INFLUENCE OF PERLITE ADDITION ON THE STRENGTH DEVELOPMENT AND THERMAL STABILITY OF CALCIUM ALUMINATE CEMENT MORTARS

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INFLUENCE OF PERLITE ADDITION ON THE STRENGTH DEVELOPMENT AND THERMAL STABILITY OF CALCIUM ALUMINATE CEMENT MORTARS

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ABSTRACT

INFLUENCE OF PERLITE ADDITION ON THE STRENGTH DEVELOPMENT AND THERMAL STABILITY OF CALCIUM ALUMINATE CEMENT MORTARS

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Calcium aluminate cement is a special cement that reaches high strength in a short time but suffers a considerable loss of strength due to moisture and temperature-related conversion of metastable calcium aluminum hydrates. The study aimed to produce strätlingite as a stable hydration product to completely stop or reduce this chemical conversion using an inexpensive and abundant silica source. Ground perlite was chosen as the source of silica. Perlite was mixed with calcium aluminate cement in different proportions and two different water-to-binder ratios. The paste and mortar samples obtained were cured under different temperature and humidity conditions. Na_2SO_4 and $Ca(OH)_2$ were also added in small quantities to these mixtures to investigate their influence on strength development and hydrated phases at early ages.

A strength loss is observed in the pure cement samples due to conversion, after 20-30d for the dry-cured samples but after only 2-3d for the wet-cured samples. The loss is small and slow (<10-20 %) for the dry-cured samples, but quite significant (up to ~ 80 %) and rapid in wet-cured cases.

As the amount of ground perlite that replaces the cement increases strength decreases. However, the early strength gained is maintained more for the perlite-incorporated mixtures. Strätlingite formation is confirmed by X-ray diffraction analysis in several of the perlite-containing mixtures. Loss of strength was completely prevented by the addition of 1-2 % Na_2SO_4 to mixtures containing more than 50 % perlite. Addition of $Ca(OH)_2$ was not very effective against conversion, however, it greatly reduced setting time. Addition of perlite also decreased setting time. In contrast, Na_2SO_4 addition delayed setting. The heat of hydration decreased with increasing perlite content. Although the addition of perlite or chemicals proved beneficial, none of the mixtures were able to maintain a significant portion of their original strengths or masses after exposure to 600 °C or 1100 °C.

Keywords: Calcium aluminate cement, perlite, strätlingite

ÖZ

PERLİT İLAVESİNİN KALSİYUM ALÜMİNAT ÇİMENTOSU PASTALARININ DAYANIMININ GELİŞİMİNE VE TERMAL STABİLİTESİNE ETKİSİ

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Kalsiyum alüminat çimentosu, kısa sürede yüksek dayanım kazanan, fakat neme ve sıcaklığa bağlı olarak yarı kararlı kalsiyum alüminat hidratlarının bozunmasından dolayı bu dayanımını önemli ölçüde kaybeden özel bir çimentodur. Bu çalışmada, bu bozunmayı azaltmak ya da tamamen durdurmak için stratlingit oluşturmak, stratlingit oluşumunu sağlamak için de ülkemizde çok bulunan bir silis kaynağı kullanmak hedeflenmiştir. Silis kaynağı olarak perlit seçilmiştir. Perlit, kalsiyum alüminat çimentosu ile farklı oranlarda ve iki farklı su-bağlayıcı malzeme oranıyla karıştırılmıştır. Çimento numuneleri farklı sıcaklık ve nemde kürlenmiştir. Dayanım gelişimine olan etkilerini ve erken yaşlarda hidrate olan fazları araştırmak için bu karışımlara az miktarlarda Na_2SO_4 ve $Ca(OH)_2$ ilave edilmiştir.

Bozunmaya bağlı olarak saf çimento numunelerinde dayanım kaybı gözlemlenmiştir. Bu kayıp kuru numunelerde 20-30 günden sonra, ıslak numunelerde ise sadece 2-3 günden sonra gerçekleşmektedir. Bu kayıp kuru numunelerde az ve yavaş (< % 10-20), ıslak numunelerde çok ve hızlıdır (~ % 80'e kadar).

Çimento yerine kullanılan perlitin miktarı arttıkça dayanım düşmektedir. Bununla birlikte, erken dayanım perlitli karışımlarda fazladır. Stratlingit oluşumu, perlit içeren birçok karışımda X ışını difraksiyonu ile teyit edilmiştir. % 50’den fazla perlit içeren karışımlara % 1-2 Na_2SO_4 eklenerek dayanım kaybı tamamen engellenmiştir. $Ca(OH)_2$ ilavesi bozunmaya karşı çok etkili olmamış, fakat priz süresini önemli ölçüde düşürmüştür. Perlit ilavesi de priz süresini düşürmektedir. Buna karşılık, Na_2SO_4 priz süresini arttırmıştır. Hidratasyon ısısı, perlit içeriği arttıkça azalmaktadır. Perlit veya kimyasalların ilavesi yararlı olmasına rağmen, karışımların hiçbiri 600 °C veya 1100 °C’ye maruz kaldıktan sonra dayanımlarının ya da kütlelerinin önemli bir bölümünü muhafaza edememişlerdir.

Anahtar Kelimeler: Kalsiyum alüminat çimentosu, perlit, stratlingit

To my parents,
Şirin and Hasan Şengül

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ASTM: American Society for Testing and Materials.
EN: European Norms.
CEN: European Committee for Standardization.
TS: Turkish Standards.

CHAPTER 1

INTRODUCTION

1.1 General

Portland cement (PC) concrete is the most widely used material in the construction sector in Turkey and all over the world owing to the fact that it has many advantages in terms of strength and durability. Also, it is economical and easily procurable. According to The Turkish Ready Mixed Concrete Association, approximately 107 million m^3 of concrete was produced in Turkey in 2014 (THBB, 2015).

Although PC concrete has many advantages over other conventional construction materials it can be inadequate for some applications such as when rapid hardening or high-temperature resistance or acid and sulphate resistance are desired. For these cases, special types of cement are employed. Calcium aluminate cement (CAC) is one such special cement. The ability to gain strength in a short time and high-temperature resistance are some of the most outstanding properties of CAC. However, a chemical conversion of hydration products can occur under certain temperature and humidity conditions, greatly reducing the strength of structures made with CAC. Therefore, CAC is not used in load-bearing structures. In general, it is preferred in refractory applications and used for applications such as rapid repair, floor leveling, tile adhesives and grouts (Scrivener, 2003).

1.2 Objective and Scope

This study aimed to create a CAC mixture that does not experience (much) conversion, hence does not lose its strength over time. This may be achievable by creating strätlingite as a hydration product, by adding ground perlite as a source of soluble silicates. The reason for using perlite is that it is inexpensive and quite abundant in Turkey. Also, Na_2SO_4 and $Ca(OH)_2$ were used to influence the hydration of CAC-perlite mixtures and influence of water-cementitious material ratio (W/CM), curing humidity conditions, and temperature on the durability of CAC was investigated. For this purpose, 36 mixtures containing different amounts of water, perlite, Na_2SO_4 and $Ca(OH)_2$ were prepared and the hydration process and products investigated using various laboratory characterization techniques.

This thesis consists of five chapters. An introduction of the topic is given in the first chapter. A theoretical background with a literature review on CAC and perlite are presented in the second chapter. In the third chapter, the experimental methods used in this study are described. The results of the tests and analyses are given and discussed in the fourth chapter. In the fifth chapter, the conclusions of the study and recommendations for future studies are given.

CHAPTER 2

LITERATURE REVIEW

2.1 Calcium Aluminate Cement

2.1.1 General

Calcium aluminate cement is one of the most important special types of cement. Nevertheless, the quantity used is about one-thousandth of that of ordinary Portland cement (OPC) (Scrivener, 2003). It is quite a bit more expensive than OPC, around four to five times as expensive (Scrivener et al., 1999).

Rapid hardening, resistance to high temperatures, temperature changes and aggressive chemical environments, and high resistance to abrasion are some of the outstanding properties of CAC (Sucu & Delibaş, 2015). The color of CAC is grey-black. It is much darker than OPC. Its color is mainly related to its iron content. The iron content may be up to 18 % in CAC. When the alumina content increases in CAC, the grey-black color turns to white (Kırca, 2006). For this reason, CACs with alumina content higher than 40 %, especially those containing 70 to 80 %, are whitish.

CAC is a cement that can reach the 28-day compressive strength of OPC in about 6 hours. However, this strength can decrease due to chemical conversion of metastable hydration products, particularly at high temperature and humidity and cause serious structural problems. Previously, it was used in load-bearing systems of some structures and damages took place. As such it is no longer used in load-bearing systems due to the conversion problems (Kırca, Yaman, & Tokyay, 2013). Owing to its rapid hardening, CAC is used in emergency situations (rapid repair). Besides, owing to the fact that it can resist high temperatures, acid, and sulphate attack, it is used as a refractory material and in sewers (Scrivener, 2003).

2.1.2 Mineral Composition of CAC

CAC contains a much greater amount of alumina and less silica than OPC. The major phases in OPC and CAC are compared in Table 2.1.

Table 2.1 The major phases of OPC and CAC (Barborak, 2010)

	Phase	OPC (%)	CAC (%)
Silicates	C_3S	50 - 70	0
	C_2S	15 - 30	< 10
Aluminates	C_3A	5 - 10	0
	C_4AF	5 - 15	10 - 40
	CA	0	40 - 50

The position of OPC and CAC in a CaO, Al_2O_3, SiO_2 ternary diagram is given in Figure 2.1.

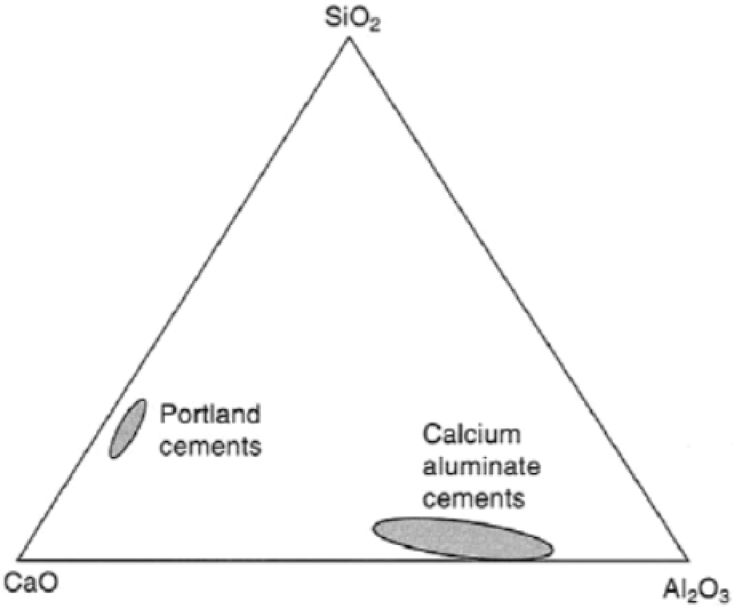

Figure 2.1 Ternary diagram of OPC and CAC (Scrivener, 2003)

Calcium monoaluminate (CA) is the principal mineral of all CACs (Eng & Reza, 2007). It provides the early strength of hydrated CAC (Klaus et al., 2015). Another reactive mineral is dodecacalcium heptaaluminate (mayenite) ($C_{12}A_7$). It helps to start the setting process. Due to the fact that much mayenite causes undesirably rapid setting and hardening, its content is limited by cement producers (Scrivener, 2003). Tetracalciumaluminoferrite (C_4AF) is the second most abundant component of CAC. However, it makes no or very little contribution to the setting and strength development (Betoniek, 1998). Another component is dicalcium silicate (C_2S). Due to its hydration being slow, it contributes to strength at later ages rather than at early ages (Kırca, 2006). Yet another one is dicalcium aluminosilicate (gehlenite) (C_2AS). C_2AS behaves similar to C_2S, its hydration is slow and it contributes to later-age strength (Robson, 1962).

The main constituents of CAC raw meal are Al_2O_3, CaO, SiO_2, FeO, Fe_2O_3, TiO_2, MgO, Na_2O and SO_3. Ratios of these constituents depend on the grade of CAC (Antonovič et al., 2013) to be produced. The oxides in and various properties of some grades of CAC are given in Table 2.2.

Table 2.2 Composition of different grades of CACs (ÇİMSA, 2016)

Class	Colour	Al_2O_3	CaO	SiO_2	Al_2O_3 +FeO	TiO_2	MgO	Na_2O	K_2O
Standard Low Alumina	Gray / faded black	36-42	36-42	3-8	12-20	< 2	~ 1	~ 0.1	~ 0.15
Low Alumina, Low Iron	Gray / light gray	48-60	36-42	3-8	1-3	< 2	~ 0.1	~ 0.1	~ 0.05
Normal Alumina	White	65-75	25-35	< 0.5	< 0.5	< 0.05	~ 0.1	~ 0.3	~ 0.05
High Alumina	White	> 80	< 20	< 0.2	< 0.2	< 0.05	< 0.1	< 0.1	~ 0.05

The most widely used CAC, in Turkey, and abroad contains approximately 40 % alumina (Kırca, 2006).

2.1.3 Hydration of CAC

The hydration of CAC is very different than that of OPC. While in OPC 60 - 80 % of hydration takes place in 28 days and the hydration reactions go on after 28 days (even though slowly), in CAC the majority of hydration takes place within the first 24 hours. Actually, after CAC is mixed with water, a little heat is released within minutes. Then the hydration stops for 2-3 hours. This period is called the induction (dormant) period. After the induction period, CAC reacts with the water rapidly and most of the hydration is completed within 24 hours. This situation reveals another desirable property of CAC, slow setting and rapid hardening (Betoniek, 1998). Figure 2.2 summarizes the hydration process of CAC.

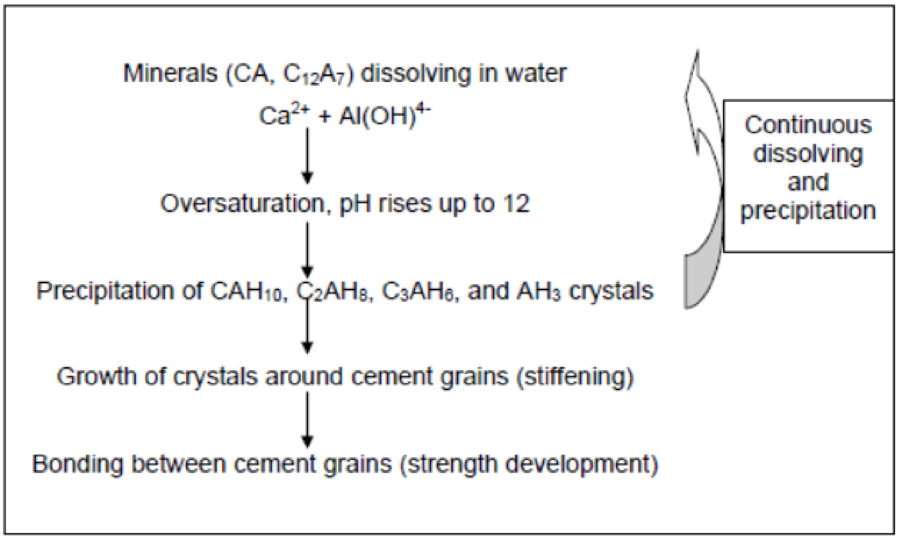

Figure 2.2 Summary of hydration process of CAC (Garsel, 1996)

Due to the fact that the most abundant components in CAC are CA and $C_{12}A_7$, they dominate the properties of cement. Therefore, calcium aluminates give CAC its specific properties. As a consequence of hydration reactions of mainly CA, different hydration products are formed depending on temperature (Kırca, 2006). CAH_{10}, C_2AH_8, C_3AH_6, AH_3, C_4AH_{19} and $C_4A_3H_3$ are possible hydration products of calcium aluminate (Kırca, 2006). Owing to the fact that there is no portlandite (CH) among the hydration products, CAC has a high resistance to lots of aggressive agents (CEN/TC 51 N 645, 2000).

2.1.4 Conversion of CAC

The nature of the hydration products of CAC is temperature and time dependent (Eng & Reza, 2007). At temperatures under 15 °C, the hydration product of CA is CAH_{10}, while between 15 °C and 27 °C, C_2AH_8 and AH_3 can be observed in addition to CAH_{10}. At higher temperatures, C_2AH_8 is the dominant product. Above 50 °C, C_3AH_6 and AH_3 dominate (Gosselin, 2009). Equations 2.1-2.3 describe the formation of different hydration products at different temperatures.

$$CA + 10H \rightarrow CAH_{10} \quad (< 15\ ^\circ C) \tag{2.1}$$

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \quad (\text{between } 15\ ^\circ C \text{ and } 27\ ^\circ C\ ) \tag{2.2}$$

$$3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \quad (> 50\ ^\circ C) \tag{2.3}$$

The change of hydrates from metastable to stable is called “conversion”. Conversion of CAH_{10} and C_2AH_8 to C_3AH_6 is the main problem of CAC. As a consequence of conversion, porosity increases thereby decreasing strength (Gosselin, 2009). The rate of conversion of CAH_{10} and C_2AH_8 to C_3AH_6 is dependent on temperature and is given in Table 2.3.

Table 2.3 The rate of conversion of CAH_{10} and C_2AH_8 to C_3AH_6 depending on temperature (Odler, 2000)

Temperature (°C)	C_2AH_8	CAH_{10}
5	> 20 years	> 20 years
10	19 years	17 years
20	2 years	21 months
30	75 days	55 days
50	32 hours	21 hours
90	2 minutes	35 seconds

The hydration and conversion reactions of CA at different temperatures are summarized in Figure 2.3.

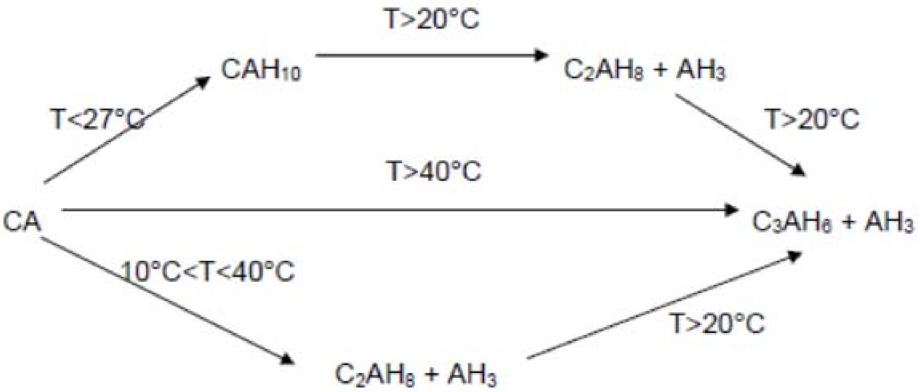

Figure 2.3 Hydration and conversion behavior of CA at different temperatures (Kırca, 2006)

In addition to time and temperature, W/CM and humidity also affect the conversion of CAC. As W/CM or humidity increases, the conversion rate increases (Odler, 2000). Table 2.4 shows this effect. To provide long term durability, it has been suggested that W/CM should be 0.4 or lower (Sucu & Delibaş, 2015).

Table 2.4 The effect of temperature and humidity on conversion (Odler, 2000)

Moisture Condition	Low Temperature (< 20 °C)	Elevated Temperature (> 20 °C)
Dry	relative stability	dehydration $CAH_{10} \rightarrow CAH_4$ $C_2AH_8 \rightarrow C_2AH_5$
Humid	slow conversion to $C_3AH_6 + AH_3$	fast conversion to $C_3AH_6 + AH_3$

2.1.5 Setting Time of CAC

Although the six-hour-compressive strength of CAC can reach up to 40 MPa, its setting time is almost the same as that of OPC. This is one of its advantageous properties (ÇİMSA, 2018). Even though the setting time of CA, the principal mineral in CAC, is about 18 hours, CAC has a much shorter setting time due to C_2AH_{17}.

Up to about 27 °C, setting time increases with increasing temperature. Beyond this temperature, setting time starts to decrease. The change in setting time of CAC with pastes temperature is given in Figure 2.4. This is observed in pastes in small quantities. In larger quantities (e.g. in concrete), this cannot be observed easily due to self-heating and friction during mixing of the aggregates present in the concrete (Scrivener, 2003).

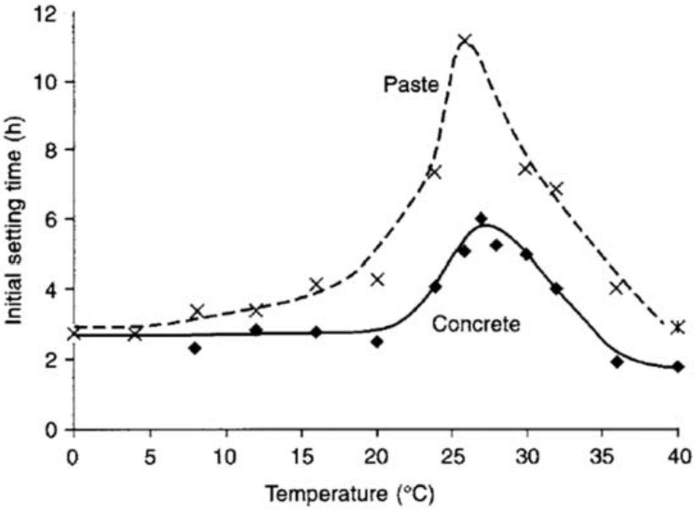

Figure 2.4 Effect of temperature on setting time of CAC paste and concrete (Cottin and George, 1982)

Certain additives can significantly influence the setting time of CAC systems (Hewlett, 2006). Calcium, potassium, lithium and sodium hydroxieds are other accelerators whereas sodium chloride and potassium chloride are retarders. Some chemicals, like magnesium chloride and calcium sulphate hemihydrate can act as either retarders or accelerators depending on the concentrations.

2.1.6 Thermal Resistance of CAC

Widely used for refractory concretes, CAC can resist high temperatures and thermal shock. Because of this feature, it is used for the floors in foundries, fire training centers or other environments exposed to high temperatures (Scrivener, 2003). CAC containing 40 % Al_2O_3 is used up to 1300 °C. If corundum is used as aggregate with

CAC containing 70 % Al_2O_3, it can resist temperatures of 1500-1800 °C. Clearly, Al_2O_3 content and aggregate type can change the temperature resistance of CAC mixtures (Antonovič et al., 2013).

2.2 CACs with Supplementary Cementitious Materials

Supplementary cementitious materials (SCMs) have an important place in the developing cement industry owing to their numerous benefits. Even though each SCM has different properties and reacts differently in the presence of water, generally speaking, they affect the most important properties of cement paste and concrete such as strength, durability, setting time, the heat of hydration and resistance to chemical attacks. In Figure 2.5 below, the ternary diagram of cementitious materials is given.

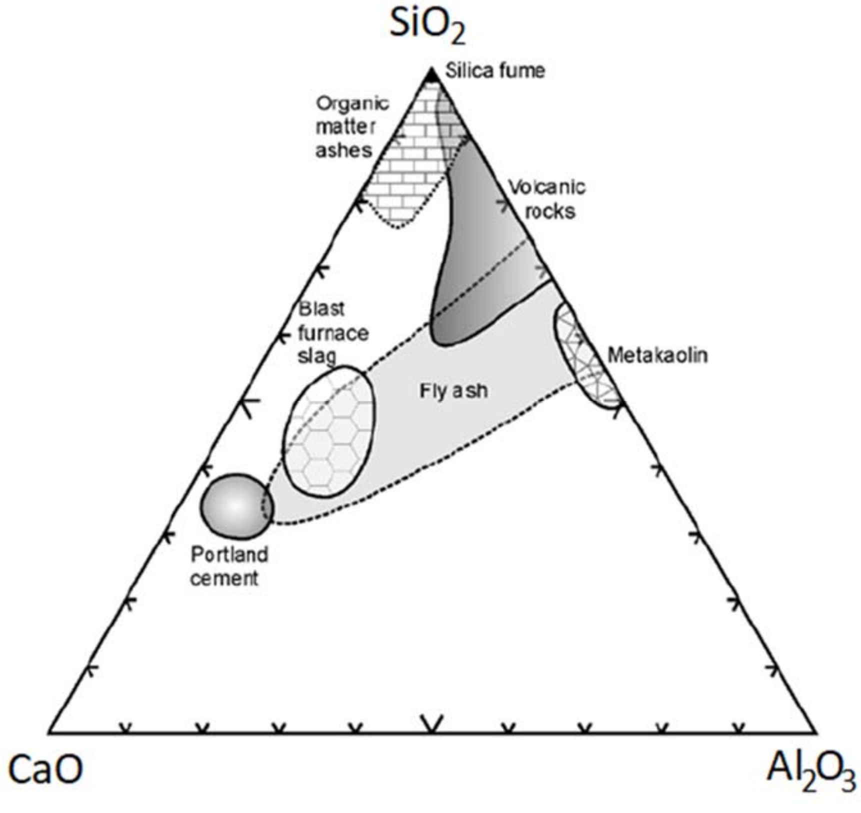

Figure 2.5 Ternary diagram of cementitious materials (Snellings et al., 2012)

2.3 Perlite as a Natural Pozzolan

When selected, processed and used suitably, natural pozzolans can improve many properties of concretes such as strength, durability or resistance to chemical attacks. Additionally, they can reduce the cost. Even though several types of natural pozzolans such as diatomaceous earth and volcanic tuffs or ashes can be named, each of them shows differences in reactivity. Therefore, estimating the results, obtained from a natural pozzolan taken from a specific location, is very difficult. Accordingly, it can be useful to determine the behavior of natural pozzolans which show limited variability and are plentiful. Also, pozzolans can be found in different locations. Perlite is one such pozzolan which fits these properties, particularly in Turkey (Erdoğan & Sağlık, 2013). Perlite is a volcanic glassy rock containing 70 - 75 % SiO_2, 12 - 18 % Al_2O_3 and lesser amounts of sodium, iron, magnesium, calcium and potassium (Erdoğan & Sağlık, 2013; Rashad, 2016)

Perlite expands up to 15 to 20 times its initial volume when heated rapidly. Expanded perlite is used as thermal and sound insulation material. Also, it is fire resistant and has low density. By virtue of its low density, it is used in lightweight concrete (Vosoughi et al., 2015). Finely ground perlite is an effective pozzolan (Erdoğan & Sağlık, 2013). As such, perlite increases strength and protects concrete against chemical attacks. As mentioned in Section 2.2, a silica source may modify the hydration of CAC (Gosselin, 2009). Ground perlite may contribute silica to the hydrating CAC system that may result in the formation of strätlingite. Hence, the use of ground perlite may prevent conversion. According to the United States Geological Survey Mineral Resources Program (USGS, 2015), approximately 21 % of the perlite in the world is produced in Turkey. Table 2.5 lists the 14 countries which are major producers of perlite.

Table 2.5 Production of perlite in various countries (USGS, 2015)

PERLITE: WORLD PRODUCTION, BY COUNTRY					
(Metric tons)					
Country	2011	2012	2013	2014	2015
Armenia	229	181	53	14	20
Australia	NA	NA	NA	5	7
Bulgaria	-	4,000	5,000	5,000	5,000
China	2,500,000	2,100,000	1,800,000	1,800,000	1,800,000
Greece	842,870	876,396	890,000	985,328	1,000,000
Hungary	39,254	40,129	35,957	37,957	40,000
Iran	20,000	30,000	55,100	55,000	60,000
Mexico	31,779	29,950	27,200	26,000	26,000
New Zealand	NA	NA	NA	22,000	25,000
Philippines	6,272	9,221	14,249	17,194	19,000
Slovakia	23,000	24,000	16,000	17,000	18,000
Turkey	702,673	887,600	1,075,949	897,125	925,000
United States	420,000	393,000	419,000	462,000	459,000
Zimbabwe	1,000	1,000	1,000	1,000	1,000
Total	4,590,000	4,400,000	4,340,000	4,330,000	4,380,000

Six countries produce 97 % of all perlite: Turkey, Greece, USA, Japan, Italy and Hungary (Rashad, 2016). Approximately 70 % of the perlite reserves in the world are in Turkey (Meral, 2004). Owing to the fact that perlite is readily available in several countries which are main producers of cement, it plays a significant role in the construction sector.

2.4 Structure and Formation of Strätlingite (C_2ASH_8)

Strätlingite forms as a consequence of the reaction between silicate and aluminate phases. Some pozzolanic additives such as silica fume and fly ash favor the formation of strätlingite when mixed with CAC (Fu & Ding, 1996). The common point of these additives is their high silica content. Hence, perlite which exists in abundance in Turkey could possibly be expected to form strätlingite when used together with CAC. Formation of strätlingite, a stable hydration product, prevents conversion and subsequent strength loss. In order to promote the formation of strätlingite in pozzolan-blended CAC systems several additives have been reported as useful (Ding et al., 1996). Different sodium salts such as sodium sulphate, sodium silicate, sodium carbonate and sodium nitrate have been found to promote strätlingite formation and significantly inhibit hydrogarnet formation in CAC pastes. Sodium sulphate was found to be particularly effective and to yield CAC-pozzolan pastes with both high early strength and high ultimate strength (Ding et al., 1995; Ding et al., 1996; Mostafa et al., 2012). Adding sodium sulphate causes an increase in the pH of CAC paste to above 12. When the pH value is above 12, it has a part in strätlingite formation as a contributor. High pH favors the dissolution of silica from the pozzolan which can react with the metastable products to form strätlingite. Strätlingite formation might also be responsible for the strength recovery after conversion of hexagonal calcium aluminum hydrates (CAH_{10} or C_2AH_8) to the cubic hydrogarnet (C_3AH_6) phase (Fu & Ding, 1996).

CHAPTER 3

EXPERIMENTAL

This chapter describes the materials used as well as the tests and analyses performed in this study.

3.1 Materials Used

This study investigated the influence of the addition of ground perlite, Na_2SO_4, and $Ca(OH)_2$ on the hydration of CAC pastes and mortars, and their properties. The CAC used was produced by Çimsa Cement Factory, in Mersin, Turkey, and is sold under the trade name Isıdaç 40 (ÇİMSA, 2002).

Unexpanded perlite from a quarry in Erzincan was used after being ground in a ball mill until its fineness was high enough to give pozzolanic properties. The desired Blaine fineness for natural pozzolans is usually between 3500 and 6000 cm^2/g (Tokyay, 2016) and the fineness of the perlite that was used in this study was approximately 5500 cm^2/g.

In preparing samples for the compressive strength tests, in addition to the materials mentioned above silica sand was used. Sands of different fineness, supplied by Çeliktaş Silis, were blended according to TS EN 196-1 (2016) to obtain a continuously graded sand mixture. The particle size distribution of the silica sand used in this study is given in Figure 3.1.

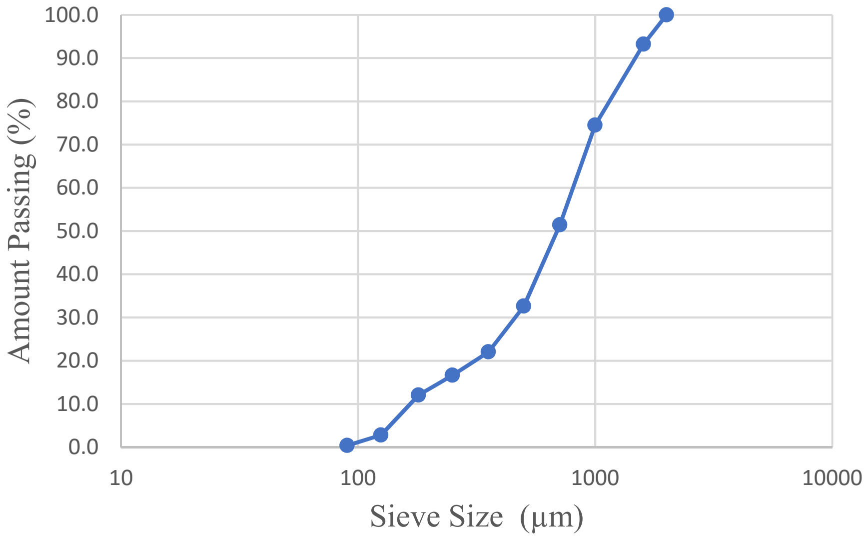

Figure 3.1 Size distribution of the silica sand used in this study

The oxide composition of the powder materials used in this study are given in Table 3.1 through Table 3.4. These results were obtained by X-ray fluorescence (XRF) spectroscopy performed at METU Central Laboratory.

Table 3.1 The composition of the CAC used in the study

Component	Content (%)
Al_2O_3	38.1
CaO	34.9
Fe_2O_3	15.7
CO_2	4.2
SiO_2	4.0
TiO_2	2.0
MgO	0.64
K_2O	0.16
Na_2O	0.14
SO_3	0.08
MnO	0.07
P_2O_5	0.06
SrO	0.03

Table 3.2 The composition of the perlite used in the study

Component	Content (%)
SiO_2	69.5
Al_2O_3	13.6
K_2O	4.7
CO_2	4.6
Na_2O	4.0
Fe_2O_3	1.6
CaO	1.5
MgO	0.36
SO_3	0.11
Cl	0.11
Rb_2O	0.02
ZrO_2	0.01

As Al_2O_3 and CaO are the principal oxides in CAC, its SiO_2 content is very low. As mentioned before, perlite was used in this study because of its high silica content (~70 %) in an attempt to form strätlingite.

Reagent grade Na_2SO_4 and $Ca(OH)_2$, obtained from Fisher Chemical and Tekkim Kimya, respectively, were used in this study.

Table 3.3 The composition of the Na_2SO_4 used in the study

Component	Content (%)
SO_3	54.8
Na_2O	45.2

Table 3.4 The composition of the $Ca(OH)_2$ used in the study

Component	Content (%)
CaO	84.2
CO_2	11.7
MgO	1.83
SO_3	0.884
SiO_2	0.691
Al_2O_3	0.3
Fe_2O_3	0.216
K_2O	0.101
Cl	0.0778
SrO	0.0399

3.2 Mixture Proportioning

Within the scope of this study, 36 different mixtures were prepared. A paste or a mortar was prepared with the mixture proportions given in Table 3.5 depending on the requirements of each test method employed.

Table 3.5 The mixtures properties used in the tests

Mixture	W/CM	CAC (%)	Perlite (%)	Silica Sand* (%)	$Ca(OH)_2$ ** (%)	Na_2SO_4 ** (%)	Notes/Details
1	0.4	100	0	275	None	None	blended mortars without any additives
2	0.4	75	25	275	None	None	
3	0.4	50	50	275	None	None	
4	0.4	25	75	275	None	None	
5	0.4	100	0	275	None	2	blended mortars with sodium sulfate
6	0.4	75	25	275	None	1.5	
7	0.4	50	50	275	None	1	
8	0.4	25	75	275	None	0.5	
9	0.4	75	25	275	None	2	
10	0.4	50	50	275	None	2	
11	0.4	25	75	275	None	2	
12	0.4	100	0	275	1	None	blended mortars with lime
13	0.4	75	25	275	0.8	None	
14	0.4	50	50	275	0.6	None	
15	0.4	25	75	275	0.4	None	
16	0.4	75	25	275	1	None	
17	0.4	50	50	275	1	None	
18	0.4	25	75	275	1	None	
19	0.6	100	0	275	None	None	blended mortars without any additives
20	0.6	75	25	275	None	None	
21	0.6	50	50	275	None	None	
22	0.6	25	75	275	None	None	
23	0.6	100	0	275	None	2	blended mortars with sodium sulfate
24	0.6	75	25	275	None	1.5	
25	0.6	50	50	275	None	1	
26	0.6	25	75	275	None	0.5	
27	0.6	75	25	275	None	2	
28	0.6	50	50	275	None	2	
29	0.6	25	75	275	None	2	
30	0.6	100	0	275	1	None	blended mortars with lime
31	0.6	75	25	275	0.8	None	
32	0.6	50	50	275	0.6	None	
33	0.6	25	75	275	0.4	None	
34	0.6	75	25	275	1	None	
35	0.6	50	50	275	1	None	
36	0.6	25	75	275	1	None	

* Silica sand was used only for compressive strength test samples.

** By mass of CAC + perlite.

Owing to the fact that strätlingite formation was observed with 2 % Na_2SO_4 (Ding et al., 1995), that amount of Na_2SO_4 was used as the maximum in this thesis. Also, 1 % $Ca(OH)_2$ shortens the setting time (Kırca, 2006). Hence, 1 % $Ca(OH)_2$ was used as the maximum.

As seen in Table 3.6, the various mixtures contained 0-75 % ground perlite, 0-2 % Na_2SO_4, 0-1 $Ca(OH)_2$ and had W/CM of 0.4 and 0.6. The contents of the chemicals were selected to either be a fixed amount for all CAC-Perlite blends or to vary with the content of CAC in the mixture.

3.3 Identification of Mixtures

In order to distinguish the mixtures easily in the subsequent chapters, all mixtures were named as described in Figure 3.2. The mixture identified in Figure 3.2 has W/CM of 0.4 and a CAC content of 75 % (hence a ground perlite content of 25 %), and contains 1 % Na_2SO_4 by mass of the cementitious powder, and is “dry” cured.

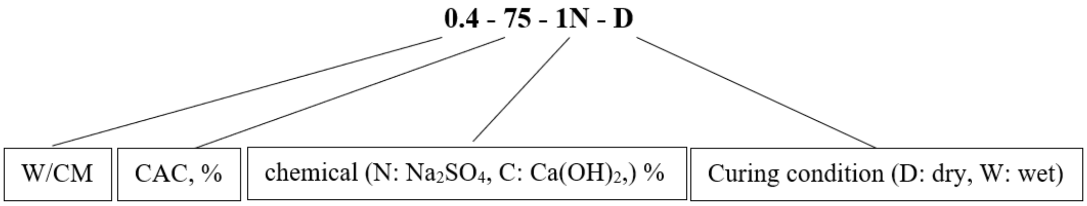

Figure 3.2 Identification of mixtures

Owing to the fact that some mixtures contain no chemicals, their names have three parts (rather than four). For instance 0.6 - 50 - D does not contain any chemicals. Similarly, only one type of curing was applied to all specimens used for some of the tests such as the setting time test. Therefore, a curing condition is not indicated for these mixtures (e.g. 0.6-50-1C).

3.4 Methods

3.4.1 Determination of Compressive Strength

Compressive strength tests were performed according to TS EN 196-1 (2016) at 8 different specimen ages (3h, 6h, 24h, 48h, 7d, 14d, 28d, 90d). Also, two curing conditions were chosen: dry at 23 °C ("dry") and wet at 40 °C ("wet"). For each mix, time and curing condition combination, 3 specimens were prepared. Specimen dimensions were 50 mm x 50 mm x 50 mm as shown in Figure 3.3. Each compressive strength presented was obtained by averaging strength measured on 3 specimens.

Figure 3.3 Curing of 50-mm cube specimens (a) covered with plastic wrap, (b) covered with a wet cloth

The specimens were cast, then cured at ambient conditions with a plastic sheet and a wet cloth over them. After 24h, all specimens were demolded. Dry specimens were kept in the curing room at 23 °C and 79 % RH, and wet specimens were kept under water at 40 °C until the test day.

3.4.2 Water Requirement For Normal Consistency and Setting Time

After determining the water requirement for normal consistency for each mix according to ASTM C187 (2016), initial and final setting time were determined according to ASTM C191 (2013).

3.4.3 Isothermal Calorimetry

A Tam Air isothermal conduction calorimeter (Figure 3.4) was used to measure the heat evolution of the hydrating CAC pastes. The weight of each specimen was approximately 10 g. Silica sand was used as an inert reference material in all tests.

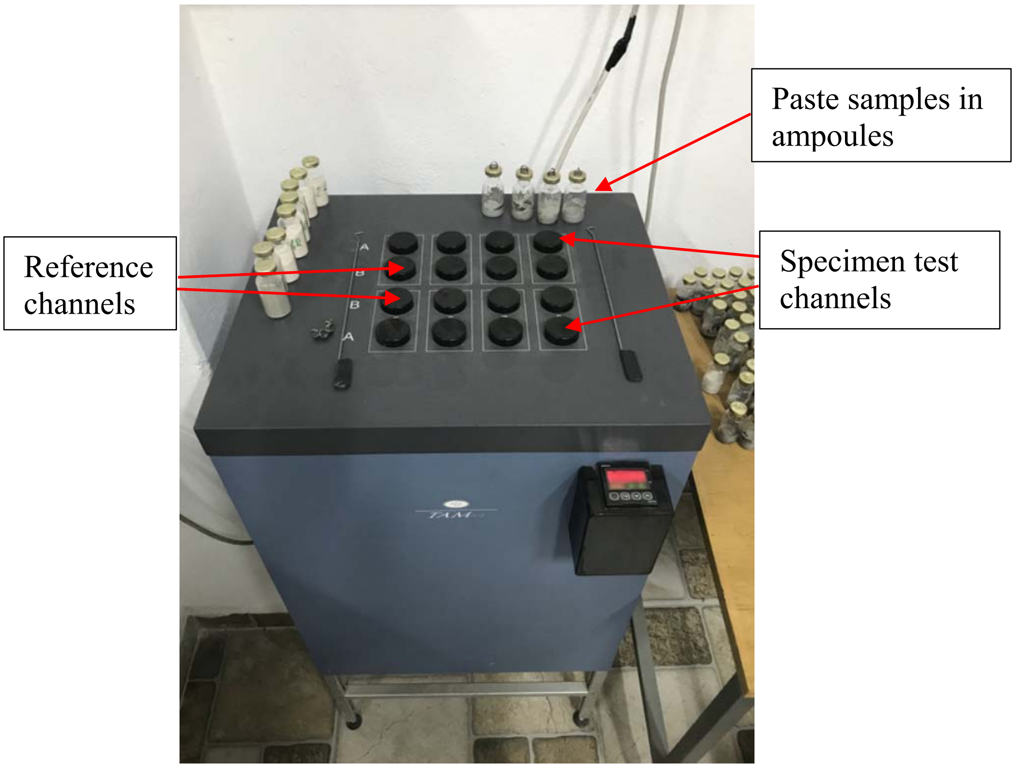

Figure 3.4 TAM Air Calorimeter

The pastes were mixed and immediately placed in the test ampoule and the ampoule was put in the calorimeter without delay. The opening of the calorimeter channel to insert the specimen disturbs the temperature in the channel and a time of about 30 minutes is needed before the measurement results can be considered correct. In normalization of W/g and J/g, CAC+perlite was used as the denominator.

3.4.4 High-Temperature Resistance Tests

In order to investigate the high-temperature performance of CAC pastes, the mass losses of the specimens were measured after exposure to elevated temperatures. Their residual flexural and compressive strengths were also determined.

To perform these tests, 40 mm x 40 mm x 160 mm paste specimens were prepared. After 24h in the mold, all specimens were kept in a curing room at 23 °C. There were 3 groups of specimens, a reference group, a group exposed to 600 °C, and one exposed to 1100 °C. 3 specimens were used for each mixture one from each group.

After 28 days, the flexural and compressive strength tests of the reference group were performed. Then, the masses of the specimens in group 2 were measured. After that, they were exposed to 600 °C for two hours. The heating rate in the dry oven was ~ 50 °C/h. The specimens were allowed to cool naturally in the oven, this process took 12-24 h. After cooling down to room temperature, their masses were measured again and their flexural and compressive strengths determined.

As the final step, masses of the specimens in group 3 were measured. Then, they were exposed to 1100 °C for two hours. The measured heating rate was ~ 90 °C/h. Specimens were allowed to cool naturally in the oven, this process took 12-24 h. After cooling down to room temperature, the same measurements and tests performed on group 2 specimens were performed.

3.4.5 XRD Analysis

For this analysis, an Olympus BTX 175 X-ray diffractometer was used. In order to do XRD analysis, experiments must be performed on finely ground particles which are then pressed into a pellet. This requirement is formed by the need to make of the certain sufficiently random orientation of the crystals in the sample. The machine uses a ~ 15 mg sample (Olympus, 2018) and makes analysis between 5-55° 2θ. To investigate the development of phases during the hydration of CAC pastes, the analyses were performed at 5 different ages (12h, 24h, 7d, 28d, and 90d). 288 XRD analyses were performed in total.

3.4.6 Thermal Analyses (Differential Thermal Analysis [DTA] / Thermogravimetric Analysis [TGA])

DTA was used to investigate the critical temperatures related to the thermal decomposition of different phases in the paste, while TGA was used to simultaneously measure the mass loss associated with the decomposition. The mixtures with 50 % perlite and without any perlite were selected for the DTA/TGA analyses. A total of 13 specimens dry-cured at 23 °C and 79 % RH were tested. Ages of the specimens are approximately 90 days.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Compressive Strength Tests

In this section, the compressive strength development of the mortar mixtures is presented. Tables in Appendix A present the same data but make it easier to compare the strengths of different mixtures at early ages.

As shown in Figure 4.1, as the perlite content increases, compressive strength decreases at all ages. Although there is an almost linear reduction in the strength of wet specimens with increasing perlite, this proposition is not quite accurate for dry conditions. The compressive strength of 0.4-75-D is almost the same as that of the specimen without any perlite at all ages.

A small drop in strength is observed for the dry-cured samples with ≤ 25 % perlite, from 14d to 90d. This could be slow progressing conversion and the ultimate drop in strength, over a period of several years, could be significant.

The drop in strength of the wet-cured samples is very significant from 3d to 14 d, up to 50 % for the control CAC-only sample, but less for the perlite-blended samples. The sample with 25 % perlite even reaches a higher ultimate strength than the reference, owing to its similar early strength and smaller strength loss. A steady increase of strength beyond 14d is noteworthy for 0.4-100-W and 0.4-75-W. This retarded gain in strength is about 20-25 % of the “converted” strength, hence quite meaningful.

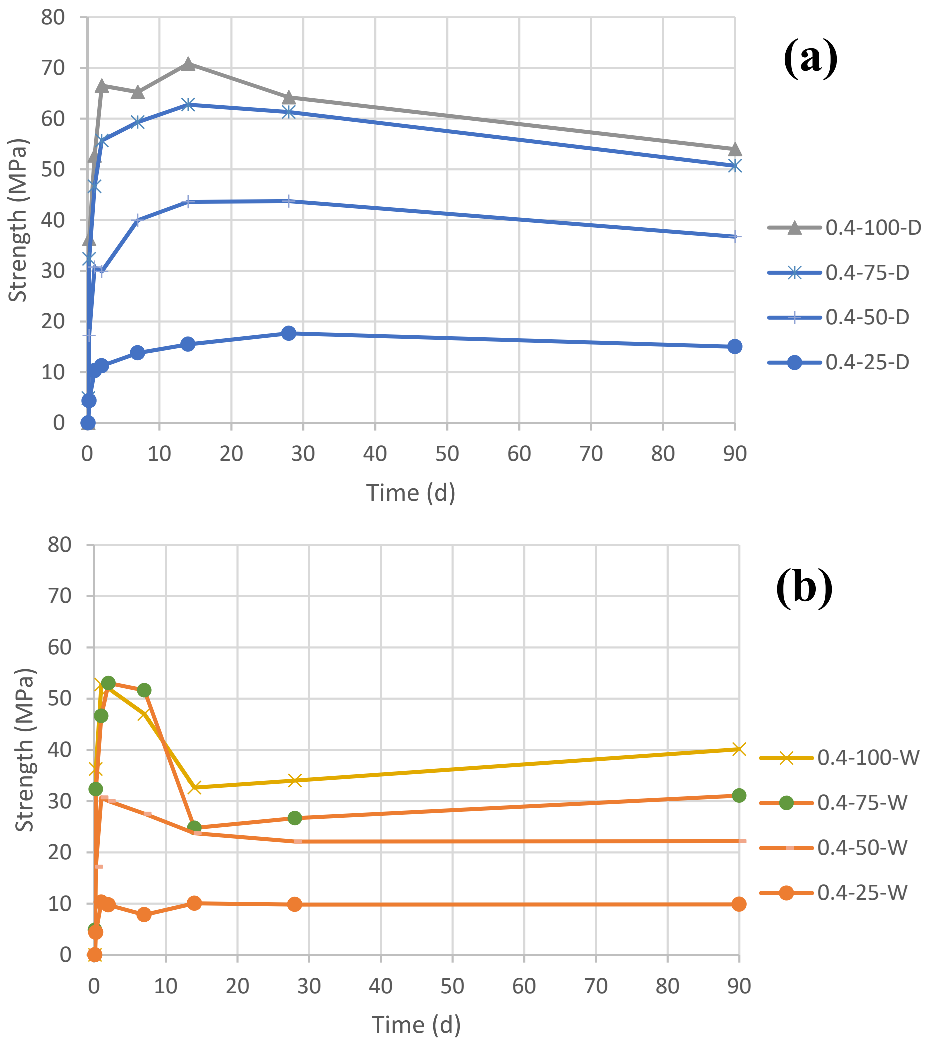

Figure 4.1 Influence of perlite quantity on compressive strength (W/CM = 0.4 and no chemical) (a) dry curing, (b) wet curing

As seen in Figure 4.2, while the addition of chemicals (at the dosages used in this study) does not affect later age compressive strength much, they decrease the early compressive strengths of the dry-cured specimens when no perlite is present in the system. On the contrary, for the specimens cured wet and at 40 °C, while the chemicals do not affect early compressive strength or even slightly increase it, they decrease the later age compressive strength. The strength loss due to conversion is even greater than in the control samples. Once again, a steady drop and a steady increase in strength are noted for the dry and wet cases, respectively, beyond 14d to 28d. One exception is the mixture with 2 % Na_2SO_4 which despite having the lowest strength at early ages, doesn't experience strength loss after 28d.

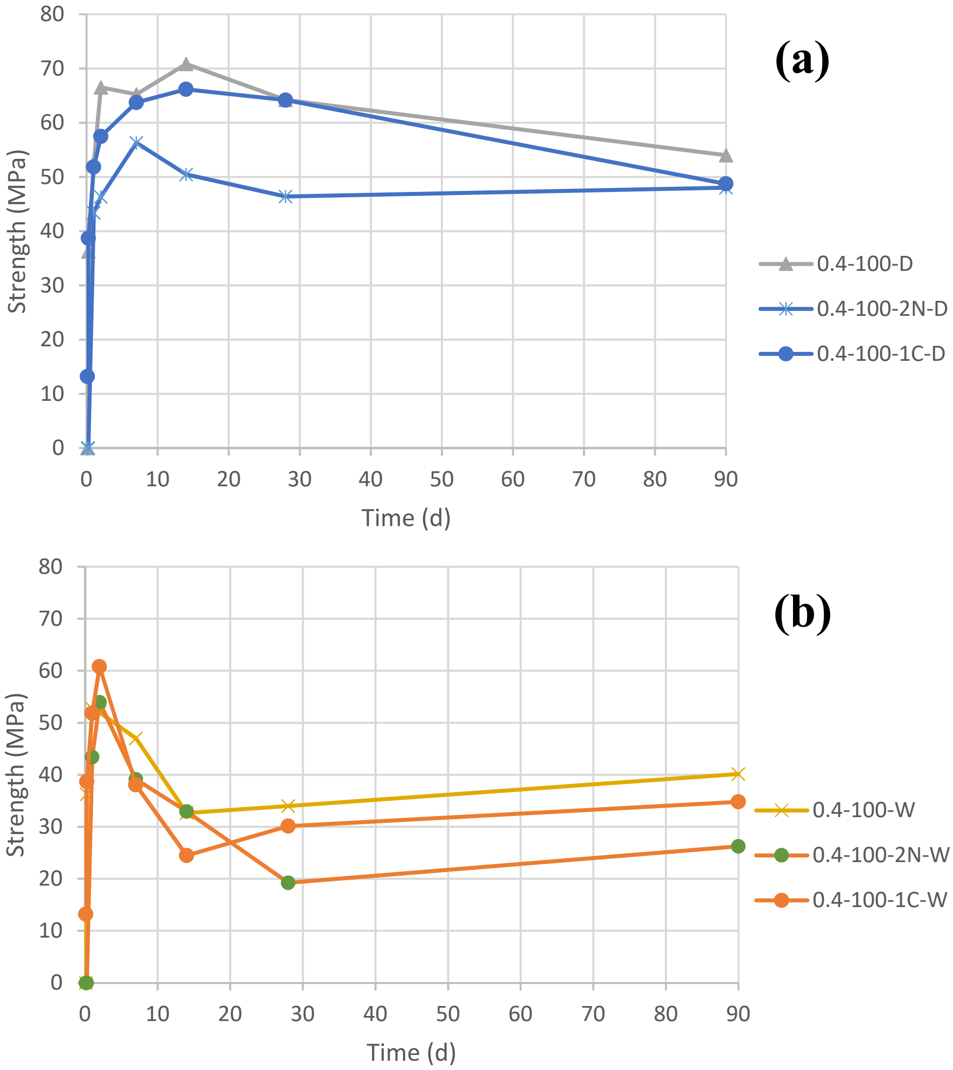

Figure 4.2 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.4 and 100 % CAC) (a) dry curing, (b) wet curing

The relevance of curing moisture level and temperature on conversion is clearly seen when Figure 4.2 is evaluated. In Figure 4.3 below, mixtures containing 25 % perlite are compared. The addition of chemicals decreases both the early and later age compressive strengths of dry specimens. Once again, however, the delayed steady loss of strength is prevented in the Na_2SO_4-containing specimens. On the contrary, they affect the compressive strengths of wet specimens at neither early nor later ages noticeably. The influence of curing conditions on conversion is clearly seen. While the strength loss is slow for some of the dry specimens, the strength of the wet specimens decreases sharply in the second week.

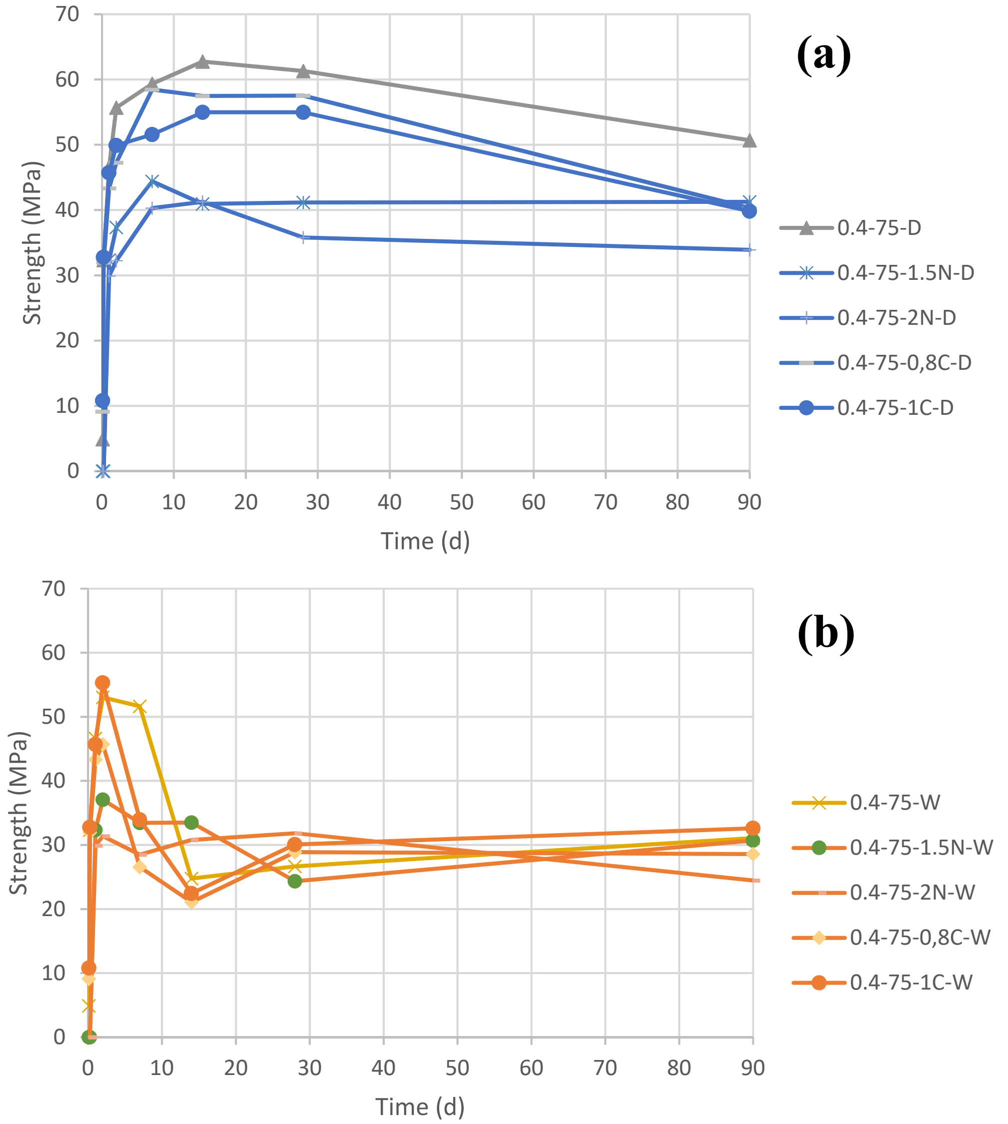

Figure 4.3 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.4 and 75 % CAC) (a) dry curing, (b) wet curing

In Figure 4.4 below, in specimens containing 50 % perlite, the addition of chemicals decreases both the early and later age compressive strength of dry-cured specimens. The Na_2SO_4-containing specimens do experience a slow loss in strength but smaller in magnitude than the others. However, for the wet-cured specimens, their effects are different. While $Ca(OH)_2$ decreases the later-age compressive strength, Na_2SO_4 increases it. In fact, the Na_2SO_4-containing specimens don’t experience any strength loss, ever, indicating that conversion is prevented. XRD analyses of these specimens (Section 4.6) reveals the formation of strätlingite in these specimens. Comparing 0.4-50-2N-W with 0.4-50-W, the importance of Na_2SO_4 in perlite blended CAC systems is clear. Compressive strengths of 30 MPa or even higher are possible with only 50 % CAC.

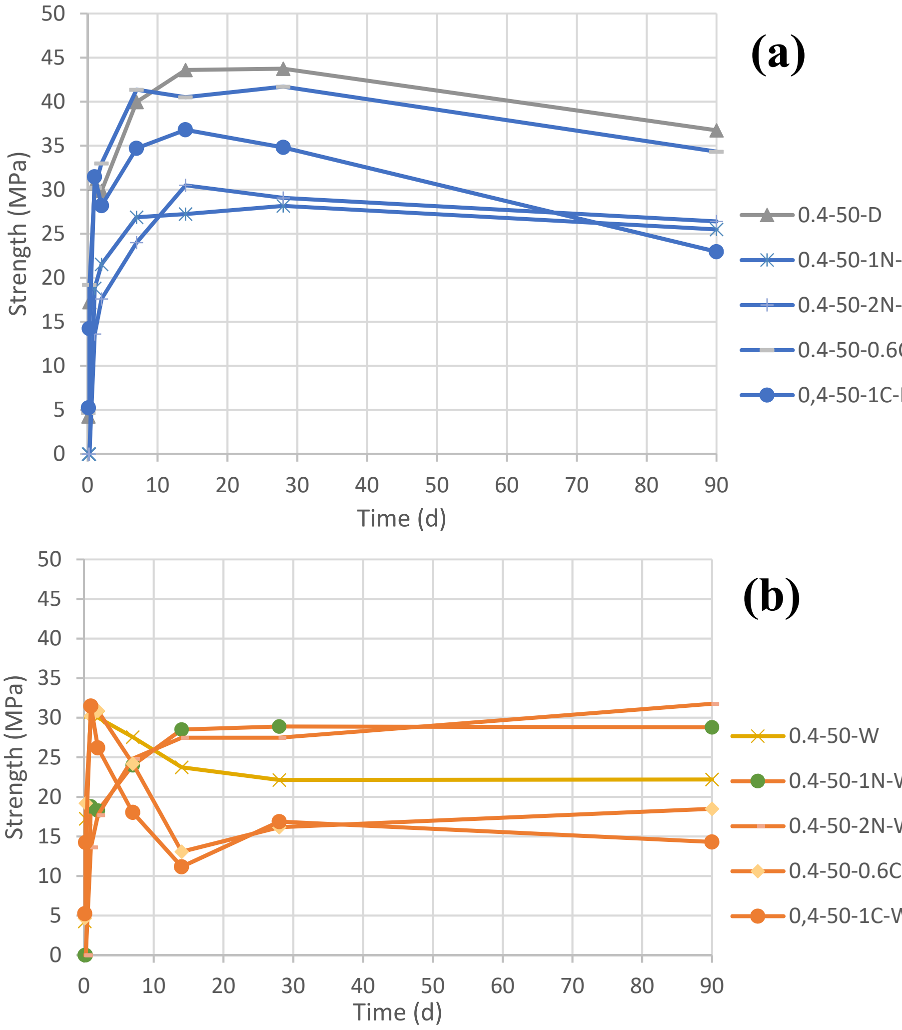

Figure 4.4 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.4 and 50 % CAC) (a) dry curing, (b) wet curing

The strength development of mortars with 75 % perlite is shown in Figure 4.5. The addition of chemicals decreases both the early and later age compressive strength of dry specimens. But, for the wet specimens adding 0.4 % $Ca(OH)_2$ had a positive effect on compressive strength, owing to strätlingite formation.

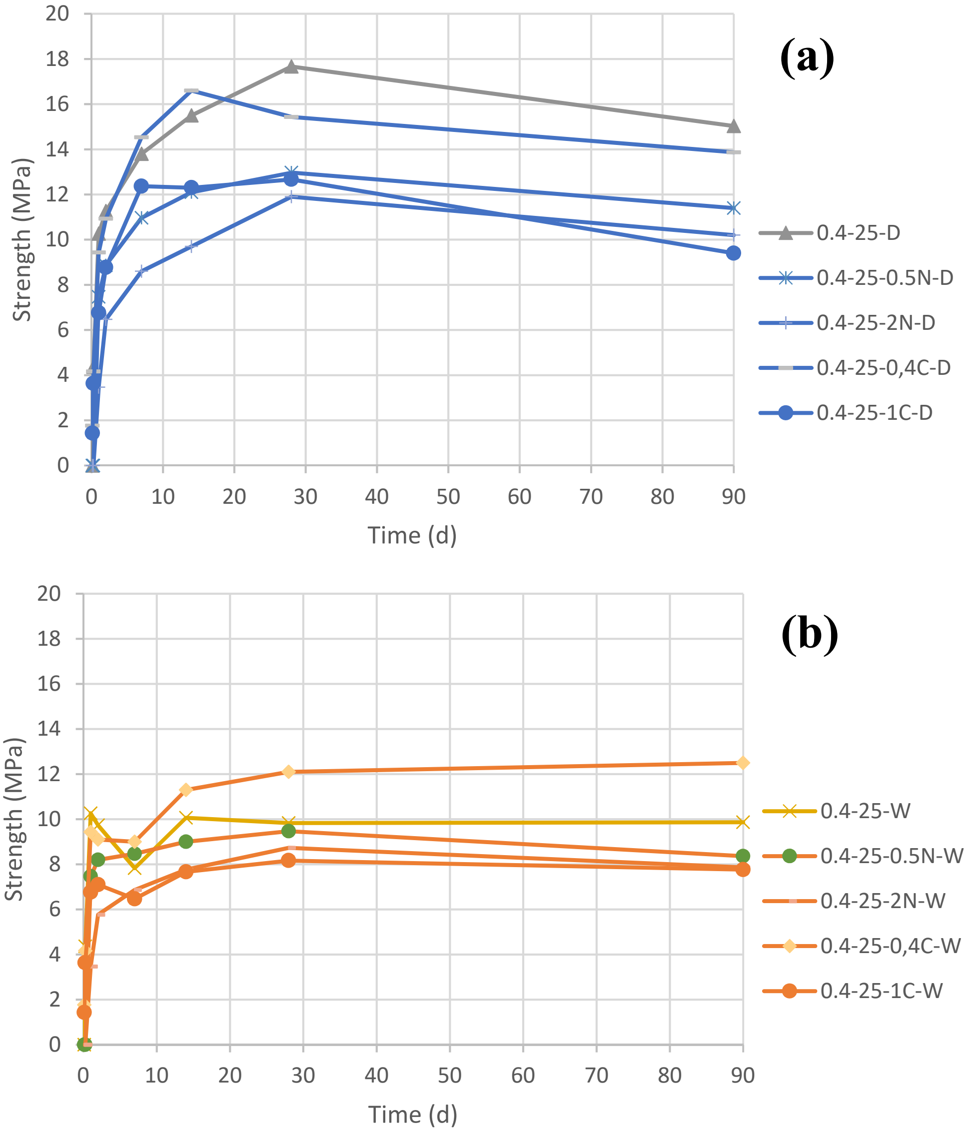

Figure 4.5 Influence of changing Na_2SO_4 and $Ca(OH)_2$ quantities on compressive strength (W/CM = 0.4 and 25 % CAC) (a) dry curing, (b) wet curing

At such a high perlite content, the early and late strengths are quite low (5-15 MPa). None of the wet-cured specimens experiences much conversion and $Ca(OH)_2$ addition appears to give the best results.

For a fixed Na_2SO_4 addition of 2 %, as the perlite content increases in the system, both early and later age compressive strength of dry specimens decrease (Figure 4.6a). But, for the wet specimens, their effects are different (Figure 4.6b). Excluding the 25 % perlite-containing-specimen, 2 % Na_2SO_4 has a positive effect on later age compressive strength.

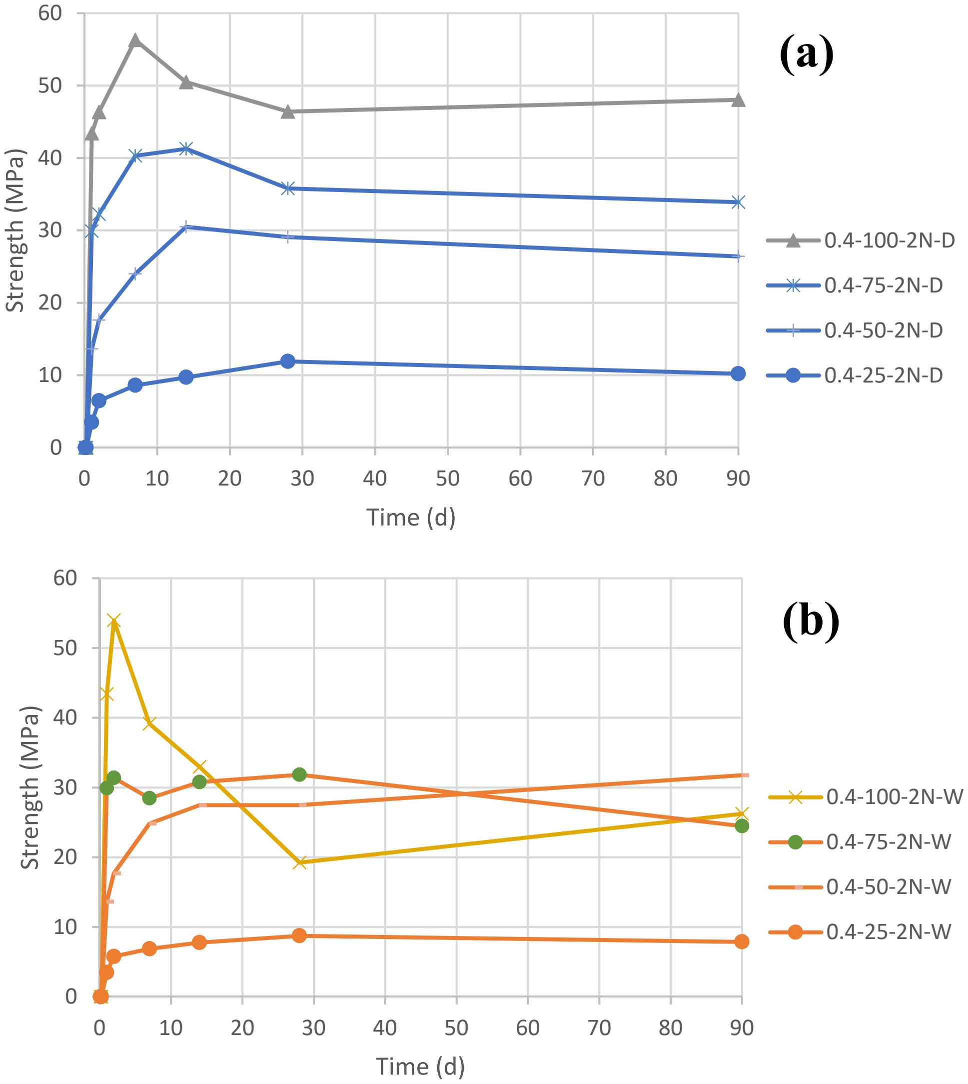

Figure 4.6 Influence of perlite quantity on compressive strength of mixtures have Na_2SO_4 (W/CM = 0.4) (a) dry curing, (b) wet curing

In Figure 4.7a, as perlite increases, compressive strength decreases for dry specimens. Using $Ca(OH)_2$ did not prevent this reduction. On the other hand, there is an important difference for wet specimens (Figure 4.7b). The compressive strength of the specimen containing 25 % perlite and 1 % $Ca(OH)_2$ was almost the same as those of the specimen with no perlite.

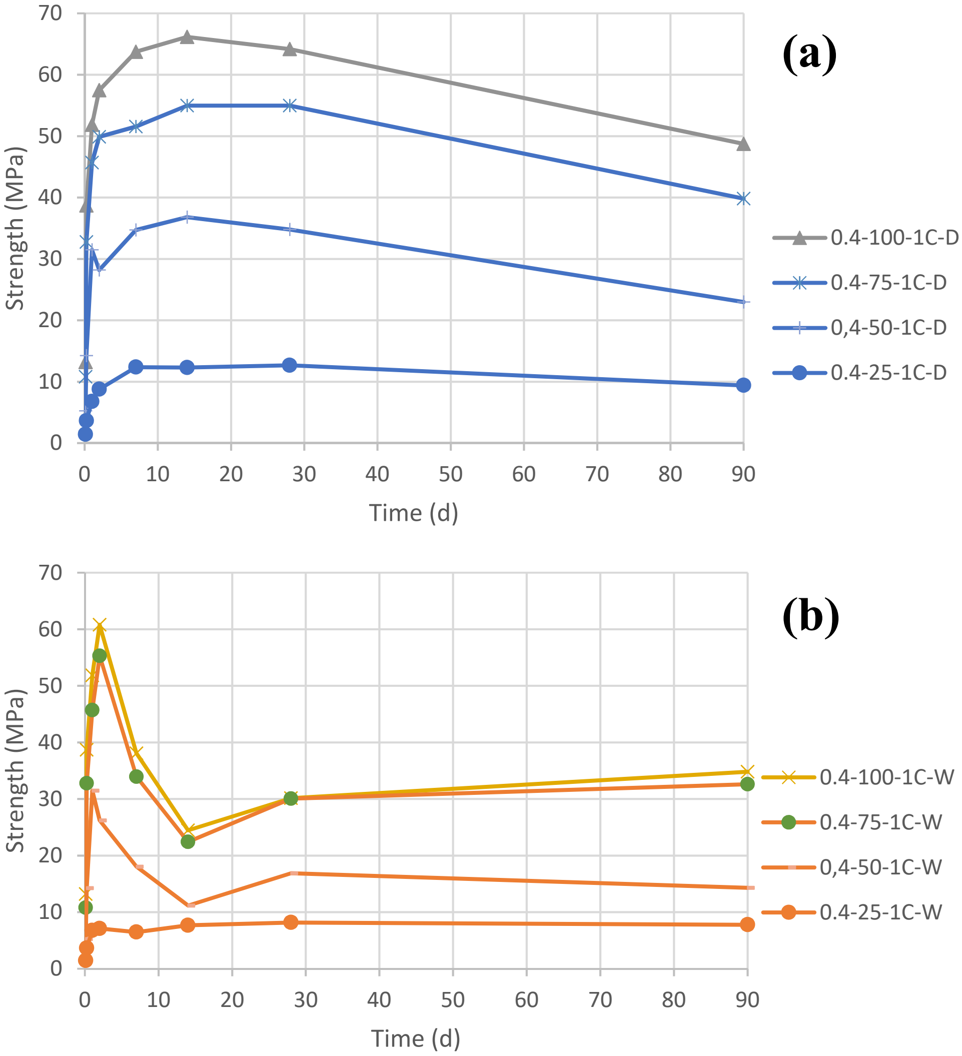

Figure 4.7 Influence of perlite quantity on compressive strength of mixtures containing $Ca(OH)_2$ (W/CM = 0.4) (a) dry curing, (b) wet curing

From this point, the figures belong to the mixtures W/CM=0,6. As shown in Figure 4.8, the decrease in compressive strength is directly proportional to the amount of perlite. There was no significant difference between the specimens which contains 25 % perlite and no perlite when W/CM=0,4. But here, this situation was not observed. As expected comparing Figure 4.1 with Figure 4.8, increasing W/CM decreases the compressive strength. The drop in strength of the wet-cured samples is very significant from 3d to 14 d, up to 50 % for the control CAC-only sample, but less for the perlite-blended samples. A steady increase of strength beyond 14d is remarkable for 0.4-100-W and 0.4-75-W.

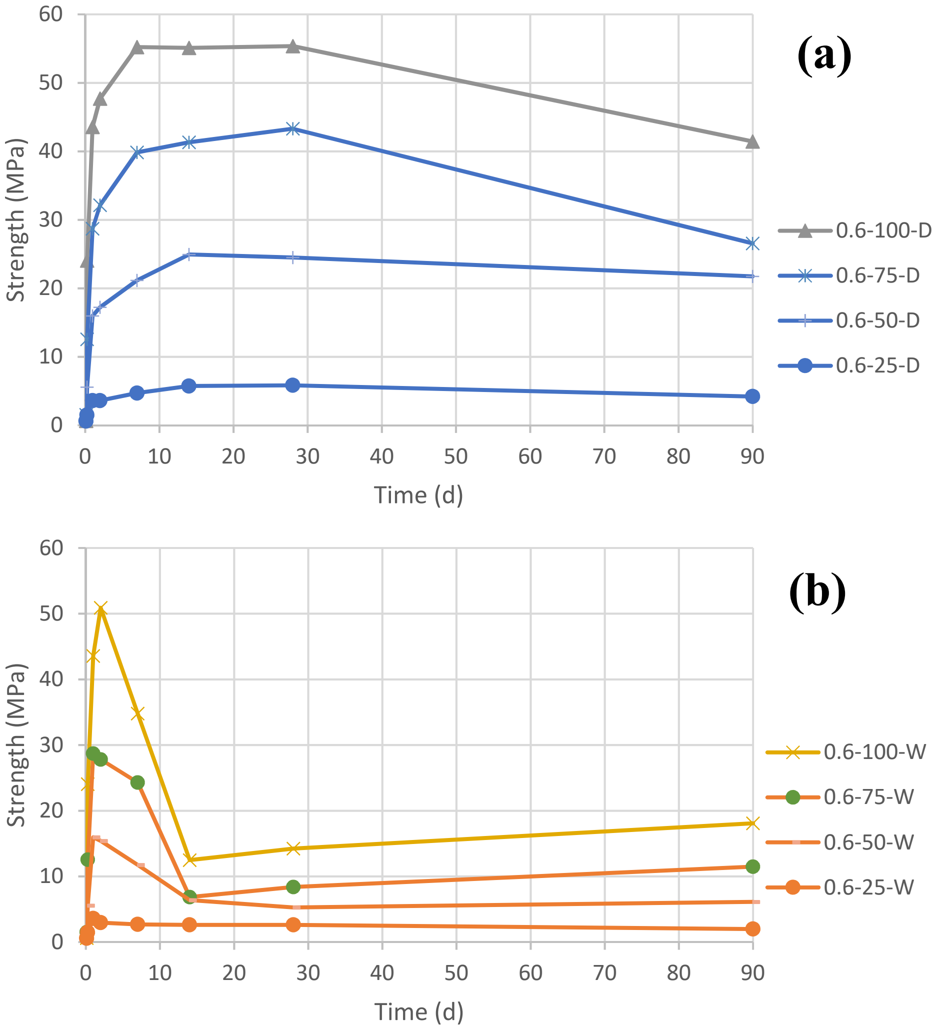

Figure 4.8 Influence of perlite quantity on compressive strength (W/CM = 0.6 and no chemical) (a) dry curing, (b) wet curing

As seen in Figure 4.9, when no perlite is present in the system, while the chemicals used in this study don't affect later-age strength much, they slightly decrease the compressive strength of the dry specimens. On the contrary, for specimens which are wet, the chemicals affect neither early- nor later-age compressive strength noticeably. Besides, after wet specimens reached the maximum compressive strength, a sharp decrease exists. In 2 weeks, there is almost 50 % strength loss due to conversion.

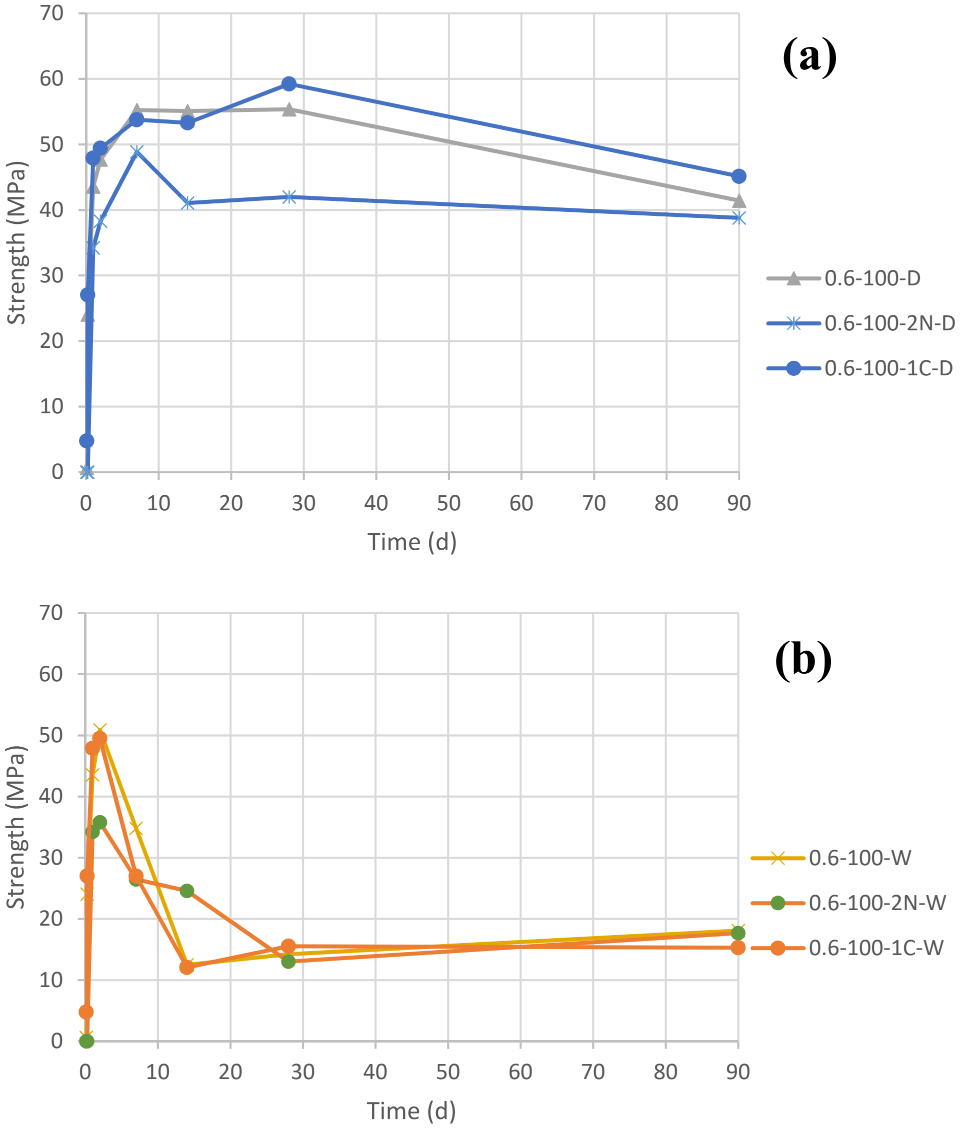

Figure 4.9 Influence of 2 % Na_2SO_4, and 1 % $Ca(OH)_2$ on compressive strength (W/CM = 0.6 and 100 % CAC) (a) dry curing, (b) wet curing

When there is 25 % perlite in the system, the chemicals decrease both the early and later age compressive strength of dry specimens (Figure 4.10a). On the contrary, they affect the compressive strength of the wet specimens at neither early nor late ages. While the strength loss is slow in dry specimens, the strength of the wet specimens decreases sharply at the second week (Figure 4.10b).

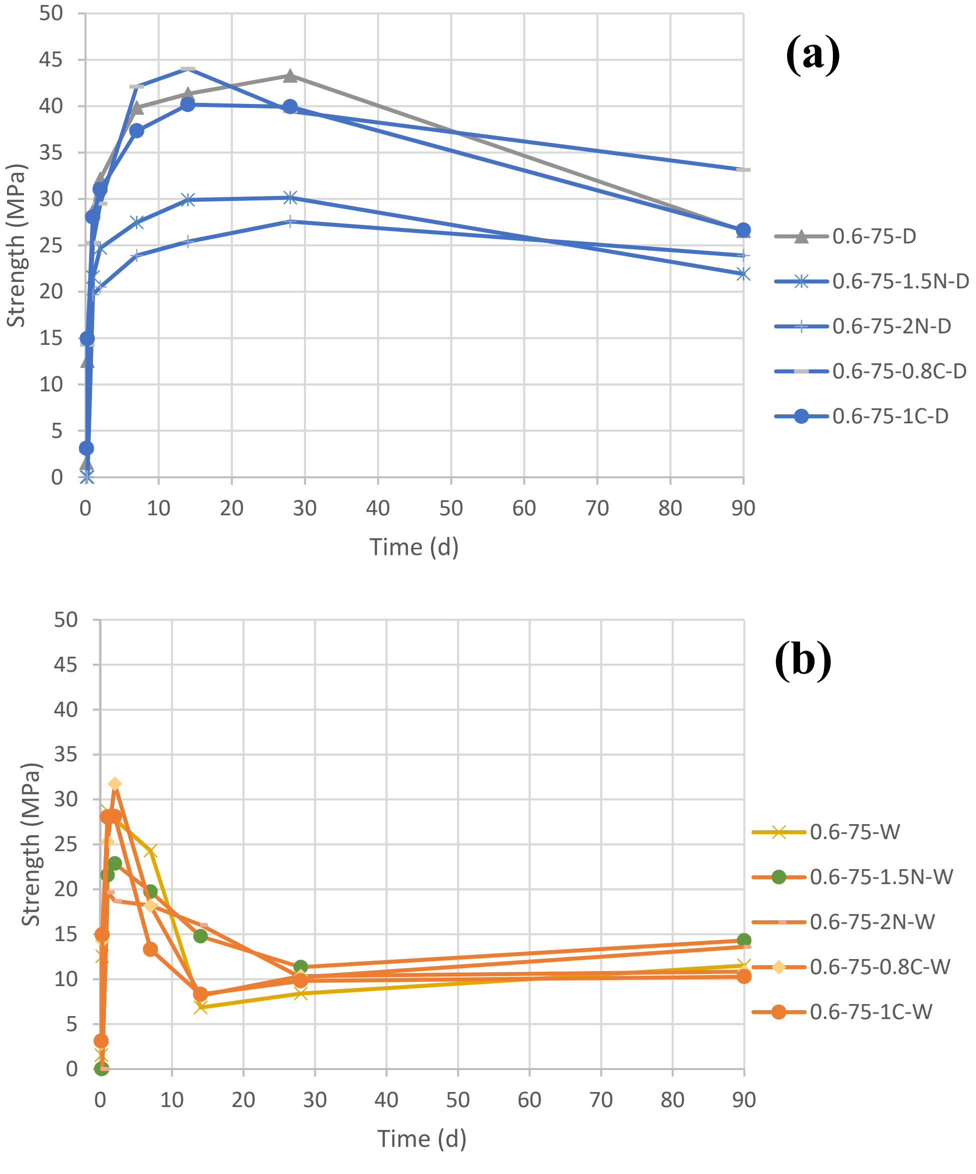

Figure 4.10 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.6 and 75 % CAC) (a) dry curing, (b) wet curing

In Figure 4.11 below, if there is 50 % perlite in the system, the chemicals decrease both the early and later-age compressive strength of dry specimens. But, for the wet specimens, their effects are different. While $Ca(OH)_2$ decreases the later-age compressive strength, using Na_2SO_4 increases owing to strätlingite formation. In fact, the Na_2SO_4-containing specimens don't experience any strength loss, ever, indicating that conversion is prevented. Comparing 0.6-50-2N-W and 0.6-50-1N-W with 0.6-50-W, the importance of Na_2SO_4 in perlite blended CAC systems is clear.

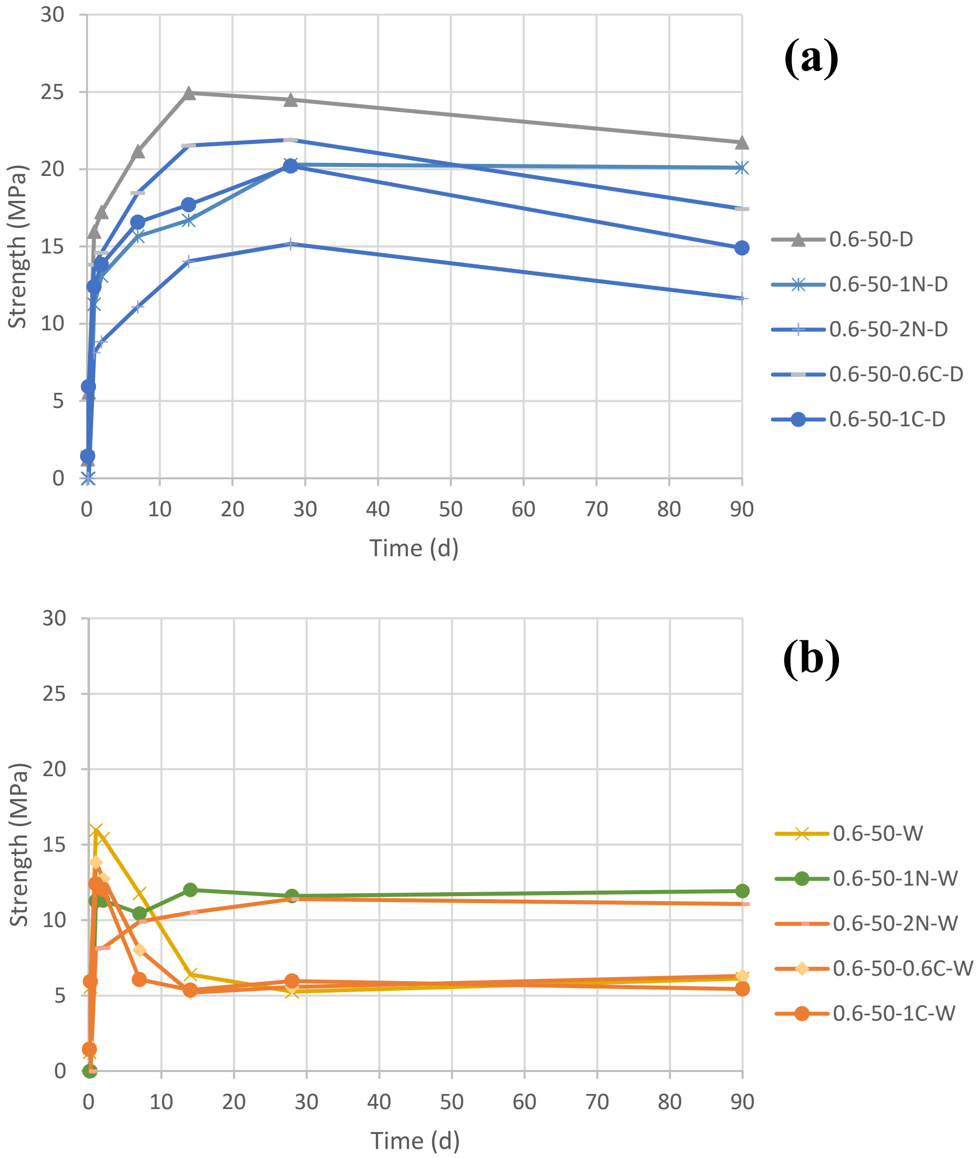

Figure 4.11 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.6 and 50 % CAC) (a) dry curing, (b) wet curing

The strength development of mortars containing 75 % perlite is shown in Figure 4.12. Excluding the use of 2 % Na_2SO_4, all chemicals positively impacted the later-age compressive strength of specimens. Mostly, as the quantity of chemicals used (their dosages with respect to the CAC) increases, early-age compressive strength decreases.

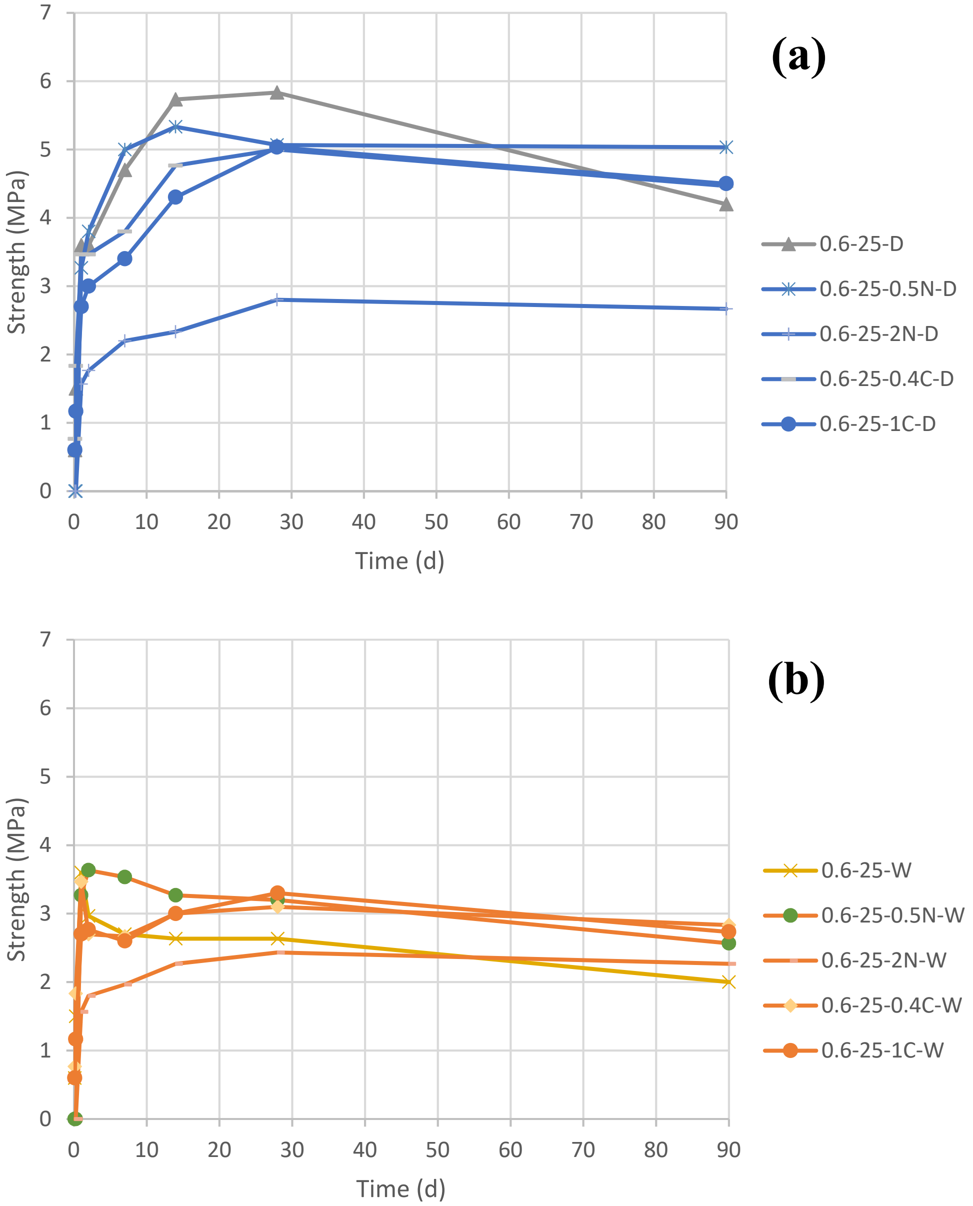

Figure 4.12 Influence of Na_2SO_4 and $Ca(OH)_2$ on compressive strength (W/CM = 0.6 and 25 % CAC) (a) dry curing, (b) wet curing

Figure 4.13 shows the influence of using 2 % Na_2SO_4 on the compressive strength of mortars with varying amounts of perlite. As perlite content increases, both early and later age compressive strength of dry specimens decrease despite chemicals. But, for the wet specimens, the effects of them are different. Excluding 75 % perlite-content-specimen, the chemicals show a positive behavior on later age compressive strength.

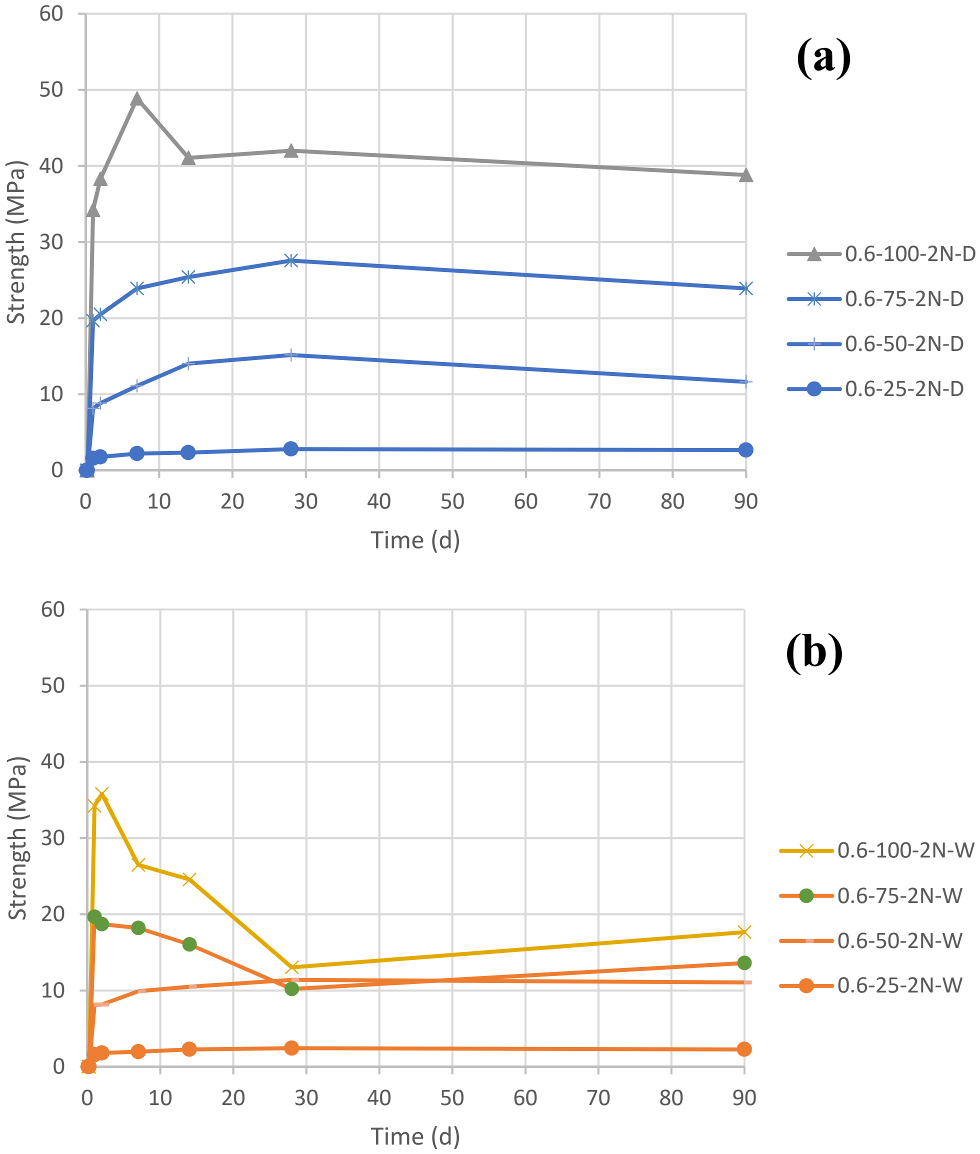

Figure 4.13 Influence of perlite quantity on compressive strength of mixtures have Na_2SO_4 (W/CM = 0.6) (a) dry curing, (b) wet curing

Figure 4.14 shows the influence of using 1 % $Ca(OH)_2$ on the compressive strength of mortars with varying amounts of perlite. As perlite content increases, the compressive strength decreases for both the dry and wet specimens. Using 1 % $Ca(OH)_2$ did not prevent this reduction. Looking at the XRD results of wet specimens, it is understood that the conversion took occur from the 7th day.

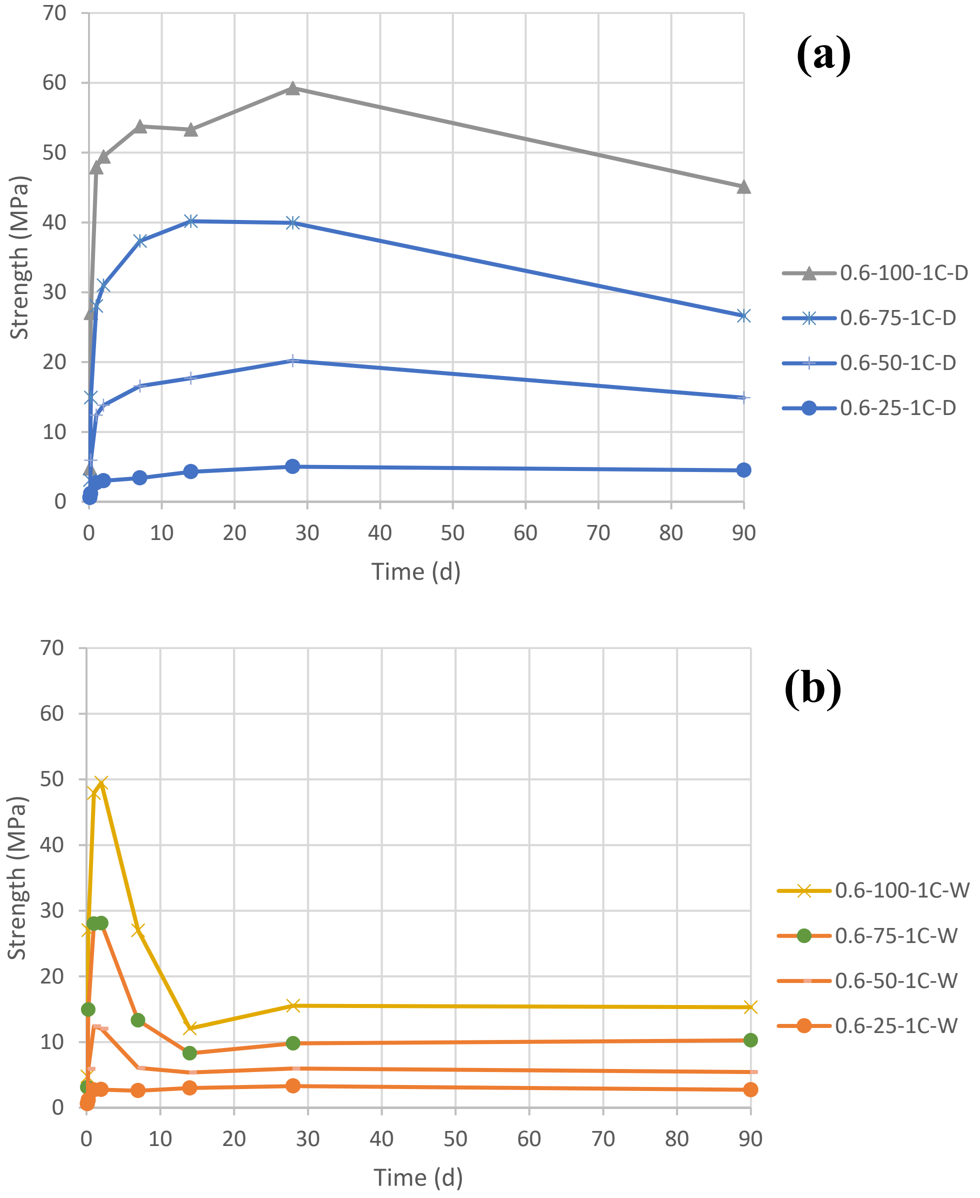

Figure 4.14 Influence of perlite quantity on compressive strength of mixtures have $Ca(OH)_2$ (W/CM = 0.6) (a) dry curing, (b) wet curing

4.2 Compressive & Flexural Strength Retention After Exposure to High Temperatures

The conditions of the specimens before and after exposure 600 °C are shown in Figure 4.15.

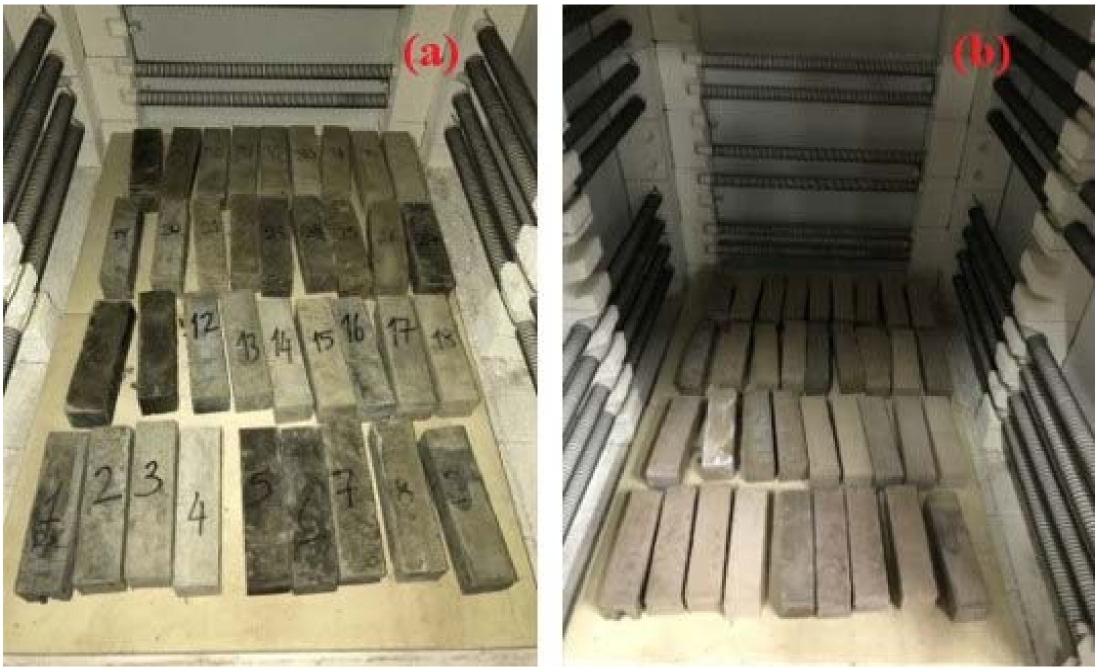

Figure 4.15 Effect of exposure to 600 °C on CAC-perlite specimens (a) before exposure, (b) after exposure & cooling

The conditions of the specimens before and after exposure to 1100 °C are shown in Figure 4.16.

Figure 4.16 Effect of 1100 °C on CAC specimens (a) before exposure, (b) after exposure & cooling

Table 4.1 shows the mass losses experienced by the specimens shown in Figure 4.15 and 4.16 after one heating and cooling cycle. It is observed that with or without chemicals or perlite, none of the CAC pastes can truly resist high temperatures. However, as perlite content increases the mass loss experienced generally decreases. Residual mass at 1100 °C is generally lower than that of 600 °C. Besides, there is more mass loss in the mixtures W/CM = 0.6 that W/CM = 0.4.

Table 4.1 Effect of high temperatures on mass

Mixture ID	Mass Before 600 °C (g)	Mass After 600 °C (g)	Mass Before 1100 °C (g)	Mass After 1100 °C (g)	Residual Mass 600 °C (after/before)	Residual Mass 1100 °C (after/before)
0,4-100	481.3	373.2	489.2	367.5	0.78	0.75
0,4-75	463.2	347.5	467.4	337.4	0.75	0.72
0,4-50	442.7	343.2	441.4	333.3	0.78	0.76
0,4-25	377.9	322.6	377.2	314.7	0.85	0.83
0,4-100-2N	506.8	375.0	510.4	371.0	0.74	0.73
0,4-75-1,5N	473.2	361.9	484.7	358.0	0.76	0.74
0,4-50-1N	432.9	340.3	436.0	335.4	0.79	0.77
0,4-25-0,5N	382.8	328.3	393.0	326.2	0.86	0.83
0,4-75-2N	492.6	368.7	488.7	353.7	0.75	0.72
0,4-50-2N	471.8	359.4	469.4	347.3	0.76	0.74
0,4-25-2N	465.9	324.8	459.2	315.6	0.70	0.69
0,4-100-1C	505.2	373.9	507.8	366.8	0.74	0.72
0,4-75-0,8C	482.4	366.1	483.1	356.4	0.76	0.74
0,4-50-0,6C	430.0	343.0	421.4	326.9	0.80	0.78
0,4-25-0,4C	424.9	323.8	422.2	329.7	0.76	0.78
0,4-75-1C	499.8	356.5	485.8	340.5	0.71	0.70
0,4-50-1C	469.7	342.6	462.9	338.1	0.73	0.73
0,4-25-1C	408.4	316.7	431.4	317.8	0.78	0.74
0,6-100	428.6	296.7	436.4	283.5	0.69	0.65
0,6-75	383.8	281.8	384.5	270.1	0.73	0.70
0,6-50	351.2	271.3	350.5	260.2	0.77	0.74
0,6-25	359.0	255.5	362.8	253.4	0.71	0.70
0,6-100-2N	427.1	298.7	436.4	291.7	0.70	0.67
0,6-75-1,5N	407.5	292.9	401.3	276.5	0.72	0.69
0,6-50-1N	417.3	287.1	419.6	278.1	0.69	0.66
0,6-25-0,5N	373.4	277.4	348.3	264.0	0.74	0.76
0,6-75-2N	415.3	295.7	412.4	284.7	0.71	0.69
0,6-50-2N	376.0	282.6	378.5	273.3	0.75	0.72
0,6-25-2N	325.8	268.6	331.7	261.5	0.82	0.79
0,6-100-1C	454.6	296.5	443.9	286.3	0.65	0.64
0,6-75-0,8C	431.2	291.0	421.3	278.4	0.67	0.66
0,6-50-0,6C	385.7	270.1	408.6	268.1	0.70	0.66
0,6-25-0,4C	326.6	263.8	310.7	249.7	0.81	0.80
0,6-75-1C	405.6	282.6	397.4	267.2	0.70	0.67
0,6-50-1C	377.0	281.1	378.4	271.6	0.75	0.72
0,6-25-1C	320.6	271.5	337.9	270.8	0.85	0.80

The effect of exposure to 600 °C on the compressive and flexural strengths of the samples is given in Table 4.2. In all cases without perlite, the compressive and flexure strength of CAC decrease. But, some mixtures which have 75 % perlite, with or without chemicals, show a positive behavior in terms of both compressive and flexure strength. This probably originated from the partial melting of perlite at high temperatures and resolidification upon cooling. In most of cases, the flexural strength loss is greater than the compressive strength loss.

Table 4.2 Effect of exposure to 600 °C on strength

Mixture ID	Flexural Strength at 23 °C (MPa)	Flexural Strength After 600 °C (MPa)	Comp. Strength at 23 °C (MPa)	Comp. Strength After 600 °C (MPa)	Residual Flexural Strength 600 °C (after/before)	Residual Compressive Strength 600 °C (after/before)
0,4-100	4.20	0.80	30.10	22.85	0.19	0.76
0,4-75	6.00	2.10	40.25	15.20	0.35	0.38
0,4-50	3.90	3.10	24.70	13.50	0.79	0.55
0,4-25	1.90	1.20	7.45	5.30	0.63	0.71
0,4-100-2N	7.50	2.50	40.65	17.75	0.33	0.44
0,4-75-1,5N	4.00	1.10	23.50	16.20	0.28	0.69
0,4-50-1N	4.10	1.10	22.75	14.30	0.27	0.63
0,4-25-0,5N	1.90	1.30	6.55	7.15	0.68	1.09
0,4-75-2N	2.80	1.50	32.40	11.35	0.54	0.35
0,4-50-2N	4.50	1.20	16.90	19.60	0.27	1.16
0,4-25-2N	1.20	0.90	3.95	4.35	0.75	1.10
0,4-100-1C	4.10	1.20	31.70	17.20	0.29	0.54
0,4-75-0,8C	3.70	3.50	33.70	18.30	0.95	0.54
0,4-50-0,6C	3.40	0.90	20.85	12.40	0.26	0.59
0,4-25-0,4C	1.90	1.20	5.95	9.20	0.63	1.55
0,4-75-1C	5.80	2.20	25.90	16.75	0.38	0.65
0,4-50-1C	4.90	0.50	17.60	14.40	0.10	0.82
0,4-25-1C	1.50	1.00	4.95	6.95	0.67	1.40
0,6-100	5.70	1.50	42.55	8.50	0.26	0.20
0,6-75	4.70	1.10	23.45	7.05	0.23	0.30
0,6-50	3.40	0.80	11.00	5.00	0.24	0.45
0,6-25	2.30	0.40	1.65	1.30	0.17	0.79
0,6-100-2N	4.90	1.00	27.50	8.30	0.20	0.30
0,6-75-1,5N	2.40	1.00	17.25	7.85	0.42	0.46
0,6-50-1N	1.80	0.10	7.50	4.80	0.06	0.64
0,6-25-0,5N	0.30	0.40	1.15	1.25	1.33	1.09
0,6-75-2N	3.80	0.60	16.85	8.40	0.16	0.50
0,6-50-2N	2.30	0.70	6.65	6.00	0.30	0.90
0,6-25-2N	0.20	0.40	0.90	1.05	2.00	1.17
0,6-100-1C	3.20	0.70	21.50	8.60	0.22	0.40
0,6-75-0,8C	2.40	1.20	15.50	6.10	0.50	0.39
0,6-50-0,6C	2.50	0.40	7.20	4.60	0.16	0.64
0,6-25-0,4C	0.50	0.40	2.00	1.90	0.80	0.95
0,6-75-1C	4.10	0.30	14.55	6.30	0.07	0.43
0,6-50-1C	2.30	1.00	6.60	4.45	0.43	0.67
0,6-25-1C	0.70	0.40	2.05	2.00	0.57	0.98

Although there is strength loss at 600 °C, a strength increase is observed at 1100 °C for mixtures with high perlite content. This can be partly explained by melting of the perlite and the tests being performed after cooling. If the strength tests were performed at the maximum temperature reached, such a positive change would probably not be recorded. The effect of exposure to 1100 °C on compressive and flexure strength is given in Table 4.3.

Table 4.3 Effect of exposure 1100 °C on strength

Mixture ID	Flexural Strength at 23 °C (MPa)	Flexural Strength After 1100 °C (MPa)	Comp. Strength at 23 °C (MPa)	Comp. Strength After 1100 °C (MPa)	Residual Flexural Strength 1100 °C (after/before)	Residual Compressive Strength 1100 °C (after/before)
0,4-100	4.20	0.40	30.10	11.20	0.10	0.37
0,4-75	6.00	0.40	40.25	12.50	0.07	0.31
0,4-50	3.90	0.70	24.70	14.95	0.18	0.61
0,4-25	1.90	1.60	7.45	28.80	0.84	3.87
0,4-100-2N	7.50	0.50	40.65	9.50	0.07	0.23
0,4-75-1,5N	4.00	0.50	23.50	10.65	0.13	0.45
0,4-50-1N	4.10	1.10	22.75	19.55	0.27	0.86
0,4-25-0,5N	1.90	2.30	6.55	37.25	1.21	5.69
0,4-75-2N	2.80	0.50	32.40	6.45	0.18	0.20
0,4-50-2N	4.50	0.50	16.90	24.50	0.11	1.45
0,4-25-2N	1.20	1.30	3.95	16.00	1.08	4.05
0,4-100-1C	4.10	0.50	31.70	8.65	0.12	0.27
0,4-75-0,8C	3.70	1.30	33.70	13.30	0.35	0.39
0,4-50-0,6C	3.40	*0.60	20.85	16.45	0.18	0.79
0,4-25-0,4C	1.90	0.20	5.95	29.45	0.11	4.95
0,4-75-1C	5.80	1.10	25.90	12.85	0.19	0.50
0,4-50-1C	4.90	2.60	17.60	14.15	0.53	0.80
0,4-25-1C	1.50	1.00	4.95	20.00	0.67	4.04
0,6-100	5.70	0.10	42.55	3.70	0.02	0.09
0,6-75	4.70	0.20	23.45	5.35	0.04	0.23
0,6-50	3.40	0.50	11.00	7.20	0.15	0.65
0,6-25	2.30	2.70	1.65	15.80	1.17	9.58
0,6-100-2N	4.90	0.30	27.50	4.45	0.06	0.16
0,6-75-1,5N	2.40	0.10	17.25	5.25	0.04	0.30
0,6-50-1N	1.80	0.60	7.50	7.40	0.33	0.99
0,6-25-0,5N	0.30	4.30	1.15	13.05	14.33	11.35
0,6-75-2N	3.80	0.30	16.85	5.00	0.08	0.30
0,6-50-2N	2.30	0.20	6.65	12.15	0.09	1.83
0,6-25-2N	0.20	3.30	0.90	15.10	16.50	16.78
0,6-100-1C	3.20	0.10	21.50	3.90	0.03	0.18
0,6-75-0,8C	2.40	*0.40	15.50	5.30	0.17	0.34
0,6-50-0,6C	2.50	0.60	7.20	7.15	0.24	0.99
0,6-25-0,4C	0.50	1.90	2.00	24.95	3.80	12.48
0,6-75-1C	4.10	0.50	14.55	4.75	0.12	0.33
0,6-50-1C	2.30	0.80	6.60	7.55	0.35	1.14
0,6-25-1C	0.70	1.40	2.05	17.75	2.00	8.66

* Specimens split into two after 1100 ℃.

In all mixtures without perlite, the compressive and flexural strength of CAC decrease. But, some mixtures with 75 % perlite, with or without chemicals, show a highly positive behavior on both compressive and flexure strength. This originated from melting of perlite after high temperature.

4.3 Water Requirement For Normal Consistency and Setting Time

The water requirement for normal consistency and initial and final setting times are given in Table 4.4.

Table 4.4 Water requirement for normal consistency and setting time

MIXTURE	W/CM	Initial Setting Time (min)	Final Setting Time (min)
100	0.23	185	345
75	0.26	229	256
50	0.28	157	202
25	0.31	82	167
100-2N	0.22	30	130
75-1.5N	0.24	26	106
50-1N	0.27	30	145
25-0.5N	0.29	60	327
75-2N	0.23	30	110
50-2N	0.26	24	94
25-2N	0.29	23	109
100-1C	0.29	100	133
75-0.8C	0.30	83	120
50-0.6C	0.32	70	115
25-0.4C	0.35	83	118
75-1C	0.33	90	110
50-1C	0.30	110	130
25-1C	0.32	115	140

As mentioned in Chapter 2, perlite addition prolongs the setting of OPC pastes. Unlike OPC, perlite shortens setting time of CAC pastes, when there are no chemicals in the mixture. The addition of Na_2SO_4 or $Ca(OH)_2$ also shortens the setting time.

When perlite and Na_2SO_4 are used together, the setting time shortens until a certain point, but after that, it starts to prolong. If enough $Ca(OH)_2$ is used in the CAC-perlite mixture, the setting will prolong.

4.4 Heat Evolution

The measurement of the heat of hydration of the mixtures up to 48h revealed much information about the influence of ground perlite on CAC systems. As perlite content in the system increases, the dormant period shortens and the acceleration period starts earlier owing likely to the nucleation effect since the perlite was quite finely ground (Figure 4.17a). On the other hand, a reduction in the heat of hydration is observed by increasing perlite, as expected (Figure 4.17b). The height of the heat peak for CAC i.e. the maximum rate of heat evolution is ~ 23 mW/g for 0.4-100, and the total evolved heat up to 48h is ~ 340 J/g. As expected, the heat evolution is greater than in Portland cement systems. Heat evolution peaks at ~ 9-10h, consistent with the final setting time (give in subsequent sections). The decrease in the total heat of hydration is smaller than the amount of CAC replaced, indicating the contribution of perlite in the reactions. This is also consistent with the strength development results (Figure 4.1).

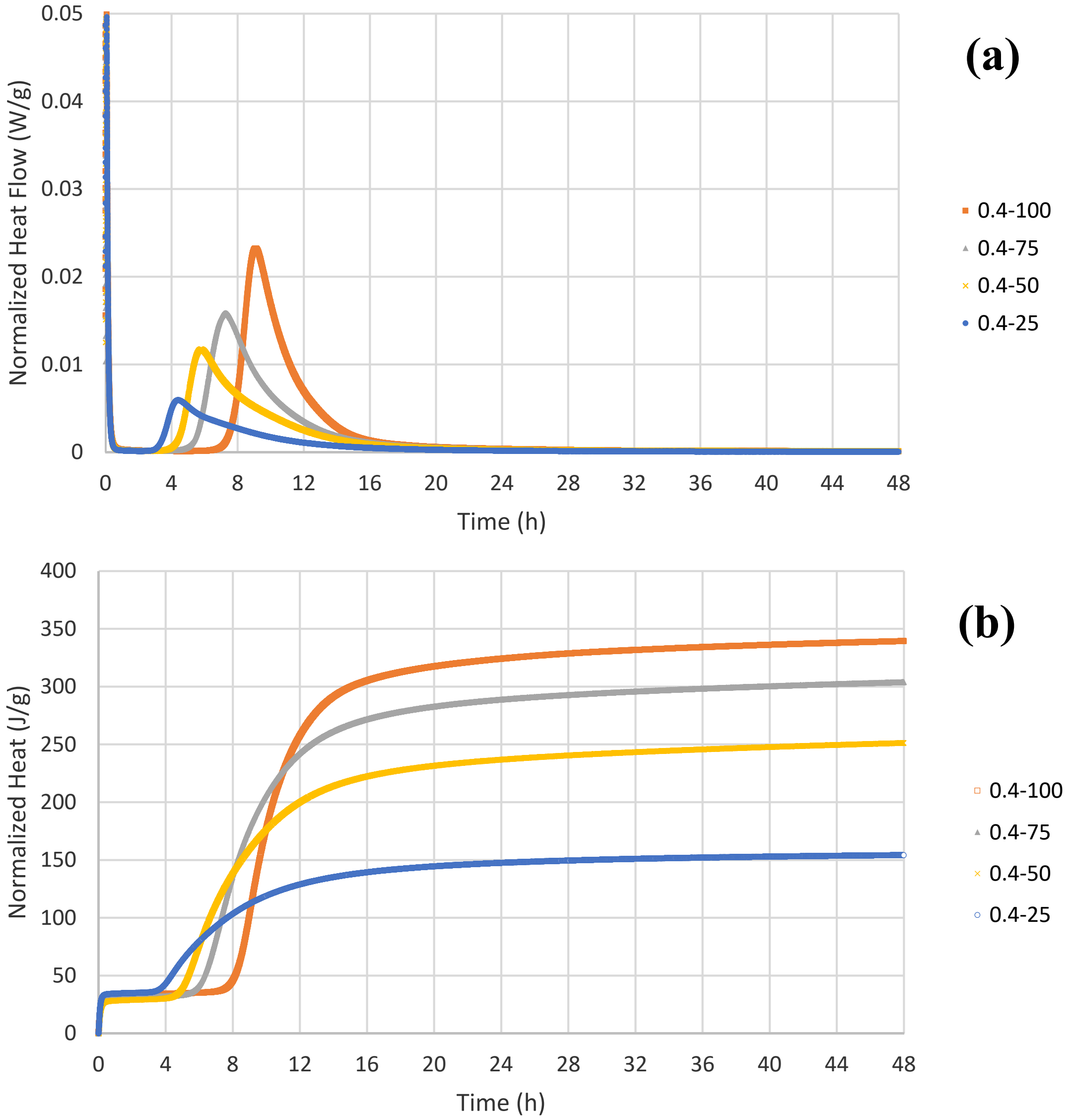

Figure 4.17 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.4 and no chemical)

The occurrence of the maximum heat evolution peak shifts from ~ 10h to ~ 5h as perlite content is increased from 0 to 75 % (Figure 4.18). The decrease is nearly linear with the amount of perlite.

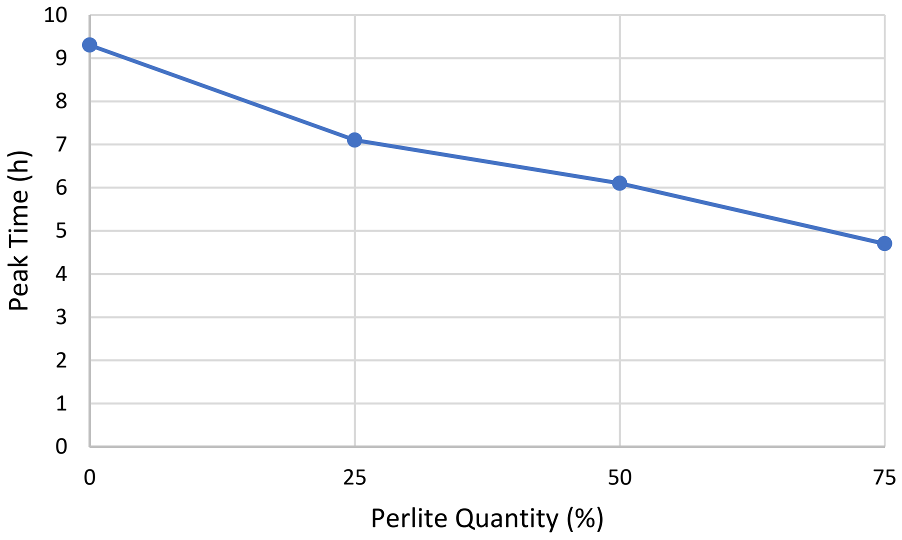

Figure 4.18 Peak time vs. perlite quantity of Figure 4.17a

As shown in Figure 4.19, while the addition of 2 % Na_2SO_4 retards the hydration, 1 % $Ca(OH)_2$ facilitates the early hydration of CAC. In all three cases, 48-h heat of hydrations are almost equal indicating that the addition of chemicals merely changes the timing of the hydration reactions but probably not their amounts. Also, when their early compressive strengths are compared (Figure 4.2), it is seen that 0.4-100-1C has the highest 3-h compressive strength of the three.

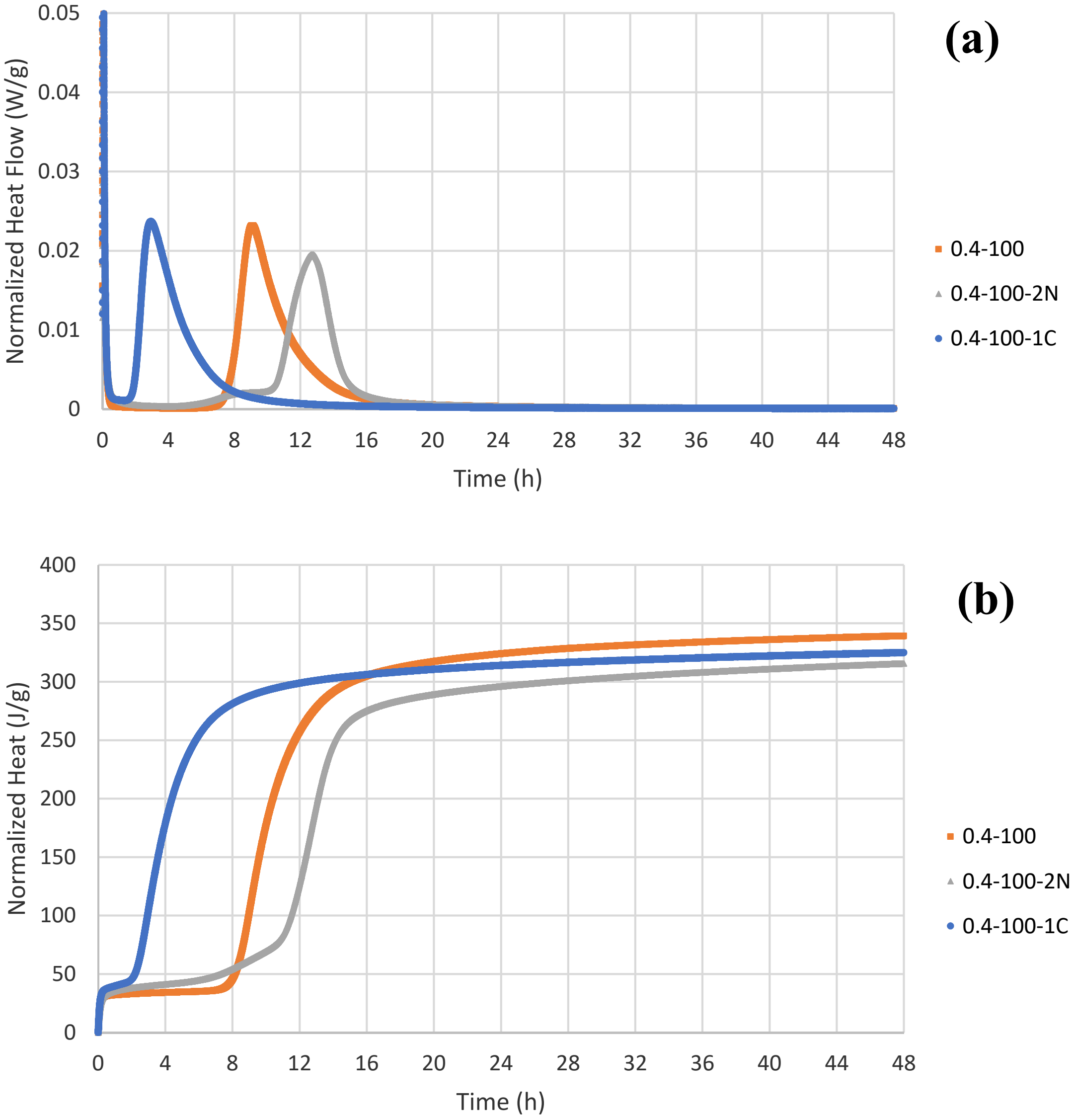

Figure 4.19 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.4 and 100 % CAC)

The influence of adding chemicals into pastes containing 25 % perlite and 75 % CAC is quite similar to the effect on pure CAC pastes (Figure 4.20).

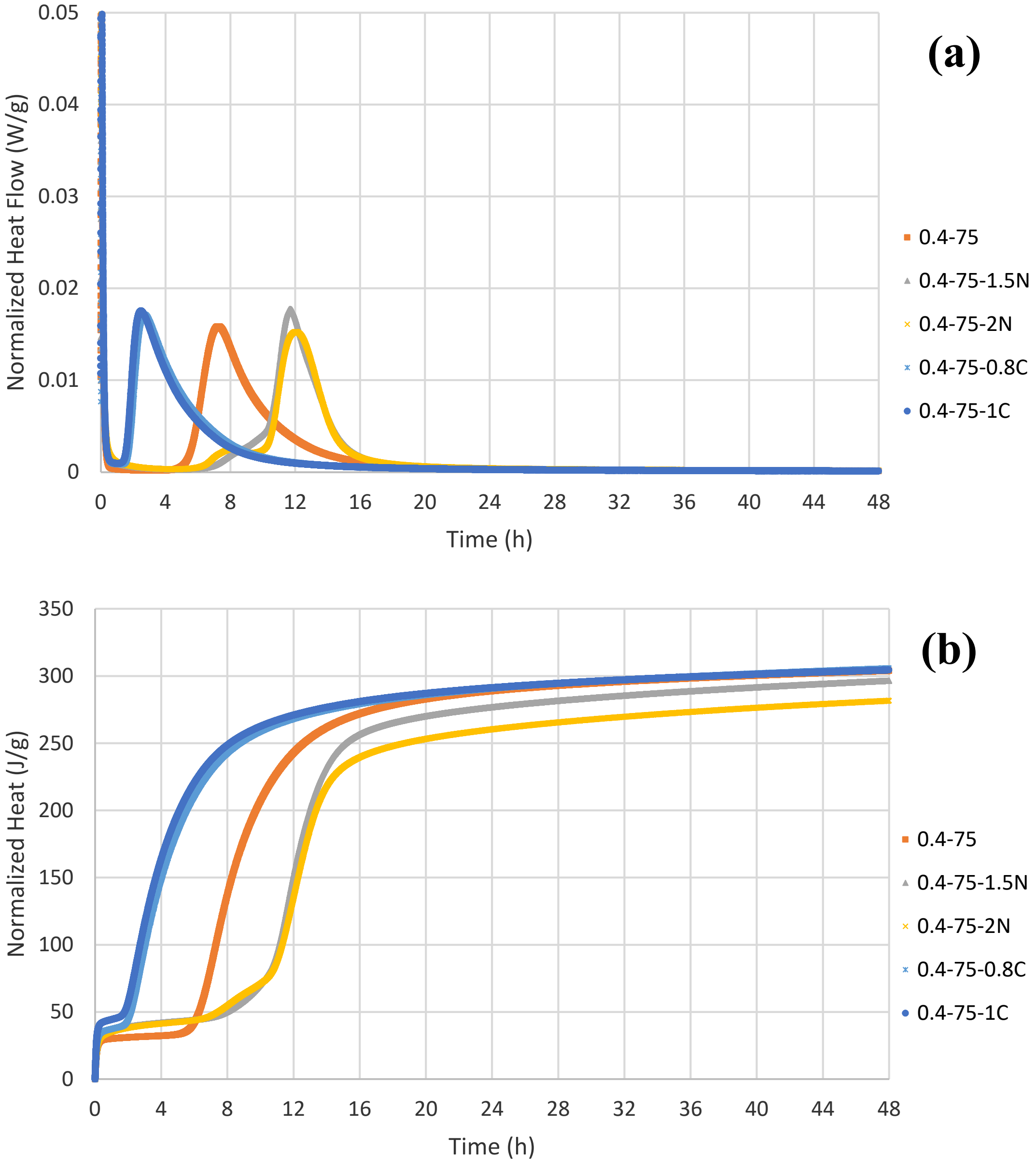

Figure 4.20 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.4 and 75 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.21).

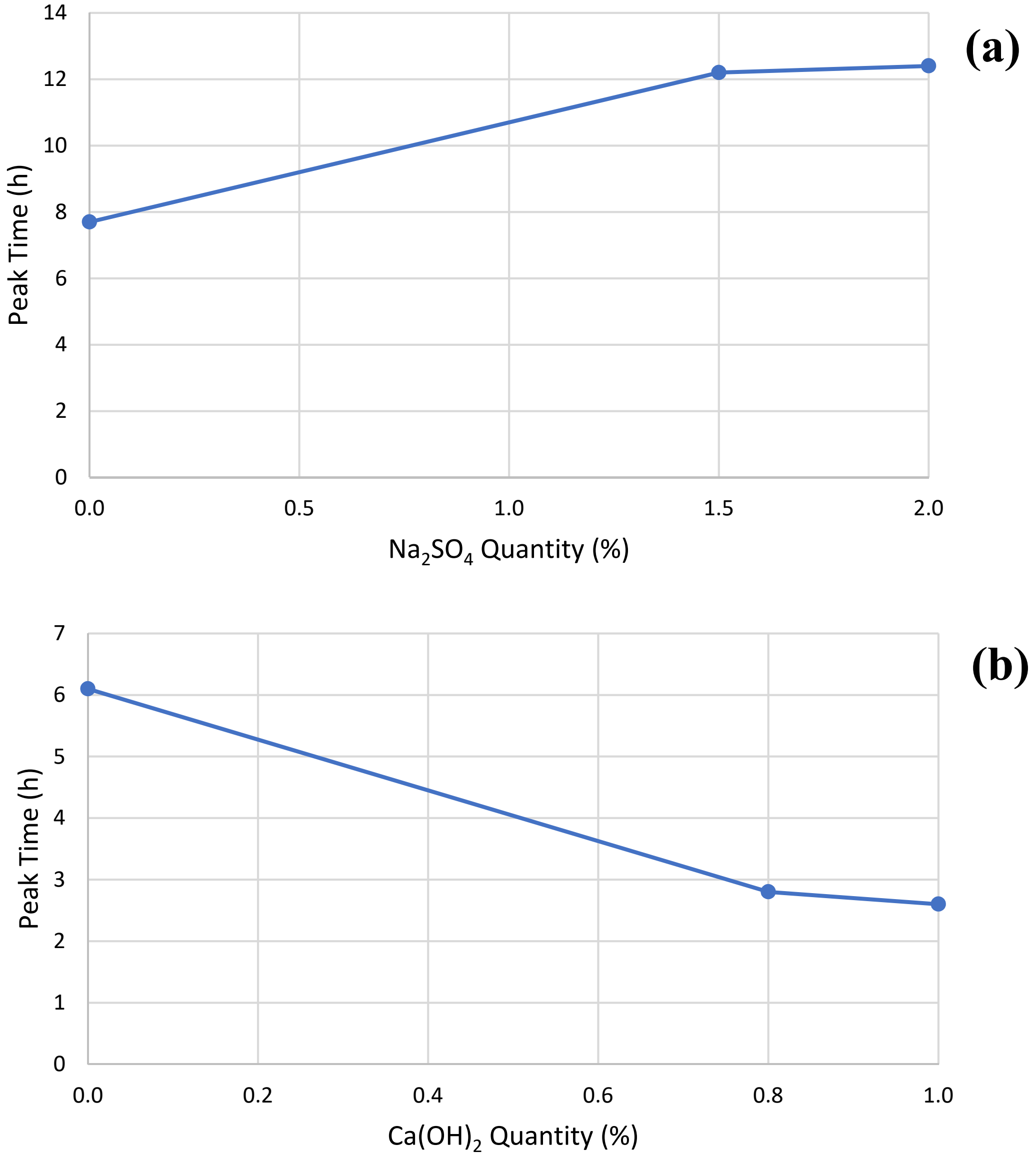

Figure 4.21 Influence of Na$_2$SO$_4$ and Ca(OH)$_2$ (a) peak time vs. Na$_2$SO$_4$ quantity, (b) peak time vs. Ca(OH)$_2$ quantity (W/CM = 0.4 and 75 % CAC)

The effect of the chemicals is similar also for the 50 % perlite pastes (Figure 4.22). Different from the others 0.4-50-2N has two heat peaks. A small shoulder peak precedes the main peak. In all five pastes the 48-hour-heat of hydrations are close to each other.

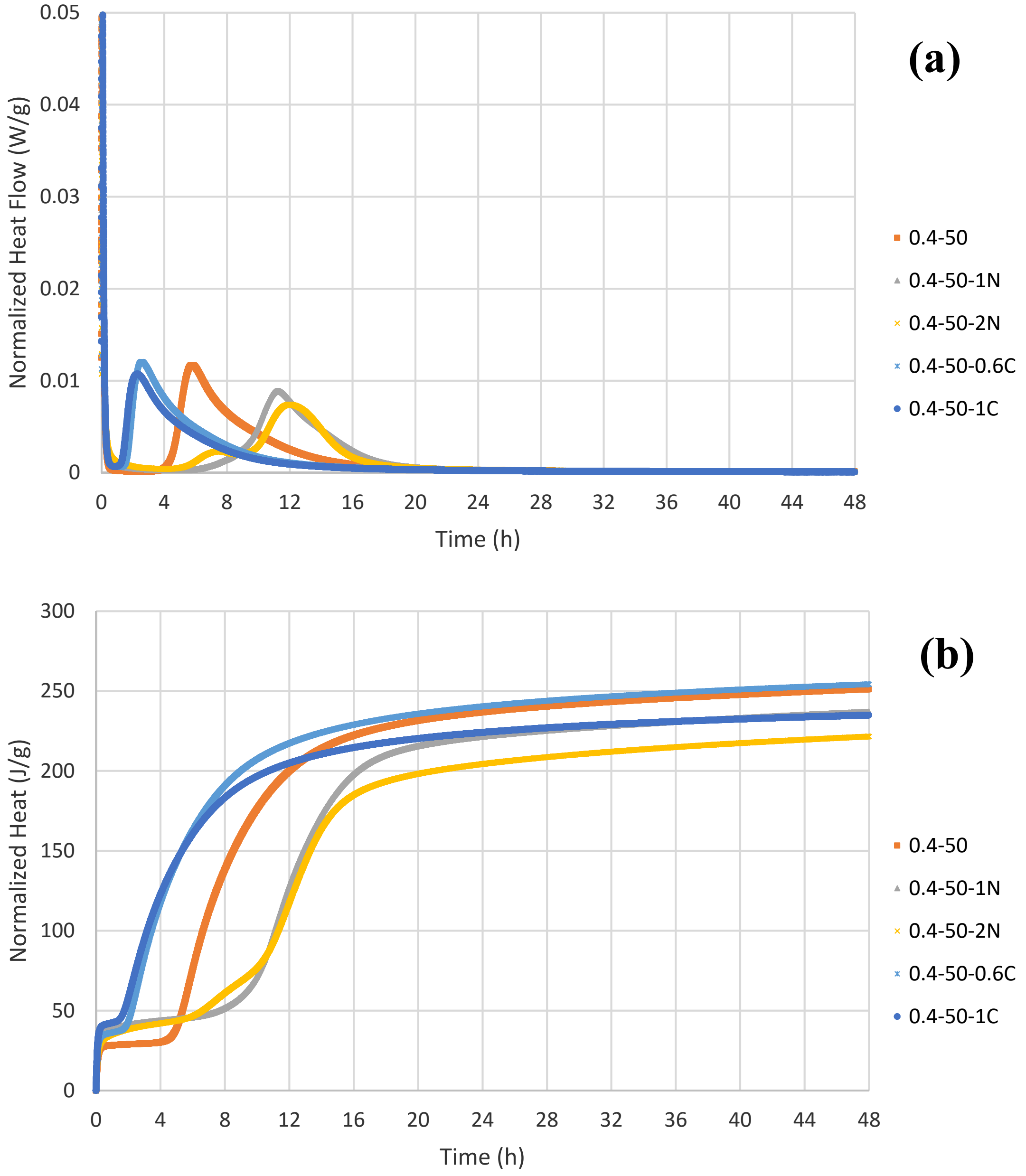

Figure 4.22 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.4 and 50 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.23).

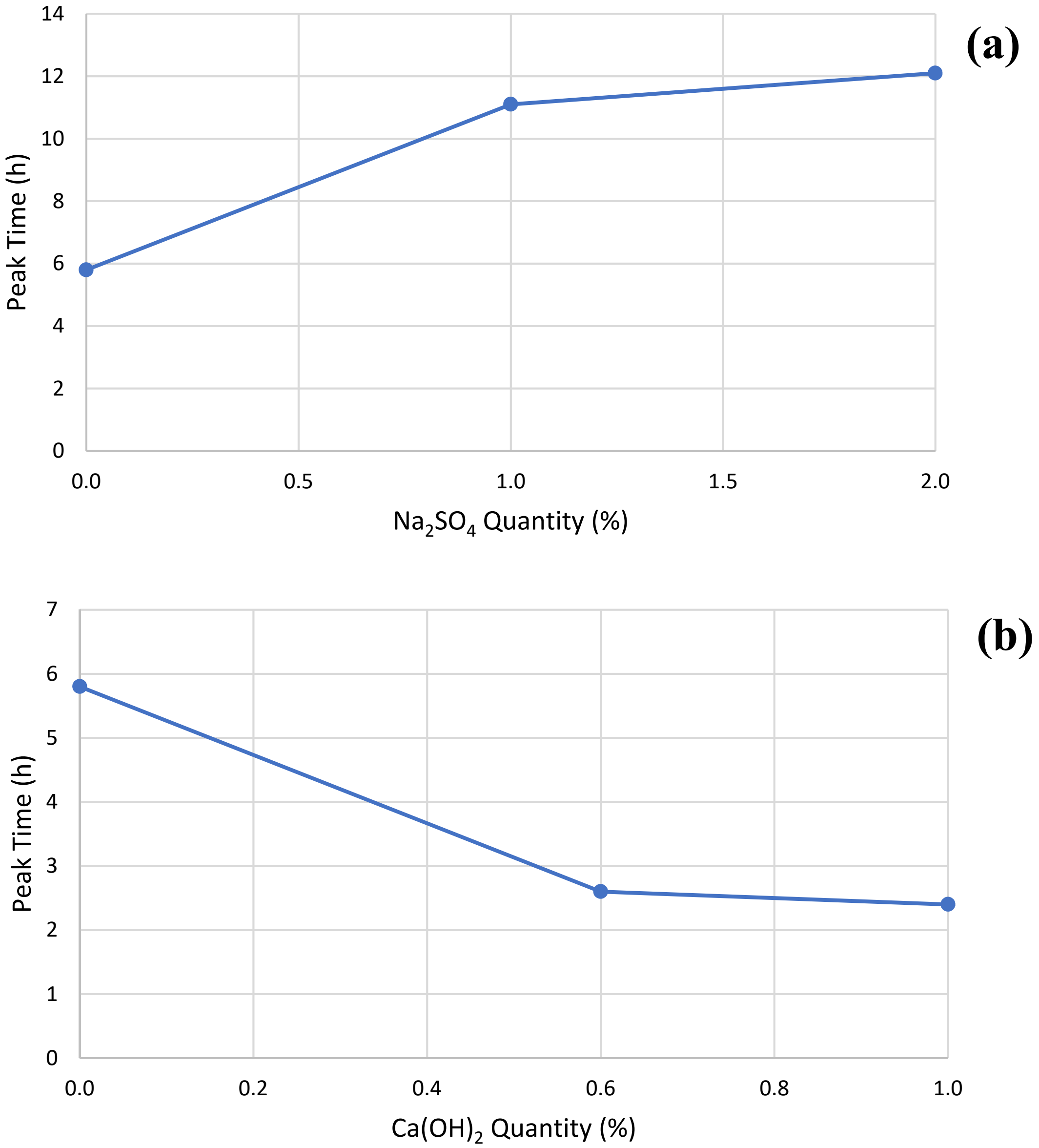

Figure 4.23 Influence of Na_2SO_4 and $Ca(OH)_2$ (a) peak time vs. Na_2SO_4 quantity, (b) peak time vs. $Ca(OH)_2$ quantity (W/CM = 0.4 and 50 % CAC)

As seen in Figure 4.24, the influence of the chemicals on the 25 % perlite pastes is similar to their effect on the 50 % perlite pastes.

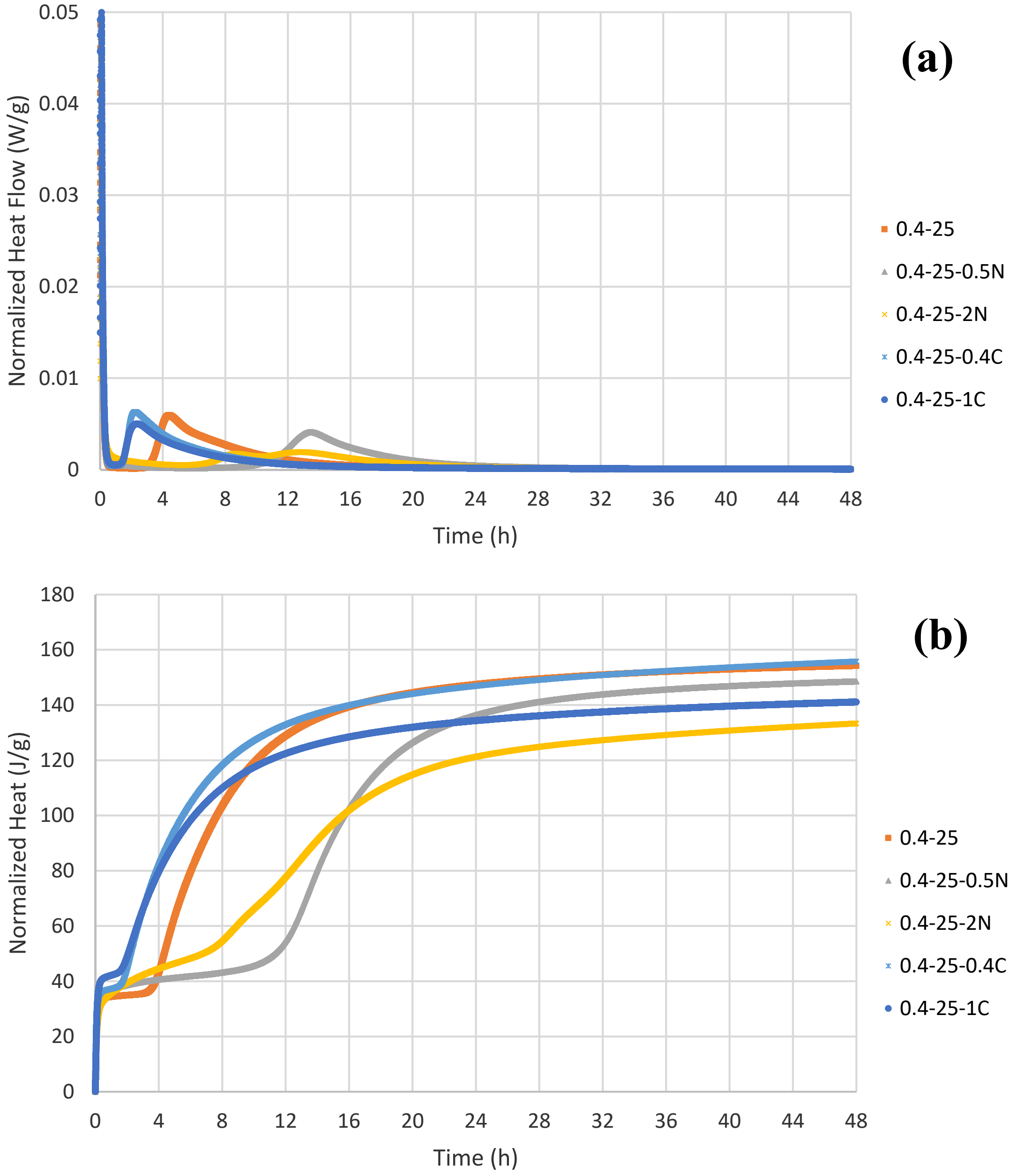

Figure 4.24 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.4 and 25 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.25).

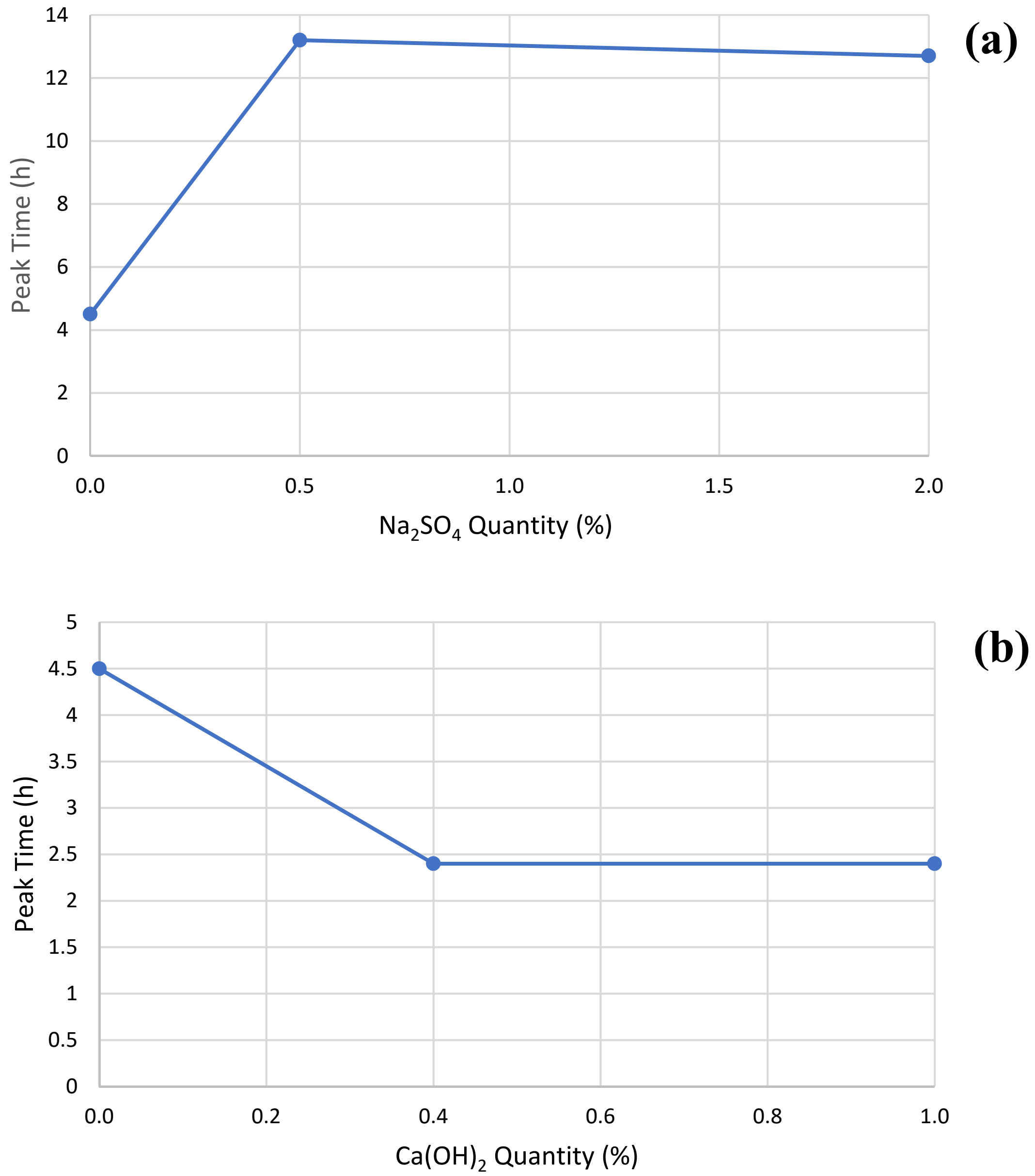

Figure 4.25 Influence of Na_2SO_4 and $Ca(OH)_2$ (a) peak time vs. Na_2SO_4 quantity, (b) peak time vs. $Ca(OH)_2$ quantity (W/CM = 0.4 and 25 % CAC)

In Figure 4.26, the combined effect of perlite and 2 % Na_2SO_4 on heat evolution was investigated. As the perlite content increases, the rate of heat evolution decreases and two peaks appear. Besides, increased perlite quantity decreases the heat of evolution. The decrease in cumulative heat is greater than in the case without any Na_2SO_4.

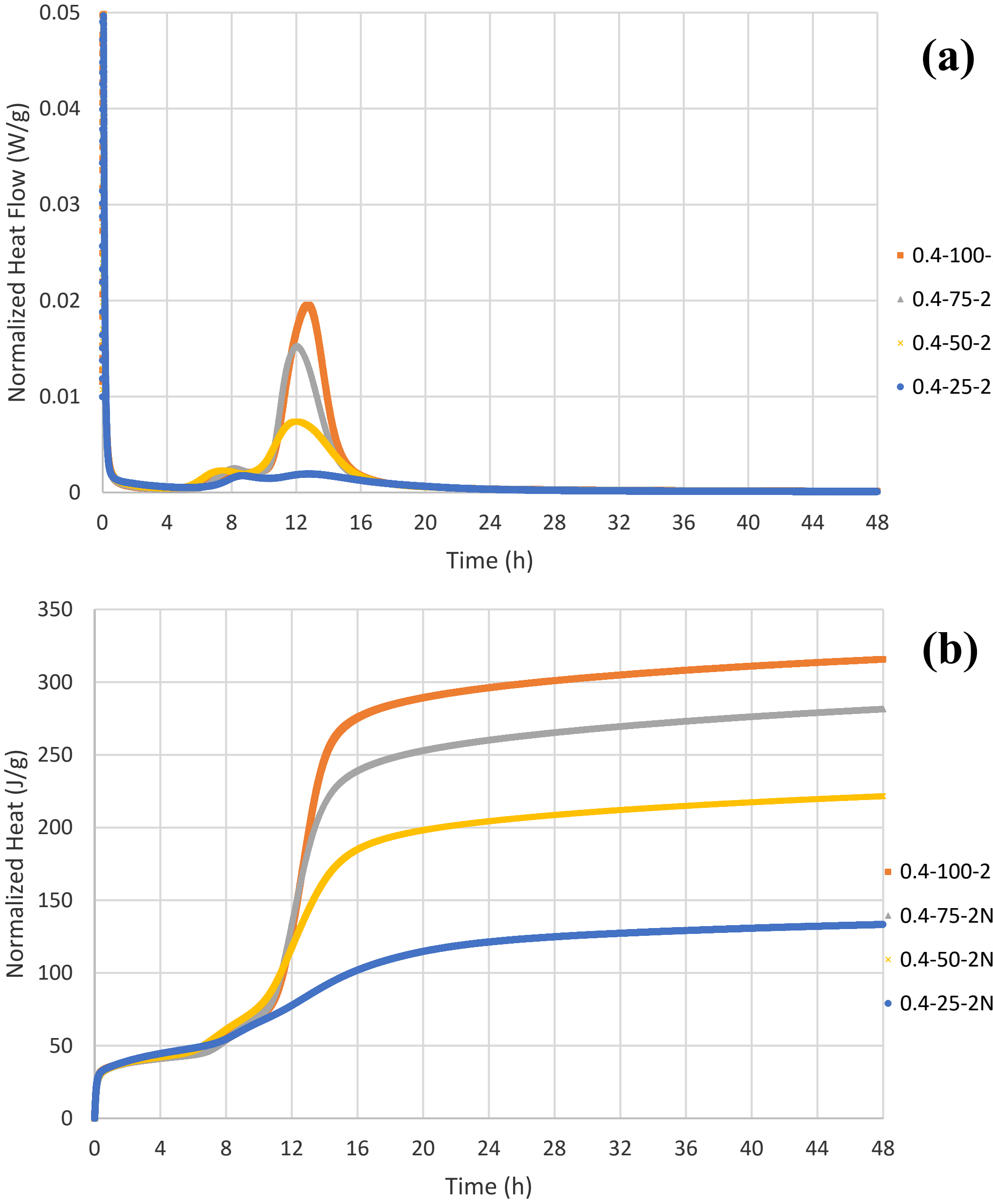

Figure 4.26 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.4 and with Na_2SO_4)

Influence of perlite quantity on peak time is given in Figure 4.27.

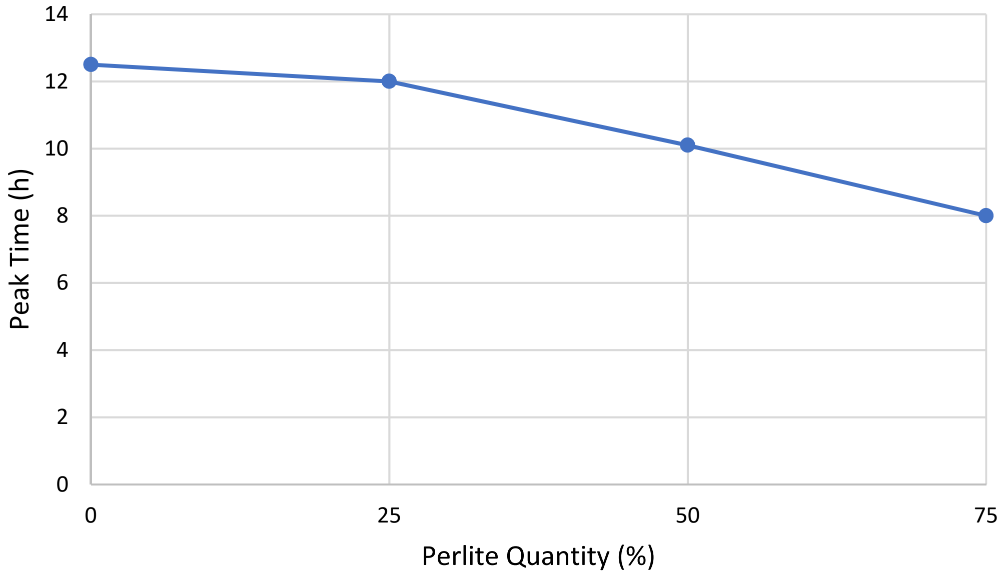

Figure 4.27 Influence of perlite quantity on peak time (W/CM = 0.4 and with Na_2SO_4)

As shown in Figure 4.28, the addition of 1 % $Ca(OH)_2$ to the system causes the hydration reactions to start at almost the same time regardless of the amount of perlite. As perlite increases the 48h total heat and the height of the heat peak decrease.

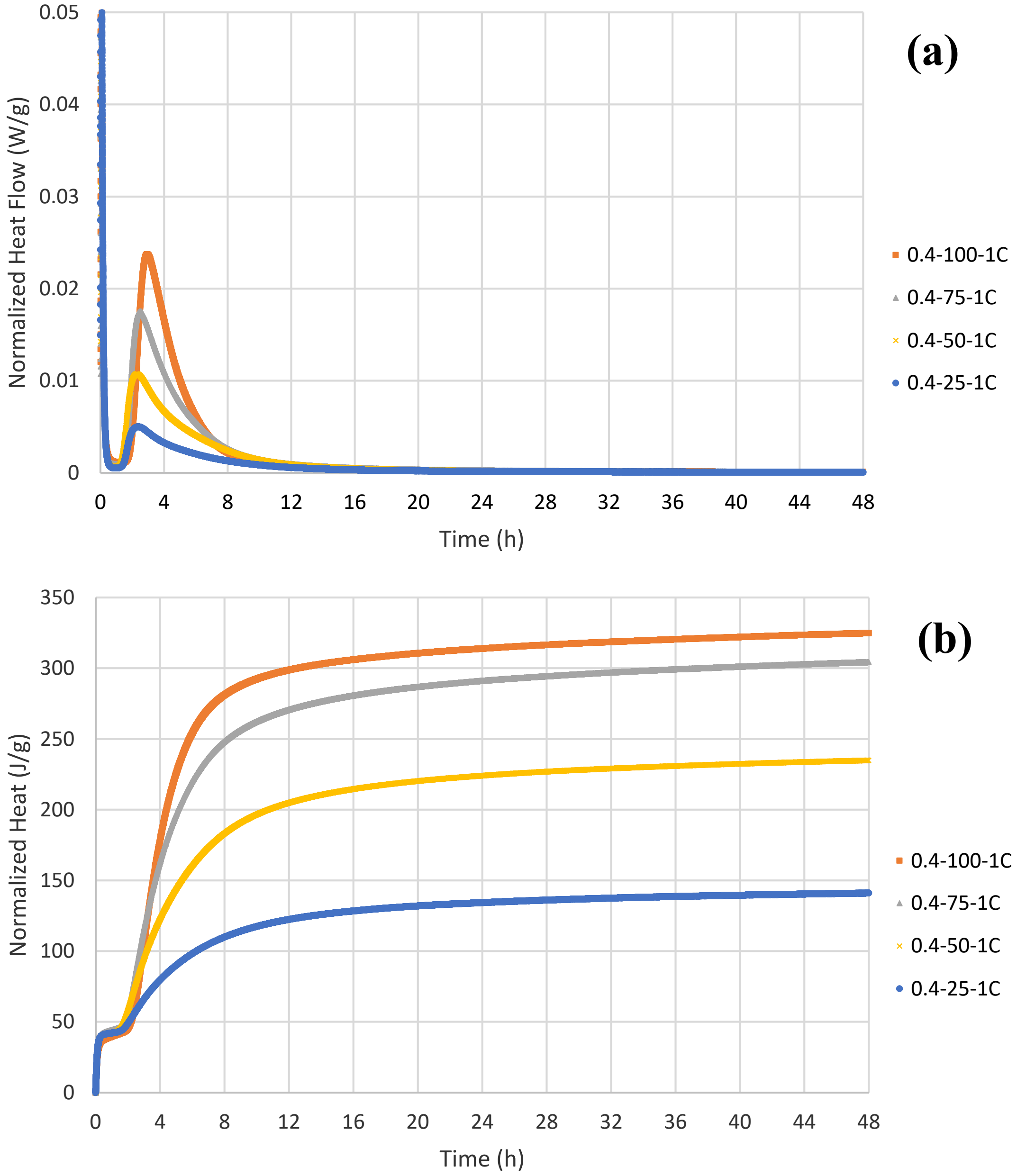

Figure 4.28 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.4 and with $Ca(OH)_2$)

In Figure 4.29, the influence of perlite quantity on peak time is shown.

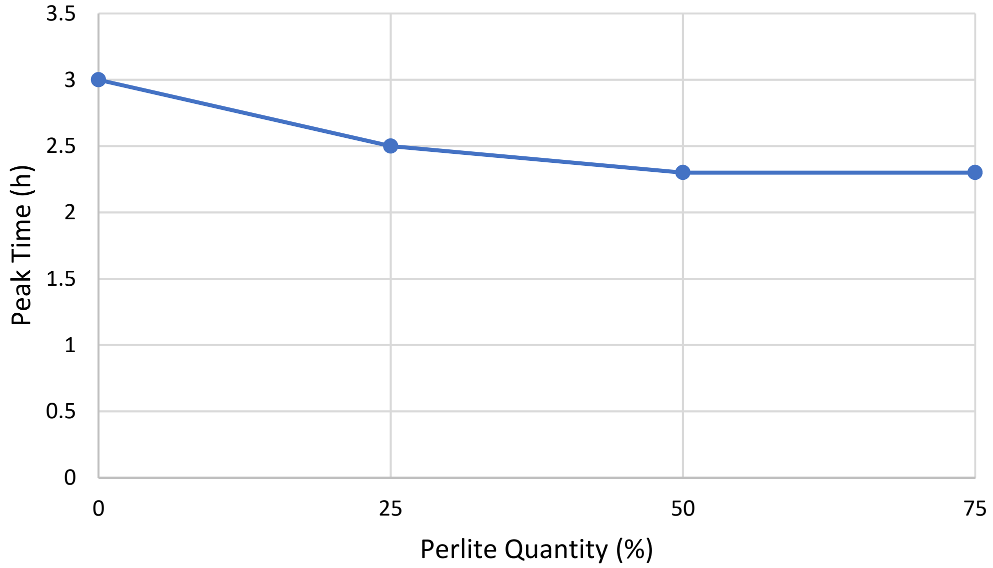

Figure 4.29 Influence of perlite quantity on peak time (W/CM = 0.4 and with $Ca(OH)_2$)

The pastes W/CM=0.6 is similar to the W/CM=0.4 pastes in terms of heat evolution. When W/CM=0.6, peak heights and cumulative heat slightly increased.

In Figure 4.30 below, as perlite increases in the system, dormant period shortens and acceleration period starts earlier owing to nucleation effect. On the other hand, as perlite increases heat of hydration decreases as expected.

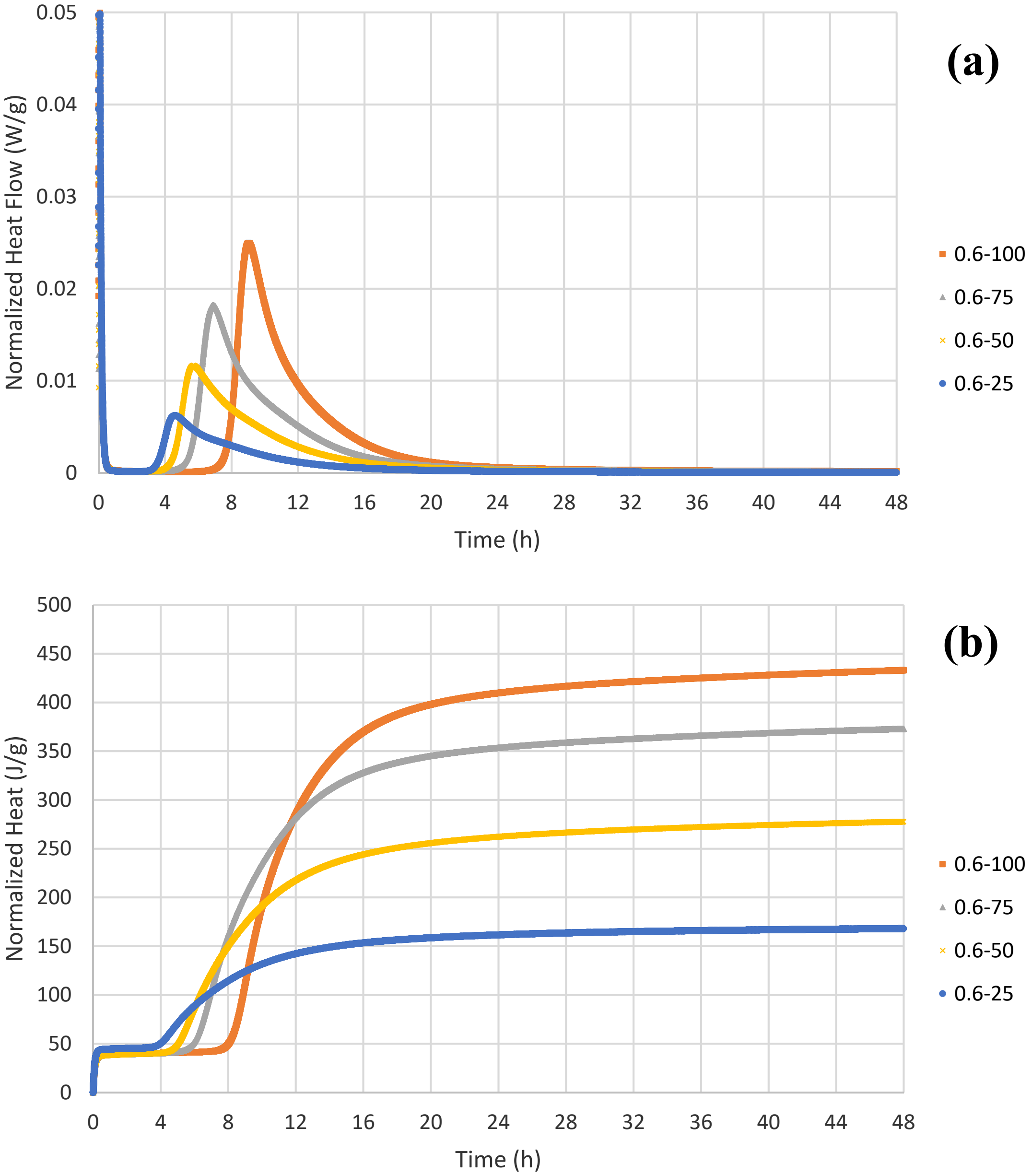

Figure 4.30 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.6 and no chemical)

In Figure 4.31, the influence of perlite quantity on peak time for W/CM=0.6 is shown.

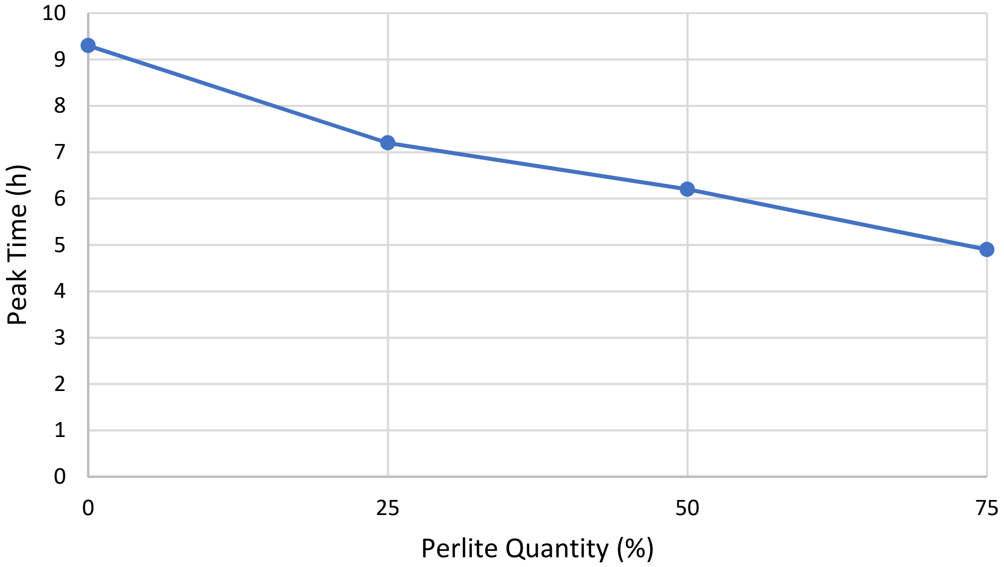

Figure 4.31 Influence of perlite quantity on peak time (W/CM = 0.6 and no chemical)

As shown in Figure 4.32, while Na_2SO_4 retards the hydration, $Ca(OH)_2$ facilitates the early hydration of CAC. In all three situations, 48-hour-heat of hydrations are almost same.

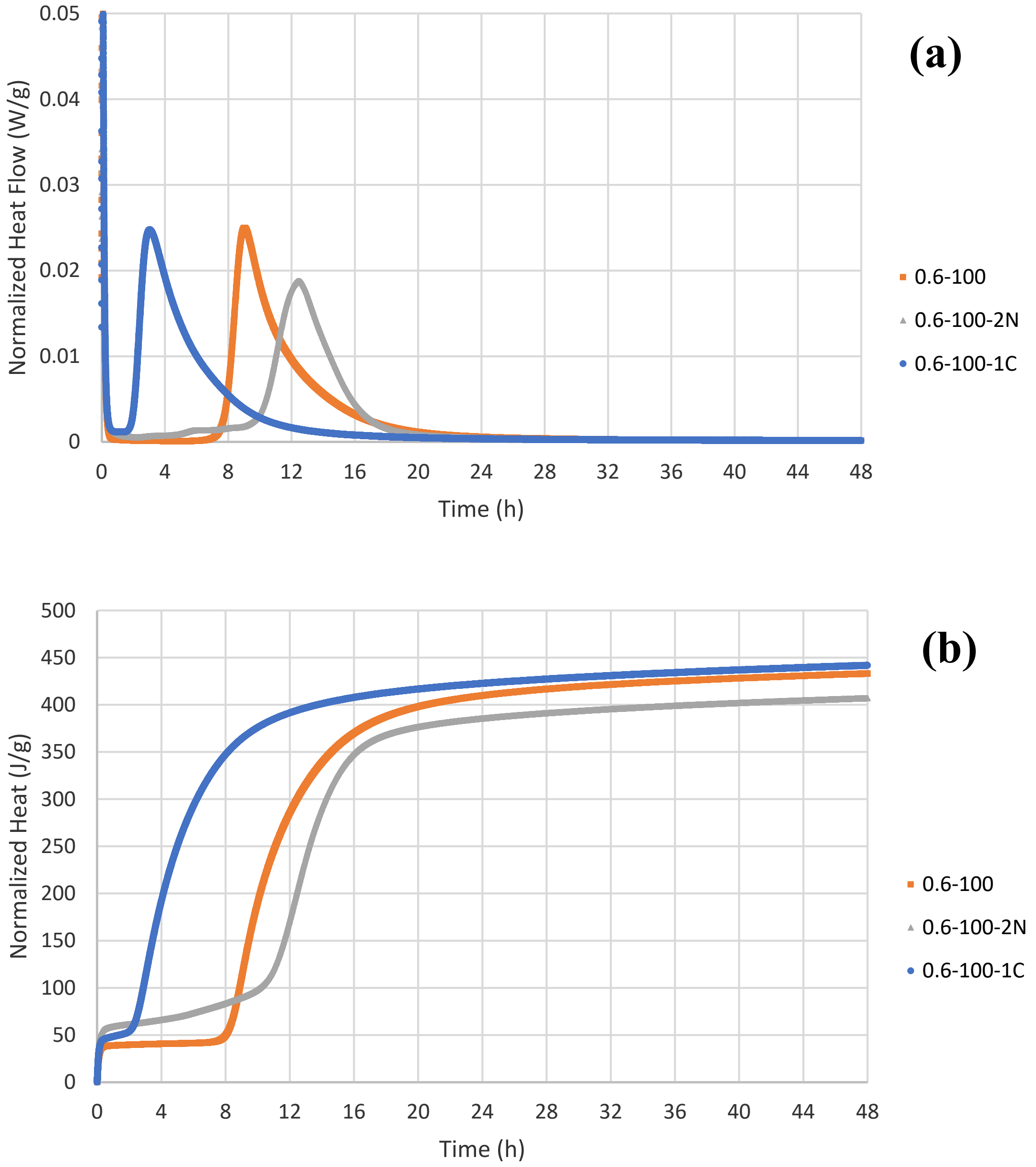

Figure 4.32 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.6 and 100 % CAC)

As seen in Figure 4.33, while Na_2SO_4 retards the hydration, $Ca(OH)_2$ facilitates the early hydration of CAC. The chemicals do not affect the 48-hour-heat of hydrations.

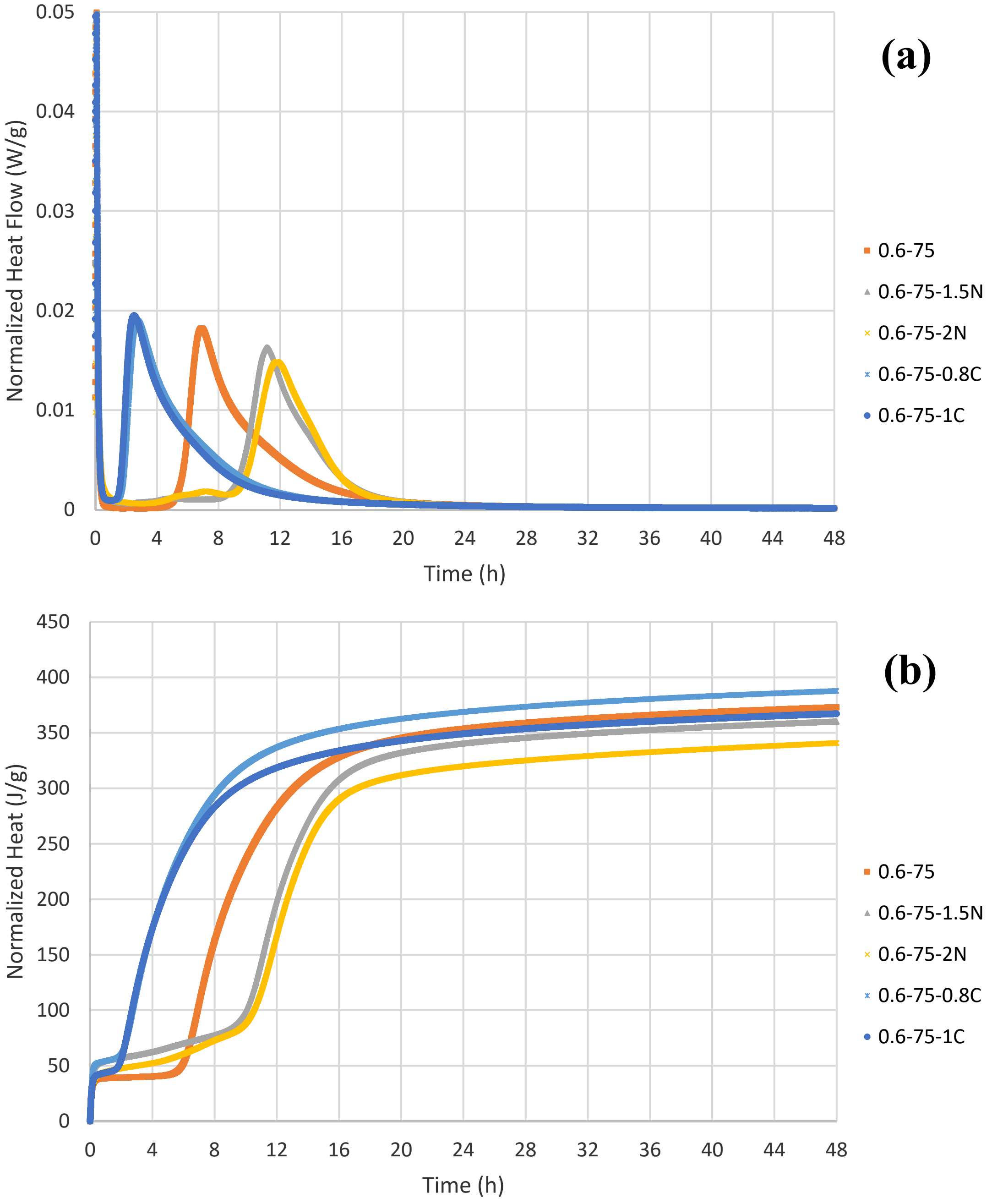

Figure 4.33 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.6 and 75 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.34).

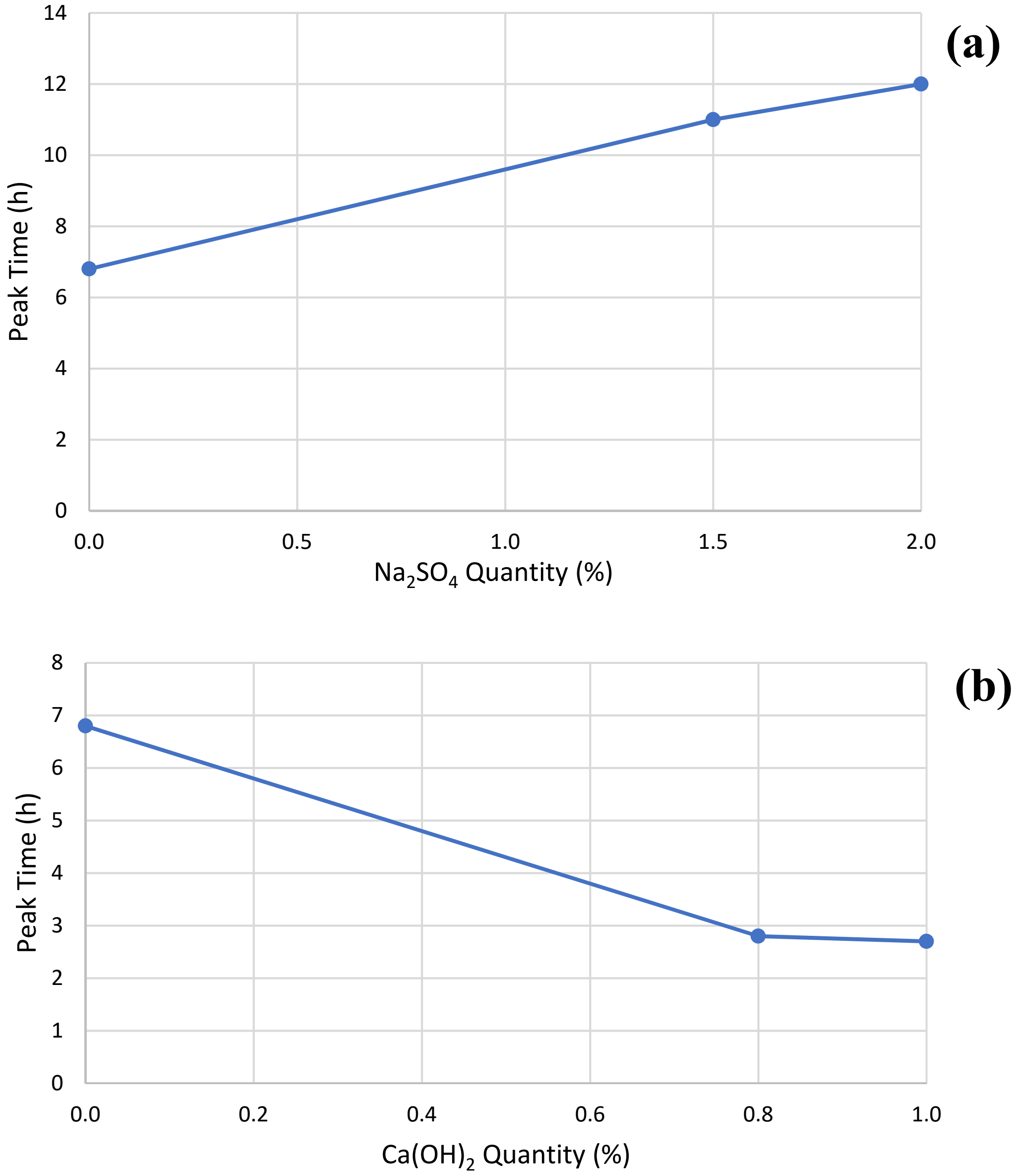

Figure 4.34 Influence of Na_2SO_4 and $Ca(OH)_2$ (a) peak time vs. Na_2SO_4 quantity, (b) peak time vs. $Ca(OH)_2$ quantity (W/CM = 0.6 and 75 % CAC)

As seen in Figure 4.35 below, while Na_2SO_4 retards the hydration, $Ca(OH)_2$ facilitates the early hydration of CAC. Different from the others, The mixture contains 2 % Na_2SO_4 has two peaks. In all five situations, 48-hour-heat of hydrations are close to each other.

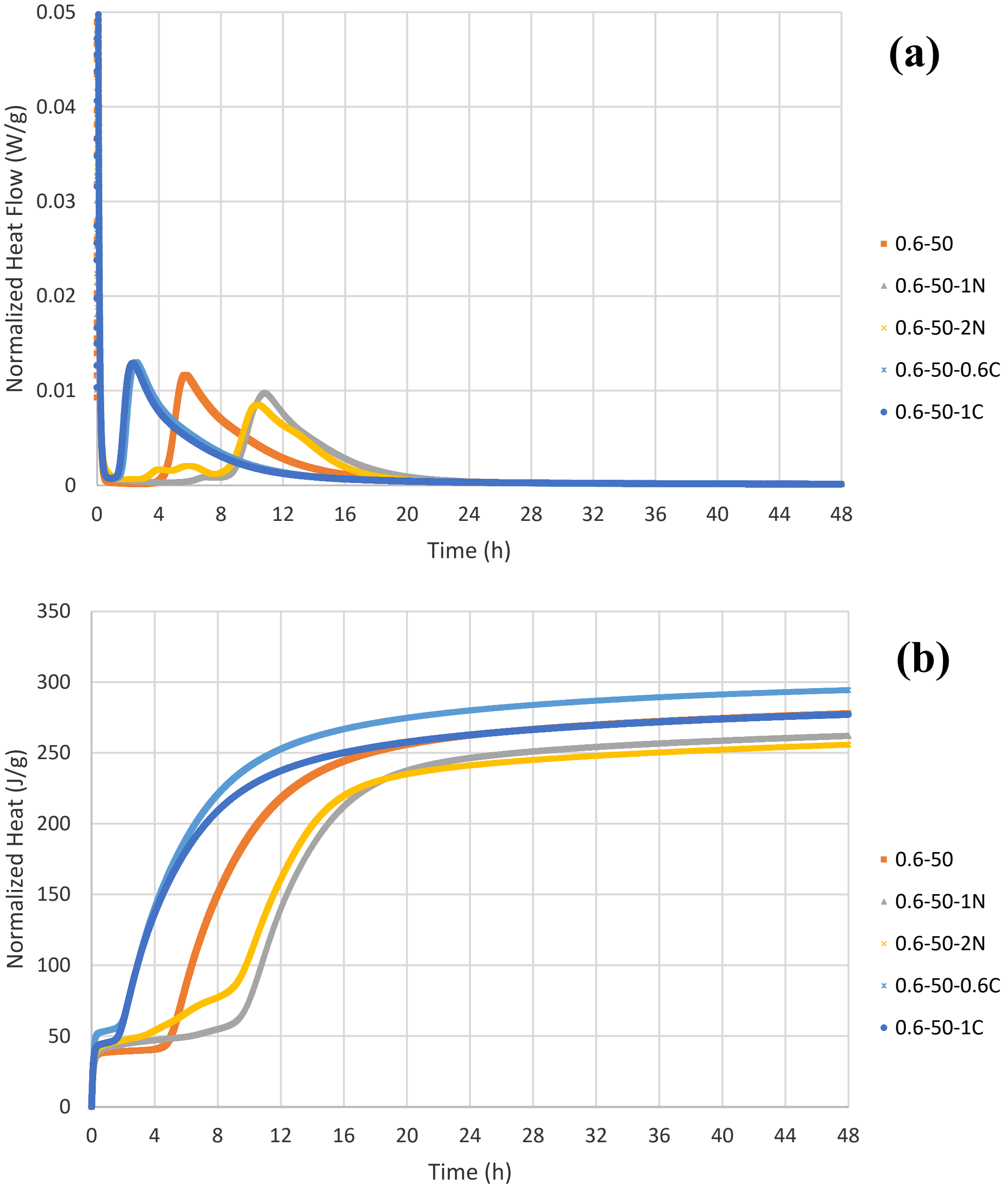

Figure 4.35 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.6 and 50 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.36).

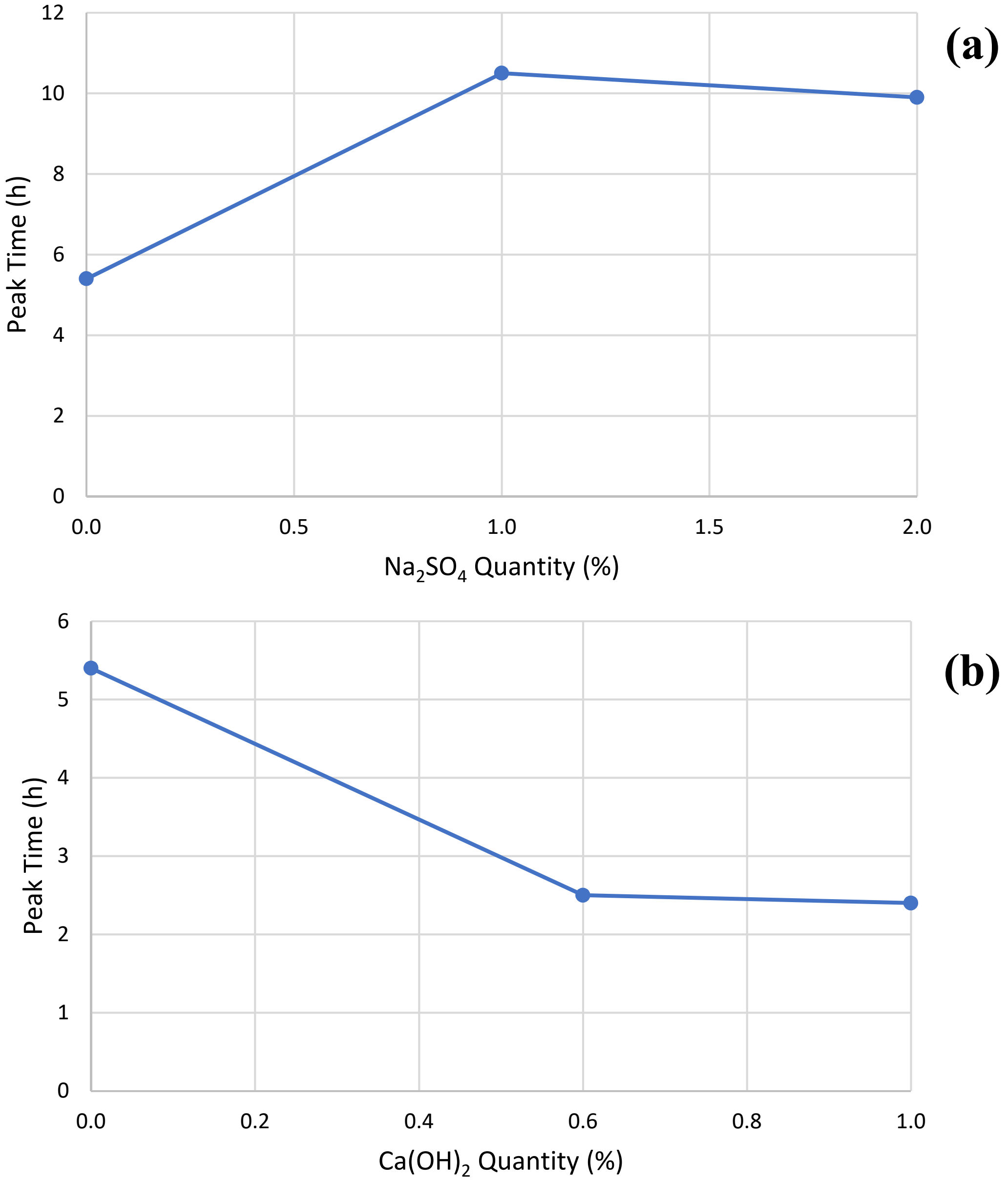

Figure 4.36 Influence of Na_2SO_4 and $Ca(OH)_2$ (a) peak time vs. Na_2SO_4 quantity, (b) peak time vs. $Ca(OH)_2$ quantity (W/CM = 0.6 and 50 % CAC)

As understood in Figure 4.37, while Na_2SO_4 retards the hydration, $Ca(OH)_2$ facilitates the early hydration of CAC. The mixture contains 2 % Na_2SO_4 has two peaks. 48-hour-heat of hydrations are close to each other.

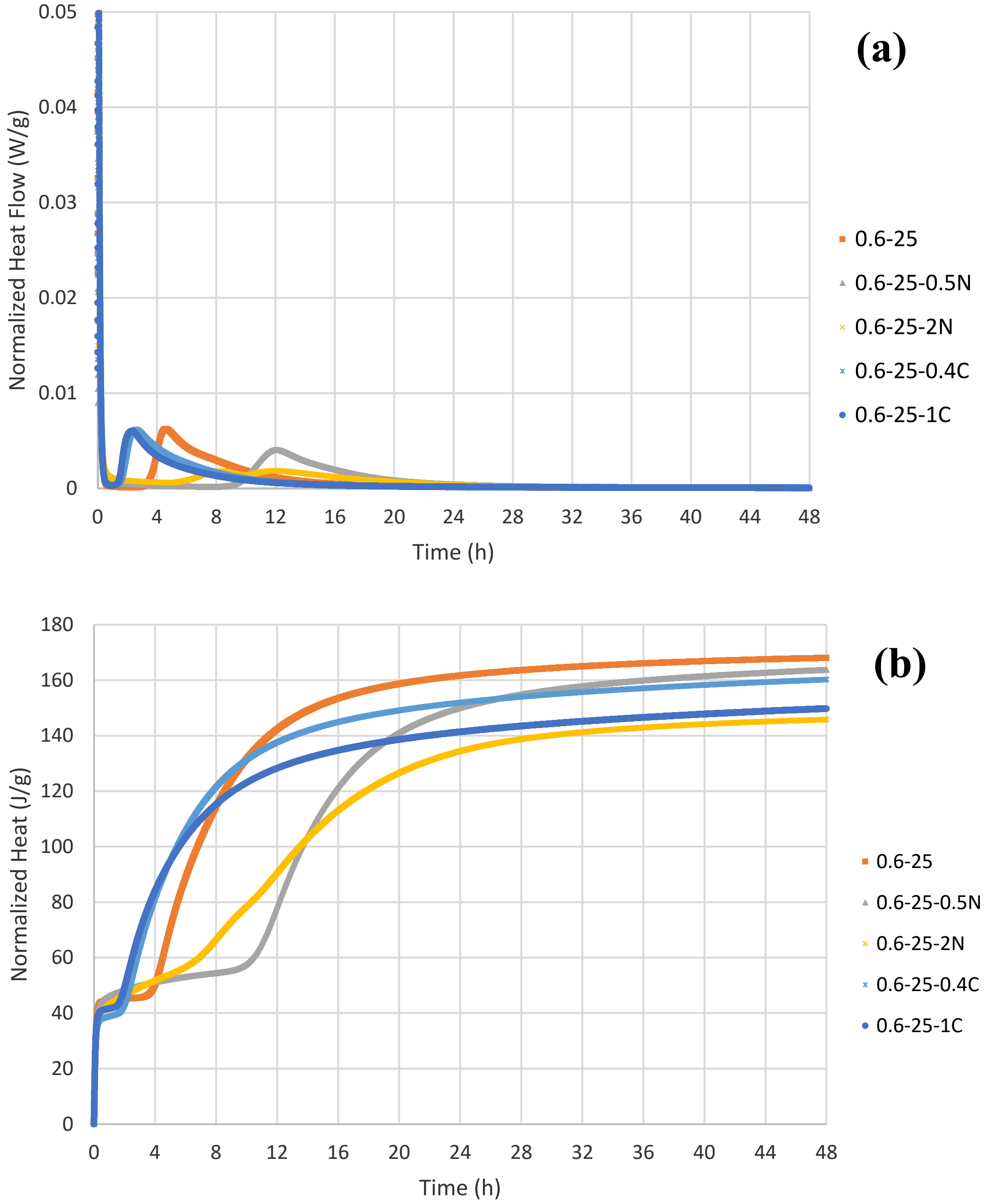

Figure 4.37 Influence of Na_2SO_4 and $Ca(OH)_2$ on (a) normalized heat flow vs. time, (b) normalized heat vs. time (W/CM = 0.6 and 25 % CAC)

The effectiveness of the chemicals in retarding/accelerating the reactions decreases with increasing dosage (Figure 4.38).

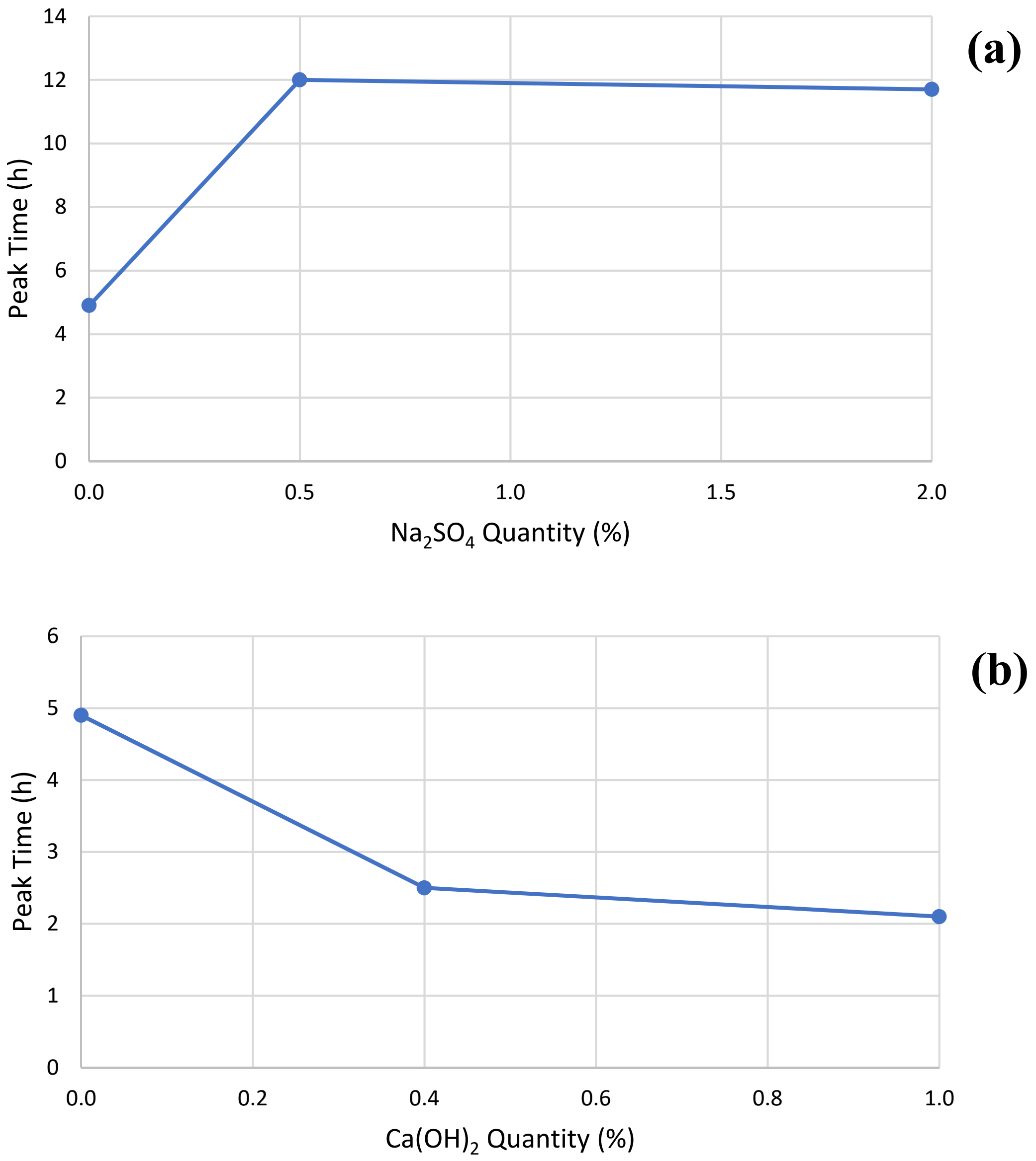

Figure 4.38 Influence of Na_2SO_4 and $Ca(OH)_2$ (a) peak time vs. Na_2SO_4 quantity, (b) peak time vs. $Ca(OH)_2$ quantity (W/CM = 0.6 and 25 % CAC)

In Figure 4.39, perlite effect on heat evolution was investigated when there is 2 % Na_2SO_4 in the mixtures. As the perlite increases, the rate of heat evolution decreases and two peaks starts to occur. Besides, increased perlite quantity decreases the heat of evolution.

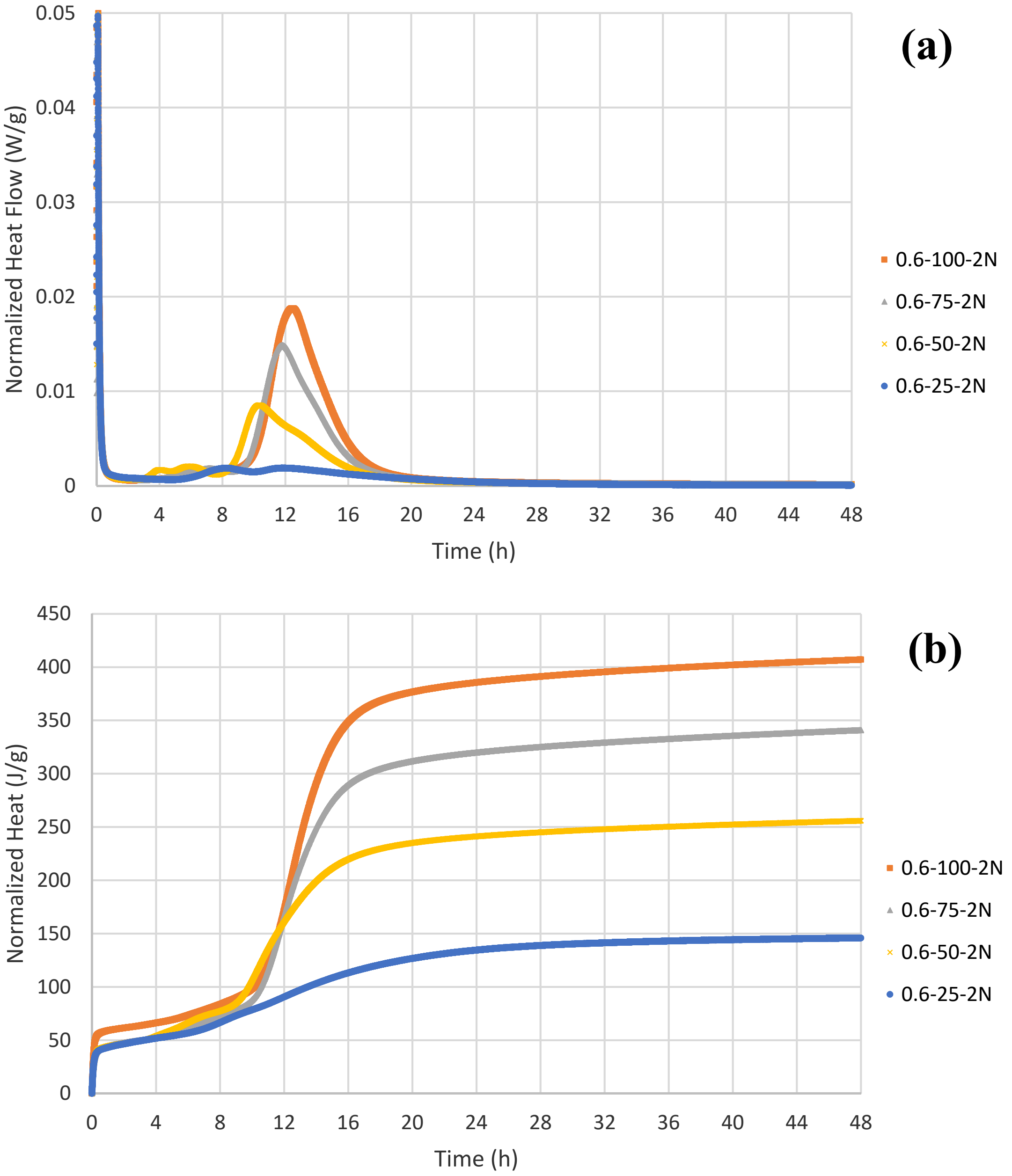

Figure 4.39 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.6 and with Na_2SO_4)

In Figure 4.40, the influence of perlite quantity on peak time is shown.

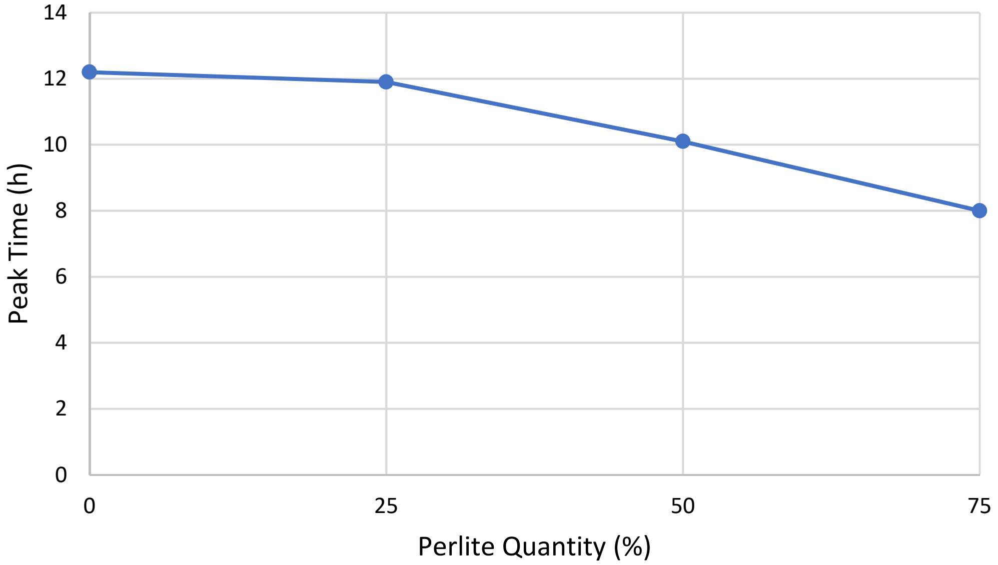

Figure 4.40 Influence of perlite quantity on peak time (W/CM = 0.6 and with Na_2SO_4)

As shown in Figure 4.41, 1 % $Ca(OH)_2$ in the system cause the hydrations to start at the almost same time whatever the amount of perlite.

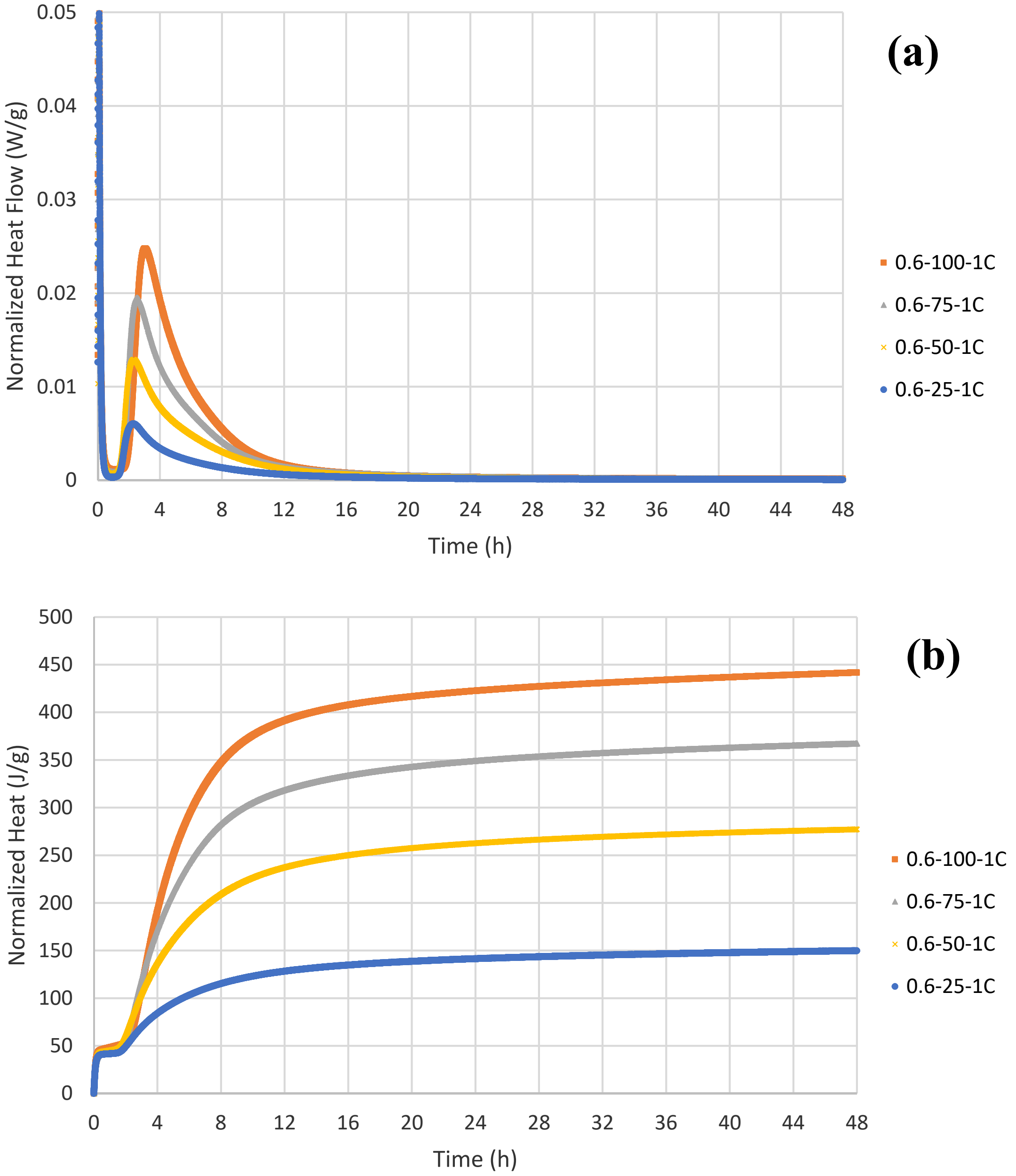

Figure 4.41 Influence of perlite quantity on (a) normalized heat flow, (b) normalized heat (W/CM = 0.6 and with $Ca(OH)_2$)

Influence of perlite quantity on peak time is shown in Figure 4.42.

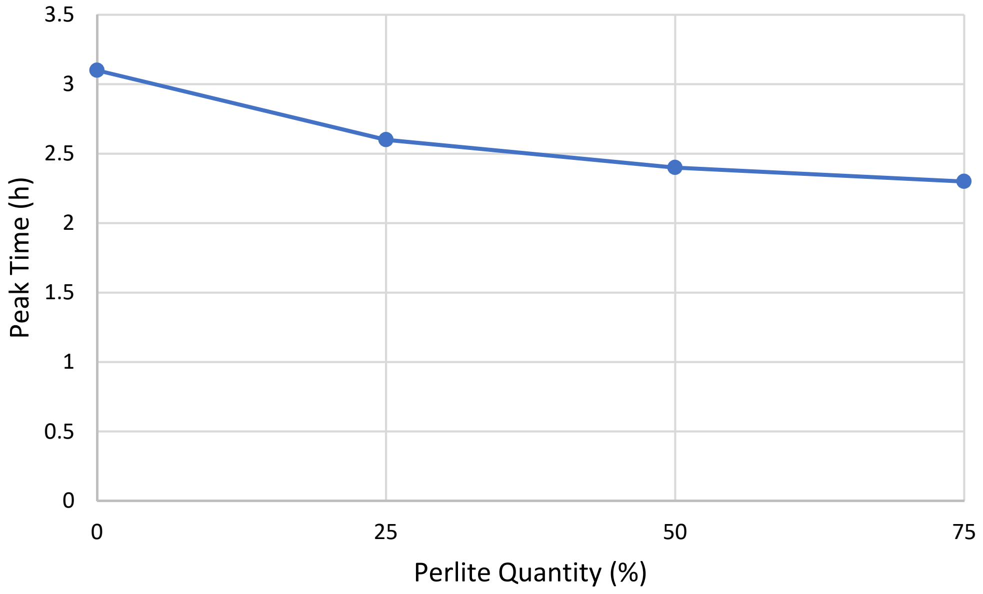

Figure 4.42 Influence of perlite quantity peak time (W/CM = 0.6 and with $Ca(OH)_2$)

The influence of W/CM on normalized heat and normalized heat flow is illustrated in Figure 4.43. Main peak times are similar in both W/CM. However, normalized heat is lower when W/CM=0.4 in all cases.

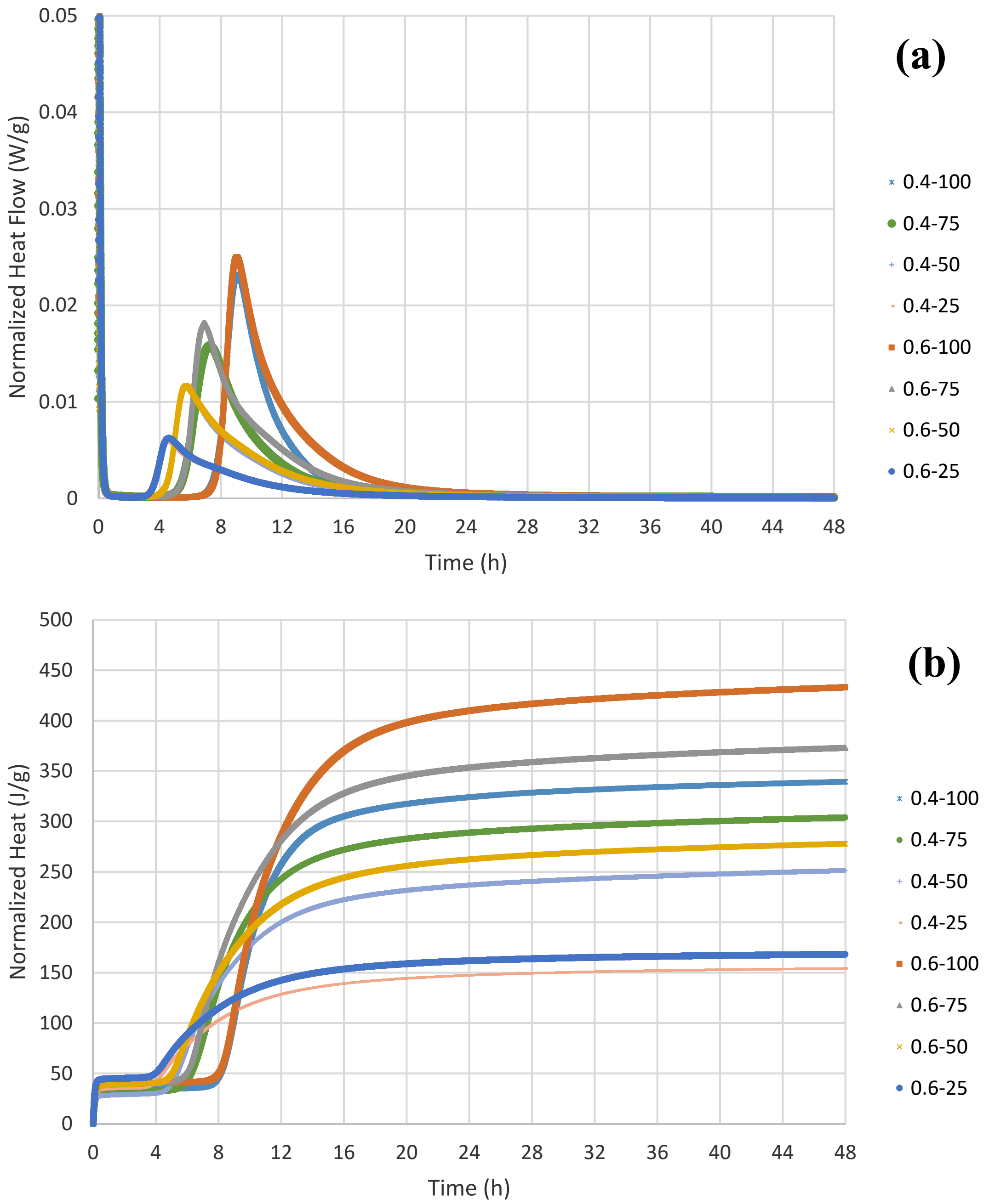

Figure 4.43 Influence of W/CM (a) normalized heat flow, (b) normalized heat (no chemical)

4.5 Thermal Analyses (DTA/TGA)

The thermal analysis of the reference (no perlite or additives) mixture is given in Figure 4.44. Three distinct temperatures at which mass loss due to dehydration are observed. The first loss of about 15 % from ~ 100 to 200 °C. This loss is associated with CAH_{10} (Kırca, 2006). The next mass loss occurs at ~ 300 °C and corresponds to about 5-10 %. This loss is probably associated with the dehydration of C_2AH_8 (Kırca, 2006). The last happens at ~ 700 °C is only 2-3 %. This is probably related to decarbonation of $CaCO_3$ (Moropoulou et al., 2004). Approximately 27 % of mass is lost in total and most of this takes place up to 400 °C.

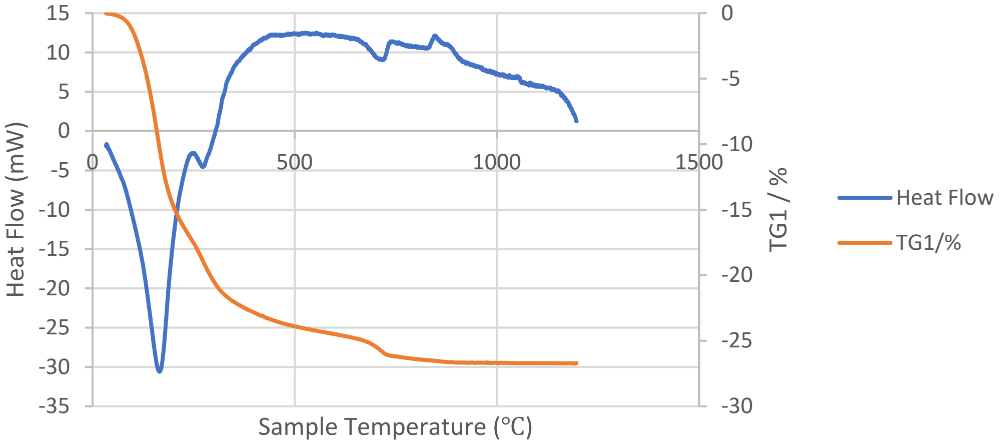

Figure 4.44 Thermal analysis of 0.4-100

The thermal analysis of 0.4-50 is given in Figure 4.45. There are two main mass losses centered around 275 °C and 762 °C, respectively. Also, there is an approximately 6 % mass loss between 650-800 °C. It is seen that 50 % perlite addition suppresses the main CAC hydration product peak. Only 3-4 % mass loss is seen from 100 to 200 °C and the mass loss from 200 to 300 °C is also small. The loss at 600-800 °C however is ~ 6 %. A smaller total mass loss of ~ 18 % indicates a stabler hydrated paste with less bound water.

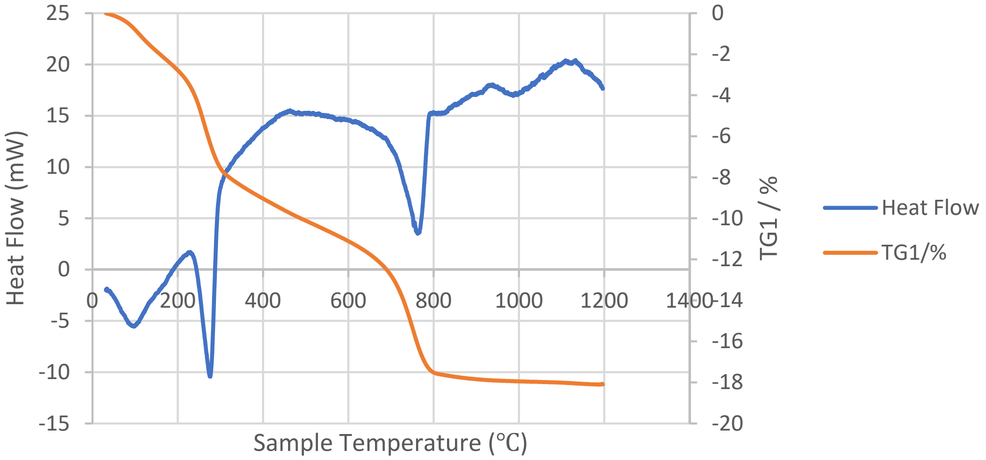

Figure 4.45 Thermal analysis of 0.4-50

The thermal analysis of 0.4-100-2N is given in Figure 4.46. There are two main mass losses centered around 288 °C and 784 °C, respectively. The total mass loss is almost same that in Figure 4.44. However, this mass loss took place at higher temperatures.

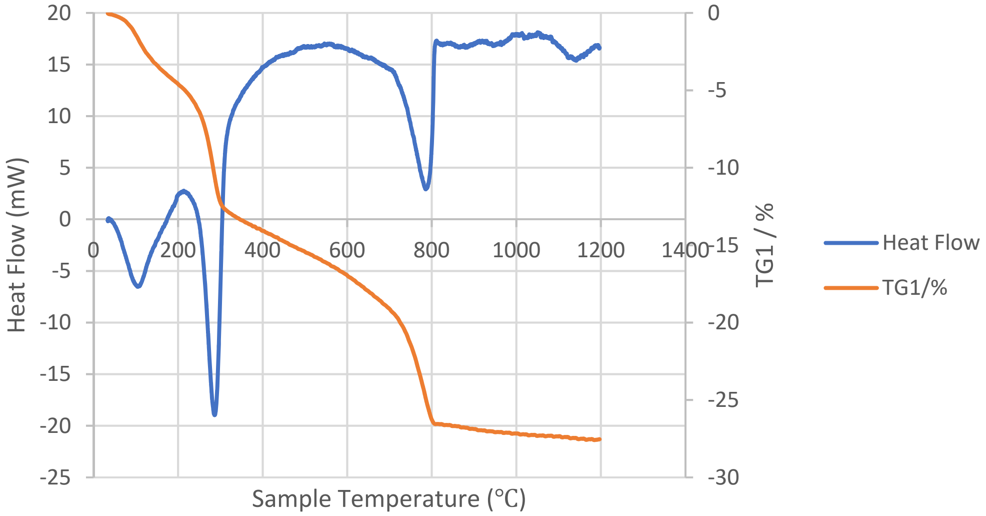

Figure 4.46 Thermal analysis of 0.4-100-2N

The thermal analysis of 0.4-50-1N is given in Figure 4.47. The main mass loss with a maximum at 148 °C. The total mass loss almost same that in Figure 4.45. But, this mass loss took place at lower temperatures.

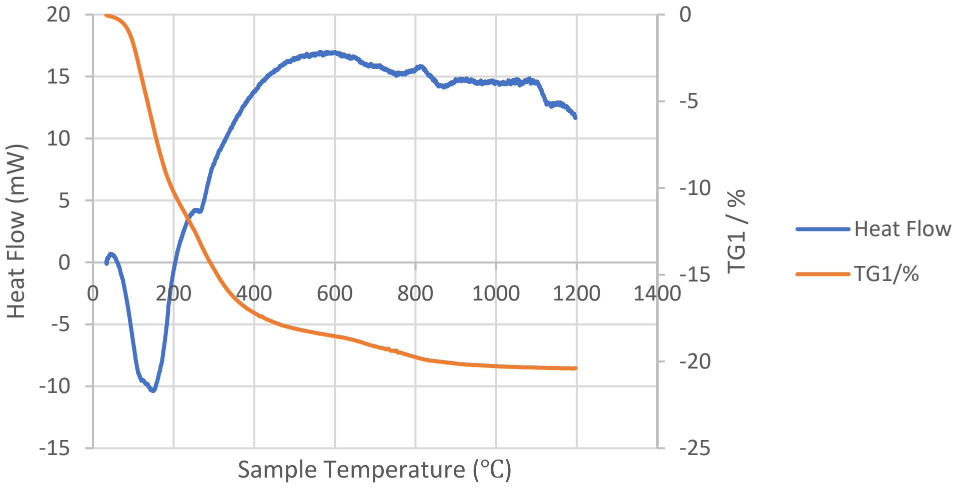

Figure 4.47 Thermal analysis of 0.4-50-1N

Figure 4.46 and Figure 4.47 show that the addition of small quantities of Na_2SO_4 doesn't significantly change the nature of the hydration products.

The thermal analysis of 0.4-50-2N is given in Figure 4.48. It shows three DTA peaks centered around 109 °C, 276 °C, 751 °C. The main difference between Figure 4.47 and Figure 4.48 appears to be the amount of mass loss at ~ 750 °C, greater for 0.4-50-2N.

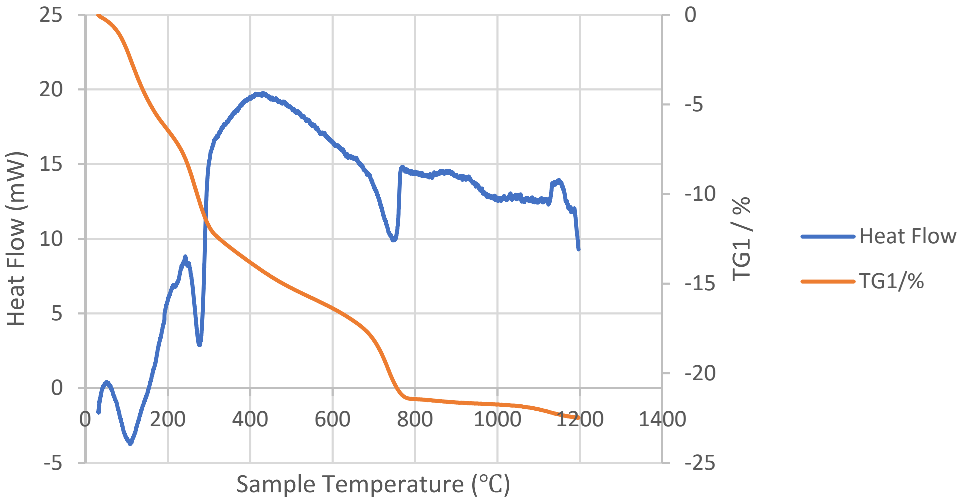

Figure 4.48 Thermal analysis of 0.4-50-2N

In Figure 4.49, the thermal analysis of 0.4-100-1C is given. There are two main mass losses centered at 283 °C and 762 °C, respectively. When compared with Figure 4.44, the total mass approximately equal. But, it is seen that existence of $Ca(OH)_2$ in the mixture shifts the mass loss to higher temperatures.

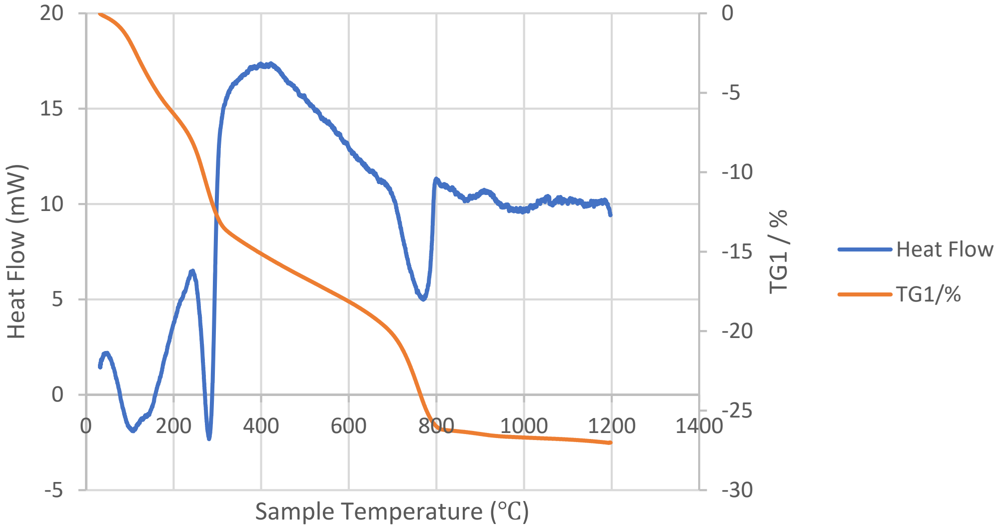

Figure 4.49 Thermal analysis of 0.4-100-1C

In Figure 4.50, the thermal analysis of 0.4-50-0.6C is given. There are two main mass losses at 272 °C and 750 °C, respectively. It is similar to Figure 4.49. But, the total mass loss is lower.

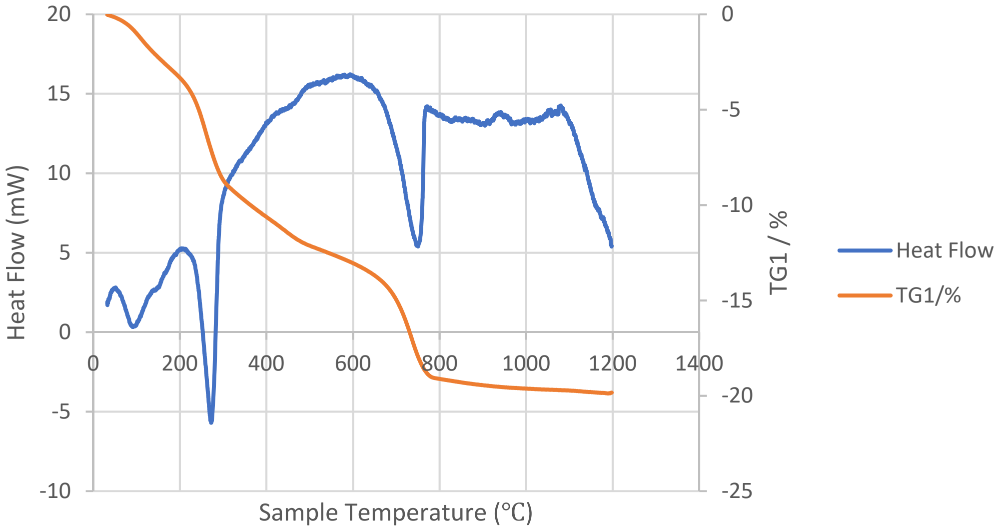

Figure 4.50 Thermal analysis of 0.4-50-0.6C

The thermal analysis of 0.6-100 is given in Figure 4.51. It shows three peaks at around 165 °C, 283 °C, 728 °C. When compared with Figure 4.44, all peaks are similar. The total mass loss is 2 % lower.

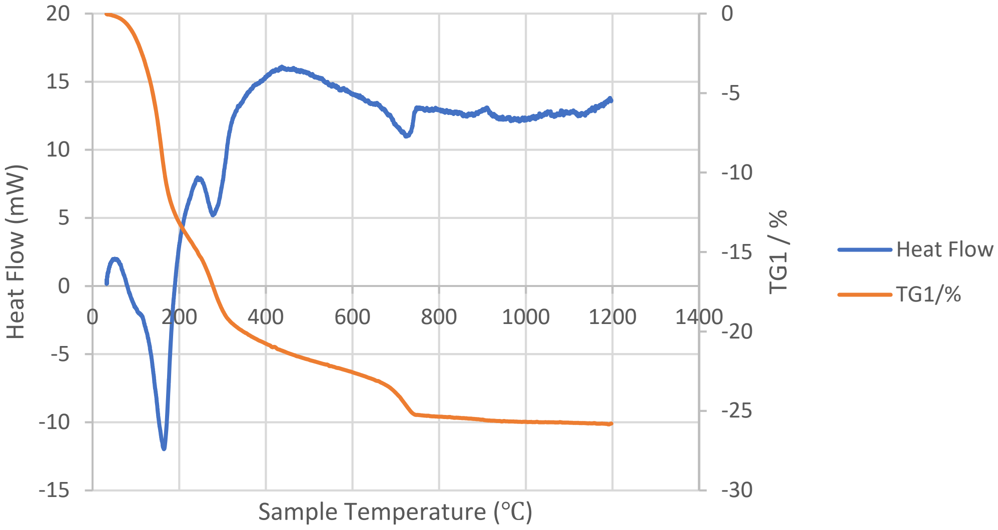

Figure 4.51 Thermal analysis of 0.6-100

The thermal analysis of 0.6-50 is given in Figure 4.52. It shows three peaks around 90 °C, 268 °C, 739 °C. The DTA peak temperatures and mass loss are similar to those of 0.4-50.

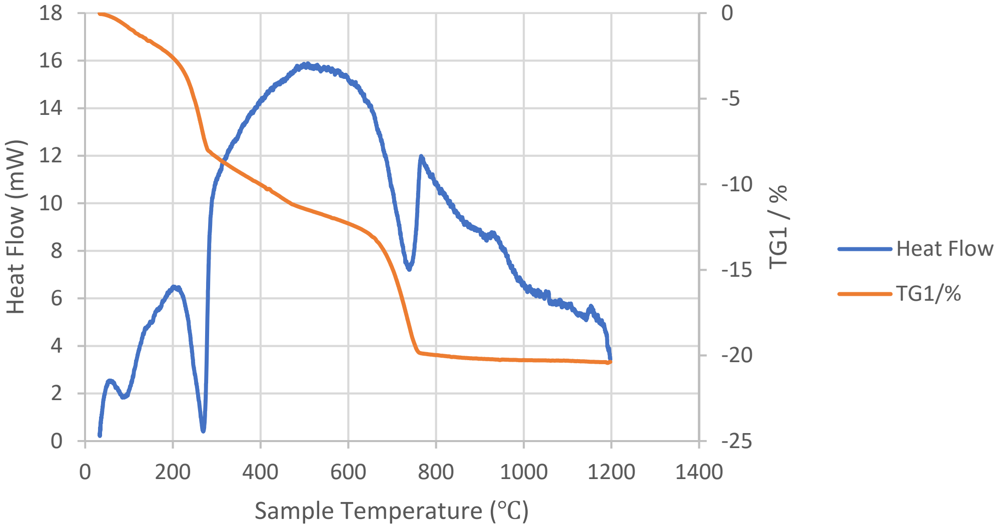

Figure 4.52 Thermal analysis of 0.6-50

The thermal analysis of 0.6-100-2N is given in Figure 4.53. There are three main mass losses around 117 °C, 277 °C, 748 °C, respectively. The total mass loss reaches ~ 30 %, greater than for 0.6-100.

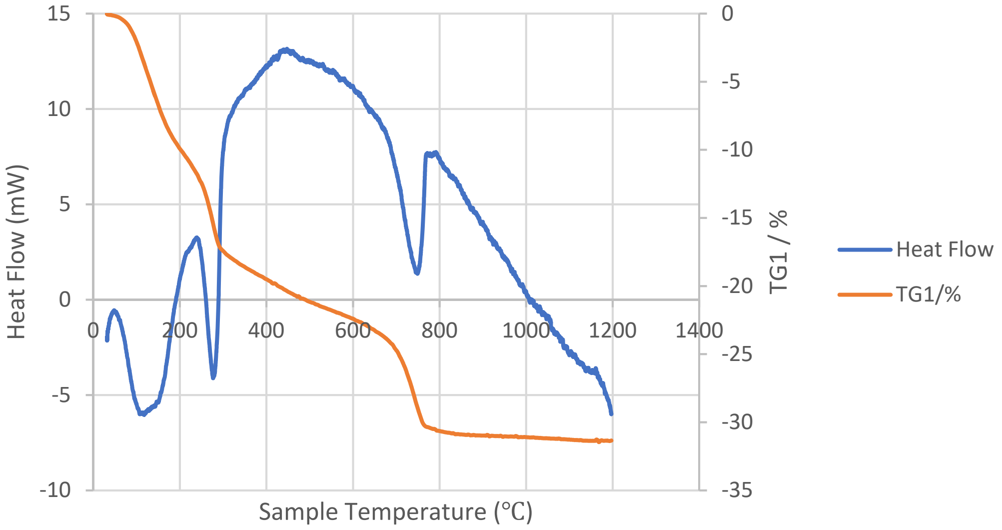

Figure 4.53 Thermal analysis of 0.6-100-2N

In Figure 4.54, the thermal analysis of 0.6-50-1N is given. It shows three peaks around 88 °C, 271 °C, 750 °C. It is highly similar to Figure 4.52 which contains no Na_2SO_4.

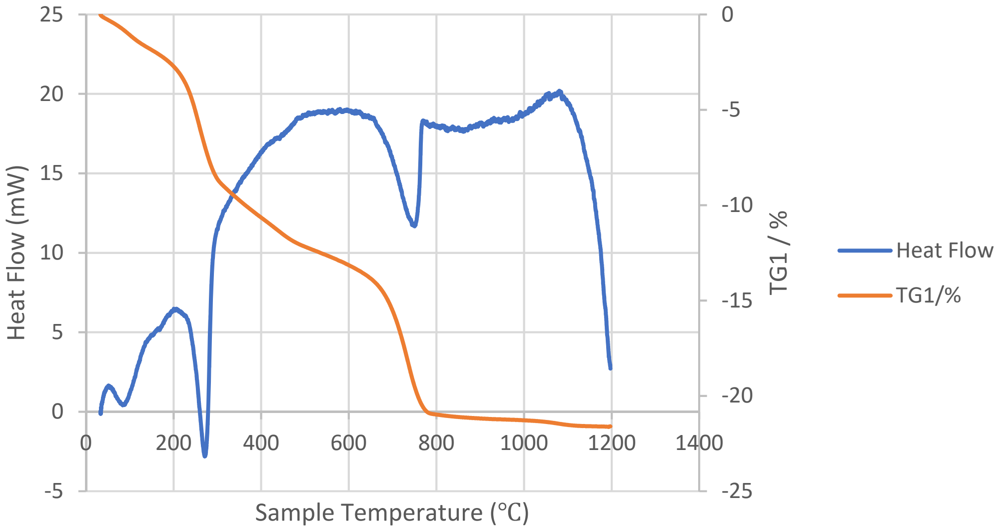

Figure 4.54 Thermal analysis of 0.6-50-1N

The thermal analysis of 0.6-100-1C is given in Figure 4.55. There are three main mass losses around 111 °C, 274 °C, 748 °C, respectively. When compared with Figure 4.51, the peaks locations are close, the mass loss is higher.

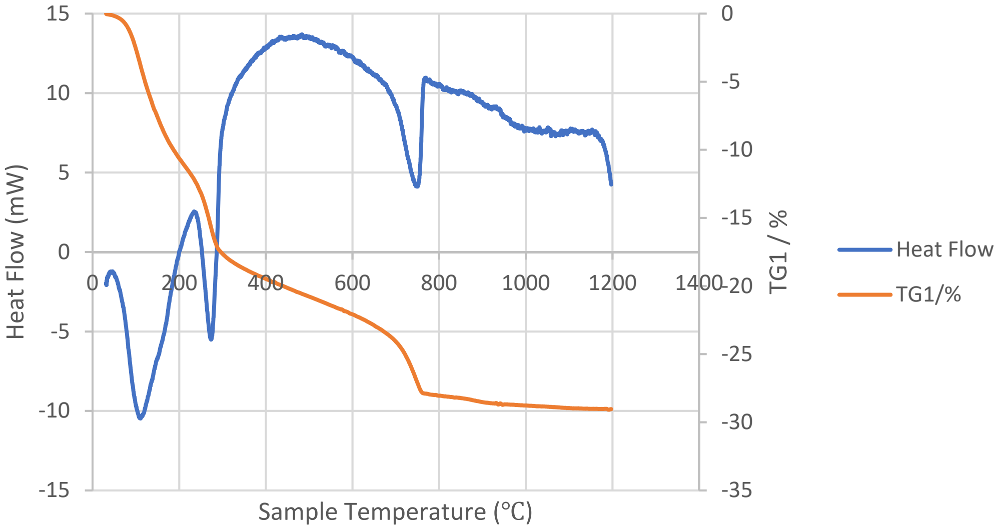

Figure 4.55 Thermal analysis of 0.6-100-1C

The thermal analysis of 0.6-50-0.6C is given in Figure 4.56. There are three main mass losses around 93 °C, 261 °C, 721 °C, respectively. When compared with Figure 4.52, the peaks locations and the total mass are similar.

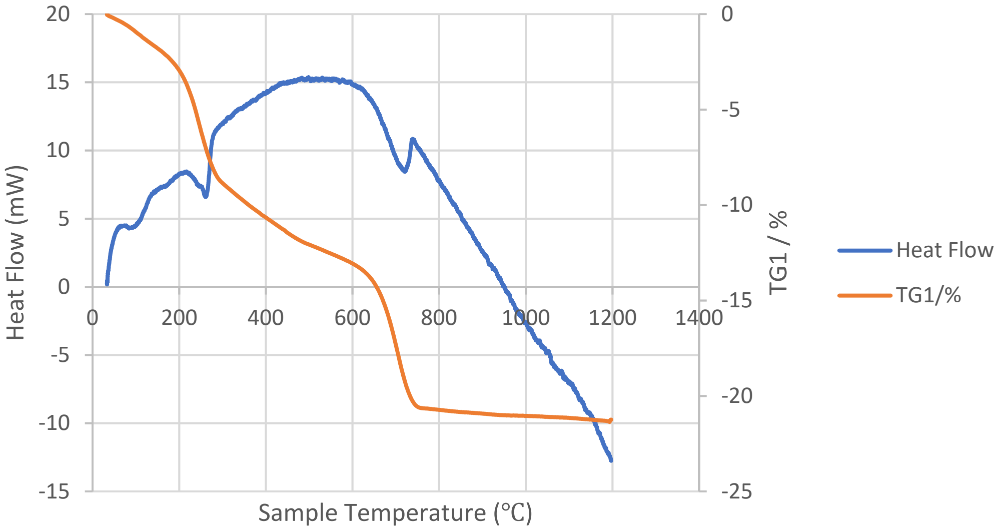

Figure 4.56 Thermal analysis of 0.6-50-0.6C

In general, the addition of ground perlite appears to produce a hydrated paste that loses a lower fraction of its mass due to dehydration. While this would hint of a staller system, it could also be the result of dilution of the CAC and the ground perlite remaining relatively unaffected by the heating up to 1200 °C, since it doesn’t contain more than ~ 3 % in its structure typically.

4.6 XRD Analysis

Within the scope of this thesis, 288 XRD analyses were performed. However, many of the diffractograms are quite similar to each other due to the materials and curing conditions being the same. Therefore, XRD results belonging to four mixtures are given: 0.4-100 (the reference mixture), 0.4-50, 0.4-50-1N and 0.4-50-0.6C. Results for both dry and wet cured samples have been given for each.

The phases observed in the X-ray diffractograms were designated with letters as given in Table 4.5.

Table 4.5 Letters used to represent different phases in the x-ray diffractograms

Designations	Phases
a	CA
b	C_4AF
c	$C_{12}A_7$
d	CAH_{10}
e	C_3AH_6
f	AH_3
g	C_2ASH_8
h	$C\hat{C}$

XRD patterns for hydrated 0.4-100-D for ages 12h to 90d are given in Figure 4.57. CAH_{10} appears to form after 24h and grows in amount afterwards. This is accompanied by the natural decrease in CA. Not much C_2AH_8 appears to form at this low temperature. No evidence of C_3AH_6, the product of conversion is seen either.

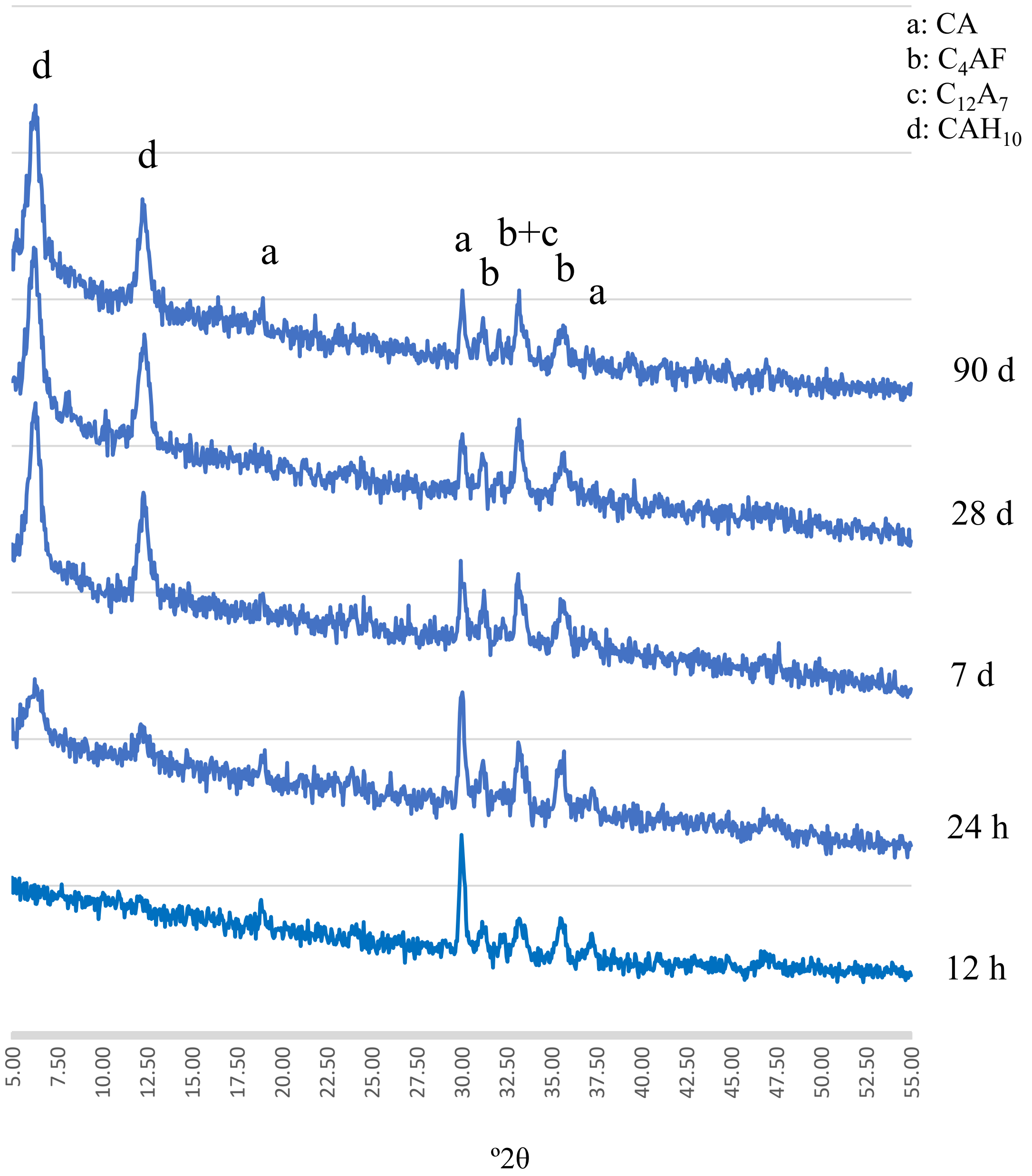

Figure 4.57 XRD pattern of 0.4-100-D

XRD patterns for 0.4-100-W are given in Figure 4.58. Under wet curing at 40 °C, CAH_{10} is observed from 24h to 7d. Beyond ~ 7d, C_3AH_6 and AH_3 are observed indicating conversion of CAH_{10}. Hence, a sharp strength loss is observed after this time (see Figure 4.1b).

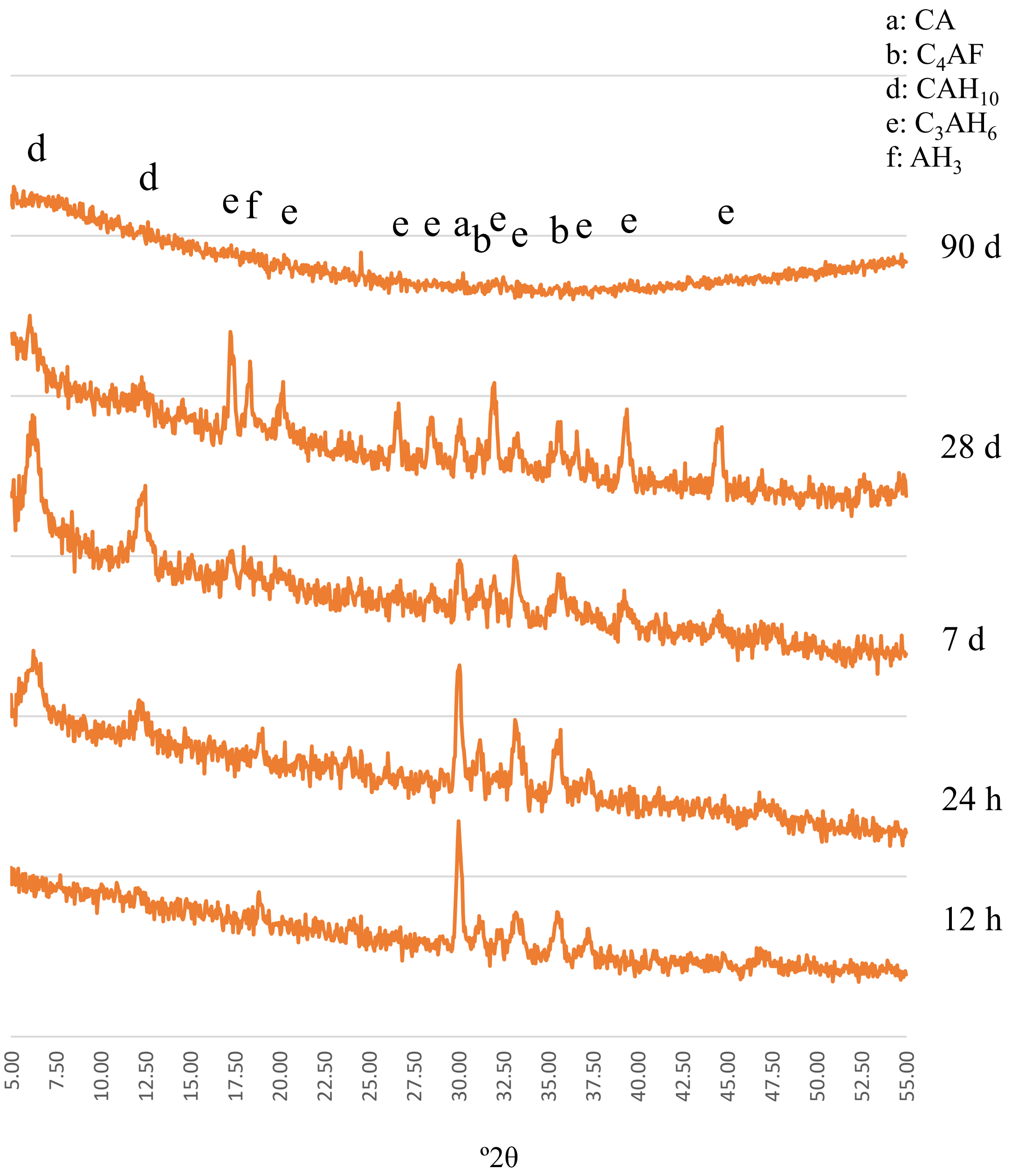

Figure 4.58 XRD pattern of 0.4-100-W

XRD patterns for 0.4-50-D are given in Figure 4.59. CAH_{10} is observed as early as 24h and its content grows with time. Also, AH_3 is observed beyond 28d in small quantities.

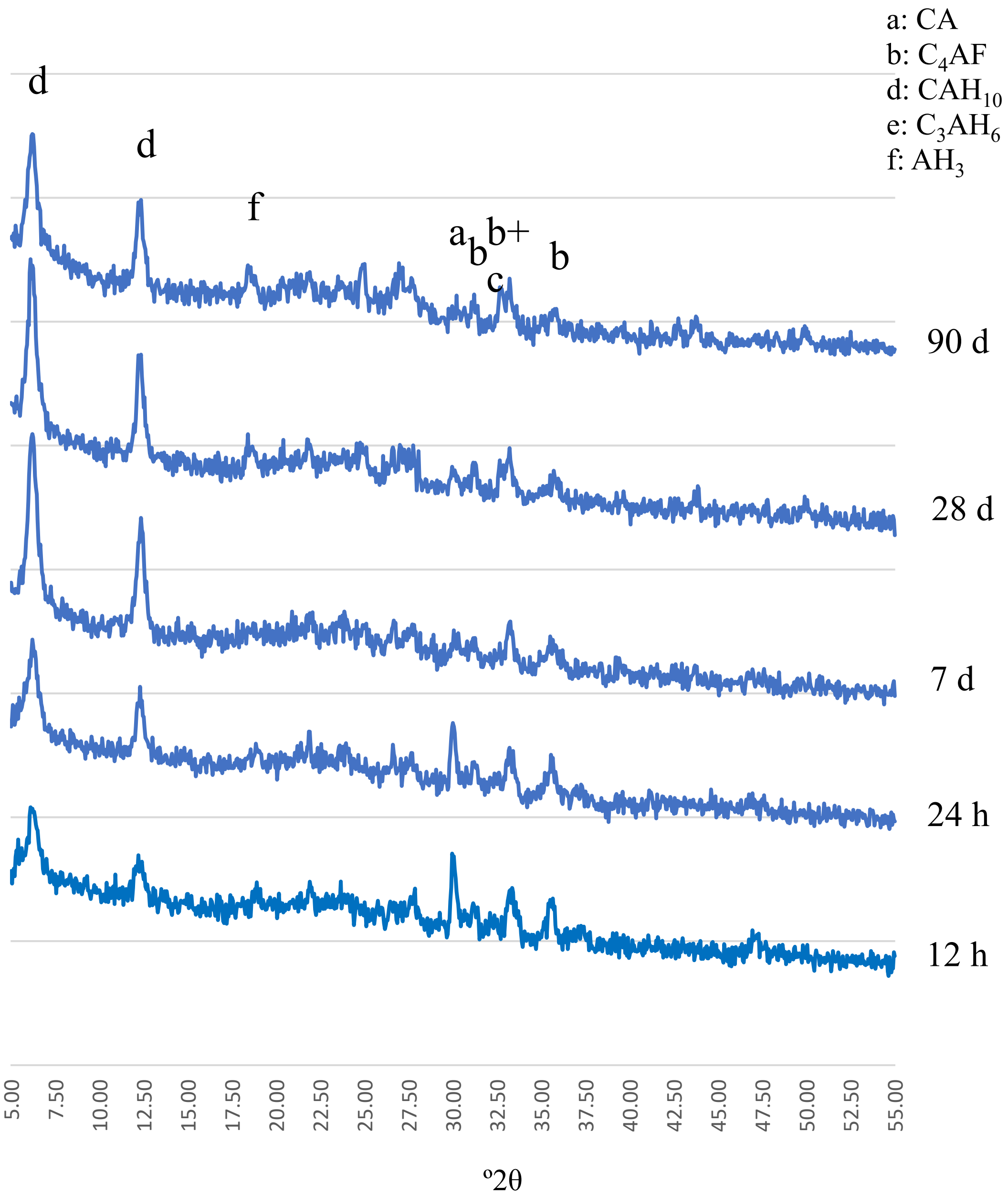

Figure 4.59 XRD pattern of 0.4-50-D

For 0.4-50-W (Figure 4.60) CAH_{10} is observed very early. From 7d, C_2ASH, the stable reaction product, is also observed. As expected, not much strength loss occurs after this time (Figure 4.4b). No C_3AH_6 is observed for this paste.

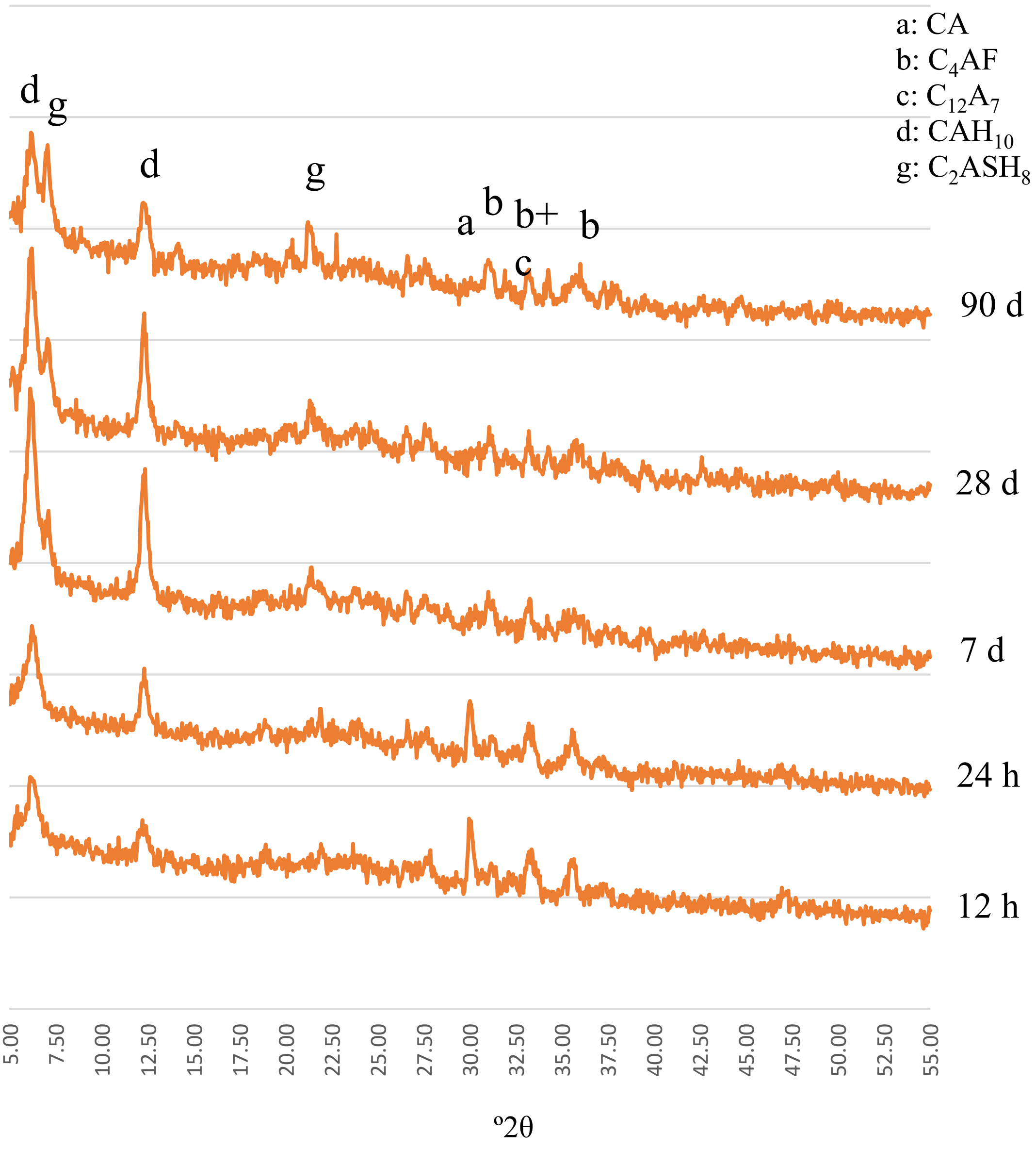

Figure 4.60 XRD pattern of 0.4-50-W

XRD patterns for 0.4-50-1N-D are given in Figure 4.61. Again, CAH_{10} is observed from 24h to 28d. From 28d, AH_3 was observed. With the addition of 1 % Na_2SO_4, the disappearance of CAH_{10} and the appearance of AH_3 more complete. At 90d, calcium carbonate is observed. This late product is likely formed by the carbonation of the calcium aluminate hydrates, supported by the disappearance of CAH_{10}, from 28d to 90d. Fernández-Carrasco et al. (2001) also reported the formation of vaterite and aragonite in CAC pastes after several months.

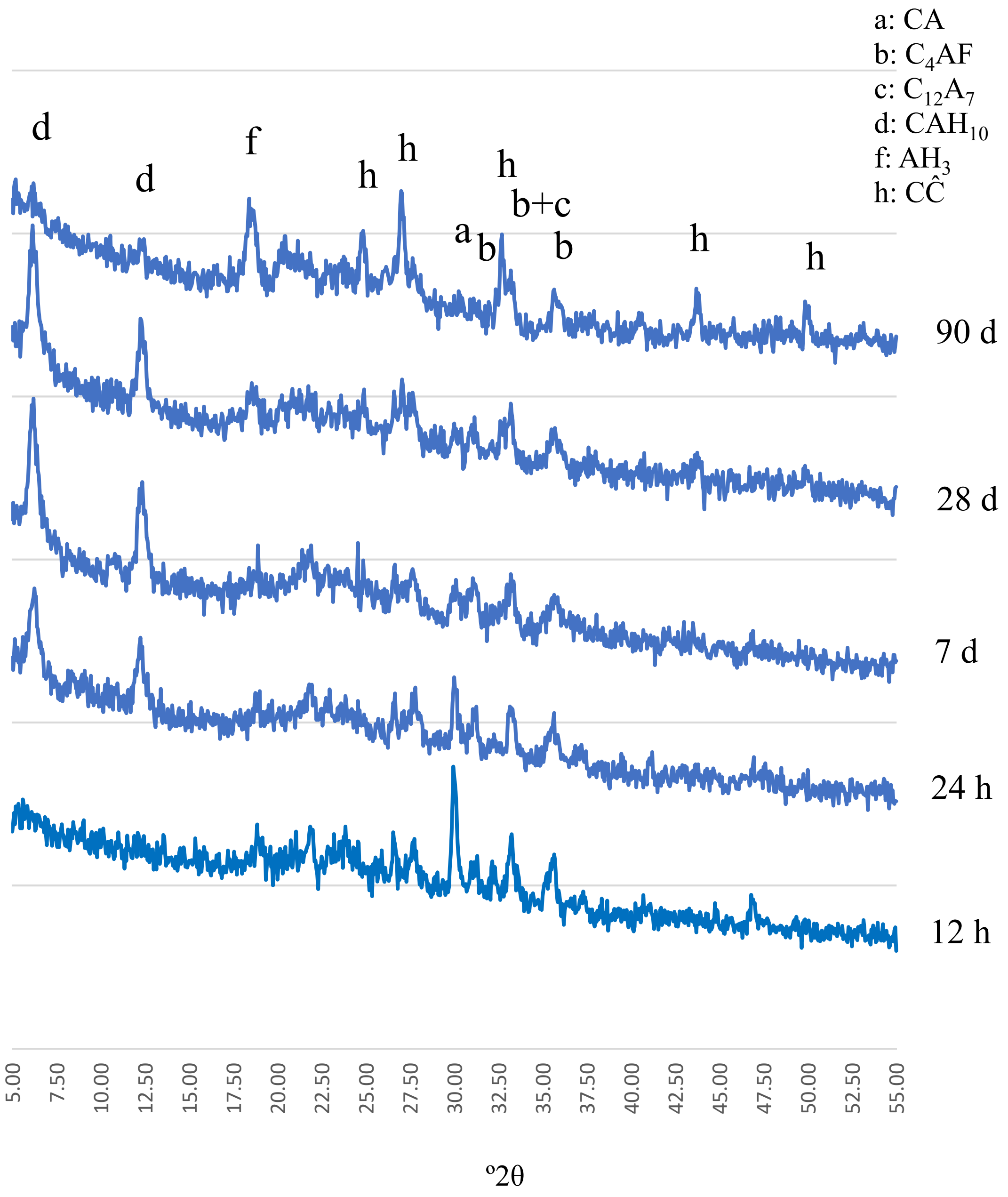

Figure 4.61 XRD pattern of 0.4-50-1N-D

XRD patterns for 0.4-50-1N-W are given in Figure 4.62. Once again, CAH_{10} is observed from 24h to 28d. Similar to in 0.4-50-W from 7d, C_2ASH_8 is observed. At 28th and 90th days, it dominates all other hydration product. The presence of C_2ASH_8 clearly explains the compressive strength results in Figure 4.4b. There is no strength loss beyond ~ 14d.

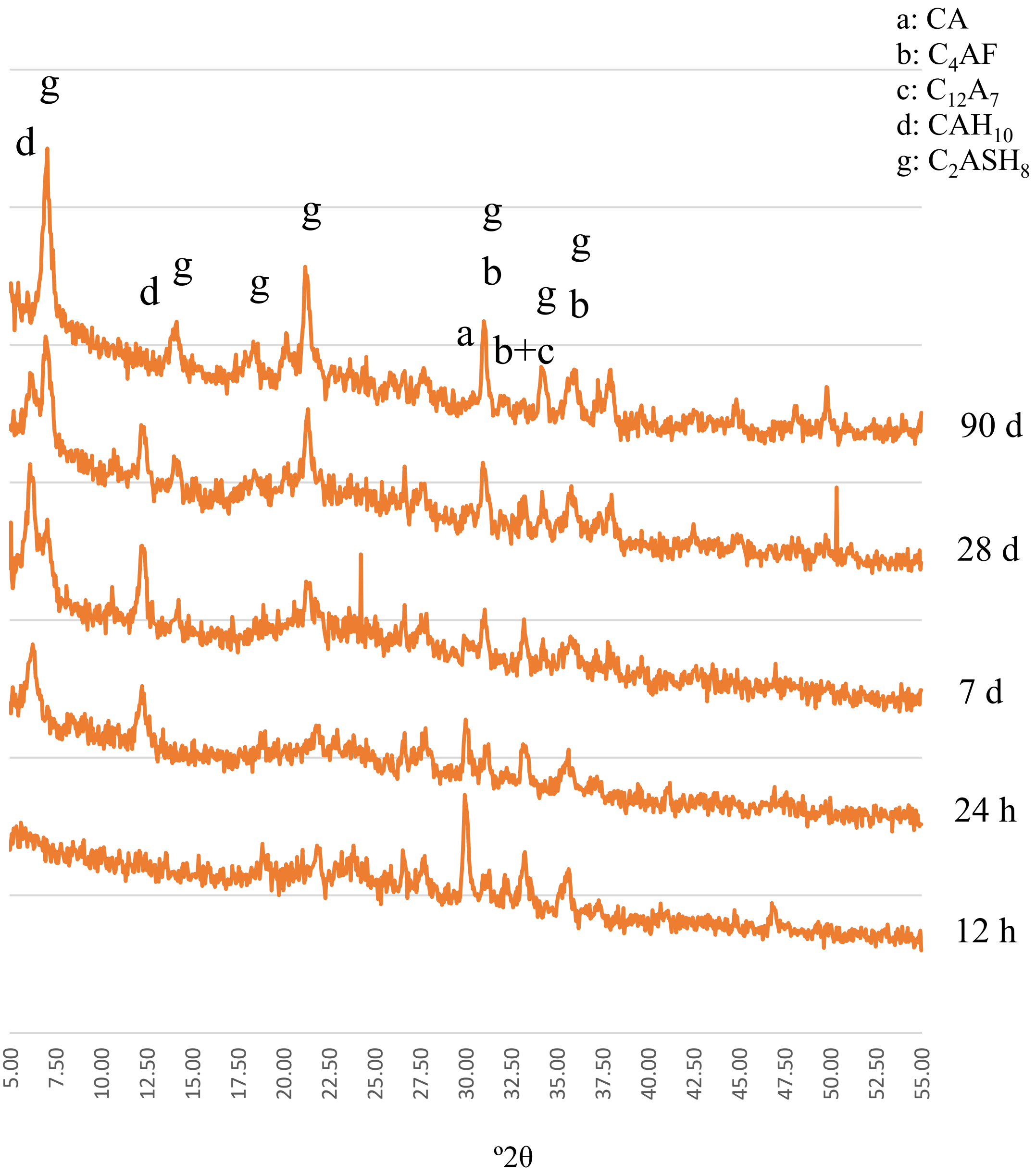

Figure 4.62 XRD pattern of 0.4-50-1N-W

XRD patterns for 0.4-50-0.6C-D are given in Figure 4.63. According to the results, CAH_{10} is observed from the 12th hour. From 7d, C_2ASH_8 and C_3AH_6 were also observed, but they are quite limited in amount. Compared with 0.4-50-D (Figure 4.59), some C_2ASH_8 is formed and the overall rate of hydration of CA to CAH_{10} appears increased, based on the diffractograms at 12h and 24h.

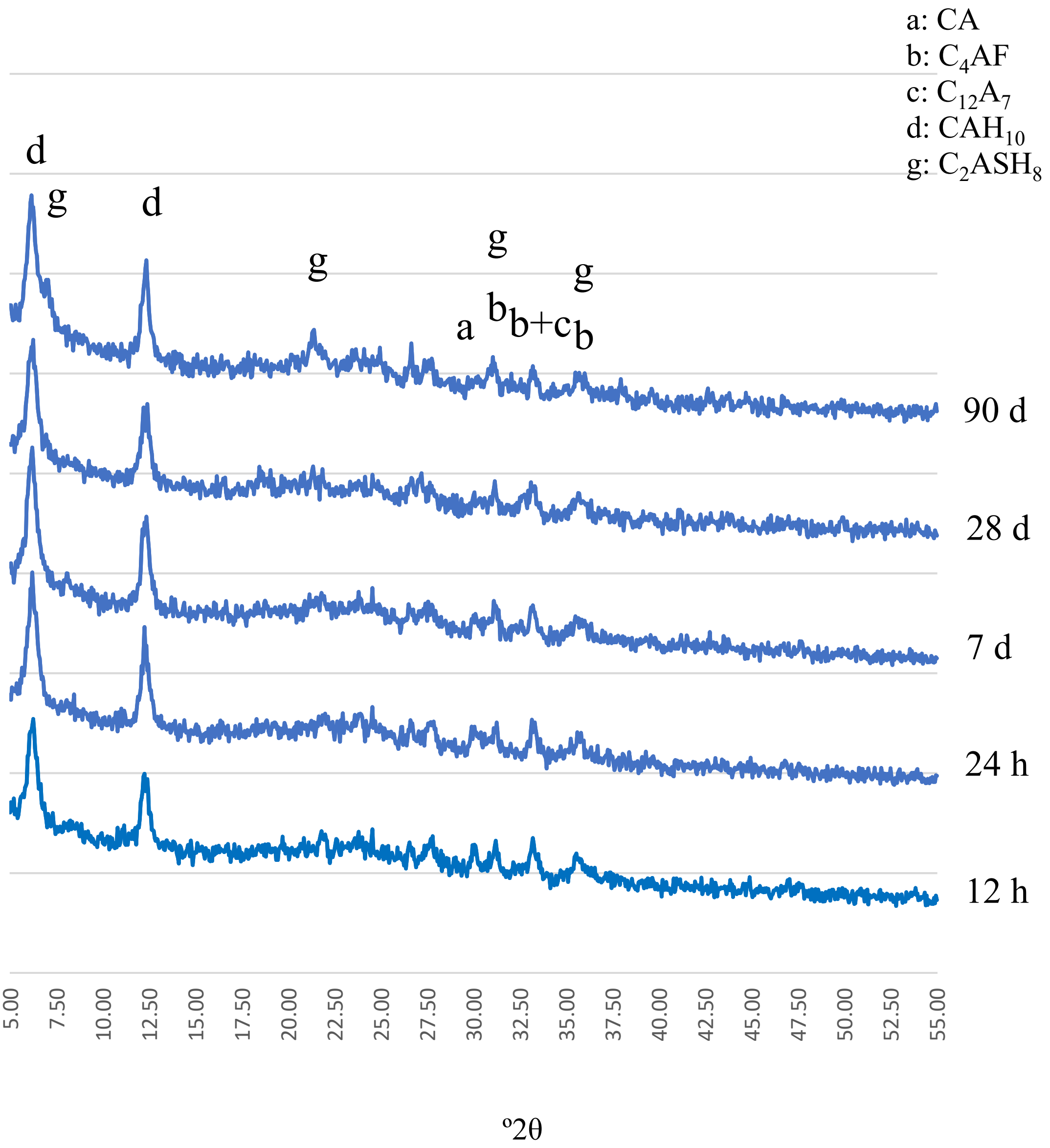

Figure 4.63 XRD pattern of 0.4-50-0.6C-D

The influence of the addition of $Ca(OH)_2$ to the XRD pattern 50 % perlite mixture (0.4-50-0.6C-W) is in Figure 4.64. CAH_{10} is observed from 24h to 28d. From 7d, C_2ASH_8, C_3AH_6 and AH_3 were observed. Although strätlingite is formed, its intensity is low indicating limited content. As such, conversion cannot be prevented (Figure 4.4). In fact, the loss is greater, and it is seen in Figure 4.64 that the C_3AH_6 is much greater than in 0.4-50-W (Figure 4.60).

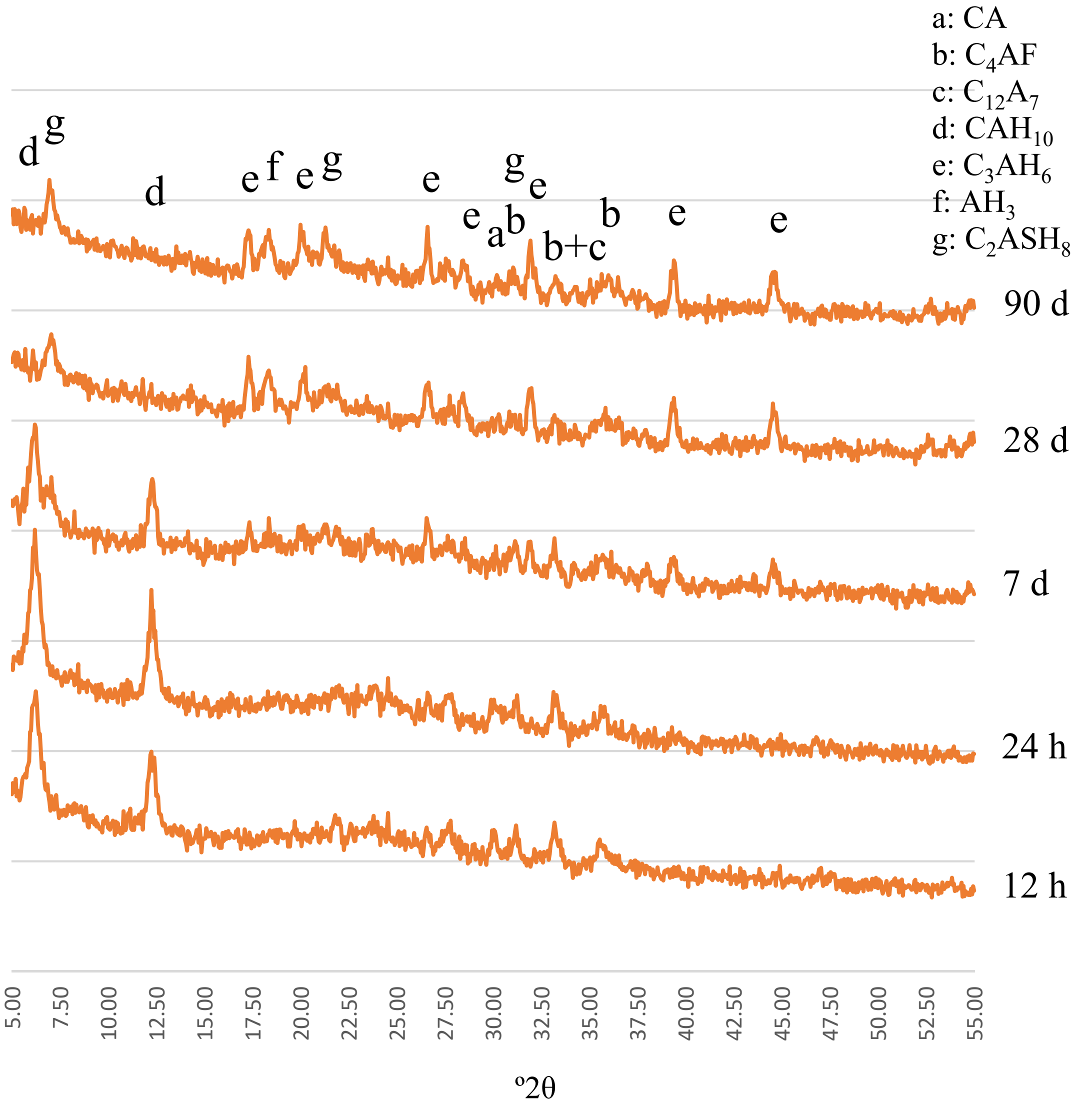

Figure 4.64 XRD pattern of 0.4-50-0.6C-W

In Figure 4.65, the influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern for dry pastes is shown. C_2ASH_8 was not observed in any mixtures below. There is slight strength decrease from 14d to 90d in 0.4-100-D and 0.4-100-2N-D. In 0.4-100-1C-D, it was observed from 7d to 28d.

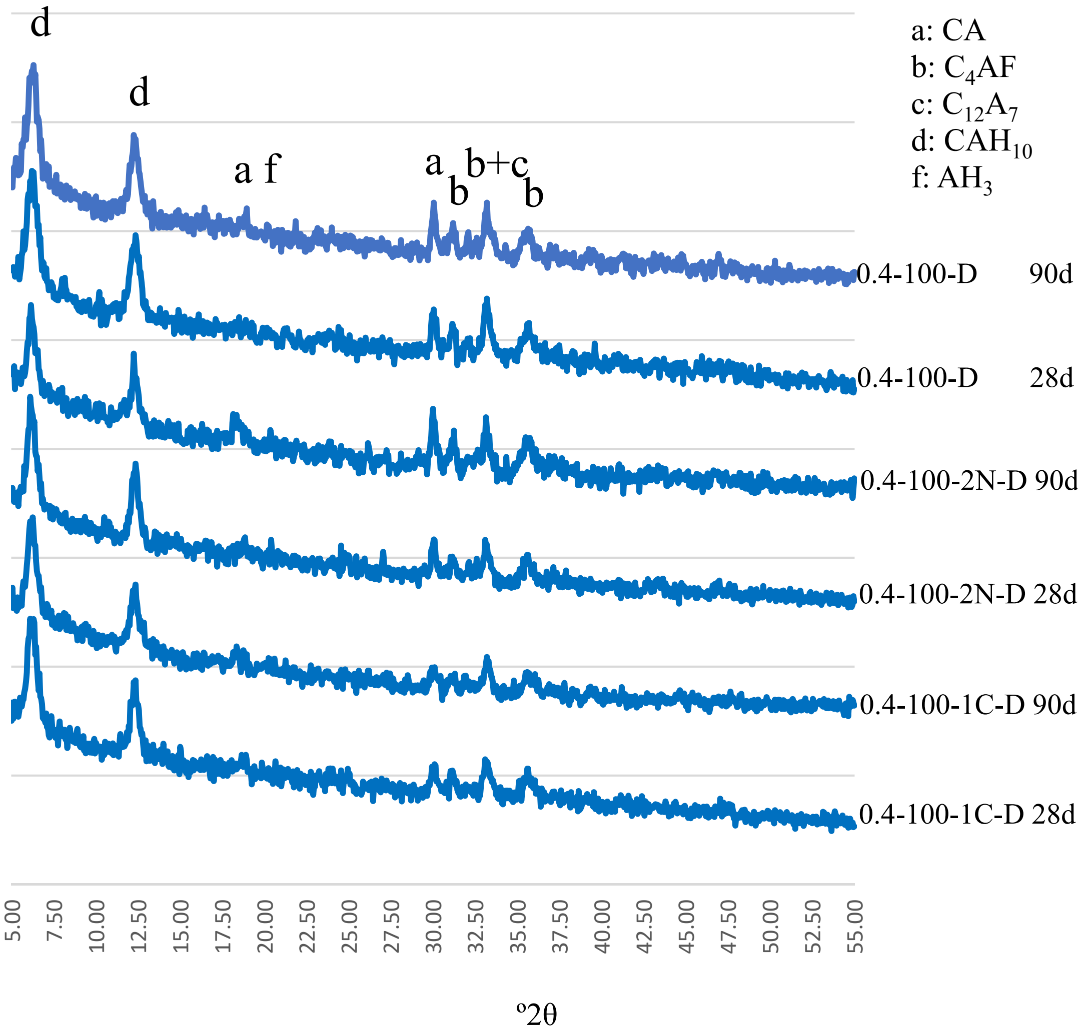

Figure 4.65 Influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern (W/CM = 0.4 and 100 % CAC - dry)

In Figure 4.66, the influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern for wet pastes is shown. While the strengths of 0.4-100-W and 0.4-100-1C-W decrease from 48h to 14d, the strength decrease of 0.4-100-2N-W is between 48h to 28d. After that, the strengths of all mixtures slightly increase to 90d.

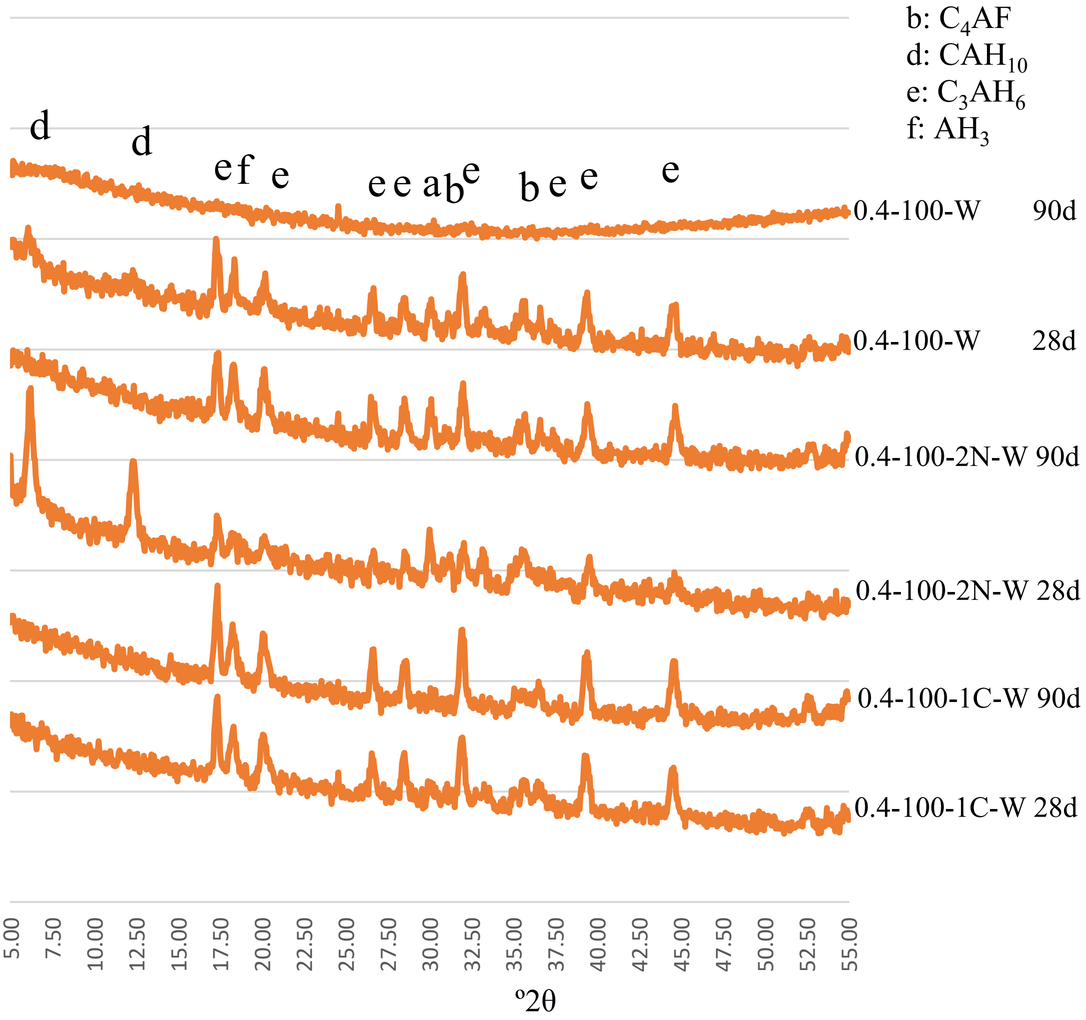

Figure 4.66 Influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern (W/CM = 0.4 and 100 % CAC - wet)

In Figure 4.67, the influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern for dry pastes with 50 % perlite is shown. C_2ASH_8 was not observed in any mixtures below. In all mixtures below, strength loss was observed from 14d to 90d.

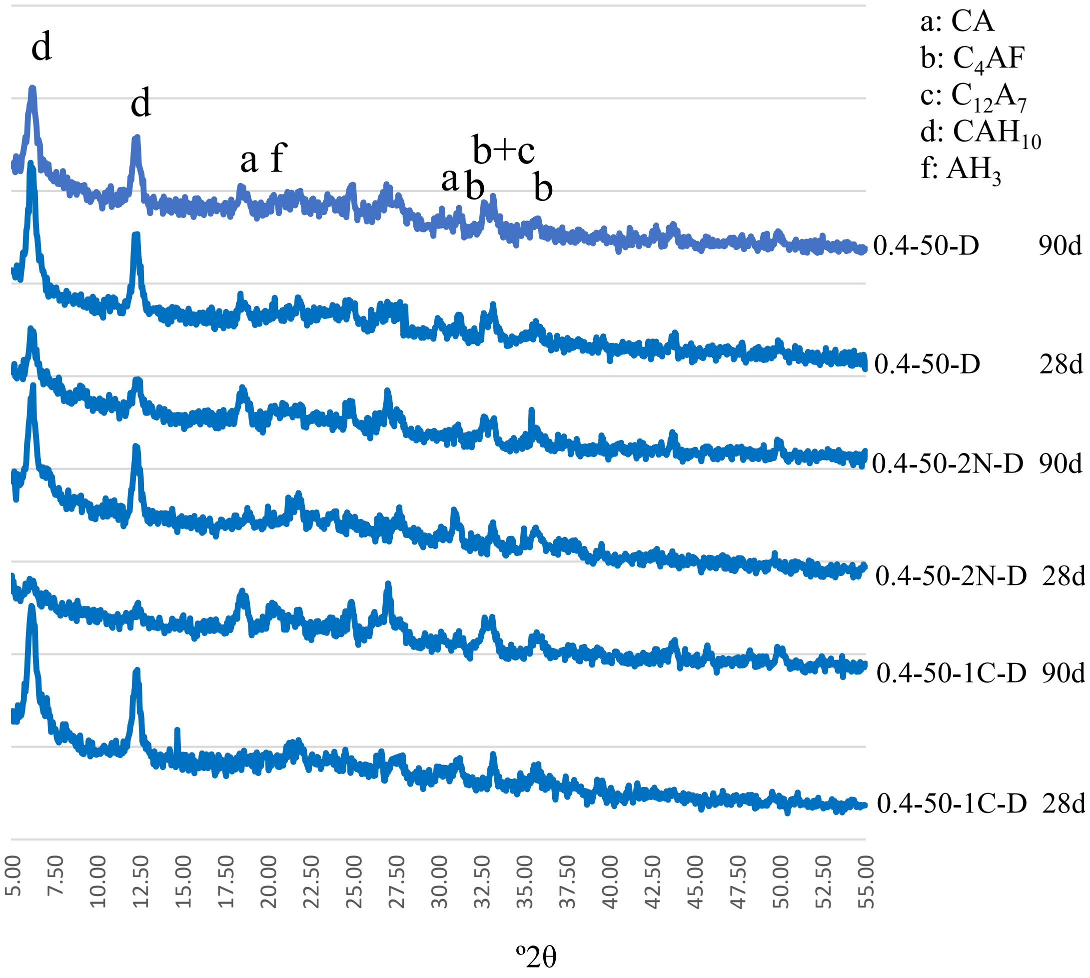

Figure 4.67 Influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern (W/CM = 0.4 and 50 % CAC - dry)

In Figure 4.68, the influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern for wet pastes with 50 % is shown. In all mixtures below, C_2ASH_8 was observed. But, the peak heights of C_2ASH_8 are different. Therefore, while a strength gain was observed in 0.4-50-2N-W, there is a strength loss in 0.4-50-W and 0.4-50-1C-W (see Figure 4.b).

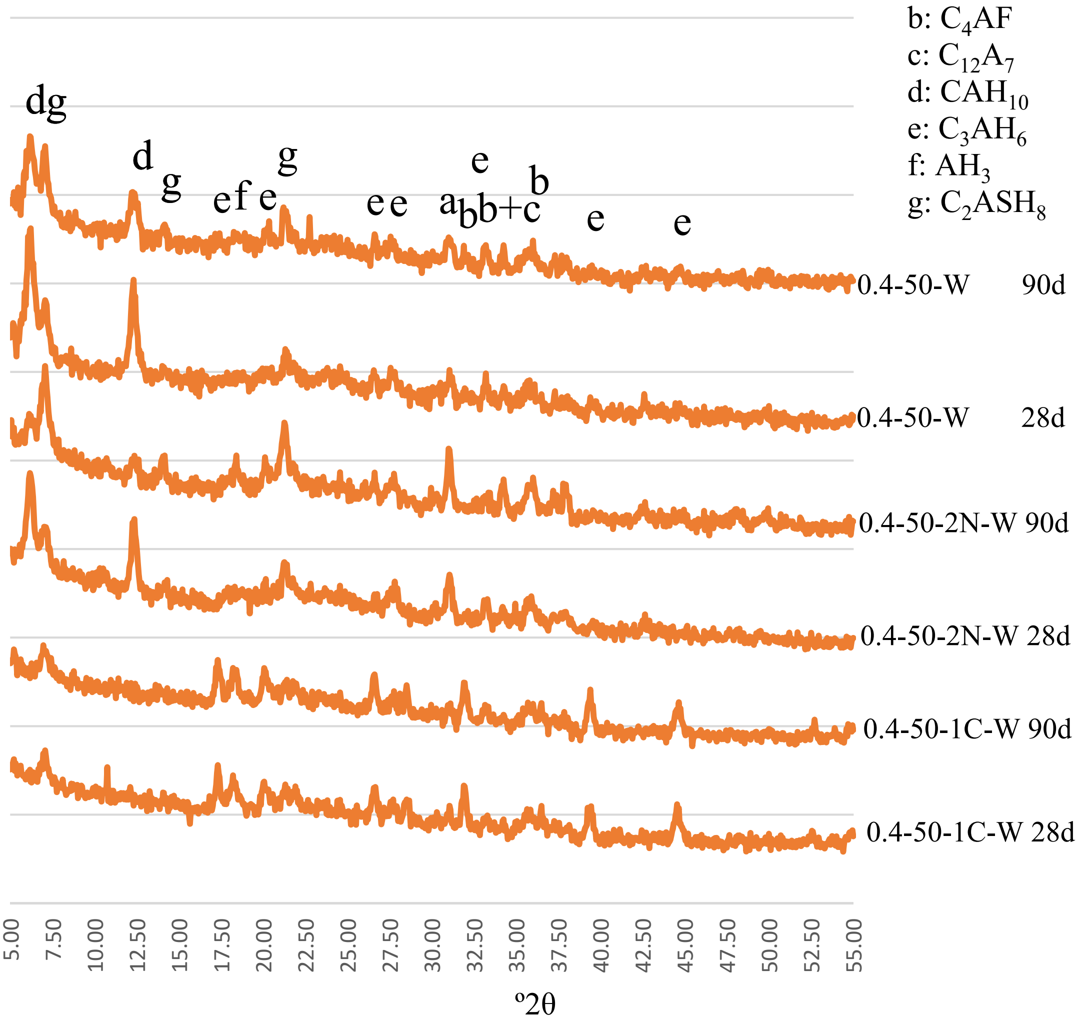

Figure 4.68 Influence of 2 % Na_2SO_4 and 1 % $Ca(OH)_2$ on XRD pattern (W/CM = 0.4 and 50 % CAC - wet)

According to the XRD analyses, strätlingite is formed in wet specimens only. It is mostly formed in the mixtures with 50 % perlite. The compressive strengths of the wet-cured mixtures containing 50 % perlite are ordered as:

mixtures with Na_2SO_4 > mixtures with $Ca(OH)_2$ > mixtures without any chemical

This ranking is not valid for the other mixtures. For the others, the mixtures without any chemical generally have the higher compressive strength (see Section 4.1). The XRD results for mixtures with W/CM = 0.6 are similar to these shown. In general, it can be said that when W/CM increases, the amount of strätlingite that forms decreases.

CHAPTER 5

CONCLUSIONS

5.1 General

In this thesis, the influence of the addition of perlite as an SCM on the hydration and properties of CAC pastes and mortars was investigated. W/CM and curing conditions were varied to study their effect on the chemical conversion of calcium aluminate hydrates. Na_2SO_4 and $Ca(OH)_2$ were added in an attempt to stabilize the hydration products by forming strätlingite and to alter the rate of hydration. Compressive strength, water requirement for normal consistency and setting time tests (of pastes with normal consistency), XRF (on starting materials), XRD, isothermal calorimetry and thermogravimetric analyses were employed and the residual strengths of samples after exposure to high temperatures were determined. Some important findings of this study can be summarized as follows:

1. The addition of 25 % ground perlite to CAC mortars decreases their compressive strength very minimally under dry conditions at 23 °C. The difference is small at early ages under wet conditions at 40 °C but the drop in ultimate strength is roughly proportional to the cement replacement. However, ultimate strengths higher than 30 MPa can be reached, even after the conversion reactions in the wet case. The drop in strength is proportional to perlite content for W/CM = 0.6, for both dry and wet-cured mortars.

2. Na_2SO_4 addition has a beneficial effect mainly for the wet-cured mortars containing greater than 25 % perlite. This is linked to the formation of strätlingite in the system. $Ca(OH)_2$ addition greatly accelerates hydration and

can give greater strengths than the control (no chemical) samples but only up to 3d, after which the effect on strength is generally detrimental.

3. None of the 75 % perlite samples experiences noticeable loss of strength due to conversion, but reach low ultimate strengths of 8-10 MPa for W/CM=0.4 and 2-3 MPa for W/CM=0.6. This is probably due to the limited amount of CAC in the system.

4. None of the CAC-perlite mixtures studied can successfully withstand exposure to either 600 °C or 1100 °C. The control samples lose 20-35 % of their original masses whereas perlite-containing samples lose less, 15-30 %. The use of chemical additives does not appear to help much. In fact, it appears to worsen the performances of most samples studied. The strength losses of the control samples are even greater (up to 90-95 %), and the loss in flexural strength is often much greater than in compressive strength. Perlite-containing samples outperform the control samples when W/CM=0.4 but not when W/CM=0.6.

5. The addition of ground perlite reduces the setting time of CAC pastes, as do Na_2SO_4 and $Ca(OH)_2$. Perlite addition increases water demand. However, when $Ca(OH)_2$ is used water demand is not affected by the perlite quantity.

6. Perlite addition affects the heat of hydration positively. It reduces the total heat and the height of the main hydration peak. Also, the dormant period shortens and the acceleration period starts earlier owing likely to the nucleation effect since the perlite was quite finely ground. While Na_2SO_4 increase the dormant period, $Ca(OH)_2$ decrease it. These chemicals do not affect the height of the heat peak and the total heat significantly.

5.2 Recommendations

1. The addition of ground perlite and the use of chemical additives has resulted in the formation of strätlingite. However, a more reactive natural pozzolan

could perhaps produce more and more positively influence strength development.

2. The addition of other chemical additives could increase the amount of reaction between CAC and perlite.

3. The degree of hydration of the CAC and the amount of reacted perlite could be measured to better evaluate strength development.

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APPENDIX A

COMPRESSIVE STRENGTH DEVELOPMENT OF MORTARS

Tables A.1 through A.36 give the compressive strength measurements for all mortars.

Table A.1 Compressive strengths of 0.4-100-D and 0.4-100-W

Age	Compressive Strength (MPa)	
	0.4-100-D	0.4-100-W
3h	0.00	0.00
6h	36.27	36.27
24h	52.73	52.73
48h	66.50	52.00
7d	65.25	47.00
14d	70.83	32.63
28d	64.20	34.00
90d	54.00	40.13

Table A.2 Compressive strengths of 0.4-75-D and 0.4-75-W

Age	Compressive Strength (MPa)	
	0.4-75-D	0.4-75-W
3h	4.90	4.90
6h	32.33	32.33
24h	46.63	46.63
48h	55.70	53.03
7d	59.33	51.63
14d	62.75	24.77
28d	61.30	26.67
90d	50.70	31.07

Table A.3 Compressive strengths of 0.4-50-D and 0.4-50-W

Age	Compressive Strength (MPa)	
	0.4-50-D	0.4-50-W
3h	4.27	4.27
6h	17.23	17.23
24h	30.73	30.73
48h	29.87	30.03
7d	39.97	27.57
14d	43.60	23.73
28d	43.73	22.13
90d	36.73	22.20

Table A.4 Compressive strengths of 0.4-25-D and 0.4-25-W

Age	Compressive Strength (MPa)	
	0.4-25-D	0.4-25-W
3h	0.00	0.00
6h	4.37	4.37
24h	10.27	10.27
48h	11.27	9.73
7d	13.80	7.83
14d	15.50	10.07
28d	17.67	9.83
90d	15.03	9.87

Table A.5 Compressive strengths of 0.4-100-2N-D and 0.4-100-2N-W

Age	Compressive Strength (MPa)	
	0.4-100-2N-D	0.4-100-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	43.40	43.40
48h	46.33	53.97
7d	56.30	39.13
14d	50.47	32.97
28d	46.40	19.23
90d	48.03	26.23

Table A.6 Compressive strengths of 0.4-75-1.5N-D and 0.4-75-1.5N-W

Age	Compressive Strength (MPa)	
	0.4-75-1.5N-D	0.4-75-1.5N-W
3h	0.00	0.00
6h	0.00	0.00
24h	32.33	32.33
48h	37.33	37.07
7d	44.40	33.43
14d	40.93	33.50
28d	41.17	24.33
90d	41.27	30.70

Table A.7 Compressive strengths of 0.4-50-1N-D and 0.4-50-1N-W

Age	Compressive Strength (MPa)	
	0.4-50-1N-D	0.4-50-1N-W
3h	0.00	0.00
6h	0.00	0.00
24h	18.80	18.80
48h	21.53	18.27
7d	26.87	24.00
14d	27.23	28.50
28d	28.17	28.90
90d	25.50	28.80

Table A.8 Compressive strengths of 0.4-25-0.5N-D and 0.4-25-0.5N-W

Age	Compressive Strength (MPa)	
	0.4-25-0.5N-D	0.4-25-0.5N-W
3h	0.00	0.00
6h	0.00	0.00
24h	7.47	7.47
48h	8.87	8.20
7d	10.97	8.47
14d	12.10	9.00
28d	12.97	9.47
90d	11.40	8.37

Table A.9 Compressive strengths of 0.4-75-2N-D and 0.4-75-2N-W

Age	Compressive Strength (MPa)	
	0.4-75-2N-D	0.4-75-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	29.90	29.90
48h	32.23	31.37
7d	40.30	28.47
14d	41.27	30.77
28d	35.80	31.83
90d	33.90	24.47

Table A.10 Compressive strengths of 0.4-50-2N-D and 0.4-50-2N-W

Age	Compressive Strength (MPa)	
	0.4-50-2N-D	0.4-50-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	13.63	13.63
48h	17.60	17.70
7d	24.00	24.83
14d	30.50	27.47
28d	29.07	27.47
90d	26.40	31.77

Table A.11 Compressive strengths of 0.4-25-2N-D and 0.4-25-2N-W

Age	Compressive Strength (MPa)	
	0.4-25-2N-D	0.4-25-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	3.47	3.47
48h	6.47	5.77
7d	8.60	6.87
14d	9.70	7.77
28d	11.90	8.73
90d	10.20	7.87

Table A.12 Compressive strengths of 0.4-100-1C-D and 0.4-100-1C-W

Age	Compressive Strength (MPa)	
	0.4-100-1C-D	0.4-100-1C-W
3h	13.20	13.20
6h	38.70	38.70
24h	51.83	51.83
48h	57.47	60.80
7d	63.73	38.07
14d	66.17	24.47
28d	64.17	30.13
90d	48.73	34.80

Table A.13 Compressive strengths of 0.4-75-0.8C-D and 0.4-75-0.8C-W

Age	Compressive Strength (MPa)	
	0.4-75-0.8C-D	0.4-75-0.8C-W
3h	9.13	9.13
6h	31.97	31.97
24h	43.33	43.33
48h	47.27	45.70
7d	58.47	26.57
14d	57.47	21.10
28d	57.53	28.87
90d	40.30	28.57

Table A.14 Compressive strengths of 0.4-50-0.6C-D and 0.4-50-0.6C-W

Age	Compressive Strength (MPa)	
	0.4-50-0.6C-D	0.4-50-0.6C-W
3h	4.67	4.67
6h	19.20	19.20
24h	30.23	30.23
48h	33.00	30.87
7d	41.37	24.20
14d	40.50	13.07
28d	41.70	16.17
90d	34.33	18.50

Table A.15 Compressive strengths of 0.4-25-0.4C-D and 0.4-25-0.4C-W

Age	Compressive Strength (MPa)	
	0.4-25-0.4C-D	0.4-25-0.4C-W
3h	1.77	1.77
6h	4.17	4.17
24h	9.43	9.43
48h	10.93	9.10
7d	14.53	9.00
14d	16.60	11.30
28d	15.43	12.10
90d	13.87	12.50

Table A.16 Compressive strengths of 0.4-75-1C-D and 0.4-75-1C-W

Age	Compressive Strength (MPa)	
	0.4-75-1C-D	0.4-75-1C-W
3h	10.80	10.80
6h	32.77	32.77
24h	45.70	45.70
48h	49.90	55.30
7d	51.57	33.93
14d	54.97	22.43
28d	54.97	30.07
90d	39.83	32.60

Table A.17 Compressive strengths of 0.4-50-1C-D and 0.4-50-1C-W

Age	Compressive Strength (MPa)	
	0.4-50-1C-D	0.4-50-1C-W
3h	5.23	5.23
6h	14.23	14.23
24h	31.47	31.47
48h	28.20	26.20
7d	34.70	18.03
14d	36.80	11.17
28d	34.80	16.87
90d	22.97	14.30

Table A.18 Compressive strengths of 0.4-25-1C-D and 0.4-25-1C-W

Age	Compressive Strength (MPa)	
	0.4-25-1C-D	0.4-25-1C-W
3h	1.43	1.43
6h	3.63	3.63
24h	6.77	6.77
48h	8.77	7.10
7d	12.37	6.47
14d	12.30	7.67
28d	12.67	8.17
90d	9.40	7.77

Table A.19 Compressive strengths of 0.6-100-D and 0.6-100-W

Age	Compressive Strength (MPa)	
	0.6-100-D	0.6-100-W
3h	0.63	0.63
6h	24.05	24.05
24h	43.57	43.57
48h	47.70	50.90
7d	55.23	34.80
14d	55.10	12.50
28d	55.37	14.23
90d	41.43	18.10

Table A.20 Compressive strengths of 0.6-75-D and 0.6-75-W

Age	Compressive Strength (MPa)	
	0.6-75-D	0.6-75-W
3h	1.53	1.53
6h	12.55	12.55
24h	28.70	28.70
48h	32.15	27.80
7d	39.85	24.30
14d	41.33	6.85
28d	43.30	8.40
90d	26.55	11.50

Table A.21 Compressive strengths of 0.6-50-D and 0.6-50-W

Age	Compressive Strength (MPa)	
	0.6-50-D	0.6-50-W
3h	1.23	1.23
6h	5.57	5.57
24h	15.97	15.97
48h	17.23	15.40
7d	21.17	11.77
14d	24.93	6.40
28d	24.50	5.27
90d	21.73	6.13

Table A.22 Compressive strengths of 0.6-25-D and 0.6-25-W

Age	Compressive Strength (MPa)	
	0.6-25-D	0.6-25-W
3h	0.60	0.60
6h	1.50	1.50
24h	3.60	3.60
48h	3.60	2.97
7d	4.70	2.70
14d	5.73	2.63
28d	5.83	2.63
90d	4.20	2.00

Table A.23 Compressive strengths of 0.6-100-2N-D and 0.6-100-2N-W

Age	Compressive Strength (MPa)	
	0.6-100-2N-D	0.6-100-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	34.23	34.23
48h	38.30	35.80
7d	48.87	26.47
14d	41.07	24.57
28d	42.00	13.03
90d	38.80	17.67

Table A.24 Compressive strengths of 0.6-75-1.5N-D and 0.6-75-1.5N-W

Age	Compressive Strength (MPa)	
	0.6-75-1.5N-D	0.6-75-1.5N-W
3h	0.00	0.00
6h	0.00	0.00
24h	21.57	21.57
48h	24.70	22.87
7d	27.47	19.73
14d	29.90	14.77
28d	30.13	11.33
90d	21.90	14.30

Table A.25 Compressive strengths of 0.6-50-1N-D and 0.6-50-1N-W

Age	Compressive Strength (MPa)	
	0.6-50-1N-D	0.6-50-1N-W
3h	0.00	0.00
6h	0.00	0.00
24h	11.27	11.27
48h	13.10	11.30
7d	15.67	10.43
14d	16.70	12.00
28d	20.30	11.60
90d	20.10	11.93

Table A.26 Compressive strengths of 0.6-25-0.5N-D and 0.6-25-0.5N-W

Age	Compressive Strength (MPa)	
	0.6-25-0.5N-D	0.6-25-0.5N-W
3h	0.00	0.00
6h	0.00	0.00
24h	3.27	3.27
48h	3.80	3.63
7d	5.00	3.53
14d	5.33	3.27
28d	5.07	3.20
90d	5.03	2.57

Table A.27 Compressive strengths of 0.6-75-2N-D and 0.6-75-2N-W

Age	Compressive Strength (MPa)	
	0.6-75-2N-D	0.6-75-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	19.67	19.67
48h	20.50	18.70
7d	23.90	18.20
14d	25.40	16.03
28d	27.57	10.20
90d	23.90	13.60

Table A.28 Compressive strengths of 0.6-50-2N-D and 0.6-50-2N-W

Age	Compressive Strength (MPa)	
	0.6-50-2N-D	0.6-50-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	8.13	8.13
48h	8.83	8.17
7d	11.10	9.90
14d	14.03	10.50
28d	15.17	11.40
90d	11.63	11.07

Table A.29 Compressive strengths of 0.6-25-2N-D and 0.6-25-2N-W

Age	Compressive Strength (MPa)	
	0.6-25-2N-D	0.6-25-2N-W
3h	0.00	0.00
6h	0.00	0.00
24h	1.57	1.57
48h	1.77	1.80
7d	2.20	1.97
14d	2.33	2.27
28d	2.80	2.43
90d	2.67	2.27

Table A.30 Compressive strengths of 0.6-100-1C-D and 0.6-100-1C-W

Age	Compressive Strength (MPa)	
	0.6-100-1C-D	0.6-100-1C-W
3h	4.77	4.77
6h	27.03	27.03
24h	47.90	47.90
48h	49.43	49.50
7d	53.77	27.00
14d	53.30	12.07
28d	59.23	15.53
90d	45.13	15.30

Table A.31 Compressive strengths of 0.6-75-0.8C-D and 0.6-75-0.8C-W

Age	Compressive Strength (MPa)	
	0.6-75-0.8C-D	0.6-75-0.8C-W
3h	2.83	2.83
6h	14.27	14.27
24h	25.27	25.27
48h	29.50	31.73
7d	42.10	18.17
14d	44.03	8.17
28d	39.47	10.33
90d	33.13	10.83

Table A.32 Compressive strengths of 0.6-50-0.6C-D and 0.6-50-0.6C-W

Age	Compressive Strength (MPa)	
	0.6-50-0.6C-D	0.6-50-0.6C-W
3h	1.70	1.70
6h	5.87	5.87
24h	13.83	13.83
48h	14.60	12.73
7d	18.47	8.03
14d	21.53	5.20
28d	21.90	5.57
90d	17.43	6.30

Table A.33 Compressive strengths of 0.6-25-0.4C-D and 0.6-25-0.4C-W

Age	Compressive Strength (MPa)	
	0.6-25-0.4C-D	0.6-25-0.4C-W
3h	0.77	0.77
6h	1.83	1.83
24h	3.47	3.47
48h	3.47	2.70
7d	3.80	2.67
14d	4.77	3.00
28d	5.00	3.10
90d	4.47	2.83

Table A.34 Compressive strengths of 0.6-75-1C-D and 0.6-75-1C-W

Age	Compressive Strength (MPa)	
	0.6-75-1C-D	0.6-75-1C-W
3h	3.10	3.10
6h	14.93	14.93
24h	28.03	28.03
48h	31.00	28.10
7d	37.33	13.30
14d	40.17	8.30
28d	39.93	9.80
90d	26.63	10.27

Table A.35 Compressive strengths of 0.6-50-1C-D and 0.6-50-1C-W

Age	Compressive Strength (MPa)	
	0.6-50-1C-D	0.6-50-1C-W
3h	1.43	1.43
6h	5.93	5.93
24h	12.40	12.40
48h	13.83	12.03
7d	16.57	6.07
14d	17.70	5.37
28d	20.20	5.97
90d	14.90	5.43

Table A.36 Compressive strengths of 0.6-25-1C-D and 0.6-25-1C-W

Age	Compressive Strength (MPa)	
	0.6-25-1C-D	0.6-25-1C-W
3h	0.60	0.60
6h	1.17	1.17
24h	2.70	2.70
48h	3.00	2.77
7d	3.40	2.60
14d	4.30	3.00
28d	5.03	3.30
90d	4.50	2.73