Performance of High Performance Concrete HPC in Low pH and Sulfate Environment

Final Report Contract No. BDK80 977-16 May 2013



Prepared by: Dr. Nakin Suksawang (Principal Investigator) Mr. Shuo Zhang (Research Assistant) Florida International University

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Prepared for:



Research Center Florida Department of Transportation 605 Suwannee Street, MS 30 Tallahassee, FL 32399-0450

Prepared by:

Dr. Nakin Suksawang (Principal Investigator) Mr. Shuo Zhang (Research Assistant) Department of Civil & Environmental Engineering Florida International University 10555 W. Flagler Street, EC 3602 Miami, FL 33174 Tel: (305) 348-0110 E-Mail: <u>suksawan@fiu.edu</u>

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DISCLAIMER

The opinions, findings and conclusion expressed in this publication are those of the authors and not necessarily those of the State of Florida Department of Transportation.

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
		AREA		
in ²	squareinches	645.2	square millimeters	mm ²
ft ²	squarefeet	0.093	square meters	m²
yd ²	square yard	0.836	square meters	m²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	square kilometers	km ²
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft ³	cubic feet	0.028	cubic meters	m ³
yd ³	cubic yards	0.765	cubic meters	m ³
NOTE: volumes	s greater than 1000 L shal	l be shown in m ³		
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
Т	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
	TEM	PERATURE (exact degree	ees)	
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in ²	poundforce per square inch	6.89	kilopascals	kPa

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Project Manager for this project	••			
16. Abstract	.	C 1 TT 1	16	1.1.0
The goal of this research is to d	etermine the impact of	t low pH and su	litate environment on	high-performance
concrete (HPC) and if the current	suluctural and materials	s specifications p	two proposed opproved	ctions for concrete
conducted which includes (1) file	d investigation and (2)	laboratory experi	iment. The field invest	tigation involved a
review of bridge environmental	database visual inspe	ection of selecte	d HPC bridges and	auantifying their
deterioration Considering that the	concrete mixtures of th	e selected HPC h	a fife onleges, and	btained laboratory
experiments were conducted to ev	aluate the effect of poz	zolanic and ceme	entitious materials on	concrete structures
exposed to low pH and sulfate en	vironment. Results indi	cated that bridge	s exposed to both low	v pH and moderate
sulfate environment are prone to	significant deteriorat	ion as compared	to bridges with sir	nilar classification
(moderately aggressive). In fact, co	prrosion was detected in	the steel reinforc	cement on two bridges	that had only been
in service for less than 30 years. W	Vhile similar classified I	oridges (moderate	ely aggressive) that we	ere only exposed to
either moderately low pH (betwee	en 5.0 and 6.5) or mod	lerate sulfate (be	tween 150 and 1500	ppm) environment
showed slight surface deterioration	on but not interior. Th	e reason for this	is because structure	s exposed to both
environment will undergo exchang	e reaction between the	acids present in t	he low pH environme	nt that increase the
concrete porosity allowing the sul	fate to attack even at a	moderate level.	The expansion manife	sted by the sulfate
attack cause cracks to form allo	wing aggressive water	to penetrate the	embedded steel ren	nforcement, which
eventually lead to corrosion. Th	erefore, it is recomm	ended that the	Department reviews	the environmental
classification to include an exposu	and a stand stand that I	low pH "and" m	oderate sulfate as "ex	tremely aggressive
environment. The laboratory re	suits indicated that H	PC provided be	ther resistance to love	w pH and sufface
recommended that slag comment and	Vor silica fume he used	in regions where	both sulfate and low n	U ara provolent
recommended that stag cement and	for since runne de useu	in regions where	both surface and low p	Ti ale prevalent.
17. Key Word		18. Distribution Stat	ement	
High-Performance Concrete, Sulfate Attack, Low				
pH, Durability				
				-
19. Security Classif. (of this report)	20. Security Classif. (c	of this page)	21. No. of Pages	22. Price
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EXECUTIVE SUMMARY

The Florida Department of Transportation (FDOT) has been using high-performance concrete (HPC) since 1976 to enhance the durability performance of reinforced concrete structures. Over the years, through research and field implementation, FDOT developed several guidelines on HPC and concrete cover for various environment prevalent in Florida. One of major concerns is the marine environment, where the presence of chloride can initiate corrosion of the steel reinforcement. Intrinsically, the State's design philosophy of a 75-year design service life of concrete structures was developed on the basis of its experiences with HPC in chloride environment. However, Florida bridges are also affected by other environment, particularly low pH and sulfate environment, which do not have the same deterioration mechanism caused by chloride. Thus, there is a need to investigate the performance of HPC in low pH and sulfate environments.

Sulfate attack on concrete is a highly complex phenomenon and is considered as a physicochemical process that leads to certain physical and mechanical consequences, such as change in volume, porosity, permeability, and mechanical properties. It is well established in the literature that sulfate attack in concrete can be limited by controlling the material's composition and transport properties. These controlling factors can be achieved by limiting the water-tocementitious material (w/cm) ratio, limiting tricalcium aluminate (C₃A) in Portland cement, use of supplementary cementitious materials, proper compaction and curing, and use of air entrainment. These controlling factors are implicitly achieved through the State's HPC mixtures guidelines. However, reinforced concrete structures are not only affected by sulfate attack but by other chemicals such as acids. Similarly to sulfate attack, acids can adversely affect concrete by dissolving both hydrated and unhydrated cement compound. The level of deterioration depends on the concentration of the acidic compound but it is well established that any environment with less than 6.5 pH would be detrimental to concrete. As a consequence, the presence of both low pH (< 6.5) and sulfate environment could potentially accelerate the rate of deterioration that may not be accounted for when developing the design and materials specification. Therefore, there is a need to understand the impact of sulfate attack and exposure to low pH on the State's HPC mixtures

The goal of this research is to identify whether the risk of deterioration of HPC in low pH and sulfate environment would shorten the 75-year design service life, based on the current state material design philosophy. The research has seven main objectives:

- 1. Determine the potential risk of significant deterioration of HPC in low pH and sulfate environments present in Florida.
- 2. Identify the concentration of sulfate and pH for deterioration of HPC to occur.
- 3. Reevaluate the state environmental classification system.
- 4. Identify the best curing practice that reduces the risk of material deterioration for HPC in low pH and sulfate environments.
- 5. Identify the time scale to degradation.
- 6. Determine the effect of material degradation in low pH and sulfate environments on the structural integrity or reinforced concrete structures.

7. Determine the effect of material degradation in low pH and sulfate environments on the corrosion resistance of HPC.

In pursuit of the stated objectives, a two pronged approach was conducted: (1) field and (2) laboratory investigations. The field investigation consisted of the inspection of HPC bridges exposed to pH values between 4.0 and 6.5 (based on the lowest recorded values) and sulfate content of 130 ppm and greater. The field inspection involved a survey of bridge environmental data, coring of field concrete samples, and analysis of cored field samples. Eight HPC bridges had been identified with potential risk of significant deterioration in low pH and sulfate environments. At each location, environmental data was collected and compared to the state's environmental database. Four cores were taken and evaluated using scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS) to characterize the chemical composition of the samples.

Results show that the pH and sulfate values recorded in the State's bridge environmental data cannot be fully relied on as these values fluctuate. In some cases, the variation between the recorded and recently measured data is very large (at least in an order of magnitude) making it difficult to accurately determine the bridge environmental classification. For this reason, an alternative classification method was proposed by associating the bridge surroundings with its potential risk of significant deterioration. Bridges that cross river at or near the ocean or the everglades present the highest risk of exposure to low pH and sulfate environments. Based on the field investigation, HPC structures exposed to moderate sulfate (150 – 1500 ppm) and low pH (< 6.5) have higher risk of deterioration as compared to bridges with the same environmental classification. In fact, corrosion of the steel reinforcement was detected on two such bridges after only been in service for 21 years. One newer bridge (built in 2009) also had significant surface abrasion that is not expected for a 4-year-old bridge exposed to moderately aggressive environment. The reason for these bridges to have higher risk of deterioration is because of the increase in porosity caused by the exchange reaction between acidic solution present in low pH environment that allow sulfate to attack even at moderate level. As a result, cracks are form allowing aggressive water to penetrate more easily into the concrete causing the embedded steel reinforcement to corrode.

The laboratory investigation involved six experiments to evaluate the performance of HPC in low pH and sulfate environments. These experiments were designed to evaluate the expansion, modulus of rupture and water absorption of concrete through accelerated tests. Accelerated tests were performed through scaling factors. Fifteen HPC mix proportions, i.e., five fly ash mixtures, four slag cement mixtures, three silica fume mixtures, and three metakaolin mixtures, were evaluated. Of all these mixtures, the slag cement mixture and the silica fume mixture performed the best and provided the best resistance to low pH and sulfate environment.

To estimate the service life of concrete structures, various service life models were evaluated. Unfortunately, none of the models provided adequate prediction for sulfate and acid attacks as the failure mechanism often involved crack formation. These models relied heavily on the diffusion through concrete, which worked well for chloride transport but are not accurate for sulfate and acid attacks. A better approach is to use sorptivity-base model to estimate the service life of concrete structures exposed to sulfate. However, the sorptivity-base model still do not

cover acid attack and should not be used when the pH is below 7.0. Therefore, a new model needs to be developed in order to accurately predict the service life.

In conclusion, low pH and moderate sulfate environment present potential risks of significant deterioration to HPC structures. Luckily there are only a few bridges in the State (mainly in the northern region of Florida in District 2) that are exposed to this environment. However, considering that the deterioration detected on bridges in moderate sulfate (150 - 1500 ppm) and low pH (5.0 - 6.5) environment, it is recommended that the environmental classification of these bridges be changed from moderately aggressive to extremely aggressive. Furthermore, based on the laboratory results, it is also recommended that slag cement and/or silica fume be added to HPC mix design when the reinforced concrete structures are exposed to low pH and moderate sulfate environments.

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CHAPTER 1: INTRODUCTION

The Florida Department of Transportation (FDOT) has comprehensive guidelines and specifications on high-performance concrete (HPC) mixtures that account for the environmental impact. These guidelines are documented in the Structures Design Guidelines [FDOT, 2011a] and Section 346 of the Standard Specification for Road and Bridge Construction [FDOT, 2010] to ensure a minimum 75-year service life of the design of reinforced concrete structures. Despite these comprehensive guidelines and specifications, questions have been raised regarding the performance of HPC in low pH and sulfate environment. This research is to determine potential risks of significant deterioration of HPC in low pH and sulfate environment.

1.1. BACKGROUND AND RESEARCH NEED

According to the American Society of Civil Engineers (ASCE) Report Card in 2013 [ASCE, 2013], the Florida infrastructure received a grade of "C-", while bridges received a grade of "B". The "B" grade is quite good considering that the national average grade is a "C+". The reason for this is because Florida has a comprehensive design and material specifications to ensure a 75 year design service life of their structures. One particular specification to improve the bridge service life is the use of high-performance concrete (HPC). In Florida, HPC is defined as low water-to-cementitious (w/cm) ratio concrete with pozzolanic materials and/or cementitious materials and chemical admixtures.

The fundamental theory for improving the durability performance of concrete, particularly the increase in chemical resistance, is by lowering its permeability. The addition of pozzolanic and other cementitious materials as well as lowering the w/cm ratio can significantly reduce permeability but cannot totally eliminate the diffusion process of chemical attack in concrete. Thus, in addition to the use of HPC, the FDOT also provides specification on concrete cover to further prevent corrosion of the steel reinforcement. These specifications as documented in the Structures Design Guidelines [FDOT, 2011a] and Section 346 of the Standard Specification for Road and Bridge Construction [FDOT, 2010] are based on environmental classification and are designed to provide a minimum 75-year design service life of reinforced concrete structures. The specifications are based on years of research and implementation but with an emphasis on coastal environment where chloride and sulfate are the two dominating compounds that deteriorate concrete. Less known, however, are other environmental conditions that also exist in Florida, particularly the exposure to both low pH and moderate sulfate environment. Based on the current FDOT classification, bridges exposed to both low pH and sulfate environment would be in the moderately aggressive environmental classification range because the pH is above 5.0 and the sulfate content is below 1500 ppm. It should be noted that despite the current specification describes low pH as a level below 5.0, concrete does suffer from deterioration when the pH level is below 6.5 [Mehta and Monteiro, 2006; Mindes et al, 2003, as well as other sources, including: http://www.cement.org/tech/cct_dur_acid.asp]. As such, the authors feel that a pH value of 6.5 or less should be considered low pH in this report. The problem with the exposure to both low pH and moderate sulfate environment is their failure mechanism is not well established. It is possible that the combination of low pH and sulfate could potential lead to significant deterioration of the

concrete structures. Therefore, there is a need to investigate the impact on HPC in low pH and moderate sulfate environment.

1.2. GOAL AND OBJECTIVES

The goal of this research is to identify whether the risk of deterioration of HPC in low pH and sulfate environments would shorten the 75-years design service life based on the current State material design philosophy. The research objectives are:

- 1. Determine the potential risk of significant deterioration of HPC in low pH and sulfate environments present in Florida.
- 2. Identify the concentration of sulfate and pH for deterioration of HPC to occur.
- 3. Reevaluate the State environmental classification criteria.
- 4. Identify the best curing practice that reduces the risk of material deterioration for HPC in low pH and sulfate environments.
- 5. Identify the time scale to degradation.
- 6. Determine the effect material degradation in low pH and sulfate environments on the structural integrity or reinforced concrete structures.
- 7. Determine the effect of material degradation in low pH and sulfate environments on the corrosion resistance of HPC.

In pursuit of the stated objectives, a two pronged approach was conducted: 1) field investigation and 2) laboratory study. The field investigation entailed the evaluation of field cored samples of bridges exposed to low pH and moderate sulfate environments. The laboratory study consisted of the evaluation of performance of HPC mixtures using accelerated expansion, modulus of rupture, and absorption tests when exposed to low pH and high sulfates media.

1.3. REPORT ORGANIZATION

The rest of the report is organized as follows. Chapter 2 discusses the review of literature on concrete exposed to sulfate and low pH environment. Chapter 3 covers the methodology, which include filed investigation and laboratory experiment. Chapter 4 provides the field and laboratory results. Chapter 5 describes detail discussion of test results and failure mechanism. Finally, Chapter 6 provides the relevant conclusions and recommendations

CHAPTER 2: LITERATURE REVIEW

Understanding the deterioration mechanism from sulfate attacks on concrete and exposure to low pH environment is vital in developing the methodology for evaluating the performance of HPC in these environments. Sulfate attack is highly complex phenomenon that involves physicochemical processes leading to changes in porosity, volume, and mechanical properties. While an exposure to low pH by itself may not necessary cause deterioration in concrete, the acidity in such environment, particularly carbonic-acid bearing water, could dissolve both hydrated and unhydrated cement compounds as well as calcareous aggregate. Thus, the exposure to both low pH and sulfate environment could potentially accelerate the deterioration processes in concrete. This chapter first describes sulfate attack, the roles of cementitious materials in resisting sulfate attack, and laboratory test methods. The chapter also covers acid attack and measures for protecting the concrete. The review of literatures provided a framework for developing the methodology for evaluating HPC in low pH and sulfate environment.

2.1. FORMS OF SULFATE ATTACK

Sulfate attack is a highly complex phenomenon and in some cases not completely understood. All sulfate attack mechanisms are treated as physicochemical processes that lead to certain physicochemical consequences, such as changes in porosity and permeability, volumetric stability, compressive and flexural strengths, modulus of elasticity, and hardness. All these physicochemical consequences ultimately will result in loss of durability and shortening of service life. Sulfate attack can be from internal or external sources and manifest in the form of expansion and cracking of concrete. It can also take the form of a progressive decrease in the strength and loss of mass due to loss of cohesiveness of the cement hydrating products. It is noted that, in this research project, only the external attack was examined as FDOT has a rigorous quality assurance and control program that would prevent the inclusion of sulfates in the concrete mixes.

In general, sulfate attack mechanism can be described by the following processes [Skalny et al., 2002]:

- 1. Dissolution or removal from the cement paste of calcium hydroxide.
- 2. Complex and continuous changes in the ionic composition of the pore liquid phase.
- 3. Adsorption or chemisorption of ionic components present in the pore liquid phase on the surface of the hydrated solids present in the cementing system.
- 4. Decomposition of still unhydrated clinker components.
- 5. Decomposition of previously formed hydration products
- 6. Formation of gypsum.
- 7. Formation of ettringite.
- 8. Formation of thaumasite.
- 9. Formation of brucite and magnesium silicate hydrate.
- 10. Formation of hydrous silica (silica gel).
- 11. Penetration into concrete of sulfate anions and subsequent formation and repeated recrystallization of sulfate salts.

It should be noted that it is possible to have severe deterioration of concrete due to sulfate attack in the absence of extensive volumetric expansion. The following section summarizes the three main deterioration mechanisms on hydrated cement compounds:

2.1.1 Action on Calcium Hydroxide (CH)

A common form of sulfate attack on concrete is the formation of gypsum due to cation-exchange reactions. Depending on the cation type associated with the sulfate solution, i.e., sodium sulfate ($N\overline{S}$) and magnesium sulfate ($M\overline{S}$), both calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) may be converted to gypsum ($C\overline{S}H_2$), sodium hydroxide (NH) and magnesium hydroxide (MH or brucite) by sulfate attack as shown in equations 2-1 & 2-2:

CH + NS +	$2H \rightarrow CSH_2 +$	NH	Eq. 2-1
$CH + M\overline{S} +$	$2H \rightarrow C\overline{S}H_2 +$	МН	Eq. 2-2

The formation of gypsum is believed to be associated with a limited increase in volume and becomes an issue at sulfate concentrations above 3,000 ppm. However, its formation uses up the available sources of calcium, thus gypsum formation may have secondary consequences by promoting other sulfate-related phenomena [Skalny et al., 2002]. Although it is not understood if gypsum formation causes any volumetric expansion, it has been observed [Mehta, 1983] that the deterioration due to gypsum formations goes through a process that first leads to reduction of pH of the system and loss in the stiffness and strength, followed by expansion and cracking, and eventually transformation of concrete into a noncohesive mass. Gypsum can also combine with other hydration products to produce ettringite as described in the next section.

2.1.2 Action on Aluminates and their Hydration Products

The gypsum as shown in section 2.1.1 can react further with hydrated calcium aluminates (C_4AH_{13}) , hydrated calcium sulfoaluminates $(C_4A\bar{S}H_{12.18})$, or hydrated tricalcium aluminate (C_3A) to form ettringite, $C_6A\bar{S}_3H_{32}$, as shown by the following equations:

$$C_4AH_{13} + 3C\overline{S}H_2 + 14H \rightarrow C_6A\overline{S}_3H_{32} + CH$$
 Eq. 2-3

$$C_4ASH_{12.18} + 2CSH_2 + (10-16)H \rightarrow C_6AS_3H_{32}$$
 Eq. 2-4

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} + CH$$
 Eq. 2-5

It should be noted that ettringite formation is still a controversial subject, but, in general, it is widely accepted that the sulfate-related expansion in concrete is associated with ettringite, which can lead to cracking and spalling, and thus, accelerate rebar corrosion.

2.1.3 Action on C-S-H

As can be examine further from Eq. 2-2, the magnesium hydroxide, MH, is practically insoluble, while calcium sulfate, CSH_2 , possesses a limited, but distinct solubility. Their reaction proceeds

in more detail as shown below:

$C_8S_2H_x + 3M\bar{S} + (x+21)H \rightarrow 3C\bar{S}H_2 + 3MH + 3SH_y + (2 + x - y)H$ Eq. 2-6

This reaction produces more gypsum and goes to another cycle of reactions to produce more ettringite. Moreover, the MH can react further with calcium hydroxide, which decomposes the C-S-H phase. Ultimately, this phase converts to a silica hydrate (SH_y) to form a magnesium silicate hydrate (M-S-H) phase that has been identified as a poorly crystalline serpentine with no cementitious properties [Bonen and Cohen 1992; Gollop and Taylor 1992–1996; Brown and Taylor 1999]. The equation below show the reaction that form the M-S-H phase:

 $4MH + SH_v \rightarrow M_4SH_{8.5} + (4.5 - y)H$ Eq. 2-7

The decalcification of the C-S-H phase does not actually take place until the pH drops to a value below 10. Furthermore, this process is a very advanced stage of deterioration and can only be achieved by MS. In the case of NS, as indicated in Eq. 2-1, the formation of NH helps maintain the alkalinity. However, after all the CH is consumed by the reaction, the NS may cause a direct attack on the C-S-H phase leading to the formation of thaumasite. Thus, the decalcification of C-S-H may eventually occur. Fortunately, the formation of thaumasite is believed to form at low temperature (between 0° and 5°C), which is not typical in Florida. Nevertheless, the decalcification of C-S-H is a very important phenomenon that cannot be overlooked. According to the US Geological Survey [Johnson and Bush, 1988], the dominant cations in Florida aquifer are Ca, Mg, Na, and K. Additionally, these cations are also present in seawater.

2.2. SOURCE OF SULFATES IN SULFATE ATTACK

2.2.1 Ground Water

Ground water is one of the main source for external sulfates in Florida. Natural sulfates such as calcium, magnesium, and sodium sulfates are commonly found in Florida's soil and ground water as indicated in Figure 2-1. The coastal region of Florida is dominated by sodium sulfate whereas inland calcium sulfate is the main source. Both of these source will cause the concrete to expand and crack. There are also some small areas containing magnesium sulfate, which can dissolve cementitious compounds.



Figure 2-1. Hydrochemical facies of the Upper Florida aquifer [Johnston and Bush, 1988]

2.2.2 Solid Industrial Wastes

Solid industrial wastes, especially from the mining industry, are also responsible for providing additional sources of sulfate to the ground water. Agricultural waste and waste water may also contain sulfates that can be discharge into the ground water but less common.

2.2.3 Atmospheric Pollution

The sulfate in ground water can also be increased by the sulfates originated from atmospheric pollution.

2.2.4 Seawater

The corrosion of concrete by seawater is the result of the simultaneous action of several ions present in the water in different concentrations. The main ions present are Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻, together with smaller amounts of K⁺, Ca²⁺, HCO⁻ and Br⁻. The initial product of seawater attack on concrete are brucite [Mg(OH)₂] and aragonite [CaCO₃], formed by the action of Mg²⁺ and dissolved CO₂ [Mehta and Haynes 1975]. Additional phases formed in seawater attack may include magnesium silicates, gypsum, ettringite and calcite, and in concrete mixes made with a carbonate-based aggregate also thaumasite. The main deleterious effects results from the degradation of the C-S-H phase and its ultimate conversion to magnesium silicate [Mehta 1991]. In summary, the external sulfate attack related issues are summarized in Figure 2-2.

2.3. SULFATE-RESISTIVITY

The ability for concrete to sustain sulfate attack depends heavily on the hydration chemistry and permeability of the concrete. The sulfate resistance of ordinary Portland cement (ASTM C150 Type I) is rather limited, mainly due to the presence of significant amounts of tricalcium aluminate (C_3A). In the course of hydration, this phase yields first ettringite which – after the added calcium sulfate had been consumed – converts completely or to a significant degree to monosulfate. If later, in the course of service, the hardened concrete is exposed to sulfates from an external source, the monosulfate present converts back to ettringite, and this reaction is associated with expansion, resulting in scaling, cracking, and loss of cohesion. As a result, the first step in controlling sulfate attack is to produce concrete with a cement that is low in C_3A . For moderate sulfate in soil is between 0.1 and 0.2 % by mass, ASTM C150 Type II cement is often specified because of its maximum amount of 8% C_3A . For higher sulfate exposure, ASTM Type V cement (C_3A below 5%) can also be used to control sulfate attack.

The FDOT Standard Specification (Section 346) requires designers to use ASTM C150 Type II and Type II (MH) for moderate and extremely aggressive environment, respectively. For these types of cement, the aluminum oxide (Al_2O_3) content of the clinker is reduced, and this oxide is bound predominantly or exclusively within the ferrite phase, which decrease the amount of C_3A . Thus, the formation of ettringite or other expansive compounds in the hydration process is significantly reduced. However, controlling the hydration chemistry alone will not eliminate the deterioration of concrete due to sulfate attack as these measures only reduce its expansiveness. They do not apply to the degradation of other compounds. Reducing the permeability of concrete also plays an important role as less sulfate will be absorbed, which could be achieved with the addition of pozzolans and slag cement into concrete (i.e., use of HPC).



Figure 2-2. Summary of external sulfate related issues [Mehta 1991]

2.3.1 Use of Fly Ash

As mentioned earlier, the permeability of concrete also play an important role in controlling sulfate attack on concrete. In general, the addition of pozzolans and slag cement will significantly lower the porosity and improve the concrete permeability. There are numerous research [Djuric et al. 1996; Giergiczny 1997; Irassar and Ans-Batic 1989; Krizan and Zivanovic 1997; Mangat and Khatib 1992, 1995; Miletic and Ilic 1997; Soroushian and Alhozami 1992 and others] indicated that replacing about 30% of cement with fly ash, particularly Class F [Soroushian and Alhozami 1992; Biricik et al. 2000], by weight can improve the sulfate resistance of ordinary concrete. The effect of ternary blend concrete by combining fly ash and natural pozzolans (Sersale et al. 1997) or with silica fume (Akoz et al. 1999; Giergiczny 1997) also improve the concrete resistance to sulfate attack. However, just as ordinary concrete, the addition of fly ash does not improve the concrete resistivity to magnesium sulfate attack.

2.3.2 Use of Slag Cement

The addition of slag cement in concrete helps reduce the C_3A content in the cement and in turn helps improve sulfate resistance. Concrete with high slag content of 60% or more by weight exhibits a better resistance to sulfate attack than at low substitution levels [Giergiczny 1997; Gollop and Taylor 1992–1996; Krizan and Zivanovic 1997; Mehta 1992; Sersale et al. 1997]. It should be noted, however, that this is only true when using slag cement from North America where the alumina content is relatively low (8-11%) while the alumina content of slag cement obtained from the Pacific Rim and elsewhere could be larger (12-18%), which may not yield the same sulfate resistivity [Hooton, 2011]. An improved sulfate resistance of slag cement may be observed only in alkali or calcium sulfate attack, where the main mode of the deleterious action is the formation of ettringite [Skalny et al, 2002]. Similarly to other pozzolans, slag cement will not improve the degradation of C-S-H phase as a result of magnesium sulfate attack.

2.3.3 Use of Silica Fume

In general silica fume is added in conjunction with other pozzolans. However, it has been reported that a 10% cement replacement improves the sulfate resistance [Hooton, 1993]. Likewise, in another study by Cohen and Bentur (1988) indicated a reduction of ettringite formation in concrete containing silica fume but does not provide the resistance to the degradation of the C-S-H phase.

2.3.4 Metakaolin

Portland cements, at approximately 20% of clinker replaced by metakaolin, exhibit a better resistance to sulfate attack, particularly on sodium sulfate solution [Khatib and Wild 1998; Courard et al. 2003; Talero 2005; Al-Akhras 2006; Guneyisi et al, 2010]. Although, the degradation of the C-S-H phase has yet to be examined, it is believed that there should not be any improvement in the resistance when exposed in magnesium sulfate.

2.3.5 Other Materials

Structures built with calcium aluminate cement perform rather well if exposed to sulfate solutions, especially if made with a high cement content and low water-to-cement ratio. This good performance is attributed to a surface densification of the hardened material, resulting in a very low permeability of the surface layer and/or to the absence of calcium hydroxide in the system [Scrivener and Capmas, 1998]. Unlike Portland cement and related binders, magnesium sulfate solutions are less aggressive to calcium aluminate cement based concrete than alkali sulfate solutions. This is due to the absence of the C-S-H phase in the hydrated cement paste, as this constituent is particularly susceptible to magnesium sulfate attack.

Cements completely resistant to sulfate attack include phosphate cements, alkali silicate cement, and geopolymer cement. Each of them possesses a completely different mechanism of setting and hardening than binders discussed above.

Based on the literatures, the percentage of cement replacement by pozzolans and slag cement can be compared to the current FDOT specification on HPC mixtures. Table 2-1 illustrates the

comparison between FDOT specification and literatures. Overall, the percentages of cement replacement with pozzolans and slag cement seem to agree well with the literature on sulfate resistance with the exception of metakaolin. Thus, it is anticipated that the FDOT recommended HPC mixtures should provide adequate resistance to sulfate attack.

Tuble 2 T comparison of comon replacement materials in extremely aggressive environment				
Cement Replacement	FDOT Section 346	Literatures		
Materials				
Fly Ash Class F		<30%		
- Drilled Shaft	33% to 37%	70% for action on C-S-H		
- Precast Concrete	18% to 25%			
- Other Concrete	18% to 22%			
Slag Cement		>60%		
- Drilled Shaft	58% to 62%	Not recommended for action		
- Precast Concrete	50% to 70%	on C-S-H		
- Other Concrete	50% to 70%			
Silica Fume	7% to 9%	>10%		
Metakaolin	8% to 12%	~20%		

Table 2-1 Comparison of cement replacement materials in extremely aggressive environment

2.4. EXPOSURE TO LOW pH ENVIRONMENT

Although the exposure to low pH by itself may not cause any deterioration in concrete, it does indicate the presence of acidity that could potentially harm concrete. The most typical source of acidity in the natural environment is from rainfall. Rainwater react with carbon dioxide in the atmosphere to form carbonic acid. Other main source of acidity is through the agriculture activity, e.g. fertilizer use, plant roots, and weathering of minerals. In general, concrete does not have good resistance to acids. In fact, concrete begins to deteriorate when the pH drops below 6.5 [PCA, 2013]. The deterioration mechanism of acid attack is the dissolution of calcium hydroxide. The decomposition of the concrete depends on the concrete acid resistance, the concrete composition should be designed to be the most impermeable as possible. Protecting coatings can also be used to protect the concrete surface from contacting the acid source. Furthermore, the environment could be modify to make it less aggressive to the concrete.

2.5. EFFECT OF TEMPERATURE AND CURING

The effect of temperature on the kinetics of hydration of cement and its components is well known, as is the effect of curing conditions on the mechanical properties of concrete. It is less appreciated, however, that temperature also affects the microstructure and crystal habit of the hydrates formed during hydration and that these effects, in turn, are causing, at least to some degree, the observed physical changes. Currently, there is very little research related to these effects on external sulfate attacks. Major emphasis has been made on the internal sulfate attack, particularly on delayed ettringite formation [Skalny and Locher, 1999]. However, in general

steam curing is not recommended for concrete structures exposed to internal sulfate attack. The sensitivity of concrete to steam curing seems to be related to at least these phenomena: (a) decomposition or non-formation of ettringite due to high temperature; (b) adsorption of the released sulfate by C-S-H; (c) possible formation of microcracks due to thermal expansion; (d) release of sulfate from C-S-H upon cooling and subsequent ambient temperature moist curing; (e) formation of microcracks as a result of drying shrinkage; (f) formation of ettringite nuclei in the preexisting cracks, and (g) growth of the nuclei resulting in paste expansion.

2.6. TEST METHODS

There are many questions regarding the reliability of the current ASTM test methods for assessing sulfate attack, particularly ASTM C 1012 (currently specified by FDOT) and ASTM C 452. According to many researchers [Mehta, 1975, Monteiro et al, 2000, Skalny and Pierce, 1999], the current standards tend to overlook some important issues that do not correspond to the concrete performance in the field. Table 2-2 summaries some of the criticism of the standard tests. As a result, new approaches were proposed by several researchers [Monteiro et al, 2000, Ferraris et al, 2006] to address some of the issues with current testing standards.

Table 2-2 Criticism of the current ASTM test methods for assessing sulfate attack [Monteiro et al, 2000]

• ·	
Criticism	Reference
Cause of expansion not determined by the tests; tests do not address	Idorn, Johansen, and
formation of ettringite during storage and expansion	Thaulow (1992) (13)
Addition of sulfate in ASTM C452 is not representative of field conditions; both ASTM C452 and ASTM C1012 are too sensitive to specimen size and geometry.	Tumidajski and Ture (1995) (<i>15</i>)
ASTM C452 does not represent field conditions because inadequate curing of cement results in anhydrous cement compounds being exposed to attack; softening-spalling attack is ignored by both ASTM C452 and ASTM C1012.	Mehta and Gjorv (1974) (<i>10</i>)
ASTM specifications for sulfate testing of cements (ASTM C452 and C1012) generally ignore the acid-type sulfate attack, which is more typical in the field.	Mehta (1975) (11)
Cement composition affects the rate of consumption of sulfate ion and introduces variability in ASTM C1012; pH during testing is 3 to 5 orders of magnitude different from field conditions; C1012 tests are protracted because of decreasing amount of sulfate ion in solution.	Brown (1981) (12)

Monteiro et al (2000) proposed new accelerating method for California Department of Transportation. The new method has the ability to control the pH level at a slight acidic condition as typically present in the field. The sulfate resistance of concrete is evaluated by comparing the specimens' 28-days to 7-days strengths—a reduction of 25% or more means that the concrete is not sulfate resistant. Figures 2-3 and 2-4 illustrate their testing schematic and a flowchart depicting all the steps for evaluating the sulfate resistance of concrete.



Figure 2-3. Schematic of pH-controlled accelerated test apparatus to measure sulfate resistance of 0.5 in cube cement mortar with w/cm ratio of 0.5. Type I/II, V, and III as well as Type III containing 10% fly ash and 8% silica fume were evaluated. Additionally, calcium aluminate cements and calcium sulfoaluminate cements were also evaluated in this study [Monteiro et al, 2000].

Ferraris et al presents a more holistic approach to measure the sulfate resistance of concrete and to perform service life predictions. They developed a model by using both concrete and cement characteristics to predict it service life. Figure 2-5 illustrates the flowchart of their model. The rate of the sulfate attack is based on the rate of diffusive transport. An empirical approach based on Fick's law is used to develop the transport equation, which depends on the concrete porosity. They also proposed new absorption test that can be used to evaluate samples partially saturated. They also recommended a new wet-dry cycle experiment.



Figure 2-4. Basic flowchart showing the steps for the proposed accelerated test for sulfate resistance of cement [Monteiro et al, 2000]

As mentioned earlier, SEM provides a powerful tool for evaluating sulfate attack in concrete as it allows one to focus at the paste composition, examines the change in microstructure, detects micro cracks, and perform chemical analysis. This method was used for evaluating field and laboratory specimens in this study. Figure 2-6 illustrates how SEM can provide useful images to study sulfate attack.

Some researchers [Al-Tayyib and Shamim Khan, 1991, Yilmaz et al, 1997] have evaluated the effect of sulfate solution on rebar corrosion. They agreed that the rebar corrosion depends on various factors such as temperature and concentration. At high sulfate solution concentration of more than 3500 ppm, the concrete would deteriorate faster allow more aggressive water to penetrate inside accelerating rebar corrosion. Fortunately, this high level of concentration is rarely the case for Florida. However, the reduction in concrete strength and the growth of ettringite could lead the concrete to crack which could ultimately lead to rebar corrosion. Currently, there is no standard test method and the methods provided by both research teams do not represent real condition as they directly submerge the sample in sulfate solution.



Figure 2-5. Flow chart for determination of the sulfate resistance of concrete or cement paste [Ferraris et al, 2006]



Figure 2-6. SEM image of concrete exposed to sulfate solution [Ferraris et al, 2006]

CHAPTER 3: METHODOLOGY

The research project was divided into two phases: (1) field evaluation of HPC structures in low pH and sulfate environments; and (2) laboratory evaluation of HPC mixtures. Phase 1 of the project consisted of the inspection and sampling of 10 HPC bridges. As there was no data on the actual concrete composition, these bridges were selected based on the assumption that no HPC bridges were constructed in Florida before 1976. The pH and sulfate content at each site were based on FDOT environmental data and the United State Geological Survey (USGS) database as well as actual field testing. Cored samples were evaluated using scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) for chemical characterization. Phase 2 involved the laboratory testing of various HPC mixtures as recommended by the Section 346 of the FDOT Standard Specification.

3.1. PHASE I – FIELD INVESTIGATION

The field investigation was divided into two stages. Stage 1 consisted of the site selection process and stage 2 consisted of sampling and testing of cored field specimens. The primary objective of the field investigation was to determine the actual deterioration mechanism and performance of HPC structures exposed to low pH and sulfate environments as well as evaluating the current environmental classification.

3.1.1 Stage 1 – Site Selection Process

The site selection process was performed through a review of the Florida bridge information and the bridge environmental data. One of the most important criteria in selecting bridge sites was the built year since HPC was only utilized in Florida after 1976. Unfortunately for this project, the actual concrete composition of each bridge was not available, and thus, the effect of pozzolans and slag cement cannot be evaluated from the field investigation. There were three main tasks performed during Stage 1 of the field investigation phase, which included:

- 1. Validate bridge databases
- 2. Select bridge sites for further investigation
- 3. Conduct field pH and sulfate tests at the selected bridge sites.

3.1.1.1 Validation of Databases

Although the FDOT has comprehensive environmental information about all its bridges, the reliability of the database was put into question at the time of this study because not all data were up-to-date and in some cases not completed¹. Furthermore, it is well established that the pH and sulfate concentration fluctuate overtime depending on the rainfall, agricultural activities, and minerals in the area. Figure 3-1 illustrates the fluctuation of pH values that were continuously

¹ It should be noted that the data contained in the 2013 Bridge Environmental Data is up-to-date. However, this study was conducted in 2012 before the updated data was available.

monitored daily by the USGS. It is observed that the pH fluctuated between 6.6 and 7.5 in one location. It should also be noted that the USGS did not continuously monitor environmental data for every site but they do provide historical data. For this project the FDOT database was compared with the USGS *Water-Quality Data for Florida* (will be referred as USGS database).



Figure 3-1. Daily pH value of USGS sites (Ref. www.usgs.org)

The USGS database was used in this research to identify the environmental condition of the water at the bridge sites. Although, the USGS database contained various water quality and meteorological parameters, its data on sulfate concentration was not useful for this research project because it was mainly obtained from ground water rather than around the water surface. The sulfate concentration around the water surface provides better characteristic of the deterioration mechanism of concrete structures because sulfate attack is most prevalent around areas subjected to wet-dry cycles. Moreover, the data was obtained by different test methods and cannot be easily converted into meaningful form for the project. Therefore, the sulfate concentration obtained from the USGS database was omitted.

On the other hand, the pH of the USGS database was more useful and could be directly compared with the FDOT database. However, the data was relatively limited with only 1994 out of 9870 data points matching Florida bridge sites. To compare the databases the bridge locations provided by the Florida bridge information needed to be identified. This identification process was performed using a website called *uglybridges.com* that gathers information from the National Bridge Inventory in one single place. Unlike the Florida bridge information, the website provides latitudinal and longitudinal coordinates that could be easily compared with the USGS database. In general, most of the environmental sites used in the comparison were within 10 miles of the bridge radius. Table 3-1 provides a summary of information sources used for validation process.
Information Sources	Application, Pros, Cons	Source			
	Environmental information of Florida bridges with ID number				
Florida Bridge Environment	Pros: clearly states environmental condition of each bridge				
	Cons: Only contains bridge ID, hard to locate; data is out of date; only one-time test have been recorded				
	Environmental information of USGS sites with coordinates				
USCS Water Quality Data for Florida	Pros: rich information of each site; multi- time tests				
USUS water-Quality Data for Florida	Cons: does not contain sulfate information; disconnected with bridges; some test method differs from FDOT requirements; system is complex to access	0505			
	Bridge name and location with ID number				
Florida Bridge Information 1 st Qtr 2011	Pros: contains bridge built year, county and name.	FDOT			
	Cons: only contains name and county, hard to locate accurately				
	Bridge name and ID with coordinates				
Uglybridges.com	Pros: provide bridge description, coordinate, ID and name	NBI			
	Cons: not complete				

Table 3-1 Summary of information sources.

3.1.1.2Selected bridges

The bridges were selected on the basis of the built year, pH, and sulfate concentration. As stated earlier, the built year played an important role in this research project because it distinguished HPC from ordinary concrete structures. In this study, it was assumed that structures built in 1976 or later were constructed using HPC as the concrete composition was not available. Although the FDOT classified water or soil pH below 6.0 as moderately aggressive environment, in this study a pH below 6.5 was considered low pH. The reason for selecting a pH of 6.5 was based on data fluctuation shown by USGS data. The sulfate concentration was based in the 150 ppm to 1500 ppm range (or in other words moderate sulfate concentration).

In all 6953 bridges provided by FDOT environment data, 23 bridges met these criteria but only 8 bridges were selected because 15 of 23 bridges had no record of their locations. Table 3-2 summarizes the list of selected bridges and their locations are displayed in Figure 3-2. It could be seen that for the most part, the FDOT recorded pH values agreed well with the USGS recorded pH values. Table 3-3 shows a summary of bridges that met the search criteria but could not be identified through the Florida bridge information, Pontis, or any other database readily available at that time.

Low pł	H and high su	ilfate								
Bridge No.	Year built	USGS pH (min)	FDOT pH	FDOT Sulfate	Sample Date	Samples				
900077	1981	8.3	6.3	2800	1979	2				
720476	1984	6.1	6.4	800	1965~1976	7				
490030	1986	6.2	5.9	552.04	1974~1975	2				
740033	1992	5.2	6.3	280	1965~1970	>10				
780088	1982	7.2	6.3	220	1955	1				
Lowest pH value										
Bridge No.	Year built	USGS pH (min)	FDOT pH	FDOT Sulfate	Sample Date	Samples				
290045	1977	4.3	4.2	130	1970-1978	6				
Highest sul	Highest sulfate value									
Bridge No.	Year built	USGS pH (min)	FDOT pH	FDOT Sulfate	Sample Date	Samples				
160227	1998	6.4	7.8	8174	1967~1990	3				
740087	1978	5.2	7	3750	1965~1970	>10				

Table 3-2 Summary of selected bridges.

Note: USGS pH shows historical lowest pH value based on USGS data of nearby sites.

FDOT pH and FDOT sulfate show pH value and sulfate value based on "*Florida Bridge Environment*".

Sample date represents the sample taken time or period of USGS data.

Samples represents the number of historical samples of related USGS site.

3.1.1.3Field Investigation

After the eight bridges had been identified, trips were made to collect pH and sulfate information as well as to visual inspect the concrete conditions of these bridges. Testing of sulfate was performed in accordance with the Florida Method of Test for Sulfate in Soil and Water (FM 5-553). Sulfate reagent system - Sulfate, Pocket Colorimeter II Test Kit, 2 to 70 mg/L by Hach Company (Figure 3-3) was used for determining the sulfate concentration. Testing of pH was conducted in accordance with the Florida Method of Test for pH of Soil and Water (FM 5-550). The pH meter and electrode system – Portable pH Test Kit Model 5050T by Hach Company (Figure 3-4) was used for this purpose.

In addition to the pH and sulfate concentration tests, the bridges were visually inspected to approximate the degree of material deterioration. Measurements of depth and width of material degradation were also carried out. The results from the field investigation are shown in the Appendix of this report.

Bridge No.	Material	Date	SULF ppm	pН
790046	Water	12/22/1976	2800	6.3
170011	Water	12/2/1975	2500	6.2
860034	Water	6/4/1976	2400	6.3
150066	Water	9/3/1976	1500	6.3
704005	Soil	6/20/1978	880	6
160198	Water	3/3/1978	400	5.2
780082	Water	3/3/1981	400	5.9
780010	Water	3/3/1981	400	6.3
730019	Water	3/3/1981	370	5.6
780027	Water	3/2/1981	340	6.3
460058	Water	6/10/1981	320	6.2
170043	Water	6/22/2004	282	6.2
700038	Water	3/20/1981	256	6.3
730026	Water	3/4/1981	220	6.3
570041	Water	2/18/1980	215	6.3

Table 3-3 Potential bridges that were not located.

3.1.1.4Stage 1 - Summary

In summary, the primary objective of Stage 1 of the field investigation was to identify HPC bridges affected by low pH and sulfate environment. Ten bridges (shown in Table 3-4) were inspected to evaluate their environmental and deterioration conditions. It should be noted that two bridges were added to the list of bridges on Table 3-2. These two bridges consisted of one ordinary concrete bridge in Mulberry (160087) and one newer HPC bridge in Sarasota (170067). The former bridge (160087) was added to the list because of its close proximity to Bridge 160277 and to determine the effect of low pH and sulfate on ordinary concrete since the bridge was constructed before 1976 when HPC was introduced in Florida. The latter bridge (170067) was originally omitted from the original list because of its age. The bridge was built in 2009 so it was only two years old during the initial inspection and no deterioration was anticipated. However, upon inspection of this bridge significant surface scaling was detected. Thus, the bridge was also included as part of the Stage 2 study where samples were cored and analyzed in the laboratory.



Figure 3-2. Selected bridges pinned on map. (Ref. www.dot.state.fl.us)



Figure 3-3. a) Pocket Colorimeter II Test Kit and b) Portable pH kit (Ref. www.hach.com)

Bridge No.	Cities	Year Built	Measured pH value (Min. pH)	FDOT pH value	Measured Sulfate ppm	FDOT Sulfate ppm	Location
900077	Islamorada	1981	7.80 (7.75)	6.3	2800	2800	US-1 & Cross Ocean
780088	St. Augustine	1982	7.26 (6.81)	6.3	8	220	I-94 & Pond
720476	Jacksonville	1984	7.53 (7.42)	6.4	860	800	8A & River & Close to Ocean
740087	Yulee	1978	7.80 (7.73)	7.0	2675	3750	1A & Bay
740033	Yulee	1992	7.47 (7.39)	6.3	750	280	I-94 & River & Close to Ocean
290045	Lake City	1977	4.35 (4.23)	4.2	-	130	CR 250 & Forest
490030	Carrabelle	1986	7.61 (6.85)	5.9	1417	552	US-98 & River & Face to Ocean
160087	Mulberry	1971	7.69 (7.35)	5	127	560	CR 676 & River & Everglade
160227	Mulberry	1998	7.71 (7.70)	7.8	300	8174	SR37 & River & Everglade
170067	Sarasota	2009	7.60 (7.03)	5.4	55	1074	SR72 & River & Everglade

Table 3-4 Inspected field bridges.

3.1.2 Stage 2 – Field Sampling and Testing

Stage 2 of the field investigation included the coring of field specimens and laboratory testing of cored specimens. As mentioned in Stage 1, ten bridges were inspected, out of these, six bridges showed signs of material deterioration and were selected for the Stage 2 investigation. These bridges included Bridges 170067, 290045, 490030, 720476, 740033, and 780088 (see Table 3-4 for details). One additional bridge in Santa Rosa (580017) was also included in the Stage 2 study as the State Material Office was alerted of significant scaling on the bridge piles. Figure 3-4 illustrates the deterioration on this bridge. These bridges were selected based on their environmental conditions as well as visual signs of material deterioration. The main deterioration detected on all selected bridges was surface scaling and cracks on the bridge piles (see Figure 3-4).



Figure 3-4. Bridge 58017 in Santa Rosa, FL.

3.1.2.1 Cored Specimens

The cored specimens were taken from above and below the highest water level of the bridge piles, which were determined roughly by the piles' watermarks. Bridge 580017 for example (see Figure 3-5), the water stain clearly marked the highest water level. At least 4 cores were taken from each pile. If necessary, more samples were taken at different levels. The cores were 2-inch-diameter and 2 to 4 in. long depending on the depth of the concrete covers. The pile selection process was based on visual observation of scaling on the piles as well as their accessibility. Distances between coring center and water level were recorded. Figures 3-6 and 3-7 illustrate the side and front views of the cored specimens, respectively.



Figure 3-5. Drilling locations of core samples.



Figure 3-6. Core samples of Bridge 290045 side view.



Figure 3-7. Core samples of Bridge 290045 exterior view.

3.1.2.2Laboratory Analysis of Field Cored Specimens

Scanning electron microscope (SEM), JEOL JSM 5900LV, was used to inspect cored samples' microstructures (Figure 3-8). Samples (Figure 3-9) were sliced every ½ in. increments. Prepared samples were washed, sealed and stored separately to avoid contamination and oxidization.

As shown in Figure 3-10, at 100 times the magnification, cement paste and aggregates could be easily distinguished by their colors and shapes. Ettringite was harder to verify but could be seen as faveolate form spreading around the cement paste (Figure 3-11). To precisely distinguish the ettringite, energy-dispersive X-ray spectroscopy (EDS) was used to characterize the chemical composition.



Figure 3-8. Scanning electron microscope. (ref: http://www2.fiu.edu/~emlab/inst_SEM.html)



Figure 3-9. Cored sample with 2-inch diameter.



Figure 3-10. One hundred times magnification SEM image of bridge 290045 at depth of $\frac{1}{2}$ inch.



Figure 3-11. 1000 times magnification SEM image of ettringite's faveolate formation.

To identify the ettrigite, the EDS spectrum was also used to characterize the chemical composition of the sliced cores. Figure 3-12 shows the EDS spectrum of ettringite and nearby cement paste. It could be observed that the aluminum and sulfur contents in the area with ettringite were higher when comparing to the area containing only cement paste. The spectrum results were then mapped on the sliced core as shown in Figures 3-13 and 3-14 where they illustrate the EDS mapping at high and low magnification, respectively. It should be noted that at lower magnification, it was much easier to distinguish ettringite, cement, and aggregates by looking at the color (see Fig. 3-14). The EDS mapping was also compared to the SEM images to validate the ettringite's faveolate formation. The EDS spectrum or more specifically the percentage of sulfur atom was also used to identify the level of sulfate attack in the concrete by analyzing the amount at different depths of the cored specimens.



Figure 3-12. EDS spectrum of a) ettringite and b) nearby cement paste.



Figure 3-13. EDS mapping of ettringite particles and surrounding cement.



Figure 3-14. EDS mapping of ettringite particles within concrete.

As mentioned earlier the percentage of sulfur atom was used to identify the level of penetration by sulfate attack because sulfate and its derivatives were the only sulfur atom source in concrete. However, sulfur was not evenly distributed within cement as shown in Figure 3-14. Thus, to obtain accurate results and avoid the influence of aggregate, two SEM images were taken for each slice in this study. For each SEM image, several sampling areas were chosen to ensure only the paste was covered in the measured area. The average value was taken for these 10 measurements to reduce artificial error. Table 3-5 shows the statistical results of the 10 measurements for evaluating the atom content of cored sample taken from bridge 720476-1 at a 3 in. depth. The average result of the sulfur content at different depths were then plotted to evaluate the sulfate penetration.

					200000							
Flomont	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Maan	Standard
Elemeni	1	2	3	4	5	6	7	8	9	10	wiean	Deviation
С	17.65	17.79	17.4	18.29	16.84	17.19	17.11	16.98	16.63	18.43	17.43	0.60
0	56.08	56.96	53.66	55.94	57.13	51.49	51.37	50.58	50.89	50.96	53.51	2.75
Na	0.56	0.29	0.42	0.63	0.47	0.73	0.44	0.42	0.31	0.22	0.45	0.16
Mg	1.47	0.93	1.84	1.41	1.13	1.35	1.24	1.12	0.95	0.97	1.24	0.29
Al	1.5	1.16	1.32	1.04	1.17	2.22	1.94	1.93	1.52	1.63	1.54	0.39
Si	6.06	6.23	6.68	7.26	7.03	7.82	7.31	7.05	7.17	7.38	7.00	0.54
S	0.73	0.82	1.08	0.69	0.64	1.32	1.08	0.97	0.96	1.08	0.94	0.21
Cl	0.36	0.28	0.32	0.23	0.23	1.27	1.38	2.12	1.81	1.48	0.95	0.74
K	0.15	0.14	0.16	0.17	0.15	0.07	0.1	0.09	0.09	0.1	0.12	0.04
Ca	15.05	14.97	16.66	13.91	14.75	16.08	17.47	18.21	19.22	17.31	16.36	1.70
Fe	0.4	0.43	0.47	0.42	0.48	0.47	0.56	0.52	0.47	0.44	0.47	0.05

Table 3-5 Element atom content of core samples 720476-1 at 3 inch from surface.

3.2. PHASE II – LABORATORY EVALUATION

Phase II of the project is the laboratory evaluation of HPC mixtures that are specified in the FDOT Standard Specification. Twelve HPC mixtures containing fly ash, slag cement, silica fume and metakaolin were evaluated.

3.2.1 Mixture Proportions

A total of 15 HPC mixtures were evaluated for their performance in low pH and sulfate environments. These mixtures were based on concrete exposed to moderately to extremely aggressive environment. Class IV concrete, which is typically used for the substructure, was used to develop the mixture proportions. As such, the maximum water-to-cementitious materials (w/cm) ratio was limited to 0.41 for mixtures containing fly ash or slag cement and 0.35 for mixture containing silica fume or metakaolin. It should also be noted that the fly ash used in this study was Class F as it is more readily available in Florida. Type II Portland Cement was also used for all mixture to conform to FDOT specification. The pozzolans and slag cement were

used to replace cement by weight and their replacement percentages were based on FDOT limitations. The 15 HPC mixtures are summarized in Table 3-6.

Mix Design for Cement Paste Specimens				Mix Desi	gn for Conc	rete Speci	mens lb/y	d ³					
								Coarse					
No.	Fly Ash	Slag	Silica Fume	Matakaolin	W/CM	Water	Cement	А.	Fine A.	Fly Ash	Slag	Silica F.	М.
FA-1	10%	-	-	-	0.41	340.00	746.34	1744.20	978.38	82.93	-	-	-
FA-2	18%	-	-	-	0.41	340.00	680.00	1744.20	960.64	149.27	-	-	-
FA-3	25%	-	-	-	0.41	340.00	621.95	1744.20	945.11	207.32	-	-	-
FA-4	35%	-	-	-	0.41	340.00	539.02	1744.20	922.93	290.24	-	-	-
FA-5	50%	-	-	-	0.41	340.00	414.63	1744.20	889.67	414.63	-	-	-
S-1	-	30%	-	-	0.41	340.00	580.49	1744.20	934.02	-	248.78	-	-
S-2	-	50%	-	-	0.41	340.00	414.63	1744.20	889.67	-	414.63	-	-
S-3	-	60%	-	-	0.41	340.00	331.71	1744.20	867.49	-	497.56	-	-
S-4	-	70%	-	-	0.41	340.00	248.78	1744.20	845.32	-	580.49	-	-
SF-1	-	-	5%	-	0.35	340.00	922.86	1744.20	865.91	-	-	48.57	-
SF-2	-	-	7%	-	0.35	340.00	903.43	1744.20	860.71	-	-	68.00	-
SF-3	-	-	9%	-	0.35	340.00	884.00	1744.20	855.52	-	-	87.43	-
M-1	-	-	-	4%	0.35	340.00	932.57	1744.20	868.51	-	-	-	38.86
M-2	-	-	-	8%	0.35	340.00	893.71	1744.20	858.11	-	-	-	77.71
M-3	-	-	-	12%	0.35	340.00	854.86	1744.20	847.72	-	-	-	116.57

Table 3-6 HPC Mixture Proportions

3.2.2 Mixing

As stated earlier, the deterioration mechanism of concrete exposed to low pH and sulfate environment lies within the paste composition. Hence, in lieu of mixing concrete specimens, cement mortars were made using controlled speed blender. For larger mixtures, a small mortar mixer was used to fabricate the test specimens.

3.2.3 Curing Methods

All specimens were cured in water for 14 days prior to submerging them into a low pH and high sulfate solutions. Other curing methods were also used on selected HPC mixtures. These methods include dry curing, steam curing, and coating the specimen with curing compound (called compound curing for the rest of this report). For the steam curing, the specimens were subjected to elevated temperature of 140 degrees Fahrenheit for period of 24 hours. After 24 hours, the specimens were removed and stored in air at room temperature for 13 more days before subjected to the sulfate and low pH solution. The compound curing was applied to the exposed surface immediately upon the initial set. After the specimens hardened and removed from the molds, the exposed surface was coated with curing compound. The coated specimens were also stored in air until they reached an age of 14 days after which they were submerged in the sulfate and low pH solution. The dry curing specimens were simply stored in air for 14 days before they were exposed to the sulfate and low pH solution. Figure 3-15 illustrates the curing regime used in this study.



Figure 3-15. Curing Methods

3.2.4 Accelerated Test Setup

The accelerated test setup followed the setup proposed by Monteiro et al., 2000 as illustrated previously in Figure 2-3. Monteiro et al. (2000) provided a well-designed system that maintained the sulfate content and pH value. However, they only exposed the test specimens to the same concentration provided by the current ASTM C1012, which is not effective for HPC. As a result, the accelerated test method developed by Ferraris et al. (2006) was adopted in this study using increased sulfate concentration and reduced specimens' size. The sulfate concentration proposed by Ferraris et al. (2006) was 50,000 ppm. Two types of sulfate solution were used in this study: 1) sodium sulfate and 2) magnesium sulfate. Unfortunately, the effect of pH was not studied by them. Thus, assuming the sulfate concentration of 50,000 ppm for accelerated laboratory test is equivalent to 1,500 ppm in the field, an equivalent pH could be approximated if a field number is assumed. For this study a field pH of 5.0 was assumed and through a computation of the acidic level in the solution, an equivalent pH of 3.48 was obtained and used in this study. Figure 3-16 illustrates the high sulfate and low pH set-up used for storing the test specimens.



Figure 3-16. Sulfate and Low pH Bath for the laboratory evaluation.

3.2.5 Experimental Test Matrix

The experimental test matrix was designed to cover a variety of parameters that are affected by sulfate and acid attack on concrete. These parameters include changes in volume, porosity, and mechanical properties. Table 3-7 summarizes the experimental test matrix performed on the HPC mixtures.

3.2.5.1 Expansion Test

The expansion test is based on the test method proposed by Ferraris et al (2006) to study sulfate attack in HPC. The test is very similar to the current ASTM C1012 test but using higher sulfate concentration and smaller specimens. The specimens used in this study were $0.5 \times 0.5 \times 2.0$ in. cementitious prisms with embedded stainless steel studs at both ends. A length comparator conforming to the requirements of ASTM C 490 was used to measure the expansion. The stand of the comparator was modified to accommodate measurements of the 2.0 in. prisms. Figure 3-17 and 3-18 illustrate the expansion test setup and the cementitious prism, respectively.

The fabrication of the prism molds were made in two lifts and the consolidation was performed simply by tapping on mold's sides. After casting, the mold was placed in a closed plastic bag with some water to maintain 100% relative of humidity (RH). The bag was stored for 24 hours in a curing cabinet at a constant temperature of 23 °C \pm 2 °C.

Table 3-7 Experimental Test Matrix

Tests	Specimen	Dimensions	Testing Age	Lasting Time
Expansion Test [Ferraris et al., 2006]	3 × Cement paste prism	$\frac{1}{2} \times \frac{1}{2} \times 2$ in.	After 7 days curing, expansion is measured 5 days a week in first 2 weeks and once a week thereafter.	2 Months
Modulus of Rupture [Monteiro et al., 2000; Xiao et al., 2006]	56 × Cement paste prisms	$1 \times 1 \times 4$ in.	4 th week, 12 th week, 16 th week, and 20 th week.	20 Weeks
SEM	Slices taken from cement prism used in the expansion test	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{4}$ in.	At the end of the expansion testing cycles	N/A
ASTM C1585 Standard Test Method for Measurement of Rate of Absorption of Water by HydraulicCement Concretes	2 × Concrete disks	Φ 4 × $\frac{3}{4}$ in.	Every min. in first hour, 4 times an hour in next 2 hours, 2 times an hour in next 3 hours, once a day in next 6 days.	7 Days

After 24 hours, the specimens were removed from their molds and cured in limewater at 23 °C \pm 2 °C for 3 days. After the curing period, the specimens were removed from limewater and threaded studs were screwed into the end pins, which were embedded in the specimens. To ensure that the stud remained stationary during the expansion experiment, small amounts of epoxy were used to fasten the studs to the pins. Additionally, small amounts of epoxy were also applied 5 mm along the top sides of the specimen to minimize sulfate penetration from the ends (Figure 3-18). The epoxy was cured by leaving the specimens in a container with 100 % RH between 5 and 6 hours. Water should not contact the specimen or the epoxy during this curing process. The specimens were then returned to the limewater or applicable curing method until the specimens reached an age of 14 days before exposing to the sulfate and low pH solution.

A reference bar (Figure 3-17) made of the same stainless steel as the studs was used to determine the comparator reading in accordance with ASTM C490. The reference bar was also submerged in the sulfate and low pH solution. The comparator readings were made daily for the first two weeks and then weekly thereafter.



Figure 3-17. Expansion Test Setup: a) Length Comparator, b) Reference Bar, and c) Specimens' Molds



Figure 3-18. Cementitious Prism for Expansion Test.

3.2.5.2 Modulus of Rupture Test

The strength degradation of concrete exposed to low pH and sulfate environment was evaluated using the modulus of rupture test. The modulus of rupture of concrete was determined through a 3-point bending test as shown in Figure 3-19. Smaller specimens with dimension of $1 \times 1 \times 4$ in. were used to accelerate the deterioration. The fabrication of test specimens followed the same procedure used for the expansion test. The beam was tested at 3-inch-apart using triangular shaped steel supports. Steel rod was used at the load point. In addition to the modulus of rupture test, the tested samples were later sliced in half and compressed to determine their compressive strengths. It should be noted that only the mixture containing 25% fly ash (FA3) was evaluated and reported in this report for the modulus of rupture test. The reason for not evaluating other mixtures was because of the instability of test results. Furthermore, it would be inaccurate to directly compare the test results of different mixtures because they all have different target strength and hydration process. For example, mixtures containing large quantities of fly ash would have lower strength. The effect of curing method was evaluated using the modulus of rupture test.



Figure 3-19. Specimen under rupture test.

3.2.5.3 Water Absorption Test

The water absorption test was performed in accordance with ASTM C1585. The test is an indirect method for evaluating the porosity of the concrete, which can be used to determine the concrete resistance to external sulfate attack. To perform the test, a 2 in. thick concrete disk's side was sealed with epoxy and then placed in water where only the bottom surface was directly in contact with the water. The top surface was covered with a plastic bag to prevent evaporation of the absorbed water. Figure 3-20 illustrates the water absorption testing schematic. The absorption, *I*, was calculated using the change in mass divided by both the cross-sectional area of the test specimen and the density of water. The initial rate of water absorption (mm/s^{1/2}) is defined as the slope of the line that is the best fit to the *I* plotted against the square root of time (s^{1/2}). This slope is obtained by using least-squares, linear regression analysis of the plot. For the regression analysis, all points from 1 minute to 6 hours or until the plot showed a clear change of slope (Nick point, see Figure 3-21) were used in calculating *I*.



Figure 3-20. Schematic of concrete absorption test (Ferraris, 2006)



Figure 3-21. Water absorption test of concrete disk. Note that the red diamond represented the measured data and the black lines represented the linear best fit using regression analysis.

3.3. SERVICE LIFE MODELS

From the viewpoint of structural design, service life is often defined as the time of damage initiation. In the AASHTO LRFD Bridge Design Specifications, service life is defined as the period in which the statistical derivation of transient loads is based. In ASTM Book of Definitions, service life is defined as "the period of time after installation during which all properties exceed the minimum acceptable values when routinely maintained."

A bridge's ability to fulfill its intended function can be compromised by concrete degradation. Severe environmental condition is one of the major causes. Environmental conditions that cause degradation include carbonation, sulfate attack, freeze-thaw cycles and chlorides ingress. Harmful environmental conditions could cause physical and/or chemical reactions within concrete and lead to cracking and spalling. The most damaging consequence of these reactions is corrosion of reinforcing steel.

Figure 3-22 illustrates the relation between environmental load and concrete resistance. Concrete resistance decreases along with time due to concrete cracks, spallings and strength degradation. The penetration of sulfate and chloride increase environmental load. Therefore, the possibility of concrete environmental resistance failure increases along the time scale. The end of the service life is when the accumulated damage in the bridge materials exceeds the tolerance limit.



Figure 3-22. Relation between environmental load and concrete resistance (Ref.: Adopted from Tuutti Model (1982))

3.3.1 Concrete Service Life Prediction

To predict the concrete service life, the end of service life should be connected with concrete performances and defined as a specific value. For example, in the case of chloride initiated pitting corrosion, concrete service life depends on the time of chloride penetration to the reinforced steel depth, which is known as Time to Initiation of Corrosion (TIC) (Figure 3-23). TIC depends on many factors, such as concrete diffusivity, concrete cover and concrete mix design. It also depends on environmental conditions and protective strategies.



Figure 3-23. Service life of concrete structures. A two-phase modeling of deterioration. (Ref.: Adopted from Tuutti Model (1982))

To calculate TIC, Fick's second law is widely used in diffusion-based models. For example, modified Fick's second law is used in DuraCrete Model (2000), which is shown below:

$$C_{(x,t)} = C_0(1 - erf\frac{x}{2\sqrt{D_ct}})$$

Where:

C(x,t) = chloride concentration at depth and time,

Co= surface chloride concentration,

Dc= apparent diffusion coefficient,

t = time for diffusion,

x = depth

erf = statistical error function.

Although the diffusion-based models are widely used and accepted as models for computing concrete service life, particularly with the corrosion of steel reinforcement, these models ignore cracks within concrete. However, for sulfate and acid attack on concrete the failure mechanism often involve the formation of ettrigite that leads to cracking in the cement paste as shown in Figure 3-24. Therefore, the validity of these diffusion-based models needs to be put into question for sulfates and acid attack service life predictions.



Figure 3-24. Cracks found in a concrete core taken from a bridge built in 2009.

As a result, a sorption-based model should be used instead. The sorption-based model uses internal factors, such as concrete properties, concrete cover, and external factors, such as degree of exposure, and sulfate concentration to predict service life. A freeware program, CONCLIFE, is based on the concrete sorption model. The program was developed by D. Bentz from NIST for estimating the service life of concrete pavements and bridge decks exposed to sulfate attack and freeze-thaw deterioration. The software was developed jointly between researchers at NIST and the Federal Highway Administration (FHWA). CONCLIFE uses three concrete models and user-specified data on concrete properties and external environmental conditions to estimate the time at which the concrete spalls beyond a user-specified limit. Sorptivity of sulfate ions and water are the primary means of degradation; the software uses a laboratory test for measuring concrete sorptivity, annual precipitation, and estimated rates of concrete spalling. The model is given as:

$$X_{spall} = (2\alpha \gamma_f (1-\nu))/(E(\beta C_E)^2)$$

where $C_E = \text{concentration of reacted sulfate as ettringite (mol/m³)}$

$$\begin{split} E &= Young's \ modulus \ (GPa) \\ X_{spall} &= spalling \ depth \ (m) \\ \alpha &= roughness \ factor \ for \ fracture \ path \\ \beta &= linear \ strain \ caused \ by \ one \ mole \ of \ sulfate \ reacted \ (m^3/mol) \\ \gamma_f &= fracture \ surface \ energy \ of \ concrete \ (N/m) \\ \sigma &= surface \ tension \ (N/m) \\ v &= Poisson's \ ratio \ (e.g., \ for \ concrete, \ probably \ close \ to \ 0.2, \ for \ paste \ 0.25, \ and \ for \ mortar \ 0.22) \end{split}$$

It should be noted, however, that CONCLIFE is intended for computing concrete pavement and bridge deck service life. Furthermore, the effect of pH is not included in the model. For this model to be used for predicting the service life of concrete piles, a new finite difference heat transfer model for estimating the surface temperature and time-of-wetness of the concrete piles is needed. Furthermore, the sorption model for concrete under sulfate attack need to be calibrated using available field data. Additionally, the primary degradation model used by the program needs to be adjusted from freeze-thaw deterioration to steel corrosion. Thus, to realistically predict the service life of concrete the three models need to be developed. The development of these models is beyond the scope the study as the model development is a research in itself. To this end, the results obtained from existing models are not reported to avoid misleading conclusion.

CHAPTER 4: FINDINGS

As mentioned in the previous chapter, the project was divided into two phases. Phase 1 was the field investigation of HPC bridges and phase 2 was the laboratory investigation of HPC mixtures exposed to low pH and sulfate environment. The findings described in this chapter correspond to the two phases of the investigation. The major findings of the first and second phases were:

- 1) The combination of moderate sulfate concentration (between 150 and 1500 ppm) and low pH (< 6.5) could potentially impact HPC structures directly in contact with the water to deteriorate prematurely.
- 2) The State should consider reviewing its environmental classification for environmental sites with sulfate concentration more than 500 ppm and pH below 6.5 as the current design guidelines would consider these locations moderately aggressive. However, based on the field study corrosion was detected on bridges exposed to similar environments even though the bridges have only been in service for 20 years.
- 3) The pH reported in the FDOT environmental database may not provide a clear picture of the acidity of the water as pH fluctuates over time. If a bridge site has moderate sulfate concentration of more than 500 ppm and a pH below 7.5, the site should be further reviewed to determine its potential for material degradation in low pH and high sulfate environments.
- 4) Steel corrosion seems to be the dominant deterioration mechanism that directly impact the structures in low pH and high sulfate environments. No sign of significant decomposition of cement compound was detected on the field cores. This also mean that the main sources of natural sulfate are sodium sulfate and calcium sulfate.
- 5) Cross river bridges at or near the ocean or the everglades presents the highest risk of exposure to low pH and sulfate environments.
- 6) Slag cement and silica fume provided the best performance in its potential to improve concrete durability when exposed to high sulfate and low pH environments.

4.1. Phase I – Results

As stated earlier Phase I of the project was divided into two stages. The first stage is the validation of FDOT environmental data and the second stage was the evaluation of field cores. This section of the report summarizes the findings of this phase.

4.1.1 Environmental Data Assessment

Table 3-2 and 3-4 summarize the bridge environmental data obtained from the FDOT, USGS, and field sampling. Like ocean level changing with tide, bridges' environmental condition is changing continuously, such as temperature, pH level, sulfate concentration, chloride concentration, water level, humidity, and so on. One time investigation cannot represent all the conditions that could happen in the field. Thus, FDOT environmental data and USGS data were both considered in this research.

It is assumed that if low pH and high sulfate concentration appear in either FDOT or USGS data, bridges located in this kind of environment have the potential of facing combination attack by sulfate and acid. For the same reason, even when there is not enough data representing low acid and high sulfate condition, we cannot conclusively state that the environmental condition for such bridge is not severe. The environmental condition is continuous. Due to the limitation of field information, it's hard to identify the accurate region of such condition. Therefore, multi environmental conditions are investigated in the first phase of field investigation. Similar environmental conditions are summarized to conclude several classified regions as reference for further study.

It is observed that the data fluctuates widely and seems to depend on the location and time the data was collected. Thus, to better understand the bridge environmental condition or more specifically determine the potential for material degradation in low pH and high sulfate environments, the list of bridges were re-categorized into 6 categories in accordance with their geographical locations. The proposed categories were based on the bridge location, water body condition, approximate pH level, approximate sulfate concentration, and waterline. The 6 categories are summarized in Table 4-1.

4.1.1.1 Category 1 Cross Ocean/Bay Bridges

Category 1 bridges are bridges that cross ocean or bays. These bridges tend to have relatively stable and high sulfate concentration usually above 2,000 ppm. The pH for these bridges typically ranges from 7.6 to 8.1 and rarely drop below 7.0 because the water body is seawater. For example, Bridges 900077 and 740087 are bridges in this category. The surrounding body of water is entirely seawater with high pH level and high sulfate concentration. Figure 4-1 illustrates the concrete condition that was observed on 740087.

It is observed that the bridge suffered from scaling and cracking. However, it was difficult to tell if the deterioration is a result of sulfate attack alone. In fact, the most likely cause of the deterioration is a combination of attack by magnesium, chloride and sulfate ions and carbonation that are present in seawater. As a consequence, the environmental classification of these bridges are typically extremely aggressive, and hence, these bridges are designed with HPC with lower porosity and thicker concrete cover, which pose no potential risk for material degradation using the current specification.

Category	Location	Water body Condition	pH Level	Sulfate Concentration	Waterline Height
1. Cross Ocean/Bay Bridges	Cross ocean or bay	Seawater all-around bridges; non-directional or less	pH value stays high and stable all year around. Range: 7.6~8.1	Sulfate concentration stays high and stable all year around. Range: around 2000 ppm	Waterline range depends on the ocean tides. Range: around 0.6 meters (2 feet)
2. Cross River & Face to Ocean Bridges	At the mouth of rivers	Seawater at one side and river water at the other side; Directional	pH value changes daily or seasonally. Range: 6.5~8.1	Sulfate concentration changes daily or seasonally. Range: 100~2000 ppm	Waterline range depends on ocean tides and river flows. Range: $0.6 \sim 1$ meters (2 ~3 feet)
3. Cross River & Close to Ocean Bridges	Cross rivers that flows to ocean and close to mouth	River water at both side of bridges; Non-directional or less	pH value usually changes seasonally. Range: 6.5~7.6	Sulfate concentration stays stable. It could be high depends on local groundwater condition. Range: 500 ~ 1000 ppm	Waterline range depends on river flows. Range: around 1 meter (3 feet) depends on local groundwater condition.
4. Inland Cross Pond/River Bridges	Cross rivers or ponds that far away from ocean	River water all around the bridge; Non-directional or less	pH value usually changes seasonally. Range: 6.0~7.6	Sulfate concentration stays stable. It usually stays low depends on local groundwater condition. Range: 0 ~ 500 ppm	Waterline range depends on river flows. Range: around 1 meter (3 feet) depends on local groundwater condition.
5. Inland Cross Pond/River Bridges in Forest Area	Cross rivers or ponds in forest area	Impregnated water all around the bridge; Non-directional or less	pH value usually stays stable. It could changes yearly. It could be very low. Range: 4.0~7.5	Sulfate concentration stays stable. It usually stays low depends on local groundwater condition. Range: 0 ~ 500 ppm	Waterline range depends on river flows or rainwater. Range: $0.1 \sim 1$ meters ($0.3 \sim 3$ feet)
6. Inland Cross Pond/River Bridges in Everglades Area	Cross rivers or ponds in everglades area	Impregnated water or seawater all around the bridge; Directional or seasonal	pH value usually changes seasonally. Range: 4.5 ~ 8.1	Sulfate concentration changes seasonally. Range: 100~2000 ppm	Waterline range depends on ocean tides and groundwater flows. Range: around 1 meters (6 feet)

Table 4-1 Classification of bridges according to environmental conditions



Figure 4-1. Concrete structure of bridge 740087. Extensive cracking can be seen above waterline.

4.1.1.2 Category 2 Cross River & Face to Ocean Bridges

Category 2 bridges are bridges that cross the mouth of rivers and have the possibility of facing seawater at high tide. Because of the change of ocean tide, the water body that these bridges face is changing between river flow and seawater. This change results in unstable pH levels and sulfate concentration. The lowest pH depends on the river flow, which could be as low as 6.5. The lowest sulfate concentration also appears when river flow dominates the water body. It could be 100~500 ppm depending on local conditions. The high level of sulfate concentration and pH level is the same as the ocean, which are above 2000 ppm and 8.1, respectively. The height of the waterline level usually changes daily due to ocean tides and seasonally due to river flows. Typically, the highest waterline level appears during rainy season when the bridges are exposed to lower sulfate concentration. Bridge 490030 is located at the mouth of a river adjacent to the ocean falls in category 2 bridges. Due to low level of the riverbed, seawater intrusion happened in high tide. When seawater dominates the body of water around the bridge, the pH level and sulfate concentration increases. When the river flow dominates the body of water around the bridge, the pH level and sulfate concentration decreases. Figure 4-2 illustrates the deterioration of the bridge pile. Dependent on the level of pH of these bridges, they are more prone to combination of acid and sulfate attack.



Figure 4-2. Concrete pile of bridge 490030. Seashells and concrete deterioration can be seen on every pile near waterline level.

4.1.1.3 Category 3 Cross River & Near Ocean Bridges

Category 3 bridges are bridges that cross rivers close to the ocean but are not in direct contact with seawater. Because the water body is not influenced by seawater, the exposed pH levels of these bridges are relatively stable and low ranging between 6.5 and 7.6. Although the water is not in direct contact with the ocean, the rainfall and marine environments play an important role in the sulfate concentration, which tends to be above 500 ppm. The height of the waterline level also changes seasonally with the river flow, which also accelerate cracking in concrete. Two bridges, 720476 and 740033, that were investigated fall in this category. Figure 4-3 illustrates the spalling that was observed on these two bridges. If the bridges in this category experience low pH (< 6.5) then they are also prone to low pH and sulfate attack. The pH level of these bridges should be monitored regularly to ensure that they are higher than 7.0.



Figure 4-3. Spallings of bridges 720476 and 740033.

4.1.1.4 Category 4 Inland Cross Pond/River Bridges

Category 4 bridges are inland bridges that cross rivers or ponds. Usually, the sulfate concentration is not high (0~300 ppm). But there might be some exemptions depending on local groundwater condition (300~700 ppm). The pH level is usually stable and low (6.0~7.6). The waterline level usually changes seasonally or depending on local raining condition. Bridge 780088 belong to category 4 bridges. According to Table 3-4, the measured pH value and sulfate concentration of this bridge is slightly different from the values reported in the FDOT environmental data. These variation may be a result of seasonal changes. As illustrated in Figure 4-4 there was no water flowing underneath the bridge at the time of inspection. Furthermore, the bridge supports suffer from surface spalling. Category 4 bridges are prone to low pH and sulfate attack if the bridges are exposed to a sulfate concentration of 500 ppm or more.



Figure 4-4. Concrete pile of bridge 780088. Spalling can be seen below the level of highest waterline.

4.1.1.5 Category 5 Inland Cross Pond/River Bridges in Forest Area

Category 5 bridges are inland bridges that are also located in the forest. The water surrounding these bridges is influence by microorganism, which lowers the pH level significantly. In some area the pH level could be as low as 4.0. The sulfate concentration of the water in this area is typically lower than 500 ppm. The waterline level is stable comparing to other categories. Bridge 290045 falls into this category. Figure 4-5 illustrates the deterioration of the bridge substructures, which are crumbling as a result of acid attacking the hydrated cement compound. Depending on the acidity and its composition, bridges in this area are deteriorated by acid attack only.



Figure 4-5. Concrete piles of bridge 290045 in forest area.

4.1.1.6 Category 6 Inland Cross Pond/River Bridges in the Everglades

Category 6 bridges are inland bridges located near the everglades. The body of water surrounding these bridges usually changes seasonally by rainfall and seepage. Due to the microorganism in the everglades, the pH level could be as low as 4.5. The influence of seawater also affected the sulfate concentration to reach above 2,000 ppm. The waterline level also changes seasonally, but unlike category 2 the sulfate concentration is at its peak when the waterline level is also high. Bridges 160087, 160227 and 170067 fall into this category. The problem with bridges in this region is the variation in the pH and sulfate concentration that could provide false readings. Taking 170067 as an example, upon examining the measured and FDOT

data the difference between the two records is enormous. Part of the reason is the fact that during the field visit, this bridge was not exposed to any water. However, the visual inspection painted a different picture as shown in Figure 4-6. The bridge suffered surface scaling despite being only 3 years old. Bridges in this category suffer the most from acid and sulfate attack and, if not already is, should be reclassified and designed as bridges in extremely aggressive environment.



Figure 4-6. Concrete pile of bridge 170067. Wet-dry cycling increases the damage of concrete due to low pH level and sulfate attack.

4.1.2 Field Cored Samples

The cored samples were taken from bridges exposed to both low pH and high sulfate environments. Among the 32 cored samples, corrosion was only discovered on 2 of them. Table 4-2 shows illustrations of the cored samples obtained from the field. Front and side views of the cored samples are shown to illustrate their conditions. Detailed inspection figures and data can also be found in Appendix-1.

Table 4-2 Bridge piles inspection summary

Bridge No.	County	Year Built	Measured pH value (Min. pH)	FDOT pH value	Measured Sulfate ppm	FDOT Sulfate ppm	FDOT Cl* ppm (Max)
170067	Sarasota	2009	7.60 (7.03)	5.4	55	1074	43 (60)
SR72 & River & Evergla de	Scaling Condition	Face		Coring Sample	Exterior	A A	
290045	Lake City	1977	4.35 (4.23)	4.2	-	130	74
CR 250 & Forest	Scaling Condition			Coring Sample		S.	
490030	Carrabelle	1986	7.61 (6.85)	5.9	1417	552	10313 (19394)
US-98 & River & Face to Ocean	Scaling Condition	A CONTRACT		Coring Sample			
580017	Santa Rosa	1971	7.12 (7.02)	5.6	18	4	209
SR-87 & River Estuary	Scaling Condition	E STOR		Coring Sample			

Bridge No.	County	Year Built	Measured pH value (Min. pH)	FDOT pH value	Measured Sulfate ppm	FDOT Sulfate ppm	FDOT Cl* ppm (Max)
720476	Jacksonville	1984	7.53 (7.42)	6.4	860	800	4700
8A & River & Close to Ocean	Scaling Condition	Face		Coring Sample	Exterior	Q.	
740033	Yulee	1992	7.47 (7.39)	6.3	750	280	600 (1680)
I-94 & River & Close to Ocean	Scaling Condition			Coring Sample			3
780088	St. Augustine	1982	7.26 (6.81)	6.3	8	220	568
I-94 & Pond	Scaling Condition	The second		Coring Sample			

4.1.3 SEM Evaluation

As stated in Chapter 3, to examine the impact of sulfate attack on concrete, SEM and EDS were used to determine the sulfur atomic percentages at different depths. These results are plotted in Figures 4-7 and 4-8. The first figure illustrates the amount of sulfate penetrated through the concrete of the three bridges with the lowest pH. These bridges also had low sulfate concentration (up to 220 ppm). Based on the results, it is observed that there is a decrease in sulfur atomic percentages along the depth of the concrete (i.e., there is a downward trend in sulfur atomic percentage). This is expected as these samples were less likely affect by sulfate attack but rather by acid attack. Ettrigite was also rarely seen in the concrete upon the inspection of the SEM images as shown in Figure 4-9. In the same figure, the average crack widths also followed the same downward trend as the sulfur atomic percentages, which eliminates the likelihood of deterioration mechanism by expansion commonly found with ettrigite formation.

On the other hands, Figure 4-8 tells a different story. Here, the sulfur atomic percentages shown an upward trend where more sulfur atomic percentages were found inside the concrete for the four bridges located in moderate pH and sulfate environments. This upward trend indicates the sorption of sulfate into concrete typically found in sulfate attack. The SEM images illustrated in Figure 4-10 also confirms this showing ettrigite formation inside the concrete. There was also an increase in the average crack width as one moves deeper into the concrete. Moreover, corrosion was also detected on two of these bridges (see Figure 4-11). Considering that these bridges were relatively new (21 and 29 years old), they may not meet the 75 year designed service life. These conditions indicate that the presence of low pH and sulfate environment even at a moderate level cannot be ignored and should not be treated separately.



Figure 4-7. Sulfate distribution within concrete under extreme acid condition.



Figure 4-8. Sulfate distribution within concrete under low pH and moderate sulfate condition.


Figure 4-9. SEM images of bridge 290045 and 780088 at different depths [Note: Wcrack = average crack width in micrometer (1 µm = 0.39 mil)]



Figure 4-10. SEM images of bridge 490030 and 720476 at different depths. [Note: Wcrack is average crack width in micrometer (1 μ m = 0.39 mil)].



Figure 4-11. Rusting found on bridge 720476 (left) and 740033 (right).

4.2.PHASE 2 – LABORATORY TESTING

Several laboratory experiments were performed under this study to evaluate the performance of HPC mixtures. These experiments include accelerated expansion, water absorption, and modulus of rupture tests. In addition, the effect of curing method was also evaluated. This section of the report describes these results.

4.2.1 Accelerated Expansion Test

There are varieties of sulfate ions in the natural environment. However, sodium sulfate and magnesium sulfate are two forms of sulfate with different deterioration mechanism and used in the accelerated expansion test. The impact of these chemicals on HPC can be found in Figure 4-12 where a mixture containing 10% fly ash was exposed to sodium sulfate and magnesium sulfate. As stated in the literatures the failure mechanism of magnesium sulfate is the dissolution of calcium hydroxide, the specimen subjected to magnesium sulfate attack clearly suffered from crumbling and softening of the paste near the surface. For this, the expansion results of the specimens subjected to sodium sulfate are higher than specimen subjected to magnesium sulfate as shown in Figure 4-13.

Figure 4-13 also compares ordinary concrete with HPC. Overall, HPC significantly improved the durability performance of concrete structure in low pH and sulfate environment. Among the HPC mixtures, the mixture containing slag cement performed the best, while mixture containing fly ash performed the worst. Mixtures containing silica fume and metakaolin also performed well. Figure 4-14 illustrates the best performing percentages of pozzolans and slag cement, which consisted of 70% slag cement, 7% silica fume, 12% metakaolin, and 10% fly ash.



Figure 4-12. Fly ash cement paste with moist curing after 1 week of submerging under sodium and magnesium sulfate.



Figure 4-13. Specimens with different cementitious materials under sodium and magnesium attack.



Figure 4-14. Test results of accelerated expansion test on cement paste with fly ash, silica fume, slag, and metakaolin.

In addition, the effect of curing method was evaluated in this study. Three different curing methods were evaluated using the expansion test. The steam curing was not included because of its effect on the stainless steel and initial expansion of the specimens that may lead to error readings. Figure 4-15 depicts the visual condition of the specimens after 6 weeks exposure to sodium sulfate solution. Overall, visually the compound curing had the best surface condition. There seems to be very little difference in the surface condition between dry curing and moist curing. To better quantify the results, the expansion results are plotted in Figure 4-16. In the figure, mixtures containing 10% and 25% fly ash were exposed to magnesium sulfate and sodium sulfate solutions. For the samples exposed to magnesium sulfate, dry curing clearly performed the worst with the highest expansion. The difference between the performance of dry curing and other curing method was less pronounced for samples exposed to sodium sulfate. Overall, both moist curing and curing compound performed well and comparable to each other.



Figure 4-15. Fly ash cement paste with dry curing, moist curing and compound curing after 6 weeks of submerging in sodium sulfate solution.



- a. 10% Fly Ash concrete in magnesium sulfate
- b. 10% Fly Ash concrete in sodium sulfate
- c. 25% Fly Ash concrete in magnesium sulfate
- d. 25% Fly Ash concrete in sodium sulfate

Figure 4-16. Comparison of expansion of various fly ash specimens under different curing conditions.

4.2.2 Water Absorption Test

Figure 4-17 illustrates the water absorption test results for mixture containing fly ash. Overall, the increase in pozzolans and slag cement in concrete improved the concrete absorption. This is to be expected as pozzolans and slag cement help increase the porosity of concrete. It should be noted, however, that the water absorption results cannot be totally relied on to establish the best concrete mixtures for HPC in low pH and sulfate environments. As shown from the expansion test, increasing the amount of fly ash does not necessary reduce the expansion of concrete exposed to low pH and sulfate environment,



Figure 4-17. Relation of fly ash content and water absorption rate at early and later age.

4.2.3 Modulus of Rupture Test

A mixture with 25% fly ash was used to evaluate the modulus of rupture as well as understand the effect of curing methods. Figure 4-18 illustrates the modulus of rupture results. In this case, moist and steam curing performed the best and the dry curing did not do well and is not recommended.



Figure 4-18. Comparison between different curing conditions (under sodium sulfate attack if not noted).

CHAPTER 5: DISCUSSION

This section provides further clarification of the findings described in Chapter 4. To better understand the sulfate attack on concrete, the sulfur atomic percentages were studied to determine the sulfate transport in concrete structures. Unlike chloride transport that has higher chloride concentration on the external surface, the expansion in concrete caused by ettrigite formation allows more sulfate to penetrate in concrete particularly in the area that is rarely exposed to the sulfate solution. The problem here lies with the fact that material deterioration could be found in areas where no visual sign of deterioration exists. To make the matter worst, the low pH environment indicated the presence of some forms of acids. The acids react with concrete to form soluble calcium salts increasing the porosity and permeability of the system. As the concrete become more permeable, the sulfate solutions (even at the moderate range) are able to penetrate inside forming expansive products cracking the concrete. As the concrete cracks, aggressive water can penetrate leading to the corrosion of the embedded steel. Thus, concrete structures exposed to both low pH and sulfate environment needs to be carefully examine. Furthermore, as indicated earlier, the environmental conditions vary greatly from season to season, so bridges with potential problems with low pH and high sulfate environment are mapped using statistical analysis to provide a better pictures of bridges with potential risk in Florida

5.1. Sulfate Transport

Due to sulfate's transport mechanism, sulfur content is not always found to be higher externally and lower internally. It varies with the number of cracks, depth of the concrete cover, water level and so on. It is found to be interacted with crack distribution. The more cracks there are, the higher sulfur content there is.

As shown in Figure 5-1, the sulfate content has a downward trend (i.e., more sulfate content is found externally than internally as indicated with the plot corresponding to fully submerged concrete portion) for concrete located near the low water mark. On the other hand, an upward trend (i.e., more sulfate content is found internally than externally as indicated with the plot corresponding to the rarely submerged concrete portion) is found on concrete located near the high water mark.

The reason for these sulfur distributions is due to the wick action and the drying shrinkage occurred in the portions of the structure rarely in contact with the water. Furthermore, water also evaporates through concrete that is under rarely submerged and occasionally submerged conditions, which increase the sulfate content within those portions. Therefore, for some of the core samples under rarely and occasionally submerged condition, sulfate content was higher from the inside compare to the outside.

Furthermore, ettringite formation also cause the concrete to crack allowing more sulfate to penetrated into the concrete. The crack formation is also a result of the drying process that occurs in the occasionally and rarely submerged condition.



Figure 5-1. Relation between concrete location and sulfur distribution.

To make the matter worst, the low pH environment or more specifically the acids in the water most likely react with the cement paste to form soluble calcium salts. As a consequence, the porosity and permeability of the system increase allowing the sulfate solution to leach inside the concrete. This can be seen in all bridges exposed to low pH and sulfate environment as upon inspection of the cores, they all suffered from surface abrasion and expansive products. Whereas bridges only exposed to low pH suffered only surface abrasion. Similarly, bridges only exposed to high sulfate environment do not have significant surface abrasion. The expansive products caused more cracks to form, which allow the water surrounding concrete structures to be absorbed by the concrete. After getting into concrete, water migrates upward by capillary force. Migration of water within concrete is also influenced by gravity force. Therefore, water within concrete is only observed within certain height depending on the porosity of concrete. Besides migrating by capillary force, water can also be driven by dry and evaporation force above water level. Sulfate ion can only be carried by water absorbed into concrete and will not be taken out of concrete with water evaporation. Such unsaturated flow within concrete carries sulfate into concrete continuously at this condition. Meanwhile, sulfate would react with hydrated cement and result of expandable materials, such as ettringite and gypsum, and largely increase concrete porosity at this region. Such large porosity would result of increasing water absorption, concrete decomposition, rebar corrosion, and concrete spalling.

5.2. High Risk Regions

Acid is considered as a severe environmental condition for concrete structures when pH level is lower than 4.0. pH level between 4 and 6.5 is considered as moderate condition, which will not cause much damage to the concrete structures. Though acid is severely dangerous to concrete, acid attack only is not considered as the most considerable threats to concrete structures. Increasing protecting concrete cover is one of the technics to ensure 75-year concrete service life.

Sulfate is largely present in ocean water, which has pH value larger than 7.5. For these structures, sulfate attack is not a considerable issue unless the concentration is more than 1500 ppm. Chloride penetration or diffusion within concrete is the dominating issue for concrete degradation. For condition like this, many researches have been done. During the field investigation, for bridge 900077, built in 1981, no obvious degradation has been observed. Even though sulfate concentration of surrounding water is 2800 ppm, both reported by FDOT and field investigation of this research, alkalinity of seawater protected concrete from softening and destruction of C-H-S gel.

Although sulfate concentration between 150 and 1500 ppm is considered as moderate sulfate condition, severe damage has been observed under the sulfate concentration of 1500 and above 500 ppm. For example, for bridge 720476 and 740033, even at young age, 21 years and 29 years, rebar bleeding are found in field inspection. Sulfate is carried by water that absorbed into concrete through cracks. The more porous concrete is, the more easily sulfate can get into. Expandable materials, such as ettringite or gypsum will form within concrete under sulfate attack. The formation of these materials will cause more cracks inside concrete, which can highly increase the porosity and permeability of concrete. Besides the transition with absorbed water, drying and evaporation above water level can cause additional sulfate concentration in concrete. The concrete structure in this kind of environmental condition will face different sulfate distribution compare to those attack by acid with limited sulfate or those attacked by high sulfate and chloride. As investigated using SEM and EDS, bridges locate in such condition have the similar trend of sulfate distribution within concrete. Different from the ones at high sulfate region and low pH region, sulfate concentration within concrete tends to increase from external to internal. Thus, simply increasing concrete cover for bridge piles cannot ensure concrete service life at low pH and high sulfate environment. Since this special environmental condition would result of increasingly dangerous of shorten concrete service life, an analysis of field region is crucial and necessary.

As mentioned earlier the environmental data vary greatly from season to season. Thus, a new method is needed to identify bridges that potentially can be affected by low pH and sulfate environment. Taking the Florida bridge environment data and through curve fitting it is shown that 20% of Florida bridges are located at non-negligible sulfate condition (see Figure 5-2). Most of these bridges are located in area with pH above 7.0, such as cross ocean bridges.

For those bridges that are exposed to low pH (less than 6.5 or 7.0 for more conservative) and high sulfate (larger than 500 ppm, or 150 ppm for more conservative) are in the high risk region. The acid-sulfate combinations attack could result in reducing the bridge's service life. Figure 5-3 illustrates the distribution of Florida bridges in accordance with their sulfate concentration and pH level. Most of the bridges are located in negligible condition, in which environmental sulfate content is lower than 150 ppm. Based on the field investigation no corrosion or serious deterioration was detected for bridges falling in this condition. The remaining 80% of the bridges are located in non-negligible condition (a condition with sulfate content higher than 150 ppm and pH level greater than 7.0). Most of these bridges are not covered in this research (due to the high pH level). The other 20% of bridges fall in the high risk region and should be further studied in the future as they were not all covered in this study. These bridges are located in the map shown

in Figure 5-4. Overall, most of the bridges affected by low pH and sulfate environment are in the northern region of Florida. This could be attributed to the heavy agriculture activity in this region.



Figure 5-2. Florida environmental sulfate concentration curve fitting.



Figure 5-3. Florida bridges' environment distribution (Concentration).



Figure 5-4. Florida bridges' sulfates and pH environment distribution (Location).

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

The goal of this research was to identify whether the risk of deterioration of HPC in low pH and sulfate environments would shorten the 75-years design service life based on the current State Materials Office design philosophy. The research objectives are:

- 1. Determine the potential risk of significant deterioration of HPC in low pH and sulfate environments present in Florida.
- 2. Identify the concentration of sulfate and pH for deterioration of HPC to occur.
- 3. Reevaluate the State environmental classification.
- 4. Identify the best curing practice that reduces the risk of material deterioration for HPC in low pH and sulfate environments.
- 5. Identify the time scale to degradation.
- 6. Determine the effect of material degradation in low pH and sulfate environments on the structural integrity or reinforced concrete structures.
- 7. Determine the effect of material degradation in low pH and sulfate environments on the corrosion resistance of HPC.

Based on these objectives the following conclusion and recommendation can be made:

6.1 POTENTIAL RISK

According to the FDOT Florida Bridge Environment Data, 20% of bridges are exposed to sulfate environment. Luckily, only few of these bridges are also located in low pH environment. However, they are in high risk of significant deterioration that may result in the reduction of service life. To make the matter worst is that these bridges are only exposed to moderate pH (ranging from 5.0 to 6.5) and moderate sulfate (ranging from 500 ppm to 1500 ppm) environment, which make their environmental classification fall in the moderately aggressive category. Upon inspection of field specimens only the specimens taken from bridges with low pH and moderate sulfate environment experienced the wick action where the sulfate content was found to be rising as we examined deeper into the cored specimens. Please note that the sulfate attack found using the SEM is of external source and the only reason it can penetrate the concrete is because of the acidic solution (low pH environment) in the water reacts with the concrete exterior transforming it into highly soluble products. The same specimens also had higher amount of microcracks, which allow water to ingress into the concrete and lead to the corrosion of the steel reinforcement. In fact, three bridges falling into this category all showed signs of significant deterioration (corrosion in two 21+ years old bridges and significant surface scaling in one 4 years old bridge) even at an early-age of their service life. Therefore, it is recommended that the State review its environmental guidelines such that sites like those for these bridges would change from moderately aggressive to extremely aggressive.

6.2 SULFATE AND pH CONCENTRATION

Based on the field investigation, deterioration of HPC occurs on bridges with sulfate concentration greater than 500 ppm and pH lower than 6.5. It should be noted that these two concentrations cannot strictly be based on the FDOT environmental data because of the variability of the data. Thus, to better use the FDOT environmental data, the site location is needed to provide a clearer picture of the potential risk of the presence of both environmental conditions. As summarize in Table 4-1, site locations can be divided into 6 categories, the categories that pose potential risk are 2 (cross river bridge near to the ocean), 3 (cross river bridge near the ocean), and 6 (cross river bridge in the Everglades). For instance, if the FDOT environmental data indicates that a bridge is exposed to sulfate concentration of 600 ppm and pH of 7.2, then going by these numbers alone would indicate that the environmental conditions pose no risk to the HPC bridges. However, if the bridge is located in a Category 2 (Table 4-1) location then the potential risk for deterioration is much higher because it is more than likely that bridges in this category have much lower pH than the values indicated in the environmental data.

6.3 REEVALUATION OF ENVIRONMENTAL CLASSIFICATION

As stated earlier, it is recommended that the State reviews its environmental classification for sites that are affected by **both**; (a) moderate sulfate concentration of more than 500 ppm **and** (b) pH below 6.5. Currently, substructures in sites that have these conditions would be designed using the moderately aggressive classification. Considering that the moderately aggressive classification was used in the design of the 4-year-old bridge suffered from premature surface scaling, it is highly unlikely that the current environmental classification would provide adequate design service life for the substructure of bridges with these conditions. It should be noted that the current specification is still valid, the only recommended changes to the specification should only be apply to structures exposed to both low pH and moderate sulfate environment.

6.4 EFFECT OF CURING

Moist curing is proven to provide the best curing practice for HPC and should be recommended for reinforced concrete structures in low pH and sulfate environment. Dry curing or no curing should be prevented as extra water is needed for the formation of CSH in HPC. Concrete strength should not be used as an indicator for the removal of curing. In fact, dry cured specimens provided the least resistance to sulfate and acid attack, especially for higher strength concrete (when concrete strength is larger than 5,000 psi). Curing compound and steam curing also provided good performance in enhancing the sulfate and acid attack resistance. Overall, any form of curing that help the concrete to hydrate will improve the concrete permeability as well as resistance to chemical attack.

6.5 TIME SCALE TO DEGRADATION

Unfortunately for this project the time scale to degradation cannot be directly quantified as there are too many variables that cannot be simply modeled. One particular variable is the pH. As stated earlier the pH level is not a direct indication of acid attack but rather just a measure of acidity in the water or soil. Even if the actual quantification of acid attack on concrete can be made, no service life model exists for concrete exposed to acid. To this end, a new model needs to be developed, which is beyond the scope of this study. However, based on the cored samples, corrosion was detected on two bridges that were at around 20 years old. The corrosion seems to be at an initial stage and the propagation rate could be further studied on the two bridges. The propagation rate could be monitor in real time using the resistivity of concrete. Furthermore, as discussed in Chapter 5, there are more bridges in Florida that may also be affected by low pH and sulfate environments. These bridges should be further evaluated through field cores as discussed in Chapters 3 and 4 to definitively conclude the time scale to degradation.

6.6 EFFECT OF MATERIAL DEGRADATION ON THE STRUCTURAL INTEGRITY

The material degradation of HPC structures exposed to low pH and sulfate environments follows the same deterioration mechanism as sulfate attack, which consists of the formation of expansive compounds, formation of microcracks, and decomposition of the cement compound. The laboratory results using accelerated tests indicated that the decomposition of the cement compound plays an important role, which can lead to a loss of the structural integrity by means of strength reduction. However, this deterioration mechanism was rarely observed from the field cores. The only field cores with structural integrity problem were the samples taken from a bridge exposed to very low pH (below 4.5) while the sulfate concentration is below 200 ppm, which is most definitely affected by only acid attack and not the two environmental conditions. Therefore, it can be concluded that the material degradation in low pH and sulfate environments prevalent in Florida do not significantly impact the structural integrity.

6.7 EFFECT OF MATERIAL DEGRADATION ON THE CORROSION RESISTANCE OF HPC

Unlike the structural integrity, the material degradation in low pH and sulfate environment do impact the corrosion resistance of HPC. The combination of the formation of expansive compound such as ettrigite and drying caused more microcracks to form allowing the air and water to penetrate inside the concrete, which lead to the corrosion of the steel reinforcement. To make the matter worst, the corrosion was found hidden in area above the water line (due to the wick action) with little indication of the problem since there is no sign of surface degradation here.

To minimize these problems, slag cement and silica fume could be added to concrete to provide resistance to sulfate attack. Both fly ash and metakaolin also improved the concrete sulfate and

low pH resistance but not as well as slag cement and silica fume. For fly ash, it is also recommended that a maximum of 25% Portland cement replacement be specified for HPC mix design in low pH and sulfate environments.

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APPENDIX-1 FIELD BRIDGE PILES INSPECTION

A1.1.Field Bridge 170067 (Built in 2009)



Figure A1-1. Overall environment and marked coring locations of bridge 170067.





(170067-2)



(170067-3)

(170067-4)

Figure A1-2. Core samples of bridge 170067.

Table A1-1	Environmental	conditions	and core s	amples c	of bridge 1	170067
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			1 0	
Bridge Environmental Condition		Sample #	Distance to Cap	Type of Sample [‡]
Year Built	2009		(inch)	(Submerged/Dry)
pH Value	7.03	170067-1	65.5	Submerged
Sulfate Concentration (ppm)	1074	170067-2	65.5	Submerged
Water Level* (inch)	Dry	170067-3	80	Dry
Max Watermark ⁺ (inch)	70	170067-4	80	Dry

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.



(170067-3)

(170067-4)



A1.2.FIELD Bridge 290045 (BUILT IN 1977)



Figure A1-4. Overall environment and marked coring locations of bridge 290045.



(290045-1)

(290045-2)



(290045-3)

(290045-4)



(290045-5)

(290045-6) Figure A1-5. Core samples of bridge 290045.

Table A1-2 Environmental conditions and core samples of bridge 290045							
Bridge Environmental Cond	lition	Sample #	Distance to Cap	Type of Sample [‡]			
Year Built	1977		(inch)	(Submerged/Dry)			
pH Value	4.23	290045-1	39.5	Submerged			
Sulfate Concentration (ppm)	-	290045-2	39.5	Submerged			
Water Level* (inch)	48	290045-3	24.5	Submerged			
Max Watermark ⁺ (inch)	14	290045-4	24.5	Submerged			
		290045-5	7.5	Dry			
		290045-6	7.0	Drv			

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* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.



Figure A1-6. Concrete piles surface scaling condition of bridge 290046.

A1.3.FIELD Bridge 490030 (BUILT IN 1986)



Figure A1-7. Overall environment and marked coring locations of bridge 490030.



Figure A1-8. Core samples of bridge 490030.

Tuble III 5 Environmental conditions and core samples of offage 190050						
Bridge Environmental Condition		Sample #	Distance to Cap	Type of Sample [‡]		
Year Built	1986		(inch)	(Submerged/Dry)		
pH Value	6.85	490030-1	51.5	Submerged		
Sulfate Concentration (ppm)	1417	490030-2	51.5	Submerged		
Water Level* (inch)	59	490030-3	43.0	Dry		
Max Watermark ⁺ (inch)	48	490030-4	43.0	Dry		

Table A1-3 Environmental conditions and core samples of bridge 490030

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.



(490030-3)

Figure A1-9. Concrete piles surface scaling condition of bridge 490030.

A1.4.Field Bridge 580017 (Built in 1971)



Figure A1-10. Overall environment and marked coring locations of bridge 580017.



(580017 -1)



(580017 - 3)

(580017 - 4)



(580017 - 5)

(580017 - 6)

Fig	ure A1-11.	Core san	nples of	bridge 58	30017.
nental co	onditions a	nd core s	amples o	of bridge	580017

Table A1-4 Environmental conditions and core samples of bridge 580017							
Bridge Environmental Conc	lition	Sample #	Distance to Cap	Type of Sample [‡]			
Year Built	1971		(inch)	(Submerged/Dry)			
pH Value	5.90	580017 -1	50.5	Submerged			
Sulfate Concentration (ppm)	4	580017 -2	50.75	Submerged			
Water Level* (inch)	55	580017 -3	41.0	Dry			
Max Watermark ⁺ (inch)	44	580017 -4	40.0	Dry			
		580017 -5					
		580017 -6					

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.





A1.5.FIELD Bridge 720476 (BUILT IN 1984)



Figure A1-13. Overall environment and marked coring locations of bridge 720476.



(720476-1)

(720476-2)



(720476-3)

(720476-4)

Figure A1-14. Core samples of bridge 720476.

Tuble TT 5 Environmental conditions and core samples of orage 720470	Table A1-5	Environmental	conditions a	and core	samples	of bridge	720476
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Bridge Environmental Conc	lition	Sample #	Distance to Cap	Type of Sample [‡]
Year Built	1984		(inch)	(Submerged/Dry)
pH Value	7.42	720476-1	127.5	Submerged
Sulfate Concentration (ppm)	860	720476-2	126.5	Submerged
Water Level* (inch)	139.5	720476-3	114.0	Dry
Max Watermark ⁺ (inch)	115.5	720476-4	113.0	Dry

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.





(720476-1)





(720476-3)

(720476-4)

Figure A1-15. Concrete piles surface scaling condition of bridge 720476.


(720476-2a)



(720476-2b)



(720476-2c)



(720476-2d)



A1.6.Field Bridge 740033 (Built in 1992)



Figure A1-17. Overall environment and marked coring locations of bridge 740033.



(740033-1)

(740033-2)



(740033-3)

(740033-4)

Figure A1-18. Core samples of bridge 740033.

Table A1-0 Environmental conditions and core samples of bridge 740050				
Bridge Environmental Condition		Sample #	Distance to Cap	Type of Sample [‡]
Year Built	1992		(inch)	(Submerged/Dry)
pH Value	7.39	740033-1	65.5	Submerged
Sulfate Concentration (ppm)	750	740033-2	65.5	Submerged
Water Level* (inch)	97	740033-3	54.5	Dry
Max Watermark ⁺ (inch)	61	740033-4	54.5	Dry

Table A1-6 Environmental conditions and core samples of bridge 740030

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.

* Submerged means coring location is below max watermark; Dry means coring location is above max watermark.





(740033-3)

(740033-4)

Figure A1-19. Concrete piles surface scaling condition of bridge 740033.



Figure A1-20. Rebar bleed-out and inner cracks of bridge 740033.

A1.7.FIELD Bridge 780088 (BUILT IN 1982)



Figure A1-21. Overall environment and marked coring locations of bridge 780088.





(780088-2)



(780088-3)

(780088-4)

Figure A1-22. Core samples of bridge 780088.

Table A1-7 Environmental conditions and core samples of brid	lge 780088
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Bridge Environmental Conc	lition	Sample #	Distance to Cap	Type of Sample [‡]
Year Built	1982		(inch)	(Submerged/Dry)
pH Value	6.81	780088-1	30.5	Submerged
Sulfate Concentration (ppm)	8	780088-2	31.0	Submerged
Water Level* (inch)	Dry	780088-3	24.3	Dry
Max Watermark ⁺ (inch)	28	780088-4	24.5	Dry

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.

* Submerged means coring location is below max watermark; Dry means coring location is above max watermark.



(780088-3)

(780088-4)



APPENDIX-2 SCANNING ELECTRON MICROSCOPE INSPECTION ON FIELD CORE SAMPLES

A2.1.Field Bridge 170067 (Built in 2009)



Figure A2-1. Environment condition and coring locations of bridge 170067.



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Figure A2-3. SEM images of coring sample 170067-1 @ 1/2 inch depth.



Figure A2-4. SEM images of coring sample 170067-1 @ 1 inch depth.



Figure A2-5. SEM images of coring sample 170067-1 @ 4 inch depth.



Figure A2-6. SEM images of coring sample 170067-3 @ 1/2 inch depth.



Figure A2-7. SEM images of coring sample 170067-3 @ 1.5 inch depth.



Figure A2-8. SEM images of coring sample 170067-3 @ 3.5 inch depth.

			0	
Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	2009		Depth	%
pH Value	7.03	170067-1	0.5	0.182
Sulfate Concentration (ppm)	55	Dist. to Cap	1	0.192
Water Level* (inch)	Dry	65.5 inch	4	0.196
Max Watermark ⁺ (inch)	70			
		170067-3	0.5	0.48
		Dist. to Cap	1.5	0.34
		80 inch	3.5	0.41

Table A2-1 Environmental conditions and sulfur content of bridge 170067

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles. watermark.

A2.2.Field Bridge 290045 (Built in 1977)



Figure A2-9. Environmental condition and coring locations of bridge 290045.



Figure A2-10. Sulfur distribution of bridge 290045.



Figure A2-11. SEM images of coring sample 290045-1 @ 1/2 inch depth.



Figure A2-12. SEM images of coring sample 290045-1 @ 1.5 inch depth.



Figure A2-13. SEM images of coring sample 290045-1 @ 4 inch depth.



Figure A2-14. SEM images of coring sample 290045-2 @ 1/2 inch depth.



Figure A2-15. SEM images of coring sample 290045-2 @ 1 inch depth.



Figure A2-16. SEM images of coring sample 290045-2 @ 3.5 inch depth.

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Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	1977		Depth	%
pH Value	4.23	290045-1	0.50	0.97
Sulfate Concentration (ppm)	-	Dist. to Cap	1.50	0.25
Water Level* (inch)	48	39.5 inch	4.00	0.20
Max Watermark ⁺ (inch)	14			
		290045-2	0.50	0.34
		Dist. to Cap	1.00	0.27
		39.5 inch	3.50	0.24

Table A2-2 Environmental conditions and sulfur content of bridge 290045

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.

A2.3.Field Bridge 490030 (Built in 1986)



Figure A2-17. Environment condition and coring locations of bridge 490030.



Figure A2-18. Sulfur distribution of bridge 490030.



Figure A2-19. SEM images of coring sample 490030-1 @ 1/2 inch depth.



Figure A2-20. SEM images of coring sample 490030-1 @ 1.5 inch depth.



Figure A2-21. SEM images of coring sample 490030-1 @ 2.5 inch depth.



Figure A2-22. SEM images of coring sample 490030-1 @ 4 inch depth.



Figure A2-23. SEM images of coring sample 490030-4 @ 1/2 inch depth.



Figure A2-24. SEM images of coring sample 490030-4 @ 1 inch depth.



Figure A2-25. SEM images of coring sample 490030-4 @ 2 inch depth.



Figure A2-26. SEM images of coring sample 490030-4 @ 3.5 inch depth.

Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	1986		Depth	%
pH Value	6.85	490030-1	0.50	0.48
Sulfate Concentration (ppm)	1417	Dist. to Cap	1.50	0.47
Water Level* (inch)	59	51.5 inch	2.50	0.56
Max Watermark ⁺ (inch)	48		4.00	0.70
		490030-4	0.50	0.44
		Dist. to Cap	1.00	0.39
		43 inch	2.00	0.52
			3.50	0.66

Table A2-3 Environmental conditions and sulfur content of bridge 490030

* Water level is recorded by the distance from water level to bridge cap on the day of visit. It may change periodically.

⁺ Max watermark is the maximum water level determined roughly from the stain on piles.

A2.4.Field Bridge 580017 (Built in 1971)



Figure A2-27. Environment condition and coring locations of bridge 580017.



Figure A2-28. Sulfur distribution of bridge 580017.



Figure A2-29. SEM images of coring sample 590017-4 @ 1/2 inch depth.



Figure A2-30. SEM images of coring sample 580017-4 @ 1.5 inch depth.


Figure A2-31. SEM images of coring sample 580017-4 @ 3 inch depth.



Figure A2-32. SEM images of coring sample 580017-1 @ 1/2 inch depth.



Figure A2-33. SEM images of coring sample 580017-1 @ 1.5 inch depth.



Figure A2-34. SEM images of coring sample 580017-1 @ 3.5 inch depth.

Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	1971		Depth	%
pH Value	5.90	580017 -4	0.50	0.70
Sulfate Concentration (ppm)	4	Dist. to Cap	1.50	0.60
Water Level* (inch)	55	40 inch	3.00	0.48
Max Watermark ⁺ (inch)	44			

Table A2-4 Environmental conditions and sulfur content of bridge 580017

A2.5.Field Bridge 720476 (Built in 1984)



Figure A2-35. Environment condition and coring locations of bridge 720476.



Figure A2-36. Sulfur distribution of bridge 720476.



Figure A2-37. SEM images of coring sample 720476-1 @ 1/2 inch depth.



Figure A2-38. SEM images of coring sample 720476-1 @ 1.5 inch depth.



Figure A2-39. SEM images of coring sample 720476-1 @ 3.5 inch depth.



Figure A2-40. SEM images of coring sample 720476-3 @ 1/2 inch depth.



Figure A2-41. SEM images of coring sample 720476-3 @ 2 inch depth.



Figure A2-42. SEM images of coring sample 720476-3 @ 3.5 inch depth.

Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	1984		Depth	%
pH Value	7.42	720476-1	0.50	1.25
Sulfate Concentration (ppm)	860	Dist. to Cap	1.50	0.63
Water Level* (inch)	139.5	127.5 inch	3.50	0.94
Max Watermark ⁺ (inch)	115.5			
		720476-3	0.50	0.60
		Dist. to Cap	2.00	0.43
		114 inch	3.50	0.65

Table A2-5 Environmental conditions and sulfur content of bridge 720476

A2.6.Field Bridge 740033 (Built in 1992)



Figure A2-43. Environment condition and coring locations of bridge 740033.



Figure A2-44. Sulfur distribution of bridge 740033.



Figure A2-45. SEM images of coring sample 740033-1 @ 1/2 inch depth.



Figure A2-46. SEM images of coring sample 740033-1 @ 1 inch depth.



Figure A2-47. SEM images of coring sample 740033-1 @ 2.3 inch depth.



Figure A2-48. SEM images of coring sample 740033-3 @ 1/2 inch depth.



Figure A2-49. SEM images of coring sample 740033-3 @ 1.5 inch depth.



Figure A2-50. SEM images of coring sample 740033-3 @ 2.5 inch depth.

Bridge Environmental Condition		Sample #	Concrete	Sulfur Content
Year Built	1992		Depth	%
pH Value	7.39	740033-1	0.50	0.51
Sulfate Concentration (ppm)	750	Dist. to Cap	1.00	0.50
Water Level* (inch)	97	65.5 inch	2.30	0.44
Max Watermark ⁺ (inch)	61			
		740033-3	0.50	0.53
		Dist. to Cap	1.50	0.56
		54.5 inch	2.50	0.56

Table A2-6 Environmental conditions and sulfur content of bridge 740030

A2.7.Field Bridge 780088 (Built in 1982)



Figure A2-51. Environment condition and coring locations of bridge 780088.



Figure A2-52. Sulfur distribution of bridge 780088.



Figure A2-53. SEM images of coring sample 780088-1 @ 1/2 inch depth.



Figure A2-54. SEM images of coring sample 780088-1 @ 1 inch depth.



Figure A2-55. SEM images of coring sample 780088-1 @ 2 inch depth.

Bridge Environmental Cond	lition	Sample #	Concrete	Sulfur Content
Year Built	1982		Depth	%
pH Value	6.81	780088-1	0.50	0.79
Sulfate Concentration (ppm)	8	Dist. to Cap	1.00	0.53
Water Level* (inch)	Dry	30.5 inch	2.00	0.40
Max Watermark ⁺ (inch)	28			

Table A2-7 Environmental conditions and sulfur content of bridge 780088

APPENDIX-3 LABORATORY EXPERIMENTS RESULTS



A3.1.Accelerated Expansion Test on Cement Paste

Figure A3-1. Cement paste with 10% fly ash in sodium sulfate solution.



Figure A3-2. Cement paste with 10% fly ash in magnesium sulfate solution.



Figure A3-3. Cement paste with 25% fly ash in sodium sulfate solution



Figure A3-4. Cement paste with 25% fly ash in magnesium sulfate solution



Figure A3-5. Compound cured cement paste with 10% and 25% fly ash in sodium sulfate solution.



Figure A3-6. Compound cured cement paste with 10% and 25% fly ash in magnesium sulfate solution.



Figure A3-7. Dry cured cement paste with 10%, 25% and 50% fly ash in sodium sulfate solution.



Figure A3-8. Dry cured cement paste with 10%, 25% and 50% fly ash in magnesium sulfate solution.



Figure A3-9. Dry cured cement paste with 10%, 25% and 50% fly ash in sodium sulfate solution.



Figure A3-10. Dry cured cement paste with 10%, 25% and 50% fly ash in magnesium sulfate solution.



Figure A3-11. Cement paste with 10% fly ash in sodium sulfate and magnesium sulfate solution.



Figure A3-12. Cement paste with 25% fly ash in sodium sulfate and magnesium sulfate solution.



Figure A3-13. Cement paste with 10% and 25% fly ash in sodium sulfate solution



Figure A3-14. Cement paste with 10% and 25% fly ash in magnesium sulfate solution



Figure A3-15. Cement paste with 5% silica fume in sodium sulfate and magnesium sulfate solution.



Figure A3-16. Cement paste with 7% silica fume in sodium sulfate and magnesium sulfate solution.



Figure A3-17. Cement paste with 9% silica fume in sodium sulfate and magnesium sulfate solution.



Figure A3-18. Cement paste with 5%, 7% and 9% silica fume in sodium sulfate solution.



Figure A3-19. Cement paste with 5%, 7% and 9% silica fume in magnesium sulfate solution.



Figure A3-20. Cement paste with 30% slag in sodium sulfate and magnesium sulfate solution.



Figure A3-21. Cement paste with 50% slag in sodium sulfate and magnesium sulfate solution.



Figure A3-22. Cement paste with 70% slag in sodium sulfate and magnesium sulfate solution.


Figure A3-23. Cement paste with 30%, 50% and 70% slag in sodium sulfate solution.



Figure A3-24. Cement paste with 30%, 50% and 70% slag in magnesium sulfate solution.



Figure A3-25. Cement paste with 4%, 8% and 12% metakaolin in sodium sulfate solution.



Figure A3-26. Cement paste with fly ash, silica fume, and slag in sodium sulfate solution.



Figure A3-27. Cement paste with fly ash, silica fume, and slag in magnesium sulfate solution.



A3.2.Water Absorption Test on Fresh Made Concrete Disk

Figure A3-29. 18% fly ash concrete disk water absorption rate.



Figure A3-30. 35% fly ash concrete disk water absorption rate.



Figure A3-31. 50% fly ash concrete disk water absorption rate.



Figure A3-33. 50% slag concrete disk water absorption rate.



Figure A3-34. 70% slag concrete disk water absorption rate.



Figure A3-35. Relation of fly ash content and water absorption rate at early and later age.



Figure A3-36. Relation of slag content and water absorption rate at early and later age.