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Corrosion of Epoxy-Coated Reinforcement in Marine Bridges

with Locally Deficient Concrete

by

Kingsley Lau

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Civil and Environmental Engineering College of Engineering University of South Florida

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Keywords: Crack, Chloride Penetration, Impedance, Durability, Modeling

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TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
ABSTRACT	vi
PART I	1
1.1. Introduction	1
1.1.1 Concrete as a Medium in the Corrosion Process of Steel	
Reinforcement	3
1.1.2 Chloride Induced Corrosion Degradation of Reinforced	
Concrete Structures	5
1.1.2.1 Corrosion Initiation	5
1.1.2.2 Corrosion Propagation	11
1.1.3 Corrosion Control Strategies	12
1.1.4 Epoxy-Coated Steel Reinforcement	12
1.1.5 Electrochemical Aspects	16
1.1.6 Electrochemical Measurement of Steel Corrosion in	
Concrete	19
1.2 Problem Statement and Research Objectives	
1.2.1 Research Approach	26
1.2.2 Bridges Investigated	30
1.2.3 General Bridge Substructure Information	30
PART II	
2.1 Present ECR Bridge Condition	
2.1.1 Bridge Survey Methodology	32
2.1.2 Damage Characteristics	33
2.1.2.1 Group 1 Bridges	
2.1.2.2 Group 2 Bridges	34
2.1.2.3 Group 3 Bridges	41
2.1.2.4 Group 4 Bridges	43
2.1.3 Damage Progression	45
PART III	
3.1 Concrete Bulk and Crack Transport	
3.1.1 Concrete Cracking and Corrosion	48
3.1.2 Chloride Penetration at Sound and Cracked Locations	48
3.1.2.1 Methodology	48
3.1.2.2 Results	49
3.1.3 Preferential Carbonation in Sound and Cracked Concrete	55
3.1.3.1 Methodology	55
3.1.3.2 Results	56

3.1.4 Moisture Penetration in Sound and Cracked Concrete	57
3.1.4.1 Methodology	57
3.1.4.2 Concrete Resistivity- Results	
3.1.4.3 Electrochemical Impedance Spectroscopy-	
Results	60
3.1.5 Porosity	62
3.2 Corrosion Development in ECR at On-Crack Locations	64
3.2.1 Methodology	64
3.2.2 Results	65
3.2.3 Solid Corrosion Product Formation in De-aerated	
Conditions.	70
3.2.3.1 Methodology	70
3.2.3.2 Results	71
PART IV	74
4.1. ECR Coating Characterization Techniques	74
4.1.1 Epoxy Coating Adhesion	74
4.1.1.1 Methodology	74
4.1.1.2 Results	75
4.1.2. Estimation of Coating Defect Area by EIS	76
4.1.2.1 Methodology	76
4.1.2.2 Results	78
4.1.3 High Frequency Dispersion in EIS Measurements of EC	CR86
4.1.3.1 Idealized Extended Circuit Analog	87
4.1.3.2 Truncated Transmission Line Extended	
Circuit Model	93
PART V	
5.1. Performance Projections	
5.1.1 Modeling Approach	98
5.1.2 Modeling Results	103
5.1.3 Validity and Limitations of the Model Projections	107
5.1.4 Overall Considerations and Behavior in Locally	
Deficient Concrete	109
5.2. Forecast Modeling in Locally Cracked Concrete	111
5.2.1 Basic Statements	112
5.2.2 Implementation	114
5.2.3 Cases examined	115
5.2.4 Results and Implications	116
PART VI	119
6.1. Conclusions	119
REFERENCES	122
ABOUT THE AUTHOR	END PAGE

LIST OF TABLES

Table 1.	Typical Composition of Ordinary Portland Cement	
Table 2.	ECR Bridges Investigated	
Table 3.	Solution Constituents (g) per 1 L H ₂ O	71
Table 4.	Supplemental EIS Test Concrete Properties	77
Table 5.	Idealized Extended Circuit Analog Model Cases	
Table 6.	Transmission Line Extended Circuit Analog Model Cases	
Table 7.	Model Input Parameters	101

LIST OF FIGURES

Figure 1.	Large Concrete Spall Exposing Corroding Steel Reinforcement	2
Figure 2.	EIS Equivalent Circuit Analogs	22
Figure 3.	Idealized Impedance Diagram of Coated Metal System with	
-	Coating Breaks and Equivalent Circuit Analog.	23
Figure 4.	ECR Bridge Sites.	29
Figure 5.	Widest Crack per Substructure Unit.	34
Figure 6.	Severe ECR Corrosion in Group 2 Bridges	35
Figure 7.	Epoxy Coating Thickness.	
Figure 8.	Open Circuit Potential Evaluation as Function of Elevation	
Figure 9.	Concrete Surface Resistivity as Function of Elevation	40
Figure 10.	Progress of Concrete Corrosion Damage as Function of Time.	46
Figure 11.	Chloride Penetration Profiles.	51
Figure 12.	Chloride Penetration Into the Side Walls of Cracks	52
Figure 13.	Comparison of Chloride Concentration Profiles with 10x and 100x	
U	Multiplier of D _{Ann} for Idealized Diffusion	54
Figure 14.	On crack Carbonation Testing	55
Figure 15.	Field-Extracted ECR Concrete Core EIS Test Set-Up.	58
Figure 16.	Concrete Surface Resistivity Comparison On and Off	
C	Crack. SSK High Elevation Trestle Caps	59
Figure 17.	Concrete Surface Resistivity Comparison On and Off	
C	Crack. HFB Footers.	59
Figure 18.	Solution Resistance Measured by EIS (SSK).	60
Figure 19.	ECR Impedance Manifestation of Presence of a Crack in the Core	61
Figure 20.	Pore Resistance in ECR from SSK Sound and	
C	Crack Concrete Locations.	62
Figure 21.	Concrete porosity.	63
Figure 22.	ECR Corrosion at Crack Location	64
Figure 23.	Cross Section of ECR Bar Showing Severe Corrosion at a	
-	Crack Location of HFB 59E1	65
Figure 24.	Corrosion product - Base Metal Interface Showing Progression of	
-	Corrosion Into the Microstructure of the Rebar Steel	65
Figure 25.	SEM Image of Corrosion Product (HFB59W1).	68
Figure 26.	SEM/EDS Analysis of Corrosion Product Obsverd in HFB59E1	
Figure 27.	External and Undercoating Corrosion Development in De-	
-	Aerated and Aerated Environments.	73
Figure 28.	Epoxy Coating Pull-Off Strength	76
Figure 29.	Impedance Manifestation of Disbondment.	79

Figure 30.	Comparison of Observed Coating Defects to Estimated Coating	
	Defects.	82
Figure 31.	Polarization Behavior of ECR from Supplemental Test Setup of ECR	
	Embedded in Concrete	83
Figure 32.	Estimated Apo as Function of Time after Initial Concrete Casting	83
Figure 33.	Pore Resistance and Concrete Resistivity as Function of Time	
	after Inital Cathodic Polarization	85
Figure 34.	Correlation of Yo and n for Coating CPE Component.	87
Figure 35.	Idealized Extended Circuit Analog Model Abstraction	88
Figure 36.	Detailed Schematic of Extended Circuit Model Abstraction	89
Figure 37.	Example Impedance Spectra for Extended Circuit Analog Model	
	Case A-F for ρ_B =300 k Ω -cm.	92
Figure 38.	Frequency Dispersion Quantified by Coating CPE n	
	Term for Idealized Extended Circuit Analog	92
Figure 39.	Yo-n Correlation from Idealized Extended Circuit Analog	
	Model EIS Analysis.	93
Figure 40.	Transmission Line Extended Circuit Analog Abstraction.	94
Figure 41.	Frequency Dispersion Quantified by Coating CPE n Term for	
	Truncated Transmission Line Extended Circuit Analog.	97
Figure 42.	Projected Damage Function for Group 1 Bridges	103
Figure 43.	Projected Damage Function for Group 2 Bridges	105
Figure 44.	Projected Damage Function for Group 3 Bridges	106
Figure 45.	Projected Damage Function for Group 4 Bridges	106
Figure 46.	Schematic of Idealized Model Geometry.	112
Figure 47.	Model Projections for the High, Nc=0.19m ⁻¹ and Low,	
	Nc=0.01m ⁻¹ Cracking Incidence Cases	117

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ABSTRACT

Epoxy-coated rebar (ECR) has been used in approximately 300 Florida bridges, in an attempt to control corrosion of the substructure in the splash-evaporation zone. Early severe ECR corrosion was observed in the substructure of several Florida ECR bridges (Group 1) where the substructure was built with permeable concrete of high apparent chloride diffusivity D_{App} . Other ECR bridges built during the same period and having similar D_{App} were projected to show corrosion damage starting on the following decade. Examination of several of those bridges (Group 2) confirmed that projection. Other recently examined Florida ECR bridges (Groups 3 and 4) were built with very low to moderate permeability concrete having correspondingly low to moderate D_{App} values at normally sound concrete locations. Those bridges were projected not to show early corrosion at normal locations and that projection has also been confirmed. However, some incidence of thin structural cracks exists affecting a small fraction of the substructure. Chloride transport there is much faster than through the matrix in otherwise low permeability concrete and work has confirmed that early corrosion can develop there.

A predictive ECR corrosion model was applied that replicated most of the damage function features observed in the field. The model divides the substructure in separate elements with individual chloride exposure, concrete permeability, concrete rebar cover, and extent of ECR coating imperfections. Additionally, a model for projecting impact of preexisting cracking on corrosion damage was developed. The projections indicate that relatively isolated cracking should only create topical concrete damage with reduced maintenance requirements. However, model projections indicated that even though assuming that the incidence of damage is limited to a small region around the crack, if the crack orientation with respect to the rebar were adverse and chloride transport were greatly enhanced (as it could be expected in relatively wide cracks), corrosion damage from localized concrete deficiencies could significantly increase maintenance costs.

Electrochemical Impedance Spectroscopy (EIS) measurements of ECR in extracted cores showed good potential for non destructive characterization of the extent of coating damage. A possible method accounting for frequency dispersion effects in the high frequency response (of importance to assess extent of defects) was introduced.

PART I

Part I provides background information on corrosion durability of building materials for civil infrastructure, identifies corrosion of epoxy coated reinforcement in locally deficient concrete as the focus of this investigation and establishes research tasks.

1.1. Introduction

Reinforced concrete has been widely used in modern construction of civil infrastructure as it combines the mechanical resistance of concrete under compressive loads and steel reinforcement under tensile loads. In non-severe environments, reinforced concrete is known to have long service lives with minimal maintenance requirements. In severe environments however, with exposure to chlorides, carbon dioxide, sulfates, certain alkalis, and frost for example, concrete deterioration can occur with subsequent consequences on the serviceability of the structure. In the presence of chloride ions or carbonation of concrete pore water from atmospheric carbon dioxide, corrosion of the steel reinforcement can initiate. Reinforcing bars are normally made of hypoeutectoid plain carbon steel (ASTM A615M-09b, 2009), where iron constitutes >97% of the material. The iron corrosion product is larger in volume than the originating metal, creating expansive stresses in the surrounding hardened concrete. Given the low resistance of the latter to tensile stresses (Mindess et al., 2003), damage in the structure ensues in the form of cracking, delamination, and spalling of the concrete (Figure 1).



Figure 1. Large Concrete Spall Exposing Corroding Steel Reinforcement. Channel 2, Florida Keys (Photograph by author).

Loss of steel cross section and concrete integrity degrades the strength and serviceability of the structure. Corrosion of steel reinforcement is among deterioration mechanisms of particular interest due to high cost of remediation and repair. The cost of all forms of corrosion in the United States is approximately 3% of the gross national product with similar estimates in other developed countries. In particular, approximately \$8.3 billion in direct costs is spent annually for highway bridges in the United States with estimated indirect costs as much as ten times that amount (Materials Performance, 2002). Corrosion control for Florida bridges is of particular importance in this study due to the large number of bridges in aggressive marine environments and the investment associated with design, construction and maintenance of them. In Florida, 12% of the state budget is spent on transportation and approximately \$300 million is spent annually for bridge construction with additional yearly maintenance costs (People's Budget, 2008). A large cost would be associated for repair, rehabilitation or replacement if bridges falls short of their design life, presently 75 years, due to corrosion damage. There is need to improve design to control corrosion and to be able to assess future maintenance requirements. 1.1.1 Concrete as a Medium in the Corrosion Process of Steel Reinforcement

Concrete is a heterogeneous composite material consisting of coarse and fine aggregates that act as bulk filling material held together by hardened hydraulic cement binder. Chemical admixtures and cement replacement materials can be present as well.

Chemical Name	Chemical Formula	Shorthand Notation
Tricalcium Silicate	$3CaO \cdot SiO_2$	C ₃ S
Dicalcium Silicate	$2CaO \bullet SiO_2$	C_2S
Tricalcium Aluminate	$3CaO \bullet Al_2O_3$	C ₃ A
Tetracalcium aluminoferrite	$4CaO \bullet Al_2O_3 \bullet Fe_2O_3$	C ₄ AF
Calcium Sulfate Dihydrate	CaSO ₄ •2H ₂ O	$C\overline{S}H_2$

Table 1. Typical Composition of Ordinary Portland Cement (after Mindess et al., 2003)

Cement hydration results in solid cement paste that binds the aggregates. The most commonly used cement is *ordinary portland cement*, OPC, with typical components listed in Table 1. The rate of hydration and the type of hydration products of these components differ and thus cement properties can be controlled by varying proportions of each component (Mindess et al., 2003). Ordinary portland cement typically contains >70% C₃S and C₂S by weight and their hydration products consists of calcium hydroxide and calcium silicate hydrate, designated as C3S2H8 or C-S-H -the exact stochiometric makeup of the compound is not well defined. Other hydrates from the other OPC components can form as well. For brevity only the main constituent of the cement hydration products, C-S-H is further discussed. C-S-H is considered to have a porous layered structure with interlayer pores, gel pores, and capillary pores that can contain pore solution. The interlayer and gel pores are intrinsic to C-S-H and the larger capillary pores are the void spaces between hydrated cement grains (Mindess et al., 2003). The structure of the hydrated cement continues to densify with time. However, cements with a higher water-to-cement, w/c, ratio tend to be more permeable as less cementitious material is present and more numerous capillary pores >10nm diameter form (Bentur et al., 1997). Diffusion of dissolved species occurs mostly through water present in the

larger capillary pores, thus the effective diffusivity of such species tends to be larger for concretes with higher w/c.

Use of pozzolanic cement replacement admixtures, such as *fly ash* and *silica fume*, also called *microsilica* (Hooton et a., 1997), can further decrease concrete permeability. Silica from these pozzolans reacts with calcium hydroxide mostly available from hydration of C_3S and C_2S to form additional C-S-H. The hydration rate of fly ash is slow and requires sufficient amounts of calcium hydroxide. Thus the hydration products that form occur much later than that of cement and typically forms in pore spaces further densifying the concrete (Bentur et al., 1997). Similarly, due to the significantly smaller grain size of silica fume than OPC, hydration of silica fume creates finer pore structures (Bohni, 2005). The pozzolanic reaction products eventually decrease -often to a great extent- the interconnectivity of the concrete pore network.

Less permeable concrete mitigates corrosion of steel reinforcement in various ways. A low permeability concrete decreases the rate of transport of aggressive chemical species such as chloride ions from the external concrete surface to the steel, thus delaying the initiation of corrosion. For a given water content, a denser concrete has larger electrical resistivity that will impede transport of dissoloved ions required for the corrosion process. Additionally, larger electrical resistivity reduces the extent of macrocell coupling of anodic and cathodic sites thus mitigating possible enhanced corrosion activity due to galvanic area effects (Fontana and Greene, 1986).

Upon cement hydration, the pore water solution that is contained in the cement pore network typically contains high concentrations of alkalis such as Na⁺ and K⁺ as well as hydroxyl ions OH⁻. Other ions such as Ca²⁺ also exist in the pore water solution to lesser extents. The exact pH of the pore water solution depends on the concrete mix and service environment, but the pH in non-severe environments is typically ~13 (Bentur et al., 1997; Mindess et al., 2003).

1.1.2 Chloride Induced Corrosion Degradation of Reinforced Concrete Structures

Steel embedded in concrete with highly alkaline pore water becomes immune to corrosion by forming a protective passivating oxide layer; however, processes such as carbonation of the pore solution by atmospheric carbon dioxide CO₂ and contamination with a critical concentration of ions such as chlorides may disrupt this *passive layer* and support corrosion initiation. In bridge service environments such as in bridge decks exposed to de-icing salts and in marine bridges, chloride induced corrosion is the key deterioration mechanism. The corrosion deterioration process of these structures can be viewed in two stages: corrosion initiation and propagation (Tuuti, 1982).

1.1.2.1 Corrosion Initiation

In the corrosion *initiation stage*, chloride ions are transported through the concrete to the steel surface until a critical chloride concentration C_T at the steel surface is reached and the passive layer is disrupted allowing active corrosion to ensue. The length of the initiation stage can be estimated by determining the value of time t at which chloride concentration C at the steel surface equals C_T . The exact concentration needed to depassivate the steel protective layer is not well known and in part due to uncertainty in the chemical process, wide variation of test conditions in research, and the poor definition of C_T in concrete (Angst et al., 2009). C_T has been expressed as a fixed quantity or as function of pore water solution pH. C_T has also been expressed as only the concentration dissolved in the pore water, free chloride, or also as the total chloride content including chloride ions that may be bound to the cement hydrate products or reacted with components such as tricalcium aluminate C_3A (Glass et al., 1996).

However, considering only the free chloride content to specify C_T may be risky as other processes may cause the release of bound chlorides and contribute to the depassivation of steel. For conservative purposes, it may be advisable to express C_T in terms of the total chloride content. Since the cement is the source of the species, alkali and Ca ions, that promote high pH and a stable passive film on steel, it is customary to express C_T as a percentage of the cement -or cementitious with appropriate correctioncontent of the concrete. However, for simplicity C_T is often simply expressed as a percentage of the total cement mass or in terms of chloride mass per unit concrete volume.

In the review by Angst et al., 2009, $C_T \sim 0.15\%$ as total chloride by weight of cement was among the most conservative estimates for steel in concrete and is consistent with a value of 0.7kg/m^3 often considered as a conservative C_T value for concretes with a typical cement factor, e.g.~400 kg/m³. Field evidence suggests that $C_T > 0.4\%$ of the cement factor may be characteristic for marine substructure (Sagüés, 2001; Bamforth, 1999; Papadakis and Tsimas, 2002)

Chloride transport in sound -that is, free of cracks and other local deficienciesconcrete is a complex process but in the structures considered here it approximately behaves as a diffusional process, at least starting at a short distance from the external surface (Bohni, 2005). Treating concrete for simplicity as a homogeneous medium addressing a spatial scale larger than the aggregate size- an apparent Cl⁻ diffusion coefficient D_{App} may be defined such that for one-dimensional transport and with chloride concentration, C, time t and depth x inside the concrete Fick's second law of diffusion applies (Crank, 1975).

$$\frac{\partial \mathbf{C}}{\partial t} = \frac{\partial}{\partial \mathbf{x}} \left(\mathbf{D}_{\mathrm{App}} \frac{\partial \mathbf{C}}{\partial \mathbf{x}} \right) \tag{Eq. 1}$$

The concentration C at a given depth is understood to be also locally averaged over a lateral scale greater than the aggregate size (Yu and Hartt, 2007). Assuming that concrete properties don't vary much from the external surface into the bulk, D_{App} may be considered to be spatially independent so Eq. (2) applies.

$$\frac{\partial C}{\partial t} = D_{App} \frac{\partial^2 C}{\partial x^2}$$
(Eq. 2)

The solution to Equation 2 is determined by the appropriate boundary conditions. Assuming space and time invariant diffusivity D_{App} and constant chloride surface concentration C_s the following initial and boundary conditions and solution apply (Crank, 1975).

$$\begin{split} C &= C_s & \quad \text{for } x = 0 \text{ and } t \geq 0 \\ C &= C_o & \quad \text{for } x > 0 \text{ and } t = 0 \end{split}$$

$$C(x,t) = C_{s} - (C_{s}-C_{o}) \operatorname{erf}\left(\frac{x}{2\sqrt{D_{App}t}}\right)$$
(Eq. 3)

For concrete bridges, these assumptions may not wholly describe actual material and service conditions. However, equation 3 does represent a reasonable working approximation in many marine concrete bridge cases particularly those with longer service times where concrete hydration is expected to be mature (Poulsen and Mejlbro, 2006). D_{App} for typical conventional concrete mixes range from 10^{-7} to 10^{-9} cm²/s. For marine bridges, the concrete chloride surface concentration can be high in the splash zone due to evaporative accumulation of chlorides as the concrete is intermittently submerged and dried due to changing tidal levels (Bertolini et al., 2003). That condition results in near chloride saturation of the pore water in the concrete surface In field studies of marine bridges by Sagüés et al., 2001; and Lau et al., 2007, C_s in the evaporative splash zone was of the same order (~20kg/m³) for several bridges even though the water chloride content ranged from 5,000 to 25,000 ppm.

Chloride diffusivity may be time dependent due to concrete hydration and differential curing of pozzolans if present (Nilsson and Olliver, 1997); the value of D_{App} is a strong function of the connectivity of the pore network, the moisture content of the pores, and temperature. The latter two may be on first approximation considered to be constant and equal to their average values through seasonal cycles. The pore network matures and becomes less interconnected as concrete ages so the value of D_{App} tends to be smaller as time progresses. This effect has been noted particularly in the case of fly-

ash cement replacement where the pozzolanic reaction has a relatively slow rate. Thomas and Bamforth, 1999 has proposed that the time-averaged value of D_{App} for fly ash concretes with age t follows an expression:

$$\mathbf{D}_{\mathrm{App},t} = \mathbf{D}_{\mathrm{App},28} \left(\frac{\mathbf{t}_{28}}{\mathbf{t}}\right)^{\mathrm{m}}$$
(Eq. 4)

where $D_{App,t}$ and $D_{App,28}$ are the apparent diffusion coefficient at time t and 28 days t_{28} , respectively with m~0.7.

Bridge decks cyclically exposed to deicing salts would have a time dependent surface chloride concentration and equation 3 may not well represent the chloride penetration profile there. The cyclic chloride exposure has been represented as a square-wave function by Bentz et al., 1996. Poulsen and Meljbro, 2006 give a solution to this diffusion equation by representing surface chloride concentration by means of the Heaviside function. D_{App} here is also assumed to be time and spatially constant. A summary of their derivation follows.

The first deicing cycle is on time $t_0 \le t < t_1$ and resumes on $t_2 \le t < t_3$ and continues until time $t_n \le t < t_{n+1}$. A deicing/relaxation period is repeated where $t_{n+2}=t_n+12$ months. During deicing periods, the surface chloride concentration $C_s = Cs'$. Before t_0 and in the intermediate time periods, C_s is effectively 0.

The heaviside function is given as

$$H(t-t_j) = \begin{cases} 0 & \text{for } t < t_j \\ 1 & \text{for } t \ge t_j \end{cases}$$
(Eq. 5)

Initial and boundary conditions to Equation 2 include :

$$\begin{split} & C = 0 & \text{for } x = 0 \text{ and } 0 \leq t < t_0 \\ & C = C_{s'} \; x \; \sum_{j=0}^n (-1)^{\; j} \; x \; H \; (t\text{-}t_j) & \text{for } x = 0 \text{ and } t_n \leq t < t_{n+1} \\ & C = C_o & \text{for } x > 0 \text{ and } t = 0 \end{split}$$

The chloride penetration profile can be expressed as

$$C(x,t) = C_{s'} \sum_{j=0}^{n} (-1)^{j} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{App}(t-t_{j})}}\right) \text{ for } t_{j} \le t < t_{j+1}$$
(Eq. 6)

The chloride profile obtained by this diffusion equation gives a depression in chloride concentration at the near surface of the concrete which is often observed in field chloride penetration profiles.

Of particular interest is the transport of chloride ions through pre-existing concrete cracks. Sagüés et al., 2001 examined chloride penetration through cracked concrete in several concrete marine substructures. Thin cracks were typical features with crack incidence observed every several meters of waterline perimeter. Substantial preferential chloride penetration through cracks, especially in tidal areas, was observed with chloride concentrations typically greater than C_T at reinforcement depths. Win et al., 2004 showed by Electron Probe Microanalysis that cracked reinforced concrete samples with low water to cement ratio, w/c=0.25, had more shallow chloride penetration depths both from the exposed surface and around the crack than compared to w/c=0.65. Transport of bulk solution and chloride ions there can occur not only by diffusion but also by capillary suction. Similarly, studies by Jaffer and Hansson, 2008 and Djerbi et al., 2008 showed similar results of chloride transport through cracks in comparison of high performance concrete to OPC.

Edvardsen (Nilsson and Ollivier, 1997) discusses chloride transport by water flow through cracked concrete by modification of Poiseuille law.

$$q = \Delta p b w^3 / (12 \eta d) \xi$$
 (Eq. 7)

where q is water flow $[m^3/s]$, Δp is the differential water pressure $[N/m^2]$, b is the crack length [m], w is the crack width [m], d is the crack depth [m], η is viscosity [Pa], and ξ is a reduction factor to account for crack wall surface roughness.

Chloride transport through cracks was modeled by Kranc and Sagüés (Sagüés et al., 2001) assuming simple diffusion and rectilinear crack geometry. Ignoring chloride binding for brevity of review, chloride transport can be formulated as

$$\frac{\partial C_{c}}{\partial t} = D_{o} \frac{\partial^{2} C_{c}}{\partial y^{2}} + D \frac{\partial C}{W \partial x} \Big|_{+} + D \frac{\partial C}{W \partial x} \Big|_{-}$$
(Eq. 8)

where C_c is the chloride concentration in the crack, C is the chloride concentration in the concrete pore water, D_o is the chloride diffusivity in free water, D is the chloride diffusivity in concrete, w is the crack width and +/- represents flux into both side walls of the crack. In the system, chloride diffusion through sound concrete portion of the outer face –formulated as the time rate of change of chloride concentration given similar treatment as Equation 1- was simultaneously solved by setting the chloride concentration in the pore water adjacent to the crack equal with the concentration in the crack. Model calculations showed that there could be greater chloride transport for wider cracks and greater chloride accumulation at specific depths for more shallow crack permeation.

Ishida et al., 2009 discusses modeling of chloride transport though cracked concrete as a distribution of macro-scale pores in a control volume -that can represent the scale of concrete crack geometry- as well as smaller scale pores representing gel and capillary pore spaces as described earlier. Generally, if chloride binding can be ignored for brevity in review of their derivation, chloride transport can be formulated as

$$\frac{\partial}{\partial t} (\Phi SC_{Cl}) + \text{div } J_{Cl} = 0$$
(Eq. 9)

where Φ is the volume fraction of pore space, S is the degree of saturation, C_{Cl} is the chloride ion concentration and J_{Cl} is the flux of chloride ions. The first term represents the rate of change of chloride ion concentration in pore spaces which can act as transport paths and the second term represents the flux of chloride ions. In consideration of crack presence, chloride transport is separated for sound and crack concrete; the chloride flux is formulated as:

$$J_{Cl} = -\left(\frac{\Phi S}{\Omega}\delta D_{Cl} + \zeta \frac{\Phi_{cr}S_{cr}}{\Omega_{cr}}\delta_{cr}D_{Cl}\right)\nabla C_{Cl}$$
(Eq. 10)

where δ and Ω are transport reduction factors due to constriction and tortuosity of the pore network, either mesoscopic pores in hydrated cement or macroscopic cracking. The first term in the bracket represents flux through gel and capillary pore space in sound concrete and the second term in the bracket represents flux through the crack. D_{Cl} represents chloride diffusivity in solution and the apparent chloride diffusivity in concrete is appropriately modified in the equation. An additional modifier ζ is placed for chloride transport through the crack to accommodate convection in the crack.

More sophisticated treatments could also include other transport mechanisms such as permeation from pressure gradients and capillary action inside the cement hydrated paste (Delagrave et al., 1997), as well as the effect of chloride ion binding on hydrated cementitious chemical species (Glass et al., 1996).

1.1.2.2 Corrosion Propagation

In the corrosion *propagation stage*, active corrosion ensues until physical manifestation of concrete deterioration in the form of cracks, spalls, or delamination appears. The length of the propagation stage depends on the rate of corrosion, system geometry, and corrosion localization (Torres-Acosta and Sagüés, 2004). The duration of the propagation stage can be estimated by either a fixed value representative of field

experience (Ramniceanu et al., 2008), or by calculation of how long it takes for corrosion at a given rate to consume enough steel to reach a critical buildup of corrosion products that cause internal stresses to crack concrete (Torres-Acosta and Sagüés, 2004).

1.1.3 Corrosion Control Strategies

Several strategies have been implemented in recent decades in newly constructed structures to control chloride-induced reinforcement corrosion, particularly by extending the time necessary for chloride ions to diffuse through the concrete and to depassivate the steel surface. Strategies include the use of advanced concrete formulation including the use of pozzolanic materials to reduce concrete permeability, changing bridge design specifications, e.g. concrete cover depth, to increase diffusional length of chlorides to the steel surface, and choice of reinforcement material including galvanized and stainless steel —to increase the critical concentration for initiation of corrosion— and epoxy polymer coated reinforcement.

1.1.4 Epoxy-Coated Steel Reinforcement

Epoxy polymer coatings act as a physical barrier to moisture and the accumulation of chloride ions at the steel surface. Epoxy coated reinforcement, ECR, is manufactured by a fusion bonded technique where thermosetting resins, cross-linking agents, and other additives are applied in powder form to an abrasive blasted steel substrate and heated until a continuous coating is formed on the bar (ASTM A775, 2004). ECR typically costs only about 30% more than plain steel so it is relatively inexpensive compared to other corrosion control methods, and has been widely used in the United States in the last few decades, particularly in bridge decks in deicing salt service — involving some 60,000 bridges (Sagüés and Lee, tbp). However, the effectiveness of its use in marine reinforced concrete substructures is in question as will be shown later. Of particular interest is the corrosion performance of ECR with the presence of local concrete deficiencies such as preexisting structural cracks from loading and concrete shrinkage.

The corrosion process for ECR is thought to begin with initial coating imperfections within quality guidelines during fabrication and bridge construction. Initial coating disbondment may occur during storage in the construction yard due to exposure to moisture and salt water. During initial service in hardened concrete, interaction of the metal-coating interface with constituents of concrete pore water at coating breaks and disbonded regions causes further coating disbondment. Upon arrival of chloride ions to the steel surface with adequate oxygen permeation, crevice corrosion occurs under disbonded regions. Such sequence implies that the corrosion mechanism of ECR involves the disbondment of coating from the steel substrate as an initial required stage (Clear, 1992; Sagüés, 1994; Weyers and Sprinkel, 1997).

Separation of the polymer coating from the steel substrate before significant anodic corrosion activity is caused by several different mechanisms. Water uptake —as much as ~2% in the epoxy coating— causes adhesion loss as the tendency of water to bond to steel oxide surface is greater than that of epoxy hydroxyls to steel oxide surfaces (Nguyen and Martin, 2004). The process is reversible upon drying if other disbondment processes are not involved. Cathodic delamination occurs at corrosion cathodic reactions sites —described in next section— particularly in the presence of Na⁺ (Sagüés, 1994; Nguyen and Martin, 1996; 2004). Proposed mechanisms include dissolution of iron oxide, polymer alkaline hydrolysis, and coating displacement by alkaline water (Nguyen and Martin, 1996; 2004).

Performance studies of ECR have been conducted over the last 30 years (Clear, 1992; Sagüés, 1994; Weyers and Sprinkel, 1997; Weyers et al., 2006; Griffith and Laylor, 1999; Fanous and Wu, 2005; Yeomans, 1993; Covino et al., 2000, Cui et al., 2007; Darwin and Scantlebury, 2002). In depth reviews of field investigations were written by Hansson et al., 2000 and Clear, 1995 so for brevity, only major findings from recent investigations will be discussed here.

Investigations on ECR corrosion durability in bridge decks in Canada, Virgina, Ohio, Iowa, Indiana, Utah, New York, and Pennsylvania have with some exceptions reported, in general, good performance. Less information concerning ECR durability in marine concrete substructures is available in the literature, but there has been reported some supporting field performance observations on the beneficial use of ECR to extend bridge service life in Georgia and North Carolina. However in marine bridges in Oregon, Virginia, Georgia, and Florida, significant to severe early corrosion development has been observed.

It is noted that the advent of ECR in the late 1970s coincided with improved construction standards and the use of higher quality concrete for bridge decks. It is also noted that in some investigations, the service times were not long, <20 years, and chloride contents at reinforcement depths were below conservative C_T estimates. As such, in general, field performance of ECR available in the literature showing relatively good performance can be argued to be inconclusive.

Investigations consistently showed extended coating disbondment regardless of corrosion activity and ECR corrosion was mostly observed in areas with poor construction practice such as locations with low concrete cover or damaged epoxy coatings. For these reasons, advocates for use of ECR argue that structures in chloride environments can have extended service life if proper construction and material quality assurance can be provided.

Other factors that may be responsible for differences in field results include service environment, presence of concrete cracks, and concrete permeability. A key difference in service environment includes how chloride ions reach the structures. In bridge decks exposed to deicing salts, chloride ions are only applied for a few months of the year and chlorides at the surface of the concrete may be washed out in the remaining months. Marine bridges instead have a constant source of chloride ions from sea spray with accumulation due to cyclic wetting and drying at the splash zone. The degree of salinity may also be a contributing factor to the difference in performance, but there is evidence that a high and roughly constant value of concrete surface chloride concentration is often reached under most conditions due to saturation of pore water (Sagüés et al., 2001; Lau et al., 2007).

Cracks in concrete can act as fast channels for chloride intrusion, as introduced earlier, more notably so in relative terms if the bulk concrete has low permeability. Moreover, some modern low permeability concrete formulations may be susceptible to cracking due to complex curing requirements. Studies have been made on the transport of chloride ions through cracks including ECR field corrosion evaluations (Weyers and Sprinkel, 1997; Fanous and Wu, 2005; Sagüés et al., 2001; Lindquist et al., 2005; Jaffer and Hansson, 2008). Bridge decks with cracked concrete in Virginia have not been shown to have any significant reduction in bridge service life (Weyers and Sprinkel, 1997). In contrast, evidence of significant corrosion of ECR in cracked concrete bridge decks was reported by Clear, 1992. Evidence of enhanced chloride penetration at cracks was reported in Florida marine ECR bridges by Sagüés et al., 2001, but information on ECR durability in such environments is still limited.

The most notable cases of corrosion of ECR in marine environments concerns early corrosion initiation of five Florida ECR marine bridges built with highly permeable concrete, with chloride diffusivity in the order of $D_{App}=10^{-7}$ cm²/s. Those bridges include Niles Channel, Seven-Mile, and Long Key bridges in the Florida Keys (Sagüés et al., 1994). Initial corrosion prediction models projected corrosion initiation at later dates for other Florida marine bridges, including those with newer concrete formulations resulting in dramatically lower values of D_{App} , e.g. $D_{App} = 10^{-9}$ cm²/s— with lower water to cement ratio and with pozzolanic cement replacement such as fly ash and silica fume. Bridges with pozzolanic additions typically have not only lower permeability, but it also tends to further decrease in time as the concrete continues to hydrate (Thomas and Bamforth, 1999). Florida marine bridges with these additions and others with lower permeability concretes did not show corrosion initiation at the time of earlier investigations (Sagüés et al., 1994) as chloride concentrations at steel cover depths for sound concrete were found to be largely still below critical threshold level. In general however, information on ECR condition in marine bridges with low to medium permeability and long service times is limited. Assessment methodologies involving not only direct examination but also reliable non-destructive electrochemical methods are commonly used in field investigations but their development is until now limited.

1.1.5 Electrochemical Aspects

The corrosion kinetics of steel in concrete has been studied extensively (Bentur et al., 1997; Bertolini et al., 2003; Broomfield, 1997). Corrosion of steel involves electrochemical reactions including the oxidation of iron (Eq. 11) and typically the reduction of atmospheric oxygen (Eq. 12).

$$\operatorname{Fe}(s) \to \operatorname{Fe}^{2^{+}}(aq) + 2e^{-} \tag{Eq. 11}$$

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$
(Eq. 12)

The electrochemical cell for corroding steel in concrete comprises of anodic sites on the steel reinforcement, cathodic sites on neighboring steel surface locations, and concrete pore water electrolyte in cement pores. Electronic transport between anodic and cathodic sites is made by electrical continuity of the steel reinforcement assembly, and ionic transport occurs in the concrete pore water electrolyte.

In non-severe environments, the steel in concrete is protected from corrosion because steel forms a protective passive oxide layer in the highly alkaline concrete pore water solution typically with pH~13 (Bentur et al., 1997). The passive layer of iron can be in the form of ferrous hydroxide, ferric hydroxide, oxyhydroxides, and other species from the electrolyte such as salts. (Bertolini et al., 2003; Cornell and Schwertmann, 2003; Pourbaix, 1974). The passive layer, only nanometers in thickness, has been suggested to consist of two layers with an Fe^{II} oxide inner layer and an Fe^{III} outer layer (Cornell and Schwertmann, 2003). The development of the passive layer generally as γ -FeOOH following initial iron dissolution in Equation 11 is as follows (Bentur et al., 1997):

$$\operatorname{Fe}^{2^{+}}(aq) + 2\operatorname{OH}^{-}(aq) \to \operatorname{Fe}(\operatorname{OH})_{2}(s)$$
(Eq. 13)

$$Fe(OH)_2(s) + O_2(g) \rightarrow \gamma \text{-FeOOH}(s) + H_2O(l)$$
(Eq. 14)

In the presence of a critical concentration of chloride ions, the stability of the passive layer is disrupted and active corrosion can ensue. Chloride ions react with ferrous hydroxide:

$$Fe(OH)_2(s) + Cl^{-}(aq) \rightarrow [FeCl]_x(aq)$$
(Eq. 15)

that competes with formation or regeneration of the passive layer (Bentur et al., 1997). In the case of carbonation, atmospheric carbon dioxide reacts with concrete calcium hydroxide and calcium-silicate-hydrate hydration products and the pore water solution resulting in a drop of pore water pH and consequently depassivation of the steel (Bentur et al., 1997).

The corrosion mechanism for ECR likely involves crevice corrosion under disbonded epoxy coating locations as described above. Under the disbonded regions, oxygen is depleted due to transport limitations to the crevice, but anodic dissolution continues as cathodic sites remain at local defect sites. Chloride ion concentration increases in the crevice to balance electro-neutrality. Hydrolysis of iron chlorides forms iron hydroxides and lowers the pH inside the crevice (Fontana and Greene, 1986) as described in Equation 16 for a generic metal M.

$$M^{+}Cl^{-}(aq) + H_{2}O(l) = MOH \downarrow + H^{+}Cl^{-}(aq)$$
(Eq. 16)

For iron, the reaction is as shown in Equation 17.

$$\operatorname{Fe}^{2+}(aq) + 2\operatorname{H}_{2}\operatorname{O}(l) + 2\operatorname{Cl}^{-}(aq) \to \operatorname{Fe}(\operatorname{OH})_{2}(s) + 2\operatorname{HCl}(aq) \qquad (\text{Eq. 17})$$

Continual metal dissolution within the crevice causes additional migration of chloride ions resulting in an autocatalytic corrosion process.

Information on the identification of ECR undercoating corrosion product that formed in field service is among details where there is a shortcoming in the current literature. In typical crevice conditions, acidification of solution within the crevice can occur, and undercoating moisture in ECR has been measured to have pH<5 (Nguyen and Martin, 1996; Sagüés et al., 1991). In this environment, solid corrosion products such as $Fe(OH)_2$ and Fe_3O_4 are not thermodynamically stable (Pourbaix, 1974) yet magnetite, Fe_3O_4 and ferrous hydroxide $Fe(OH)_2$ has been observed under disbonded epoxy coating (Singh and Ghosh, 2005; Kahhaleh et al., 1998). This may in part explain observations of corrosion product precipitation at or near coating defects where there could be some exchange with external concrete pore solution or due to local alkalinization outside the crevice where cathodic reactions can occur. Also, the presence of chloride ions in the morphology of precipitated corrosion product is not well documented. Hydrated $FeCl_2 \cdot H_2O$ is thought to form at anodic sites by the following reaction (Nguyen and Martin, 1996):

$$Fe^{2^+}(aq) + 2Cl^-(aq) + 4H_2O(l) \rightarrow FeCl_2(s) + 4H_2O(l)$$
 (Eq. 18)

The presence of chloride ions also causes formation of stable chlorocomplex corrosion products such as *green rust* containing mixed iron valencies Fe^{2+} , Fe^{3+} , and Cl^{-} ions. This compound can form even in anoxic conditions and within a wide pH range ~5-12 (Sagoe-Crentsil and Glasser, 1993; Refait et al., 1997; 1998; 2003; Scott and Eggert, 2009).

The presence of low oxidation state iron oxides is consistent with a low oxygen environment (Singh and Ghosh, 2005; Sagüés et al., 1991; Kahhaleh et al., 1998), and oxygen can be transport limited to formed crevices. Other higher oxidation state oxides may also form if oxygen becomes available due to extensive epoxy coating disbondment, blistering and other modes of degradation. X-ray diffraction studies by Singh and Ghosh, 2005 suggest that chloride substituted akaganeite β -FeOOH may also be among possible corrosion product morphology in ECR. Sagoe-Crentsil and Glasser, 1993 and Refait, 1997 also suggest that upon oxygen availability, green rust would oxidize to akaganeite but in the process would liberate some chloride ions and exacerbate further formation of green rust.

1.1.6 Electrochemical Measurement of Steel Corrosion in Concrete

For corroding steel in oxygen aerated systems, reactions shown in Eq. 11 and 12 occur simultaneously on the steel surface. As a result, the corrosion system has a mixed potential of both reactions in between the equilibrium potentials of each reaction (Piron, 1994). This open-circuit potential, OCP, is typically quite negative compared to that of passive steel. ASTM had established criteria for interpretation of OCP where potentials more negative than -350 mV in the copper/copper-sulfate electrode scale were empirically established to define a high risk of corrosion (ASTM C876, 2009). Interpretation of OCP in actual reinforced concrete in moist environments is complicated where there is limited oxygen availability, especially in wet concrete where oxygen transport through the saturated pore network is slow. In such case, concentration *polarization* will result in similarly negative potentials indicative of active corrosion even with the absence of corrosion initiation. Also, for epoxy-coated reinforcement, the polymer layer —in the absence of coating defects— acts as an electrical insulator on the metal surface from the electrolyte. Other complications that may be present in field measurements of reinforced concrete structures include ohmic *IR drop*, *junction potential*, and temperature effects among others (Dimond and Ansuini, 2005). These effects may lead to erroneous interpretation of OCP measurement and the corrosion condition of the steel reinforcement.

Concrete resistivity measurements have shown good correlation to corrosion risk of reinforced concrete structures where larger concrete resistivity typically corresponds cases of low corrosion rates for reasons explained earlier (Carino, 1999; Broomfield, 1997). Complications in field measurement interpretation include electrical interference with underlying steel reinforcement, concrete surface carbonation, and concrete surface drying (Broomfield, 1997). Concrete resistivity can be measured on extracted concrete cores in controlled conditions with appropriate geometric corrections (Morris et al., 1996).

Corroding systems can be characterized also by artificially altering the potential of the metallic component from its OCP by a small amount, and measuring the amount of electric current needed for the potential change. The *polarization resistance*, Rp, of a corrosion system is defined as the ratio of that change in potential to the amount of required current, at the limit of very small changes (Vetter, 1967). This ratio Rp is found to be mostly a simple function of the corrosion rate expressed by Faradaic conversion (Fontana and Greene, 1986) in terms of current density, i_{corr}, by

$$I_{corr} = \frac{B}{Rp}$$
(Eq. 19)

where B is a function of the polarization characteristics of the cathodic and anodic reactions. In many systems a practical estimate of the corrosion rate from Rp measurements can be made by using the value B~0.026 V. For ECR in concrete structures, corrosion rate estimates from electrochemical techniques to measure polarization resistance such as *linear polarization resistance*, LPR, are complicated due to coating electrical insulation, unknown exposed steel area, and other current confinement issues (Broomfield, 1997).

Electrochemical impedance spectroscopy, EIS, is a measurement technique that can be used to examine electrochemical properties of corrosion systems. EIS offers a non-destructive method that may provide insight on coating and metal surface reaction parameters for ECR systems. The impedance behavior of electrochemical systems, measured as function of frequency of a small sinusoidal signal perturbation, is due to system physical and chemical properties, processes, and reaction rates. Similar to other electrochemical measurement techniques, EIS is measured with a 3-electrode configuration cell. The working electrode is the sample being measured. Electrochemical behavior here is typically associated with surface and interface processes. The potentiostat for EIS measurements maintains the desired levels of polarization of the working electrode with respect to the reference electrode. The counter electrode completes the electrical circuit and is ideally placed for unifrom excitation current distribution to the working electrode. The measured impedance spectra for a range of signal frequencies is interpreted as that corresponding to an electrical analog to possible physico-electrochemical properties and processes in the corrosion system (Barsoukov and Macdonald, 2005). For corrosion systems, the metal and solution interface of the working electrode consists of a *double layer capacitance*, C_{dl}, -due to separation of charge in the inner surface of the metal interface and orientation of charged ions in solution- and polarization resistance as described earlier. The *solution resistance*, Rs, is measured as the high frequency limit of the electrical resistance of the electrolytic medium between the working and reference electrode.



Figure 2. EIS Equivalent Circuit Analogs

These electical analog components among others are combined to characterize *equivalent circuit analogs* to corrosion system properties and processes, but its interpretation must be made with careful consideration of possible actual physicoelectrochemical processes and not with data fitting to the impedance spectra alone. Other complications are involved in EIS interpretation and pertinent discussions are later presented. For a simple ideal corrosion system, the *Randles circuit*, Figure 2a, is often used, with Rs, C_{dl}, and Rp as described earlier. For ideal coated metal systems of finite porosity coatings, the equivalent circuit in Figure 2b is commonly used where C_C represents the capacitive behavior of the polymer coating and Rpo is the resistance through pores in the polymer coating (Agarwal et al., 1992). The equivalent circuit in Figure 2c incorporates a diffusional impedance element with separate branches for cathodic and anodic processes (Sagüés, 1988; Lau and Sagüés, 2009; Agarwal et al., 1992) where Ra_A is the polarization resistance of the activation limited component of the anodic process, RcA is the corresponding component of the cathodic process, and W represents the cathodic diffusional impedance. This listing is by no means meant to be an exhaustive review of possible equivalent circuit analogs but rather a general view of how

equivalent circuit analogs are used to describe impedance spectra of corrosion systems. The total system impedance in terms of equivalent circuit analogs is the combined electrical impedance of the electrical analog components. As an example, the impedance of an ideal capacitor Z_C is frequency dependent and formulated as $Z_C=1/j\omega C$ where j is the imaginary number, ω is the angular frequency and C is the capacitance.



Figure 3. Idealized Impedance Diagram of Coated Metal System with Coating Breaks and Equivalent Circuit Analog.

Impedance behavior of ECR embedded in concrete can be modeled by a similar analog of coated metal with coating breaks, depicted in Figure 3, as that described above. The system in Figure 3 is regarded as a partially blocked electrode (Orazen and Tribollet, 2008). At the metal interface within the defect or pore, the impedance is similar to that of a corroding metal as discussed earlier. Within the defect pore space, the electrolyte resistance is given as Rpo. In parallel to the impedance of the pore, the coating has capacitive behavior given by C_c . The impedance response diagram in the figure is of an idealized case. For non-ideal behavior, due to surface heterogeneity or distributed charge-transfer reactivity for example (Orazem and Tribollet, 2008), the impedance of the epoxy

coating and metal-solution interfacial capacitive behavior can be represented by *constant phase elements*, CPE, with admittance

$$1/Z_{CPE} = Y_o(j\omega)^n$$
 (Eq. 23)

where Y_o is the pre-exponential admittance term, ω is the angular frequency, and n is a real number 0<n<1. The total impedance for the equivalent circuit analog shown in Figure 3 is given in Equation 24 where the subscripts C and M represent the polymer coating and metal/solution interface, respectively.

$$Z = Rs + \frac{1}{Y_{oC}(j\omega)^{n_{c}} + \frac{1}{Rpo + \frac{1}{Y_{oM}(j\omega)^{n_{M}} + \frac{1}{Rp}}}}$$
(Eq. 24)

The analog of the impedance of ECR with no coating flaws may be further simplified as a plain capacitor with capacitance C_C

$$C_{\rm C} = \varepsilon \varepsilon_0 \, {\rm A}/{\rm d}$$
 (Eq. 25)

where ε is the dielectric constant of the coating, ~5; ε_0 is the permittivity of free space, 8.85x10⁻¹⁴ F/cm; A is the area of the metal coating; and d is the coating thickness, ~0.2 mm.

1.2 Problem Statement and Research Objectives

The Florida Department of Transportation, FDOT, specified the use of ECR from the 1970's to the early 1990's. Following the Florida Keys experience, the use of ECR for new bridge design was discontinued by FDOT in 1992. Nevertheless, there remain over 300 ECR bridges in the state inventory including major structures like the Sunshine Skyway Bridge. Those structures represent a potentially large future corrosion control and maintenance liability. Representative concrete permeability parameters for these bridges have been documented in earlier investigations (Sagüés, 1994; Sagüés et al., 2001). Based on diffusional parameters, some of those bridges beyond the initial Florida Keys group are expected to have initiated corrosion of the ECR by now. Concrete bridges with high permeability are expected to have earlier corrosion initiation than those bridges with higher quality concretes. Verification of this assumption would help elucidate long term ECR durability. That verification should benefit from development and application of assessment technologies beyond direct observation of corrosion condition. As noted earlier, the effect of pre-existing structural cracks on the transport of chloride ions may also be significant, especially for otherwise low permeability concrete. Given the severity of early corrosion observed in some of the Florida ECR marine bridges, damage projections for those and the remaining FDOT ECR bridges are needed to evaluate future maintenance needs and provide information that will serve for future corrosion mechanistic understanding.

The objective of this study is therefore to evaluate marine ECR bridges to anticipate their long-term corrosion performance. To achieve this objective, the following questions need to be answered:

1. What is the prognosis for future corrosion progression in all Florida ECR bridges?

2. What is the prognosis for ECR bridges with local concrete cracking?

3. How can corrosion predictive models be improved based on new evidence and mechanistic insight?

4. How can nondestructive electrochemical techniques be better interpreted to assess ECR corrosion condition?

1.2.1 Research Approach

The research approach included to:

1. Assess the present condition of Florida marine ECR bridges after approximately three decades in service and determine the effect of concrete cracking on ECR corrosion initiation.

2. Model corrosion damage projections of ECR bridges with local concrete cracks over remaining service lives.

3. Use and improve interpretation of electrochemical methods to evaluate corrosion condition of ECR.

The study examined the present condition of 13 Florida ECR bridges in aggressive marine environments, Table 1, with specific attention to the possible effect of thin structural cracks on early corrosion. Recently available data on the corrosion condition of 5 Florida ECR bridges that had already propagated early severe corrosion, referred as Group 1 bridges in this study, were also assessed. The choice in field locations reflected various service environments varying from brackish water, ~10,000 ppm chloride, to sea water, ~25,000 ppm chloride, and locations from the Florida Panhandle to the Florida Keys, Figure 4.

Measurements and observations made in this study were either in-situ on field structures or in the laboratory with representative concrete/ECR samples extracted from
field locations. Corrosion model projections were made to predict damage in existing bridges and to evaluate corrosion prognosis in new structures.

Some content in this dissertation has been published in reports to the sponsoring agency (Lau and Sagüés, 2009a; 2009b), and subsequently published in manuscript form (Sagüés et al., 2010; Lau et al., 2010) and has been in part reproduced here.

ECR cover (cm)	7.6					15.3	15.3 15.3			7.6	10.2	10.2	10.2	12.0	1	10.9	c	9. Z	
Widest crack width (mm)	× 1 ⁺ × 1 ⁺ × 1 ⁺		>1†	>1 ⁷ 0.28		0.28	× +1+	0.64	0.25	ž	0.18	hairline	0.18	и С	G7.0	nents.			
Fly ash	2					ę				20% Type F	Yes	35% Type C	Yes	2			ure compo		
Cement factor (kg/m³)	388					388					445		388						substruct
م) (kΩ-cm)	5-24		•			0.4-12 4-50		4-50	16-128	150	113-275	high MΩ-cm	9-180	ı	4-10	4-12		n for different	
Average D (cm²/s)	2x10 ⁻⁷	2x10 ⁻⁷	~10 ⁻⁷	~10 ⁻⁷	2.9x10 ⁻⁷	~10 ⁻⁷	2.6x10 ⁻⁷		9.0x10 ⁻⁸	1.8x10 ⁻⁸	1.1x10 ⁻⁹	3.1x10 ⁻⁹	7.3x10 ⁻⁹	3.8x10 ⁻⁹	1.8X10 ⁻⁸	2.5x10 ⁻⁷	3.9x10 ⁻⁸		concrete desig
Year Built	1982	1980	1981	1982	1982	1981	1982	1982	1981	1979	1986	1981	1991	1989	1981	1989	1983	1983	ions in c
Bridge Name	900026	900117	900095	860006	900094	900097	900126	900124	900077	570082	150189	480140	150210	860467	860319	860466	870607	870606	lable, * Variat
	IWL	NIL	NN	CH5	LoK	CH2	VA1	VA2	SNK	сно	SSK	PER	HFB	ITB	NWR	ITA	IT2	IT3	not avai
	Seven Mile	Niles Channel	Indian Key	Channel 5	Long Key	Channel 2	Channel 2 Vaca Cut		Snake Creek	William Marler (over Choctawachee Bay)	Sunshine Skyway	Lillian (over Perdido Bay)	Howard Frankland	Sunrise Blvd. (over Intracoastal Waterway)	S. Andrews Ave. (over New River)	Sunrise Blvd. (over Intracoastal Waterway)	Lehman Cswy. (over Intracoastal Waterway)		alled Concrete Data
		G	roup	01	•	Group 2					Group 3				Group 4				† Sp

Table 2. ECR Bridges Investigated







Figure 4. ECR Bridge Sites. (Maps from Microsoft Virtual EarthTM)

1.2.2 Bridges Investigated

Bridges investigated in this study, Table 1, were selected to be representative of the following categories:

1. Group 1: Structures with documented severe early ECR corrosion (Sagüés et al., 1994) to determine the progression of damage having already a well established baseline.

Group 2: Bridges not showing ECR corrosion in a study by Sagüés, 1994 after ~15 years service but determined to have a high likelihood of ECR corrosion development during the following decade based on high chloride ion diffusivity.

3. Group 3: Bridges with overall low to very low chloride ion diffusivity but where some narrow cracks have been detected that permit fast localized chloride ingress.

4. Group 4: Bridges with intermediate chloride diffusivity with some chances of ECR corrosion development at present.

1.2.3 General Bridge Substructure Information

Table 1 lists the structures of all groups, construction information, and the bridge identifications used in the rest of the dissertation. Information on concrete properties is listed in the table.

Group 1 Bridges: 7MI, NIL, and INK were built with drilled shafts supporting columns with connecting struts. The LOK bridge has capped drilled shafts joined by a strut, and V-Piers rested on synthetic rubber pads placed on the caps. The CH5 bridge has drilled shafts with spread footers and precast posttensioned box columns.

Group 2 Bridges: The CH2, VAC, and SNK bridges have capped drilled shafts supporting columns. The CHO bridge has reinforced concrete columns with connecting struts, supported by capped prestressed piles.

Group 3 Bridges: The SSK substructure consists of reinforced concrete columns with footers and struts in the low approach spans and elliptical posttensioned columns for the high approaches. The PER substructure consists of reinforced concrete piles for the low approach and reinforced concrete columns on footers for the main span. The HFB substructure consists of reinforced concrete columns on footers. ITB substructure consisted of bascule and rest piers.

Group 4 Bridges: Substructure in marine service for NWR and ITA include the bascule and rest piers. IT2 and IT3 consist of reinforced concrete columns with footers. The substructure on these bridges was painted with a texture coating above the high tide level.

PART II

Part II assesses the development of corrosion in Florida ECR bridges over ~30 years of marine service and presents updated field survey results documenting present condition.

2.1 Present ECR Bridge Condition

2.1.1 Bridge Survey Methodology

Examination of the structures was conducted at various levels. Group 1 bridges already had documented corrosion activity so further discussion of bridge condition information is limited to the observations of external concrete distress. Special bridge surveying and core sampling of concrete and ECR were conducted for the 13 structures from Groups 2-4. Representative locations from several substructure component types — columns, footers, struts— were selected for examination, focusing on cracks on concrete sections at low elevations exposed to sea splash. For SSK, higher elevations, 7-8 m above high tide, where wide cracks were prevalent were also examined. Elevations are reported as distance above the high tide level, AHT.

All surveys included visual examination of all or part of the substructure and soundings to assess extent of corrosion spalls if any was present. If evidence of concrete cracking or other distress was observed, the substructure element was tested by sounding with a hammer for evidence and extent of internal concrete delamination. An area of delaminated concrete thus detected is designated as a concrete spall. A delaminated area which extended from an area found to be spalled in a previous inspection was designated as a progressive spall.

During the survey of Group 2-4 bridges, concrete cores ~10 cm diameter and extending past steel reinforcement depth were extracted. Extracted ECR segments —

typically ~ 2 cm diameters, ~10 cm length— were perpendicular to the core axis. Concrete clear cover was noted. When cracks were observed, pairs of cores were typically collected along the same elevation typically ~15 cm apart on center with one core centered on crack. Crack widths were measured on site using a crack width comparison reference gage. The in-situ condition of the exposed ECR coating was noted. Spot knife tests for coating disbondment were conducted. Half-cell potentials were measured with a copper/copper-sulfate reference electrode, CSE, along the elevation of the substructure component. Concrete surface resistance was measured using a Wenner array probe with an inter-probe spacing of 5 cm, chosen as a compromise between sampling size and possible interference from embedded rebar.

Additional characterization of material properties and conditions were conducted in the field or in laboratory shortly after extraction and are discussed later in the manuscript.

2.1.2 Damage Characteristics

2.1.2.1 Group 1 Bridges

The following is a brief description of corrosion observations for this group (Sagüés et al., 1994) with updated results. Typical spalls affected a projected area of ~ 0.3 m² on the surface of the concrete. Longitudinal cuts on the ECR surface with a sharp knife permitted easy peeling of the coating from the corroded regions, revealing extensive solid dark undercoating corrosion products typically magnetic and electronically conductive (Sagüés et al., 1990). Occasionally, significant amounts of acidic liquid rich in chloride and iron were found as well (Sagüés and Powers, 1990; Sagüés et al., 1991). Coating disbondment was also found on rebar location adjacent and away from corroding regions. This disbondment without significant corrosion was found to be widespread in ECR after it was in service for a few years in Florida marine substructure conditions of all this and the other groups, even in the absence of chloride contamination of the concrete next to the rebar (Sagüés, 1994; Sagüés and Powers, 1996). Examination of the underside of coatings from numerous ECR samples did not reveal any

correlation between this disbondment and the usual forms of surface contamination expected in the coating process (Sagüés, 1994; Sagüés and Powers, 1996). Concrete resistivity readings were as low as $1k\Omega$ -cm in the tidal region indicative of high concrete permeability (Sagüés, 1994; Berke and Hicks, 1992; Andrade et al., 1993).



Figure 5. Widest Crack per Substructure Unit.

2.1.2.2 Group 2 Bridges

Vaca Cut (VA1/2) and Snake Creek (SNK). For simplicity, the side-by-side bridges VA1 and VA2 are treated as one bridge in the following unless indicated otherwise. The substructure from VA1/2 and SNK in contact with the seawater has only reinforced concrete drilled shafts. Concrete deterioration was generally inconspicuous with the exception of vertical cracks, 0.08-0.3 mm wide, on one shaft each in VA1 and VA2 and one in SNK, out of a combined total of 26 shafts in water for those bridges. The drilled shaft containing the largest crack in VA1/2, 0.3 mm width, Figure 5, and ~13 cm deep, had also internal cracks— diagonal and transverse— leading from reinforcement depth, that had not yet propagated to the concrete surface. The crack at SNK was 0.08 mm thick, from 4 cm below high tide line to 26 cm AHT, and ~18 cm deep. Concrete delamination could not be detected by hammer sounding on the any of the concrete sections, sound or cracked, from either bridge likely due to the large concrete cover, \sim 13-15 cm.



a) VA2 Drilled Shaft ~45 cm AHT on crack (0.33 mm).



b) CHO. Footer. ~9 cm AHT.

Figure 6. Severe ECR Corrosion in Group 2 Bridges.

In VA1, two shafts were cored in five locations fully exposing ECR in three cores. Two of those cores were an on-crack and off-crack pair at the largest vertical crack, 46 cm AHT. The ECR, both on- and off- the main crack showed extensive corrosion, Figure 6a. Lesser but still significant corrosion distress was observed on samples from a core at 165 cm AHT. There, the distress was limited to small coating breaks of rusty appearance and to thin rust spots and discoloration on as much as 10% of the steel substrate observed after removal of the coating. ECR was fully exposed at four core locations in SNK, including a low elevation on- and off-crack pair that showed significant corrosion but not as severe as in VA1/2. The average epoxy coating thickness was ~0.2 mm, Figure 7 —generally consistent with product specifications and not showing deficiency in this respect. However, complete coating disbondment was observed on all ECR samples from both bridges. Where it could be examined, backside contamination was ~1%. Vertical and horizontal ECR exposed by coring in the same column were mostly found to be electrically continuous.

Half-cell potential mapping of the ECR, Figure 8a generally showed potential values, more negative than -300mV CSE, traditionally indicative of corrosion activity for plain rebar in atmospherically exposed concrete. Although potential may not be a reliable indicator of active corrosion of ECR in marine concrete, it is noted that all the rebar which had showed visual signs of corrosion were similarly negative. Concrete resistivity, Figure 9a reached <5 k Ω -cm, indicative of highly permeable concrete. A general trend of lower resistivity at low elevations was consistent with expectations of near water saturation there.

William Marler (CHO). Two of 20 footers from the ten high elevation piers had cracks wider than 1.0 mm; ten of the footers had cracks larger than 0.2 mm. Minor concrete cracking was typical on all of the footers. Vertical and map-type cracking was observed on one of 20 columns from the high elevation piers. Rust bleedout was observed on two columns and one strut. The origin of that bleedout was not confirmed as samples of reinforcement were not obtained, but corrosion of reinforcement may be possible. Core samples were extracted from two footers each with one wide vertical

crack, 1.0 and 0.63 mm wide respectively. Approximately 0.42 m^2 and 0.1 m^2 , respectively, of concrete around the crack locations seemed to be delaminated as determined by hammer sounding. Extensive corrosion of the reinforcing steel, Figure 6b was observed on both footers at elevations 8.9 to 17.8 cm above high tide level, both where the crack intersected steel and in adjacent sound concrete locations. The epoxy coating thickness exceeded specifications therefore is not attributable to the early corrosion development. The lack of coating adhesion to the steel substrate however would provide environment for corrosion. The concrete cover to vertical bar ranged from 7.1-10.4 cm; nominal design cover was 10.2 cm.

Highly negative half-cell steel potentials were measured, -400 to -552 mV CSE. In plain steel rebar such potentials would likely be reflective of the observed ongoing corrosion, but it is cautioned that potential readings in epoxy coated rebar, especially in wet concrete, may not be always reliable indicators of corrosion condition. Concrete surface resistivity measurements on the columns ranged from 46 to 128 k Ω -cm on the columns at elevations 0.6 to 2.4 m AHT. Concrete resistivity on the footer ranged from 16 to 63 k Ω -cm at elevations 0 to 0.55 m AHT.

Channel 2 (CH2). Corrosion evaluations at CH2 for the current investigation were cursory but those and records (Simmons et al., 2005) from FDOT routine surveys showed extensive corrosion damage, Figure 1, not unlike that observed at the Group 1 bridges. Typical corrosion distress is characterized by extensive concrete cracking— as wide as 1.3 mm with spalled concrete, average ~2.9 m²— typically in the splash area but with several instances extended to above and below it. As in the Group 1 bridges, the concrete in CH2 showed indications of high permeability. At 25 year age the chloride concentration at ~15 cm reinforcement depth and elevations 0.3-2 m AHT was as much as 6.5 kg/m³. Assuming a typical chloride surface concentration value (Sagüés et al., 2001) Cs~20 kg/m³, D_{App} was estimated to be in the order of ~10⁻⁷ cm²/s. Low concrete resistivity, 3-30 k Ω -cm, was measured as well at elevations 0.3-1.5 m AHT. Severe

coating distress and disbondment was observed at spalled concrete locations. ECR in areas away from distressed concrete locations was not tested.



Figure 7. Epoxy Coating Thickness.







2.1.2.3 Group 3 Bridges

Figures 7-9 for epoxy-coating thickness, OCP, and concrete resistivity data are to be referred in the following section.

Sunshine Skyway (SSK). The low approach span substructure consists of 512 reinforced concrete columns with footers and struts exposed to direct sea splash, and 256 cap beams at ~7 m AHT. The high approaches have elliptical post-tensioned columns. The average clear cover of the outer mat steel ranged from 9-11 cm in the various substructural components.

At low elevations, hairline cracks, <0.03 mm, were commonly observed on the concrete footers, <60 cm AHT, and columns, <200 cm AHT. Larger vertical cracks, Figure 5, ~0.3 mm, with efflorescence were found on the elliptical post-tensioned columns. No concrete delamination was observed or detected by hammer sounding on any cracked or sound sections. A total of 16 cores were extracted from these low elevation locations. In the field, no evidence of corrosion was observed on the surface of the epoxy coated reinforcement exposed by coring, except for vestigial rust at small coating breaks such as high points on ribs where the coating had been damaged during or before construction. That rust did not appear to reflect ongoing corrosion. Half cell potentials ranged from values indicative of passive behavior to <- 600 mV. The more negative values were observed at some— but not all— of the lowest elevations. As mentioned above, the significance of these values is limited. The surface resistivity of the concrete at elevations where the concrete was very wet, e.g. <=0.3 m AHT, ranged from ~15-150 kΩ-cm, consistent with the low permeability concrete used in this bridge.

The trestle cap beams, at elevations ~7-8 m AHT, often had wider structural cracks, Figure 5, up to 0.6 mm, some with heavy efflorescence. No concrete delamination was observed or detected. Moisture was more prevalent at some of the cap beams which were exposed to runoff water at deck expansion joints. Isolated concrete spalls— apparently not corrosion related— in the same vicinity of the cracks were occasionally

found in cap beams. A total of 10 cores were extracted from the cap beams. As in the lower elevations, minor to no corrosion was observed on the reinforcement exposed by coring except for vestigial rust at small breaks in the polymer coating. Potentials measured at exposed ECR locations ranged from -70 mV_{CSE} > E >-490 mV_{CSE}. The concrete surface resistivity was 70-300 kΩ-cm with no clear difference between sound and cracked locations.

Howard Frankland (HFB). Vertical cracks were frequently observed on the concrete footers; several large cracks were as wide as 1.0 mm, Figure 5. The trace of the crack observed on the top of the footers of the larger cracks was as deep as a meter. Cracks of this type had been documented in previous inspections and are likely due to differential curing in the bulk of the concrete. Subsequent coring revealed that cracking sometimes propagated past reinforcement depth, 10.2 cm. Six pairs of on-crack/off-crack core samples were extracted at 9.7 to 47 cm AHT from 5 footers- in one of those footers, coring was done on two separate faces. Significant localized corrosionmorphology discussed later— was observed on 4 out of 7 on-crack bars extracted from 4 locations at 3 of the footers. In one instance where two bars were extracted from the same core, only the bar with deeper cover, 11.6 cm, 1.6 cm deeper than the bar with lower cover, showed corrosion. No physical indication of corrosion was observed at any of the matching sound concrete locations. Concrete delamination was not detected at either sound or cracked locations. Concrete clear cover to horizontal reinforcement was 10.9 to 11.7 cm, meeting nominal design requirements, 10.2 cm. Half-cell potentials ranged from -200 to -690 mV_{CSE} measured at elevations from tidal zone to 0.9 m AHT. The more negative values were from locations where ECR corrosion took place. As noted above, caution is in order on generalizing the significance of this observation. Concrete surface resistivity was very high, M Ω -cm range, even in the tidal zone.

The corrosion observed on the four epoxy coated reinforcement samples extracted from cracked locations from this bridge merits note. The crack plane was usually perpendicular to the rebar. Corrosion products were generally observed around locations with coating defects, especially near the intersection of the crack plane with the rebar. Upon removal of the coating —which was found to be fully disbonded— the underlying surface was relatively dry, with dark corrosion product regions. Coating thickness was generally consistent with product specification.

Lillian (PER). Very little concrete deterioration was observed. Thin hairline cracks were observed occasionally. The main span footer had larger cracks, ~0.3 mm, with indication of efflorescence, some of which had been repaired earlier on by epoxy-injection. Concrete cores were extracted sampling on and off a crack location at 1.1 m AHT. Also cores were extracted from a column with no concrete deterioration at 0.9 and 1.2 m AHT. Concrete cover ranged from 10.4 to 13 cm. Half-cell potentials ranged from -183 to -656 mV_{CSE} at tidal to 1.5 m AHT. Concrete resistivity of the footer and column ranged from 113 to 275 k Ω -cm at 0.3-2 m AHT. No corrosion or only vestigial signs of surface corrosion discoloration were observed on extracted epoxy coated reinforcement.

Sunrise Blvd (ITB). Like the Group 4 bridges described in the next section, the substructure concrete had a surface coating extending down to the high tide level. Only minor concrete cracking, <0.2 mm— Figure 5, combined with ITA— was observed. A concrete core was extracted on a vertical crack at ~80 cm AHT and another core extracted on sound concrete offset 15 cm on center but at an elevation 20 cm above the crack concrete location to avoid other concrete cracks. The crack propagated deep into the concrete past reinforcement depth, Xc~11 cm. The half-cell potential ranged from -61 to -218 mV_{CSE} at tidal zone to 1.2 m AHT. Concrete resistivity ranged from ~9 to 180 k Ω -cm from the tidal zone to 1.2 m AHT. No observation of corrosion was observed on the surface of ECR. The ECR in cracked concrete was found to be disbonded, but good adhesion was maintained for ECR in the sound concrete location.

2.1.2.4 Group 4 Bridges

Figures 7-10 in the previous subsection for epoxy-coating thickness, OCP, concrete resistivity, and concrete porosity data are to be referred in the following section.

Lehman Causeway (IT2/3). Very little concrete deterioration was observed, although pre-existing damage prior to application of surface texture paint may have been obscured. Concrete cracks, Figure 5, typically ~0.08 mm wide were thin yet penetrated deep into the concrete. The cracks were often traced across the width of the footers and penetrated past reinforcement depths, Xc~7-10 cm. Concrete cores were extracted sampling ECR on and off crack locations ~50-120 cm AHT. Half-cell potentials ranged from -41 to -627 mV_{CSE} at tidal level to 1.2m AHT; low concrete resistivity was observed, 4 to 12 k Ω -cm at 0.1-1.2 m AHT. Only vestigial surface corrosion under defects of the epoxy coating was observed.

S. Andrews Ave (NWR). Only the bascule rest pier was accessible. There, no concrete deterioration was externally observed. However, surface paint may have masked pre-existing cracks as one thin vertical crack, Figure 5, 0.05 mm was revealed after removing some of the paint. One core was extracted to sample the underlying bar there, \sim 1 m AHT and another core on sound concrete at an elevation \sim 40 cm below— no side by side cores were extracted at this location. The crack was found to be very shallow, propagating only a few centimeters below the concrete surface. The half-cell potential of exposed ECR in the cracked concrete location was -400mV_{CSE}. Concrete surface resistivity was not measured as it would have necessitated removing the paint coating and damaged surface finish in a tourist attraction bridge. Only vestigial surface corrosion of steel under breaks in the epoxy coating was observed.

Sunrise Blvd (ITA). Like the other bridges in Group 4, the substructure concrete had a surface coating extending down to the high tide level. Only minor concrete cracking, <0.2 mm— Figure 5, combined with ITB— was observed. A core was extracted from concrete with no deterioration ~62 cm AHT. The half-cell potential ranged from -200 to -370 mV_{CSE} at tidal zone to 1 m AHT. Concrete resistivity ranged from ~4 to 10 k Ω -cm from the tidal zone to 1 m AHT. No observation of corrosion was observed on the surface of ECR and was found to be disbonded.

2.1.3 Damage Progression

The damage function in Figure 10 depicts the cumulative progression of external manifestation of concrete distress for the ECR bridges in this study. The figure contains documented data from Sagüés, 2003, updated bridge inspection data from FDOT and results from Lau and Sagüés, 2009a; 2009b

Only Group 1 and 2 bridges have exhibited external manifestations of corrosion damage in the visual and sounding examinations reported, which were conducted from 1986 to 2007. The number of new spalls or progressive spalls observed on a bridge at a given inspection date was recorded. Spalls that occurred in regions formerly repaired, either by conventional patching or otherwise, were considered new spalls. That number was then added to those observed in previous inspections of the same bridge. In Figure 10, the cumulative spall count was normalized by the number of bridge bents. For VAC, SNK, and CHO, only the number of bridge bents with ECR in marine service were counted. For VAC and SNK, the areas where severe corrosion was observed at cracked concrete locations were considered as spalls even though concrete separation by hammer sounding could not be verified. This absence of sounding evidence may be due to the large, ~15cm, concrete cover at these bridges. The damage functions are expressed in terms of spalls per bent to normalize for bridge size.



Figure 10. Progress of Concrete Corrosion Damage as Function of Time.

The damage function trends provide important insight on the extent of the corrosion and its future development. For Group 1 Bridges the corrosion damage into the 3rd decade of service is conspicuous, with multiple spalls per bent on average. That damage affects a significant fraction of the area of the splash zone of each bridge, where the concrete surface area on the splash zone of a typical bent is $\sim 20 \text{ m}^2$ and a typical spall affects $\sim 0.3 \text{ m}^2$. Damage is likely to have been worse without the application of protective anodes. Except for an offset toward shorter times for NIL, the functions are remarkably similar to each other. The damage at present appears to increase

approximately linearly with time. If those trends were to continue, the total extent of damage would roughly more than double over the next 20-30 years of service. As repairs in marine substructure are very costly, corrosion would place a continuing and heavy repair and maintenance burden during the remaining service life of these structures.

In Group 2 Bridges, corrosion propagation at CH2 started the earliest and appeared to increase roughly linearly with time similar to Group 1 bridges. Significant damage in the other Group 2 bridges appeared to have started after ~25 years in marine service. Corrosion deterioration was evident in CHO where spalled areas could easily be detected. Damage at VAC and SNK was not as conspicuous, and the origin of concrete cracking at corroded bar locations there could not be established as resulting exclusively from expansive corrosion products. The corrosion propagation trends at VAC and SNK may be anticipated to be similar to those at CH2 and the Group 1 bridges, but future confirmation is needed. In any event, the observation of significant ECR corrosion in the Group 2 Bridges verifies earlier damage projections for ECR structures in the Florida inventory having concrete with high D_{App} values (Sagüés et al., 1994).

For the Group 3 and 4 bridges, no concrete delamination or spalling was observed at any of the structures examined, but significant ECR corrosion was observed at cracked concrete locations of HFB. This latter observation is an important warning of potentially severe local damage in the future, so frequent monitoring of these and similar locations is advisable. Due to the otherwise high quality concrete, thick concrete cover and low surface chloride concentration in Group 4 bridges, early corrosion damage is not anticipated for sound concrete locations. However, there was typically widespread disbondment of the epoxy coating in all these structures even in sound concrete locations. This disbondment together with the observed frequent coating breaks is expected to facilitate corrosion initiation as chloride levels at the rebar depth increase in future decades.

PART III

Part III presents examination of field extracted concrete and ECR, and laboratory experiments, with emphasis on the mechanism of corrosion in concrete with preexisting cracks.

3.1 Concrete Bulk and Crack Transport

3.1.1 Concrete Cracking and Corrosion

The field survey confirmed the presence of usually minor cracks —but sometimes severe— as a regular feature of marine substructure elements. Concrete cracking was expected to promote a local increase of permeability manifested by increases in chloride ion penetration, carbonation, and enhanced moisture resulting in lowered resistivity, all of which would promote early corrosion. The cracks in the Group 2 bridges in places where ECR showed corrosion may be ascribed to corrosion that was initiated first by fast chloride transport through the bulk of the concrete. The rest of the cracks observed were likely preexisting and, with the exception of HFB, did not show any evidence of having originated early ECR corrosion. The multiple observations of corrosion of ECR at some of the wider cracks in HFB is of particular concern given the short age of the bridge at the time of the survey and the low permeability of the otherwise sound concrete used there. The factors that may have caused that early deterioration are examined in the following.

3.1.2 Chloride Penetration at Sound and Cracked Locations

3.1.2.1 Methodology

Chloride ion penetration profiles were obtained for the field-extracted concrete cores. Concrete powder for chloride analyses was obtained from ~4cm deep holes made using a ~1cm diameter drill bit. The holes were drilled perpendicular to the core axis, at various depths from the face of the core that corresponded to the external concrete

surface. For cracked concrete, the drill bit axis was placed to follow the approximate plane of the crack surface, effectively sampling a ~ 1 cm wide band of concrete centered in the immediate vicinity of the crack. For selected cores, additional powder was sampled with the drill axis ~1cm offset from the crack, to assess chloride penetration into the side walls of the crack. The powdered concrete samples (typically > 7 g each) obtained at various depths from the surface were analyzed for total acid-soluble chloride concentration. A variation of a standard FDOT analysis methods was used (FM5-516, 2005) in which each powder sample was in the largest majority of cases parceled into two 3g subsamples and the average of both was reported. The percent difference between duplicate measurements (or between the highest and lowest value in the few instances in which more than two replicates were tested), expressed as a percentage of the reported value, followed approximately a lognormal distribution with a median of 2.8% indicating generally good reproducibility. In only 10% of the cases the difference was more than 20%. Results are given in mg of Cl⁻ ion per gram of dry concrete. Diffusion coefficients, D_{App}, for the sound concrete profiles were estimated by least-error-fitting of the chloride content data profile to a solution to Fick's second law expressed in Equation 3.

3.1.2.2 Results

Chloride transport at cracks may involve convective as well as diffusional flow, with different parameters responsible for transport along and into the sides of the crack (Sagüés et al., 2001; Ishida et al., 2009). Consequently, the on-crack concentration profiles obtained by the sampling procedure used here cannot be described by a relatively simple solution to Fick's second law as it was done via Eq. 3 for sound concrete. Thus a value for D_{App} was calculated from the chloride profiles from off-crack cores, but not from on-crack cores. Instead, comparison of the relative chloride penetration at cracked and adjacent sound concrete is made by presenting both profiles together. As it will be shown in the modeling section, a fictitious enhanced diffusion coefficient for on-crack transport was used there but only as a rough working approximation.

The chloride penetration profiles, solid and open symbols for sound and cracked concrete respectively, are shown in Figure 11.

Results for Groups 2 and 3 are considered first. For sound concrete, the average D_{App} values for VA1/2 and SNK were very high: ~3x10⁻⁷ and ~9x10⁻⁸cm²/s, respectively. The average D_{App} for CHO was lower than that of the other Group 2 bridges but chloride concentrations in sound concrete for the entire group at reinforcement depths were nevertheless larger than 0.7kg/m³, which is a commonly assumed conservative chloride ion threshold value (Angst et al., 2009). In contrast, the average D_{App} values for sound concrete in Group 3 bridges were very low: $1.1x10^{-9}$, 3.1×10^{-9} , 7.3×10^{-9} , and 3.8×10^{-9} cm²/s for SSK, PER, HFB, and ITB respectively. These observations are in keeping with the relative permeability differences expected from the respective concrete mixture proportions used in these two groups. The average Cs value for low elevation locations in both groups, in the order of 20 kg/m³, was comparable to that measured in other Florida marine bridges at similar elevations and consistent with expectations (Sagüés et al., 2001; Law et al., 2007). Likewise, Cs for SSK at higher elevations was consistently less.

The profiles for on-crack locations in Groups 2 and 3 were on average higher than those for sound concrete confirming the expectation of preferential chloride penetration through cracks. In Group 2 the difference was moderate, indicating that the effect was overshadowed to some extent by fast bulk diffusion through the sound concrete in that group. In contrast the difference was dramatic for Group 3 where bulk diffusion in sound concrete is low, especially for SSK and HFB. The effect for those bridges was notable at the low elevations where the conservative threshold level was exceeded in most instances at the reinforcement depth. In the SSK higher elevation trestle caps the chloride penetration enhancement was less consequential, not markedly exceeding typical native chloride concentrations at depths greater than a few centimeters from the concrete surface. This lesser effect at high elevations likely reflects, as noted earlier, both a lower external surface concentration and drier conditions in the crack with consequentially less efficient transport. Enhanced chloride penetration was not observed in the limited number of samples extracted from PER, but there conditions similar to those encountered for SSK at the higher elevations may exist. Enhanced chloride penetration through cracks in ITB was moderate and may have been somewhat mitigated by low Cs, <10 kg/m³, reflecting presence of concrete surface coating, as noted also in Group 4 which is discussed next. The overall findings for Group 3 agree also with initial observations made by Sagüés et al., 2001.



Figure 11. Chloride Penetration Profiles. Solid symbols: sound concrete. Open symbols: cracked concrete. Thick line, arrowed: high elevation trestle cap SSK locations. Horizontal line: conservative chloride threshold value $\sim 0.3 \text{ mg/g} (C_T \sim 0.7 \text{ kg/m}^3)$.

The Group 4 bridges cores were all from low elevations but had consistently low surface chloride contents. As in the case of ITB, Cs values for Group 4 bridges were very low, $<2kg/m^3$, which is one order of magnitude lower than that typically encountered for similar marine environments. Those lower concentrations reflect the presence in these bridges of concrete surface coatings, a feature not commonly used by the owner agency in marine substructure The D_{App} values were moderate to high; $~4x10^{-8}$, $~2x10^{-8}$, and $3x10^{-7}$ cm²/s for IT2/3, NWR, and ITA respectively; as manifested by the deep penetration of the concentration profiles when viewed as a fraction of the surface content. In common with the Group 2 bridges and for similar reasons, there was only modest differentiation between on- and off-crack locations. Due to the low value of C_S the overall chloride content at the reinforcement depth was nevertheless small so the corrosion risk to date remained low and consistent with the lack of observation of corrosion manifestations.



Figure 12. Chloride Penetration into the Side Walls of Cracks. On-crack profiles obtained following the usual procedure. Offset-crack profiles are for the same cores as On-crack but sampled ~1cm away from the approximate crack plane. A sound concrete profile from the matching core of one the on-crack locations is shown as well. Circle: cores SSK117E1-3. Triangle:SSK117E4.

The results of limited experiments to assess chloride penetration into the side walls of the cracks are shown in Figure 12 for selected cores from Group 3 SSK Bridge. All three cores were from the same column and about the same elevation. Cores 117E1 and 117E3 were a matching on-and off-crack pair extracted ~0.5m AHT; Core 117E4 was from the same column at elevation ~1m AHT. While the data are limited, the results indicate chloride penetration into the side walls of the cracks was minor. This is consistent with observations by Sagüés et al., 2001, Win et al., 2004, Jaffer and Hansson, 2008 and Djerbi et al., 2008 for low permeability concretes. Neglecting possible enhanced chloride penetration around the interface of ECR with its surrounding concrete, greater chloride transport should be limited to the small vicinity of the crack transport path.

Chloride penetration as discussed earlier is complicated by mixed transport mechanisms among other factors intrinsic to the concrete medium and service environment. If, for the sake of argument, transport through cracks can be assumed to be dominantly by diffusion, the extent of enhanced chloride penetration in concrete by other factors may simply be considered as a multiplier to chloride diffusivity in the bulk medium. The Group 3 bridge chloride concentration profile data was compared to an ideal diffusional system described by Equation 3 with $C_s\sim 10mg/g$, $C_o\sim 0.05mg/g$, and $D_{App}\sim 1x10^{-9}cm^2/s$ and parameterization of D_{App} diffusivities 10 and 100 times larger, Figure 13. For the Group 3 bridge data set, these multiplier values seem like plausible ranging values to give rough working approximation of an enhanced chloride diffusion coefficient for transport through cracks. Modeling by Ishida et al., 2009 used a similar modifier for chloride transport to accomodate for convection in the crack; in their work, in addition to parameterization of mesoscopic pore size distribution, constrictivity, and tortuosity, an additional modifier $\zeta=50$ was used. Forecast modeling of corrosion damage of ECR is later detailed in the manuscript.



Figure 13. Comparison of Chloride Concentration Profiles with 10x and 100x Multiplier of D_{App} for Idealized Diffusion per Equation 3. Group 3 Case. Solid symbols: sound concrete. Open symbols: cracked concrete. (Data reproduced from Figure 11b)

In summary, preferential chloride transport at cracks when enough moisture is present has been documented in most instances but it became of greater relative importance when the bulk concrete was the least permeable. That local chloride ingress was the most likely primary cause of the early corrosion of ECR at HFB. The appearance of corrosion only there so far may have resulted from an adverse combination of wider cracks, somewhat higher bulk permeability, and perhaps a greater extent of coating imperfections than at the other bridges in the group. The observation of similar penetration patterns at some other Group 3 bridges -in particular SSK, a major bridge 20 years old at the time of the survey- creates concern that similar corrosion may occur there too in the near future as it will be discussed in the next section. Frequent inspection of low elevation crack locations of these structures is advisable.

3.1.3 Preferential Carbonation in Sound and Cracked Concrete

3.1.3.1 Methodology

The depth of concrete carbonation, from the external surface, was measured by lightly spraying 1% phenolphthalein in ethanol solution on freshly fractured concrete core samples. In concrete cores from cracked locations, the core was separated exposing the cracked surface, and phenolphthalein was sprayed on it. The depth, if any, from the external surface to which the crack surface remained colorless was recorded as the on-crack carbonation depth. In selected cores, the halves corresponding to each side of the crack were further broken transversely to the crack, to determine how carbonation had progressed into the sides of the crack.



Figure 14. On Crack Carbonation Testing: SSK High Elevation Trestle Cap Concrete core. A) On site crack location, SSK140E1. B) Transverse cross section from crack surface, SSK33W1. C) On crack surface, SSK33W1.

3.1.3.2 Results

Carbonation penetration from the external surface of sound concrete at elevations exposed to sea splash was typically negligible, <1mm. This is as expected due to the slow transport of CO_2 in a pore network with high moisture content, and in agreement with similar observations in the past (Sagüés et al., 1997). The on-crack carbonation —that is, carbonation noted on the surface of the crack sides— at those elevations was also typically shallow, suggesting that water was filling much of the crack space itself. However, in a few low elevation cases, the on-crack carbonation extended to >1cm from the external surface and in the case of ITB, to past reinforcement depths. In high elevation SSK cores, there was also evidence of deep on-crack carbonation, reaching up to reinforcement depth, Figure 14. In all cases of significant on-crack carbonation depths, the carbonation penetration into the sides of the crack was found to be very small, < 1mm, indicating that the bulk of the concrete still retained sufficient moisture to impede efficient CO_2 transport.

Carbonation could seriously lower locally the chloride initiation threshold (Sagüés et al., 1997), thus further aggravating conditions at a narrow region around where a crack intersects the rebar and damaged coating is also present. However, that does not appear to be a concern at most splash zone locations since carbonation penetration was minor as noted above. At the splash zone of ITB carbonation did penetrate to the rebar depth, but no corrosion was observed there. Factors such as the higher quality concrete there and the concrete surface coating may have contributed to mitigate any resulting corrosion by decreasing chloride ingress and creating a dryer local environment (Bertolini et al., 2003). It is also possible that rebar coating distress was not significant at the affected locations. Even lower chloride exposure and dryer concrete would have more efficiently mitigated corrosion induced by carbonation in the higher elevation trestle cap cracks.

3.1.4 Moisture Penetration in Sound and Cracked Concrete

3.1.4.1 Methodology

Preferential moisture penetration at cracks was examined indirectly by seeking evidence from concrete resistivity and electrochemical impedance measurements. Resistivity measurements were conducted at both off and on crack locations following procedures indicated in Section 2.1.1. Side-by-side field surface resistivity measurement for on-crack / off crack concrete location pairs were made for SSK at high elevations and for HFB, both of which included comparatively wide concrete cracking, Figure 5. The average resistivity readings from measurements made with electrode array orientation parallel and perpendicular to the crack were recorded. It is noted that in the case of cracked concrete the reported resistivity is actually a nominal value reflecting the contribution of the conductive paths of the bulk concrete and the crack zone.

Nominal concrete resistivity was also indirectly examined for cores extracted from SSK containing embedded ECR, by means of electrochemical impedance spectroscopy, EIS, measurements. A schematic of the test set-up is shown in Figure 15. Pre-autopsy EIS measurements were made at the open circuit potential within 10 days of original extraction from the field. On the cross-sectional cuts of the rebar, the circumference of the metal/epoxy interface was ground down and coated with acrylic, except at measurement contact point, to ensure electrical isolation of the steel substrate from the concrete matrix from the external surface of the sample. The signal amplitude was 10 mV and test frequency typically ranged from 100 kHz to 1 mHz.

Further details of EIS measurement procedures and results are given elsewhere (Lau and Sagüés, 2007) and only selected findings will be presented here. The results are presented as the high frequency limit cell solution resistance, R_s, between the embedded ECR and the outer concrete core face plane which contained both the reference electrode and a counter electrode. A sponge wetted with tap water was placed to improve counter electrode contact with the concrete face. This arrangement samples the parallel combination of the conductive path along the entire crack and that of the surrounding

bulk concrete, providing high sensitivity to any conductance enhancement due to preferential moisture presence in the crack. In contrast, the more varied current paths and comparatively smaller sample volume in the Wenner probe field surface resistivity measurements tend to obscure the contribution of the crack.



Figure 15. Field-Extracted ECR Concrete Core EIS Test Set-up.

3.1.4.2 Concrete Resistivity- Results

Concrete resistivity, ρ , for sound concrete locations, Figure 9 was ~5< ρ <100k Ω cm for Group 2 and 4 bridges and 10< ρ <1,000k Ω -cm for Group 3 bridges below 1m AHT. Surface concrete resistivity measurements in the field are subject to many complicating influences such as variations in the degree of water saturation and coarse aggregate presence, but the measured concrete resistivity was differentiated as expected among the high and low diffusivity of concretes in Group 2,4 and 3 bridges in the order of 10k Ω -cm and 100 k Ω -cm, respectively in the evaporative splash area >50cm AHT.

The side-by-side field surface resistivity determinations for on- /off- crack concrete location pairs made for SSK at high elevations and HFB (Figures 16-17) did not show any significant differentiation. However, as noted earlier this lack of differentiation

does not preclude the presence of significantly greater moisture content within the crack due to the limitations of the probe method.



Figure 16. Concrete Surface Resistivity Comparison On and Off crack. SSK High Elevation Trestle Caps line: Sound concrete. Dotted line: Cracked concrete.



Figure 17. Concrete Surface Resistivity Comparison On and Off Crack. HFB footers. Solid line: sound concrete. Dotted line: cracked concrete.

3.1.4.3 Electrochemical Impedance Spectroscopy- Results

The EIS measurements did show differentiation between both conditions, as shown in Figure 18. The solution resistance was smaller not only at low elevation locations —already observed in the surface resistivity tests— but also in cracked samples consistent with the increased moisture content and water penetration expected for the latter. For a typical EIS cell geometry, core diameter d=10cm, cover length L~10cm, the nominal concrete resistivity can be approximated by $\rho = R_s \pi d^2/4L$. The resulting value for sound concrete was in the range $\sim 40-140 \text{k}\Omega$ -cm, comparable to that obtained in the field surface resistivity measurements. The nominal ρ in cracked concrete was in the range \sim 8-80 k Ω -cm, smaller than in sound concrete and indicative of increased electrolyte presence in the cracks. The effect was stronger at low elevations, where ρ for cracked concrete was as much as 10 times smaller than for sound concrete. It is noted that some of the moisture in the crack in the EIS tests may have been recharged from the sponge used to enhance counter electrode contact. Nevertheless, the increased conductance of the cracked cores underscores the ability of that region to retain moisture and consequently facilitate chloride transport. The effect would be expected to be greater in bridges such as HFB where cracks were on average twice as large as in the others, and where the observation of corrosion of the ECR at crack locations was actually observed.



Figure 18. Solution Resistance Measured by EIS (SSK).● High elevations. □ Low elevations

Impedance curves generally showed high frequency, hf, loops with diameters that varied by orders of magnitude in side by side comparisons of EIS responses of epoxy coated rebar from cracked and on-cracked concrete from low elevations. As seen in Figure 19, the ECR from cracked locations generally had smaller hf loops than the ECR from the sound concrete. The hf loop diameter corresponds to the combined coating pore resistance, Rpo. Cumulative fraction curves of the pore resistance for all ECR measured with EIS, cracked/non-cracked concrete, are shown in Figure 20. Smaller Rpo values generally observed at cracked concrete locations are likely indicative of larger electrolyte conductance to the steel at crack locations.

From the above, it may be concluded that while not manifested by surface resistivity measurements, substantial moisture penetration can take place at crack locations with subsequent potential for locally accelerating corrosion.



Figure 19. ECR Impedance Manifestation of Presence of a Crack in the Core (Low Elevation SSK Samples). A,B,C Sound concrete core; A', B', C' Companion on-crack core; crack widths were 0.13, 0.25 and 0.23 mm respectively. A, A':118W4,118W3. B, B': 118W2, 118W1. C,C': 117E3, 117E1.



Figure 20. Pore Resistance in ECR from SSK Sound and Crack Concrete Locations. – sound concrete, -- crack concrete.

3.1.5 Porosity

Concrete porosity was measured following ASTM C642, 1997. Figure 21 shows that concrete porosity results, while being generally in the range or values normally expected for concrete, did not have good correlation to other permeability factors, such as D_{App} or ρ , nor to extent of corrosion. Porosity instead was influenced by the type of coarse aggregate, tending to be smaller for concrete with denser aggregate such as granite. This overall behavior is not unexpected as chloride transport tends to be dominated by the connectivity of the pore network rather than the total porosity (ACI 2004). Coarse aggregate such as limestone contains large pores but relatively little of the chloride resides there (Yu and Hartt, 2007). These measurements were performed for completeness and to rule out extraneous factors that might have changed the interpretation of the other findings.


Figure 21. Concrete Porosity.

3.2 Corrosion Development in ECR at On-Crack Locations

3.2.1 Methodology

Corrosion products developed in four separate cracked concrete locations in the Group 3 bridge HFB, examples shown in Figure 22, were examined with metallographic cross sections by optical metallography; two of those samples were further analyzed by secondary and backscatter Scanning Electron Microscopy, SEM, supplemented by elemental analysis with Energy-Dispersive X-Ray Spectroscopy, EDS.



Figure 22. ECR Corrosion at Crack Location, HFB 59E1 A. Corrosion products on bar surface. The line represents the location of the crack intersection. B. Appearance after partially removing the coating and exploring into the corrosion products.



Figure 23. Cross Section of ECR Bar Showing Severe Corrosion at a Crack Location of HFB 59E1. Left: Entire Bar cross-section. Right: Close up of corrosion penetration.



Figure 24. Corrosion Product - Base Metal Interface Showing Progression of Corrosion into the Microstructure of the Rebar Steel, HFB 59W1.

3.2.2 Results

Initiation of significant corrosion on ECR requires the combined presence of coating degradation and sufficient chloride ion contamination of the surrounding concrete. Prior work suggests that the corrosion initiation threshold of ECR is in the order of that required for plain rebar steel (Sagüés et al., 1994). As shown earlier and elsewhere (Sagüés, 1994; Ramniceanu et al., 2008; Fanous and Wu, 2005) coating breaks, often

clearly associated with initial mechanical distress, were a commonly observed feature in cores extracted from the bridges surveyed. A severe form of ECR coating degradation affecting all the structures examined was widespread disbondment of the metal-polymer interface, often with complete loss of adhesion and occurring early in the life with no need for chloride contamination. As discussed earlier and elsewhere (Sagüés et al., 1994) these deficiencies provide numerous sites for corrosion initiation and its propagation in the coating-metal crevice. The chloride contamination associated with cracks is not limited to just the narrow width of the crack itself but it also extends sidewise to some distance (Sagüés et al., 2001; Ishida et al., 2009). In addition, the epoxy coating-concrete interface is not adhesively bonded, as demonstrated by the clean separation achieved in extracted cores with embedded rebar and by the reduced bond strength measured in pullout experiments (Treece and Jirsa, 1989) so easy moisture and chloride transport on that interface is likely. Thus, initiation of ECR corrosion due to preexisting cracks is not expected to require the statistically rare precise intersection of a coating break with the crack plane. That expectation is supported by the observation of the multiple events of ECR corrosion at crack locations that took place in HFB. Consequently, it may be assumed that intersection of ECR with a crack that creates a local concentration in excess of threshold levels for plain carbon steel creates a high probability of corrosion initiation at or near that intersection. That assumption has been given a quantitative character in the modeling section of this manuscript.

Previous work has also shown that ECR coating breaks and associated disbondment elsewhere in the structure can provide sufficient cathodic reaction sites for efficient macrocell coupling to aggravate corrosion at anodic spots were corrosion has already been initiated (Sagüés et al., 1991). The extent of aggravation would depend on how effective the cathodic region is (Kranc and Sagüés, 1998; Raupach, 1996). The resulting duration of the corrosion propagation period would then be a combined function of the extent of coating deterioration that would affect both the number of anodic spots and the efficiency of the cathodic coupling. That effect too has been given a quantitative character in the modeling section and adapted for crack conditions.

The on-crack ECR undercoating corrosion products from HFB were compact and dark, consistent with a low state of oxidation, suggestive of anaerobic conditions in agreement with laboratory tests elsewhere (Zayed and Sagüés, 1990). Exploration with a sharp knife tip at the dark corrosion region pried out some of the products, revealing pitlike features as shown in Figure 22. Sectioning of the bar with a thin diamond blade and water-free lubrication was performed at a pit-like location, with subsequent metallographic mounting of the section. The cross section, Figure 23 revealed that corrosion had affected a wide region, having proceeded in relatively uniform fashion within the region to as much as ~ 1 mm dep. The corrosion product-base metal interface was examined at higher magnification revealing upon etching a ferrite-pearlite grain structure in the metal that extended, with no indication of microstructural alteration, all the way up to the corrosion penetration front where it was being consumed. Representative features are shown in Figure 24. This observation nearly rules out ascribing the observed features to causes alternative to corrosion, for example the presence of an isolated defect in the form of trapped slag or mill scale during rolling, since such condition would have been manifested by microstructural changes near the interface. Metallographic sections of the other bar samples from crack locations revealed corrosion penetration of depth and morphology similar to the one shown, always near the region of intersection of the rebar with the crack. No indications of severe corrosion were externally observed or revealed metallographically on ECR from the peer cores on the sound concrete location next to the cracks.

SEM micrographs, Figure 25-26, of the corrosion products showed a porous structure. Consistent with optical observations, the pearlitic grain structure of the steel extended to the corrosion front with no indication of microstructural alteration, further confirming the identification of the observed material as a corrosion product rather than manufacturing imperfections mentioned above. The larger pores in the corrosion product were in the order of 1 μ m. EDS results are exemplified for bulk steel and bulk corrosion product in Figure 23. The EDS analysis of the corrosion product shows a region rich in

iron (17 to 30at%) and oxygen (29 to 51at%), consistent with steel corrosion, and also significant presence of chlorine (2 to 7at%), likely a chloride form.

Trace amounts of other elements such as chromium, manganese, nickel, copper, silicon, and aluminum are attributed to steel alloy elements and contamination from metallographic preparation. Space-resolved EDS elemental analysis did not show any marked difference in relative chloride content when sampling points in the bulk of the corrosion product —light gray in Figure 26— and within the pore regions. This observation suggests that the electron beam simply excited the bottom of the pores with no indication of large chloride segregation there.

A solid corrosion product consistent with the SEM-EDS compositional observations and also capable of creating a significant in-crevice decrease in pH through hydrolysis of Fe ions (Fontana and Greene, 1986) is chloride-substituted Akaganeite, which has the nominal composition $Fe(OH)_{2.7}$ Cl_{0.3} (Schwertmann and Cornel, 2003; Selwyn et al., 1999). Such product would account for the formation of an expansive increvice solid and the ability to sustain crevice corrosion by promoting substantial local acidification.



Figure 25. SEM Image of Corrosion Product (HFB59W1).



Figure 26. SEM/EDS Analysis of Corrosion Product Observed in HFB59E1.

3.2.3 Solid Corrosion Product Formation in De-aerated Conditions.

Corrosion was accelerated for laboratory epoxy coated steel samples with introduced defects placed in simulated concrete pore water solution in aerated and deaerated conditions to compare corrosion development and morphology with that observed in HFB field samples, and to determine whether enhanced oxygen access is needed for the in-crevice corrosion produce development.

3.2.3.1 Methodology

Laboratory experiments were conducted with 1.6 cm diameter ECR newly manufactured, 2007, by a major rebar manufacturer. In these tests coating breaks were introduced intentionally and the ECR was subject to accelerated corrosion in simulated concrete pore water solution, SPS, with chloride ions in aerated and deaerated conditions. The SPS solution constituents and pH are listed in Table 3. The coating defects were introduced, between adjacent deformation ribs, by drilling with a 1.6 mm diameter drill bit to a nominal depth from the coating outer surface to the tip of the drill cavity of 1 mm. Each bar had 8 coating breaks for a total exposed steel area of ~0.45 cm². The two cut ends of the bar samples were coated with epoxy patch compounds.

The bar samples were partially immersed so that 19 cm length (~95 cm² surface area) were in contact with the test solution. The test cells were sealed from external air. In the aerated cell, air scrubbed of carbon dioxide through a filter cell with saturated calcium hydroxide was bubbled into the test solution at a rate ~0.01cm³/s. In the deaerated cell, 99.999% purity nitrogen gas with <1ppb O₂ was continuously bubbled in the cell at a similar flow rate as the aerated cell. In both cells, the gas outlet was fed into a bubbler to create a small positive overpressure. Solution temperature was 22 ± 2 °C. Each cell contained duplicate ECR specimens. The samples were potentiostatically polarized anodically at ~100mV_{SCE} to accelerate corrosion for 1 week after which the specimens were removed and the corrosion products formed were examined.

Table 3. Solution Constituents (g) per 1 L H_2O

	NaOH	КОН	$Ca(OH)_2^{\dagger}$	NaCl	pН	
SPS	3.7	10.5	2.1	35	13	
† Not fully dissolved in solution.						

3.2.3.2 Results

Anodic currents for the aerated and deaerated cells were similar throughout the experiment. The effect of concentration polarization where lower corrosion would occur in the deaerated condition was not manifested due to the large applied anodic polarization at $\pm 100 \text{mV}_{\text{SCE}}$. The cumulative charge for the aerated and de-aerated cells was similar for both conditions, ~900 coulombs. A steel volume of ~ 5-10 mm³ was consumed beneath each break in a roughly semicircular region centered on the break and undercutting it. The sound metal loss was comparable to that expected from Faradaic conversion for formation of Fe²⁺ ions. A solid corrosion product filled the space left by the consumed metal. Further corrosion products in the form of a tubercle extended outside the coating attesting to the expansive nature of the corrosion. There was considerable coating disbondment with some moisture accumulation around the defects, with a morphology that has been described in detail elsewhere (Zayed and Sagüés, 1990; Lau and Sagüés, 2009).

Visual differences were seen externally between the aerated and deaerated samples throughout the duration of the experiment, Figure 27. The external corrosion product tubercles in the aerated cells were reddish, consistent with a high oxidation state of iron oxidation (Evans, 1960). In contrast, greenish tubercle formation was observed in deaerated cells consistent with a lower state of oxidation (Broomfield, 1997). However, the underlying corrosion appearance for both conditions was similar, the solid corrosion product being dark and with visual appearance similar to that found in the HFB field samples. The pH, of the surrounding undercoating moisture, determined by applying pH paper there shortly after extraction of the samples from the test cells, was also similar, ~5-6 for both cases. These observations are consistent with those expected from an occluded cell under externally imposed anodic polarization (Fontana and Greene, 1986;

Lau and Sagüés, 2009), but noting that in the present case conditions allow for the precipitation of an internal solid corrosion product with expansive overflow.

Importantly, although the nature of the external corrosion product may have been influenced somewhat by oxygen availability, it was not a requisite for the formation of a substantial amount of expansive corrosion products. Thus, the results suggest that damage could develop even with thin, moisture filled cracks that would restrict oxygen flow to the corroding region.

In summary, ample opportunity for corrosion of ECR at cracked concrete regions exists, as confirmed by multiple events in the field. The corrosion depth was significant and solid undercoating corrosion products developed consistent with the expected occluded cell conditions. Oxygen transport to the corroding zone itself does not appear to be necessary.



Figure 27. External and Undercoating Corrosion Development in De-aerated (left) and Aerated (right) Environments.

PART IV

Part IV concerns direct examination and development of electrochemical methods for coating defect characterization of the epoxy coating in cracked concrete.

4.1. ECR Coating Characterization Techniques

Coating pull-off strength measurements and coating condition impedance characterization were made in the laboratory with extracted field samples. Coating pulloff strength measurement supplemented field and laboratory knife test observations. Supplemental EIS measurements were made with newly manufactured ECR following current specifications.

4.1.1 Epoxy Coating Adhesion

4.1.1.1 Methodology

To quantify coating disbondment, the coating adhesion strength was measured with a mechanical pull-off device (Sagüés and Powers, 1996). A metal dolly, 4.8 or 6.4 mm diameter, contoured to the surface curvature of bar between deformation ribs was attached with a cyanoacrylate adhesive to the outer polymer surface, lightly roughened and degreased, directly adjacent to the defect location. The polymer coating on the perimeter of the dolly was removed with a rotating dental drill bit. The dolly was then pulled until separation using a gimbal joint fixture to avoid shear stresses. The strength was recorded as the pull-off force divided by the nominal dolly area.

ECR samples extracted from all bridges were tested except for those from VAC where no coating adhesion was retained throughout the bar samples. The pulloff strength was calculated as the applied force divided by nominal dolly cross-sectional area, either 0.048 or 0.028cm².

4.1.1.2 Results

Figure 28 presents the pull-off strength results. It is noted that the pull-off tests were conducted on various spots of some of the ECR samples, and that large variations in strength values were noted in some cases from one part of the sample to another. Pull-off strengths for ECR from Group 2 bridges ranged from low to negligible, in agreement with the observations of significant corrosion and extended coating disbondment described in Section 2.1.2.

For ECR from Group 3 Bridges the coating pull-off tests gave results generally consistent with observations noted earlier ranging from instances of good coating adhesion to widespread coating disbondment. In high elevation SSK samples, where the coating had generally been found to have good coating adhesion, most of the pull-off strength tests resulted in the cyanoacrylate failing instead of the epoxy-steel substrate bond; indicating that its strength was above ~10 MN/m². In contrast, the coating failed at stresses as low as ~0.6 MN/m² in the low elevation samples, consistent with prevalent coating disbondment there as noted earlier. Coating failed at stresses below ~1 MN/m² on some of the HFB samples but the cyanoacrylate adhesive limit was reached for the majority of the sample spots tested. Samples from PER, noted earlier to be disbonded, had also pull-off strengths that were as low as 0.6 MN/m².

The polymer coating on ECR from Group 4 Bridges had pull-off strength levels consistent with disbondment measurements as described above. Of note, samples from IT2/3 had among the lowest pull-off strengths.



Figure 28. Epoxy Coating Pull-Off Strength. The pull-off strengths for Vaca Cut samples were negligible. Solid black symbols represent measured pull-off strengths. The other symbols represent lower bound pull-off strength failure at cyanoacrylate adhesive.
 Vertical lines represent minimum measurable strengths using metal dollys, nominal area 0.049 and 0.028 cm².

Being able to locate areas of ECR that have extended disbondment particularly in areas most susceptible to corrosion would be beneficial to isolate locations that may develop corrosion deterioration. Knife tests and pull-off strength tests are not practical as it involves destructive methods to sample only small sections of ECR. EIS methods to estimate coating ECR coating defects are described next.

4.1.2. Estimation of coating defect area by EIS

4.1.2.1 Methodology

EIS measurements for SSK ECR samples embedded in extracted concrete cores, described in Section 3.1.4, were conducted in part to examine the coating condition of ECR after ~20 years of service. As earlier mentioned, concrete cores were extracted from representative locations focusing on thin preexisting structural cracks on concrete

sections at low elevations exposed to sea splash as well as on drier higher elevation trestle caps.

On- and off- crack concrete core pairs, ~10 cm diameter, were typically drilled 15 cm apart and typically 4 cm past reinforcement depth, >10 cm. The ECR segments embedded in the cores, ~2 cm diameter, ~10 cm length, were perpendicular to the core axis. The cracks typically ran through the entire cover thickness and the plane of the crack was usually perpendicular to the rebar. The EIS measurements were made on the embedded ECR at the open circuit condition within 10 days of original extraction from the field. Within that time, samples were sealed to prevent moisture content change in the concrete. The signal amplitude was 10 mV and test frequency typically ranged from 100 kHz to 1 mHz. A Solartron Analytical SI1287 Electrical Interface and SI1260 Impedance Analyzer were used. An activated titanium mesh at the core outer end face was used as a counter electrode and a short activated titanium wire, calibrated against a copper/copper-sulfate, CSE, was used as a reference electrode held at the same end face. Both electrodes were separated and held by sponges saturated with tap water.

water/cement ratio	Cl ⁻ concentration (pcy)	Slump (in)	%air	Unit Weight (pcy)	28 day ρ (kΩ-cm)	30 day comp. strength (psi)
0.5	0.260	5.25	13	127	6.6	4290

Table 4. Supplemental EIS Test Concrete Properties

Supplemental EIS measurements were periodically made to evaluate the condition of the polymer coating of ECR subjected to cathodic polarization as part of another test program concerning mechanistic issues of alternative polymer-coated steel reinforcement (Lau and Sagüés, 2009; tbp). Test samples in these measurements were newly manufactured, 2008, commercial ECR, diameter ~1.6cm, cast in concrete, briefly disconnected from cathodic polarization from an external corroding steel anode during EIS testing. Testing began approximately 40 days after initial concrete casting. Similar EIS test parameters described above were used except 1MHz>f>1Hz. Activated titanium reference electrodes were embedded ~1.3 cm from each ECR. The disconnected steel rebar anode was used as a counter electrode. Defects exposing steel ~1% of the bar surface were intentionally introduced. The bars were set in a ladder-array configuration where the lowest of five bars per duplicate concrete columns would have the greatest cathodic over-voltage, while connected to the steel anode, and the top bar the least due to IR drop phenomena in resistive electrolytic mediums, i.e. concrete. Concrete mix properties are given in Table 4. Concrete resistivity was measured utilizing the 4-point Wenner-array described in section 2.1.1 with an inter-electrode spacing of 5cm.

4.1.2.2 Results

Figure 29 shows all EIS results, as Nyquist representations, from disbonded and non-disbonded SSK ECR samples from the high elevation trestle caps. The nondisbonded sample, which correspondingly did not have any visually observed coating breaks, as expected had an impedance response closely approaching that of an ideal capacitor. The curves from samples which were found to be disbonded, however, showed high frequency hf loops with diameters that varied by orders of magnitude. Similar hf loops were observed in side by side comparisons of EIS responses of ECR samples , all exhibiting complete disbondment, from cracked and non-cracked concrete from low elevations; results are shown in Figure 19 in Section 3.1.4.c.

The observation of the hf loops provide information on the presence of coating defect sites of varying severity of exposed metal and subsequent coating disbondment. The following analysis was conducted to examine to what extent EIS information of this type may be used to nondestructively estimate the extent of coating defects, so as to serve as an additional or alternative coating condition assessment method in future investigations.



Figure 29. Impedance Manifestation of Disbondment. ECR from high elevations. A,B Sound concrete core. A',A' Companion on crack core. (A, A': 140E2, 140E1. B, B': 33W2, 33W1).

Starting from earlier treatments by Haruyama et al., 1987 and Tsai and Mansfeld, 1993, the total ohmic resistance associated with a coating defect or pore¹ includes the electrolytic resistance R_{pos} ' of the pore which is assumed to be filled with electrolyte, and the resistance R_{poc} ' due to current constriction in the electrolyte immediately outside of the pore opening. The total ohmic resistance of a pore is then

$$R_{po}' = R_{pos}' + R_{poc}'.$$
 (Eq. 26)

The electrolytic resistance of a pore, R_{pos} ' is a function of the resistivity of the liquid filling the pore ρ and the geometry of the pore. Assuming cylindrical pore geometry,

$$R_{pos}' = \rho d/A_{po}'$$
(Eq. 27)

¹ In the following derivation, the term "defect" or "pore" will be used indistinctly reflecting common usage in the literature of EIS of coated materials.

where d is the thickness of the coating and A_{po} ' is the cross-sectional area of exposed metal at the bottom of the pore.

The resistance R_{poc} ' due to current constriction in the electrolyte immediately outside of the pore opening is proportional to ρ and the characteristic radius, r, of the pore (Oltra and Keddam, 1988).

$$R_{poc}' = \rho/4r \tag{Eq. 28}$$

Therefore

$$R_{po}' = \frac{\rho d}{A_{po}'} + \frac{\rho}{4r}$$
(Eq. 29)

and if the pore is assumed to be circular

$$R_{po}' = \frac{\rho d}{\pi r^2} + \frac{\rho}{4r}$$
(Eq. 30)

For ECR where there can be a distribution of coating pores, the total exposed metal area would be $\Sigma A_{po} = n\pi r^2$. If all n pores on a coating had approximately the same dimensions, the combined pore resistance R_{po} measured by EIS would be given by the corresponding parallel combination:

$$R_{po} = \frac{R_{po}'}{n} = \frac{\rho d}{n\pi r^2} + \frac{\rho}{4nr}$$
(Eq. 31)

If the resistance of the pore would be known, for example from EIS measurements, the cross-sectional area of coating pore defects, A_{po} , can be estimated as being inversely proportional to the ohmic resistance of the electrolyte assumed to be filling the defect, R_{po} .

$$A_{po} = k x \rho / R_{po}$$
(Eq. 32)

where k is a proportionality constant. The proportionality constant $k \propto d$ and would also incorporate the attributing resistance R_{poc} .

Combining Equation 31 and 32, it can be shown that $k=(4d+\pi r)/4$ or $k=d+\pi r/4$. The characteristic defect radius r for each sample tested was determined by calculating the equivalent radius of a pore of nominal Apo' which was correspondingly calculated by dividing the observed total A_{po} per sample by n of each sample. Assuming typical coating $d\sim0.03$ cm, the average r for the sample population was ~0.15 cm. The corresponding k would be ~0.15cm. This estimated k value for was ~5 times greater than d; for smaller defect areas, the influence of current constriction would be less and the value of k would approach d. The above may be considered as a rough approximation of k for the typical defect size observed for the sample population. Due to possible variability of d and current constriction artifacts, k was also assessed by correlating the observed coating damage area with the quotient of solution resistivity and pore resistance. Further evaluation is required, but for the sample population measured so far, a direct correlation between ρ/R_{po} and A_{po} was observed with similar k~0.15cm. Figure 30 shows the comparisons for ECR samples where direct coating defect observations and impedance measurements could be made, indicating better than order-of-magnitude correlation. In cases where there were no observable coating breaks, a nominal detection area of 0.1x0.1mm total defect area was assumed to give an upper limit of defect size.



Figure 30. Comparison of Observed Coating Defects to Estimated Coating Defects. Black symbols represent SSK data. Grey data from Lau and Sagüés, tbp.

The difference of pore resistance from cracked and non-cracked concrete locations, as seen in Figure 20 in Section 3.1.4.c, is not expected to significantly affect the estimated coating defect areas for the SSK field samples as the ratio of ρ/R_{po} is expected to be constant. If coating disbondment processes had occured, the ratio of ρ/R_{po} would increase assuming a simplified system with no impedance dispersion effects (Sagüés, 1991) for the disbonded coating region.

Additional EIS measurements to determine coating breaks were made as part of the supplemental experiments; the polarization behavior of the ECR samples is shown in Figure 31. Instability of electrochemical surface conditions of the rebar during the disconnect recovery period are not a concern as they are not consequential to the high frequency portion of the EIS measurements which reflects the polymer coating properties. The increase of potential in the polarized condition after ~30 days likely reflects accumulation of corrosion products on the surface of the steel rebar anode and subsequent decrease in overall cathodic overpotential for the ECR samples. This change in magnitude of cathodic polarization to the ECR is less than ~50mV and is not expected to greatly affect overall trends.



Figure 31. Polarization Behavior of ECR from Supplemental Test Setup of ECR Embedded in Concrete. All potentials are mixed-potentials while the system was connected to the steel bar anode. Dotted lines- steel bar anodes. Gray and black lines represent bars from duplicate concrete specimens.



Figure 32. Estimated Apo as Function of Time After Initial Concrete Casting. Vertical line represents time of initial cathodic polarization. Horizontal line represents nominal intentional defect area. . Gray and black lines represent bars from duplicate concrete specimens.

The nominal defect area of each of the eight intentional defects was ~0.2cm² so the nominal A_{po} was ~1.6cm². Apo at periodic time intervals after concrete casting was estimated from the EIS data by the relationship expressed in Eq. 32 using the k value determined earlier and is shown in Figure 32. For all ten samples, with varying extent of cathodic polarization, there was a relatively minor increase in the estimated Apo with time. The change may indicate some cathodic disbondment of the polymer coating, but the observed change is small in comparison to the uncertainty in estimating defect size. The difference of cathodic polarization from the upper to lower bars was <20mV and all cathodic potentials were -650<E<-550mV_{SCE}. At these moderate polarization levels, no discernable trend of estimated Apo and the extent of applied cathodic polarization were observed.

The extent of possible coating disbondment of ECR at OCP for the first 40 days after initial concrete casting was not evaluated by direct observation since exposure is still in progress. However, experiments in SPS by Lau and Sagüés, 2009 showed that after ~40 days of static polarization at OCP, $-150mV_{SCE}$, and $-500mV_{SCE}$ in SPS solution, ECR showed coating disbondment for both conditions. The disbondment radial length from the edge of circular coating defects for both of those cases was ~2mm, but disbondment measurements made there by applying force to the coating may not necessarily correspond to the insitu A_{po} of ECR embedded in concrete.

It is noted that the increase in ρ/R_{po} with time may be a result of the test column configuration used rather than an evolution in the extent of coating disbondment. As mentioned earlier, concrete resistivity was measured with a Wenner array probe where current density is greatest in the outer regions, a few cm, of the concrete. If as expected the moisture of that outer concrete region is removed at a faster rate —by evaporation in addition to cement hydration for example— than the interior, or if carbonation of the outer concrete surface occurs, then the probe may report a concrete resistivity substantially larger than that near the rebar surface in the bulk. Consequently, the apparent ρ/R_{po} ratio would increase at a faster rate than that corresponding to the conditions at the rebar surface which may have remained constant after all. As seen in Figure 33, there was only a moderate difference in the trend observed for R_{po} and ρ . Further testing is in progress and final verification of coating disbondment will be made after sample demolition and autopsy. In anycase, A_{po} was generally constant and consistent with expected values despite large changes in concrete resistivity.

In summary, in the concrete tests the high resistivity of the medium was manifested as a large pore resistance that depended on the characteristic size of the coating breaks. Relationships taking into account current distribution in the medium were developed to evaluate the coating break size from the measured pore resistance and number of defects present. Also, relationships taking into account the pore resistance, solution resistivity, and pore geometry may describe in-situ possible coating disbondment. These results are a first step toward applying EIS as a diagnostic method to assess the performance of ECR in quality evaluation and field applications.



Figure 33. Pore resistance and Concrete Resistivity as Function of Time after Inital Cathodic Polarization, ~40 days After Concrete Casting.

4.1.3 High Frequency Dispersion in EIS Measurements of ECR

Referring back to SSK samples, the coating CPE impedance component showed sometimes strong frequency dispersion as manifested by n values as low as ~0.5, as shown in Figure 34. This observation is striking since the capacitance of polymeric coatings of this type is usually near ideal (Orazem and Tribollet, 2008). Elucidation of this effect is important for any detailed interpretation of EIS response behavior of ECR. For example, frequency dispersion introduces large uncertainty in the value of the coating capacitance, which would in turn lead to improper estimates of the amount of water absorbed in the polymer coating characterized by the change in apparent coating capacitance with exposure time. Precise determination of water absorption trends is important in future mechanistic studies of the mechanisms responsible for coating disbondment.

An explanation for the frequency dispersion is that it reflects markedly uneven excitation current distribution due to the spatially extended cell configuration combined with high and uneven concrete resistivity. Such effect would be expected to be more noticeable in combination with breaks resulting in higher metal surface admittances and indeed, smaller R_{po} values, typically from cracked concrete samples, were associated with low n values. There was only one instance where a low n value, <0.7, was observed from a sound concrete sample. Yo varied widely but as seen in Figure 34, after normalizing for the coating thickness, d, and surface area, A, log Yo showed clear correlation with the value of n that can be expressed as Yo/Yo|_{n=1}=10^{4.5(1-n)}. Extrapolation of the trend to n=1 yields a value Yod/A~4x10⁻¹³. Per Eq. 25, that value corresponds to a coating dielectric constant ε =(Yod/A)/ ε_0 ~5 which is consistent with values typical for polymers such as the epoxy used on the bars (Orazem and Tribollet, 2008). This plausible result suggests that a representation as in Figure 34 can serve to deconvolute the effect of obscuring artifacts from uneven current distribution.



Figure 34. Correlation of Yo and n for Coating CPE Component.

4.1.3.1 Idealized Extended Circuit Analog

The frequency dispersion was thought to be due to uneven excitation current distribution from the outer plate counter electrode to ECR defect sites caused by the high quality concrete resistivity, >100k Ω -cm, reflecting the very low permeability concrete used in SSK, large concrete core test cell geometry, and in the cases of cores with cracks, uneven current paths via moisture in the cracks.

In exploratory modeling of the causes of the high frequency dispersion, the test cell was abstracted as an extended circuit mesh of resistor and capacitor elements representing solution resistance, coating pore resistance and coating capacitance, as described in Figure 35.



Figure 35. Idealized Extended Circuit Analog Model Abstraction.

The model corresponded to the typical cylindrical core geometry idealized as a prism of height 14cm and width 10cm. The rebar geometry was approximated by a prism with side length 2cm. For simplicity and benefiting from geometric symmetry, a two dimensional model of half of the system was implemented consisting of a mesh of 10x6 nodes as shown in Figure 36. The coarse mesh reduced the amount of necessary computation; as the analysis was exploratory in nature the model geometry was greatly idealized and simplified. The distance between each node in the mesh corresponded to 1cm except for the last row of vertical nodes where mesh elements had values that correspond to 6cm. The distance from the bottom edge of the mesh to elements corresponding to the ECR was 10cm, consistent with typical cover depths.



Figure 36. Detailed Schematic of Extended Circuit Analog Model Abstraction.

Each bulk resistance mesh element corresponded to a value $R_B = \rho_B x 1 \text{ cm}/10 \text{ cm}^2$ where ρ_B is the concrete resistivity. The concrete resistivity was assumed to be either 100 or 300k Ω -cm consistent with the concrete in the samples examined experimentally, Section 3.1.4. A crack in the concrete core, when considered, was implemented in the model by adjusting the values of the series of mesh resistors in the model geometry corresponding to the location where the crack propagated through the cover length intersecting the rebar— to a smaller value to represent preferential charge conductance through the moisture filled crack channel. For simplicity, the crack was treated as running along the length of the rebar. As shown in Figure 18 in Section 3.1.4.c, Rs measured by EIS was ~2-4 times greater in sound concrete than in cracked concrete. Thus the conductance of a mesh element in the crack region was assumed to be 5 times greater than the bulk. For the model geometry used, this would correspond to an edge mesh resistor in the crack region $R_C=2x(R_B/k)$ where k was 25. Due to the model geometry, the edge mesh resistor elements were given a value 2xR. For the bottom row of vertical mesh elements, the values of the resistors were correspondingly larger. Also, the horizontal mesh elements in the bottom row of the mesh were each given small resistances, 0.001Ω , to reflect uniform initial current distribution from the counter electrode. From a lead resistor connecting to these points, simulation of an alternating current voltage source was applied as shown in Figure 36.

Coating breaks were assumed to have uniform distribution around the circumference and length of the bar. The breaks along with the coating capacitance, were implemented in the uniaxial symmetric mesh by 8 parallel combinations of resistors and capacitors radially placed from a center node to the eight surrounding adjacent nodes. A pore resistance mesh element $R_B=R_{po}x8$. Corresponding to variability in coating defects determined by EIS measurements, R_{po} was assigned a value of $20k\Omega$, $200k\Omega$, or $2M\Omega$. Similar to the bulk resistance mesh elements, the edge resistors were given a value 2xR.

The total coating capacitance was calculated using Eq. 23 for and area of \sim 50cm² and coating thickness 0.23mm. C_C~1nF. A coating capacitance mesh element C_B=C_C/8. Edge capacitor elements were given a value C_B/2. The center node was treated as an electrical ground. Table 5 summarized the model cases tested. The model output consisted of the magnitude of impedance and phase angle for a range of frequencies 1MHz > f > 1mHz.

Case	Rpo (Ω)	Crack	$ ho_{\rm B}$ (k Ω -cm)
Α	2M		
В	200k	No	
С	20k		100 or
D	2M		300
Е	200k	Yes	
F	20k		

Table 5. Idealized Extended Circuit Analog Model Cases

The modeled impedance spectra results are illustrated in Figure 37 for Cases A-F for ρ_B =300 k Ω -cm. The frequency dispersion noticed experimentally was replicated by the model outputs such that the hf loop was somewhat elongated, particularly evident in

Case F. It is noted that charge transfer processes related to steel corrosion were not considered in this analog circuit model. Impedance parameters for these spectra and all the other implemented realizations were calculated using impedance analysis fitting software and the equivalent circuit analog shown in Figure 2b, except that Rp and C_{dl} components relating to charge transfer corrosion processes were neglected and a CPE component for the coating capacitance was used. The frequency ranges used in the analysis were 100kHz to 100Hz, 1kHz, and 10kHz. Frequency dispersion was quantified in this case by the resulting coating CPE n term calculated from those frequency regimes of the impedance spectra. A summary of all the modeling results is shown in Figure 38.

More apparent frequency dispersion was seen with cases of higher concrete resistivity in which it could be remarked that the capacitive impedance of the polymer coating would be lower compared with that of the electrolyte. This was also apparent where analysis was made for frequency regimes with confined ranges at the higher frequencies. Apparent frequency dispersion was calculated from impedance spectra for smaller Rpo as well in which much of the high frequency impedance response would be dominated by the higher apparent capacitive impedance of the electrolyte. Also, there was more apparent frequency dispersion with crack presence which would be attributed to less uniform current distribution.

The model calculations accurately replicated the experimental Yo-n correlation as shown in Figure 39 and give supporting evidence that current distribution from cell geometry and high concrete resistivity resulted in high frequency dispersion in EIS measurements. A more analytical approach to examine the cause of high frequency dispersion is detailed next.



Figure 37. Example Impedance Spectra for Extended Circuit Analog Model Case A-F for ρ_B =300 k Ω -cm. Point 1, 100kHz; Point 2, 10kHz, Point 3, 1kHz, Point 4, 100Hz.



Figure 38. Frequency Dispersion Quantified by Coating CPE n Term for Idealized Extended Circuit Analog.



Figure 39. Yo-n Correlation from Idealized Extended Circuit Analog Model EIS Analysis. The trendline overimposes experimental Yo-n correlation.

4.1.3.2 Truncated Transmission Line Extended Circuit Model

In the idealized extended circuit analog described in the previous section, uneven excitation current distribution, viewed to be caused in part by high solution resistance and enhanced conductance through moisture-filled crack space, was analyzed by impedance analysis of a mesh of resistors and capacitors relating to cell component properties. Here, the system was similarly analyzed but the current distribution beyond the solution resistance was treated rather as having characteristics of an electrical transmission line, TL. This approach is one-dimensional and more simplified than the numerical simulation presented above, but offers the opportunity of obtaining further insight into the mechanistic reasons behind the observed frequency dispersions. Analysis of impedance behavior of electrochemical systems as TL have been introduced by deLevie, 1964 and Keiser, 1976 and have been used to interpret electrochemical behavior under disbonded coatings by Sagüés and Zayed, 1991. The total impedance Z_{T} of TL is expressed as

$$Z_{\rm T} = \frac{\sqrt{R_{\rm L} Z_{\rm L}}}{\tanh\left(L\sqrt{\frac{R_{\rm L}}{Z_{\rm L}}}\right)}$$
(Eq. 33)

where L is the length of the TL, R_L is the resistance per unit length of the TL, and Z_L is impedance of the system interface per unit length of the TL.



Figure 40. Transmission Line Extended Circuit Analog Abstraction.

For the impedance response of the portion of the system being considered, Figure 40, R and Z in the TL would be characteristic of solution resistances and the impedance of the coating capacitance along the length of the TL, respectively. In the following, it is reminded that the impedance response to properties relating to the polymer coating is typically observed at relatively high frequencies, ie f>>Hz.

In the low frequency limit of the TL, the impedance would be

$$Z_{\rm T}|_{\rm lf} = \frac{1}{j\omega C_{\rm T}} \tag{Eq. 34}$$

where C_T is the total coating capacitance. If the impedance of the coating capacitance is viewed in terms of a CPE, one could consider an apparent $Yo = C_T$ for an apparent n=1. The ratio $Yo/C_T = 1$. It is noted that pre-admittance CPE term Yo is not equivalent to a capacitance.

In the high frequency limit of the TL, the impedance would be

$$Z_{\rm T}|_{\rm hf} = \sqrt{R_{\rm L} Z_{\rm L}} \tag{Eq. 35}$$

Equation 35 can be rewritten as

$$Z_{\rm T}|_{\rm hf} = \sqrt{\frac{R_{\rm T}}{j\omega C_{\rm T}}} = \frac{1}{C_{\rm T}} \left(\frac{\tau}{j\omega}\right)^{\frac{1}{2}}$$
(Eq. 36)

where $R_T = R_L L$, $C_T = C_L L$, $Z_L = 1/j\omega C_L$, and $\tau = R_T C_T$. As such, similar to inference made at the low frequency limit, one could consider per Eq. 21 an apparent Yo = $C_T \tau^{-0.5}$ for an apparent n=0.5. The ratio Yo/ $C_T = \tau^{-0.5}$.

 R_T could be approximated as $\rho_B \Phi/A$ where Φ is the bar diameter and A is the core cross-sectional area. For typical core geometry, $R_T \sim 2-6k\Omega$. The polymer coating capacitance was assumed to be in the order of $\sim 1nF$. τ was approximated to be $\sim 6-18\mu$ s, and the low frequency limit ratio Yo/ $C_T < 200$ to 400. This coarse estimate is not inconsistent with empirical observations and is within an order of magnitude of extrapolated values from the observed Yo-n trend described earlier.

	Case	τ=RxC (sec)	Rpo (kohm)	Rs (kohm)	Yo epoxy (Ssec ⁿ)	n epoxy	Rp (kohm)	Yo interface (Ssec ⁿ)	n metal
A	1	6x10 ⁻⁶ 18x10 ⁻⁶	20	30	1x10 ⁻⁹	1	-	-	-
B ·	2	6x10 ⁻⁶ 18x10 ⁻⁶	20	30	1x10 ⁻⁹	1	40	2.5x10 ⁻⁸	1
	3	6x10 ⁻⁶ 18x10 ⁻⁶	20	30	1x10 ⁻⁹	1	40	5×10^{-7}	0.7

Table 6. Transmission Line Extended Circuit Analog Model Cases

An equivalent circuit analog of the concrete/ECR system incorporating current attenuation by TL is shown in Figure 40. The impedance response for three cases with $\tau = 6\mu$ s or three times larger, 18µs, were examined; Table 6. The latter time constant was

considered to compensate for uncertainty in the coarse approximation of R_T in the TL and possibly larger coating capacitance due to water absorbtion. Similar to procedures described earlier, impedance parameters for these spectra were calculated using impedance analysis fitting software. For cases 2-3, the equivalent circuit analog shown in Figure 2b was considered. For case 1, Rp and C_{dl} components were neglected. CPE coating capacitance terms were used in all cases. The frequency ranges used in the analysis were 100kHz to 1mHz, 100Hz, 1kHz, and 10kHz. Frequency dispersion was quantified by the resulting coating CPE n term. A summary of results is shown in Figure 41.

Generally, little frequency dispersion was manifested for any case when $\tau = 6\mu s$. More frequency dispersion was observed for all cases when $\tau = 18\mu s$. The greater solution resistance in the TL that can be attributed to the larger time constant would cause uneven current distribution to be even more greatly manifested.



Figure 41. Frequency Dispersion Quantified by Coating CPE n Term for Truncated Transmission Line Extended Circuit Analog

In summary, the unexpected frequency dispersion in the coating capacitance observed at high frequencies was shown to result from uneven excitation current distribution due to an extended cell geometry, high concrete resistivity, and preferential crack conductance. This explained why more apparent frequency dispersion was observed for cases with or in combination of larger coating surface admittance, higher concrete resistivity, and crack presence.

Based on the understanding developed here, the use of a Yo-n correlation to deconvolute results so as to obtain the true coating capacitance was proposed. The correlation was further justified by independent transmission line calculations that supplemented those of the coarse 2D model abstractions.

PART V

Part V introduces and conducts advanced forecast modeling of the progression of corrosion damage of bridges with ECR and locally deficient concrete.

5.1. Performance Projections

5.1.1 Modeling Approach

To better understand the factors responsible for corrosion development and anticipate future needs for maintenance and repair, an effort was conducted to obtain quantitative damage projections. A statistical model to project performance of marine bridge substructures was successfully applied by Sagüés, 2003 and Lau and Sagüés, 2007 in previous interpretations of damage progression data. Application to the current expanded data set is presented here.

Briefly, the model divides the substructure surface into N_i discrete elements, each experiencing damage evolution with a corrosion initiation stage, of duration ti, and a propagation stage of duration tp (Berke and Hicks, 1992; Tuutti, 1982) at the end of which the element is declared damaged. Each element is assumed to have its own value of surface chloride concentration C_s , concrete cover x, D_{App} , threshold concentration C_T . Those parameters together establish the local value of ti by assuming for simplicity a one-dimensional diffusion geometry (Sagüés, 2003). The value of tp for each element is determined by assuming that the element has its own effective corrosion rate R resulting in corrosion penetration P that increases linearly with t-ti, where t is time. There is growing evidence that cracking/spalling takes place when P reaches a given value P_{CRIT} which for macroscopically uniform corrosion is proportional to the ratio x/Φ , where Φ is the rebar diameter (Torres-Acosta and Sagüés, 2004). Rebar size –mostly near size #6, ~20mm diameter– varies relatively little over the structural elements of interest so by
treating Φ as constant tp may be approximated for modeling purposes (Torres-Acosta and Sagüés, 2000) as tp = k'x, where k is proportional to R⁻¹. R is strongly influenced by the condition of the coating (Clear, 1992; McDonald et al., 1998) such that ECR with substantial coating distress should corrode faster than in the absence of imperfections. Thus k' is treated as a distributed model parameter, and assigned a value that becomes smaller as the extent of ECR coating distress increases.

Following the treatment by Sagüés, 2003, the time to corrosion spalling for these conditions can be expressed as ts.

$$ts = \frac{x^2}{4D_{App}\left(erf^1\left(1 - \frac{C_T}{C_S}\right)\right)^2} + k'x$$
(Eq. 37)

The values of Cs, D_{App} and x were assumed to have average values and element-toelement variability consistent with field observations in these structures. The variabilities were treated as stemming from normal distributions truncated as indicated below (Sagüés, 2003). A fixed value of C_T was assumed for simplicity. Laboratory observations suggest that under simple conditions C_T for ECR is on the order of the value for plain steel bar (Sagüés et al., 1994), which may in turn be estimated as being proportional to the cement content, CF of the concrete, $C_T \sim 0.004CF$ (Bentur et al., 1997). The parameter k' was assigned variability but implemented only stepwise over 3 different finite levels, plus another level designating elements with essentially unblemished rebar coating. The fraction of elements having each of the coating distress levels, or lack thereof, was also a model input.

The time to corrosion spalling on an element per arguments above is a function of x, D_{App} , C_S , C_T , and k'.

$$ts = f(x, D_{App}, C_S, C_T, k')$$
 (Eq. 38)

As such, if the values of the parameters other than x were at a given value, then elements with concrete cover smaller than a critical depth, x_s would result in a corrosion spall such that

$$x_s = F(ts, D_{App}, C_s, C_T, k')$$
 (Eq. 39)

For ts given in Equation 37, Equation 39 could be expressed as

$$x_{s} = -\frac{k'\Psi}{2} + \frac{1}{2}\sqrt{k'^{2}\Psi^{2} + 4 \text{ ts }\Psi}$$
(Eq. 40)

where

$$\Psi = 4D_{App} \left(\text{erf}^{1} \left(1 - \frac{C_{T}}{C_{S}} \right) \right)^{2}$$
(Eq. 41)

The fraction of elements for given values of D_{App} , C_S , C_T , and k' that would have a critical depth x_s for time ts is obtained by integrating the probability distribution of x:

$$\int_{0}^{X_{s}} P(x) dx = P_{cum}(x_{s})$$
(Eq. 42)

Likewise, in consideration of the probability that the concrete surface elements would have a given value for each of the variables described above and integrating over all possible parameter values of Cs and D for all ECR coating defect conditions k', the number of elements having a corrosion spall by time t would be as follows:

$$Nd(t)/N = (1/\Sigma_i N_i) \Sigma_i N_i \int_D \int_{C_s} P_{cum}(x_s) P(D_{App}) dD_{App} P(C_s) dC_s \quad (Eq. 43)$$

Damage projections were made by applying the above parameter distributions to a large population of elements, and tallying the fraction of elements reaching ti+tp for increasing time intervals (Sagüés, 2003). Each element was assigned the same surface area value, equal to that of a typical spall, and the total number of elements corresponded to a multiple of the typical portion of a bent exposed to aggressive conditions. Thus the fraction of cracked/spalled elements at a given time was equal to the number of spalls per bent, allowing direct comparison to the field data.

Cases modeled corresponded to the Group 1 bridges, two subsets of the Group 2 bridges, and speculative cases for Group 3 and 4 bridges. All calculations assumed initially chloride-free concrete.

		Group Group 2		Group	Group	
		1	(VSC)	(C)	3	4
Af	Surface area of bent exposed to severe corrosion	20 m ²				
Ae	Typical spall area	0.32 m^2				
CT	ECR chloride concentration threshold	1.55 kg/m^3				
μCs	Average surface chloride concentration	$12 \text{ kg/m}^3 \qquad \qquad$				
σCs	Standard deviation of surface chloride conc.	μCs/4				
Cs _{max}	Maximum surface chloride concentration	25 kg/m ³				
μx	Average rebar cover (mm)	76	148	87	10)2
σx	Standard deviation of rebar cover	μx/4				
μD_{App}	Average apparent chloride diffusion coefficient (m^2/s)	2x10 ⁻¹¹	1.7x10 ⁻¹¹	1.3x10 ⁻¹²	3x10 ⁻¹³	3x10 ⁻¹²
σD_{App}	Standard deviation of app. diff. coeff.	$\mu D_{App}/4$				
	Proportionality constant for propagation	0.14 yr/mm (2%) 0.28 yr/mm (4%) 0.56 yr/mm (8%)				
k'	time (Percentages indicate fraction of the					
	surface assigned to the value)					

Table 7.	Model	Input	Parameters
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Note: Cs, x and D_{App} were assumed to be normally distributed but truncated by zero and as shown by Cs_{max} .

Table 7 lists the values selected for model input for each case. The exposed bent area Af and element area Ae were based on typical prevalent structure and spall dimensions. The value of C_T reflects a representative value of CF, 388 kg/m³, consistent with those noted earlier. The average C_S , x and D_{App} values and their standard deviations were representative of those encountered in the affected bridges (Sagüés et al., 1994). It

is recognized that as those magnitudes cannot assume negative values, the actual distributions must depart from simple Gaussian shape. However, as more precise information on distribution character is not available, truncated normal distributions were used instead as a compromise. Thus all distributions were truncated at zero, and C_S was furthermore truncated at 25 kg/m³ which is representative of a salt-saturated pore water condition (Sagüés et al., 2001). The severe exposure regime and high concrete permeability conditions in Group 1 –reflected in the high average C_S and D_{App} values—yielded projections where the threshold concentration at the rebar depth was exceeded very early, e.g one year or so, in the life of the structure even for average cover locations. Consequently, for Group 1 the corrosion development projected by the model is dominated by the propagation stage, the value of tp, and less sensitive to the parameters that affect only ti (Sagüés et al., 2001).

The projected value of tp did depend strongly on x and k' values. The x values were determined by direct measurement in the field, but the k' distribution could only be inferred. Toward representing closely the actually observed damage progression, the assignment of k values over the rebar assembly was made by assuming that only a small fraction, 2%, of the rebar assembly was responsible for the earliest observations of damage. For that fraction a low value of k' = 0.14 y/mm was chosen, which corresponds to tp=7 years when x=50 mm. Since the value of ti given the other model variables was very short, the k'=0.14 y/mm fraction of the rebar assembly would consequently be responsible for the very first failures projected. Increasingly large fractions of the assembly, 4% and 8%, were assumed to have correspondingly less distress, k'=0.28 and 0.56 respectively, and consequently larger propagation times. This approach reflected the expectation that rebar segments with a high incidence of coating distress are likely to have the highest corrosion rates and therefore the shortest tp values. The chosen distribution for k' then effectively stated that there was a small fraction of the rebar with severe coating distress, and proportionally less distress on increasingly larger fractions of the assembly.

5.1.2 Modeling Results

The damage projections resulting from the above choice of parameters for each of the bridge groups, thick solid line, are shown in Figures 42-45. The corresponding actual damage functions from Figure 10 are reproduced for each pertinent case. The model projection for Group 1 bridges, Figure 42, reasonably reproduced the duration of the initial period where damage was minimal, and the subsequent steady rise of damage with time. The present choice of input parameters replicates that used by Sagués, 2003, which was based on fitting to data that terminated at earlier times for two of the bridges, NIL and LOK, but the overall match continues to be similarly adequate for the newer data as well. Sensitivity tests confirmed that the damage projection was only modestly influenced by changes in the distribution of D_{App} or Cs, or by variations in C_T , in agreement with the basis for the choice of model parameters used.



Figure 42. - Projected Damage Function for Group 1 Bridges. Thick bold line: total damage projection. Dashed lines: partial damage from each of the rebar assembly fractions considered: 2% of the rebar with k'=0.14 y/mm; 4% with k'=0.28 y/mm and 8% with k'=0.56 y/mm.

The dashed lines in Figures 42-45 represent the separate contribution to the total damage of each of the assumed finite distress fractions; addition of which corresponds to the thick solid line. As best seen in Figure 42, as time progresses a greater share of the projected damage increase results from fractions with increasingly greater k'. Whether future damage will continue along the present trend depends, in this scheme, on the extent of coating distress on the rest of the rebar assembly. If the remaining rebar coating were in very good condition, damage would continue for some time at the present nearly constant rate and then saturate at some intermediate level. The present choice of the distribution of k' values assigns finite values to only the first 14% of the rebar assembly, so projected damage saturation would take place at ~9 spalls per bent. As of this writing the highest recorded damage value —for NIL, evaluated in 2008— reached 4.4 spalls per bent without signs of slowing down, but the available data cannot preclude development of saturation in the relatively near future. Conversely, if the surface condition of the remaining rebar were poor or marginal, damage progression could easily continue to reach increasingly higher levels.

Data for the Group 2 bridges are too limited for detailed evaluation, but the model projections are in the order of the observed deterioration. Calculations for two subsets of Group 2 projected later damage development than for Group 1. The bridges in the subset VAC, SNK, and CH2 —VSC on Table 7— had values of D_{App} that were comparable to each other but not much smaller than those for Group 1. However, the average rebar cover of subset VSC was twice as high as that for Group 1. The model ruling equations imply that doubling the cover results in a fourfold increase in ti, and in a doubling of the value of tp, delaying the projected development of damage accordingly. The actual damage evolution in CH2 was somewhat faster than as projected by the model, but that difference should at least partially stem from imprecise information on the range of D_{App} for that bridge as only a cursory examination was performed there. CHO was placed into another subset —C on Table 7— as its average D_{App} was notably smaller than for the other bridges. That difference resulted in a significant increase of projected ti, toward increasing initiation stage control of the deterioration. Thus, CHO had longer projected

times to damage than in the first Group 2 subset, even though the average cover value was less than for that first subset.



Figure 43. Projected Damage Function for Group 2 Bridges. Thick bold line: total damage projection. Dashed lines: partial damage from each of the rebar assembly fractions considered: 2% of the rebar with k'=0.14 y/mm; 4% with k'=0.28 y/mm and 8% with k'=0.56 y/mm.



Figure 44. Projected Damage Function for Group 3 Bridges. Thick bold line: total damage projection. Dashed lines: partial damage from each of the rebar assembly fractions considered; 2% of the rebar with k'=0.14 y/mm; 4% with k'=0.28 y/mm and 8% with k'=0.56 y/mm.



Figure 45. Projected Damage Function for Group 4 Bridges. Thick bold line: total damage projection. Dashed lines: partial damage from each of the rebar assembly fractions considered; 2% of the rebar with k'=0.14 y/mm; 4% with k'=0.28 y/mm and 8% with k'=0.56 y/mm.

More speculative projections for sound concrete in Group 3 and 4 over a 100 year time frame are given in Figures 5-6. Those projections were made by assuming that the distributions of rebar damage and relative parameter variance and truncations were equal to those in Group 2, and changing only the average values of the concrete cover, chloride diffusivity, and surface concentration to reflect those obtained from concrete cores. These projections are only tentative as there are not as of yet direct observations of finite damage for comparison as it was the case for Groups 1 and 2. The projections essentially indicate that in sound concrete for Groups 3 and 4, widespread damage from ECR corrosion is not expected for several decades into the future. As noted above when considering similar expectations from earlier model predictions, much of the projected extended durability in these groups is a consequence of either high quality concrete or mild surface chloride load, and essentially no credit is taken for the use of ECR.

5.1.3 Validity and Limitations of the Model Projections

The model projections served primarily to provide insight as to the causes of the seemingly linear damage progression with time observed for the Group 1 bridges, and as to whether and at which rate similar damage functions would develop in the other groups. The calculations showed that the observed damage function in the Group 1 bridges was consistent with a relatively small fraction of the rebar assembly causing much of the damage in the first decade or two, with that fraction representing places were the rebar had experienced the most distress by the time it was put in service. Due to the fast chloride transport in the concrete, entered as a model input, the projections described a propagation stage-controlled damage progression. Accordingly, the damage at later bridge ages would correspond to other regions in the rebar assembly with lesser distress, where the effective corrosion rate was lower. The calculations showed that a roughly linear projected damage function, descriptive of that actually observed for the Group 1 bridges, resulted from assuming that the remainder of the rebar surface could be divided into fractions that were increasingly larger, and increasingly less free of distress. Such assumption is reasonably consistent with visual observations of ECR in place before concreting, showing obvious damage on only a small fraction of the rebar surface, while

much of the remaining surface was apparently defect free (Sagüés, 1994; Sagüés et al., 1990). Less visible initial distress, such as disbondment at rebar bends or from saltwater exposure in a storage yard, would also be expected to be severe in only a small portion of the assembly and less important elsewhere. The widespread coating disbondment in ECR observed even for chloride-free concrete would be present on areas with and without coating distress, but access to the disbonded metal-polymer interface would still be more efficient at the locations with more distress.

The projections successfully approximated too the limited observed damage progression data for the Group 2 bridges. In support of the applicability of the model, it is noted that for that group the input distribution of k' values was the same as that for Group 1 since the rebar sources were generally the same in both groups (Sagüés et al., 1994), and not treated as an adjustable parameter to force a fit. The approximation between projections and observed damage for this group supports also the interpretation that the process became more initiation-stage controlled as expected from the lower chloride diffusivity. The applicability of the model projections for sound concrete in Groups 3 and 4 was also supported, albeit by default, by the absence of observed damage in those locations up to the present.

The model provides a supported explanation of the observed damage and a tool for estimating future evolution. Such explanation and forecast are useful in developing an understanding of the factors responsible for the corrosion, and in having a structured method for anticipating maintenance and rehabilitation needs at least in a comparative manner. However, the model projections should be viewed only as provisional estimates subject to considerable modification as new information develops. Such caution applies as the field data and mechanistic knowledge available at present are not enough to resolve substantial uncertainty in the model assumptions and in the value of the input parameters. Importantly, the assumptions linking coating distress with corrosion rate represent gross simplifications that would require significant improvements in mechanistic knowledge to verify and refine. Even after such validation, a multiple regression fit to the data to optimize the parameter choice for the distribution of k' values would be very poorly resolved given the variability and limited amount of field damage data. Other factors, such as the effect of the extensive disbondment noted earlier for ECR after a few years of service in chloride free concrete, were not explicitly considered in the model. Advances in modeling of these systems are in progress that should improve future forecasts. For example, the present model assumes simple Fickian diffusion with time and depth independent D_{App} with constant surface concentration Cs, factors that may be better quantified as additional information develops (Sagüés, 2003). Alternative C_T regimes may be considered as reported elsewhere (Hartt et al., 1998), including possible higher C_T due to coupling with nearby anodic regions (Sagüés and Kranc, 1998) which could substantially alter the damage projection. This latter factor has been examined in detail recently and has good potential for implementation in next generation models (Sagüés et al., 2008).

5.1.4 Overall Considerations and Behavior in Locally Deficient Concrete

The field observations and insight from the above modeling projections indicate that ECR corrosion in the Florida bridges resulted from a combination of factors. Those include a highly aggressive service environment which, in the absence of a thick cover of highly impermeable concrete, rapidly left the epoxy film as the only remaining corrosion protecting barrier on the steel bar. Given also the inherent vulnerability of the film to flaws and disbondment from the base metal, corrosion quickly ensued with electrochemical aggravating factors noted earlier. As the modeling arguments showed, significant corrosion of even a relatively small fraction of the rebar assembly could manifest itself as extensive and conspicuous damage, which can continue increasing for many years.

As shown by the absence of external signs of damage in the Group 3 bridges, no severe ECR corrosion developed when the coated bar was protected by a thick cover of sound, very low permeability concrete with D_{App} values nearly two orders of magnitude lower than those in Group 1. Significant amounts of coating flaws existed in those cases too, as well as widespread loss of adhesion between coating and base metal, so corrosion

is expected to ensue once the chloride content at the rebar exceeds an effective threshold level. However, such event would likely be many decades into the future given the very slow chloride penetration. It is cautioned that part of the inventory of ECR Florida bridges has substructure with intermediate D_{App} values not unlike those in CHO (Sagüés et al., 1994). In those bridges corrosion may well begin to develop in the relatively near future, albeit per experience from the Group 2 bridges and per model projections, at a more moderate rate of increase than that seen in Group 1.

As noted above and from findings in related investigations (Sagüés et al., 1994; Lau and Sagüés, 2009a) the protection of a thick cover of low permeability concrete can be seriously diminished locally in the presence of cracks, lift lines or other local deficiencies. Corrosion may not only develop locally as noted in HFB, but the strong deterioration seen there may reflect also adverse galvanic coupling with nearby passive steel at other coating break locations (Kranc and Sagüés, 1998; Raupach, 1996). Such effect could lead to severe local reduction of cross section and associated risk of reinforcement failure (Tinnea, 2002). The consequences of that form of deterioration may be mitigated in part by the relatively small incidence of cracking (Sagüés et al., 2001) when viewed in terms of number of cracks per length of waterline perimeter, thus representing a limited number of spots with likely incidence of damage. Continuing monitoring of these locations is recommended.

5.2. Forecast Modeling in Locally Cracked Concrete

The observation of severe local corrosion of ECR at one of the bridges with otherwise low permeability concrete brings up interest in forecasting the extent of possible resulting damage in that bridge and in similar structures that showed preferential chloride transport at crack locations. The following is an initial formulation that may serve as a starting point pending the development of additional field evidence.

The modeling is based on the premise of spatially discretized sound concrete surfaces exposed to corrosion risk with independent corrosion initiation and propagation processes and distributed concrete parameters described earlier but also explores the added effect of the presence of cracks on ECR corrosion development. As noted earlier, the effect would be relatively more important in the case of less permeable sound concrete, so the model implementation uses as a baseline the projections for the lowdiffusivity Group 3 bridges that had been presented earlier. The following assumptions and simplifications were made, referring to Figure 46 for a schematic of the idealized geometry considered. The factors affecting corrosion opportunity at the concrete crack-ECR intersection zone were mentioned in the previous section and are tentatively quantified here.



Figure 46. Schematic of Idealized Model Geometry.

5.2.1 Basic Statements

1. Per extension of the findings by Sagues et al., 2001, preexisting cracks exist at the rate of Nc cracks per unit length of substructure perimeter on water.

2. The average preexisting crack length is h'

3. The portion of the substructure subject to corrosion has a height h and a total perimeter length W, so its total area is $A_T=h$ W

4. The portion of rebar subject to corrosion when a preexisting crack intersects the rebar crosswise is small, with a length $Lc \sim \Phi$ where Φ is the rebar diameter. When the rebar is aligned lengthwise with the crack reaching it, the entire affected length is assumed to be subject to corrosion.

5. Rebar diameter Φ is significantly smaller than the average rebar cover Xc'

6. The corrosion-induced crack emanating from the affected rebar results in a spall corresponding to a crack front fanning out at a 90 degree angle from the corroded zone. Therefore the resulting spall has a width $Ws \sim 2 Xc'$

7. For crosswise intersections, the preexisting crack is considered to affect multiple parallel rebars. On first approximation the resulting multiple corrosion-induced crack fronts are assumed to merge forming a spall region of length h' and width Ws. Per assumption (4) above when the rebar is aligned lengthwise with the preexisting crack the spall region is also of size h' by Ws.

8. The total area potentially affected by spalls at preexisting cracks and the rest of the substructure area subject to corrosion develop corrosion separately, e.g mutual macrocell effects and mutual spall mechanical interference are ignored for simplicity.

9. In the model for sound concrete described earlier, a value Ae was assigned to the area of a typical spall. For consistency with that model, the cumulative area from spall regions from preexisting cracks is tallied and the spall count is increased by one unit every time that sum reaches an integer multiple of Ae.

10. Chloride transport into the preexisting crack is assumed on first approximation to occur by simple diffusion, with an apparent diffusivity $D_{cApp} = \beta D_{App}$, where D_{App} is the apparent diffusivity in the concrete bulk and β is a multiplier >1.

11. The corrosion initiation threshold for rebar portions reached by a preexisting crack is the same as the value C_T prevalent at rebar in contact elsewhere with the bulk of the concrete.

12. Once corrosion starts at a crosswise rebar/preexisting crack intersection the local corrosion rate is macrocell-enhanced with respect to that in the bulk by a

factor $\gamma > 1$. When the rebar is aligned lengthwise with the crack reaching it, the anode/cathode configuration is assumed to be comparable to a normal case and γ is assigned a value of 1.

13. Per extension of the arguments made by Torres-Acosta and Sagüés, 2004, the amount of metal penetration by corrosion needed to cause a spall by corrosion where the rebar intersects the preexisting crack is greater than that prevalent at the bulk by a factor $\delta = (1+Xc/Lc)^2$. It is noted that for crosswise intersections Lc is effectively equal to Φ per assumption (4) above. For lengthwise intersections Lc is equal to the length of the crack.

14. From the above, it may be said on first approximation that, of the total substructure area subject to corrosion A_T , there is a portion αA_T that is subject to crack-induced corrosion and a portion (1- α) A_T that corrodes regularly as in initially sound concrete.

15. The fraction of the surface experiencing regular corrosion that spalls by time t shall be called fr(t); the fraction of the surface potentially affected by crack-induced corrosion that spalls by time t shall be called fc(t).

5.2.2 Implementation

Based on the above assumptions and definitions the value of α is given by

$$\alpha = 2 \text{ Xc' Nc h' W / (h W)} = 2 \text{ Xc' Nc h'/h}$$
 (Eq. 44)

The function fr(t) for the part corroding regularly can be calculated using common treatments for sound concrete. For these simulations, a statistically distributed approach was used as detailed earlier and by Sagüés, 2003 with the parameters listed in Table 7. For the crack portion the function fc(t) can be calculated in the same manner but using βD_{App} instead of D_{App} , and $\epsilon k'$ instead of each k' where $\epsilon = \delta/\gamma$ because the propagation time would be shortened by the increase γ in the local corrosion rate, and extended by the increase δ in the amount of corrosion needed for local cracking. All the other parameters remain the same as for the sound concrete model

The number of spalls per bent by time t is therefore given by

$$N(t) = (Af/Ae) \left(\alpha fc(t) + (1-\alpha) fr(t) \right)$$
(Eq. 45)

5.2.3 Cases Examined

Because of the paucity of actual data noted earlier, only illustrative calculations are presented.

The conditions chosen correspond to a Group 3 bridge with 20 m² surface area (~200 sq. ft.) bents, and declaring a spall when the spall area is 0.32 m^2 (~3 sq.ft). Numbers smaller than one spall per bent may be interpreted as indicating the appearance of only one spall in a correspondingly large number of bents.

Rebar size and cover are assumed Φ =1 in (2.54 cm) and Xc'=4 in (10.2 cm), so δ = 25. As a variation, a condition will be considered in which the crack runs parallel to the rebar length instead of crosswise. In such case the length of the corroded zone can be Lc>>Xc', so δ is simply =1.

The macrocell acceleration factor is unknown but experiments and calculations (Kranc and Sagüés, 1998) suggest that there may be an order-of-magnitude effect so γ =10 will be assumed.

Acceleration of chloride transport into the crack will be also assumed to be an order-of magnitude effect but possibly greater for concrete with very low D_{App} in the bulk, so cases with β =10 and β =100 will be adopted per arguments earlier in the manuscript.

Visual observations suggested that most cracks are in the 3 to 6 ft [0.9 to 1.8 m] length range which is in the order of half of the elevation range normally associated with potential for sever corrosion, so h'=0.5 h will be assumed. The value of Nc observed in Ref. 13 ranged from 0.01 m⁻¹ to 0.19 m⁻¹ so calculations were conducted for those two extreme values, as well as for Nc=0 as a sound concrete baseline.

The above conditions and variations are named as follows:

No crack:	Baseline, sound concrete.
C:	Crack perpendicular to rebar, $\delta=25$, $\gamma=10$
L:	Crack along rebar, $\delta=1$, $\gamma=1$
10X:	Transport along crack 10 times faster than in bulk, $\beta=10$
100X:	Transport along crack 100 times faster than in bulk, β =100
Nc:	0.01 m ⁻¹ . Low incidence of preexisting cracking
Nc:	0.19 m ⁻¹ . High incidence of preexisting cracking

All other parameters are as in case Group 3 described in Table 7.

5.2.4 Results and Implications

The results must be qualified by observing that the model assumptions are sweeping and there is ample room for added complexity in future development. Among many such issues, it is noted that assumption 8 on independent corrosion progression of individual regions may benefit from consideration of the effect of potential on local corrosion threshold (Sagüés et al., 2009). Consequently, the following should be viewed as tentative findings.

Results keyed to the nomenclature used above are presented in Figure 47 for a 100 years time base. As can be seen there, the model projects no dramatic effect on the damage function for any of the variations concerning the case of low incidence of cracking. Substantial effects are projected however for some of the variations in the high incidence case, 0.19 m^{-1} , or one crack each ~5 m of linear substructure waterline. The greatest effect is equivalent to a 300% increase in the incidence of spalling for service

ages from about 15 years to 50 years compared to the sound concrete case, for lengthwise cracks and a 100X multiplier in chloride transport at the cracks compared with sound concrete. The smallest projected effect for the high incidence cases is comparatively small –maximum ~ 20% increase in damage– and corresponds to cracks crosswise to the rebar length, and only a 10X increase in chloride ransport in the crack.



Figure 47. Model Projections for the a) High, Nc=0.19m⁻¹ and b) Low, Nc=0.01m⁻¹ Cracking Incidence Cases.

The projections indicate that, as expected, relatively isolated cracking should only create topical concrete damage with limited maintenance requirements. However, even though assuming that the incidence of damage is limited to a small region around the crack, if the crack orientation with respect to the rebar were adverse and chloride transport were greatly enhanced –as it could be expected in relatively wide cracks– corrosion damage from localized concrete deficiencies could significantly increase maintenance costs. It is also noted that remedial measures such as cathodic protection, which can be readily implemented for plain steel rebar, may be impractical in the case of

ECR due to connectivity limitations (Sagüés et al., 1994). These findings underscore the need for continuing monitoring of locally deficient concrete locations in otherwise high quality concrete structures exposed to aggressive environments. Judicious application of the predictive model developed in this project may aid in exploring the cost effectiveness of alternative corrosion protection methods, such as corrosion resistant rebar to prevent local damage for a given extent of existing or anticipated concrete deficiency.

In summary, the model calculations indicate that while corrosion of ECR at cracked locations may result in conspicuous early local damage instances, only the most pessimistic scenarios yielded projections of a sizable increase in the total corrosion damage relative to that expected by the rest of the substructure. However, given the tentative character of these projections it is important to continue monitoring the performance of ECR in these structures to reduce uncertainty in subsequent damage forecasts.

PART VI

Part VI presents conclusions.

6.1 Conclusions

Damage from corrosion of ECR has continued to develop steadily in the substructure of five major Florida Keys bridges (Group 1). Since the first indications of corrosion ~6 y after construction, damage increased until the present near-30 y age of the structures, with no indication of slowdown. Externally recognizable ECR corrosion damage began to be noticeable at four other Florida bridges (Group 2) ~2 decades after construction and continuing into the 3rd decade.

Early corrosion in the Florida bridges resulted from a combination of factors, including a highly aggressive service environment which, in the absence of a thick cover of highly impermeable concrete, rapidly left the epoxy film as the only remaining corrosion protecting barrier on the steel bar. Given also the inherent vulnerability of the film to flaws and disbondment from the base metal, corrosion quickly ensued with electrochemical aggravating factors such as the formation of extended macrocells.

No severe ECR corrosion developed in situations where the coated bar was protected by a thick cover of sound, very low permeability concrete (Group 3 and 4 bridges). However, there was widespread disbondment of the epoxy coating in all these structures even in sound concrete locations. This disbondment together with the observed frequent coating breaks are expected to facilitate corrosion initiation as chloride levels at the rebar depth increase in future decades.

A field survey confirmed the presence of usually minor cracks as a regular feature of marine substructure elements. Some cracks in bridges with highly permeable concrete may be caused by corrosion of the ECR resulting from chloride ingress through the bulk of the concrete. The rest of the cracks were most likely preexisting.

There was marked preferential chloride intrusion at preexisting cracks in bridges built with low permeability concrete. Preferential chloride intrusion was relatively less in bridges with higher permeability concrete, were bulk diffusion was rapid enough to mask any faster transport through cracks.

In most cases preexisting cracking at bridges with otherwise low permeability concrete was not associated with ECR corrosion. However, multiple instances of early severe corrosion of ECR occurred at one of those bridges where ~1mm wide cracking existed near the water level.

The corrosion products in that case were solid and grew underneath the epoxy coating. The composition was consistent with that of chloride-substituted Akaganeite, which can be stable in the locally acidified conditions present in an occluded cell. Laboratory experiments showed that oxygen presence was not necessary for the formation of similar corrosion products, suggesting that corrosion damage could develop even with thin, moisture filled cracks that would restrict oxygen flow to the corroding region.

Experimental results and predictive model calculations indicate that the propagation stage of corrosion dominated damage development in the structures that showed early deterioration. Significant corrosion of even a relatively small fraction of the rebar assembly could manifest itself as extensive and conspicuous damage, which can continue increasing for many years.

A model for projecting impact of preexisting cracking on spall damage was developed based on tentative assumptions. The projections indicated that relatively isolated cracking should only create topical concrete corrosion damage with limited maintenance requirements. However, adverse crack orientation with respect to the rebar and chloride transport enhanced by wider cracks resulted in significantly increase damage projections. Continuing monitoring of the structures showing preexisting cracking was recommended.

EIS response was sensitive to moisture content. Lower solution resistance was observed at locations with greater moisture content and presence of crack. Smaller R_{po} values are generally observed at cracked concrete locations for ECR core samples. The differences of R_{po} values in cracked to noncracked samples are likely indicative of larger electrolyte conductance to the steel at crack locations.

In EIS tests, the high resistivity of the concrete medium was manifested as a large pore resistance that depended on the characteristic size of the coating breaks. Relationships taking into account current distribution in the medium were developed to evaluate the coating break size from the measured pore resistance. The results were discussed as a first step toward applying EIS as a diagnostic method to assess the performance of ECR in quality evaluation and field applications.

Frequency dispersion at high frequencies was shown to result from current distribution effects from cell geometry and high concrete resistivity. More apparent frequency dispersion was observed for cases with or in combination of larger coating surface admittance, higher concrete resistivity, and crack presence. Yo-n correlation for coating CPE was observed. Deconvolution of dispersion effects on coating capacitance may be possible.

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