

7-7-2014

Feasibility of Application of Cathodic Prevention to Cracked Reinforced Concrete in Marine Service

Kevin Williams

University of South Florida, kmwilli6@mail.usf.edu

Follow this and additional works at: <https://scholarcommons.usf.edu/etd>

 Part of the [Engineering Commons](#)

Scholar Commons Citation

Williams, Kevin, "Feasibility of Application of Cathodic Prevention to Cracked Reinforced Concrete in Marine Service" (2014).
Graduate Theses and Dissertations.
<https://scholarcommons.usf.edu/etd/5333>

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.

Feasibility of Application of Cathodic Prevention to Cracked
Reinforced Concrete in Marine Service

by

Kevin Williams

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering
with a concentration in Structures
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Major Professor: Alberto Sagüés, Ph.D.
Rajan Sen, Ph.D.
Margareth Dugarte, Ph.D.

Date of Approval:
July 7, 2014

Keywords: Corrosion, Steel, Protection, Chloride

Copyright © 2014, Kevin Williams

DEDICATION

...to my parents, Chris and Brad, who have always supported me since day one.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Alberto Sagüés, whose knowledge, guidance, support and patience enabled me to complete this thesis. I would also like to thank my committee member Dr. Margareth Dugarte. In addition, I am grateful for my committee member Dr. Sen, whose wisdom encouraged me to pursue a career in the field of repair and rehabilitation of structures.

A special thanks to Sandra Hoffman and Dr. Ezeddin Busba, whose assistance and knowledge with this investigation was very much appreciated.

I also wish to show my appreciation to all my colleagues from the Corrosion Laboratory at USF, Leo Emmenegger, Andrea Sánchez, Enrique Paz, Joe Fernandez, Mike Walsh, Joseph Scott, and William Ruth, who have all helped me in various ways to complete this thesis.

Finally, I would like to thank Tatiana Carvajalino, who has always managed to put a smile on my face and encourage me when I needed it most.

The author gratefully acknowledges the support provided by the Florida Department of Transportation for this project. The opinions, findings, and conclusions presented here are those of the author and not necessarily those of the State of Florida Department of Transportation.

TABLE OF CONTENTS

LIST OF TABLES.....	iii
LIST OF FIGURES.....	iv
ABSTRACT.....	vi
CHAPTER 1: INTRODUCTION.....	1
1.1 The Basics of Corrosion of Steel in Concrete.....	1
1.2 Potential-pH Relationship.....	3
1.3 Steel Passive Layer.....	4
1.4 Chloride Ion Induced Corrosion.....	5
1.5 Reinforced Concrete Corrosion Damage.....	8
1.6 Cathodic Protection of Steel in Concrete.....	9
1.7 Cathodic Prevention of Steel in Concrete.....	10
1.8 Concrete Cracking.....	15
CHAPTER 2: OBJECTIVES AND METHODOLOGY.....	18
2.1 Objectives.....	18
2.2 Approach.....	18
2.3 Methodology.....	20
2.3.1 Experimental Setup.....	20
2.3.2 Monitoring of OC Specimens.....	27
2.3.3 Monitoring of Polarized Specimens.....	30
2.3.4 Determination of Feasibility of CPrev.....	31
2.3.5 Cathodic Polarization after Activation.....	31
CHAPTER 3: RESULTS AND DISCUSSION.....	33
3.1 Unpolarized (OC) Control Specimens.....	33
3.1.1 Potential Measurements.....	33
3.1.2 Macrocell Current Measurements.....	34
3.1.3 Discussion of Results from Unpolarized Specimens.....	34
3.2 Polarized Specimens.....	35
3.2.1 Potential Measurements.....	35
3.2.2 Current Measurements.....	36
3.2.3 Discussion of Results from Polarized Specimens.....	40
3.2.4 Cathodic Protection Depolarization Results.....	43
3.2.5 Discussion of Results from Depolarization Test.....	48
CHAPTER 4: CONCLUSIONS.....	50

REFERENCES.....	51
APPENDICES.....	53
Appendix A Permission for Use of Figure.....	54

LIST OF TABLES

Table 1 Exposure Conditions Indicating Crack Width and Potential for each Specimen.....	24
Table 2 Likelihood of Active Corrosion per Measured Potential	29

LIST OF FIGURES

Figure 1 E-log $ i $ Graph	3
Figure 2 Steel Pourbaix Diagram of Iron in an Aqueous Solution	4
Figure 3 E-log $ i $ Graph of Passive Steel	5
Figure 4 Potential vs Chloride Content Effect on E_{pitt}	11
Figure 5 C_{Prev} Effect on Anodic and Cathodic Current	13
Figure 6 Wood Mold and Steel Reinforcement Configuration	21
Figure 7 General Specimen Arrangement.....	21
Figure 8 Three Point Bending Test Configuration	22
Figure 9 Specimen Connection to Potentiostat	26
Figure 10 Typical Specimen Setup	26
Figure 11 Testing Arrangement.....	27
Figure 12 Half Cell Potential Reading for Specimen	28
Figure 13 Average Potential for the OC Specimens.....	28
Figure 14 Average Macrocell Current Density for OC Specimens	34
Figure 15 Cumulative Distribution of Instant-off Potentials.....	35
Figure 16 Cathodic Current Demand for -330 mV Specimens	37
Figure 17 Timeline for Specimens Initially Polarized to -330 mV	38
Figure 18 Cathodic Current Demand for -430 mV Specimens	38
Figure 19 Timeline for Specimens Initially Polarized to -430 mV	39
Figure 20 Cathodic Current Demand for -540 mV Specimens	39

Figure 21 Average Current Density for each Potential Level Before Activation.....	40
Figure 22 Detailed Summary of each Specimen's Time to Activation	43
Figure 23 1 Hour Depolarization Test.....	45
Figure 24 4 Hour Depolarization Test.....	45
Figure 25 24 Hour Depolarization Test.....	46
Figure 26 Current Demand for Activated Specimens Switched from -330 mV to - 430 mV.....	46
Figure 27 Current Demand for Activated Specimens Switched from -330 mV to - 540 mV.....	47
Figure 28 Current Demand for Activated Specimens Switched from -430 mV to - 540 mV.....	47
Figure 29 Average Current Density for each Potential Level After Activation.....	48

ABSTRACT

Corrosion can take place as chloride ions accumulate above a critical concentration (C_T) at the surface of a reinforcing bar inside concrete in marine service. The initiation of corrosion can be delayed by polarizing the steel cathodically, which is known to increase the value of C_T . That effect is the basis of the cathodic prevention (CPrev) method to control corrosion of reinforcing steel in concrete. However, concrete cracks are a common occurrence and at cracks, the buildup of chloride ions is accelerated to the extent that CPrev may be less effective. The findings from an ongoing investigation to determine the effectiveness of cathodic prevention on cracked concrete exposed to a marine environment are presented. Experiments were conducted on reinforced concrete blocks with controlled-width cracks placed along the length of a central reinforcing steel bar. A ponding area on top of each specimen allowed for cyclic exposure to a 5% NaCl solution to imitate a marine environment. Crack widths ranging from 0.01 inch to 0.04 inch and polarization levels ranging from -330 mV to -540 mV were used. The onset of corrosion as a function of time of exposure was determined by measurements of the cathodic current demand needed to reach each target polarization level. The ranking of time to onset of corrosion was used as an indicator to determine how much cathodic prevention is necessary to effectively extend the life of cracked concrete. Results to date suggest that a minimum cathodic polarization level in the range of -540 mV would be needed.

CHAPTER 1: INTRODUCTION

1.1 The Basics of Corrosion of Steel in Concrete

Steel is susceptible to corrosion when exposed to the atmosphere. In fact, most pure metals, barring a few exceptionally noble metals like gold and platinum, will corrode in atmospheric conditions. These metals, including iron (main element in steel) are found in nature as ores, combined with sulfur and oxygen and tend to return to that natural state as ores [1]. In engineering however, metals are used in their pure form and corrosion frequently causes the need for repair and replacement; and it is not cheap to account for corrosion damage. A study in 2002 by NACE International found that the direct cost of corrosion per year was approximately 3.1% of the Gross Domestic Product for the United States, translating to \$276 billion. If indirect costs like loss of productivity, delays, failures, and cost of corrosion goods and services are included in the previous figure, the total cost of corrosion could double to \$552 billion [2]. Proper techniques to mitigate the costly effects of corrosion are of mounting importance.

Corrosion is an electrochemical process requiring four components: anodic reaction, cathodic reaction, electrolyte, and electronic path. For the case of steel in concrete, the anodic reaction is the dissolution of iron atoms (Fe) from the bulk of the steel reinforcement into iron ions (Fe^{2+}), losing two electrons in the process. The iron ions are released into the concrete pore water. If the electrons left behind by the anodic reaction are allowed to build up, the corrosion process will cease. The electrons are consumed, however, by the cathodic reaction. The cathodic reaction occurs when

oxygen gas and water gather at the surface of the reinforcement and combine with the electrons left behind from the anodic reaction [1]. The cathodic reaction produces hydroxide ions (OH), which can later combine with Fe^{2+} to form rust, one of the most common byproducts associated with corrosion. The pore water provides the electrolyte and the steel itself is the electronic path.

Iron in equilibrium in a solution containing its own ions develops a characteristic electrical potential (E) associated with the oxidation-reduction process of the system. In fact all metals, when they are in equilibrium with their own ions in a solution under standard conditions will have a potential value that can be represented in a table known as the electrochemical series of metals [3]. This table generally uses the hydrogen/hydrogen ion reaction as a reference point, and metals with more negative potentials may corrode first when they are paired with a metal that has a more positive potential. At any given potential the anodic reaction $Fe \rightarrow Fe^{2+} + 2e$ occurs at a rate that tends to be greater for more positive values of potential. The rate q of the reaction (mols/unit area-unit time) can also be represented by a current density $i = q n F$, where n is the number of electrons associated with the reaction (2 in this case) and F is Faraday's constant (~96,500 coul/mol of electrons). The cathodic reaction can be represented likewise. By convention, anodic current densities are assigned positive values, while cathodic current densities are assigned negative values.

When two systems are combined (anodic reaction of a metal and a cathodic reaction), it is possible to represent the corrosion process with an E-log $|i|$ graph. If steel were to be submerged in an electrolyte and oxygen molecules able to reach the surface of the steel, its E-log $|i|$ graph for the system would resemble Figure 1.

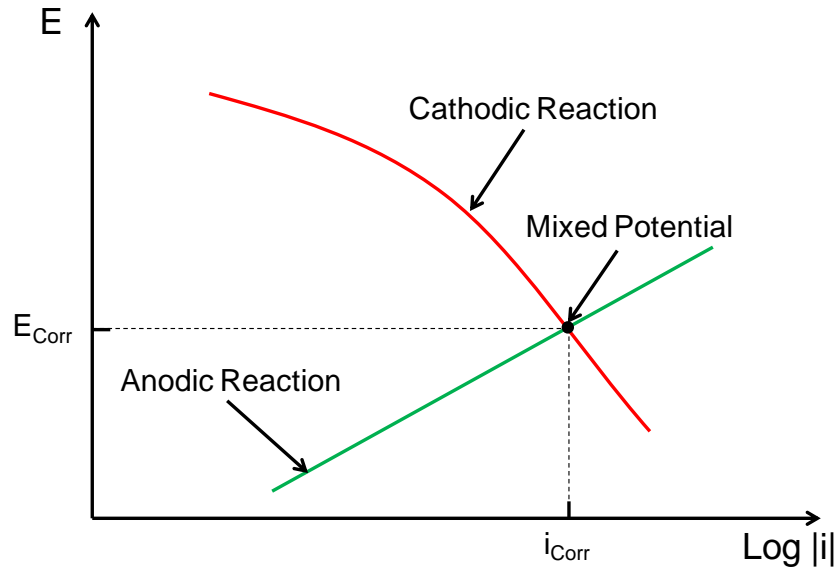


Figure 1 E-log |i| Graph

The potential for the intersection of the anodic and cathodic reaction is called the mixed potential, or corrosion potential and has a corresponding corrosion rate, i_{corr} . This is indicative of steel being exposed to the atmosphere; however, a wide range of conditions are possible depending on factors such as E and pH [3].

In this thesis potentials will be given in the Saturated Calomel Electrode (SCE) scale unless otherwise indicated.

1.2 Potential-pH Relationship

It is desirable to summarize the relationship between E and pH in graphical form. At various combinations of E and pH, metal can corrode, be immune to corrosion, or passivate. These E-pH graphs, commonly referred to as Pourbaix diagrams, consider common reactions that can take place for a certain metal. A simplified Pourbaix diagram for iron in an aqueous solution is shown below in Figure 2.

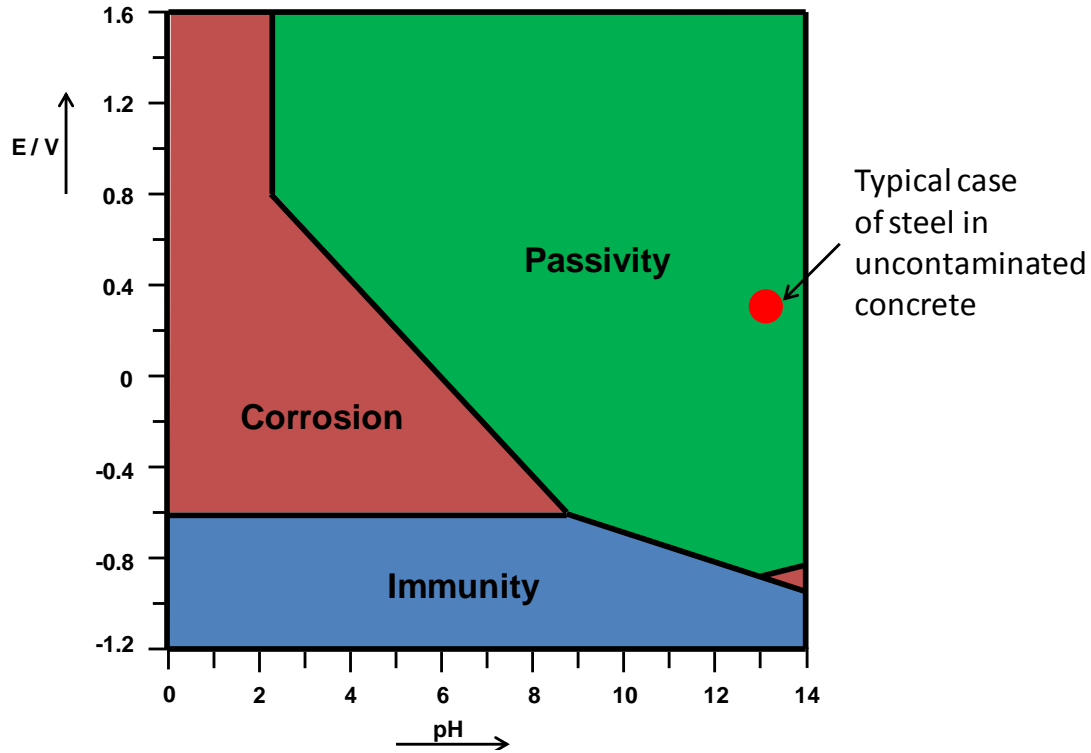


Figure 2 Steel Pourbaix Diagram of Iron in an Aqueous Solution (E in the Standard Hydrogen Electrode (SHE) scale). Note: potential vs SCE = potential vs SHE -241 mV.

Steel is immune to corrosion at a low enough potential for all pH values. Above the potential where steel is immune, corrosion may take place, though steel can develop a passive layer at high pH values. A passive layer is a very thin film of metal oxide which forms on the surface of a metal and slows corrosion to a near standstill. Steel can form a passive layer at potentials in the usual range of interest, but only in a high pH environment.

1.3 Steel Passive Layer

Conveniently, concrete has a pH between 13 and 14 due to the alkaline solution in the hydrated cement paste [4]. This high pH environment is ideal for the formation of a passive film on steel in reinforcing steel. This passive layer consists of an iron oxide

which remains stable as long as the steel is embedded in concrete. In this condition, the corrosion rate of the reinforcing steel is negligible ($\ll 1 \mu\text{m/y}$) [5], and the E-log $|i|$ graph changes to account for the passive steel, as shown in Figure 3.

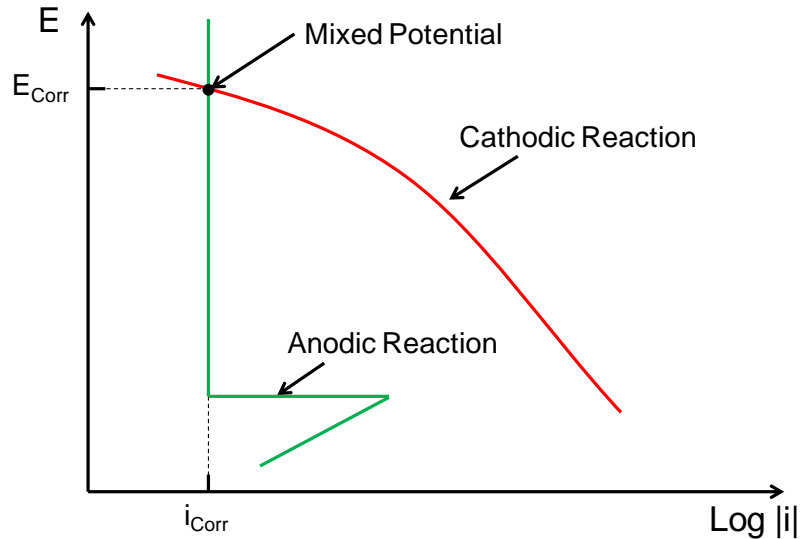


Figure 3 E-log $|i|$ Graph of Passive Steel

When examining Figure 3, E_{Corr} is an appreciably higher value while i_{Corr} is much lower when compared to those observed in Figure 1. The high pH environment allows the steel to remain passive under the right conditions. Unfortunately, the passivity is not permanent and the passive layer is subject to being broken down by factors like concrete carbonation and chloride ions.

1.4 Chloride Ion Induced Corrosion

A dominant factor which oftentimes disrupts the passive film on reinforcing steel is the presence of chloride ions. The substructures of bridges in marine service accumulate chloride ions from the splashing of seawater. The chloride ions accumulate

at the surface of the concrete due to the constant seawater spray. When the water evaporates, chloride containing salt is left behind, and as this process continues, the content of chlorides at the concrete surface increases. Chloride ions transport through the porous concrete to the reinforcing steel.

One property of concrete that has a significant influence on its corrosion resistance is permeability [6]. Permeability is the property of concrete that allows ingress of gas, liquid, and dissolved ions through the pore network [7]. High quality concrete is known to have a low permeability, i.e. the chloride ions take longer to reach the steel surface, while poor quality concrete allows for the ions to ingress much more rapidly. The mechanism which allows for the chloride ions to travel from the surface toward the reinforcement of a structure is usually a combination of capillary suction and diffusion [4]. In sound concrete, the pore network is very tortuous and chloride ions have no direct path to the reinforcement. They must diffuse through the narrow, twisting capillary pores and when they finally reach the steel surface, the chloride ions have travelled a much greater distance than the actual rebar depth distance, and also through a narrower effective cross section as well as in the presence of chloride traps that bound some of the chloride in the solid concrete matrix. With this considered, and if high quality concrete is used, it could take many years for chloride ions to reach the steel surface in a significant quantity.

Eventually, enough chloride ions build up at the steel surface to cause a localized breakdown in the passive layer. The amount of chlorides needed to breakdown the passive layer is called the critical chloride threshold (C_T). C_T depends on many variables like concrete quality, availability of oxygen, temperature, and even the

potential of the steel while it is still passive [8]. C_T is generally in the range of 0.4 to 1 percent of the cement weight used in the concrete [9]. Once the passive layer breaks down, corrosion, specifically pitting corrosion, can initiate.

Pitting corrosion is particularly associated with the presence chloride ions [10]. It often occurs in metals that have a passive layer, including steel used in reinforced concrete. The passive layer will experience a local break down due to chloride ions exceeding the C_T , which lowers the pitting potential (E_{pitt}). Above E_{pitt} , pitting corrosion can initiate and propagate. Below E_{pitt} , pitting corrosion can initiate, but will not propagate. Sufficiently low potential will not allow initiation or propagation of pitting corrosion. See Figure 4.

Locations on the steel surface where the passive layer has been destroyed generally act as an anode, while locations where the passive film will remain act as a cathode [9] [10]. The pit occupies a very small amount of the steel's surface area, while the rest of the steel's surface area remains in the passive condition until another localized pit forms [10]. This active-passive element creates a very high potential difference usually in the range of 0.5 to 1 Volt between anodes and cathodes [3]. This large potential difference may cause local accelerated corrosion of the reinforcement, producing a relatively large amount of corrosion product despite the very small pit.

E_{pitt} is not a fixed value, gradually decreasing over time. The reason for this decrease depends somewhat on temperature, pH, and cement type, but primarily on chloride content. Initially, E_{pitt} is much greater than the potential of the steel (-100 mV when passive). As long as the steel's potential is less than E_{pitt} , the passive layer will remain intact. Once C_T is reached, E_{pitt} becomes less than the potential of the steel and

the passive layer experiences a localized breakdown. If corrosion of steel in concrete is to be mitigated, the relationship between steel potential and E_{pitt} must be considered [9].

1.5 Reinforced Concrete Corrosion Damage

The corrosion of steel in concrete, especially in marine service, can have an adverse effect on the service life of a structure. The area most likely to be damaged by corrosion is in the emerged part of the structure up to about six feet high in calm seas and greater in rougher seas. Though submerged parts of bridges are constantly in a chloride environment, the lack of oxygen is such that corrosion is less of a concern in these areas [11]. Oftentimes, chunks of concrete, called spalls, break off from the structure, where the expansive corrosion products have exerted enough tensile stress [4]. These spalls expose the rebar to the outside environment. As a result, the exposed steel no longer experiences the high pH of the concrete pore water and thus is subject to accelerated corrosion. Spalls must be repaired quickly as to maintain structural integrity, but repairing spalls is very costly. In addition, most repairs involving corrosion of reinforced concrete typically do not last more than five years due to what is known as the halo effect [12].

Spalls must be patched with fresh, chloride free, high pH material that is suitable for the formation of steel's passive layer. Given that concrete surrounding the repair is still contaminated with chloride ions, the potential of the steel in that region is at a lower potential value than that of the steel in the repaired area. Corrosion related damage occurs quickly due to the large difference in potential between repaired and contaminated regions. The term halo effect was coined due to the ring of corrosion that is observed around the perimeter of the repair. In addition, a large cathode in the

repaired concrete in contact with a small anode in the contaminated concrete results in accelerated corrosion. It is desirable to increase the lifetime of a repair by employing additional repair techniques, like cathodic protection [13].

1.6 Cathodic Protection of Steel in Concrete

One such technique often implemented to attain a longer lasting repair, or mitigate reinforcement corrosion, is to install a cathodic protection (CP) system. CP for concrete was applied in significant amounts by about 1973, mainly for bridge deck applications [9]. It works by dropping the potential of the steel to a potential where corrosion cannot propagate, or where the corrosion rate is minimal. CP is usually considered to be the only technique that can truly stop corrosion in chloride contaminated concrete [13]. The negative shift in potential is the main beneficial effect, which reduces the driving force for the anodic reaction and increases the resistance to the anodic process [9].

The desired potential drop is most effectively achieved by using an outside voltage source to deliver current to the reinforcement, called a potentiostat. A voltage source is connected to permanent anodes installed inside or at the surface of the concrete. The current runs through the permanent anodes, which are made from an inactive metal, such as titanium with activated mixed metal oxide. Current is delivered as evenly as possible to the reinforcement and protection is achieved. Steel is considered to be protected if a decay of 100 mV is observed after the system is disconnected for a period of 4 to 24 hours [9].

1.7 Cathodic Prevention of Steel in Concrete

Though CP is a viable protection method, it is costly and difficult to install, especially in a marine environment. Instead of repairing concrete damaged by reinforcement corrosion, it may be possible to prevent damage altogether. A relatively new technology developed in the early 1990s by Pedferri and collaborators offers a promising alternative to costly corrosion repairs. Cathodic prevention (CPrev) is the application of cathodic currents while the steel is still in its passive condition, and has the ability to be installed during construction. By cathodically polarizing the steel while it is still passive, it is possible to delay the initiation of corrosion, improve durability of the concrete and reduce maintenance costs [14].

CPrev aims to increase the C_T value and keep the steel in a passive condition, even when chloride levels in the concrete reach well above the C_T for steel that has not utilized CPrev. Since CPrev is applied while the steel is still passive, the steel potential remains less than E_{pitt} even as E_{pitt} drops with increasing chloride levels [13]. CPrev maintains the potential of the steel in this regime, where corrosion can propagate, but cannot initiate. Steel that has already experienced corrosion initiation and had CP applied will tend to corrode in this regime. Typical cathodic current density needed to achieve CPrev conditions is reported to be between 0.5-2 mA/m² for laboratory and field tests for atmospherically exposed concrete. Under more aggressive environments, a current density of 2-5 mA/m² is required [14]. To achieve CP conditions, much higher current densities are required: 15 mA/m² to achieve the 100 mV decay criterion, and 20 mA/m² to achieve repassivation [9].

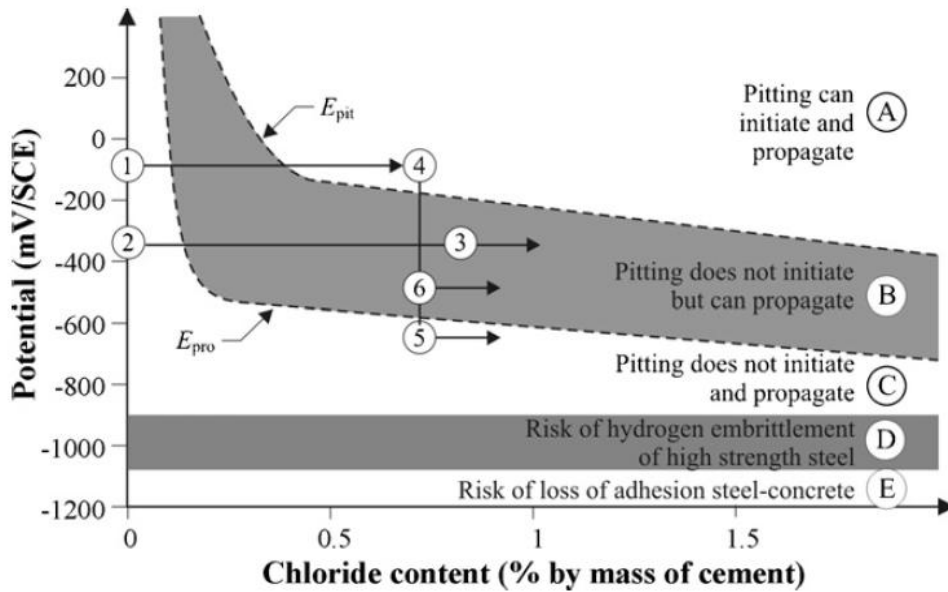


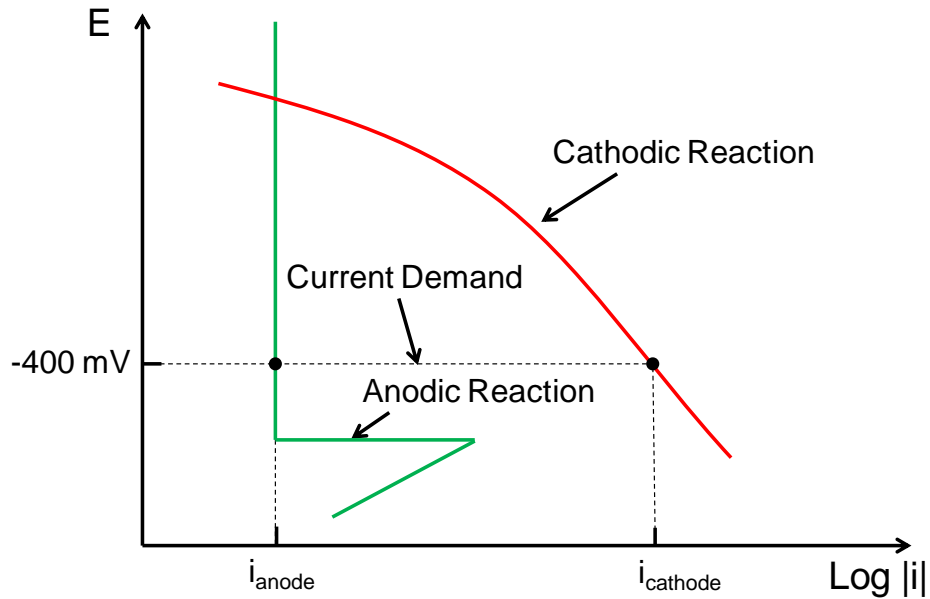
Figure 4 Potential vs Chloride Content Effect on E_{pitt} [13]

In a normal situation where steel is simply embedded in concrete without CPrev, corrosion in an aggressive marine environment is almost unavoidable. This situation is shown by the path 1-4 in Figure 4 and demonstrates how E_{pitt} becomes less than the potential of the steel over time and corrosion is initiated. In order to mitigate corrosion in this situation, the potential of the steel must be lowered enough so corrosion can no longer propagate, or the corrosion rate is minimal. These two CP situations are represented by paths 4-5 and 4-6, respectively.

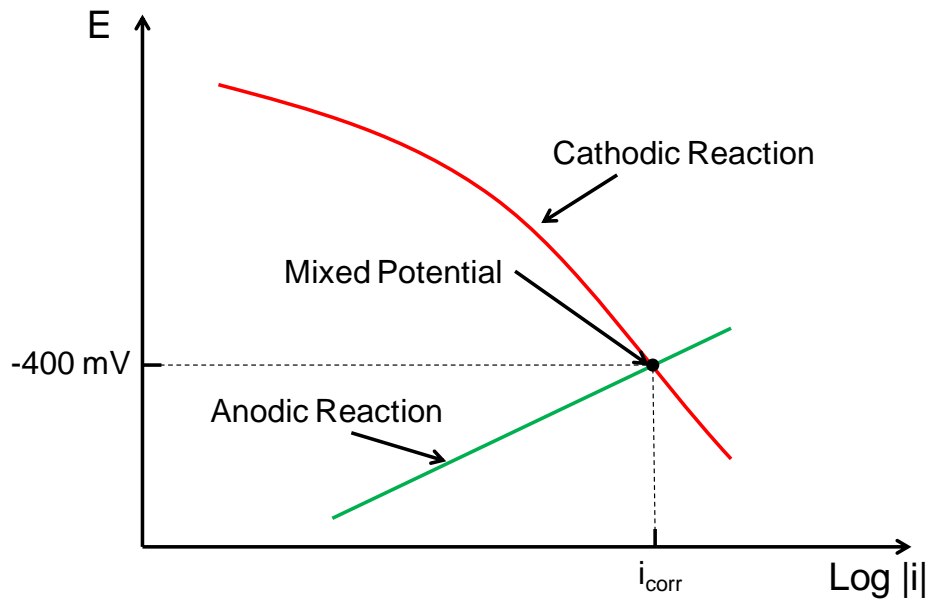
If steel is embedded in concrete with the application of CPrev, path 1-2-3 applies. It is evident that a marked increase in time to corrosion initiation is achieved by negatively polarizing the passive steel so that pitting corrosion cannot initiate. This is achieved by the initial cathodic polarization, which puts the steel in zone B, where corrosion can propagate, but not initiate. The level of polarization used in CPrev determines how beneficial the effects are: a slight polarization may not be beneficial,

while a larger cathodic polarization can have great benefits. It has been found by Sánchez et al [8] that polarizing to a level of -600 mV SCE can increase the C_T by as much as three times compared to the C_T of non-polarized specimens in the same condition.

CPrev is most commonly applied to the reinforcing steel of a concrete structure by using a potentiostat to deliver electronic current into the steel through permanent anodes. In many laboratory tests, it is desirable to maintain a fixed level of potential for CPrev by application of the necessary amount of cathodic current. Current demanded by steel in CPrev is almost entirely equal to that needed to support the cathodic reaction, since the current corresponding to the anodic reaction on passive steel is negligible in comparison. As the passive film begins to break down, the anodic reaction begins to release electrons into the metal in considerable amounts, thus decreasing the demand for cathodic current from the external circuit. When the current demand eventually becomes zero, the point has been reached where the open circuit potential of the system is equal to the fixed potential level used for CPrev. This condition is a good indication that the passive film has experienced a local breakdown and pitting corrosion has initiated. If the potential of the system were to become even more negative than in that condition, as is often the case, then the potentiostat would begin to deliver a net anodic current, which would expedite corrosion instead of mitigating it. In Figure 5 these different scenarios are illustrated for a hypothetical case where CPrev was being applied to achieve a fixed potential of -400 mV SCE. It is noted that this situation would not develop if the CPrev system were operated instead under galvanostatic control.



(a)



(b)

Figure 5 CP_{prev} Effect on Anodic and Cathodic Current. Figure 5a represents CP_{prev} application (potentiostatic control) on passive steel. Figure 5b represents the condition of zero current demand that could be reached if steel became active . Figure 5c represents a later stage where the anodic reaction would be actually accelerated if applied potential were kept at the initial level.

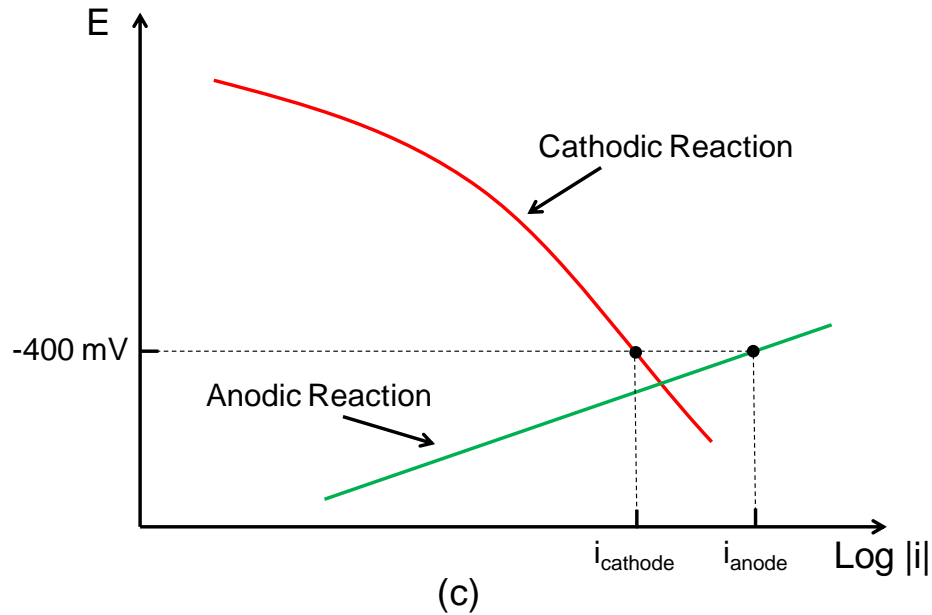


Figure 5 continued.

Though the application of CPrev may be a means for controlling steel corrosion, it may induce other undesired consequences that can affect concrete and steel-concrete bond, and may cause hydrogen embrittlement of high strength steel. The application of CPrev can excessively increase pH of the pore solution near the reinforcement and thus enhance alkali-silica reaction in concretes which use aggregates susceptible to this phenomenon. Bond between the concrete and reinforcement could be compromised if very negative potentials in the order of -1.1 V (SCE) or more negative are used. Hydrogen embrittlement can also occur at potentials more negative than -950 mV (SCE) [9]. The very negative potentials induce hydrogen formation, which could cause sudden brittle failure in some cases. It is noted that only high strength steel is susceptible to hydrogen embrittlement. Low strength carbon steel, used in many reinforced concrete structures, is generally considered not to be at risk of hydrogen embrittlement. However, concrete structures which use prestressed or post-tensioned

concrete contain high strength steels, and therefore may be subject to hydrogen embrittlement at very negative potential levels [15].

1.8 Concrete Cracking

Unfortunately, cracks prior to any corrosion damage often occur in concrete, and are of particular interest to corrosion when formed in the substructure of bridges. In field observations by Lau [16], the Sunshine Skyway Bridge (SSK) and Howard Frankland Bridge (HFB) were found to have crack with widths as large as 0.6 mm (0.024 in) and 1 mm (0.04 in), respectively. The cracks in SSK, along with four additional bridges surveyed, were concluded to be preexisting cracks due to the lack of corrosion observed. In HFB, the large-width cracks were observed and documented in past bridge inspections. The cracks were confirmed to extend to a depth that exceeded the reinforcing steel cover. Cracks in HFB were likely a result of differential temperature conditions during curing of the concrete [16]. These cracks in concrete structures can cause major localized durability problems. For structures in marine environment, these preexisting cracks can cause rapid chloride ion transport to the reinforcement. When compared with sound concrete, cracked concrete had a significantly higher local chloride concentration at the depth of the reinforcement [16]. Chloride concentrations of about 2.4 kg/m^3 were found at the steel/concrete interface in cracked concrete locations in SSK and HFB, compared to about 0.24 kg/m^3 or less at the steel/concrete interface in sound concrete locations. It has been found that concrete quality plays a larger role in corrosion of the reinforcement than does crack width [17]. Paradoxically, high performance concrete is more susceptible to *relative* acceleration of corrosion due to

cracking when compared with low quality concrete. In high quality concrete, the chloride concentration at the rebar depth at cracked areas is observed to be comparatively very high compared with chloride levels at the rebar depth at sound portions of the structure. Corrosion in poor quality concrete is relatively less affected by cracks because chloride concentrations at the reinforcement surface and at sound portions of the structure (where chloride penetration is relatively fast anyway) are comparable to chloride concentrations at the reinforcement at cracked portions [16]. In other ways, corrosion development is relatively fast everywhere. In contrast, early corrosion in high performance concretes is likely to develop only at crack locations. For this reason, performance in cracked concrete is becoming a dominant concern in modern design with high performance concrete [16] [17].

In view of the above considerations, it would be desirable to apply a corrosion control method like CPrev to concrete with preexisting cracks. However, up to this point in time, laboratory studies investigating the efficacy of CPrev seem to have been limited to only sound concrete; the author is unaware of an investigation on the efficacy of CPrev for reinforcing steel embedded in cracked concrete.

It is thus important to establish whether it is feasible to apply CPrev to rebar in cracked concrete to extend service life, as well as to determine what level of cathodic polarization is needed to make a CPrev system viable for cracked concrete in marine service. In case CPrev provided insufficient corrosion control, it could be advantageous to convert the CPrev system already in place to operate in a conventional CP regime to further extend service life. The issues mentioned above merit experimental investigation

in order to establish if they are achievable and work toward that end is described in the following chapters.

CHAPTER 2: OBJECTIVES AND METHODOLOGY

2.1 Objectives

This research was aimed at investigating the efficacy of utilizing a cathodic prevention system in cracked concrete in marine service, and the objectives are as follows:

1. Determine the feasibility of applying successful cathodic prevention to cracked concrete in a marine environment.
2. Establish cathodic polarization levels required for a cathodic prevention system to be effective in cracked concrete in a marine environment.
3. Investigate the effectiveness of cathodically polarizing specimens into a conventional CP regime if the extent of CPrev application was insufficient.

2.2 Approach

The above objectives were addressed by creating an experiment which applied various levels of CPrev to cracked reinforced concrete specimens. Polarized and non-polarized, open circuit (OC) specimens were monitored throughout the duration of the experiment for signs of corrosion activation over a period of >200 days. The absence of activation during that period was considered to be indicative of promising CPrev effectiveness. By applying various levels of CPrev by means of a multiple channel potentiostat, it was possible to determine the required amount of polarization to make

CPrev feasible. For specimens that reached activation during that period, the length of time required to reach activation was considered to be an inverse indicator of the efficacy of CPrev for the exposure conditions of the specimen.

In addition, after specimens experienced corrosion activation, they were put into a conventional CP regime to determine if corrosion could be mitigated by that means. Depolarization tests were then conducted to test for 100 mV decay which is an indication that CP is effectively mitigating corrosion.

30 concrete prisms were created to enable a range of experimental conditions with appropriate reproducibility. Prisms contained three reinforcing steel bars, two activated titanium mesh anodes, and one activated titanium reference electrode embedded. Cracks were induced parallel to the central rebar to simulate the worst case scenario. CPrev was then applied to the reinforcement of 24 concrete prisms at predetermined values of potential representing various levels of CPrev application. The remaining six specimens were used as controls without any applied CPrev, with their potential evolving in the natural open circuit condition. To simulate a severe marine environment exposure, each specimen was exposed to 2 week wet and 2 week dry salt water cycles for ~170 days. After that, all specimens were subjected to a permanent wet condition starting after cycle 6. The wet cycle used a 5% NaCl solution to introduce chlorides to the reinforcing steel.

2.3 Methodology

2.3.1 Experimental Setup

30 wood molds, with interior dimensions of 15.75 in x 14.25 in x 5 in were assembled to cast concrete prisms (Figure 6). Figure 7 shows the general specimen arrangement and dimensions. The prisms consisted of 3 reinforcing steel bars, size #4 (1/2 in nominal diameter) running the length of each specimen. The molds each contained three slots for the reinforcing steel bars. The steel was 18 in long with about 3 in at each end coated with Sikadur® 32 Hi-Mod epoxy so as to protect from any corrosion in the part of the bar where it emerged from the concrete surface. The steel length in contact with concrete was 12 in. The rebar was inserted so that it was centered in the mold as shown in Figure 6.

In addition to the reinforcing steel, two anodes and a reference electrode were placed into each mold prior to pouring concrete. The anodes were 0.5 in wide activated titanium mesh strips made by Siemens. The activated titanium mesh was sufficiently long to enable exterior connections after concrete was poured. A 1.5 in long activated titanium rod was inserted horizontally in the mold and served as a reference electrode [18] and assisted in potential measurements and adjustments when specimens strayed from their desired potential level.

In order to successfully initiate cracks parallel to the direction of the steel reinforcement, a crack initiator was included in the wood mold. The crack initiator was simply a thin strip of wood which protruded a short distance from the bottom of the wood mold and is shown in Figure 7. Thus, upon removal from the mold, each prism contained a small notch that promoted the formation of a longitudinal crack. Two ¼ in

diameter fiberglass reinforcing bars (non conducting and hence not interfering with the flow of applied current) were placed as shown in Figure 6 to offer some crosswise reinforcement and preventing splitting of the specimen during crack formation.



Figure 6 Wood Mold and Steel Reinforcement Configuration

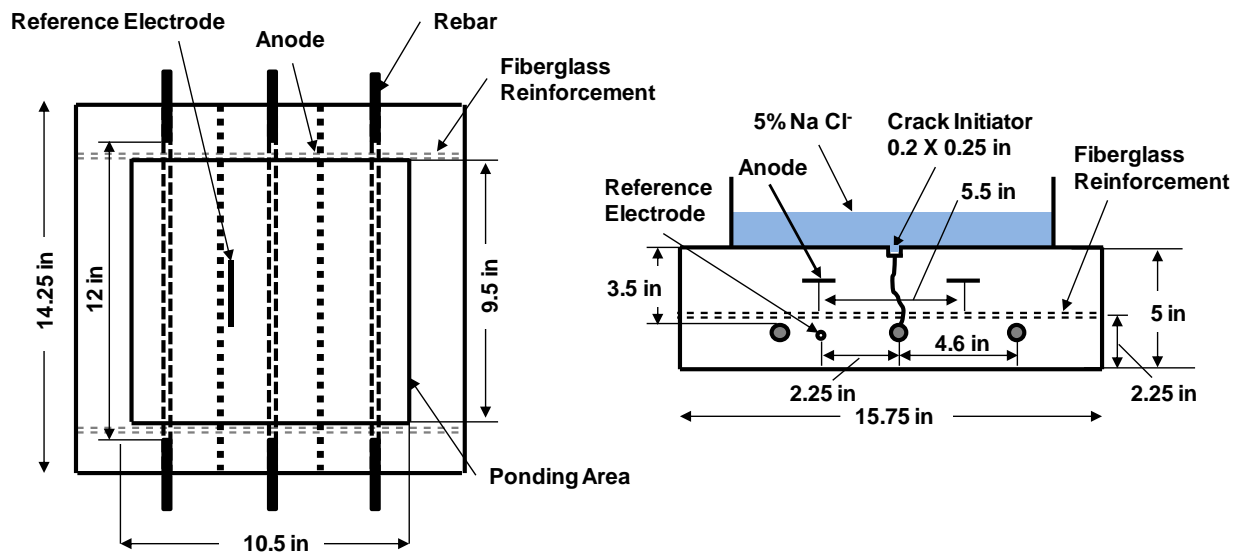


Figure 7 General Specimen Arrangement

After all 30 molds were prepared, concrete was poured. The concrete formulation used was a FDOT class IV concrete mix, with 590 pcy ordinary Portland cement with 20% fly ash replacement, $w/c = 0.39$ and limestone coarse aggregate with #67 gradation. The concrete was left to wet cure for 28 days. After curing, the concrete prisms were cracked. It was predetermined that crack widths of 0.01 in, 0.02 in and 0.04 in would be used to represent a typical range of cracks that may be found in a structure in service. Cracks were created using a three point bending procedure. The specimen was arranged in the three point bending procedure so that the surface containing the crack initiator experienced a tensile force large enough to form a crack. Once the crack formed, stainless steel shims sized to the desired crack widths were inserted in the crack opening to a depth of $\frac{1}{2}$ in before the tensile force was relieved and the fiberglass reinforcement restoring force would act. The shims kept the crack open to the desired surface width after the three point bending procedure was completed, and were left in place for the duration of the investigation. The three point bending procedure configuration is shown in Figure 8.



Figure 8 Three Point Bending Test Configuration

After cracking and shimming, a ponding area was established on the cracked concrete surface. The ponding, as shown in Figure 7, was created to simulate splash-evaporation conditions found in marine environments by containing a 5% NaCl saltwater solution during the wet cycle. Each cycle consisted of 2 weeks 5% NaCl solution exposure followed by 2 weeks dry. After cycle 6, specimens were permanently exposed to 5% NaCl solution to create a severe long term regime. In order to avoid leaks due to cracks, epoxy (same as that used to cover the steel bar ends) was used to completely cover any areas susceptible to leaking. After epoxy was sufficiently applied, each specimen was leak tested. If leaks were observed, additional epoxy was applied until there were no observable leaks.

Per the plan described in the Approach section, six specimens were evaluated as controls at the open circuit (OC) potential, with no connection to the potentiostat. The remaining 24 specimens were polarized using a multiple potentiostat to obtain instant-off potentials (with the procedure described subsequently) of -330 (9 specimens), -430 (9 specimens) and -540 mV SCE (6 specimens). The behavior at each potential was evaluated with specimens having each of the three chosen crack widths. Table 1 shows the crack width and instant-off potential assigned to each specimen, and the degree of replication for each experimental condition.

Table 1 Exposure Conditions Indicating Crack Width and Potential for each Specimen

Crack width (in)	Non-Polarized (Control)	E_1 -330 mV*	E_2 -430 mV*	E_3 -540 mV*
0.01	X (11)	X (2)	X (9)	X (5)
	X (28)	X (13)	X (18)	X (24)
	-	X (23)	X (12)	-
0.02	X (4)	X (3)	X (1)	X (6)
	X (14)	X (15)	X (21)	X (27)
	-	X (25)	X (29)	-
0.04	X (7)	X (16)	X (10)	X (8)
	X (20)	X (17)	X (19)	X (30)
	-	X (26)	X (22)	-

*All Potentials are in the SCE scale. Specimen numbers are in parenthesis.

The three rebar were externally interconnected via a stainless steel wire. This array is shown as W in Figure 9. The wire was attached between stainless steel washers, nuts and screws inserted into tapped ends of each rebar. This rebar assembly is representative of a reinforcement mat in a concrete structure, where tie wires that are used in rebar placement also create rebar connectivity throughout the structure [14]. In order to obtain the desired cathodic polarization, a multiple-channel adjustable potentiostat was built to maintain the correct polarization level supplied to each specimen. Current runs through the anode and is approximately evenly distributed to the steel reinforcement, aided by the half-way placement of the anodes.

The two anodes are coupled via a stainless steel wire. This arrangement is labeled as C in Figure 9. The anode was connected to the positive end of the potentiostat, which delivered cathodic current to the rebar assembly. Anodes were

equipped with a 1N914 or comparable silicon switching diode. The diode function was to ensure the rebar assembly received only cathodic current at all times. When activation occurred, the diode prevented the rebar assembly from receiving a net anodic current, which would occur if the open circuit potential of the steel dropped below the initial polarization potential (shown in Figure 5). This also allowed for specimens polarized to -330 mV and -430 mV to be switched to a more negative potential after activation.

Switches were installed between potentiostat and anodes on polarized specimens. The rebar assembly during the polarization can exhibit capacitor-like behavior and store charge on its surface, which can interfere with potential measurements. It is advisable to release this charge; by turning off the switch, the charge dissipates and a drop in potential is experienced. This change in potential is known as the ohmic drop and is a function of the resistance of the concrete and the current applied to the rebar assembly. The difference between the on potential and the ohmic drop is referred to as the instant off potential. The switches allowed for the current to be interrupted for one second to obtain the instant off potential, which is a close indication of the actual value of the steel potential against its immediately surrounding concrete. Figure 10 shows a typical specimen and Figure 11 shows the testing arrangement.

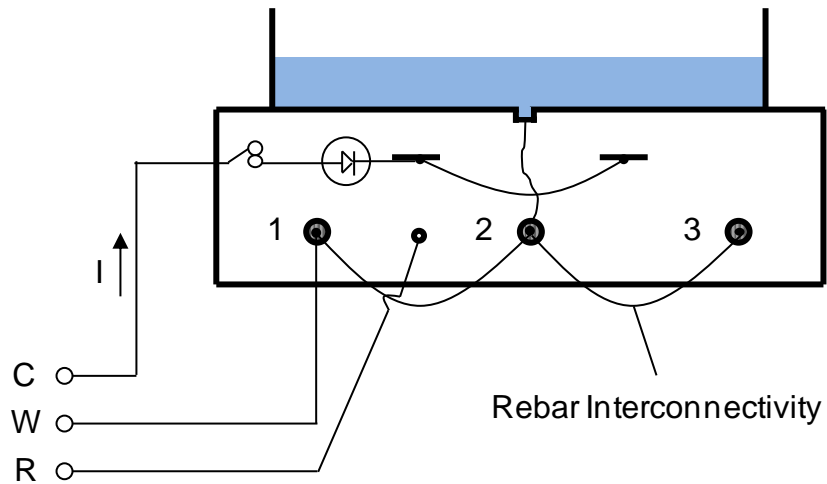


Figure 9 Specimen Connection to Potentiostat. C is the counter electrode, W is the working electrode, and R is the reference electrode terminal respectively of the potentiostat. C and W complete the circuit and allow for current to flow, and the potential difference between W and R is the potentiostat control signal. The diode ensures that only net cathodic current is supplied to the rebar assembly.

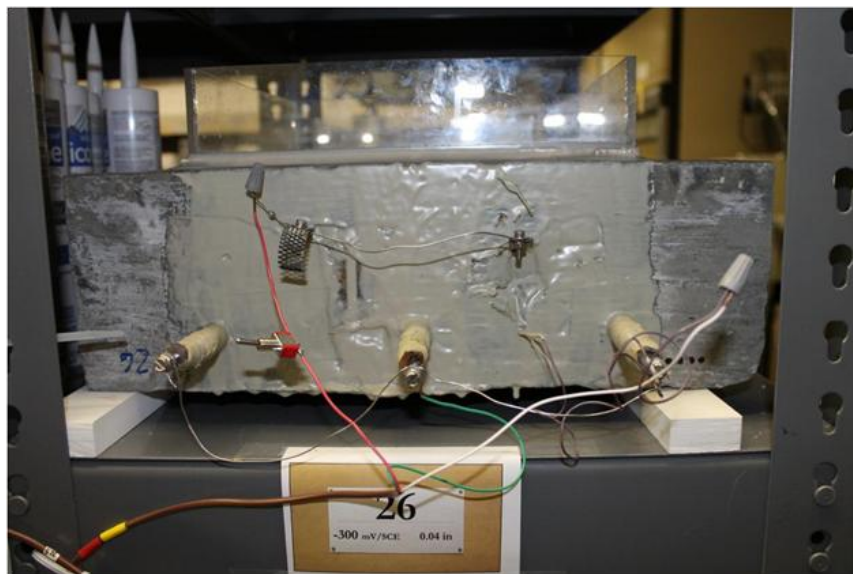


Figure 10 Typical Specimen Setup



Figure 11 Testing Arrangement

2.3.2 Monitoring of OC Specimens

Before exposure to the NaCl solution, OC specimens were monitored for corrosion activity to ensure no activation had occurred by means of potential measurements.

Monitoring of OC specimens for corrosion activation by half-cell potential measurements was routinely performed. Potential measurements are conducted using a voltmeter, SCE/embedded titanium electrodes, and rebar assembly. The reference electrode, connected to the negative terminal of the voltmeter, represents one half of the cell and the rebar assembly, connected to the positive end, represents the other half of the cell. The full cell is formed when the SCE is placed on the surface of the concrete (when the permanent embedded reference electrode is used in place of the SCE the corresponding full cell is already formed). The concrete pore water serves as an electrolytic path between the rebar assembly and reference electrode.

Figure 12 displays the half-cell potential measurement performed for this experiment. Half-cell potential measurements were conducted differently for wet and dry cycles. During the wet cycle, a uniform potential is observed across the entire surface of the ponding area, and subsequently, only one potential is recorded for this condition. Under dry conditions, potentials were measured at three locations, equidistance apart spanning the central rebar in the ponding area with a wet sponge between reference electrode and concrete to ensure electrolytic path.

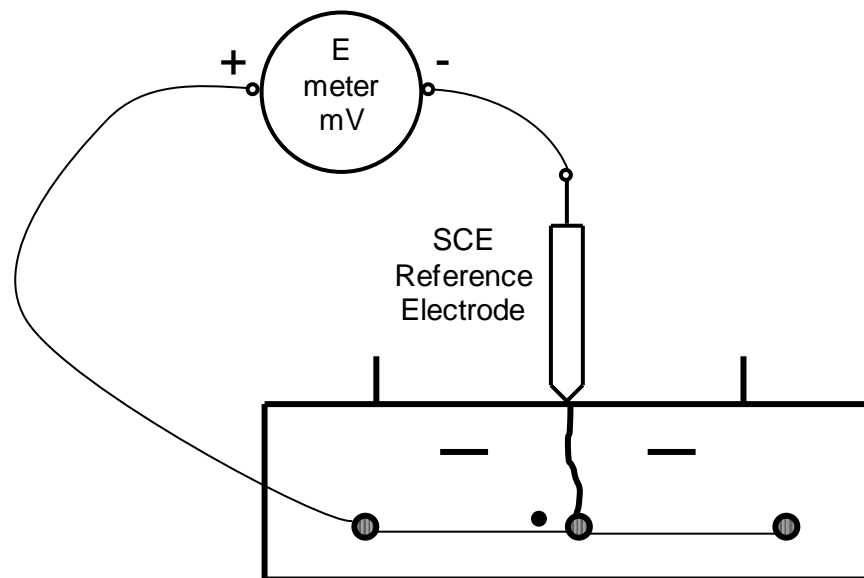


Figure 12 Half Cell Potential Reading for Specimen

ASTM C876 [19] gives guidelines which are used to estimate the likelihood of corrosion activity based on the measured potential. Table 2 shows these guidelines for copper copper-sulfate (CSE) and SCE. It should be noted that the values in Table 2 are representative of bridge deck service conditions, so they may be considered to be

useful only as a first approximation of determination of corrosion activity in the present case.

Table 2 Likelihood of Active Corrosion per Measured Potential

Measured Potential (mV/CSE)	Measured Potential (mV/CSE)	Corrosion Risk
>-200	> -126	Low (10% Risk)
-200 - -350	-126 - 276	Intermediate (uncertain)
<-350	< -276	High (90% Risk)

Note: potential vs SCE = potential vs CSE +77 mV

Macrocell currents are the total current delivered to the central rebar from the two outer rebars. The central bar (anode) sends electrons to the outer bars (cathode) once active corrosion initiates. Macrocell currents were measured to determine the amount of current being transferred from outer bars to the central bar., shown as a positive current. These measurements were conducted using a Fluke 27 multimeter (configured as ammeter in the A/mA range, with an effective resistance of 5 ohm) with the negative end connected to the central rebar 2, and the positive end connected to outer rebar 1. Referring to Figure 9, rebar 1 was disconnected from the rebar assembly by loosening the nut on the stainless steel screw at rebar 1 and removing the stainless steel wire so that rebar 1 is isolated from rebars 2 and 3. Current was then recorded at rebar 1 and referred to as current 1-2. The stainless steel wire was reconnected to rebar 1 and measurements were conducted in the same manner for rebar 3 and referred to as current 3-2. With that configuration, currents resulting from rebar 2 actively corroding and rebars 1 and 3 in the passive condition were >0.

2.3.3 Monitoring of Polarized Specimens

Before energizing and 5% NaCl solution exposure to specimens, potentials were measured to confirm initially passive condition of the steel reinforcement.

Measurements for polarized specimens differed from the measurements for OC specimens. Since OC specimens were not polarized, it was possible to use half-cell measurements to gauge how likely corrosion activity was. Instead, current demanded by the rebar assembly from the potentiostat was used to determine if active corrosion had been initiated for polarized specimens as explained in Chapter 1.7. When current demand reached zero (it could not be negative due to the diode) it was deemed that significant active corrosion was in progress in the rebar assembly.

Half cell potential measurements of polarized specimens in the “on” condition were conducted in the same manner as the half-cell potential measurements of OC specimens when the switch was on, utilizing both SCE and embedded titanium reference electrodes. Half-cell “on” measurements were also conducted immediately after activation to aid in switching to a CP regime. However, an instant-off-potential was measured as well in all cases. The voltmeter was closely observed as the switch was moved to the off position for approximately one second. After one second interruption, the value displayed by the voltmeter was recorded and considered to be the instant-off-potential. The instant off potential was representative of the actual potential of the rebar assembly with respect to the concrete immediately adjacent to the steel surface. If the instant-off-potential was more than 5 mV away from the intended polarized potential of the specimen, an adjustment was needed and performed.

The adjustments were made by manually turning the control screw of the potentiostat channel controlling a given specimen, depending on the instant-off-potential value measured. For example, if a specimen that should be polarized to -540 mV was found to have an instant-off-potential of -520 mV SCE, the potentiostat would be manually adjusted so that the potential of the rebar assembly against the embedded reference electrode experienced a 20 mV shift in the negative direction. The new setting was maintained until the next scheduled data acquisition date, when it was newly adjusted or left unchanged depending on whether or not the potential had drifted outside the 5 mV desired bandwidth.

2.3.4 Determination of Feasibility of CPrev

In order to determine the efficacy of CPrev application, the time to corrosion activation was compared with the time to corrosion activation for the OC specimens. If a significant increase in time to corrosion activation was observed between polarized and OC specimens, it may be appropriate to suggest CPrev is feasible. The various levels of polarization would give different times to corrosion activation, and depending on those times, it could be determined which polarization levels were sufficient or insufficient for CPrev feasibility.

2.3.5 Cathodic Polarization after Activation

If a polarized specimen experienced activation (indicative that CPrev was no longer effective, as outlined in the previous section), the potentiostat channel for the specimen was adjusted to obtain a higher level of polarization (to either -430 mV or -540

mV) to determine if the steel could now be protected under CP conditions. Potential and current measurements were conducted as per pre-activation conditions. The potentiostat continued to be monitored and adjusted to maintain the new desired potential level.

As mentioned before, in conventional cathodic protection applied to steel in concrete, steel is considered to be protected if a 100 mV depolarization decay (toward more positive values) is achieved after 4 hours of current interruption [9]. It is noted that it is possible to regenerate with the application of CP the steel's passive film which had previously experienced breakdown due to chloride ion ingress [20]. In such cases over time, the current demanded by the rebar assembly decreases if active zones on the rebar repassivate, which can make the depolarization decay more pronounced. The 100 mV criterion is used nevertheless even if the steel does not achieve passivity [20]. The depolarization tests were thus conducted for selected specimens, and applied only to specimens that experienced corrosion initiation and subject to CP. The depolarization tests were conducted during the dry condition. Instant-off potentials were conducted by first placing the SCE tip at nine locations on the surface of the concrete (three along each of the three rebars) before current interruption. Switches were then turned to the off position and remained in the off position, allowing the specimen to depolarize. The recorded depolarization for a given time was the measured "off" potential minus the initial instant-off potential. Potentials were measured at 1, 4, and 24 hours after current interruption. After 24 hours, switches were turned back to the "on" position.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 Unpolarized (OC) Control Specimens

3.1.1 Potential Measurements

Initial potential values, before exposure to 5% NaCl solution, were in the order of -50 mV SCE. As indicated earlier, potentials of this order are usually deemed to indicate [19] that the steel was in the passive condition before exposure to NaCl, as expected.

After exposure to the NaCl solution, a significant drop in the potential readings was observed for all specimens in this OC regime within 8 days, regardless of crack width, as shown in Figure 13. This indicates very early corrosion activation for all crack widths. Also as expected the largest crack width (0.04 in) showed signs of activation a few days before the smaller crack widths (0.01 in and 0.02 in) and exhibited the most negative potentials.

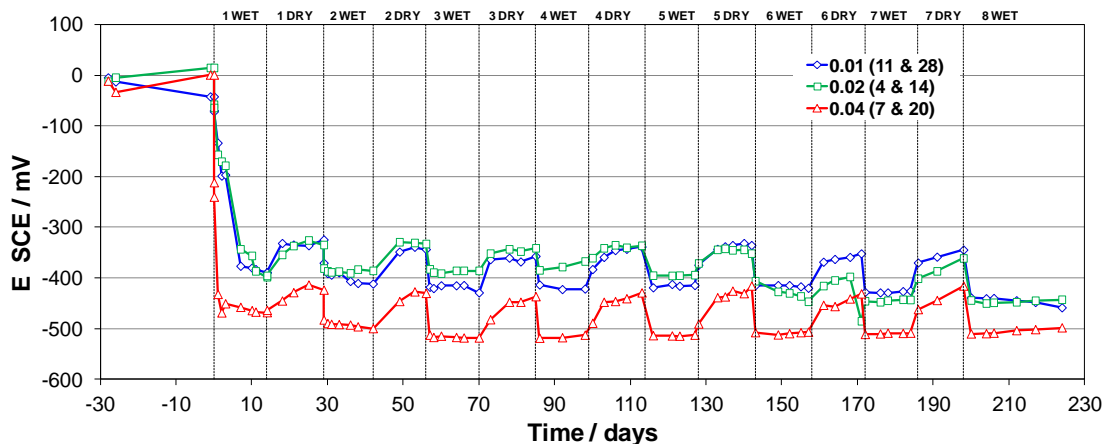


Figure 13 Average Potential for the OC Specimens. Legend shows crack width. The average potential range in potential measurements from replicate specimens was 14 mV, 30 mV, 27 mV for 0.01 in, 0.02 in, and 0.04 in crack widths, respectively.

3.1.2 Macrocell Current Measurements

Small macrocell current values were observed shortly after starting exposure to the 5% NaCl solution, but quickly increased with time. The increase in macrocell current is indicative of corrosion activity. Figure 14 shows the current density v. Time, averaged for each crack width. Following the work of Sanchez [8] the criterion for corrosion initiation adopted here was a current density greater than $0.2 \mu\text{A}/\text{cm}^2$. In less than a week's time, all specimens exhibited current density greater than the $0.2 \mu\text{A}/\text{cm}^2$ criterion. Notably, and as expected, the largest crack width (0.04 in) corresponded to the highest macrocell current indicating more corrosion activity.

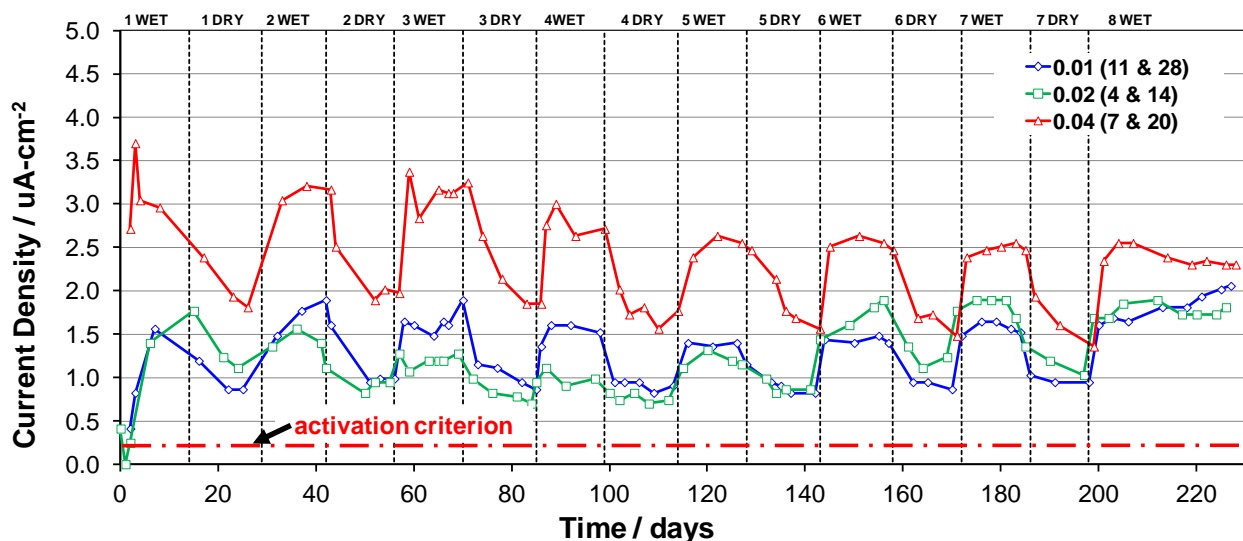


Figure 14 Average Macrocell Current Density for OC Specimens. Legend shows crack width. The average current density range in current measurements from replicate specimens was 0.04 for 0.01 in crack widths, 0.12 for 0.02 in crack widths, and 0.13 for 0.04 in crack widths.

3.1.3 Discussion of Results from Unpolarized Specimens

The increases in current density coincided with the sharp decreases in potential noted earlier, so both indicators consistently suggested an early onset (8 days or less, first wet cycle) of corrosion activity for the unpolarized control specimens. Corrosion

severity was greater for the greatest crack width (0.04 in), also as expected. The results indicated that with no form of corrosion protection or prevention, in the presence of cracks (even at the smallest width investigated, 0.01 in) in a simulated marine environment reinforcing steel was liable to corrode quickly. Such early onset of corrosion would be clearly detrimental to achieving the desired service life in the part of the structure affected by the cracks.

3.2 Polarized Specimens

3.2.1 Potential Measurements

The steel assembly of each specimen was cathodically polarized to maintain a certain level of potential, regardless of corrosion behavior. Figure 15 displays the time-averaged potential distribution for all polarized specimens in the pre-activation condition, showing that specimens were generally polarized and maintained near the target potential level.

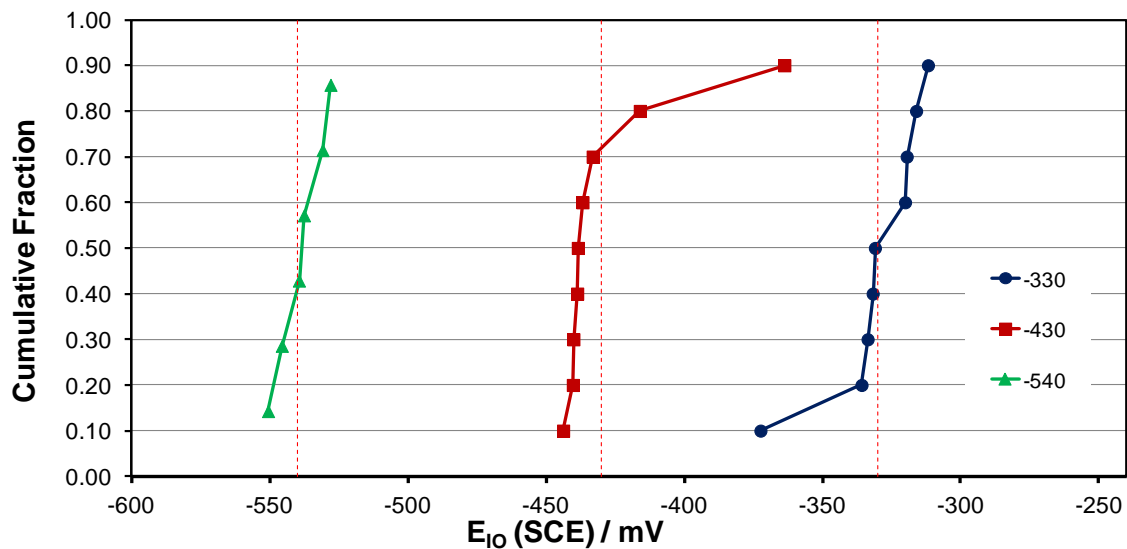


Figure 15 Cumulative Distribution of Instant-off Potentials. The potentials are averaged over the exposure period for all polarized specimens in the pre-activation condition. Legend indicates the target potential (mV SCE) for each group.

3.2.2 Current Measurements

Figure 16 summarizes evolution of current demand for specimens polarized to -330 mV SCE. Time is counted from the day of energizing (same as for the first wet cycle). After a period of a few days, current demand stabilized. Eight of the 9 specimens polarized to -330 mV exhibited corrosion initiation after 50 days of being energized. Specimens with 0.04 in crack widths activated within 10 days, before specimens with 0.01 and 0.02 in crack widths. There was no correlation between crack width and time to corrosion activation for specimens with 0.01 in and 0.02 in crack widths. Activated specimens were afterwards polarized to a more negative potential (either -430 mV or -540 mV) as shown in Figure 17. The increase in time to corrosion activation of the -330 mV group compared to those of the OC specimens was minimal.

Figure 18 summarizes the evolution of current demand for specimens polarized to -430 mV SCE. Current demand stabilized within a few days of being polarized. Seven of the 9 specimens activated within 190 days of being energized. Two specimens polarized to -430 mV have not activated after >200 days of exposure. Specimens with 0.04 in crack widths all activated within 90 days of being energized. Again, there was no distinction between crack width and time to initiation for specimens with crack widths of 0.01 in and 0.02 in. Activated specimens were afterwards polarized to -540 mV as shown in Figure 19. Though specimens polarized to -430 mV showed an increase in time to corrosion activation when compared to those for specimens polarized to -330 mV, the increase was not substantial.

Figure 20 summarizes the current demand for specimens polarized to -540 mV SCE. Current demand stabilized within a few days of being energized. After > 200 days

since energizing and exposure to chloride, no specimen polarized at -540 mV has activated. The results hence indicate a significant increase in time to corrosion activation when compared to OC specimens and specimens polarized to -330 mV and -430 mV.

Figure 21 shows the nominal average current density with respect to rebar area (0.4 ft²) and concrete area (1.15 ft²)¹, derived from Figure 16, Figure 18 and Figure 20. To account for high values of current soon after polarization and low values soon before activation, the range of values from 14 days after polarization up until 5 days before activation are averaged. As expected, current density was lowest for specimens polarized to -330 mV and highest for those polarized to -540 mV. The current density values are nominal averages recognizing that currents to center and side rebars were different.

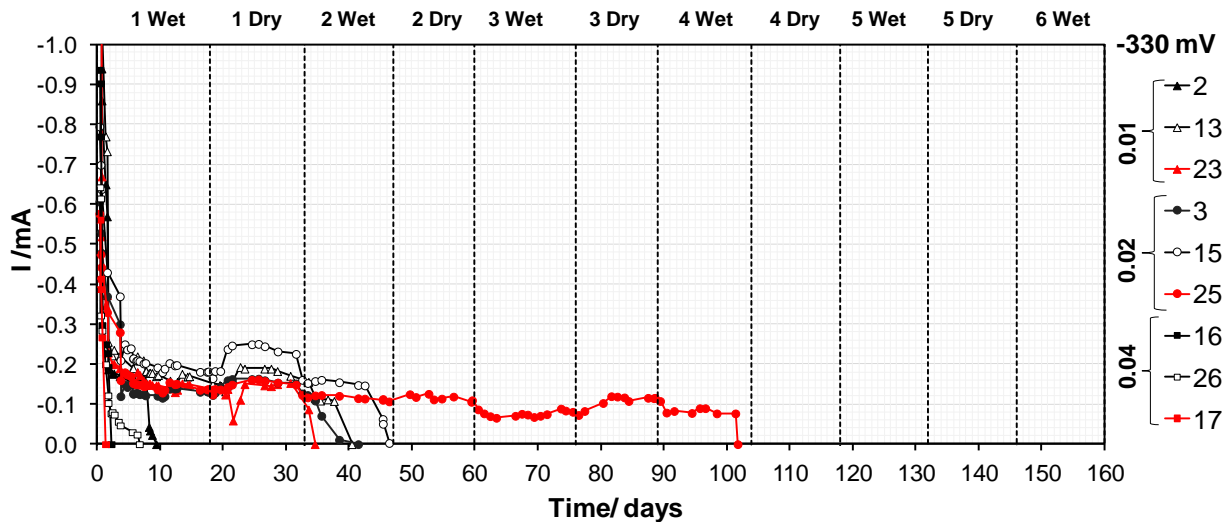


Figure 16 Cathodic Current Demand for -330 mV Specimens. Specimens are organized by crack width.

¹ Assuming 3 rebars with exposed length 12 inch, diameter 0.5 in, on a footprint of 3 spaces 4.6 inch wide each based on center-center distance shown in Figure 7.

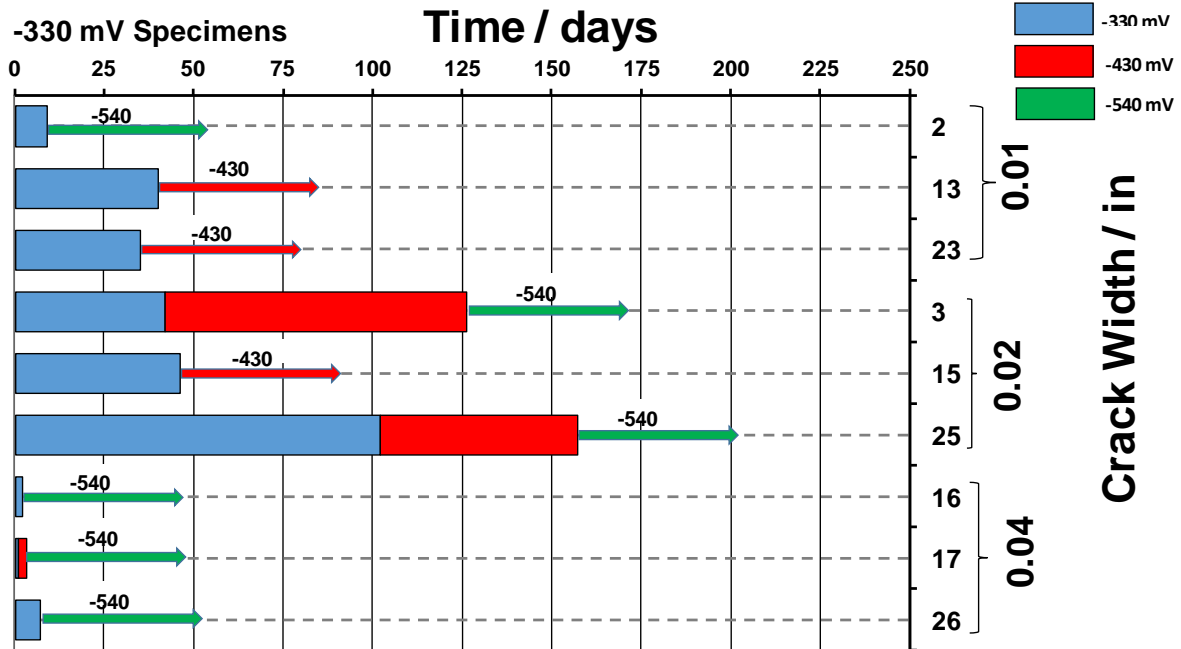


Figure 17 Timeline for Specimens Initially Polarized to -330 mV. Indicated is the day each specimen activated and the potential level it was subsequently switched to. Arrows indicate the specimen is still polarized to the specified potential level.

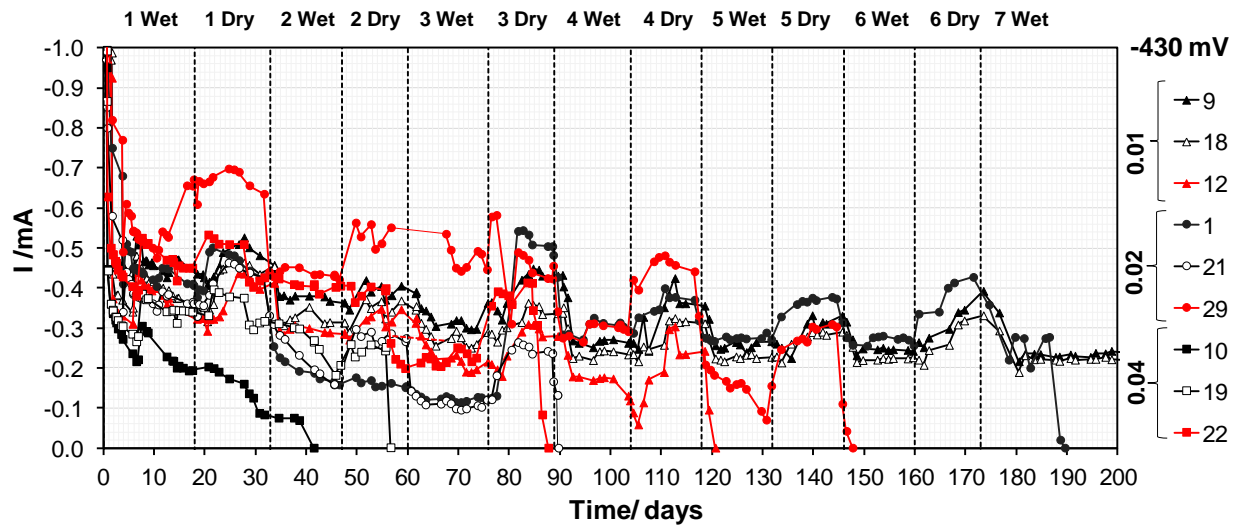


Figure 18 Cathodic Current Demand for -430 mV Specimens. Specimens are organized by crack width.

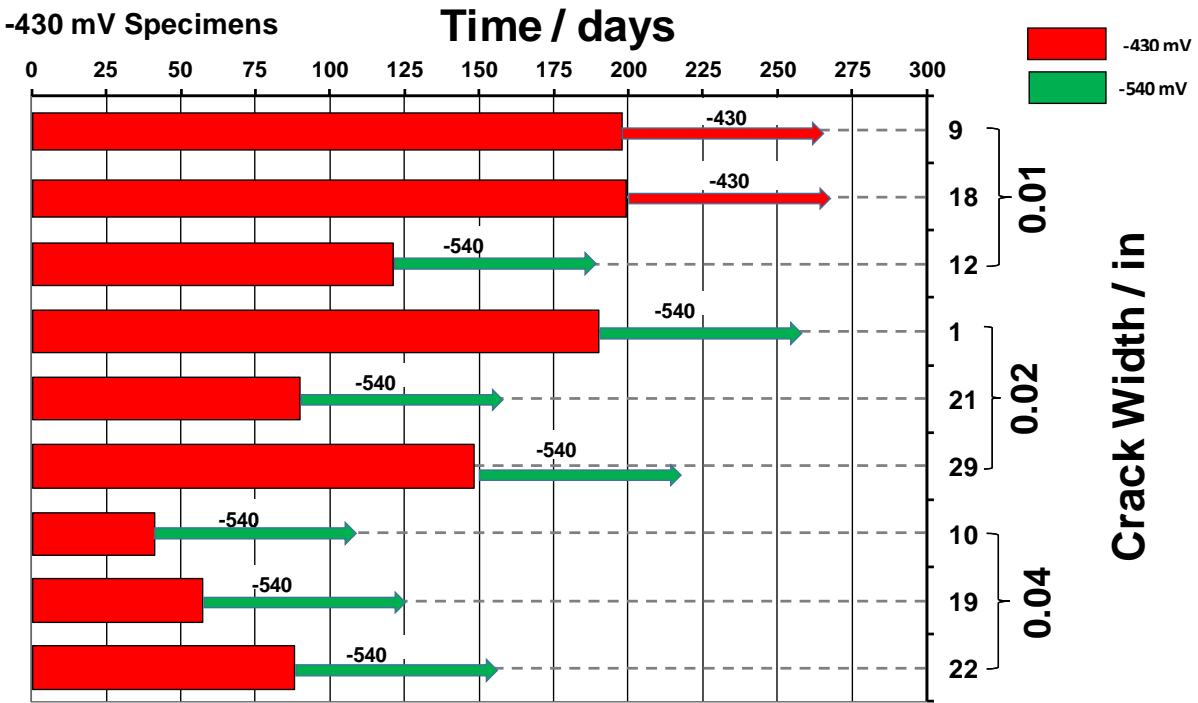


Figure 19 Timeline for Specimens Initially Polarized to -430 mV. Indicated is the day each specimen activated and the potential level it was subsequently switched to. Arrows indicate the specimen is still polarized to the specified potential level.

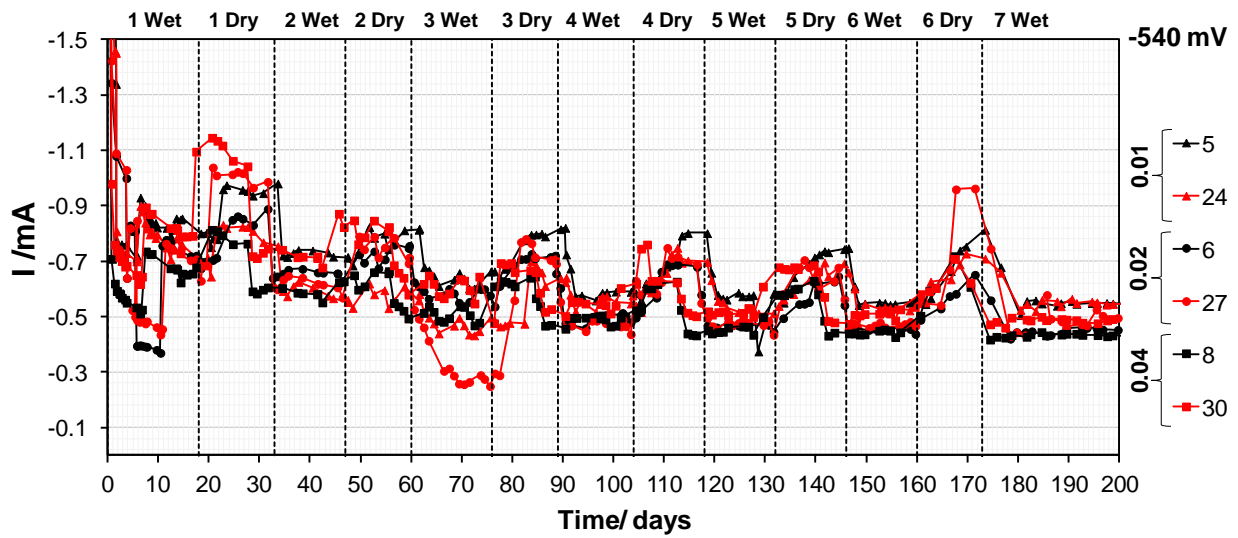


Figure 20 Cathodic Current Demand for -540 mV Specimens. Specimens are organized by crack width.

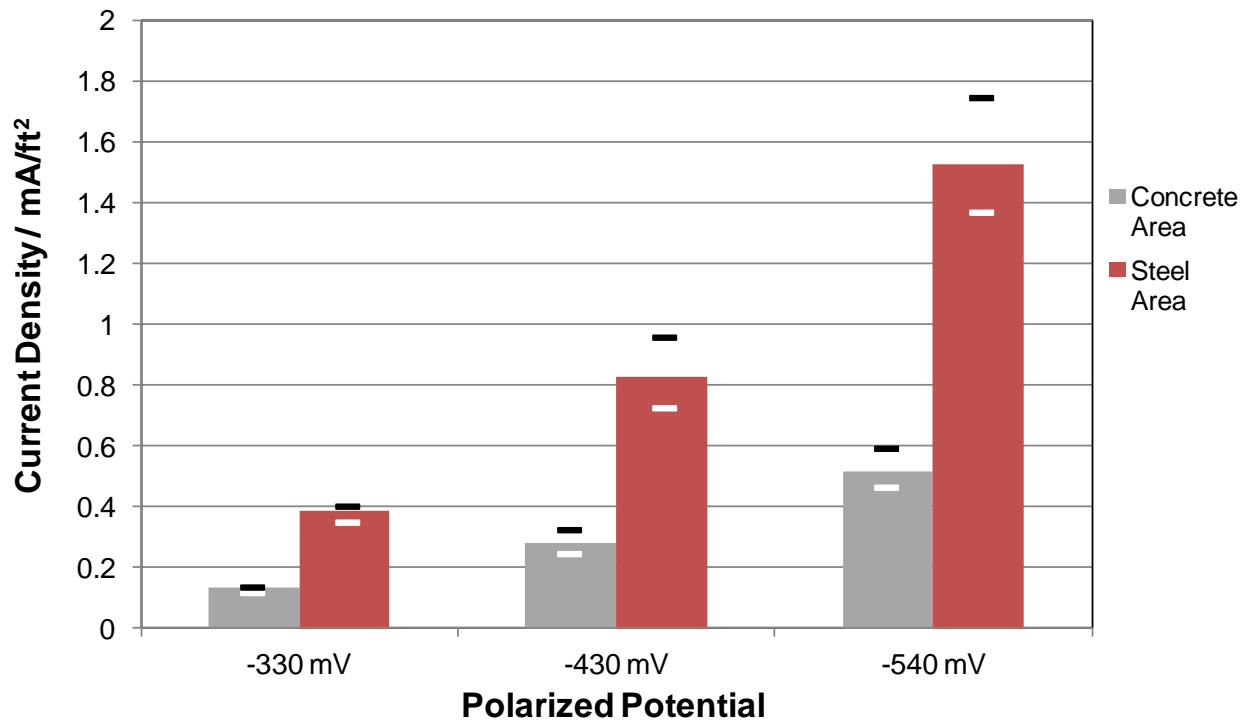


Figure 21 Nominal Average Current Density for each Potential Level Before Activation. White dashes represent the average current density during wet cycles. Black dashes represent the average current density during dry cycles.

3.2.3 Discussion of Results from Polarized Specimens

Specimens polarized to -330 mV containing 0.04 in crack widths met the zero current demand criterion for corrosion activation within 10 days, notably before those with 0.02 and 0.01 in crack widths, as expected. This finding indicates that large-width cracks may require greater levels of CPrev to increase time to activation compared to those for 0.02 and 0.01 in crack widths. Eight of 9 specimens polarized to -330 mV activated within 50 days, regardless of crack width. The increase in time to corrosion activation for specimens polarized to -330 mV is minimal compared to OC specimens. From the data obtained, it appears that CPrev at -330 mV is likely not a feasible means

of providing marked service life increase for reinforced concrete structures in marine service in the part of the structure affected by the cracks.

Specimens polarized to -430 mV containing crack widths of 0.04 in met the corrosion activation criterion within 90 days, noticeable before specimens with 0.02 in and 0.01 in crack widths did. This finding, along with the similar result for -330 mV specimens mentioned above, indicates that large-width cracks may require greater levels of CPrev to increase time to activation compared to those required for 0.02 and 0.01 in crack widths. After 190 days, 7 of 9 specimens polarized to -430 mV, regardless of crack width, had activated, with 2 specimens still operating in the CPrev regime after >200 days. Though specimens polarized to -430 mV showed an increase in time to corrosion activation when compared to those for specimens polarized to -330 mV, the increase is not substantial, especially considering that some specimens containing large width cracks activated before specimens polarized to -330 mV. From these data, it appears that applying CPrev at -430 mV is not an effective means of providing marked service life increase for reinforced concrete structures in marine service in the part of the structure affected by the cracks.

All specimens polarized to -540 mV, regardless of crack width, are still in a CPrev regime, with no well defined activation after >200 days since exposure. This finding is significant considering the early activation of specimens polarized to -330 mV and -430 mV, as mentioned above. In particular, all specimens with 0.04 in crack widths polarized to -430 mV and -330 mV activated within 90 days, while specimens with 0.04 in crack widths polarized to -540 mV are still in CPrev after >200 days. A detailed summary of each specimen's time to activation arranged by potential level and crack width is shown

in Figure 22. All specimens polarized to -540 mV have endured 7 exposure cycles to NaCl solution with no activation, whereas OC specimens and specimens polarized to -330 mV activated in the first wet cycle. This suggests a considerable increase in the steel's C_T is possible in cracked concrete in a simulated marine environment. This increase in the steel's C_T may translate to a marked increase in service life for a cracked reinforced concrete structure in marine service in the part of the structure affected by the cracks, suggesting that CPrev application at -540 mV may be feasible as an effective corrosion control measure.

Nominal current density values were higher than typical for CPrev application [14] in sound concrete, but within the range of current density values for CP in sound concrete [9]. This may be attributed to the presence of cracks in the concrete. Current densities during wet cycles were noticeably lower than current densities during dry cycles. It should be recalled that the system was under potentiostatic control so the difference does not necessarily reflect differences in overall concrete resistance between the wet and dry conditions. Rather, the effect is likely to involve the relative resistance distribution in bulk and crack between both conditions, as well as variations in the extent of junction potentials developed at the reference electrode / concrete contact zone which may have influenced the set point used for the potentiostat. This issue, together with a more detailed interpretation of the distribution of current between center and side rebars, should be examined in follow up research.

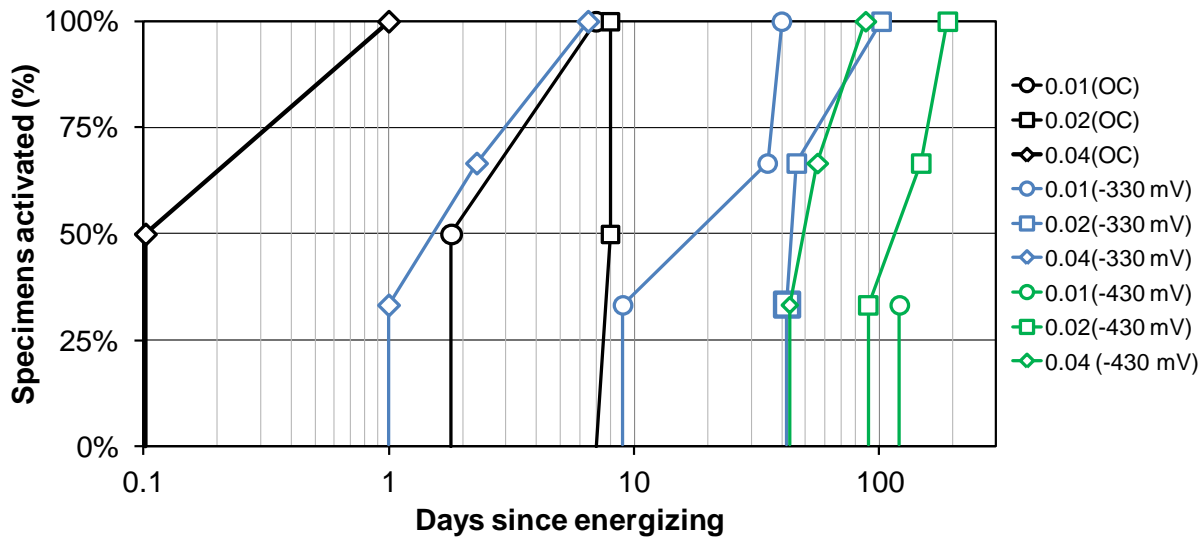


Figure 22 Detailed Summary of each Specimen's Time to Activation. Specimens are arranged by potential level and crack width plotted and against days since energizing.

3.2.4 Cathodic Protection Depolarization Results

Six specimens which had previously activated were tested, with samples from CP levels of -430 mV and -540 mV. Figure 23-25 summarize the 1 hour, 4 hour, and 24 hour depolarization for each of the six specimens, respectively. The averaged depolarization value along each rebar is tabulated (locations 1,2,3 for the left rebar, locations 4,5,6 for the central rebar, and locations 7,8,9 for the left rebar). The specimen number, crack width and the time in days the specimen has been under CP are displayed beneath each set of data. All specimens polarized to -540 mV surpassed the 100 mV decay required within 4-24 hours of depolarization to be considered protected. 1 of 2 specimens polarized to -430 mV surpassed the 100 mV decay required after 4-24 hours. Despite being polarized for 134 days, specimen 23 did not experience a 100 mV decay for all three rebars after 24 hours of being switched off.

Figure 26-28 show the current demand for all specimens switched into a CP regime. Specimens 3 and 25 appear in both Figure 26 and Figure 28 (yellow fill) because they were originally moved from -330 mV to -430 mV, activated and were switched to -540 mV. The current demand fluctuated for all specimens due to wet and dry cycle conditions but then remained relatively constant for the remainder of the experiment. Specimens switched from -330 mV to -540 mV show a decrease in current demand of a few tenths of a mA after stabilizing at about day 30, but is likely due to initially over-polarizing these specimens.

Figure 29 shows the nominal average current density after activation with respect to rebar area (0.4 ft^2) and concrete area (1.15 ft^2) and is derived from Figure 26-28. Nominal average values are calculated after from data obtained after specimens are polarized to their new potential level. As expected, current density was lower for specimens switched to -430 mV and higher for specimens switched to -540 mV. Current densities were also higher during the dry condition when compared with current densities during the wet condition, the same as findings from specimens in the CPrev regime. Notably the nominal current densities were actually somewhat smaller than those shown in Figure 21 for the corresponding CPrev conditions.

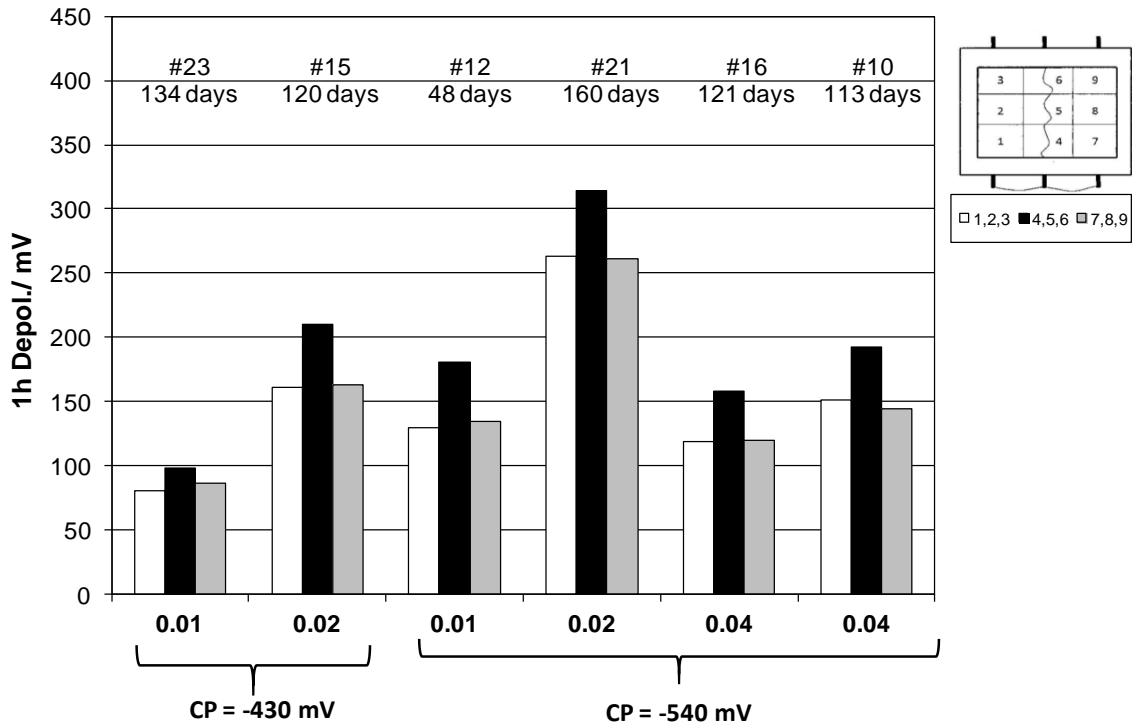


Figure 23 1 Hour Depolarization Test. Depolarization values shown are the average of three points measured along each rebar. Specimen number and days under CP noted above data.

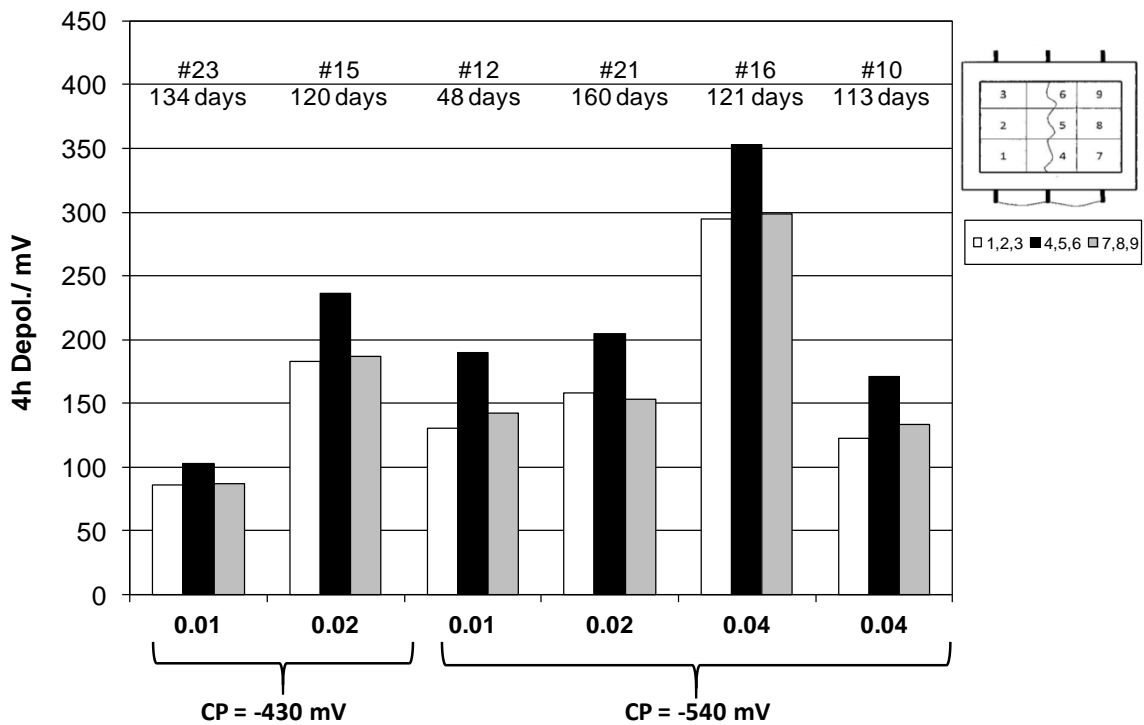


Figure 24 4 Hour Depolarization Test

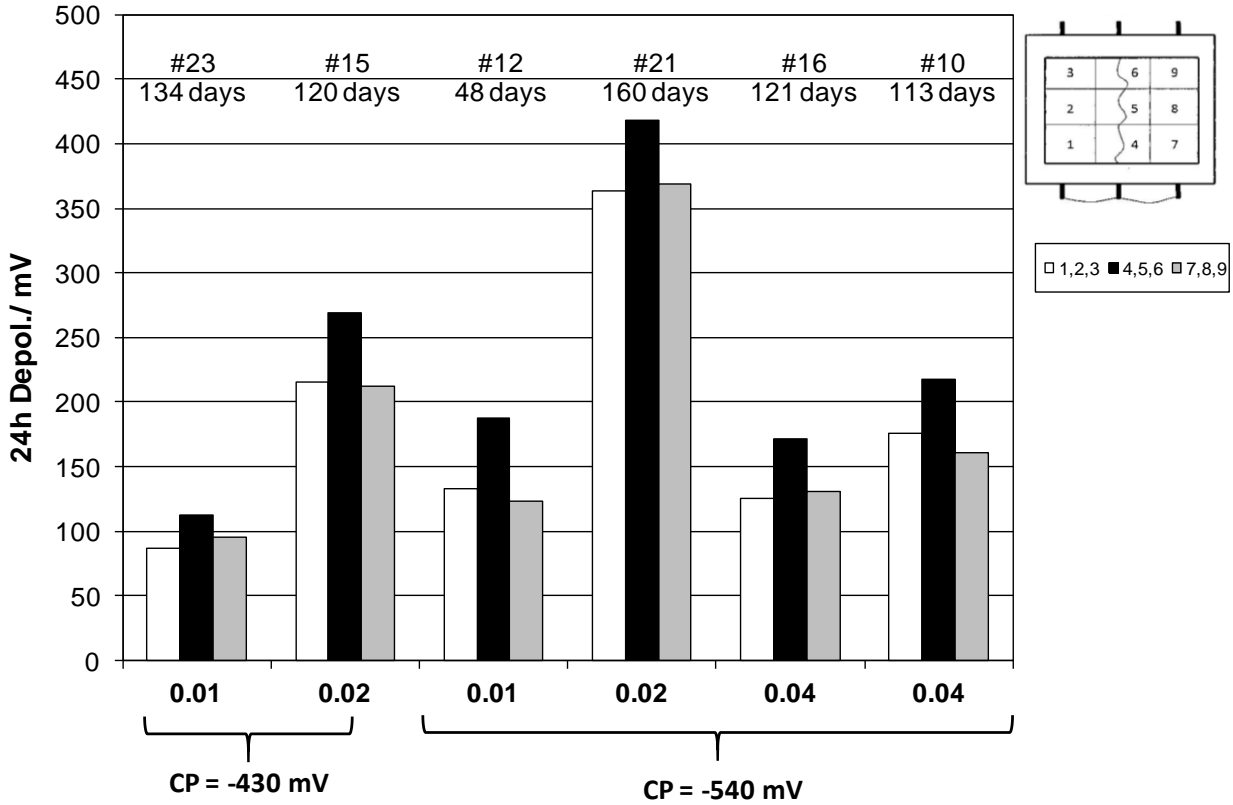


Figure 25 24 Hour Depolarization Test

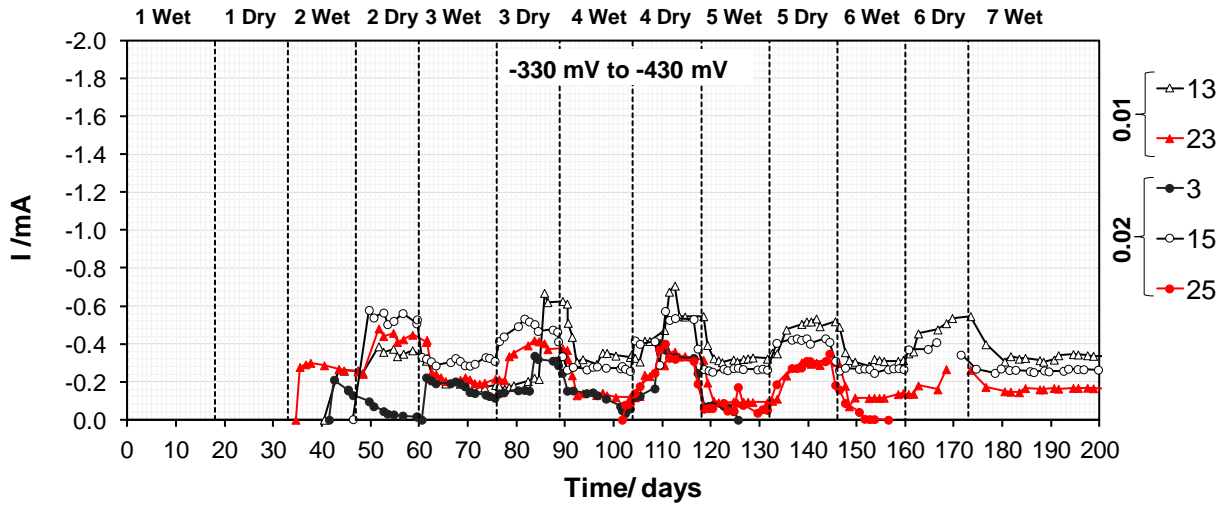


Figure 26 Current Demand for Activated Specimens Switched from -330 mV to -430 mV.

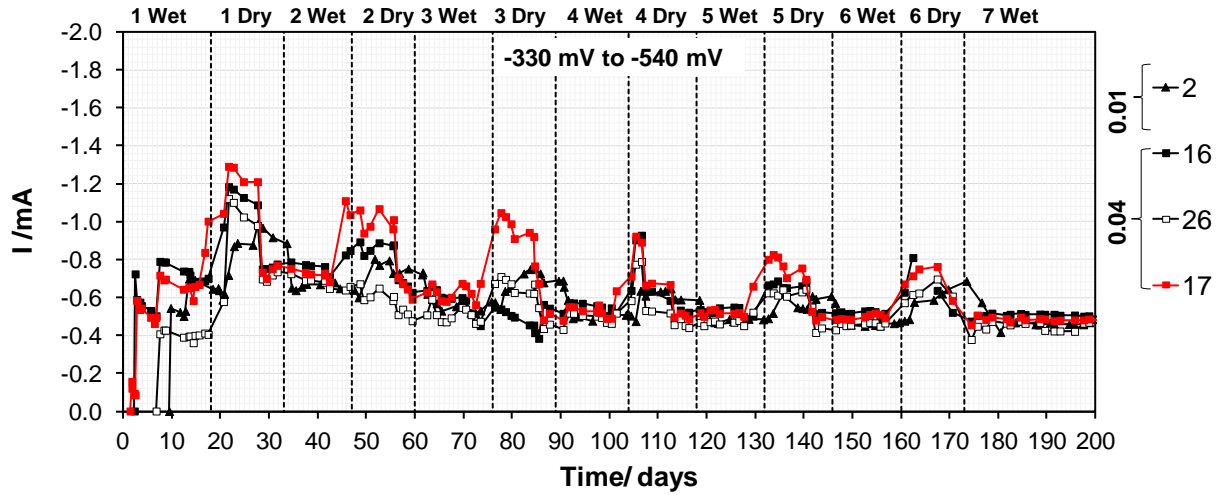


Figure 27 Current Demand for Activated Specimens Switched from -330 mV to -540 mV.

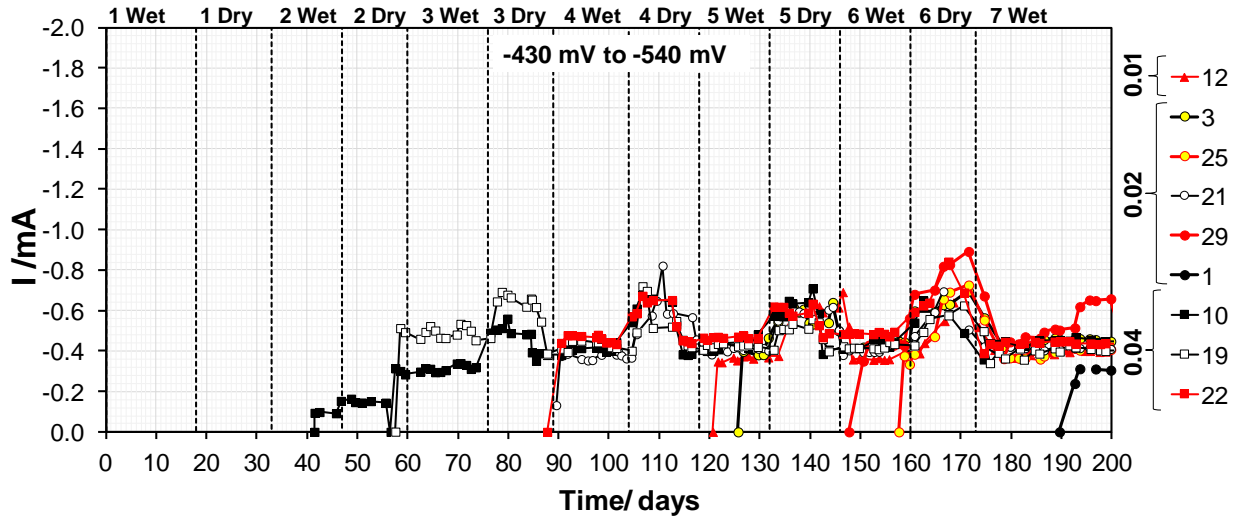


Figure 28 Current Demand for Activated Specimens Switched from -430 mV to -540 mV.

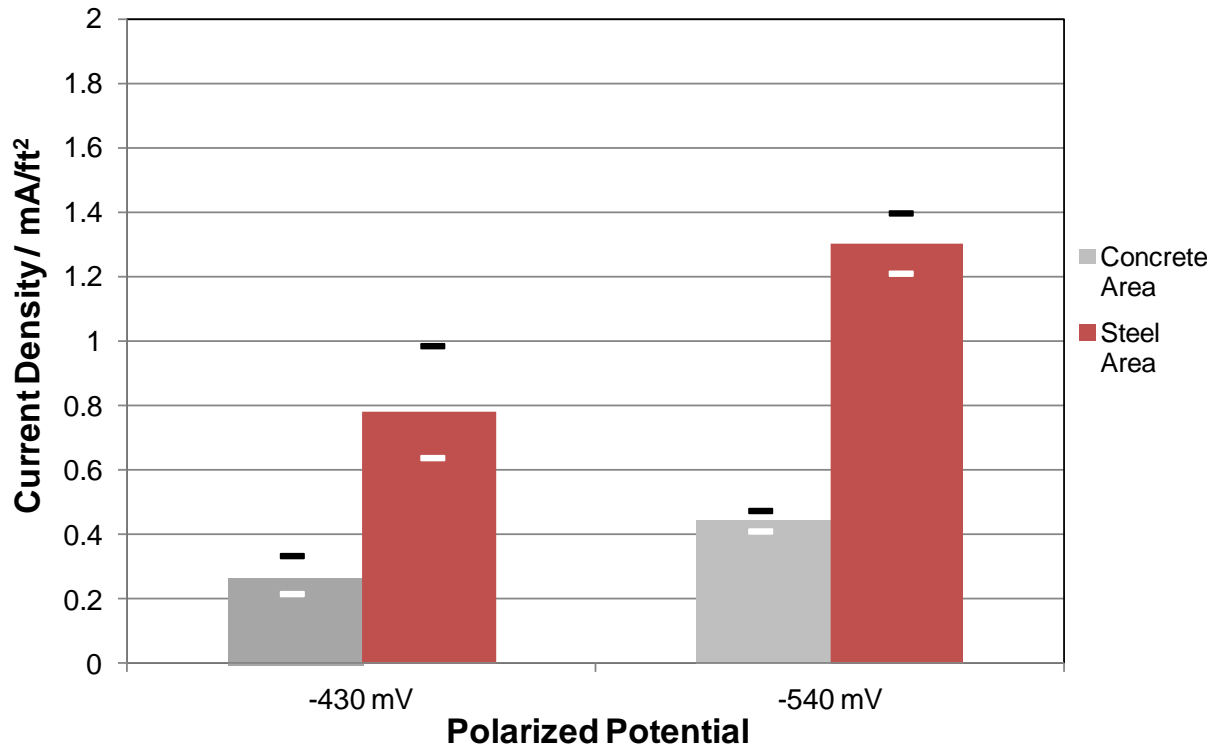


Figure 29 Average Current Density for each Potential Level After Activation. White dashes represent the average current density during wet cycles. Black dashes represent the average current density during dry cycles.

3.2.5 Discussion of Results from Depolarization Test

After activation, cathodically polarizing specimens to -540 mV and into a conventional CP regime seems to be effective in achieving the desired 100 mV depolarization decay protection criterion for cracked concrete exposed to a simulated marine environment. This finding is supported by the depolarization test results whereby all four specimens tested at -540 mV CP achieved a 100 mV decay after 1 hour of current interruption. In contrast, polarizing to -430 mV did not always provide a 100 mV depolarization decay for cracked concrete exposed to a simulated marine environment. Current demand remained relatively stable for specimens put into a CP regime after activation, suggesting that the passive layer did not regenerate [20].

Nominal current density values for specimens in the CP regimes were comparable, or slightly lower, than those for specimens in the CPrev regimes applied at the same potential level. The result is seemingly intriguing as CPrev in sound concrete is usually considered to require less current than CP, because CPrev is generally expected to be applied to a much lower polarization level. However, the present results indicated that to prevent corrosion in cracked concrete a fairly high level of cathodic polarization (down to about -540 mV) would be needed. That corresponds to more than 400 mV below a typical open circuit potential, and in that case nearly all of the current is demanded by the cathodic reaction. Hence in these conditions the benefit of CPrev would appear to fully avoid any corrosion initiation event, and not a decrease in current demand compared to a CP system. The CP current demand may be somewhat lower than for CPrev because at -540 mV there may still be an appreciable residual amount of anodic reaction taking place in the previously corroding system. If that proves to be the case in follow up research, the results would in that event be to some extent still supportive of CPrev as the more strict corrosion control method, albeit without much benefit from the standpoint of lowered current needs.

CHAPTER 4: CONCLUSIONS

- With no form of corrosion protection or prevention, in the presence of cracks ranging from 0.01 in to 0.04 in width in a simulated marine environment, reinforcing steel was liable to corrode quickly. Such early onset of corrosion would be clearly detrimental to achieving the desired service life in the part of the structure affected by the cracks.
- The increase in time to corrosion activation for specimens polarized to -330 mV and -430 mV (SCE) was not substantial compared to OC specimens. These results suggest that CPrev with these levels of cathodic polarization may be of limited or no benefit in the case of cracks aligned lengthwise to the rebar.
- The observation that no specimen polarized to -540 mV (SCE), regardless of crack size, has activated after >200 days of exposure to NaCl solution, suggests that CPrev with cathodic polarization levels of -540 mV (SCE) may be considered effective for steel in cracked concrete in a marine environment. Longer term test confirmation is needed. Average nominal cathodic current density values required to achieve -540 mV (SCE) were high, in the order of 1.5 mA/ft² of steel surface near the crack zone.
- The results indicated that the 100 mV depolarization decay [9] criterion for protecting already corroding steel may be satisfied for cracked concrete conditions by applying -540 mV (SCE) of conventional CP.

REFERENCES

- [1] A. Sagüés, *Class Notes, Structural Life Prediction*. University of South Florida Course CGN 6933 Sec.901, CRN: 83180, 2011.
- [2] G. Koch, M. Brongers, N. Thompson, Y. Virmani, J.H. Payer. "Corrosion Costs and Preventive Strategies in the United States," Publication No. FHWA-RD-01-156, NACE International.
- [3] P. Gellings, *Introduction to Corrosion Prevention and Control*. Enschede, Netherlands: University of Twente, 2005.
- [4] L. Bertolini. "Performance-based Service Life Design of Reinforced Concrete Structures Exposed to Chloride Environment," *The New Boundaries of Structural Concrete* Ancona, Italy, Session A, pp.17-30, 2011.
- [5] ACI 222R-01, "Protection of Metals in Concrete Against Corrosion" American Concrete Institute Detroit, MI, 2001.
- [6] A. Poursaee, C. Hansson. "The Influence of Longitudinal Cracks on the Corrosion Protection Afforded Reinforcing Steel in High Performance Concrete," *Cement and Concrete Research* vol. 38 pp 1098-1105, 2008.
- [7] L. Bertolini, B. Elsener, P. Pedferri, R. Polder, *Corrosion of Steel in Concrete*. Weinheim, Germany: Wiley, 2004.
- [8] A. Sánchez, A. Sagüés."Chloride Corrosion Threshold Dependence on Steel Potential in Reinforced Concrete," *Corrosion/14*, paper no. 4118, NACE International, San Antonio, 2014.
- [9] P. Pedferri. "Cathodic Protection and Cathodic Prevention," *Construction and Building Materials* vol. 10 No. 5 pp. 391-402, 1996.
- [10] G. Burstein, C. Liu, R. Souto, S. Vines. "Origins of Pitting Corrosion" *Corrosion Engineering, Science and Technology* vol. 39, pp. 25-30, 2004.
- [11] L. Bertolini, M. Gastaldi, M. Pedferri, E. Redaelli. "Prevention of Steel Corrosion in Concrete Exposed to Seawater with Submerged Sacrificial Anodes," *Corrosion Science* vol. 44 pp 1497-1513, 2002.

- [12] J. Broomfield. *Corrosion of Steel in Concrete: Understanding, Investigation and Repair*. CRC Press, 1997.
- [13] L. Bertolini, F. Bolzoni, M. Gastaldi, P. Pedferri, E. Redaelli. "Effects of Cathodic Prevention on the Chloride Threshold for Steel Corrosion in Concrete" *Electrochimica Acta* vol. 54, pp. 1452-1463, 2009.
- [14] A. Cheaitani, P. Karajayli, C, Fu. "Application of Cathodic Prevention to Sea Cliff Bridge, Lawrence Hargrave Drive," *Corrosion and Prevention*, Paper 6, pp. 1-12, 2006.
- [15] M. Louthan. "Hydrogen Embrittlement of Metals: A Primer for the Failure Analyst," Savannah River National Laboratory, Aiken, South Carolina, 2008.
- [16] K. Lau, A. Sagüés "Approach to Modeling Corrosion Progression of Epoxy Coated Rebar in Structures with Cracked Concrete," *Corrosion/10*, paper no. 10128, NACE International, San Antonio, 2010.
- [17] P. Schiessl, M. Raupach. "Laboratory Studies and Calculations on the Influence of Crack Width on Chloride-Induced Corrosion of Steel in Concrete," *ACI Materials Journal*, January/February, pp. 56-61, 1997.
- [18] P. Castro, A. Sagüés, E. Moreno, L. Maldonado, J. Genesca. "Characterization of Activated Titanium Solid Reference Electrodes for Corrosion Testing of Steel in Concrete," *Corrosion*, Vol 52, issue 8, pp. 609-617, 1996.
- [19] ASTM C867 "Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete" American Society for Testing and Materials Philadelphia, PA, 2009.
- [20] L. Bertolini, F. Bolzoni, P. Pedferri, L. Lazzari, T. Pastore. "Cathodic Protection and Cathodic Prevention in Concrete: Principles and Applications," *Journal of Applied Electrochemistry*, vol. 28, pp. 1321-1331, 1998.

APPENDICES

Appendix A Permission for Use of Figure

The subject license applies to Figure 4.

This request for permission made by Marilyn Burke on behalf of Kevin Williams to use the image from Electrochimica Acta.

Effects of cathodic prevention on the chloride threshold for steel corrosion in concrete

V.54 2009

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

May 29, 2014

This is a License Agreement between Marilyn Burke ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Marilyn Burke
Customer address	4202 E. Fowler Ave Tampa, FL 33620
License number	3398380725836
License date	May 29, 2014
Licensed content publisher	Elsevier
Licensed content publication	Electrochimica Acta
Licensed content title	Effects of cathodic prevention on the chloride threshold for steel corrosion in concrete
Licensed content author	L. Bertolini, F. Bolzoni, M. Gastaldi, T. Pastore, P. Pedferri, E. Redaelli
Licensed content date	1 February 2009
Licensed content volume number	54
Licensed content issue number	5
Number of pages	12
Start Page	1452
End Page	1463
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

Title of your thesis/dissertation	Feasibility of Cathodic prevention
Expected completion date	Jul 2014
Estimated size (number of pages)	75
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

For journal authors: the following clauses are applicable in addition to the above: Permission granted is limited to the author accepted manuscript version* of your paper.

***Accepted Author Manuscript (AAM) Definition:** An accepted author manuscript (AAM) is the author's version of the manuscript of an article that has been accepted for publication and which may include any author-incorporated changes suggested through the processes of submission processing, peer review, and editor-author communications. AAMs do not include other publisher value-added contributions such as copy-editing, formatting, technical enhancements and (if relevant) pagination.

You are not allowed to download and post the published journal article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

Posting to a repository: Authors may post their AAM immediately to their employer's institutional repository for internal use only and may make their manuscript publically available after the journal-specific embargo period has ended.

Please also refer to [Elsevier's Article Posting Policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only.. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

20. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Elsevier Open Access Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals.

Authors publishing in an Open Access journal or who choose to make their article Open Access in an Elsevier subscription journal select one of the following Creative Commons user licenses, which define how a reader may reuse their work: Creative Commons Attribution License (CC BY), Creative Commons Attribution – Non Commercial - ShareAlike (CC BY NC SA) and Creative Commons Attribution – Non Commercial – No Derivatives (CC BY NC ND)

Terms & Conditions applicable to all Elsevier Open Access articles:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation.

The author(s) must be appropriately credited.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: You may distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), to

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

include in a collective work (such as an anthology), to text or data mine the article, including for commercial purposes without permission from Elsevier

CC BY NC SA: For non-commercial purposes you may distribute and copy the article, create extracts, abstracts and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text and data mine the article and license new adaptations or creations under identical terms without permission from Elsevier

CC BY NC ND: For non-commercial purposes you may distribute and copy the article and include it in a collective work (such as an anthology), provided you do not alter or modify the article, without permission from Elsevier

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Promotional purposes (advertising or marketing)
- Commercial exploitation (e.g. a product for sale or loan)
- Systematic distribution (for a fee or free of charge)

Please refer to [Elsevier's Open Access Policy](#) for further information.

21. Other Conditions:

v1.7

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number 501315695. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customer care@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014

license for your reference. No payment is required.

<https://s100.copyright.com/App/PrintableLicenseFrame.jsp?publisherID=70&publisherNa...> 5/29/2014