing. The 2002 research report reshuffled the categories to fit under two headings:

- Sociocultural values: which include historical, cultural/symbolic, social, spiritual/religious
- Economic values: which include use (market) value, nonuse (nonmarket value), existence, option, bequest 59

The point of listing these value typologies is not to say that there are some fixed number of categories for heritage sites to be confined by but is to say that preservation practitioners should use these value typologies as a starting off point. In doing so, conservators can use these values to guide their treatment choices.

This theory may be applied more specifically to concrete heritage. In the past, older concrete structures were generally valued less for their artistic value, “value stemming from [their] sensate qualities – [their] capacity to stimulate the senses”60 as Mason and Avrami define it, and more for the other value typologies in their list. This is simply due to the fact that concrete didn’t begin to be used as an expressive material by architects until the early to mid-20th century.


Older civic concrete structures for example are often associated with social and civic values. For example, as the former U.S. federal prison, the main cell house on Alcatraz Island in San Francisco Bay, built in 1912, is associated with a significant amount of social and civic value for Americans (figure 5). Today, the island and this massive concrete structure are a National Landmark and major tourist attraction.\textsuperscript{61} The utilitarianly-designed building has no notable architect; its construction was overseen by Major Reuben Turner.\textsuperscript{62} Values are placed in the overall structure, specifically in its iconic outcropping from the island itself. Little to no value is placed in the aesthetic of the concrete used, the structure’s technological advances, or the architect’s fame. Alcatraz is a good example of value being imbued in the building as a whole, in its function and symbolism, as opposed to in the concrete itself.

More recently, as mid-century modern buildings become old enough to be considered “historic,” the preservation field is seeing an increasing amount of artistic and aesthetic values being associated with concrete heritage. The Solomon R. Guggenheim Museum (1952) for example, designed by one of the biggest protagonists in the history of reinforced concrete, architect Frank Lloyd Wright, is considered a mastery of the material and valued by an international community for its design and its innovative use of gunite, a relatively new sprayed-on concrete technology at the time.\textsuperscript{63} Faced with structural failures caused by the original design’s lack of continuous reinforcement within the concrete, and with both aesthetic and technological values guiding the conservation choices, the project team strove to fix these

\textsuperscript{61} “Concrete Preservation Institute - Field School at Alcatraz: History,” BASF, accessed April 29, 2018, 

\textsuperscript{62} Donald Langmead, \textit{Icons of American Architecture: From the Alamo to the World Trade Center} (Greenwood Publishing Group, 2009).

structural issues while maintaining the building’s external appearance and Wright’s original vision.\textsuperscript{64} One way in which they did so was through a destructive intervention from the interior to embed carbon fiber reinforced polymer (CFRP) strips within the concrete as new reinforcement.\textsuperscript{65} Secondly, they repaired exterior damages with a combination of patching compounds, acrylic crack fillers, and expandable surface coatings after a long series of weathering tests on the products.\textsuperscript{66} Afterward, the exterior façade was painted.\textsuperscript{67} Had the value of this structure not lay in the aesthetic continuity of the exterior, curving, concrete façade or in the original material’s technological novelty for its time, the project team might have looked into removing and replacing heavily damaged areas for example. Instead, the aesthetic and historic values and the elements of the building they were associated with were used to drive the conservation treatment choices.

Conservation projects like that of the Guggenheim Museum exemplify the importance of looking through the lens of values in order to evaluate treatment options for concrete heritage. Today, a division exists between preservation theorists and conservation practitioners. Many of today’s conservators might argue that there is no need or place for preservation theories such as Mason and Avrami’s values-based approach, focusing more on questions of efficacy and cost, for example. But conservation treatment decisions would benefit from some level of integration


\textsuperscript{66} Trienens, Boornazian, and Weiss, “Guggenheim Museum: Laboratory and Field Evaluation of Concrete Repair Products.”

with preservation theories, specifically that of a values-based approach. What follows is an overview of the available treatment options for corrosion in concrete and an assessment of the ways in which each of these treatments interact with the values associated with concrete heritage structures.

B. EXISTING TREATMENT OPTIONS

The question of the “hand” of the conservator and how visible it should be has always been a debate at the center of the field: should one be able to see the work carried out by a conservator, should it be regarded as part of the architectural history of the structure, an art in and of itself, or should the work be to make it seem as if he or she was never there? Different time periods and locations have seemed to have taken different stances on the subject. The infamous dispute between the 19th century conservation theories of French architect and author Eugène Emmanuel Viollet-le-Duc and English art critic John Ruskin, for example, is the near the center of this question. On one hand, Viollet-le-Duc felt that as a preservation architect he had the right to bring a structure back to a certain time period in its past by removing and adding elements with no indication of where he had done so. Ruskin, on the other hand, abhorred this idea and argued for more honest indications of the conservator’s “hand” if intervention was necessary at all.68

Today in the United States, much of the field leans towards the “invisible hand” theory, although certain projects will warrant some indication that the conservator had been there. In the corner of the mural on the ceiling of Grand Central Terminal’s Main Concourse is a tiny square

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that is significantly darker than the rest of it. Conservators who cleaned the ceiling in a 1996-98 restoration decided to leave this small patch of soiling as a sign of their hand and in an attempt to be honest about their work and the space’s layers of history. These considerations are central to treatment options for concrete heritage.

The first treatment to consider for concrete experiencing failure from corrosion is localized replacement. If the concrete in question is determined to be deteriorated beyond repair, the said concrete may be removed, and the surface may be prepared for replacement material. According to the ACI Guide to Concrete Repair, failing concrete can be removed by blasting, cutting, impacting, milling, hydrodemolition, or presplitting methods, to which small hand tools should also be added. All of these have risks and benefits in relation to the specific site in question.69

Impacting, for example, delivers large blows to the structure. Milling is also associated with a significant amount of vibration which could be detrimental to the structure as a whole or to surrounding concrete kept in place. Additionally, removal methodologies like these may cause micro-cracking in remaining concrete.70 If vibrations and impacts are not problematic for the structure, removal in this manner and replacement may be a worthwhile option.

On the other hand, vibration-heavy removal methods are would not be a viable option for historic structures in fragile condition. For more unsound structures, a conservator might explore other removal options such as abrasive blasting or hydrodemolition. These techniques employ small abrasive media and water respectively to remove damaged concrete. These methods are

69 ACI Committee 546, “ACI 546R-96: Concrete Repair Guide” (American Concrete Institute, 1996).

70 Ibid., 5-8.
associated with a significant amount of debris, and therefore environmental effects. They can also can be more expensive and rely more on contractors’ skills than other removal methods. Sites which may not have as much funding for the work, such as smaller privately-owned museums for example, might find these methods unfeasible. Sites unable to temporarily shut down their programming or protect the rest of the site effectively and cheaply during the work, would also not find this removal process viable. Evidently, if removal of concrete is necessary, the method chosen to do so involves an analysis of existing resources, the site’s management context, and how it functions on a daily basis.

When it comes to replacement materials, a value-based assessment becomes necessary. In some cases, project teams may determine that value lies most in the specific original material and therefore removed concrete warrants aesthetically different replacement material in an attempt to be didactic about what is old and what is new. An example of this theory in practice exists in the Alte Pinakothek in Munich, Germany (figure 6). Built in 1836 and bombed in World War II, the section of the building that was lost was replaced with bricks that very clearly differentiate themselves from the original material. Although this building is not built of concrete, it exemplifies this type of didacticism through materiality that sometimes guides preservation treatment. While this practice has previously been less common in concrete structures, the thought process is certainly useful and should be considered in their conservation in the future.

Some projects may find that more value lies in the aesthetic cohesiveness of the structure. In these cases, a lot of research and design goes into attempting to replicate the exact aesthetic of

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71 Lauren R. Millman, “Surface Assessment and Modification of Concrete Using Abrasive Blasting” (University of Miami, 2013).

the replacement material, as was the case in the Guggenheim restoration.73 In order to match the original concrete’s texture with imprints from plywood forms, patching material was hand worked while fresh.74 Here, the repair of historic concrete also becomes a question of craft.75 The exterior was then painted to match the original color found through a finishes analysis.76 This type of work can take a lot of time and money. This is where the project team’s work of assessing physical condition, values, and management context comes in to play in determining the best way forward.77

When concrete remains in acceptable condition, or the deteriorated concrete has already been removed and replaced, conservators then look for treatments that will slow existing and prevent future corrosion. One option that is available to conservators is cathodic protection. Cathodic protection effectively turns the entire embedded reinforcement into a cathode, thereby slowing corrosion. Cathodic protection can be done by connecting another less noble metal to the reinforcement (sacrificial anode system) or by applying an external charge to the reinforcement (impressed current cathodic system).78

In a sacrificial anode system, the added metal connected to the embedded reinforcement corrodes sacrificially to the reinforcement because it is lower in the galvanic series (figure 7).

73 Trienens, Boornazian, and Weiss, “Concrete Repairs and Coatings for Frank Lloyd Wright’s Solomon R. Guggenheim Museum.”
74 Trienens, Boornazian, and Weiss, “Guggenheim Museum: Laboratory and Field Evaluation of Concrete Repair Products,” 17.
76 Ibid., 50-52.
78 Ibid., 30.
The galvanic series is a table in which metals are organized according to their nobility and thus their preferentiality to corrode. Zinc, a metal near the bottom of the galvanic series, along with aluminum and magnesium, is often used as the external anode.\textsuperscript{79}

One study evaluated the viability of a particular zinc sacrificial anode system and MCIs on a carbonated concrete building in Honolulu, Hawaii.\textsuperscript{80} The study concluded that both systems were viable, and only recommended the sacrificial anode system if economic considerations allowed for it.\textsuperscript{81} While the zinc systems are also easier and faster to install than impressed current cathodic protection, they are arguably also less effective than them.\textsuperscript{82} The efficacy of sacrificial anode systems depends on the longevity of the anodes, i.e., their ability to continue to generate current. Not only is this reliant on the characteristics of the metal itself, but also on environmental factors such as temperature and humidity.\textsuperscript{83} Furthermore, although sacrificial anode systems do not require monitoring after installation, one cannot know exactly when the anode has stopped working until signs of deterioration occur. To avoid this, frequent visual inspections are necessary.\textsuperscript{84}


\textsuperscript{80} Seung-Kyoung Lee and Paul D. Krauss, “Methodology for Evaluation of Migrating Type Corrosion Inhibitors and a Discrete Zinc Sacrificial Anode Cathodic Protection Systems Applied on a 30-Year Old Carbonated Concrete Building,” \textit{Korea Concrete Institute}, 2003, 1081–90.

\textsuperscript{81} Ibid., 1084.

\textsuperscript{82} Paul Gaudette and Deborah Slaton, “Preservation Brief 15: Preservation of Historic Concrete,” 15.


\textsuperscript{84} Ibid., 19–25.
More often than not, impressed current cathodic protection (ICCP) systems are used. In ICCP systems, a small charge is delivered to the embedded reinforcement in order to override the current produced by corrosion (figure 8). The treatment can be very effective in slowing and preventing future corrosion and is advantageous in that removal of sound concrete, even if contaminated by chlorides, is not necessary. Therefore, structures which seek to retain as much original material as possible are good candidates for the system. Historic reinforced concrete bridges have successfully installed ICCP systems.

On the other hand, ICCP is more expensive than sacrificial anode systems, and than most other corrosion treatments in general. The system also requires highly skilled labor for installation and long-term monitoring. Failures of the system or of its components are a costly risk. Therefore, conservators would only recommend putting these systems in place in well-funded conservation projects. Concrete heritage sites that do not have these resources, both during installation and beyond, would not be good candidates for the treatment. ICCP systems also often involve a substantial amount of damage for installation and then can be visible from the exterior of the structure. Structures in which critical value lies in the aesthetic whole of the


88 Lee and Krauss, “Methodology for Evaluation of Migrating Type Corrosion Inhibitors and a Discrete Zinc Sacrificial Anode Cathodic Protection Systems Applied on a 30-Year Old Carbonated Concrete Building,” 1081–90.


90 Lee and Krauss, “Methodology for Evaluation of Migrating Type Corrosion Inhibitors and a Discrete Zinc Sacrificial Anode Cathodic Protection Systems Applied on a 30-Year Old Carbonated Concrete Building,” 1081–90.
exterior would therefore not be good candidates for the treatment if it meant disrupting the exterior composition.

Electrochemical realkalization of carbonated concrete is another more recently developed treatment for corrosion in reinforced concrete. The underlying principal behind the treatment is to restore passivity of the steel by restoring the alkalinity of the concrete (figure 9). The treatment is a non-destructive process which consists of applying a cathodic current to the embedded steel from an external anode in an alkaline electrolyte. The external anode can be anything from titanium meshes to mortar containing graphite powder for smaller applications.

This treatment can be an appealing option for structures because of its temporary nature. The cathodic current is only applied to the embedded steel for a few days, which is a very feasible option for a structure without the means to monitor longer-term systems and for a structure in which there is aesthetic value in the original concrete. In its brief and non-destructive approach, electrochemical realkalization thereby finds its intrigue for conservators in its ability to provide them an “invisible hand.” Electrochemical realkalization has therefore been picked up as treatment in the conservation of historic concrete structures, such as in the case of the San Antonio Abate Church bell tower (1930) in Valmadera, Italy. Unfortunately, cases like these also highlight how the brevity of the treatment can also be associated with a shorter-term durability. In an article on the bell tower’s treatment, the authors concluded that protection of the reinforcement after the treatment could only be attributed to an increase in alkalinity in the

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91 Böhni, *Corrosion in Reinforced Concrete Structures*, 165.


vicinity of the reinforcement, which would only last until the concrete became carbonated again.94

If the historic concrete is in good enough condition at the time of conservation, or if failing concrete has been removed and replaced, conservators may also consider surface treatments to prevent or slow future corrosion. The ACI Guide to Concrete Repair divides surface treatments into the following classifications:

1. penetrating sealers
2. surface sealers
3. high-build coatings
4. membranes
5. overlays 95

Not all surface treatments fit specifically into one of these classifications. Some are hybrids, such as semi-transparent hydrophobic stains. The basic principal behind these treatments is to reduce free water within the concrete pore structure and deter further infiltration of moisture or chlorides from the exterior environment.96 In deciding whether surface treatments may be a viable option for a specific concrete heritage project, conservators have a number of factors to consider in relation to the project’s values and needs.

For one, surface treatments pose the risk of changing the color or texture of the concrete.97 In most cases, this is not desirable in a concrete heritage conservation project, specifically for those in which the structure holds a significant amount of aesthetic and artistic value through its materials. Before using any surface treatments, conservators have to do mock-

94 Ibid., 376–85.
96 Ibid., 25.
97 Ibid., 25.
up areas on the structure to be sure no change in appearance occurs. Some surface treatments may not show signs of change in appearance until years later. Epoxies, for example, have been known to darken or yellow over time and are therefore often avoided by conservators.\textsuperscript{98} Other coatings have been known to become milky with exposure to moisture.\textsuperscript{99}

Conservators must also consider the effects on water and vapor permeability of a surface treatment. Water and vapor permeability are indirect factors in corrosion – less water and vapor infiltration will lead to a lower corrosion rate. Conservators therefore undertake long term testing programs to evaluate the treatment’s effects on these characteristics in the specific material and structure in question.\textsuperscript{100} Crack bridging is also a characteristic of surface treatments that may be important for conservators’ work. A certain surface treatment may be successful in the preceding categories, but if cracks are an issue in the concrete in question and a surface treatment is not successful at bridging them, the treatment is less effective as the cracks continue to let in corrosive species.\textsuperscript{101}

High-build coatings, one classification of surface treatment, are products that are applied at a thickness greater than 0.025 cm on the surface that act as a protective barrier and are almost always opaque, i.e. paints. These can be composed of acrylics, styene-butadienes, polyvinyl acetates, chlorinated rubbers, urethanes, polyesters, or epoxies, but this is not an exhaustive list.


\textsuperscript{101} ACI Committee 546, “ACI 546R-96: Concrete Repair Guide” (American Concrete Institute, 1996), 25.
They generally have good resistance to water absorption and can reduce corrosion in this manner. Furthermore, coatings can be prone to loss of adhesion, even with proper surface treatment due to the trapping of water, at this interface.\textsuperscript{102} Coatings therefore may not be a viable option in buildings or locations subject to heavy contact with water. In relatively dry locations in which cracking is not an issue and in which the coating has been determined to not change the concrete’s appearance, this treatment may be a viable option if the cause of corrosion being addressed is the ingress of corrosive species.\textsuperscript{103}

Overlays, another classification of surface treatment, are products that are applied at a thickness of 0.6 cm or more on to the surface of concrete to bond with the substrate. Overlays can be composed of epoxies, certain methyl methacrylates, polymer-modified concrete, polymer concrete, and concrete itself.\textsuperscript{104} Most important to consider in the use of overlays for historic structures are their addition to the profile of the concrete surface and weight of the structure. Sometimes, overlays will incorporate MCIs as an admixture.\textsuperscript{105}

Sealers, another group of surface treatments, which include penetrating sealers and surface sealers, are chemicals applied at about 0.025 cm or less on to the surface of the concrete. Sealers can be composed of a combination of epoxies, polyurethanes, methyl methacrylates, moisture-cured urethanes, or acrylic resins. Penetrating sealers are generally low molecular weight water repellents while surface sealers are generally transparent coatings. Surface sealers

\textsuperscript{102} Ibid., 27.
\textsuperscript{103} Paul Gaudette and Deborah Slaton, “Preservation Brief 15: Preservation of Historic Concrete”; Laura N. Buchner and Raymond M. Pepi, “Restoration of the Cast-in-Place Concrete at the New York Hall of Science,” 2–3.
\textsuperscript{104} ACI Committee 546, “ACI 546R-96: Concrete Repair Guide,” 27.
can be generically classified into boiled linseed oil, high-molecular weight methacrylate, and alkylalkoxy silane or siloxanes.\(^{106}\)

Boiled linseed oil sealers are known to slightly darken the surface of the concrete and cannot bridge cracks, meaning corrosive species could still enter through cracks that already exist.\(^{107}\) It should also be considered that these some of these sealers often require frequent applications, which can be disruptive and costly to a site. If the risk of a slight darkening of the concrete is not a problem for the structure in question, and if there are not a significant number of cracks that need sealing, then this type of sealer might be a good option. Furthermore, these sealers can be good in improving freeze-thaw durability. As opposed to linseed-oil-based sealers, high-molecular weight methacrylate sealers can in fact bridge cracks, sealing them and thereby preventing the ingress of corrosive species.\(^{108}\)

Some sealers are film formers and pore fillers while some are not. So called “breathable” sealers are often alkylalkoxy silanes or silane/siloxanes. Alkylalkoxy silane and silane/siloxanes-based sealers cannot bridge cracks but do improve resistance to water absorption and salt penetration through their filling of pores. Often times, silane- and siloxane-based sealers are recommended by manufacturers to be applied to concrete after the application of another treatment, specifically MCIs. This is due to their ability to prevent the entry of water, and therefore the exit of water-borne treatments. Cortec produces a line of products that are sealers that include MCIs.\(^{109}\)


\(^{108}\) Ibid., 25.

\(^{109}\) “MCI-2018 Sealer Product Data Sheet” (Cortec Corporation, 2011); Bavarian and Reiner, “MCI Surface Applied Corrosion Protection Systems for Reinforced Concrete: The Efficacy of Using Migration Corrosion Inhibitors (MCI-2020 & MCI-2020 M) for Reinforced Concrete.”
MCIs may represent an appropriate conservation treatment for existing concrete heritage, but still have a number of questions surrounding them despite over 30 years of use in the construction industry. Conservation professionals are not yet convinced of MCIs efficacy and some are fearful of its side-effects.\textsuperscript{110} What follows in the next chapter is a description of MCIs, their classifications and compositions, to aid in the understanding of the treatment and the questions that surround it.

IV. MIGRATING CORROSION INHIBITORS

A. CLASSIFICATIONS

Migrating corrosion inhibitors (MCIs) are a subset of substances called corrosion inhibitors that reduce corrosion rates. MCIs are intended to diffuse through permeable materials such as concrete. Corrosion inhibitors are generally classified by the following characteristics:

- Chemical composition
- Means of application
- Means of protection
- Film forming properties
- Capability to passivate the steel

Using these classifications, most MCIs may be defined as organic; admixture or surface-applied to hardened concrete or steel; mixed inhibition; film forming; and steel passivating. Each of these classifications and its relevance to historic concrete is expanded on hereafter.

MCIs are divided into two categories based on how they are applied: admixture and surface-applied. Both types find applications in the conservation of historic concrete. Admixture MCIs are those that are mixed-in to fresh concrete. If effective, admixture MCIs are clearly useful as a preventative measure in new construction applications, as they can be mixed into

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114 Ibid.
fresh concrete. They are also useful for conservation applications when they are mixed in to concrete repair material used on an existing structure. Repair mortars with admixed MCIs are also useful in historic concrete structures, as was the case in the repair of San Agustin Church in Puerto Rico (figure 10).

Surface-applied MCIs are believed to be even more useful for conservation applications. They are ostensibly absorbed by concrete upon application and then are said to migrate through the concrete’s pore structure to the embedded reinforcement. The inhibitor is purported to travel in both liquid and vapor phases, carried by capillary action, vapor diffusion, and ionic attraction. The inhibitor is said to form a monolayer film on the surface of the steel, analogous to the passive layer that naturally forms on steel in an alkaline environment. This monolayer film is said to protect the steel from corrosive forces.

B. COMPOSITIONS & MECHANISMS

Commercial MCIs are proprietary mixtures. Information on an MCIs chemistry can be found in some product’s Safety Data Sheets (SDS). Here, only compounds required by law to be disclosed are reported. A review of manufacturer literature suggests that alkanolamines and aminecarboxylate salts are common ingredients in commercial MCIs. While it has been claimed


117 “Case History: Repair of San Agustin Church” (Cortec Corporation, 2009).

118 L. Holloway, K Nairn, and M Forsyth, “Concentration Monitoring and Performance of a Migratory Corrosion Inhibitor in Steel-Reinforced Concrete,” Cement and Concrete Research 34, no. 8 (August 1, 2004), 1435.
that monofluorophosphates are found in certain migrating corrosion inhibitors,\textsuperscript{119} a review of manufacturer literature shows no commercial products currently on the market contained them.\textsuperscript{120}

Alkanolamines and aminecarboxylate salts contain amino groups. Once at the surface of reinforcement, nitrogen in the amino groups is believed to bond with the metal oxide on the substrate. This reaction forms a film on the metal surface that may inhibit both anodic and cathodic reactions. If MCIs do in fact behave in this manner, these products would be defined as mixed inhibitors. There have been arguments that alkanolamines only inhibit corrosion by blocking sites where oxygen collects electrons making them cathodic inhibitors rather than mixed inhibitors.\textsuperscript{121}

There is also an argument that MCIs can actually accelerate corrosion more in certain areas by shutting it down in others.\textsuperscript{122} This may be attributed to the fact that MCIs have to work their way through the complex microstructure of concrete and navigate around coarse aggregate. This may lead to uneven arrival at the embedded reinforcement and non-uniform coverage of it. In this instance, the inhibitor would shut down certain corrosion cells along the metal’s surface, which could serve to accelerate them in others and cause pitting corrosion. Because of this phenomenon, studies have proven that, in some cases, using too little an amount of an MCI is worse than not using inhibitors at all.\textsuperscript{123}

\textsuperscript{119} Söylev and Richardson, “Corrosion Inhibitors for Steel in Concrete: State-of-the-Art Report,” 610.

\textsuperscript{120} Myrdal, “Corrosion Inhibitors – State of the Art,” 28.

\textsuperscript{121} Ibid., 14.


\textsuperscript{123} Dariva and Galio, “Corrosion Inhibitors - Principles, Mechanisms and Applications,” 369.
Other questions also exist about the inhibition mechanisms of MCIs. While the science behind the formation of the protective layer is generally accepted thanks to studies and evaluations of mixed-in inhibitors,\textsuperscript{124} literature has not addressed how the formation of the protective layer takes place when rust already exists on the surface of the metal. Questions also surround the migration abilities of MCIs. For example, high-performance concrete’s relatively dense and non-continuous pore structure would seem to make it difficult for an inhibitor to travel through it.\textsuperscript{125} It is also curious that while it can take chlorides years to travel through concrete, MCIs are able to do so in just about a month’s time.

C. PRODUCTS & MANUFACTURER CLAIMS

The five most common commercially available surface-applied MCIs come from three manufacturers: Cortec, BASF, and Sika. Both Cortec and BASF produce two MCI products each. It seems that compositions of a particular product may differ somewhat from country to country (table 1).\textsuperscript{126} For example, while Sika’s product, Ferrogard 903, is aminoethanol based in Norway, it is composed of alkanolamines and ethyl alcohols in Canada. One of Cortec and BASF’s products at one point shared the same name, MCI-2020, which BASF has since renamed MasterProtect 8020CI. BASF has since changed the name of their MCI-2006-NS product to Masterlife 2006,\textsuperscript{127} and now describes it as a powdered admixture in its Product Data Sheet.


\textsuperscript{125} Kosmatka, Kerkhoff, and Panarese, \textit{Design and Control of Concrete}, 14th ed. (Portland Cement Association, 2002), 309.

\textsuperscript{126} Myrdal, “Corrosion Inhibitors – State of the Art,” 28.

(PDS) and therefore will not be further discussed.\textsuperscript{128} Almost all of the commercial MCIs on the market have an aminecarboxylate component and furthermore are water-soluble.

The claims made by two of the manufacturers about the depth of penetration are essentially the same. Cortec claims its MCI-2020 and MCI-2020 V/O can migrate up to 3 inches in 30 days,\textsuperscript{129} while Sika claims 3 inches in 28 days for its Ferrogard 903.\textsuperscript{130} BASF does not make a specific claim for its MasterProtect 8020CI about penetration depth and time in its PDS.\textsuperscript{131}

A look at common mixed-in (admixture) MCIs adds W.R. Grace, Euclid Chemical, and Axim to the list of manufacturers (table 2).\textsuperscript{132} To this list should also be added Cortec’s MCI-2000. A review of the manufacturer literature on these mixed-in inhibitors indicates a bit more variety in chemical composition than surface-applied MCIs. The common chemical ingredients amongst most mixed-in inhibitors are calcium nitrite or alkanolamines. Again, products of the same name from the same manufacturer differ when produced in different countries. This disparity could be due to different rules for disclosing chemical ingredients or differing environmental regulations.\textsuperscript{133}

\begin{itemize}
\item \textsuperscript{128} “BASF Masterlife 2006 Product Data Sheet” (BASF), accessed April 22, 2018, \url{https://assets.master-builders-solutions.basf.com/Shared%20Documents/PDF/English%20(Australia)/basf-masterlife-2006-tds.pdf}.
\item \textsuperscript{129} “MCI-2020/MCI-2020 V/O Product Data Sheet” (Cortec Corporation, Revised 2010), \url{https://www.cortecvci.com/Publications/PDS/MCI-2020_and_VO.pdf}.
\item \textsuperscript{130} “Sika FerroGard 903 Product Data Sheet, Ed. 5.5.2011” (Sika Corporation, n.d.).
\item \textsuperscript{131} “BASF Masterprotect 8020ci Product Data Sheet” (BASF), accessed April 22, 2018, \url{https://assets.master-builders-solutions.basf.com/Shared%20Documents/PDF/English%20(Australia)/basf-masterprotect-8020ci-tds.pdf}.
\item \textsuperscript{132} Myrdal, “Corrosion Inhibitors – State of the Art,” 26.
\item \textsuperscript{133} Myrdal, “Corrosion Inhibitors – State of the Art,” 26.
\end{itemize}
D. MONITORING & TESTING METHODOLOGIES

MCIs were first introduced to the construction industry by Cortec Corporation in the mid-1980’s. The technology originates from “vapor phase inhibitor” technology that has existed in the shipping and storage industry for decades for the protection of steel machinery. Despite being on the market for over 30 years in the construction industry, MCIs, the science behind how they work, their efficacy, and their side effects are still being reviewed by practitioners. The biggest barrier to answering these questions is a lack of acceptable monitoring and testing methodologies specifically for the evaluation of MCIs. Traditional corrosion monitoring poses issues when used to evaluate the efficacy of MCIs.

Two types of monitoring systems have been used historically to measure corrosion in reinforced concrete successfully, but both of them present their own issues when utilizing them to evaluate MCIs. The first, called a half-cell survey, specified by ASTM C876, measures electrochemical corrosion potential (ECP) of reinforcement by using a reference electrode to measure the difference in potential energy between the reinforcement and that electrode (figure 11). ECP is a measurement of electromotive force (EMF) measured in units of voltage and also referred to as a potential. ECP indicates the probability of corrosion, as opposed to a

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135 Ibid., 24.


measurement of corrosion that is actually occurring, but the value may be used in Ohm’s Law to calculate a corrosion current. Corrosion current, otherwise known as Icorr, represents the flow of electrons from the anode to the cathode, otherwise thought of as the corrosion rate (the rate at which the steel oxidizes and converts to rust). In half-cell surveys the reference electrode may be placed on the surface of the concrete or embedded within the concrete itself near the reinforcement. When used to measure corrosion, extremely wet concrete may cause results to misrepresent the corrosion occurring in it. Therefore, one may measure an extremely high potential at the base of a column with a high moisture content, only to open up the column and see that the reinforcement is in fine condition. Evaluations of the methodology have concluded that half-cell potentials are problematic because there are based on probability and interpretive data.

When applying the half-cell survey methodology to an evaluation of MCIs, the possibility of misrepresentative results increases. In order for the half-cell survey to give accurate results, the concrete must be conductive all the way through from the reinforcement to the electrode at the surface. MCIs have been believed to act as pore blockers and would thereby disrupt the conductivity of the concrete necessary for the half-cell survey’s accuracy.

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141 W. Spencer Guthrie, Thad M. Pinkerton, and Dennis L. Eggett, “Sensitivity of Half-Cell Potential Measurements to Properties of Concrete Bridge Decks” (Brigham Young University Department of Civil and Environmental Engineering, 2008), 11.

explore this, in Columbia University’s laboratory, a petri dish containing a few drops of MCI-2020 was left out to evaporate out for 4 days. After 4 days, what remained was a significant volume of residue (figure 12). This residue could represent the material that can potentially block the pores of concrete after the liquid carrier has evaporated, which would lead to less oxygen for corrosion but also difficulties in measuring corrosion.

Moreover, manufacturers often suggest the application of a silane- or siloxane-based sealer to the surface of the concrete after an MCI has been applied.143 This is intended to ensure that the MCI is not able to egress the concrete in the same manner it entered, that is, through water and vapor diffusion. The issue with silane- or silane/siloxane-based sealers is that they block conductivity. Therefore, a half-cell survey methodology in which the reference electrode is at the surface of the concrete and silane- or silane/siloxane-based sealers have been applied becomes ineffectual. If the electrode is placed inside the concrete, the problem then becomes the difficulty in confirming that the inhibitor has reached the reinforcement and the reference electrode. If, for example, the inhibitor reaches the reference electrode and not the reinforcement, the results will misrepresent corrosion occurring at the reinforcement.144

The second of the two common monitoring systems used to measure corrosion of reinforcement in concrete is called linear polarization resistance (LPR) and is outlined in RILEM TC154 – EMC Electrochemical Techniques for Measuring Metallic Corrosion.145 LPR is based on the theory that introducing a certain amount of energy to a reaction will result in the return of


144 “Evaluation of Half-Cell Corrosion Detection Test for Concrete Bridge Decks.”

a specific amount of energy to balance this reaction. Based on this theory, by applying a change in potential to a corrosion cell one can measure the current that was returned to balance it out. The issues with LPR are similar to those of half-cell surveys in that the method relies on a reference electrode. If one cannot be sure that full conductivity exists between the reference electrode on the surface and the reinforcement or that inhibitor has reached the reinforcement if it is below the surface, then results from LPR may misrepresent corrosion of reinforcement.\(^{146}\) On the other hand, LPR is less vulnerable to moisture content affecting results because it measures the rate of corrosion as opposed to measuring just corrosion potential.

Laboratory-based studies on MCIs are often structured in a similar manner to one another: a large number of concrete samples with embedded reinforcement are produced and MCI is applied to some while the other are kept as controls with no MCI. These studies will often then employ traditional corrosion monitoring methodologies, such as half-cell surveys and LPR, to evaluate the difference in corrosion between the two sets of samples. Many of these testing programs fail to address some important real-world factors in their sample preparation. No tests, for example, have attempted to model historic concrete in their samples, and most tests use new reinforcement.\(^ {147}\) This new reinforcement often does not have existing rust on its surface.\(^ {148}\) If this is the case, the test cannot fully confirm the efficacy of the MCI in the structures that are candidates for MCIs in which this is the state of existing reinforcement.


Lastly, samples are often not assembled with cracks, another real-world factor important to include in the evaluation of MCIs.149

Other testing programs have attempted to model the chloride concentration of existing structures by including chlorides in the concrete mixes and by soaking the entire concrete samples in salt solution before applying MCI.150 In these cases, too much salt may act as a pore-blocker, denying oxygen to the corrosion cells at the reinforcement as well as rendering corrosion measurement methodologies questionable.151 Moreover, if results from these types of modeled-reality methodologies are successful, they only prove that the inhibitor can slow corrosion in a relatively small sample size, which does not consider the issue raised earlier about the risk of uneven inhibitor coverage of reinforcement causing worse corrosion than with no inhibitor at all.152

For example, a study carried out by Dubravka Bjegovic and Boris Miksic, President of Cortec, titled, “Migrating Corrosion Inhibitor Protection for Concrete,” and published in 1999 in Materials Performance, is often cited in other studies and literature on MCIs as a valuable testing program in its proof of MCIs efficacy, but raises some of the issues with model-reality testing methodologies.153 The authors’ test on surface-applied MCIs involved the assemblage of 13 cm diameter concrete samples with embedded 13 mm diameter polished steel reinforcement

149 Ibid., 1435–40.
150 Dubravka Bjegovic and Boris Miksic, “Migrating Corrosion Inhibitor Protection of Concrete,” Materials Performance; Houston 38, no. 11 (November 1999).
153 Dubravka Bjegovic and Boris Miksic, “Migrating Corrosion Inhibitor Protection of Concrete.”

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with 3 cm of concrete coverage.\textsuperscript{154} Firstly, in their use of polished steel, the test cannot be said to have proved that the MCIs could be effective in an existing structure with existing rust. Furthermore, the authors attempted to accelerate corrosion by including 3kg/m\textsuperscript{3} NaCl in the concrete mix and subsequently placing a 3.5\% NaCl solution on the surface of the samples for a week and drying them out for a week.\textsuperscript{155} Through the combination of aggressive chloride pre-treatments and the subsequent addition of MCI, the samples may have completely denied oxygen by pore blockage that was necessary for corrosion to continue. Furthermore, the test employed half-cell potentials, known to be hindered by pore blockage.\textsuperscript{156} This effect may explain the very low corrosion rate of \textasciitilde{}10 to 12 \mu m/y or little to no corrosion whatsoever of MCI treated samples. Results still indicated MCI treated samples had a corrosion rate reduction of 83\% compared to control samples.\textsuperscript{157} Further study of the pore-blocking effects of chloride pre-treatments is necessary. Lastly, in the small sample sizes, the testing program did not address the possibility of uneven application and reinforcement cover in actual structures.

Testing and evaluation methodologies specifically for the migration of MCIs are also less than adequate. These techniques have to address that the question of the MCI having migrated through the concrete is separate from the question of the actual inhibitor having reached the embedded reinforcement. In other words, proving that the MCI has saturated through the concrete to the reinforcement depth is not the same as proving that the inhibitor has reached the reinforcement. Additionally, concluding that some inhibiting chemicals have reached the

\footnotesize{\textsuperscript{154} Ibid., 54.}

\footnotesize{\textsuperscript{155} Ibid., 54.}

\footnotesize{\textsuperscript{156} Guthrie, Pinkerton, and Eggett, “Sensitivity of Half-Cell Potential Measurements to Properties of Concrete Bridge Decks.”}

\footnotesize{\textsuperscript{157} Dubravka Bjeogovic and Boris Miksic, “Migrating Corrosion Inhibitor Protection of Concrete,” 54 -55.}
embedded reinforcement is not necessarily concluding that they have reached in sufficient quantity to form a continuous protective layer around it.

Some practices for evaluating the migration of MCIs through concrete involve taking cores from the structure or from samples produced in the laboratory.\textsuperscript{158} This is problematic in the coring process’ introduction of heat and water to the concrete which can alter the location and amount of the MCI. One of these methods involves the use of a quaternary ammonium compounds (QAC) test kit. These kits measure the concentration of QACs in a solution. QAC tests can thereby identify the inhibiting chemicals of amine- and alkanolamine-based MCIs. Cortec suggests this method in their literature and describe its steps.\textsuperscript{159}

The procedure involves first taking cores from the structure or samples that have been treated with MCI and dividing them into 1-inch disc-shape samples and labeling them according to their depth (figure 13). Each of these samples can then be ground up or pulverized into a powder, passed through mesh, and placed into separate containers. After adding deionized water to create a 1:1 slurry of the samples and letting them soak for at least 30 minutes, the QAC test kit can be used to determine the concentration of QACs at the specific depth of each disc-shaped sample.\textsuperscript{160}

The major issue with this test method is the introduction of heat and water by the coring process. Results obtained from this test are thus problematic. Even if this fact is ignored, this technique only proves that inhibitor has reached a certain depth but does not prove that it has formed a protective layer in sufficient quantities on the metals surface.

\textsuperscript{158} Ibid., 54.

\textsuperscript{159} Bavarian and Reiner, “MCI Surface Applied Corrosion Protection Systems for Reinforced Concrete: The Efficacy of Using Migration Corrosion Inhibitors (MCI-2020 & MCI-2020 M) for Reinforced Concrete.”

\textsuperscript{160} Ibid.
Other studies on MCIs have used X-ray photo electron spectroscopy (XPS) techniques to locate the inhibitor.\textsuperscript{161} XPS is a quantitative surface analysis technique in which X-rays are irradiated at a material and wavelength distributions sent back by its constituents are analyzed to determine elemental compositions.\textsuperscript{162} One study published in 2003 in \textit{NACE Corrosion} by Behzad Bavarian and Lisa Reiner of California State University, Northridge, titled “Corrosion Protection of Steel Reinforcement in Concrete by Migrating Corrosion Inhibitors,” employed XPS analysis to demonstrate that inhibitor had migrated to the surface of the reinforcement.\textsuperscript{163} The study also used XPS depth profiling using a 2 kV Argon ion gun to demonstrate that a 140 nm layer of amine-rich compound was on the surface of the reinforcement.\textsuperscript{164} This approach is more suitable for the evaluation of MCIs than coring and cutting in the fact that it does not introduce heat or water to the concrete. Still, XPS does not go as far as to prove that the inhibitor has reached the reinforcement in a sufficient quantity. The inspection window of XPS is extremely small and it would thereby take a large amount of readings to determine MCI cover on the entire metal surface.

Ultraviolet-visible (UV) spectroscopy is another technique used for studying MCI migration. The machinery sends out wavelengths in the UV spectrum as opposed to an X-ray.\textsuperscript{165} Similarly to XPS, UV spectroscopy can determine the presence of inhibitor but cannot prove


\textsuperscript{164} Ibid.

quantities. In a 2013 study carried out by Ming Shen, Alla Furman, and Joshua Hicks published in *Materials Performance*, for example, UV spectroscopy was used to identify surface-applied MCI at a depth of 3 inches below the surface of concrete.\(^{166}\) This procedure also included the cutting of cored samples into discs and pulverizing them into powders in order to be analyzed using UV spectroscopy.

\(^{166}\) Shen, Furman, and Hansen, “Protecting Concrete Reinforcement Using Admixture with Migrating Corrosion Inhibitor and Water-Repellent Component,” 18–21.
V. EXPLORING NEW METHODOLOGIES

Within the timeframe of this thesis, laboratory work was carried out to explore simplified testing methods. Evaluation was broken into two parts to more specifically evaluate the efficacy of MCIs based upon the questions of migration and of inhibition. The testing used a simple product, Cortec’s surface-applied MCI-2020, in order to focus on the development of methods, rather than on the evaluation of different products.

A. INHIBITION

Two testing methods were explored for the question of inhibition to determine if an MCI could inhibit corrosion in solution without the obstacles that the many variables of concrete introduce. Confidence that MCIs work in solution could confirm the belief that surface-applied inhibitors could inhibit corrosion in a sufficient way if they were in fact able to reach the reinforcement. In this way, future questions of how various MCI products perform in concrete would be more predominantly questions of migration.

A secondary goal arose during experimentation of determining at what concentration of NaCl the chemical would be effective. The tests were time-based and aimed to produce relatively fast results. The NaCl solutions can be understood as a simplified model of the pore water in chloride-contaminated concrete. In more fully-realized tests, measures to more closely model the chemistry of this pore water could be undertaken.
i. JAR TEST

The first approach explored was adapted from the jars that Cortec representatives (and other MCI manufacturers) often display at trade shows and conferences (figure 14). The jars come in sets of two: one of the jars with steel wool and solution labeled “tap water with MCI-2020,” and the other with steel wool and a solution labeled “steel wool unprotected in Water.” The former shows no visible change in color or appearance of the steel wool, or of the surrounding solution whatsoever. The latter appears to have corrosion products, which have turned the liquid very black. It was thought that this proof of efficacy demonstration could be adapted into a reasonable qualitative approach to the study of inhibition with surface-applied MCIs in solution, and one that did not necessitate reliance on laboratory experiments.

a. TEST A: FILINGS

These tests were carried out in Columbia University’s laboratory. Eisco iron filings were used in place of the steel wool. It was believed that with more surface area, the iron filings would corrode more rapidly, and produce faster results. Commercial steel wool is also likely to be contaminated with surfactants and inhibitors. Three 4oz Wheaton clear glass jars with screw caps were filled with 100 mL of deionized water and another three jars were filled with 100 mL of a 3% NaCl solution prepared with reagent-grade sodium chloride. The three jars of deionized water received 1 g, 2 g, and 4 g of iron filings respectively. The same was done for each of the three jars containing the salt solution. All of the jars were vigorously shaken and left in the lab.
After 48 hours, neither set of jars showed a change in color attributable to corrosion products (figure 15). The iron filings themselves also all appeared to be the same color as at the start of the experiment. Rust appeared on the upper rims of the glass and the inner rim of the lids of all of the 3% NaCl jars (figure 16). Another jar was set up with an increased chloride content with 100 mL of a 12% NaCl solution and 4 g of iron filings and left for 72 hours. Again, no change in the liquid or the iron filings was observed (figure 17). Despite vigorous shaking, the results suggested that the iron filings were not receiving enough oxygen in the solution for corrosion to commence in a short period of time. This was consistent with the deposition of rust formed on the upper areas of the jars and lids where oxygen was more readily available. In an attempt to remedy this, additional jars were prepared with reduced amounts of solution and a range of methods of shaking, opening, and closing the jars. The results were still unsatisfactory showing no change in color or appearance of the solution.

b. TEST B: COUPONS

In further jar testing, 10 cm x 1.9 cm steel coupons were used in place of iron filings, so that the metal could extend out of jars and be exposed to oxygen. The iron coupons were placed in the jars with 100 mL of a 12% NaCl solution without lids (figure 18). One jar was prepared with no MCI, another with 4 mL of Cortec’s MCI-2020, and another with 4 mL of Cortec’s MCI-2020 V/O (Cortec’s version of MCI-2020 for vertical and overhead applications). After 24 hours all of the coupons began to discharge an orange color, presumably rust, into the liquid. The jar containing no MCI showed the most orange color. The jar containing MCI-2020 displayed less of the orange color, and the jar with the MCI-2020 V/O showed somewhat less.
Interestingly, this version of the product began to turn the iron coupon and solution a blue color (figure 19).

c. CONCLUSIONS

It was concluded that this methodology was probably not sophisticated enough in design to model the situation of inhibitors working within concrete. A more fully-realized version of these experiments might include the introduction of oxygen, along with pH adjustment to simulate the chemistry of pore water in carbonated concrete. The Cortec demonstration jars, and how they were prepared, remain a mystery.

i. CELL TEST

A second inhibition testing method involved assembling a single corrosion cell with reinforcing steel as electrodes. The primary goal was an exploration of what concentrations of MCI would slow corrosion.

a. TEST A: PROOF OF CONCEPT

As an initial proof of concept, a corrosion cell was set up in EChem’s laboratory in Poughkeepsie, New York. The corrosion cell consisted of a 3” long #4 black rebar acting as the anode and a 3” long #6 316 stainless-steel rebar acting as the cathode. Both were placed in a 275 mL Eisco plastic jar filled with about 150 mL of a 3% NaCl solution and held in place by
clamping brackets. The ordinary rebar had previously been soaked in a 3% NaCl solution for about 24 hours to initiate corrosion. Each rebar was connected by copper stranded wire to a WAGO lever-nut and these two lever-nuts were connected by a DALE LVR-3 1Ω 3W resistor. The lever-nut was then connected with two more pieces of copper stranded wire, which connected the entire cell through an input terminal to a Thermo Fischer Scientific DT85 Series 3 DataTaker. The DataTaker then measured the voltage in microvolts as it crossed the resistor. An increase in voltage would indicate an increase in current and therefore corrosion. A decrease in voltage below the equilibrium of the cell before the addition of MCI would indicate corrosion inhibition by the MCI.

- After about 5 minutes, the voltage of the assembled corrosion cell was reading at a relatively stable value of around 68 μV, and 3 mL of MCI-2020 was then added to the solution in the plastic jar. The DataTaker instantly recorded a spike in microvolts from to about 106 μV and the potential quickly began to fall back down to below the original baseline voltage, stabilizing at about 45 μV. Another 3 mL of MCI-2020 was added to the solution and the voltage spiked to about 71 μV and then again immediately began decreasing, reaching about 27 μV. When air was introduced to the solution by blowing through a straw into it, the voltage increased.

The cause of spikes in voltage directly after the addition of MCI was not fully understood but might be attributed to a brief increase in conductivity of the solution caused by the salts in the MCI. A yellowish substance, suspended in the solution began to surround the anode in the jar almost immediately after the addition of MCI. The color did not gather around the cathode in the same manner (figure 20). This may be some indication that the claims from manufacturers about
the attraction of MCI to the location where corrosion takes place (that is, the anodic locations) were accurate. It was also observed that introducing air into the solution in the jar would produce a spike in voltage, showing the essentiality of oxygen to the corrosion cell and therefore to this testing method. This observation suggested that a more fully-realized version of this test should also introduce and control the partial pressure of oxygen. From this first test, it was concluded that the assembly of a corrosion cell with a stainless-steel rebar as the cathode and the introduction of an MCI and would produce voltage changes that could be monitored.

b. TEST B: COLUMBIA UNIVERSITY

An iteration of this test was done in Columbia University’s laboratory. Four corrosion cells were constructed in the 275 mL Eisco plastic jars using 3” long #4 black rebar (as anodes) and 3” long #6 stainless-steel rebar (as cathodes). 100 mL of a 3% NaCl solution was added to the jars to serve as the electrolyte (figure 21). The cells were left to reach equilibrium with the DataTaker reading the voltages every minute (figure 22). The immediate spike in voltage in the proof of concept test was not observed due to less frequent data recording in this iteration, every 1 minutes as opposed to every 5 seconds previously. Rising and falling patterns amongst the four cells were determined to be identical and negligible, and were attributed to instrument noise or ambient variations. When the cells had remained in relative equilibrium for about 4 days, 2 mL and 4 mL of Cortec’s MCI-2020 was added to two of the samples, Sample 3 and Sample 4 respectively. Data was plotted, and some other observations were recorded (figure 23).

- The voltages of Sample 1 and 2, which had not received any MCI, along with Sample 4, which had received the most MCI, continued to move together in a
consistent manner with a small initial drop followed by a steady rise for 2 days after the MCI was added, reaching a relative equilibrium right around where it had been before the addition of MCI.

- The voltage of Sample 3, which received the least amount of MCI, behaved as with the other samples for 2 days after the MCI was added, at which point, the current sharply dropped to the lowest value just below 0.

The instrument noise in this test was unsatisfactory. Furthermore, the results indicated the largest amount of MCI would have no effect on corrosion, while the smallest amount of MCI would bring the voltage down significantly, to below 0.

c. TEST C: ECHEM’S LABORATORY

Another version of this test was assembled at EChem’s laboratory to address some of the issues noted in the previous one. One issue identified was the erratic temperature and humidity in Columbia’s laboratory. An effect of this may have been the relatively rapid evaporation of the solutions in the jars over the course of the week. An environment with a more stable temperature and humidity was sought, and it was noted that a more sophisticated version of this test design would have to incorporate temperature and relative humidity control.

New data loggers, one per cell, were used. These new data loggers measured current in mA rather than voltage. Electrodes were spaced from each other by measuring a distance of 1.5” between the metal clamps. Each electrode was marked on its connecting wire at 3” from the bottom of the electrode so that this mark could line up with the bottom of the clamp and ensure that all of the electrodes were immersed evenly in the solution (figure 24). 150 mL of 3% NaCl
was added to each of the four cells and each cell was then covered with a ziplock bag to reduce evaporation (figure 25). The cells were left to reach equilibrium which took 48 hours. This was based on an initial sample cell that had been set up and observed for the time it took to reach equilibrium in the new, more controlled, temperature and relative humidity environment (figure 26).

After 48 hours, Cortec’s MCI-2020 was added to three out of the four cells (figure 27). One cell, Sample 1, remained without MCI as a control. Sample 2 received 7.5 mL of MCI-2020, representing 5% of the total solution. Sample 3 received 3.75 mL of MCI-2020, representing 2.5% of the total solution. Sample 4 received 1.5 mL of MCI-2020, representing 1% of the total solution (figure 28).

- All of the samples reached a relatively stable average equilibrium of 16 ± mA within 48 hours. Sample 2, 3, and 4, which received the most to least amount of MCI respectively, showed no significant difference in current reached after the addition of MCI, averaging at 21 ± mA (figure 29, 30, 31 and 32).

These results indicated that the MCI did not have a significant effect on the current that could have been interpreted as inhibition. A new sample, Sample 5, was assembled with 150 mL of 1% NaCl solution and was given 7.5 mL of MCI-2020, representing 5% of the total solution. The largest dosage of MCI was repeated from the previous test and a significantly lower concentration of salt was used to observe if a higher dosage of MCI could inhibit corrosion.

- Sample 5 reached an equilibrium around 0.22 ± mA, and 48 hours after the addition of MCI, the current steadily rose reaching its highest point 4 days out at 0.34 ± mA at which point the current dramatically dropped to 0.125 ± mA followed by a steady rise in current for the remainder of the time (figure 33).
d. TEST D: HIGHER DOSAGE

Cortec’s MCI-2020/MCI-2020 V/O product data sheet states that “MCI-2020 is applied in a single coat at 150 ft²/gallon (2.68 m²/liter) to horizontal surfaces. It also states that it should be applied in two coats at 300 ft²/gallon (7.36 m²/liter) to vertical and overhead surfaces.”\(^{167}\) Using these values, it was deduced that a significant increase of MCI in the experiments would be required for MCI to be able to shut down the corrosion cell in solution, and thereby establish this testing method as viable.

A new cell test, Sample 6, was done with 75 mL of the lower 1% NaCl solution previously used, and 25 mL of added MCI-2020 to achieve a desired solution:

- Sample 6 reached a relative equilibrium current around 0.15 ± mA after 48 hours, and after the addition of MCI, the current sharply dropped to about 0.06 ± mA and then began to rise for the next 24 hours until reaching a current of about 0.12 ± mA. At this point, the current dropped slightly again but continued to stay at this general range hovering just below 0.10 ± mA (figure 34).

This was the first cell that, after the addition of the MCI, exhibited a current significantly lower than its original equilibrium with no signs of steady rising. This test was replicated two more times to confirm that the results could be achieved again (figures 35, 36, and 37). These additional samples exhibited a drop in corrosion current with the addition of MCI and a continuation of this low current for the remainder of the time. The relatively uniform results in these three tests indicated that at a sufficient dose of the MCI (and a lower chloride ion

\(^{167}\) “MCI-2020/MCI-2020 V/O Product Data Sheet” (Cortec Corporation, Revised 2010).
concentration) this testing methodology, in its most basic form, could prove an MCIs ability to inhibit corrosion in solution.

**B. MIGRATION**

Two methods for identifying the migration of MCI in concrete samples were also explored. These aimed to avoid coring, cutting, or pulverizing samples so as not to introduce heat and water to the treated concrete. A fully-realized test could involve the use of the splitting tensile function on a compression machine to break samples and then employ one of these identification methods, if successful, to identify MCI had migrated. This would eliminate the need to use problematic cutting techniques.

First, Cortec’s MCI-2020 and MCI-2020 V/O were examined underneath a dual-wavelength UV light to see if either product would fluoresce. It was hoped that this might be a viable way to identify if the MCI had migrated in a treated samples once they were broken open roughly perpendicular to the treated surface. Neither of the products fluoresced under short wave or long wave UV illumination.

Second, Cortec MCI-2020 was applied with a brush to the 10 cm² area on the surface of a historic concrete core sample. It was broken open after 3 days using the back of a ball-peen hammer. It was thought that if the MCI could be observed through a change in appearance from saturation it could lead to a viable identification method. No change in color was observed indicating that a simple visual test was not possible.

Investigation into chemical compounds that may react with one or more of the amines in the MCI with a distinct change in color (such as copper compounds) may be a valuable next step.
Overall, these methods still did not offer an answer of whether inhibitor had reached reinforcement in sufficient quantities.
VI. SUMMARY & AREAS FOR FURTHER STUDY

This thesis began by presenting the issue of corrosion in reinforced concrete heritage. A discussion of concrete as a material, the differences between historic and modern concrete as they relate to conservators’ work, and an explanation of corrosion in reinforced concrete, its causes, and its effects, provided a basis for understanding available treatment options. It was concluded that historic concrete is a very different material from modern concrete, which has implications on both its deterioration and its treatment. A valuable area for further study is a compilation of the introduction dates of admixtures throughout the concrete’s history to aid practitioners in the care of historic concrete.

A methodology was then offered for conservators to choose treatment paths by analyzing the ways in which these treatments support or oppose the specific values and needs of the structure in question. It was concluded that conservators could benefit from an integration of preservation theory in their practice. While preservation theories can often be considered as too abstract for practical application, this thesis argued that with more analysis, some theories can aid in a conservator’s decision-making process. A study should be undertaken in which the combination of these preservation theories with the practical realities of heritage sites (such as cost, management context, on-going programming, and availability of skilled-labor) is explored.

The discussion of available treatment options led to the questions that surround one treatment in particular, MCIs, because surface-applied chemicals seem to represent an appropriate conservation treatment for existing concrete heritage, but still have a number of questions surrounding them. The theoretical benefits of MCIs for concrete heritage were
analyzed and the limitations of existing evaluation methods for the class of products were investigated. A deeper dive into corrosion monitoring systems and their applications in studies on MCIs would be valuable.

Finally, a preliminary exploration of how to improve these methodologies was begun. This undertaking indicated that there is still a significant amount of work to do in developing methodologies designed specifically for the evaluation of MCIs. For one, both the jar and the cell procedures for testing inhibition exhibited the importance of air to the corrosion cell. Secondly, these two tests indicated that additional steps towards more closely modeling the pore solution of concrete were necessary. Additionally, all of the tests needed temperature and relative humidity control.

The more fully-realized laboratory version of the cell test would therefore use the cell assembly in which two pieces of rebar, one larger than the other, would be secured in a jar by clamps at a specified distance from one another and from the bottom of the jar. The temperature and relative humidity of the lab would be controlled and monitored. A solution modeled after the pore water of concrete would be added to the jars and air would be introduced continuously to the solution through the use of an air pump. Samples would vary in chloride content and amount of MCI added, as well as in type of MCI, in order to test the efficacy of different concentrations of MCI and NaCl and different products.

In conjunction with the inhibition test, a fully-realized migration test would involve preparing concrete samples with a range in chloride contents and with embedded rebar. The rebar would vary in existing rust formation. Different amounts and types of MCI would be applied to each type of concrete sample. After 30 days, the samples would be broken using the splitting tensile function on a test stand. The question of how to determine migration depths in
these broken samples needs further study. Compounds, such as copper compounds, that may react with certain components of MCIs, resulting in a color change, should be explored. An ideal detection method would be able to identify quantity and would detect the specific inhibiting chemical on the surface of the rebar as opposed to within the vicinity of it.

The next iteration of this fully-realized test would combine the questions of inhibition and migration while still employing the concept of using two known electrodes, as opposed to using methodologies such as LPR and half-cell surveys, which rely on reference electrodes. The test would embed sets of two rebar electrodes in an actual concrete structure and measure voltage from attached conductive wires that run out of concrete and connect to a data logger on the exterior. Varying amounts of MCI and different products could be applied in to different cells. Additionally, different degrees of existing rust on rebar could be explored as a variable. Change in appearance could also be assessed using reflectance colorimetry instruments before and after application.

The trials and errors of the cell test indicated the importance of solution concentrations for the efficacy of MCIs. In the early samples, lower dosages of MCI did not allow the inhibitor to shut down corrosion. In light of the belief that too low of an MCI dosage can lead to corrosion inhibition in some areas of a structure but acceleration in others,¹⁶⁸ this has major implications for conservators considering the use of MCIs on historic structures. Any risk of increasing corrosion in certain areas of a concrete heritage structure would often outweigh the benefits of decreasing it in others. It also raises questions about application uniformity: are there risks in the failure to apply the MCI in uniform amounts across the entire structure?

One of the goals of this thesis was to take a step closer towards evaluating the efficacy of MCIs for corrosion in reinforced concrete heritage. The ability to evaluate efficacy is only one part of this investigation. Equally important is the evaluation of the risk involved in using MCIs. This includes, not only the development of testing methodologies for identifying specific risks, but also an assessment of the probability of those risks, and at what probability conservators should use them.

Another important area for further study exists in the use of MCIs in conjunction with other treatments. MCIs, or any conservation treatment for that matter, are rarely applied as the only treatment in a project. Rather, conservation projects are often a network of treatments. The conservation of the New York Hall of Science’s Great Hall (1964-1956) in Queens, New York has served as a good example of a project in which conservators had to implement a combination of a handful of treatments in one structure (figure 38).169 A project like this one usually entails years of testing (in this case three) in order to arrive at a combination of treatments that are compatible with each other. Projects like these also make it difficult to isolate and evaluate one of the treatments applied to the building. While the New York Hall of Science’s Great Hall offers an example of concrete heritage in which MCIs were employed, the efficacy of the MCI specifically cannot be evaluated, as a number of other treatments were used before and after it in the same locations.170

The theoretical benefits of MCIs for aesthetically valued historic concrete are unquestionable. These benefits are further underscored in projects where critical value lies in

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169 Laura N. Buchner and Raymond M. Pepi, “Restoration of the Cast-in-Place Concrete at the New York Hall of Science,” 2–3.

170 Ibid., 2–3.
preserving the authenticity and appearance of the original concrete. Nonetheless, the viability of MCIs for concrete heritage conservation depends on better monitoring and testing methods designed specifically for the treatment’s evaluation, and on further study of the treatment’s risks. These studies will need to focus on historic concrete and the specific issues it presents in relation to corrosion and treatment if they are to be used as empirical evidence in the architectural conservation field.
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### TABLES

Table 1. Commercial surface-applied MCIs on the market as of 2010.

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<tr>
<th>SUPPLIER</th>
<th>NAME OF PRODUCT</th>
<th>CHEMICAL INGREDIENTS DISCLOSED IN MSDS</th>
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Data adapted from Roar Myrdal, 2010
Table 2. Commercial mixed-in MCIs on the market as of 2010.

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<td>Calcium nitrate</td>
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</tr>
<tr>
<td>AXIM</td>
<td>CATEXOL CN-CI</td>
<td>Calcium nitrate</td>
<td>30-40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcium nitrate</td>
<td>&lt;5</td>
</tr>
<tr>
<td>CORTEC</td>
<td>MCI-2005 NS</td>
<td>Disodium metasilicate</td>
<td>10-25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>proprietary ammonia derivate</td>
<td>2.5-10</td>
</tr>
</tbody>
</table>

Source: Data adapted from Roar Myrdal, 2010 with additional information from “MCI-2005 NS SDS (USA),” Cortec Corporation, 2015
FIGURES

Figure 1. The Pantheon, Rome, Italy, 118-125 A.D.

Figure 2. Notre-Dame du Raincy, Le Raincy, France, Auguste Perrett, 1922.

Source: Martin Charles.
Figure 3. TWA Flight Center, Queens, New York, Eero Saarinen, 1962.

Source: Ezra Stoller.
Figure 5. The main cell house at Alcatraz Island, San Francisco Bay, 1912.

Source: Daniel Ramirez.
Figure 6. Alte Pinakothek, Munich, Germany, 1836, restored in 1957.

Source: Gregory Tinus.
Figure 7. Basic assembly of sacrificial anode system in concrete.

Source. John P. Broomfield.
Figure 8. Basic assembly of impressed cathodic protection (ICCP) system.

Source: John P. Broomfield.
Figure 9. Basic diagram of Electrochemical realkalization.

Source: John P. Broomfield.
Figure 10. San Agustin Church, San Juan, Puerto Rico, 1910s, restored 2008.

Source: Enciclopedia de Puerto Rico.
Figure 11. Schematic showing basics of the half-cell potential measurement technique.

Figure 12. Residue from MCI-2020 left out to evaporate out for 4 days.

Source: Author, 2018.
Figure 13. The cutting of cored samples for QAC test.

Figure 14. Jars passed out by Cortec representatives at a trade show.

Figure 15. 48 hours showed no change in color from corrosion products in early iterations of the jar test.

Figure 16. Rust formed on the upper rim of the glass jar and the inner rim of the lids.

Figure 17. No change in color from corrosion after increase in NaCl concentration.

Figure 18. Set up of jars using electrodes.

Figure 19. Change in color produced after 24 hours.

Figure 20. MCI visibly attracted to the anode.

Source: Author, 2018.
Figure 21. First full run of cell test in Columbia's laboratory.

Source: Author, 2018.
Figure 22. Change in color of solutions from corrosion after 24 hours.

Source: Author, 2018.
Figure 23. Data from first full run of test in Columbia’s laboratory.

Source: Author, 2018.
Figure 24. Second full run of cell test assembled in EChem’s Laboratory.

Source: Author, 2018.
Figure 25. Cells assembled with plastic bags to reduce evaporation.

Source: Author, 2018.
Figure 26. Test run sample.

Source: Author, 2018.
Figure 27. Adding MCI.

Figure 28. Data collected from all four samples in EChem’s laboratory.

Source: Author, 2018
Figure 29. Sample 1.

Source: Author, 2018.
Figure 30. Sample 2.

Source: Author, 2018.
Figure 31. Sample 3.

Source: Author, 2018.
Figure 32. Sample 4.

Source: Author, 2018.
Figure 33. Sample 5.

Source: Author, 2018.
Figure 34. Sample 6.

Source: Author, 2018.
Figure 35. Sample 7.

Source: Author, 2018.
Figure 36. Sample 8.

Source: Author, 2018.
Figure 37. Data collected from Sample 6, 7 and 8.

Source: Author, 2018.
Figure 38. New York Hall of Science’s Great Hall, Queens, New York, Todd Schliemann, 1964.

Source: Ezra Stoller.