ABSTRACT

THE IMPACT OF CONVERSION ON THE DURABILITY OF CALCIUM ALUMINATE CEMENT CONCRETE SYSTEMS

by
Marwa Mohsen Korayem

The deterioration of infrastructure in North America has resulted in a significant need for concrete repair materials that can be used to maintain service life of these structures. Hydraulic cement based rapid repair materials can be used to repair pavement and bridge deterioration with minimal impact on economic activities such as freight handling or public transportation. While there are many options for use in repair situations, calcium aluminate cements have become more popular recently, particularly in situations where repairs must be completed rapidly.

Calcium aluminate cement (CAC) is a cement characterized by its rapid strength gain, even at low temperatures approaching 0℃. This key feature has made CACs extremely useful in certain concrete repair applications, particularly in cold regions. CAC systems undergo a unique process known as conversion, in which metastable hydrates convert to stable hydrates, resulting in an increase in porosity and strength loss. Understanding the time at which this conversion occurs, and the magnitude of strength loss is important for long-term design decisions involving repaired concrete systems. There has been significant previous research work on the kinetics of the conversion process in the CAC systems. However, there is very little information available on the impact of conversion on long-term concrete durability.

This dissertation discusses the capability of using electric resistivity measurements in order to assess conversion in CAC systems in the field. A rapid procedure is recommended to detect when conversion occurs in different aspects. The validity of this approach is studied on CAC systems with various robustness factors including different cement formulations, different types of aggregates, different water to cement ratios, and different time to convert. This work also studies the relationship between converted and unconverted CAC concrete in terms of drying shrinkage; focusing on understanding the impact of conversion on CAC systems long term durability. A discussion is presented on various CAC systems using different water to cement ratios, different cement formulations, and different time to convert.

This work shows a proof-of-concept that the electric resistivity measurement may be a promising tool to assess time to conversion in CAC systems. The presented data shows a significant reduction in electric resistivity correlating with a reduction in the compressive strength, which indicates that full conversion has occurred. This work also studies the impact of conversion on long term durability in CAC systems in terms of drying shrinkage. The presented data shows a much higher total shrinkage and mass loss in samples after conversion occurs than in unconverted ones. This work shows that it will be essential to ensure that the CAC system will gain enough strength and they should be prevented from converting at an early age, before it builds up stresses that occur due to drying shrinkage.

THE IMPACT OF CONVERSION ON THE DURABILITY OF CALCIUM ALUMINATE CEMENT CONCRETE SYSTEMS

by
Marwa Mohsen Korayem

A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Civil Engineering

John A. Reif, JR. Department of Civil and Environmental Engineering

May 2020

.

APPROVAL PAGE

THE IMPACT OF CONVERSION ON THE DURABILITY OF CALCIUM ALUMINATE CEMENT CONCRETE SYSTEMS

Marwa Mohsen Korayem

Dr. Matthew P. Adams, Dissertation Advisor	Date
Assistant Professor of Civil and Environmental Engineering, NJIT	

Dr. Taha F. Marhaba, Committee Member	Date
Professor and Department Chair of Civil and Environmental Engineering, NJIT	

Dr. Methi Wecharatana, Committee Member	Date
Professor of Civil and Environmental Engineering, NJIT	

Dr. Matthew J. Bandelt, Committee Member	Date
Assistant Professor of Civil and Environmental Engineering, NJIT	

Dr. Megan E. O'Neill, Committee Member	Date
Assistant Professor, Humanities, NJIT	

Author: Marwa Mohsen Korayem

Degree: Doctor of Philosophy

Date: May 2020

Undergraduate and Graduate Education:

- Doctor of Philosophy in Civil Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2020

- Master of Science in Civil Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2013

- Bachelor of Science in Civil Engineering,
  Alexandria University, Alexandria, Egypt, 2000

Major: Civil Engineering

Presentations and Publications:

Marwa M. Korayem, Aaron J. Strand, Matthew P. Adams, and Anthony Bentivegna,
    Electric resistivity testing method to assess conversion in calcium aluminate
    cement concrete, Calcium Aluminates: Proceedings of International Conference,
    Cambridge, England, article in press, October 2020.

Marwa M. Korayem and Matthew P. Adams, Impacts of conversion on drying shrinkage
    of calcium aluminate cement using finely ground limestone, Calcium Aluminates:
    Proceedings of International Conference, Cambridge, England, article in press,
    October 2020.

Matthew P. Adams, Marwa M. Korayem, and Jason H. Ideker, Aggregate impacts on
    chemistry, conversion, and strength in calcium aluminate cement concrete
    systems, Calcium Aluminates: Proceedings of International Conference,
    Cambridge, England, article in press, October 2020.

Marwa M. Korayem and Matthew P. Adams, Methods for promoting conversion and
    determining converted strength of calcium aluminate cement concrete, Bridge
    Engineering Institute Conference (BEI-2019), Honolulu, Hawaii, July 2019.

To my parents, Mohsen and Mervat,
My siblings, Ibrahim and Maha,
and my daughters, Nour and Jana

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(CONTINUED)

LIST OF FIGURES
(CONTINUED)

CHAPTER 1

INTRODUCTION

1.1 Background

The deterioration of infrastructure in North America has resulted in a significant need for concrete repair materials that can be used to maintain service life of these structures [1]. Hydraulic cement based rapid repair materials can be used to repair pavement and bridge deterioration with minimal impact on economic activities such as freight handling or public transportation. While there are many options for use in repair situations, calcium aluminate cements have become more popular recently, particularly in situations where repairs must be completed rapidly.

Calcium aluminate cement (CAC) is a cement characterized by its rapid strength gain, even at low temperatures approaching 0℃ [2]. This key feature has made CACs extremely useful in certain concrete repair applications, particularly in cold regions [3]. In the early 20th century, it was used to quickly construct gun emplacements during WWI in France because of its rapid strength gain properties [4]. Other uses included wearing surfaces to provide scour resistance in dam spillways [2], [5], as a temperature resistant material in refractory applications [2], [6]–[11], and as an acid resistant material in manufactory and wastewater applications [12]–[18]. CAC is a specialty cement that can be used in a wide range of applications and has led to an increase in interest in concrete rapid repair applications. Despite the higher cost of CAC (about 4-5 times of ordinary portland cement, OPC), it can provide solutions to specific rapid repair applications where the use of ordinary portland cement may not be feasible. CAC is favorable to be used where there

is an intensive need for rapid return to service, especially in industrial applications when several severe conditions are present [19].

Even though CAC hydration has been studied significantly in the past, specifically its microstructure, it's not quite understood within the general construction practice. Previous research studies have focused on studying the kinetics of conversion, a process that will be explained later in Section 2.3. There has been very limited work done to understand the long-term durability of CAC and what impact this conversion may have on it.

There has been significant previous research work on the kinetics of the conversion process in the CAC systems. However, there is very little information available on the impact of conversion on long-term concrete durability. There are concerns over how the increase in porosity may impact the transport properties of aggressive chemicals through the system. In particular, given its limited use in field applications up to now, there is not sufficient data on how CAC concrete may perform in the field after conversion, particularly when exposed to the harsh conditions seen on our nation's roadways. This work studied the capability of using electrical resistivity measurements as a tool to assess conversion in situ. The work presented examined the impact of conversion in CAC systems on drying shrinkage. It also focused on understanding the relationship between converted and unconverted CAC concretes in terms of drying shrinkage.

1.2 Scope and Objectives

This dissertation consists of a literature review, experimental methods, two chapters derived from papers (under press) submitted to CAC UK proceedings, October 2020, and a conclusion. The layout of this dissertation is as follows:

Chapter 1 Introduction. This chapter provides an introduction and background on calcium aluminate cement concrete (CAC) systems. It also presents the motivation and objectives for this research work. This chapter also presents a detailed literature review presenting CAC history and its uses. Additionally, it includes a review of CAC hydration process, concrete properties, durability issues, promoting conversion procedures.

Chapter 2 Means and Methods. This chapter provides an overview of the experimental methods used throughout this dissertation.

Chapter 3 Electric Resistivity Measurement as a Tool to Assess Conversion. This chapter discusses the potential of using electric resistivity as an indication of conversion in CAC systems under different variables. These variables included different water to cement ratios, different cement formulations, different aggregate sources, and different time to convert.

Chapter 4 Impact of Conversion on Drying Shrinkage in CAC Systems. This chapter provides an understanding of the impact of conversion on drying shrinkage. A comparison is presented between converted and unconverted systems. Also presents the impact of different variables including different water to cement ratios, different time to convert, and using small dosages of finely ground limestone (FGLS).

Chapter 5 Conclusions and Recommendations. This chapter provides a unified conclusion to the presented work; summarizing the key findings. Future work is also recommended based on this work.

Chapter 6 References. This chapter provides a list of all the references used throughout this dissertation.

The main objectives of the work presented in this dissertation are as follows:

1- Determine if the electric resistivity test can be used to detect conversion in the field.
2- Understand the effect of conversion on the durability of CAC in terms of its drying shrinkage.

These objectives will help support use of CAC by increasing understanding of how CAC can be used in aggressive environments.

1.3 Literature Review

1.3.1 History of CAC

Calcium aluminate cement (CAC) also known as "ciment alumineux" in French and "cemento aluminoso" in Spanish [2], is a rapid hardening cementitious material that rapidly gains strength, even at temperatures approaching freezing. It was developed in the late 19th and early 20th century as an alternative to portland cement for situations where the latter may not perform well [5], [20]. By the end of the 1800s many researchers had begun to examine cements with high alumina contents [21]. In the 1840s, Louis Vicat determined that by combining silica and alumina ratio greater than one to magnesia and calcium would result in a highly sulfate resistant cement that would be an "indestructible" material [20], [22]. However, the increase in silica content led to a less reactive material with no strength development and the increase of alumina content led to flash setting. Building on Vicat's work, Jules Bied was able to develop high alumina cement with very good cement properties that did not undergo flash setting [23]. The motivation for this discovery was due to the need for a sulfate resistant material to be used in various areas in France where sulfate attack was a major deterioration issue [19], [23]. In 1908, Bied patented the manufacture of cements with alumina and low silica contents through the use of a fusion furnace rather than the more standard cement manufacturing process of clinkering [24]. Bied's cement product was eventually manufactured while working at J and A Pavin de Lafarge by 1913 under the name of "Ciment Fondu Lafarge" (CFL) [2], [20], [25].

This evolution of CACs was extremely important at that time because it was found that CACs could resolve issues of rapid degradation of mortars and concrete placed in areas

where the ground had high-sulfate content [2]. Unlike the OPC, CAC doesn't contain calcium hydroxide (CH) which dissolves rapidly in the presence of acids allowing for more ingress of corrosive chemicals. However, the aluminates in CAC are stable to low pH levels which make it more resistant to acid attack. This proved useful in tunnel linings, some of which have shown very good durability over time. An example is the durability of the "tunnel des Valois" located in southern France and subjected to harsh environment. This tunnel used CAC cement Fondu to reinforce it. It has shown a good durability over a 90 years of service period [26]. Cements containing high percentages of Al_2O_3 within a range 1of 30-40 % were named as "high-alumina cement" (HAC) and were used in UK after WWI [5], [20], [25]. Later other alumina cements were produced with higher alumina percentages ranging from 50-90 % which were mainly used in refractory applications [2], [27]–[30]. These cements have become to be known as calcium aluminate cements (CAC).

The centenary of the first patent on CAC was celebrated in 2008; however, since its original inception, the use of CACs has gone through several ups and downs [20]. In addition to the above mentioned uses of CAC, CACs were also used in structural applications. In the 1940, the U.K. building code was modified to allow uses of CAC in structural applications. In the 1950s, CAC was used extensively in precast concrete construction due to its rapid strength gain properties, which made it an economical choice for precast plants. CAC was in use for structural concrete applications through the 1960s, until it fell out of favor because of three major structural collapses. A collapse of prestressed beams made of CAC occurred at the University of Leicester (built in 1965), the Camden school of girls (built in 1955), and Sir John Cass school [2]. It was concluded later that the collapse in some of the roof beams at the Sir John Cass school was due to the

lack of knowledge of conversion process, a process unique to CACs which causes strength loss but was not well understood in the construction industry [2]. The collapses at the University of Leicester and the Camden School of Girls were found to be due, in part, to improper structural steel detailing which then was exacerbated by the strength loss associated with conversion[25] [2]. At the time, these collapses changed the perception of the use of CAC and led to significant limitations in its structural use [2], [25]. Despite this, many years of CAC use have shown that with proper design a good quality and good performance concrete system can be created. Design guides today note that the use of CAC should be based on the converted strengths for structural design to ensure long term performance [2]. The conversion phenomenon, however, makes it more prone to misuse than Portland cement, emphasizing the importance for better design guides and education on the use of the product.

Compared to OPC, CAC materials are often more expensive. The cost difference has limited the use of CAC to niche applications where the specific properties of the material are required [5]. These unique characteristics of CAC also expands the range of applications of using cementitious materials [5], [19]. Concrete has always been thought of as a highly durable construction material, yet an additional perspective would be taken when looking into the versatility of CAC. It can be used as the only binder or as one component in a mixture of cement, which would extend the range of its applications [31], [32]. The impact of temperature, moisture and type of aggregates on mechanical properties of CAC concretes have been extensively studied [33]–[36] [37]. Lamour et al. studied and compared some mechanical properties other than compressive strength in converted and unconverted states on CAC concrete at w/c ratio of 0.4 [37]. The authors inferred that the

elastic properties, ductility and resistance to crack propagation were less affected by conversion than are the tensile and compressive strengths.

1.3.2 Composition and Microstructure of CAC

1.3.2.1 Composition of CAC   Calcium aluminate cement composition differs significantly from ordinary Portland cement as shown in Figure 1.1 and Table 1.1 [2], [31]. CAC contains mainly alumina and calcium oxides and little to no silica while OPC contains mainly calcium and silica oxides and little alumina. CACs are produced by fusing a mixture of limestone and bauxite (a pure source of alumina) which due to its high cost makes CAC more expensive than OPC [2], [19]. The composition of CAC varies according to its grade and applications. Table 1.2 shows the approximate chemical compositions for the standard grades of CAC. It can be seen that typical CAC with standard alumina content contains 36-42% of AL_2O_3 and small amounts of ferric or ferrous oxides up to 20%. The purer materials (medium and high alumina) contains 65-80% with less than 0.3% of iron oxides.
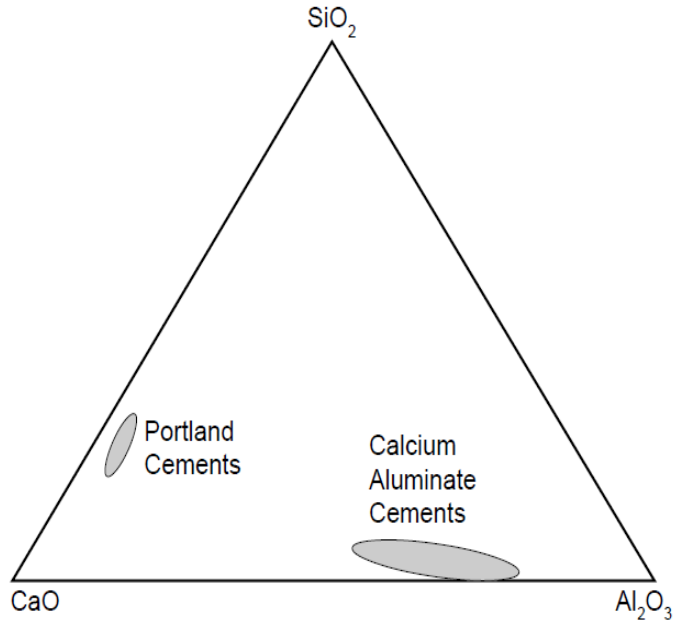
Figure 1.1 Comparison in composition of CAC and OPC.
Source: [31].

Table 1.1 Range of Hydrates Formed by OPC and CAC

	Phase Hydrate	Ordinary Portland Cement	Calcium Aluminate	
Silicates	C_3S	50--70	0	
	C_2S	15--30	< 10	
	C_3A	5--10	0	Aluminates
	C_4AF	5--15	10--40	
	CA	0	40--50	

Table 1.2 Calcium Aluminate Cement Grade Compositions
Source: [5]

Grade	Colour	Al_2O_3	CaO	SiO_2	Fe_2O_3 + FeO	TiO_2	MgO	Na_2O	K_2O	Countries of manufacture
Standard low alumina	Grey or buff to black	36–42	36–42	3–8	12–20	<2	~1	~0.1	~0.15	France, Spain, Croatia, USA, India, eastern Europe
Low alumina, low iron	Light buff or grey to white	48–60	36–42	3–8	1–3	<2	~0.1	~0.1	~0.05	France, USA, India, Korea, Brasil
Medium alumina	White	65–75	25–35	<0.5	<0.5	<0.05	~0.1	<0.3	~0.05	France, UK, USA, Japan, China, India, Korea, Brazil
High alumina	White	≥80	<20	<0.2	<0.2	<0.05	<0.1	<0.2	~0.05	USA, France, Japan, Brasil, Korea

1.3.2.2 Unhydrated constituents of CAC   CAC consists of several unhydrated phases of which monocalcium aluminate ($CaAl_2O_3$ or CA) is the main phase. CA typically constitutes 40% or more of the CAC system depending on its type [2]. The composition of this phase takes place in the general form of $Ca_xAl_yFe_zSi_tO_{x+3/2(y+z)+2t}$ where the variables are within the following ranges : $4.4 \leq x \leq 4.8$, $4.7 \leq y \leq 5.0$, $z \leq 2.13$ and $t \leq 0.1$ [38]. Calcium dialuminate ($CaAl_4O_7$ or CA_2) also exists in large quantities in CAC systems, and its amount is proportional to the amount of CaO in the system. Dodecalcium heptaaluminate ($Ca_{12}Al_{14}O_{33}$, $C_{12}A_7$, manyenite) may also be present in CACs and will increase the reactivity of the system when present, playing a vital role in the setting time of CACs. Some other minor constituents may also be found in the CAC system such as dicalcium aluminate (C_2A) and hibonite (CA_6) which mainly form in higher alumina CACs [2]. A summary table of these unhydrated phases is shown below in Table 1.3.

Table 1.3 Calcium Aluminate Cement Unhydrated Phases

Unhydrated component	Standard chemical notation	Cement chemistry notation
Monocalcium Aluminate	$CaAl_2O_3$	CA
Calcium Dialuminate	$CaAL_4O_7$	CA_2
Dodecalcium Heptaaluminate(Manyenite)	$Ca_{12}Al_{14}O_{33}$	$C_{12}A_7$
Dicalcium Aluminate	$2CaO \cdot Al_2O_3$	C_2A
Hibonite	$(Ca,Ce)(Al,Ti,Mg)_{12}O_{19}$	CA_6

1.4 Hydration and Conversion of CAC

The chemical process in which cements react with water to produce solid materials is called "hydration". The main phase in CAC is monocalcium aluminate- $CaO \cdot Al_2O_3$ (CA) [23]. CAC hydration has been extensively studied for over a century since they were originally developed [2], [5], [23], [39] [40]–[43]. The hydration of CA initially produces CAH_{10} and C_2AH_8 which are metastable hydrates. These metastable hydrates undergo a process known as conversion in which the two stable hydrates, C_3AH_6 and AH_3, are formed. This conversion process is accompanied by the release of water, which will react with the remaining unhydrated CA, forming new hydrates and reducing long-term porosity that was formed from conversion. The formation of metastable or stable hydrates from the hydration of calcium aluminates depends strongly on temperature, unlike the hydration of calcium silicates which produce the similar hydrates at all temperatures below 100℃ [2]. The preference of which hydration product will form during CAC hydration depends significantly on the temperature at which the system is cured. If the temperature is below 15℃ the initial -metastable hydrate CAH_{10} is formed, while if the temperature is above 30℃ the initial metastable C_2AH_8 is formed. If the temperature lies between 15 ℃ and 30 ℃, then neither is preferred between the two metastable hydrates regarding the order to be formed [2], [5], [44], which can result in a delay of setting time.

The hydration of CAC is a highly exothermic chemical reaction and the rapid precipitation of its hydrates may result in self-heating in the CAC system. Gosselin et al. studied the heat evolution in pure CACs at different w/cm ratio at 20˚C. As shown in Figure 1.2, a single sharp peak occurs within the first few hours of CAC hydration which is attributed to the precipitation of its hydrates [45]. This peak is followed by an induction

period which is associated by small heat flow and low activity. It was observed that lower

w/cm will slightly reduce the induction period due to the early ionic concentration in the

solution [45].
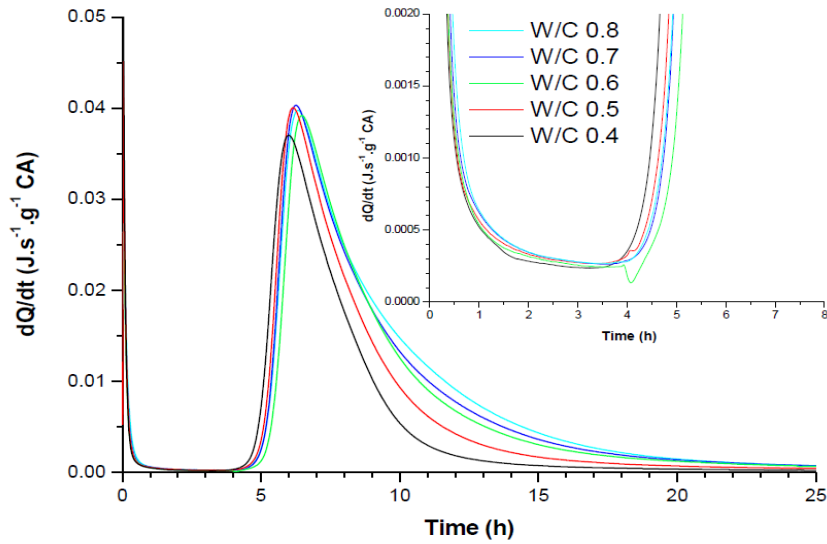
Figure 1.2 Heat evolution for pure CAC hydrated at 20˚C for several w/cm.
Source: [45]

Gosselin also studied the heat evolution in pure CAC system hydrated at 38˚C for

0.4 w/cm. The calorimetry of CAC at 38˚C has shown different patterns than that at 20˚C

with and without the presence of lithium sulfates as shown in Figure 1.3 [45], [46]. In the

presence of Li_2SO_4, there was an early peak and all heat evolved ended in the first 5 hours.

However, in the absence of Li_2SO_4 the hydration of CAC showed a high peak followed by

a lower one which is correlated to the dissolution of C_2AH_8 during conversion [46].
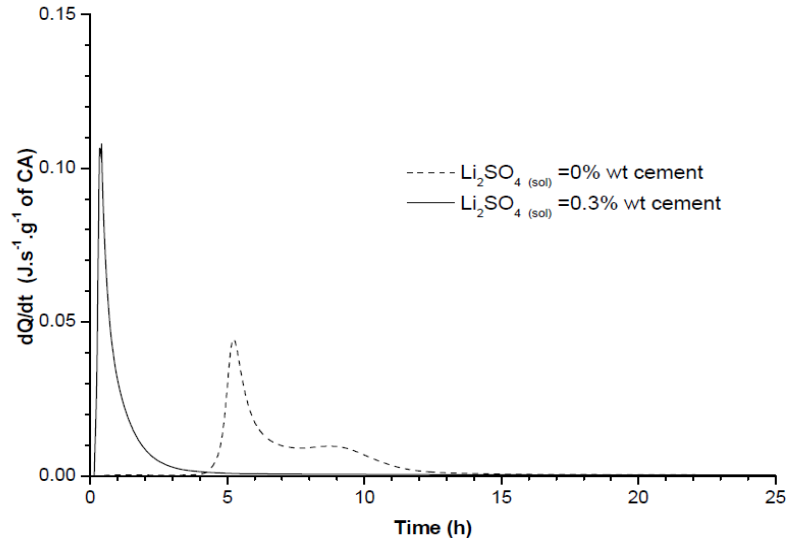
Figure 1.3 Heat evolution for pure CAC hydrated at 38˚C with or without Li_2SO_4.
Source: [46]

The time of conversion depends on the temperature history of the concrete. Fryda et al. showed that the CAC concrete that was placed into a heated tub at 100 ˚C directly after casting reached its converted strength only within 15 minutes. The specimens that were placed in a water tub at temperature 30 ˚C reached their minimum strength at 20 days [47]. This work explains the impact of the temperature history to which CAC concrete is subjected on the time of its conversion. For that reason, it is extremely important to monitor the temperature history of CAC and to record specific temperatures when dealing with specifications for use with CAC.

The hydration equations for CAC were given in literature as shown below [2], [19], [23],[48].

$$CA + 10H \rightarrow CAH_{10} \qquad\qquad 1.1$$

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \qquad\qquad 1.2$$

$$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H \qquad\qquad 1.3$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \qquad\qquad 1.4$$
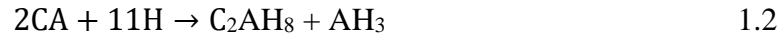
All these reactions take place "through solution" which means that the reactants dissolve to form products which are precipitated from solution [19], [49].

The speed of the reaction in the conversion process depends upon temperature, moisture content and water to cementitious ratio. These hydration reactions are exothermic. The rapid hydration in CAC leads to a higher and faster heat evolution than that in calcium silicate cement (CSC) systems. Further temperature increase is noted to accelerate the hydration process [2], [19], [50].

During the conversion process, the metastable hydrates are converted to stable hydrates as mentioned above. This formation of these denser hydrates within the paste matrix increases the porosity in the system and thus decreases the compressive strength [37]. The densification of the hydrates during conversion results in a change in volume. The amount of water needed for hydration depends mainly on the nature of the hydrates being formed [2]. Adams et al. examined the microstructures of CAC concrete specimens showing backscatter scanning electron images (BSEM) images before and after conversion as shown in Figure 1.4 [51]. The images taken on day 1 showed a dense structure with some porosity, indicating unconverted CAC paste. The images taken on day 14 showed higher level of porosity in the cement paste compared to the unconverted sample.
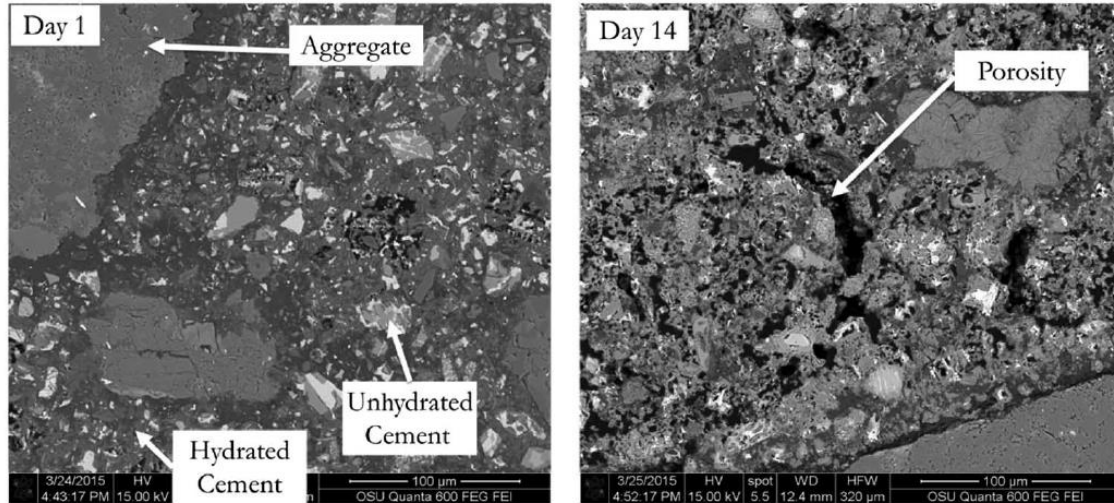
Figure 1.4 BSEM images of KRC sample at w/cm 0.40 for unconverted (left) and unconverted (right) samples.
Source: [51]

The hydration reactions can strongly be affected by the different morphology and particle size of the hydrates [52].The metastable hydrates, formed at lower temperatures, nucleate easily due to its non-isotropic crystal structure. CAH_{10} is poorly crystallized, while C_2AH_8 with its hexagonal morphology is more crystalized [46]. Also the C_3AH_6 hydrates are formed of cubical crystals, while the AH_3 is poorly crystallized gel [19]. The metastable hydrates, CAH_{10} and C_2AH_8, have higher solubility than the stable hydrates C_3AH_6 and AH_3. Thus once the stable hydrates nucleate, the metastable phases dissolve [46]. Therefore, the C_3AH_6 precipitates from solution which is driven by the dissolution of metastable hydrates. It will nucleate directly from the unhydrated CA once it has already formed. This elucidates the reason that the a second conversion is not observed in CAC systems despite continued hydration of anhydrate cement [37], [45].

1.5 Strength Development in CAC

The strength development in CAC systems is different than that of CSC systems due to the conversion process from metastable hydrates to stable hydrates. When conversion occurs in CAC systems the dense stable hydrates C_3AH_6 and AH_3 are formed from the less dense metastable hydrates. This densification of the hydrates in the CAC system causes the absolute volume of the system to decrease without an accompanied macroscopic volume change in the whole system. Therefore, porosity opens up within the system resulting in a decrease in strength over time [2], [39]. After the conversion process occurs a minimum strength is reached. However, the water released through the conversion process continues to hydrate any remaining and available anhydrate cement grains. This results in continuous long term strength gain [23]. The metastable hydrates CAH_{10} and C_2AH_8 are responsible for the early strength gain while the stable hydrates C_3AH_6 and AH_3 are responsible for the long-term strength gain. The effect of conversion on strength of CAC can be shown in Figure 1.5 [2], [5]. The graph shows the strength development of CAC cured at ambient temperature and at higher temperatures. The system cured at ambient temperatures shows a transient high strength before 28 days. Then due to conversion and porosity of the system a gradual decrease in strength is observed till it reaches a minimum strength value. Later additional strength is gained over time due to further hydration. However, the other system cured at elevated temperatures had continuous strength gain as the high temperature caused rapid conversion to stable hydrates where it was for a large section. That is why it didn't reach its minimum converted strength even after about 100 years [2]. That is quite different than the hydration of OPC where it continues to gain strength over time.
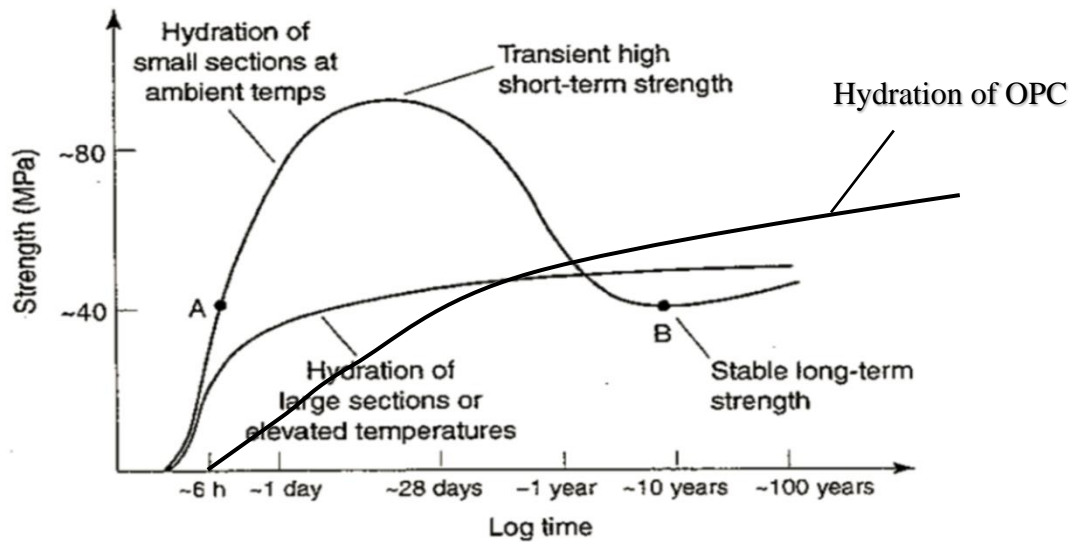
Figure 1.5 Schematic diagram for strength development for CAC and OPC adapted from Scrivener et al.
Source: [2]

1.6 Heat Generation and Internal Heat in CAC

As mentioned previously, conversion in CAC from metastable hydrates to stable hydrates are affected by temperature and humidity. The rate of heat dissipation from CAC is then important to know the temperature reached during its hydration. Fryda et al. examined the impact of concrete size on internal heating [53]. The authors observed high internal temperatures about 40° C and 58°C that occur in smaller elements within 3 hours of curing. Larger elements can generate high internal temperatures of 9°C within the first 9 hours. The temperature profiles for the tested elements can be shown in Figure 1.6. This may have suggested that a larger element may have fully converted at an earlier stage than smaller sections due to high internal temperatures generated.
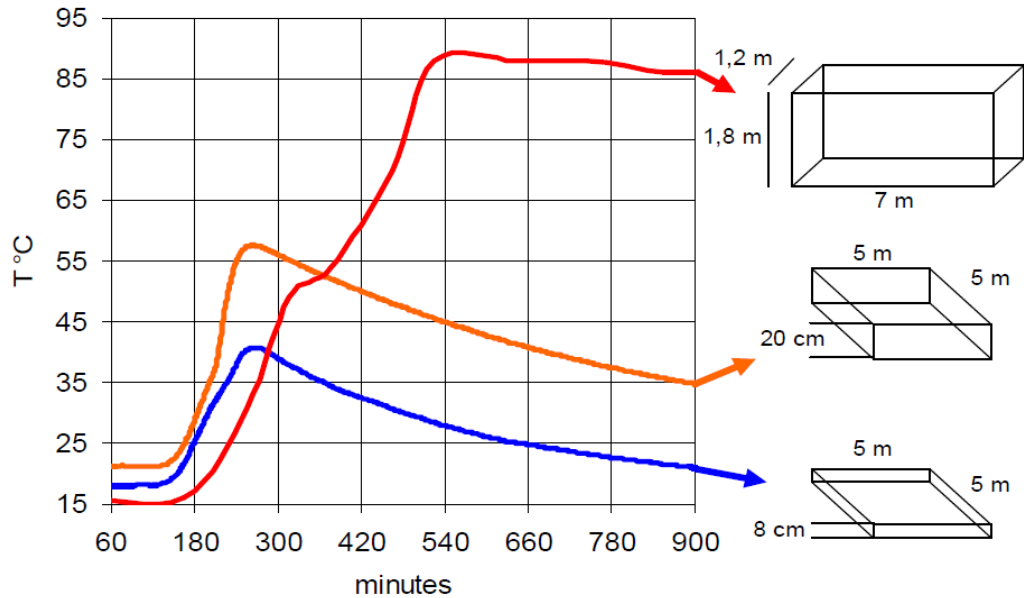
Figure 1.6 Internal heat temperatures for CAC in different size elements.
Source: [53]

1.7 Factors Affecting Setting Time of CAC

As discussed in section 1.4, the temperature influences speed of conversion in CACs. Earlier studies have shown that the setting time of CACs are significantly impacted by temperature. The set time of CAC systems is retarded between 18℃ and 30 ℃, where it decreased again when temperature gets higher than 30 ℃ [54]. This was in contrast to what Robson observed, where he stated that the set time of high alumina content cement retards when the temperature is between 18℃ and 30 ℃, but accelerates when the temperature gets higher than 30 ℃ [54]. Bushnell-Watson's and Sharp's work agreed with this, indicating that the setting time of CACs is directly proportional with the temperature and it reaches its maximum between 26℃ and 30 ℃ followed by a decrease in set time above or below these temperature limits [29]. The authors illustrated this relationship on two different grades of CAC as shown in Figure 1.7 [29]. The authors discussed several theories that were earlier reported which may explain the unusual behavior of the setting time. They

suggested that the retardation in setting time between the temperatures 20℃ and 30 ℃ is due to difficulty of the nucleation of C_2AH_8 and noted the importance to state the temperature when quoting the set time for CAC [29]. Campas have returned this retardation due to the difficulty of nucleating of CAH_{10} as temperature increases, until it becomes almost impossible to nucleate when temperature gets above 29℃ [55].

An earlier theory stated that the unusual behavior of set time was attributed to the presence of C_2S in the CAC [56]. However, Bushnell-Watson and Sharp were not in total agreement with that observation. The authors observed the same setting behavior to CAC pastes that do not contain CA_2, and suggested that the retardation is associated with the CA hydration [29].
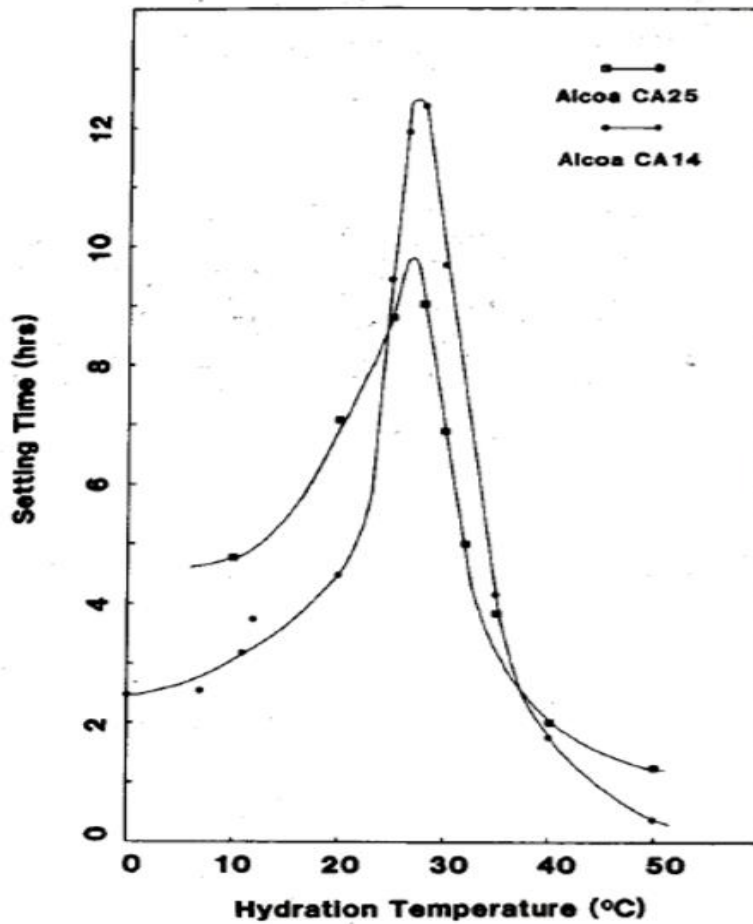
Figure 1.7 The impact of temperature on setting time of CAC samples.
Source: [29]

1.8 Hydration of CAC in the Presence of Calcium Carbonate

Previous work has shown that the hydration of CAC occurs at an earlier stage in the presence of calcium carbonate compared to pure CAC systems [57]. Fentiman has observed that conversion of CAC was delayed in the presence of $CaCO_3$ [58]. A minimum converted strength was observed after six months for such mix which was similar to the minimum strength on days 5-7 in pure CAC as shown in Figure 1.8. Both systems were cured at 20˚C for 24 hours followed by long term curing at 38˚C. The author attributed that delay in conversion to the formation of a secondary metastable hydrate monocarboaluminte

(C_4ACH_{11}) that will eventually convert to stable hydrate (C_3AH_6); at a slower rate, however.
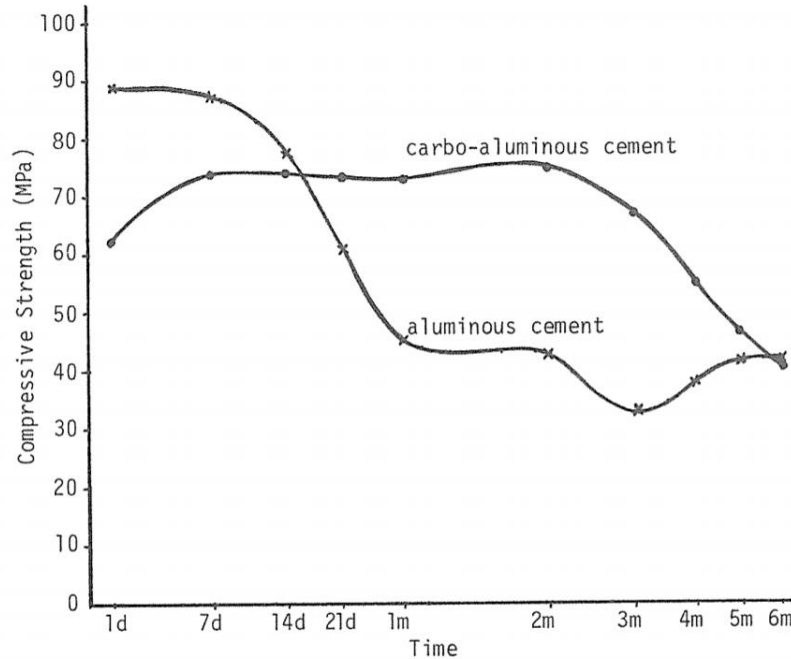
Figure 1.8 Compressive strength for pure CAC (aluminous cement) and 70% CAC & 30% $CaCO_3$ (carbo-aluminous cement).
Source: [58]

Later, Adams et al. showed that using smaller dosages of finely ground limestone (FGLS) can be beneficial to CAC systems [51]. The authors observed that incorporating 5% to 10% of FGLS will mitigate the minimum converted strength without delaying the time to convert. The compressive strength for different mixes with different cement replacement levels is shown in Figure 1.9. These systems were cured at ambient temperatures for 24 hours, then placed in heated water at 50˚C until the day of testing to promote conversion.
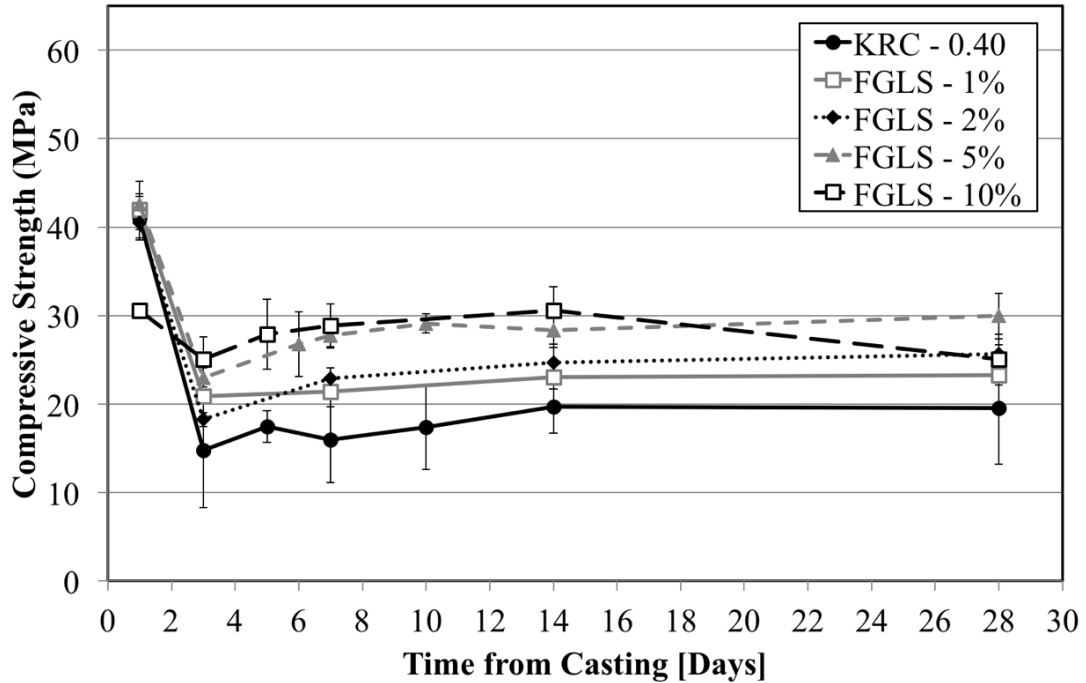
Figure 1.9 Compressive strength for CAC with different replacement levels of FGLS.
Source: [51]

1.9 Durability of CAC

The durability of CAC, as with OPC, is a function of its quality in addition to the intensity of the environment being exposed to. Almost all deteriorations are determined by the chemical ingress into the concrete and the resistance to that ingress. The resistance of CAC is assessed through its pore structure and pore connectivity. CACs are well known for their high early strength gain, however, those materials should also survive for the remaining life of the structure [59]

As mentioned above, amongst the earlier applications of CAC was the external sulfate resistance. The durability of CAC concrete in aggressive environments is considered one of its major benefits of the material. It was used in south of France where the severe deterioration of OPC in the Paris-Lyon-Marseille railway tunnel occurred due

to CaSO$_4$ formation [60]. The OPC failed after five years, where a 20% loss of strength in 5 years and 50% in 10 years was observed [2]. CAC was also used to anchor haulage cables in a sulfate mine which was completely immersed in a saturated solution of gypsum. The absence of free lime during CAC hydration allows the material to be a highly resistant to sulfate attack [54], [61]. However, the resistance to alkalis (especially strong alkalis) is weak [39].

It was a common belief that concrete rich in alumina content would have a high chemical resistance to sulfate attacks. For that reason, CACs were used in sulfate bearing soils. However, few collapses that occurred in early 1970s [62], [63] raised some red flags for the use of precast high alumina cement concrete components. Some of these failures were attributed to poor detailing and practice, but others were a direct result of excessive strength loss of CAC [2], [63]. In 1990, Crammond conducted some tests on CAC specimens of precast cylinders and in-situ piles buried in sulfate bearing soils at Northwick Park in London [63]. He noted that the low permeability of good quality unconverted concrete is the reason that CAC cement has good sulfate resistance properties [63]. However, sulfate attack will occur in poor quality converted concrete as the concrete has high permeability to sulfate solutions and also the additional free water in the system create mobility of sulfate anions. Some other long term performance tests [2], [62] came to the same conclusions which states that "a good quality high alumina cement concrete not subjected to higher temperatures performed very well in sulfate rich environments". The term "good quality" is discussed in the next paragraph.

In 1973, the British Standards Institution (BSI) mandated in its code of practice that CAC cement materials to be used should keep its w/c to 0.4 or below [56]. This ratio

requires using sufficient cement to achieve the desired workability so that the minimum content is 400 kg/m^3. Later, Lafarge Fondu International adopted this approach as well [56], [64]. Adding to those guidelines, it recommended to keep the cast concrete cool and prevent surface drying.

Some difficulties are posed within the compositions of very strong chloride mine waters. Kurdowski et al. observed a very dense layer of AH_3 on the surface of CAC cubes (immersed in strong chloride solutions) accompanied with a large amount of salt [65]. They also found higher concentration of C_3AH_6 in the inner paste, while higher concentration of CAH_{10} in the outer layer. The authors attributed the high resistivity of CAC concrete to corrosive solution to the low porosity of the outer layer that hinders the mobility of the chloride ions into the inner paste. Earlier it was suggested that the reason for the low porosity was due to the presence of AH_3 [66]. In addition to that, some authors attributed the durability of CACs to corrosion to the decomposition of hydrates and aggregate materials which is followed by the dissolution of salts that are formed [67]. Additionally, Dunster et al. observed O_2 permeability on 60-year old CAC concretes exposed to sea water in two different cases [68]. For samples with w/c around 0.6 the permeability for the outer shell (denser) was different to that of the inner paste. On the other hand, for samples that met the guidelines of keeping the w/c below or equal to 0.4 with cement content more than 400 kg/m^3 had same permeability values with respect to various depth levels [2], [68].

1.10 Reinforcement Corrosion and Carbonation in CAC

The converted CACs hydrates are characterized by their high porosity; however, they can still have a reasonable low permeability level when adhering to the recommended w/c ratio of 0.4 or lower [23].

CACs have a pH of about 11.97 for the stable phase and 12.13 for the metastable phase [69].

Although CACs have low alkalinity, it is released into the pore solution and concentrated during hydration [2]. However due to the lower binding capacity of CAC to alkali ions, the pH level (about 12.50) of CAC is very similar to that of OPC. Field and experimental work have confirmed that the conversion of CAC has very little impact on the passive layer on steel reinforcement [69], [70]. Thus, conversion of CAC doesn't change its capacity to protect reinforcement against corrosion. Adams et al. showed that the pH can be significantly impacted by the aggregate type [44]. As the chemical analysis of the CAC pore solution showed that the pH of the carbonate limestone was significantly higher than that of siliceous aggregates due to more dissolution of unhydrated cement in the limestone carbonate system.

In 1993, a series of laboratory tests were conducted at the BRE on CAC to provide a comprehensive understanding on the rate of carbonation and corrosion of its reinforcement. Dunster et al. observed that the carbonation in CAC spreads in the same way as in OPC with similar design mix [71]. Mammoliti et al. conducted short term experiments on CAC cylinder samples and stated that the steel corroded for fully converted CAC at a higher rate factor ($\sim 50\%$) than with unconverted ones [72].

1.11 Volume Reduction and Drying Shrinkage in CAC

As discussed previously, CAC systems will undergo conversion when metastable hydrates convert to stable hydrates. This is accompanied by a significant release of water and densification in the system [2]. After conversion, CAC systems experience a significant reduction in its strength which may adversely impact its long-term durability. The change in pore structure may drastically impact drying shrinkage.

Drying shrinkage in concrete is the loss of water from its pore structure to the environment. It occurs when the ambient relative humidity is less than within the concrete. It will continue to occur until the relative humidity inside concrete stabilizes with the external humidity [73]. The loss of this water creates pressure, which eventually causes these pores to collapse [74]. As drying shrinkage occurs in hardened concrete after setting due to the loss of capillary water, its volume decreases. A rapid rate of volume reduction begins for the first few months and then decreases over time and starts to stabilize. If concrete is not restrained, it can shrink freely with no impact due to drying shrinkage. In condition concrete is used in deck slab, being a part of a bridge structure, will be restrained from adjacent structures such as a pier. A restrained concrete that undergo drying shrinkage will build up tensile stress which can eventually lead to crack propagation [75]. These cracks are undesirable as they create paths to aggressive chemicals which can cause corrosion and can impact the sustainability and life cycle cost of the structure. There are many factors that affect drying shrinkage such as water to cement ratio, aggregate types, aggregate size, and curing regimes [76].

Previous work has shown that the total drying shrinkage in CAC is similar to that in OPC [2]. However, drying shrinkage occurs in CAC at a more rapid rate compared to

OPC system [2], [77]. This can be attributed to conversion in CAC systems and water movement in its pore structure. No previous study was done to understand the drying shrinkage before and after conversion in CAC. It is important to study the impact of conversion in CAC on drying shrinkage and to understand how different cement formulations, different w/cm, and different time to conversion may affect the drying shrinkage. The volumetric change due to drying shrinkage is an important durability issue that need to be studied in CAC systems. In particular when used as a rapid repair material which requires to maintain volumetric stability without cracking when bonded to an existing substrate.

1.12 Electric Resistivity for CAC

Measuring the electrical resistivity of concrete has gained popularity especially for in situ applications due to its easiness and rapidness in running the test. Based on the speed of the electric current, it measures its electric resistivity, which is a quantitative measurement that is impacted by moisture content, permeability, tortuosity, and pore size within the concrete. Various techniques have been studied for measuring the electric resistivity in concrete such as bulk and surface resistivity. The bulk resistivity of concreted is measured by using the uniaxial method, standardized by ASTM C1760 [78]. The surface resistivity has been adopted by the American Association of State Highway and Transportation Officials (AASHTO), which is a standard test method outlined in AASHTO T 358-17 [79]. While both methods have proven giving consistent results, the latter is more convenient for in-situ measurements. The electrical resistivity of concrete can be described as its ability to resist the flow of ions through its structure. Thus, the properties of the microstructure of

concrete that is will impact its durability which may be correlated to the electrical resistivity measurements. This is related to the pore structure of concrete, its distribution, and the interconnection between its pores. For instance, the more porous the structure with high degree of interconnectivity; the higher its porosity. When measuring electrical resistivity, the higher the porosity the more interconnectivity between pores which will result in lower electrical resistance measurements. That is because the pores in concrete allow the movement of ions between them and thus make it more conductive to electric current.

The electric resistivity of concrete can be correlated to corrosion because higher resistivities generally mean that there is less likelihood that chloride (or other aggressive elements) can transport easily through the concrete [80]. Another application for electric resistivity measurements is using it to detect the concrete ability to withstand chloride penetration. This method was used as an alternative test to the Rapid Chloride Penetration Test (RCPT) [81], [82]. Electric resistivity of concrete is considered to be a qualitative test that can detect the porosity of concrete according to the ions movement but cannot quantify its compressive strength.

1.13 Promoting Conversion in CAC

This section is derived from the following paper: M M Korayem and M P Adams; "Methods for promoting conversion and determining converted strength of calcium aluminate cement concrete"[83], Bridge Engineering Institute Conference 2019 (BEI-2019) Honolulu, Hawaii, USA, July 22-25, 2019.

1.13.1 Synopsis

Rapid repair materials have become commonplace for bridge and pavement repairs since the need to reduce lane closure times has become more important to local economies and users. Rapid repair materials can vary in chemistry, and often, standard test methods do not apply for testing the quality of these materials. Calcium aluminate cement (CAC) concretes are high early strength systems that are particularly useful in cold environments where the system will still rapidly set and gain strength at temperatures near freezing. CAC systems undergo a unique process known as conversion, in which metastable hydrates convert to stable hydrates, resulting in an increase in porosity and strength loss. Understanding the time at which this conversion occurs, and the magnitude of strength loss is important for long-term design decisions involving repaired concrete systems. Methods promoting conversion for quality assurance testing are discussed including immediate submersion in 38°C and 50°C water baths, delayed submersion in 50°C water bath, and self-heating with the use of a semi-adiabatic box. Mechanical properties testing is discussed with a review of required modifications to existing test methods. Finally, determination of time to conversion through a concrete maturity method, non-destructive testing, and destructive testing techniques is discussed with a presentation of a novel method of using electrical resistivity to detect conversion of CAC concrete.

1.13.2 Introduction

Calcium aluminate cement (CAC) is characterized by its rapid strength gain, even at low temperatures approaching 0°C [2]. This key feature has made CACs extremely useful in certain concrete repair applications, particularly in cold regions (Banfill 2014). CAC is a specialty cement that can be used in a wide range of applications and has led to an increase

in interest in concrete rapid repair applications. Despite the higher cost of CAC (about 4-5 times of ordinary portland cement, OPC), it can provide solutions to specific rapid repair applications where the use of ordinary portland cement may not be feasible [19]. CAC has also performed well as a corrosion resistant material and has been widely used in sewer pipe lining and repair [17], [18], [23].

CAC composition differs significantly from ordinary portland cement (OPC). CAC contains mainly alumina and calcium oxides and little to no silica while OPC contains mainly calcium and silica oxides and little alumina [23],[31]. The hydration of monocalcium aluminate (CA, the main phase in the unhydrated CAC cement) initially produces CAH_{10} and C_2AH_8 which are metastable hydrates. These metastable hydrates undergo a process known as "conversion" in which the two denser stable hydrates, C_3AH_6 and AH_3, are formed. This conversion process is accompanied by the release of water, an increase in porosity, and significant reduction in its strength. Whether metastable or stable hydrates form during the hydration of CAC depends strongly on temperature, unlike the hydration of calcium silicates which produce the similar hydrates at all temperatures below 100˚C [2]. If the temperature is below 15˚C the initial metastable hydrate CAH_{10} is formed, while if the temperature is above 30ºC the initial metastable C_2AH_8 is formed. If the temperature lies between 15ºC and 30ºC, then neither is preferred between the two metastable hydrates regarding the order to be formed and a reduced setting time is observed [2], [5], [44]. The time to conversion varies and depends mainly on the temperature history to which concrete is subjected. Previous work has shown that CAC concrete has converted within 15 minutes from being cast when placed directly in a 100˚C water bath. When placed in a water bath of 30°C, CAC was shown to not reach its minimum converted strength until

30 days after casting [47]. Some systems have lasted up to 70 years without undergoing conversion [84] It is important to note that the conversion process only occurs in systems that contain only CAC as the binding material. As additions are made to create binary or ternary binder systems, different hydrates will form, and conversion will not occur.

The conversion process has a significant impact on the strength of CAC systems. Due to the densification of hydrates during conversion, pore space opens up inside the bulk cement paste reducing compressive strength of the concrete [37] Once a minimum compressive strength is reached (i.e., the system has full converted) the strength will again increase as the remaining unhydrated cement grains continue to hydrate [2], [23] It should be noted that despite the loss in strength, good quality concrete of acceptable compressive strengths can be achieved after conversion with acceptable mixture design. The minimum converted strength should be used as the design strength for the system, however, to ensure that the system is not structurally deficient.

The standard method used for curing hydraulic cement concrete for compressive strength testing, ASTM C31[85] in the US, mandates that cylinders are to be cast on site and allow to cure for up to 48 hours. Then these cylinders can be placed in a water bath at 23˚C ± 2˚C until the day of testing. This method is not applicable to CAC as this curing regime will not allow for reaching the minimum converted strength within a convenient time at this given temperature. Therefore, alternative methods of curing must be used that will promote conversion. This method should ensure that the minimum converted strength that is used for design can be measured within a reasonable time period (i.e., within 28 days). This paper reviews the current methods used for promoting conversion such that the

minimum compressive strength in CAC systems that are used for rapid repair of pavements and transportations structures can be measured.

1.13.3 Existing Methods of Promoting Conversion to Determine Design Strength

There are two existing methods that are used to promote conversion of CAC and to obtain the minimum converted compressive strength within a reasonable time. The first method, described in European committee for standardization, calcium aluminate cement-composition, specifications, and conformity criteria (EN 14647), is used primarily in Europe. This method states that to achieve the minimum converted strength of CAC concrete rapidly, the test specimens should be submerged directly in a 38°C water bath after cast. According to this standard, the minimum converted strength will occur at the fifth day after being cast [86]. Figure 1.10 shows the effect of temperature on the speed of conversion.
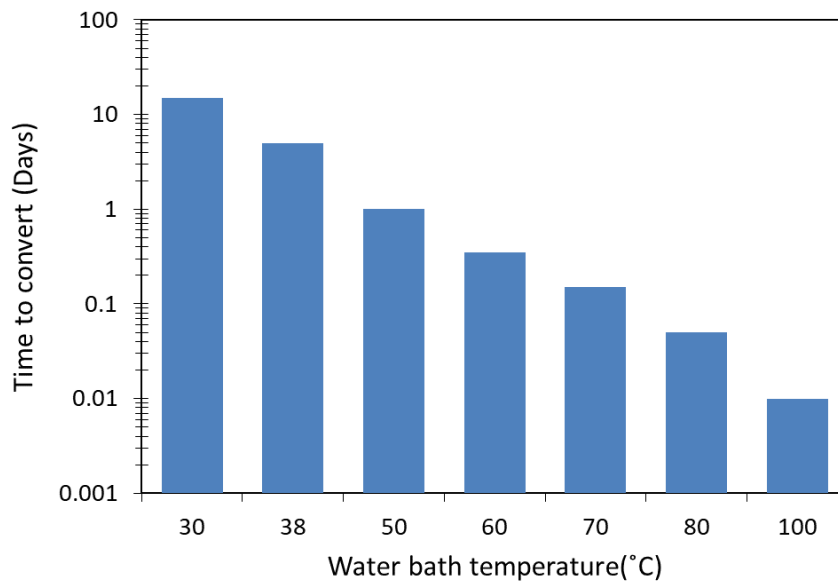
Figure 1.10 The impact of temperature on time to convert in CAC systems.
Source: [47], [51], [53]

The second method is described by standard SS-4491 used by the Texas Department of Transportation, in Texas, U.S.A. This method states that the specimens should be placed immediately in a heavily (semi-adiabatic) insulated box after casting. The insulated box takes advantage of the high heat of hydration produced during CAC hydration which is captured to encourage "self-heating" of the specimens [87]. These samples that are stored in the insulated box will in turn generate heat to promote the rapid conversion of the metastable hydrates. A heavily insulted box similar to that suggested by the Texas DOT can be seen in Figure 1.11 [88].

Figure 1.11 Semi-adiabatic insulated box for curing CAC.
Source: [88]

These test methods are useful for determining the converted strength of CAC concrete within a reasonable time; however, they are not field-friendly and are not practical to be used for infrastructure applications. That is because these methods do require bulky equipment, or equipment that requires a power source. It is not easy to be transported to the site, so samples can be directly placed into the heated water bath or the insulated box directly after being cast. Additionally, it is not clear if these curing methods produce a conservative estimate of the design strength. When the system is encouraged to convert even before the system has completely hardened, this may result in a different microstructure compared to a system that converts after the concrete has reached final set.

1.13.4 Proposed Method of Promoting Conversion to Determine Design Strength

Fryda et al. [53] proposed a test method that overcomes these challenges by allowing the CAC concrete specimens to cure on site at ambient temperatures for up to 48 hours. Then the specimens can be transported to the laboratory and placed in a heated water bath at 50°C [53]. Adams et al. suggested a modification to the method to reduce the time on site to 24 hours, and also studied the robustness of the test method with various parameters (aggregate types, curing time, w/cm ratio and the temperature of curing) in order to examine the robustness of this test [51], [88]. The proposed method suggests that when cured on site at normal ambient conditions for 24 hours, and then transported to the laboratory and placed into a water bath at 50°C, minimum converted strength will be reached at 48 hours after casting. This proposed method is convenient to be used on site as it permits the curing of the cylinders in the field at ambient temperatures and then they can be transported to the laboratory at a later time for curing till the day of testing. Therefore, no additional equipment will be required on site beyond the standard concrete sampling tools. A heated water tank for curing the CAC samples at temperature 50°C ± 2°C in the laboratory is shown in Figure 1.12. This system uses two submersible heaters in a horse trough tank filled with water, a submersible circulation pump, and a programmable temperature relay to maintain temperature. The tank is then covered with insulation to better maintain temperature. Such a system can be made for as little as $600 USD.

Figure 1.12 Heated curing tank at 50˚C (left) and temperature relays set at temperature of 50˚C±2˚C (right).

CAC concrete systems can be very useful in bridge and road repairs as they are known to gain early strength at very low temperatures approaching freezing. CAC systems undergo a unique process known as conversion that results in an increase in porosity and strength loss. It is crucial then to know when conversion occurs and to get the minimum converted strength for design. Different existing methods for promoting conversion including immediate submersion heated water baths and self-heating with the use of a semi-adiabatic box have shown good results. However, they are not field-friendly for repair situations and it may be difficult to have all cylinders well sealed when placed in the water tank. A recently developed accelerated method to promote conversion by allowing to cure samples for 24 hours at ambient temperatures followed by submersion in a heated water tank at 50˚C is recommended instead.

1.14 Summary

This chapter summarized a literature for CACs including its features, properties, and applications. This literature review presented CAC history, microstructure, cement hydration, strength, conversion, durability issues, promoting conversion procedures, and curing methods.

In conclusion, previous research has extensively studied the kinetics of CAC conversion. Very limited work has been done to understand how this conversion may impact the CAC durability. CAC is a specific material and is useful for some niche applications (low temperature rapid repair material, harsh acidic environments). However, there is a lack of understanding of CAC durability after conversion. In response to the above mentioned research gaps, this work is intended to help to improve the understanding of CAC durability after conversion to help engineers to better assess this material in its special applications. It is also intended to help as a guidance on long term properties of CAC and to propose a preliminary test method to detect conversion easily in the field.

CHAPTER 2

MEANS AND METHODS

This chapter describes the experimental methods used throughout this work.

2.1 Mixture Design and Mixing Procedures

2.1.1 Mixture design

The European standard for CAC has set recommendations for the design of CAC concrete systems in order to ensure a feasible strength after conversion. These guidelines suggest a minimum cement content of 400kg/cm and maximum water to cement ratio of 0.40 [86], [87]. The cement and concrete mixtures used in this research are described in detail in the following chapters.

2.1.2 Mixing procedures

A Marshalltown 600CM mixer, as shown in Figure 2.1, was used for all the mixtures done throughout this dissertation.

Figure 2.1 The mixer drum used for CAC concrete mixes.

All concrete mixtures were done following the procedures used in previous work by Adams et al. [51] as follows:

1. All coarse then fine aggregates with half of the mixing water are added to the mixer,

2. Cover the mixer and allow to mix for 1 minute,

3. While mixing add the fondu retader and the superplasticizer,

4. Then add the cement and the remaining water,

5. Continue to mix for three more minutes,

6. Finally, discharge all the mix and cast the specimens.

The total mixing time was 4.5 minutes ±10 seconds. All aggregates were brought near to their SSD conditions before mixing. The total mixture water was then adjusted to ensure that the required water to cement ratio was reached.

Concrete mixtures were done in the laboratory ambient temperature of $23 \pm 2°C$ and the relative humidity was not controlled. For each mix the concrete temperature, unit weight and slump were measured directly after mixing. Unit weight was measured as per ASTM C138 [89] and the slump was measured as per ASTM C143 [90].

2.2 Aggregate Properties Testing

Aggregate properties were measured for all coarse and fine aggregates used in this work. These properties included assessing specific gravity and absorption capacity for all aggregates. Specific gravity and absorption capacity were measured according to ASTM C128 for fine aggregates [91] and ASTM C127 for coarse aggregates [92]. All sieve analyses were done according to ASTM C136 [93].

2.3 Curing Procedures

Curing procedures varied for different experiments done throughout this work. Each curing method is explained in detail in the following chapters for both unconverted and converted systems.

2.4 Compressive Strength Testing

Compressive strength testing was measured for 4 in. diameter by 8 in. height (100 mm by 200 mm) cylinders. The compression testing presented in this dissertation was performed using testing machine FHS-700 B-T PILOT as shown in Figure 2.2. Compressive strength testing for cylinders followed ASTM C 39 [94].

Figure 2.2 FHS-700B-T PILOT compressive strength testing machine.

2.5 Free Drying Shrinkage Testing

Drying shrinkage in concrete occurs when water in the pore structure is lost to the environment. This will occur if the ambient relative humidity is less than 100%. It will continue to occur until it equalizes with the relative humidity inside the concrete. As water leaves the capillary pores, it creates pressure and build up tensile stresses in the system [2], [74]. This will eventually lead to the formation of cracks. These cracks are undesirable as they increase the maintenance repairs and shorten the service life of the structure. Drying shrinkage and mass loss measurements were taken on CAC hardened specimens of 3 in. x 3 in. x 11.25 in. (75 mm x 75 mm x 285 mm). The measurements were taken for a set of 3 prisms for each mixture and was measured according to ASTM C 157 [95]. All prisms were cast into steel molds and allowed to cure for 24 hours at ambient temperatures. Then they were demolded and kept in the drying shrinkage controlled room at temperature 23 ± 4˚C and RH 50%, where change in length and mass were measured over time. A detailed description of the curing procedures is explained in chapter 4 for each mixture. Figure 2.3 illustrates the comparator set up for measuring length change of prisms over time. Using the comparator, a comparison is made to a rod of fixed length. This rod is made of invar; a material that is well known for its low coefficient of thermal expansion. Therefore, it relatively does not undergo expansion or contraction due to temperature changes. That feature makes it a viable material for length change measurement comparison over longer time periods.

Figure 2.3 Drying shrinkage comparator setup.

2.6 Electrical Resistivity Testing

Electrical resistivity for concrete resembles its ability to withstand the ionic mobility in its pore structure. There are various techniques in measuring both the bulk and surface resistivity. In the work presented, only surface resistivity measured for concreted is of interest. Surface resistivity is measured using the wenner probe as shown in Figure 2.4. This measurement procedure is standardized by AASHTO T 358-17[79].

Figure 2.4 The wenner probe for electrical surface resistivity measurement.

The wenner probe has four equally spaced probes, where upon contact to concrete surface, the outer probes apply electric current (I) to the concrete and the inner ones measure the electric voltage (V) as illustrated in Figure 2.5.

Figure 2.5 The wenner probe setup.

The electrical resistivity testing method is a non-destructive test which can be performed on concrete cylinders, similar to the ones used in compression testing. Despite the easiness and rapidity of the surface resistivity measurements, the composite structure of concrete makes it challenging to get reliable resistivity measurements. For instance, a dry sample would give a higher electric resistivity than when placed in a moist condition. Not only the saturation condition may impact the resistivity measurements in concrete, but the temperature fluctuation as well. As the temperature affects the movements of the ions and therefore impact the resistivity measurement. As temperatures get higher, the electric resistivity readings will decrease. It was reported that a change of 1˚C in temperature can result in a 3% change in electric resistivity measurements[82]. For these reasons, user should be very cautious with curing conditions and ambient temperatures to mitigate any possible variables. Additionally, as mandated by standard test method multiple readings are taken for each sample in order to get a reliable average electric resistivity measurement.

CHAPTER 3

USING ELECTRIC RESISTIVTY MEASUREMENTS TO ASSESS CONVERSION

This work is being prepared for submission to ASTM Advances in Civil Engineering Materials Journal. Part of this work has been accepted for publication in Calcium Aluminates: Proceedings of International Conference, Cambridge, England, October 2020 [96].

3.1 Synopsis

Calcium aluminate cement (CAC) systems are used for a wide range of applications including rapid concrete repair, scour resistance, protection of sewage systems, and refractory applications. Concrete, mortars, and pastes using 100% CAC as the binder undergo a process known as conversion, in which metastable hydrates initially formed during hydration convert into denser, stable hydrates. The densification of the hydrates causes increased porosity in the cement paste matrix which results in a loss of strength. Determining when conversion occurs is generally completed through ongoing compressive strength tests until a minimum concrete strength is reached. The rate of conversion is dependent on the temperature history of the concrete, and therefore determining when conversion happens through specimens in the lab will not necessarily relate to when conversion happens in the field. In situ measurements of concrete using electric resistivity have gained ground due to the ease and rapidity in doing the test. The objective of this research was to determine if there is a distinct trend between the electric resistivity and higher porosity to detect conversion in CAC systems. A comparison was made between

converted and unconverted systems with respect to strength. The electric resistivity measurements were done on same mixtures on the same days. Initial work to validate the robustness of this test and its universal applicability, was done on systems with different mixture design variables including different w/c ratio, different types of aggregates, and different cement replacement levels. A significant decrease in electrical resistivity was observed to be correlated with conversion and associated with strength reduction. The CAC systems that were prevented from converting showed a steady increase in electrical resistivity measurements, indicating that the conversion process results in changes that will show a significant change in electrical resistivity. Results presented indicate that electrical resistivity measurement may be a useful tool for determining time to conversion in CAC systems in situ.

Keywords: assess conversion, calcium aluminate cement, electric resistivity, strength testing.

3.2 Introduction

The deterioration of infrastructure in North America has resulted in a significant need for concrete repair materials that can be used to maintain service life of these structures [1]. Hydraulic cement based rapid repair materials can be used to repair pavement and bridge deterioration with minimal impact on economic activities. While there are many options for use in repair situations, calcium aluminate cement (CAC) has become more popular, particularly in situations where repairs must be completed rapidly and at low temperatures. CACs have unique properties as they have high early strength even at temperatures approaching freezing [2], [3].

The chemical composition of CAC systems differs significantly from Portland cement (PC). CAC contains mainly aluminium and calcium oxides and little to no silica while PC contains mainly calcium and silicon oxides and only small amounts of alumina [19], [31]. CAC systems undergo an inevitable process called conversion. In this process the metastable hydrates (CAH_{10} and C_2AH_8) convert to denser stable hydrates (C_3AH_6 and AH_3). The densification of the system increases the porosity and is accompanied by a significant reduction in the compressive strength. The minimum converted strength is the compressive strength that should be used in the design process. The speed of the reaction of the conversion process depends upon temperature history, moisture content, and water to cementitious materials ratio [2], [19], [50]. Determination of when conversion has occurred is important as during quality testing of the systems the minimum converted strength needs to be determined to ensure the design requirements are met. Current techniques for determining when conversion has completed involve casting many samples, storing the samples at high temperature, and testing them in compression over a series of days. The minimum strength of the tests is what is used as the minimum strength [51], [53], [97] . This process is prohibitive because it is labour and material intensive.

In recent years, measuring the electrical resistivity of concrete has gained popularity, especially for *in situ* applications, due to the ease and rapidity of the test. Measuring surface resistivity of concrete has been standardized around the world, including in the United States under AASHTO T 358-17 [79] . The electric resistivity measurement is based on the speed of the electric current and is impacted by moisture content, permeability, tortuosity, and pore size within the concrete. Whittington et al. showed that the electric resistivity in different PC concrete mixes was able to be used as an indicator to its strength

gain and degree of hydration [98]. Others concluded that there is a linear trend between electric resistivity and compressive strength for the same PC mixing design at the same w/c ratio [99]. In CAC systems, it is known that conversion is associated with an increase in porosity and is accompanied by a release of water. This will result in a significant and sudden reduction in the resistivity of the concrete, which can be measured to determine when concrete has undergone conversion. By doing this, one set of cylinders could be used to monitor when conversion has occurred, and then compressive strength testing can be completed to determine the minimum converted strength. Thus, it would be beneficial to understand if there is a distinct relationship between the electric resistivity and time to conversion in CAC systems. This paper presents work that was done to determine whether this method could be used effectively in a variety of CAC systems.

3.3 Experimental Work

3.3.1 Cement

A standard grade CAC was used for all the concrete mixtures examined in this study. The oxide composition of the CAC used is shown in Table 3.1.

Table 3.1 Oxide Composition of CAC

Oxide (% wt)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	Mn_2O_3	P_2O_5	SrO	Loss
CAC	5.0	38.2	15.4	37.5	0.7	0.03	0.23	0.06	2.0	0.23	0.13	0.02	0.65

3.3.2 Finely ground limestone

The finely ground limestone used in this study had 99% calcium carbonate. It had a specific gravity of 2.70 and a Blaine fineness of 9800 m^2/kg.

3.3.3 Aggregates

A wide range of aggregates were used in this study for the concrete mixtures. Absorption capacities and bulk specific gravities, oven dry ($G_{sb,OD}$) for all aggregates were measured according to ASTM C127 for coarse aggregates and according to ASTM C128 for fine aggregates [91], [92]. A description of the coarse and fine aggregates used are shown in Table 3.2.

Table 3.2 Coarse and Fine Aggregates Description

Aggregate name	Absorption capacity (%)*a	$G_{sb,OD}$	Source	Mineralogical description
Siliceous_Coarse	2.58	2.44	Oregon, USA	Siliceous
Limestone_Coarse	0.67	2.68	Washington, USA	Carbonate Limestone
Granite_Coarse	0.52	2.69	New Jersey, USA	Crushed Granite
Siliceous_Fine	3.08	2.41	Oregon, USA	Siliceous
Limestone_Fine	0.71	2.69	Washington, USA	Carbonate Limestone
Granite_Fine	0.54	2.60	New Jersey, USA	Crushed Granite

*a Absorption capacity is measured as the mass percentage of water that can be absorbed into the aggregate's permeable pores compared to the dry mass of the aggregate

3.3.4 Concrete mixtures

The concrete mixtures prepared for this study are described below in Table 3. The w/c presented is an effective w/c of 0.40, 0.35, or 0.45, with total water content adjusted to take into account the moisture content of the aggregates. The maximum size aggregate for the coarse aggregate used was 19 mm (3/4"). Mixture data are labelled as described in Table 3.3; systems that underwent the conversion promotion process have "_conv" appended to the mixture label. Systems that did not undergo a conversion promotion process have "_unconv" appended to the mixture label.

Table 3.3 Concrete Mixture Design

Mixture Label	w/cm	Fine Aggregate content (kg/m^3)	Coarse Aggregate content (kg/m^3)	Cement content (kg/m^3)	FGLS content (kg/m^3)	Aggregate Type
S_0.40	0.40	730	890	440	0	Siliceous
L_0.40	0.40	855	938	440	0	Carbonate Limestone
G_0.40	0.40	836	922	440	0	Crushed Granite
G_0.35	0.35	808	896	440	0	Crushed Granite
G_0.45	0.45	855	945	440	0	Crushed Granite
FGLS_3%	0.40	835	920	427	13	Crushed Granite
FGLS_7%	0.40	840	919	409	31	Crushed Granite
FGLS_10%	0.40	852	919	396	44	Crushed Granite

3.4 Experimental Methods

3.4.1 Sample preparation

The CAC concrete was mixed and cast following the mixing procedures presented in Adams et al. [51] . The concrete was mixed in a rotary drum mixer by first adding all the coarse and fine aggregates and half of the mixing water to the mixer. The mixer was covered and allowed to mix for 1 minute. Following this, while still mixing the cement and then the remaining water along with retarder, and superplasticizing admixtures were added over a 1-minute period. The mixer was then covered again and allowed to mix for an additional minute before being turned off. The mixture was then deposited into a large plastic container and concrete was scooped from here to make test specimens. Concrete cylinders of 100 mm diameter and 200 mm height were cast for all testing completed in this study. Cylinders were cast according to procedures specified in ASTM C39 [94] . After casting, the cylinders were finished and sealed with plastic lids to maintain moisture in the cylinders. Then they were covered with wet burlap and plastic cover to ensure that

moisture loss was prevented. All samples were cured at 23˚C ± 5˚C (laboratory ambient temperatures) for 24 hours in the plastic moulds in which they were cast before being demoulded. After demoulding the cylinders, they were placed either in a moist curing room at 23˚C ± 5, which would maintain the concrete in the unconverted state during the testing period (labelled with _unconv); or they were placed into a heated water bath to promote conversion (labelled with _conv). Figure 3.1 presents a timeline of the curing procedure for both specimens that were maintained in the unconverted state and specimens that were placed in a heated water bath to promote conversion.

Conversion promotion procedure [a]

Day 0

Casting cylinders in plastic molds, sealed and covered with burlap. All cylinders were allowed to cure at ambient temperatures for 24 hours

Day 1

Placed in a heated water bath at 50°C after demolding

Day 3

All cylinders in the tank were tested for their compressive strength and electrical resistivity on days 3, 7, 14, and 28. Day 3 showed the minimum converted strength

Day 28

Systems prevented from conversion [b]

Cured at moist curing room at 23°C after demolding

All cylinders were cured at 23°C did not undergo conversion. All samples were tested for their compressive strength and electrical resistivity on days 3, 7, 14, and 28

Figure 3.1 Graphical timeline for curing procedures for unconverted and converted systems on Day 3.

[a]: Specimens that underwent the conversion promotion procedure are denoted by " _conv" in graphs.
[b]: Specimens that were prevented from converting are denoted by " _unconv" in graphs.

3.4.2 Promoting conversion

In order to achieve conversion within a reasonable time period, a curing regime to promote conversion at an accelerated rate was used for the concrete samples. As shown in Figure 3.1, the samples which were to undergo accelerated conversion were submerged in a heated water bath at $50°C \pm 2°C$ after they were demoulded from the plastic moulds; after 24 hours from casting. This curing procedure for converted samples was proposed by Fryda et al. [47] in order to reach the minimum converted strength on the third day after casting, this method has been confirmed through an extensive research program undertaken by Adams et al. [44], [51] . These samples were kept in the water bath till the day of testing. Previous work has shown that this method is effective for producing concrete with a minimum converted strength at 3 days after casting [44], [47], [51] , as such examination of the hydrates to confirm conversion on these samples was not necessary. A set of three specimens from all mixture types were put through the conversion promotion process. A subset of these mixtures had a set of three specimens that were maintained at $23°C \pm 5°C$ to prevent conversion from occurring for comparison. Systems that had specimens that were prevented from converting were the G_0.40, G_0.35, and G_0.45 systems.

3.4.3 Electrical resistivity testing

Electrical resistivity measurements were collected on CAC cylinders throughout the testing program. Electrical resistivity measurement was done per AASHTO T358-17 [100]using a surface resistivity measurement device known as a wenner probe. Measurements were taken on cylinders on days 1, 3, 7, 14, and 28 after casting. A set of three cylinders was cast for each mixture and conversion combination and surface electrical resistivity

measurements were taken on these same cylinders throughout the testing program. After removing the samples from the plastic moulds, all samples were kept in the moisture curing room at temperature 23 ± 2ºC until tested. Prior to being placed in the curing room or water baths, the cylinders were kept sealed and under wet burlap and plastic to prevent any moisture loss. For each cylinder, two perpendicular axes were marked on the circular face marking the 0, 90, 180 and 270 degree points of the circumference [100] . These marks were extended on the longitudinal sides of each sample to facilitate a visual reference to ensure testing was done at the same location throughout testing. Two readings were taken at each location for each cylinder and then the total eight readings were averaged. The surface resistivity readings were measured for a set of 3 prisms using a four-point wenner probe as shown in Figure 3.2. Per AASHTO T358, a curing condition correction factor of 1.0 was taken for the surface resistivity measurements for both moist room and the water tank. Each sample was kept moist during testing as well as the probes' tips to reduce testing variability. The samples that were placed in the heated water bath were removed were removed from the heated water bath and were left to cool to 23 ± 2˚C while covered with wet burlap and plastic prior to measurement. This was to avoid thermal shock and to refrain from any influential factor that may impact the surface resistivity measurement.
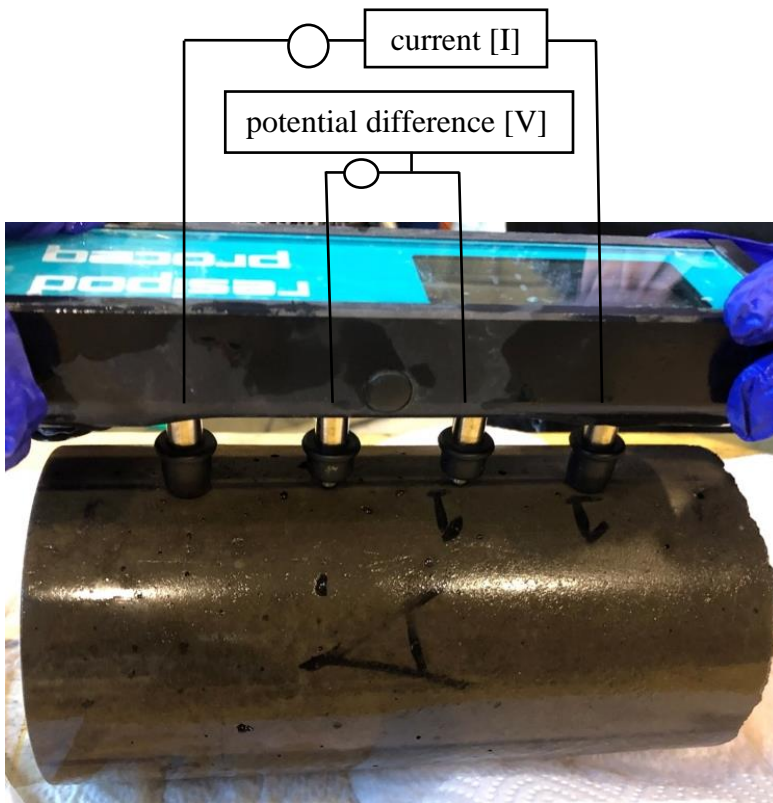
Figure 3.2 Electric resistivity measurement using wenner probe.

3.4.4 Compressive strength testing

The compressive strength measurements were done per ASTM C39 [94] on days 1, 3, 7, 14, and 28.

3.4.5 Robustness factors

In order to understand whether this test method may be valid across mixture types, several robustness factors were examined to validate the test. These included using different sources of aggregate, altering the w/c, and including small amounts of finely ground limestone. Previous work has shown that different aggregate sources and types may have a significant impact on converted strength for pure CAC concrete [44] . Work by Adams et al. indicated that the CAC systems made with carbonate limestone had less porosity after

conversion compared to those made with siliceous aggregates, which may impact the ability of electrical resistivity to identify conversion. Additionally, their work indicated that CAC concrete systems made with limestone may experience delayed conversion compared to systems made with siliceous aggregates [51] .

Previous work showed that varying of w/c ratio of CAC concrete systems had a minimal impact on the converted strength and time to reach conversion under the same curing conditions [51] . This low impact was attributed to the choice of limestone and siliceous aggregates. The work presented examines the impact of varying the w/c using a higher strength concrete system with crushed granite aggregates. Thus, observing if the change in w/c may impact the minimum converted compressive strength and the time to convert for different concrete mixtures.

Previous work has shown that adding finely ground limestone (FGLS) as cement replacement to CAC concrete systems may delay or disrupt conversion. This delay was attributed to the formation of monocarboaluminate as a metastable hydrate [25], [37], [101], [102] . Adams et al. showed that adding FGLS at 5% replacement level may increase the converted strength without impacting the early strength gain [51]. In the presented work, different cement replacement levels of FGLS at 10% and lower were used to investigate the ability of electric resistivity to detect time to conversion in CAC systems.

For these reasons, the robustness variables selected to validate using electrical resistivity measurements as a tool to assess conversion were as follows:

- Three aggregate types: a crushed granite, a siliceous river gravel, and a limestone (coarse and fine aggregates from the same source);

- Three w/c: 0.35, 0.40, and 0.45; and

- Different cement formulations using various replacement levels of FGLS by mass: 0%, 3%, 7%, and 10% FGLS.

- Different time to conversion using curing procedures to promote conversion on day 3 and day 28 after casting.

3.5 Results

3.5.1 Impact of different aggregate types

The compressive strength data for CAC concrete systems using the three different types of aggregates (crushed granite, limestone and siliceous aggregates) is shown in Figure 3.3. All three systems experienced signficant compressive strength reductions on day three, consistent with conversion promotion per the curing procedure noted above. The CAC systems made with siliceous or granite aggregates had lower minimum converted strengths compared to the limestone. The strength reduction percentage from day 1 to day 3 ranged from 10% in limestone, 65% in siliceous and 44% in granite. The G_0.40_unconv system was observed to have increased strength development over the first 28 days, indicating that it had not undergone conversion, as observed in the systems that were submitted to the conversion promotion procedure.
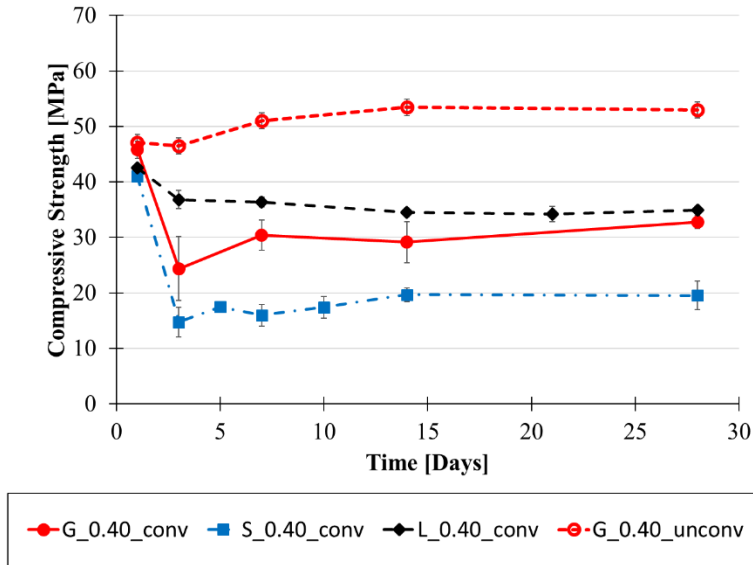
Figure 3.3 Compressive strength for different aggregates types for converted CAC samples and unconverted crushed granite samples.

Electric resistivity measurements for the G_0.40_conv, L_0.40_conv, and S_0.40_conv are shown in Figure 3.4a. All specimens that were subjected to the conversion promotion procedure experienced a significant reduction in electric resistivity on day 3, this is correlated to the time of conversion per the compressive strength results in Figure 3.2 and the conversion promotion procedure described above. The crushed granite and limestone aggregate systems exhibited a higher reduction in their electric resistivity than that of the system made of siliceous aggregates. The electric resistivity of the systems made with granite and limestone showed a reduction of 82% and 73% respectively, while the siliceous system showed a reduction of 30% from day 1 to day 3. After day 3, the electric resistivity for both the granite and the limestone systems remained almost constant while that of the siliceous system increased.

The electric resistvity of the G_0.40_conv and G_0.40_unconv samples are shown in Figure 3.4b. This graph shows a comparison between samples that were maintained in

the unconverted state and samples that underwent the conversion promotion procedure. The electric resistivtiy in the unconverted samples steadily increased over the testing period. The converted samples experienced a reduction in the electric resistivity on day 3 which was correlated to conversion.
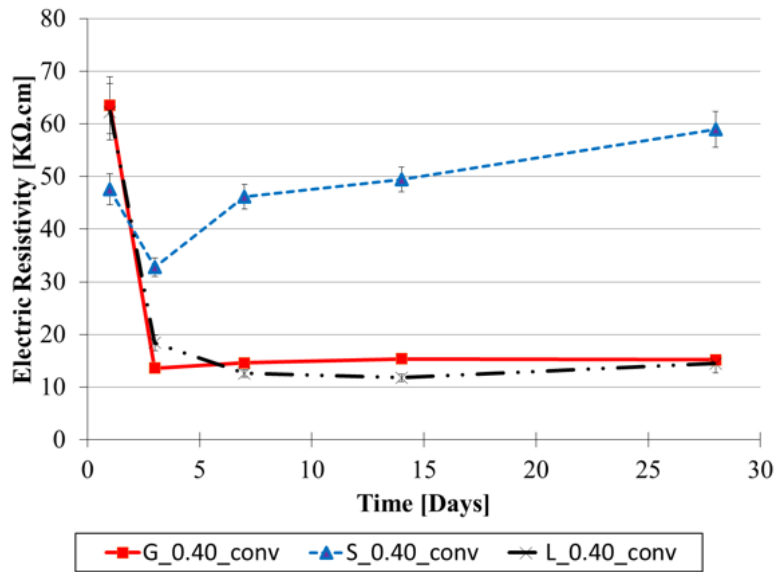
Figure 3.4a Electric resistivity for converted samples made with all aggregate types
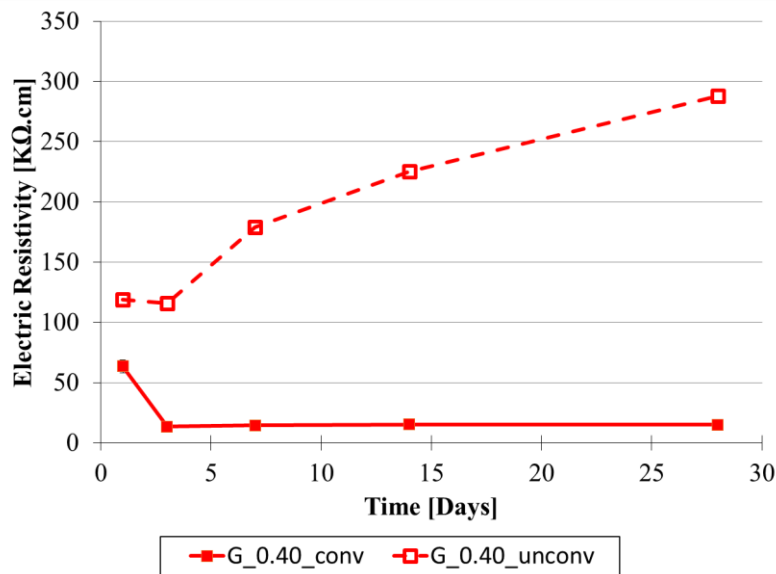
Figure 3.4b Electric resistivity for unconverted samples made with crushed granite aggregates.

3.5.2 Impact of different w/c ratio

The second robustness factor considered was examining CAC mixtures with different w/c. All mixtures examined for this work used coarse and fine aggregate from the same granite source. Compressive strength measurements for the unconverted and converted systems are shown in Figure 3.5. The unconverted samples showed an increase in their compressive strength from day 1 throughout day 28 for all w/c. All systems that underwent the conversion promotion procedure reached their minimum converted strength on day 3, regardless of w/c. The mixture with a w/c of 0.35 had a higher minimum converted strength than that of the mixtures with w/c of 0.40 and 0.45. The mixture with w/c ratio of 0.35 showed 30% strength reduction after conversion, while those of w/c ratios 0.40 and 0.45 showed 48% strength reduction after conversion.
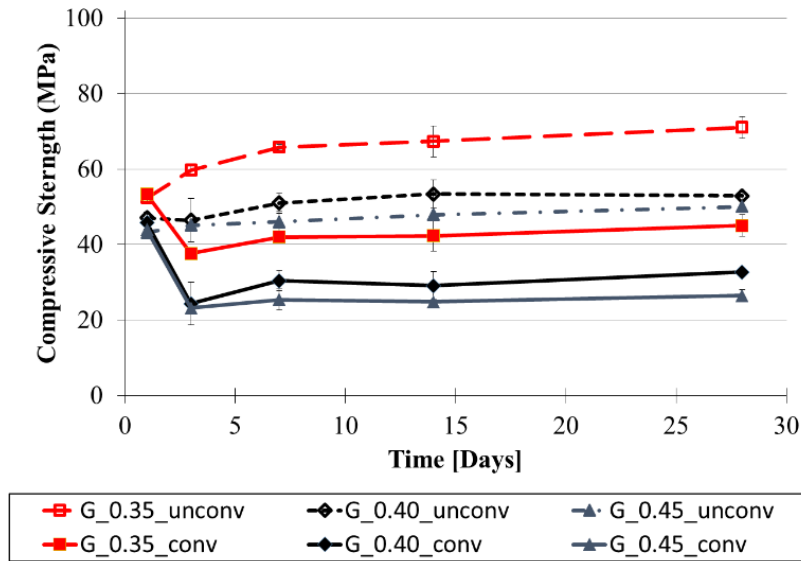
Figure 3.5 Compressive strength for crushed granite aggregates with different w/c ratio for unconverted and converted samples.

Figure 3.6 shows the electrical resistivity data for the samples maintained in an unconverted state and the samples that underwent the conversion promotion procedure for all three w/c (note: the research group was unable to collect electric resistivity measurements for mixture G_0.45_uncov due to a laboratory failure in the curing environment). The electrical resistivity data of the three different mixtures were collected on the same corresponding days. All mixtures showed significant reductions in electric resistivity on day three. The mixture with a w/c ratio of 0.35 showed the highest resistivity reduction 82%, compared to 79% for 0.40 w/c ratio system, and 65% for 0.45 w/c ratio system. The unconverted samples showed an increase in electrical resistivity over the testing period. The G_0.35_unconv systems showed a higher electric resistivity than the G_0.40_unconv system.
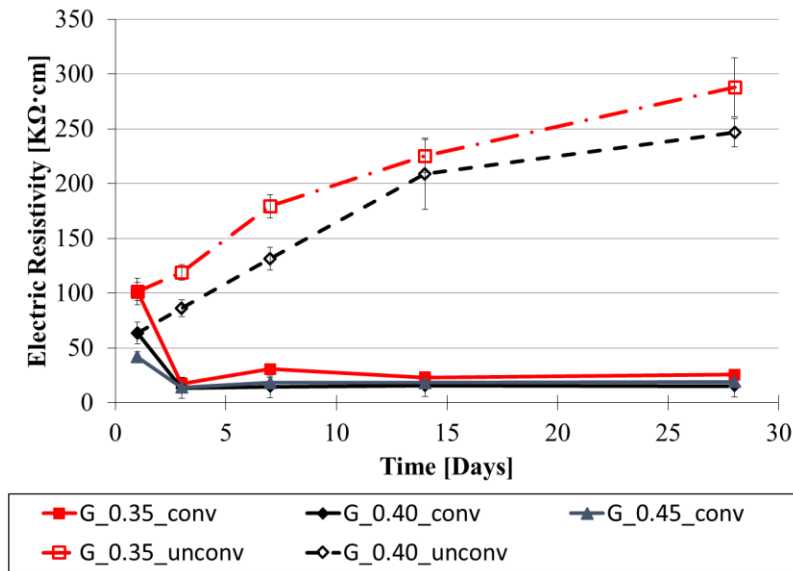
Figure 3.6 Electric resistivity for crushed granite aggregates with different w/c ratio for unconverted and converted samples.

3.5.3 Impact of different cement compositions

The third robustness factor considered in this work was the impact of different replacement levels of finely ground limestone (FGLS) as a replacement for cement. A comparison between the behaviour of electric resistivity of four different mixtures with 0%, 3%, 7%, and 10% FGLS as a replacement of cement, by mass. All samples were subjected to the conversion promotion procedure and their compressive strength measurements over the testing period are shown in Figure 3.7. All samples were made with fine and coarse crushed granite aggregates from the same source.

The compressive strengths of the mixtures with 0%, 3%, and 7% FGLS were observed to have a decrease in compressive strength on day three, which is correlated to conversion. However, the mixture with 10% FGLS exhibited no strength reduction from day 1 to day 3. This mixture showed a minimal reduction after day 7 over the 28-day testing period.
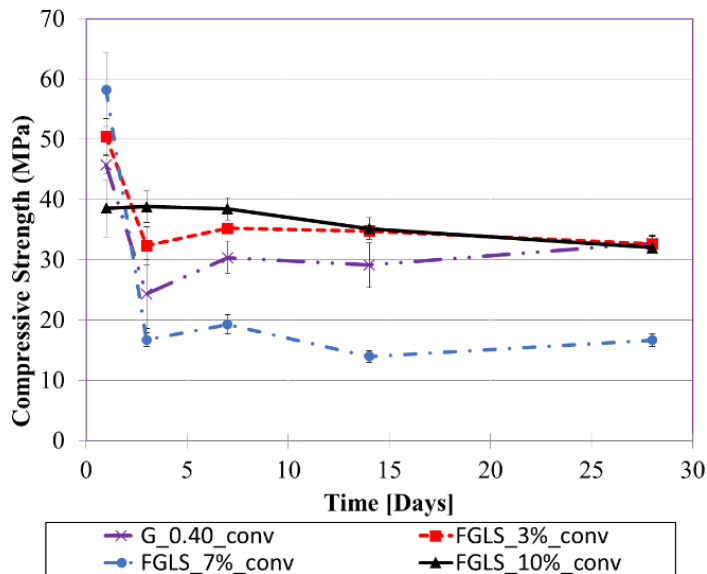
Figure 3.7 Compressive strength for crushed granite aggregates with different levels of replacement of FGLS for converted samples.

The electrical resistivity measurements for all mixtures with different levels of FGLS can be seen in Figure 3.8. All mixtures, including the 10% FGLS, experienced a significant reduction in resistivity on day 3. For all but the 10% FGLS, this reduction in electrical resistivity corresponded to the time to conversion as observed in Figure 3.7.
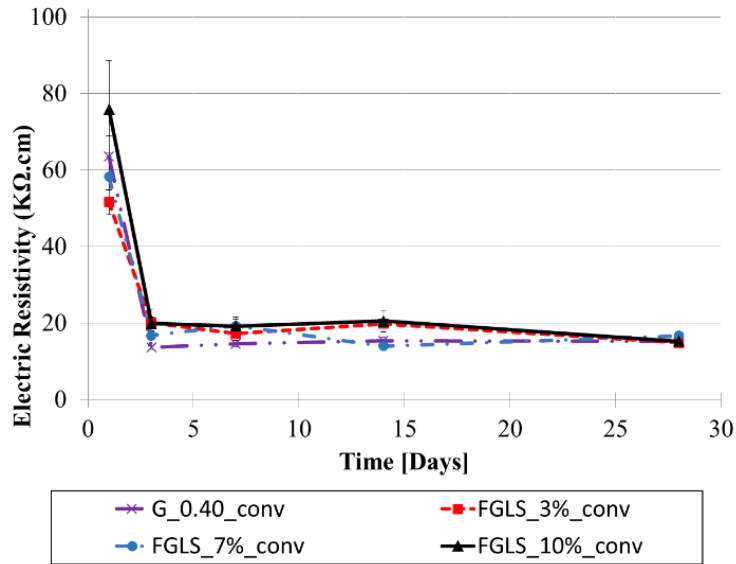
Figure 3.8 Electric resistivity for crushed granite aggregates with different levels of replacement of FGLS.

Additionally, compressive strengths were measure for mixes prevented from converting with different replacement levels of FGLS, these mixes are having the suffix of "_Unconv". The mix with 0% FGLS was denoted as G_0.40 for consistency. The strength showed an increase in strength over the curing time period of 28 days. All mixes were made of crushed granite aggregates. The mix with 0% FGLS showed the lowest strength, while that of 10% FGLS showed the highest as shown in Figure 3.9.
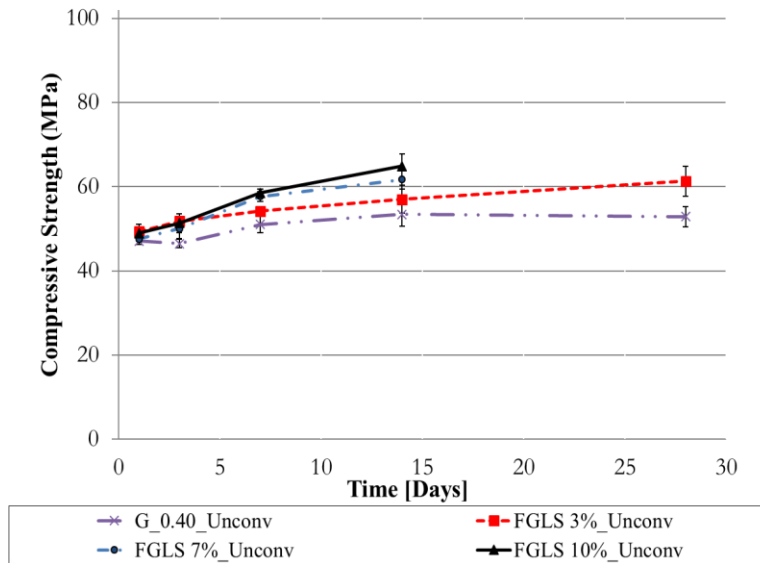
Figure 3.9 Compressive strength for crushed granite aggregates with different levels of replacement of FGLS for unconverted samples.
Note: Strengths for day 28 were not measured for mixes with FGLS 7% and 10% due to COVID-19 shutdown.

The electric resistivity for these unconverted samples were measured as well on the same corresponding days as in compression testing (1, 3, 7,1 4, and 28). The mix with 0% FGLS showed the highest values for resistivity. The electric resistivity in all mixes did not experience any significant reduction over the 28 days period but continued to increase over time. Only for mix with 3% FGLS there was a minor reduction of about 15% between day 14 and day 28.
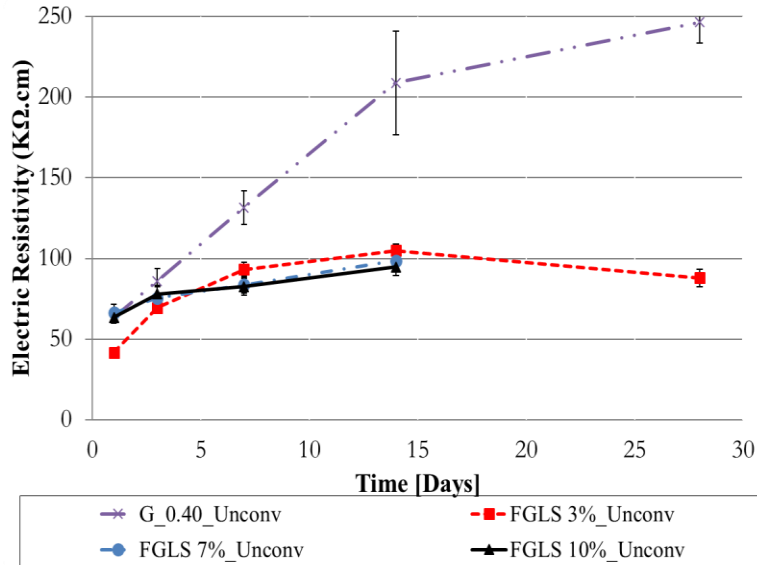
Figure 3.10 Electric resistivity for crushed granite aggregates with different levels of replacement of FGLS for unconverted samples.
Note: Electric resistivity measurements for day 28 were not measured for mixes with FGLS 7% and 10% due to COVID-19 shutdown.

3.5.4 Impact of different time to conversion

The final robustness factor was to promote conversion at different times from casting other than on day 3. The same curing regime as mentioned above in section 4.3.1 was followed where all samples used fine crushed granite for fine and coarse aggregates. These systems were promoted to convert on day 28 after casting instead of day 3. The samples that were promoted to convert on day 28 were placed in a heated water bath at temperature $50 \pm 2°C$ on day 26 (two days prior day 28 compression testing). This was to replicate the same procedure and follow same duration of curing that was confirmed in literature [51], [53]. The compressive strengths of these cylinders were measured on days 1, 3, 7, 14, 28, and 56. Figure 3.11 presents a timeline for the curing procedures for unconverted and converted systems that were promoted to convert 28 days after casting. These systems were denoted here in this work as G_0.40_Unconv_Day 28 and G_0.40_Conv_Day 28.

Conversion promotion procedure [a]

Day 0

Casting cylinders in plastic molds, sealed and covered with burlap. All cylinders were allowed to cure at ambient temperatures for 24 hours

Day 1

Cured at moist curing room at 23°C after demolding

Day 26

Placed in a heated water bath at 50°C

Day 28

Day 56

All cylinders in the tank were tested for their compressive strength and electrical resistivity on days 3, 7, 14, 28, and 56. Day 28 showed the minimum converted strength

Systems prevented from conversion [b]

Cured at moist curing room at 23°C after demolding

All cylinders were cured at 23°C did not undergo conversion. All samples were tested for their compressive strength and electrical resistivity on days 3, 7, 14, 28, and 56

Figure 3.11 Graphical timeline for curing procedures for unconverted and converted systems on Day 28.

[a]: Specimens that underwent the conversion promotion procedure are denoted by "_conv_Day 28" in graphs.
[b]: Specimens that were prevented from converting are denoted by "_unconv_Day 28" in graphs.

The compressive strength was measured for both unconverted and converted systems which were promoted to convert on day 28. Figure 3.12 shows an increase in compression values for G-0.40_Unconv_Day 28 throughout the curing period of 90 days. About an 8% decrease was observed for compressive strength between day 28 and day 56. As for the samples promoted to convert, a significant reduction of about 35% was observed on day 28 which elucidates conversion of samples on that day.
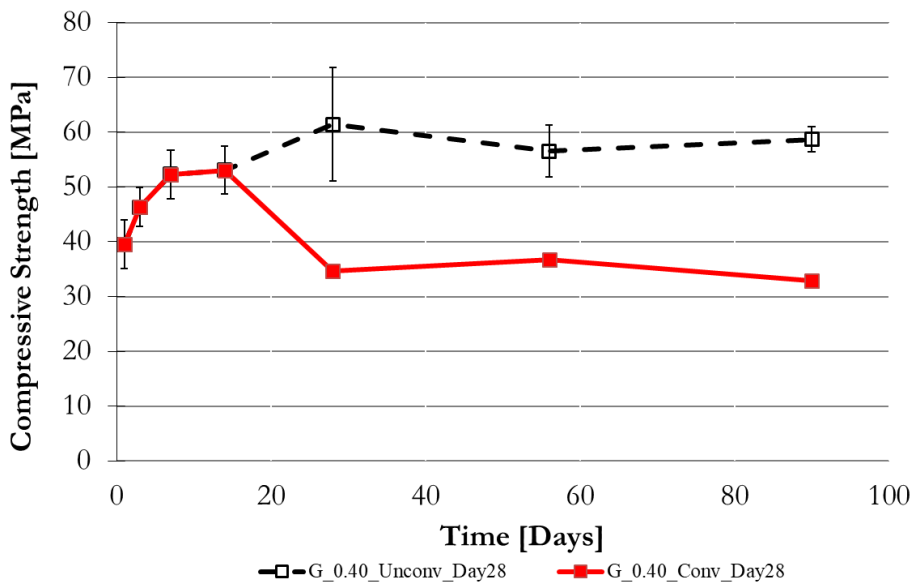
Figure 3.12 Compressive strength for crushed granite aggregates unconverted and converted on day 28.

The electrical resistivity was measured as well on companion samples on the same corresponding days as in compressive strength. Figure 3.13 presents a comparison between systems maintained in the unconverted state and systems promoted to convert on day 28. The unconverted systems showed an increase in its electric resistivity from day 1 to day 90, except for a slight decrease on day 56. The converted systems that had undergone conversion showed a significant reduction in its resistivity on day 28 and then continued to be almost steady throughout the 90 days period.
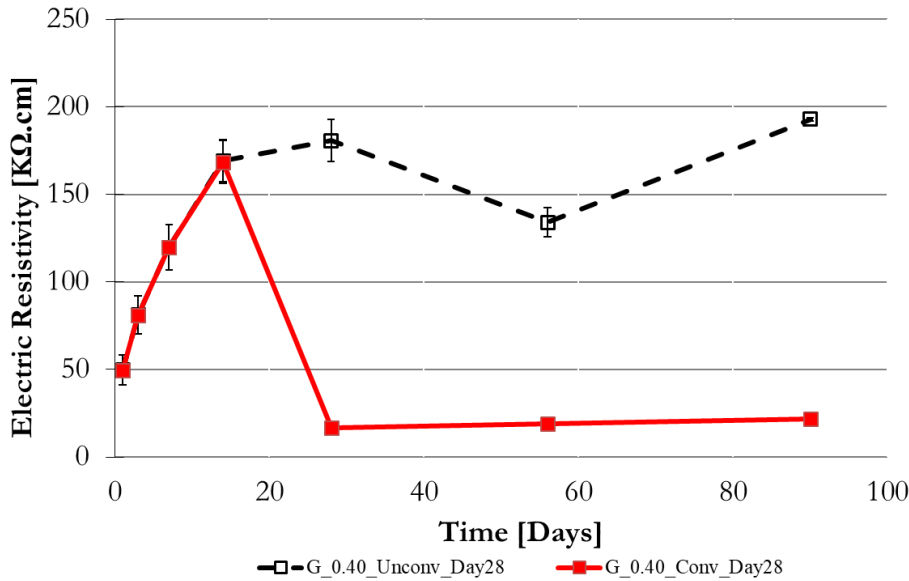
Figure 3.13 Electric resistivity for crushed granite aggregates unconverted and converted on day 28.

3.6 Discussion

Electrical resistivity of concrete is, in part, related to the overall permeability of concrete. A more porous concrete will have a lower electrical resistivity (assuming that the pores are filled with water). Dry systems, which have high levels of porosity may present high levels of resistivity because of the difficulty for a charge to pass through the system [99], [103], [104]. Since CAC conversion results in the opening of porosity and flooding of the system with water, electrical resistivity measurements are a good candidate for a non-destructive test method to determine if a CAC concrete system has undergone conversion. The presented work indicates that conversion is associated with a significant decrease in the electrical resistivity that can be observed through simple surface resistivity measurements. The reduction in electrical resistivity was correlated to the decrease in compressive strength associated with conversion. While this work did not directly examine the hydrates to ensure conversion, the conversion promotion procedure used is a well-established method for

promoting conversion in system [51], [53]. The decrease in compressive strength at day 3 for systems subjected to the heated curing procedure indicates that conversion has occurred. The only system where a significant strength reduction was not observed was the system made with 10% FGLS, which may be due to the formation of monocarboaluminate. The time to conversion matched with the time to the significant decrease in electrical resistivity.

All samples placed into the heated water tanks experienced significant decreases in electrical resistivity after being placed into the water tanks. There may be some concern that the submersion in water may have flooded the system resulting in higher resistivity that would not be correlated to conversion; or, alternately that the samples kept in the moist curing room to prevent conversion may be drier than the samples placed in the water bath. However, the samples kept in the moist curing room were kept in the saturated condition, as the room was always maintained at a > 95% relative humidity and the specimen surfaces were remoistened just before testing to ensure a good connection of the probe to the surface. Additionally, unconverted CAC samples have extremely dense microstructures with very low permeability [44] . This means that the specimens that were unconverted would not lose any water in the system, and even if they were submerged, would not have been able to uptake too much water to impact the resistivity measurements. Nonetheless, it is recommended that further work on this test examine the impact of saturation state on the reliability of the test method to confirm these results. All samples were tested at standard room temperatures to remove any impact of water content or temperature variations. Given this information, the results indicate that the decrease in resistivity was due to the opening of porosity due to conversion. The resistivity stayed relatively constant for most samples

after conversion occurred. Therefore, this test method may be useful for detecting conversion in CAC systems.

The variance in aggregate types had an impact on the compressive strengths, but not the time to conversion. It has been shown previously that the siliceous aggregate mixtures had higher strength reductions compared to limestone [44]. The work presented showed that the limestone system had less strength reduction compared to both the crushed granite and siliceous systems. The CAC system made of limestone aggregates had a higher converted strength on day three compared to systems made of siliceous or crushed granite. The three types of systems, however, had similar early compressive strengths one day after mixing. The siliceous, limestone, and granite aggregate systems experienced a significant reduction in electric resistivity values on day three which matched with the time to conversion. Both limestone and crushed granite aggregate systems had relatively constant electric resistivity values after day three. Whereas the siliceous aggregate system saw increased electric resistivity over time, which may indicate more rapid hydration of this system after conversion compared to the other two systems.

When examining the impact of w/c ratio on whether electrical resistivity could determine time to conversion, no significant impacts were observed. The system using a 0.35 w/c had a higher compressive strength compared to the 0.40 and 0.45 w/c systems. The w/c did not appear to have any impact on the time to conversion as all systems showed significant decreases in electrical resistivity on day three, when conversion was complete. It has been shown that w/c impacts strength of CAC systems similar to calcium silicate cement systems: a higher w/c will result in lower strengths [102]. The 0.35 w/c system

showed a spike in resistivity on day 7, for which the research team was unable to find an explanation. Further work should be completed to confirm whether this was an anomaly.

The amount of FGLS in the system also did not seem to impact the ability of the electrical resistivity measurement to detect time to conversion for systems with 7% replacement and below. No reduction in strength was observed for the system using 10% FGLS over the testing period, however a significant decrease in resistivity was noted starting at day three. Systems with high amounts of FGLS have been shown to form calcium monocarboaluminate instead of converting to C_3AH_6 [101]. This may result in a reduced resistivity while maintaining a higher strength. Further work needs to be done to investigate the hydrates that were formed in these systems to determine whether the 10% FGLS actually converted or formed a different hydrate.

The varying of time to convert didn't seem to have an impact on the efficacy of electric resistivity to assess conversion in CAC systems. Systems that were promoted to convert 3 days after casting, denoted here as G-0.40-Conv, showed a resistivity reduction on the same day as it converted. The systems that were allowed to convert after 28 days from casting were denoted here as G_0.40_Conv_Day 28. These systems showed a significant reduction in electric resistivity on day 28 which was correlated to the minimum converted strength on the same day. Upon comparing systems that converted on different times; on days 3 and 28, the electrical resistivity was able to assess conversion by showing a significant reduction on their corresponding days. However, it will be important to further investigate this factor and its impact on resistivity readings by elongating the time to convert.

No trend was observed that would allow for linking specific electric resistivity measurements to compressive strength magnitudes. There was a distinct trend between the electric resistivity and indication of higher porosity in order to assess conversion in CAC systems. Electric resistivity of concrete is a qualitative test that can detect the porosity of concrete according to the ions movement but cannot quantify its compressive strength. When measuring electrical resistivity, the higher the porosity the more interconnectivity between pores which will result in lower electrical resistance measurements. That is due to the pores in concrete allowing for the movement of ions between them and thus a more conductive system. However, the trend that electrical resistivity shows a significant decrease correlated to the time of conversion indicates that this test method may be a valuable tool for detecting conversion in CAC concrete systems. This will help limit the number of specimens needed to test for converted strength in CAC or allow for monitoring of systems *in situ*.

Further work needs to be completed to verify these results, particularly when examining longer times to conversion; other than two or twenty-seven days after casting. Additional analysis needs to be completed to understand how the storage conditions may impact electrical resistivity measurements on CAC concrete. Additionally, confirmation of the hydrates in all systems will be necessary before full acceptance of this test method, however current work indicates that there is promise for this test method. Users should be careful to use the method only on systems that will convert to C_3AH_6, as indicated by the systems using high levels of FGLS. Extended work on the hydrate structures present in these systems is required to confirm that conversion occurred.

3.7 Conclusion

This work has shown a proof-of-concept that the electric resistivity measurement may be a promising tool to assess time to conversion in CAC systems. The presented data showed a significant reduction of electric resistivity correlated with a reduction in compressive strength three days after mixing, which indicated that full conversion had occurred. All samples showed a decrease in electric resistivity that matched with the same time to conversion. All samples tested were maintained at high relative humidity and at standard room temperatures to hold constant any variables that may impact the electric resistivity measurements.

In order to validate the electric resistivity method as a reliable tool to assess conversion, several robustness factors were used. The granite, limestone and siliceous aggregates have shown a significant decrease in their electric resistivity three days after mixing which matched the same day of conversion. The electric resistivity of limestone and granite remained almost constant after the significant reduction, while that of the siliceous kept gaining higher resistivity values over time. Further investigation to such behaviour in the CAC made with siliceous aggregates need to be examined. The variance in w/c ratio showed no significant impact on the time to convert. All samples showed significant drops in electric resistivity on day 3 correlated with the same day when full conversion occurred. Further tests may be needed to find a reason for the spike in electric resistivity in w/c of 0.35 on day 7. The impact of adding different replacement levels of FGLS of 7% and below showed no impact on the using the electric resistivity method in order to detect conversion. However, a higher amount of 10% was used and no strength reduction was shown on day three. The factor of varying time to convert on days 3 and 28

seemed to have no impact on the capability of electric resistivity measurements to assess conversion. Electric resistivity showed a significant reduction for both mixes that were promoted at different times corresponding to same day when conversion occurred. Conversion was confirmed by a reduction in compressive strength on days 3 and 28.

Further work will be needed to examine if the 10% FGLS systems have reached the full conversion or just formed a different hydrate. Extended work is planned to validate the proposed test by examining samples that are allowed to convert on a longer time to conversion other than two days and 27 days after mixing as well as examining different sources of CAC.

CHAPTER 4

THE IMPACT OF CONVERSION ON DRYING SHRINKAGE

This work is to being prepared for submission to the ASCE Materials Journal. Part of this work has been accepted for publication in the Calcium Aluminates: Proceedings of International Conference, Cambridge, England [105].

4.1 Summary

Calcium aluminate cement concrete (CAC) systems are characterized by their high early strength gain while maintaining similar setting times to portland cement systems. During their lifetime, CAC systems will undergo conversion during which metastable hydrates are converted into denser stable hydrates. This densification of the stable hydrates increases the porosity in the system and decreases its strength. The rate of this process depends mainly on temperature and humidity. There has been significant previous research work on the kinetics of the conversion process in the CAC systems. However, there is very little information available on the impact of conversion on long-term concrete durability. Volume change due to drying (drying shrinkage) is an important durability issue for concrete, and in particular for rapid repair systems which need to maintain volumetric stability without cracking when they are bonded to an existing substrate. Drying shrinkage is significantly impacted by porosity changes in the cement matrix which are correlated with conversion in CAC systems. The objective of this work was to examine the impact of conversion in CAC systems on drying shrinkage. Shrinkage measurements and mass change of CAC concrete systems were measured for CAC systems with (i) different w/c,

(ii) different time to convert, (iii) and systems containing small amounts of finely ground limestone (FGLS). Results indicate that conversion will result in higher levels of drying shrinkage and mass loss in concrete. These results are discussed and potential improvements for construction techniques are provided. A comparison between unconverted and converted systems is presented for each robustness factor.

4.2 Introduction

Calcium aluminate cement (CAC) concrete systems are a specialty type of cement due to their unique features [23]. CAC is often used as a rapid repair material in infrastructure settings because of its ability to gain strength rapidly at temperatures approaching freezing [2], [3], [83]. While CACs are also used heavily in building chemistry, refractory, and pipe lining applications [17], [18], drying shrinkage is a particular concern for rapid repair situations. In most construction settings, proper curing can be completed to ensure that the system gains strength quick enough to prevent cracking during shrinkage. Many rapid repairs, however, are cast and allowed to harden and gain strength with no curing. Therefore, temperature changes and moisture loss are all but guaranteed. These both can have significant impacts in CAC systems and change the microstructure significantly.

The composition of CAC hydrates is quite different than that of ordinary portland cement (OPC). The main phase in CAC is monocalcium aluminate- $CaO \cdot Al_2O_3$ (CA) [23]. CAC hydration has been extensively studied for over a century since they were originally developed [2], [5], [23], [39]. The hydration of CA initially produces CAH_{10} and C_2AH_8 which are metastable hydrates. These metastable hydrates undergo a process known as conversion in which the two stable hydrates, C_3AH_6 and AH_3, are formed. This conversion

76

process is accompanied by the release of water, which will react with the remaining unhydrated CA, forming new hydrates and reducing long-term porosity that was formed from conversion [40]–[43]. The formation of metastable or stable hydrates from the hydration of calcium aluminates depends strongly on temperature, unlike the hydration of calcium silicates which produce the similar hydrates at all temperatures below 100℃ [2]. The preference of which hydration product will form during CAC hydration depends significantly on the temperature at which the system is cured. If the temperature is below 15℃ the initial -metastable hydrate CAH_{10} is formed, while if the temperature is above 30℃ the initial metastable C_2AH_8 is formed. If the temperature lies between 15 ℃ and 30 ℃, then neither is preferred between the two metastable hydrates regarding the order to be formed [2], [5], [44], which can result in a delay of setting time. The strength loss associated with conversion can sometimes be quite severe, depending on w/cm, cement content, and aggregate type [44]. Recent work has shown that small doses of finely ground limestone (FGLS) can help mitigate the strength reduction associated with conversion without changing the hydrate structure of the system [51]. Previous studies have shown that the addition of FGLS to CAC systems may have may result in the formation of monocarboaluminate [25], [37], [102]. However, more Adams et al.'s work indicated that small doses may not result in significant changes to the microstructure, but instead that it may behave as a filler material reducing porosity [51]. Its impact as a possible filler or the formation of additional hydrates from the addition of FGLS may also impact the rate and magnitude of shrinkage that the concrete may undergo is unknown.

Guidelines have been set by the European Standards and CAC manufacturers for the optimum w/c to be at 0.40 or lower to achieve a viable converted strength [86]. Recent

work by Adams et al. [51] has shown a minimal impact for varying w/c on conversion time. The authors stated that when using siliceous aggregates for CAC systems, higher w/c systems showed lower strengths, but long term strength increase. The impact of w/c on conversion when using higher strength CAC systems is note quite understood, however.

One of the concerns for concrete deterioration is the drying shrinkage. This durability issue results in significant levels of cracking which can provide fast paths for aggressive chemicals and water which can initiate corrosion or freeze/thaw damage. Drying shrinkage occurs when the water in the pore structure is lost to the environment and continues till the internal relative humidity (RH) stabilizes with the ambient RH [106]. Drying shrinkage will occur as long as the RH outside the concrete is lower than the RH humidity within the concrete [107]. Since drying shrinkage is a result of water moving through pores, and its loss to the environment, the conversion of CAC and the changes that causes to pore structure and water availability means that converted concrete may be more susceptible to drying shrinkage [77]. Although drying shrinkage may not impact the concrete strength, it will certainly impact its long-term durability [75]. In patch repairs, where CAC products are often used, it can result in volume change which may disturb the integrity of the patch or result in worse damage than what was repaired. In overlays, the bond between the repair layer and the old concrete forms an external constraint. During drying, volumetric changes in the concrete around this bond induce tensile stresses which will eventually cause cracking in the system [108]. The amount of drying shrinkage that will occur and its rate depends on the size of the specimens and the surrounding conditions [106], [109]. The free drying shrinkage test determines how much free shrinkage an unrestrained system will undergo, not necessarily if the system may crack or not. However,

in industry it is used as a proxy for that; i.e., the more a prism of concrete exposed to dry conditions shrinks the more likely it is to crack.

The conversion process can result in significant changes in porosity and since drying shrinkage is impacted by both the amount, size, and interconnectivity of pores in concrete, it is important to study how conversion may impact drying shrinkage in CAC systems. As discussed above, the temperature at which the concrete cures will change the speed of conversion. If CAC concrete is cured at high temperatures (or self-heats in a larger element) it will result in rapid conversion [53] and the concrete will have more porosity. Therefore, understanding the impact of conversion on drying shrinkage is an important factor for determining proper curing procedures and construction practices when using CAC. Presented are the results of a study that examined the drying shrinkage of CAC concrete systems that have and have not undergone conversion. Samples were also cast using small amounts of FGLS (up to 10% cement replacement) to reduce overall porosity and lower the shrinkage in systems. Other sets of samples had different w/c and others were promoted to convert at varied times.

4.3 Materials

4.3.1 Cement

A standard grade CAC was used for all the concrete mixtures examined in this study. The oxide composition of the CAC used is shown in Table 4.1.

Table 4.1 Oxide Composition of CAC

Oxide (% wt)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	Mn_2O_3	P_2O_5	SrO	Loss
CAC	4.98	38.23	15.4	37.53	0.71	0.03	0.23	0.06	1.8	0.23	0.13	0.02	0.65

4.3.2 Aggregates

Crushed granite aggregates were used in this study for the concrete mixtures. Absorption capacities and specific gravities ($G_{sb.OD}$) for all aggregates were measured according to ASTM C127 for coarse aggregates and according to ASTM C128 for fine aggregates[91], [92]. A description of the coarse and fine aggregates used are shown in Table 4.2.

Table 4.2 Coarse and Fine Aggregates Description

Aggregate name	Absorption capacity (%)	Gsb, OD	Source	Mineralogical description
Granite_Coarse	0.34	2.72	New Jersey, USA	Crushed Granite
Granite_Fine	0.536	2.604	New Jersey, USA	Crushed Granite

4.3.3 Concrete Mixtures

The concrete mixtures prepared for this study are described below in Table 4.3. The w/cm presented is an effective w/cm of 0.40 for all mixtures with total water content adjusted to take into account the moisture content of the aggregates.

Table 4.3 Concrete Mixture Design

Mixture Label	w/cm	Fine Aggregate content (kg/m^3)	Coarse Aggregate content (kg/m^3)	Cement content (kg/m^3)	FGLS content (kg/m^3)	Aggregate Type
FGLS_0%	0.40	836	922	440	0	Crushed Granite
FGLS_3%	0.40	835	920	427	13	Crushed Granite
FGLS_7%	0.40	840	919	409	31	Crushed Granite
FGLS_10%	0.40	852	919	396	44	Crushed Granite

4.4 Experimental Methods

4.4.1 Sample Preparation

The CAC concrete was mixed and cast following the mixing procedures presented in Adams et al.[51]. Concrete prisms of 75 mm x 75 mm x 285 mm were cast for all testing completed in this study. Prisms were cast according to procedures specified in ASTM C 57/C157M-17 [95]. Concrete was placed into steel molds in approximately two equal layers. After casting, the prisms were finished, and excess material was patted off the surface using a straight edge. The molds were then covered with wet burlap to prevent moisture loss. All samples were allowed to cure at ambient temperatures for 24 hours in the steel molds. Companion compressive strength specimens were also cast using plastic molds to create 100 mm diameter x 200 mm high concrete cylinders. Molds were spaced apart to allow adequate airflow to prevent self-heating and conversion during curing. Cylinders used for compressive strength testing were cast and cured according to the procedures presented in Adams et al. [51].

4.4.2 Promoting Conversion

In order to achieve conversion within a reasonable time period, a curing regime to promote conversion at an accelerated rate was used for the concrete samples. The samples which were to undergo accelerated conversion were submerged in a heated water bath at 50˚C ± 2˚C after they were demolded from the steel molds. The curing procedure for converted samples was proposed by Fryda et al. [47] in order to reach the minimum converted strength on the third day after casting, this method has been confirmed through an extensive research program undertaken by Adams et al. [44], [51]. In addition to promoting

conversion on the third day after casting, other samples were also promoted to convert on days 28 and 90. Following the same curing procedures samples were first cured in the moist curing room at $23 \pm 2°C$ after demolding and were then moved to the heated water tank. Each set of prisms and cylinders was placed in the $50 \pm 2°C$ two days prior the desired converted time.

4.4.3 Drying Shrinkage Testing

The Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete ASTM C157/C157M-17 [95] was followed to measure the change in length of concrete specimens in a controlled environment; without being impacted by a change in temperature or applied external forces. Mass change was also measured to know how much water was lost to the environment. This was done on different cement combination of CAC samples using different levels of replacement of finely ground limestone (FGLS), different w/c, and systems converted at different times. The unconverted prisms were cured in a moist curing room at $23°C \pm 2°C$ after being demolded for 28 days and then were moved to the drying curing room. The converted prisms were placed in the heated water tank at $50°C \pm 2°C$ two days prior the desired converted time to promote conversion as previously mentioned. Before moving them to the dry curing room they were removed from the heated water tank and left to cool down in a bucket filled with water at the same temperature for 24 hours to avoid thermal shock. All specimens were then stored in a dry curing room set at temperature $23°C \pm 2°C$ and RH of $50\% \pm 4\%$ as specified in ASTM C157/C157M-17 [95]. The specimens were placed on racks allowing air circulation and had a clearance of at least 25 mm on all sides as shown in Figure 4.1a. The length change was calculated for each specimen and averaged for each set (set of three prisms per mixture) with respect to

the initial comparator reading as shown in Figure 4.1b. Mass of the prisms was also recorded.
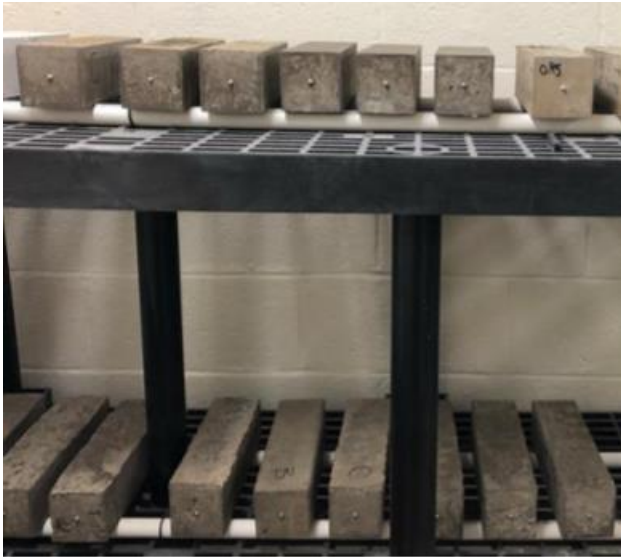
Figure 4.1a Drying shrinkage prisms cured in a controlled chamber at temperature $23°C \pm 2°C$ and RH of $50\% \pm 4\%$.

Figure 4.1b Length change measurement using comparator.

4.4.4 Compressive Strength Testing

Compression testing for the concrete cylinders were done as per ASTM C39/39M-18-Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens [94]. The compressive measurements were collected for days 1, 3, 7, 14, and 28 for systems with different w/c and different cement formulations. This period was extended to day 56 for systems promoted to convert on day 28. The curing conditions were done following the guidelines set in Adams et al. [51].

4.5 Results

4.5.1 Impact of different replacement levels of FGLS

The compressive strength results were recorded for CAC cylinders for different mixtures with 0%, 3%, 7% and 10% FGLS. Samples denoted herein as G_0.40 represents the 0% FGLS. The compressive strength data for converted samples are shown in Figure 4.2. All converted samples for 0%, 3%, and 7% showed conversion, represented by the, minimum strength on day 3 and then continued to increase again. Only the CAC samples with 10% FGLS showed a minimal reduction after day 7.
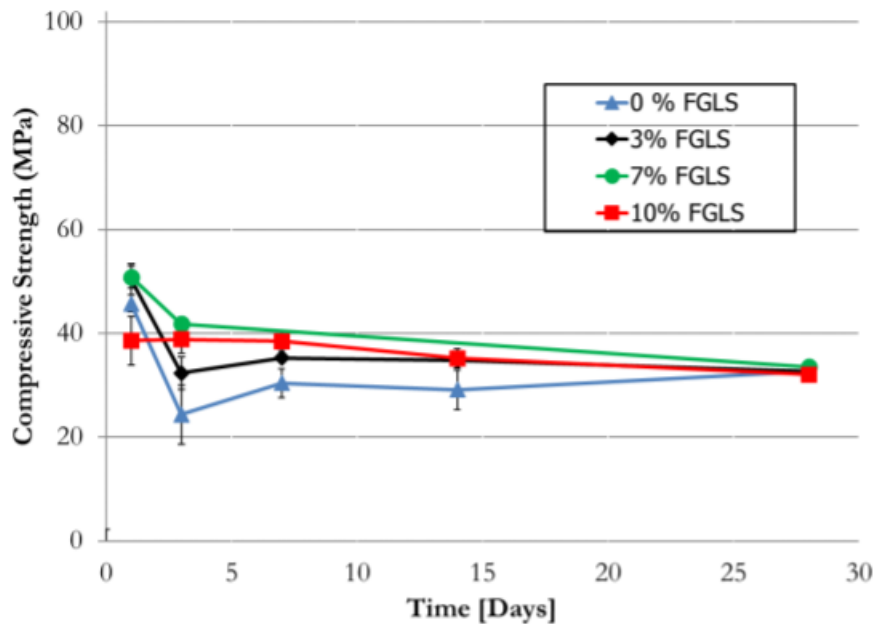
Figure 4.2 Compressive strength for converted CAC systems using different levels of FGLS.

Drying shrinkage was monitored along with the mass change for the concrete prisms. The percentage of length change and mass change were calculated for the specimens for both converted and unconverted CAC systems. The specimens were at different replacement levels of finely ground limestone (FGLS) as a replacement for cement. A comparison between the behavior of drying shrinkage of four different mixtures

with 0%, 3%, 7%, and 10% FGLS, for unconverted and converted systems is shown in Figure 4.3. All converted systems showed higher levels of drying shrinkage than the unconverted ones.
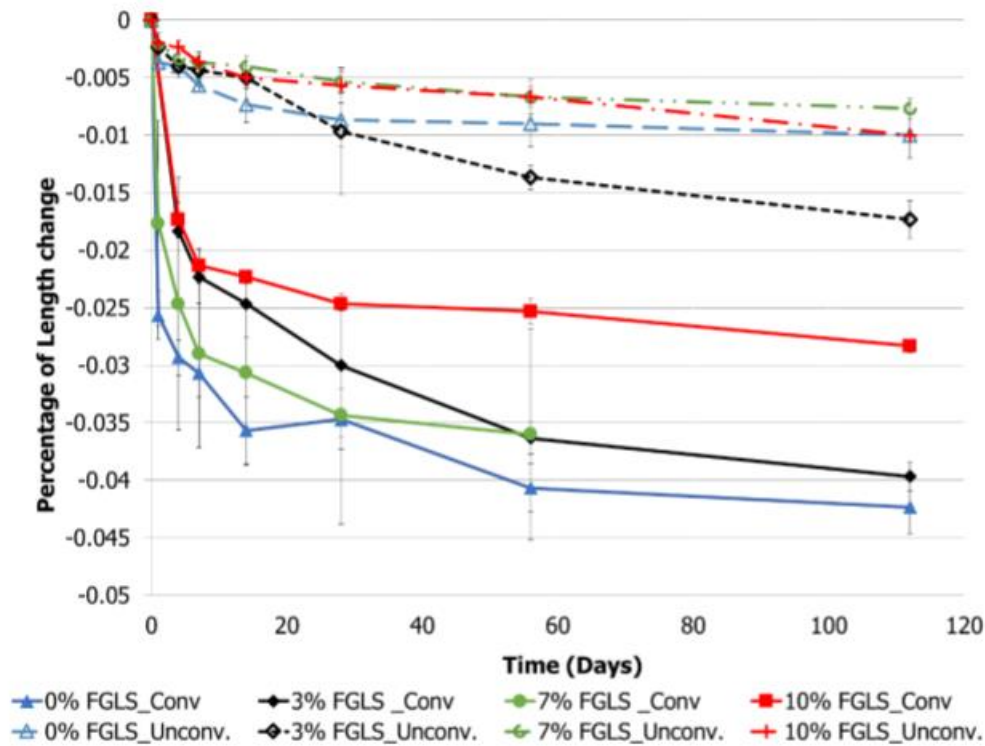
Figure 4.3 Percentage of length change for unconverted and converted CAC systems using different levels of FGLS.
Note: The drying shrinkage data for 7% FGLS_Conv on day 112 was not taken due to laboratory shutdown due to COVID-19.

For the unconverted systems, the 7% FGLS and 10% FGLS showed almost same levels of shrinkage which were less than the shrinkage in systems with 0% FGLS and 3% FGLS systems. In the converted systems, systems with 0% FGLS observed the highest shrinkage at 112 days followed by the 3% and 10% FGLS systems. The variability in all systems was relatively high, however.

Figure 4.4 shows the mass loss of all drying shrinkage specimens out to 112 days of dry curing. Similarly to the drying shrinkage results, the converted specimens showed significantly higher mass loss than the unconverted specimens. However, the trends within the converted and unconverted specimens do not match what was seen in the drying shrinkage.

Figure 4.4 Percentage of mass change for unconverted and converted CAC systems using different levels of FGLS.
Note: The drying shrinkage data for 7% FGLS_Conv on day 112 was not taken due to laboratory shutdown, which was due to COVID-19.

The unconverted prisms all had similar levels of mass change with the 10% FGLS systems having the highest mass loss, and the 3% FGLS system having the lowest till day 28. By day 112, the 10% FGLS had the least mass loss and the 0% FGLS the highest. In

the converted systems the 0% FGLS system had the highest level of mass loss while the 3% FGLS and 7% FGLS systems had the lowest.

The difference in values between the drying shrinkage in microstrains (μƐ) was calculated for the four different mixes between uncoverted and unconverted specimens. Also a comparison was made for the same mixes with repect to the mass change in grams (g) as shown in Table 4.4.

Table 4.4 Summary of Drying Shrinkage and Mass Change Values at 56 Days for Converted and Unconverted Samples at Different FGLS Percentages

Mix Name	Day 56_ Drying Shrinkage (μƐ)	Difference between unconverted and converted samples (μƐ)	Day 56_Mass Change (g)	Difference between unconverted and converted samples (g)
0%_Unconv	-90	317	-0.5	2.3
0%_Conv	-407		-2.9	
3 %_Unconv	-137	227	-0.4	2.3
3 %_Conv	-363		-2.7	
7 %_Unconv	-67	293	-0.5	2.2
7 %_Conv	-360		-2.7	
10 %_Unconv	-67	187	-0.4	2.8
10 %_Conv	-253		-3.2	

CAC with 0% FGLS showed 70% higher shrinkage difference between unconverted and converted samples compared to those with 10% FGLS. While the mass change difference between unconverted and converted samples for 10% FGLS were about 17% higher compared to the 0% FGLS. For each mix, the unconverted specimens showed much higher values than converted ones. These values varied in range from 187 μƐ to 317 μƐ in drying shrinkage and 2.2 g to 2.8 g for mass change. No trend was observed in the amount of difference in shrinkage in relation to the amount of FGLS in the system.

4.5.2 Impact of varying w/c

The compressive strength results were recorded for CAC cylinders for different mixtures with varied w/c ratios. The compressive strength data for converted samples are shown in Figure 4.5. All converted samples for w/c 0.35, 0.40, and 0.45 showed conversion represented by a minimum strength on day 3 and then continued to increase again.
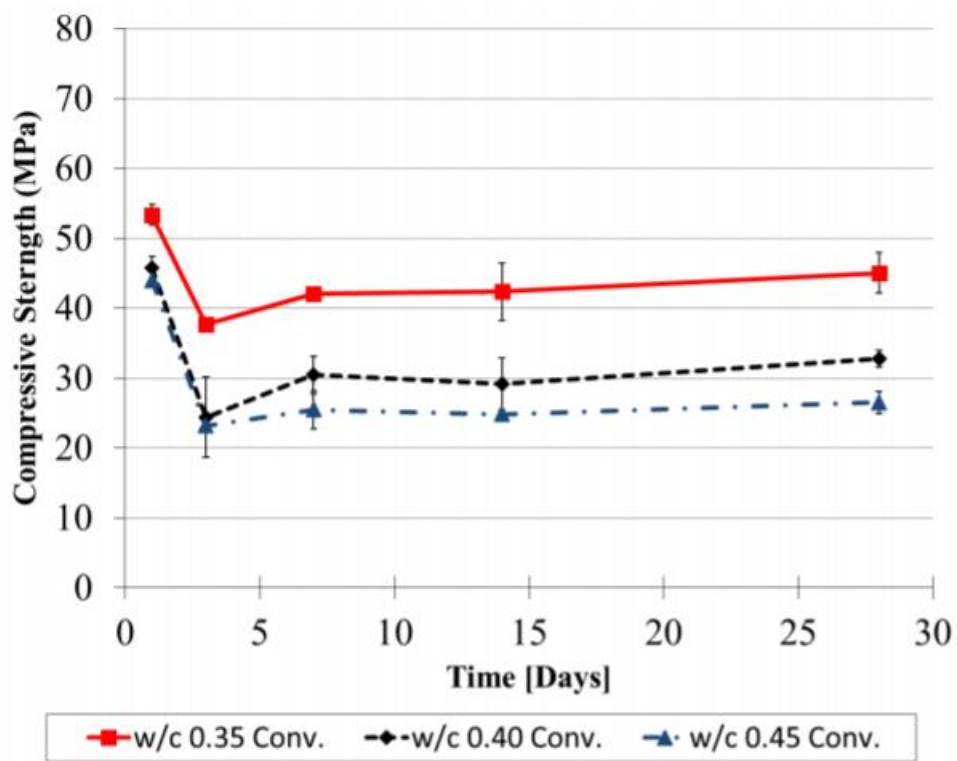
Figure 4.5 The compressive strength for unconverted and converted CAC systems at different w/c ratios.

Drying shrinkage was monitored for all the samples in unconverted and converted conditions at various w/c ratios. As shown in Figure 4.6, at day 56, the unconverted samples with w/cm 0.4 showed the least amount of shrinkage while that with w/c 0.45 showed the highest. At the same time interval, a different trend was observed for the converted samples. The systems with w/c 0.35 and 0.40 had a closer amount of shrinkage which was

higher than in systems with 0.45 w/c ratio. At the same w/c, the drying shrinkage for unconverted systems was a bit higher than the unconverted ones.

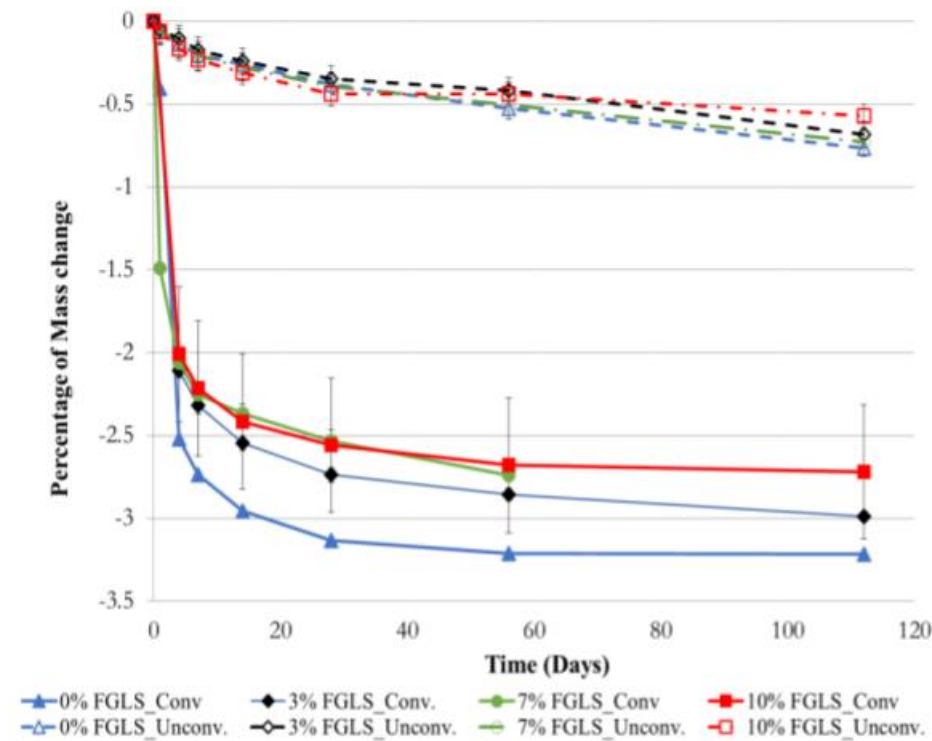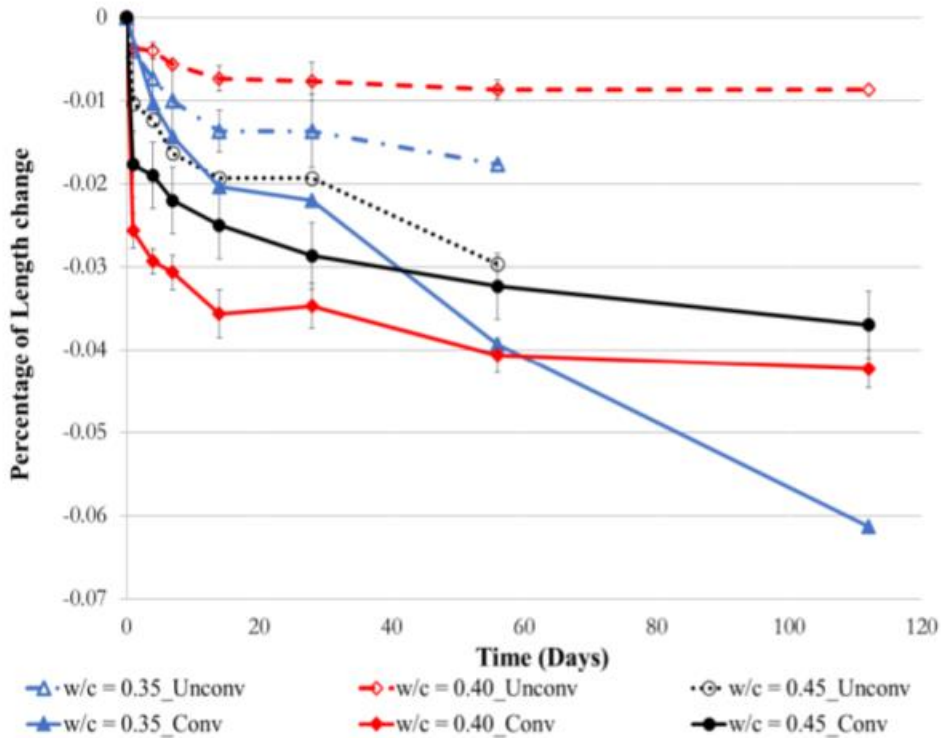**Figure 4.6** Percentage for length change for unconverted and converted CAC systems at different w/c ratios.
Note: The drying shrinkage data for w/c 0.35_Unconv and 0.45_Unconv on day 112 were not taken due to laboratory shutdown, which was due to COVID-19.

Upon observing the mass loss in systems with varied w/c, the converted systems showed a higher values than unconverted ones. For unconverted systems the w/c of 0.35 and 0.40 showed similar mass loss, while that of w/c 0.45 showed the lowest as shown in Figure 4.7. For converted systems, the system with w/c 0.45 showed the highest level of mass loss followed by 0.40 and 0.35 respectively.
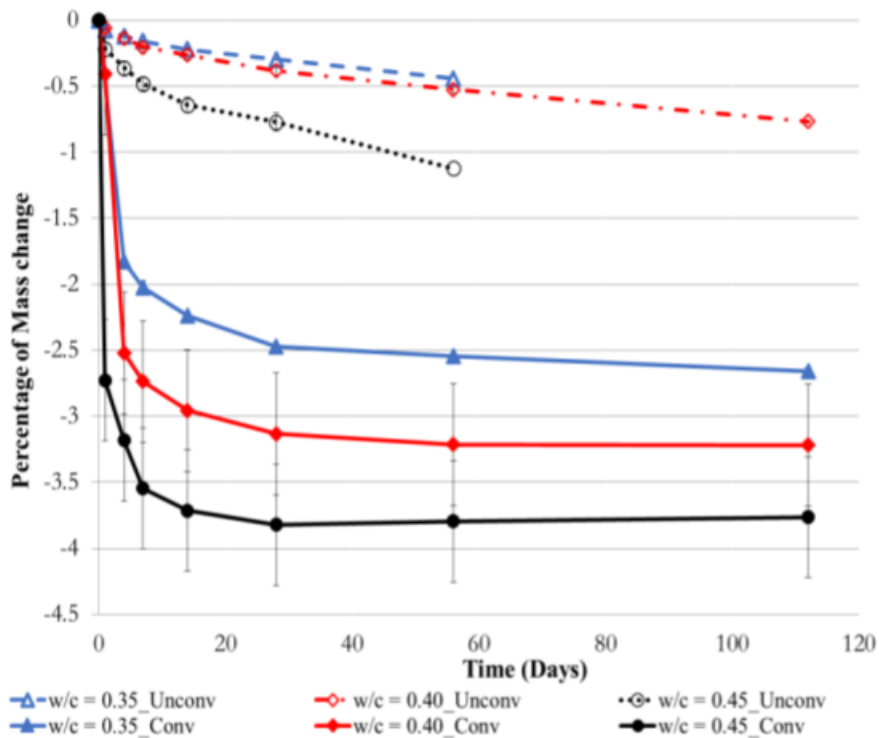
Figure 4.7 Percentage for mass change for unconverted and converted CAC systems at different w/c ratios.

Note: The mass change data for w/c 0.35_Unconv and 0.45_Unconv on day 112 were not taken due to laboratory shutdown, which was due to COVID-19.

The difference in values between the drying shrinkage in microstrains ($\mu\mathcal{E}$) was calculated for the three different mixes between uncoverted and unconverted specimens. Also, a comparison was made for the same mixes with repect to the mass change in grams (g) as shown in Table 4.5. The difference in shrinkage between converted and unconverted systems was about 32% higher in systems with w/c 0.40 compared to systems with 0.35. The system with 0.45 w/c showed a minimal difference between its unconverted and converted systems of 27$\mu\mathcal{E}$, compared to the other two systems. The mass change difference between unconverted and converted samples was very similar in all mixes, which varied between 2.2g and 2.3g. For each mix, the unconverted specimens showed

higher values than converted ones. No trend was observed in the amount of difference in shrinkage in relation to the varying of w/c.

Table 4.5 Summary of Drying Shrinkage and Mass Change Values at 56 Days for Converted and Unconverted Samples with Various w/c Ratios

Mix Name	Day 56_ Drying Shrinkage (µε)	Difference between unconverted and converted samples (µε)	Day 56_Mass Change (g)	Difference between unconverted and converted samples (g)
w/c 0.35_Unconv	-177	217	-0.5	2.3
w/c 0.35_Conv	-393		-2.9	
w/c 0.40_Unconv	-87	320	-0.4	2.3
w/c 0.40_Conv	-407		-2.7	
w/c 0.45_Unconv	-297	27	-0.5	2.2
w/c 0.45_Conv	-323		-2.7	

4.5.3 Impact of different time to convert

In this robustness factor, it was required to understand the impact of changing time to converting on days other than day 3. For that reason, systems were promoted to convert on day 28. To attain this, systems were placed in heated water bath at 50°C ± 2 °C two days prior the targeted converting time. This was following the previous curing procedures studied by Fryda et al.[53] and confirmed by Adams et al.[51]. Companion prisms for each mix were prepared and were kept in moist curing condition at 23°C ± 2°C and RH >95% in order to prevent conversion. These samples had the suffix "_Unconv" and were labelled with their corresponding day they were moved to the drying curing room (day 3, 28 or 90).

Drying shrinkage was monitored for all the samples in unconverted and converted conditions at different time to converting other than day 3. For unconverted prisms, the Unconv_Day 3 showed the lowest shrinkage, while the Unconv_Day 90 showed the highest one. The difference between the level of shrinkage between the three unconverted

mixes was very little, however. For converted mixes, Conv_Day 28 showed higher amount of shrinkage, after day 28, compared to Conv_Day 3. The converted samples showed higher levels of shrinkage than the corresponding unconverted ones. That was true for systems promoted to converted on day 3 and day 28. Measurements for Conv_Day 90 were not taken due to failure in curing conditions in the laboratory.
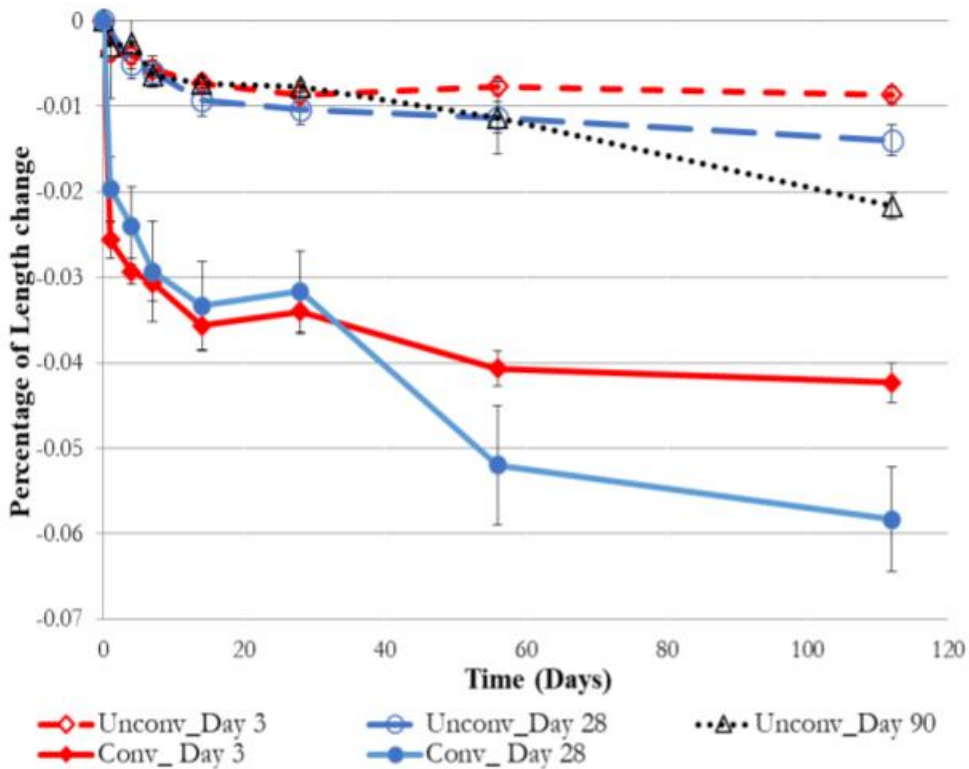
Figure 4.8 Percentage for length change for unconverted and converted CAC systems at different converting times.
Note: The drying shrinkage data for "Conv_Day 90" due to failure in curing conditions.

As for the mass loss in systems at different times to converting, the converted systems showed much higher values than unconverted ones. The unconverted systems for the three mixes showed relatively similar levels of shrinkage. For the converted systems, Conv_Day 3 showed more shrinkage compared to Conv_Day 28 as shown in Figure 4.9.
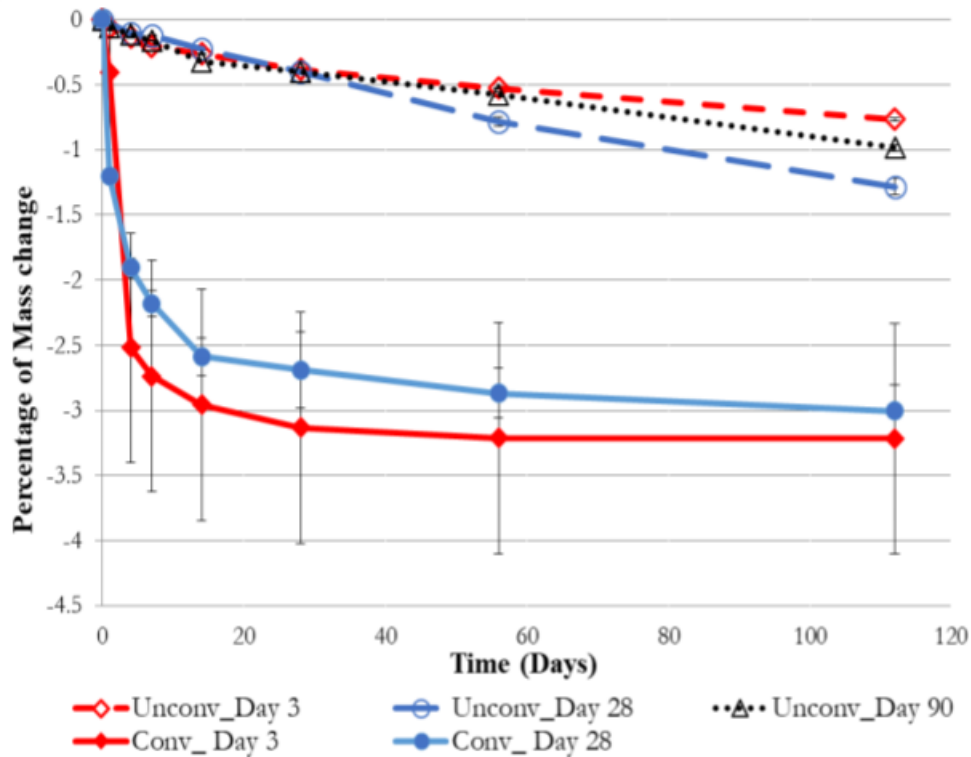
Figure 4.9 Percentage for mass change for unconverted and converted CAC systems at different converting times.

Note: The mass change data for "Conv_Day 90" due to failure in curing conditions.

The difference in values between the drying shrinkage in microstrains ($\mu\mathcal{E}$) was calculated for the two different mixes between uncoverted and unconverted specimens. Also a comparison was made for the same mixes with repect to the mass change in grams (g) as shown in Table 4.6. The difference in shrinkage between converted and unconverted systems was about 24% higher than in systems converted on day 28 compared to systems converted on day 3. The mass change difference between unconverted and converted samples varied between 1.7g and 2.5g. For each mix, the unconverted specimens showed higher levels in drying shrinkage than converted ones. No trend was observed in the amount of difference in shrinkage in relation to the different time to converting.

Table 4.6 Summary of Drying Shrinkage and Mass Change Values at 112 Days for Converted and Unconverted Samples with Different Time to Converting

Mix Name	Day 112_ Drying Shrinkage (µℰ)	Difference between unconverted and converted samples (µℰ)	Day 112_Mass Change (g)	Difference between unconverted and converted samples (g)
Unconv_Day 3	-87	337	-0.8	2.5
Conv_Day 3	-423		-3.2	
Unconv_Day 28	-140	443	-1.3	1.7
Conv_Day 28	-583		-3.0	

4.6 Discussion

Mass loss and shrinkage in the converted systems were characterized by a large amount of change early on with much lower rates of mass loss and volume change after that. That is attributed to the high porosity in the converted system with more voids opened to the air. This rapid mass loss and shrinkage slow down after day 3, with much slower mass loss continuing out to 112 days. The unconverted CAC systems showed a steady rate of shrinkage and mass loss throughout the 56 days in systems with w/c_0.35, w/c_ 0.45 and throughout the 112 days in the remaining samples, with no early period of rapid mass loss. This can be attributed to the dense microstructure of the unconverted system which resulted in less shrinkage. That was true for long term curing periods out to 112 days in terms of mass-loss and shrinkage. This is a key finding in terms of construction when using CAC systems as a rapid repair material. It will be extremely important to ensure that the CAC system does not convert early on, so as to reduce the amount of mass loss and thus to slow down the drying shrinkage. This slow rate of mass loss will allow more time for the CAC system to gain strength before it develops more stresses that occur due to shrinkage. If the

CAC system undergoes conversion instantly during hydration, it will then lose a lot of water and develop a lot of stress. This is undesirable as it will develop more cracks making the CAC system more prone to chloride penetration that would lead to corrosion and freeze thaw deterioration. As shown in Fryda et al. [53], even fairly thin sections can self-heat rapidly to a temperature which may promote earlier conversion. Care should be taken to understand the heat gain that will be experienced in all placements where drying shrinkage may be a concern.

It was noticeable that the addition of FGLS with different percentages had minimal impact on drying shrinkage behavioral pattern for both converted and unconverted systems. While the 10% FGLS system had less shrinkage than the 0% FGLS the amount of difference was minimal and within variability for the systems. The CAC with 0% FGLS showed the highest difference in mass change. The addition of FGLS helped to reduce the water loss amount in the CAC system. This small amount of difference may be due to a mineral filler effect filling porosity and making a more tortuous path for water to escape from the system. As for the compressive strength, the CAC systems with 10% FGLS showed about 20 MPa more than that with 0% FGLS for the minimum converted strength. This pattern continued over time until they all reached almost the same value on day 28. This matches with previous studies by Adams et al. [51] which showed that the addition of FGLS to CAC systems helps improve the strength. However, the system with 10% FGLS did not see a significant loss of strength due to conversion. This may indicate that the system did not convert and instead formed monocarboaluminate. Further microstructural studies will need to be completed to determine if this occurred. If so, the system may undergo conversion at a later, unpredictable date [58].

It was also observed that the w/c had a minimal impact on the drying shrinkage and mass loss. The mass loss was higher in systems with 0.45 w/c compared to systems with 0.35 w/c throughout the 112 days curing period. The higher the w/c the more mass loss in the system. That was true in converted and unconverted systems. As for the drying shrinkage in the unconverted samples, systems with 0.45 w/c showed higher level than that of 0.35. The unconverted systems with w/c 0.40, showed the lowest amount of shrinkage. In the converted samples, systems with w/c 0.35 had lower shrinkage than that of 0.40 and 0.45 until day 28. After that the systems with w/c 0.35 experienced a higher level of shrinkage that exceeded the other two converted systems. The reason for such trend is not quite understood why exactly samples behaved in this manner. CAC systems have high variability, and this may impact the average values showing a larger increase in shrinkage [51]. The samples might have got wet and the pores may have been filled with water. Further work needs to be done to study the microstructures of these samples for further investigation.

It was observed that changing time to converting did not significantly impact much the drying shrinkage. For the converted samples, systems converted on days 3 and 28 showed close levels of shrinkage till day 28 of curing time in the drying controlled curing chamber. After that, samples converted at day 28 showed higher shrinkage than systems converted on day 3 up to day 112. The difference between the systems was still within the variability of the CAC.

4.7 Conclusion

The work herein presented a study on the impact of conversion on the drying shrinkage in CAC systems. The following can be concluded:

- The total shrinkage for converted systems were much higher than the unconverted ones. That shows that the special curing systems should be considered for larger sections which may self-heat rapidly promoting conversion. This will be imperative in order to prevent conversion from occurring early on; giving better performance of drying shrinkage in rapid repair materials applications.

- The converted systems experienced a significant rapid mass loss, whereas the unconverted systems experienced a much slower rate of shrinkage and mass loss. The lower amount of shrinkage in the unconverted systems may be attributed to their lower porosity. The pore structure of a converted system which have more water has driven that increase in drying shrinkage. When CAC is used in construction, a restrained system will build up stresses rapidly but not necessarily giving enough time to gain enough strength. As converted systems have more pores that are ready to collapse and are prone to higher amount of drying shrinkage. It will be essential to ensure that the CAC system will gain strength and do not convert at an early age, before it builds up stresses that occur due to drying shrinkage.

Further work should be completed to examine the microstructure of converted and unconverted CAC. A detailed SEM analysis can help to understand the interconnectivity between the pores and to compare the pore size as well. In particular examining what hydrates formed through the use of FGLS will be key to understanding if it behaves as a mineral filler or participates in hydration.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Calcium aluminate cement concrete system is a specialty type of concrete with unique features. They are characterized by gaining rapid strength at very low temperatures approaching freezing. A reason for which CACs have gained more grounds recently to be used as a rapid repair material. CACs have been also used in wide range of applications such as an acid resistant material in wastewater applications, scour resistant material in dam spillways, and high temperature resistant material in refractory kiln applications.

CACs are known to undergo an inevitable process known as "conversion". In this process metastable hydrates convert into stable hydrates. A process that is accompanied by release of water and significant reduction of strength. Literature review has studied extensively the hydration process and kinetics of the conversion process in CAC systems. Very little information was, however provided studying the impact of conversion on the concrete long term durability.

The work presented pushed forward a method that showed promise to be used in the field in order to assess conversion. It studied the impact of conversion on the long term durability of CAC in terms of its drying shrinkage. It also addressed recommended future work that need to be done building on the key findings.

5.1 Key Findings

The key findings in this research include following:

- Electric resistivity measurement can be a promising tool to detect conversion in the field.
    - This work was done testing several robustness factors in order to test variabilities to validate this test. These factors included using different w/c, different cement formulations using FGLS, different aggregate types, and different time to converting.
    - Using different variables, a significant reduction in electric resistivity was observed correlated with the reduction in compressive strength. This reduction in strength represented when full conversion occurred in the system.

- Understanding the impact of conversion on long-term CAC durability in terms of drying shrinkage.
    - This work observed a much higher drying shrinkage and mass loss in converted CAC systems compared to unconverted ones.
    - This study was held on CAC systems with different variables such as different w/c, different cement formulation, and different time to convert.
    - Special curing procedures should be considered for larger sections which may self-heat rapidly. This is essential in order to prevent conversion to occur early on, before it builds up stresses due to drying shrinkage. This is imperative in order to ensure better performance in CAC when used as a rapid repair material.

5.2 Future Work

- Further investigation needs to be done on siliceous aggregates in order to examine why they kept gaining higher electric resistivity measurements after significant reduction. As it was observed that siliceous aggregates didn't keep relatively constant after time correlated to conversion as in other types of aggregates.

- SEM analysis need to be done on systems with 10% FGLS in order to understand the reason for not showing strength reduction when promoted to convert two days after casting. This work will help to understand if the systems fully converted or just formed a different hydrate.

- Testing the validation of the electric resistivity measurement as a tool to assess conversion with extended time to converting. This will be other than promoting conversion two days or 27 days after casting. This will be to observe if the electric

resistivity will continue to show reduction on times correlated to reduction in strength.

- Further examination needs to be done to investigate the microstructure of the converted and unconverted CAC systems to better understand the impact of conversion on drying shrinkage. SEM analysis can help better understand the porosity in these systems and how well they are interconnected. Understand if these pores are filled with air or water.

REFERENCES

[1] American Society of Civil Engineers (ASCE) Report Card, "INFRASTRUCTURE REPORT CARD 2017-ASCE," 2017.

[2] K. L. Scrivener and A. Campas, "Calcium Aluminate Cements," in Lea's Chemistry of Cement and Concrete, Elsevier Science, Oxford, UK, 2003.

[3] P. F. G. Banfill, "10 years exposure of ciment fondu mortars in a marine environment," in Calcium Aluminates: Proceedings of the International conference, IHS, Avignon, France, 2014, pp. 545–555.

[4] M. P. Adams and J. H. Ideker, "Volume stability of calcium aluminate cement and calcium sulfoaluminate cement systems," in International Conference on Calcium Aluminate Cements, IHS, Avignon, France, 2014.

[5] K. L. Scrivener, J. L. Cabiron, and R. Letourneux, "High-performance concretes from calcium aluminate cements," Cement Concrete Research, vol. 29, no. 8, 1999, pp. 1215–1223.

[6] S. R. Klaus, J. Neubauer, and F. Goetz-Neunhoeffer, "Application of heat flow calculations to synthetic calcium aluminate cement mixes," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 65–74.

[7] J. M .Auvray, H. Fryda, C. Zetterstrom, C. Wohrmeyer, and C. Parr, "Hydration and properties of calcium magnesium aluminate cement," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp.130–139.

[8] D. Madej, J. Szczerba, and W. Kagan, "Investigations on the hydratable compounds in the CaO-Al2O3-ZrO2 system," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 140–150.

[9] C. Stancu, N. Angelescu, and M. Muntean, "The influence of mineralogical composition of high alumina cement on its physical-mechanical properties," in Calcium Aluminates:Proceedings of the International Conference, Avignon., France, 2014, pp. 364–370.

[10] A. Buhr, D. Schmidtmeier, G. Wams, S. Kuiper, and S.Klaus, "Testing of calcium aluminate cement bonded castables and influence of curing conditions on the strength development," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 437–449.

[11] J. Kasper and O. Krause, "Mixing optimization of an alumina based LC-castable by applying variable power inputs," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 450–456.

[12] J.Herisson, M.Geugeuen-Minerbe, T.Chaussadent, and E. D. V. Hullebusch, "Development of a reproducible, representative and accelerated biogenic corrosion test to deliver durable structures in sewer networks," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 645–658.

[13] J. Herisson, E. D. V. Hullebusch, M. Gueguen-Minerbe, and T. Chaussadent, "Biogenic corrosion mechanism:study of parameters explaining calcium aluminate cement durability," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 633–659.

[14] M. P. Lavigne, J. N. Foussard, A. Cockx, E. Paul, A. Bertron, and G. Escadeillas, "A new method for evaluation of cement-based material resistance against biogenic attacks in sewer-like environments:comparison between CAC and BFSC linings," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 621–632.

[15] N. Motseiloa, M. G. Alexander, and H. Beushausen, "Acid resistance of calcium aluminate cement concrete blended with supplementary cementitious materials for application in sewer pipes," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 608–620.

[16] T. Sugiyama, K. Tabara, M. Morioka, and E. Sakai, "The influence of water/powderratio on the resistance to sulfuric acid of hardened calcium aluminate cement containing blast furnace slag," in Calcium Aluminates:Proceedings of the International Conference, Avignon., France, 2014, pp. 600–607.

[17] M. Valix and A. W. H. Cheung, "The impact of calcium aluminate cement and aggregates on conversion and on field performance in sewers," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 585–599.

[18] A.M.Goyns and M.G.Alexander, "Performance of various concretes in the Viginia experimental sewer over 20 years," in Calcium Aluminates:Proceedings of the International Conference, Avignon, France, 2014, pp. 573–584.

[19] K. L. Scrivener, "Advanced Concrete Technology," in Calcium Aluminates Cements, Elsevier, Oxford, UK, 2009, pp. 1-31.

[20] K. L. Scrivener, "100 years of calcium aluminate cement," in Calcium aluminate cement concrete: Proceedings of the Centenary Conference, Avignon, France, 2008, pp. 3–6.

[21] Concrete Society Technical Report, Calcium aluminate cements in construction: a Reassessmemt. Concrete Society, 2010, pp. 1-6.

[22] L. J. Vicat, "Recherches sur les causes chimiques de la destruction des composés hydrauliques par l'eau de mer et les moyens d'apprécier leur résistance à cette action", 2nd Edition, Valmont, Paris, 1857.

[23] K. L. Scrivener and A. Capmas, "Calcium aluminate cements. Advanced concrete technology: Constituent materials, Elsevier, Butterworth-Heinemann, Oxford, UK, 2003, Ch 2, pp.2/1-2/31.

[24] Bied, J. 'Aluminous cement.' British Patent 8193 (1909).

[25] H. G. Midgley, "High alumina cement in construction-a future based on experience," in Calcium Aluminate Cements Proccedings of the International Symposium held at Queen Mary and Westfield College, University of London, 1990, pp. 1–13.

[26] F. Sorrentino and D. Damidot, "Mineralogy of a 90 year old structure"Le Tunnel des Valois"," in Calcium Alumnates Proceedings of the International conference, IHS, BRE Press, Avignon, France, 2014, pp. 535–544.

[27] D. Konakova, "The influence of high temperatures on selected properties of calcium aluminous composites," in International conference of numerical analysis and applied mathematics (ICNAAM), 2016.

[28] L. Scheinherrova and A. Trnik, "Hydration of calcium aluminate cement determined by thermal analysis," in American Institute of Physics "AIP" conference Proceedings 1866, 2017.

[29] S. M. Bushnell-Watson and J. Sharp, "The effect of temperature upon the setting behaviour of refractory calcium aluminate cement," in Concrete and Cement Research, 1986, vol.16, pp.875-884.

[30] S. M. Bushnell-Watson and J. Sharp, "Further Studies of the effect of temperature upon the setting behaviour of refractory calcium aluminate cement" in Cement and Concrete Research, 1990, vol.20, pp 623–635.

[31] K. L. Scrivener, "Historical and Present Day Applications of Calcium Aluminate Cements," in Proceedings of the International conference on Calcium Aluminate Cements held at Heriot Watt University Edinburgh, Scotland, UK, 2001, pp. 3–23.

[32] N. Ukrainczyk and T. Matusinović, "Thermal properties of hydrating calcium aluminate cement pastes," Cement and Concrete Research, vol. 40, no. 1, 2010, pp. 128–136.

[33] H. G. Midgley and A. Midgley, "The conversion of High Alumina Cement," in Magazine of Concrete research, vol.27, 1975, pp. 59–77.

[34] R. J .Collins and W. Gutt, "Research on long-term properties of High Alumina Cement Concrete," in Magazine of Concrete Research, vol.40, 1988, pp. 195–208.

[35] A. M. Neville, "Properties of concrete," Fourth Edi., John Wiley & Sons Inc., NY, 1996, pp. 91–102.

[36] D. C. Teychenne, "Long term research into the charecteristics og high alumina cement concrete," in Magazine of Concrete research, vol.27, 1975, pp. 78–102.

[37] V. H. R. Lamour, P. J. M. Monteiro, K. L. Scrivener, and H. Fryda, "Mechanical Properties of Calcium Aluminate Cements," in Proceedings of the International conference on Calcium Aluminate cement Held at Heriot Watt University Edinburgh, Scotland, UK, 2001, pp. 199–213.

[38] H. Pollmann, "Calcium Aluminate Cements-Raw materials, Differences, Hydration and Properties," in Reviews in Minerology and Geochemistry, vol. 74, 2012, pp. 1–82.

[39] P. Barnes and J. Bensted, "Structure and Performance of cements," in Calcium Aluminate Cements, CRC Press, 2001, pp. 114–140.

[40] Calcium Aluminate Cement: Proceedings of the International Symposium in London, England, E & F N Spon, London, 1990.

[41] Calcium Aluminate Cement: Proceedings of International Conference in Edinburgh, Scotland, IOM Communications, 2001.

[42] Calcium Aluminate Cement: Proceedings of the centenary conference in Avignon, France, IHS BRE Press, London, England, 2008.

[43] Calcium Aluminates:Proceedings of the International Conference, Avignon., France, IHS BRE Press, UK, 2014.

[44] M. P. Adams and J. H. Ideker, "Influence of aggregate type on conversion and strength in calcium aluminate cement concrete," Cement and Concrete Research, vol. 100, 2017, pp. 284–296.

[45] C. Gosselin, "Microstructural Development of Calcium Aluminate Cement Based Systems with and without Supplementary Cementitious Materials," ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, 2009.

[46] C. Gosselin and K. L. Scrivener, "Microstructure development of calcium aluminate cements accelerated by lithium sulphate," in Calcium Aluminate Cements: Proceeding of the centenary conference, 2008, pp. 109–122.

[47] H. Fryda, K. L. Scrivener, G. Chanvillard, and C. Feron, "Relevance of laboratory tests to field applications of calcium aluminate cement concretes," Calcium Aluminate Cement, IOM Communications, Edinburgh, Scotland,UK, pp. 227–246, 2001.

[48] C. M. George and R. G. J. Montgomery, "Hormigon de cemento aluminoso: Durabilidad y conversion. Un nuevo punto de vista sobre un tema antiguo," Materiales de construcción, vol. 42, no. 228, 1992, pp. 33–50.

[49] Y. Zhang, G. Ye, W. Gu, D. Ding, L. Chen, and L. Zhu, "Conversion of calcium aluminate cement hydrates at 60°C with and without water," Journal of the American Ceramic Society, vol.7, 2018, pp. 2712–2717.

[50] M. Schmidt and H. Pollmann, "Hydration behaviour of CAC at various temperstures by isoperibolic heat flow calorimetry using acetates," in Calcium Aluminate Cements: Proceeding of the centenary conference, 2008, pp. 93–108.

[51] M. P. Adams, R. D. Lute, E. G. Moffatt, and J. H. Ideker, "Evaluation of a Procedure for Determining the Converted Strength of Calcium Aluminate Cement Concrete," Journal of Testing and Evaluation, vol. 46, no. 4, 2018, pp. 1659-1672.

[52] B. Raab, S. Stober, and H. Pollmann, "Investigations of the hydration behaviour of pure cement phases by different synthesis methods," in Calcium Aluminate Cements: Proceeding of the centenary conference, 2008, pp. 79–92.

[53] H. Fryda, E. Charpentier, and J. M. Bertino, "Accelerated Test for Conversion of Calcium Aluminate Cement," IHS BRE Press, Avignon, France, 2008.

[54] T.D. Robson, "High alumina cements and concrete," in Contractors Record Ltd, 1962.

[55] A. Campas, "Effect of temperature on setting time of calcium aluminate cement," in Calcium Aluminate Cement: Proceedings of the international Symposium in London, England, 1990, pp. 65–80.

[56] C. M. George, Industrial Aluminous Cement, Structure and Performance of cements, Applied Science, London, vol.1," in 7th International conference on the chemistry of cements, 1980, pp.415-470.

[57] A. Negro, A. Bachiorrini, and M. Murat, "Interaction , in aqueous medium , between calcium carbonate and monocalcium aluminate at 5 ° C , 20 ° C and 40 ° C," Bulletin Mineral., vol. 105, 1982, pp. 284–290.

[58] C. H. Fentiman, "Hydration of carbo-aluminous cement at different temperatures," Cement and Concrete Research, vol. 15, 1985, pp. 622–630.

[59] E. G. Moffatt and M. D. A. Thomas, "Performance of rapid-repair concrete in an aggressive marine environment," Constuction. Building Materials, vol. 132, 2017, pp. 478–486.

[60] A. Campas, "Durability of calcium aluminate cement concretes," in Advances in cement and concrete. Proceedings of an engineering foundation conference, 1994, pp. 377–405.

[61] P. Soukatchoff, Étude de résistance à l'eau douce de quelques ciments, Matériaux et constructions, vol.18, 1985, pp. 115–122.

[62] S. C. Bate, "High alumina cement concrete in existing building superstructures," Gratson, Watford, London, vol.109,1984.

[63] N. J. Crammond, "Long-term performance of high alumina cement in sulfate bearing environment," in Calcium Aluminate Cement. Proceedings of the International Symposium, University of London, 1990, pp. 208–221.

[64] Lafarge Fondu International, "Guide for using cement fondu Lafarge in structural units for civil engineering." France, 1979.

[65] W. Kurdowski, L. Taczuk, and B. Trybalska, "Behavior of high alumina cement in chloride solutions," in Calcium Aluminate Cements: Proceedings of the international synposium, 1990, pp. 222–229.

[66] C. M. Goerge, "Structure and performance of cements," P.Barnes, Ed. London, Applied Science Publishers, 1983.

[67] J. P. Bayoux, J. P. Letourneux, and S. Marcdargent, "Acidic corrosion of high alumina cement," in *Calcium Aluminate Cement:* Proceedings of the international Symposium in London, England, 1990, pp. 230–240.

[68] A. M. Dunster, N. J. Crammond, K. Pettifer, and D. L. Rayment "An assessment of ageing calcium aluminate concrete from marine structures.," in Mechanisms of Chemical Degradation of cement-based system, London, E & F N Spon,1997.

[69] A. Macias, A. Kindness, and F.P.Glasser, "Corrosion behaviour in steel in high alumina cement mortar cured at 5, 25 and 55 C:chemical and physical factors," Journal of Materials Science, vol. 31, 1996, pp. 279–289,.

[70] S. Goñi, C. Andrade, and C. Page, "Corrosion behaviour in steel in high alumina cement pastes," Cement and Concrete Research., vol. 21, 1991, pp. 635-646.

[71] A. Dunster and G. SERGI, "Carbonation and reinforcement corrosion in CAC concrete" in Calcium Aluminate Cements: Proceeding of the centenary conference, 2008, pp. 221–234.

[72] L. Mammoliti, B. P. Bergsma, and C. M. Hansson, "Corrosion of rebar in pore solutions simulating calcium aluminate cement," in Calcium Aluminate Cement Proceedings of the Centenary Conference 2008, pp. 235–248.

[73] J. Bae, N. S. Berke, R. J. Hoopes, and J. Malone, "Freezing and thawing resistance of concretes with shrinkage reducing admixtures.," International RILEM Work. Frost Resistance Concrete, RILEM Publications SARL., 2002, pp. 327–333.

[74] P. Mehta and P. J. M. Monteiro, Concrete Microstructure, Properties, and Materials, 4th ed., MacGraw Hill, 2014.

[75] T. Fu, T. Deboodt, and J. H. Ideker, "Development of shrinkage limit specification for high performance concrete used in bridge decks," Cement and Concrete Composition, vol. 72, 2016, pp. 17–26.

[76] C. K. Nmai, R. Tomita, F. Hondo, and J. Buffenbarger, "Shrinkage-Reducing Admixtures," Concrete International , 1998, pp. 31–37.

[77] J. H. Ideker, "Early-Age Behavior of Calcium Aluminate Cement Systems," in Civil Engineering, The University of Texas, Austin, 2008.

[78] American Society for Testing and Materials, ASTM C1760 Standard test method for bulk electric conductivity of hardened concrete, ASTM International, 2012.

[79] American Association of State Highway and Transportation Officials, AASHTO T 358-17, Standard Method of Test for Surface Resistivity Indication of Concrete's Ability to Resist Chloride Ion Penetration, vol. 1, 2017, pp. 1–8.

[80] M. R. Hornbostel, K. Larsen, and C. K. Geiker, "Relationship between Concrete Resistivity and Corrosion Rate—A Literature Review," Cement and Concrete Composites, vol. 29, 2013, pp. 60–72.

[81] American Society for Testing and Materials , ASTM C1202, "Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration,"American Society Testing Materials, 2012, pp. 1–8.

[82] H. Layssi, P. Ghods, A. R. Alizadeh, and M. Salehi, "Electrical Resistivity of Concrete,"Concrete International, 2015, pp. 1–33.

[83] M. M. Korayem and M. P. Adams, "Methods for promoting conversion and determining converted strength of calcium aluminate cement concrete," in Bridge Engineering Institute Conference, BEI 2019, pp.66-71.

[84] H. Fryda, S. Lamberet, and A. Dunster, "Calcium Aluminate Cement concrete in an Old concrete structure," 2008, pp. 209–220.

[85] American Society for Testing and Materials , ASTM C31/C31M-19a, "Standard Practice for Making and Curing Concrete Test Specimens in the Field," 2019.

[86] European Committee for Standarization, Calcium Aluminate cement-Composition, specifications, and conformity criteria, EN 14647, Brussels, 2005.

[87] Texas Department of Transportation , TX DoT SS-4491 Class CAC Concrete, Austin, TX, 2009.

[88] M. P. Adams, "Factors Influencing Conversion and Volume Stability in Calcium Aluminate Cement Systems," Oregon State University, 2015.

[89] American Society for Testing and Materials , ASTM C138/C138M-17a, Standard Test Method for Density (Unit Weight), Yield , and Air Content (Gravimetric), 2017, pp. 1–6.

[90] American Society for Testing and Materials, ASTM C143/C143M-15a, Standard Test Method for Slump of Hydraulic-Cement Concrete, 2015, pp. 1–4.

[91] American Society for Testing and Materials, ASTM C128-18, Standard Test Method for Relative Density (Specific Gravity) and Absorption of Fine Aggregates, 2018, pp. 2–7.

[92] American Society for Testing and Materials, ASTM C127-15, Standard Test Method for Relative Density (Specific Gravity) and Absorption of Coarse Aggregate, 2015, pp. 1–5.

[93] American Society for Testing and Materials, ASTM C136/C136M-19, Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates, 2019, pp. 1–5.

[94] American Society for Testing and Materials, ASTM C39/C39M-18 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, 2018, pp.1-5.

[95] American Society for Testing and Materials, ASTM C157/157/M, Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar, 2017, pp. 1–7.

[96] M. M. Korayem, M. P. Adams, A. J. Strand, and A. Bentivegna, "Electric resistivity testing method to assess conversion in calcium aluminate cement concrete," in Calcium Aluminates: Proceedings of International Conference, 2020.

[97] M. M. Korayem and M. P. Adams, "Methods for promoting conversion and determining converted strength of calcium aluminate cement concrete," in *Bridge Engineering Institute*, 2019, vol. 2019.

[98] K. B. Oldham and J. C. Myland, "The Conduction of Electricity," Fundamentals of Electrochemical Science, 1994, pp. 1–27.

[99] P. Azarsa and R. Gupta, "Electrical Resistivity of Concrete for Durability Evaluation: A Review," Advanced Materials Science Engineering, 2017.

[100] American Association State Highway Transportation Officials, AASHTO TP 95. Method of test for surface resistivity indication of concrete's ability to resist chloride ion penetration, 2011.

[101] C. H. Fentiman, "Hydration of carbo-aluminous cement at different temperatures,"Cement and Concrete Research, vol. 15, no. 4, 1985, pp. 622–630.

[102] F. Indelicato, "On the correlation between porosity and strength in high-alumina cement mortars," Materials Structures, vol. 23, 1990, pp. 289–295.

[103] S. H. Kosmatka and M. L. Wilson, Design and Control of Concrete Mixtures :The Guide to Applications, Methods and Materials, Portland Cement Association, 15th edition, First Printing 2011.

[104] R. Spragg, K. Snyder, D. Bentz, J. W. Bullard, and J. Weiss, Electrical Resistivity Measurements in Cementitious Systems: Observations of Factors that Influence the Measurements, 2013, pp. 1–17.

[105] M. M. Korayem and M. P. Adams, "Impacts of conversion on drying shrinkage of calcium aluminate cement using finely ground limestone," in Calcium Aluminates: Proceedings of International Conference, England, UK, 2020.

[106] B. Bissonnette, P. Pierre, and M. Pigeon, "Influence of key parameters on drying shrinkage of cementitious materials," vol. 29, 1996, pp. 1655–1662.

[107] A. Al-Manaseer and S. Ristanovic, "Predicting Drying Shrinkage of concrete," Concrete International, vol. 26, no. 8, 2004, pp. 79–83.

[108] M. Pigeon and F. Suacier, "Durability of Repaired Concrete Structures," in Proceedings of the International Conference on Advances in Concrete Technology, 1992, pp. 741–773.

[109] X. Huo, "Early-Age Shrinkage of HPC Decks under Different Curing Methods," Structures Conference Congress, 2000.