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Compressive Strength Development of Mortar from Partially Cement Substitution by
Limestone Powder and Metakaolin

Miss Thanyarat Buasiri



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Civil Engineering

Department of Civil Engineering

Faculty of Engineering

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ัญญารัตน์ บัวศิริ : การพัฒนากำลังอัดของมอร์ตาร์โดยการแทนที่ซีเมนต์ด้วยผงหินปูนและดินขาวเผา (Compressive Strength Development of Mortar from Partially Cement Substitution by Limestone Powder and Metakaolin) อ.ที่ปรึกษา วิทยานิพนธ์หลัก: รศ. ดร. วิจิต ปานสุข, 59 หน้า.

วัตถุประสงค์ของงานวิจัยนี้เพื่อศึกษากลไกที่มีผลกระทบต่อการพัฒนา กำลังอัดของมอร์ตาร์ โดยการแทนที่ซีเมนต์ด้วยผงหินปูนและดินขาวเผา โดยการแทนที่ของซีเมนต์ด้วยผงหินปูนและดินขาวเผาคิดเป็นร้อยละ 45 โดยน้ำหนักแห้งของซีเมนต์ การทดสอบกำลังอัดดำเนินโดยใช้ตัวอย่างมอร์ตาร์ และการศึกษาโครงสร้างระดับไมโครดำเนินการศึกษาตัวอย่างที่อยู่ในลักษณะเพสต์ ผลที่ได้จากการทดสอบพบว่ามอร์ตาร์ที่แทนที่ซีเมนต์ร้อยละ 45 โดย ผงหินปูนร้อยละ 15 และดินขาวเผาร้อยละ 30 และมีการผสมสารผสมเพิ่มประเภทสารลดน้ำจำนวนมากร้อยละ 1 ให้ค่ากำลังอัดของมอร์ตาร์ที่อายุ 28 วัน ใกล้เคียงกับซีเมนต์มอร์ตาร์ คิดเป็นร้อยละ 97 เมื่อกำหนดกำลังอัดที่ 28 วันของซีเมนต์มอร์ตาร์เป็นร้อยละ 100 จากการทดสอบยังพบอีกว่าการแทนที่ซีเมนต์ด้วยผงหินปูนและดินขาวเผาทำให้เกิดปฏิกิริยาที่เสริมกันระหว่างอลูมินेटและคาร์บอเนต ซึ่งสามารถสังเกตพบได้จากการก่อตัวของ เฮมิการ์บออลูมินेट และโมโนคาร์บออลูมินेट ซึ่งถือเป็นกลไกสำคัญในการทำปฏิกิริยาและมีส่วนช่วยในการพัฒนากำลังอัดของมอร์ตาร์ที่แทนที่ซีเมนต์ด้วยผงหินปูนและดินขาวเผา นอกจากนี้ความไม่บริสุทธิ์ของดินขาวเผาเป็นตัวจำกัดการเกิดปฏิกิริยาเสริมกันของอลูมินेटและคาร์บอเนต ซึ่งมีผลทำให้กำลังอัดของมอร์ตาร์ที่มีการแทนที่ด้วยผงหินปูนและดินขาวเผาน้อยกว่าความเป็นจริง

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The aim of this study is to investigate the mechanism that has an effect on compressive strength development of mortar from partially substitution cement by combination of limestone powder and metakaolin. The percentage of binding material between limestone powder and metakaolin is 45% by dry weight of cement. The strength was tested by mortar and the microstructure determination was done by paste. The results show that 45% cement replacement by 15% limestone powder and 30% metakaolin with 1% PCEs (B45S 1:2) have the compressive strength reached almost the same with mortar reference at 28 days with 97% relative. The results also show that the cement replacement by limestone powder and metakaolin leads to the synergetic reaction between aluminate and carbonate. It can be observed by more forming supplementary AFm phases (hemicaluminate and monocarboaluminate phases). That is the main mechanism which develop the compressive strength of ternary blend mortar. Moreover, it has limitation of synergetic reaction cause of impurity of metakaolin and it make the compressive strength not well as an expected.

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CHAPTER 1

INTRODUCTION

1.1 Background

In a present day, the rate of consumption Portland cement over the world is increasing rapidly. According to Portland Cement Association (PCA), the world cement consumption is about 3,313 Million Metric ton in 2010 and it is predicted to significantly increase to 4,367 Million Metric ton in 2016 [1]. That leads to impact the environment in term of Carbon dioxide (CO_2) emission. Many several studies try to find the substitution materials of cement to reduce the clinker factor of cement and decrease the greenhouse effect.

Limestone is sedimentation of calcium carbonate and performs as rock; it is widely added as a partial cement replacement material. ASTM C 595-12 allowed up to 15% limestone powder as a cement replacement. It is defined a Type IL cement. It has been shown that cement Type IL has better properties [2]. The most important of limestone powder in concrete are: improve acceleration of hydration, slightly increase strength of early state, control of bleeding in concrete, reducing the initial and final setting time and relatively inexpensive because there is abundant natural material and environmentally-friendly material. [3]

Metakaolin, the supplementary cementitious material, has been one of the most interesting materials for the replacement material in cement. Metakaolin is a dehydrated material from the kaolinite clay which is easy to be found in both nature and industry. The color of kaolinite clay is mostly white; however Impurities can make the color of kaolinite clay change, sometimes red or light brown. Metakaolin is burned in a quite low temperature ($600\text{-}800^\circ\text{C}$) compare to clinker ($1,450^\circ\text{C}$). The CO_2 of metakaolin is reducing approximately 96 kg CO_2 per ton [4]. Therefore, it can be classified as an eco-friendly material of concrete. It reduces the size of pores and transforms many finer particles into discontinuous pores, therefore decreasing the permeability of concrete substantially. Metakaolin also increases compressive and

flexural strengths and reduces heat of hydration leading to better shrinkage and crack control. [5]

With many interesting facts about limestone powder and metakaolin, it is a fabulous idea to studies the effect of using limestone powder and metakaolin which founded in Thailand (South East Asia country) as a partial of cement replacement in mortar by concerning the mechanism and reaction which has an effect on compressive strength.

1.2 Research objectives

- 1.2.1 To study the mechanism of cement-limestone powder-metakaolin mortar which effect to the compressive strength.

1.3 Scope and limitations of study

- 1.3.1 Use ordinary Portland cement Type 1 in this research.
- 1.3.2 Limestone powder is by-product from rock production process from Saraburi province. The median particle size (D_{50}) is less than 20 micron.
- 1.3.3 Metakaolin is a dehydrated material from the kaolinite clay which is mineral material from Uttaradit Province. The median particle size (D_{50}) is less than 20 micron.
- 1.3.4 Standard sand is from the market.
- 1.3.5 The specimen size of mortar is cube 50 x 50 x 50 mm.
- 1.3.6 Water-cement or water-binder ratio is fixed at 0.485.
- 1.3.7 The cement to sand ratio or binder to sand ratio is fixed at 1:2.75.
- 1.3.8 The combination between limestone powder and metakaolin are replaced about 45% by dry weight of cement.
- 1.3.9 The limestone powder to metakaolin ratio is varying to 1:1, 1:2 and 2:1 by dry weight of cement replacement.
- 1.3.10 Workability of mortar is adjusted by superplasticizer type F.
- 1.3.11 The mechanical strength is tested by mortar and the microstructure consideration is done by paste.

- 1.3.12 The reference mix is 100% of Portland cement paste or mortar.
- 1.3.13 The specimens are seal curing at the first date and submersion until the date of test.
- 1.3.14 The compressive strength of mortar is tested at age of 1, 3, 7 and 28 days.
- 1.3.15 The heat of hydration reaction is tested until 7 days by using the isothermal calorimeter.
- 1.3.16 Stop hydration before XRD test by microwave method.
- 1.3.17 XRD is tested at 1, 3, 7, and 28 days.



CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Hydration reaction [6]

Hydration reaction is a chemical reaction occurs when cement and water mix together and lead cement to setting and hardened. The rate of hydration reaction depends on the amount of chemical composition in cement.

Portland cement consists of 4 main compounds which are in Table 2.1.

Table 2.1. Main compound of cement

Name of Compound	Chemical compound	Abbreviation
Tricalcium Silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium Silicate	$2 \text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium Aluminate	$3 \text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium Aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF

The amount of 4 main compounds in cement calculate from the amount of main oxide in cement by use Bogue equation.

$$\begin{aligned} \text{The amount of } \text{C}_3\text{S} (\%) &= 4.07 (\% \text{CaO}) - 7.60 (\% \text{SiO}_2) - 6.72 (\% \text{Al}_2\text{O}_3) \\ &\quad - 1.43 (\% \text{Fe}_2\text{O}_3) - 2.85 (\% \text{SO}_3) \end{aligned} \quad (2.1)$$

$$\text{The amount of } \text{C}_2\text{S} (\%) = 2.87 (\% \text{SiO}_2) - 0.754 (\% \text{C}_3\text{S}) \quad (2.2)$$

$$\text{The amount of } \text{C}_3\text{A} (\%) = 2.65 (\% \text{Al}_2\text{O}_3) - 1.69 (\% \text{Fe}_2\text{O}_3) \quad (2.3)$$

$$\text{The amount of } \text{C}_4\text{AF} (\%) = 3.04 (\% \text{Fe}_2\text{O}_3) \quad (2.4)$$

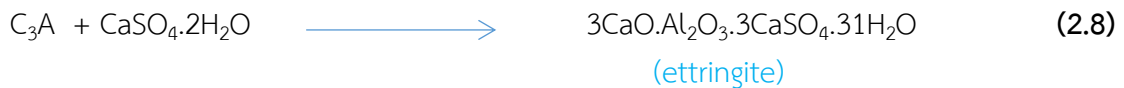
- Hydration of Calcium Silicate (Alite- C_3S , Belite- C_2S)



- Hydration of Calcium Aluminate (C_3A)



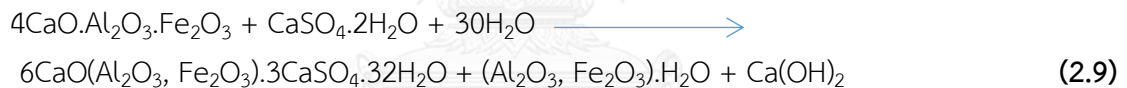
The Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added for retarding the hydration reaction of C_3A , and the ettringite reaction will be occurred.



Ettringite will retarding the hydration reaction of C_3A until it do not have enough Sulphate ion to perform ettringite. Finally ettringite will change to monosulphate.

- Hydration of Tetracalcium Aluminoferrite (C_4AF)

First, C_4AF will react with gypsum and $\text{Ca}(\text{OH})_2$. Then, it perform the particle which look like needle shape of Sulphoaluminate and Sulphoferrite.



2.1.1 Stage of hydration reaction [7]

2.1.1.1 Rapid heat generation

On mixing cement with water, calcium and hydroxide ions are released from the surface of the C_3S ; pH rises to a very alkaline solution. When the calcium and hydroxide reach critical concentrations, crystallization of CH and C-S-H begins. Early chemical reactions are temperature dependent.

2.1.1.2 Dormant period

In this state, cement remain plastic, the hydration reaction slows. CH crystallizes from the solution; C-S-H develops on the surface of the C_3S and forms a coating. As the thickness increases, the time it takes water to penetrate the coating increases, thus the rate of reaction becomes diffusion controlled. C_2S hydrates at a slower rate because it is a less reactive compound.

2.1.1.3 Acceleration period

Critical concentration of ions is reached and silicate hydrates rapidly, maximum rate occurs at this stage. Final set has passed and early hardening begins (4-8 hours).

2.1.1.4 Deceleration

The rate of reaction slows; completely diffusion dependent reaction.

2.1.1.5 Steady state

In this state, it has constant rate of reaction. Temperature has little effect on hydration at this point.

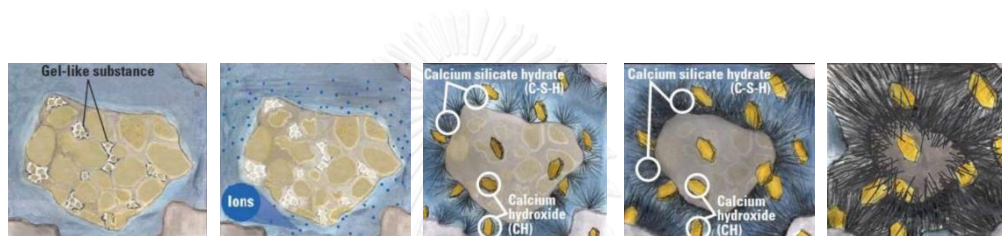


Figure 2.1 : Stage of hydration reaction

2.1.2 Heat of hydration reaction

The process of hydration begins when the molecules of cement and water are mixed. Loss of mass on a molecular level, necessarily results in an energy release. In this case, the bonding of molecules results in an exothermic chemical reaction. This is known as the heat of hydration. The relation between heat evolution and hydration reaction shows in Figure 2.2.

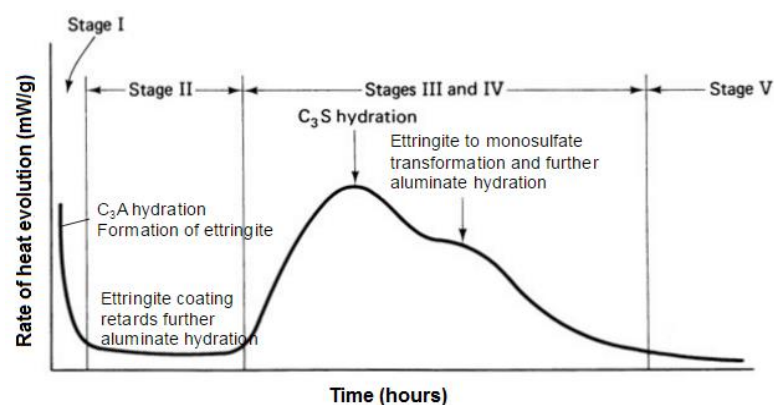


Figure 2.2 : General heat evolution of Portland cement [8].

2.1.3 Effect of aggregate on heat of hydration [9]

Lars Wadsö (2001) measured the heat generated by the hydration reaction by using TAM Air isothermal calorimeter with 3 different samples. For the measurement a cement paste was mixed by water to cement ratio at 0.5 and divided into 3 parts. The one part is used for cement paste sample. One part was added the equal mass of aggregate to cement paste. The last part was mixed cement paste with half the mass of aggregate. The results of rate of hydration are rather similar for both cement paste and mortar as shown in Figure 2.3.

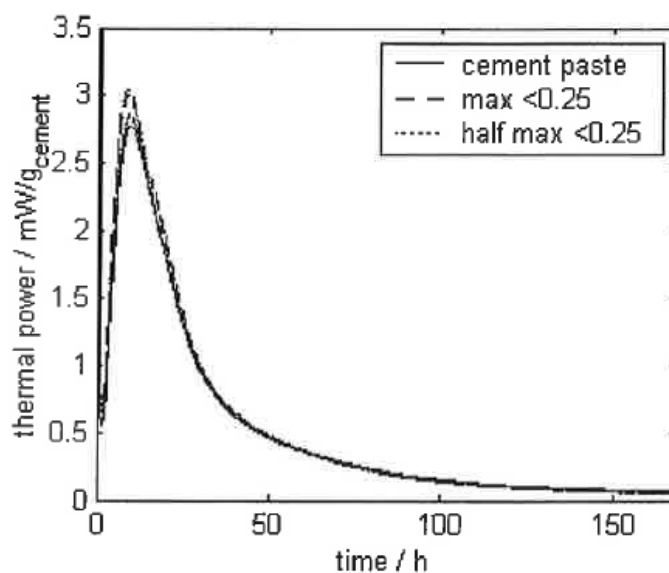


Figure 2.3 : Heat evaluation of cement paste and mortar with different amount of aggregate.

2.1.4 Effect of heat of hydration for the structure [10]

If the heat of hydration is not properly controlled, it can cause damage to the structure especially with a large structure because heat cannot escape easily. It also can cause an expansion while the cement is in the process of hardening and curing. Heat of hydration can lead to very high internal temperatures within a structure, it can create significant cracks.

2.2 Supplementary cementitious material (SCMs)

Supplementary cementitious materials, also known as pozzolan, is a material conjunction with portland cement, it contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both. It is high composition of siliceous or siliceous and aluminous materials. There are 2 types of SCMs; first is artificial pozzolan such as fly ash, silica fume, metakaolin and granulated blast furnace slag; the second is natural pozzolan such as calcined clay, volcanic ash, volcanic tuff and pumicite. [11]

2.2.1 Kaolinite and metakaolin [12]

Kaolinite can be formed as a residual weathering product, by hydrothermal alteration, and as a sedimentary mineral.

Metakaolin is a dehydrate material from clay mineral kaolinite. It classified as artificial pozzolanic material. The theoretical formula of metakaolin is $Al_2O_3 \cdot 2SiO_2$ or AS_2 . Thermal activation at 600-900 °C increased disorder structure in alumina sheet (see in Figure 2.4), it causes particle breakdown of the crystal lattice structure to amorphous. [13]

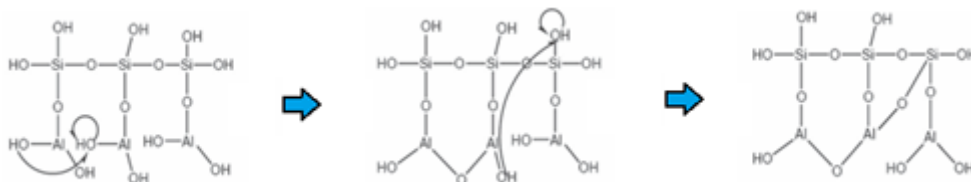


Figure 2.4 : Heat treatment of kaolinite to increase disorder in alumina sheet].

There are various parameters influence to the dehydroxylation process of kaolinite which are temperature, heating time as well as cooling parameter. [14]

Brindly and Nakahira (1959) attempt to compile a crystallographic to model structure of metakaolin and proposed well-ordered lattice as shown in Figure 3. If metakaolin has a structure that shown in Figure 2.5, it should be founded by XRD analysis. In reality, it cannot to find the metakaolin structure by XRD. Then, it must consider as an ideal structure. [15-17]

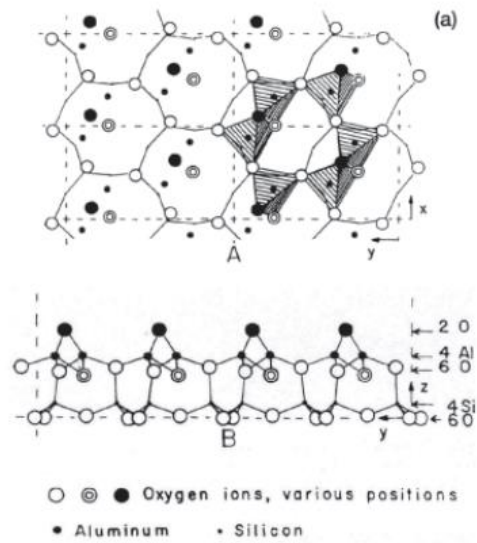


Figure 2.5 : Lattice of metakaolinite supposed by Brindley and Nakahira

For use of metakaolin as cement replacement material, Silica and Alumina from the pozzolanic material react with calcium hydroxide (CH) which is the product of Portland cement hydration reaction and lead to the secondary cementitious product (C-S-H or C-A-H).

It perform more cementitious product and increase the strength. The pozzolanic reaction show this process can be written as Figure 2.6.

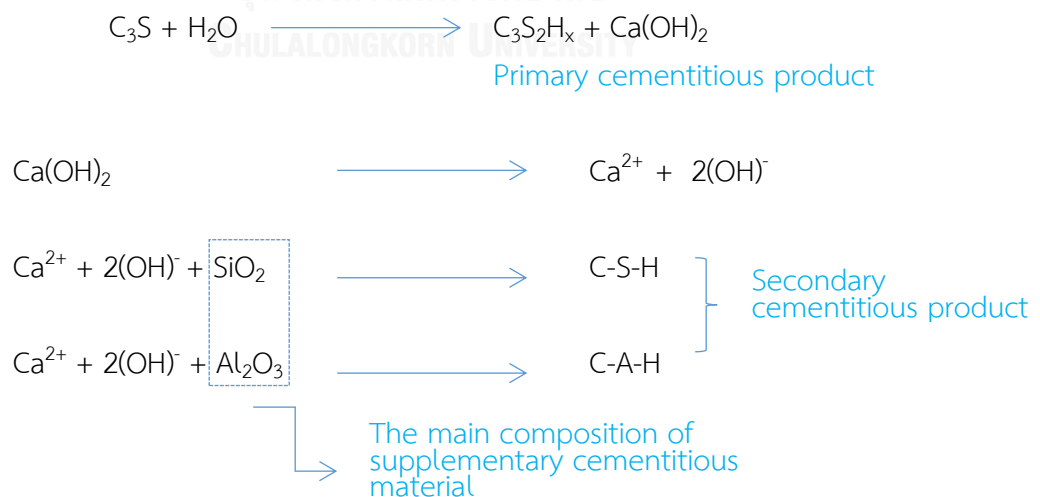


Figure 2.6 : The pozzolanic reaction

2.3 Binding material

2.3.1 Limestone powder

Limestone is a carbonate rock formed mostly of calcium carbonate (CaCO_3). These rocks are composed of more than 50% carbonate minerals, generally the minerals calcite (pure CaCO_3) or dolomite (calcium-magnesium carbonate, $\text{Ca}\{\text{Mg}(\text{CO}_3)_2$ or both. Limestone powder is a product when grinding limestone rock into a very small particle size. Fine limestone is a binding material; it can fulfill the pore of the concrete (filler effect). The chemical composition of limestone powder as shown in Table 2.2. [18]

Table 2.2. Chemical composition (%) of limestone.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
0.55	0.40	0.17	53.47	1.02	0.01	0.03	43.13

The fine limestone powder may accelerate the early hydration of cement clinkers. For use of limestone powder instead of cement, it has limitation to add the limestone powder instead of cement due to dilution effect and free lime effect. [19]

2.4 Compressive strength development

Compressive strength is the capacity that concrete can withstand when receive axial loads. There are many factors influence the compressive strength such as water-cement ratio, compaction of concrete and the quality of mixtures. In this research mention on the quality and quantity of limestone powder and metakaolin which effect to the compressive strength.

2.4.1 Effect of compressive strength due to various time and temperature in burning process to performed metakaolin

Charoenchai and Prarinya (2007) Ranong Metakaolin is design to be used for mortar. The results show in Figures 2.7 and 2.8 that the suitable time and temperature in burning process is 3 hours and 600 °C respectively. Metakaolin has the most reactive state when the temperature leads to loss of hydroxyls and its structure collapse and amorphous. [20]

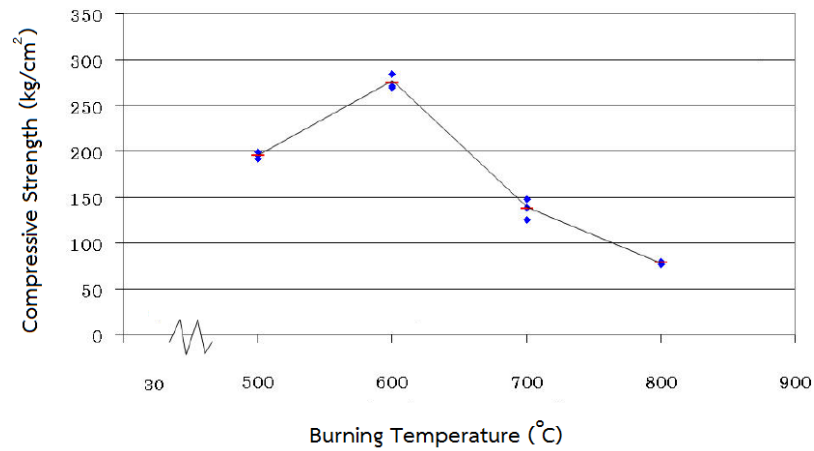


Figure 2.7 : The relationship between 7 day compressive strength and burning time

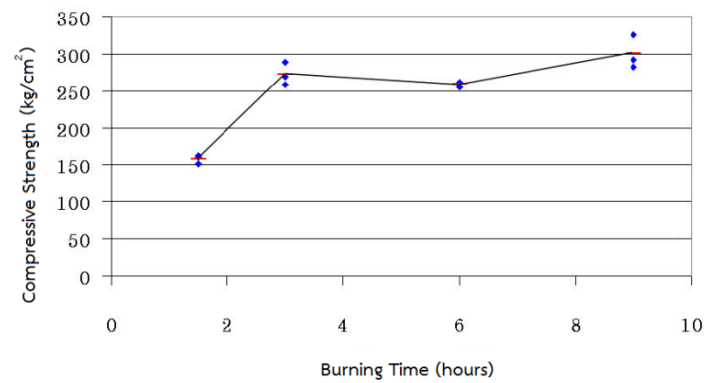


Figure 2.8 : The relationship between 7 day compressive strength and burning temperature

Torres et al (2007) study the treated of Columbian kaolinite at 600, 700 and 800 °C, the treated at 800 °C for 2 hours show greatest structural disorder and therefore amorphous and reactivity. They research about the durability in mortar by replacement concrete by 20% of Metakaolin. The experiment is fixed the water binder ratio at 0.5 and cement to sand ratio is 1:2.75. The results show use of 800 °C also has lowest capillary permeability in mortar. Therefore, the suitable temperature for perform metakaolin is 800 °C in 2 hours. [21]

2.4.2 Effect of compressive strength due to amount of metakaolin instead of cement

Wild et al (1996) researched about replacement level of Portland cement type 1 by commercial metakaolin as 0, 5, 10, 15, 20, 25 and 30% and water-binder ratio is fixed at 0.4. The gain in strength with time for OPC concrete is principally dependent on the rate of Portland cement hydration and combination of the rates of Portland cement hydration and the MK-CH reaction. The influence factors to the compressive strength of concrete containing metakaolin are filler effect, which immediately acceleration of Portland cement hydration and pozzolanic reaction. The suitable proportion that gain the highest strength is 25 % replacement. The results show in Figure 2.9 [22] It is also reported by Brooks and Johari (2001), the compressive strength increase when increase the amount of metakaolin Table 2.3.

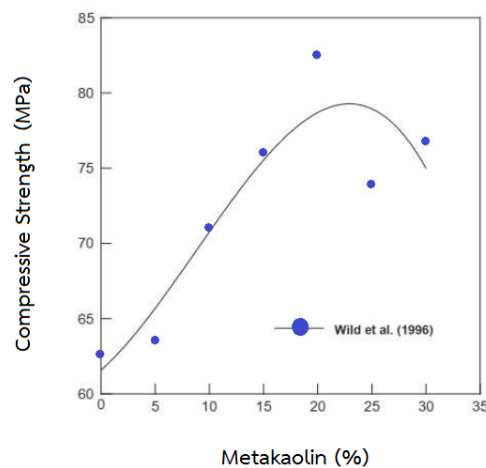


Figure 2.9 : Maximum possible percentage replacement VS compressive strength

Table 2.3. 28-day compressive strength of concrete.

Concrete mixes	28-day cube Compressive Strength (MPa)
OPC	87.0
MK5	91.5
MK10	104.0
MK15	103.5

2.4.3 Effect of compressive strength due to median particle size of limestone powder

Krick et al (2013) researched about the three difference median size of limestone powder (0.7, 3 and 15 micron) has an effect in compressive strength by 10% and 20% replacing of cement. The results are shown in Figure 2.10 that the mixture containing 10%, 0.7 micron limestone has the highest 1 day compressive strength than the Portland cement paste. If replacement the limestone particle size larger than Portland cement, it has the lower strength.

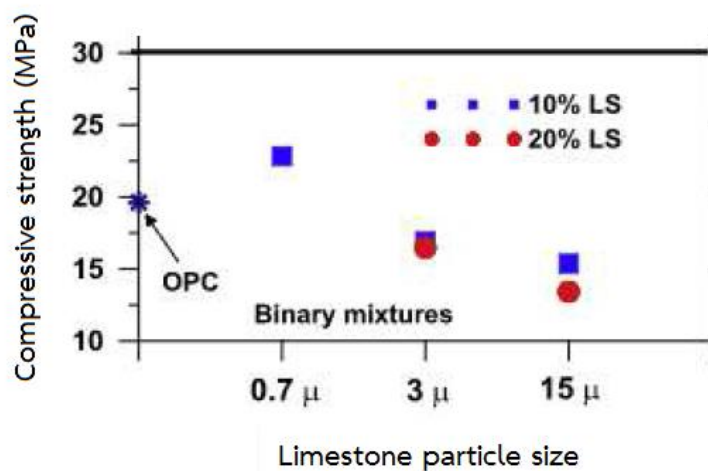


Figure 2.10 : 1-Day compressive strengths of binary blends of limestone

2.4.4 Effect of compressive strength due to amount of limestone powder instead of cement

Beeralingegowda and Gundakalle (2013) researched about the partial supplement limestone powder 0, 5, 10, 15, 20, 25, and 30% by weight of cement. The result of 28 day cube compression test is increase 17.74% at 20% replacement of cement gain the highest compressive strength [23]. The results show in Figure 2.11.

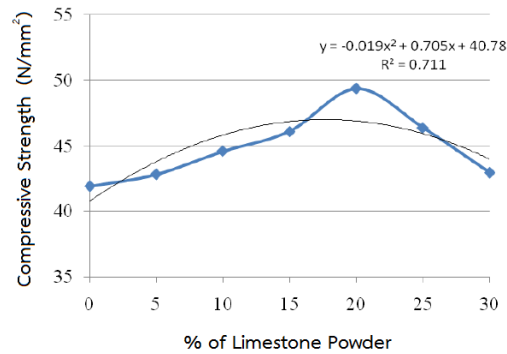


Figure 2.11 : 28 day compressive strenght VS the percentage of cement replacement by limestone powder

2.4.5 Effect of compressive strength when couple replacement limestone powder and metakaolin;

Antoni et al. (2012) researched about mortar by coupled substitution of metakaolin and limestone in microstructural development. The results show that replacing 30% Metakaolin and 15% limestone in Portland cement gives better mechanical properties than 100% use Portland cement. The calcium carbonate in limestone reacts with aluminate in the Metakaolin forming the hemicarboaluminate and to a lesser extent monocarboaluminate in AFm phase and stabilizing ettringite. The stoichiometric formulation of monocarbonate hydrate is corresponding weight ratio 2:1 Metakaolin : limestone powder.

The phase that obtained by 24 hours hydration of substitute 30% Matakaolin and 15% limestone by weight of cement is show in Figure 2.12 and the relative mechanical strength shown in Figure 2.13.

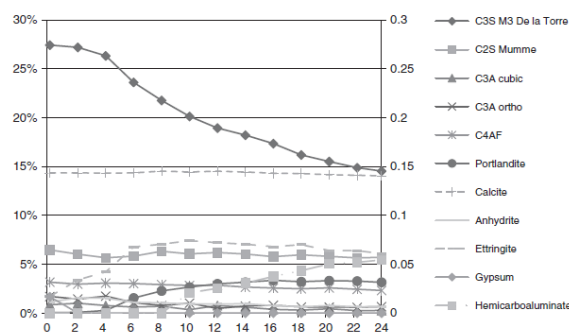


Figure 2.12 : Evaluation of phase obtained by Rietveld refinement of in-situ XRD during the first 24 h hydration for 15% limestone and 30% metakaolin

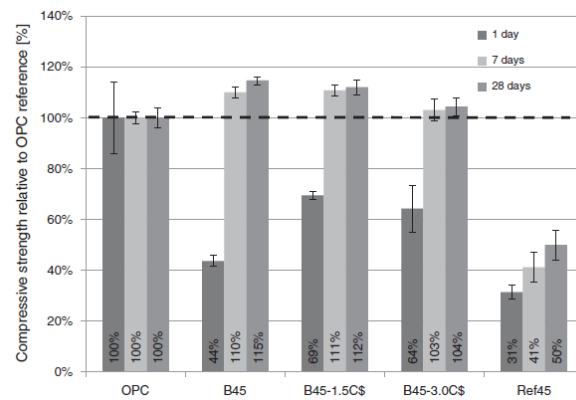


Figure 2.13 : Evaluation of mechanical strength

Krick et al (2013) founded the couple replacement 10% 0.7 micron limestone powder and 10% metakaolin resulted highest compressive strength when compare with other fineness limestone and metakaolin proportion. The results shown in Figure 2.14.

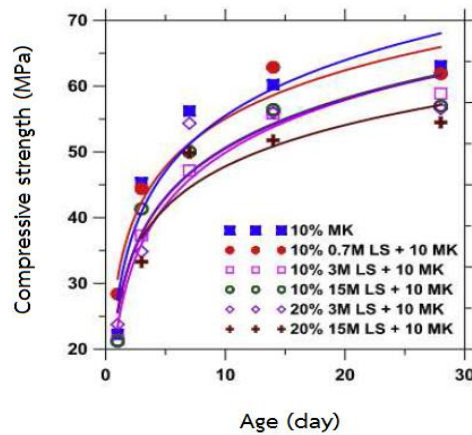


Figure 2.14 : 28 day compressive strength development of OPC-limestone-metakaolin paste

Chapter 3

Research Methodology

In this chapter, it is focusing on the research details which consist of the experimental design, material, apparatus and tools, and testing techniques. The flow chart of the project and process is described as follows:

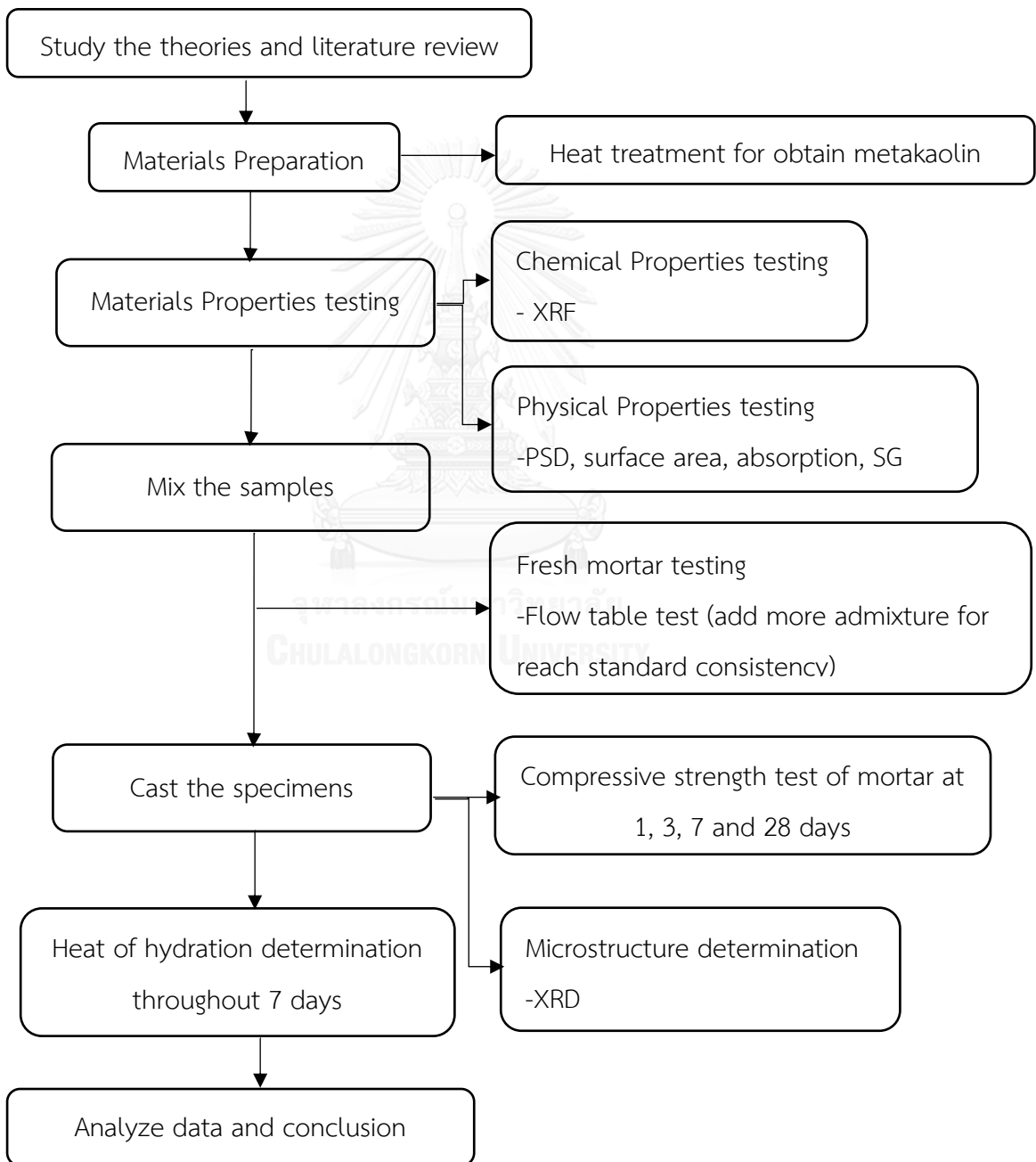


Figure 3.1 : Experimental procedure flow chart

3.1 Experimental design

3.1.1 Specimens

The mortar specimen is cube as shown in Figure 3.2, it have dimension of 50 x 50 x 50 mm.

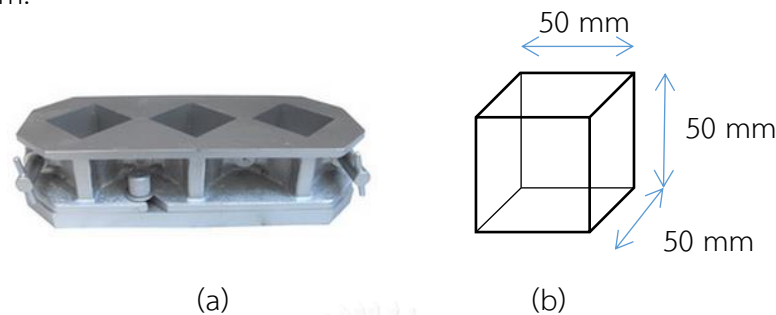


Figure 3.2 : (a) Mortar cube mold (b) Specimens size

3.1.2 Mixture proportion

Mortar specimens were mixed proportion as demonstrated in Table 3.1, by fixing the water to cement ratio or the water to binder ratio to be 0.485 and the cement to sand ratio or the binder to sand ratio is 1:2.75. The ratio between limestone powder and metakaolin are 1:1 1:2 and 2:1 and the 100% Portland cement mortar is for reference. There are 2 systems of mortar which are mortar with and without superplasticizer, the dosage of admixture due to flow table test. For the paste samples have the same proportion as mortar but excluding sand.

Table 3.1. Mixture proportion for mortar.

	OPC (%)	LP (%)	MK (%)
100% CM	100	0	0
B45 1:2 *	55	15	30
B45 1:1 *	55	22.5	22.5
B45 2:1 *	55	30	15
B45S 1:2 *	55	15	30
B45S 1:1 *	55	22.5	22.5
B45S 2:1 *	55	30	15

* The ternary blends are labelled as "BxxS y:z" , xx is the level of cement substitution, S is superplasticizer is added and no alphabet mean without admixture, y is the proportion of limestone powder by dry weight of cement and z is the proportion of metakaolin by dry weight of cement.

3.1.2.1 Adjustment for moisture in the aggregate

If the fine aggregate is not in the suitable condition, it should be adjusted of the amount of water. The moisture content of the aggregate has an effect to the water content of the mortar

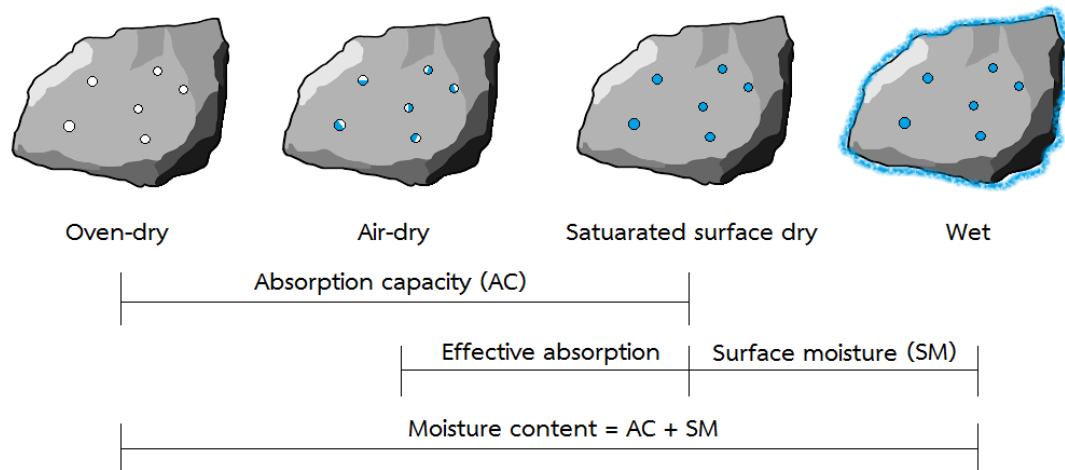


Figure 3.3 : the status of aggregate

The weight of saturated surface dry aggregate is

$$\text{weight of aggregate}_{\text{SSD}} = \text{weight of aggregate}_{\text{oven dry}} \times (1 + \text{MC}) \quad (3.1)$$

The change in the weight water due to the moisture of the aggregate from the stock is

$$\Delta \text{weight}_{\text{water}} = \text{weight of aggregate}_{\text{oven dry}} \times (\text{SM}) \quad (3.2)$$

$$\text{Adjustweight}_{\text{water}} = \text{weight}_{\text{water}} - \Delta \text{weight}_{\text{water}} \quad (3.3)$$

3.2 Mix procedure

Using mixer mix the paste and mortar and the mix procedure according to ASTM C305 [24] ; Standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency.

3.3 Material

The materials that used in this research were the Portland cement type I (Elephant brand) according to ASTM C150 standard [25], the limestone powder (LP) from grinding rock process from Saraburi Province, the metakaolin (MK) is obtained from heat treatment of kaolinite clay from Uttaradit province, the standard sand according to ASTM C33 [26], the clean water that has pH value of 7.0 and the Glenium ACE32 high range water reducing superplasticizer.

3.4. Testing

3.4.1 Chemical composition determination of main powder

To find the chemical composition by using XRF (X-ray Fluorescence) in order to analysed in term of quantity analysis of cement, limestone powder and metakaolin.

3.4.2 Physical properties determination of materials

3.4.2.1 Particle size distribution (PSD)

It can obtain the particle size distribution by using Laser particle size analyser (See in Figure 3.4)



Figure 3.4 : Laser particle size analyser machine

PSD is using Equivalent Sphere Theory which is comparing the volume of the object with the sphere object by resulting it as Unique Number. The Unique Number is the diameter of the sphere. PSD is the fast technique to calculate the particles, using the small object and having similar result event though the object has been calculate many times. The particles can be calculate in amount 0.1 to 1000 micron. [27]

3.4.2.2 Specific gravity of materials and absorption of aggregate

Refer to ASTM C128 [28] and ASTM C70 [29] for determining the specific gravity and absorption of fine aggregate. To find size distribution of aggregate by sieve analysis method according ASTM C136. [30]

3.4.2.3 Blain fineness test of main powder

To find fineness of cement according to ASTM C204 [31], limestone powder and metakaolin use the air permeability technique of Blain air-permeability apparatus. The Blaine surface area is a value which showing the fineness.

3.4.3 Fresh mortar determination

3.4.3.1 Flow table test

Refer to ASTM C1437 [32] ; Standard test method for flow of hydraulic cement mortar; the test is created to find the consistency of mortar by flow table apparatus.

3.4.4 Compressive strength test

According to ASTM C109 [33], the test of compressive strength of hydraulic cement mortar specimens, the number of specimens is 3 cube samples per set. The compression test is 1, 3, 7 and 28 day-curing-time. The compressive strength is calculated from the failure load divided by cross-sectional are which receive the load.

$$f_m = \frac{P}{A} \quad (3.4)$$

3.4.5 Hydration stop

It is necessary to stop hydration before determining the phase composition of the hydration product. There are several methods for hydration stopping to remove free water. Microwave method is the fastest [34]. In this research, the microwave method is used to stop hydration before X-Ray Diffraction test. For the procedure the paste samples were stopped hydration reaction by the microwave method. The commercial microwave oven operated with 1000W, 2.45 GHz frequency. The 3-5 mm grind samples were ovened for the interval duration times until the constant weight was occurred. Also, it has a number of drawbacks (see in Appendix C) but the suitable method should be selected for the further microstructure experimental.

3.4.6 Heat of hydration reaction determination

Use the isothermal calorimeter to determine the heat that generated from hydration reaction of cement paste and cement-limestone powder-metakaolin paste according to ASTM C186 [35]. The isothermal calorimeter is shown in Figure 3.5.

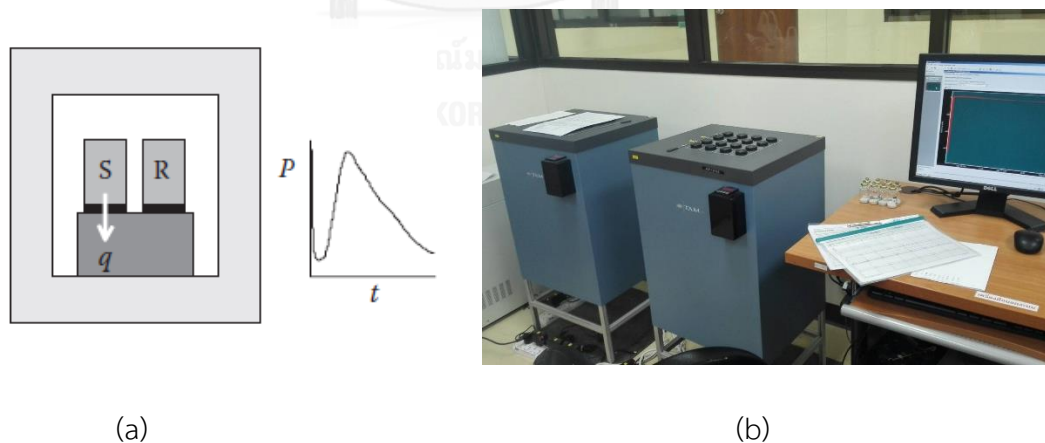


Figure 3.5 : (a) Schematic illustrations of isothermal (heat conduction) calorimetry (b) TAM AIR isothermal calorimeter

3.4.7 X-ray diffractogram determination [27]

To analyze the crystal and quantity of paste by X-ray method and comparing limestone powder-metakaolin-cement paste crystal with Portland cement paste reference. XRD is the machine that used x-ray to detect the object and using the detector to analyze the component. Each sample has the different component which can be proved by the study of crystal structure and atomic spacing. XRD is providing the X-Ray wavelength to the plane of crystal lattice with all diffraction angles, the angle of the wavelength is satisfy Bragg's Law ($n\lambda=2d \sin \theta$), to the object in order to analyze the object. The wavelength is scanning the sample through a range of 2θ angles. With this angle, all the possible diffraction direction to the lattice can be attained. The XRD machine is shown in Figure 3.6.



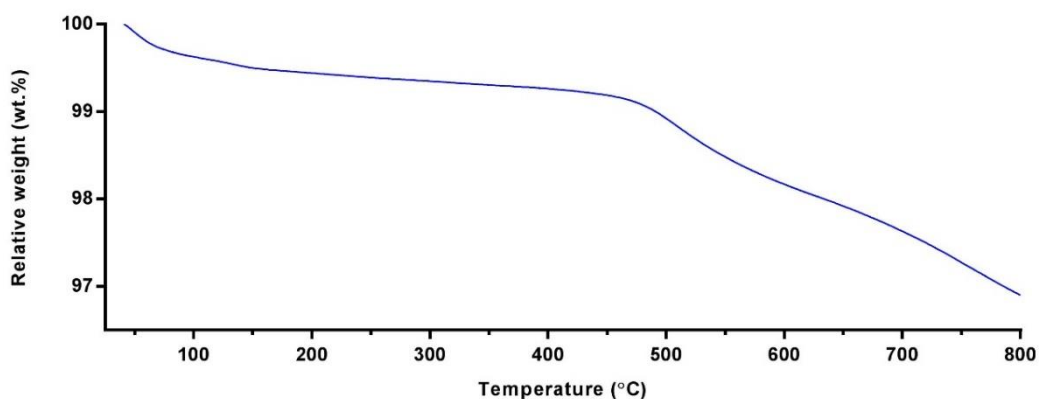
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Figure 3.6 : X-ray Diffraction machine

Chapter 4

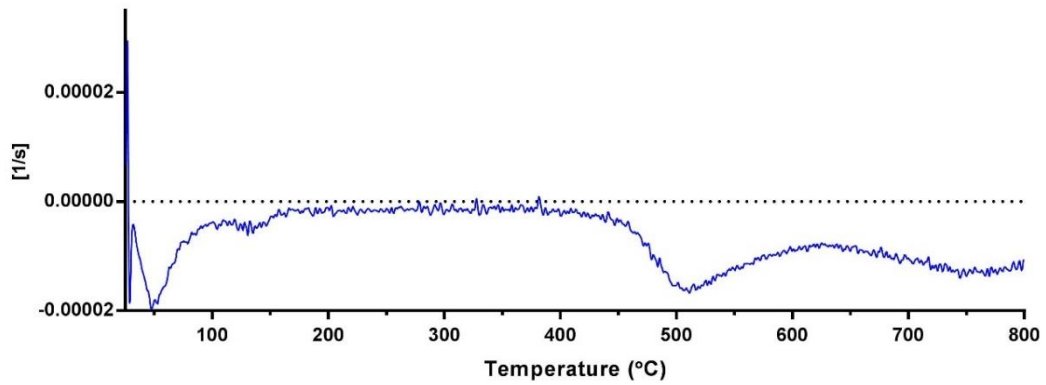
Results and Discussion

4.1 Metakaolin preparation

Pure kaolinite clay is difficult to find in Thailand. The low content of kaolinite clay that was available in the market was mixed between several reactive and non-reactive clay and other substances. So, kaolinite clay was randomly collected from Uttaradit province (The Northern province of Thailand), with kaolinite content about 20%. Thermal treatment was used to obtain meta-phase of kaolinite called “Metakaolin”. The burning temperature was determined from dehydroxylation process by Thermogravimetry (TG), the analysis is presented in Figure 4.1. It is evident that when the temperatures below 450°C, water inside the pores and the surface of the clay are released. This means that it has attributed to the pre-dehydrated process. Between 450°C and 800°C, metakaolin was formed. Therefore, the selected conditions of thermal treatment for this research was to burn kaolinite clay at 800°C for a duration of 1.5 hours. After heating kaolinite clay was quenched to room temperature to protect amorphous recrystallization.



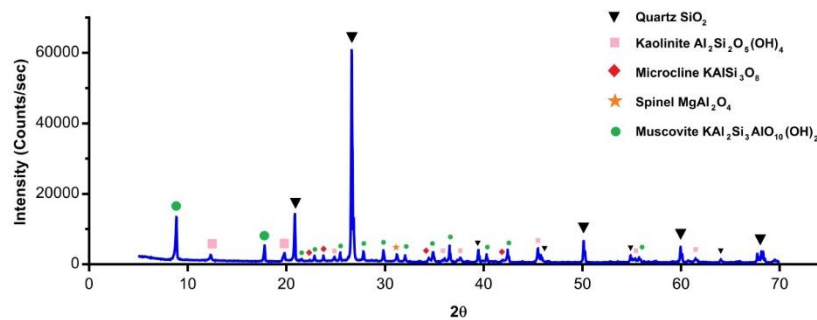
(a)



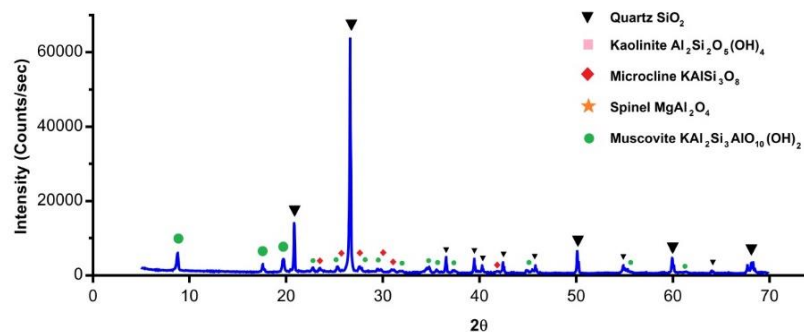
(b)

Figure 4.1 : TG analysis curve (a) mass loss of kaolinite clay (b) Time derivative of mass loss of kaolinite clay

To confirm formation of metakaolinite, X-Ray Diffraction (XRD) measurements were compared between the initial state of kaolinite clay and after heat treatment; in order to observe disappearance of kaolinite peaks as shown in Figure 4.2.



(a)



(b)

Figure 4.2 : (a) XRD pattern of starting kaolinite clay (b) XRD pattern of kaolinite clay after burning at 800° C for 1.5 hours

4.2 Properties of raw materials

4.2.1 Chemical and physical properties of main powders

The chemical composition, quantifications by X-Ray Fluorescence method and some physical properties of 3 main raw materials are given in Table 4.1. The general compositions of cement are calcium oxide, silica oxide and alumina oxide. Limestone powder contain approximately 98% of calcium carbonate. Metakaolin is pozzolic material consist of silica oxide and alumina oxide as the main components. The size distribution is also shown in Figure 4.3. The median particle size (D_{50}) of cement, limestone powder and metakaolin are 38.623 μm , 5.891 μm , and 7.459 μm , respectively.

Table 4.1. The physical and chemical properties of the main powder.

Oxide/Compound	Cement (wt%)	Limestone powder (wt%)	Metakaolin (wt%)
CaO	67.820	-	-
CaCO ₃	-	97.950	-
SiO ₂	18.035	1.649	76.982
Al ₂ O ₃	3.921	-	14.027
K ₂ O	0.560	-	4.704
TiO ₂	0.348	-	0.159
MgO	-	-	1.990
SO ₃	4.067	-	-
Fe ₂ O ₃	3.831	0.401	2.140
Total	100.000	100.000	100.000
Blain surface area (m ² /g)	0.117	2.240	1.180
Specific gravity	3.116	2.674	2.420

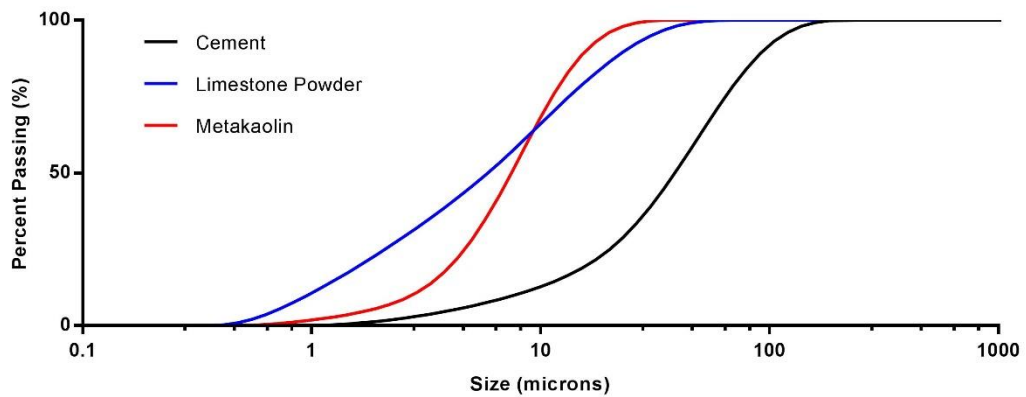


Figure 4.3 : Particle size distribution of the main powder by laser diffraction analyzer

4.2.2 Physical properties of fine aggregate

The percentage absorption of sand is 0.633 and the specific gravity of sand is 2.606. The size distribution shows in Figure 4.4.

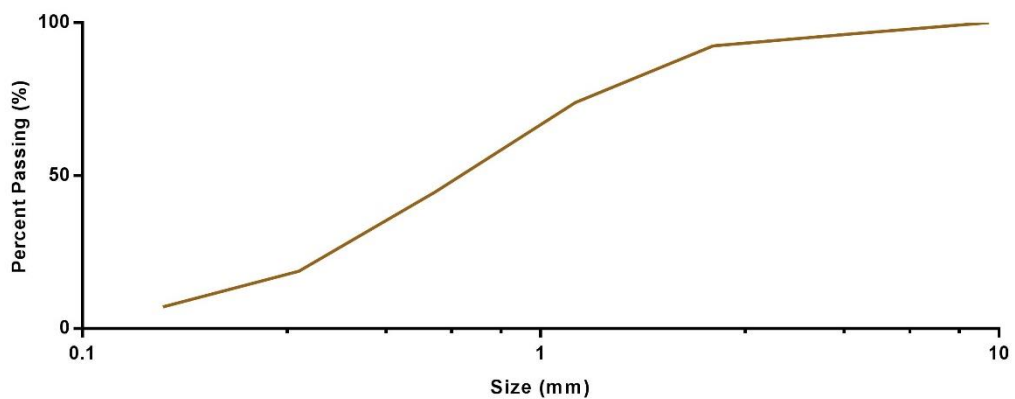


Figure 4.4 : Particle size distribution of sand by sieve analysis method

4.3 Workability of blend mortar tested by flow table method

Polycarboxylic Ether superplasticizer (PCEs), Glenium ACE32 was added to adjust the workability of ternary blends mortar. The proper dosage was obtained by adjusting the amount of superplasticizer. The adjustment should cause the percentage of flow table of ternary blends mortar to be almost the same as cement mortar reference and also has the percentage of flow table in the standard normal

consistency range of 110 ± 5 %. The results of each mixed proportion is illustrated in Table 4.2. 1% of PCEs was used by dry weight of binder in this study.

Table 4.2. The percentage of flow table for ternary blends mortar with various dosage of superplasticizer

Formula	Amount of superplasticizer (wt% of binder)		
	0	1	2
	Flow table of mortar (%)		
100% CM	110.99	-	-
B45S 1:2	103.35	110.24	140.57
B45S 1:1	105.31	113.19	140.75
B45S 2:1	108.26	112.21	141.73

4.4 Heat of hydration

4.4.1 Effect of limestone powder and metakaolin

Figure 4.5 shows the heat evolution for different blend pastes, compared to the reference, for the period of 100 hours at 25°C. Whilst, Figure 4.6 illustrates the cumulative heat curve reported on basis of grams of Portland cement.

From these results, it can be seen that without superplasticizer system, limestone powder-metakaolin mixtures have the highest heat evolution rates due to aluminate components. An observation can be made on the second peak that it is due to replacing cement with high aluminate content material. There are similar effects on the hydration process for any ratio of limestone powder and metakaolin. Adding limestone powder and metakaolin can accelerate the early age hydration reaction.

The addition of superplasticizer clearly retards hydration reaction of blends paste as shown in Figures 4.5 and 4.6. During the initial slow stage, the superplasticizer can prompt the formation with calcium ion, it had to be prolonged, inhibition of C-S-H gel forming and display better fluidity retention. Which also had an effect on the initial and final setting time. B45S 1:2 and B45S 2:1 paste have rather similar heat flow,

whereas B45S 2:1 exhibited a longer delay for the hydration process. The final setting time was shifted from 5 hours to 30-35 hours in superplasticizer system.

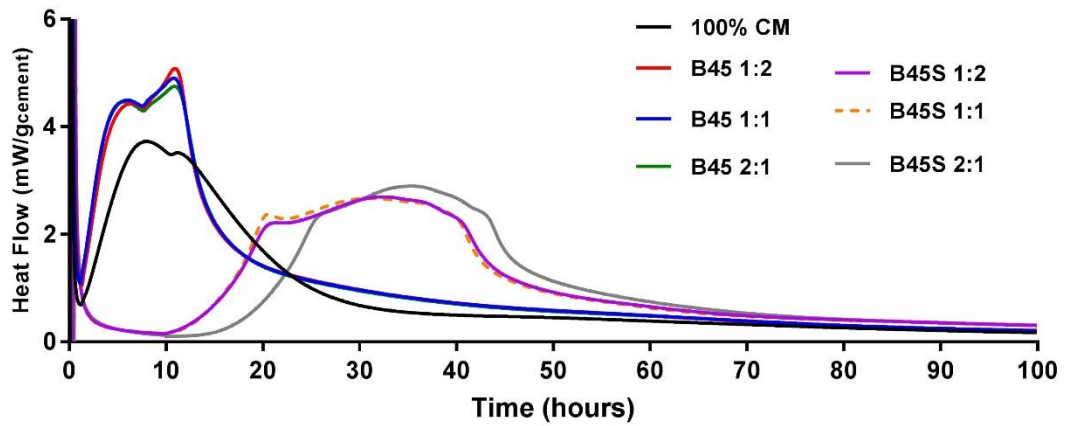


Figure 4.5 : Heat flow reported on basis of grams of cement by isothermal calorimeter of the blend paste compared to cement paste reference (100% CM) until 100 hours

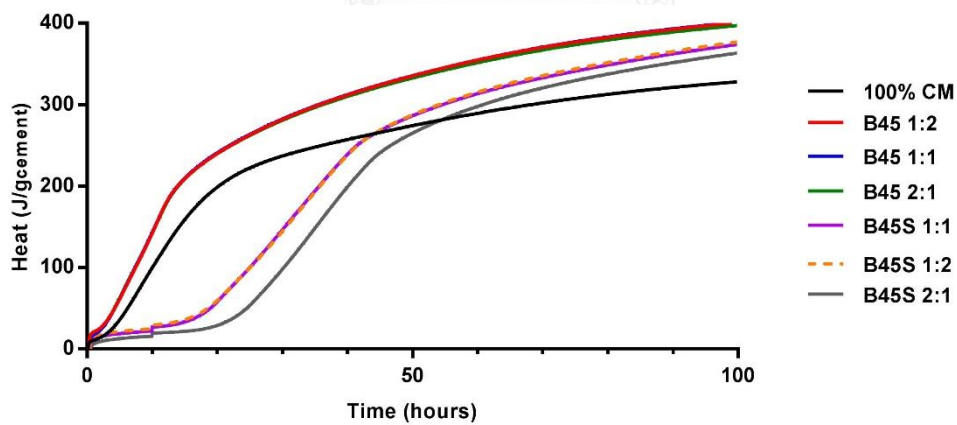


Figure 4.6 : Cumulative heat reported on basis of grams of binder paste compared to cement paste reference (100% CM) until 100 hours

4.4.2 Effect of ternary blends on heat of hydration

Figure 4.7 shows the heat flow reported on basis of grams of binder that and Figure 4.8 demonstrate the accumulate heat. It can be observed that when replacement cement by partially limestone powder and metakaolin can be reduced the heat evaluation of hydration process rather than 100% cement paste. It have a benefit for use in massive structure. In some situation, the heat cannot be readily released. The mass concrete may then attain high internal temperatures and cracks occurs. Therefore, replacement cement by limestone powder and metakaolin can be tackled this problem.

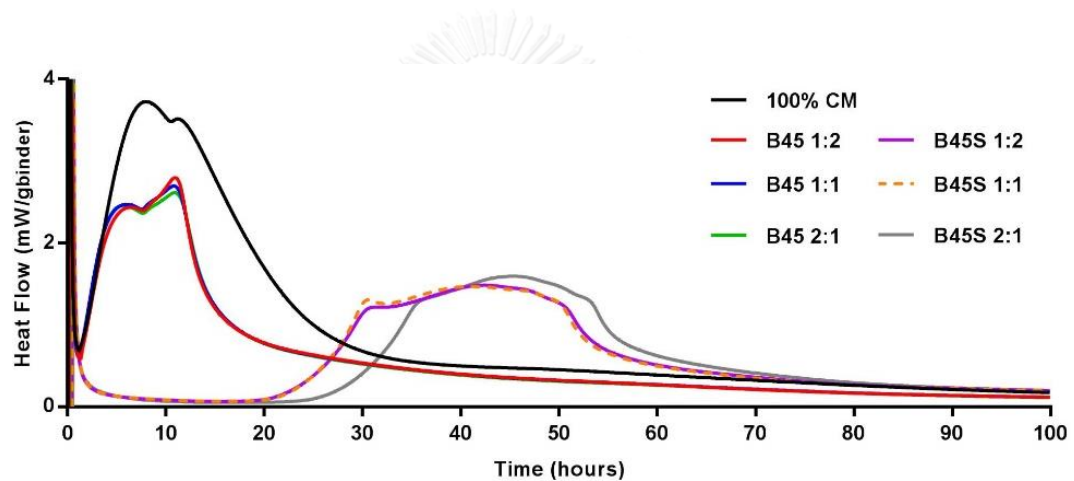


Figure 4.7 : Heat flow reported on basis of grams of binder by isothermal calorimeter of the blend paste compared to cement paste reference (100% CM) until 100 hours

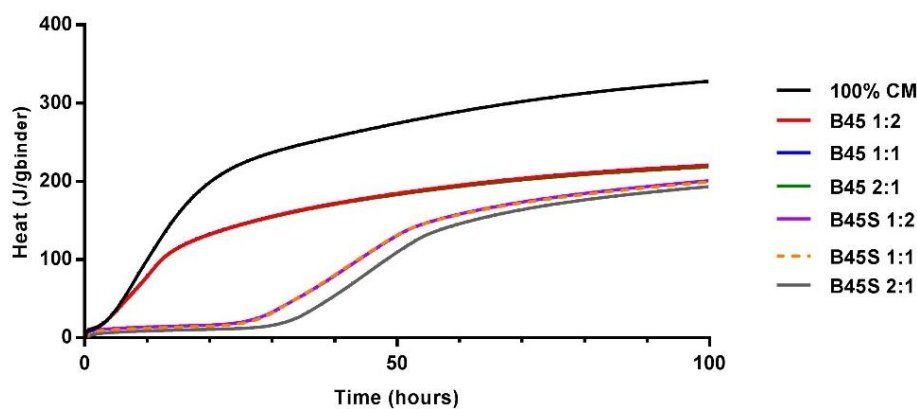


Figure 4.8 : Cumulative heat of binder paste compared to cement paste reference (100% CM) until 100 hours

4.5 X-Ray Diffraction

The selected XRD patterns of all paste samples at 1, 3, 7 and 28 days are given in Figure 4.9. XRD measurement of grinding paste powder samples were accomplished by Bruker diffractometer using $\text{CuK}\alpha$ source with wavelength 1.5418740 Å, rotating stage between 5 and 70 °2 θ , step size of 0.0199 °2 θ and a time per step 30 second. The Rietveld refinement strategy was used for determining the trend of appearance crystalline substances in XRD technique.

In this research used the fully functional Reitveld program called “TOPAS” by Bruker Corporation. The quantitative analysis in percentage for all detected phases for 28 days paste samples shown in Table 3. The results from Reitveld refinement analysis cannot directly comparing in term of quantity due to inappropriate preparing the specimen for XRD test. Stop hydration reaction by microwave method can be explained in term of qualitative analysis. It does not suitable for quantitative analysis. Therefore, Reitveld refinement in this research exhibited trend of amount of crystal which appear after hydration reaction throughout the age of study.

For the 100% CM paste, there was formation of ettringite, an increase in amount of Portlandite (CH) and a decrease in the main compounds of cement (C_2S , C_3S , C_3A , C_4AF) due to hydration reaction over the age of cement paste. The XRD results for the B45 blend without admixture systems show the formation of ettringite, also the growing quantity of Portlandite and hemicarboaluminate appears from day 1 throughout the age of study and then conversion into monocarboaluminate. Some components of clay can be observed from the amount of calcined clay added. For the B45S blend with PCEs systems, the appearance of crystal substances are in similar manner with B45 blend system, but the formation is slower due to the effect of superplasticizer, especially the hemicarboaluminate detected from day 3.

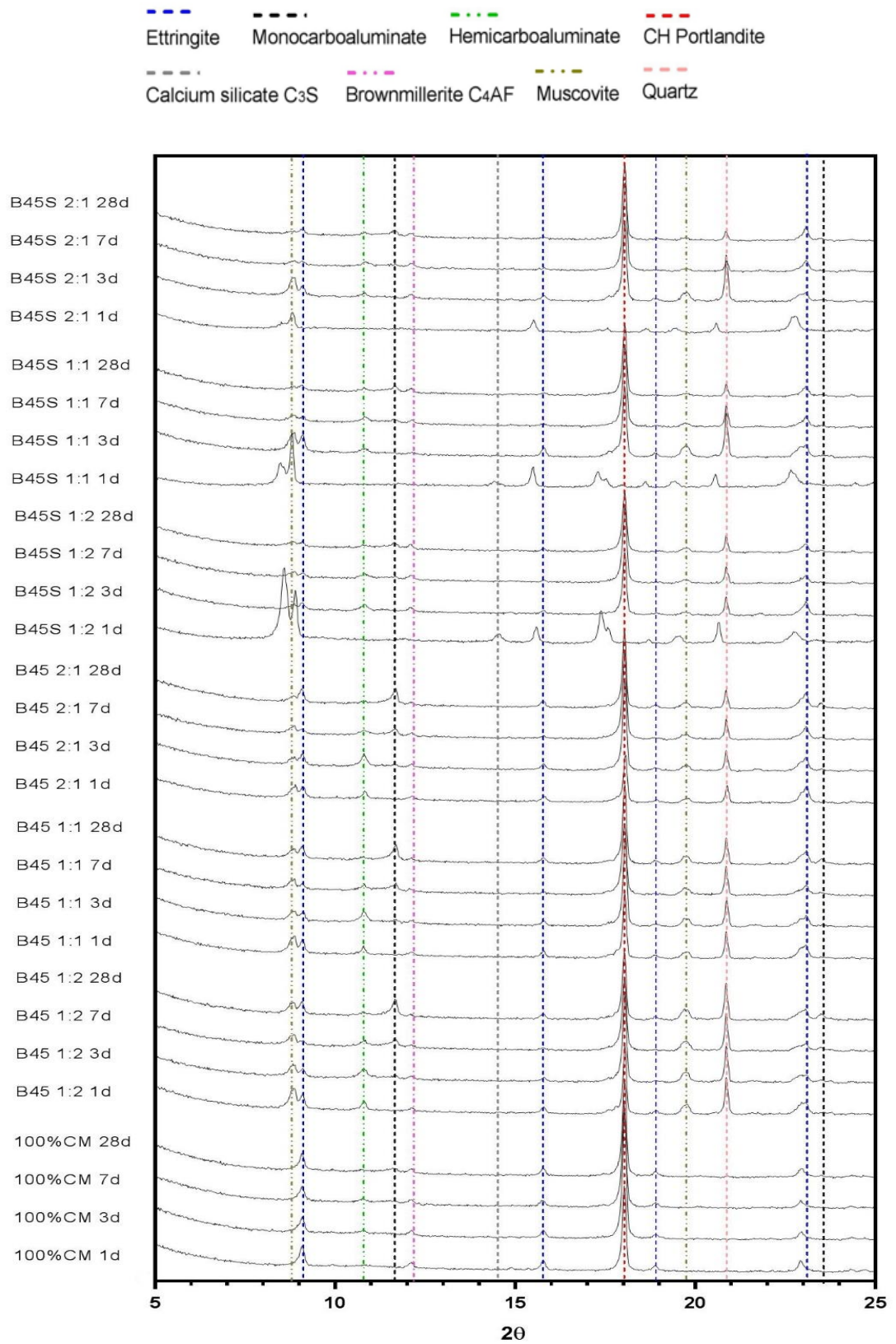


Figure 4.9 : XRD patterns for 100% cement paste and ternary blend paste with and without admixture at 1, 3, 7 and 28 days

Table 4.3. Phases obtained by Reitveld refinement of XRD at 28 days of hydration.

The substances obtained (%)		Formula						
		100% CM	B45 1:2	B45 1:1	B45 2:1	B45S 1:2	B45S 1:1	B45S 2:1
C3S	C3S-M3	0.96	0.25	0.29	0.24	0.24	0.51	4.07
	C3S-M1	2.60	0.22	0.19	0.28	3.81	4.85	1.67
C2S		4.46	2.02	2.43	2.50	2.53	2.69	2.90
C3A	C3A Cub.	0.57	0.09	0.19	0.00	0.74	0.72	0.99
	C3A Orht.	0.17	0.34	0.27	0.82	0.00	0.31	0.29
C4AF		5.75	2.83	2.81	2.84	3.20	3.30	3.53
Portlandite		11.02	6.37	7.04	7.42	7.67	8.64	9.17
Calcite		5.13	12.21	16.36	20.24	11.47	16.30	19.31
Ettringite		4.62	2.67	2.57	2.37	1.07	0.96	0.94
Monocarboaluminate		2.98	6.50	6.34	6.05	3.80	3.37	2.80
Hemicarboaluminate		1.19	1.19	0.08	0.04	1.20	0.76	0.54
Quartz		0.00	12.45	9.76	6.96	6.57	5.24	3.36
Muscovite		0.00	9.01	6.35	4.86	3.95	3.68	1.44
Dolomite		0.00	0.56	1.68	1.83	1.82	2.08	2.49

The results of XRD measurement with Reitveld refinement of all paste at the age of 28 days are shown in Table 4.3. It can be observed that the Portland cement contain a few amount of limestone powder because of the hemicarboaluminate and monocarboaluminate phases appear. For the ternary blend show that at 28 days the substitution cement by limestone powder and metakaolin has the beneficial effect for increase the amount of hemicarboaluminate phase.

4.6 Mechanical strength

Compressive strength of all mortar specimens were tested at the age of 1, 3, 7 and 28 days. The results are presented in Figure 4.10 and the relative compressive strength compared to 100% CM mortar reference is illustrated in Figure 4.11.

The values of compressive strength obtain for the ternary blend with and without superplasticizer mortar show the same trend as in case of Portland cement mortar reference; a continuous increase compressive strength with increasing age of mortar. For all mix proportions, the compressive strength value was lower than the reference for all ages. In this study, the best result of ternary blend mortar is B45S 1:2 mortar. As for the 45% blend mortar, the cement was replaced by limestone powder (15%) and metakaolin (30%) with 1% of superplasticizer; which caused it to almost reach the same compressive strength as the control reference approximately of 97% relative at 28 days.

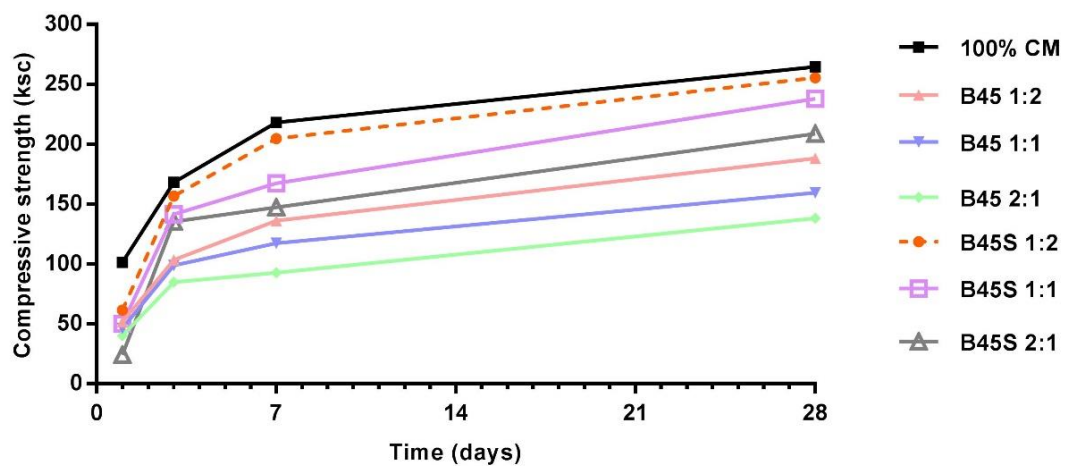


Figure 4.10 : Compressive strength of blend mortars at 1, 3, 7 and 28 days

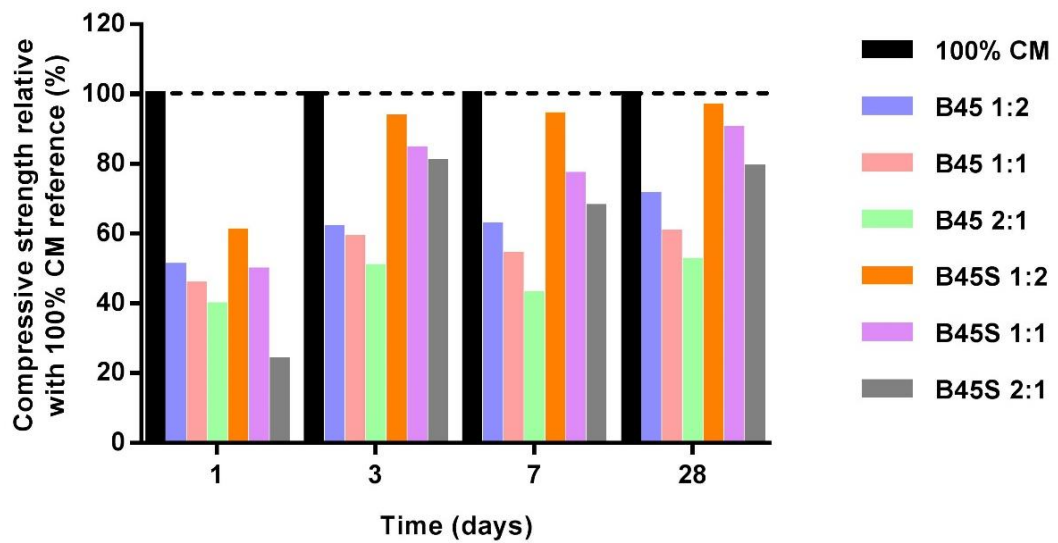


Figure 4.11 : Relative compressive strength to 100% cement mortar for varying limestone powder to metakaolin ratio

Generally, there are no direct relation between heat of hydration and strength of mortar but it can possible correlating strength with cumulative heat for any mix proportion at any aged. Figure 4.12 shows the correlation between compressive strength of mortars and heat of hydration. It is supposed that the higher cumulative heat generated by hydration reaction cause of higher compressive strength.

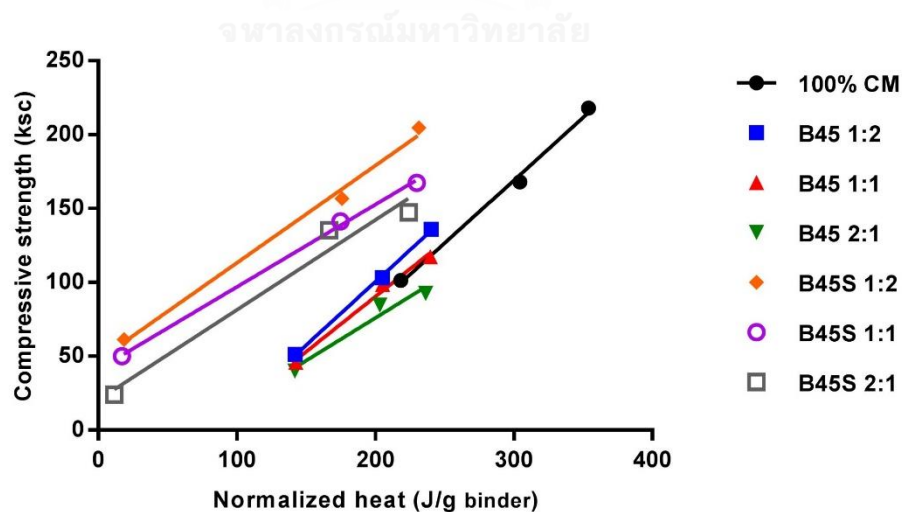


Figure 4.12 : Compressive strength (1, 3 and 7 days) vs cumulative heat release per gram of binder

Chapter 5

Conclusion

5.1 Conclusion

This study shows the compressive strength development of mortar with the 45% replacement cement by combination substitutions of limestone powder and metakaolin by varying limestone to metakaolin ratio into 1:2, 1:1 and 2:1 with and without PCE superplasticizer comparing to 100% cement mortar reference. In this research investigating that 45% cement replacement by 15% limestone powder and 30% metakaolin with 1% PCEs have the highest compressive strength value and reached almost the same as compressive strength of 100% cement mortar reference. The key mechanism which has an effect on compressive strength as following:

1. PCE superplasticizer make the dispersing mechanism in the early stage of reaction. The main polymer chains (carboxylate group $-\text{COO}^{-}$) adsorb on the surface of cement particles and then become a negative charge particle. Then, electrostatic repulsion between the cement particles occurred. After that, the cement particle rearrangement and improve compactness which leads to a decrease in the total porosity of the hardened mortar. It cause of superplasticizer system have higher compressive strength rather than non-superplasticizer system.
2. XRD results show that the aluminate in metakaolin react with calcium hydroxide and water to form calcium aluminate hydrate. Presenting of calcium carbonate in limestone powder cause forming hemicarboaluminate in the early age and conversion to monocarboaluminate throughout the age of study. The formation indicate that the role of calcium carbonate is not only that of inert filler but also being a reactive component take place by solid state mechanism. There are increase the AFm phase which has an effect on the compressive

strength. The cement replacement by limestone powder and metakaolin leads to the synergetic reaction between aluminates and carbonate. It also supported by trend of Reitveld refinement analysis show that the higher amount of both hemicarboaluminate and monocarboaluminate in ternary blends system rather than cement paste.

3. The quality of metakaolin has an effect on development compressive strength in ternary blend mortar. Impurity of metakaolin cause of the limitation of reaction. It has low level of aluminate oxide in clay. So, it cause of the compressive strength not well as expected.

5.2 Recommendation

The quality of metakaolin is the most important in the study. For the further investigation, pure kaolinite clay, or high kaolinite content clay, should be used for heat treatment process for obtain the high reactive material. Moreover, there are several method for hydration stopping so it should be selected the proper method for the further microstructure test.

Last but not least, the microstructure determination experiment should be done by high experience person because of it can be effected to the accuracy of the results.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX A

ABBREVIATIONS

C ₃ S :	3CaO.SiO ₂	Tricalcium silicate (Alite)
C ₂ S :	2CaO.SiO ₂	Dicalcium silicate (Blite)
C ₃ A	3CaO.Al ₂ O ₃	Tricalcium aluminate
C ₄ AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	Ferrite
C-S-H	CaO.SiO ₂ .H ₂ O	Calcium silicate hydrate
C-A-S-H	CaO.Al ₂ O ₃ . SiO ₂ .H ₂ O	Calcium silicate aluminate hydrate
CH	Ca(OH) ₂	Calcium hydroxide (Portlandite)
Calcite	CaCO ₃	Calcium carbonate
Ettr	3CaO.Al ₂ O ₃ .3CaSO ₄ .32H ₂ O	Ettringite
Hemicarboaluminate	3CaO.Al ₂ O ₃ .0.5Ca(OH) ₂ .0.5CaCO ₃ .11.5H ₂ O	
Monocarboaluminate	3CaO.Al ₂ O ₃ .CaCO ₃ .11H ₂ O	
Quartz :	SiO ₂	
Muscovite :	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	
Dolomite :	CaMg(CO ₃) ₂	
Kaolinite :	Al ₂ Si ₂ O ₅ (OH) ₄	
Microcline :	KAlSi ₃ O ₈	
Spinel :	MgAl ₂ O ₄	
TGA :	Thermalgravimetric Analysis	
PSD :	Particle Size Distribution	
XRF :	X-Ray Fluorescence	
XRD :	X-Ray Diffraction	
100% CM :	100% cement paste or mortar	
BxxS y:z :	Ternary blend with couple substitution limestone powder and metakaolin xx% by dry weight of cement with or without superplasticizer S and the ratio between limestone powder and metakaolin y:z	

APPENDIX B
EXTENDED RESULTS

B1. XRD Results and Reitveld refinement analysis

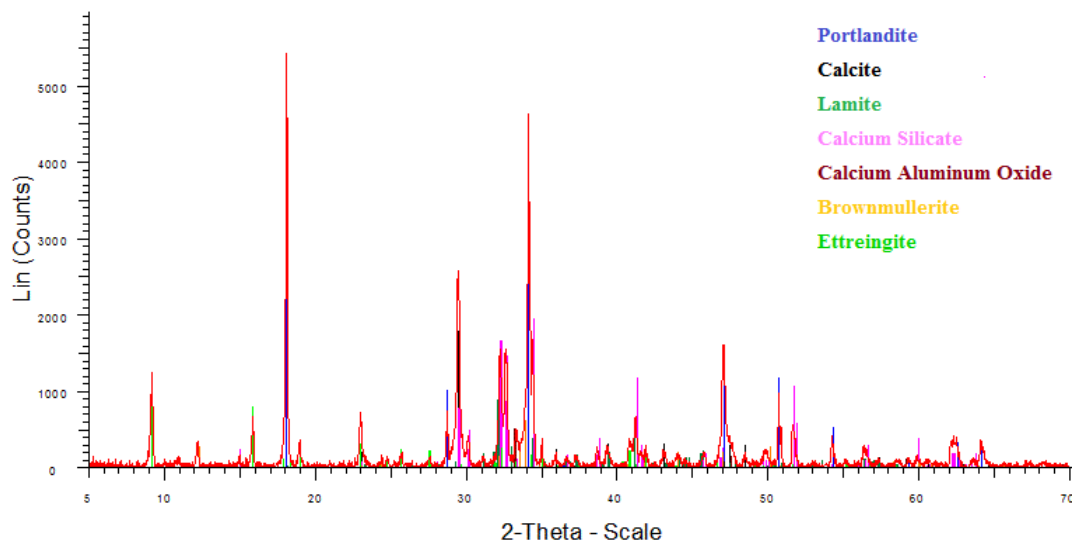


Figure B 1 : XRD pattern for 100% CM paste at 1 day

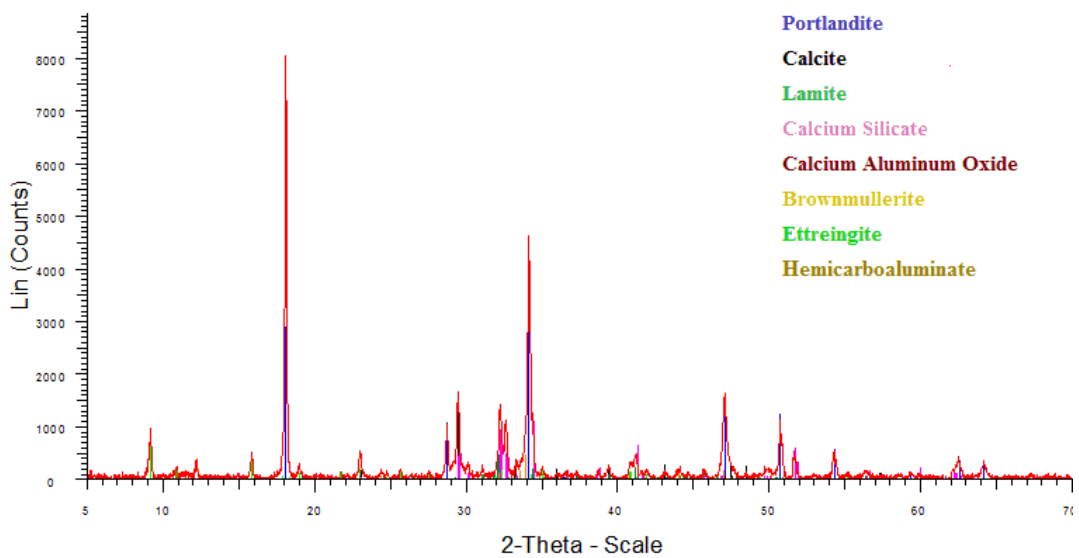


Figure B 2 : XRD pattern for 100% CM paste at 3 days

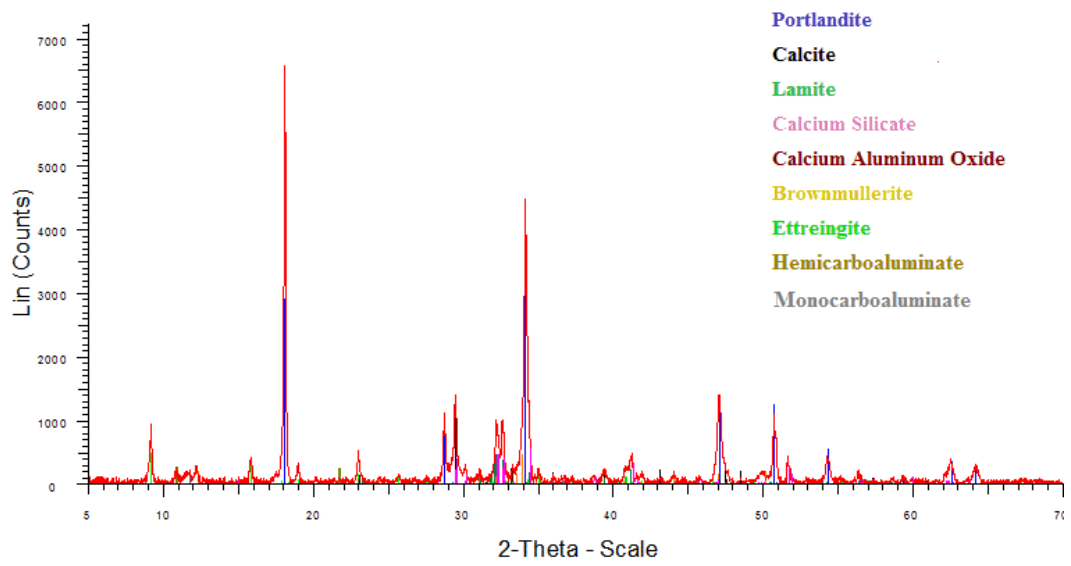


Figure B 3 : XRD pattern for 100% CM paste at 7 days

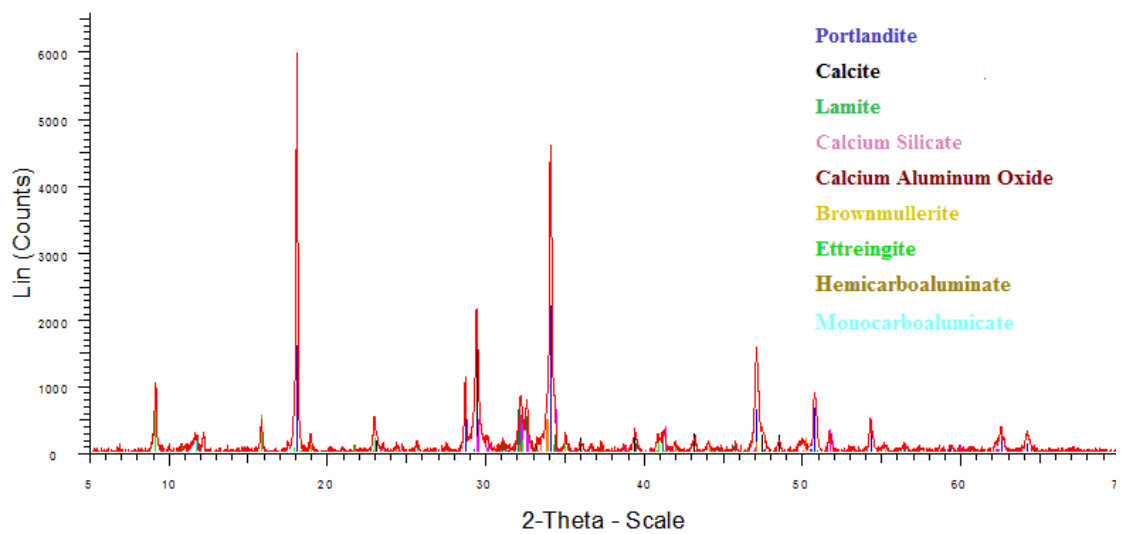


Figure B 4 : XRD pattern for 100% CM paste at 28 days

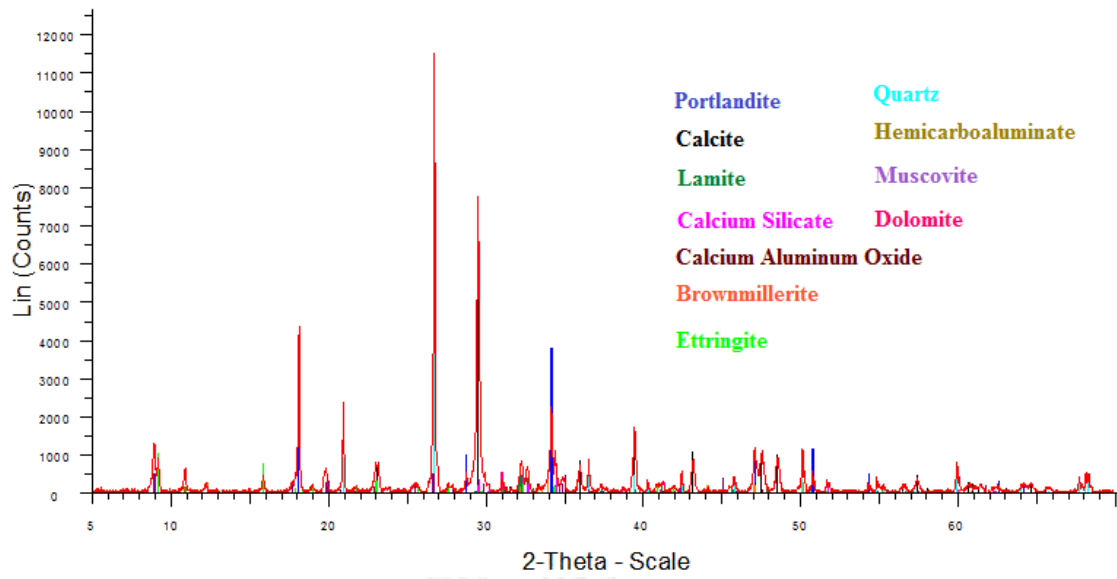


Figure B 5 : XRD pattern for B45 1:2 paste at 1 day

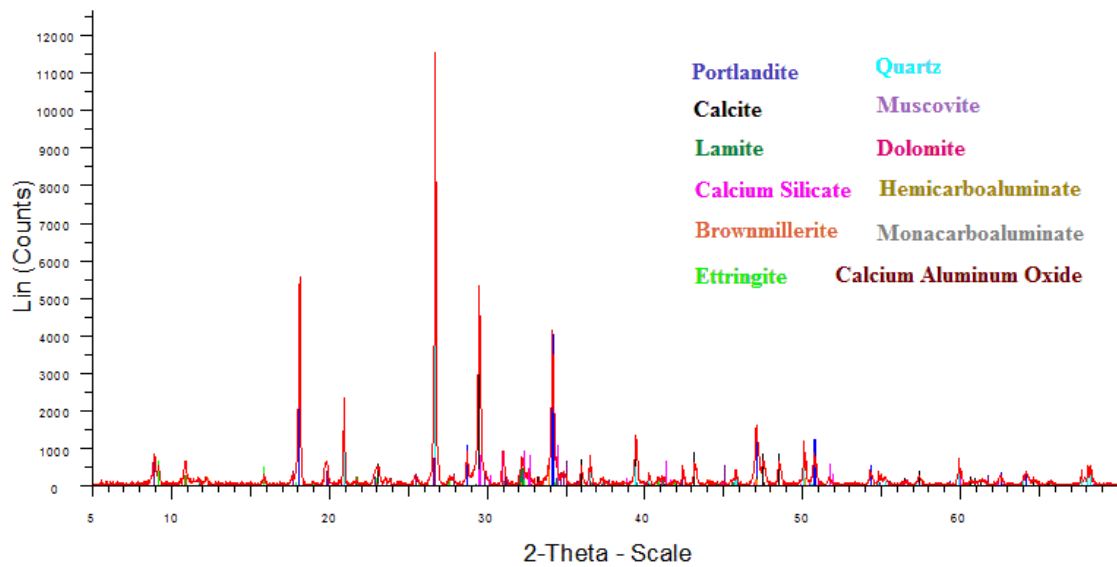


Figure B 6 : XRD pattern for B45 1:2 paste at 3 days

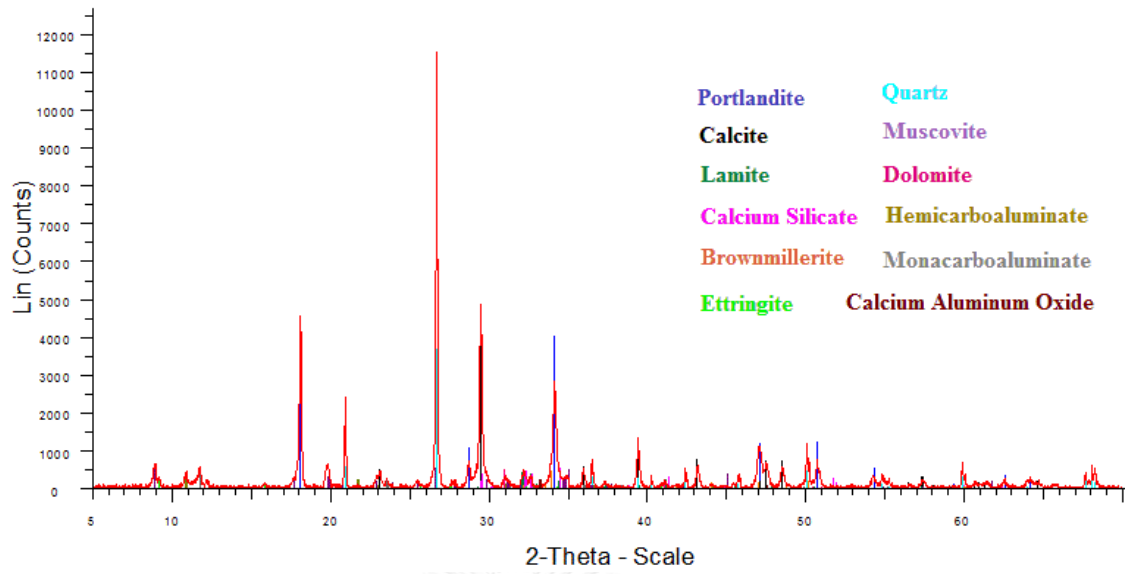


Figure B 7 : XRD pattern for B45 1:2 paste at 7 days

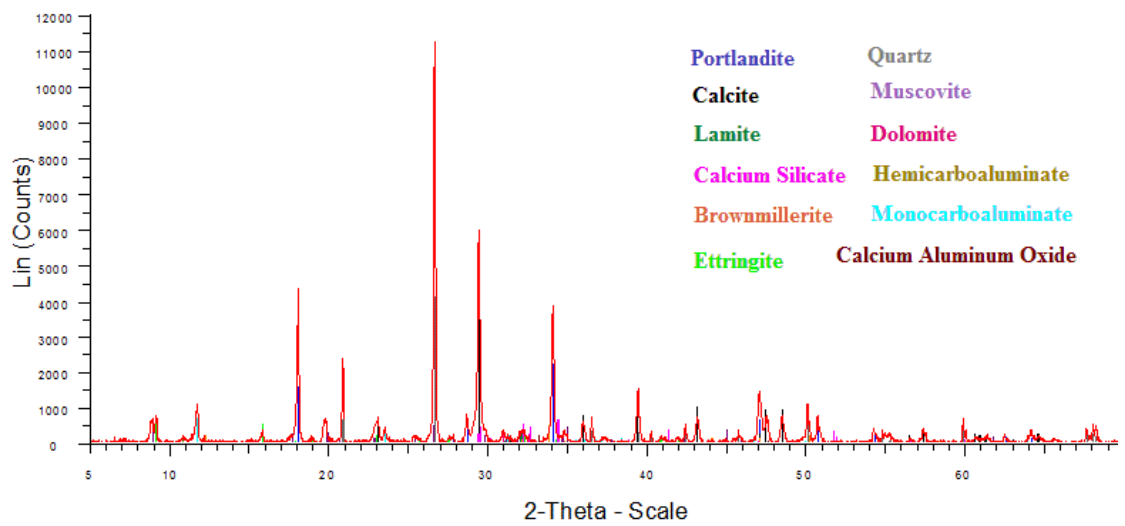


Figure B 8 : XRD pattern for B45 1:2 paste at 28 days

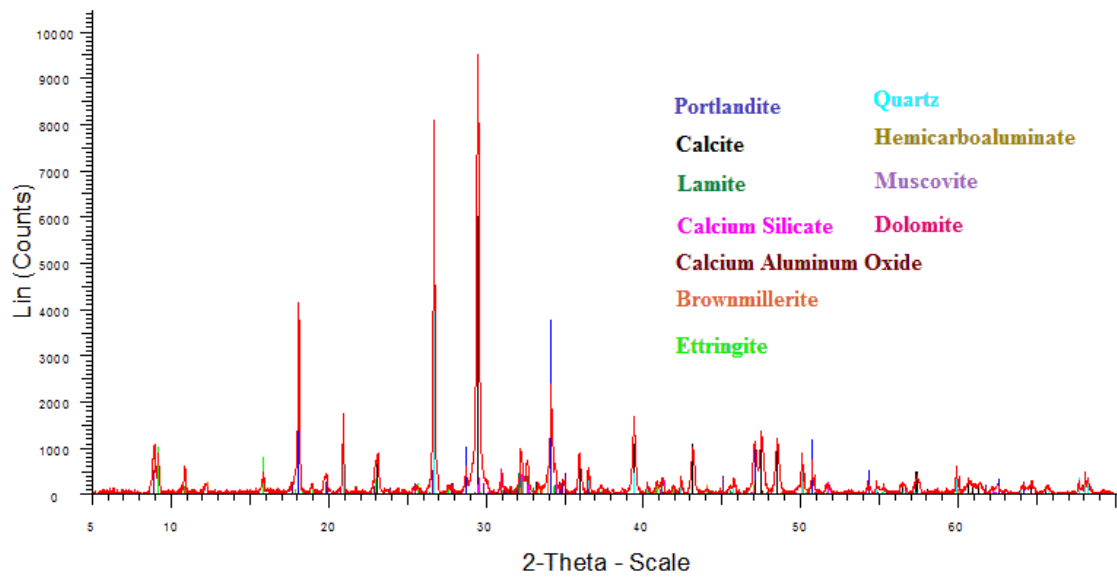


Figure B 9 : XRD pattern for B45 1:1 paste at 1 day

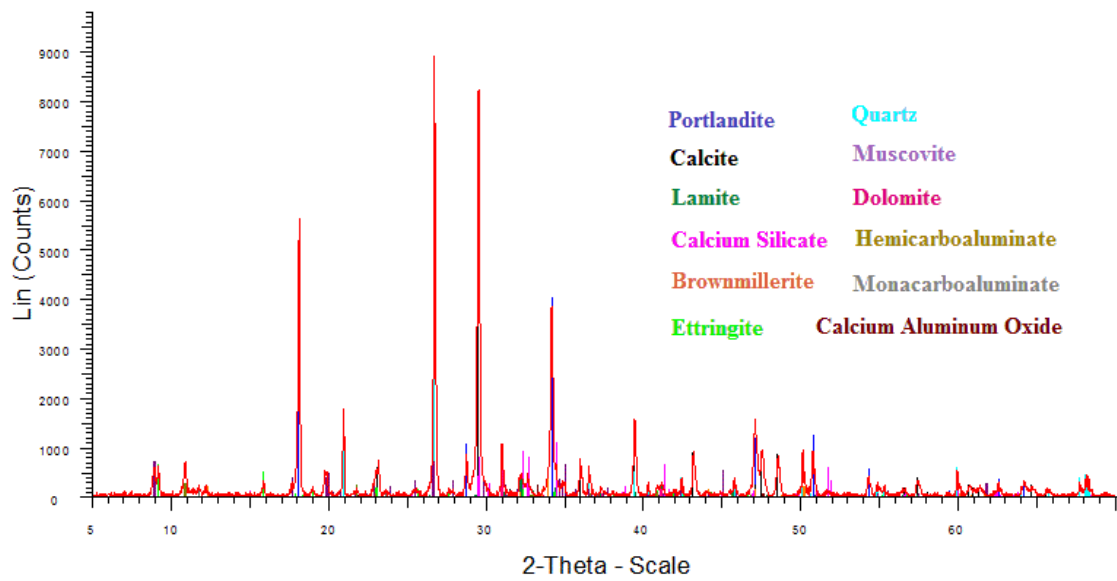


Figure B 10 : XRD pattern for B45 1:1 paste at 3 days

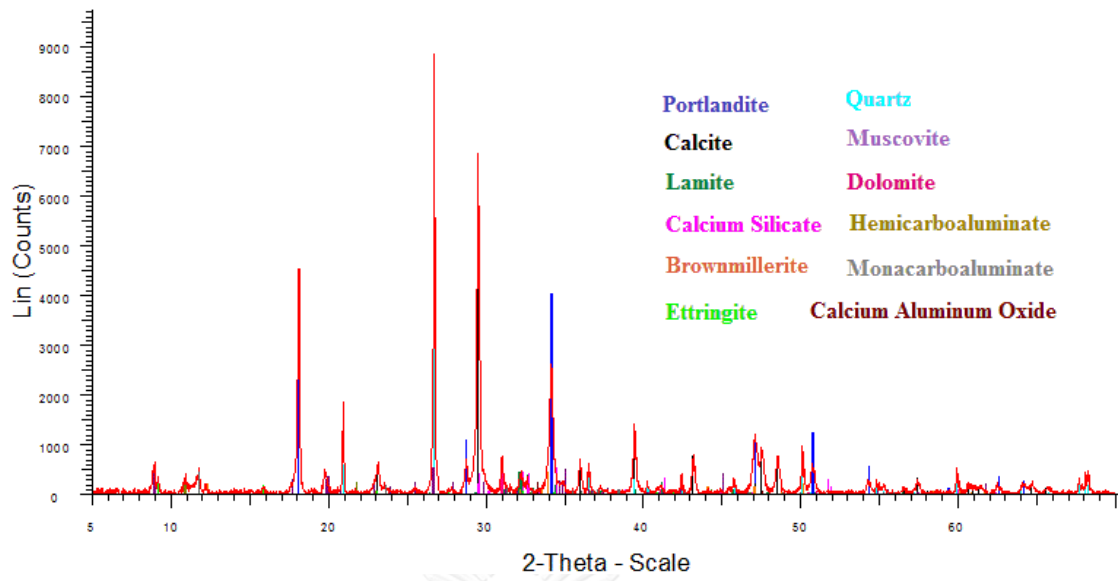


Figure B 11 : XRD pattern for B45 1:1 paste at 7 days

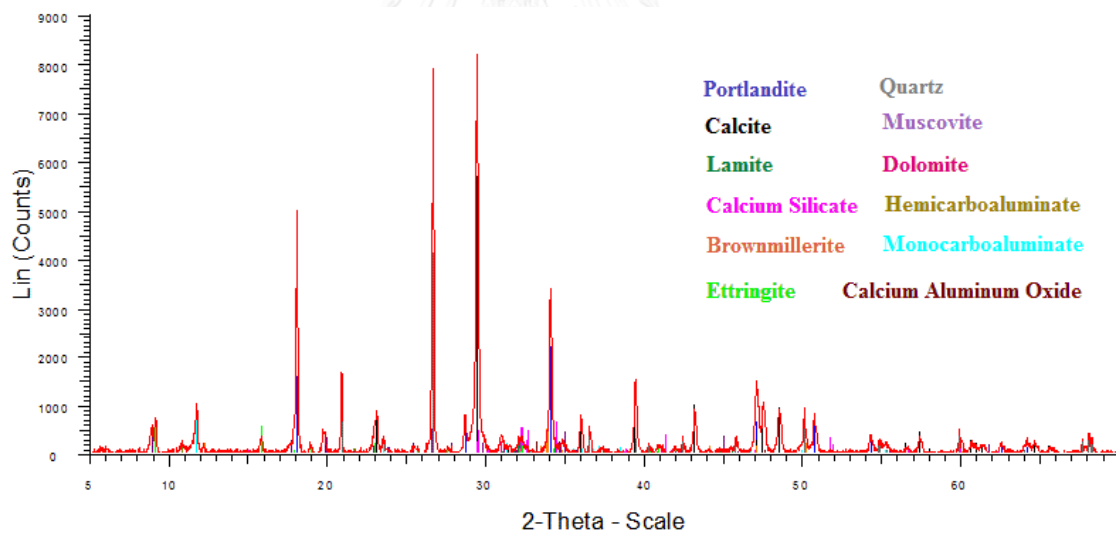


Figure B 12 : XRD pattern for B45 1:1 paste at 28 days

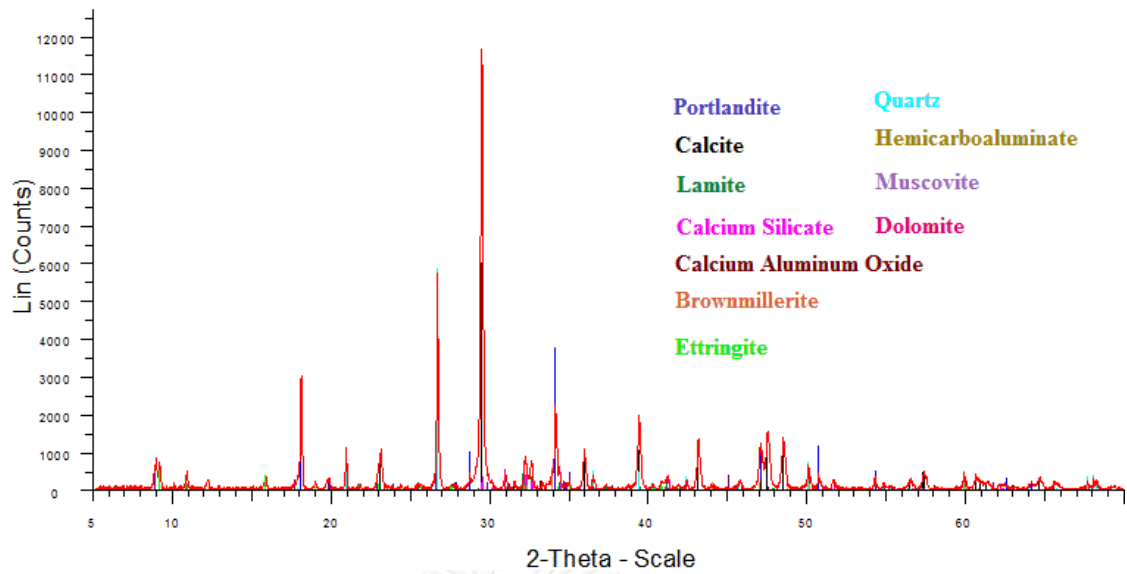


Figure B 13 : XRD pattern for B45 2:1 paste at 1 day

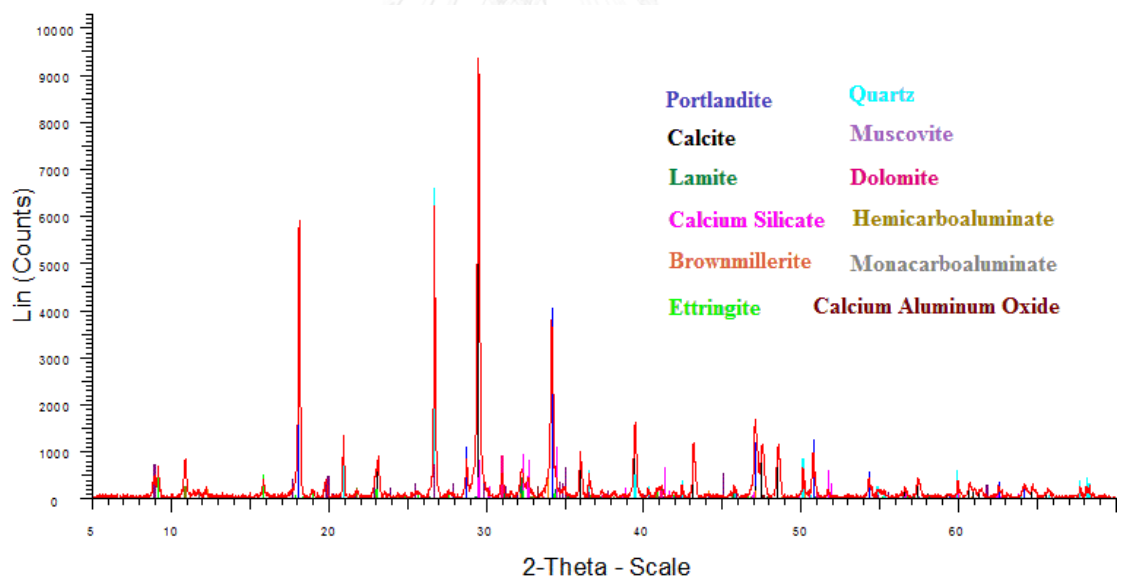


Figure B 14 : XRD pattern for B45 2:1 paste at 3 days

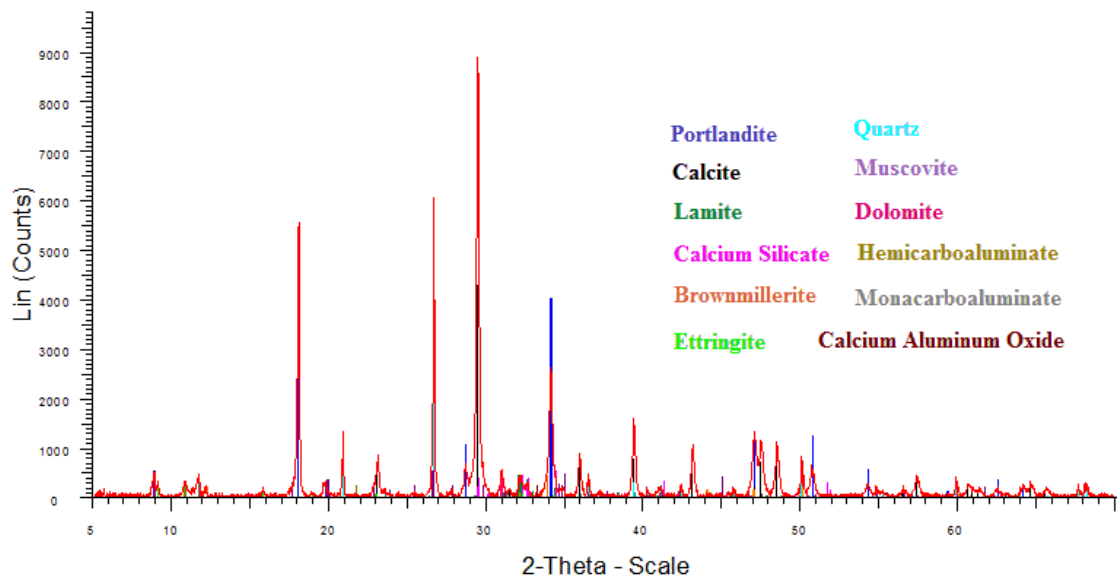


Figure B 15 : XRD pattern for B45 2:1 paste at 7 days

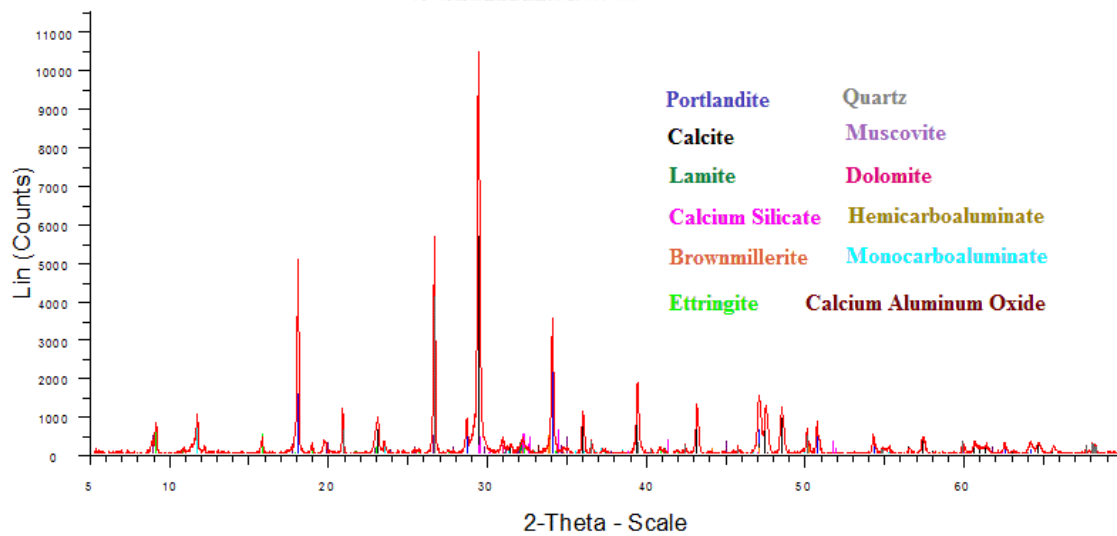
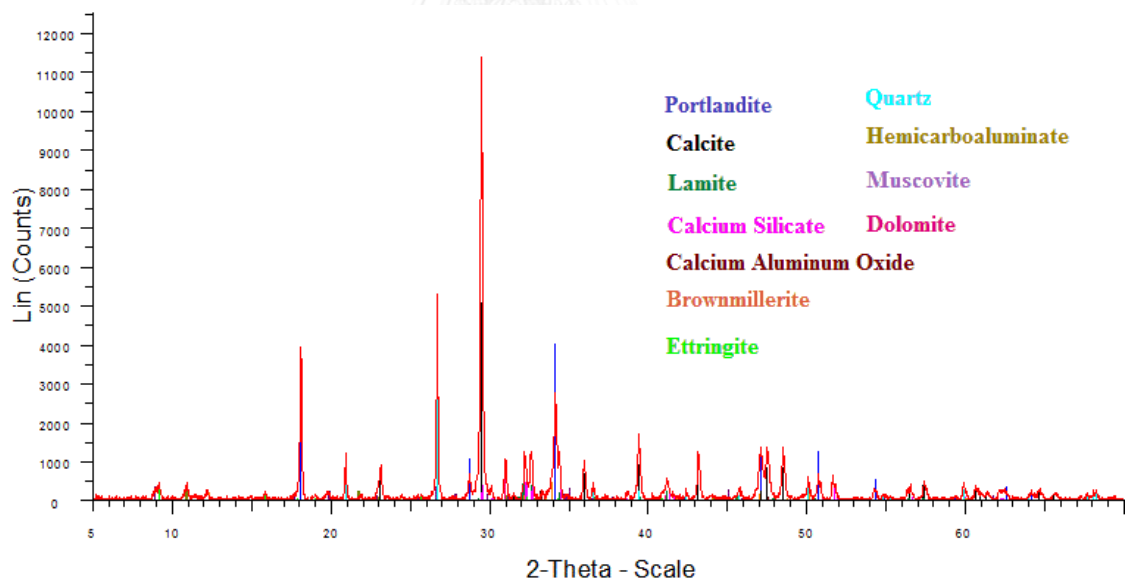
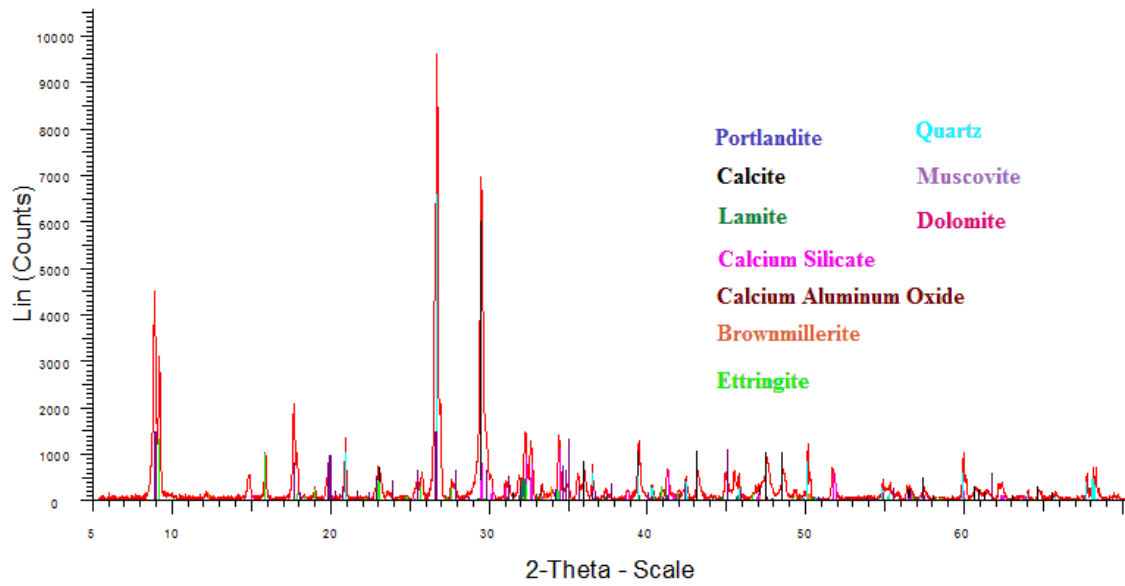


Figure B 16 : XRD pattern for B45 2:1 paste at 28 days



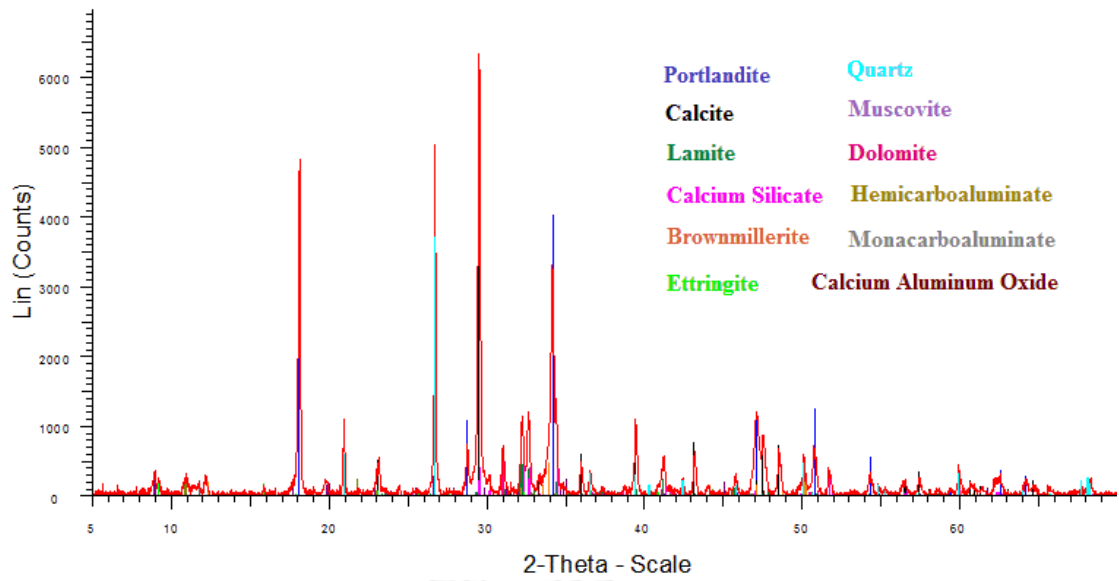


Figure B 19 : XRD pattern for B45S 1:2 paste at 7 days

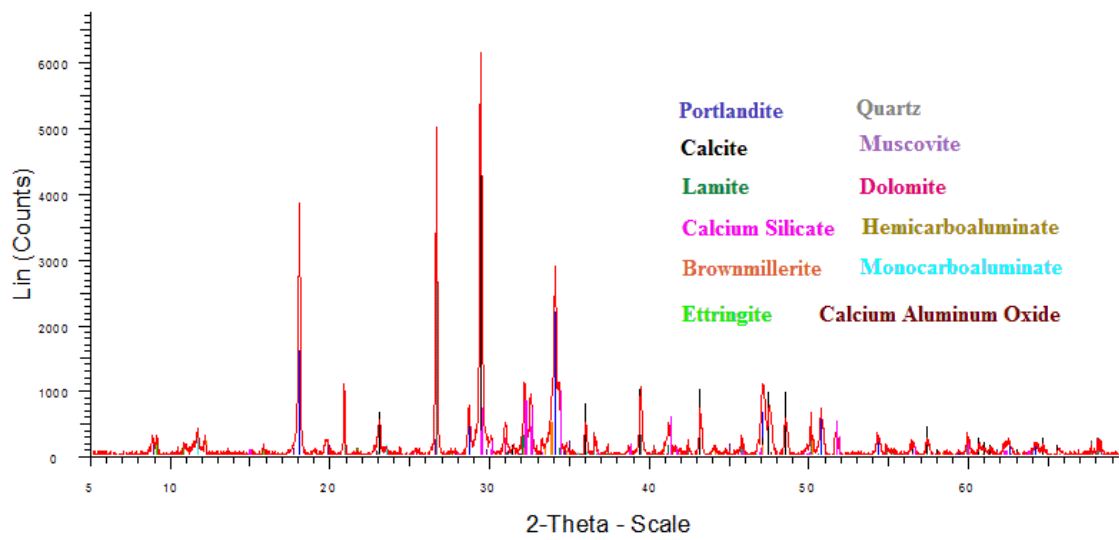


Figure B 20 : XRD pattern for B45S 1:2 paste at 28 days

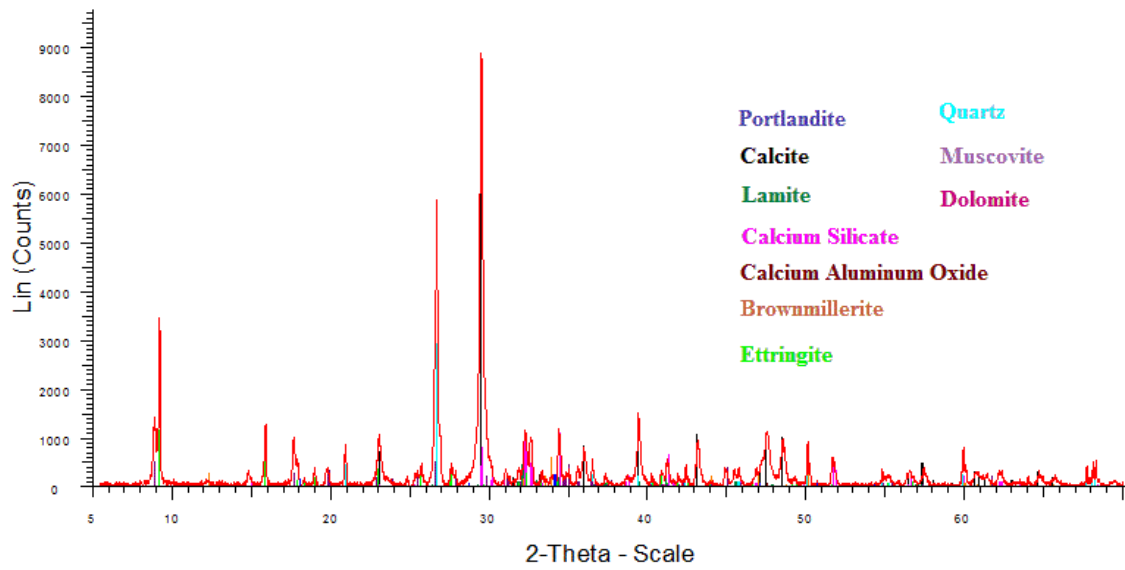


Figure B 21 : XRD pattern for B45S 1:1 paste at 1 day

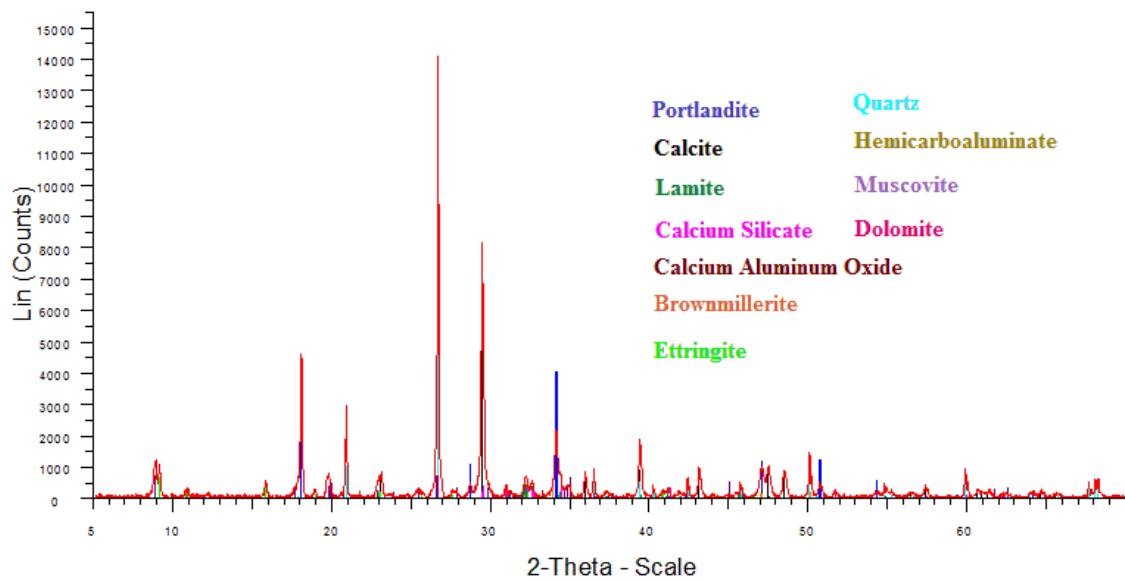


Figure B 22 : XRD pattern for B45S 1:1 paste at 3 days

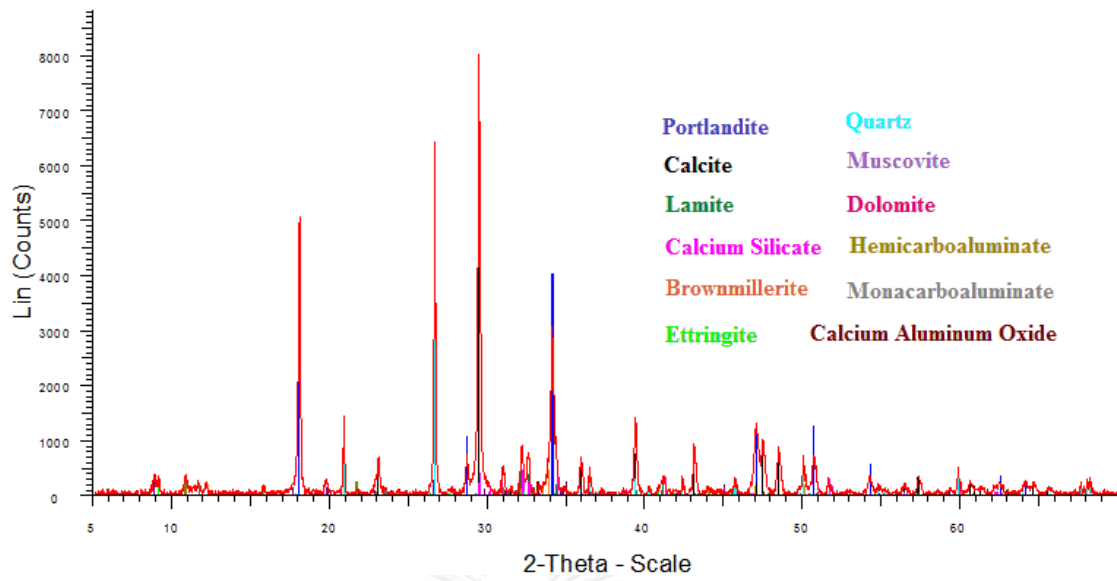


Figure B 23 : XRD pattern for B45S 1:1 paste at 7 days

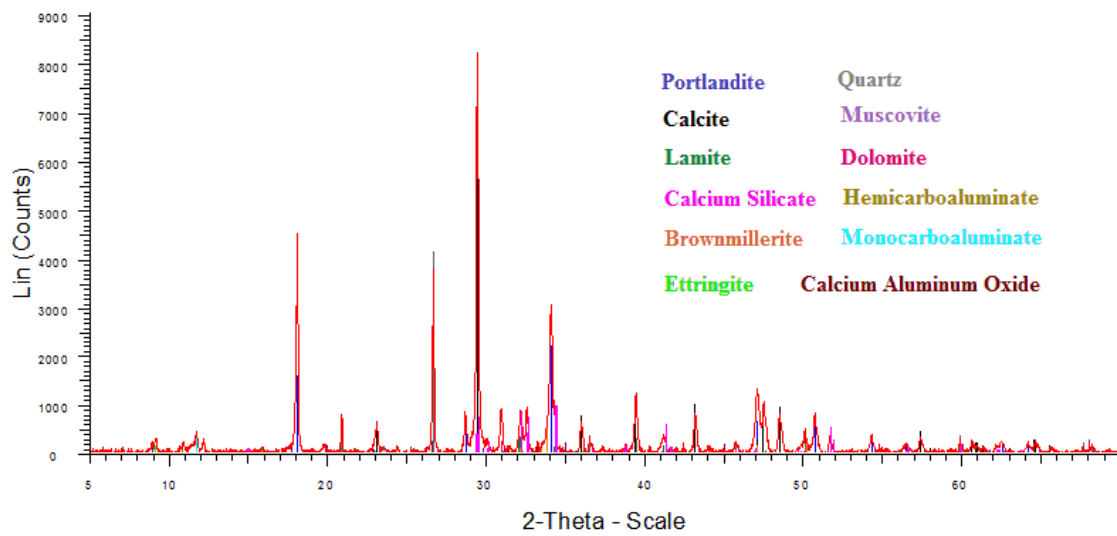


Figure B 24 : XRD pattern for B45S 1:1 paste at 28 days

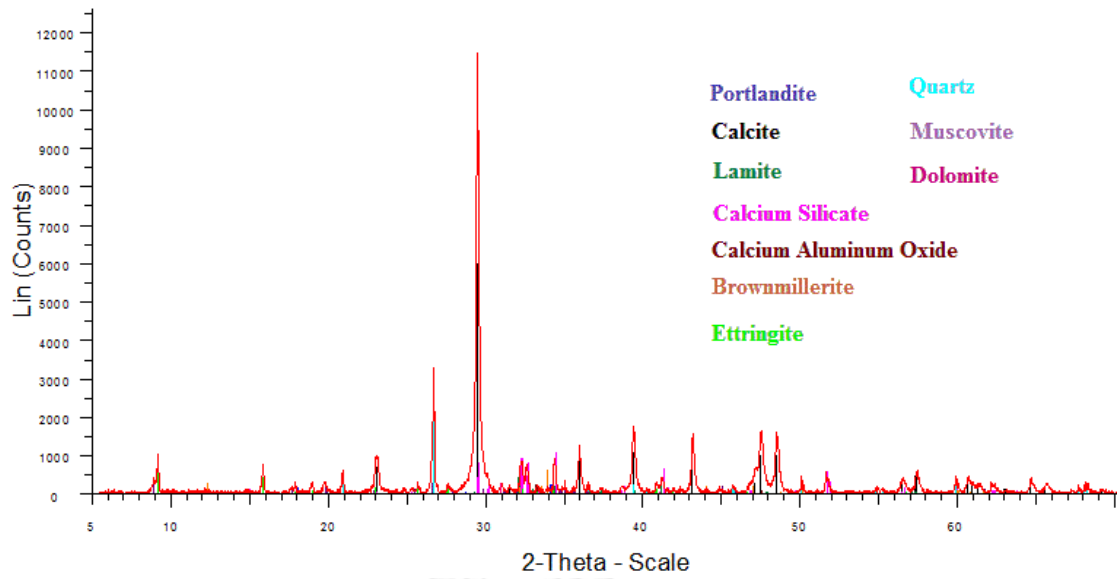


Figure B 25 : XRD pattern for B45S 2:1 paste at 1 day

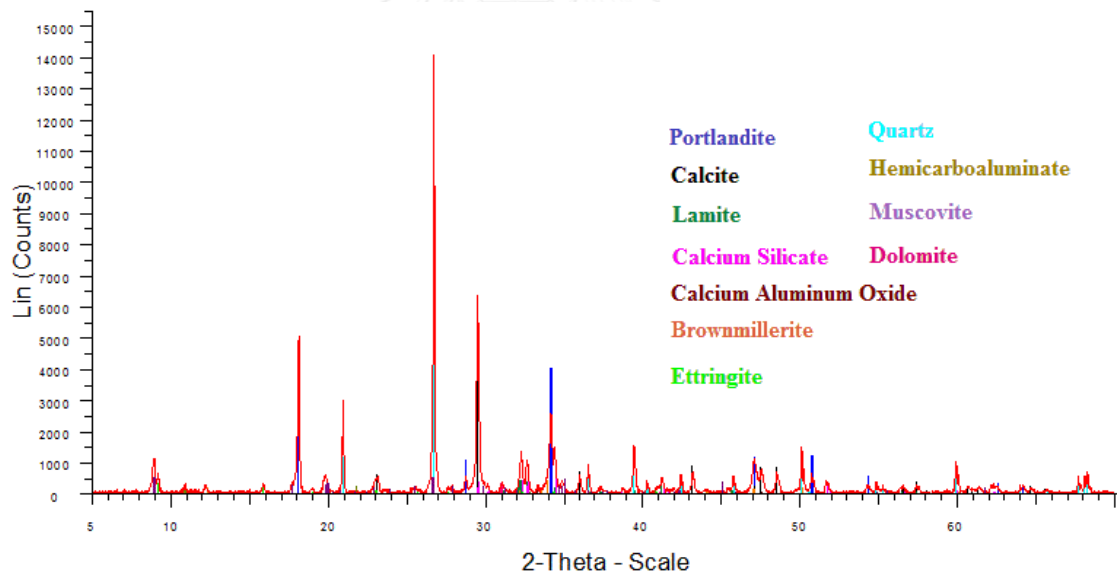


Figure B 26 : XRD pattern for B45S 2:1 paste at 3 days

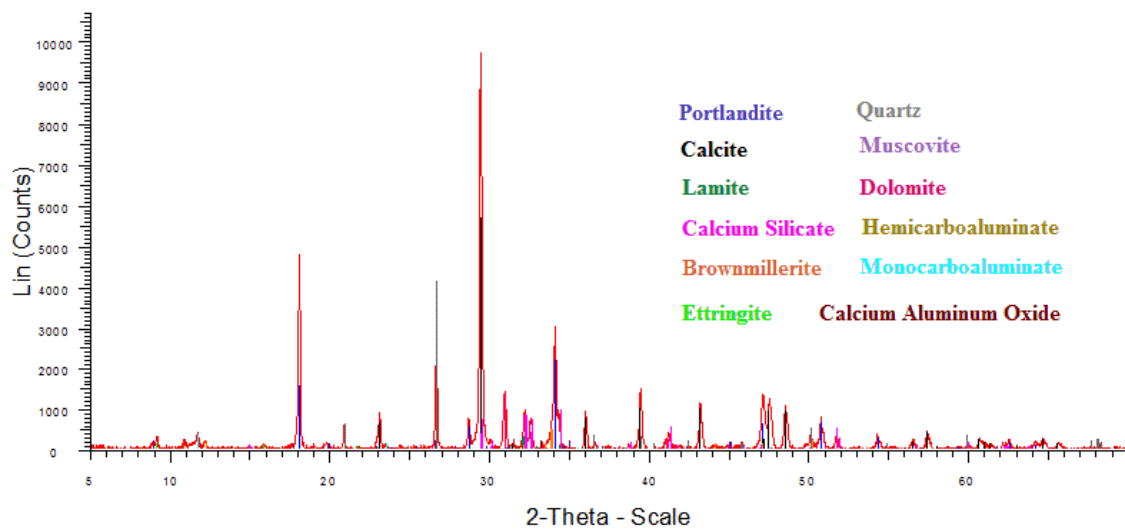
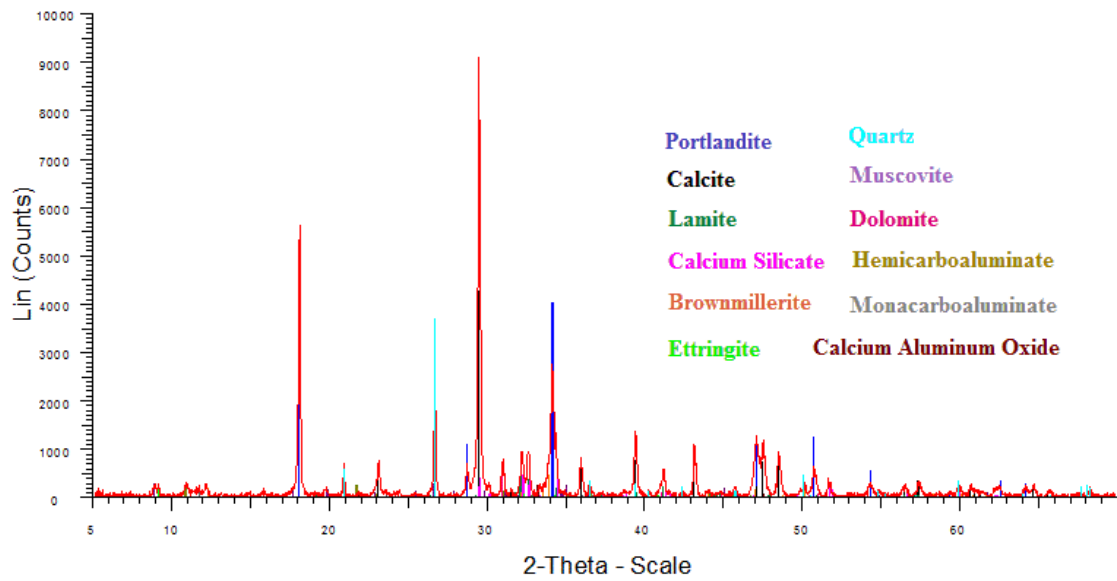


Table B 1 : Reitveld refinement analysis of ternary blend paste comparing with cement paste reference at 1, 3, 7 and 28 days

Formula	Age (days)	The substances obtained by XRD technique in percentage													
		C3S		C2S	C3A		C4AF	Portlandite	Calcite	Ettringite	Monocarboaluminate	Hemicarboaluminate	Quartz	Muscovite	Dolomite
		C3S-M3	C3S-M1		C3A Cub.	C3A Orht.									
100% CM	1	6.27	1.17	3.99	1.36	0.03	4.21	6.79	4.21	5.55	-	-	-	-	-
	3	4.96	0.89	4.35	0.87	0.19	4.91	12.70	2.24	4.66	0.11	-	-	-	-
	7	4.25	0.26	4.54	0.84	0.28	5.12	11.85	1.40	4.26	0.84	-	-	-	-
	28	0.96	2.60	4.46	0.57	0.17	5.75	11.02	5.13	4.62	1.19	-	-	-	-
B45 1:2	1	0.47	2.47	2.42	0.28	0.51	2.33	3.29	13.95	2.21	0.95	10.01	6.47	0.52	
	3	1.72	0.44	3.13	0.79	0.00	2.34	8.13	10.33	1.50	1.47	13.92	8.77	0.88	
	7	0.82	1.09	2.57	0.00	0.54	3.50	8.29	10.81	0.82	4.55	14.27	8.92	1.10	
	28	0.25	0.22	2.02	0.09	0.34	2.83	6.37	12.21	2.67	6.50	12.45	9.01	0.56	
B45 1:1	1	0.60	2.45	2.59	0.27	0.65	2.29	2.66	16.46	2.64	0.40	7.98	3.93	0.61	
	3	1.38	0.54	3.20	0.27	0.58	2.98	8.15	15.70	1.75	1.57	10.91	7.58	1.81	
	7	0.68	1.02	1.80	0.07	0.75	4.59	7.77	16.05	0.81	3.78	10.76	6.93	1.94	
	28	0.29	0.19	2.43	0.19	0.27	2.81	7.04	16.36	2.57	6.34	9.76	6.35	1.68	
B45 2:1	1	1.40	1.80	2.97	0.64	0.39	2.65	2.98	21.36	2.48	1.15	5.91	2.54	1.26	
	3	1.40	0.34	3.58	0.55	0.29	2.83	7.81	19.59	2.24	1.63	5.29	4.99	1.59	
	7	1.01	0.35	2.43	0.33	0.41	4.43	7.35	21.37	1.06	3.48	7.04	3.89	1.51	
	28	0.24	0.28	2.50	0.00	0.82	2.84	7.42	20.24	2.37	6.05	6.96	4.86	1.83	
B45S 1:2	1	28.87	3.64	1.38	2.98	0.33	4.84	0.11	10.80	0.72	-	10.09	5.43	1.98	
	3	3.19	3.39	4.26	0.58	0.46	3.80	6.55	19.03	1.21	1.61	6.05	2.69	1.74	
	7	0.00	7.06	3.91	0.96	0.55	4.70	9.15	10.86	0.76	2.02	6.70	4.33	1.36	
	28	0.24	3.81	2.53	0.74	0.00	3.20	7.87	11.47	1.07	3.80	6.57	3.95	1.82	
B45S 1:1	1	29.54	3.06	2.97	2.88	0.41	4.84	0.40	18.29	0.72	-	9.89	2.93	2.50	
	3	1.44	2.12	1.45	0.03	0.73	2.01	5.20	16.57	3.68	1.15	8.63	9.60	1.31	
	7	3.73	0.46	2.53	0.70	0.59	3.22	8.45	14.98	0.90	1.96	7.36	3.80	1.72	
	28	0.51	4.85	2.69	0.72	0.31	3.30	8.84	16.30	0.96	3.37	5.24	3.68	2.08	
B45S 2:1	1	14.24	24.61	5.28	3.40	0.40	5.66	0.42	20.55	0.64	-	5.48	1.54	2.32	
	3	3.86	3.75	2.48	0.42	1.06	3.20	6.74	12.50	2.36	0.13	6.86	8.99	0.96	
	7	2.46	4.48	3.83	0.73	1.03	4.46	8.82	12.39	0.52	1.99	6.86	3.41	1.33	
	28	4.07	1.67	2.90	0.99	0.29	3.53	9.17	19.31	0.94	2.80	3.36	1.44	2.49	

B2. Compressive strength and compressive strength relative of mortar

Table B 2 : Compressive strength of mortar at 1, 3, 7 and 28 days

Age (days)	Compressive strength of mortar (ksc)						
	100% CM	B45 1:2	B45 1:1	B45 2:1	B45S 1:2	B45S 1:1	B45S 2:1
1	101.33	51.33	46.00	40.00	61.33	50.00	24.00
3	168.00	103.33	98.67	84.67	156.67	141.33	135.33
7	218.00	136.00	117.33	92.67	204.67	167.33	147.33
28	264.67	188.00	159.33	138.00	255.33	238.00	208.67

Table B 3 : Compressive strength relative with 100% CM mortar at 1, 3, 7 and 28 days

Age (days)	Compressive strength relative (%)						
	100% CM	B45 1:2	B45 1:1	B45 2:1	B45S 1:2	B45S 1:1	B45S 2:1
1	100.00	50.66	45.39	39.47	60.53	49.34	23.68
3	100.00	61.51	58.73	50.40	93.25	84.13	80.56
7	100.00	62.39	53.82	42.51	93.88	76.76	67.58
28	100.00	71.03	60.20	52.14	96.47	89.92	78.84

APPENDIX C

PROS AND CONS OF STOP HYDRATION TECHNIQUES

Table C.1 : Comparison various techniques of stop hydration

Technique	Process	Pros	Cons	effective	Suitable for analysis
Oven drying	Atmospheric pressure, 35 ≤ T(°C) ≤ 105	fast	Microcracking, degrade C-S-H, ettringite	no	
Microwave drying	Lower power, several minutes	fastest	Destroy microstructure	yes	
D-drying	Vacuum < 4.2 Pa, solid CO ₂ +alcohol at -79°C, 14 days	Definition of "non-evaporable" water	Remove some bound water	no	
P-drying	1.1 Pa, room temperature		Contains residual pore water	no	
Vacuum drying	Vacuum chamber 0.1 Pa		Degrade ettringite and monosulphate, increase pore volume, damage pore structure.	no	
			Remove less water		
Freeze drying	Submerge in liquid N ₂ > 15 min, then place in a freeze dryer for > 1 day	Less damage to structure, No hydration product change	Degrade ettringite and monosulphate	yes	MIP, TGA
Supercritical drying	Replace pore water by solvent. then freon, supercritical drying of freon	Preserve pore structure	Expensive complex process	yes	Microscopy
Solvent exchange	Solvent renewed regularly, then dried in a desiccator	Small damage to pore structure; gives finest pore size distribution applies least stress Isopropanol is the best solvent	Many partially dehydrate the C-S-H and ettringite; interaction with cement, could be sorbed into cement phases and not be removed without affecting microstructure	yes	MIP, NAS microscopy

VITA

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