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Improving engineering properties of cement-based materials by internal curing

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Improving engineering properties of cement-based materials by internal curing

by

Payam Vosoughi

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Civil Engineering (Civil Engineering Materials)

Program of Study Committee:
Peter Taylor, Co-major Professor
Kejin Wang, Co-major Professor
Robert Horton
Jeramy Ashlock
Simon Laflamme

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2019

DEDICATION

To my family and especially my parents who I have not had the chance to visit for more than four years…

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ABSTRACT

Cement-based mixtures are assumed to be saturated right after placement, other than the air bubbles. Hydration of cementitious materials results in the formation of cement matrix, and change the state of the mixture from plastic to a weak solid. Further moisture loss, due to water consumption during hydration reactions or water evaporation from the free surface, leads to the development of negative capillary pore water potential. Excessive pore water potential is recognized as the source of capillary tension and increased early-age shrinkage cracking potential. Internal curing by substitution of fine aggregate with lightweight fine aggregate is an alternative curing method to uniformly provide additional water through the whole volume of the mixture and compensate the capillary pore water potential. Internal curing water is sucked out of the pre-saturated porous lightweight fine aggregate as of increasing capillary pore water potential in the matrix. The additional internal curing moisture results in extended hydration, improved strength development and delayed pore water potential development in the cement matrix, which consequently decreases early-age shrinkage strain and cracking potential.

This dissertation aims to study the effects of internal curing on the hydration and pore water potential development in early ages as well as mechanical and transport properties of cement-based materials (with various water-to-cement, supplementary cementitious materials and lightweight fine aggregate substitutions) under different curing (sealed and standard moist curing methods) and exposure (ambient temperature and relative humidifies) conditions.

The results indicate that internal curing using lightweight fine aggregate is a very effective method to delay pore water potential development, especially for the mixtures with low water to cementitious materials ratio, or incorporating fine supplementary cementitious materials like silica fume. It is also beneficial in high-temperature exposure conditions to suppress pore water potential development. The results of isothermal calorimetry and setting time tests confirmed that internal curing extended the hydration and lead to higher heat generation while initial and final setting time are not meaningfully changed, compared to the control mixture without lightweight fine aggregate.

The effect of substitution of fine aggregate with lightweight fine aggregate on the mechanical and transport properties of concrete mixtures in both sealed and standard moist curing conditions are also investigated. The results show that the coefficient of thermal expansion of mixtures is linearly decreased by increasing lightweight fine aggregate substitution. In addition, substitution of lightweight fine aggregate up to 30% results in a slight increase in the compressive strength of concrete mixtures, particularly highlighted for the mixtures with low water to cementitious materials ratio. Internal curing is even more beneficial in increasing electrical resistivity of mixtures, particularly in sealed curing condition. The optimum lightweight fine aggregate substitution depends on absorption/desorption properties of lightweight fine aggregate, water to cementitious materials ratio, type and quantity of cementitious materials, and the target property.

CHAPTER 1. GENERAL INTRODUCTION

1.1. Problem statement

An early-age cement-based mixture can be assumed a saturated weak solid, other than the air bubbles. Water evaporation from the free surface or water consumption during hydration reactions of cementitious materials leads to moisture loss from the mixture, which in turn, results in the development of capillary pore water potential (PWP). The strength and elastic modulus development in early-age cement-based mixtures are limited, so capillary tension generated due to PWP development may result in early-age shrinkage cracking. Figure *1-1* illustrates early-age shrinkage cracking in a jointed plain concrete pavement (JPCP) in a parking lot.

Early-age shrinkage cracks are usually very shallow, but prevention of them is critical because of the aesthetic and durability properties of the concrete member. The external layer of concrete is responsible for resisting ingress of external moisture, ions and other sources that may endanger the performance of concrete over its service life.

PWP development is a physical process and the pressure can be reduced by providing extra curing water and keeping the mixture saturated. This is the main purpose of traditional curing methods. However, there are some questions and difficulties in practice to properly applying standard wet curing especially on linear elements like water channels or concrete pavements). It is also shown that due to the low permeability of cement matrix, external curing is just effective for the external surface of the member.

Standard wet curing cannot be started before the initial setting time of the mixture, as it may increase water-to-cement ratio of the cover of mixture. On the other hand, delayed curing may not be effective after early-age shrinkage cracking time. Therefore, it is important to monitor PWP development of concrete in place, so the proper timing of curing can be determined. New practical and easy-to-use test methods are required to be investigated and developed to employ in the field.

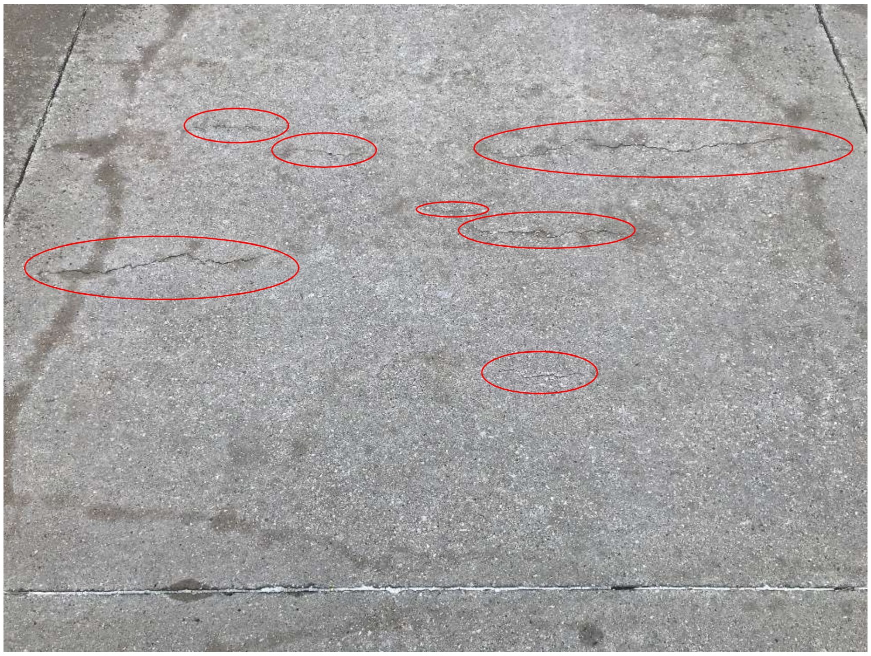


Figure 1-1- Early-age shrinkage cracking in a concrete pavement

1.2. Background

Cementitious materials start hydration reactions and cement matrix generation after mixing with free water. The schematic procedure is illustrated in Figure *1-2*. The main hydration products are C-S-H gel, but there are different types of pores in the matrix as well. The diameter of gel, capillary and air pores, the main pores in cement matrix, are in the order of 10^{-10}, 10^{-5} to 10^{-8} and 10^{-4} m, respectively [1]. Pore size distribution and the volume of pores can be significantly changed by mixture proportions, the degree of hydration and curing conditions.

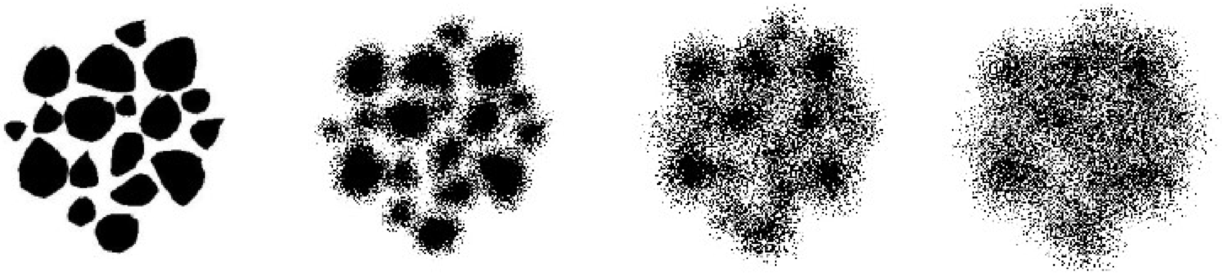


Figure 1-2- Hydration of cement particles and generation of cement matrix [2]

A fresh cement-based mixture can be assumed saturated, other than the air pores. However, moisture loss, because of water consumption during hydration reactions or water evaporation from the free surface, can decrease the saturation degree of cement matrix. Water starts to be taken out of the bigger pores with lower potential. When capillary pores with 50 nm start to lose water, pore water potential begins to be significantly increased [3,4].

The rate of hydration reactions of cementitious materials at early ages mainly depends on type and fineness of cementitious materials [5], chemical admixtures, temperature [6] and PWP [7]. Fine cementitious materials not only may have higher hydration reactivity because of their increased specific surface area but also help increase the rate of hydration of other cementitious materials due to the nucleation effect and increase the internal specific surface area [8]. This also increases the PWP development. For instance, Figure *1-3* demonstrates the effect of incorporation of three different silica fumes in decreasing the internal relative humidity of cement paste with 0.25 water-to-cement ratio [9].

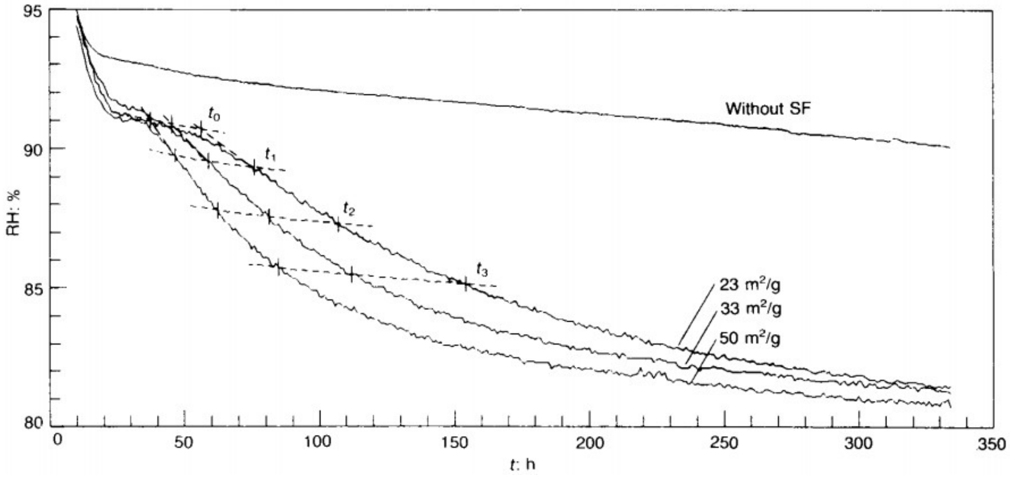


Figure 1-3- Effect of fineness of SF on relative humidity reduction [9]

The rate of water evaporation from the free surface of cement-based mixtures [10] depends on a number of parameters including environmental factors (temperature, relative humidity, light and wind speed), mixture proportion (bleeding) and PWP on the surface. Figure *1-4* illustrates water evaporation from the surface of free water and concrete mixtures with different water-to-cement ratios. It indicates that after the first hour, evaporation from the surface of concrete is much less than that from free water. Also, the rate of evaporation is decreased for mixtures with a low water-to-cement ratio.

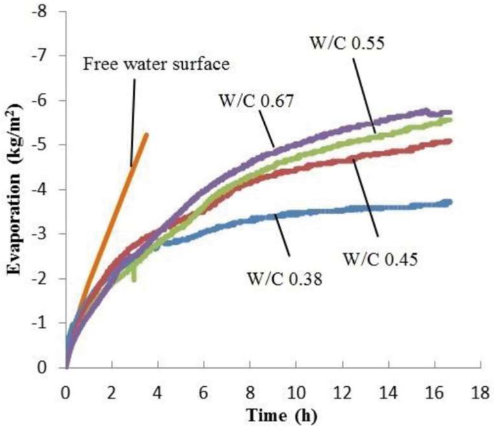
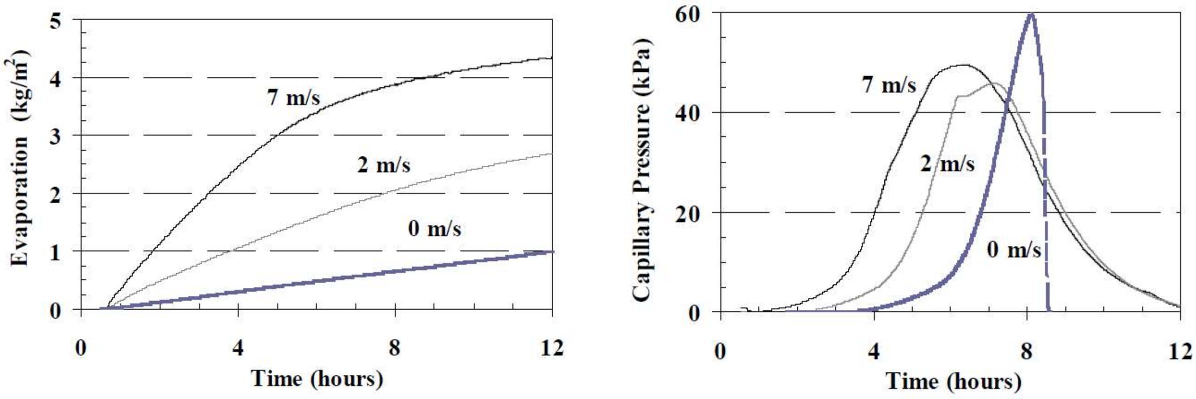


Figure 1-4- Water evaporation from the surface of free water and concrete mixtures [11]

Figure *1-5* shows the effect of wind speed in increasing water evaporation from the surface of a concrete mixture and associated capillary PWP development. It is worth noting that although the unit of water evaporation measurement from the surface is kg/m^2, what makes capillary PWP is the volume of moisture loss divided by the volume of initial moisture $\left(\frac{\Delta V}{V}\right)$ in the volume of mixture limited to the unit of surface. In other words, it emphasizes the effect of thickness $\left(\frac{volume}{surface}\right)$. Constant water evaporation from a mixture with smaller thickness generates higher PWP [10].



(a) *(b)*

Figure 1-5- Effect of wind speed on evaporation and PWP development in concrete mixtures [2]

Development of capillary PWP is a physical process, so the pressure should be reduced by rewetting the mixture [12]. However, considering hardened cement matrix, very high capillary PWP results in taking interlayer water out from the space between hydration products. This leads to an irreversible shrinkage, so rewetting cannot provide enough swelling pressure to bring the mixture back to the initial volume [13].

Figure *1-6* shows capillary PWP development in a cement paste with 0.35 W/C at two depths, 25 and 40 mm. It illustrates that external curing (rewetting) is very effective in removing capillary PWP at 25 mm depth. However, due to the impermeability of cement matrix, rewetting cannot immediately remove PWP at 40 mm depth.

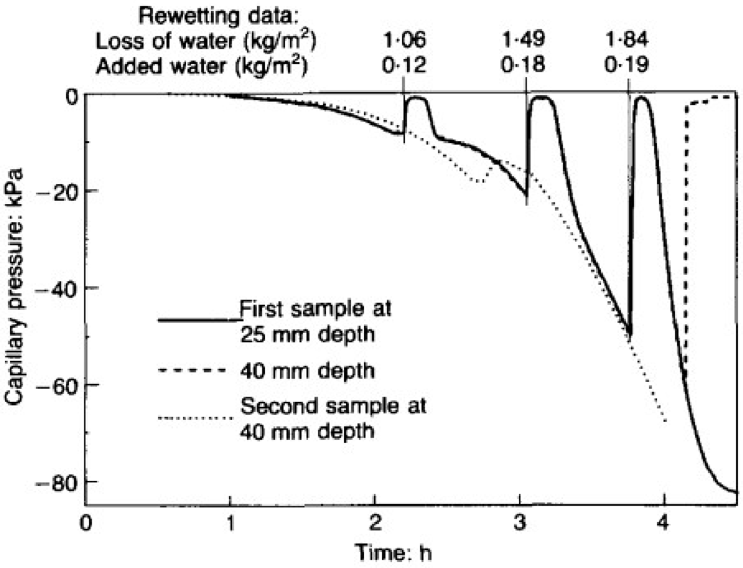


Figure 1-6- Effect of rewetting on capillary PWP development at different depths [10]

Wittmann [12] demonstrated that there is a good correlation between capillary PWP and early-age shrinkage strain development (see Figure *1-7*). Further studies [2,10,14,15] confirm that capillary PWP is the source of volume shrinkage in cement-based materials. Figure *1-8* illustrates the capillary PWP development and horizontal, vertical and volume early-age shrinkage over time. Due to the strength and elastic modulus development, the rate of early-age shrinkage development is significantly decreased over time although capillary PWP is always increasing because of growing moisture loss and decreasing size of pores in the cement matrix. The drop in PWP measurement in Figure *1-8* is because of entering air bubbles into the tensiometer, around 100 m bar, and it does not reflect the real capillary PWP in the mixture after the dropping point.

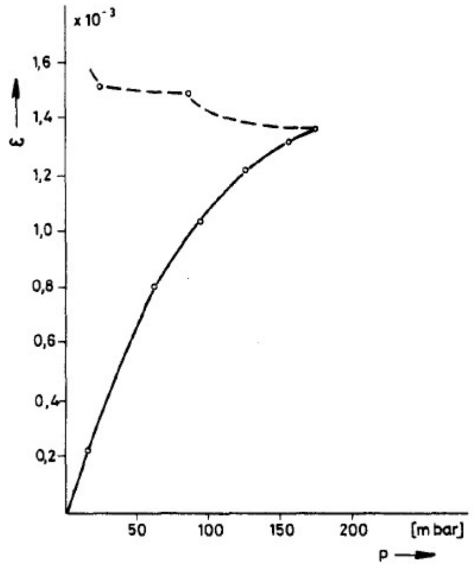


Figure 1-7- Correlation between capillary PWP and shrinkage strain between 1 to 4 hours after mixing [12]

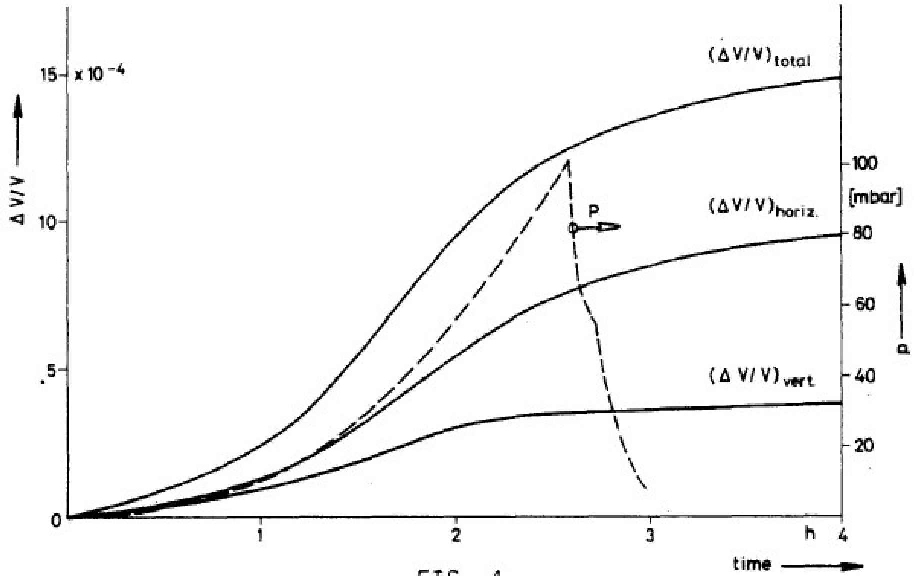


Figure 1-8- Effect of capillary PWP development on Horizontal, vertical and volume shrinkage [12]

It is possible to measure PWP in a cement matrix by measuring the moisture content of an embedded known porous material, like granular sand or ceramic, with equilibrium water potential. There is a specific nonlinear power correlation between moisture content (ω) and pore water potential (PWP) [16] as it is shown in Equation 1-1 and Figure *1-9*. Constant variables $(a \text{ and } b)$ determined based on the pore size distribution of the material. The wet side of this correlation shows that a decrease in the moisture content of the medium results in a significant increase in PWP with a power order.

The benefit of this measurement is that it is not affected by air entry to the sensor, so it is possible to monitor PWP for a longer period of time. Moisture content can be measured by monitoring the change in different thermal or electrical properties of the material.

$$\mathrm{PWP} = a\omega^{-b} \qquad \text{Equation 1-1}$$

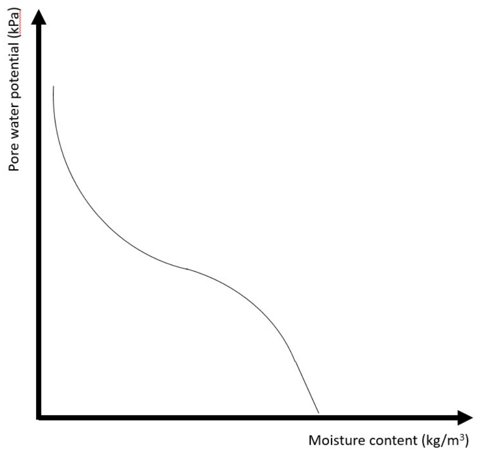


Figure 1-9- Correlation of moisture content and water potential

Another indirect method successfully used in concrete science for measuring PWP is monitoring relative humidity (RH) inside a small sealed plastic tube with a Gore-Tex cape embedded in concrete [3]. Equation 1-2 shows the nonlinear correlation between RH inside the tube and capillary pressure in a cement matrix (assuming perfect wetting and negligible contact angel between pore solution and cement matrix [17]):

$$RH = exp\left(\frac{2\,\gamma.V_m}{r.R.T}\right) = exp\left(\frac{PWP.V_m}{R.T}\right) \qquad \text{Equation 1-2}$$

Where γ is surface tension, V_m is molar volume of pore solution, r is radius of capillary pore, R is universal gas constant, T is temperature in kelvin.

However, there are two main problems for using RH sensors to evaluate pore water potential in concrete. Early-age concrete is almost saturated and has a very high internal RH. The correlation between RH and PWP is very sensitive to any error in this range of measurement (see Figure *1-10*). In addition, most commercially available RH sensors do not have a good accuracy or are out of calibration in RH more than 90-95% [18]. That is why using RH sensors to monitor PWP results in a considerable error in wet conditions [19]. However, RH meters can be successfully used on higher PWP (200 kPa to 5MPa), which makes it suitable for use in monitoring drying shrinkage [18].

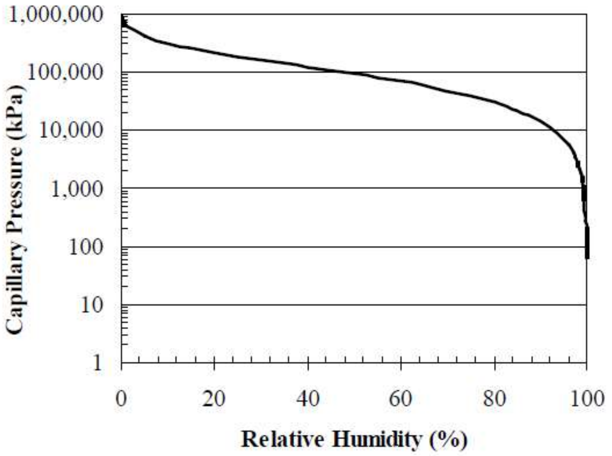


Figure 1-10- Correlation between RH and PWP [2]

There are different methods to suppress and delay capillary PWP development in cement-based mixtures by the time when the cement matrix can resist against capillary tension and prevent of early-age shrinkage cracking. PWP mainly depends on the chemical composition of pore solution, temperature, moisture content and pore size distribution of cement matrix [7,20]. The traditional method for controlling PWP development is covering and wet curing the free surface of mixture to prevent evaporation and increase the degree of saturation. The other option is modifying the chemical composition of mixture pore solution. PWP depends on the surface tension of pore solution (see Equation 1-2) which can be significantly reduced by a modification using shrinkage reducing admixtures (SRA). As an example it is worth to note that surface tension of ethyl ether, water, and mercury are 17, 72, and 430 dyn/cm at 20° C, respectively [20].

Internal curing [21] is an alternative method to uniformly provide extra curing water through the whole volume of the mixture. Lightweight fine aggregate is the most common carrier of internal curing water for cement-based materials. Pre-saturated porous lightweight fine aggregate is mixed with the mixture and uniformly distributed. Any increase in capillary PWP in the cement matrix results in sucking water out of the porous lightweight aggregate. Therefore, the time capillary pores start to lose moisture and generate a significant capillary tension in the matrix is delayed.

1.3. Objective of dissertation

The main objective of this dissertation is the investigation of PWP development in cement-based materials and mitigation of PWP by internal curing using lightweight fine aggregate (LWFA). The list of detailed objectives are as follows:

- Studying the effect of internal curing on extending hydration of mortar mixtures with different water-to-cement ratios and various supplementary cementitious materials including fly ash and silica fume
- Estimating the optimum lightweight fine aggregate substitution and the ratio of internal curing water to cementitious materials (by mass) for different mortar and concrete mixtures considering hydration, PWP development, compressive strength and electrical resistivity of mixtures
- Investigating the effect of lightweight fine aggregate substitution on mechanical and transport properties of concrete mixtures with different water-to-cement ratios and supplementary cementitious materials
- Studying the effect of mixture proportion design of concrete materials on PWP development
- Investigating the role of exposure conditions (temperature and relative humidity) in PWP development and effectiveness of internal curing in delaying PWP development

1.4. Dissertation organization

This dissertation is written in the alternative journal paper format. It is presented in five chapters as it is described below:

- Chapter one, entitled "Introduction", presents problem statement, background, objective and organization of the dissertation.
- Chapter two, entitled "Effects of Internal Curing on Hydration, Mechanical and Transport Properties of Cement-Based Materials Incorporating SCMs", presents the first journal paper. It studies the effect of internal curing using lightweight fine aggregate substitution on the hydration, mechanical and transport properties of different mortar and concrete mixtures with various water-to-cement ratios and supplementary cementitious materials.
- Chapter three, entitled "Improved Hydration and Mitigation of Pore Water Potential Development in Cement-Based Materials by Internal Curing", presents the second journal paper. This paper studies the hydration and pore water potential development in mortar and concrete mixtures. In addition, it investigates the effectiveness of internally curing in extending hydration and suppressing pore water potential development.
- Chapter four, entitled "Effect of Exposure Conditions, Silica Fume Incorporation and Internal Curing on Hydration and Pore Water Potential Development in Cement-Based Materials", presents the third journal paper. It studies the effect of exposure condition including relative humidity and temperature on the pore water potential development in the mixtures incorporating silica fume with and without internal curing.
- Chapter five, entitled "Conclusion and future works", presents a summary of all the findings of this dissertation and some recommendations for future investigations.

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CHAPTER 2. EFFECTS OF INTERNAL CURING ON HYDRATION, MECHANICAL AND TRANSPORT PROPERTIES OF CEMENT-BASED MATERIALS INCORPORATING SCMS

A journal paper to submit to Journal of Materials in Civil Engineering (ASCE)

Payam Vosoughi[1], Kejin Wang[2], Peter Taylor[3], Meysam Najimi[4], Halil Ceylan[5]

2.1. Abstract

For the complete hydration of portland cement in sealed condition, a minimum of 0.56 water-to-cement ratio (W/C) is required. However, increasing W/C results in significantly decreased mechanical and transport properties. As an alternative, internal curing (IC) uniformly provides additional water for extended hydration of cementitious materials; particularly for the ones with low W/C. This research investigates the effects of substitution lightweight fine aggregate (LWFA) as an IC water carrier on early-age, mechanical and transport properties of cement-based materials. For this purpose, five mortar and 14 concrete mixtures with different W/C (0.35, 0.42 and 0.5), supplementary cementitious materials (20% Fly Ash and 7.5% silica fume substitution) and LWFA substitutions (10, 20, 30 and 40%) cured under two different

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sealed and standard curing conditions are investigated. The results show that IC does not have a significant influence on setting time, while it improves cementitious materials hydration, mechanical and transport properties, especially for the mixtures cured under sealed condition and the ones with a low W/C. Due to the effect of IC water carrier, there is an optimum LWFA substitution considering mechanical properties while transport properties are improved on all replacement percentages.

Keywords: Lightweight fine aggregate, Coefficient of thermal expansion (CTE); Isothermal calorimetry; Electrical resistivity; Rapid chloride migration test (RCMT); Sealed curing

2.2. Introduction

The mass of water chemically absorbed by fully hydrated portland cement is around 28-29% (by the mass of cement) [1,2]. However, considering 34% saturated gel porosity in hardened cement paste, a minimum of 0.56 water-to-cement ratio (W/C) is required for complete hydration of cement with a proper rate in sealed condition [1]. The fact that W/C substantially affects all engineering properties of cement-based materials demonstrates the importance of curing for mixtures with lower W/C.

Conventionally, external curing has been using in practice to provide extra moisture for an extended hydration. However, according to the very low permeability of hardened concrete (e.g. 10-12 to 10-14 m/s), external curing is just effective on the external layer of concrete [3,4]. However, internal curing (IC) is a procedure whereby extra water is provided uniformly through the whole volume of cement-based materials to postpone water potential development after solidification and facilitates cementitious materials hydration reactions. IC can be appropriately implemented using pre-saturated materials with a specific range of pore sizes to release the majority of absorbed water before relative humidity (RH) in capillary pores drops to 93% [5–9]. RH is an indirect sign of capillary water pressure (pore water potential) in partially saturated capillary pores [10]. Water with very low potential is physically bonded and decreases the rate of hydration reactions [11]. Lightweight aggregates and super-absorbent polymers are the most common carriers of IC water although the feasibility of using other materials like recycled concrete aggregate, and natural and carbon fibers has been also investigated [12,13].

Bentz and Weiss [5] concluded that for the complete hydration of portland cement, it is required to provide 7% IC water (by mass of cement), which also results in 9.6% chemical shrinkage. Therefore, they suggested that based on the absorption and desorption properties of lightweight fine aggregate (LWFA) [14], the substitution percentage should be designed to provide the water to keep paste saturated [4,5].

Chemical shrinkage of supplementary cementitious materials (SCMs) like fly ash (FA) and silica fume (SF) is two or three times higher than portland cement [15,16], which highlights the importance of IC to decrease self-desiccation and shrinkage cracking potential when using SCMs. Through pozzolanic reactions, SCMs decrease the total porosity and pore size distribution of cement matrix and, more importantly, the interfacial transition zone (ITZ) between aggregate and cement matrix [17,18], which significantly improves the mechanical and transport properties of mixtures with low W/C. However, increasing the internal surface area of hardened cement also increases surface tension and self-desiccation shrinkage.

Due to the low permeability of hardened paste, moisture provided through external curing can just reach to a depth of 5 cm [3]. Therefore, in the absence of moisture exchange, the internal volume of concrete cured is similar to a sealed concrete. Although concrete samples are protected against moisture loss or ion leakage [19] in sealed curing, the risk of decelerating hydration reactions and reducing the ultimate degree of hydration because of moisture insufficiency and low water potential become critical. Self-desiccation shrinkage also increases the risk of cracking potential.

Despite years of research on the use of LWFA as the most common and available IC water carrier, there are limited studies covering the following subjects:

- A portion of self-desiccation shrinkage strain is irreversible and changes engineering properties of concrete. Although IC can be a very effective curing method to extend hydration reactions and decrease self-desiccation in a sealed condition, there is a lack of research studies to compare properties of IC concrete with sealed curing to the ones cured in standard laboratory conditions.
- The effect of substituting LWFA on concrete strength properties depends on a variety of parameters including curing condition, W/C, substitution percentage, properties of LWFA, type and quantity of cementitious materials. That is why there is contradictory data available, although most researchers reported a slight increase in the compressive strength of IC concrete [5,20,21].
- LWFA can successfully provide extra water and increase pore water potential in partially saturated capillary pores after solidification the cement paste, which extends hydration reactions with a higher rate. A limited number of studies have investigated the effect of IC on cement hydration in an isothermal sealed condition [22].
- Coefficient of thermal expansion (CTE) demonstrates the temperature-induced strain in concrete elements [23]. CTE of hardened cement paste is about 20 microstrain/°C while that of aggregate is usually between 4-13 microstrain/°C, and porous aggregate

has usually lower CTE [1,24]. Therefore, LWFA substitution can significantly decrease CTE and improves the resistance of concrete against temperature-induced cracking.

- Irreversible self-desiccation affects pore networks and electrical resistivity in hardened concrete. Electrical resistivity is a sign of concrete permeability and directly influence the rate of corrosion in reinforced concrete. Although studies are available on the effect of IC in mixtures with standard curing, there is a lack of information about the performance of concrete mixture in a sealed condition.
- The ability of concrete to resist against chloride ion ingress can be estimated through rapid chloride migration coefficient, also called electro-diffusion coefficient [25–27]. Few studies are available on the effect of LWFA substitution on chloride penetration resistance of concrete mixtures incorporating SCMs.

The aim of this study is to investigate effects of IC using LWFA on a variety of hydration, mechanical and transport properties of cement-based materials including density, CTE, hydration reactions, setting time, UPV, compressive strength, electrical resistivity, and rapid chloride migration coefficient. Different LWFA substitutions (10, 20, 30 and 40%), W/C ratios (0.35, 0.42 and 0.5) and SCMs (FA and SF) were investigated. In addition, the effect of different curing conditions (standard and sealed curing) on the strength and electrical resistivity of mixtures were examined. This study helps provide a better understanding of how IC affects the engineering properties of a variety of concrete mixtures under different curing conditions.

2.3. Materials and mixture designs

Type I portland cement (ASTM C150) and tap water are used in all mixtures. Fly Ash – Class C (ASTM C618) and Densified Silica Fume (ASTM C1240) are also incorporated in the design of five mixtures. Chemical compositions of cementitious materials and main components of portland cement (calculated based on the modified Bogue formula [28]) are demonstrated in **Error! Reference source not found.** and **Error! Reference source not found.**, respectively. The specific gravity of portland cement, FA and SF were 3.15, 2.65 and 2.25, respectively.

Table 2-1- Chemical composition of cementitious materials

	Portland cement	**Fly Ash_C**	**Silica fume**
SiO_2	20	38.1	94.3
Al_2O_3	4.42	20.2	0.09
Fe_2O_3	2.81	6	0.1
SO_3	2.81	1.17	0.1
CaO	63.5	24.1	0.3
MgO	2.06	4.4	0.43
K_2O	0.52	0.6	0.83
Na_2O	0.21	1.57	0.27
Total Alkali (Na_2O+0.658 K_2O)	0.55	1.96	0.82
P_2O_5	0.06	0.89	-
TiO_2	0.24	1.46	-
BaO	0	0.54	-
SrO	0.09	0.31	-
Mn_2O_3	0.06	0.04	-
LOI	2.82	0.2	2.19

Table 2-2- The main components of portland cement (% by mass)

	Abbreviation	**Calculated based on Bogue formula** [29]	**Normal range** [1]
Tricalcium silicate	C_3S	64.78	60-73
Dicalcium silicate	C_2S	8.47	8-30
Tricalcium aluminate	C_3A	6.96	5-12
Tetracalcium silicate	C_4AF	8.55	8-16

Euclid 1037 (Type A and F - ASTM C494) was used as a high-range water reducer admixture to keep relatively constant slump for all the mixtures, in the range of 5±2.5 cm. Well-graded crushed limestone coarse aggregate with 25-mm maximum size and fine aggregate with fineness modulus of 2.97 were used (both meeting ASTM C33).

In IC mixtures, a portion of fine aggregate is substituted by the same volume of expanded clay lightweight fine aggregate (provided by Arcosa, Alabama). Water release of LWFA at 93% RH was measured 91.7% of the one-day water absorption [6]. Specific gravity and one-day saturated surface dried (SSD) moisture content of all aggregates are provided in Table *2-3*.

Table 2-3- Specific gravity and moisture content of aggregates

	Specific gravity	**One-day SSD moisture content (%)**
Coarse Aggregate	2.68	0.84
Fine Aggregate	2.65	1.3
LWFA	1.23	27.1

The design of all 14 concrete mixtures is presented in **Error! Reference source not found.**, designed based on the unit volume. The proportion of five mortar mixtures used for isothermal calorimetry test are also shown in Table *2-6*. IC water suggested by Bentz and Weiss

[5] calculated for the concrete mixtures equaled to 24.5 kg/m3 while the provided IC water for each mixture is denoted in **Error! Reference source not found.**.

All concrete mixtures were mixed in standard laboratory conditions following ASTM C192. Mortar mixtures were mixed according to ASTM C305. A fog curing room with 100% relative humidity and 23±2 °C temperature was used for standard curing of samples. Sealed samples were kept in the plastic mold (with extra sealing tape) until three days before testing time. All specimens were immersed in saturated limewater before testing to have comparable moisture conditions.

Table 2-4- Design of concrete mixtures

Code	**W/CMs**	**OPC (kg/m^3)**	**SCMs**		**Aggregate (kg/m^3)**		**LWFA**	
			Type	**Quantity (kg/m^3)**	**Coarse**	**Fine**	**Substitution (%)**	**IC water (kg/m3)**
C35L0	0.35	350	-	-	916	1048	0	0
C35L10		350	-	-	916	943	10	9.6
C35L20		350	-	-	916	838	20	19
C35L30		350	-	-	916	734	30	28.5
C35L40		350	-	-	916	629	40	38.1
C42L0	0.42	350	-	-	885	1013	0	0
C42L20		350	-	-	885	810	20	18.4
C50L0	0.5	350	-	-	850	973	0	0
C50L20		350	-	-	850	779	20	17.6
FA35L0	0.35	280	FA	70	910	1042	0	0
FA35L20		280	FA	70	910	834	20	19
SF35L0		324	SF	26	915	1047	0	0
SF35L20		324	SF	26	915	838	20	19
SF35L40		324	SF	26	915	628	40	37.9

Table 2-5- Mixture proportion of mortars

	W/C	**S/B ratio**	**LWFA Substitution (%)**
M375L0	0.375	2.75	0
M375L10	0.375	2.75	10
M375L20	0.375	2.75	20
M375L30	0.375	2.75	30
M375L50	0.375	2.75	50

2.4. Experimental tests

8 different tests conducted in this study are briefly explained in this section. All the experiments were conducted under controlled temperature (23±2 °C).

2.5.1. Density

The density of fully saturated specimens after 28-day standard curing was measured following ASTM C642 [30]. The specimens were 5-cm thick discs cut from 10-cm diameter cylinders. Density was calculated based on the weight of the specimens in SSD condition in air and immersed in water.

2.5.2. Coefficient of thermal expansion (CTE)

CTE test was conducted following AASHTO T336 [31] on saturated specimens with standard curing at the age of 28 days. Temperature variation was 40 °C (between 10 to 50 °C). Temperature variation cycles were repeated for at least three times.

2.5.3. Isothermal calorimetry

Isothermal calorimetry test was performed following ASTM C1679 [32] at 22.5 °C in a sealed condition. All raw materials were conditioned to temperature prior to mixing. The first 120-minute results were ignored to minimize errors.

2.5.4. Setting time

Initial and final setting times were determined following AASHTO T197 [33] based on the penetration resistance of mortar sieved from fresh concrete mixtures.

2.5.5. Ultra-sonic Pulse Velocity (UPV)

UPV was measured over the length of cylindrical specimens with 10-cm diameter and 20-cm length following ASTM C597 [34]. P-wave transmitter with 55 kHz frequency was used to conduct the tests. The specimens were cured in a curing room until testing.

2.5.6. Compressive strength

Compressive strength tests were carried out on saturated 10 by 20-cm cylindrical specimens following AASHTO T22 [35]. The specimens were being treated with either standard curing or sealed curing before immersing in limewater three days in advance to the testing time.

2.5.7. Surface resistivity (SR)

SR tests were conducted on 10 by 20-cm cylindrical specimens following AASHTO T358 [36]. The measurements were conducted on low current and 40 Hz frequency. All the specimens were immersed in limewater three days in advance to testing.

2.5.8. Rapid Chloride Migration Test (RCMT)

RCMT was conducted following AASHTO T357 [25] on specimens with standard curing at 28-day age. Chloride migration coefficient was calculated based on chloride penetration and simplified Nernst-Planck equation.

2.5. Results and discussion

2.6.1. Density

The density of all concrete mixtures is presented in Figure *2-1*. Concrete density is controlled by the density of its ingredients, proportional to the volume in mixture design. Normal concrete mixtures consist of 60 to 80% aggregate, coarse and fine, so replacing a portion of fine aggregate with LWFA directly affect the density of concrete mixtures. The results show that LWFA substitution is a major parameter in concrete density which is linearly decreased by increasing LWFA substitution. 40% LWFA substitution results in about 10% reduction in total density.

Increasing W/C from 0.35 to 0.5 leads to a 2.5% decline in the density of mixtures with no LWFA. Although incorporating FA or SF is not making a significant change in the density of mixtures without LWFA, the results indicate a slight increase in the density of mixtures incorporated LWFA and SCMs, compared to the ones without SCMs.

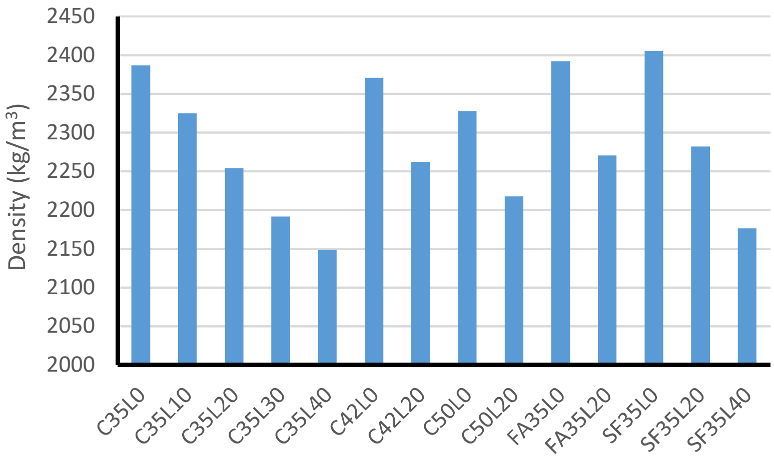

Figure 2-1- Effect of LWFA substitution on the density of concrete mixtures

2.6.2. CTE

Figure *2-2* presents CTE of all concrete mixtures. As illustrated, LWFA substitution significantly affects CTE of mixtures. Replacing up to 40% of fine aggregate with LWFA leads to a linear decrease in CTE, up to 25% reduction.

On the other hand, changes in W/C does not show a major effect on concrete CTE. CTE of cement paste is not affected by varying W/C from 0.4 to 0.6 [37], so any reduction can be mainly attributed to decreased aggregate content in the mixture design.

Incorporation of SCMs like FA or SF can decrease the porosity leading to an increase in CTE of cement paste. However, this increase, proportioned to the volume of cement paste in concrete design, does not make a major rise in concrete CTE.

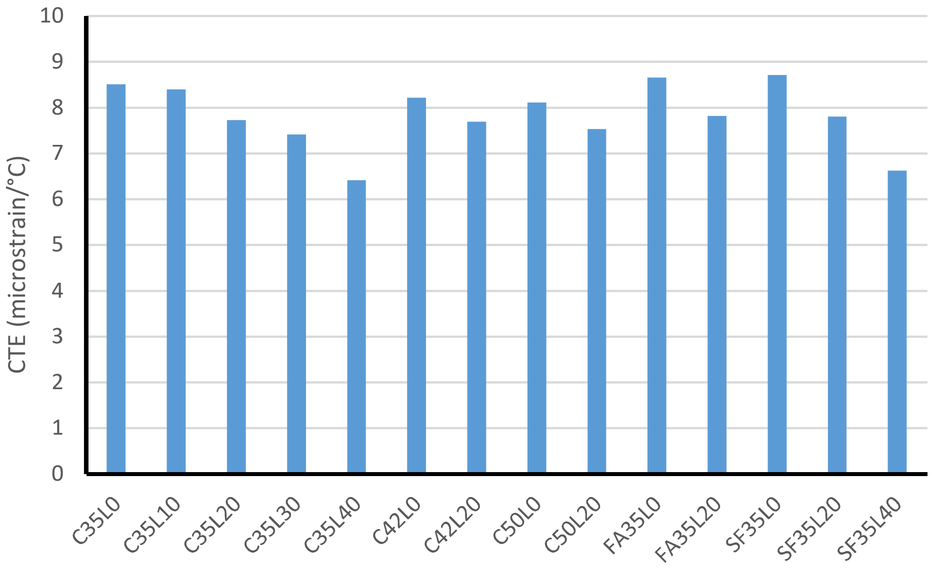

Figure 2-2- Effect of LWFA substitution CTE in concrete mixtures

2.6.3. Isothermal calorimetry

Hydration of cementitious materials can be classified in five primary stages. Portland cement particles start dissolving and releasing ions right after contact with water. The initial peak of heat evolution (usually less than 15 minutes after mixing time) is mainly attributed to C3A hydration and formation of Aft phase rods (Ettringite formation).

After a dormant period, C3S starts hydrating and heat liberation increases again. The main products in this stage are low-density C-S-H and CH. Solidification is a specific period of time in which the state of the matrix is gradually changed from plastic to solid, so the matrix starts to bear tension and resist against volume change. Another bump or shoulder might be also visible after the main peak. It can be accredited to the conversion of ettringite to monosulphate (Aft to AFm). Both C_3S and C_2S components participate in hydration reactions over this period generating high-density C-S-H gel. Hydrations reactions continue for an infinitive period of time, based on moisture availability.

The results of isothermal calorimetry tests on five different mortars substituting different percentages of LWFA are shown in Figure *2-3*. The results are normalized per gram of cement in mortar mixtures. The results indicate that LWFA substitution does not change the rate of heat generation before reaching 85% of the second peak. IC mortars, with 20% LWFA substitution and higher, shows around 15% increase in the peak of hydration heat generation rate. This increase might demonstrate the start of releasing water by LWFA.

IC mortars appear to extend the rate of heat generation after solidification. The reason is that IC water starts to be released by the carrier when pore water potential is developed. Figure *2-3* demonstrates that IC mortars have a higher rate of hydration over these stages, resulting in higher total heat generation. Total heat generated by the complete hydration of portland cement is about 500 J/gr [38], so higher heat generated can be attributed to a higher degree of hydration for IC mortars.

Although increasing LWFA substitutions up to 30% demonstrates a consistent increase in total heat generation, further increase in substitution did not provide an additional significant improvement over the first two days.

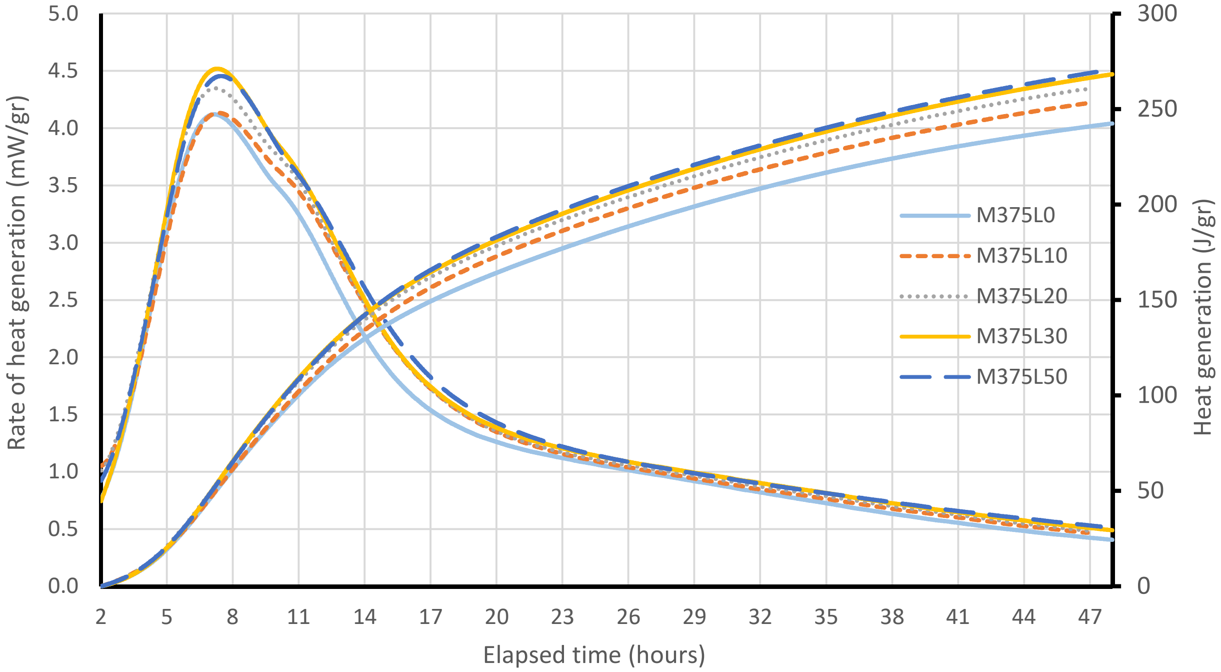

Figure 2-3- Effects of internal curing on heat generation in a mortar with w/c=0.375 and s/b=2.75

2.6.4. Setting time

Penetration resistance of the portion of concrete mixtures passing sieve #4 was measured over time after mixing. The results for the first five mixtures in **Error! Reference source not found.**, substituting different percentages of LWFA, are presented in Figure *2-4*. LWFA releases IC water after solidification and due to the tendency of the mixture to develop pore water potential. According to the results illustrated in Figure *2-3*, this starts around the main peak in the rate of heat generation. That is the reason why IC is not making a meaningful change in the penetration resistance development at the very early ages.

ASTM C403 defines the initial and final setting time of mixtures based on mechanical penetration resistance. The best power trendline with the minimum R-squared was developed for each mixture, and associated time with 3.5 and 27.6 MPa resistance was considered as initial and final setting time, respectively. The results presented in Table *2-6* show that there is not a significant difference in setting time of mixtures with different LWFA substitutions.

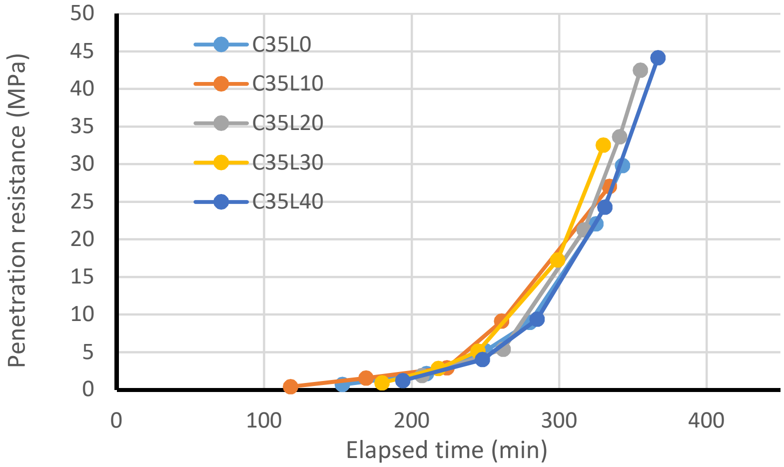

Figure 2-4- Penetration resistant development in mixtures with different LWFA substitution

Table 2-6- Initial and final setting time of concrete following ASTM C403

	C35L0	**C35L10**	**C35L20**	**C35L30**	**C35L40**
Initial setting time (min)	224	210	234	227	236
Final setting time (min)	348	354	332	324	339

2.6.5. Ultrasonic pulse velocity (UPV)

UPV development of concrete mixtures with 0.35 W/C and different LWFA substitutions are presented in Figure *2-5*. UPV have a direct correlation with both dynamic elastic modulus and density. Considering a constant density, UPV mainly depends on the properties of cement paste. Therefore, it is generally growing over time by an increase in the degree of hydration [39].

Although IC concrete mixtures may have a higher degree of hydration, their lower density leads to an almost constant UPV for IC concrete mixtures with 10, 20 and 30% LWFA replacement. However, the mixture having 40% LWFA substitution shows a meaningful decrease in UPV, attributed to the significant decrease in density.

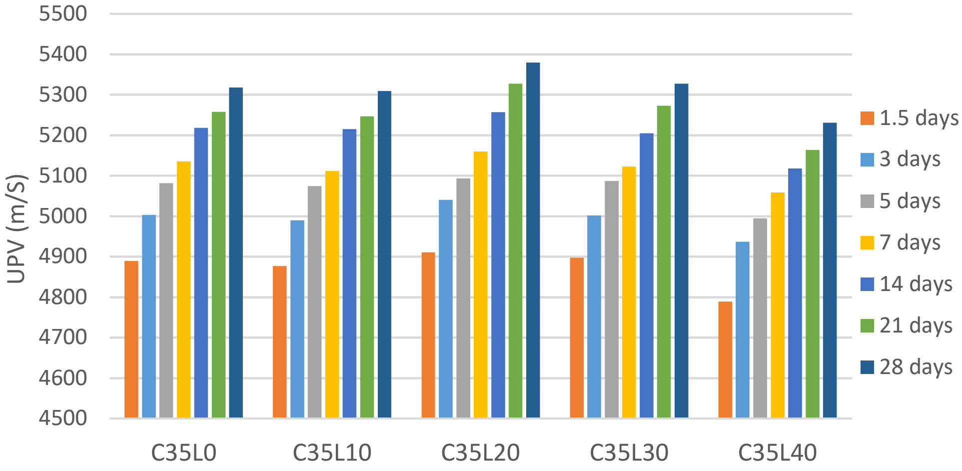

Figure 2-5- UPV development in concrete mixtures with different LWFA substitutions

2.6.6. Compressive strength

IC has two contradictory effects on concrete compressive strength. Because of moisture consumption in hydration reactions, internal RH of hardened concrete significantly drops with depth [3]. This shows water potential development and insufficiency of external curing, particularly for the ones with very low permeability. The main benefit of internal curing is providing extra water uniformly through the whole section to hinder water potential development. It leads to a higher degree of hydration, and so cement matrix with lower porosity and improved ITZ [5,22].

On the other hand, the presence of LWFA in concrete structure brings a tendency to decrease concrete compressive strength and elastic modulus because of its porous structure with low strength compared to fine aggregate [40]. Due to parameters like curing condition, W/C and type of cementitious materials, the ultimate increase or decrease in the compressive strength of an IC concrete mixture is determined by the balance between these two contradictory effects.

In addition, increased water potential (i.e. high capillary pressure) results in self-desiccation making irreversible shrinkage by taking interlayer water out [8,41,42]. This makes the cement matrix denser; therefore, the compressive strength can be slightly increased. Although re-wetting the paste generates swelling pressure between gel layers and makes up reversible shrinkage portion, decreasing the compressive strength by 30% [41], the ultimate strength would be slightly higher than the initial specimen before shrinkage.

- *Effect of LWFA substitutions and W/C*

The compressive strength of concrete mixtures with different LWFA substitutions, W/C and curing conditions are presented in Figure *2-6*, at a 28-day age. Considering the first five mixtures with constant W/C and standard curing, 20% LWFA substitution seems the optimum value which increases the compressive strength by 11%, compared to the mix without LWFA. For sealed cured samples, the benefit of IC is more notable. In addition, sealed curing (in comparison with standard curing) results in the reduction of compressive strength for control mixture with low W/C and no LWFA. However, IC can compensate for this reduction by extended hydration. The compressive strength of the sealed cured mixture with 30 or 40% LWFA substitution is even higher than the standard cured ones. However, there is still no improvement compared to the mixture with 20% LWFA substitution.

The results demonstrated in Figure *2-6* also indicate that the compressive strength of mixtures is significantly decreased with increasing W/C ratio from 0.35 to 0.42 which is mainly because of increasing the volume and porosity of ITZ and also porosity of the bulk cement matrix. Increasing W/C further to 0.5 decreases the compressive strength by increasing the porosity of cement paste.

It is also indicated that although IC is an effective method in improving the compressive strength of the mixture with 0.42 W/C, it is less beneficial for the mixture with a higher ratio. The reason is that there is enough water in the initial mixture for the hydration of portland cement. Also, because of the higher permeability of the hardened mixtures with W/C, the external curing is more efficient to provide curing water for the whole section. The increase of W/C also reduces the negative effect of sealed curing on the hydration reactions, as enough moisture was provided by initial water in the mixture.

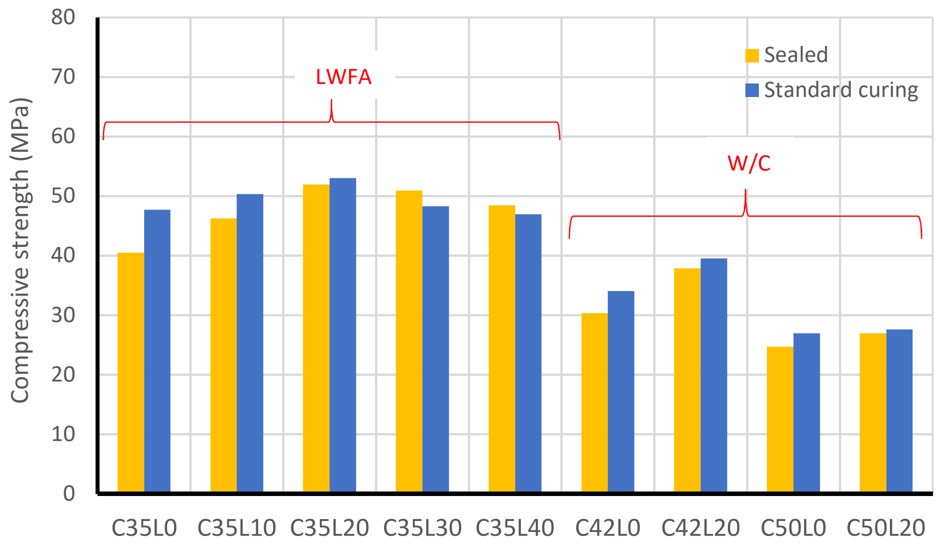

Figure 2-6- Compressive strength of mixtures with different W/C and LWFA substitutions

- *Effect of SCMs substitution*

Substitution of SCMs also has two contradictory effects on concrete properties. Replacing a portion of portland cement with SCMs results in a dilution effect which is more dominant on mixtures with low cementitious materials content, or very high substitution percentage. This effect depends on the type and reactivity of the material, and it is also time-dependent. On the other hand, some SCMs include high aluminosilicate portions which react with calcium hydroxide, pozzolanic reactions, over time. The hydration products are C-S-H gels similar to portland cement hydration products. This helps to not only densify the bulk matrix of hardened portland cement but also decreasing the volume and porosity of ITZ in concrete mixtures.

The effect of IC on the 28-day age compressive strength of mixtures incorporating different SCMs and two curing conditions is illustrated in Figure *2-7*. Comparing mix C35L0 with FA35L0 and C35L20 with FA35L20, the results show that there is a balance between dilution and pozzolanic effects of FA class C on the compressive strength of concrete mixture at 28 days.

However, replacing 7.5% of portland cement with SF leads to an increase in the compressive strength of the mixtures in both sealed and standard curing conditions. 20% LWFA substitution, in SF contained mixtures, significantly helps increase compressive strength in both curing conditions while their difference between them is also reduced. This shows the benefit of internal uniform curing for concrete with low permeability and high strength (i.e. 0.35 W/C). On the other hand, a further increase in LWFA substitution to 40% results in the reduction of compressive strength of SF contained mixtures due to the adverse effect of porous low-strength LWFA. It is worth to note that the compressive strength of this mixture (i.e. SF35L40) is still higher than the one of mixtures with no LWFA (i.e. SF35L0).

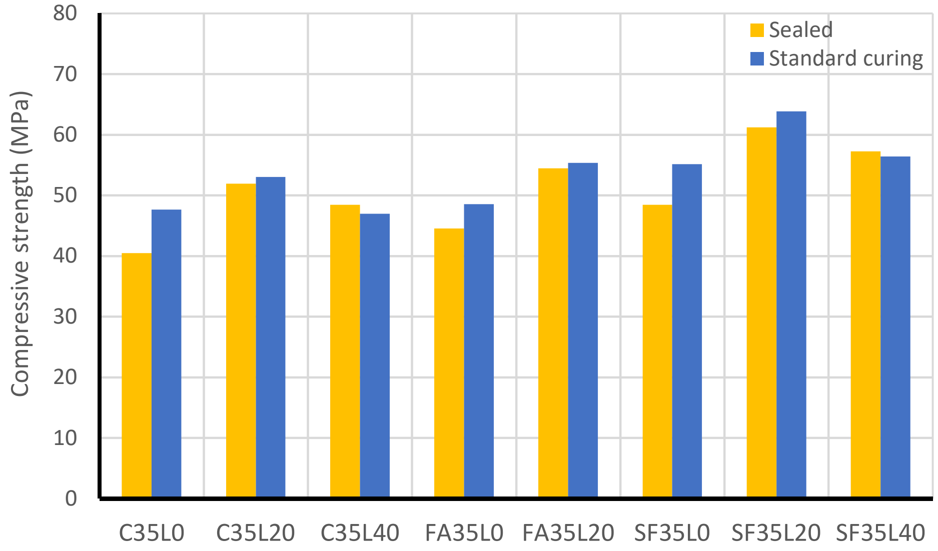

Figure 2-7- Compressive strength of mixtures with different LWFA and SCMs substitution

2.6.7. Surface resistivity (SR)

Concrete is a composite material consists of solid, gas and liquid phases. The electrical conductivity of the liquid phase is much higher than the others, so it is dominant in determining the resistivity of concrete. In other words, considering saturated specimens with relatively constant temperature, conductivity and connectivity of pore solution are the main parameters determining concrete resistivity.

Physically bonded water has high viscosity and low conductivity compared to free water. Therefore, conductive ions mainly pass through the free water in hardened concrete to convey the electrical charges. Capillary and ITZ pores are the most connected pores in concrete. Therefore, any changes in the resistivity of concrete mixtures with the unit type of cementitious materials can be explained by the connectivity of pores [19,43].

Normal concrete mixtures incorporate around 70% aggregate by volume. Therefore, ITZ pores can get very close together to be the dominant parameter in determining concrete resistivity, which is called ITZ percolation [1,44]. Reducing the volume and porosity of ITZ by lowering W/C, increasing the degree of hydration, internal curing or using SCMs makes a significant increase in SR. This effect is magnified in low W/C concrete mixtures having a cement matrix with high tortuosity.

- *Effect of LWFA substitutions and W/C*

Figure *2-8* demonstrates the electrical resistivity of concrete mixtures with two different curing conditions, sealed and standard curing, at 28-day age. Considering standard curing, the results show increases in the resistivity of concrete mixtures. This increase is attributed to reducing percolation of pores through hydration.

Samples cured under sealed condition are expected to have a lower degree of hydration and resistivity due to the lack of moisture, particularly in low W/C. However, the opposite trend is observed. Developing pore water potential leads to taking interlayer water out, irreversible self-desiccation shrinkage, which decreases the size of capillary pores and increases electrical resistivity. The electrical resistivity of the mixture with 0.35 W/C and no LWFA shows a balance between these two contradictory effects, i.e. reduction of resistivity due to low hydration degree and increase of resistivity due to self-desiccation; therefore, SR is not meaningfully changed. However, for similar W/C, there is a significant increase in SR of mixtures by sealed curing where LWFA is incorporated. Uniform IC water providing by LWFA leads to a higher degree of hydration through the whole section, lower capillary pores and decreased ITZ [22]. This leads to up to 35% increase in electrical resistivity.

Figure *2-8* also shows a significant drop when W/C reaches a certain ratio (i.e. 0.42 in this study). This demonstrates that tortuosity is substantially decreased and capillary pores are somehow interconnected, which results in a significant increase of concrete conductivity. By increasing the volume and diameter of pores, the effect of self-desiccation is much less dominant in controlling SR. However, IC is still efficient in increasing SR of mixtures with different water-to-cement ratios.

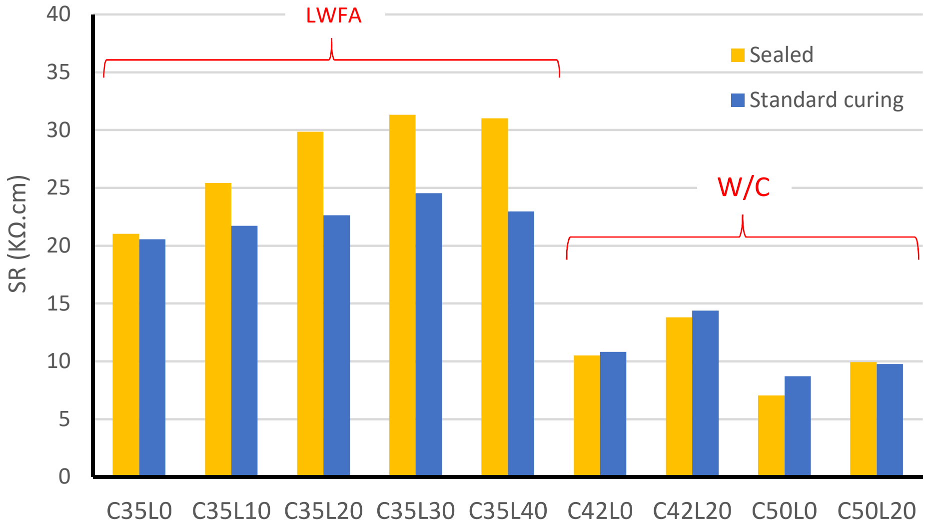

Figure 2-8- Electrical resistivity of mixtures with different W/C and LWFA substitutions

- *Effect of SCMs substitution*

There is a nonlinear correlation between ionic concentration and conductivity of pore solution [45,46]. The most conductive ions in the pore solution of hardened concrete mixtures are Na^+, K^+, and OH^- [19,47]. Therefore, any significant changes in ionic molar concentration in the pore solution directly affects concrete resistivity. SCMs are assumed to significantly change the composition of pore solution because of the pozzolanic reactions with calcium hydroxide. These reactions also densify ITZ and decrease ITZ percolation effect. That is why the effect of SCMs on concrete mixtures is more significant than on cement paste [19].

Figure *2-9* shows the 28-day electrical resistivity of mixtures incorporating different SCMs. It demonstrates that the effect of pozzolanic and hydraulic (because high CaO content) reactions of FA class C is in balanced with dilution effect of 20% FA substitution at 28 day age, on both sealed and standard curing conditions. Therefore, there is no meaningful increase in SR because of FA substitution.

However, the reactivity of SF is more significant than FA, especially at 28 day or earlier ages. Therefore, substituting 7.5% SF, considerably increases the SR of concrete mixtures (by an average of 3.1 times), in standard curing condition. The positive effect of IC on SR become more significant for SF mixtures. SR of the mixture incorporating SF and 40% LWFA is higher than those with 20% LWFA.

In addition, similar to the previous observation, but to a larger extent, sealed cured samples achieves higher SR than standard cured ones. Because of the higher reactivity and lower distribution size of pores in concrete mixtures incorporating SF, irreversible self-desiccation shrinkage is more signified, so surface resistivity of sealed samples is generally higher.

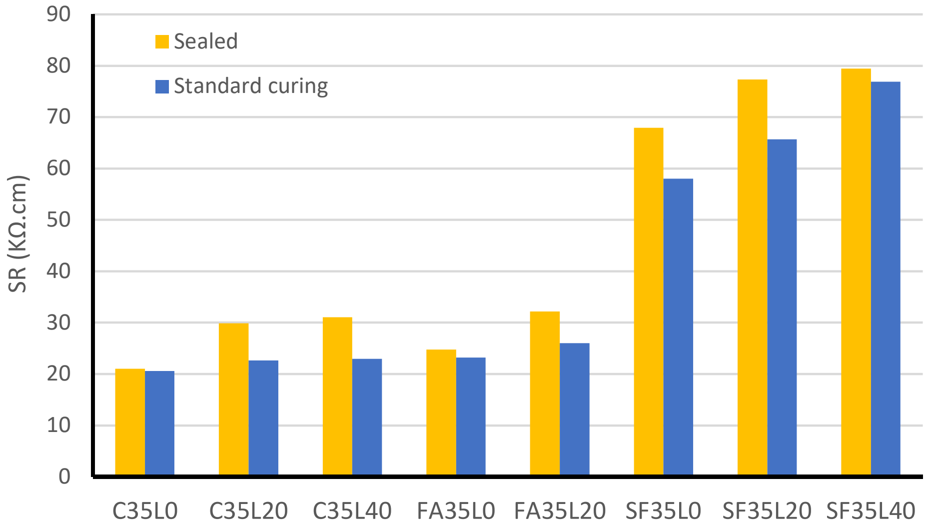

Figure 2-9- Electrical resistivity of mixtures with different LWFA and SCMs substitution

- *Electrical resistivity development over time*

Figure *2-10* to 12 demonstrate SR development of concrete mixtures over time, up to 180 days, in standard curing condition. In a constant 0.35 W/C, Figure *2-10*, the results indicate that SR is increased by substituting higher LWFA. However, the improvement is not significant between 30 and 40% LWFA substitution. In addition, for different W/C, Figure *2-11*, it is indicated that IC (with 20% LWFA substitution) is more beneficial in increasing SR of mixtures with 0.35 and 0.42 W/C than the mixture with 0.5 W/C. The volume of ITZ and porosity of cement matrix in the concrete mixture with 0.5 W/C is very high, so IC is not very efficient to increase tortuosity.

Figure *2-12* denotes that although FA class C is not making a significant improvement at 28 day age, comparing to control concrete without SCMs, the resistivity of FA contained mixtures increases over time by a higher rate because of the pozzolanic reactions. At 180 day age, concrete mixtures incorporating 20% FA has around 1.7 times higher SR than the mixtures without SCMs.

SF has a very high surface area and reactivity; therefore, it is very efficient in cutting the connectivity between pores and especially decreasing ITZ percolation. It is worth to note that in low W/C mixtures with low pore connectivity, SR significantly increases by an increase in tortuosity. That is the reason why incorporating SF significantly increases the rate of SR development over time up to 3.7 times of the mixture with no SCMs at 180 day age. It is also presented that increasing LWFA substitution from 20 to 40% in the mixture incorporating SF leads to a slight increase in SR.

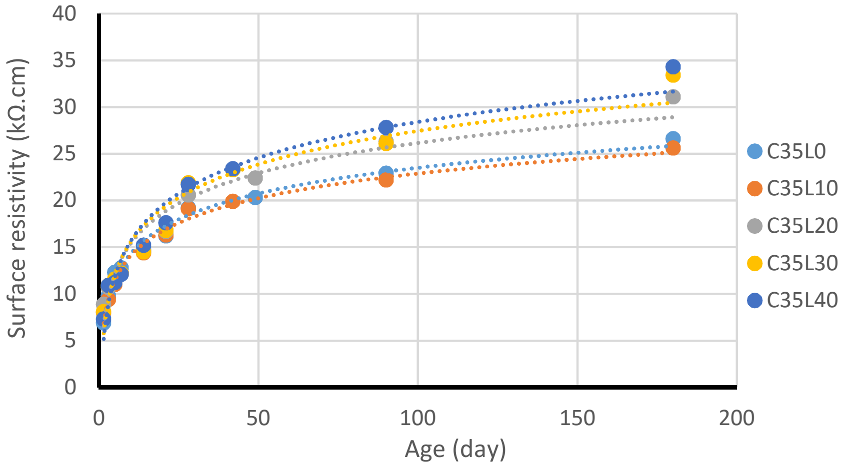

Figure 2-10- SR development of mixtures with different LWFA substitutions

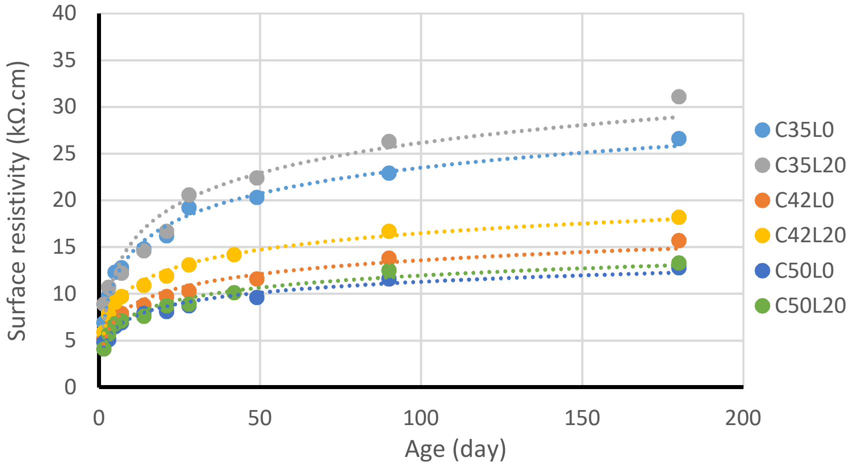

Figure 2-11- SR development of mixtures with different LWFA substitutions and W/C

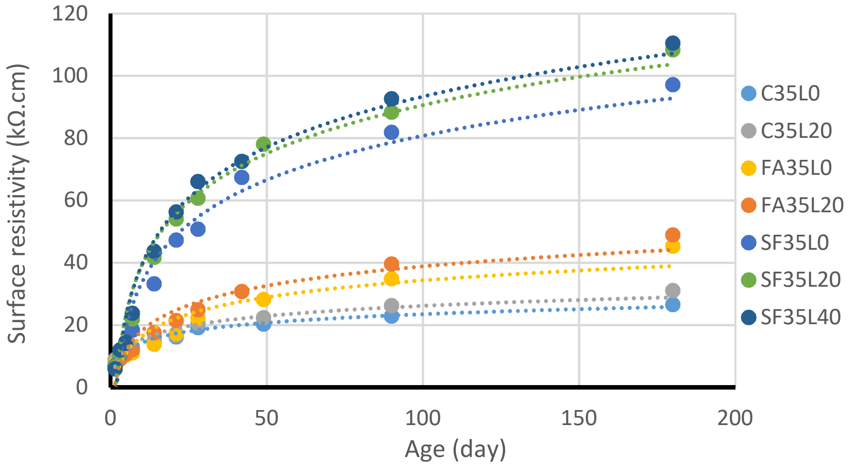

Figure 2-12- SR development of mixtures incorporating SCMs and LWFA

2.6.8. Rapid chloride migration coefficient

RCMT is an expedited test under the steady-state condition to investigate concrete resistance against electrically driven chloride ion penetration. The nature of this experiment, measuring chloride penetration depth, is different from electrical resistivity which mainly depends on concrete permeability.

Rapid chloride migration (RCM) coefficients of mixtures incorporating different SCMs and LWFA at 28 day age are presented in Figure *2-12*. The results indicate that IC using 20 and 40% LWFA substitutions results in 4 and 8% reduction in RCM coefficient, respectively. This shows the benefits of uniform IC through the whole section in decreasing porosity and also ITZ percolation.

FA substitution does not meaningfully decrease RCM coefficient at 28 days. However, based on SR development at longer ages, it can be expected that the performance and RCM coefficient of the mixtures incorporating FA would be improved over time because of pozzolanic reactions.

Incorporating SF is an efficient method to decrease RCM coefficient. In the mixture with no LWFA, incorporating 7.5% SF results in a 25% reduction in RCM coefficient. LWFA substitution intensifies this improvement; RCM coefficient reduction due to the use of SF is increased to 32% in the mixture with 40% LWFA substitution. This improvement is because of the higher water consumption of SF for hydration reactions compared to portland cement.

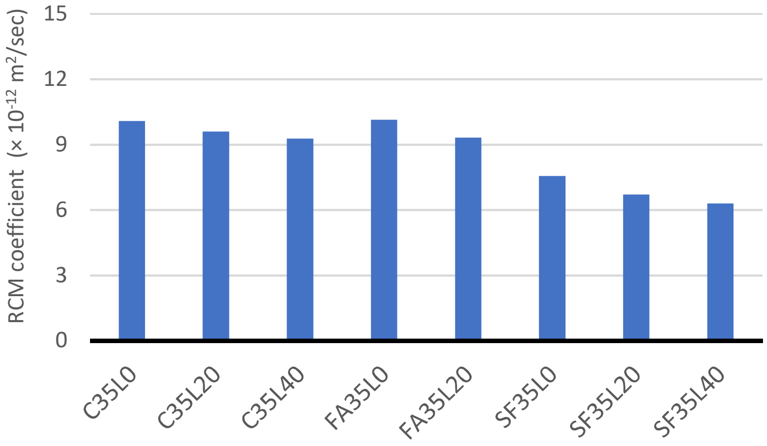

Figure 2-13- Rapid chloride migration coefficient of concrete mixtures

2.6. Conclusion

The main findings of this study can be listed as below:

- LWFA releases IC water after solidification. This leads to an increase in the rate of heat generation after setting time. Extended hydration also results in higher total heat generation per gram of portland cement in mortars. Further increase in LWFA substitution than 30% leads to an insignificant increase in total heat generation.
- IC does not change the setting time or UPV of concrete mixtures.
- LWFA substitution has a major effect on CTE of concrete mixtures. CTE linearly decreases by up to 25%, in the case of LWFA substitution by up to 40%.

- IC is more efficient for the concrete mixtures with low W/C, incorporating SF, or in sealed curing condition.
- 20% LWFA substitution appears to be the optimum percentage, for the LWFA used in this study, to improve compressive strength of concrete mixtures.
- Further substitution of LWFA increases SR of concrete mixtures, particularly in case of sealed curing or incorporating silica fume in the mixtures.
- IC is efficient in decreasing rapid chloride migration coefficient of concrete mixtures with low W/C. Incorporation of silica fume intensifies this improvement.

2.7. Acknowledgments

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2.8. References

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CHAPTER 3. IMPROVED HYDRATION AND MITIGATION OF PORE WATER POTENTIAL DEVELOPMENT IN CEMENT-BASED MATERIALS BY INTERNAL CURING

A journal paper to submit to ACI Materials Journal

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3.1. Abstract

Consumption of water during hydration reactions, or water evaporation through the surface results in the development of negative pressure in capillary pores of concrete at early ages. This pore water potential (PWP) creates early-age shrinkage strain and increases the chance of early-age cracking. The aim of this study is to investigate the effects of internal curing (IC), water-to-cementitious materials ratio (W/CMs) and incorporation of supplementary cementitious materials (SCMs) on the hydration reactions and PWP development in cement-based materials. For this purpose, 15 mortar mixtures with different W/CMs (0.3, 0.375, 0.45 and 0.525), lightweight fine aggregate (LWFA) substitutions (10, 20, 30 and 50%) and SCMs incorporation (7.5% silica fume and 20% fly ash), as well as, 14 concrete mixtures with different W/CMs (0.35, 0.42 and 0.5), LWFA substitutions (10, 20, 30 and 40%) and SCMs incorporation (7.5%

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silica fume and 20% fly ash) were evaluated through isothermal calorimetry and pore water potential tests. The results demonstrate that IC is efficient in promoting hydration kinetics after solidification. 10% is found optimum for the ratio of IC water to portland cement. IC also delays capillary PWP development, especially for the mixtures with low W/C or incorporating silica fume.

Keywords: Lightweight fine aggregate (LWFA), Supplementary cementitious materials (SCMs), Isothermal calorimetry, Tensiometer, Capillary pore water potential (PWP)

3.2. Introduction

Cement-based mixtures are assumed to be saturated right after placement, other than the presence of small air bubbles. However, moisture consumption during hydration reactions and water evaporation from the free surface of material result in a significant decrease in the degree of saturation of the system over the early ages. Moisture loss in the system decreases the rate of hydration of cementitious materials (CMs) and develops negative pore water potential (PWP) which increases early-age shrinkage cracking potential [1–5].

The main factors determining the rate of water evaporation are temperature of the mixture, ambient temperature and relative humidity, wind speed, solar radiation and bleeding. Right after placement, the free water in the mixture starts rising up to the surface, due to differences in the specific gravity of the constituents which makes a film of water on the surface, known as bleeding. The rate of water evaporation from free water is more than that at the concrete materials surface [6]. Therefore, although slow bleeding can temporarily protect the material from PWP development, severe bleeding ultimately increases the rate of moisture loss and capillary PWP development.

Pore water potential is made up of several different components, but the most important ones are gravitational, pressure, osmotic and matric potential. Gravitational water potential is related to elevation. Pressure potential arises from any applied hydro or pneumatic pressure. Osmotic potential is generated by components dissolved in water. The variation of these three potentials can be usually ignored in the study of concrete materials. However, matric potential development can significantly affect concrete properties.

Matric potential is generated because of cohesive and adhesive forces between water particles together or to cement matrix, respectively. High cohesive force between water molecules results in unbalanced forces on the surface of water, known as surface tension. The adhesive force between water and cement matrix also leads to absorbing pore water to the wall of matrix, which makes an upward meniscus curve on the surface of and negative capillary pressure in pore water as well as a capillary tension in the cement matrix. [7–9].

Capillary PWP development is a physical process that occurs when the media loses moisture. Water is initially removed from pores with the largest diameters and potentials. When capillary pores with 50 nm start to lose water and be partially saturated, negative capillary PWP starts to be substantially decreased [10,11]. Internal relative humidity (RH) in cement-based materials is controlled by the chemical properties of pore water and PWP in the capillary pores. Jensen et al. [4] showed that there is a specific relative humidity (RH) for each component of portland cement, below which the rate of hydration reactions significantly drops. This specific limiting RH for C_2S, C_3S, and C_3A are 90, 85 and 60%, respectively.

There is a linear correlation between free horizontal early-age shrinkage strain and PWP development in cement-based materials [1,12,13]. Early-age cement matrix is a weak solid material. While it resists volume changes generated by capillary PWP, its strength to tolerate the associated tensile stress is limited, so cracks may form. Although early-age shrinkage cracks occur at the surface of cement-based materials, they are important because of aesthetic and durability issues.

The early-age cracking potential of a mixture mainly depends on the degree of restraint, PWP development, early-age elastic modulus and tensile strength of cement matrix. The cracking potential can be controlled by appropriately placed contraction joints, employing proper construction techniques, optimizing mixture proportion, and using suitable curing.

Although the traditional external curing methods are successful in limiting water evaporation and delivering extra water for the external layers of concrete [14], it is not practical or easy to provide properly for some projects. External curing at the surface does not cure the whole volume of concrete. Internal curing (IC) is the alternative method to uniformly provide extra curing water for extended hydration of cementitious materials throughout the section. Pre-saturated porous lightweight fine aggregate (LWFA), the most common carrier of IC water in the USA, uniformly releases IC water through the whole body of the material during PWP development.

Due to the chemical shrinkage and water consumption of portland cement for complete hydration, Bentz and Weiss [15] concluded that the optimum IC water to provide is 7% by the mass of portland cement content. However, chemical shrinkage of supplementary cementitious materials (SCMs) like silica fume (SF) and fly ash (FA) is around two to three times higher than portland cement [16–18]. In addition, incorporation of fine highly reactive SCMs like SF significantly decreases pore size distribution of cement matrix [19,20], resulting in a higher capillary PWP. Those factors may further highlight the importance of IC as well as increase the IC water demand.

In addition, in the normal range of water-to-cement ratios, decreasing W/C is expected to promote the kinetics of CMs hydration reactions in the acceleration stage of cement hydration. It means that lower initial water is available in the mixture, and the water consumption rate is increased. Therefore, increased capillary PWP and decreased hydration rate because of moisture insufficiency are expected after the acceleration period [21,22]. This also highlights the potential benefit of IC for promoting hydration reactions and suppressing PWP in cement-based materials with low W/C.

Very limited research has been conducted on capillary PWP development in cement-based materials. In particular, there exists no comprehensive study on the effect of IC on PWP development and hydration kinetics of mixtures incorporating different cementitious materials.

This study aims to investigate the effects of various W/C, SCMs and IC water on hydration kinetics and capillary PWP development in different cement-based materials. 14 mortar and 15 concrete mixtures incorporating FA, SF and LWFA are studied. The outcome of the study is to determine the importance of IC in promoting extended hydration reactions and suppressing capillary PWP development, in particular for mixtures with low W/C and incorporating SF.

3.3. Materials and mixture designs

Portland cement Type I (ASTM C150), fly ash – class C (ASTM C618) and densified silica fume (ASTM C1240) are three different cementitious materials used in this study. The chemical compositions of the cementitious materials are presented in Table *3-1*. In addition, the main components of portland cement (based on the modified Bogue formula [23,24]) along with the normal range and heat generation of each component are shown in Table *3-2*. Tap water from the municipal network (Ames, IA) was used for mixing.

Table 3-1- Chemical composition of cementitious materials

	Portland cement	**Fly ash – Class C**	**Silica fume**
SiO_2	20	38.1	94.3
Al_2O_3	4.42	20.2	0.09
Fe_2O_3	2.81	6	0.1
SO_3	2.81	1.17	0.1
CaO	63.5	24.1	0.3
MgO	2.06	4.4	0.43
K_2O	0.52	0.6	0.83
Na_2O	0.21	1.57	0.27
Total Alkali (Na_2O+0.658 K_2O)	0.55	1.96	0.82
P_2O_5	0.06	0.89	-
TiO_2	0.24	1.46	-
BaO	0	0.54	-
SrO	0.09	0.31	-
Mn_2O_3	0.06	0.04	-
LOI	2.82	0.2	2.19

Table 3-2- The main components of portland cement (% by mass)

	Abbreviation	**Calculated based on Bogue formula** [23]	**Normal range** [7]	**Enthalpy of complete hydration (J/g)** [25,26]
Tricalcium silicate	C_3S	64.78	60-73	-517
Dicalcium silicate	C_2S	8.47	8-30	-262
Tricalcium aluminate	C_3A	6.96	5-12	-1144[a] to -1672b
Tetracalcium silicate	C_4AF	8.55	8-16	-418

[a] Monosulfate formation

[b] Ettringite formation

For concrete mixtures, Euclid 1037 (Type A and F - ASTM C494) was used as high-range water reducing admixture to keep slump relatively constant in the range of 5±2.5 cm.

Well-graded crushed limestone coarse aggregate with 25-mm maximum size and fine aggregate with fineness modulus of 2.97 were used (both meeting ASTM C33). In IC mixtures, a portion of fine aggregate was substituted by the same volume of expanded clay lightweight fine aggregate (Provided by Arcosa, Alabama). Water release of LWFA at 93% RH was measured as 91.7% of the one-day water absorption [27]. Specific gravity and one-day saturated surface dried (SSD) moisture absorption of all aggregates are presented in Table *3-3*.

Table 3-3- Specific gravity and moisture content of aggregates

	Specific gravity	**One-day SSD moisture absorption (%)**
Coarse Aggregate	2.68	0.84
Fine Aggregate	2.65	1.3
LWFA	1.23	27.1

Mixture proportions of all 15 mortars and 14 concrete mixtures are shown in Table *3-4* and Table 3-5, respectively. The ratio of IC water to cementitious materials (ICW/CMs) is also provided for all IC mixtures in Table *3-4* and Table 3-5. Mortars were mixed according to ASTM C305. Hobart mixer and raw materials were conditioned at 22.5±0.5 °C several hours before the mixing time. Concrete mixtures were mixed using a drum mixer in standard laboratory conditions following ASTM C192.

Table 3-4- Mixture proportion of mortars

	W/CMs	**S/B**	**SCMs**		**LWFA**	
			Type	**Substitution (%)**	**Substitution (%)**	**ICW/CMs [a]**
M30L0	0.30	2.75	-	-	-	0
M375L0	0.375	2.75	-	-	-	0
M45L0	0.45	2.75	-	-	-	0
M525L0	0.525	2.75	-	-	-	0
M30L30	0.30	2.75	-	-	30	0.101
M375L30	0.375	2.75	-	-	30	0.101
M45L30	0.45	2.75	-	-	30	0.101
M525L30	0.525	2.75	-	-	30	0.101
M375L10	0.375	2.75	-	-	10	0.034
M375L20	0.375	2.75	-	-	20	0.067
M375L50	0.375	2.75	-	-	50	0.169
M-FA375L0	0.375	2.75	FA	20	-	0
M-FA375L30	0.375	2.75	FA	20	30	0.126
M-SF375L0	0.375	2.75	SF	5	-	0
M-SF375L30	0.375	2.75	SF	5	30	0.107

[a] The ratio of IC water to cementitious materials

Table 3-5- Concrete mixture proportions

Code	**W/CMs**	**OPC (kg/m^3)**	**SCMs**		**Aggregate (kg/m^3)**		**LWFA**	
			Type	**Quantity (kg/m^3)**	**Coarse**	**Fine**	**Substitution (%)**	**ICW/CMs[a]**
C35L0	0.35	350	-	-	916	1048	0	0
C35L10		350	-	-	916	943	10	0.027
C35L20		350	-	-	916	838	20	0.054
C35L30		350	-	-	916	734	30	0.081
C35L40		350	-	-	916	629	40	0.109
C42L0	0.42	350	-	-	885	1013	0	0
C42L20		350	-	-	885	810	20	0.053
C50L0	0.5	350	-	-	850	973	0	0
C50L20		350	-	-	850	779	20	0.050
FA35L0	0.35	280	FA	70	910	1042	0	0
FA35L20		280	FA	70	910	834	20	0.054
SF35L0		324	SF	26	915	1047	0	0
SF35L20		324	SF	26	915	838	20	0.054
SF35L40		324	SF	26	915	628	40	0.108

[a] The ratio of IC water to cementitious materials

3.4. Experimental methods

Isothermal calorimetry and PWP tests conducted in this study are explained below in detail.

3.5.1. Isothermal calorimetry test

The purpose of the calorimetry testing is to investigate the hydration kinetics of the cementitious materials. Calorimetry tests can be divided into three categories: isothermal, semi-adiabatic and adiabatic. In isothermal calorimetry tests, heat conduction is measured, while in the other tests the temperature rise is monitored. Isothermal calorimetry tests require advanced equipment, but it gives more detailed information compared to semi-adiabatic calorimetry which actually measures the integral of the rate of heat evolution [26]. In this study, the isothermal calorimetry test is performed following ASTM C1679 [28] at an isothermal temperature of 22.5 ± 0.1 °C.

The isothermal calorimetry device consists of a thermally isolated box with internal constant temperature, eight small chambers in an internal isolated box (except the bottom side), a heat sink sensor under each chamber and a reference 129-gram aluminum block. Any heat generated inside the chambers is quickly conducted out to avoid temperature rise inside the chambers. This heat flux is measured by the heat sink sensor in contrast to the inert reference block. A separate calibration equation for each channel is used to calculate heat flux (thermal power) using the voltage output of heat sink sensors. Then, the heat flux is normalized to the mass of cementitious materials in the specimen tested. The total heat generation can be calculated as the integrated heat flux over time.

Hydration of cementitious materials can be devided into five primary stages, as illustrated in Figure *3-1*. In the dissolution stage, the release of ions starts right after contact with water. C_3A hydration and ettringite formation (Aft phase) generate a lot of heat making the initial peak, which usually lasts less than 15 minutes after mixing time. Then, hydration reactions are followed in a dormant stage with a low heat flux.

The start of hydration of C_3S substantially increases heat liberation in the third stage. A 3D cement matrix is formed in this stage. By densifying the matrix, the state of the material gradually changes from plastic to a weak solid and then to a solid material which can bear stress resisting volume change, i.e. the solidification period. The fourth stage is a deceleration period in which a bump or shoulder might be visible, attributed to the conversion of ettringite to monosulphate (Aft to AFm phase). Hydration reactions continue over the last stage for an extended period of time.

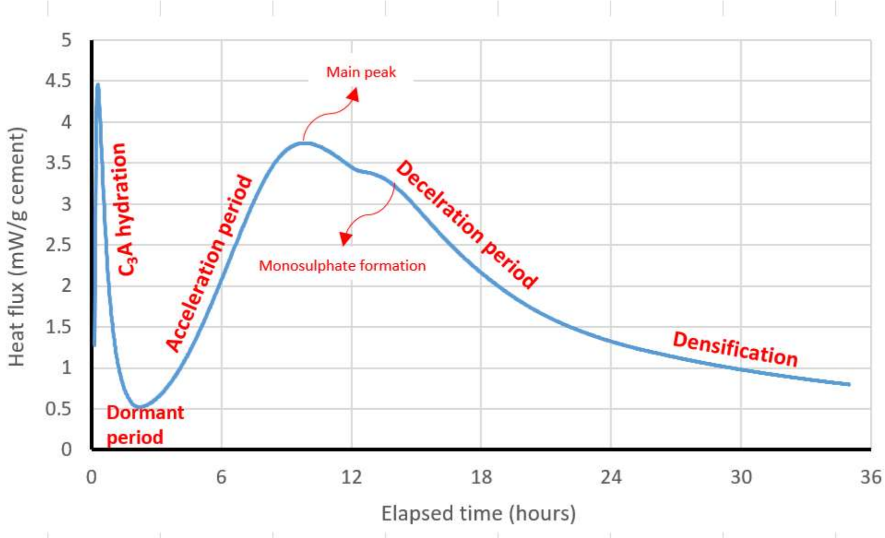

Figure 3-1- Different stages in heat flux with time during the hydration of cementitious materials

3.5.2. Pore water potential (PWP)

There are different methods available for evaluating capillary pressure in materials. Indirect estimation of capillary pressure by monitoring the moisture content of an embedded calibrated porous medium (ceramic, granular sand or a thin nylon film) is a common method used in soil physical studies [29,30]. Moisture content can be estimated by monitoring various physical properties of the medium like thermal conductivity, resistivity, permittivity or light transmission.

Another indirect method used in concrete science is to monitor RH inside a small sealed plastic tube with a Gore-Tex cap embedded in concrete [11]. **Error! Reference source not**

found. shows the nonlinear relationship between RH inside the tube and capillary pressure (matric and osmotic potential) in the concrete (assuming perfect wetting [31] and local equilibrium between vapor and water):

$$PWP = \frac{R.T}{V_m} \ln RH \qquad \text{Equation 1}$$

Where V_m is molar volume of pore solution, R is universal gas constant, T is temperature in Kelvin.

There are two main problems for using RH sensors to evaluate pore water potential in concrete. Early-age concrete is almost saturated and has a very high internal RH. The correlation between RH and PWP is very sensitive to any error in this range of measurement. In addition, most commercially available RH sensors do not have a good accuracy or are out of calibration in RH more than 90-95% [9]. That is why using RH sensors to monitor PWP results in a considerable error in wet conditions [30]. However, RH meters can be successfully used on higher PWP (200 kPa to 5 MPa), which makes it suitable for use in monitoring drying shrinkage [9].

In this study, a tensiometer, capillary pressure sensor system (CPSS), was used for direct measurements of PWP at the center of cylindrical concrete specimens with 15-cm diameter and 10-cm thickness. The specimens were kept uncovered in a room with controlled RH (30 ± 5%) and temperature (22.5 ± 2.5 °C).

Tensiometers usually consist of three main components; pressure transducer, connecting material and porous transition cap. The digital pressure transducer has a maximum range of 100 kPa at a resolution of 0.1 kPa. The tensiometer (syringe) is filled with deionized water to keep a hydraulic connection between the medium and pressure transducer. Transition cap is usually make-up of a porous ceramic or other materials with very fine pores making equilibrium pressure between the surrounding materials and connecting materials inside the sensor. In this study, a disposable plastic syringe with a very fine tip, filled with vacuumed deionized water, is used instead of a porous ceramic. The whole system is presented in Figure *3-2*.

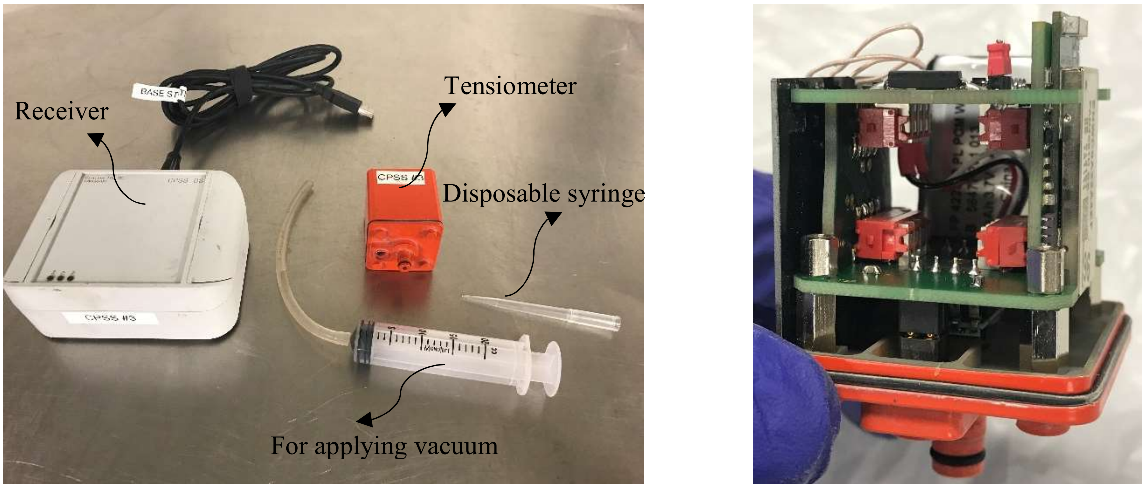

Figure 3-2- Tensiometer - capillary pressure sensor system (CPSS)

The main disadvantage of tensiometers is their limited working range. Most commercially available instruments can measure capillary pressure up to around 90 kPa [9]. The limitation is mainly attributed to maximum capillary pressure the system can tolerate before water vaporization and entering air bubbles into the tensiometer. It significantly drops the internal pressure of the transducer to that of the free atmospheric pressure, so the sensor is inoperative. The presence of unwanted air bubbles around the tip of tensiometer can also break the hydraulic connection and leave the tensiometer to be inoperative.

The literature represents that the main part of the volume instability in early-age concrete, vertical and horizontal shrinkage strain, occurs over time when capillary pressure is under 80 kPa

[2,32–34]. Therefore, tensiometers can be successfully used to monitor PWP development in early-age concrete materials.

3.5. Results and discussion

The results of isothermal calorimetry tests on mortar mixtures and PWP development in concrete mixtures are presented in the following sections.

3.6.1. Isothermal calorimetry

The results of isothermal calorimetry tests conducted on 15 different mortar mixtures are discussed below in three different categories.

- *Effect of W/C on hydration kinetics of mortars*

Figure *3-3* and Figure *3-4* illustrate the heat flux and heat generation of mortars with no LWFA and IC mortars, respectively. Mixtures with different W/C (0.3, 0.375, 0.45 and 0.525) were tested over the first two days. It is shown that decreasing W/C promotes hydration kinetics in mortars before the main peak in heat flux (acceleration stage). Mortars can be assumed to be solid and semi-saturated after this period. Moisture insufficiency in mortars with low W/C leads to a significant drop in heat flux after the main peak. That is why mortars with higher W/C generally have higher total heat generation. It is worth noting that the effect of increasing W/C on growing total heat generation at two-day age is decreased at higher W/C values. The reason is that the mixture has enough free moisture to continue hydration reactions at the rate determined by the type of cementitious materials.

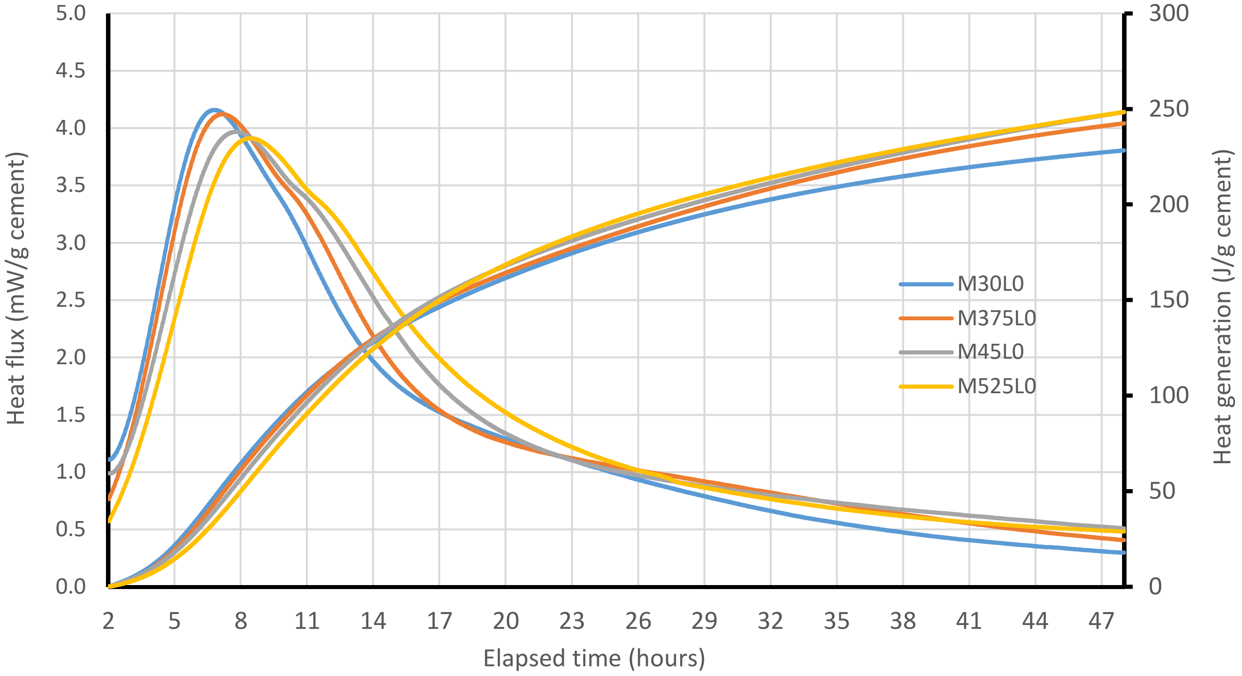

Figure 3-3- Effect of W/C on heat generation of mortars with no LWFA

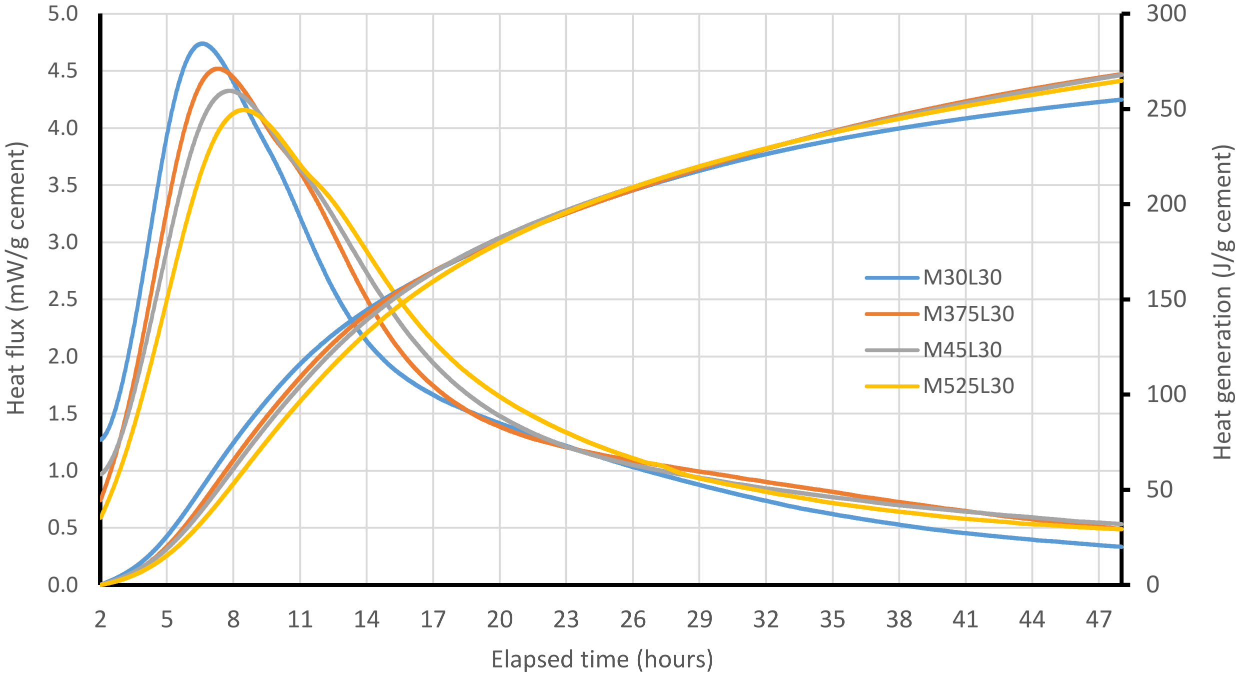

Figure 3-4- Effect of W/C on heat generation of IC mortars

Figure *3-5* shows the differences in heat generated in mortars with and without LWFA. The positive heat values mean higher heat generation for IC mixtures. It indicates the benefit of substituting 30% of fine aggregate with pre-saturated LWFA to improve the kinetics of cement hydration. Releasing IC water after solidification promotes extended hydration of portland cement. It can be particularly seen that IC is more effective in promoting hydration reactions of mortars with low W/C. The reason can be attributed to making up the main portion of the decrease in the rate of hydration reactions in this mortars because of moisture insufficiency.

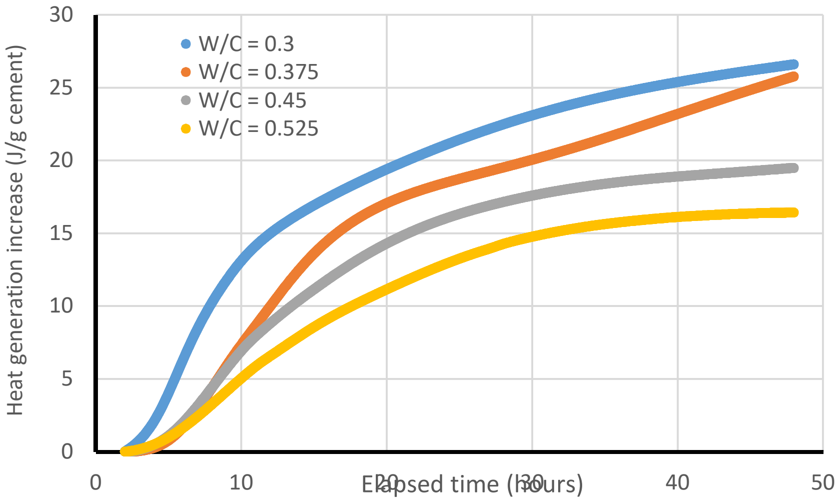

Figure 3-5- Effect of W/C on difference of heat generation between mortars with and without LWFA

- *Effect of LWFA substitutions on hydration kinetics of IC mortars*

LWFA is usually more expensive than fine aggregate. Also, substituting a high volume of LWFA may result in some side effects on compressive strength of the mixture. Therefore, it is important to investigate the optimum value for LWFA substitution. The optimum value can be defined as the LWFA substitution percentage which makes the most significant improvement on the tested property of mixture.

Figure *3-6* demonstrates improvement in hydration kinetics of mortars incorporating different LWFA substitutions. It shows that providing 0.034, 0.067 and 0.101 ICW/CMs by substituting 10, 20 and 30% LWFA, respectively, helps considerably increase both heat flux and total heat generation of the mixtures. However, substituting 50% LWFA (0.169 ICW/CMs) does not make any significant improvement in the first two days. Therefore, it can be concluded that 0.1 ICW/CMs (i.e. 30% LWFA substitution in this study) is the optimum value for the investigated mixtures.

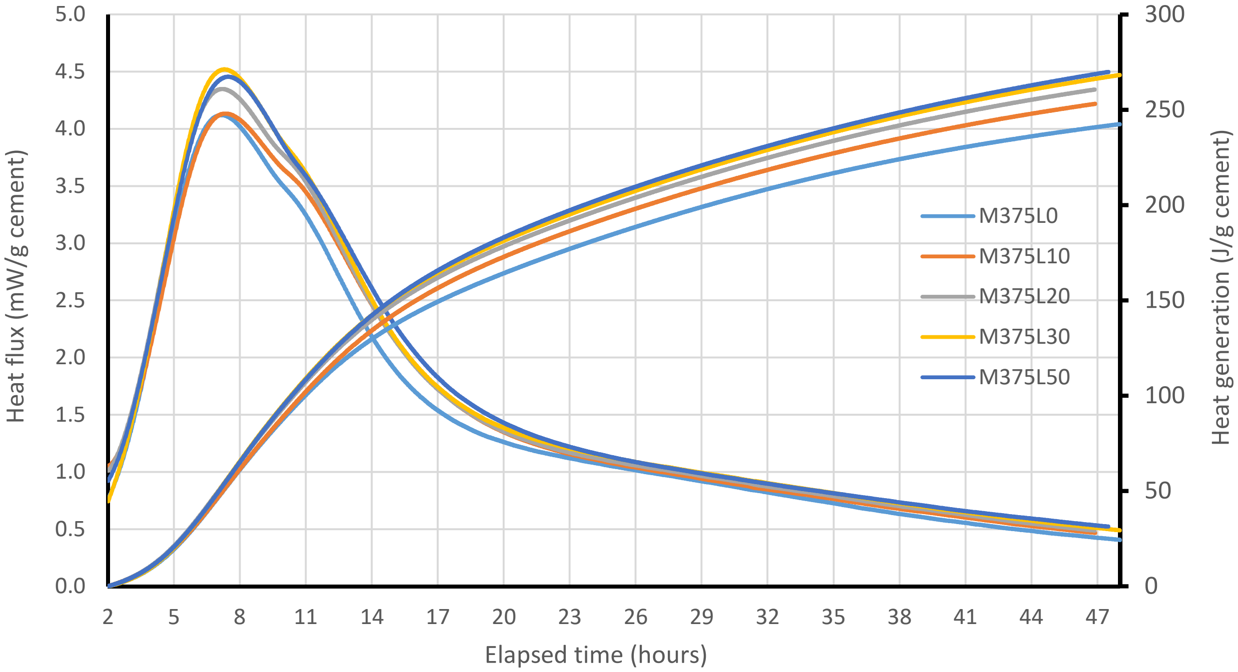

Figure 3-6- Effect of LWFA substitutions on heat generation of IC mortars

- *Effect of incorporating SCMs on hydration kinetics of mortars*

SF and FA are common pozzolanic materials substituted in concrete mixtures. SF is a by-product of the ferrosilicon smelting process. It consists of about 95% SiO_2 and also has a very high specific surface, around 20000 m^2/kg. Therefore, incorporating SF significantly increases the rate of hydration reactions and consequently heat flux and total heat generation of the mixture. Providing extra IC water can effectively help extend the hydration reactions and increase heat flux.

FA is extracted from the exhaust gases of furnaces fired by pulverized coal. Because of its spherical shape, it can help to increase the workability of the mixtures, but it can also act as a retarder and delays hydration reactions. In addition, high replacement ratio of portland cement with FA makes a dilution effect and decreases total heat generation.

Figure *3-7* shows that incorporation of 7.5% SF significantly increases the main peak of heat flux, while incorporation of 20% FA decreases the main peak and postpones the associated time. IC is beneficial in promoting hydration kinetics of all mixtures. However, the improvement is more pronounced for the mixtures incorporating SF, while it is less marked mixtures incorporating FA.

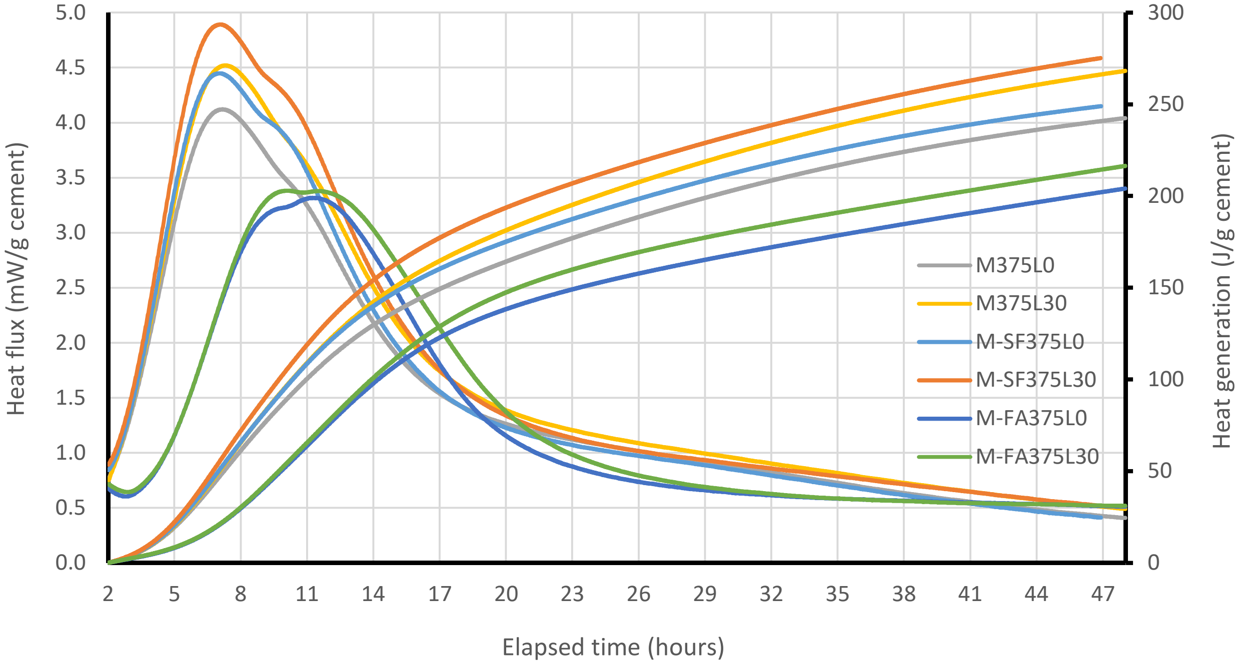

Figure 3-7- Effect of SCM incorporation on heat generation

3.6.2. Pore water potential (PWP)

PWP development can be monitored by the time of air-entry using tensiometers. Air-entry time is defined as the time when air bubbles enter the tensiometer, so the internal pressure in tensiometer is dropped, and it is not operative anymore. Air-entry time and associated capillary pressure are dependent on properties of the porous cap (the maximum capillary PWP can be measured is usually 80-100 kPa), air content of material and temperature. Therefore, air-entry time is not a property of concrete material, but a limitation in the measurement method. The following subsections discuss the effects of W/C, LWFA substitution and SCM incorporation on PWP development.

- *Effect of W/C on PWP development*

Error! Reference source not found. demonstrates PWP development in the concrete mixtures including different W/CMs (0.35, 0.42 and 0.5) with and without LWFA. The results show that the time of initiation of PWP development is substantially controlled by W/C, but the rate of PWP development is not significantly dependent on W/C variation.

PWP starts to develop after solidification when the cement matrix starts to resist volume change. Accelerated development of 3D cement matrix and higher strength development in concrete mixtures with low W/C result in decreasing the time of initiation of PWP development.

However, the rate of PWP development is dependent on the ratio of moisture loss to initial moisture content after solidification, by volume $\left(\frac{\Delta V}{V}\right)$. The rate of moisture loss (the rate of water consumption or evaporation) changes for the mixtures with different W/C (initial moisture content) in a way that rate of PWP development $\left(\frac{\Delta V}{V}\right)$ is almost constant. In other words, the rate of evaporation and the rate of water consumption in hydration reactions (deceleration stage) decreases for the mixtures with lower moisture content.

In addition, it is demonstrated that IC is efficient in providing IC water to suppress PWP development in the concrete mixtures with low W/CMs Figure *3-8*. shows that PWP development for the mixtures with 0.35 and 0.42 W/CMs are significantly postponed, while the improvement for the mixture with 0.5 W/CMs is negligible. The reason is that mixtures with high W/CMs have enough initial moisture content to keep PWP development low, so IC water is not lost from LWFA at early ages.

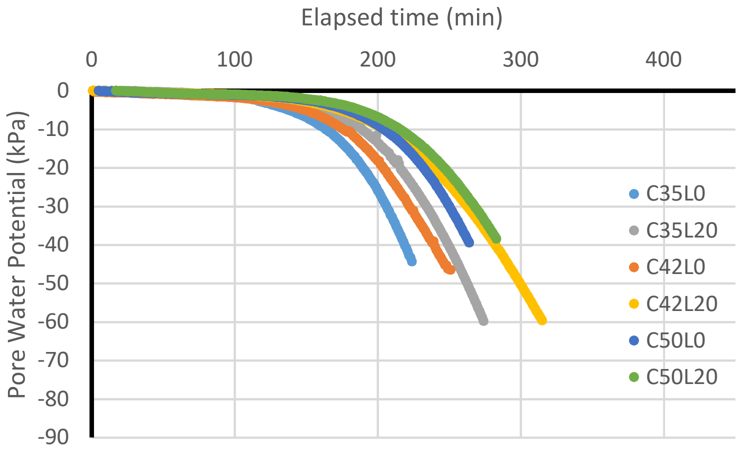

Figure 3-8- Effect of W/C and IC on PWP development

- *Effect of LWFA substitution on PWP development*

Error! Reference source not found. demonstrates that LWFA substitution postpones PWP development. Substitution of a higher percentage of fine aggregate with LWFA provides more IC water for the mixtures to suppress PWP development. In addition, Figure *3-9* shows that increasing ICW/CMs up to 8% is very effective in postponing PWP development. However, the improvement by further increases in LWFA substitution is not substantial. It is worth noting that this optimum value is also dependent on the mixture temperature, chemical admixtures and cementitious materials used, so it should be separately studied for different mixture proportions.

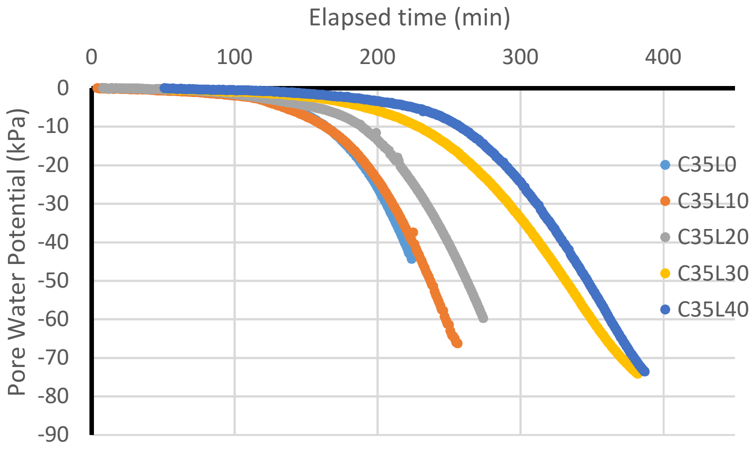

Figure 3-9- Effect of LWFA substitution on PWP development

- *Effect of incorporating SCMs on PWP development*

Incorporation of SCMs can significantly change both chemical composition and physical properties of concrete mixtures. Therefore, PWP development in the mixture is also substantially affected by the use of SCMs. The results presented in Figure *3-10* shows that incorporating 7.5% SF in concrete mixtures extensively accelerates PWP development. SF, an active pozzolan, increases the rate of hydration of portland cement because of the nucleation effect, and it makes the cement matrix denser, decreases the size of capillary pores and increases the internal specific surface area. These result in an increased PWP for a matrix with constant volumetric water content [3].

The results also illustrate the effectiveness of IC in suppressing PWP development in SF contained mixtures. A 20% LWFA substitution (providing around 5% ICW/CMs) almost compensates the effect of an SF incorporation on accelerating PWP development. Further increases in LWFA substitutions to 40% (10% ICW/CMs) are still very efficient in postponing PWP developments in the concrete mixture.

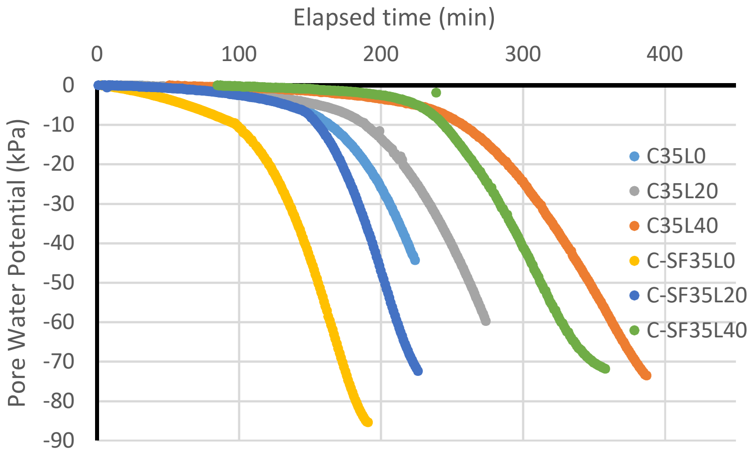

Figure 3-10- Effect of SF substitution on PWP development

Unlike SF, FA Class C is not very reactive at very early ages. It actually changes the chemical composition of pore solution and acts more like a retarder in decreasing the rate of hydration reactions in concrete materials. Figure *3-11* shows the effect of a 20% incorporation of FA on postponing PWP development. Decelerated PWP development in FA contained concrete mixtures underemphasizes the benefit of IC in suppressing PWP. In fact, decreased PWP development results in releasing lower IC water during the early ages.

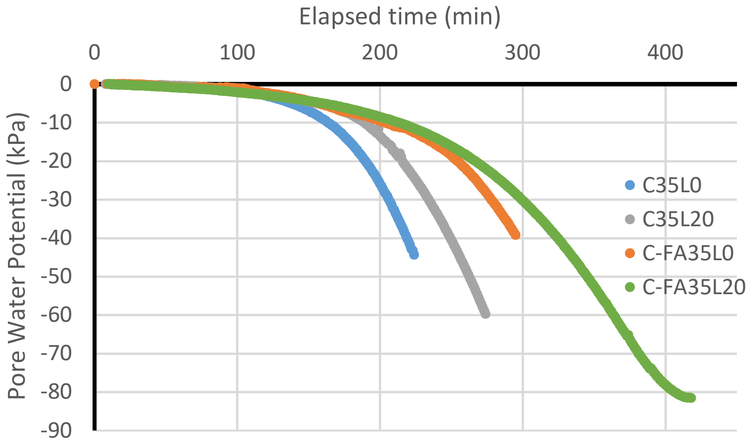

Figure 3-11- Effect of FA substitution on PWP development

3.6. Conclusion

The main findings and conclusions of this study are as follow:

- Increasing W/C decreases heat flux and kinetics of cement hydration. However, it leads to a higher total heat generation in both control and IC mortars.
- Releasing IC water starts before the main peak of heat flux in isothermal calorimetry tests and results in increased heat flux over the following hydration stages.
- The effectiveness of IC to increase heat generation is more pronounced for the mortar mixtures with low W/C.
- Increasing IC water/CMs to more than 0.10 does not significantly promote heat flux or heat generation.
- IC efficiently increases hydration kinetics of the SF incorporated mortars.
- Capillary pore water potential development is significantly postponed by increasing W/C or providing IC water. IC is particularly beneficial for low W/C concrete mixtures.
- Increasing IC water/CMs can significantly intensify the benefits of IC in postponing capillary pressure development. However, the improvement associated with IC water/CMs higher than 0.08 is negligible.
- Incorporating SF significantly accelerates capillary pore water potential development. IC is very efficient in suppressing this increase.
- Incorporating 20% of FA decreases heat flux and water consumption at early ages. Therefore, it postpones capillary pore water potential development.

3.7. Acknowledgments

Authors gratefully appreciate the financial support by Iowa and Ohio departments of transportation. The results and conclusions do not reflect the opinion of the sponsors. Authors would also like to appreciate the support of Arcosa Lightweight and Euclid Chemical Companies for providing Lightweight fine aggregate and chemical admixture, respectively. Cooperation and help of the employees of Portland Cement Concrete Research Laboratory (PCC lab) at Iowa State University were crucial for this research and gratefully treasured.

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CHAPTER 4. EFFECT OF EXPOSURE CONDITIONS AND INTERNAL CURING ON HYDRATION AND PORE WATER POTENTIAL DEVELOPMENT IN CEMENT-BASED MATERIALS

A journal paper to submit to Journal of Materials in Civil Engineering (ASCE)

Payam Vosoughi[1], Peter Taylor[2], Robert Horton[3], Meysam Najimi[4], Kejin Wang[5]

4.1. Abstract:

Moisture availability is important for ongoing hydration reactions and controlling capillary pore water potential (PWP) development in cement-based mixtures. Harsh exposure conditions (such as low relative humidity, high temperature or high wind speed) or incorporating fine cementitious materials that result in accelerated PWP development may increase the mixture susceptibility to early-age shrinkage cracking. This study aims to investigate hydration kinetics, PWP and electrical conductivity development in cement pastes and mortar mixtures with various water-to-cement ratios (from 0.25 to 0.4), silica fume substitution and internal curing in both sealed and harsh exposure conditions (ambient temperature from 10 to 35°C and relative humidity from 25 to 75%). The results indicate that although high ambient temperature and silica fume incorporation increase the rate of hydration reactions, moisture loss and PWP development

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are also substantially accelerated. The outcome of this study also showed the capability of internal curing using lightweight fine aggregate in extending hydration reactions and delaying PWP development. It is concluded that IC water provided by lightweight fine aggregate successfully mitigates PWP development in mixtures containing silica fume or exposing to low-relative humidity and high-temperature ambient environments.

Keywords: Isothermal calorimetry, Capillary pore water potential, Ambient curing conditions, Electrical conductivity, Lightweight fine aggregate

4.2. Introduction

Availability of free water is imperative for ongoing hydration of cementitious materials with a proper rate [1]. In addition, moisture loss, consumed in hydration reactions or from evaporation from the free surface, results in considerable early-age shrinkage in cement-based materials [2,3], which increases cracking potential [4]. In order to find solutions for the mitigation of early-age cracking potential, it is essential to study mixture proportions and exposure condition parameters that mainly result in moisture insufficiency in early-age state.

There are three different types of water in cement-based materials; chemically bonded water in gel pores, near-field physically bonded water in interlayer spaces and very fine capillary pores, and free water (not absorbed) in capillary pores [5]. Due to their low potential, chemically and physically bonded water cannot properly participate in hydration reactions with cementitious materials. The role of free water in the capillary pores of cement-based materials is important because it is the portion of the total moisture which can participate in hydration reactions, evaporation at normal curing temperatures, and the transfer of ion charges.

Capillary pore water potential (PWP), the negative pressure in drying capillary pores due to the surface tension of pore solution, starts to significantly decrease when free water is taken out from capillary pores with 50 nm and smaller [6,7]. This physical procedure generates a capillary tension on early-age hardened cement matrix, which can be reduced by rewetting the capillary pores [8]. The magnitude of capillary PWP mainly depends on the effective size of capillary pores in the cement matrix and surface tension of the pore solution [7]. Increasing the degree of hydration [9,10], decreasing initial water-to-cement ratio (W/C), and using supplementary cementitious materials (SCMs) with fine particle size distribution and high surface area like silica fume are the main parameters which can significantly decrease the effective pore size of cement matrix and increase PWP at a constant volumetric moisture content. Chemical admixtures like shrinkage reducing agents can be successfully used to modify the chemical composition of pore solution and substantially decrease surface tension [11].

Exposure to the environment is an important condition that affects the rate of water evaporation from the free surface of the mixture resulting in PWP development. The rate of water evaporation from the surface of a normal concrete mixture is about half of that from the surface of free water [12]. Evaporation rate depends on the ambient temperature and relative humidity [13], wind speed, solar radiation and PWP at the mixture surface. There is a lack of information regarding the effect of exposure condition on increasing water evaporation, accelerating PWP development and decreasing the rate of hydration in cement-based mixtures.

An alternative method to mitigate moisture loss is internal curing which uniformly provides extra curing water to the whole volume of the cement matrix after solidification [14]. Lightweight fine aggregate (LWFA) is the common internal curing water carrier used in North America [15]. Pre-saturated porous LWFA is mixed with and uniformly distributed through the mixture. When moisture loss results in capillary PWP development in the cement matrix, free water is taken out of the larger pores in LWFA, which leads to rewetting and suppressing of PWP in the matrix. There is a lack of information on the performance of internal curing to rewet capillary pores and suppress PWP development in harsh exposure conditions (low relative humidity and high temperature).

The aim of this study is to investigate the hydration kinetics and PWP development in cement-based mixtures with various W/C (from 0.25 to 0.4) and LWFA substitutions (from 10 to 50%) as well as 5% SF incorporation in harsh exposure conditions, including three levels of ambient temperature (from 10 to 35°C) and relative humidity (from 25 to 75%).

4.3. Materials and mixture designs

The chemical compositions of portland cement Type I (ASTM C150) and densified silica fume (ASTM C1240) used in this study, are presented in Table *4-1*. The main components of portland cement were calculated using the modified Bogue formula [16,17] based on the chemical composition. The calculated values are presented and compared to the normal ranges in Table *4-2*. Tap water from the municipal network (Ames, IA) was used for mixing.

Table 4-1- Chemical composition of cementitious materials

	Portland cement	**Densified silica fume (SF)**
SiO_2	20	94.3
Al_2O_3	4.42	0.09
Fe_2O_3	2.81	0.1
SO_3	2.81	0.1
CaO	63.5	0.3
MgO	2.06	0.43
K_2O	0.52	0.83
Na_2O	0.21	0.27
Total Alkali (Na_2O+0.658 K_2O)	0.55	0.82
P2O5	0.06	-
TiO2	0.24	-
BaO	0	-
SrO	0.09	-
Mn2O3	0.06	-
LOI	2.82	2.19

Table 4-2- The main components of portland cement (% by mass)

	Abbreviation	**Calculated based on Bogue formula** [16]	**Normal range** [1]
Tricalcium silicate	C3S	64.78	60-73
Dicalcium silicate	C2S	8.47	8-30
Tricalcium aluminate	C3A	6.96	5-12
Tetracalcium silicate	C4AF	8.55	8-16

A well-graded limestone fine aggregate with fineness modulus of 2.97, specific gravity of 2.65 and one-day saturated surface dried (SSD) moisture absorption of 1.3% was used, meeting the criteria of ASTM C33. In internally cured mortars, a portion of fine aggregate was substituted for the same volume of expanded clay lightweight fine aggregate (Provided by Arcosa, Alabama). Specific gravity and SSD moisture absorption of lightweight fine aggregate were 1.23 and 27.1%, respectively. Water release of LWFA at 93% RH was measured as 91.7% of SSD moisture absorption [18].

Mixture proportions of 10 cement pastes and 7 mortar mixtures tested in this study are presented in Table *4-3* and Table *4-4*, respectively. The ratio of internal curing water to cementitious materials (ICW/CMs) is also provided for all IC mixtures in Table *4-4*. Both pastes and mortars were mixed following ASTM C305 at 23±2°C using a laboratory Hobart mixer. Regarding the mixtures for the isothermal calorimetry test, raw materials and the bowl and paddle of the mixer were preconditioned at the test temperature (10, 22.5 and 35°C) several hours before the mixing time.

Table 4-3- Mixture proportion of cement pastes

	P250	**P275**	**P300**	**P325**	**P375**	**P400**	**PSF5**	**PSF75**	**PSF10**	**PSF15**
W/C	0.25	0.275	0.3	0.325	0.375	0.4	0.325	0.325	0.325	0.325
SF (%)	-	-	-	-	-	-	5	7.5	10	15

Table 4-4- Mixture proportion of mortars

	W/CMs	**S/B**	**SF substitution (%)**	**LWFA**	
				Substitution (%)	**ICW/CMs [a]**
M375L0	0.375	2.75	-	-	0
M375L10	0.375	2.75	-	10	0.034
M375L20	0.375	2.75	-	20	0.067
M375L30	0.375	2.75	-	30	0.101
M375L50	0.375	2.75	-	50	0.169
M-SF375L0	0.375	2.75	5	-	0
M-SF375L30	0.375	2.75	5	30	0.107

[a] The ratio of IC water to cementitious materials

Table *4-5* demonstrates five different environmental exposure conditions in which PWP and conductivity of mortar mixtures were tested.

Table 4-5- Ambient exposure conditions

	Ambient temperature (°C)	**Ambient relative humidity (%)**
Ex1	22.5	25
Ex2	22.5	50
Ex3	22.5	75
Ex4	10	25
Ex5	35	25

4.4. Experimental methods

An environmental chamber was used to control ambient RH and temperature as explained in Table *4-5*. Experimental tests including isothermal calorimetry, PWP and electrical conductivity are explained below in detail.

4.5.1. Isothermal calorimetry test

The purpose of calorimetry testing is to investigate the hydration kinetics of the cementitious materials. Calorimetry tests can be divided into three categories: isothermal, semi-adiabatic and adiabatic. In isothermal calorimetry tests, heat conduction is measured, while in the other tests the temperature rise is monitored. Isothermal calorimetry tests require advanced equipment, but they provide more detailed information than semi-adiabatic calorimetry test which actually measure the integral of the rate of heat evolution [19]. In this study, the isothermal calorimetry test is performed following ASTM C1679 [20] at an isothermal temperature of 22.5 ± 0.1 °C.

The isothermal calorimetry device consists of a thermally isolated box with internal constant temperature, eight small chambers in an internal insulated box (except the bottom side), a heat sink sensor under each chamber and a reference 129-gram aluminum block. Any heat generated inside the chambers is conducted out to avoid temperature rise inside the chambers. This heat flux is measured by the heat sink sensor in contrast to the inert reference block. A separate calibration equation for each channel is used to calculate heat flux (thermal power) using the voltage output of heat sink sensors. Then, the heat flux is normalized to the mass of cementitious materials in the specimen tested. The total heat generation can be calculated as the integrated heat flux over time.

Hydration of cementitious materials can be divided into five primary stages, as illustrated in Figure *4-1*. In the dissolution stage, the release of ions starts right after contact with water. C3A hydration and ettringite formation (Aft phase) generate heat making the initial peak, which usually lasts less than 15 minutes after mixing time. Then, hydration reactions continue in a dormant stage with a low heat flux.

The start of hydration of C3S substantially increases heat liberation in the third stage. A 3D cement matrix is formed in this stage. By densifying the matrix, the state of the material gradually changes from plastic to a weak solid and then to a solid material which can bear stress resisting volume change, i.e. the solidification period. The fourth stage is a deceleration period in which a bump or shoulder might be visible, attributed to the conversion of ettringite to monosulphate (Aft to AFm phase). Hydration reactions continue over the last stage for an extended period of time.

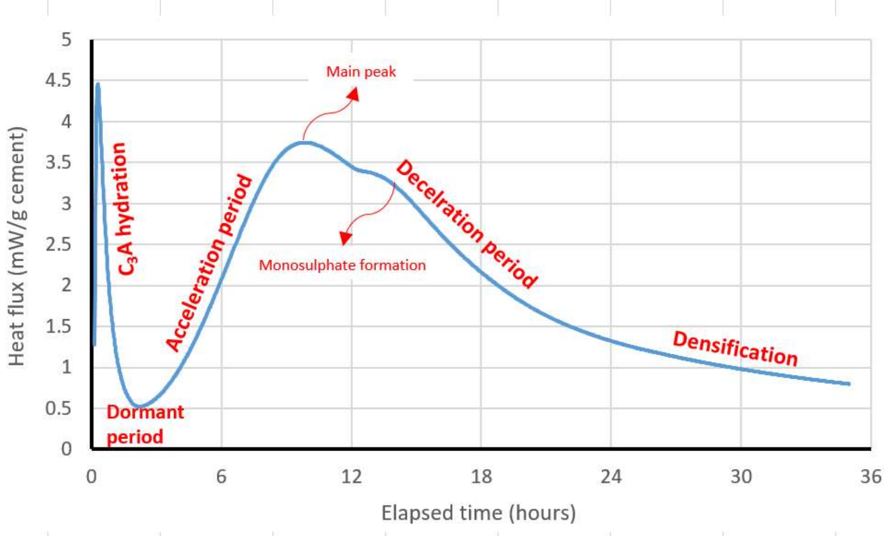

Figure 4-1- Different stages in heat flux with time during the hydration of cementitious materials

4.5.2. Pore water potential (PWP)

There are various methods available for determining capillary pressure in materials. Indirect estimation of capillary pressure by monitoring the moisture content of an embedded calibrated porous medium (ceramic, granular sand or a thin nylon film) is a common method used in soil physical studies [21,22]. Moisture content can be estimated by monitoring various physical properties of the medium like thermal conductivity, resistivity, permittivity or light transmission.

Another indirect method used in concrete materials science is to monitor RH inside a small sealed plastic tube with a Gore-Tex cap embedded in the mixture [7]. **Error! Reference source not found.** shows the nonlinear relationship between RH inside the tube and capillary pressure in the mixture (assuming perfect wetting [23] and local equilibrium between water vapor and liquid water):

$$PWP = \frac{R.T}{V_m} \ln RH \qquad \text{Equation 1}$$

Where V_m is molar volume of pore solution, R is universal gas constant, T is temperature in Kelvin.

There are two main problems when using RH sensors to evaluate pore water potential in cement-based materials. Early-age mixtures are almost saturated and have a very high internal RH. The correlation between RH and PWP is very sensitive to any error in this range of measurement. In addition, most commercially available RH sensors do not have a good accuracy or are out of calibration in RH more than 90-95% [24]. That is why using RH sensors to monitor PWP results in a considerable error in wet conditions [22]. However, RH meters can be successfully used on higher PWP (200 kPa to 5 MPa), which makes it suitable for use in monitoring drying shrinkage [24].

In this study, a tensiometer, capillary pressure sensor system (CPSS), was used to make direct measurements of PWP at two depths (1.25 and 5 cm) in cylindrical mortar specimens with 15-cm diameter and 10-cm depth. The specimens were kept uncovered in an environmental chamber with controlled ambient RH and temperature as explained in Table *4-5*.

Tensiometers usually consist of three main components; pressure transducer, connecting material and porous transition cap. The digital pressure transducer provides a maximum range of 100 kPa at a resolution of 0.1 kPa. The tensiometer (syringe) is filled with deionized water to keep a hydraulic connection between the medium and the pressure transducer. The transition cap is usually made of porous ceramic or other materials with very fine pores providing hydraulic connection between the surrounding materials and the connecting materials inside the sensor. In this study, a disposable plastic syringe with a very fine tip, filled with degassed deionized water, is used instead of a porous ceramic. The whole system is presented in Figure 4-2.

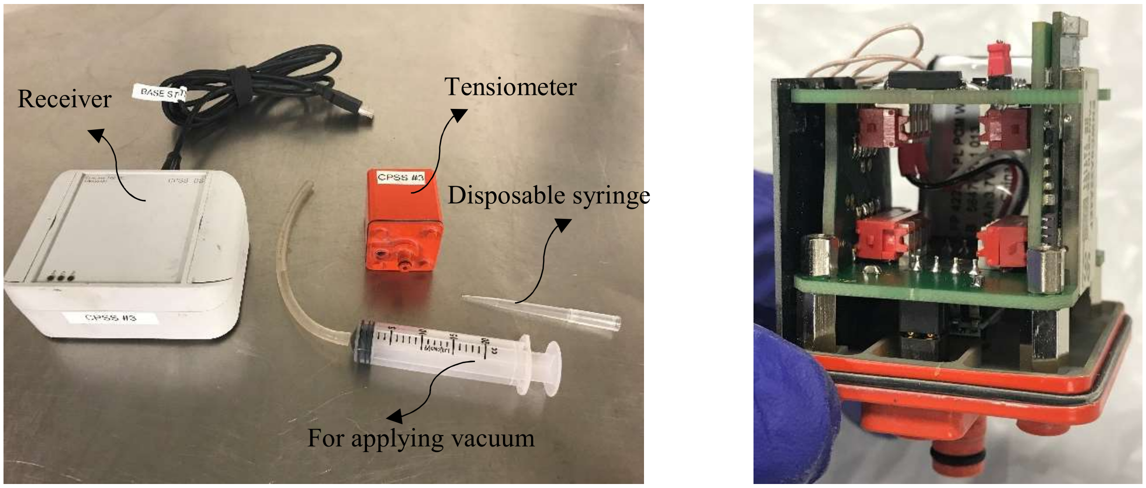

Figure 4-2- Tensiometer - capillary pressure sensor system (CPSS)

The main disadvantage of tensiometers is their limited working range. Most commercially available instruments can measure capillary pressure down to 90 kPa [24]. The limitation is partly attributed to the maximum capillary pressure the transition cap can tolerate before air bubbles enter into the tensiometer. Once air enters, the internal pressure increases to that of the free atmospheric pressure, so the sensor is inoperative. The presence of unwanted air bubbles around the tip of tensiometer can also break the hydraulic connection of the sensor to the surrounding material and the tensiometer becomes inoperative.

The literature represents that the main part of the volume instability in early-age cement-based mixtures, vertical and horizontal shrinkage strain, occurs over time when capillary pressure is greater than 80 kPa [3,8,25,26]. Therefore, tensiometers can be successfully used to monitor PWP development in early-age cement-based materials.

4.5.3. Electrical conductivity

Cement-based mixtures are composite materials consisting of aggregate, pore solution, and air voids. However, due to the negligible electrical conductivity of aggregate and air voids, that of mixtures mainly depends on electrical conductivity and connectivity of the pore solution. The electrical conductivity of the pore solution mainly depends on temperature, type, and concentration of ions and frequency of electrical measurement. In this study, electrical conductivity measurements are temperature corrected to 25°C [27]. Also, the results are normalized to the peak value to disregard the variation of ionic concentration in the pore solution of mortars with the same cementitious materials. Electrical conductivity was measured using a two-probe method (with a distance of 10 mm) and direct current (DC) with an accuracy of 0.01 dS/m. Due to the short measurement time, the polarization effect is negligible. The measurement was performed at the center of cylindrical specimens with 15 cm diameter and 10 cm depth.

Chemically and physically bonded pore solution cannot participate in the transition of ionic charges. Therefore, free pore solution in connected capillary pores is the most electrically conductive part in cement-based mixtures. Formation of dense cement matrix decreases the effective capillary pore size and increases bonded water, so the electrical conductivity of a mixture gradually drops during hydration reactions. Moisture loss from capillary pores, starting from larger pores and free water, results in partially saturated pores and accelerates this reduction over time.

4.5. Results and discussion

The results of isothermal calorimetry, PWP and electrical conductivity tests are presented and discussed in the following sections.

4.6.1. Isothermal calorimetry

The effects of temperature variation, LWFA substitution and silica fume incorporation on hydration kinetics of cement pastes and mortar mixtures are discussed in the following subsections:

- *Effect of temperature variation*

Figure *4-3* and Figure *4-4* demonstrate the effect of increased and decreased temperature on hydration kinetics of a cement past with 0.325 W/C and a mortar mixture with 0.375 W/C. The results show that increased temperature has a substantial acceleration effect on heat flux and rate of hydration, so the time associated with the main peak is decreased. In addition, the total heat generation is increased although the difference with that of control temperature (22.5°C) decreases over time. This indicates that increasing temperature leads to an advanced strength development in the sealed condition.

Although hydration reactions of cementitious materials are exothermic, the results show that decreased temperature significantly suppresses hydration reactions and heat flux. The main peak of heat flux is difficult to be determined, but it is delayed. Total heat generation is also significantly decreased, so it can be concluded that strength development is also delayed.

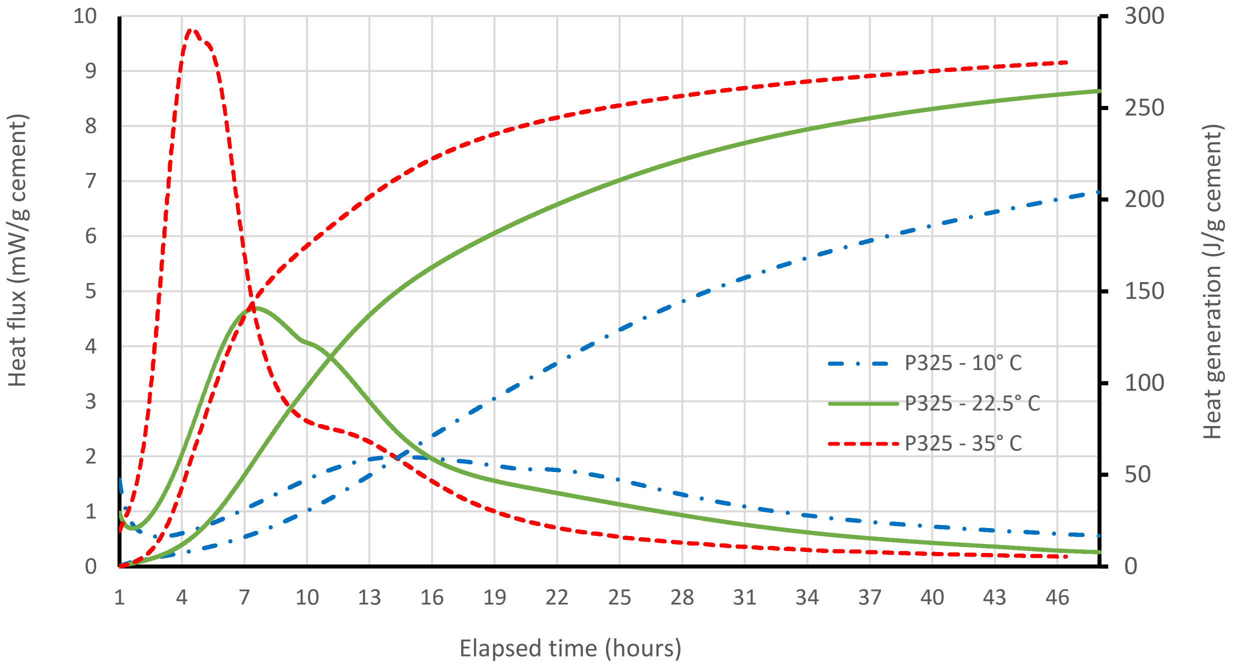

Figure 4-3- Effect of temperature variation on hydration kinetics of cement paste

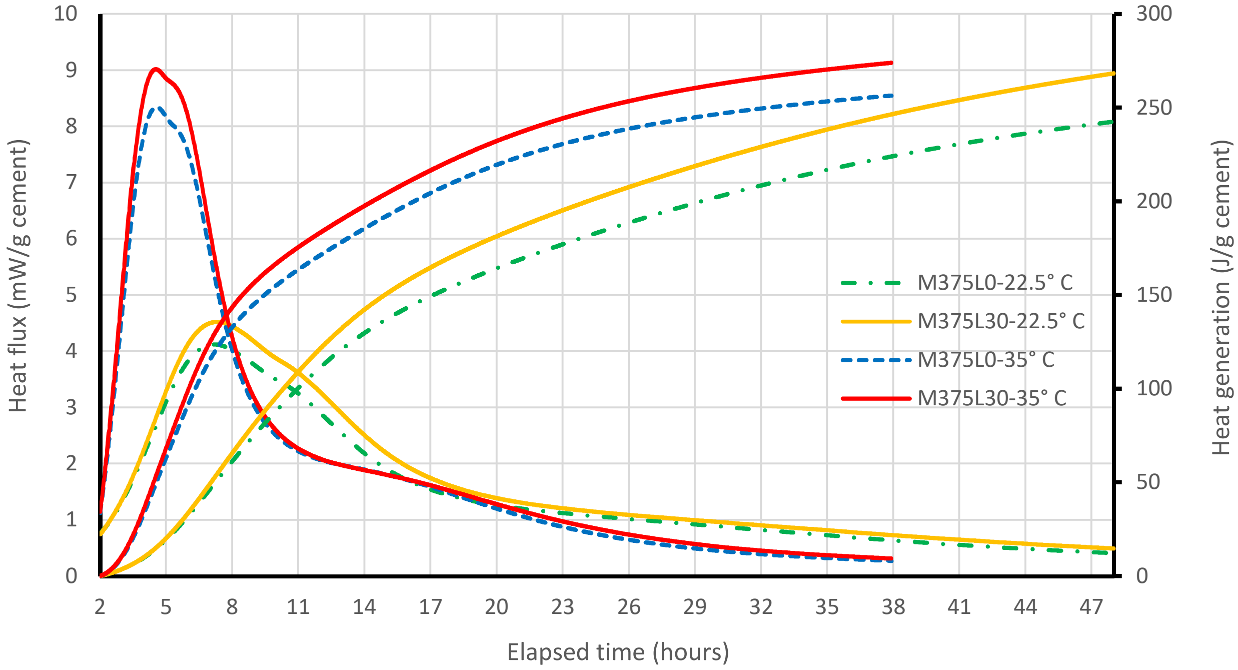

Figure 4-4- Effect of temperature rise on hydration kinetics of mortars

- *Effect of LWFA substitution*

Substitution of fine aggregate with porous pre-saturated LWFA does not have a significant effect on fresh properties of mixtures, despite a slight decrease in workability due to the rough texture of LWFA. After solidification and formation of a 3D cement matrix which can resist volume change, capillary PWP starts to develop because of moisture consumption during the hydration reactions. As the capillary pressure develops, IC water come out of the LWFA, so the rate of hydration reactions and the heat flux are increased by providing extra water. Increasing the substitution percentage increases the provided IC water to the mixture, and the effect of extended hydration is intensified. The results presented in Figure *4-5* show that not only the heat flux increased over the deceleration period, but also the total heat generation at 2-day age is improved by increasing LWFA substitution. However, it also indicates that substituting 50% LWFA makes a negligible improvement in hydration kinetics compared with that of 30% substitution. It can be concluded that a 30% substitution is the optimum value for the investigated mixture (10% ICW/CMs), and extra IC water is not effective for increasing hydration at the 2-day age.

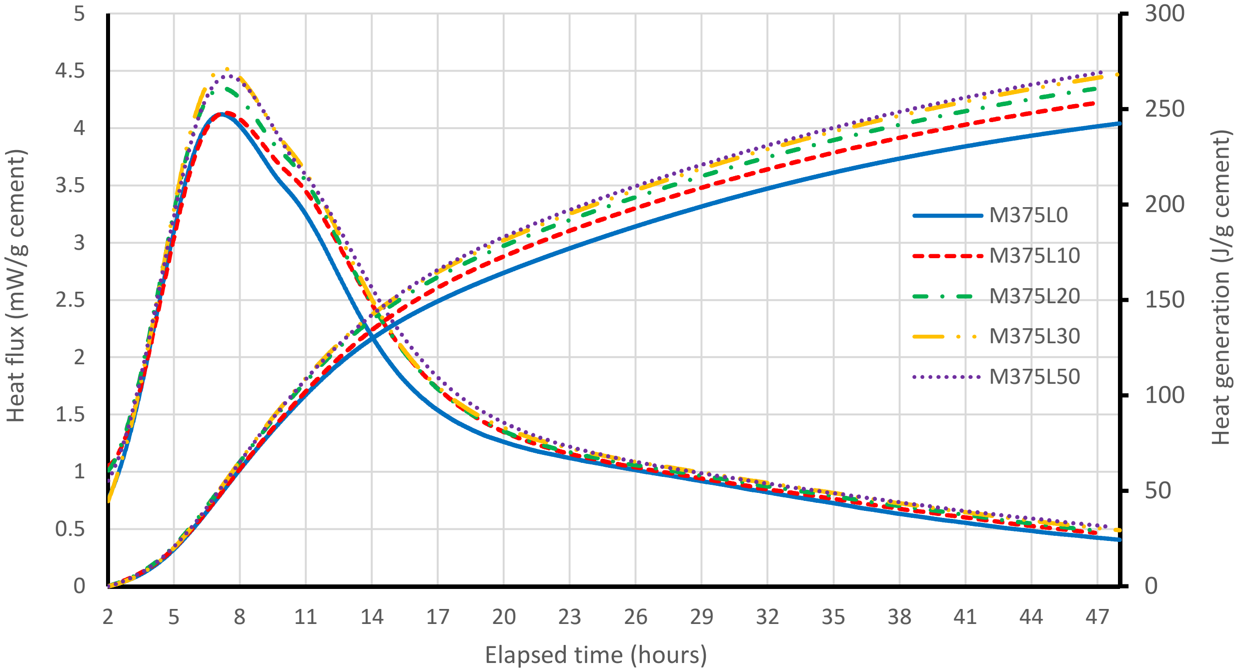

Figure 4-5- Effect of different LWFA substitutions on hydration kinetics

- *Effect of silica fume incorporation*

Silica fume is a by-product of the ferrosilicon smelting process. It consists of about 95% amorphous SiO_2 with a very high specific surface area, around 20000 m^2/kg. Its very low bulk density causes difficulties in transportation, so silica fume is usually densified. However, the weak connection between particles is easily broken by proper mechanical mixing.

Error! Reference source not found. shows that incorporation of silica fume increases heat flux of both mortar mixtures, and the time associated with the main peak is also slightly decreased. In addition, total heat generation is increased for the mixtures incorporating silica fume, which means that strength development is accelerated by the incorporation of silica fume in the mixtures. Incorporation of silica fume not only accelerates hydration reactions because of its strong pozzolanic properties, but also accelerates the rate of hydration of portland cement, because of the nucleation effect of silica fume.

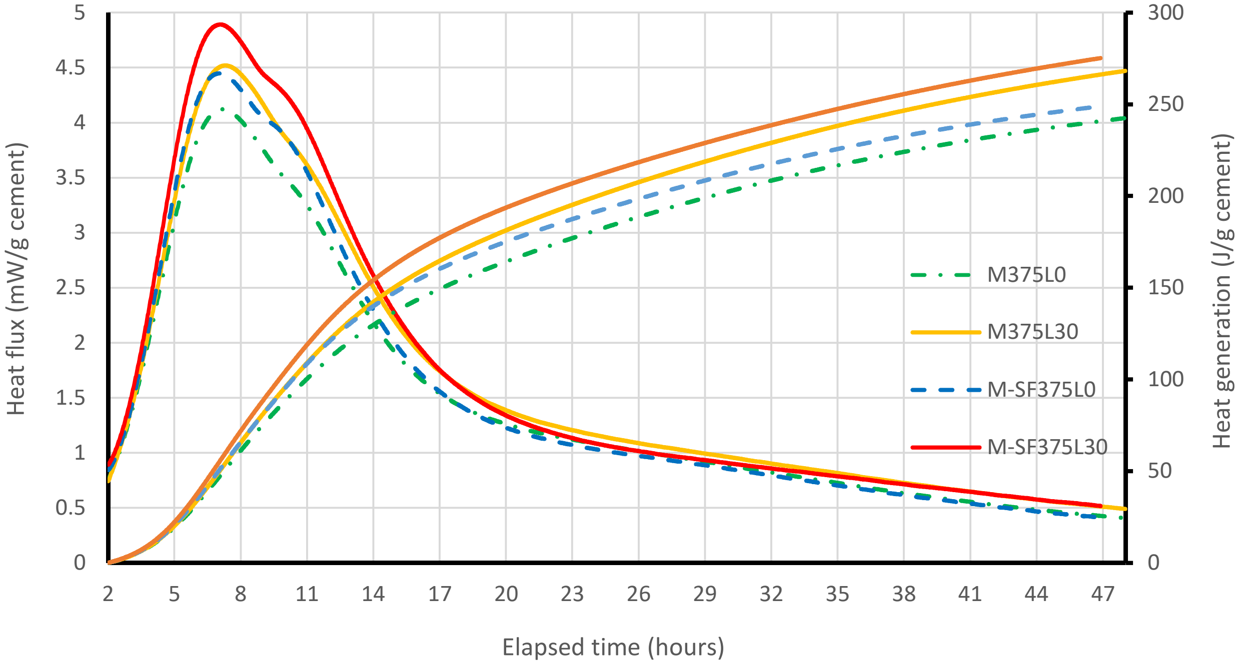

Figure 4-6- Effect of SF incorporation on hydration kinetics of mortars

4.6.2. Pore water potential (PWP)

The effects of water-to-cement ratio, silica fume incorporation and exposure condition on PWP development in cement pastes and mortar mixtures are discussed separately in the following subsections.

- *Effect of W/C on PWP development*

Figure *4-7* illustrates PWP development in six cement pastes with different W/C from 0.25 to 0.4 in a sealed condition at 23±2°C. It is shown that increasing W/C delays PWP development. It is also worth noting that visible bleeding occurred when testing cement pastes with 0.375 and 0.4 W/C. Bleeding decreases the initial W/C in the mixtures and provides extra water for the hardened cement matrix, which decreases the rate of PWP development.

Decreasing the W/C ratio increases ionic concentration and precipitation of hydration products, while increases the initial rate of hydration reactions at the acceleration stage.

Therefore, solidification, the time when the matrix starts resisting volume shrinkage, occurs at an earlier age. In addition to increase in moisture consumption during hydration reactions, mixtures with lower W/C have lower initial moisture available. Therefore, capillary PWP development, which is due to the ratio of moisture loss to initial moisture $\left(\frac{\Delta V}{V}\right)$, is accelerated for the mixtures with low W/C.

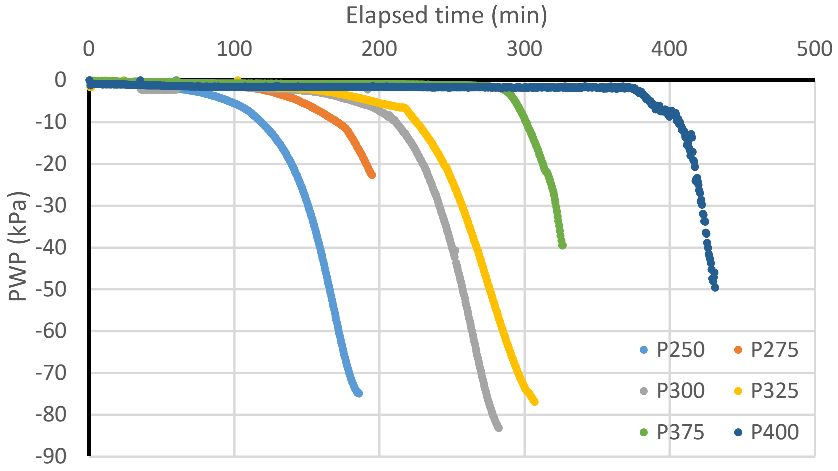

Figure 4-7- Effect of W/C on PWP development in cement pastes

- *Effect of silica fume incorporation on PWP development*

Figure *4-8* illustrates PWP development in cement pastes with 0.325 W/C and different substitutions of silica fume. Tests can performed in a sealed condition at 23±2°C. The results show accelerated PWP development in mixtures with increasing silica fume incorporation.

Silica fume has strong pozzolanic properties and increases the rate of hydration reactions in cement paste. In addition, it increases the rate of hydration of portland cement, because of the nucleation effect. Therefore, incorporation of silica fume accelerates solidification in cement paste. Furthermore, incorporation of silica fume decreases the effective pore size of the matrix due to its very fine particle size distribution. Capillary PWP is directly dependent on the size of capillary pores, so PWP development accelerates in a mixture incorporated silica fume compared to that of matrix with the same moisture content, but no silica fume.

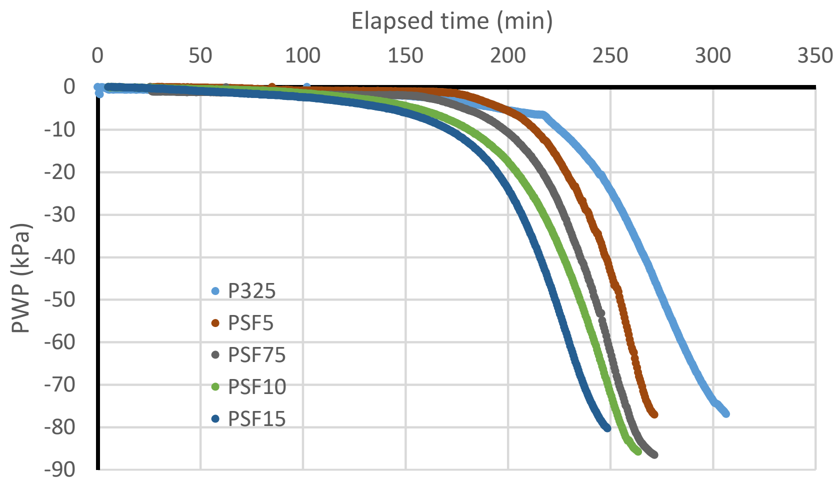

Figure 4-8- Effect of SF incorporation on PWP development in cement pastes

- *Effect of exposure condition on PWP development*

Figure *4-9* shows the effect of decreasing ambient relative humidity from 75 to 25% on accelerating PWP development in a mortar mixture with 0.375 W/C. The results show that low ambient relative humidity increases the moisture loss (water evaporation) from the mixture and accelerates PWP development at the 5-cm depth. It also demonstrates that decreasing ambient relative humidity from 75 to 50% substantially increases PWP development, while decreasing ambient relative humidity from 50 to 25% just slightly accelerates PWP development at the 5-cm depth.

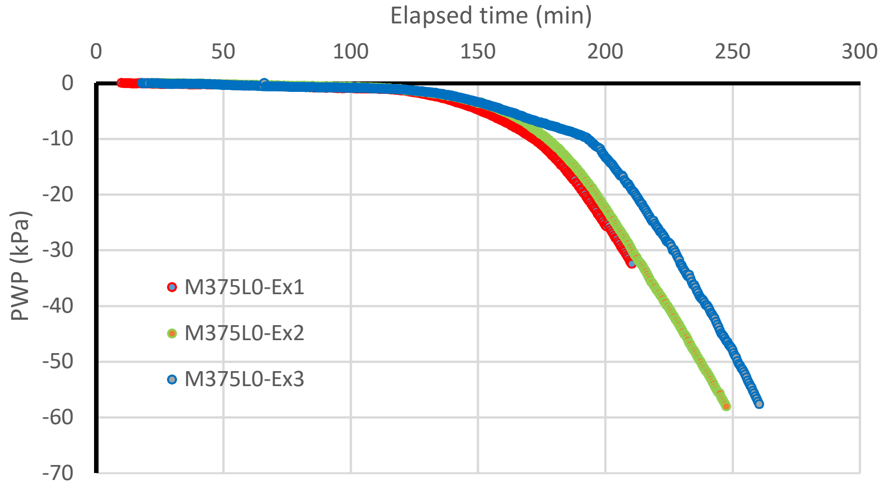

Figure 4-9- Effect of ambient relative humidity on PWP development

Figure *4-10* shows the accelerated PWP development at the depths of 5 and 1.25 cm with increasing ambient temperature. In Figure *4-10*, the code like “M375L0-EX5-1.25” means that mortar mixture “M375L0” (see Table *4-4*) tested in exposure condition “Ex5” (see Table *4-5*) at 1.25-cm depth. The results show that as long as there is a hydraulic connection between capillary pores along the depth, PWP is almost equal along the depth. However, by increasing the impermeability of the cement matrix and dropping the moisture content, this is expected to be changed.

Increasing and decreasing the ambient temperature from 22.5°C, respectively, increases and decreases water evaporation, moisture consumption and matrix densification during the hydration reactions. Therefore, PWP development is substantially affected by variations in ambient temperature.

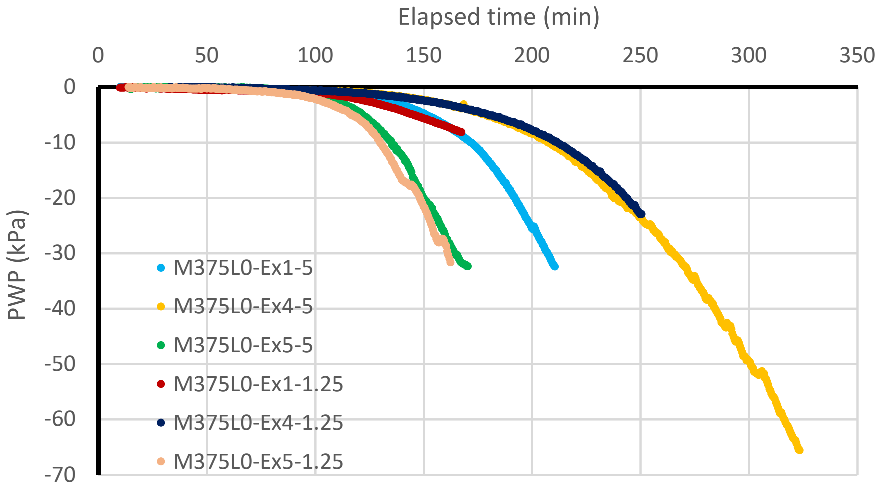

Figure 4-10- Effect of ambient temperature on PWP development at 5 and 1.25-cm depths

Although incorporation silica fume improves some mechanical and transport properties of hardened cement-based materials, it makes the mixture susceptible to early-age shrinkage cracking due to accelerated PWP development. This can be intensified in an ambient exposure condition with low relative humidity and high temperature. Internal curing can help delay PWP development by providing extra IC water for the cement matrix.

Figure *4-11* shows the improvement in delaying PWP development in the exposure condition with 25% relative humidity and 22.5°C temperature by internal curing (0.101 ICW/CMs). It also presents the effect of incorporation of silica fume along with increasing the ambient temperature to 35°C. The results show that PWP development is substantially accelerated because of increasing water evaporation, water consumption during hydration reactions and internal specific surface area (due to the fine particle size distribution of silica fume). This mixture is very susceptible to early-age shrinkage cracking; however, Figure *4-11* shows that internal curing can improve PWP development.

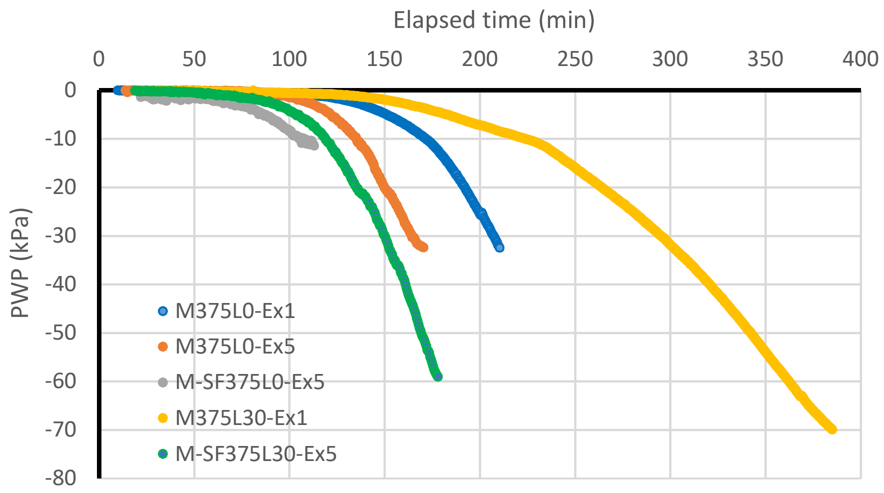

Figure 4-11- Effect of SF incorporation and IC on PWP development

4.6.3. Electrical conductivity

Temperature-corrected normalized electrical conductivity (EC) of mortar mixtures are presented in Figure *4-12*. Normalized reductions in the electrical conductivity of mortar mixtures after the peak are mainly because of cement matrix densification (disconnecting capillary pores and increasing bond water) and moisture loss [28]. The results presented in Figure *4-12* (a) show that increasing ambient temperature results in a steeper sleep and decreasing electrical conductivity compared to that at 22.5°C. This is due to a higher rate of hydration reactions disconnecting capillary pores and to moisture loss due to accelerated hydration reactions or evaporation. Decreased ambient temperature leads to a lower slope and decreasing electrical conductivity compared to that at 22.5°C.

Figure *4-12* (b) shows a reduced slope of decreasing electrical conductivity of the mortar mixture using internal curing. Although IC mixture has a higher degree of hydration and reduced capillary pores, extended internal curing results in a higher degree of saturation and smaller slope of electrical conductivity decrease compared to that of the mixture without internal curing.

Internal curing is also shown to be beneficial in reducing slope of decreasing electrical conductivity during the early ages, when it is shown from isothermal calorimetry that internal curing increases the total heat of hydration (correlated with the degree of hydration).

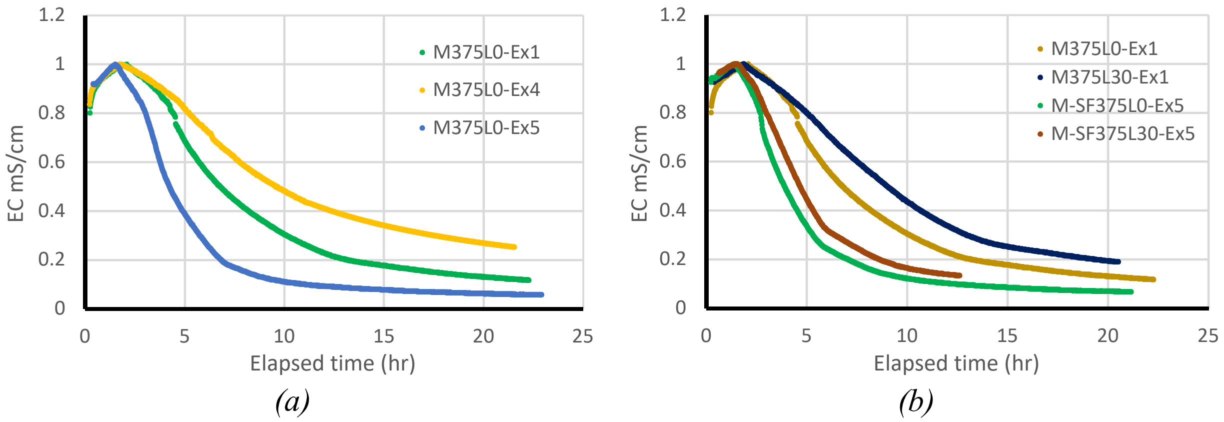

Figure 4-12- EC variation of mortars in different exposure conditions:

a)effect of ambient temperature, b)effect of internal curing and silica fume incorporation

4.6. Conclusion

The main conclusions from this study can be listed as follows:

- Increasing the temperature from 22.5 to 35°C doubles the main heat flux and significantly decreases the associated time for paste and mortar mixtures with and without LWFA. However, due to the extended rate of heat generation for mixtures at 22.5°C, total heat generation at the 2-day age is only increased by 6% for the paste mixture.
- Decreasing the temperature from 22.5 to 10°C results in spreading out the heat flux and disappearing the maximum peak. Also, heat generation at the 2-day age is decreased by 22% for the paste mixture.
- Providing extra IC water for mortar mixtures results in increasing both heat flux (without a meaningful change in associated time) and heat generation. However, there is an optimum

point beyond which further increase in the ratio of IC water to cementitious materials (ICW/CMs) does not make a significant increase. For this study the optimum ICW/CMs is 10%, which is provided by 30% LWFA substitution.

- Incorporation of 5% SF in mortar mixtures (both with and without LWFA) results in around 8 and 10% increases, respectively in the peaks of heat flux and total heat generation at 2 days.
- Increasing W/C significantly delays PWP development in sealed cement paste mixtures due to delayed solidification time and increased initial moisture content.
- Increasing the percentage of SF incorporation accelerates PWP development in sealed cement paste. This can be attributed to the increased rate of hydration for SF contained mixtures as well as the formation of a denser matrix with smaller pores.
- Decreasing the RH of the surrounding environment accelerates PWP development.
- There is not a meaningful difference between PWP at the 5 and 1.25-cm depths as long as the matrix is considerably saturated, and a good hydraulic connection between pores at early ages.
- Increasing the temperature significantly accelerates PWP development in the mortar mixture, while decreasing the temperature substantially delays it.
- IC effectively suppress the PWP development in the control mixture at 22.5°C, and the SF incorporated mixture at 35°C.

4.7. Acknowledgments

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CHAPTER 5. GENERAL CONCLUSION

5.1. Summary

Capillary pore water potential is recognized as the source of early-age shrinkage strain and increasing cracking potential in cement-based material. Internal curing by substituting lightweight fine aggregate is an alternative curing method to uniformly provide extra water through the whole volume after cement matrix solidification. However, substituting fine aggregate with lightweight fine aggregate affects other engineering properties of the mixture including the rate of hydration reactions, mechanical and transport properties. This dissertation aimed to study pore water potential development in cement-based materials. In addition, it investigated the effectiveness of internal curing as a technique to control pore water potential development as well as its effect on the mechanical and transport properties of concrete mixtures.

Effects of internal curing on engineering properties of concrete mixtures, pore water potential development in a wide range of concrete mixtures incorporated supplementary cementitious materials and pore water potential development in various exposure conditions are the main topics of chapters two to four of this dissertation.

5.2. Conclusion

The main findings and contributions of each chapter of this study can be listed as follows:

- **Chapter Two:** Effects of Internal Curing on Hydration, Mechanical and Transport Properties of Cement-Based Materials Incorporating SCMs

- LWFA releases IC water after solidification. This leads to an increase in the rate of heat generation after setting time. Extended hydration also results in higher total heat generation per gram of portland cement in mortars. Further increase in LWFA substitution than 30% leads to an insignificant increase in total heat generation.
- IC does not change the setting time or UPV of concrete mixtures.
- LWFA substitution has a major effect on CTE of concrete mixtures. CTE linearly decreases by up to 25%, in the case of LWFA substitution by up to 40%.
- IC is more efficient for the concrete mixtures with low W/C, incorporating SF, or in sealed curing condition.
- 20% LWFA substitution appears to be the optimum percentage, for the LWFA used in this study, to improve compressive strength of concrete mixtures.
- Further substitution of LWFA increases SR of concrete mixtures, particularly in case of sealed curing or incorporating silica fume in the mixtures.
- IC is efficient in decreasing rapid chloride migration coefficient of concrete mixtures with low W/C. Incorporation of silica fume intensifies this improvement.

➢ **Chapter Three:** Improved Hydration and Mitigation of Pore Water Potential Development in Cement-Based Materials by Internal Curing

- Increasing W/C decreases heat flux and kinetics of cement hydration. However, it leads to a higher total heat generation in both control and IC mortars.
- Releasing IC water starts before the main peak of heat flux in isothermal calorimetry tests and results in increased heat flux over the following hydration stages.

- The effectiveness of IC to increase heat generation is more pronounced for the mortar mixtures with low W/C.
- Increasing IC water/CMs to more than 0.10 does not significantly promote heat flux or heat generation.
- IC efficiently increases hydration kinetics of the SF incorporated mortars.
- Capillary pore water potential development is significantly postponed by increasing W/C or providing IC water. IC is particularly beneficial for low W/C concrete mixtures.
- Increasing IC water/CMs can significantly intensify the benefits of IC in postponing capillary pressure development. However, the improvement associated with IC water/CMs higher than 0.08 is negligible.
- Incorporating SF significantly accelerates capillary pore water potential development. IC is very efficient in suppressing this increase.
- Incorporating 20% of FA decreases heat flux and water consumption at early ages. Therefore, it postpones capillary pore water potential development.

➢ **Chapter Four:** Effect of Exposure Conditions, Silica Fume Incorporation and Internal Curing on Hydration and Pore Water Potential Development in Cement-Based Materials

- Increasing the temperature from 22.5 to 35°C doubles the main heat flux and significantly decreases the associated time for paste and mortar mixtures with and without LWFA. However, due to the extended rate of heat generation for mixtures at 22.5°C, total heat generation at the 2-day age is only increased by 6% for the paste mixture.

- Decreasing the temperature from 22.5 to 10°C results in spreading out the heat flux and disappearing the maximum peak. Also, heat generation at the 2-day age is decreased by 22% for the paste mixture.
- Providing extra IC water for mortar mixtures results in increasing both heat flux (without a meaningful change in associated time) and heat generation. However, there is an optimum point beyond which further increase in the ratio of IC water to cementitious materials (ICW/CMs) does not make a significant increase. For this study the optimum ICW/CMs is 10%, which is provided by 30% LWFA substitution.
- Incorporation of 5% SF in mortar mixtures (both with and without LWFA) results in around 8 and 10% increases, respectively in the peaks of heat flux and total heat generation at 2 days.
- Increasing W/C significantly delays PWP development in sealed cement paste mixtures due to delayed solidification time and increased initial moisture content.
- Increasing the percentage of SF incorporation accelerates PWP development in sealed cement paste. This can be attributed to the increased rate of hydration for SF contained mixtures as well as the formation of a denser matrix with smaller pores.
- Decreasing the RH of the surrounding environment accelerates PWP development.
- There is not a meaningful difference between PWP at the 5 and 1.25-cm depths as long as the matrix is considerably saturated, and a good hydraulic connection between pores at early ages.
- Increasing the temperature significantly accelerates PWP development in the mortar mixture, while decreasing the temperature substantially delays it.

- IC effectively suppress the PWP development in the control mixture at 22.5°C, and the SF incorporated mixture at 35°C.

5.3. Future work

Although this study provides a meaningful contribution to the literature on pore water potential development in cement-based materials and effect of internal curing on engineering properties of mixtures, there still remain several of questions in need of further investigation. Based on the experience obtained in this study the following topics are suggested for future studies:

- Investigation of hydration kinetics using isothermal calorimetry test shows that the total heat generation is increased for internally cured mixtures over the first two days. However, it is important to study the performance of mixtures over long ages to consider possible further improvements for internally cured mixtures. Long duration isothermal calorimetry test or thermogravimetric analysis (TGA) of hardened mixtures can help for this purpose. In addition, increasing the degree of hydration results in decreasing the effective pore size distribution of pores in the hardened cement matrix which can be investigated by mercury intrusion porosimetry (MIP). Decreasing the effective pore size in internally cured mixtures may lead to an increased drying pore water potential. Therefore, it is important to study the drying shrinkage of internally cured mixtures in environments with low relative humidity.
- The coefficient of thermal expansion is a key parameter of concrete mixtures determining thermal-induced strain which controls thermal curling behavior of jointed plain concrete pavements. The coefficient of thermal expansion is significantly dependent on the moisture content and internal relative humidity of concrete. Some limited studies show that it reaches the minimum value in the dry and wet conditions, while the coefficient of thermal expansion

can be at the maximum value around 60% internal relative humidity, which is close to the value measured in practice. This study, conducted in saturated conditions, shows that internal curing decreases the coefficient of thermal expansion because of the effect of replacing fine aggregate with porous lightweight fine aggregate. However, an additional study is recommended to investigate the effects of internal curing on the coefficient of thermal expansion at other relative humidity values such as 60%. This can further explain the improved behavior of internally cured jointed plain concrete pavements over temperature curling.

- It seems that the role of the interfacial transition zone (ITZ) in controlling the electrical resistivity of cement-based materials is underestimated. The electrical resistivity of high-performance concrete mixtures with 60-70% aggregate content (by volume) and low water-to-cement is mainly controlled by the volume and percolation of ITZ. One of the benefits of internal curing is decreasing the volume and increasing the density of ITZ. It helps increase the optimum volume of aggregate content without compromising concrete transport properties. In other words, internal curing may help decrease cement content in concrete mixture proportion (by improving ITZ) without affecting mechanical or transport properties of concrete. Further study is required to investigate the effects of internal curing on improving transport properties of concrete mixtures with a focus on the properties of ITZ.
- Tensiometers can be successfully used to study capillary pore water potential development in early-age cement-based materials. However, the working range of the sensor is usually very limited. There are some other indirect methods for monitoring pore water potential which can monitor capillary pore water potential development beyond the limited tensiometer range. Most of the sensors work based on measuring the moisture content of porous materials (like

porous ceramic or granular sand). Pore water potential of concrete can then be estimated using a calibration equation. A separate study is recommended to investigate the benefit of these methods in monitoring capillary pressure in partially-saturated concrete materials for an extended period of time.