INVESTIGATION OF WORKABILITY AND DURABILITY OF CONCRETE MIXES INCORPORATED WITH EXPANSIVE CEMENT, POLY-CARBOXYLATE ADMIXTURES, AND LIGHTWEIGHT AGGREGATES

by

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TABLE OF CONTENTS

LIST O LIST O ABSTR	F TABLES	vi ii xi
Chapter		
1	INTRODUCTION	1
	1.1 Scope of the Thesis	2
	1.2 Objectives of the Thesis	3
2	A BRIEF LITERATURE REVIEW	5
	2.1 Concrete Properties	5
	2.2 Hydration Process of Ordinary Portland Cement	6
	2.3 Expansive Cement-Hydration Mechanism and Properties	9
	2.4 Rheology of Concrete	1
	2.5 Chemistry of Chemical Admixtures	4
	2.6 Mechanism of Poly-Carboxylate Admixtures with Expansive Cement 1	6
	2.7 Mechanism of Air-entraining Admixtures 1	8
	2.8 Self-healing Mechanisms of Concrete	0
3	INVESTIGATION OF FRESH PROPERTIES OF TYPE K CONCRETE WITH POLY-CARBOXYLATE ADMIXTURES	:3
	3.1 Investigation of Fluidity Retention	4
	3.2 Materials and Methods	4
	3.3 Test Results and Discussion	6
	3.4 Regression Analysis of Slump Loss Trends	8
	3.5 Compatibility of Admixtures with Control Mix	0
	3.6 Compatibility of Admixtures with Type K Mix	3
	3.7 Regression Analysis of Slump Loss Trends	5
	3.8 Calorimetric Study of Type K cement with selected Admixtures	7
	3.9 Summary	0

4	DURABILITY PROPERTIES OF TYPE K CONCRETE	
	4.1 Investigation of Water Absorption Capacity	
	4.2 Materials and Methods	
	4.3 Test Results and Discussion	
	4.4 Comparison between Water Soaked and Air-Dried Samples	
	4.5 Comparison between Oven-Dried Samples	57
	4.6 Regression Analysis of Water Absorption Pattern	61
	4.7 Compressive strength Testing and Results	65
	4.8 Summary	
5	SUMMARY AND FUTURE WORK	69
REFE	RENCES	71
Appen	dix	
А	INDEX	
В	GRAPHS AND PLOTS PERTINENT TO THE THESIS	

LIST OF TABLES

Table 1	Mix Designs for Workability Analysis	.24
Table 2	Mix Designs for Durability Analysis	.44
Table 3	Essential Acronyms pertinent to the reading	.48
Table 4	List of exponential equations, R ² and adjusted R ² developed from the experimental data of Control samples	.62
Table 5	List of exponential equations, R ² and adjusted R ² developed from the experimental data of Type K samples	.63

LIST OF FIGURES

Figure 1	Stochiometric equation of C ₃ S reaction mechanism (Mindess, Young, and Darwin 2003)
Figure 2	Heat evolution profile of cement hydration (Mindess, Young, and Darwin 2003)
Figure 3	Stochiometric equations of ye'elimite hydration steps9
Figure 4	(a) Flow behavior and (b) Viscosity Difference between the Bingham Fluid and Newtonian Fluid (Aïtcin, Pierre Claude Flatt, Robert J.,2015)
Figure 5	Influence of cement additives on yield stress and viscosity of cement paste (Newman and Choo,2003)
Figure 6	(a) Diagram of PCE molecular structure and (b) Dispersion effect of PCE attached to a cement particle (Aïtcin, Pierre Claude Flatt, Robert J.,2015)
Figure 7	(a) Fresh concrete mix; (b) slump test setup; and (c) concrete kept in mixing drum at 25 rpm to provide mild agitation
Figure 8	(a) Fresh concrete mix; (b) Type-A air meter; and (c) concrete kept in mixing drum at 25 rpm to provide mild agitation
Figure 9	Slump loss comparison between Control mix and Type K mix over 60 minutes
Figure 10	Air content loss comparison between Control mix and Type K mix over 60 minutes
Figure 11	Regression analysis of Control mix slump loss over 60 minutes
Figure 12	Regression analysis of Type K mix slump loss over 60 minutes
Figure 13	Slump loss comparison between Control, Control+HRWRA, and Control+MRWRA mixes over 60 minutes

Figure 14	Slump retention comparison between Control, Control+HRWRA, and Control+MRWRA mixes
Figure 15	Slump loss comparison between Type K, Type K+HRWRA, and Type K+MRWRA mixes
Figure 16	Slump retention comparison between Type K, Type K + HRWRA, and Type K+MRWRA
Figure 17	Regression Analysis of Control+HRWRA mix slump loss over 60 minutes
Figure 18	Regression Analysis of Control+MRWRA mix slump loss over 60 minutes
Figure 19	Regression Analysis of Type K+HRWRA mix slump loss over 60 minutes
Figure 20	Regression Analysis of Type K+MRWRA mix slump loss over 60 minutes
Figure 21	(a) Sample preparation, (b) cement paste placed in an ampoule and, (c) TAM isothermal calorimeter used for the experiment
Figure 22	Heat evolution profiles for Type K, Type K+HRWRA, and Type K+MRWRA hydration process
Figure 23	Slump value comparison of all mixes at 60 minutes
Figure 24	Concrete samples being cured underwater
Figure 25	Sample preparation steps for water absorption test
Figure 26	Equations needed to calculate water absorption by concrete samples47
Figure 27	(a) Cross-sectional view; (b) Animated 3D view; and (c) real image of the setup
Figure 28	Comparison of Absorption between Control and Type K samples 49
Figure 29	Absorption rate comparison between Control and Control+LWA water-soaked samples
Figure 30	Absorption rate comparison between Control and Control+LWA air- dried samples

Figure 31	Comparison between Type K and Type K+LWA water-soaked samples	3
Figure 32	Comparison between Type K and Type K+LWA air-dried samples 5	4
Figure 33	Comparison between Type K and Type K+LWA+MRWRA water- soaked samples	5
Figure 34	Comparison between Type K and Type K+LWA+MRWRA air-dried samples	6
Figure 35	Comparison between Control and Type K oven-dried samples5	8
Figure 36	Comparison between Control and Control+LWA oven-dried samples 5	9
Figure 37	Comparison between Type K and Type K+LWA oven-dried samples 5	9
Figure 38	Comparison between Type K and Type K+LWA+MRWRA oven- dried samples	51
Figure 39	Nonlinear curve fitting of KL35MR_WS absorption data6	i4
Figure 40	Nonlinear curve fitting of KL35MR_AD absorption data6	i4
Figure 41	Nonlinear curve fitting of KL35MR_OD absorption data6	5
Figure 42	(a) Hydraulic machine setup for compressive strength Test, (b) Horizon Software to control loading rate and data collection, and (c) sample failure after loading	6
Figure 43	Comparison of all compressive strength values	7
Figure 44	Slump loss comparison between Control and Type K over 180 minutes 8	2
Figure 45	Regression Analysis of Control Mix slump loss8	3
Figure 46	Regression Analysis of Type K Mix slump loss8	4
Figure 47	Air content comparison between Control and Type K mix over 180 minutes	4
Figure 48	Regression Analysis of Control Mix air content loss	5
Figure 49	Regression Analysis of Type K Mix air content loss	5

Figure 50	Nonlinear curve fitting for C_WS absorption data	86
Figure 51	Nonlinear curve fitting for C_AD absorption data	86
Figure 52	Nonlinear curve fitting for C_OD absorption data	87
Figure 53	Nonlinear curve fitting for K_WS absorption data	87
Figure 54	Nonlinear curve fitting for K_AD absorption data	88
Figure 55	Nonlinear curve fitting for K_OD absorption data	88
Figure 56	Nonlinear curve fitting for CL17_WS absorption data	89
Figure 57	Nonlinear curve fitting for CL17_AD absorption data	89
Figure 58	Nonlinear curve fitting for CL17_OD absorption data	90
Figure 59	Nonlinear curve fitting for CL35_WS absorption data	91
Figure 60	Nonlinear curve fitting for CL35_AD absorption data	91
Figure 61	Nonlinear curve fitting for CL35_OD absorption data	92
Figure 62	Nonlinear curve fitting for KL17_WS absorption data	92
Figure 63	Nonlinear curve fitting for KL17_AD absorption data	93
Figure 64	Nonlinear curve fitting for KL17_OD absorption data	93
Figure 65	Nonlinear curve fitting for KL35_WS absorption data	94
Figure 66	Nonlinear curve fitting for KL35_AD absorption data	94
Figure 67	Nonlinear curve fitting for KL35_OD absorption data	95
Figure 68	Nonlinear curve fitting for KL17MR_WS absorption data	95
Figure 69	Nonlinear curve fitting for KL17MR_AD absorption data	96
Figure 70	Nonlinear curve fitting for KL17MR_OD absorption data	96

X

ABSTRACT

Calcium Sulfoaluminate (CSA) cement is renowned for rapid strength development, accelerated microstructure formation, and shrinkage mitigation. It has been used as a supplemental cementitious material for concrete decks of bridges, airport runways, and several other practical applications. One of the main disadvantages of using CSA cement is its high-water demand for rapid hydration processes, which adversely affects the fresh concrete workability. In this study, different poly-carboxylate admixtures have been used to prepare several concrete mix test batches. These concrete mixes include Ordinary Portland cement (OPC) and Type K (85% OPC + 15% CSA) cement mixes. Slump and air content readings were taken within 60 minutes from the time of mixing. A specific mid-range water-reducing admixture (MRWRA) effectively retained the flowable properties at the end of 60 minutes, acceptable for working conditions. Isothermal calorimetric studies were performed after preparing different cement pastes samples with added admixtures; MRWRA keeps the Type K cement paste at the dormant stage for the longest time effectively compared to other admixtures. However, this raises questions about the quality of microstructure development during the curing process. Further tests were done, adhering to the ASTM standards, incorporating the pre-soaked lightweight aggregates (LWA) and MRWRA in the concrete mix designs. Several samples were prepared for the water absorption test and compressive strength test. Data trends concluded that KL35MR (Type K samples with MRWRA at 3 fl oz/cwt and 35% replacement of fine aggregates with LWA) had demonstrated the lowest permeability after 7 days submerged underwater. Also, these samples had the highest compressive strength amongst all Type K samples. These observations were relatable to normal OPC concrete samples and can thus, KL35MR concrete mix design can be considered durable for bridge decks and other structural applications. For further justification, further analysis should be done at a micro-level, such as scanning electron microscopic imaging, to understand the impact of internal curing and retarding admixture interaction on microstructure development of expansive cementitious materials.

Keywords: Calcium Sulfoaluminate, Ordinary Portland cement, Hydration, Poly-Carboxylate Admixtures, Mid-Range Water Reducing Admixture, Workability, Lightweight Aggregates, Permeability, Slump, Air Content.

Chapter 1

INTRODUCTION

Durability is a cardinal factor of concrete structures. It is desired for a concrete bridge deck to sustain the required strength and serviceability during its lifetime. On the contrary, concrete decks having a large surface to volume ratio undergo accelerated drying shrinkage due to more exposed surfaces. Drying shrinkage forms transverse cracks, which allows corrosion of reinforcement in concrete, freeze-thaw cycles, and alkali-silica reaction (also known as 'concrete cancer') because of intrusion of deicing salts and numerous harmful chemicals in concrete which deteriorates the integrity of the structure(P K Mehta 1999; Neville 2001).

ACI committee (ACI Committee 231 2010) has recommended many strategies to curtail shrinkage in concrete. These strategies include shrinkage reducing admixtures, supplemental cementitious materials such as pozzolans, expansive additives, etc. An extensive Phase-I study (Chaunsali et al. 2013) with expansive additives was done to curb shrinkage. After experimenting with different concrete mix designs, it was concluded that the use of calcium sulfoaluminate (CSA) cement at 15% replacement of Ordinary Portland Cement (OPC) to develop Type K (85% OPC + 15% CSA) could effectively compensate for the drying shrinkage problem in laboratory conditions. In the Phase-II of this study (Ardeshirilajimi et al. 2016), a combination of Type K cement and lightweight aggregates (LWA) in mortar mixes has been beneficial against autogenous and drying shrinkage. It has been observed that Type K-LWA blend samples exhibited a surge in early-age expansion in sealed conditions compared to Type K blend with a higher water to cement ratio. Since Type K mix has higher water to cement ratio compared to Type K-LWA mix, it has been suggested that the concrete made only from the former mix has higher susceptibility to develop porous microstructure compared to the latter. Additionally, Type K-LWA mix demonstrated a lower compressive strength compared to traditional OPC mix at early ages but can show an increase in compressive strength at later ages (28 days or more). Additionally, Type K concrete mix exhibited rapid slump loss compared to normal OPC concrete mix which adversely affects the workability during transportation and construction.

1.1 Scope of the Thesis

Chemical admixtures – To tackle the workability issues, engineers have been using chemical admixtures/superplasticizers in fresh concrete for the last 50 years. Some of the benefits of using chemical admixtures are improved workability in fresh concrete, increased strength and durability, and limited

2

formation of capillary pores, resulting in less permeability in hardened concrete (Symposium, Tecnology and February 2005).

Internal curing – It can be defined as the supply of water for hydration purposes to unreacted cementitious particles using pre-soaked LWA, which is placed as a partial replacement of conventional aggregates into the volume of fresh mix concrete. When the relative humidity (RH) falls below the critical level due to self-desiccation and evaporation, LWA releases the required amount of water to replace the lost moisture and facilitate hydration. This mechanism helps prevent early cracking and ingress of aggressive chemicals, reduce porosity, and improve durability (Bentz and Weiss 2011).

1.2 Objectives of the Thesis

This thesis deals with the workability and durability issues associated with the Type K concrete mix. Adverse loss of workability stems from the accelerated use of water for ettringite formation because of expansive cement hydration results in a rapid slump and air content loss in the fresh concrete mix. Besides, self-desiccation and evaporation due to environmental conditions make the concrete mix susceptible to develop early age cracking.

Currently, little research work has been done to address the workability issue of Type K concrete mix. In this study, different commercially available chemical admixtures were incorporated into the concrete mix designs to determine slump loss and air content loss for comparison. Experimental data was studied to select the most suitable chemical admixture to be used during construction purposes. Later on, hardened concrete samples were prepared using the desired admixture and LWA to investigate the durability properties, such as the degree of water absorption and compressive strength.

Chapter 2

A BRIEF LITERATURE REVIEW

In this chapter, properties and uses of concrete, hydration process of ordinary Portland cement (OPC), hydration process of Calcium sulfoaluminate (CSA) cement, expansive properties of CSA cement, workability of concrete mix, the functionality of admixtures and lightweight aggregates, and finally, self-healing mechanisms will be discussed concisely.

2.1 Concrete Properties

Concrete is a composite made of readily available raw materials and ease of production method, which also redeems it one of the most abundantly used construction materials (Pomeroy 1978). Conventional concrete can be made by mixing OPC, coarse and fine aggregates, and water at different proportions. OPC reacts with water to form the microstructure, and this reaction is directly correlated with temperature variance, time of reaction, and water availability. The development of hardened concrete's compressive strength depends on several factors: chemical composition of OPC, water to cement ratio, uniformity and distribution of aggregate sizes, and the extent of cement hydration. Depending on the criteria, ACI design guidelines can prepare a specific concrete mix that delivers target properties for the desired application (ACI Committee 325 2017).

2.2 Hydration Process of Ordinary Portland Cement

The four essential constituents of the OPC are Tricalcium silicate (C_3S) , Dicalcium silicate (C_2S) , Tricalcium aluminate (C_3A) , and Tetracalcium aluminoferrite (C_4AF) . Early-age and late-age compressive strength of hardened concrete depends on the percentage composition of the four chemicals mentioned above and their subsequent rate of hydration mechanisms (S. Wild, B.B. Sabir, and J.M. Khatib 1995). Basics of these reaction mechanisms are important to understand as they drive to develop new mix designs of more sustainable concrete materials, with chemical admixtures and other supplemental materials, which is becoming an increasingly tough job for researchers (Bullard et al. 2011). The cement hydration process can be modeled into several chemical kinetics steps based on fundamental physics and chemistry. Additionally, mechanistic understanding of these steps at a molecular level can become integral to fathom the whole concept of cement hydration steps. The steps can be classified into the following categories:

- Dislocation/dissolution separation of molecules from solid surface to liquid (water). Kinetics involving dissolution/dislocation has been studied thoroughly by Dove et al. (Dove and Han, 2007).
- Diffusion the process in which pore solution components travel through cement paste volume (Glasstone, Laidler, and Eyring 1941).
- Growth attachment of molecules into a crystalline structure or amorphous solid through a process of self-adsorption (Physical and Communicated 1951).
- Nucleation enormous excess energy enabling chemicals to cross the solid-liquid interface barrier and forming precipitates (homogenous in

6

solution, heterogenous on a solid surface) (Kashchiev and van Rosmalen 2003).

- Complexation reactions forming complex formation of ions from simple ions (Morel 1983).
- Adsorption ions and/or other molecules accumulate on a particular interface (Morel 1983; Somorjai and Li 2010).

The common consensus is that these reaction steps occur either in series, parallel, or complex combinations. Microstructure growth from pore solution involves diffusion of solute to a close contact or proximity of a solid surface followed by adsorption and complexation of several solute molecules to form a single crystal molecular structure unit. This molecular unit forms a chemical bond with the more massive crystal structure and hence, growth. But often, that is not the case. Instead, the reaction mechanisms usually reach a state of equilibrium. The slowest step is the rate-controlling step in equilibrium conditions, ultimately determining the reaction rate (Somorjai and Li 2010). Hydration reaction of C₃S dictates the setting time and early-age strength development of the cement paste. Studies on the reaction mechanism of the C_3S -water system have helped explain the effects of temperature, the addition of admixtures, dilution, and other additional cementitious materials in the fresh concrete mix (E.M.Gartner, J.F. Young 2003). Equation (1) below shows the reaction in a stoichiometric manner. The actual product of the C₃S hydration reaction is calcium silicate hydrate or known as C-S-H. Calcium silicate hydrate has been found as an amorphous phase with different compositions,

which dictated using the 'C-S-H' acronym for identification rather than the exact chemical formula. This reaction can be classified into four sections, as shown in figure 2: (1) initial reaction, (2) dormant period, (3) acceleration period, and (4) deceleration period (S Mindess, Young, and Darwin 2003).



Figure 1: Stochiometric equation of C₃S reaction mechanism (Mindess, Young, and Darwin 2003)



Figure 2: Heat evolution profile of cement hydration (Mindess, Young, and Darwin 2003)

2.3 Expansive Cement - Hydration Mechanism and Properties

Over the past few decades, different admixtures have been developed for concrete to mitigate the shrinkage cracking problem (Liu et al. 2016). One of the most promising strategies is to use CSA expansive cement; its unrestrained expansion abilities have been touted by several studies as one of the most effective methods to compensate for tensile stress due to selfdesiccation (Ardeshirilajimi et al. 2016; Carballosa et al. 2015; Chaunsali et al. 2013). 'Type K' (combination of OPC + CSA cement) contains C_3S (tricalcium silicate), C_2S (dicalcium silicate), $C_4A_3\hat{S}$ (ye'elimite), CaSO4 (gypsum), and CaO (lime) as its' main components. In this study, the main focus will be on ye'elimite hydration, the formation of ettringite at early-age hydration and late-age hydration, decomposition of crystalline ettringite to amorphous ettringite under extreme heating conditions, compressive strength development, and its effect of reducing concrete porosity by promoting internal curing by using LWA and late-age hydration.

$$C4A3\hat{S} + 2C\hat{S}H2 + 34 H \rightarrow C3A.3C\hat{S}.32H + 2AH3$$
 (2)

$$C4A3\hat{S} + 6 CH + 8 C\hat{S}H2 + 74 H \rightarrow 3 C3A.3C\hat{S}.32H$$
(3)

$$AH3 + 3CH + 3C\hat{S}H2 + 20H \rightarrow C3A.3C\hat{S}.32H$$
(4)

Figure 3: Stochiometric equations of ye'elimite hydration steps

Ettringite, also known as ES32(Baquerizo, Matschei, and Scrivener 2016), is a natural mineral. The presence of lime makes equation (3) more likely. It can also be noted that ettringite formation requires a lot of water compared to traditional OPC cement hydrated products. A study has found that in the presence of lime, the colloidal formation of ettringite can be expected (Povindar Kumar Mehta 1973). Colloidal ettringite has been cited for absorbing water, which influence crystallization pressure on the volume of concrete and hence, causes expansion (Hargis et al. 2013; P. K. Mehta 1973). A study done by Min and Mingshu explained the growth of ettringite crystals exerts swelling pressure as tiny ettringite crystals continue to absorb water (Min and Mingshu 1994). A molecule of ettringite has a structure divided into columns and channels and have the chemical formula,

 $[Ca_3Al_2(OH)_6 \cdot 12H_2O]^{3+}[3(SO_4) \cdot 2H_2O]^{6-}$. Each calcium atom has four water molecules attached to it, which gives the cylindrical surface. In between the columns, there are channels which are made of sulfate groups and zeolitic water (Harry F W Taylor 1997). In overall, at a stable solid phase, ettringite contains 32 H₂O molecules (30 are fixed in columns and 2 are weakly bound in channels) (Skoblinskaya and Krasilnikov 1975).

In this study, it is also essential to know about the thermal stability of ettringite crystals. At around 120°C, ettringite breaks down to form monosulfoaluminate (AFm) and basanite (Hall et al. 1996). A study done by Skoblinskaya et al. (Skoblinskaya and Krasilnikov 1975) found that the decomposition of ettringite results in the loss of 24 H₂O molecules at high temperatures. It can be described in two steps: (1) firstly, the loss of 12 H₂O molecules occurs from Ca atoms until the number of bounded H₂O molecules in ettringite becomes 18. Up to this point, ettringite still maintains a crystalline structure but there is a significant reduction in lattice parameters such as intercolumn distance. And secondly, the loss of another 12 H_2O molecules happens at temperatures as high as 180°C where ettringite structure becomes amorphous. Another study done by Hartman et al. (Hartman et al. 2006) observed that ettringite loses water and/or hydroxyl groups simultaneously, which is in total contradiction with the mechanism mentioned by Skoblinskaya et al. (Skoblinskaya and Krasilnikov 1975). The decomposed product is known as metaettringite (Zhou, Lachowski, and Glasser 2004). Studies have found that ettringite decomposition and re-composition can be described as a function of temperature and relative humidity (Baquerizo, Matschei, and Scrivener 2016). Apart from shrinkage mitigation, CSA cement has been used in addition to gypsum to avoid flash set in several cases. However, delayed ettringite formation due to late-age hydration or alkali-silica reaction has been credited to the deterioration of concrete structures (Collepardi 2003; Kuzel 1996; H F W Taylor, Famy, and Scrivener 2001).

2.4 Rheology of Concrete

The primary purpose of the chemical admixtures is to alter the rheology of concrete. The flow nature of concrete, also known as 'workability,' directly impacts the quality of mixing, handling during transportation, casting, finishing, etc. The use of chemical admixtures has been directly correlated with building economic and durable structures (N. Roussel et al. 2012). The simplest way to measure the fresh concrete workability empirically is the slump test (ASTM C143/C143M 2015). This test simulates the flowing nature at a low-shear rate that has been directly associated with yield stress. On the contrary, this test does not depict the flow behavior of concrete at a higher shear rate: it has been found that two different concrete mixes can have the same slump value but contradictory flow behavior at the same time (Tattersall and Banfill 1983). In another study, variable shear rates have been found during mixing and pumping of fresh concrete (Nicolas Roussel 2006). The flow behavior of concrete is quite complex and cannot be described by using the Newtonian model. Rather than using the Newtonian model, the Bingham model is used to explain the behavior. The fundamental difference between the two models is for Bingham; the curve does not cross the origin, unlike the Newtonian model. Fluids that follow the Bingham model behaves like an elastic material below threshold yield stress (τ_0). Once this threshold is crossed, the fluid demonstrates proportionality between yield stress and shear rate, as illustrated in figure 4. This is because concrete is considered an agglomeration of heavy aggregates suspended in the mortar mix, and this created inter-particle attractions that resulted in this threshold yield stress (τ_0) value. (Nicolas Roussel, 2006). Moreover, the rheological behavior of concrete has been directly correlated with several influencing factors which are (Aïtcin and Flatt 2015):

• Colloidal forces such as Van-der-Waals, electrostatic, and steric can make the suspended particles attract or repel, depending on the presence of chemical admixtures, water content, etc.

12

- Brownian motion is triggered due to consistent rotational movements and mixing of the concrete suspension.
- Non-Newtonian fluids tend to vary in viscosity when shear thinning, and shear thickening occurs.
- The gravitational pull act can cause the aggregates to segregate from the concrete volume unless the particle size and density are in balance.



Figure 4: (a) Flow behavior and (b) Viscosity Difference between the Bingham Fluid and Newtonian Fluid (Aïtcin, Pierre Claude Flatt, Robert J.,2015)

In summary, since the rheological behavior of concrete added with chemical admixtures is a pressing concern, it is important to understand its functions. The conventional property of chemical admixtures is to interfere between the interparticle distance via the mechanism of adsorption, a process by which molecules attach themselves to the cement particles surface. As a result, it causes a dilution of attractive forces, and in turn, threshold yield stress allows the concrete to flow more easily. Figure 5 illustrates the behavioral change in the rheology of concrete in a simple manner.



Figure 5: Influence of cement additives on yield stress and viscosity of cement paste (Newman and Choo,2003)

2.5 Chemistry of Chemical Admixtures

Hydration reactions of C₃S, C₂S, and C₄A₃ \hat{S} form mainly C-S-H (calcium silicate hydrate) gel, CH (calcium hydroxide), and C₃A.3C \hat{S} .32H (crystalline ettringite). During the hydration process, cement particles undergo dissolution, precipitation, and crystallization changes, leading to the hardening of concrete. Adding chemical admixtures to freshly-mixed concrete makes it possible to alter a few basic properties to make workability favorable and improve hardened concrete properties such as durability and late-age strength. Secondary effects of using admixtures such as water reducers abate the rate of cement hydration; the degree of reduction can be directly correlated with the dosage and the molecular structure of the admixture (Uchikawa, Sawaki, and Hanehara 1995; Yamada et al. 2000). Most chemical admixtures available in the current market are made from organic compounds. In this section, a few different types of chemical admixtures have been identified, and the importance of the molecular structure of these compounds has been discussed briefly. Since the 1930s, many different types of natural polymers were used for altering concrete flow properties. But recently, since 1980s, a new generation of chemically synthesized polymers, such as polynapthalene sulphonates (PNS), polymelamine sulphonates (PMS) and polycarboxylates (PCE), were introduced into the industry as admixtures. These chemicals can be used at a very low dosage (which also makes them economical) to achieve high dispersion via electrostatic and/or steric effect (Admixtures and Khalifa 2020; Symposium, Tecnology, and February 2005). With the recent improvement in technology, it is possible to modify the molecular structure and achieve a wide range of performances. Among all the different types of admixtures, PCE has been subjected to the most improvement throughout the last few decades. Recent technologies have enabled researchers to modify the structural properties of the PCE molecule to gain a broader range of applications. Some of the modifications are:

- Length of the main chain and side chains
- Distribution category of the side chains along the main chain
- Chemical nature of the carboxylic groups and polyethers
- Charge distribution

These feature modifications gave an upper hand for PCEs to dominate in the admixture industry. Moreover, the synthesis processes of PCEs, free radical co-polymerization, and polymer analogs esterification showed the versatility needed to change such features.

2.6 Mechanism of Poly-Carboxylate Admixtures with Expansive Cement

Numerous researchers have claimed that the admixture-cement compatibility depends on several factors: the dosage of admixture, exact time of addition, and structural composition of the chemical groups. Variability of PCE molecules' structural shapes has made it intricate to fathom their effects on the rheology of concrete, hydration mechanism, and microstructure development. Usually, PCE molecules have comb-shaped copolymers, which give the researchers countless options to tailor PCE admixtures to suit the desired requirements (Uchikawa, Sawaki, and Hanehara 1995; Yamada et al. 2000). The structure of comb-shaped copolymers has side chains (polyethers) attached to the main chain (carboxylic groups). The carboxylic groups provide a negatively charged environment after dissociation with water, attracting the positively charged cement particles for adsorption. Besides, the polyether side chains provide a steric hindrance effect, which allows the cement particles to stay un-hydrated for a certain period. The dispersion effect can be ascribed towards the covalent nature side chains (Ohta, Sugiyama, and Tanaka 1997). The molecular structure and dispersion mechanism have been illustrated in figure 6.



Figure 6: (a) Diagram of PCE molecular structure and (b) Dispersion effect of PCE attached to a cement particle (Aïtcin, Pierre Claude Flatt, Robert J.,2015)

PCE admixtures are known for delaying OPC systems' initial hydration peak, making it very useful (Pourchet et al. 2007). However, the interaction between CSA cement and PCE molecules is intricate, and most PCE admixtures are ineffectual with CSA based cement (Tian et al. 2019). Ye'elimite hydration process form ettringite crystals (needle-like structure), which cause the concrete to stiffen up within 30 minutes of mixing. A study found the explanation behind the retardation effect of PCE admixtures with type K cement; they concluded that the number of carboxyl groups in PCE molecules could be directly correlated with the slump retention up to a certain degree (Yamada et al. 2000). It is common practice to combine superplasticizers with retarders to achieve best results for workability maintenance during mixing. However, a combination of such chemicals can be deleterious for concrete as it leads to complex interactions between them and the cement particles (G. Zhang, Li, and Li 2016). To address this issue, a recent study was done by researchers in China where they synthesized a new type of chemical admixture which can provide plasticization and retardation effect at the same time in CSA based cement mixes. Before performing macrolevel experiments, they did several tests using techniques such as X-ray diffraction, thermo-gravimetric analysis, nuclear magnetic resonance spectroscopy, calorimetric tests, etc. to understand the effect on hydration reactions and setting times. They concluded that, compared to PCE, the newly synthesized chemical facilitated better fluidity retention and extended the setting time (Su et al. 2019). Also, with the increase in dosage, ettringite formation is strongly retarded, unlike PCE admixtures, where dosage increase adversely affects the fresh properties.

2.7 Mechanism of Air-entraining Admixtures

Several studies have confirmed that entrained air bubbles in fresh concrete affect its rheology. Moreover, it can be attributed towards increasing durability against freeze-thaw cycles. (Aïtcin and Flatt 2015; Dodson 2013; Sidney Mindess, Young, and Darwin 2003). The average size of air bubbles formed due to the addition of air-entraining admixture can range from 1 to 100 μ m, which is comparable to cementitious particles size. Apart from that, other factors such as temperature, superplasticizer dosage, presence of other admixtures, aggregate and cement particle size, mixing techniques, etc. can contribute to the flow properties.

There are two main mechanisms in which AEA works with cement particles. Firstly, hydrophilic AEA molecules attach themselves to the positive sides of cement particles, enabling the air bubbles from each other and maintaining a fixed position on the concrete mix suspension (Kreijger 1967). And secondly, specific AEA molecules form hydrophobic precipitates that create a layer at the air-water interfacial zone. As a result, the bubbles are strongly protected by a thick film that causes steric effects and facilitates uniform dispersion of these air bubbles (Mielenz et al. 1958). It has also been observed that an increase of air bubbles directly correlates to an increase in concrete's workability. However, this, in turn, reduces the compressive strength. If the slump of fresh concrete mix goes north of 6 inches, the entrained air volume decreases. This is because the bigger air bubbles tend to move upward and escape the volume of the concrete mix due to higher instability (Dodson 2013). Additionally, water to cement ratio directly impacts air-entrainment; a decrease in w/c ratio can hinder the formation of air bubbles and hence, reduce durability (Du and Folliard 2005). Also, the addition of superplasticizers may create a state of conflict with AEA molecules; it depends on the dosage and the type of chemical being used. A study has shown that PNS superplasticizers have minimal interactions with AEA admixtures and their functionality. On the other hand, PCE admixtures create air bubbles when added to the concrete mix (Nkinamubanzi, Mantellato, and Flatt 2016). Some types of PCE admixtures molecules entrain larger air bubbles into the concrete while inhibiting the AEA admixture from producing smaller air bubbles. The larger bubbles do not protect against freeze-thaw as spacing factors become

redundant (Pigeon 2014). However, it is hard to predict whether certain PCE molecules will interact negatively with AEA molecules as PCE admixtures have different types of chemical compositions. It has been recommended that, if needed, a higher dosage of AEA should be incorporated into the mix design to counteract the defoaming effects of PCE.

2.8 Self-healing Mechanisms of Concrete

Self-healing mechanisms can be distinguished into two categories: autogenous and autonomic. Autogenic self-healing occurs when a concrete material heals cracks and other defects on its microstructure using its own chemical reaction products either by re-hydration or late-age hydration. The first explanation is the hydration reactions of unreacted C₃S, and C₂S produce C-S-H at a late age of concrete curing. Secondly, the precipitate formation of calcium carbonate results from the reaction between calcium ions and carbon dioxide dissolved in water. This precipitate deposit themselves around major cracks and ultimately reduces the porosity of concrete. However, calcium carbonate's contribution to mechanical properties is still not adequately understood yet (Edvardsen 1999; De Rooij et al. 2013).

On the other hand, autonomic self-healing is promoted by adding cement admixtures such as expansive cement (Hosoda 2007; Kishi 2007; Sisomphon, Copuroglu, and Koenders 2011), LWA releasing water and/or numerous types of self-healing agents (De Rooij et al. 2013). In an experimental study done by Sisomphon et al. (Sisomphon, Copuroglu, and Koenders 2012), the degree of self-healing was compared between a control

20

specimen and CSA incorporated specimen. Due to the high rate of reaction of CSA particles, it was concluded that it helped close down surface cracks at a higher rate. The investigation also found proof that the addition of CSA agents in cement facilitated more calcium ion production and hence, more calcium carbonate precipitation. In addition, an alkaline environment positively triggers calcium carbonate production. The study also found a new form of carbonate ettringite forms that work as a quasi-reinforcement in the cement matrix.

LWAs have been used for internal curing for multiple structural applications in aggressive environments to counteract extreme self-desiccation induced shrinkage, late-age hydration, and reduce porosity in concrete structures (Holm, Bremner, and Newman 1984). Even though LWA has a porous microstructure, pre-soaked LWA facilitates cement particle hydration around the outer edges. As a result, a continuous cement matrix can be observed on scanning electron microscopic images around LWA particles. In addition, these hydrated particles impregnate themselves inside the LWA outer layer. Due to this phenomenon, there was no evidence of interfacial transition zone (ITZ) around LWA aggregates (M.-H. Zhang and Gjørv 1990). ITZ has been observed in standard concrete with traditional aggregates. Inefficient packing, non-uniform particle size distribution, unavailability of water at internal regions of concrete form large ITZ zones, which act as a transport region for water and other harmful ions. However, many studies have claimed that LWAs become a porous structure that can provide a water transport pathway after complete hydration. In contrast, Pyc et al., after extensive

21

investigation, have found that once LWA pores become empty, re-absorption of water by LWA is not possible. Because, the presence of dense concrete microstructure around individual LWA prevent further water ingress (Pyc et al. 2008). Moreover, empty LWAs act as an efficient air-void system which provides freeze-thaw resistance to a considerable degree (Bentz and Snyder 1999).

The information, as mentioned earlier, will provide greater insight into the investigation that was performed. Different admixtures have their positive and negative effects, and by doing this literature review, a better understanding can be achieved to explain trends, scope, and shortcomings.

Chapter 3

INVESTIGATION OF FRESH PROPERTIES OF TYPE K CONCRETE WITH POLY-CARBOXYLATE ADMIXTURES

This chapter explores the behavior of selected PCE admixtures with Type K concrete mix. At an early age, Type K hydrates rapidly to form ettringite, leading to a high degree of heat evolution and rapid use of water (Huang et al. 2019). As a result, concrete made from Type K cement has a lower setting time than conventional OPC concrete, which can make pouring, dispersing, and finishing difficult. But, the use of chemical admixtures at optimal dosages can potentially offset this behavior. Therefore, research reported herein was intended to determine if there is any discrepancy between the behavior of conventional concrete versus Type K concrete in the presence of water-reducing and air-entraining admixtures. This chapter summarizes concrete mix designs, material properties, slump loss, air content loss, and isothermal calorimetric test procedures. After several trial and error and discussion with the Type K provider (CTS cement), two PCE based admixtures were selected for this study. Data points of slump loss, air content loss, and heat evolution profiles have been plotted against time and discussed for fresh cement and concrete combined with the selected admixtures. This phase of the investigation aims to find a suitable admixture for tackling the workability issues of Type K concrete.

23

3.1 Investigation of Fluidity Retention

In the next few sub-sections, mix designs, material proportions, and their properties, experimental procedure, results and discussions, and regression analysis have been presented and discussed.

3.2 Materials and Methods

Acronym	OPC (lb/yd ³)	CSA (lb/yd ³)	FA (lb/yd ³)	CA (lb/yd ³)	Water (lb/yd ³)	Water cement ratio
С	610		1130	1826	268	0.44
CHR	610		1130	1826	268	0.44
CMR	610		1130	1826	268	0.44
K	519	91	1130	1826	299	0.49
KHR	519	91	1130	1826	299	0.49
KMR	519	91	1130	1826	299	0.49
AEA ¹ – 'MasterAir AE200' dosage at 2 fl oz/cwt HRWRA ² - 'MasterGlenium 3400' dosage at 2 fl oz/cwt MRWRA ³ - 'MasterPolyheed 1020' dosage at 3 fl oz/cwt						
	Acronym C CHR CMR K KHR KMR ir AE200' terGlenium terPolyhee PC + 15%	Acronym OPC (lb/yd^3) C 610 CHR 610 CMR 610 KHR 519 KHR 519 ir AE200' dosage at terGlenium 3400' do terPolyheed 1020' d PC + 15% CSA	AcronymOPC (lb/yd^3) CSA (lb/yd^3) C610CHR610CMR610K519SI91KHR51991519KMR519913400' dosage at 2terPolyheed 1020' dosage at 3PC + 15%CSA	AcronymOPC (lb/yd^3) CSA (lb/yd^3) FA (lb/yd^3) C6101130CHR6101130CMR6101130K51991MR51991KMR5199111301130KHR51991It AE200' dosage at 2 fl oz/cwtterGlenium 3400' dosage at 2 fl oz/cwtterPolyheed 1020' dosage at 3 fl oz/cwtPC + 15%CSA	AcronymOPC (lb/yd^3) CSA (lb/yd^3) FA (lb/yd^3) CA (lb/yd^3) C61011301826CHR61011301826CMR61011301826K5199111301826KHR5199111301826KMR5199111301826ir AE200' dosage at 2 fl oz/cwt11301826ir AE200' dosage at 2 fl oz/cwtterGlenium 3400' dosage at 2 fl oz/cwtPC + 15%CSA	AcronymOPC (lb/yd³)CSA (lb/yd³)FA (lb/yd³)CA (lb/yd³)Water (lb/yd³)C61011301826268CHR61011301826268CMR61011301826268K5199111301826299KHR5199111301826299KMR5199111301826299ir AE200' dosage at 2 fl oz/cwtterGlenium 3400' dosage at 2 fl oz/cwt299PC + 15%CSAterSecondterSecond

Table 1: Mix Designs for Workability Analysis

Material composition for every concrete mix designs selected for the testing is mentioned in Table 1. Every time around 60 lbs, concrete was concrete for testing purposes according to the ASTM C 685 standards (ASTM C 685/C 685M-01 2001). However, there is a subtle difference between the slump loss test and air content loss test; after every slump reading, the concrete was placed back into the mixer to prevent stiffening of fresh concrete by keeping it in mild agitation. Whereas, after every successive air content reading, the concrete was discarded as the testing procedure introduces water
into the mix, which ultimately changes the concrete's water content. As a result, to prevent further discrepancies, every concrete batch after reading had to



Figure 7: (a) Fresh concrete mix; (b) slump test setup; and (c) concrete kept in mixing drum at 25 rpm to provide mild agitation



Figure 8: (a) Fresh concrete mix; (b) Type-A air meter; and (c) concrete kept in mixing drum at 25 rpm to provide mild agitation

be discarded. To tackle this issue, 100 lbs. concrete had to be made for air content tests for a single investigation. Figure 7 shows the slump loss test setup, and figure 8 presents the air content loss setup. For the slump loss test (ASTM C143/C143M 2015) and the air content loss measurement (ASTM C231/C231M 2010), the fresh concrete was taken out every fifteen minutes from the mixer, and five readings were taken within the first sixty minutes.

3.3 Test Results and Discussion

At the start of this investigation, it was essential to compare the slump loss and air content loss to the Type K concrete mix ("K") and standard OPC concrete mix ("C"). It should be noted at this stage that K mix has a watercement ratio of 0.49. In contrast, the C mix has a water-cement ratio of 0.44. Figures 9 and 10 compare the slump and air content measurements for the two mix designs. In both instances, it can be observed that the K mix loss is steeper compared to the C mix. Even though both mixes had the same dosage of the air-entraining agent, the K mix exhibited lower slump and air content values at zero minute; the values were 13.7% and 28.2% lower, respectively. However, the difference in percentages between the measurements remained consistent throughout the 60-minute observation period. Based on the data, the K mix shows a higher need for chemical admixtures to achieve early-age properties suitable for construction purposes. However, it was reassuring to witness the difference in behavior between the two concretes mixes remained relatively consistent.



Figure 9: Slump loss comparison between Control mix and Type K mix over 60 minutes



Figure 10: Air content loss comparison between Control mix and Type K mix over 60 minutes

3.4 Regression Analysis of Slump Loss Trends



Figure 11: Regression analysis of Control mix slump loss over 60 minutes



Figure 12: Regression analysis of Type K mix slump loss over 60 minutes

Regression analysis is an ever-growing statistical method to understand the relationship between two or more variables, develop equations at multiple orders to predict or extrapolate the dependent variable if needed. It is a crucial technique used by researchers all the time (Berk 2004). In this case, since it is vital to understand the relationship between slump loss and time, several techniques have been proposed. Regression analysis can be successfully using multiple software such Microsoft Excel, Origin Pro 2020, etc. Besides, coding languages such as python, java, C++ can also be used to write suitable code segments to run the analysis using the provided x-y data from the experiments. However, the disadvantages of using programming languages are several; these techniques are time-consuming, need the proper expertise and experience for efficacy. As a result, software with a graphic user interface, such as Origin Pro, provides a necessary environment to run analyses quickly. A striking advantage of using such software is the availability of options; for each dataset, this particular software can run multiple iterations and provide the best-suited curve, hence the closest R^2 values to 1. R^2 is a measure that presents the degree of variation of the dependent variable (slump) that can be explained by the independent variable (time). For both C and K mixes, the R² values are above 0.90, which indicates a strong dependence of slump values on the change of time. However, as the regression analyses in these cases were multiple rather than linear, another factor was essential to be noteworthy; that is known as 'Adjusted R^2 '. This factor corrects the R^2 values to nullify the overfitting condition. A regression model with increased data points may yield a higher R^2 value, which, in simple terms, can indicate a better fit with the model. But,

there is a high chance that the model may not predict any projection correctly. As a result, the adjusted R^2 takes the regression models' explanatory power to compensate and yield a lower and more accurate value. In both cases, lower adjusted R^2 values have been specified to justify the regression models; the R^2 values were still above 0.90.

3.5 Compatibility of Admixtures with Control Mix

After experimentation with a few trial batches, one mid-range waterreducing admixture (MRWRA), MasterPolyheed 1020, and one high-range water-reducing admixture (HRWRA), MasterGlenium 3400, which are commercially produced by BASF[©], were selected for use in concrete mixes. Before using the admixtures to prepare K mixes, it was essential to understand the baseline behavior for the control mix; slump loss tests were first performed using Control (C), Control+HRWRA (CHR), and Control+MRWRA (CMR) mixes and plotted against the target (TGT) value at four inches. In figure 13, the slump value for C goes below 4 in. around 10 minutes after mixing. In contrast, CHR and CMR's slump values go below the target approximately 35 minutes after mixing. These observations show the effectiveness of the admixtures with the conventional mix. At time zero, the slump values for CHR and CMR were 30.6% and 50%, respectively, compared to the C mix. Similarly, at the end of 60 minutes, the slump values for CHR and CMR were 64.6% higher than the C mix. Even though all mixes had the same water-tocement ratio, the admixtures significantly improved the workability characteristics throughout the testing period of 60 minutes. According to the product distributors, both selected admixtures contain a similar cement

30

dispersant based on poly-carboxylate groups. Both chemical admixtures are manufactured using a free radical polymerization process involving various organic monomers, among which ether and carboxylic acid monomers are significant. Both chemistries seemed to provide consistent results when used with conventional concrete.

One fundamental difference between the two admixtures is their effect at time zero. Figures 13 and 14 (which shows the percentage difference from the target 4 in. slump) show the mid-range water reducer was more effective in increasing the early-age slump than the high-range water reducer. This is interesting because the fundamental difference between MRWRA and HRWRA is the amount of water content reduction they can offer. MRWRA can reduce water content up to 10%, while HRWRA can reduce water content from 12% to 40% (Day et al. 2013). In this case, the slump values for CMR were higher than CHR until 35 minutes after mixing. The contradiction possibly is due to the higher dosage of MRWRA used in this study (3 fl oz/cwt) compared to the HRWRA dosage (2 fl oz/cwt).



Figure 13: Slump loss comparison between Control, Control+HRWRA, and Control+MRWRA mixes over 60 minutes



Figure 14: Slump retention comparison between Control, Control+HRWRA, and Control+MRWRA mixes

3.6 Compatibility of Admixtures with Type K Mix

Once the chemical admixtures' effectiveness for the control mix was established, selected agents' slump retention capabilities with the Type K mix were observed. Two mixes were designed: Type K+HRWRA and Type K+MRWRA. Figure 15 juxtaposes the slump loss results with the target value of 4 inches, and figure 16 compares the percentage differences. Both admixtures had a positive impact on improving the workability of the Type K mix. At time zero, the slump was 132% higher for the high-range water reducer (KHR) than the K mix. While the slump values remained consistently higher for KHR, slump values became smaller as the time approached 60 minutes. At the end of 60 minutes, the slump value was 1.1 in., which is only 10% more than the K mix. In contrast, the initial slump for the mid-range water reducer (KMR) was 177% higher than the K mix. Similarly, the difference in slump values remained consistently higher until the end of 60 minutes. At the end of 60 minutes, the slump for KMR was four inches, which is an approximately 250% increase compared to the slump value for K mix at 60 minutes.



Figure 15: Slump loss comparison between Type K, Type K+HRWRA, and Type K+MRWRA mixes



Figure 16: Slump retention comparison between Type K, Type K + HRWRA, and Type K+MRWRA

3.7 Regression Analysis of Slump Loss Trends

Figures 17,18,19, and 20 presents the regression models for CHR, CMR, KHR, and KMR slump loss data. For all cases, equations were developed, which can be used to predict slump loss beyond 60 minutes if needed. In addition, the R^2 and adjusted R^2 values are above 0.98, a strong indication of the reliability of the models.



Figure 17: Regression Analysis of Control+HRWRA mix slump loss over 60 minutes



Figure 18: Regression Analysis of Control+MRWRA mix slump loss over 60 minutes



Figure 19: Regression Analysis of Type K+HRWRA mix slump loss over 60 minutes



Figure 20: Regression Analysis of Type K+MRWRA mix slump loss over 60 minutes

3.8 Calorimetric Study of Type K cement with selected Admixtures

The progression of hydration reactions of cementitious particles has been a reliable indication of concrete's microstructure development as it hardens (Pane and Hansen 2005). The quality of the microstructure dictates empirical properties such as strength and durability. Isothermal calorimetry has been abundantly used by cement and concrete researchers to understand the effects of cement additives (Hanehara et al. 2001; De Schutter 1999; Y. Zhang, Sun, and Liu 2002). In this investigation, two different admixtures have shown promise in retaining the slump for Type K mixes. Moreover, MRWRA performed better to retain slump compared to HRWRA. To justify this observation, a calorimetric study was able to provide more evidence. Three different samples were prepared: K, KHR, and KMR. All three cement paste samples had a 0.49 water to cement ratio. The admixtures' dosages were adjusted accordingly to prepare three ampoules with 25 grams of cement samples in each of them. The mixing procedure has been presented in figure 21 and was done as follows: (i) mix OPC and CSA cement for fair distribution; (ii) water added with admixture if specified; and finally (iii) prepare samples by uniform mixing and proper placement inside ampoules before putting them inside the calorimeter at 25 °C. Heat evolution data was collected for 24 hours and presented in figure 22. Observations show that the Type K hydration process is rapid and starts setting at the lowest time compared to KMR and KHR heat profiles.



Figure 21: (a) Sample preparation, (b) cement paste placed in an ampoule and, (c) TAM isothermal calorimeter used for the experiment

Additionally, the heat evolution of KMR is subdued in comparison to the KHR heat profile. This trend was coherent with slump loss values and proves that the MRWRA retardation keeps the Type K hydration at the dormant period for the longest time. As a result, the KMR values stay at a lower viscous phase, which will help to retain slump and ensure proper placement during construction.



Figure 22: Heat evolution profiles for Type K, Type K+HRWRA, and Type K+MRWRA hydration process.

3.9 Summary



Figure 23: Slump value comparison of all mixes at 60 minutes

MRWRA showed the best positive results with both control and Type K mixes. This observation can be affected by the difference in the dosage and molecular structure of the admixture. Besides having the highest initial fluidity after mixing, the Type K mix with MRWRA had a 4 inches slump after 60 minutes. Some studies have found that fluidity retention is directly related to the molecular structure of the admixture used. It is possible that this particular mid-range water-reducing admixture had a higher number of carboxyl groups attached to the molecular structure, which facilitated better slump retention by keeping the hydration mechanism at a dormant phase for a longer period of time. Moreover, no drastic difference in the admixture interaction between the control and Type K mixes was observed. This is a positive sign to consider

while performing admixture dosage optimization of Type K concrete mixes for field implementation.

Chapter 4

DURABILITY PROPERTIES OF TYPE K CONCRETE

Concrete was once regarded as a durable construction material that requires minimal inspection and maintenance. However, many degradation mechanisms have been established over the past few decades, reducing the life-span of concrete structures. Concrete on highway bridges is exposed to the repetitive process of wetting and drying due to variable weather conditions (Sabir, Wild, and O'farrell 1998). These aggressive fluctuations of the conditions influence the transport of water and other agents through capillary pores influence the long-term performance of concrete; water ingression in concrete either facilitates freeze-thaw damage in cold weather or acts as a medium for harmful ions (chloride, sulfate, etc.) (Yang, Weiss, and Olek 2006).

Transport of water through cementitious materials happens in three different methods: (i) permeability, (ii) diffusion, and (iii) absorption. The capillary suction generally governs the absorption of water in the concrete near the unsaturated concrete surface. This process is comparatively faster than the general diffusion or capillary absorption process (Martys and Ferraris 1997). The water absorption test of concrete demonstrates a degree of durability of the concrete used to build aggressive environments. Three main approaches have

42

been established to determine the water transport mechanisms in cementitious materials: experimental, numerical simulation, and analytical (Wang 2009). The most dominant and accurate approach is the experimental method; highly sophisticated techniques such as nuclear magnetic resonance, gamma rays, etc. can be used to observe water transport's dynamic mechanism through the concrete capillary pores. However, the methods mentioned earlier are too expensive, and as a result, the gravimetric method is preferred to be most widely used at this point (Goual et al. 2000).

4.1 Investigation of Water Absorption Capacity

Sorptivity is widely accepted as the measure of saturation to characterize the water transport property through different concrete samples (Neithalath 2006). To perform this test, guidelines from ASTM C642, C1585, and C1757 (ASTM 2014; ASTM C1585-13 2013; ASTM C642-13 1997) have been followed to design the experiment. The details of materials, methods, and results are discussed in the sub-sections below.

4.2 Materials and Methods

Table 2 has all the mix proportions for the preparation of the samples. 24-hour absorption capacity for LWAs was found at 16.83% by using ASTM C128 standard specifications (ASTM C128 2004). LWAs were pre-soaked 24 hours before mixing. For each mix design, four 4 in. x 8 in. concrete cylinders (32 in total) were prepared by maintaining ASTM C192 standards (ASTM 2007). After each casting session, the fresh samples were kept in a temperature-controlled room 24 hours before demolding from the formwork. Later, these samples were submerged underwater for curing purposes. Samples selected for the water absorption test were cured for 14 days, and samples for the compressive strength test were cured 28 days straight.

		All units in lb/yd ³					Water	Total	
Mix Design	Acronym	OPC	CSA	FA	CA	Free water- cement ratio	supplied by LWA (lb/yd ³)	water- cemen t ratio	
Control	С	610		1130	1826	0.44	0	0.44	
Control+LWA (35%)	CL35	610		1130	1826	0.33	67	0.44	
Control+LWA (17%)	CL17	610		1130	1826	0.386	33.5	0.44	
Type K ²	K	519	91	1130	1826	0.49	0	0.49	
Type K ² +LWA (35%)	KL35	519	91	1130	1826	0.381	67	0.49	
Type K ² +LWA (17%)	K117	519	91	1130	1826	0.437	33.5	0.49	
Type K^2 +LWA (35%)+ MRWRA ³	KL35MR	519	91	1130	1826	0.381	67	0.49	
Type K ² +LWA (17%)+MRWRA ³	Kl17MR	519	91	1130	1826	0.437	33.5	0.49	
AEA ¹ – 'MasterAir AE200' dosage at 2 fl oz/cwt Type K ² - 85% OPC + 15% CSA MRWRA ³ - 'MasterPolyheed 1020' dosage at 3 fl oz/cwt									

Table 2: Mix Designs for Durability Analysis



Figure 24: Concrete samples being cured underwater

For the water absorption test, the cylinders were cut into 4 in. x 2 in. using a saw machine. Three different discs were obtained (in total, 6 for each mix design). Every two discs went through specific sample conditioning; this step is critical because the water absorption rate is responsive to the concrete sample's moisture content (Parrott 1994). As a result, for this test, three different sample conditionings were done: (i) water-soaked (WS), (ii) air-dried (AD), and (iii) oven-dried (OD). The critical steps of sample conditioning are illustrated in figure 25.



Figure 25: Sample preparation steps for water absorption test

While the WS samples and AD samples were submerged underwater immediately after conditioning, the OD samples were kept in air-tight plastic bags to cool down after removing from the oven. The temperature gradient positively affects the water absorption rate; with an increase in temperature, the water absorption rate increases. The concrete samples were cooled down to room temperature for 24 hours before submerging them underwater. To get a degree of saturation for each sample, the following formulas have been adopted. The change in mass is divided by the total surface area of the specimen, as mentioned in figure 26.

Absorption(g/mm²) =
$$\frac{\Delta \text{ mass}}{\text{Surface area}}$$

 Δ mass(g) = (mass at tth time) - (mass at time 'zero')

Surface area(mm²)= $2^*\pi^*r^2 + 2^*\pi^*r^*h$

Figure 26: Equations needed to calculate water absorption by concrete samples



Figure 27: (a) Cross-sectional view; (b) Animated 3D view; and (c) real image of the setup

In this investigation, water uptake has been simulated throughout all the concrete discs' exposed surface area. After submerging each disc at time 'zero', mass readings were taken every 30 minutes until the first 4 hours to get a measure of initial absorption. Later on, each disc's mass readings were taken

every 24 hours until 7 days were completed to measure secondary absorption. This step is vital because concrete with CSA expansive cement, chemical admixtures, and LWAs tend to behave differently compared to traditional OPC samples. In several studies, it has been found that pre-soaked LWA provided internal curing for late-age hydration of cement particles. As a result, depercolation/disconnection effects can be observed, which reduces capillary porosity in the concrete microstructure (Powers 1959). This can be categorized as 'self-healing': the process by which a material itself recovers from sustained damage and improves its performance (De Rooij et al. 2013). Studies have also found that partial replacement of OPC cement with CSA expansive cement helped with self-healing properties and, hence, improved durability (Hosoda 2007; Sisomphon and Copuroglu 2010). Based on these conclusions, it can be expected that 'Type K' samples added with LWAs and MRWRA can perform better compared to 'Control' samples. The experimental setup for the water absorption test has been illustrated in figure 27.

4.3 Test Results and Discussion

Acronyms for Samples used in Water Absorption Test							
Mix Design	Water	Air-Dried	Oven-Dried				
	Saturated						
С	C_WS	C_AD	C_OD				
CL35	CL35_WS	CL35_AD	CL35_OD				
CL17	CL17_WS	CL17_AD	CL17_OD				
K	K_WS	K_AD	K_OD				
KL35	KL35_WS	KL35_AD	KL35_OD				
K17	KL17_WS	KL17_AD	KL17_OD				
K35MR	KL35MR_WS	KL35MR_AD	KL35MR_OD				
K17MR	KL17MR_WS	KL17MR_AD	KL17MR_OD				

Table 3: Essential Acronyms pertinent to the reading

Table 3 has all the acronyms for all the samples involved in the discussion. In the next few sections, comparisons have been drawn between samples data pattern and relevant conclusions have been made.

4.4 Comparison between Water Soaked and Air-Dried Samples



Figure 28: Comparison of Absorption between Control and Type K samples

In Figure 28, to understand the problem, C and K samples' absorption rate was plotted against the square root of time. The air-dried samples had a higher absorption rate compared to water-saturated samples. Due to the drying effect, AD samples had a lower relative humidity compared to WS samples. Moreover, although K samples were touted to have a denser microstructure, that was not the case. Instead, the K samples absorbed more water compared to C in both water-soaked and air-dried conditions. In fact, at the end of 7 days, the absorption for K_WS was 45% more compared to C_WS. Similarly, the difference between K_AD and C_AD at the end of 7 days was almost 50%. Based on these observations, concrete made from CSA expansive cement will perform poorly against aggressive environments. There can be a multitude of reasons behind this observation. Firstly, the K sample had a water to cement ratio (w/c = 0.49) compared to the C sample (w/c = 0.44). As ettringite formation requires higher water demand, the Type K sample underwent rapid self-desiccation during the early stages of the hydration process. As a result, due to more significant enthalpy change and fast-paced reaction rate, and the use of higher water to cement ratio resulted in a porous microstructure for Type K samples compared to C samples. And secondly, the crystalline structure of ettringite depends on the number of hydroxyl groups attached to it. It is also possible that ettringite crystals absorbed more water as the K sample discs were taken from the inside sections. Internal sections of a concrete sample remain un-hydrated after early age hydration. The ettringite did not receive enough water molecules to achieve complete crystallinity as curing only impacts the external surface.

It was clear that mitigation strategies have to be implemented to improve the Type K samples' durability properties. Before that, two more mix designs were prepared using the control mix, CL35 (35% replacement of fine aggregates with LWAs) and CL17 (17% replacement of fine aggregates with LWAs), to justify the benefits of internal curing. Figure 29 shows a direct comparison between C, CL35, and CL17 was drawn to illustrate the absorption rate differences.



Figure 29: Absorption rate comparison between Control and Control+LWA watersoaked samples

The graph above shows that CL35 and CL17 exhibit a random absorption rate over the experiment's inital 4 hours. It can be explained with the depercolation effect: LWAs release water due to a decrease in relative humidity after self-desiccation, facilitating hydration of unreacted cement particles. However, for both CL35 and CL17, the absorption value fluctuations continued for 7 days. Besides, both samples had absorbed more water compared to the C sample. It is possible that as LWA has a high degree of porosity, excess water was absorbed due to taking the internal sections from the concrete cylinders. Petro-graphic analysis can be a viable technique to explain such observations.



Figure 30: Absorption rate comparison between Control and Control+LWA air-dried samples

In the second phase of this experiment, air-dried samples had been tested to observe the effect of LWAs under an elevated drying condition compared to water-saturated samples. In figure 30, C, CL35, and CL17 absorption data under air-drying preconditioning were juxtaposed; in this case, the opposite can be noticed. For CL35_AD and CL17_AD samples, the absorption capacities after 7 days were significantly lower than C_AD samples (8% for CL35 and 4% for CL17). The drying effect helped reduce the concrete samples' internal relative humidity, which facilitated late-age hydration. Studies have found that late-age hydration forms calcium carbonate via the reaction between free calcium ions and carbon dioxide dissolved in water, the basic functionality of autogenous self-healing (De Rooij et al. 2013; Wu, Johannesson, and Geiker 2012).



Figure 31: Comparison between Type K and Type K+LWA water-soaked samples

Later, the investigation was geared toward observing the effects of internal curing in Type K concrete samples. For this part, two more mix designs were prepared: KL35(35% replacement of fine aggregates with LWAs) and KL17 (17% replacement of fine aggregates with LWAs). The water absorption for K, KL35, KL17 data was plotted in figure 32 to draw a contrast between the performance against water ingress. It can be observed that samples with LWAs performed significantly better to reduce water absorption. For KL35_WS, at the end of 7 days, the water absorption was 7% lower compared to K_WS. On the other hand, KL17_WS water absorption for 36% lower compared to K_WS. The absorption value was more than 7% lower compared to C_WS at the end of 7 days. This data showed promise and needed a further explanation for justification.



Figure 32: Comparison between Type K and Type K+LWA air-dried samples

For air-dried samples, the water absorption for KL35 and KL17 drastically decreased. This can be credited to the relative drop in internal relative humidity, allowing LWAs to release more water for hydration purposes. Moreover, for both KL35 and KL17, free water content was decreased during mixing due to the addition of pre-soaked LWAs. According to Power's model, this will leave un-hydrated C₄A₃S particles during early-age curing, and as a result, a higher rate of late-age ettringite formation can be expected. However, late-age ettringite formation has been credited to damaging the C-S-H microstructure, disrupting the concrete samples' structural integrity



Figure 33: Comparison between Type K and Type K+LWA+MRWRA water-soaked samples

The main concern of using admixtures is the delayed formation of ettringite, which causes microcrack formation on matured concrete. As a result, concrete samples become susceptible to water ingress and demonstrate reduced durable properties. However, incorporating pre-soaked LWAs in concrete volume allows delayed hydration of cement particles that deposit calcium carbonate precipitates at the cracks, classified as a self-healing mechanism.



Figure 34: Comparison between Type K and Type K+LWA+MRWRA air-dried samples

Figures 33 and 34 illustrate the water absorption capacity of K, KL17MR, and KL35MR concrete samples. From the initial interpretation of data patterns, air-drying concrete samples' impact can be correlated with reduced water absorption after seven days. On the other hand, water-soaked samples had almost the same water absorption after seven days. Air-drying of concrete samples reduces the internal relative humidity, which triggers water release from the pre-soaked LWAs. As a result, un-hydrated cement particles receive water, which causes late-age reactions and forms a denser microstructure. Also, KL35MR_AD samples had the lowest water absorption after seven days; the absorption value was 67% lower than K_AD.

4.5 Comparison between Oven-Dried Samples

At high temperatures, it has been observed concrete experience extreme microstructural cracking and hence, become more porous. In addition, ettringite tends to lose its crystalline structure and become more amorphous due to loss of hydroxyl groups. To simulate these conditions and observe the effects, concrete samples were oven dried at 110 oC for 24 hours and water absorption test was performed. In figure 35, it can be observed that the initial absorption for K_OD was steeper compared to C_OD. However, the secondary absorption is significantly lower for K_OD. At the end of 7 days, K_OD absorption was 9% lower compared to C_OD. For both samples, initial absorption is considerably higher compared to WS and AD samples. Heating increases pore spaces and connectivity between pores due to crack formation in the mortar-aggregate interface, bridging cracks between aggregates, air voids, etc. (Henry, Darma, and Sugiyama 2014). Durability directly correlates with the degree of pore connection; increased pore spaces and connections cause a more considerable degree of loss in durability than the loss in strength (Crook and Murray 1970). But, re-curing has given evidence in decreasing pores and hence, improve durability. This recovery can be credited to the re-hydration of un-hydrated cement particles in the concrete samples' internal regions. Pore space reduction and crack-healing have been linked with the formation and deposition of calcium carbonate around cracked areas. But, its contribution toward strength recovery is still questionable.



Figure 35: Comparison between Control and Type K oven-dried samples

A possible explanation to justify the reduced absorption for K samples compared to C samples is the transformation of amorphous ettringite to crystalline ettringite. In the case of K_OD samples, it is clear that amorphous ettringite absorbed a significant amount of water, which formed crystal structures at the early stages of the water absorption test. As a result, ettringite crystals' formation inhibited water through up to a certain degree at late stages. To observe the internal curing effect before and after oven drying conditions, further studies were done, as illustrated in figures 36 and 37.



Figure 36: Comparison between Control and Control+LWA oven-dried samples



Figure 37: Comparison between Type K and Type K+LWA oven-dried samples

When a concrete sample experiences extreme heating conditions, several changes happen in the microstructure. Along with three-dimensional cracks, it is safe to assume that water evaporates from capillary pores, gel pores, and LWA pores. Overall, concrete samples with more LWAs will represent a more porous volume and a higher rate of water absorption than C or K concrete samples. For CL17, CL35, KL17, and KL35, the initial water absorption rate was higher compared to C and K. As concrete samples undergo the self-healing process, for CL17 and CL35, the secondary water absorption rate decreases; the difference is the largest for CL35 in comparison with C. This also proves that adding a higher percentage of LWAs helped CL35 develop a denser microstructure over the curing period of 14 days. However, for the type K oven-dried samples, KL17 and KL35 had a higher secondary absorption rate compared to K. This can be attributed to the decomposition of ettringite and evaporation of water from LWAs. As a result, re-curing allowed ettringite to absorb water to achieve initial crystallinity and LWAs to absorb water in the process.

Finally, in figure 38, it can be observed that KL35MR_OD samples had the highest initial and secondary water absorption. As soon as the samples underwent extreme drying conditions, the water molecules quickly evaporated from the gel pores, capillary pores, and LWA pores. As a result, the samples' water intake rate containing LWA was more extensive upon re-hydration than K_OD samples. In conclusion, the concrete decks during casting should be
adequately taken care of to prevent extreme drying during the initial curing stages.



Figure 38: Comparison between Type K and Type K+LWA+MRWRA oven-dried samples

4.6 Regression Analysis of Water Absorption Pattern

For every sample, the exponential curve was adopted; R^2 and the adjusted R^2 values for these models were the best compare to others. As a result, these parameters make these derived equations reliable. Moreover, these equations can predict exact water absorption values during a late-age for the concrete samples. This also brings a further scope of this investigation; using these equations, water absorptions can be calculated for individual samples. These predicted observations can be verified by procuring experimental data. Table 4 lists all the exponential equations generated from the regression analysis of Control samples' experimental data. For instance, it can be observed that the R^2 values for samples with LWA and preconditioned, either air-dried or water-soaked, are significantly below 0.90, which raises the question of the reliability of the equations. This is because the experimental data exhibited water absorption and desorption effects throughout 7 days. However, the model does not consider that phenomenon, and it is under the assumption that water absorption values should increase with time.

Table 4: List of exponential equations, R^2 and adjusted R^2 developed from the experimental data of Control samples

Sample Type	Acronym	Equation	R ²	Adjusted
	·			\mathbf{R}^2
Control_water-soaked	C_WS	$Y = 0.193 - 0.178 * e^{(-0.0911*X)}$	0.9254	0.9149
Control_air-dried	C_AD	$Y = 0.263 - 0.251 * e^{(-0.119 * X)}$	0.9543	0.9473
Control_oven-dried	C_OD	$Y = 3.70 - 3.705 * e^{(-0.084 * X)}$	0.9904	0.9889
Control+17%LWA_water-	CL17_WS	$Y = 0.211 - 0.163 * e^{(-0.064 * X)}$	0.6669	0.6156
soaked				
Control+17%LWA_air-dried	CL17_AD	$Y = 0.179 - 0.170 * e^{(-0.064 * X)}$	0.7604	0.7236
Control+17%LWA_oven-	CL17_OD	$Y = 3.674 - 3.775 * e^{(-0.108 * X)}$	0.9887	0.9869
dried				
Control+35%LWA_water-	CL35_WS	$Y = 0.185 - 0.176^* e^{(-0.123^*X)}$	0.8552	0.8329
soaked				
Control+35%LWA_air-dried	CL35_AD	$Y = 0.213 - 0.181 * e^{(-0.068 * X)}$	0.7908	0.7586
Control+35%LWA_oven-	CL35_OD	$Y = 3.211 - 3.378 * e^{(-0.119 * X)}$	0.9834	0.9809
dried				

Table 5 lists all the exponential equations generated from the regression analysis of Type K samples' experimental data. Similar to control samples analysis, LWAs internal curing, air-drying, or water-soaking affect the models' R^2 values and accuracy. Experimental data showed evidence of absorption and desorption effect, which varies the water absorption parameter. On the other hand, the samples with LWAs and oven-drying preconditioning had more accurate models ($\mathbb{R}^2 > 0.90$). Figures 39,40, and 41 illustrate the curve fitting of

KL35_MR equations; KL35MR samples data were selected to be presented

because these samples demonstrated the most promising data.

Table 5:List of exponential equations,	R^2 and adjusted R^2 developed from the
experimental data of Type K samples	

Sample Type	Acronym	Equation	R ²	Adjusted R ²
Type K_water-soaked	K_WS	$Y = 0.269 - 0.178 * e^{(-0.084 * X)}$	0.9670	0.9653
Type K_air-dried	K_AD	$Y = 0.376 - 0.345 * e^{(-0.065 * X)}$	0.9495	0.9417
Type K_oven-dried	K_OD	$Y = 3.204 - 3.192 * e^{(-0.120 * X)}$	0.9839	0.9815
Type K+17%LWA_water- soaked	KL17_WS	$Y = 0.175 - 0.159 * e^{(-0.086 * X)}$	0.8010	0.770
Type K+17%LWA_ air- dried	KL17_AD	$Y = 0.227 - 0.174 * e^{(-0.033 * X)}$	0.8415	0.8171
Type K+17%LWA_oven- dried	KL17_OD	$Y = 3.759 - 3.912 * e^{(-0.109 * X)}$	0.9777	0.9742
Type K+17%LWA+MR_water- soaked	KL17MR_WS	$Y = 0.278 - 0.252 * e^{(-0.053 * X)}$	0.9387	0.9292
Type K+17%LWA+MR_ air-dried	KL17MR_AD	$Y = 0.236 - 0.136 * e^{(-0.136 * X)}$	0.9224	0.9105
Type K+17%LWA+MR_oven- dried	KL17MR_OD	$Y = 3.651 - 3.776 * e^{(-0.071 * X)}$	0.9851	0.9828
Type K+35%LWA_water- soaked	KL35_WS	$Y = 0.217 - 0.187 * e^{(-0.054 * X)}$	0.8041	0.7715
Type K+35%LWA_ air- dried	KL35_AD	$Y = 0.238 - 0.205 * e^{(-0.065 * X)}$	0.8581	0.8363
Type K+35%LWA_oven- dried	KL35_OD	$Y = 3.731 - 3.844 * e^{(-0.095 * X)}$	0.9887	0.9870
Type K+35%LWA+MR_water- soaked	KL35MR_WS	$Y = 0.276_{0.087^*X)} - 0.279^* e^{(-1)}$	0.9549	0.9480
Type K+35%LWA+MR_ air-dried	KL35MR_AD	$Y = 0.233 - 0.215 * e^{(-0.083 * X)}$	0.9331	0.9229
Type K+35%LWA+MR_oven- dried	KL35MR_OD	$Y = 3.834 - 3.917 * e^{(-0.071 * X)}$	0.9918	0.9905



Figure 39: Nonlinear curve fitting of KL35MR_WS absorption data



Figure 40: Nonlinear curve fitting of KL35MR_AD absorption data



Figure 41: Nonlinear curve fitting of KL35MR_OD absorption data

4.7 Compressive strength Testing and Results

Sixteen cylinders were prepared (2 samples each mix design) and cured underwater for 28 days. After that, these cylinders were tested to measure compressive strength, adhering to the standards of ASTM C39 (ASTM C39 2015). The testing setup has been illustrated in Figure 19. Figure 20 presents all the compressive strength data of the samples tested. It can be noticed that the control mix with w/c= 0.44 has the highest compressive strength. Besides, KL35MR has compressive strength close to C (only 7% difference), which again provides durable concrete evidence.

On the other hand, the addition of LWAs helped increase the compressive strength of the samples with Type K cement (KL17 and KL35).

This can be attributed to internal curing mechanisms at late ages to hydrate unreacted cement particles to form C-S-H and ettringite crystals. The addition of admixture helped increase the strength of KL35 samples by almost 12% but, for KL17, the addition of the admixture reduced the strength by nearly 3%.



Figure 42: (a) Hydraulic machine setup for compressive strength Test, (b) Horizon Software to control loading rate and data collection, and (c) sample failure after loading



Figure 43: Comparison of all compressive strength values

4.8 Summary

LWAs made an impact in reducing water absorption of Type K concrete samples. This can be attributed to the internal curing mechanism offered by pre-soaked LWAs. During curing procedures, LWAs provide additional water for hydration of Type K. This eliminates the need for using a higher water-to-cement ratio in Type K concrete, which tends to affect concrete permeability and compressive strength negatively. Compared to the Control-air-dried samples, water absorption value after seven days, for Type K-35%LWA-MRWRA-air-dried samples was 24% lower. Based on these percentage comparisons, the choice of using Type K-35%LWA-MRWRA mix design for bridge decks would be prudent. It is important to clarify that most bridge decks, after casting, are usually exposed to air drying conditions. So, comparing the air-dried samples data is logical. Besides, Type K-35%LWA-MRWRA samples exhibited strength north of 4 ksi. As bridge decks after casting experience mild to severe drying conditions, incorporation of presoaked LWAs in mix design can help counteract the incomplete hydration of cement particles and form a denser microstructure at a late-age.

Chapter 5

SUMMARY AND FUTURE WORK

In this section, a summary of all the results, observations, and conclusions has been articulated concisely. These are:

- Fresh Type K concrete mix exhibited poor slump retention. As a result, several admixtures were added to the design mix. The investigation concluded with a poly-carboxylate based mid-range water-reducing admixture, manufactured by BASF©, demonstrating 4 inches slump after 60 minutes of mixing. This particular admixture can be categorized as a suitable additive to solve workability issues.
- Upon performing further isothermal calorimetric studies, it was concluded that the particular admixture achieved slump retention by prolonging the dormant period of the hydration reaction mechanisms.
- Delayed formation of concrete microstructure may negatively impact durability. To investigate durability properties, water absorption and compressive strength tests were performed on hardened concrete samples. Lightweight aggregates were also added into the mix to enhance internal curing. Research has found that Type K cement with 35% lightweight aggregates and mid-range admixture at 3 fl oz/cwt provide the least permeable concrete. Also, this particular mix design's compressive strength was more than 4000 psi, which is desirable.

• Since the studies involved varying several independent factors and observing the change in an experimental manner. Using the data, various equations were developed for slump loss, air content loss, water absorption trends, etc. These equations can be used to predict the 'y' variable for a future time, with reliable statistical significance.

This sections some of the future work that can be done as follows:

- Scaling down the testing to a smaller level will give the freedom to check for compatibility of various admixtures with Type K cement and optimize the results.
- However, using admixtures designed for Ordinary Portland cement on expansive cement can have negative implications. Researchers are already working to synthesize a new type of admixture, which will be perfectly suitable for expansive cement. They have used several techniques at a microscope and molecular level to alter properties and see the effect. Similar studies can also be done to explain further the observations achieved in this study.
- Further studies should be done to understand the fluctuations in absorption values, especially for the samples with lightweight aggregates.
- Using the equations, 'y' variables can be calculated to get an estimation. Experimental validation of these findings will solidify the results.

REFERENCES

- ACI Committee 231, Properties of Concrete at Early Ages. 2010. "Report on Early-Age Cracking: Causes, Measurement, and Mitigation." In American Concrete Institute.
- ACI Committee 325. 2017. "325.14R-17: Guide for Design and Proportioning of Concrete Mixtures for Pavements."
- Admixtures, Chemical, and Burj Khalifa. 2020. "Chemical Admixtures." (2013): 65–86.
- Aïtcin, Pierre Claude, and Robert J. Flatt. 2015. Science and Technology of Concrete Admixtures *Science and Technology of Concrete Admixtures*.
- American Society of Testing Materials. 2010. "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method." *ASTM International* i: 1–10.
- Ardeshirilajimi, Ardavan et al. 2016. *Bridge Decks: Mitigation of Cracking and Increased Durability*. Illinois Center for Transportation/Illinois Department of Transportation.
- ASTM. 2007. "ASTM 192 Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory." : 1–8.
- ASTM. 2014. "ASTM Standard C1757 Standard Test Method for Determination of One-Point, Bulk Water Sorption of Dried Concrete." *ASTM International* i: 14–16.
- ASTM C 685/C 685M-01. 2001. "Standard Specification for Concrete Made by Volumetric Batching and Continuous Mixing." *ASTM Standard* 11: 9.
- ASTM C128. 2004. "Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate." *Annual Book of ASTM Standards*: 1–5.

- ASTM C143/C143M. 2015. "Standard Test Method for Slump of Hydraulic-Cement Concrete." *Astm C143* (1): 1–4.
- ASTM C1585-13. 2013. "Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic Cement Concretes." *ASTM International* 41(147): 1–6.
- ASTM C642-13. 1997. "Standard Test Method for Density, Absorption, and Voids in Hardened Concrete ASTM C-642." *Annual Book of ASTM Standards* (March): 1–3.
- Baquerizo, Luis G., Thomas Matschei, and Karen L. Scrivener. 2016. "Impact of Water Activity on the Stability of Ettringite." *Cement and Concrete Research* 79: 31–44. http://dx.doi.org/10.1016/j.cemconres.2015.07.008.
- Bentz, Dale P, and Kenneth A Snyder. 1999. "Protected Paste Volume in Concrete: Extension to Internal Curing Using Saturated Lightweight Fine Aggregate." *Cement and concrete research* 29(11): 1863–67.
- Bentz, Dale P, and W Jason Weiss. 2011. *Internal Curing: A 2010 State-ofthe-Art Review*. US Department of Commerce, National Institute of Standards and Technology.
- Berk, Richard A. 2004. 11 Regression Analysis: A Constructive Critique. Sage.
- Bullard, Jeffrey W. et al. 2011. "Mechanisms of Cement Hydration." *Cement and Concrete Research* 41(12): 1208–23. http://dx.doi.org/10.1016/j.cemconres.2010.09.011.
- C39. 2015. "Compressive Strength of Cylindrical Concrete Specimens." *ASTM Standards*: 1–7.
- Carballosa, P et al. 2015. "Influence of Cement and Expansive Additive Types in the Performance of Self-Stressing and Self-Compacting Concretes for Structural Elements." *Construction and Building Materials* 93: 223–29.
- Chaunsali, Piyush et al. 2013. *Bridge Decks: Mitigation of Cracking and Increased Durability*. Illinois Center for Transportation (ICT).
- Collepardi, M. 2003. "A State-of-the-Art Review on Delayed Ettringite Attack on Concrete." *Cement and Concrete Composites* 25(4-5 SPEC): 401–7.
- Crook, D N, and M J Murray. 1970. "Regain of Strength after Firing of Concrete." *Magazine of Concrete Research* 22(72): 149–54.

- Dodson, Vance H. 2013. *Concrete Admixtures*. Springer Science & Business Media.
- Dove, Patricia M., and Nizhou Han. 2007. "Kinetics of Mineral Dissolution and Growth as Reciprocal Microscopic Surface Processes across Chemical Driving Force." *AIP Conference Proceedings* 916: 215–34.
- Du, Lianxiang, and Kevin J Folliard. 2005. "Mechanisms of Air Entrainment in Concrete." *Cement and concrete research* 35(8): 1463–71.
- E.M.Gartner, J.F. Young, D.A. Damidot and I. Jawed. 2003. 25 Engineering Structures Structure and Performance of Cements, 2nd Edition.
- Edvardsen, Carola. 1999. "Water Permeability and Autogenous Healing of Cracks in Concrete." In *Innovation in Concrete Structures: Design and Construction*, Thomas Telford Publishing, 473–87.
- Glasstone, S, K J Laidler, and H Eyring. 1941. *The Theory of Rate Processes: The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena*. McGraw-Hill Book Company, Incorporated. https://books.google.com/books?id=zb2GAAAAIAAJ.
- Goual, M S et al. 2000. "Estimation of the Capillary Transport Coefficient of Clayey Aerated Concrete Using a Gravimetric Technique." *Cement and Concrete Research* 30(10): 1559–63.
- Hall, Christopher et al. 1996. "Thermal Decomposition of Ettringite Ca 6 [Al (OH) 6] 2 (SO 4) 3. 26H 2 O." *Journal of the Chemical Society, Faraday Transactions* 92(12): 2125–29.
- Hanehara, Shunsuke, Fuminori Tomosawa, Makoto Kobayakawa, and KwangRyul Hwang. 2001. "Effects of Water/Powder Ratio, Mixing Ratio of Fly Ash, and Curing Temperature on Pozzolanic Reaction of Fly Ash in Cement Paste." *Cement and Concrete Research* 31(1): 31–39.
- Hargis, Craig W, Ana Paula Kirchheim, Paulo J M Monteiro, and Ellis M Gartner. 2013. "Early Age Hydration of Calcium Sulfoaluminate (Synthetic Ye'elimite, C4A3S) in the Presence of Gypsum and Varying Amounts of Calcium Hydroxide." *Cement and Concrete Research* 48: 105–15.

- Hartman, Michael R, Steven K Brady, Ronald Berliner, and Mark S Conradi. 2006. "The Evolution of Structural Changes in Ettringite during Thermal Decomposition." *Journal of Solid State Chemistry* 179(4): 1259–72.
- Henry, Michael, Ivan Sandi Darma, and Takafumi Sugiyama. 2014. "Analysis of the Effect of Heating and Re-Curing on the Microstructure of High-Strength Concrete Using X-Ray CT." *Construction and Building Materials* 67: 37–46. http://dx.doi.org/10.1016/j.conbuildmat.2013.11.007.
- Holm, T A, T W Bremner, and J B Newman. 1984. "Concrete Bridge Decks: Lightweight Aggregate Concrete Subject to Severe Weathering." *Concrete international* 6(6): 49–54.
- Hosoda, A. 2007. "Self Healing of Crack and Water Permeability of Expansive Concrete." In *First International Conference on Self Healing Materials*, *Noordwijk, The Netherlands, 2007. 4*,.
- Huang, Guangping, Deepak Pudasainee, Rajender Gupta, and Wei Victor Liu. 2019. "Hydration Reaction and Strength Development of Calcium Sulfoaluminate Cement-Based Mortar Cured at Cold Temperatures." *Construction and Building Materials* 224: 493–503. https://doi.org/10.1016/j.conbuildmat.2019.07.085.
- Kashchiev, D, and G M van Rosmalen. 2003. "Review: Nucleation in Solutions Revisited." *Crystal Research and Technology* 38(7-8): 555–74. https://onlinelibrary.wiley.com/doi/abs/10.1002/crat.200310070.
- Kishi, T. 2007. "Self Healing Behaviour by Cementitious Recrystallization of Cracked Concrete Incorporating Expansive Agent." In *First International Conference on Self Healing Materials, Noordwijk, The Netherlands,* 2007. 4,.
- Kreijger, P C. 1967. "Action of AE Agents and Water-Reducing Agents and the Difference between Them." In *Intl Symp Admix Mortar & Concr/Belg/*,.
- Kuzel, H-J. 1996. "Initial Hydration Reactions and Mechanisms of Delayed Ettringite Formation in Portland Cements." *Cement and Concrete Composites* 18(3): 195–203.

- Liu, Fang et al. 2016. "Enhancing Behavior of Large Volume Underground Concrete Structure Using Expansive Agents." *Construction and Building Materials* 114: 49–55.
- Martys, Nicos S, and Chiara F Ferraris. 1997. "Capillary Transport in Mortars and Concrete." *Cement and concrete research* 27(5): 747–60.
- Mehta, P. K. 1973. "Mechanism of Expansion Associated with Ettringite Formation." *Cement and Concrete Research* 3(1): 1–6.
- Mehta, P K. 1999. "Concrete Technology for Sustainable Development: An Overview of Essential Principles." In Vancouver CANMET/ACI International Symposium on Concrete Technology for Sustainable Development, Dec,.
- Mehta, Povindar Kumar. 1973. "Effect of Lime on Hydration of Pastes Containing Gypsum and Calcium Aluminates or Calcium Sulfoaluminate." *Journal of the American Ceramic Society* 56(6): 315– 19.
- Mielenz, Richard C, Vladimir E Wolkodoff, James E Backstrom, and Richard W Burrows. 1958. "Origin, Evolution, and Effects of the Air Void System in Concrete Part 4-The Air Void System in Job Concrete." In *Journal Proceedings*, , 507–17.
- Min, Deng, and Tang Mingshu. 1994. "Formation and Expansion of Ettringite Crystals." *Cement and concrete research* 24(1): 119–26.
- Mindess, S, J F Young, and D Darwin. 2003. *Concrete*. Prentice Hall. https://books.google.com/books?id=38VoQgAACAAJ.
- Mindess, Sidney, F J Young, and David Darwin. 2003. "Concrete 2nd Editio." *Technical Documents*.
- Morel, François. 1983. 446 Principles of Aquatic Chemistry. Wiley New York.
- Neithalath, Narayanan. 2006. "Analysis of Moisture Transport in Mortars and Concrete Using Sorption-Diffusion Approach." *ACI Materials Journal* 103(3): 209–17.
- Neville, Adam. 2001. "Consideration of Durability of Concrete Structures: Past, Present, and Future." *Materials and Structures* 34(2): 114–18. https://doi.org/10.1007/BF02481560.

- Nkinamubanzi, P-C, S Mantellato, and R J Flatt. 2016. "Superplasticizers in Practice." In *Science and Technology of Concrete Admixtures*, Elsevier, 353–77.
- Ohta, Al, T Sugiyama, and Y Tanaka. 1997. "Fluidizing Mechanism and Application of Polycarboxlate-Based Superplasticizers." *Special Publication* 173: 359–78.
- Pane, Ivindra, and Will Hansen. 2005. "Investigation of Blended Cement Hydration by Isothermal Calorimetry and Thermal Analysis." *Cement and concrete research* 35(6): 1155–64.
- Parrott, L. J. 1994. "Moisture Conditioning and Transport Properties of Concrete Test Specimens." *Materials and Structures* 27(8): 460–68.
- Physical, H H Wills, and N F Communicated. 1951. "The Growth of Crystals and the Equilibrium Structure of Their Surfaces." *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences* 243(866): 299–358.
- Pigeon, Michel. 2014. Durability of Concrete in Cold Climates. CRC Press.
- Pomeroy, C D. 1978. "Fourteenth John Player Lecture Concrete, an Alternative Material." 192.
- Pourchet, Sylvie, Cédric Comparet, Luc Nicoleau, and André Nonat. 2007. "Influence of PC Superplasticizers on Tricalcium Silicate Hydration."
- Powers, T C. 1959. "Capillary Continuity or Discontinuity in Cement Paste." *PCA Bullentin* 10: 2–12.
- Pyc, W A, M A Caldarone, D Broton, and D Reeves. 2008. "Internal Curing Study with Intermediate Lightweight Aggregate." *Special Publication* 256: 13–34.
- De Rooij, Mario, Kim Van Tittelboom, Nele De Belie, and Erik Schlangen. 2013. 11 Self-Healing Phenomena in Cement-Based Materials: State-ofthe-Art Report of RILEM Technical Committee 221-SHC: Self-Healing Phenomena in Cement-Based Materials. Springer.
- Roussel, N., G. Ovarlez, S. Garrault, and C. Brumaud. 2012. "The Origins of Thixotropy of Fresh Cement Pastes." *Cement and Concrete Research* 42(1): 148–57. http://dx.doi.org/10.1016/j.cemconres.2011.09.004.

- Roussel, Nicolas. 2006. "A Thixotropy Model for Fresh Fluid Concretes: Theory, Validation and Applications." *Cement and Concrete Research* 36(10): 1797–1806.
- S. Wild, B.B. Sabir, and J.M. Khatib. 1995. "(Refereed) (Received February 15; in Fmal Form May 7.1995)." *Science* 25(7): 1567–80.
- Sabir, B B, S Wild, and M O'farrell. 1998. "A Water Sorptivity Test for Martar and Concrete." *Materials and Structures* 31(8): 568.
- De Schutter, Geert. 1999. "Hydration and Temperature Development of Concrete Made with Blast-Furnace Slag Cement." *Cement and Concrete Research* 29(1): 143–49.
- Sisomphon, K., O. Copuroglu, and E. A.B. Koenders. 2012. "Self-Healing of Surface Cracks in Mortars with Expansive Additive and Crystalline Additive." *Cement and Concrete Composites* 34(4): 566–74. http://dx.doi.org/10.1016/j.cemconcomp.2012.01.005.
- Sisomphon, K, and O Copuroglu. 2010. "Some Characteristics of a Self Healing Mortar Incorporating Calcium Sulfo-Aluminate Based Agent." In Proceedings of the 2nd International Conference on Durability of Concrete Structures, , 157–64.
- Sisomphon, K, O Copuroglu, and E A B Koenders. 2011. "Surface Crack Self-Healing Behaviour of Mortars with Expansive Additives." In *3rd International Conference on Self-Healing Materials, Bath, UK*, , 44–45.
- Skoblinskaya, N N, and K G Krasilnikov. 1975. "Changes in Crystal Structure of Ettringite on Dehydration. 1." *Cement and Concrete Research* 5(4): 381–93.
- Somorjai, Gabor A, and Yimin Li. 2010. *Introduction to Surface Chemistry and Catalysis*. John Wiley & Sons.
- Su, Tong, Xiangming Kong, Hongwei Tian, and Dongmin Wang. 2019. "Effects of Comb-like PCE and Linear Copolymers on Workability and Early Hydration of a Calcium Sulfoaluminate Belite Cement." *Cement* and Concrete Research 123(May): 105801. https://doi.org/10.1016/j.cemconres.2019.105801.

- Symposium, Second International, Concrete Tecnology, and Sustainable February. 2005. "CHEMICAL ADMIXTURES TODAY Mario Collepardi, Enco, Engineering Concrete, Ponzano Veneto (Italy).": 527– 41.
- Tattersall, Geoffrey Howarth, and Phillip F G Banfill. 1983. *The Rheology of Fresh Concrete*.
- Taylor, H F W, C Famy, and K L Scrivener. 2001. "Delayed Ettringite Formation." *Cement and concrete research* 31(5): 683–93.
- Taylor, Harry F W. 1997. 2 Cement Chemistry. Thomas Telford London.
- Tian, Hongwei, Xiangming Kong, Tong Su, and Dongmin Wang. 2019.
 "Comparative Study of Two PCE Superplasticizers with Varied Charge Density in Portland Cement and Sulfoaluminate Cement Systems." *Cement and Concrete Research* 115: 43–58. http://www.sciencedirect.com/science/article/pii/S0008884618310949.
- Uchikawa, Hiroshi, Daisuke Sawaki, and Shunsuke Hanehara. 1995. "Influence of Kind and Added Timing of Organic Admixture on the Composition, Structure and Property of Fresh Cement Paste." *Cement and Concrete Research* 25(2): 353–64.
- Wang, Li-Cheng. 2009. "Analytical Methods for Prediction of Water Absorption in Cement-Based Material." *China Ocean Engineering* 23(4): 719–28.
- Wu, Min, Björn Johannesson, and Mette Geiker. 2012. "A Review: Self-Healing in Cementitious Materials and Engineered Cementitious Composite as a Self-Healing Material." *Construction and Building Materials* 28(1): 571–83.
- Yamada, Kazuo, Tomoo Takahashi, Shunsuke Hanehara, and Makoto Matsuhisa. 2000. "Effects of the Chemical Structure on the Properties of Polycarboxylate-Type Superplasticizer." *Cement and concrete research* 30(2): 197–207.
- Yang, Zhifu, W Jason Weiss, and Jan Olek. 2006. "Water Transport in Concrete Damaged by Tensile Loading and Freeze–Thaw Cycling." *Journal of materials in civil engineering* 18(3): 424–34.

- Zhang, Ge, Guoxin Li, and Yanchao Li. 2016. "Effects of Superplasticizers and Retarders on the Fluidity and Strength of Sulphoaluminate Cement." *Construction and Building Materials* 126: 44–54.
- Zhang, Min-Hong, and Odd E Gjørv. 1990. "Microstructure of the Interfacial Zone between Lightweight Aggregate and Cement Paste." *Cement and Concrete Research* 20(4): 610–18.
- Zhang, Yunsheng, Wei Sun, and Sifeng Liu. 2002. "Study on the Hydration Heat of Binder Paste in High-Performance Concrete." *Cement and Concrete Research* 32(9): 1483–88.
- Zhou, Q, E E Lachowski, and Fredrik Paul Glasser. 2004. "Metaettringite, a Decomposition Product of Ettringite." *Cement and Concrete Research* 34(4): 703–10.

Appendix A

INDEX

admixtures, xi, 13, 14, 15 adsorption, 19 air content, xi, 15, 16 alkali-silica reaction, 13 amorphous, 18, 20, 21, 23, 69, 70 autogenous, 14, 32, 65 autonomic, 32 basanite, 22 Bingham, vii, 24, 25 calcium hydroxide, 26 calcium silicate hydrate, 26 calcium Sulfoaluminate, xi, xii, 87, 88, 90, 95 calorimetric, xi, 30, 35, 49, 81 capillary, 15, 54, 60, 72 capillary pores, 15, 55 cementitious, xi, 13, 15 complexation, 19 composite, 17 compressive strength, ix, xii, 14, 16, 17, 18, 21, 31, 56, 77, 78, 79, 80, 81 concrete, iv, viii, 17, 23, 32, 54, 57, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97 crystalline, 23, 26 crystallinity, 62, 72 crystallization, 26 depercolation, 60, 63 diffusion, 18, 87, 91 dislocation, 18 durability, 1, 2, 13, 83, 86, 91, 92, 94 esterification, 28 ettringite, 15, 22, 23, 26 Ettringite, 85, 86, 87, 88, 89, 90, 94, 95, 97 freeze-thaw, 13, 30, 31, 34, 54 gel pores, 72 growth, 86, 92

hydration, vii, viii, xi, 15, 17, 18, 19, 20, 21, 23, 26, 28, 29, 32, 33, 49, 50, 51, 52, 60, 62, 63, 64, 66, 67, 69, 72, 80, 81 hydrophilic, 31 hydrophobic, 31 interfacial, 31, 33 internal curing, xii isothermal. xi lightweight aggregates, xi, 14 metaettringite, 23 microstructure, xi, 14 microstructure, 88, 97 monosulfoaluminate, 22 nuclear magnetic resonance spectroscopy, 30 Nucleation, 19, 89 ordinary Portland cement, xi, xii permeability, xii, 15, 54, 80 petro-graphic, 64 poly-carboxylate, xi polycarboxylates, 27 polymerization, 28, 43 pozzolans, 13 precipitation, 26 regression, 36, 41, 47, 73, 74 relative humidity, 15, 23 scanning electron microscopic, xii self-desiccation, 15 shrinkage, xi, 13, 21, 23, 33 slump, xi, xii, 84 sorptivity, 55, 93 superplasticizers, 14, 29, 31 thermo-gravimetric analysis, 30 *Type K, xi, 14, 15, 36, 75* water absorption test, xii water-reducing admixture, xi workability, xi, 14, 15 x-ray diffraction, 30

Appendix B

GRAPHS AND PLOTS PERTINENT TO THE THESIS



Figure 44: Slump loss comparison between Control and Type K over 180 minutes



Figure 45: Regression Analysis of Control Mix slump loss



Figure 46: Regression Analysis of Type K Mix slump loss



Figure 47: Air content comparison between Control and Type K mix over 180 minutes



Figure 48: Regression Analysis of Control Mix air content loss



Figure 49: Regression Analysis of Type K Mix air content loss



Figure 50: Nonlinear curve fitting for C_WS absorption data



Figure 51: Nonlinear curve fitting for C_AD absorption data



Figure 52: Nonlinear curve fitting for C_OD absorption data



Figure 53: Nonlinear curve fitting for K_WS absorption data



Figure 54: Nonlinear curve fitting of K_AD absorption data



Figure 55: Nonlinear curve fitting for K_OD absorption data



Figure 56: Nonlinear curve fitting of CL17_WS absorption data



Figure 57: Nonlinear curve fitting of CL17_AD absorption data



Figure 58: Nonlinear curve fitting for CL17_OD absorption data



Figure 59: Nonlinear curve fitting for CL35_WS absorption data



Figure 60: Nonlinear curve fitting for CL35_AD absorption data



Figure 61: Nonlinear curve fitting for CL35_OD absorption data



Figure 62: Nonlinear curve fitting of KL17_WS absorption data



Figure 63: Nonlinear curve fitting KL17_AD absorption data



Figure 64: Nonlinear curve fitting of KL17_OD absorption data



Figure 65: Nonlinear curve fitting of KL35_WS absorption data



Figure 66: Nonlinear curve fitting of KL35_AD absorption data



Figure 67: Nonlinear curve fitting of KL35_OD absorption data



Figure 68: Nonlinear curve fitting of KL17MR_WS absorption data



Figure 69: Nonlinear curve fitting of KL17MR_AD absorption data



Figure 70: Nonlinear curve fitting for KL17MR_OD absorption data