STRENGTH AND DURABILITY OF CLAY-FLY ASH GEOPOLYMER

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A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy in Civil Engineering

Suranaree University of Technology

Academic Year 2013

กำลังอัดและความทนทานของดินเถ้าลอยจีโอโพลิเมอร์

นางสาวปฏิมาพร สุขมาก

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
สาขาวิชาวิศวกรรมโยธา
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2556

STRENGTH AND DURABILITY OF CLAY-FLY ASH GEOPOLYMER

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

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ปฏิมาพร สุขมาก : กำลังอัดและความทนทานของดินเถ้าลอยจีโอโพลิเมอร์ (STRENGTH AND DURABILITY OF CLAY-FLY ASH GEOPOLYMER) อาจารย์ที่ปรึกษา : ศาสตราจารย์ ดร.สุขสันติ์ หอพิบูลสุข, 168 หน้า

วิทยานิพนธ์นี้ประกอบด้วยสามส่วนหลักดังนี้ ส่วนแรกศึกษาความเป็นไปได้ของการผลิตจีโอโพลิเมอร์ ซึ่งใช้ดินเหนียว (silty clay) เป็นวัตถุดิบหลัก และเถ้าลอย (fly ash, FA) เป็นวัสดุปอซโซลาน ของเหลวอัลคาไลน์ (liquid alkaline activator, L) เป็นส่วนประกอบของสารละลายโซเดียมซิลิเกต (Na_2SiO_3) และสารละลายโซเดียมไฮดรอกไซด์ (NaOH) ดินเถ้าลอยจีโอโพลิเมอร์ต้องการอัตราส่วน Na_2SiO_3/NaOH ในปริมาณที่ต่ำกว่าเถ้าลอยจีโอโพลิเมอร์ สำหรับอัตราส่วน Na_2SiO_3/NaOH คงที่ค่าหนึ่ง การเพิ่มขึ้นของอัตราส่วน L/FA ส่งผลให้กำลังอัดในดินเถ้าลอยจีโอโพลิเมอร์เพิ่มขึ้น แต่เมื่ออัตราส่วน L/FA สูงเกินความต้องการต่อการทำปฏิกิริยาจีโอโพลิเมอไรเซชั่น ของเหลวอัลคาไลน์ส่วนเกินมีผลให้จีโอโพลิเมอร์เจลตกตะกอนก่อนการเกิดปฏิกิริยาการควบแน่น อุณหภูมิและระยะเวลาให้ความร้อนที่นานเกินความต้องการทำให้เกิดรอยแตกระดับไมโครเมตรภายในตัวอย่าง

งานวิจัยในส่วนที่สอง นำเสนอปัจจัยที่มีอิทธิพลต่อการพัฒนากำลังอัดในดินเถ้าลอยจีโอโพลิเมอร์ ได้แก่ อัตราส่วน FA/clay, อัตราส่วน Na_2SiO_3/NaOH, อัตราส่วน L/FA, ปริมาณความชื้นในตัวอย่าง, ขนาดของตัวอย่าง, อุณหภูมิความร้อน และระยะเวลาในการบ่ม อัตราส่วนผสมที่เหมาะสมในดินเถ้าลอยจีโอโพลิเมอร์ คืออัตราส่วน Na_2SiO_3/NaOH เท่ากับ 0.7 สำหรับทุกอัตราส่วน FA/Clay และ L/FA อัตราส่วน L/FA ที่เหมาะสม และปริมาณความชื้นเหมาะสม (OMC) แปรผกผันกับอัตราส่วน FA/Clay ขนาดของตัวอย่างไม่มีผลกระทบต่ออัตราส่วนผสมที่เหมาะสม แต่มีผลต่ออุณหภูมิความร้อนและระยะเวลาในการบ่ม ตัวอย่างขนาดใหญ่ต้องการอุณหภูมิความร้อนที่สูงและระยะเวลาบ่มที่นานในการเร่งปฏิกิริยาจีโอโพลิเมอร์ไรเซชั่น พลังงานความร้อนต่อน้ำหนัก (E/W) ถูกนำเสนอขึ้นเพื่อรวมอิทธิพลของอุณหภูมิความร้อน ระยะเวลาและน้ำหนักของตัวอย่าง ตัวอย่างที่มีอัตราส่วน FA/clay สูงต้องการ E/W ต่ำ ความสัมพันธ์ระหว่างกำลังอัดและ E/W มีประโยชน์ต่อภาคอุตสาหกรรมในการกำหนดพลังงานความร้อนเพื่อให้ได้ตัวอย่างที่มีกำลังอัดและน้ำหนักตามความต้องการ

งานวิจัยในส่วนสุดท้าย ศึกษาความต้านทานต้านสารละลายโซเดียมซัลเฟตความเข้มข้น 5% และสารละลายแมกนีเซียมซัลเฟตความเข้มข้น 5% ของดินเถ้าลอยจีโอโพลิเมอร์ และดินปูนซีเมนต์ อัตราส่วนผสมของดินเถ้าลอยจีโอโพลิเมอร์คือ อัตราส่วน Na_2SiO_3/NaOH ที่ 0.7, L/FA ที่ 0.6, FA/Clay ที่ 0.3 และปริมาณความชื้นของตัวอย่างที่ปริมาณความชื้นที่เหมาะสม (OMC)

อัตราส่วนผสมของดินซีเมนต์คือ ปริมาณความชื้นของตัวอย่างที่ 1.2OMC และอัตราส่วน cement/Clay ที่ 0.3 ผลทดสอบแสดงให้เห็นว่าดินเถ้าลอยจีโอโพลิเมอร์มีความต้านทานสารละลายซัลเฟตสูงกว่าดินซีเมนต์ ผลการศึกษาด้านโครงสร้างทางจุลภาคแสดงให้เห็นว่าตัวอย่างทั้งสองชนิดเกิดยิปซัมและเอสทริงไกต์ ซึ่งเห็นได้ชัดกับตัวอย่างดินซีเมนต์ สารละลายแมกนีเซียมซัลเฟตทำลายโครงสร้างของดินเถ้าลอยจีโอโพลิเมอร์และดินซีเมนต์สูงกว่าสารละลายโซเดียมซัลเฟต ดินเถ้าลอยจีโอโพลิเมอร์มีความต้านทานสารละลายซัลเฟตสูงกว่าดินซีเมนต์

สาขาวิชา วิศวกรรมโยธา ลายมือชื่อนักศึกษา ____________________________

ปีการศึกษา 2556 ลายมือชื่ออาจารย์ที่ปรึกษา ______________________

PATIMAPON SUKMAK : STRENGTH AND DURABILITY OF
CLAY-FLY ASH GEOPOLYMER. THESIS ADVISOR : PROF. SUKSUN
HORPIBULSUK, Ph.D., 168 PP.

STRENGTH/MICROSTRUCTURE/ HEAT ENERGY PER WEIGHT/SULPHATE

This thesis consists of three main parts. First part presents the possibility of using a silty clay as fine aggregates to develop geopolymer and fly ash, FA as a pozzolanic material. A liquid alkaline activator, L is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH). The Na_2SiO_3/NaOH ratio required for the clay–FA geopolymer is less than that of the FA geopolymer. For a given Na_2SiO_3/NaOH content, the strength increases with increasing the liquid alkaline activator. The excess input alkaline activator causes the precipitation at very early stage before the condensation process in geopolymerization. The very high temperature and excess heat duration cause the micro-cracks on the specimens.

Second part presents the strength development with different influential factors for the manufacturing of clay–FA geopolymer. The studied factors are ingredients (FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio and molding moisture content), specimen sizes, heat temperature and duration. The optimum Na_2SiO_3/NaOH ratio is 0.7 for all FA/clay ratios, L/FA ratios and specimen sizes tested. The optimum L/FA ratio and molding moisture content decrease as the FA/clay ratio increases. The optimum ingredient is irrespective of specimen size. The larger specimens require higher heat temperature and longer duration for the geopolymerization development. The heat energy per weight (E/W) concept integrates the role of heat temperature, duration and specimen weight on the geopolymerization.

The specimens with high FA/clay ratio require low heat energy per weight (E/W). The relationship between strength and E/W is very useful for production industry to estimate the heat temperature and duration to attain the target strength for the required weight in making clay–FA geopolymer brick.

Last part examines the resistance ability of two different cementitious systems prepared using silty clay as a major component against 5% sodium sulfate and 5% magnesium sulfate solutions. The two cementitious systems are clay-Portland cement and clay-FA geopolymer. The clay–FA geopolymer is a mixture of FA/clay ratio at 0.3 by soil mass, Na_2SiO_3/NaOH ratio at 0.7, L/FA ratio at 0.6 and at optimum moisture content (OMC). For the clay-cement, a cement/clay ratio of 0.3 by soil mass and the molding moisture content providing the highest strength at 1.2OMC are used. The physical performance of clay-FA geopolymer when exposed to sulphate solution is better than that of clay-cement. Gypsum and ettringite phases are present in both specimens, especially in the clay-cement. The exposure to magnesium sulphate solution causes more degradation in both clay-FA geopolymer and clay-cement system than the exposure to sodium sulphate. Overall, clay-FA geopolymers show better resistance to sulphate attack than clay-cement mixtures.

School of Civil Engineering Student's Signature ______________________

Academic Year 2013 Advisor's Signature ______________________

ACKNOWLEDGEMENTS

Seven years ago, the author has entered the School of Civil Engineering, Suranaree University of Technology, to pursue her Bachelor's and Ph.D degrees. It was her great opportunity to work under the supervision of Professor Dr. Suksun Horpibulsuk during Ph.D. Studies. The author would like to express her deepest sincere and gratitude to Professor Dr. Suksun Horpibulsuk for his guidance valuable advices, endless kindness, encouragement and enthusiasm throughout her studies. Even with his tight and hectic schedules, he always gave his time and support every time the author needed them. It has been a very pleasant experience to work under of guidance of Professor Dr. Suksun Horpibulsuk, who has highly disciplined life style, leadership character and philosophical thoughts.

Profound gratitude is expressed to Professor Dr. Satoru Shibuya, my co-advisor, for valuable comments suggestions. The author also wish to her sincere thanks to Dr. Pre De Silva for her insights into chemical and microstructural analysis on the geopolymer, valuable comments, suggestions and support during her 6-month visit to the Australian Catholic University, New South Wales, Australia.

The examining committee has also played a significant role in the completion of this thesis. The author is grateful to Associate Professor Dr. Avirut Chinkulkijniwat for serving as a chair of the Ph.D. thesis examining committee as well as Assistant Professor Dr. Runglawan Rachan and Assistant Professor Dr. Visit Vao-Soongnern for serving as Ph.D. thesis examiners.

Sincere thanks and indebtedness are due to her respected teachers, Associate Professor Dr. Avirut Chinkulkijniwat, Assistant Professor Dr. Pornpot Tanseng, Assistant Professor Dr. Theerawat Sinsiri, Associate Professor Dr.Sittichai Seangatith and Dr. Tanongsuk Bisarnsin, the School of Civil Engineering, Suranaree University of Technology for their excellent lectures, valuable comments and suggestions. The author wishes to thank all the staff and faculty members at the School of Civil Engineering, Suranaree University of Technology for the academic, administrative and technical support during her study. The author acknowledges Mr. Somjai yubonchit, Mr. Apichat Suddeepong, Dr. Apichit Kumpala and Miss. Piyachat Supakul for discussion and encouragement. The author would like to thank the Suranaree University of Technology for facilities, equipment and financial support and the Thailand Research Fund (TRF) under Royal Jubilee program for facilities, equipment and financial support.

Finally, the author would like to appreciate her family for their love, support and understanding throughout her Ph.D. study.

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SYMBOLS AND ABBREVIATIONS

z = 1, 2, 3, or higher

M = a monovalent cation such as K^+ or Na^+

n = degree of poly-condensation

°C = degree Celsius

NMR = nuclear magnetic resonance

FTIR = fourier Transform Infrared Spectrophotometer

XRD = x-ray diffraction

SEM = scanning electron microscopy

EDX = energy Dispersive X-ray Spectrometer

XRF = X-ray fluorescence

pH = potential of Hydrogen ion

M = molar

h = hours

OPC = portland cement

CFA = classified fly ash

OFA = original fly ash

RH = relative humidity

CEC = cation exchange capacity

FSR = a free swell ratio

γ_{dmax} = maximum dry unit weight

SYMBOLS AND ABBREVIATIONS (Continued)

FA = Fly ash

OWC = optimum water content

D = state of moisture content (0.6, 0.8, 1.0, and 1.2 times)

FA/clay = fly ash/clay

L/FA = liquid alkaline

$^{o}\ 2\theta$ = 2 theta

^{o}C-h = heat energy

E/W = heat energy per weight,

CH = high plasticity

CY = cylindrical specimen

RE = rectangular specimen

DEF = delayed ettringite formation

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Clay-based bricks are mostly used in the northeastern region of Thailand as a constructional and building material. The bricks are a mixture of local soil (clay) and cement. Because production of construction materials has become an expensive business in these areas due to the high costs associated with the production processes and transportation of materials. However, bricks are a mixture of clay and cement which have low ability to resist the changes in the environment especially moisture/water content (collapse and swelling with the change in water content) and the salts in the common ground (Rajasekaran 2005). Manufacturing of Portland cement is a resource exhausting and energy intensive process that releases large amount of the CO_2 into the atmosphere, which cause the greenhouse gases (Davidovits 1991; Davidovits and Davidovics 2008). Therefore, the development of a new cementing agent with low carbon dioxide release is considered as an interesting issue. Commercial and industrial utilization of alkali-activated alumino-silicate cements, known as 'geopolymers' has been increasingly well-known over the past several decades as the search for high-performance and/or an environmentally maintainable alternative for ordinary Portland cement (Davidovits 1991).

Geopolymers belong to a group of materials with increased interest due to the possibility of low CO_2 emission as well as low energy consumption. The hardening process of geopolymers at ambient temperature results in materials with ceramic-like properties, such as resistance against acids and high temperatures. The three sources are needed for the synthesis of geopolymer, namely geopolymer liquor, inactive filter, and raw materials (Ikeda 1998). Geopolymer liquor is an alkali hydroxide solution required for the dissolution of raw materials while sodium silicate solution acts as binder. Inactive filter, mainly clay or kaolin that is used for the supply of Al^{3+} ion (Phair 2001). Generally, literature showed that clay can be used as inactive filter for the synthesis of geopolymer bricks but it must be heated at 500–700 °C (Berg et al. 1968). This materials control the manufacturing cost. Raw material could be natural (alumino silicate) mineral or industrial wastes such as fly ash, bottom ash, slag, and waste glass. In this study, fly ash is used a raw material. Fly ash geopolymerization provides the greatest opportunity for commercial utilization of this technology due to the plentiful worldwide raw material supply, which is derived from coal-fired electricity generation (Mohapatra and Rao 2001; Van Jaarsveld et al. 1998). The transportation of the fly ash from a far distance and heating process are costly. The higher the temperature, the greater the manufacturing cost. Consequently, this thesis attempts to study the possibility of using the silty clay of high silica and alumina contents (without heat) and fly ash to develop the clay-fly ash geopolymer as possible in the manufacturing processes of building products. The aim is also to investigate the factors controlling strength development of the clay-FA geopolymer and compare sulphate resistance with cement stabilized clay.

1.2 Objectives of the study

1.2.1 To investigate a possibility of using silty clay as aggregate to manufacture clay-fly ash geopolymer.

1.2.2 To study the factors influencing strength development in clay–fly ash geopolymer.

1.2.3 To study the durability of the clay-fly ash geopolymer against sodium and magnesium sulphate attack.

1.3 Structure of presentation

This thesis consists of six chapters and outlines of each chapter are presented as follows:

Chapter II presents the review of previous research on structure, properties and characterization of geopolymer. The aspects of the science and application of geopolymer are also renewed and presented.

Chapter III presents the study on the factors influencing strength development in clay-fly ash geopolymer. The possibility of using the silty clay of high silica and alumina contents (without heat) and fly ash to develop the clay-fly ash geopolymer is illustrated. The soil used in this study is high plasticity (CH) type classified by Unified Soil Classification System (USCS), which was collected from Nakhon Ratchasima, Thailand. The comparison of geopolymer ratio and manufacturing condition on the compressive strength between the fly ash geopolymer and the clay-fly ash geopolymer are revealed.

Chapter IV presents the factors influencing strength development in clay–fly ash geopolymer. This chapter presents that strength development in the clay-fly ash geopolymer with three factors: ingredients (fly ash/clay ratio, Na_2SiO_3/NaOH ratio, Liquid alkaline/fly ash ratio, and molding moisture content), specimen weights, and heating conditions (curing temperature and duration). The studied ingredients of the fly ash/clay ratio are 0.3, 0.5, and 0.7; Na_2SiO_3/NaOH ratio of 0.4, 0.7, 1.0, and 1.5; Liquid alkaline/fly ash ratio are 0.3, 0.4, 0.5, 0.6, and 0.7; and the moisture content are 80%, 100%, 120%, and 140% of the optimum moisture content are used to prepare the specimens. Two specimen weights are selected: a cylindrical sample with 50 mm in diameter and 100 mm in height and including a rectangular sample with 230 mm in length, 90 mm in width, and 75 mm in height. The heating temperatures are ranged from 55 to 140^{o}C and the heat durations are from 24 to 168 h.

Chapter V investigates the durability of clay-fly ash geopolymer when exposed to 5% sodium sulphate and 5% magnesium sulphate solutions. The durability between clay-fly ash geopolymer and clay-Portland cement is compared. The clay-fly ash geopolymer is at FA/clay ratio of 0.3 by clay mass, Na_2SiO_3/NaOH ratio of 0.7, L/FA ratio of 0.6 and the heating condition at 130^{o}C for 120 h have been selected for this study based on the work of chapters III and IV (Sukmak et al. 2013a; Sukmak et al. 2013b). These ingredient and heat condition were proved as optimal providing the highest strength. The moisture content for the highest strength is 1.0 OMC (Optimum Moisture Content). The clay-Portland cement is a combination of silty clay, Portland cement and tap water with cement/clay ratio of 0.3 by dry clay mass. The moisture

content are 80%, 100%, 120%, and 140% of the optimum moisture content are used to prepare the clay-Portland cement.

Chapter VI concludes the present work and suggests the topics for further study.

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CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

The Cordi-Géopolymère private research laboratory in Saint-Quentin in 1972 discovered a fresh inorganic material called as ‘geopolymer'. Geopolymer can be formed at low temperature and small amount of time and based on the alkaline activation of easily obtainable natural and by-product silica and alumina materials happening as a network of the alumino-silicates (Davidovits 1988c). After shorter setting and hardening time, geopolymer with tightly packed poly-crystalline structure is formed showing better mechanical properties Geopolymer is extremely environmentally attractive for various reasons. Its performance as construction materials can be compared with Portland cement in lots of ways but the geopolymer needs no heat in its manufacturing process. This implies a substantial benefit with regards to reducing global CO_2 emissions. Furthermore, the utilization of industrial by-products meets the increasing trend towards waste re-utilization (Jiminez et al. 2004). Geopolymer is definitely an alumino-silicate material which includes excellent physical and chemical properties of numerous applications (Komnitsas and Zaharaki 2007).

2.2 Chemistry

Three sources are used to form the geopolymer, i.e. raw materials, inactive filler and geopolymer liquor. Raw materials might be natural (alumino-silicate) minerals or industrial wastes e.g. fly ash, slag, and waste glass. Inactive filler, mainly kaolinite or meta-kaolinite, is employed for supplying Al^{3+} ions (Ikeda 1998). Geopolymer liquor is definitely an alkali hydroxide solution required for dissolving raw materials while sodium (or potassium) silicate solution acts as a binder, alkali activator and dispersant or plasticizer (Phair 2001). Geopolymer (poly (sialates)) contains silicate (SiO_4) and aluminate oxides (AlO_4) tetrahedral alternately linked where all oxygen atoms are exchanged (Davidovits 1976). Positive ions (Na^+, K^+ and Ca^{2+}) must certainly be contained in the framework voids to balance the negative charge of Al^{3+}.Poly (sialates) is chain polymers with Si^{4+} and Al^{3+} in 4-fold coordination with oxygen and their empirical formula could be expressed as:

$$M_n(–(SiO_2)_z–AlO_2)_n\ wH_2O$$

Where z is 1, 2, 3, or higher

M is a monovalent cation such as K^+ or Na^+

n is the degree of poly-condensation

The forms of polysialates distinguished are illustrated in Figure 1(Davidovits 1988a). The complex geopolymer structure thus contains chains, sheet-like and three-dimensional networks composed of various unit kinds of connected SiO_4 and AlO_4 tetrahedral (Singh et al. 2005).

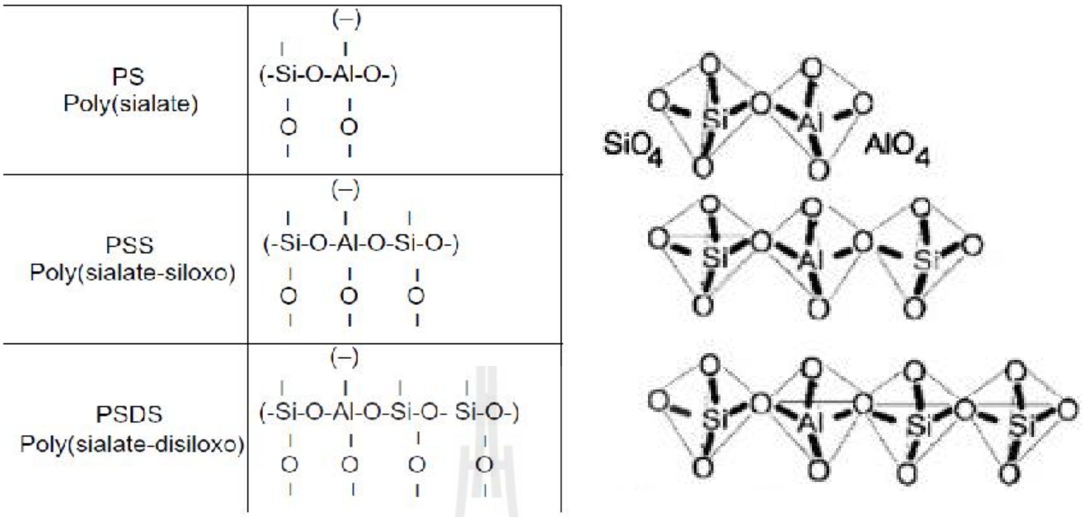

Figure 2.1 The types of polysialates (Davidovits 1988a).

Geopolymerization can be an exothermic procedure that is conducted through oligomers dimer which provide the specific unit structures for the three dimensional macromolecular edifice. Among several hardening mechanisms could be the chemical reaction of alumino-silicate oxides with alkalis and alkali–polysilicates, leading to polymeric Si–O–Al bonds with a $(Si_2O_5, Al_2O_2)n$ formula, which may be accomplished by calcining alumino-silicate hydroxides $(Si_2O_5,Al_2(OH)_4)$ through the reaction (Davidovits 1988a).

Primary steps of geopolymerization involve dissolution of solid alumino-silicate oxides in *M*OH solution (*M*: alkali metal), diffusion or transportation of dissolved Al and Si complexes from the particle surface to the inter-particle space, formation of a gel phase caused by the polymerization between added silicate solution and Al and Si complexes, and finally hardening of the gel phase (Van Jaarsveld 2000; Xu 2001) for the poly-condensation occurring during geopolymerization of minerals:

$$\text{Al–Si material}_{(s)} + M\text{OH}_{(aq)} + \text{Na}_2\text{SiO}_{3\,(s)\text{ or }(aq)}$$

$$\downarrow \quad (1)$$

$$\text{Al–Si material}_{(s)} + [M_z\,(\text{AlO}_2)_x\,(\text{SiO}_2)_y \cdot nM\text{OH} \cdot m\text{H}_2\text{O}]\text{ gel}$$

(2)

$$\downarrow$$

$$\text{Al–Si material}_{(s)} + [M_a\,((\text{AlO}_2)_a\,(\text{SiO}_2)_b)\;nMOH \cdot m\text{H}_2\text{O}]$$

(3)

In reactions (1) and (2), the amount of Al–Si material used is dependent upon the particle size, the extent of dissolution of Al–Si materials, and the concentration of the alkaline solution. The forming of $[M_z(\text{AlO}_2)_x(\text{SiO}_2)_y nM\text{OH}m\text{H}_2\text{O}]$ gel is basically on the basis of the extent of dissolution of alumino-silicate materials, while geopolymer with amorphous structure is formed during the reaction (3). Enough time necessary for the alumino-silicate solution to create a continuous gel is dependent upon raw material processing conditions (Ivanova et al. 1994).

Dissolution of the starting materials could be the major step that has a twofold role, i.e. firstly, poly-sialate forming species are liberated from the starting materials (Duxson et al. 2007a; Grutzeck and Siemer 1997), and secondly, dissolution activates the top and binding reactions occur significantly supporting the ultimate strength of the structure. The extent of the dissolution part of geopolymerization is not fully clear whilst the extent to which other factors complement or no dissolution must be further investigated (Phair 2001).

Under alkaline conditions, alumino-silicates are changed into extremely reactive materials, and generally speaking it is thought that the dissolution process is initiated by the clear presence of hydroxyl ions. Higher levels of hydroxyl ions facilitate the dissociation of different silicate and aluminate species, promoting thus further polymerization (Davidovits 1988b; Phair et al. 2000). However, in case a quite high alkaline environment (>30 mol% overall Na_2O content) is employed, the connectivity of silicate anions might be reduced, causing poor polymerization (Singh et al. 2005).

The analysis of the dissolution on different alumino-silicate industrial minerals and by-products indicated that the extent of dissolution is higher when NaOH is employed in place of KOH (Panagiotopoulou et al. 2007) due to the smaller size of Na+ that may better stabilize the silicate monomers and dimmers contained in the solution. This thus enhances the minerals dissolution rate (Xu and Van Deventer 2000a). Additionally, it absolutely was reported that Si and Al appear to possess a synchronized leaching behavior in both alkaline media.

Furthermore, there have been the studies of the dissolution on various kinds of fly ash in caustic soda solutions as much as 15 M at 25 and 80°C. It had been reported that high dissolution of Al_2O_3 is seen in 80°C, while the increased dissolution of SiO_2 occurs during leaching with increasing NaOH concentrations in 25°C.

2.3 Alkali metals

The sort of alkali metal cation is any alkali and alkali earth cation used during geopolymer synthesis based on many factors where the most crucial one is the kind of source materials, such as the foreseen application of the produced geopolymers (Van Jaarsveld 2000). Alkali can be utilized as the alkali element (*M*) in geopolymerization reactions which the majority of the studies centered on the effect of sodium (Na^+) and potassium (K^+) ions (Van Jaarsveld and Van Deventer 1999; Xu and Van Deventer 2000b). Alkali metal cations control and affect nearly all stages of geopolymerization and specifically during gel hardening and crystal formation, and the cations contribute to the structure formation of geopolymer (Van Jaarsveld 2000).

In the geopolymers synthesis, NaOH was found to significantly affect both compressive strength and structure of geopolymer. The NaOH concentration in the aqueous phase of the geopolymer system acts on the dissolution process, along with on the bonding of solid particles in the final structure (Panias et al. 2007). The optimum polymer properties are obtained once the Na concentration is enough to supply a charge balancing mechanism for the substitution of tetrahedral Si by Al, although not in sufficient excess to create sodium carbonate by atmospheric carbonation (Barbosa et al. 1999). In geopolymerization, the alkali metal content of reacting minerals might have a substantial impact on strength development. This really is on the other hand with concrete manufacture which the clear presence of metals is undesirable as a result of stresses produced by alkali activation (Xu and Van Deventer 2000b). Moreover, the mechanical properties of geopolymer cured for 7 days are not seriously affected when working with specimens with various alkali compositions (Duxson et al. 2007c).

Using a variety of analytical techniques, including differential scanning calorimetry (DSC), ^{27}Al and ^{29}Si MAS NMR, FTIR and XRD, it may be proven that although solution alkalinity (M_2O/H_2O) might enhance solid dissolution, the character of the reaction product (i.e. the geopolymer gel) was practically unaffected (Rahier et al. 1996), which means that alkalis are reactants and not reaction modifiers, since the solution alkalinity is essential in controlling how much of the reaction product is produced without affecting the character of the product. It seems therefore that the SiO_2/M_2O molar ratio of the activating is probably the most critical factor for the geopolymer synthesis (Lee 2002).

The SiO_2/M_2O ratio within an alkaline silicate solution affects the amount of polymerization of the dissolved species (Swaddle 2001). If the silica content is increased, the rate of the reaction taking place in a geopolymer-forming paste decreases accordingly. In high-silica systems, the paste solidification ahead of the completion of the reaction can also occur (Provis and Van Deventer 2007).

The limit of geopolymer synthesis should be used to create strong geopolymer products. The compositions should take the range of 0.2–0.48, 3.3–4.5, 10–25 and 0.8–1.6 for M_2O/SiO_2, SiO_2/Al_2O_3, H_2O/M_2O and M_2O/Al_2O_3 ratio, respectively. The majority of the studies supported that geopolymer materials are prepared from alumino-silicate clay minerals and sodium silicate using a restricted array of Si/Al compositions (Khale and Chaudhary 2007). Otherwise, a recent study showed that these conditions can vary and that it was possible to include tetrahedral borate and phosphate units in the framework structure, as evidenced by XRD, multi-nuclear MAS NMR and electron microscopy (MacKenzie et al. 2006).

However, high concentration of silicates becomes necessary during synthesis of geopolymer especially when working with sodium silicate. Therefore, stronger ion-pair formation is expected, leading to the forming of longer chain silicate oligomers, including Al–O–Si complexes, i.e. geopolymer precursors (McCormick et al. 1989). The concentration of soluble silicon was found to affect the distribution of porosity in metakaolin-based geopolymer, that is, low concentrations lead to the synthesis of dense gel while high concentrations produce reduced gel skeletal densities (Duxson et al. 2005).

So far as calcium is taken into consideration, the CaO content of the original material appears to strengthen the geopolymer by forming amorphously structured Ca–Al–Si gel (Yip and Van Deventer 2001). Various studies (Xu and Van Deventer 2000b) discovered that calcium includes a positive influence on the compressive strength of geopolymer binders. Once the CaO content is high, the microstructural porosity decreases and the ultimate product is strengthened by the resulting formation of amorphous structure Ca–Al–Si gel (Van Jaarsveld et al. 1998). Phair and Van Deventer (Phair et al. 2000) supported that strength development by calcium is more probably be achieved through enhancing silicate and poly-sialate network formation and hardening through the entire matrix. Minaŕková and Škvára (Minaŕková and Škvára 2005) proved that the presence of calcium ions in the geopolymer matrix improves the resistance of fly ash-based geopolymer during leaching.

Some authors (Dombrowski et al. 2007) evaluated the influence of calcium and its dosage on structure formation and property development. With prolonged reaction time and increased calcium content, fly ash based geopolymer showed an increased reaction degree and therefore acquired higher strength. Based on some authors, (Lee 2002), the quantity of calcium contained in a geopolymer reacting system, irrespective of its initial source, is essential in determining the character of the alumino-silicate gel formed, which presumably controls the macroscopic strength of a geopolymer product. Some authors (Van Deventer et al. 2007) proved that the quantity of calcium within the waste used during geopolymerization affects the procedure by giving extra nucleation sites for precipitation of dissolved species.

Furthermore some authors (Dombrowski et al. 2007) studied the influence of calcium content on the performance of fly ash and metakaolin geopolymer binders. Adding high levels of calcium hydroxide to fly ash based geopolymer improves early strength, whereas adding small levels of calcium enhances strength at later stages. For both fly ash and metakaolin binders, a change of approximately 10% of the alumino-silicate material with calcium hydroxide is possibly favored.

Some authors (Yip 2004) stated that the shape of added Ca^{2+} plays a substantial role in determining the physical properties of the ultimate geopolymer. The effect of calcium on the reaction product may be determined by the degree of dissolved silicate in the activating solution through pH control. If the solid raw material is deficient in calcium, $CaCO_3$ and CaO may be introduced in the shape of an aqueous suspension to enhance the physical and mechanical properties of geopolymers.

2.4 Raw materials

Theoretically, any material composed of silica and aluminium can be alkali-activated. So far the investigations performed have used the following raw materials:

(a) kaolinitic clays (Barbosa et al. 2000; Davidovits 1979; Davidovits and Sawyer 1985; Rahier et al. 1996; Rahier et al. 1997);

(b) metakaolin (Alonso and Palomo 2001a; Alonso and Palomo 2001b; Davidovits 1999; Pinto 2004);

(c) fly ashes (Fernandez-Jimenez and Palomo 2005; Palomo et al. 1999);

(d) blast furnace slag (Fernandez-Jimenez et al. 1999; Purdon 1940; Wang and Scrivener 1995);

(e) mixtures of fly ashes and slag (Puertas and Fernandez-Jimenez 2003; Puertas et al. 2000);

(f) mixtures of fly ashes and metakaolin (Swanepoel and Strydom Appl Geochem 2002);

(g) mixtures of slag and metakaolin (Cheng and Chiu 2003);

(h) mixtures of slag and red mud (Zhihua et al. 2002; Zhihua et al. 2003);

(i) mixtures of fly ashes and non-calcined materials like kaolin and stilbite (Xu et al. 2002).

used kaolinite and calcined kaolinite (metakaolin) as the supply of alumino-silicate oxides to be able to synthesize geopolymer (Davidovits 1984). A number of other researchers also have centered on the manufacture of geopolymer products and their industrial applications by utilizing either kaolinite or metakaolinite as the key reactant (Barbosa and MacKenzie 2003a; Barbosa and MacKenzie 2003b; Cioffi et al. 2003; Xu and Van Deventer 2002).

Kaolinite provides structure forming species to the entire geopolymerization process. Xu and Van Deventer (Xu and Van Deventer 2000b) stated that the addition of kaolinite is essential because the rate of Al dissolution from the raw materials is insufficient to generate a gel of the required composition. The lower reactivity of kaolinite requires sufficient time for interactions among the original materials or the source material and the gel phase to form. Little is known in regards to the behavior with this gel phase and the extent to which the character of the starting materials and the specific concentrations in solution are affecting its formation and setting (Xu and Van Deventer 2002). However, a massive amount added kaolinite might not take part in the synthesis reaction at all (Van Jaarsveld et al. 2002; Zaharaki et al. 2006).

Some authors (Xu and Van Deventer 2000b) studied sixteen different alumino-silicate minerals with the addition of kaolinite to be able to synthesize geopolymer and observed that for the majority of the alumino- silicate minerals the addition of kaolinite is required for the forming of gel. Only if kaolinite is utilized without the presence of other alumino-silicates, a poor structure is formed, which means synergy between different aluminosilicates is apparently quite important (Xu and Van Deventer 1999).

Furthermore, other authors (Palomo et al. 1999; Xu and Van Deventer 1999)studied the usage of natural minerals and wastes (in particular fly ash) in geopolymerization, as well as the immobilization of toxic metals was investigated extensively in recent years Also, some authors (Van Jaarsveld et al. 1998) have used black coal fly ash and construction wastes as the foundation for geopolymerization.

Some authors (Xu et al. 2002) used fly ash, kaolinite and albite (Na-rich end member of the Albite-Anorthite Series.) in several combinations for the synthesis of geopolymer. It is thought that the larger reactivity of fly ash and albite, the interaction between the original materials and the gel phase along with the reinforcing effect induced by the large unreacted albite particles are accountable for an ideal mechanical behavior (high compressive strength and low cracking probability).

Some authors (Davidovits 2005a) studied the 15 types of combustion fly ashes were tested for suitability in geopolymer cements. The samples were cured at room temperature and the compressive strength was measured after 28 days. A sizable variation in the behavior of the fly ashes was noticed which range from unworkable situations to strength of 95 MPa.

Some authors (Xu and Van Deventer 2000b) proved that calcined materials for instance slag, fly ash and metakaolinite which are generally amorphous, usually display a greater reactivity during geopolymerization in comparison to non-calcined materials. This is explained by the truth that calcination activates materials by changing their crystalline into amorphous structure with subsequent storage of the additional energy (Xu et al. 2002).

Moreover, the production of consistent geopolymer from heterogeneous industrial waste sources is really a challenging issue for the minerals industry, since raw material suitability cannot be fully guaranteed by elemental composition analysis (Fernandez-Jimenez and Palomo 2003). So far as fly ash based geopolymers are involved, the mechanical strength increases as a result of the formation of an Al-rich alumino-silicate gel during the initial stage of alkaline activation of ash particles, and may further increase as a result of the Si enrichment of the material (Fernandez-Jimenez et al. 2006). Therefore, it is important to control Al and Si dissolution from the raw materials, through pre-processing and/or utilization of combinations of raw materials with various reactivities (Duxson et al. 2007a).

2.4.1 Composition of raw materials

In order to achieve high strength and durability, some authors (Davidovits 1999), based on the zeolite chemistry, recommended the use of certain molar ratios:

- For the alkaline activator: SiO_2/Na_2O = 1.85
- For the metakaolin: SiO_2/Al_2O_3 (3.5–4.5), Na_2O/SiO_2 (0.2–0.48), and Na_2O/Al_2O_3 (0.8–1.6)
- Between the activator and the metakaolin: H_2O/Na_2O (10–25).

However, some authors argue that the parameters linked to the prime material do not connect with other prime materials for instance fly ashes and blast furnace slag, because not absolutely all the silica and aluminium are reactive (Hos et al. 2002; Rahier et al. 1996; Van Jaarsveld et al. 1997). Actually, one must remember that Davidovits used a higher purity material he named Kandoxi (Kaolin, Nacrite, Dickite, Oxide), obtained from the calcination of kaolin during 6 hours at 750°C.

Some authors (Barbosa et al. 2000) have studied seven mixtures of metakaolin pastes activated with NaOH and water glass, to be able to study the molar ratios suggested by Davidovits[46]:

- $0.2 < Na_2O/SiO_2 < 0.48$
- $3.3 < SiO_2/Al_2O_3 < 4.5$
- $10 < H_2O/Na_2O < 25$

They have summarized that the optimum composition occurs for $Na_2O/SiO_2 = 0.25$; $H_2O/Na_2O = 10$ and $SiO_2/Al_2O_3 = 3.3$. Additionally, they noticed that after using mixtures with a molar ratio $H_2O/Na_2O = 25$ extremely low mechanical strength specimens were obtained, confirming the significance of the water content.

Based on some authors (Xu and Van Deventer 2000b), the percentage of CaO and of K_2O, the ratio Si/Al in the initial mineral presents a correlation with mechanical strength. some authors (Fletcher et al. 2005) studied sodium hydroxide alkali-activated metakaolin, in mixtures varying the SiO_2/Al_2O_3 molar ratio. He summarized that mechanical strength is maximum for $SiO_2/Al_2O_3 = 16$ molar ratio. However, for $SiO_2/ Al_2O_3>24$, mechanical strength could not be determined as the hardened material behaves plastic-like, he also discovered that for high $SiO_2/Al_2O_3>24$ a thermal treatment between 100 and 250^{o}C leads water to be expelled as bubbles resulting in foam materials.

For binder execution, some authors (Davidovits 2005b) suggests these average molar ratios to the composition of the hardened material:

- Si:Al 2.854 (2.047–5.57)
- K:Al 0.556 (0.306–0.756)
- Si:K 6.13 (3.096–9.681)
- Ca:Al 0.286 (0.107–0.401)
- Si:Ca 15.02 (4.882–41.267)

Some authors (Fernandez-Jimenez et al. 2006) studied several kinds of fly ashes, having reported for the reactive phase a Si/Al molar ratio between 1.42 and 2.38, even though the molar ratio for the initial fly ashes is lower, meaning that Al has a less reactive phase than Si. Therefore, what matters most could be the Si/Al molar ratio of the reactive phase, and not really much the Si/Al molar ratio of the initial prime material.

2.5 Factors affecting of compressive strength

Measurements of compressive strength are employed by many researchers as an instrument to measure the success of geopolymerization due to the low cost and simplicity of compressive strength testing, along with of the truth that strength development is really a primary way of measuring the utility of the materials found in different applications of the construction industry (Provis et al. 2005).

The compressive strength of geopolymer is dependent upon many factors such as the gel phase strength, the ratio of the gel phase/undissolved Al–Si particles, the distribution and the hardness of the undissolved Al–Si particle sizes, the amorphous nature of geopolymer or the amount of crystallinity, and the surface reaction between the gel phase and the undissolved Al–Si particles (Van Jaarsveld et al. 2003; Xu 2001)

Furthermore, factors such as % CaO, % K_2O and the kinds of alkali have an important correlation with compressive strength. The significance of the molar Si/Al ratio during the alkaline dissolution of the individual minerals suggests that compressive strength is obtained by complex reactions between the mineral surface, kaolinite and the concentrated sodium silicate solution.

After geopolymerization, the undissolved particles remain bonded in the matrix, so the hardness of the minerals correlates positively with the last compressive strength (Xu and Van Deventer 1999; Xu and Van Deventer 2000b). During geopolymerization of natural minerals, it is known that after adding aggregate for instance granular sand to the geopolymer mixture, the compressive strength increases (Xu et al. 2002).

The quantity of metakaolinite added to the geopolymer matrix, along with the KOH concentration and the addition of sodium silicate, also play an important role on the ultimate compressive strength. some authors (Swanepoel et al. 1999) proved that the strength increases with increasing addition of metakaolinite. The main reason might be that the more metakaolinite added, the more Al gel forms in the system, causing a higher level of polymerization. Some authors (Wang et al. 2005) proved experimentally that the compressive strength, along with the apparent density and the content of the amorphous phase of metakaolinite-based geopolymer, increase with the increase of NaOH concentration within the range 4–12 mol/L. This is caused by the enhanced dissolution of the metakaolinite particulates and therefore the accelerated condensation of the monomer in the clear presence of higher NaOH concentration.

Some authors (Luz Granizo et al. 2007) supported the proven fact that the alkali activation of metakaolin using sodium silicate and NaOH containing solutions results in the production of material exhibiting higher mechanical strength compared to the activation with only NaOH. Furthermore, the flexural strength increases once the activator volume decreases or the concentration of Na increases.

Compressive strength of metakaolin based geopolymer increased linearly by approximately 400% from Si/ Al = 1.15 to Si/Al = 1.90, where it obtained its maximum value, before decreasing again at the greatest Si/Al ratio of 2.15 (Duxson et al. 2005) (Figure 2.2).

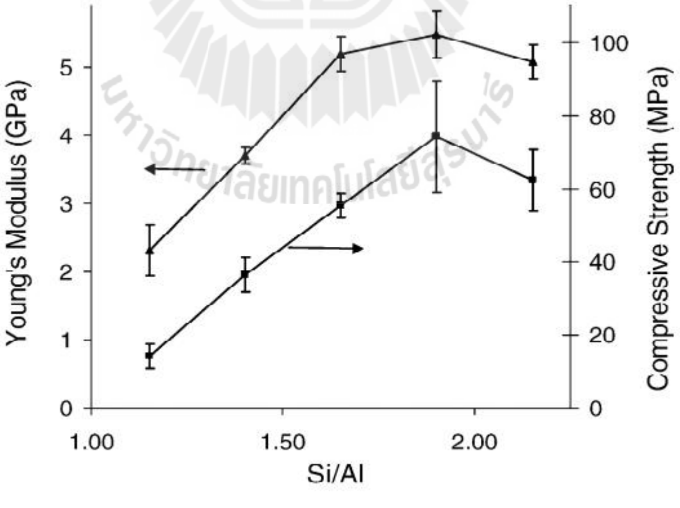

Figure 2.2 Young’s moduli (▲) and ultimate compressive strengths (■) of geopolymers. (Duxson et al. 2005).

It is thought that the quantity of unreacted materials in specimens with higher silica content acts as defect site and includes a negative impact on strength. Higher strength was recorded once the ratios SiO_2/Al_2O_3 and Na_2O/Al_2O_3 were 3.0–3.8 and approximately 1, respectively (Duxson et al. 2005; Stevenson and Sagoe-Crentsil 2005). However, these initial ratios might be changed based on the total amount of the raw materials used as Al_2O_3 and SiO_2 source (Silva et al. 2007).

Based on some authors (Phair and Van Deventer 2001), probably the most significant factor that controls the compressive strength of fly ash-based geopolymer may be the pH of the original alkali metal silicate precursor. When working with cement as a setting additive in the geopolymer matrix, the compressive strength increases almost exponentially with increasing pH (Figure 2.3 and 2.4).

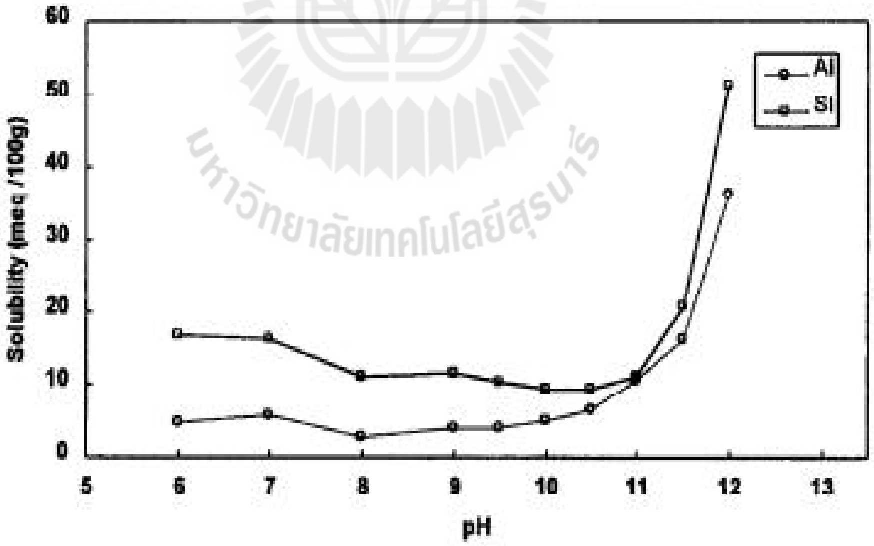

Figure 2.3 Dissolution of Al Si from metakaolin as a function of pH over a 5 h period (Phair and Van Deventer 2001).

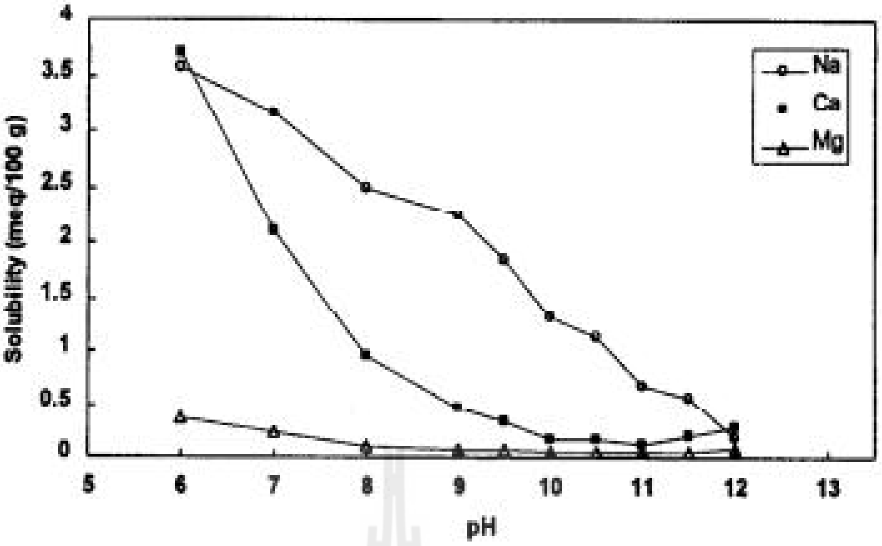

Figure 2.4 Dissolution of Na, Ca, and Mg metakaolin as a function of pH over a 5 h period. Ti and Fe concentration were negligible (Phair and Van Deventer 2001).

The larger alkali content was found to enhance solid dissolution but also to cause alumino-silicate gel precipitation at very early stages, causing lower compressive strength (Lee and Van Deventer 2002). Additionally, the calcium content in fly ash based geopolymer, along with the water/fly ash ratio, is apparently highly important (Van Jaarsveld et al. 2003).

Some authors (Palomo et al. 2007) proved that alkali activation of highly blended cements containing 30% Portland cement clinker and 70% fly ash results in acceptable mechanical strength, which will be strongly affected by the sort of the alkaline activator put into the system. Some authors (Kumar et al. 2005) indicated that mechanically activated fly ash based geopolymer exhibits higher compressive strength due to the formation of a tight microstructure. Mechanical activation of fly ash appears to favor geopolymerization, since the reaction requires less time and occurs at lower temperature.

The influence of curing temperature and time on the flexural properties of geopolymer centered on class C fly ash has been investigated by some authors . (Miller et al. 2005). It had been discovered that the curing regime includes a very significant effect on the physical and chemical properties of fly ash-based geopolymer. Indeed, the mere escalation in synthesis temperature is sufficient to boost the degree of long-range ordering in geopolymer binders (Duxson et al. 2007a).

Geopolymers include relatively massive amount water in large pores readily available for evaporation, which does not end up in capillary strain. This fact may account for the low temperature region of dimensional stability (Barbosa and MacKenzie 2003b). Once the freely evaporable water is taken from pores, the top part of the gel structure increases as water is liberated from the outer lining of the gel, and small pores leading to shrinkage are observed. In this instance, the gel contraction might be correlated with the decrease in surface area (Duxson et al. 2007b).

Moisture evaporation results in deterioration of the geopolymer product which cannot develop satisfactory strength. Furthermore, the addition of water improves the workability of the mortar (Chindaprasirt et al. 2007) (Figure 2.5, 2.6 and 2.7).

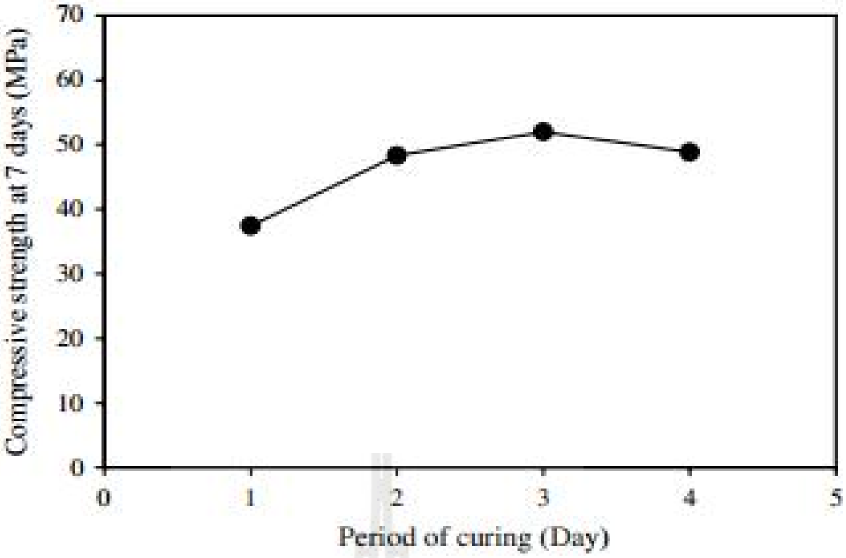

Figure 2.5 Duration of heat curing and strength cured at 60°C with delay time [94].

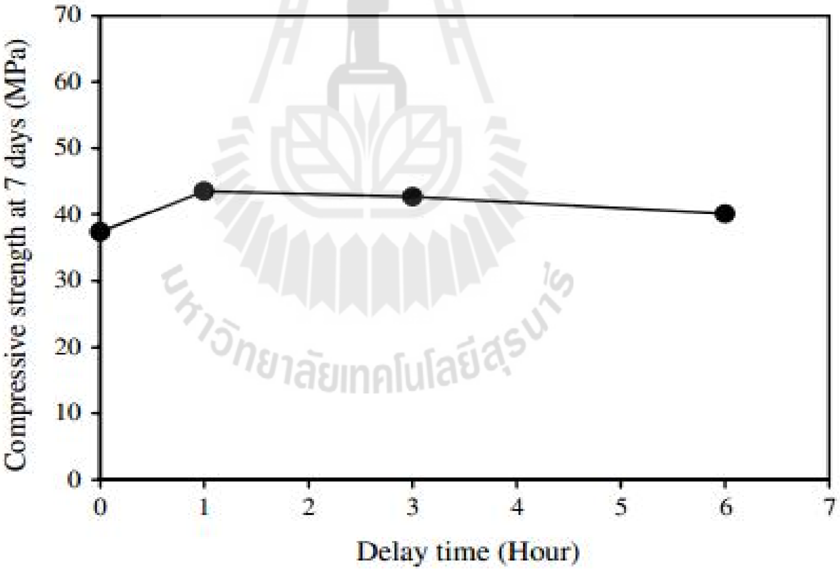

Figure 2.6 Strength and delay time of geopolymer mortar with 60°C heat curing for 24 h (Chindaprasirt et al. 2007).

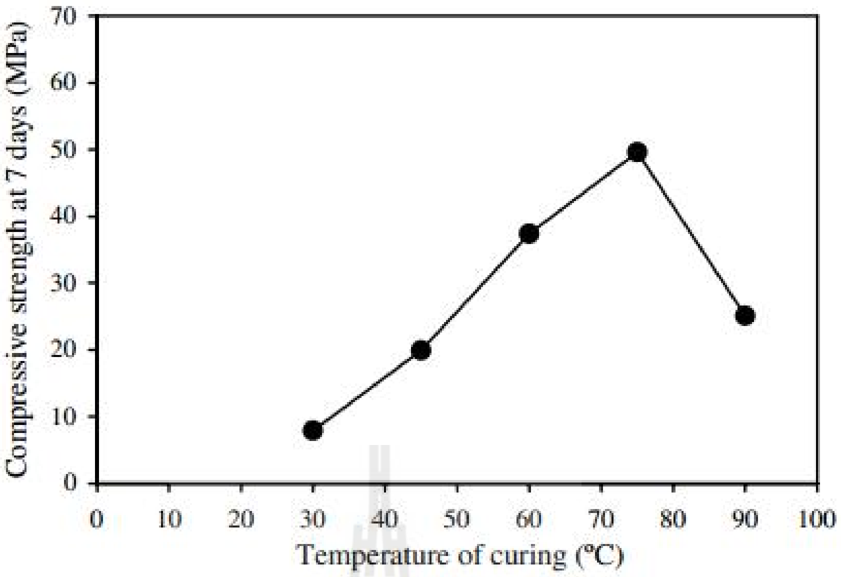

Figure 2.7 Strength and temperature of curing of geopolymer with no delay time before curing (Chindaprasirt et al. 2007).

Furthermore, some authors (Rattanasak and Chindaprasirt 2009) studied the influence of NaOH solution on the synthesis of fly ash geopolymer. To produce geopolymer paste, separate mixing and normal mixing were used. For separate mixing, NaOH solution was blended with fly ash for the initial 10 min; the subsequently sodium silicate solution was added to the mixture. For normal mixing, fly ash, sodium hydroxide and sodium silicate solution were incorporated and mixed at the same time. Geopolymer were cured at 65°C for 48 h. At 5 M NaOH, the dissolution was low because of the relatively low base condition. For 10 M NaOH, the base condition was higher and the dissolution was, therefore, increased. For the 15 M NaOH, the dissolution was again reduced owing primarily to a rise in coagulation of silica (Bergna and Roberts 2006) (Figure 2.8 and 2.9).

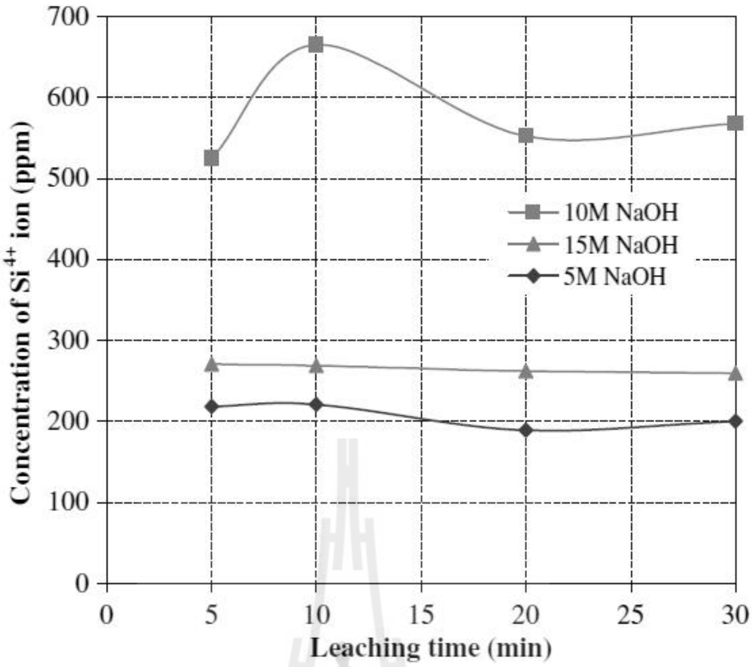

Figure 2.8 Si^{4+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH (Rattanasak and Chindaprasirt 2009).

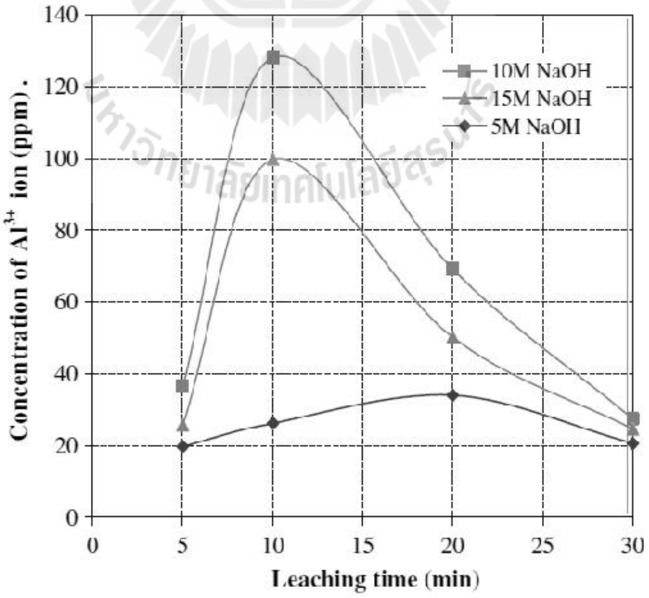

Figure 2.9 Al^{3+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH (Rattanasak and Chindaprasirt 2009).

The water within geopolymer and its subsequent removal by evaporation plays a significant role in obtaining a crack-free geopolymer, which means that rapid drying during curing ought to be avoided, while curing at less relative humidity (e.g. 30%) is advised (Perera et al. 2004). Also, it had been found that when the curing temperature is high (approximately 90°C), the geopolymer will substantially lose the moisture (Bakharev 2005b).

Other researches (Khalil and Merz 1994; Van Jaarsveld et al. 2002) proved that curing for longer amounts of time at elevated temperature generally seems to weaken the structure, suggesting that small levels of structural water must be retained to be able to eliminate cracking and maintain structural integrity. It appears that prolonged curing at elevated temperatures breaks down the gelular structure of the geopolymer synthesis mixture, leading to dehydration and excessive shrinkage, while long procuring at room temperature is good for strength development when utilizing fly ash as a raw material (Bakharev 2005b). Furthermore, J.G.S Van Jaarsveld et al.2002 (Table 2.1) stated that initial curing at higher temperatures (above 50–80°C) does not increase compressive strength substantially above that accomplished by curing at room temperature.

Table 2.1 The effect of curing conditions on the compressive strength of a matrix containing Macquarie fly ash with compositional variables: clay (kaolinite) content = 15% (mass) (J.G.S. Van Jaarsveld et al. 2002).

Time (h)	Temperature (°C)					
	30	50	70	30 B	50 B	70 B
6	6	-	14	19	-	28
12	15	26	34	7	22	21
24	20	12	33	19	24	29
48	19	-	28	21	-	15
Average (12/24 h samples)	17	19	34	13	23	25

[a] Samples were cured in an oven, open to the atmosphere except for samples denoted by "B" which were cured in sealed plastic bags under the same conditions. Compressive strength values in MPa.

Generally speaking, it is needed to adequately cure to be able to achieve advanced mechanical and durability performance. Additionally, the setting time is practically important as it defines enough time necessary for transport, placing and compaction (Teixeira-Pinto et al. 2002). In order to raise the acceptance of geopolymerization by the industry, curing conditions ought to be just like those utilized in OPC production.

Based on researches (Hardjito et al. 2004) collected the consequence of geopolymer concrete development. The binder in this concrete, the geopolymer paste, is formed by activating by-product materials, for example low-calcium (Class F) fly ash. he found that numerous variables for instance curing temperature, curing time, concentration of alkali solution, and delay time effected to compressive strength of geopolymer concrete as follows;

- The curing temperature in the range of 30 to 90°C increases, the compressive strength of geopolymer concrete also increases. Higher curing temperature triggered larger compressive strength, although a rise in the curing temperature beyond 60°C did not raise the compressive strength substantially (Figure 2.10).

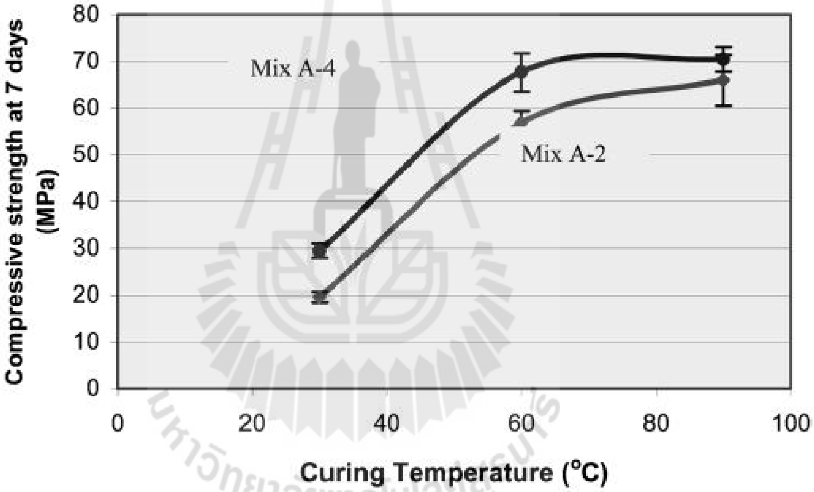

Figure 2.10 Effect of curing temperature on compressive strength (Hardjito et al. 2004).

- The influence of curing time on the compressive strength indicate that a longer did not produce weaker material as claimed by researches (Van Jaarsveld et al. 2002). However, the escalation in strength for curing periods beyond 48 h is not significant (Figure 2.11).

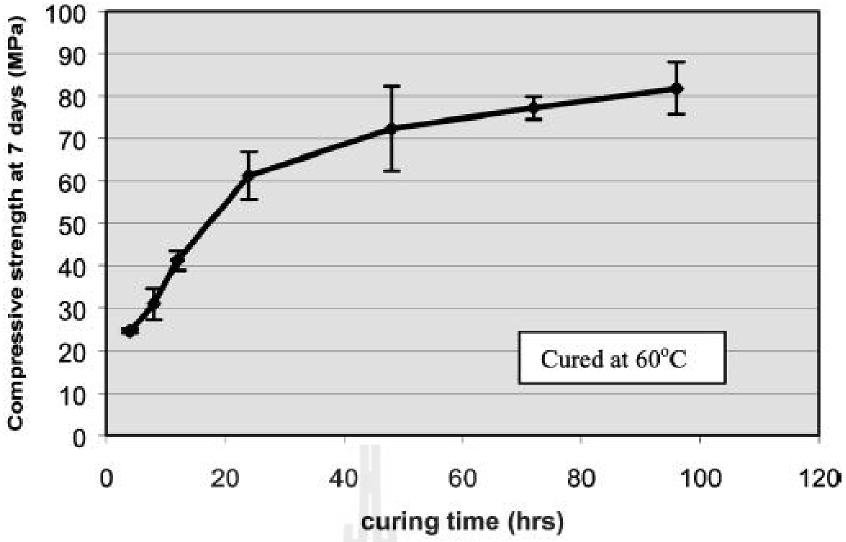

Figure 2.11 Influence of curing time on compressive strength (Hardjito et al. 2004).

- The concentration of sodium hydroxide as measured by Molarity (second column). Mixture A-3 with higher concentration of NaOH yielded higher compressive strength than Mixture A-1. The same trend can also be observed for the Mixtures A-2 and A-4 (Table 2.2)

Table 2.2 Effect of parameter on compressive strength (Hardjito et al. 2004).

Mixture	Concentration of NaOH liquid in molarity (M)	Sodium silicate/NaoH liquid ratio by mass	7-day compressive strength after curing at 60°C for 24 h. (MPa)
A-1	8 M	0.4	17.3
A-2	8 M	2.5	56.8
A-3	14 M	0.4	47.9
A-4	14 M	2.517.3	67.6

- The new concrete was permitted to stand at room temperature after mixing and just before being put into molds for a particular amount of time. The new geopolymer concrete is easily handled as much as 120 min without the sign of the setting and the degradation in the compressive strength (Figure 2.12).

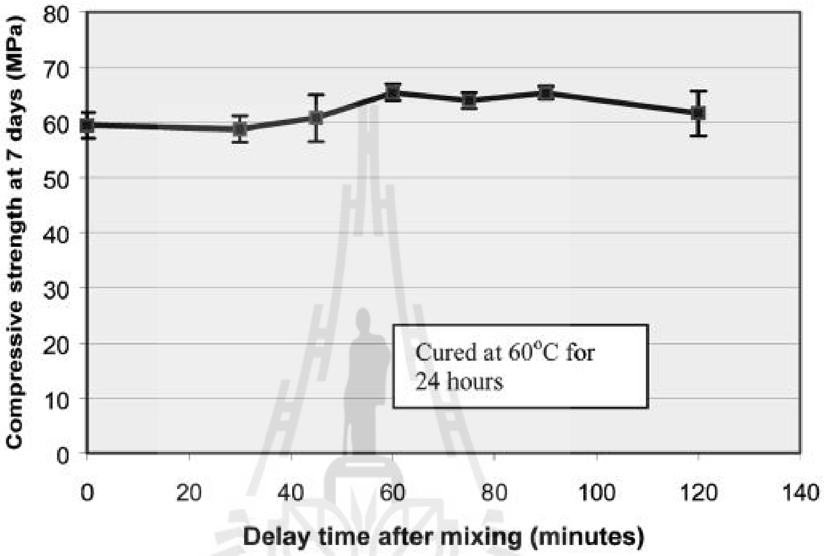

Figure 2.12 Influence of delay time on compressive strength (Hardjito et al. 2004).

- The compressive strength does not vary with the age of concrete, when cured for 24 h. This observation is in contrast to the well-known behavior of OPC concrete, which undergoes a hydration process and hence gains strength over time (Figure 2.13).

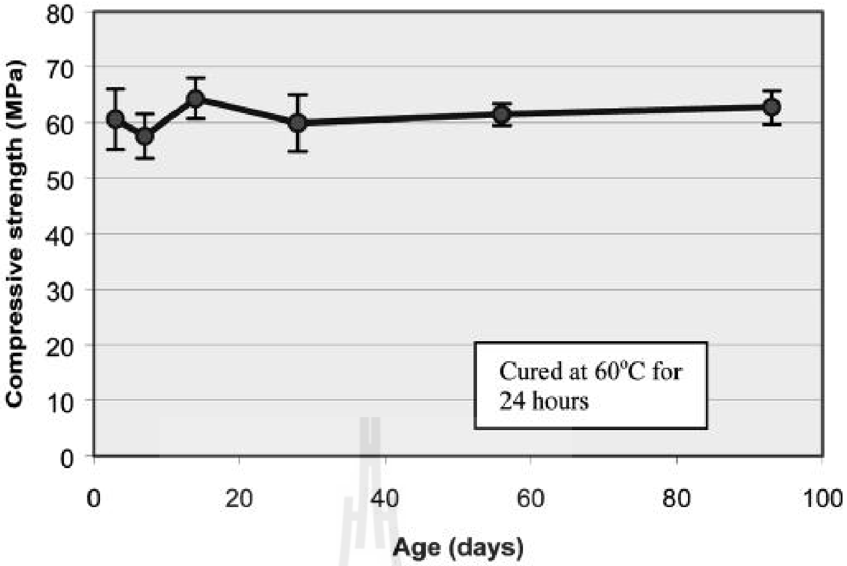

Figure 2.13 Compressive strength at different ages (Hardjito et al. 2004).

Some authors (Guo et al. 2010) indicated that the high compressive strength was obtained once the class C fly ash (CFA) was activated by the mixed alkali activator (sodium hydroxide and sodium silicate solution) with the optimum modulus viz., molar ratio of SiO_2/Na_2O of 1.5. The appropriate content of the mixed activator was 50% as evaluated by the mass proportion of Na_2O to CFA. The compressive strength of those samples was 63.4 MPa when these were cured at 75°C for 8 h accompanied by curing at 23°C for 28 days (Figure 2.14 and 2.15).

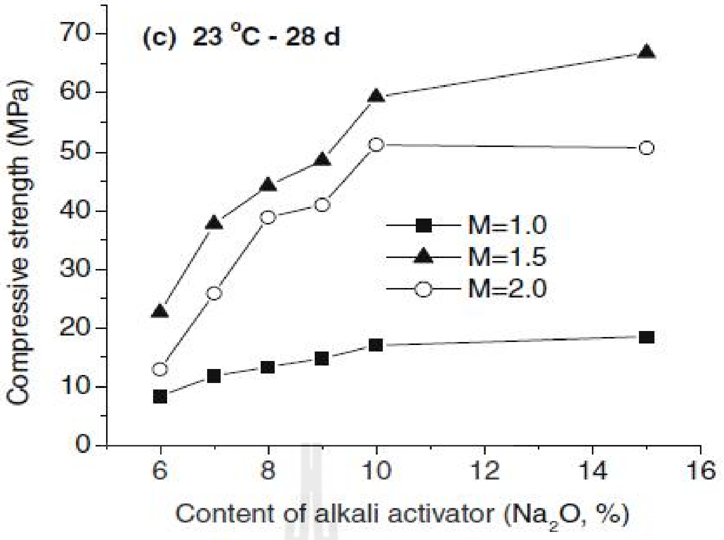

Figure 2.14 Effects of modulus (M) and content of the mixed alkali activator on the compressive strength of fly ash geopolymer cured at room temperature of 23°C for 28 days (Guo et al. 2010).

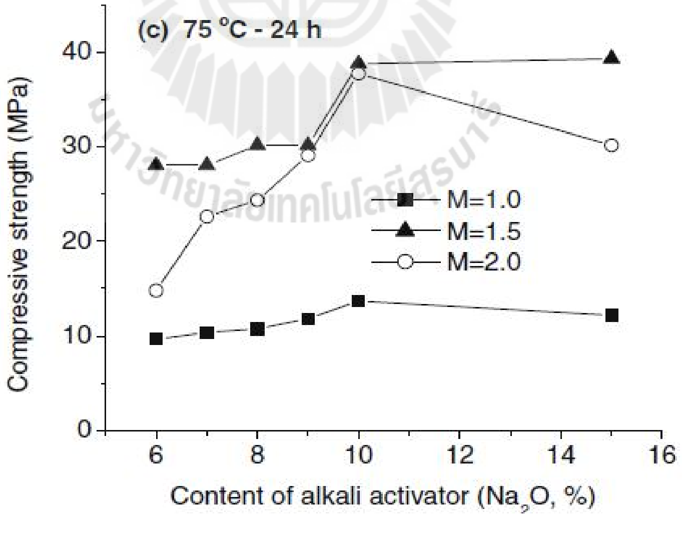

Figure 2.15 Effects of modulus (M) and content of the mixed alkali activator on the compressive strength of fly ash geopolymer cured at room temperature of 75°C for 4, 8, and 24 h (Guo et al. 2010).

Some authors (Provis et al. 2009) showed that the compressive strength of Geopolymer samples was prepared by mixing the fly ash with sodium silicate activating solutions and discovered that the greatest compressive strength of liquid/fly ash mass and SiO_2/Na_2O mole ratio were 0.5-0.8 and 1.0 -1.5, respectively (Figure 2.16).

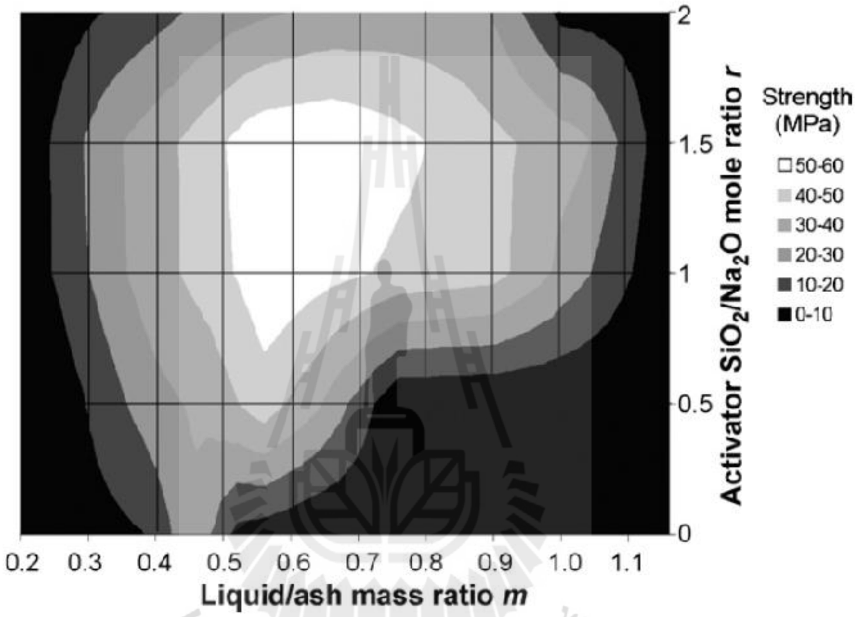

Figure 2.16 Contour plot of compressive strength data for all samples (Provis et al. 2009)

Some authors (Diop et al. 2011) revealed that the performance of clay from the Niemenike deposit (Niem) and clay pre-treated at 700°C (NiemC). The performance of both clays is dependent upon the temperature of curing and on the full time of curing. In long-term tests (1 week to 3 months), for bricks kept at 40°C/60% RH, strength did not increase with time for both clays (natural and calcined) activated with sodium hydroxide but this is dependent upon the NaOH concentration (4, 8, and 12 M). The utmost strength is obtained after 14 days for all concentrations. For all concentrations and periods, strength obtained with natural clay is greater. The calcined clay gave the best mechanical performances. For all cases, long-term or short-term, calcined or not, strength increased with concentration. The bricks manufactured in this fashion are durable and relatively inexpensive to produce (Figure 2.17).

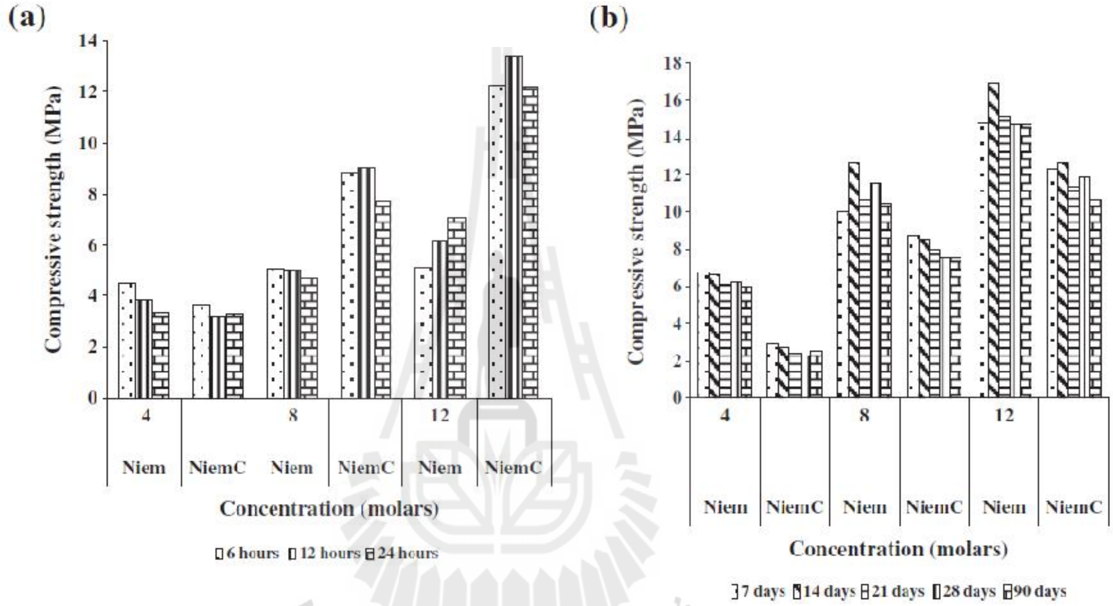

Figure 2.17 Summary of compressive strength of samples cured at (a) 120°C and (b) 40°C (Diop et al. 2011).

Durability is an essential function to assess the utilization of waste and recycled materials for geopolymer material in construction (Khoury and Zaman 2007). It may be stated that the durability of the clay-fly ash geopolymer brick induced by environmental conditions in alkali, hot and rainfall regions may have the impact on their performance. For this reason, the effect of environmental conditions is highly recommended to judge the performance of the clay-fly ash geopolymer brick stabilized. Environmental features, namely wet–dry cycles, adsorption, and sodium and magnesium sulphate attack are regarded as one of the most destructive actions that will help damage the structure for construction. Author (Bakharev 2005a) presented an investigation into the durability of geopolymer materials manufactured using class F fly ash and alkaline activators when subjected to a sulfate environment. The tests involved immersions for an amount of 5 months into 5% solutions of sodium sulfate and magnesium sulfate, and a solution of 5% sodium sulfate+5% magnesium sulfate. He discovered that in the sodium sulfate solution, significant fluctuations of strength occurred with strength reduction 18% in the 8FASS material prepared with sodium silicate and 65% in the 8FAK material prepared with a combination of sodium hydroxide and potassium hydroxide as activators, while 4% strength increase was measured in the 8FA specimens activated by sodium hydroxide. In the magnesium sulfate solution, 12% and 35% strength increase was measured in the 8FA and 8FAK specimens, respectively; and 24% strength decline was measured in the 8FASS samples. Probably the most significant deterioration was observed in the sodium sulfate solution and it seemed to be linked to the migration of alkali into solution. In the magnesium sulfate solution, migration of alkali into the solution and diffusion of magnesium and calcium to the subsurface areas was observed in the specimen prepared using sodium silicate and a combination of sodium and potassium hydroxides as activators. The smallest amount of strength changes was present in the solution of 5% sodium sulfate+5% magnesium sulfate. The material prepared using sodium hydroxide had the most effective performance, which has been related to its stable cross-linked alumino-silicate polymer structure (Figure 2.18, 2.19 and 2.20).

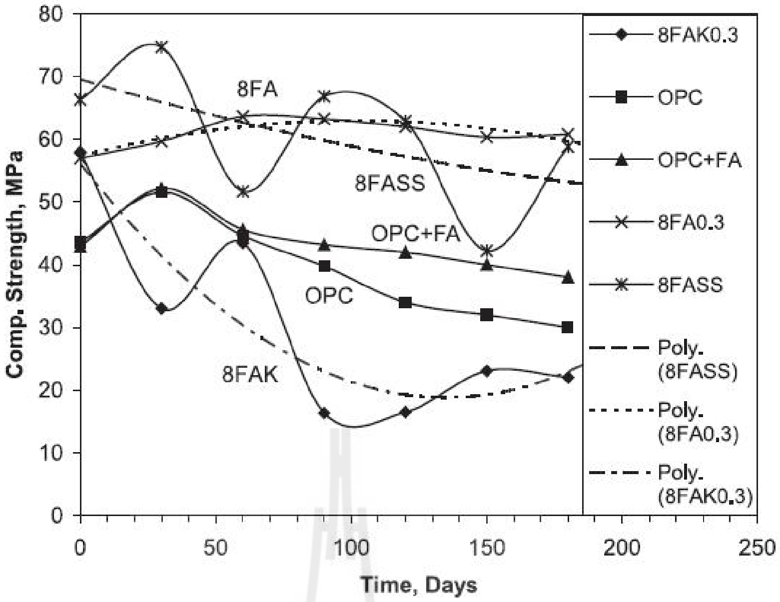

Figure 2.18 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to 5% sodium sulfate solution (Bakharev 2005a).

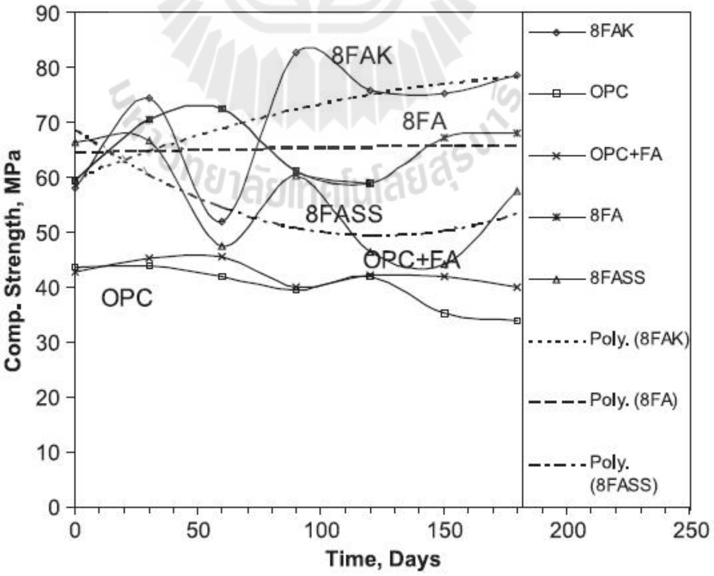

Figure 2.19 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to 5% magnesium sulfate solution (Bakharev 2005a).

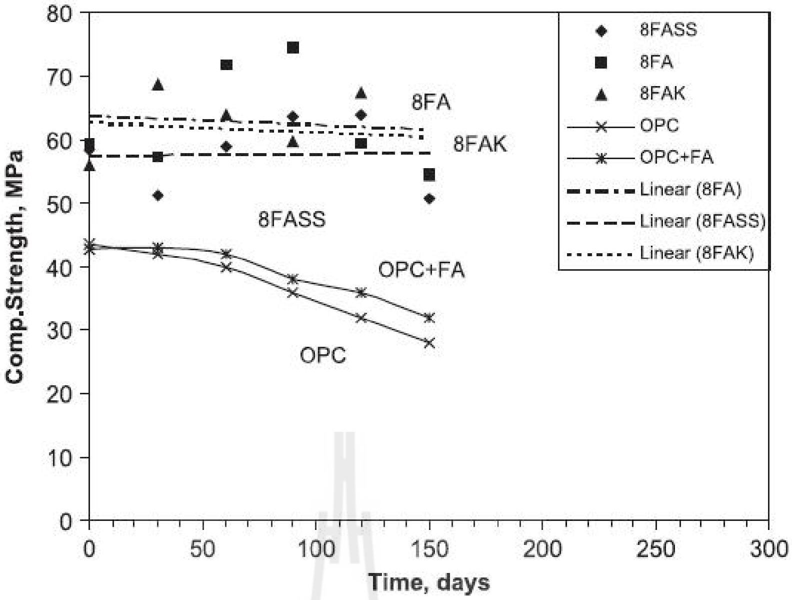

Figure 2.20 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to a solution of 5% sodium sulfate+5% magnesium sulfate (Bakharev 2005a).

2.6 Analytical techniques

Several easy or advanced techniques can be utilized to acquire maximum information and elucidate geopolymerization mechanisms. The capability of Al–Si minerals to undergo geopolymerization might be predicted by specific surface area measurements, which offer an indication of how much surface area participates in heterogeneous reactions inside a solid–fluid system (Van Jaarsveld et al. 2002).

Optical microscopy provides a visible description of the microstructure because it is shown in scale the physical size and model of the different aspects of geopolymer. X-ray fluorescence (XRF) spectrometry works extremely well for elemental analysis of Al–Si minerals. X-ray diffraction (XRD) might be also a helpful tool although the quantity of information which may be obtained is restricted as a result of substantial amorphous nature of geopolymer. However it will provide information concerning the extent to which crystalline starting materials have reacted (Van Jaarsveld et al. 2002). Figure 2.21 presents the XRD pattern of geopolymer when fly ash is employed as raw materials and activated employing a NaOH (8M) solution and cured at 85°C (20 h) (Fernandez Jiminez et al. 2004).

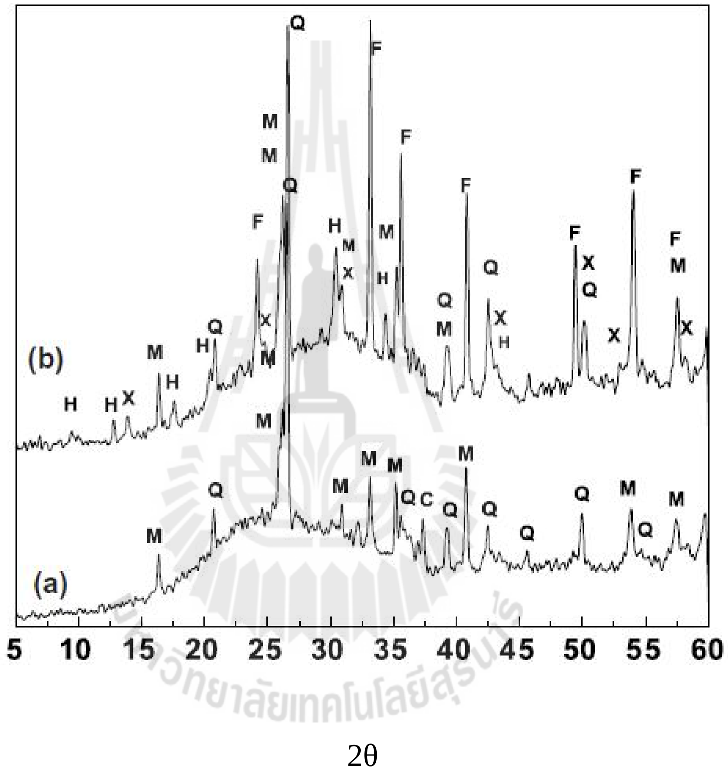

Figure 2.21 XRD spectra (a) un-reacted fly ash; (b) alkali-activated fly ash 20 h at 85°C Q=Quartz; M= Mullite; F=Hematite; C=CaO; H=Herschelite; X=Hydroxysodalite (Fernandez Jiminez et al. 2004).

Scanning electron microscopy (SEM) allows visual examination of a product from millimeters to micrometers to yield definitive topographical information along with good physical and mechanical description of the microstructure of crystalline and amorphous materials, which may not be detected by other techniques (Duxson et al. 2006; Lee 2002). Some authors (Jiminez et al. 2004)provided the geopolymer microstructures (Figure 2.22 - 2.25) are characterized by way of a dispersion of distinctive morphologies in a large of predominantly featureless hydration product (alumino-silicate gel). Occasionally, cracking in the item is observed. This might be because of the thermal treatment carried out within the activation process, mechanical damage during sample preparation or to drying shrinkage in the vacuum of the electron microscope. The relatively low magnification images (Figure 2.22 and 2.23) offer a summary of the distribution of numerous constituent phases with an increase of local detail being provided in Figure. 2.24 and 2.25.

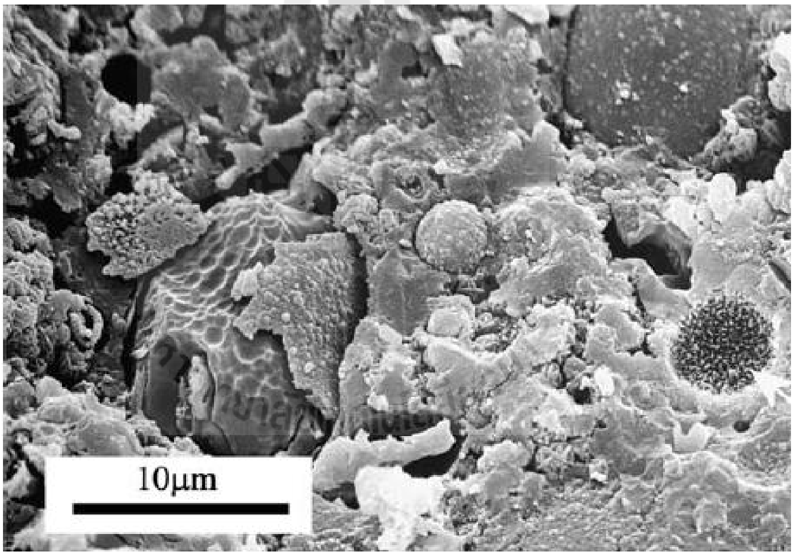

Figure 2.22 SEM micrograph of fracture surface of alkali-activated PFA geopolymer. Fe_2O_3 is arrowed (Jiminez et al. 2004).

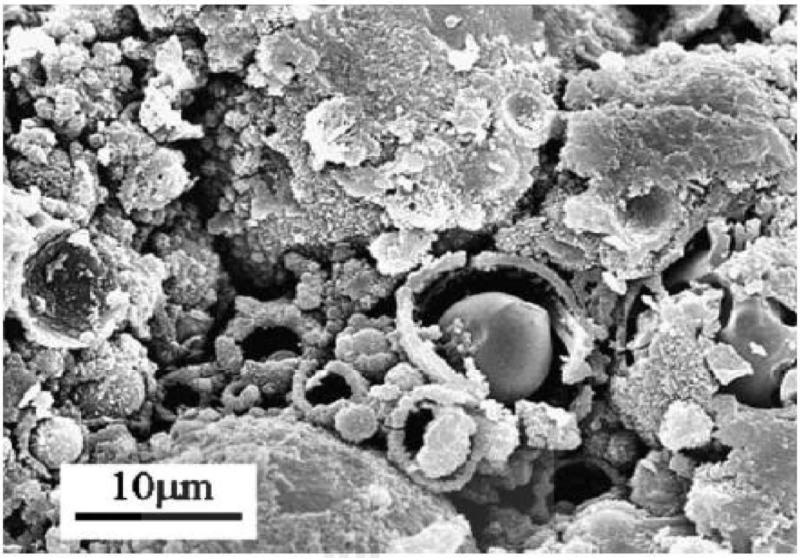

Figure 2.23 SEM micrograph of fracture surface of alkali-activated PFA geopolymer (Jiminez et al. 2004).

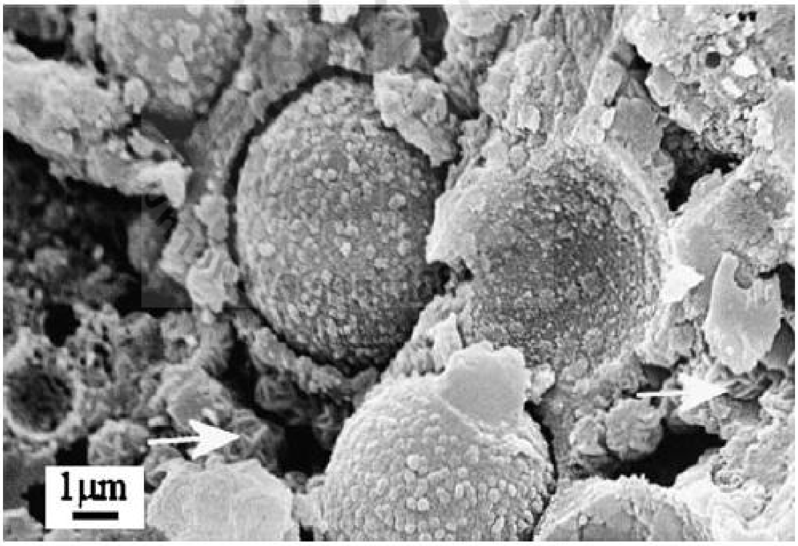

Figure 2.24 SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing PFA particle with reaction shells and also unidentified spherical assemblages (arrowed) [110].

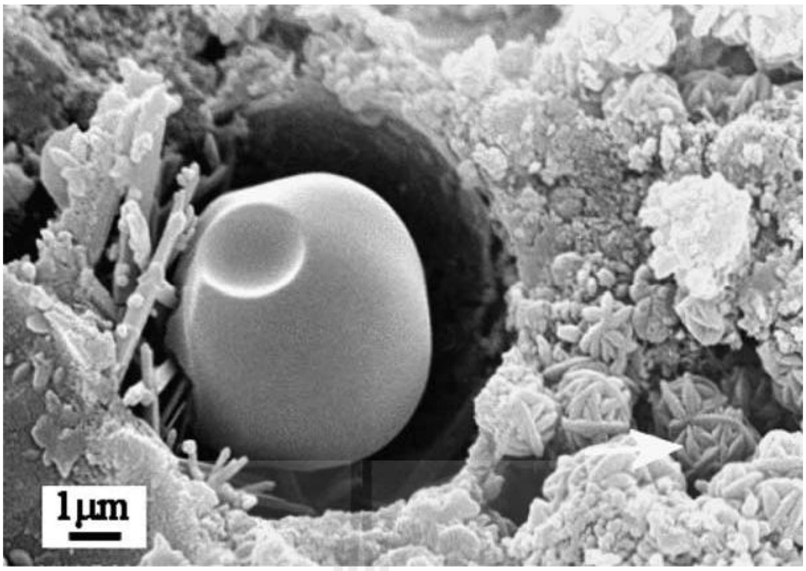

Figure 2.25 SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing considerably eroded PFA particle and also unidentified spherical assemblages (arrowed) (Jiminez et al. 2004).

2.7 The new information obtained from this thesis

The thesis attempts to study the possibility of using the silty clay of high silica and alumina contents (without heat) and fly ash to develop the clay-fly ash geopolymer and then, presents the factors influencing strength development in clay–fly ash geopolymer. The factors are different ingredients (fly ash/clay ratio, Na_2SiO_3/NaOH ratio, Liquid alkaline/fly ash ratio, and molding moisture content), specimen weights, and heating conditions (curing temperature and duration). Finally, presents the durability of the clay-fly ash geopolymer against sodium and magnesium sulphate attack; which are the causes for most destructive damages in northeast Thailand soil. The outcome of this work would provide choices and be beneficial for the production of building materials in the saline soil areas or near the coast and thus lead to the reduction in the cement consumption and environmental problems.

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CHAPTER III

STRENGTH DEVELOPMENT IN CLAY-FLY ASH GEOPOLYMER

3.1 Statement of problem

The bricks are a mixture of cement and local soil; therefore they are sensitive to the climate change. And then, Portland cement manufacture causes greenhouse effects and global warming. The development of a new cementing agent with low carbon dioxide release is considered as an interesting issue. Commercial and industrial utilization of alkali-activated aluminosilicates cements, known as '*geopolymers*' belong to a group of materials with increased interest due to low CO_2 emission and energy consumption. The silica rich materials such as clay or kaolin (Buchwald and Kaps 2002), fly ash, and bottom ash (Davidovits et al. 1999) can be used as a pozzolanic material to react with the liquid alkaline activator. Fly ash provides the greatest opportunity for commercial utilization of this technology due to the plentiful worldwide raw material supply, which is derived from coal-fired electricity generation (Mohapatra and Rao 2001; Van Jaarsveld et al. 1998). This chapter attempts to study the possibility of using silty clay and fly ash, FA as a raw material to develop the clay–fly ash geopolymer. The silty clay, which is abundant inland soil in northeast Thailand, is used as aggregates. The effects of liquid alkaline activator, heat condition and curing time on the strength development in the clay–FA geopolymer are illustrated. The strength developments in both FA geopolymer and clay–FA geopolymer were measured and compared to understand the role of clay particles on the mix ingredient. The scanning electron microscope (SEM) and X-ray diffraction (XRD) tests were performed to investigate the growth of geopolymerization products. Based on the critical analysis of the test results, the mechanism controlling the strength development of the clay–fly ash geopolymer is revealed. The outcome of this study is useful as fundamental to further study the suitable mix ingredient of the other clay–FA geopolymers to attain target strength and durability.

3.2 Materials and methods

3.2.1 Soil, fly ash and liquid alkaline activator

Silty clay was used as fine aggregates and fly ash was used as a pozzolanic material to react with liquid alkaline activator for geopolymerization. The silty clay was collected from the Suranaree University of Technology campus in Nakhon Ratchasima, Thailand, at a depth of 3 m. Its specific gravity is 2.70. The liquid and plastic limits are approximately 54% and 28%, respectively. The soil consists of 2% sand, 45% silt and 53% clay. The cation exchange capacity, CEC for the silty clay, which is the number of positive charges that the clay can contain, was measured according to the ASTM D7503-10. It is 31.5 meq/100 g soil, which is considered as high. According to the Unified Soil Classification System (USCS), the clay is classified as high plasticity (CH). The natural water content was 7.5%. The free swell test result shows that the clay is classified as low swelling with a free swell ratio (FSR) of 1.0 (Prakash and Sridharan 2004). The chemical composition and grain size distribution of the clay are shown in Table 3.1 and Figure 3.1, respectively.

The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum water content, OWC of 16% and maximum dry unit weight, γ_{dmax} of 17.3 kN/m^3.

Fly ash (FA) was obtained from the Mae Moh power plant in the north of Thailand. Table 3.1 summarizes the chemical composition of FA using X-ray fluorescence (XRF). Total amount of the major components SiO_2, Al_2O_3 and Fe_2O_3 in FA are 81.48%. It is thus classified as class F fly ash in accordance with ASTM C 618. The grain size distribution curve of the FA is also shown in Figure 3.1. The morphology of the silty clay and the FA is shown in Figure 3.2. It is shown that the FA particles are normally fine and spherical while the clay particles are irregular in shape. The liquid alkaline activator is a mixture of sodium silicate solution (Na_2SiO_3), which contains 9% Na_2O and 30% SiO_2 by weight and sodium hydroxide solution (NaOH) with 10 M concentration. FA is used in the development of geopolymer even though the grain size distribution of both clay and FA is approximately the same (Figure 3.2) because of its better reactivity with the liquid alkaline activator. Table 3.2 shows the leaching results of SiO_2 and Al_2O_3 in the clay and FA using the X-ray fluorescence (XRF). Both clay and FA were mixed with 10 M NaOH of 40 mL and the solution was passed through a filter paper for measurement. The results show that the maximum SiO_2 and Al_2O_3 contents were detected at approximately 15 min. After certain leaching time with sufficient amount of ions, gel formation started. The gel of $Si(OH)_4$, $Al(OH)_3$ and alumino-silicates formed results in thickening of solution and lower mobility of solution and ions particularly (Rattanasak and Chindaprasirt 2009). Results from Tables 3.1 and Table 3.2 illustrate the leaching results of SiO_2 and Al_2O_3 in the clay and FA. The clay exhibits leaching capacity of SiO_2 and Al_2O_3 less than the FA because the silica and alumina in FA are mostly amorphous (Palomo et al. 1999; Xu and Van Deventer 2000). For example, the difference in the initial SiO_2 between FA and clay (before leaching test) is about 2.45 times (49.32/20.10) while it is 3.40 times (16.63/4.89) after 15 min of leaching.

Table 3.1 Chemical composition of fly ash and silty clay using

Chemical composition (%)	**Clay**	**OFA**
SiO_2	20.10	49.32
Al_2O_3	7.55	12.96
Fe_2O_3	32.89	15.64
CaO	26.15	5.79
MgO	0.47	2.94
SO_3	4.92	7.29
Na_2O	NA	2.83
K_2O	3.17	2.83
LOI	3.44	7.29

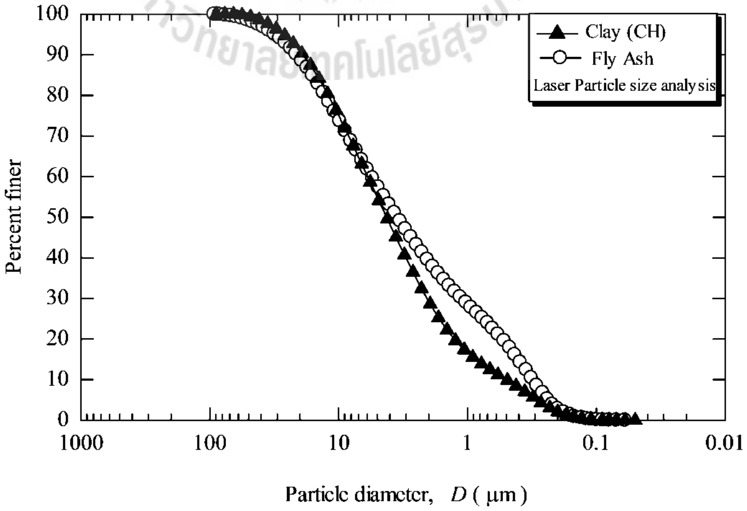


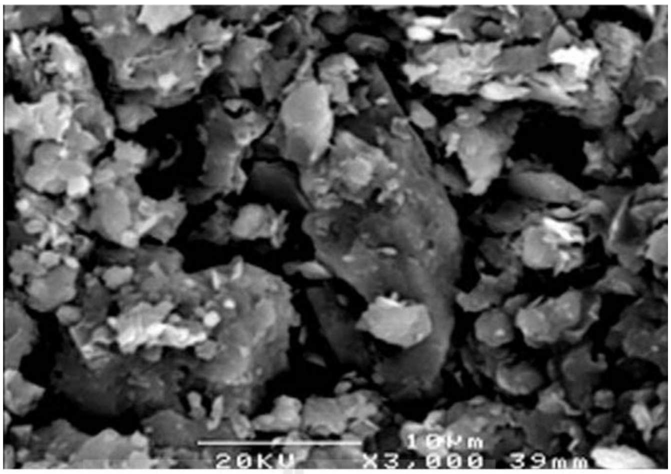
Figure 3.1 Grain size distribution of the clay, and FA.

Table 3.2 Leaching test results of the clay and FA using X-ray fluorescence

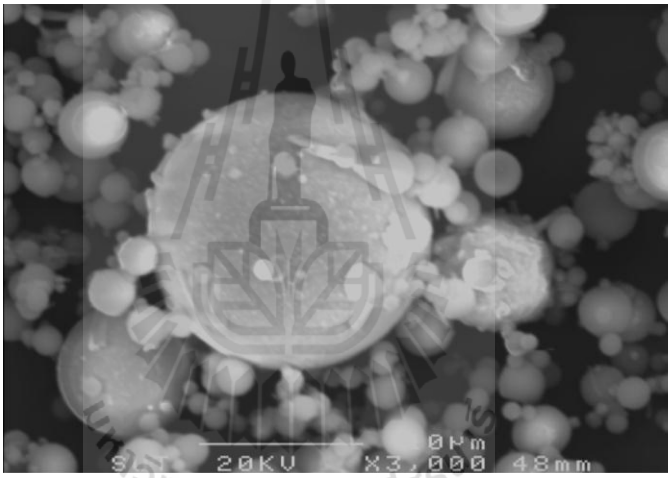
Material	**Leaching time (Min.)**	**Chemical composition (%)**		
		NaO_2	**SiO_2**	**Al_2O_3**
FA	10	84.67	13.136	2.19
	15	80.60	16.63	2.77
	30	83.37	14.97	1.66
	60	82.90	15.39	1.71
CLAY	10	96.17	3.77	0.06
	15	95.06	4.89	0.05
	30	96.98	3.00	0.02
	60	96.40	3.53	0.07

3.2.2 Fly ash geopolymer

FA geopolymer is a mixture of FA and liquid alkaline activator, which is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH) of 10 M concentration. To obtain the optimum ingredient, the Na_2SiO_3/NaOH and the activator to FA (L/FA) ratios were varied. The Na_2SiO_3/NaOH ratios were 0.4, 0.7, 1.0, 1.5, and 2.3 and the L/FA ratios were 0.4, 0.5, 0.6, and 0.7. The geopolymer paste (mixture of FA and liquid alkaline activator) was mixed thoroughly for 10 min in a mixer (Rattanasak and Chindaprasirt 2009) and transferred to plastic molds with 50 mm in diameter and 100 mm in height, kept at ambient temperature (27–30^{o}C) for 24 h, so that the specimens hardened before dismantling from the molds. The cylindrical specimens were then cured at 65^{o}C for 48 h to complete the geopolymerization (Chindaprasirt et al. 2009).



(a) The silty clay



(b) The fly ash

Figure 3.2 Scanning Electron Microscope (SEM)**.**

3.2.3 Clay-fly ash geopolymer

The clay–fly ash geopolymer is a mixture of liquid alkaline activator (Na_2SiO_3 and NaOH), fly ash, and clay. In this study, the ratio of fly ash to clay ratio was 0.3, the Na_2SiO_3/NaOH ratios were 0.4, 0.7, 1.0, 1.5 and 2.3 and the L/FA ratios were 0.4, 0.5, 0.6, and 0.7 by dry clay mass. After thoroughly mixing clay, fly ash and liquid alkaline activator, the clay–FA–activator mixture was statically compressed in a cylindrical mold with 50 mm in diameter and 100 mm in height, kept at ambient temperature (27–30^{o}C) for 24 h, and then cured at 65, 75, and 85^{o}C for 24, 48, and 72 h. The compression was performed by a hand-operated hydraulic jack at the optimum water content (OWC) to attain γ_{dmax}. The OWC and γ_{dmax} were obtained from the laboratory compaction under modified Proctor energy. The symbols for both FA and clay–FA geopolymer specimens are shown as follows:

A–B FA for FA geopolymer

A–B CLAY–FA for clay–FA geopolymer

Where A is the Na_2SiO_3/10 M NaOH ratio (liquid alkaline activator) and

B is the liquid alkaline activator/fly ash ratio (L/FA).

3.2.4 Methods

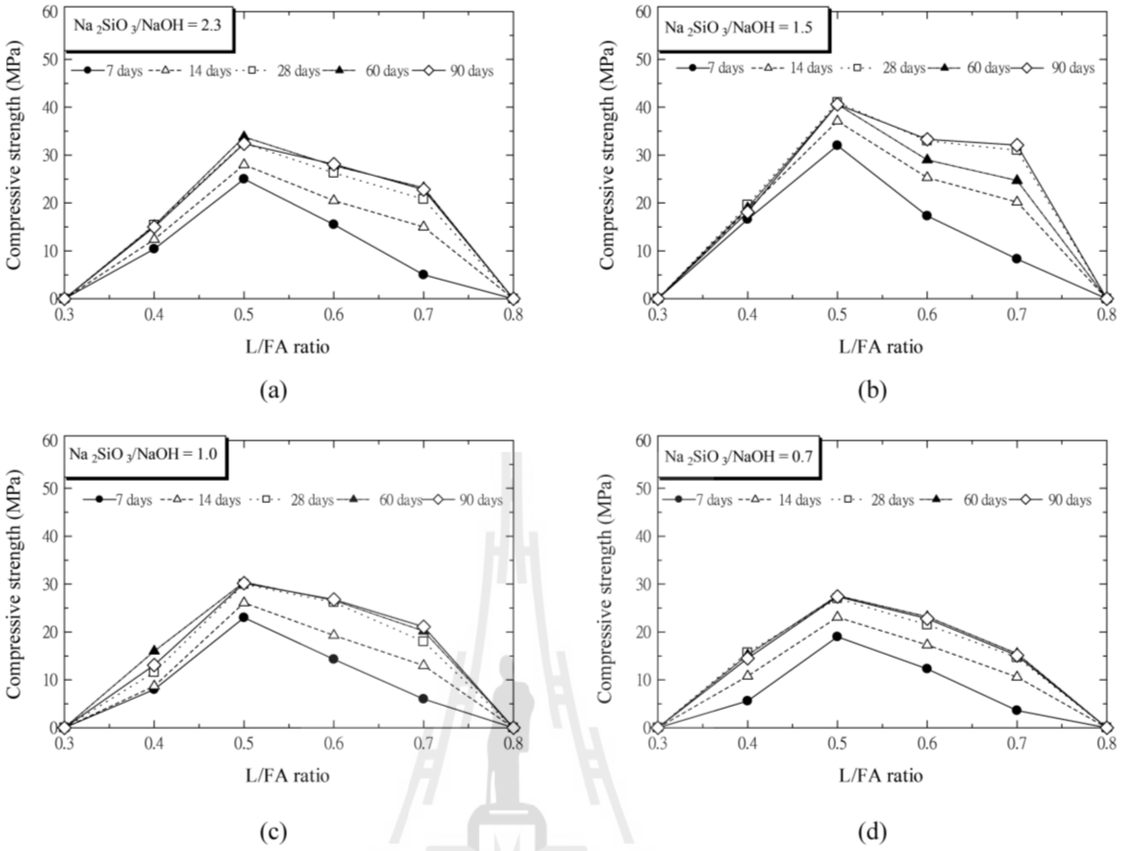
Compressive strengths of both FA and clay–FA geopolymer specimens were measured at different mix ingredients and heat conditions. Compressive strength tests were performed after 7, 14, 28, 60, and 90 days of curing according to the American Standard for Testing and Materials (ASTM D 1633). The reported results were the mean compressive strength of at least five specimens to check for consistency of the test. In most cases, the results under the same testing condition were reproducible with a low mean standard deviation, SD (SD = x<10%, where x is the mean strength value).

The growth of the geopolymerization structures on the specimens was illustrated using X-ray diffraction (XRD) and scanning electron microscope (SEM).

The XRD traces were used to provide fundamental information on geopolymerization structures. The SEM images were used to study the morphology of geopolymer. The SEM specimens were broken from the center into small fragments. They were frozen at -195 ^{o}C by immersion in liquid nitrogen for 5 min and evacuated at a pressure of 0.5 Pa at -40 ^{o}C for 5 days (Horpibulsuk et al. 2010; Horpibulsuk et al. 2009b; Miura et al. 1999). All specimens were coated with gold before SEM (JOEL JSM-6400) analysis.

3.3 Results

The strength test results of the FA geopolymer specimens for different Na_2SiO_3/NaOH ratios and L/FA ratios are shown in Figure 3.3. It shows the 7, 14, 28, 60, and 90 day compressive strengths of the FA geopolymer specimens heated at 65^{o}C for 48 h. For all Na_2SiO_3/NaOH ratios, the strength increases with increasing L/FA ratio up to an optimum value and then tends to decrease. The strength is null at very low and high L/FA ratios of 0.3 and 0.8. The optimum L/FA ratio providing the highest strength is at about 0.5. The maximum compressive strength of the FA geopolymer is at the Na_2SiO_3/NaOH ratio of 1.5 for all L/FA ratios. It is thus concluded that the optimum ingredient for the tested FA geopolymer is the Na_2SiO_3/NaOH ratio of 1.5 and the L/FA ratio of 0.5.



(a) (b)

(c) (d)

Figure 3.3 Compressive strengths of the FA geopolymer specimens heated at 65°C for 48 h for different L/FA and Na_2SiO_3/NaOH ratios.

Figure 3.4 shows the typical strength development with curing time. The figure shows the strength development of the FA geopolymer specimens heated at 65°C for 48 h and L/FA ratio of 0.5. The strength development is rapid for the curing times shorter than 28 days, similar to the strength development in cement paste. Beyond this time, the strengths gradually increase. The 1.5–0.5 FA specimen gives the maximum strength for all curing times.

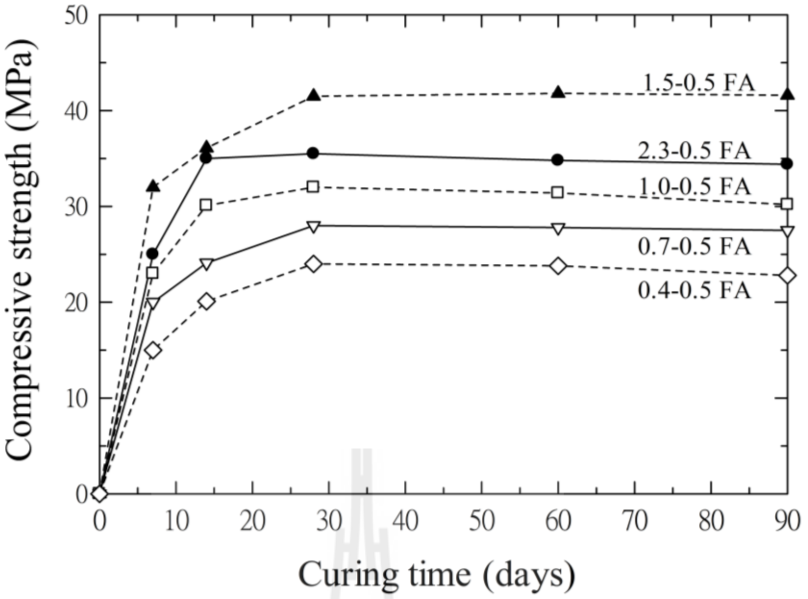


Figure 3.4 Strength development of the FA geopolymer specimens manufacturing heated at 65°C for 48 hours for L/FA ratio of 0.5.

It is now to investigate the compaction behavior and strength development in the clay–FA geopolymer that the clay is used as fine aggregates. Figure 3.5 shows the compaction curves of the clay–FA geopolymer at different ingredients compared with those of the clay and the clay–FA mixture. The compaction curves of the clay–FA mixture and clay–FA geopolymer are essentially the same for all ingredients tested. The maximum dry unit weight of the clay–FA geopolymer is slightly higher than that of the compacted clay. The increase in maximum dry unit weight is associated with the reduction in optimum water content.

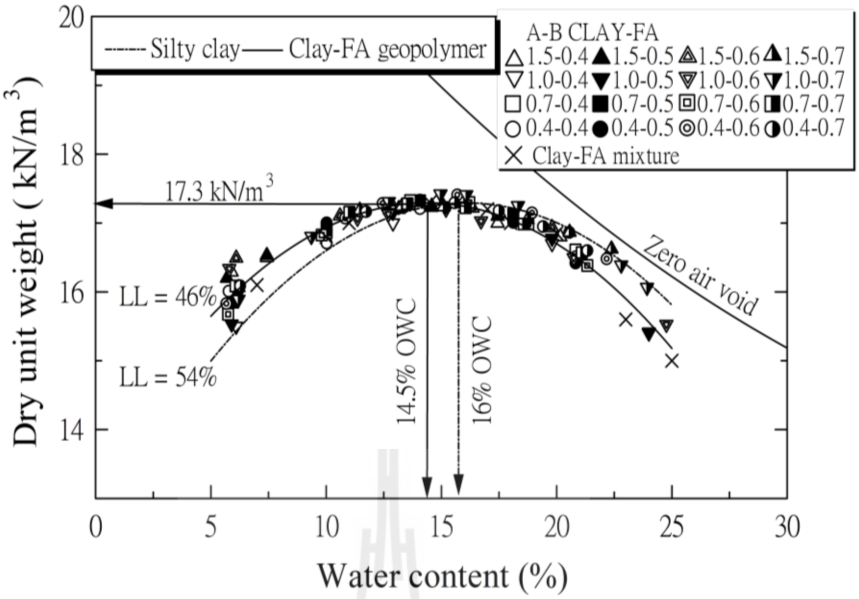


Figure 3.5 Compaction curves of the clay-FA geopolymer at different ingredients compared with the curve of compacted clay.

Figure 3.6 shows the typical strength development in the clay–FA geopolymer specimens for different Na_2SiO_3/NaOH ratios and L/FA ratios at different curing times. The clay–FA geopolymer specimens were heated at 75 ^{o}C for 48 h. The result shows that the strength development with L/FA ratio is in similar pattern to that of the FA geopolymer (vide Figure 3.3). The L/FA ratios of less than 0.3 and greater than 0.8 are not suitable to manufacture the specimen. The optimum ingredient is Na_2SiO_3/NaOH ratio of 0.7 and L/FA ratio of 0.6. The optimum Na_2SiO_3/NaOH ratio is higher while the L/FA ratio is lower than those of the FA geopolymer.

The effects of heat condition on the strength development in the clay–FA geopolymer specimens are illustrated in Figure 3.7. The strengths increase with logarithm of curing time for 65 and 75^{o}C for all heat durations. The longer heat duration is needed for the lower heat temperature to develop high strength as shown that the maximum strength for the 65°C is at 72 h while the maximum strength for the 75°C is at 48 h. The strength gradually increases and the maximum strength is at about 60 days of curing. Yet, the strength tends to decrease with curing time for the specimens heated at 85°C for all heat durations. It is of interest to mention that the maximum strengths for the three temperatures are essentially the same (about 12–14 MPa).

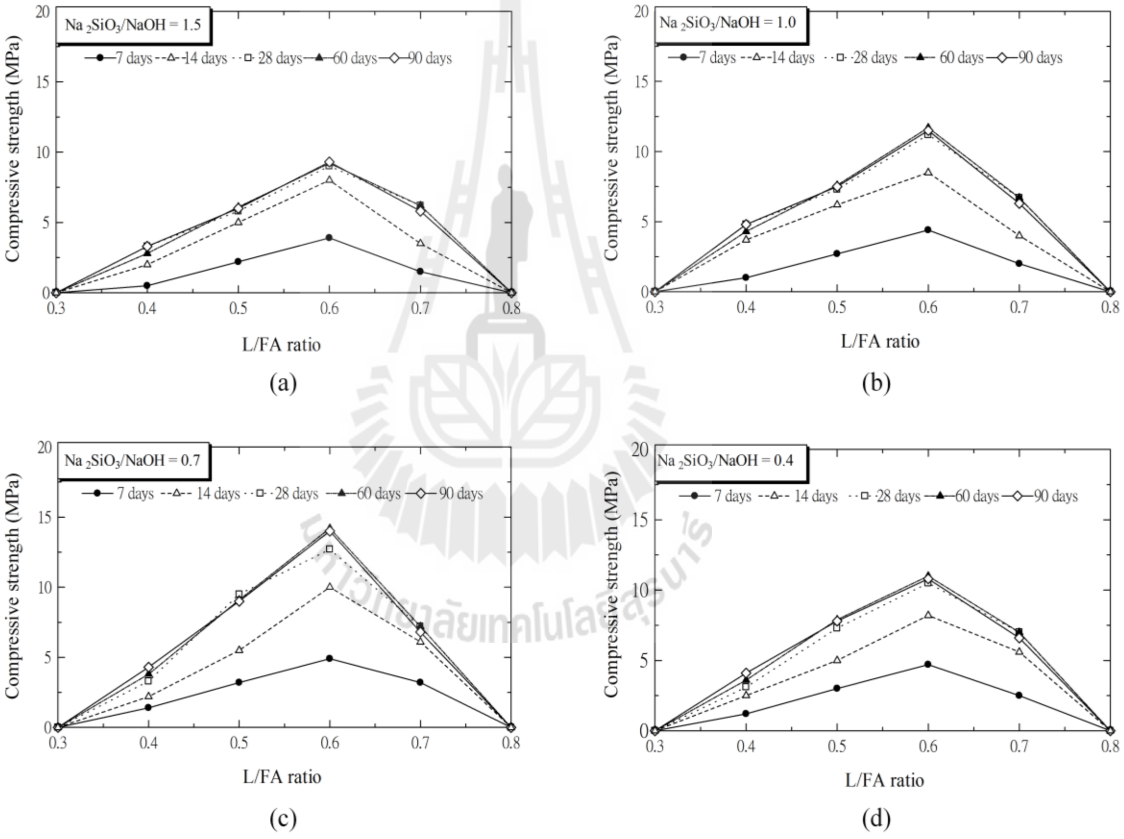


Figure 3.6 Compressive strengths of the clay–FA geopolymer specimens heated at 75°C for 48 h for different L/FA and $Na_2SiO_3/NaOH$ ratios.

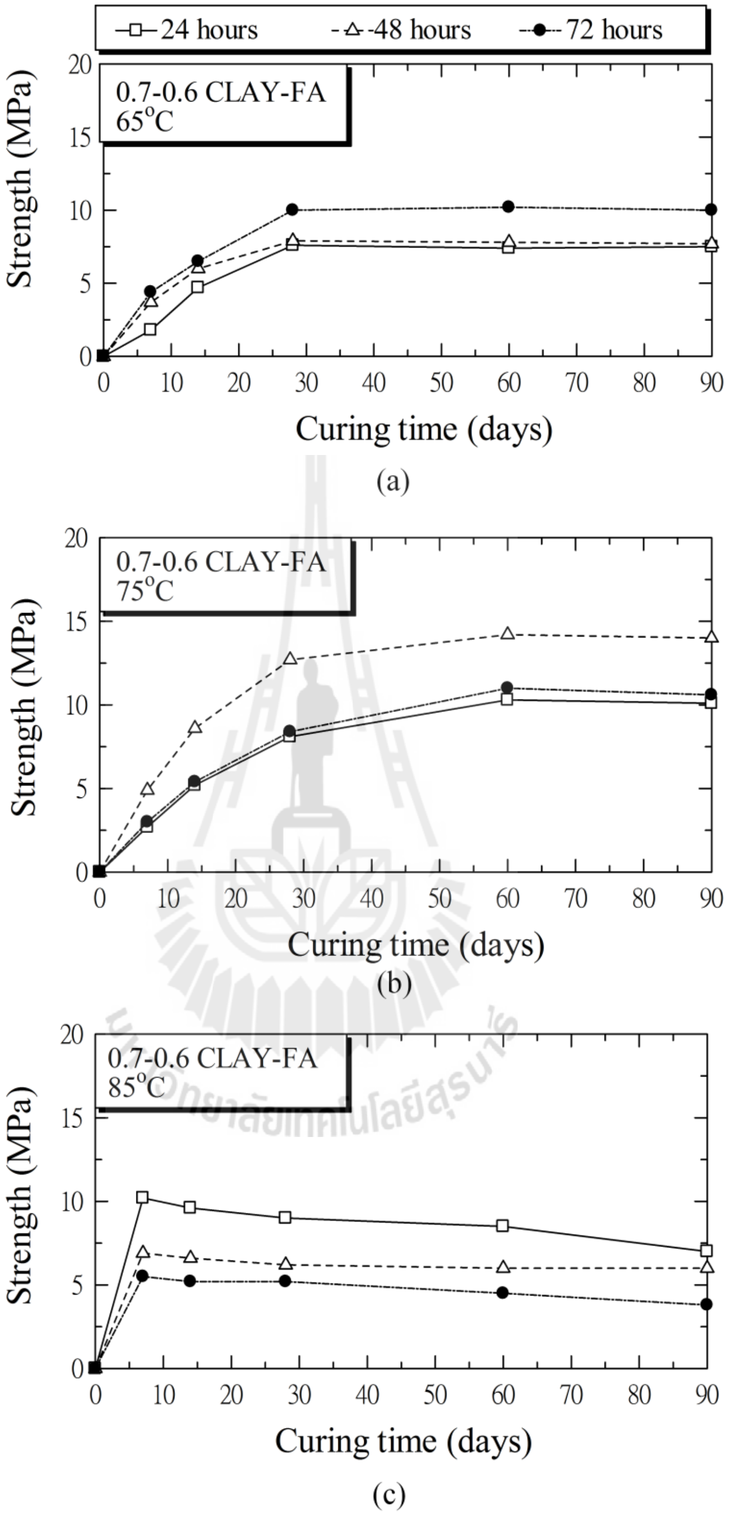


Figure 3.7 Effects of heat condition on the compressive strength of the 0.7–0.6 CLAY–FA specimens heated at (a) 65°C, (b) 75°C, and (c) 85°C.

3.4 Analysis and discussion

It is known that the liquid limit controls the compaction characteristics of the low swelling clays (Horpibulsuk et al. 2008; Horpibulsuk et al. 2009a; Nagaraj et al. 2006; Y. Gurtug and A. Sridharan 2002). Because the input of FA decreases the liquid limit of the silty clay, the optimum water content of the clay–FA mixture decreases, which is associated to the increase in the maximum dry unit weight. The compaction curves of the clay–FA geopolymer are insignificantly changed with the input liquid alkaline activator and are essentially the same with the compaction curve of the clay–FA mixture. This is because the liquid alkaline activator changes inconsequentially the index properties of the clay and FA mixture (vide Table 3.3).

The strength development in the clay–FA geopolymer specimen is controlled by two factors; namely, liquid alkaline activator and heat condition. In the present work, the liquid alkaline activator is the mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH). The sodium hydroxide solution (NaOH) leaches the silicon and aluminum in amorphous phase of FA and the sodium silicate solution (Na_2SiO_3) acts as a binder. The optimum Na_2SiO_3/NaOH ratios to provide the maximum strengths for the FA and the clay–FA geopolymer specimens are different. They are 1.5 and 0.7 for the FA geopolymer and the clay–FA geopolymer, respectively. The clay contains alumino-silicates layers with both external and internal negative layer surfaces, indicated by its relatively high CEC of 31.5 meq/100 g soil. The negative layers act as a huge anion and a swarm of positively charged cations (such as Na+, K+, Ca+, and Mg+) (Horpibulsuk et al. 2011; Mitchell 1996; Van Olphen 1963). Therefore, some of the input NaOH content to leach the silicon and aluminum in amorphous phase of FA were absorbed by the negative charges between clay layers (diffusion double layers) and form an ionic interlayer. Consequently, the clay–FA geopolymer specimens need more NaOH for geopolymerization than the FA geopolymer specimens; hence lower optimum Na_2SiO_3/NaOH ratio.

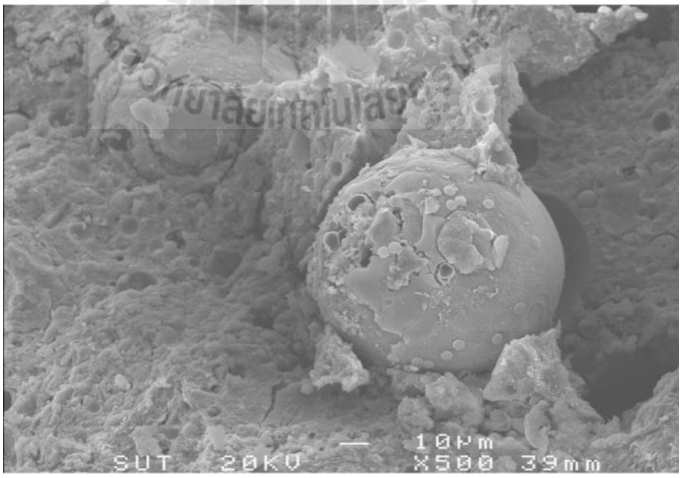
Table 3.3 The index properties of the clay–FA geopolymer specimens.

Name of sample	Liquid limit (%)	Plastic limit (%)
1.5-0.4 CLAY-FA	46	27
1.0-0.4 CLAY-FA	45	28
0.7-0.4 CLAY-FA	45	28
0.4-0.4 CLAY-FA	46	27
1.5-0.5 CLAY-FA	46	28
1.0-0.5 CLAY-FA	46	27
0.7-0.5 CLAY-FA	46	28
0.4-0.5 CLAY-FA	46	28
1.5-0.6 CLAY-FA	46	28
1.0-0.6 CLAY-FA	46	28
0.7-0.6 CLAY-FA	46	28
0.4-0.6 CLAY-FA	47	28
1.5-0.7 CLAY-FA	44	28
1.0-0.7 CLAY-FA	45	27
0.7-0.7 CLAY-FA	46	28
0.4-0.7 CLAY-FA	46	28

The role of L/FA ratio on the compressive strength development in the FA and the clay–FA geopolymer specimens are shown in Figure 3.3 and Figure 3.6, respectively. The compressive strength development with L/FA ratio of the FA and the clay–FA geopolymer specimens is of the same manner. The compressive strength increases rapidly with L/FA ratio until a certain value; this zone is referred to as active zone. Beyond this value, the compressive strength decreases with L/FA ratio. The optimum L/FA ratios are different for both specimens. They are 0.5 and 0.6 for the FA and the clay–FA geopolymer specimens, respectively. For the L/FA ratios less than 0.3, the strength is null for both FA and clay–FA geopolymer specimens. The insignificant strength development is because the amount of liquid alkaline activator is not enough to leach the silicon and the aluminum in amorphous phase of FA for the geopolymerization process. The reduction in strength at very high L/FA ratio is because the amount of OH^- from the liquid alkaline activator exceeds the requirement for geopolymerization process.

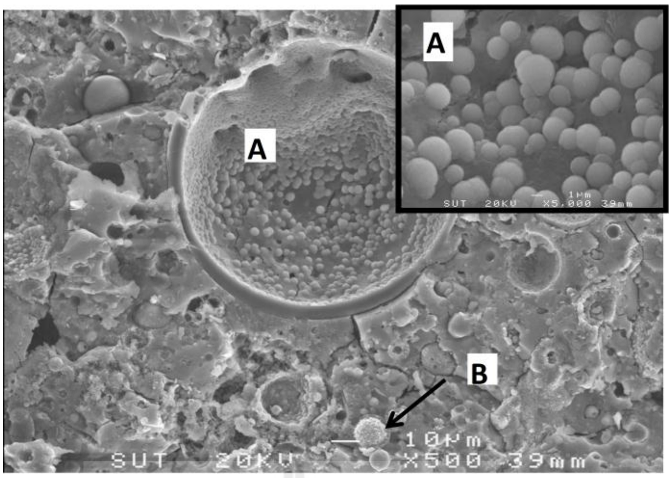
The growth of the geopolymerization products, which controls the strength development, for different L/FA ratios is illustrated using the scanning electron microscope (SEM) images. Figures 3.8–3.10 show the morphology of the FA and clay–FA geopolymer specimens. The FA geopolymer specimens were made up from the Na_2SiO_3/NaOH ratio of 1.5 and L/FA ratios of 0.3, 0.5 (optimal) and 0.7 and the clay–FA geopolymer specimens were from the Na_2SiO_3/NaOH ratio of 0.7 and the L/FA ratio of 0.3, 0.6 (optimal) and 0.7. All the specimens were heated at 65^{o}C for 48 h. The smooth FA particles are detected for the L/FA ratio of 0.3. The low alkaline activated condition (low amount of OH^-) was not enough to leach the silicon and the aluminum for producing alumino-silicate gel (vide Figure 3.8). The same is not true at the optimum L/FA ratio. The precipitation in the geopolymerization is indicated on the fly ash surface (vide Figure 3.9). The geopolymerization products, hydration 'shells' (point A) and 'unidentified spherical assemblages' (point B), are detected on the FA particles (Jiminez et al. 2004). The cracks on the FA particles (point C) with less alumino-silicate gel are observed for the specimens with very high L/FA ratio (vide Figure 3.10). The precipitation at very early stages before poly-condensation process in geopolymerization may be due to the excess alkaline activated condition causes the cracks on the FA particles (Guo et al. 2010; Somna et al. 2011).

(a) The FA geopolymer

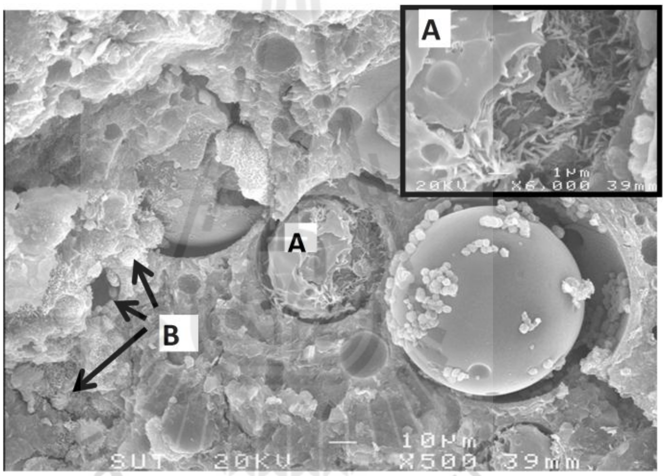


(b) The clay-FA geopolymer

Figure 3.8 SEM images of specimens at L/FA = 0.3.

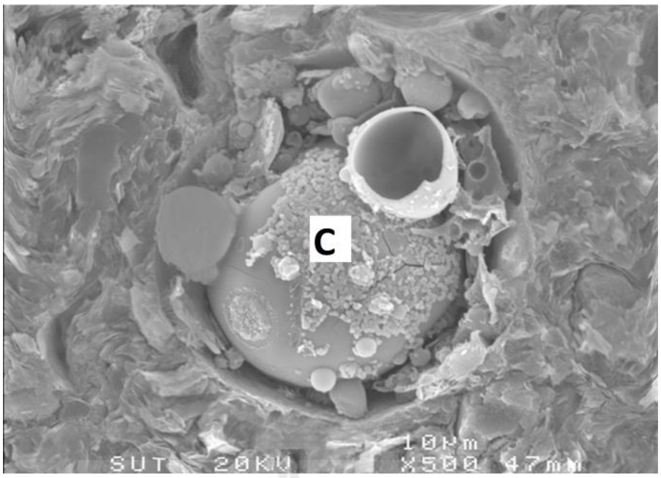


(a) The FA geopolymer on active zone (L/FA=0.5)

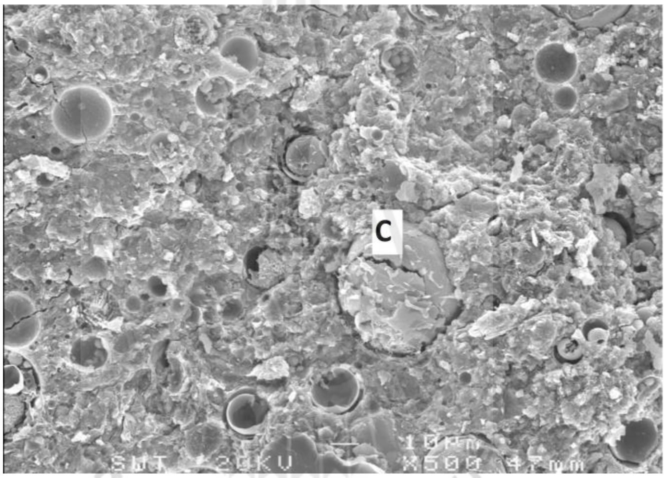


(b) The clay-FA geopolymer on active zone (L/FA=0.6)

Figure 3.9 SEM images on active zone.



(a) The FA geopolymer



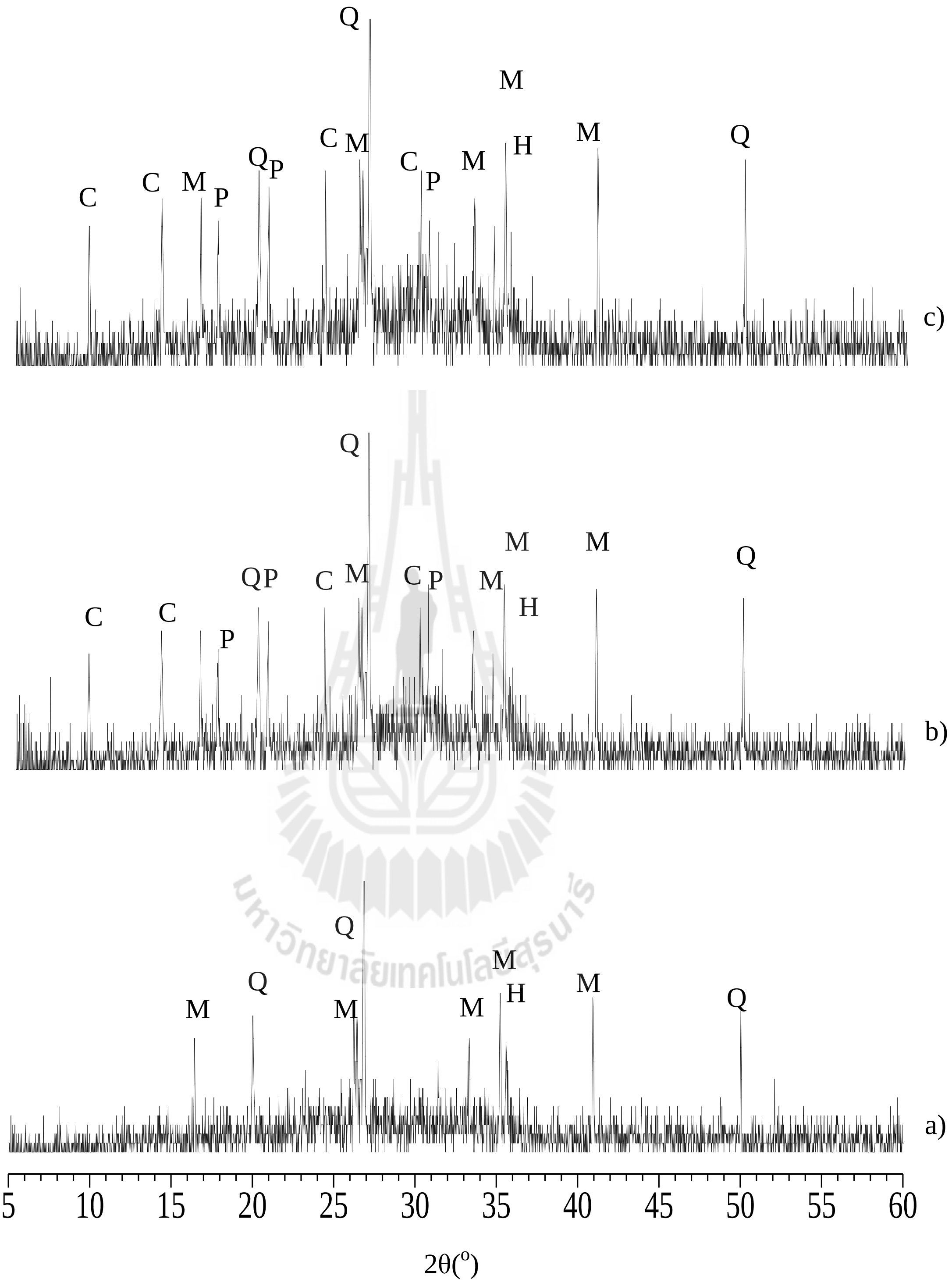
(b) The clay-FA geopolymer

Figure 3.10 SEM images of specimens at L/FA = 0.7.

The role of heat condition on the strength development is illustrated by the XRD results (vide Figure 3.11 and 3.12). Figure 3.11 shows the comparison of XRD patterns between the FA and the FA geopolymer specimens. The FA geopolymer specimens were made up with Na_2SiO_3/NaOH ratio of 1.5 and L/FA ratios of 0.5 and heated at 65^{o}C for 48 h. Peak intensity of Quartz, Mullite, and Herschelite of Crystalline components in the FA is clearly seen especially in the region of 17–35^{o} 2θ

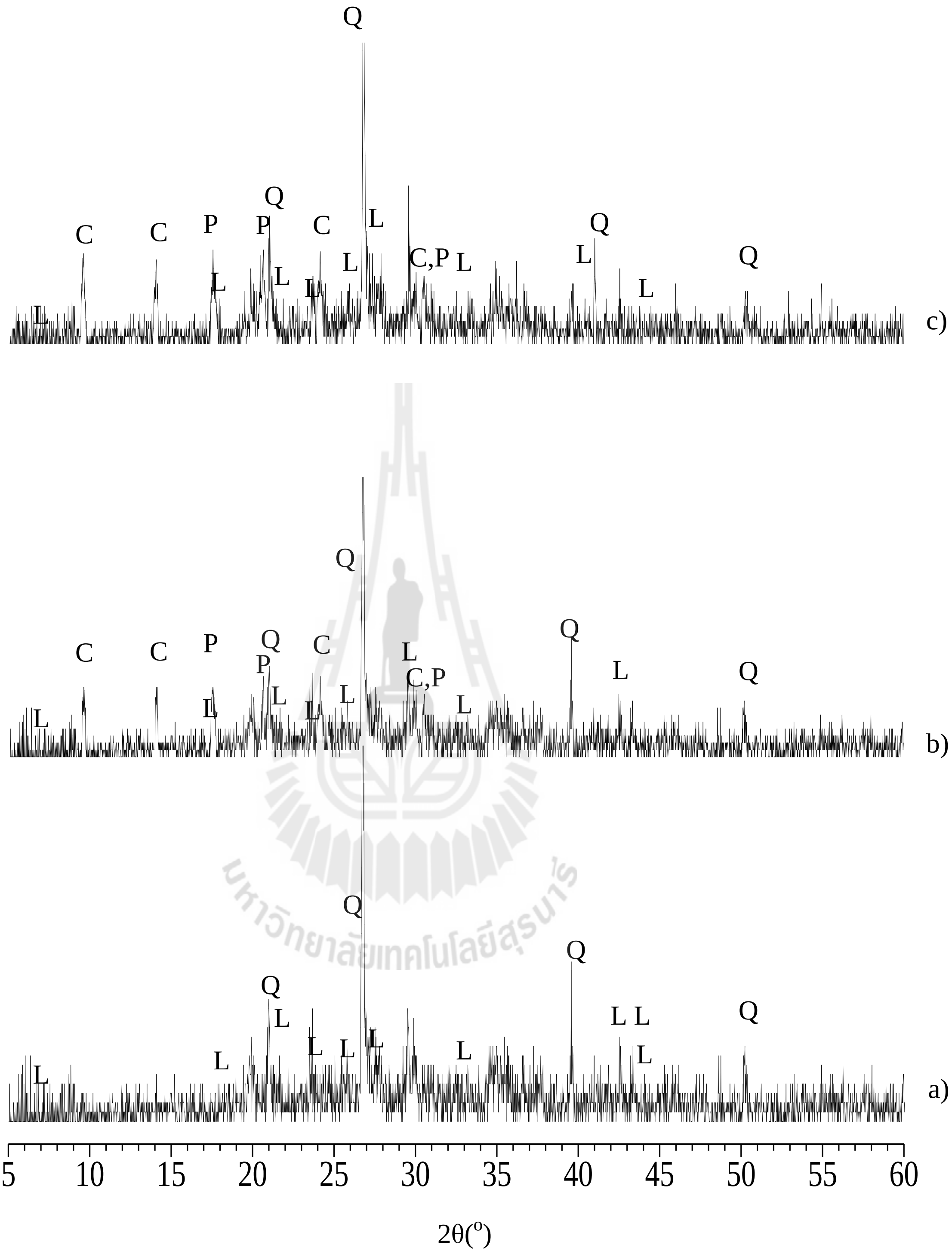
(Figure 3.11a). For longer curing times (28 and 90 days), the broad and amorphous humps between 9.5 and 30.5^o 2θ, which indicate the alumino-silicate gel including chabazite- Na and gismondine (zeolites), are clearly observed. This result indicates the growth of alumino-silicate gel (geopolymerization products) with curing time, hence the strength development.

Similarly, the XRD traces of the silty clay and the clay–FA geopolymer after 28 days of curing are shown in Figure 3.12. All clay–FA geopolymer specimens were made up with the Na_2SiO_3/NaOH ratio of 0.7 and L/FA ratio of 0.6 (optimum ingredient) but with different heat conditions: at 75^{o}C for 48 h and at 85^{o}C for 24 h. The main mineral components of the silty clay are Quartz and Illite (vide Figure 3.12a). These main components remain in both clay–FA geopolymer specimens, indicating that some of the silicon and aluminum in the clay is mainly in the crystal form. The broad and amorphous humps of chabazite and gismondine at 9.5–30.5^o 2θ for all the specimens are clearly observed, which are the same as the FA geopolymer specimens.



C=Chabazite, Q=Quartz, M=Mullite, P=Gismondine and H = Hematite

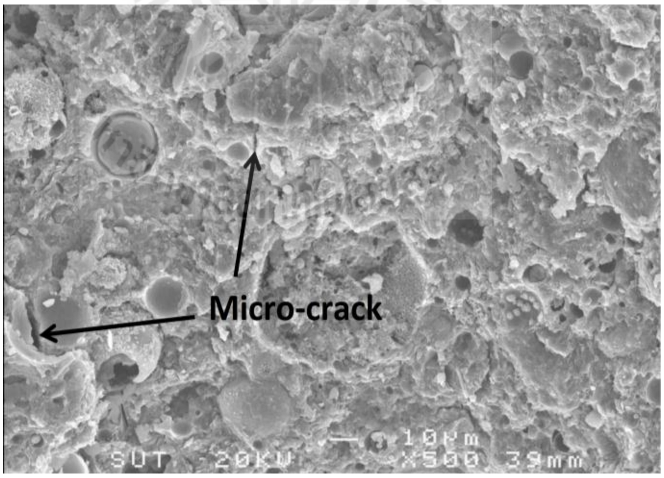
Figure 3.11 XRD patterns of (a) the FA and the 1.5–0.5 FA specimens heated at 65^{o}C for 48 h, (b) at 28 days, and (c) at 90 days.



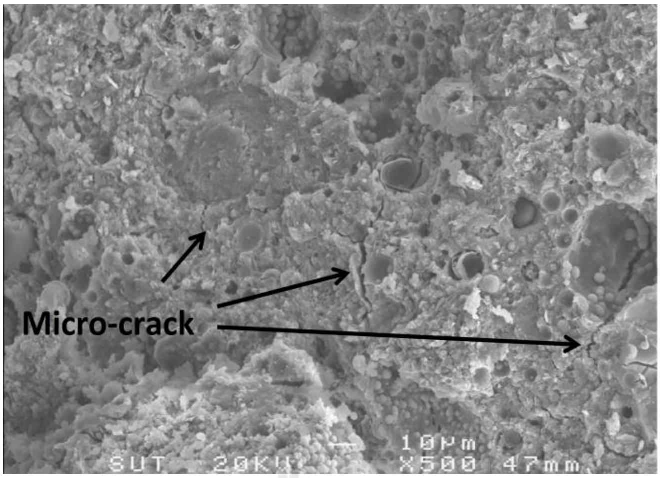
C=Chabazite, Q=Quartz, P=Gismondine and L=Illite ($K(Al_4SiO_2O_9(OH)_3)$)

Figure 3.12 XRD patterns of (a) silt clay and the 0.7–0.6 CLAY–FA specimens heated (b) 75°C for 48 h, and (c) 85°C for 24 h after 28 days of curing.

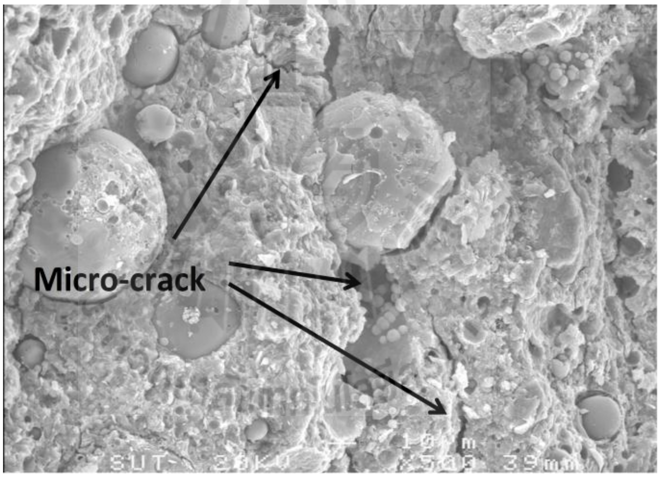
Figures 3.13 and 3.14 show the effect of the heat condition on the microstructure of the clay–FA geopolymer specimens at 85 and 75^{o}C, respectively. For high temperature of 85^{o}C, the micro-cracks are clearly observed at very early heat duration as seen in Figure 3.13 for 24 h. The result is in agreement with that by Bakharev (Bakharev 2005). Bakharev (Bakharev 2005) revealed that the geopolymer experiences a substantial loss of moisture when subjected to high curing temperature. The loss of moisture plays a major part in obtaining a crack-free geopolymer. This fact indicates that rapid drying during curing should be avoided, while curing at a lower relative humidity is preferable (Perera et al. 2007). For lower temperature of 75^{o}C, the heat duration stimulates the reaction as shown by the increase in the geopolymerization products (compare Figure 3.14a and b).



(a) 0.7-0.6 CLAY-FA heated at 85^{o}C for 24 hours

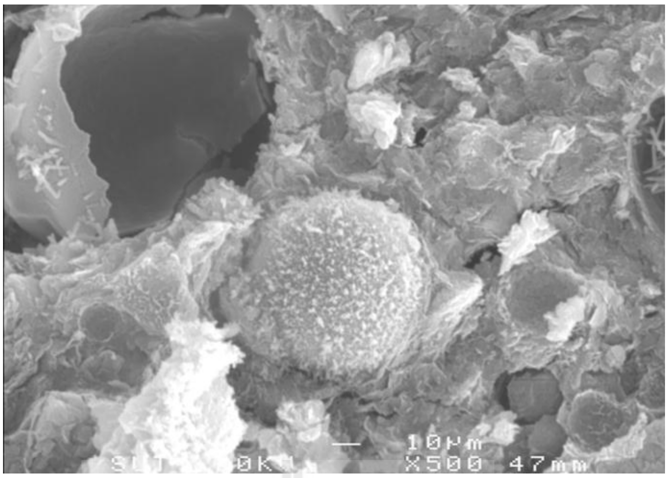


(b) 0.7-0.6 CLAY-FA heated at 85^{o}C for 48 hours

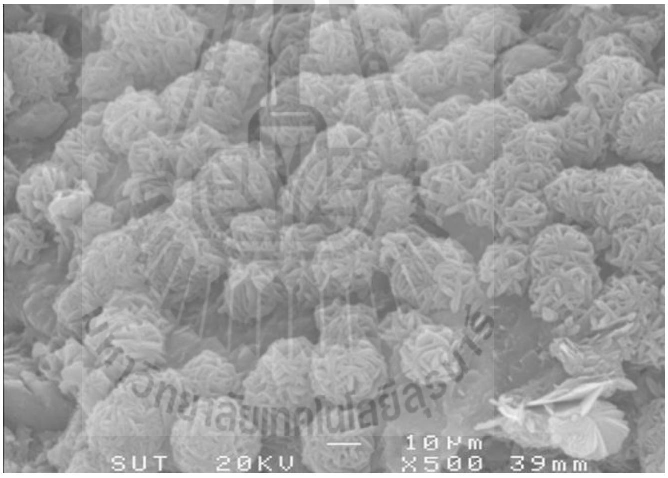


(c) 0.7-0.6 CLAY-FA heated at 85^{o}C for 72 hours

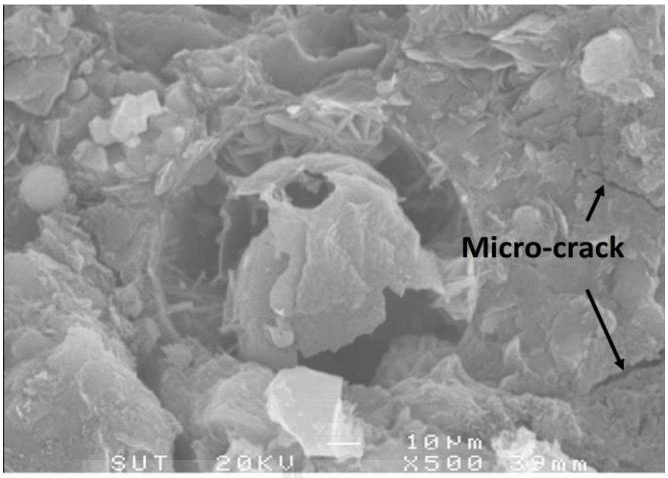
Figure 3.13 SEM images of the clay-FA geopolymer at 28 days



(a) 0.7-0.6 CLAY-FA heated at 75^{o}C for 24 hours



(b) 0.7-0.6 CLAY-FA heated at 75^{o}C for 48 hours



(c) 0.7-0.6 CLAY-FA heated at 75^{o}C for 72 hours

Figure 3.14 SEM images of the clay-FA geopolymer at 28 days.

However, the heat duration is not always positive. Figure 3.14c clearly shows the disadvantage of the excess heat duration, indicting the micro-cracks on the specimen structure. The cracks are caused by the loss of pore fluid needed to maintain structural integrity. Consequently, the specimen heated at 48 h exhibits the highest strength for all curing times.

For optimum temperatures between 65 and 75^{o}C, it is found that the heat energy controls the geopolymerization reaction and hence strength development. Figure 3.15 shows the strength development and heat energy relationship for 7 and 14 days of curing where the heat energy is determined from the product of heat temperature and duration. The fit curves with degree of correlation of higher than 0.89 for both curing times are presented. The variation of the test data is within 5%. The strengths increase with the heat energy up to a certain level and then decrease. The optimum heat energy is found at about 4300^{o}C-h for both curing times. The relationship is very useful to determine the heat temperature and duration to attain the strength requirement with effective manufacturing cost. It must be kept in mind that this proposed relationship is developed based on the specific specimen size and weight. More test results of different specimen sizes and weights are required to develop a generalized relationship.

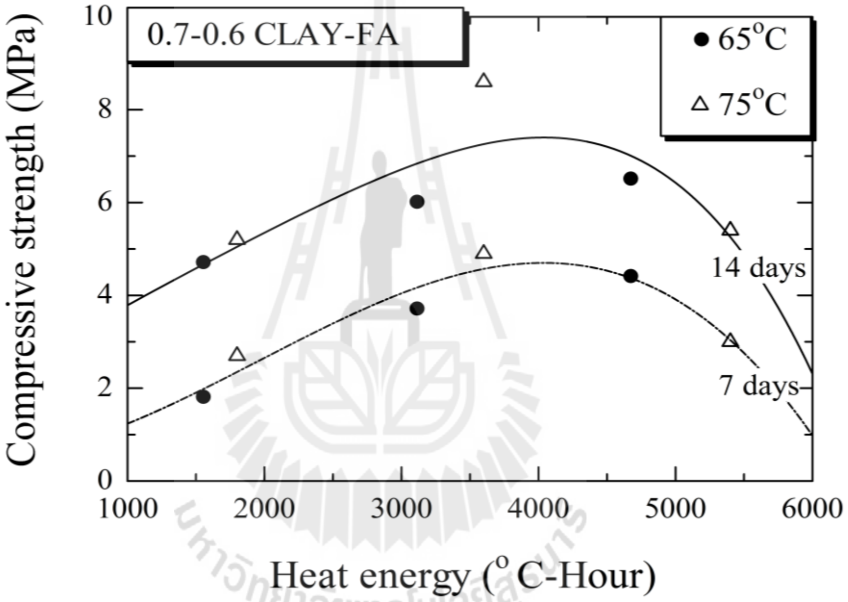


Figure 3.15 The strength and heat energy relationship cured at 7 and 14 days

3.5 Conclusions

This chapter studies the possibility of using the silty clay and the fly ash as a raw material to manufacture the clay–fly ash geopolymer. The following conclusions are drawn.

(1) The compaction curves of the clay–FA mixture and clay–FA geopolymer are essentially the same because the index properties insignificantly alter with the input of liquid alkaline activator.

(2) The sodium hydroxide solution (NaOH) leaches the silicon and aluminum in amorphous phase of FA and the sodium silicate solution (Na_2SiO_3) acts as a binder. The optimum ingredient for the clay–FA geopolymer specimen is Na_2SiO_3/NaOH ratio of 0.7 and activator/FA ratio of 0.6.

(3) The role of the liquid alkaline activator, L/FA ratio on the strength development is illustrated. The excess L/FA ratio causes the precipitation at very early stage before poly-condensation process in geopolymerization. The geopolymerization products in the active zone are clearly observed both by the SEM images and the XRD patterns.

(4) The heat temperature significantly governs the microstructure and strength of the clay–FA geopolymer. The optimum temperature and duration stimulate the geopolymerization reaction and hence strength development with structural integrity. The overheating (very high temperature) and excess heat duration however causes the micro-cracks due to the loss of the pore fluid and hence the strength reduction.

(5) Based on the analysis of the test results, the relationship between strength and heat energy is proposed. The relationship is useful in estimating the cost-effective heat temperature and duration. The formulation of the proposed relationship is on sound principle and is useful as fundamental for future researches on the mix design of the clay–FA geopolymer to attain the target strength.

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CHAPTER IV

FACTORS INFLUENCING STRENGTH DEVELOPMENT IN CLAY-FLY ASH GEOPOLYMER

4.1 Statement of problem

Recently, the chapter III (Sukmak et al. 2013) investigated the possibility of using FA as a raw material and silty clay as aggregates to develop the clay–FA geopolymer brick. The liquid alkaline activator (L) was a mixture of Na_2SiO_3 and NaOH. The suitable ingredient for the clay–FA geopolymer is Na_2SiO_3/NaOH ratio of 0.7 and L/FA ratio of 0.6, which are lower than those of FA geopolymer. The research was limited to specific FA/clay ratio of 0.3, molding moisture content and specimen size. The present work is thus to investigate strength development with different ingredients (FA/clay ratio, Na_2SiO_3/NaOH, L/FA ratio, and molding moisture content), specimen weights, and heating conditions (curing temperature and duration). The microstructure of specimens was examined by the scanning electron microscope (SEM) to illustrate the effect of the geopolymerization products on the strength development. The outcome of this result is possibly applied to other clay–FA geopolymer.

4.2 Materials and methods

4.2.1 Materials

The studied soil is silty clay collected at a depth of 3–4 m from the Suranaree University of Technology campus in Nakhon Ratchasima, Thailand. The specific gravity is 2.70. The soil is weathered from claystone, which consists of clay, silt and sand (Udomchore 1991). Its liquid and plastic limits are approximately 54% and 28%, respectively. The soil contains 2%, 45% and 53% of sand, silt and clay, respectively. The natural moisture content is 5.3%. This clay is classified as high plasticity (CH), according to the Unified Soil Classification System (USCS). The free swell test result reveals that the clay is a low swelling type with a free swell ratio (FSR) of 1.0. The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum moisture content (OMC) of 16%, and maximum dry unit weight (γ_{dmax}) of 17.3 kN/m^3.

FA was acquired from the Mae Moh power plant in the northern region of Thailand. Table 4.1 illustrates the chemical composition of FA using X-ray fluorescence (XRF). Total amount of the major components (SiO_2, Al_2O_3 and Fe_2O_3) are 77.27%; therefore, in accordance with ASTM C 618, it is classified as class F fly ash. Figures 4.1 and 4.2 show the grain size distribution curve and SEM photos of FA, compared with those of the silty clay, respectively. The silty clay's grain size distribution is similar to the FA's. The FA particles are fine and spherical whereas the clay particles are irregular in shape. Although the grain size distribution of both clay and FA is approximately the same, FA shows higher reactivity with the liquid alkaline in the development of geopolymer (Sukmak et al. 2013). The liquid alkaline activator

(L) is a mixture of Na_2SiO_3, consisting of 9% Na_2O and 30% SiO_2 by weight, and NaOH with a concentration of 10 molars

Table 4.1 Chemical composition of fly ash and silty clay

Chemical composition (%)	Clay	FA
SiO_2	20.10	39.18
Al_2O_3	7.55	22.64
Fe_2O_3	32.89	15.45
CaO	26.15	11.3
MgO	0.47	1.69
SO_3	4.92	4.29
Na_2O	NA	1.81
K_2O	3.17	2.03
LOI	3.44	1.61

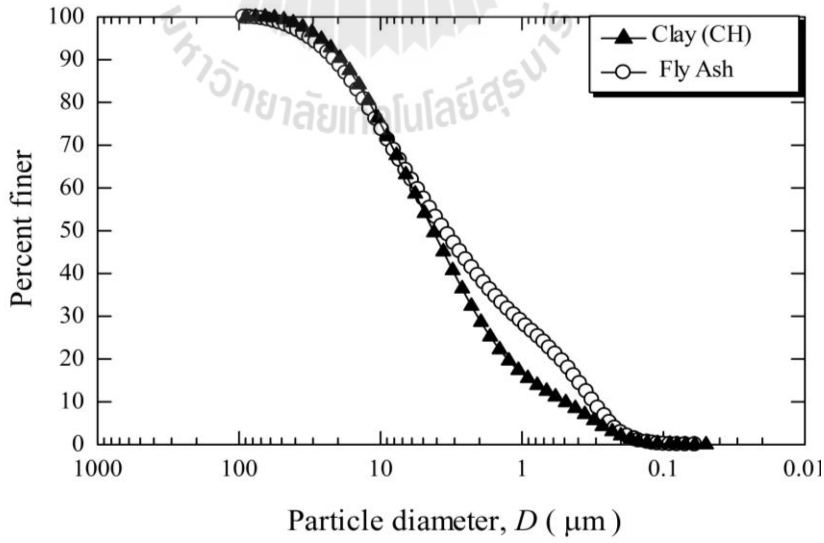
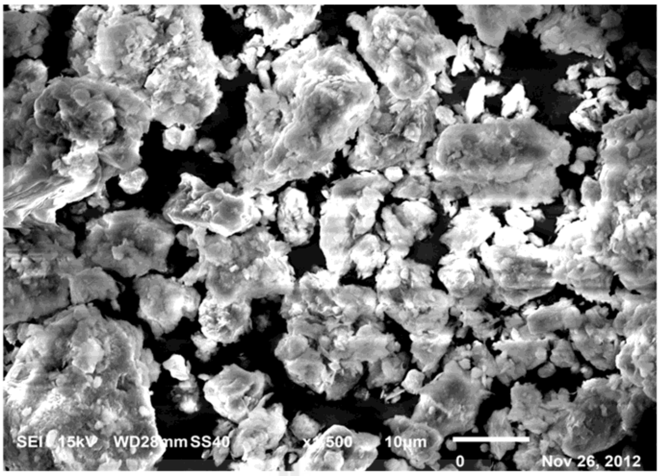
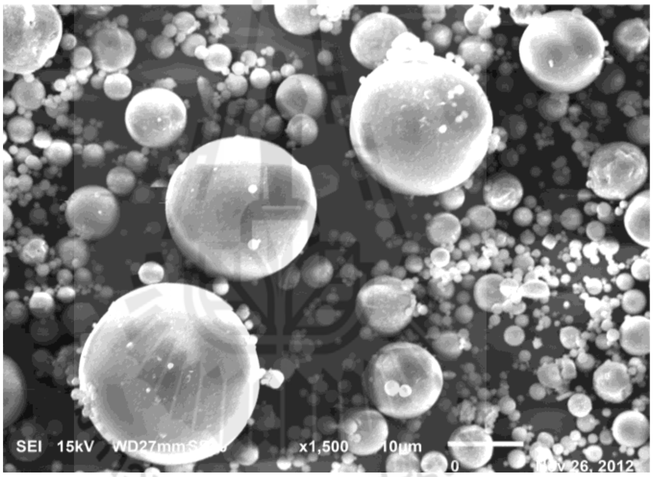


Figure 4.1 Grain size distribution of the clay, and FA.



(a) The silty clay



(b) The fly ash

Figure 4.2 Scanning Electron Microscope (SEM)**.**

4.2.2 Sample preparation

The clay–FA geopolymer specimen is a combination of silty clay, FA, liquid alkaline activator (Na_2SiO_3 and NaOH), and tap water. The FA/clay ratios of 0.3, 0.5,and 0.7; Na_2SiO_3/NaOH ratios of 0.4, 0.7, 1.0, and 1.5; L/FA ratios of 0.4, 0.5, 0.6, and 0.7 were used. The clay, FA, and L were thoroughly mixed with water to conduct the modified compaction test. Having obtained the compaction curves, the clay–FA–L–water mixture at the moisture contents between 0.6 and 1.2OMC was statically compressed in a cylindrical mold with 50 mm in diameter and 100 mm in height and in a rectangular mold with 230 mm in length, 90 mm in width, and 75 mm in height. The compression was performed by a manual hydraulic jack. According to this procedure, all the specimens for different molding water contents have the same compression (modified Proctor) energy per volume. Practically, the OMC value at any compaction energy can be easily and rapidly approximated from the one known at a particular energy (Horpibulsuk et al. 2008; Horpibulsuk et al. 2009a; LR. Blotz et al. 1998). The specimens were dismantled, wrapped within vinyl sheet and stored in ambient temperature (27–30°C) for 24 h, and then cured at 55 to 140°C for 24 to 168 h.

The symbols for clay–FA geopolymer specimens are shown as follows:

A – B CLAY – FA – C – DOMC (CY or RE)

where A is the Na_2SiO_3/NaOH ratio,

B is the L/FA ratio, C is the FA/clay ratio,

D is the state of moisture content (0.6, 0.8, 1.0, and 1.2 times), and

(CY or RE) is small (cylindrical) or large (rectangular) specimens.

4.2.3 Methods

Compressive strengths of clay–FA geopolymer specimens were measured after 7, 14, 28, 60, and 90 days of curing in accordance with ASTM D 1633. The reported results were the average of at least five specimens in order to obtain reliable test results. In most cases, the results under the same testing condition were reproducible with a low standard deviation, SD (SD= x<10%, where x is the mean strength value).

The clay–FA geopolymer specimens were carefully broken and small fragments were taken from the centre for microstructure test. The SEM specimens were frozen at -195^{o}C by immersion in liquid nitrogen for 5 min and evacuated at a pressure of 0.5 Pa at -40^{o}C for 5 days (Horpibulsuk et al. 2010; Horpibulsuk et al. 2009b; Miura et al. 1999). All specimens were coated with gold before SEM (JOEL JSM-6400) analysis.

4.3 Result

Figure 4.3 depicts the plots of dry unit weight versus molding moisture content of clay–FA geopolymer samples with different ingredients compared with those of clay and clay–FA mixtures (FA/clay ratios of 0.3, 0.5, and 0.7), under modified Proctor energy. For a given FA/clay ratio, the compaction curves of both clay–FA mixtures and clay–FA geopolymers are approximately the same for all Na_2SiO_3/NaOH and L/FA ratios. The maximum dry unit weight for compacted clay–FA mixture of 0.3 is slightly higher than that of compacted silty clay. However, for FA/clay ratios greater than 0.3, the clay–FA mixtures possess lower maximum dry unit weight than the compacted clay. The decrease in maximum dry unit weight is associated with the increase in OMC. The OMCs of the clay–FA mixtures and clay–FA geopolymers are almost the same.

The 28 day strength of clay–FA geopolymers at OMC with different ratios of Na_2SiO_3/NaOH, L/FA and FA/clay, and specimen dimensions are illustrated in Figure 4.4. The small specimens were heated at 75^{o}C for 48 h while the large specimens were heated at 130°C for 120 h. The result shows that the relationship between strength versus Na_2SiO_3/NaOH ratio and L/FA ratio for a given FA/clay ratio exhibits similar pattern with almost the same maximum strength, regardless of specimen sizes (weight). The maximum compressive strengths for both specimen dimensions are at Na_2SiO_3/NaOH ratio of 0.7 for all L/FA and FA/clay ratios. For a given Na_2SiO_3/NaOH ratio, the strength increases with increasing L/FA ratio until its optimum value and then tends to decrease. The strength is null at very low and high L/FA ratios of 0.3 and 0.8. The optimum L/FA ratio for the highest strength varies between 0.5 and 0.6 and tends to reduce with the increase in FA/clay ratio. It is 0.6 for FA/clay ratio of 0.3 and is 0.5 for FA/clay ratio of 0.7. These results identify that the optimum Na_2SiO_3/NaOH ratio is 0.7 for all FA/clay ratios, L/FA and specimens as well as the L/FA ratios of less than 0.3 and greater than 0.8 are not suitable to manufacture the clay–FA geopolymer.

Table 4.2 Index properties of the clay–FA geopolymer specimens

Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)
1.5-0.4 CLAY-FA-0.3	46	27	1.5-0.4 CLAY-FA-0.5	44	25	1.5-0.4 CLAY-FA-0.7	40	22
1.0-0.4 CLAY-FA-0.3	45	28	1.0-0.4 CLAY-FA-0.5	45	25	1.0-0.4 CLAY-FA-0.7	41	23
0.7-0.4 CLAY-FA-0.3	45	28	0.7-0.4 CLAY-FA-0.5	43	26	0.7-0.4 CLAY-FA-0.7	38	23
0.4-0.4 CLAY-FA-0.3	46	27	0.4-0.4 CLAY-FA-0.5	44	25	0.4-0.4 CLAY-FA-0.7	40	22
1.5-0.5 CLAY-FA-0.3	46	28	1.5-0.5 CLAY-FA-0.5	44	26	1.5-0.5 CLAY-FA-0.7	41	21
1.0-0.5 CLAY-FA-0.3	46	27	1.0-0.5 CLAY-FA-0.5	43	26	1.0-0.5 CLAY-FA-0.7	38	24
0.7-0.5 CLAY-FA-0.3	46	28	0.7-0.5 CLAY-FA-0.5	44	27	0.7-0.5 CLAY-FA-0.7	39	24
0.4-0.5 CLAY-FA-0.3	46	28	0.4-0.5 CLAY-FA-0.5	43	26	0.4-0.5 CLAY-FA-0.7	38	22

Table 4.2 Index properties of the clay–FA geopolymer specimens (continuous)

Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)
1.5-0.6 CLAY-FA-0.3	46	28	1.5-0.6 CLAY-FA-0.5	44	26	1.5-0.6 CLAY-FA-0.7	40	21
1.0-0.6 CLAY-FA-0.3	46	28	1.0-0.6 CLAY-FA-0.5	44	25	1.0-0.6 CLAY-FA-0.7	41	22
0.7-0.6 CLAY-FA-0.3	46	28	0.7-0.6 CLAY-FA-0.5	44	27	0.7-0.6 CLAY-FA-0.7	40	24
0.4-0.6 CLAY-FA-0.3	47	28	0.4-0.6 CLAY-FA-0.5	44	25	0.4-0.6 CLAY-FA-0.7	42	23
1.5-0.7 CLAY-FA-0.3	44	28	1.5-0.7 CLAY-FA-0.5	43	26	1.5-0.7 CLAY-FA-0.7	40	23
1.0-0.7 CLAY-FA-0.3	45	27	1.0-0.7 CLAY-FA-0.5	42	25	1.0-0.7 CLAY-FA-0.7	39	24
0.7-0.7 CLAY-FA-0.3	46	28	0.7-0.7 CLAY-FA-0.5	44	27	0.7-0.7 CLAY-FA-0.7	40	24
0.4-0.7 CLAY-FA-0.3	46	28	0.4-0.7 CLAY-FA-0.5	44	25	0.4-0.7 CLAY-FA-0.7	40	24

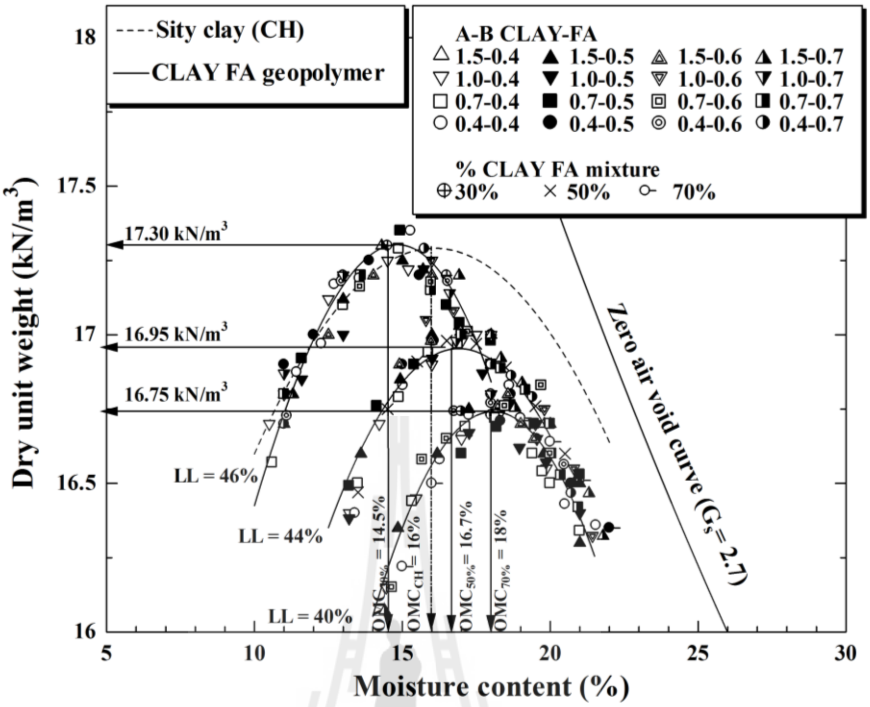


Figure 4.3 Plots of dry unit weight versus molding moisture content of clay and clay–FA geopolymer for FA/clay ratios of 0.3, 0.5, and 0.7.

Figures 4.5–4.7 show the effects of heat curing on strength development for both specimen sizes. For FA/clay ratios of 0.3 and 0.5, the optimum temperatures are between 65^{o}C and 75^{o}C for the small specimens and between 120^{o}C and 130^{o}C for the large specimens. However, the optimum temperatures are lower for FA/clay ratio of 0.7, which are between 55^{o}C and 65^{o}C for the small specimens and between 110^{o}C and 120^{o}C for the large specimens. Figures 4.5–4.7 also indicate that the long curing duration is needed for the low heat temperature in order to develop high strength clay–FA geopolymers. The maximum strengths are found at 75^{o}C for 48 h (for small specimens) and 130^{o}C for 120 h (for large specimens) for FA/clay ratios of 0.3 and 0.5, and at 65^{o}C for 48 h (for small specimens) and 120^{o}C for 120 h (for large specimens) for FA/clay ratio of 0.7. For these heat conditions, the strengths of both specimen sizes gradually increase with curing time and the maximum strengths are at about 60 days. However, the strength tends to decrease with curing time for the specimens heated at very high temperature i.e. 85°C (for small specimens) and 140°C (for large specimens) for FA/clay ratio of 0.3 and 0.5.

Figure 4.8 depicts the effects of curing time and molding moisture content on the strength development of compacted clay and clay– FA geopolymer for both small and large specimens. Figure 4.8b–d show that the strengths of the compacted silty clay and clay–FA geopolymers are controlled by the moisture (water and liquid alkaline activator) content. For both compacted clay and geopolymer specimens, the strengths of cylindrical and rectangular specimens are essentially identical for the same moisture content. In other words, the specimen size has minimum effect on the strength development. The strength of compacted clay increases with moisture content up to the OMC (densest package) and decreases when the moisture content is on the wet side of OMC. At a particular curing time, the strength curve of the clay–FA geopolymer is strongly dependent on the FA/clay ratio. As the FA/clay ratio increases, the maximum strength increases while molding moisture content at maximum strength decreases. The relationship between strength and moisture content is of the same pattern for different curing times, indicating that the maximum strengths are at the same moisture content. The moisture content for the maximum strength is 1.0OMC ($m=14.5\%$), 0.8OMC ($m=13.4\%$) and 0.6OMC ($m=10.8\%$) for FA/clay ratios of 0.3, 0.5 and 0.7, respectively.

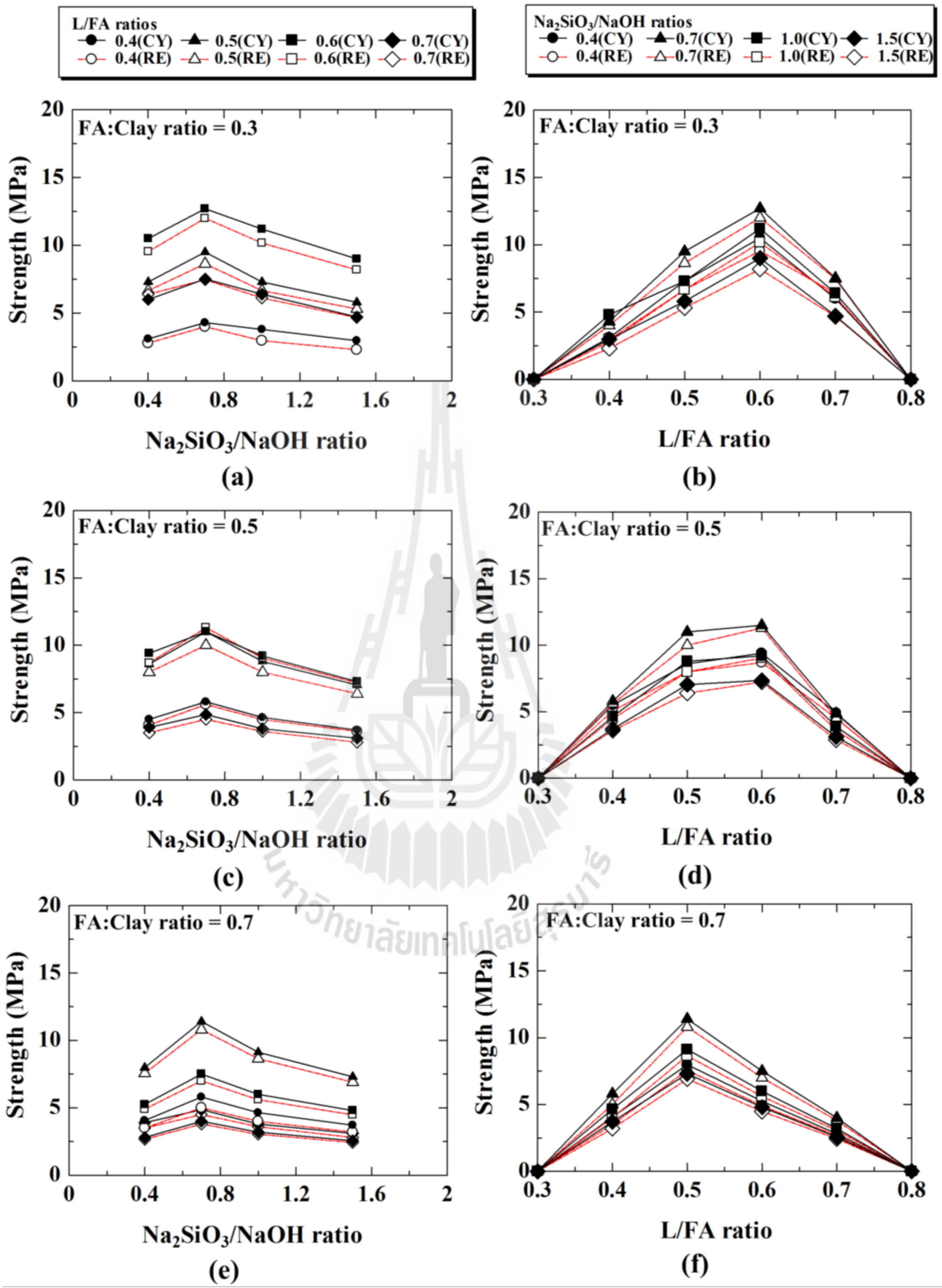


Figure 4.4 The 28 day compressive strengths of clay–geopolymer.

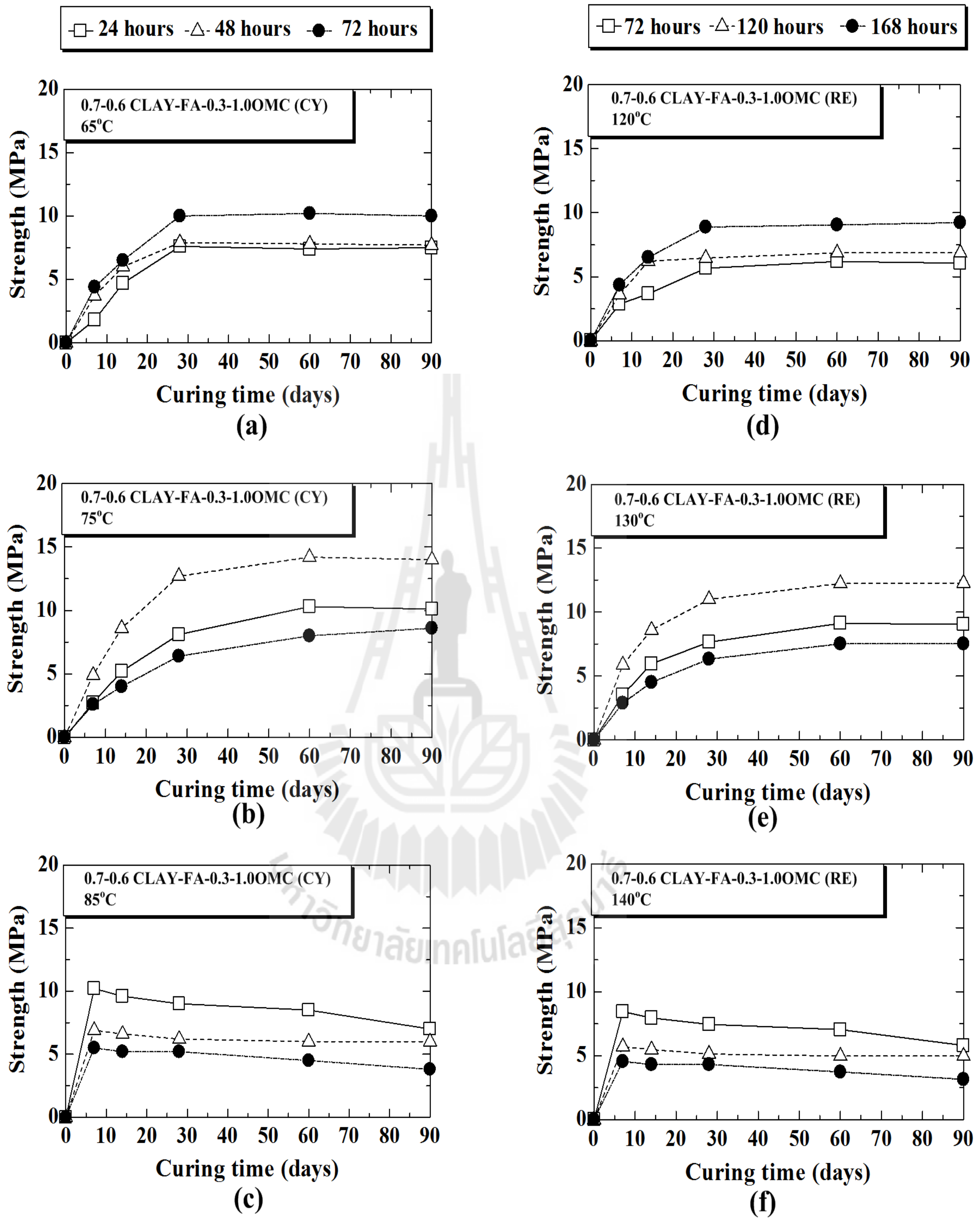


Figure 4.5 Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.3 at different heat conditions.

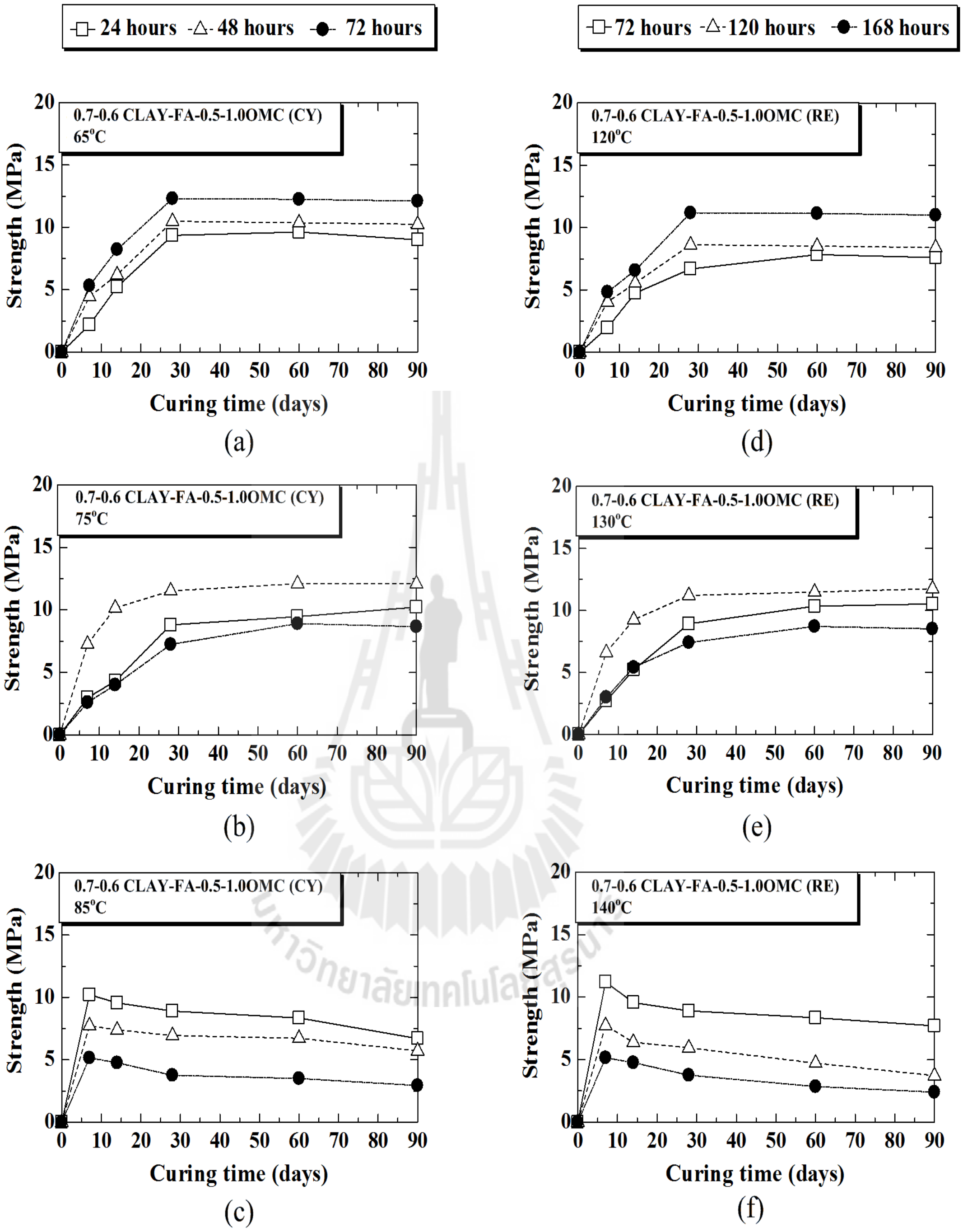


Figure 4.6 Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.5 at different heat conditions.

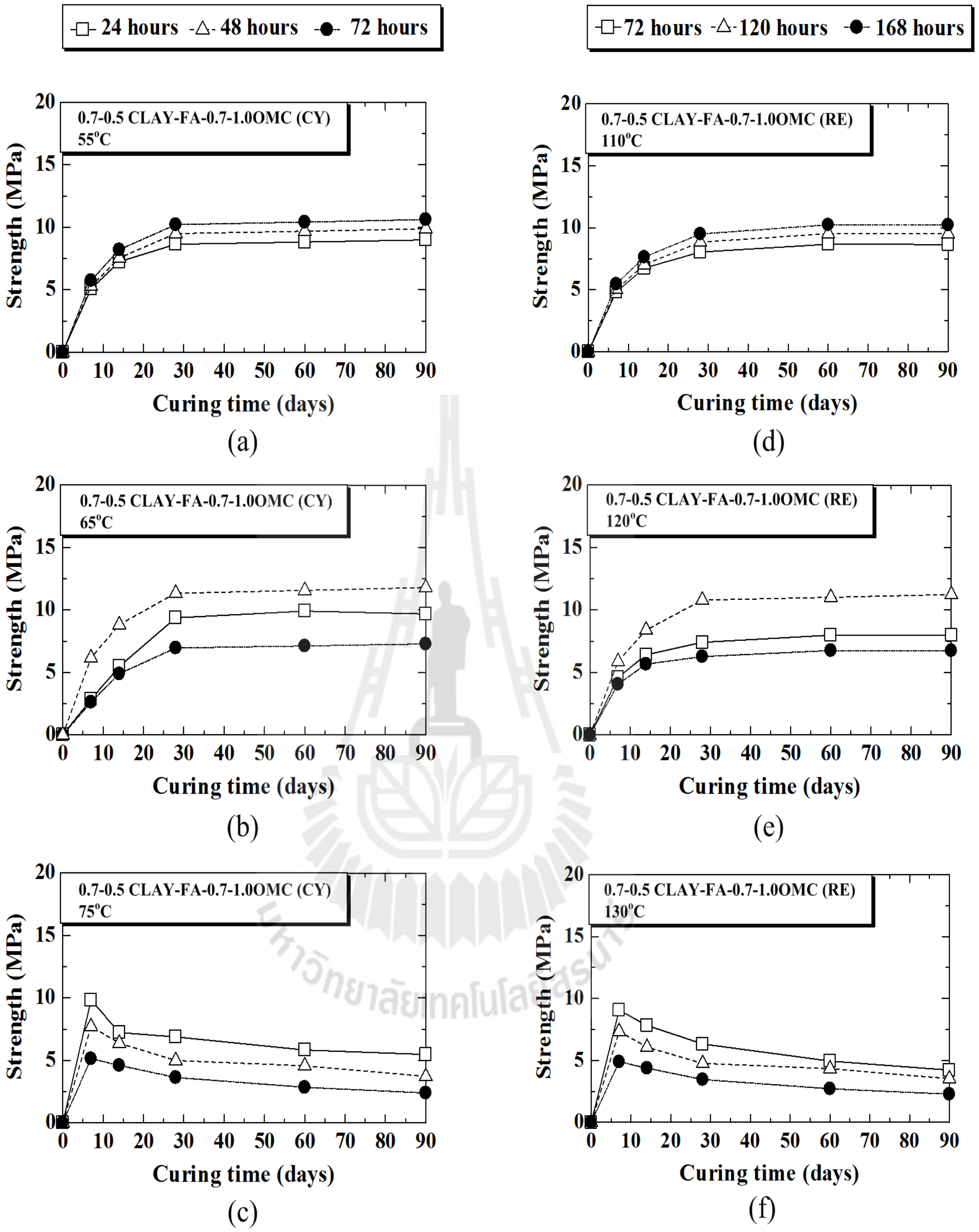


Figure 4.7 Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.7 at different heat conditions.

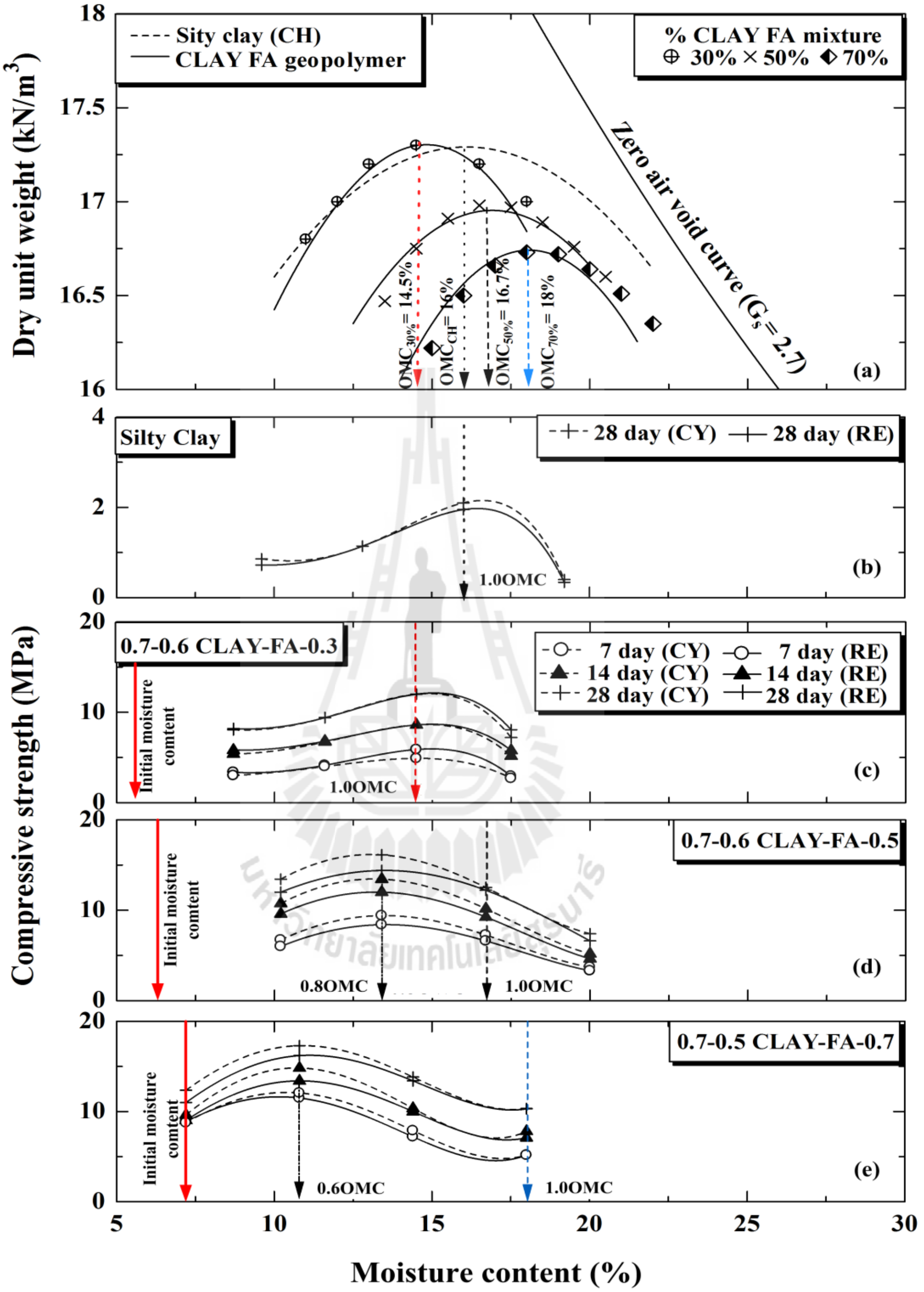


Figure 4.8 Role of curing time and molding moisture content on the strength development of clay–FA geopolymer.

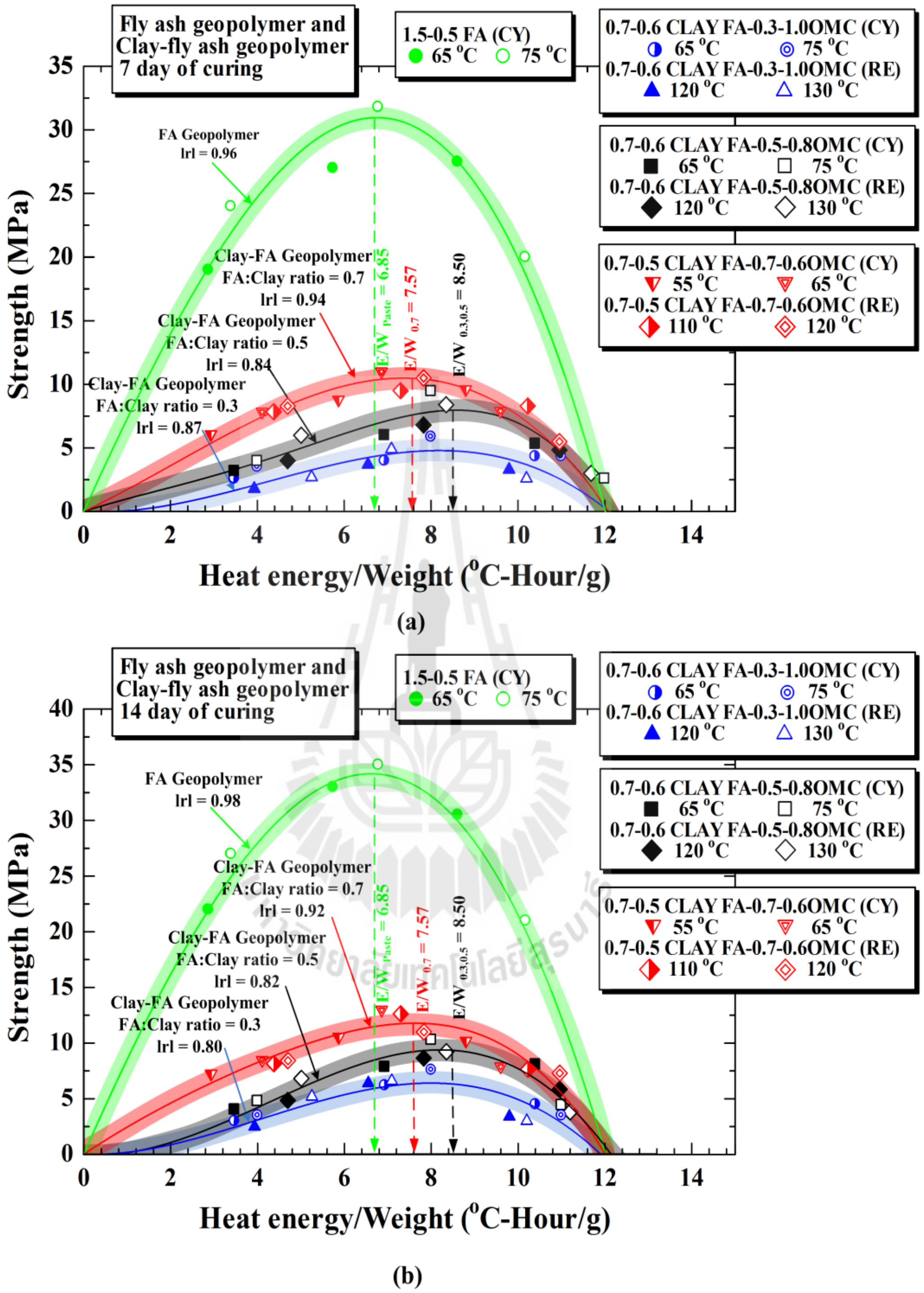


Figure 4.9 Strength development and heat energy/weight relationship for: (a) 7 and (b) 14 days of curing.

4.4 Analysis and discussion

Generally, gradation and specific gravity controls the compaction curve. Because the grain size distribution of FA and clay is essentially the same (vide Figure 4.1), the specific gravity controls the dry unit weight when compacted. The specific gravity of clay–FA mixture is lower than that of clay, so the clay–FA mixture possesses lower dry unit weight. The reduction in maximum dry unit weight is associated with the increase in optimum moisture content. When compared the test results of index properties between the clay–FA mixture and clay–FA geopolymer, it is found that the input L insignificantly affects the soil plasticity; i.e. the index properties of clay–FA mixture and clay–FA geopolymer are identical for the same FA/clay ratio (vide Table 4.2). Because the liquid limit controls the compaction curve (Horpibulsuk et al. 2008) the compaction curves of compacted clay–FA mixture and clay–FA geopolymer are essentially identical for the same FA/clay ratio (Figure 4.3).

The strength development in clay–FA geopolymer specimen is controlled by four factors; namely, L, heat condition, FA/clay ratio and molding moisture content. For both specimen sizes, at a particular Na_2SiO_3/NaOH ratio and curing condition, the compressive strength increases rapidly with L/FA ratio until a maximum value. Beyond this value, the compressive strength decreases with L/FA ratio. It is of interest to note that the optimum L/FA ratio is dependent upon FA replacement (FA/clay ratio) and irrespective of specimen size. It is approximately 0.6 for FA/clay ratio of 0.3 and 0.5 for FA/clay ratio of 0.7. It is a fact that the clay contains alumino-silicate layers with both external and internal negative layer surfaces as indicated by its relatively high CEC of 31.5 meq/100 g clay. The negative layers act as a huge anion and a swarm of positively charged cations (such as Na, K, Ca, and Mg) (Horpibulsuk et al. 2011; Mitchell 1996; Van Olphen 1963) when the clay content decreases (FA/clay ratio increases), the negative layer surfaces decrease. In addition to the reduction in negative surfaces, the increase in FA/clay ratio increases the alumino-silicate for the geopolymerization reaction (Palomo et al. 1999; Xu and Van Deventer 2000). Sukmak et al. 2013 showed the leaching results of SiO_2 and Al_2O_3 in the clay and FA using the X-ray fluorescence (XRF). The clay exhibited the leaching capacity of SiO_2 and Al_2O_3 less than the FA because the silica and alumina in FA are mostly amorphous. Both the reduction in negative surfaces and the increase in amorphous alimino-silicate result in the decrease in L required for the cation exchange and the increase in the degree of the geopolymerization reaction. Consequently, the optimum L/FA ratio decreases as FA/clay ratio increases.

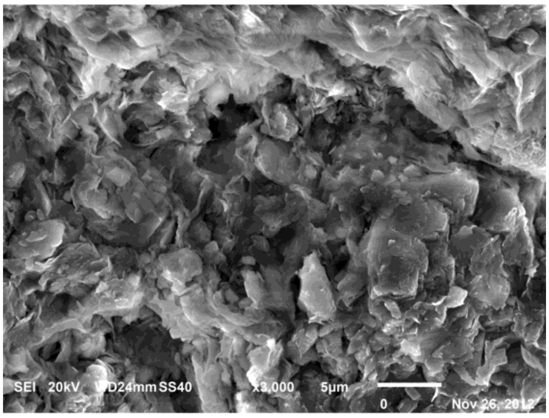
It is now to examine the effect of the heat conditions on the strength development. For all Na_2SiO_3/NaOH and L/FA ratios, the heat temperature and the duration required for the geopolymerization are dependent upon the specimen dimension and FA/clay ratio. With larger specimen size (weight) and lower FA/clay ratio, the higher temperature and longer duration are required to attain the highest strength. Sukmak et al. 2013 depicted the effect of the heat condition on the microstructure of clay–FA geopolymer specimens at a particular FA/clay ratio. For a very high temperature, the clay–FA geopolymer experienced a substantial loss of moisture. The loss of moisture played a major part in obtaining a crack-free geopolymer. Consequently, the rapid drying during curing should be avoided, while curing at a lower relative humidity was preferable. For low temperature, the heat duration stimulated the geopolymerization reaction as shown by the increase in the geopolymerization products. However, the heat duration is not always positive. The excess heat duration also caused the micro-cracks on the specimen structure. In this study, it is found that the excess temperature is strongly dependent upon the specimen size and FA/clay ratio. For FA/clay ratios of 0.3 and 0.5, it is 85°C for the small specimen and 140°C for the large specimen. For FA/clay ratio of 0.7, it is 75°C for the small specimen and 130°C for the large specimen.

The combined effect from the heat temperature and duration was taken into account by the heat energy parameter (Sukmak et al. 2013). The heat energy is the product of heat temperature and duration. At low heat temperature, even though the temperature and duration are different, the strength at a given curing time and weight is practically identical as long as the heat energy is the same. The strength increases with the heat energy up to a certain level and then decreases. It is found from this investigation that the heat energy is not the controlled parameter for different specimen sizes. In other words, the specimen weight must be taken into consideration. The larger specimens with higher weights require higher energy for the geopolymerization development. Consequently, the heat energy per weight, E/W is thus proposed as a key parameter controlling the strength development. Figure 4.9 shows the applicability of E/W for FA/clay ratios of 0.3, 0.5 and 0.7. Even with different specimen weights and heat conditions, the strength development for both 7 and 14 days is governed by the E/W and FA/clay ratio. Higher degrees of correlation of 0.80 are found for both curing times. For FA/clay ratios of 0.3 and 0.5, the optimum E/W (providing the highest strength) is approximately 8.5°C h/g for both curing times. It is approximately 7.57°C h/g for FA/clay ratio of 0.7. This result shows that the optimum E/W increases as FA/clay ratio decreases. For better understanding of the role of FA content on the required E/W, the test data of the FA geopolymer (no clay) is compared in the Figure. It is shown that the optimum E/W for FA geopoplymer is lower than that of clay–FA geopolymers. This is a fact that silica and alumina in FA are mostly amorphous and therefore the heat energy required for geopolymerization reaction is lower. Beyond this optimum value, the specimens shrink and crack due to the loss of pore fluid, which results in the strength reduction.

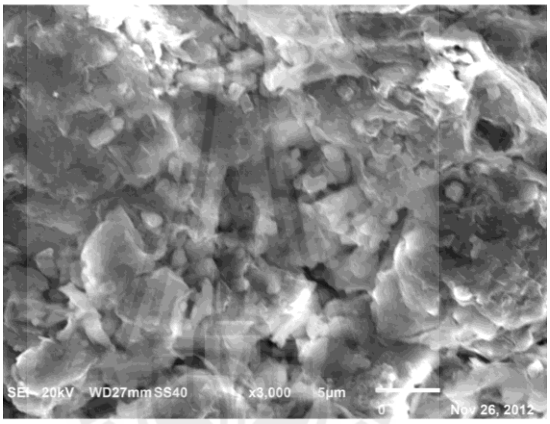
The relationship between strength and E/W is very useful for the production industry to estimate the optimum E/W value as well as heat temperature and duration to attain the target strength for the required weight of clay–FA geopolymer brick. The optimum E/W value is essentially the same as long as the FA/clay ratio is the same, irrespective of the sample weight. This relationship is also useful for the cost analysis to select the optimized FA/clay ratio and heat energy. For the optimum ingredient L, the high FA/clay ratio with low E/W can be designed or vice versa to obtain the same strength. With different possible FA/clay ratios and E/W values, the cost optimization can be performed. For a selected brick weight, the required heat energy is then estimated; hence the duration for a specific heat temperature. The manufacturing of geoploymer bricks at E/W values beyond the optimum value is not recommended even with high strength. This is because micro-crack in the brick might cause the low durability. The formulation of the proposed relationship is on sound principle and developed from two weights of the geopolymer specimens. The relationship can be further refined with the analysis of more data for different specimen weights, temperatures and durations.

The effect of molding moisture content on the strength development of compacted clay and clay–FA geopolymer is being illustrated. For compacted silty clay, the clay structure, which is governed by molding moisture content, mainly controls the strength (Horpibulsuk et al. 2010). Figure 4.10 shows the SEM photos of the compacted specimen under the modified Proctor energy at different moisture contents ranging from (0.8–1.2)OMC. On the wet side of optimum (vide Figure 4.10c), a dispersed structure is likely to develop because the quantity of pore water is sufficient to develop a complete double layer of the ions that are attracted to the clay particles. As such, the clay particles and clay clusters easily slide over each other when sheared and results in low strength. On the dry side of optimum (vide Figure 4.10a), there is not sufficient water to develop a complete double-layer; thus, the distance between two clay platelets is small enough for van der Waals type attraction to dominate. Such an attraction leads to flocculation with more surface to edge bonds; thus, more aggregates of platelets lead to compressible flows, which make up the overall structure. At the OMC, the structure results from a combination of these two characteristics (vide Figure 4.10b). Under this condition, the compacted specimen exhibits the highest strength (vide Figure 4.8b).

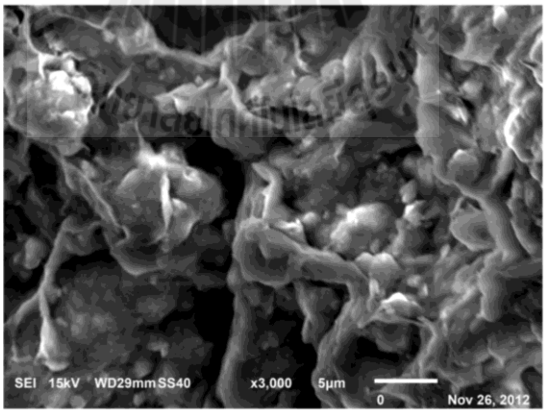
Unlike the compacted clay, the strength of the clay–FA geopolymer is contributed from two components: mechanical and chemical. Because the geopolymer specimens were prepared at the same compression energy per volume (modified Proctor), the mechanical component is mainly governed by the soil densification, where the OMC provides the densest packing. At very low moisture content, the L is not sufficient for geopolymerization reaction because it is taken by the clay particles for developing the soil structure. With increasing moisture content (densification), the clay and FA particles come closer due to the water lubrication and thus the gopolymerization reaction can be better developed. As such, the strengths of each ingredient increase with molding moisture content up to the highest values and the highest strengths of clay– FA geopolymer specimens are not at the OMC. The contribution from the chemical component (geopolymerization) decreases with the excessive molding moisture content due to the reduction in L concentration. The moisture content providing the highest strength is thus the combination of these two components. Figures 4.11–4.13 show the SEM photos of the clay–FA geopolymers cured for 60 days, at different molding moisture contents for FA/ clay ratios of 0.3, 0.5 and 0.7 respectively. The geopolymerization products are clearly seen at OMC, 0.8OMC and 0.6OMC for FA/clay ratios of 0.3, 0.5 and 0.7, respectively, which are associated with the highest strength. Geopolymerization products produced are clearly observed around FA particles and in the pores. The geopolymer gel is in a form of colloid with different sizes ranging from less than 1 lm to about 20 lm. As more gel is formed, it overwhelms clay and FA particles and forms a continuous mass of gel resulting in a relatively dense alumino-silicate and strong bond among clay particles (Rattanasak and Chindaprasirt 2009).



(a) m = 12.8% (0.8OMC)

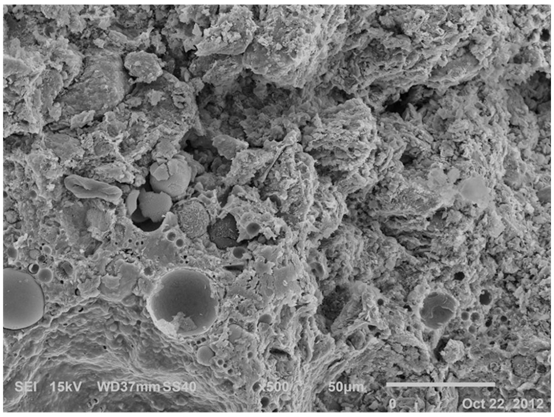


(b) m = 16% (OMC)

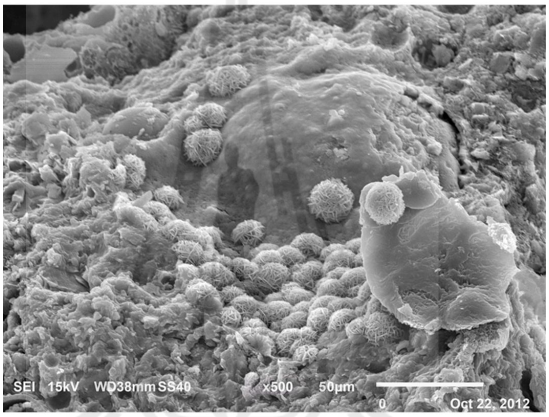


(c) m = 19.2% (1.2OMC)

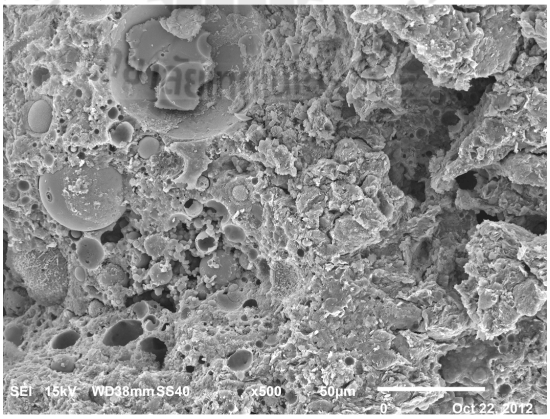
Figure 4.10 SEM images of compacted clay for: (a) m = 12.8%, (b) m = 16% and (c) m = 19.2%.



(a) 0.7-0.6 CLAY-FA-0.3
m = 11.6% (0.8OMC)

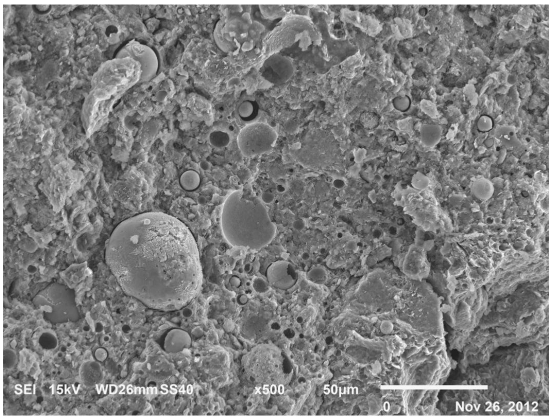


(b) 0.7-0.6 CLAY-FA-0.3
m = 14.5% (OMC)



(c) 0.7-0.6 CLAY-FA-0.3
m = 17.4% (1.2OMC)

Figure 4.11 SEM images of clay–FA geopolymer at FA/clay of 0.3 for: (a) m = 11.6%, (b) m = 14.5% and (c) m = 17.4%.

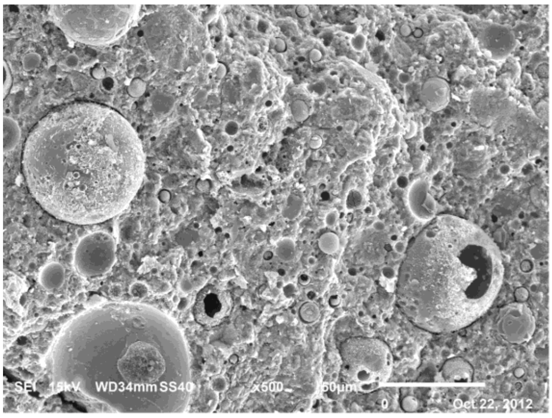


(a) 0.7-0.6 CLAY-FA-0.5
m = 10.0% (0.6OMC)

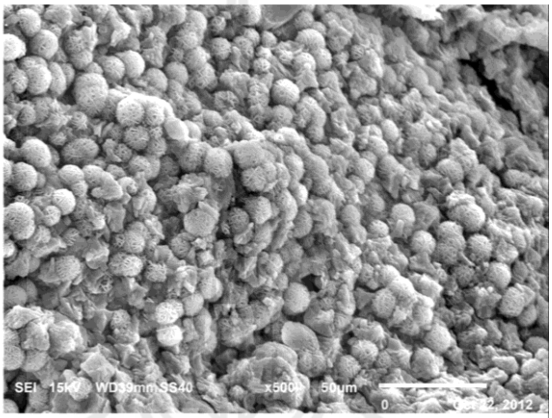
(b) 0.7-0.6 CLAY-FA-0.5
m = 13.4% (0.8OMC)

(c) 0.7-0.6 CLAY-FA-0.5
m = 16.7% (OMC)

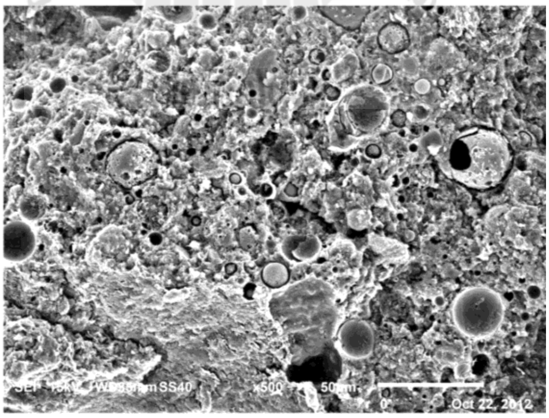
Figure 4.12 SEM images of clay–FA geopolymer at FA/clay of 0.5 for: (a) m = 10.0%, (b) m = 13.4% and (c) m = 16.7%.



(a) 0.7-0.5 CLAY-FA-0.7
m = 7.2% (0.4OMC)



(b) 0.7-0.5 CLAY-FA-0.7
m = 10.8% (0.6OMC)



(c) 0.7-0.5 CLAY-FA-0.7
m = 14.4% (0.8OMC)

Figure 4.13 SEM images of clay–FA geopolymer at FA/clay of 0.7 for: (a) m = 7.2%, (b) m = 10.8% and (c) m = 14.4%.

4.5 Conclusions

This chapter investigates the effect of ingredients (FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio), molding moisture content, specimen sizes, and heating conditions (heat temperature and heat duration) on the strength development in clay–fly ash geopolymer. The following conclusions are drawn.

(1) The FA replacement reduces liquid limit and dry unit weight of the clay, although the particle size distribution of FA and clay is almost the same. The compaction curves of clay–FA mixture and clay–FA geopolymer for the same clay–FA ratio are identical because the L insignificantly affects the index properties for the same FA/clay ratio.

(2) The NaOH leaches the silicon and aluminum in amorphous phase of FA and the Na_2SiO_3 acts as a binder. In this study, the liquid alkaline activator (L) is a mixture of Na_2SiO_3, consisting of 9% Na_2O and 30% SiO_2 by weight, and NaOH with a concentration of 10 molars. With this condition, the Na_2SiO_3/NaOH ratio of 0.7 can be considered as constant for the manufacturing of clay–FA geopolymer.

(3) The optimum L/FA ratio is dependent upon only the FA replacement (FA/clay ratio). When the clay content decreases (the FA/clay decreases), the L required for the reaction decreases. It is approximately 0.6 for FA/clay ratio of 0.3 and 0.5 for FA/clay ratio of 0.7.

(4) The relationship between strength and E/W is proposed. The optimum E/W at the highest strength is approximately 8.50^{o}C h/g for FA/clay ratios of 0.3 and 0.5 and approximately 7.57^{o}C h/g for FA/clay ratio of 0.7. The relationship is very useful

for production industry to estimate the heat temperature and duration to attain the target strength for the required weight of clay–FA geopolymer brick.

(5) The molding moisture content for the highest strength is the combination of mechanical and chemical components. The mechanical component is governed by the soil densification, where the OMC provides the densest packing. The contribution from the chemical component (geopolymerization) decreases with increasing the molding moisture content due to the reduction in L concentration. At very low moisture content, the L is not sufficient for geopolymerization reaction because it is taken by the clay particles for developing the soil structure, hence low strength is obtained. The moisture contents for the highest strength are 1.0OMC, 0.8OMC and 0.6OMC for FA/clay ratios of 0.3, 0.5 and 0.7, respectively.

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CHAPTER V

SULPHATE RESISTANCE OF CLAY-PORTLAND CEMENT AND CLAY- FLY ASH GEOPOLYMER

5.1 Statement of problem

In the northeast of Thailand, bricks are made by mixing local soil and Portland cement. Bricks are a mixture of clay and cement with low ability to resist the changes in the environment especially moisture/water content (collapse and swelling with the change in water content) and the attack of salts (Rajasekaran 2005). Northeast Thailand covers more than one-third of the country; 16.9 million ha with 2.8 million ha of saline soil (Yavaniyama et al. 2005). The saline soil contains sodium sulphate, calcium sulphate and magnesium sulphate (Horpibulsuk et al. 2012; Rajasekaran 2005). One of the main deteriorations of concrete structures is sulphate attack (Rajasekaran 2005). In hardened cement, tricalcium aluminate (C_3A) reacts with sulphate ions in the presence of calcium hydroxide and forms ettringite and gypsum, leading to degradation of concrete into a non-cohesive granular mass and disruptive expansion (Al-Amoudi 1995; Rasheeduzzafar et al. 1994). Previous experience with Portland cement and blended cement concretes showed cases of concrete deterioration when exposed to sulphate attack in the environment (Mehta 1993; Wakely et al. 1993). The sulphate attack on Portland cement concretes has a complicated mechanism and manifests in various ways. From these reactions, expansion and cracking are caused, directly or indirectly, via ettringite and gypsum formation (Ferraris et al. 1997; Santhanam et al. 2003; Taylor and Gollop 1997).

Geopolymer is a material prepared by alkaline activation of alumina-silica materials. According to Davidovits (Davidovits 1991), geopolymer possess high early strength and low creep, low shrinkage and good resistance against acid and sulphate attack in addition to its environment friendliness. According to the studies of the sulphate attack on geopolymer, when exposed to various sulphates with different exposure durations, fly ash-based geopolymers have indicated excellent performance.

Recently, the strength improvement of soil with the incorporation of fly ash geopolymer has been studied by the chapters III and IV (Sukmak et al. 2013a; Sukmak et al. 2013b). However, the durability properties of the clay–fly ash geopolymers have not been investigated and need to be explored. The present work investigates the durability of clay-fly ash geopolymer manufactured using fly ash, silty clay (low swelling) and alkaline activators when exposed to high sulphate environments. It is anticipated that the outcome of this work would provide choices and be beneficial for the production of building materials in the saline soil areas or near the coast and thus lead to the reductions in Portland cement consumption and environmental problems.

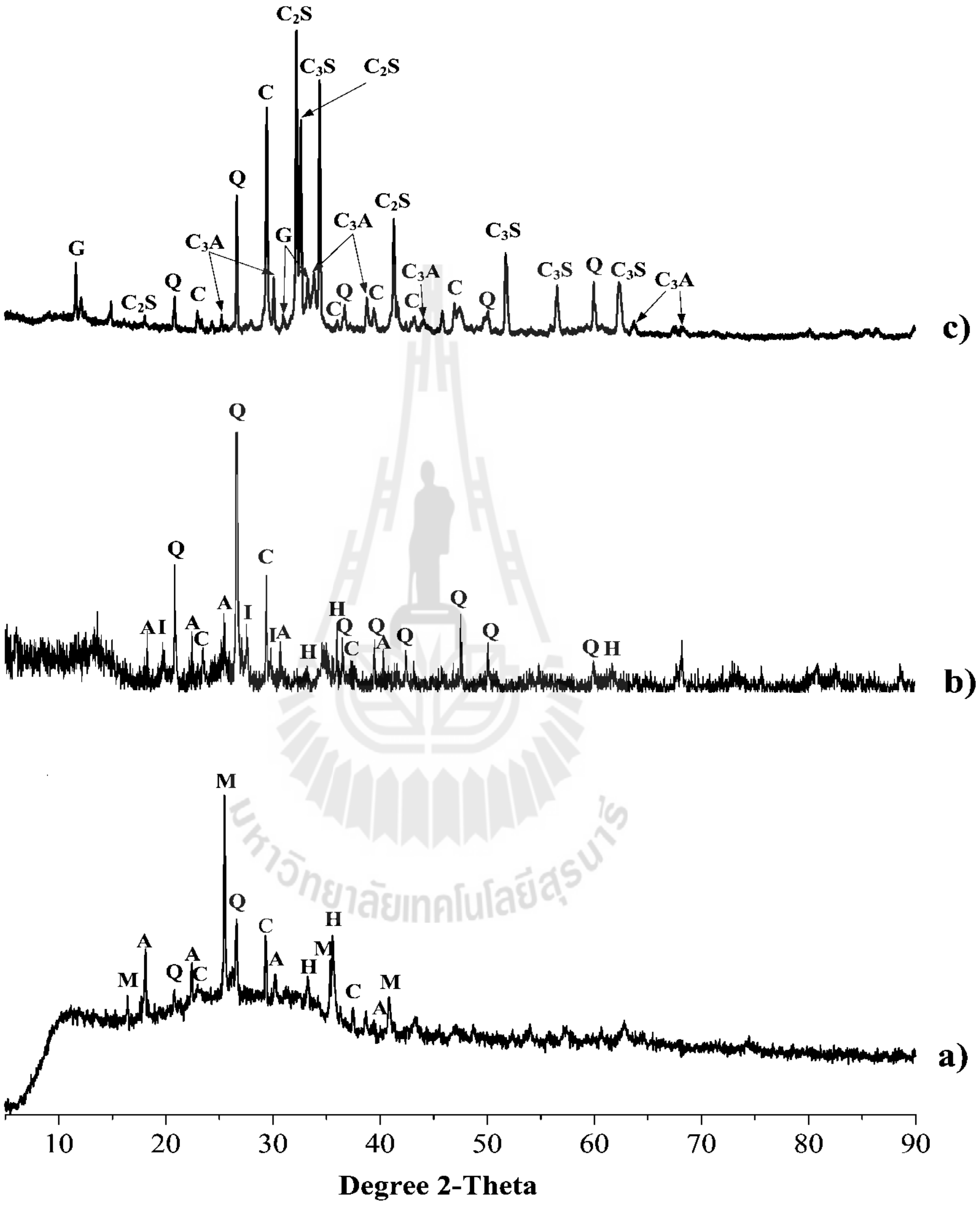
5.2 Materials and methods

5.2.1 Materials

The silty clay (specific gravity of 2.70) at a depth of 3-4 meters from the Suranaree University of Technology campus in Nakhon Ratchasima, Thailand was used. The natural water content, liquid limit and plastic limit are 5.3%, 54% and 28%, respectively. The soil contains 2% sand, 45% silt and 53% clay. This soil is classified as high plasticity clay (CH) according to the Unified Soil Classification System (USCS). The free swell test result revealed that this clay can be classified as low swelling with a free swell ratio (FSR) of 1.0 [14]. The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum moisture content (OMC) of 16% and maximum dry unit weight, γ_{dmax} of 17.3 kN/m^3. The chemical and mineralogical compositions of silty clay are shown in Table 5.1 and Figure 5.1. The main mineral components of the silty clay are quartz, hematite, calcite, calcium sulphate and illite.

Fly ash (FA) used in this study was obtained from the Mae Moh power plant in the north of Thailand. The chemical and mineralogical compositions of fly ash and Type I Portland cement (PC) are shown in Table 5.1 and Figure 5.1. FA consists of mainly glassy phase materials with some crystalline inclusions of mullite, hematite, calcite, calcium sulphate and quartz. The main mineral components of Portland cement are quartz, illite, hematite, calcite, tricalcium silicate, dicalcium silicate, gypsum and tricalcium alumiate. The particle size distribution of PC, FA and silty clay were obtained from laser particle size analyses. The median particles of silty clay, FA and PC are 4.3, 3.4 and 14.8μm, respectively (Figure 5.2). The specific gravity values are 2.31 and 3.17 for FA and PC, respectively.

The liquid alkaline activator is a mixture of sodium silicate solution (Na_2SiO_3), consisting of 9% Na_2O and 30% SiO_2 by weight, and sodium hydroxide solution (NaOH) with a concentration of $10 \mathrm{molL}^{-1}$. The sulphate solutions are 5% sodium sulphate and 5% magnesium sulphate solutions.



Q = Quartz, I = Illite, M = Mullite, H = Hematite, C = Calcite, A = Calcium Sulfate, C_3S = Tricalcium Silicate, C_2S = Dicalcium Silicate G = Gypsum and C_3A = Tricalcium Alumiate

Figure 5.1 X-ray diffraction (XRD) of a) the FA and b) silty clay c) Portland cement.

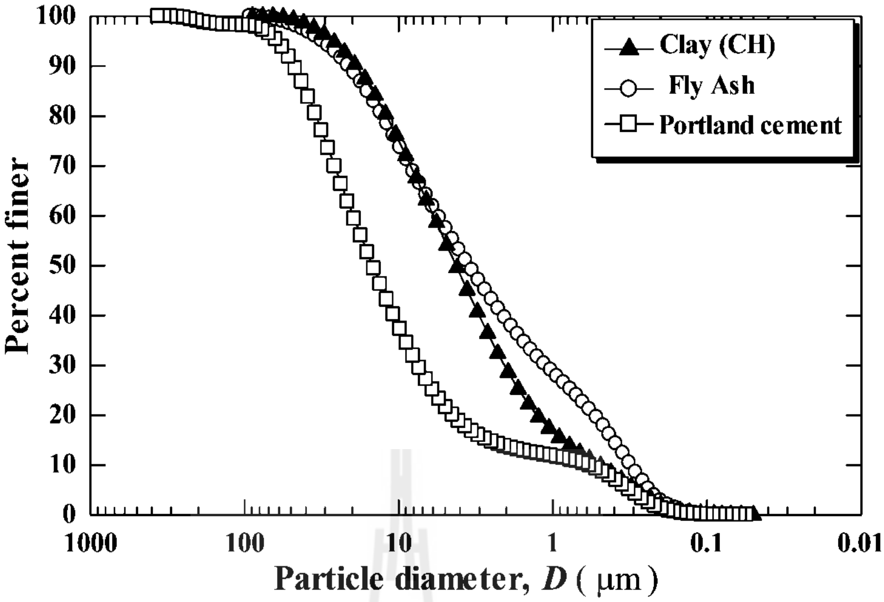


Figure 5.2 Grain size distribution of the clay, Portland cement and FA.

5.2.2 Sample Preparation of Clay-FA geopolymer

Clay-FA geopolymer at FA/clay ratio of 0.3 by mass, Na_2SiO_3/NaOH ratio of 0.7 and L/FA ratio of 0.6 have been selected for this study based on the work of Sukmak et al. (Sukmak et al. 2013a; Sukmak et al. 2013b). This ingredient was proved as optimal providing the highest strength. The moisture content for the highest strength is 1.0 OMC (Optimum Moisture Content). The clay, FA, liquid alkaline activator and water were thoroughly mixed to obtain a uniform mixture. The mixture was then statically compressed in a rectangular mold with 230 mm in length, 90 mm in width and 75 mm in height. The compression was performed by a manual hydraulic jack to attain the optimum point (OMC, $\gamma_{d,max}$) based on the compaction curve of clay-FA geopolymer as shown in Figure 5.3. Practically, the OMC at any compaction energy can be easily and rapidly approximated from the Modified Ohio's compaction curves (Blotz et al. 1998; Horpibulsuk et al. 2008; Prakash and Sridharan 2004). The specimens were dismantled, wrapped in vinyl bags and stored in ambient temperature (27-30^{o}C) for 24 hours and then cured at 130^{o}C for 120 hours. Basic properties of the clay-FA geopolymer samples are shown in Table 5.2.

Table 5.1 Chemical composition of fly ash, Portland cement and silty clay

Chemical composition (%)	**Clay**	**FA**	**Portland cement**
SiO_2	20.10	39.18	21.89
Al_2O_3	7.55	22.64	4.83
Fe_2O_3	32.89	15.45	3.41
CaO	26.15	11.3	65.44
MgO	0.47	1.69	**NA**
SO_3	4.92	4.29	2.7
Na_2O	**NA**	1.81	0.1
K_2O	3.17	2.03	0.69
LOI	3.44	1.61	0.94

Table 5.2 Mix proportions and basic properties of the clay-FA geopolymer and clay-cement samples

Sample ID	Liquid limit (%)	Plastic limit (%)	moisture content (%)	γ_d (kN/m^3)
0.7-0.6 CLAY FA	46	28	14.5 **(1.0OMC)**	17.3
Clay-cement	53.8	35.3	19.4 **(1.2OMC)**	18.7

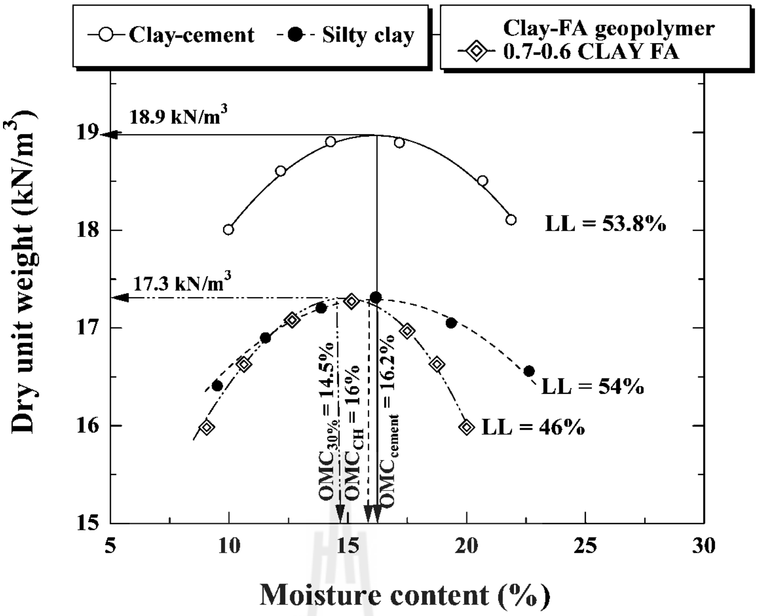


Figure 5.3 Plots of dry unit weight versus molding moisture content of clay and clay–FA geopolymer with those of the clay and the clay-cement under modified Proctor.

5.2.3 Sample Preparation of Clay-cement

The clay-cement sample is a combination of silty clay, Portland cement and tap water with cement/clay ratio of 0.3 by dry clay mass. The silty clay and cement were thoroughly mixed with water to obtain a uniform mixture with moisture contents between 0.8 and 1.4OMC. The silty clay-cement samples were prepared using the same compaction procedure of Clay-FA geopolymer but based on the compaction curve of clay-cement as shown in Figure 5.3. Mix proportions and basic properties of the clay-cement samples are shown in Table 5.2.

5.3 Testing

5.3.1 Compressive strength test

Compression strength test was performed at the age of 28 days in accordance with ASTM D1633. The reported results were the average of at least five specimens in order to obtain reliable test results. In all cases, the results under the same testing condition were reproducible with low standard deviations, SD ($SD/\bar{x}$ < 10%, where $\bar{x}$ is the mean strength value).

5.3.2 Durability test

After 28 days of curing, the samples were immersed in 5% sodium sulphate and magnesium sulphate solutions. The samples were tested for compressive strengths after 30, 60, 90, 120,150, 180, 210 and 240 days of immersion. The sulphate solution was replaced with fresh sulphate solution after immersion of 30, 60, 90, 120,150, 180, and 210 days.

5.3.3 The pH test

At 30, 60, 90, 120,150, 180, 210 and 240 days of immersion, a fraction of the sample exposed to sulphate environments was taken out of the solution, dried and ground to a fine powder. A known amount of this powder was then mixed with distilled (DI) water at sample/DI water ratio of 1:1 and stored at ambient temperature (27-30^{o}C) for 3 minutes before the pH values of solutions were determined.

5.3.4 Microstructural test

The microstructures of sulphate exposed samples were analyzed using scanning electron microscope, EDX spectrum (SEM-EDX) and X-ray diffraction (XRD). The portions were taken from the surface (0–1 mm depth) of samples exposed to the solutions (Bakharev 2005). All specimens were coated with gold before SEM (JOEL JSM-6400) analysis. The XRD analysis were done on powdered samples and patterns were obtained by scanning at 0.1^o (2θ) per min and steps of 0.05^o (2θ).

5.4 Result

5.4.1 Compaction and optimum moisture content

Figure 5.3 presents the dry unit weight versus molding moisture content plots under modified Proctor energy for both clay-FA geopolymer and clay-cement samples compared with those of compacted silty clay. The compaction curves of both clay-FA geopolymer and silty clay are approximately the same whereas the maximum dry unit weight for compacted clay-cement is higher than that of both clay-FA geopolymer and silty clay. The OMCs of the silty clay and the clay-cement samples are almost the same.

The role of moisture content in the strength development of clay-cement samples at a cement/clay ratio of 0.3 is examined and presented in Figure 5.4. The figure shows the strength development with moisture content of the clay-cement samples compressed under the modified Proctor energy after 28 days curing. The result shows that the strengths of compacted clay-cement samples are controlled by the moisture content. The strength of clay-cement increases with moisture content up to 19.4% (1.2OMC) and decreases when the moisture content is on the wet side of 1.2OMC.

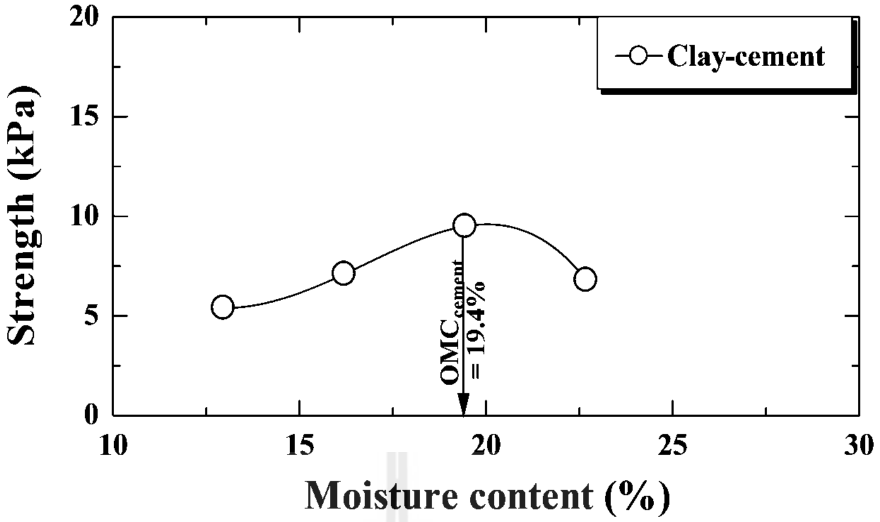


Figure 5.4 Effect of moisture content on strength development of clay-cement at 28 days.

5.4.2 External appearance and compressive strength

Prior to exposure to sulphate solutions both clay-fly ash geopolymer and clay- cement samples appeared to have smooth surfaces with no visible cracks. However, the continuous exposure to sulphate has caused deterioration of the clay-cement samples with visible cracks and white deposits on the surface. This was not observed with clay-fly ash geopolymer samples exposed to sulphate solutions.

Figure 5.5 shows the compressive strength evolution of clay-FA geopolymer and clay-cement specimens unexposed and exposed to 5% sodium sulphate and 5% magnesium sulphate solutions. The initial strength of clay-FA geopolymer and clay-cement were 12.0 and 9.5 MPa, respectively. The strength of both samples gradually decreases with time when exposed to sulphate solutions. However, the rate of decrease seems to be higher in clay-cement mixtures than in clay-FA geopolymer mixtures. In 5% sodium sulphate solution, the clay-FA geopolymer sample performed better than the clay-cement, with only 19% decrease in strength at 240 days of exposure compared to 82% decrease in the clay-cement. A similar trend can be seen with the samples exposed to magnesium sulphate solutions.

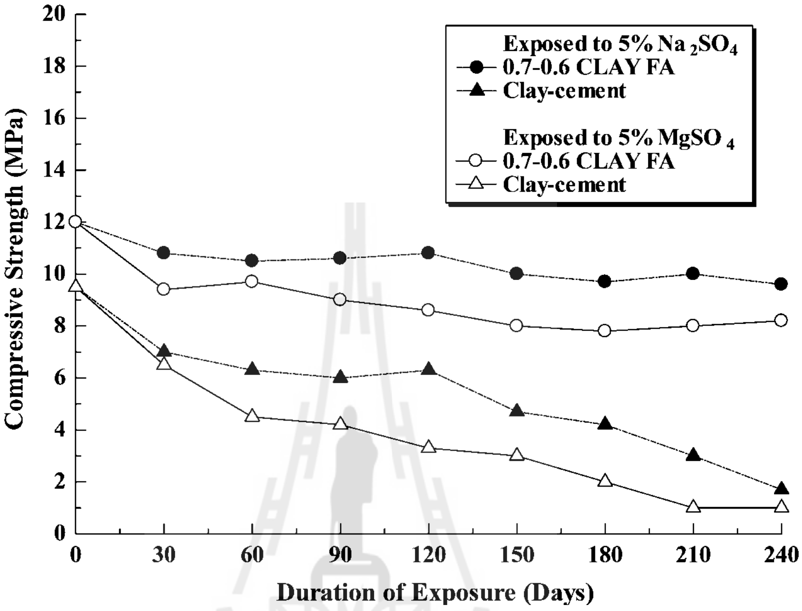


Figure 5.5 Compressive strength evolution of clay-FA geopolymer and clay-cement specimens exposed to a solution of 5% sodium sulfate and 5% magnesium sulfate.

The two different sulphate solutions (sodium sulphate and magnesium sulphate) appear to have a slightly different effect on both clay-cement and clay-FA geopolymer samples. The initial rates of decrease in strength of both clay-cement and clay-FA geopolymer are higher with magnesium sulphate than those with sodium sulphate. At 30 days, the decrease in strength of clay-FA geoplymer with sodium sulphate is 10.8% compared to 21.6% with magnesium sulphate. Similarly, at 30 days, the decrease in strength of clay-cement with sodium sulphate is 26.3% compared to 31.6% with magnesium sulphate. Overall, the least strength reduction was observed with the clay-FA geopolymer samples exposed to sodium sulphate solutions.

5.4.3 pH variation

Figure 5.6 shows the pH results of clay-FA geopolymer and clay-cement samples unexposed and exposed to the solutions of 5% sodium sulphate and 5% magnesium sulphate at different curing intervals. The initial pH values of clay-FA geopolymer and clay-cement were 12.1 and 11.9, respectively. The pH values of both these samples gradually decrease with time with a higher rate of decrease for the clay-cement sample. It is also apparent that the pH level of both clay-cement and clay-FA geopolymer samples exposed to magnesium sulphate solution is comparatively higher than that of sodium sulphate solution. When exposed to magnesium sulphate, the overall reduction in pH for clay-cement and clay-FA geopolymer systems are from 11.9 to 10 and from 12.1 to 11.6, respectively. Comparative values for the two systems with sodium sulphate exposure are from 11.9 to 8.9 and from 12.1 to 11.2, respectively. Irrespective of the source of sulphate, the least pH reduction was observed with the clay-FA geopolymer samples.

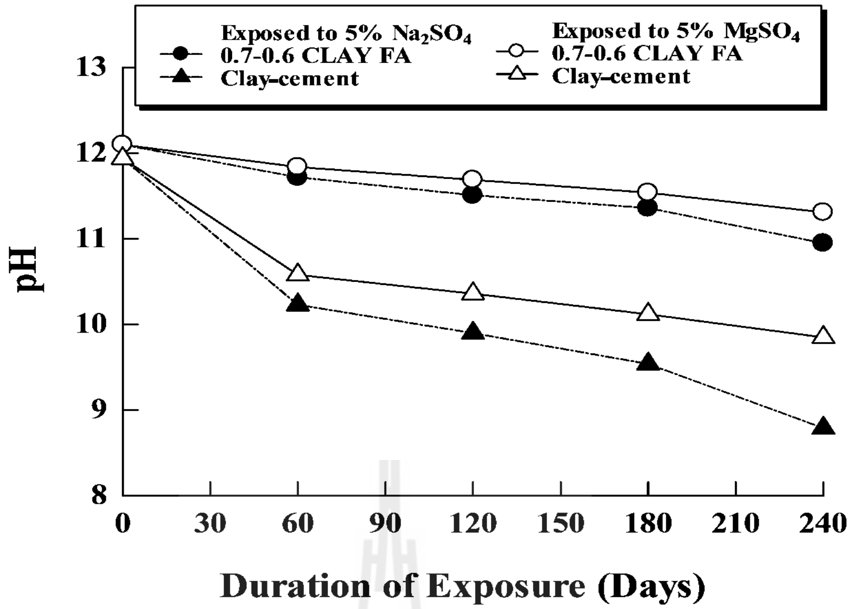


Figure 5.6 pH level of clay-FA geopolymer and clay-cement.

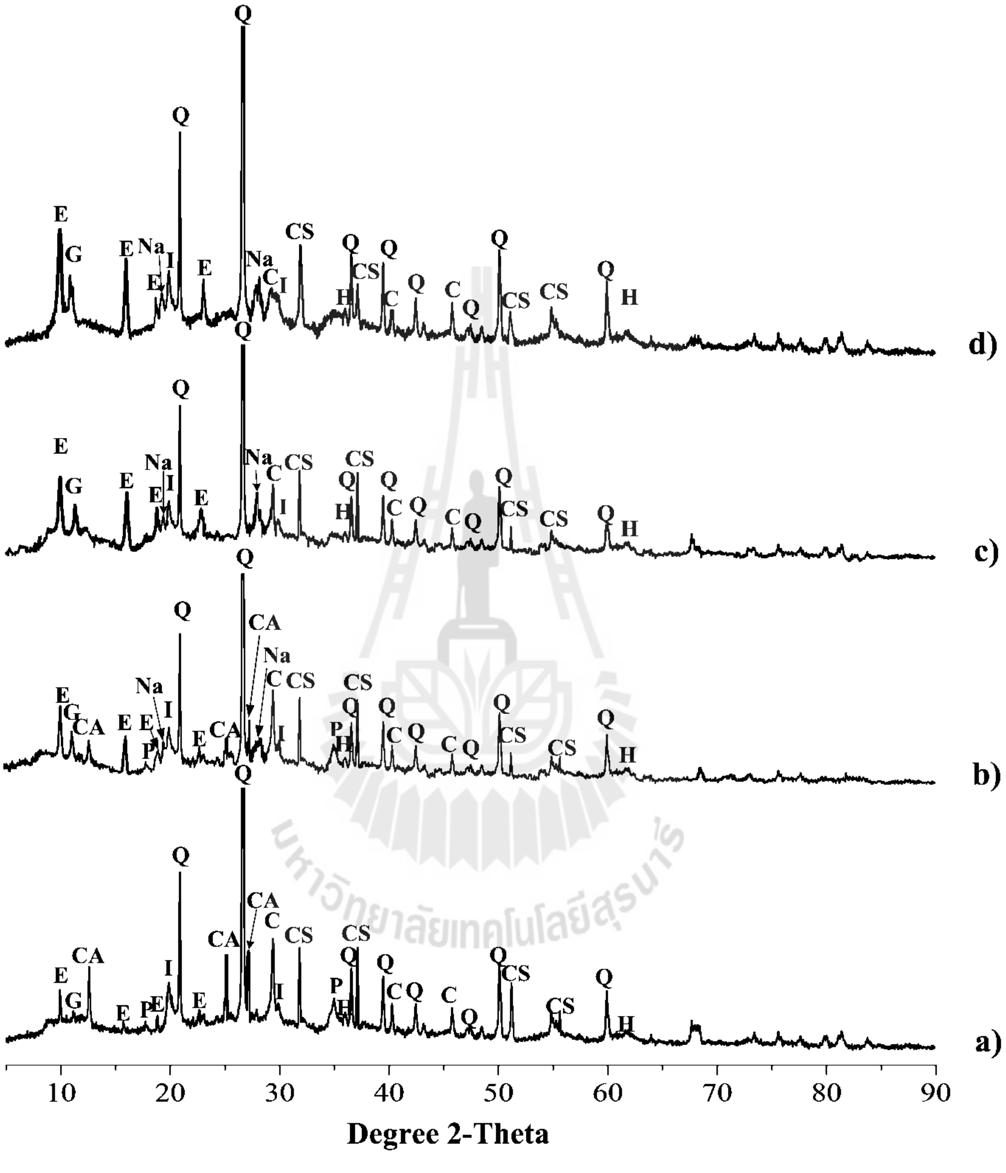
5.4.4 Microstructural analysis

5.4.4.1 Phase development by XRD

Figures 5.7 and 5.8 show the XRD patterns of clay-cement exposed to sodium sulphate and magnesium sulphate solutions, respectively. Before the exposure, (Figures 5.7a and 5.8a), the clay-cement sample at 28 days of curing contains the phases of quartz, illite, hematite, calcite, calcium silicate hydrate (CSH), portlandite (CH), calcium aluminate hydrate (CAH), gypsum and ettringite. When these samples were exposed to 5% sodium sulphate solution for 60, 180, and 240 days (Figures 5.7b - d), the peaks corresponded to CAH and CH decrease with no significant change in the CSH peaks. In contrast, peaks corresponded to gypsum and ettringite become more prominent with increasing exposure times. The disappearance of CAH and CH phases is associated with the formation of ettringite and gypsum phases. Furthermore, peaks corresponded to sodium sulphate also appears in these samples with continuous exposure to sodium sulphate solutions with time and becomes a dominant phase.

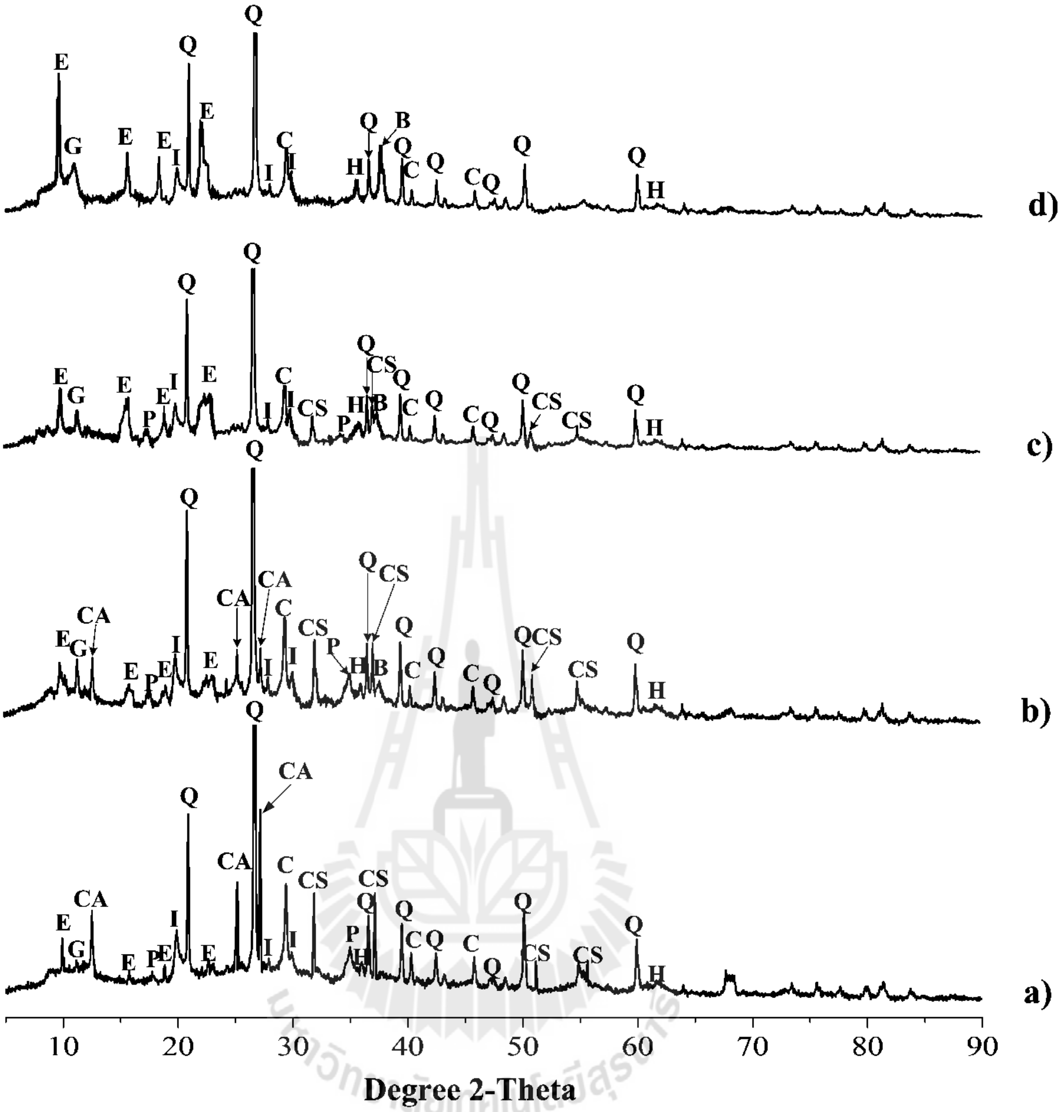
A similar trend in phase development, i.e. the disappearance of CAH and CH phases with the formation of ettringite and gypsum phases has been observed for the clay-cement specimens exposed to magnesium sulphate solution (Figure 5.8b - d). In addition, the CSH phase also seems to disappear with continuous exposure to magnesium sulphate solution. Traces of brucite (magnesium hydroxide) can also be detected in the samples exposed for 240 days.

Figures 5.9 and 5.10 show the XRD peak intensities of clay-FA geopolymer unexposed and exposed to a sulphate solution. Before exposure to sulphate solutions, (Figures 5.9a and 5.10a), the clay-FA geopolymer at 28 days contained phases of geopolymer (as shown by the characteristic broad band around 30^0 2θ), quartz, illite, hematite, mullite, calcite, chabazite, gismondine and muscovite. When the specimen was exposed of 5% sodium sulphate and 5% magnesium sulphate solutions at 60, 180, and 240 days (Figures 5.9b - d and 5.10b - d), the results obtained are similar, i.e. the calcite phase decreases significantly with the appearance of gypsum and ettringite phases. However, the presences of these phases are not as dominant as those of the clay-cement samples. When considering the specimen exposed to a solution of 5% sodium sulphate (Figures 5.9b - d), it can be noticed that peaks corresponded to sodium sulphate also occurs but it is relatively stable and does not fluctuate with exposure time. Likewise, traces of brucite can be identified with the increase in exposure time in samples exposed to magnesium sulphate solutions. It is important to note that, irrespective of the type of sulphate solution, the broad band at 30^{o} 2θ corresponded to geopolymers do not change as shown in the XRD patterns.



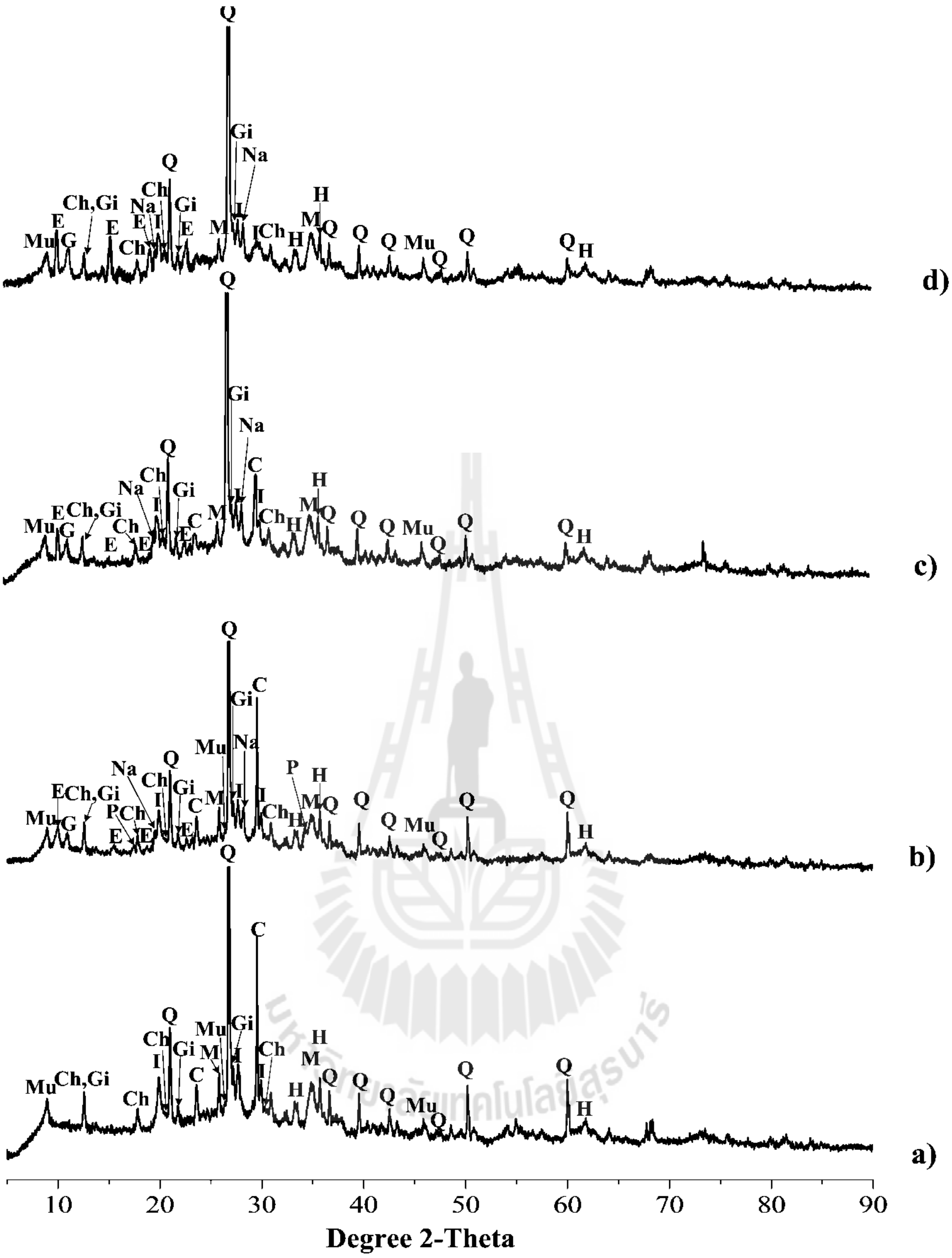
Q = Quartz, I = Illite, H = Hematite, C = Calcite, CS = Calcium Silicate Hydrate,P = Portlandite G = Gypsum, E = ettringite, CA = Calcium Alumiate Hydrate and Na = Sodium Sulfate

Figure 5.7 XRD peak intensities of clay-cement exposed to a solution of 5% sodium sulfate at 0, 60, 180, and 240 days.



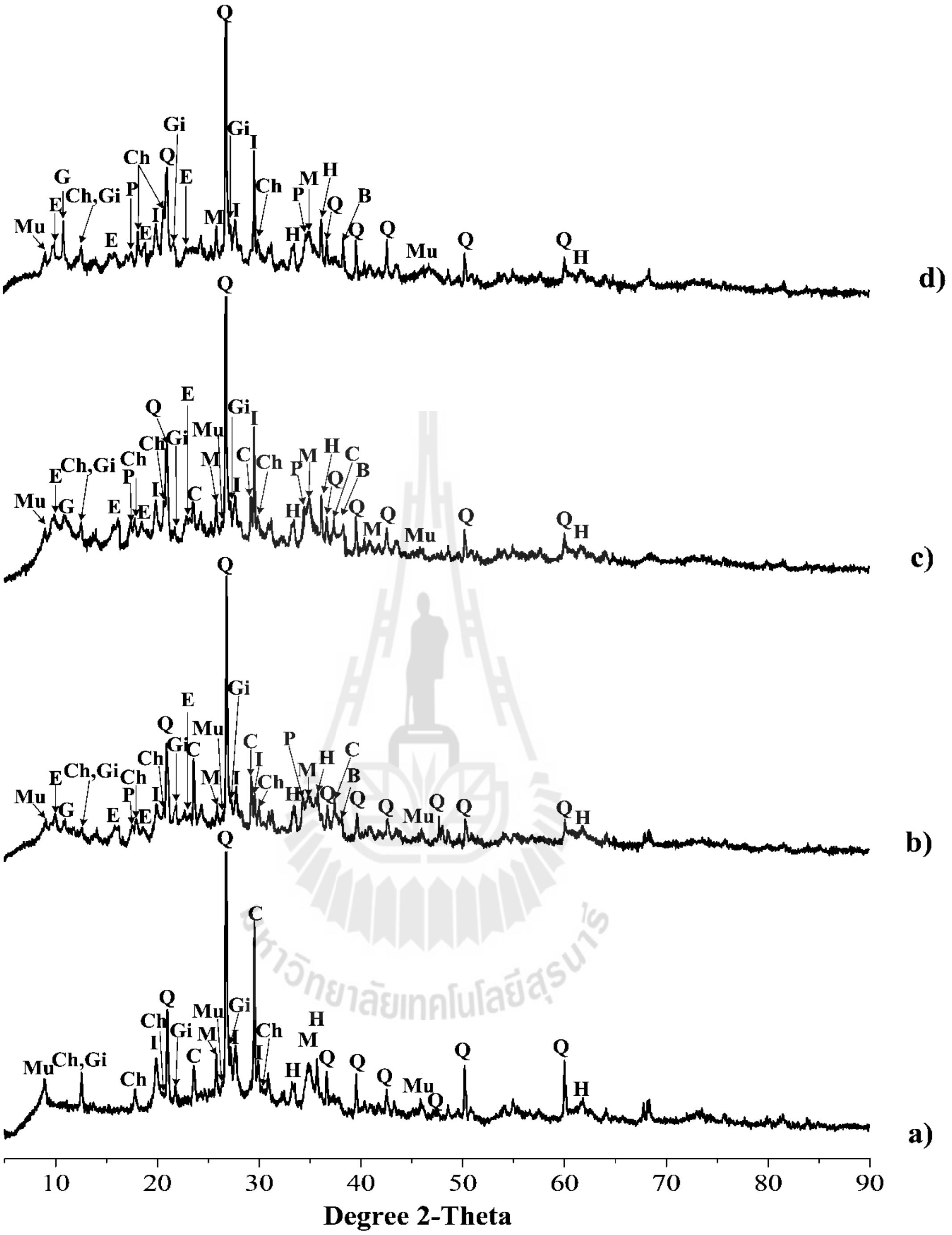
Q = Quartz, I = Illite, H = Hematite, C = Calcite, CS = Calcium Silicate Hydrate,P = Portlandite, G = Gypsum, E = ettringite, B = Brucite and CA = Calcium Alumiate Hydrate

Figure 5.8 XRD peak intensities of clay-cement exposed to a solution of 5% magnesium sulfate at 0, 60, 180, and 240 days.



Q = Quartz, I = Illite, H = Hematite, M = Mullite, C = Calcite, P = Portlandite, G = Gypsum, E = ettringite, Ch = Chabazite Gi = Gismondine, Mu = Muscovite and Na = sodium sulfate

Figure 5.9 XRD peak intensities of clay-FA geopolymer exposed to a solution of 5% sodium sulfate at 0, 60, 180, and 240 days.



Q = Quartz, I = Illite, H = Hematite, M = Mullite, C = Calcite, P = Portlandite, G = Gypsum, E = ettringite, B = Brucite, Ch = Chabazite Gi = Gismondine and Mu = Muscovite

Figure 5.10 XRD peak intensities of clay-FA geopolymer exposed to a solution of 5 % magnesium sulfate at 0, 60, 180, and 240 days.

5.4.4.2 Electron Microscope analysis

Figure 5.11 shows the SEM and EDX analysis of clay-cement samples before and after exposure to sulphate solutions. Before exposed to sulphate solution (Figure 5.11a), clay-cement has a reasonably homogeneous microstructure with the presence of a small quantity of needle-like phases. As shown by EDX analysis, these needle-like phases have the elemental ratio similar to ettringite. XRD results of these samples also show the presence of trace amount of ettringite before exposure to sulphate solutions. When exposed to sulphate (Figure 5.11b and c), irrespective of the type of sulphate solution, the microstructure of clay-cement sample contains massive growth of ettringite and is the dominant phase. Figure 5.12 shows the SEM images of the clay-FA geopolymer samples before and after exposure to sulphate solutions. The unexposed sample (Figure 5.12a) is dominated by the presence of glassy aluminosilicate geopolymer matrix. EDX analysis data of an enlarged area of the matrix confirms that geopolymer phase with elemental ratio Si/Al = 1.67 and Na/Al = 0.95 mainly present on the surface of fly ash particle. The overall matrix looks continuous and fairly homogeneous. There is no major change in the microstructure of these samples when exposed to sulphate solutions (Figures 5.12b and 5.12c). Small pockets of needle-like growths are found within the geopolymer matrix and the matrix seems to be intact. These needle-like growths are identified as ettringite by EDX analysis.

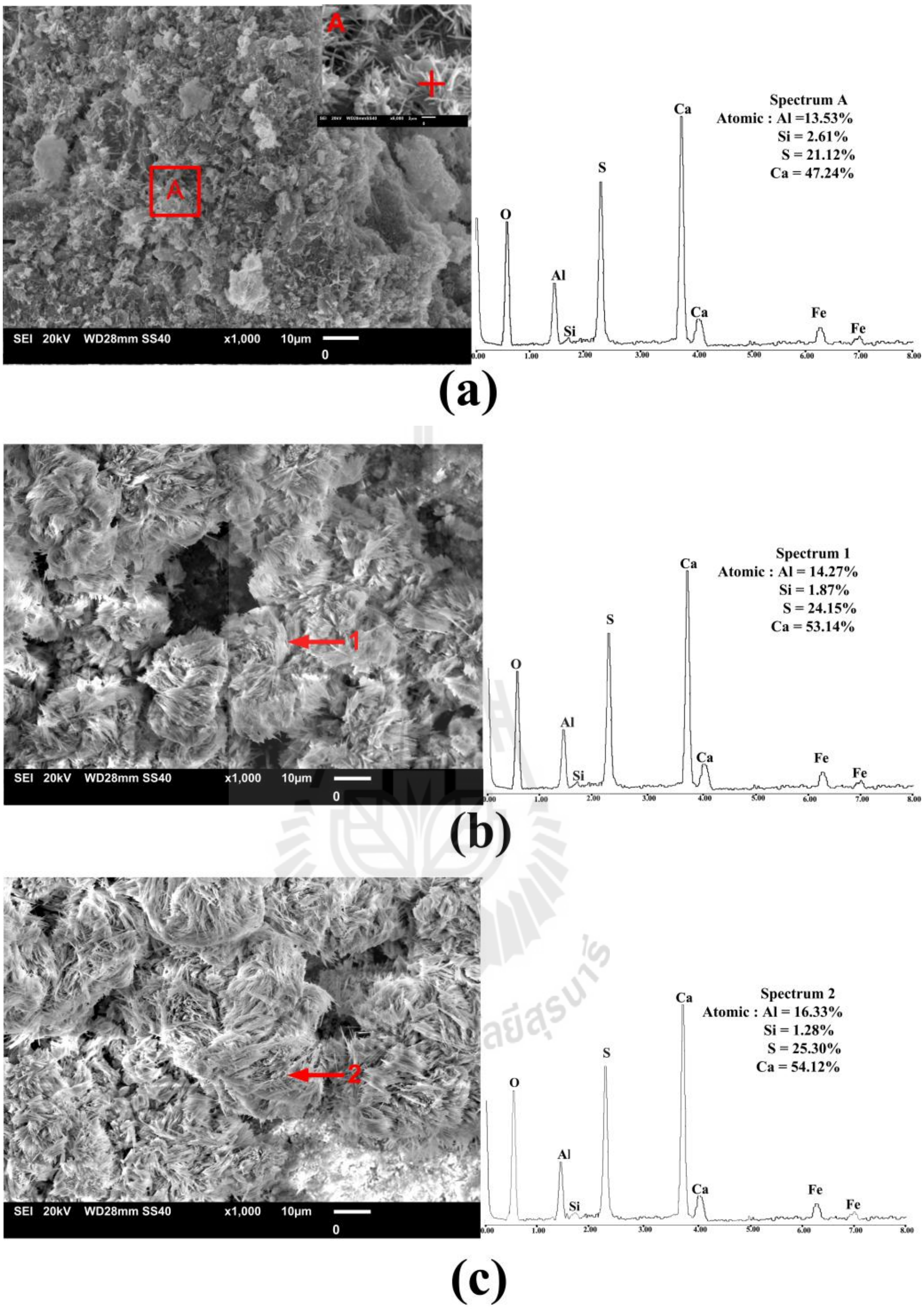


Figure 5.11 The SEM and EDX analysis of clay-cement a) unexposed to a sulfate solution at 28 days, b) exposed to 5% sodium sulfate at 240 days and c) exposed to 5% magnesium sulfate at 240 days.

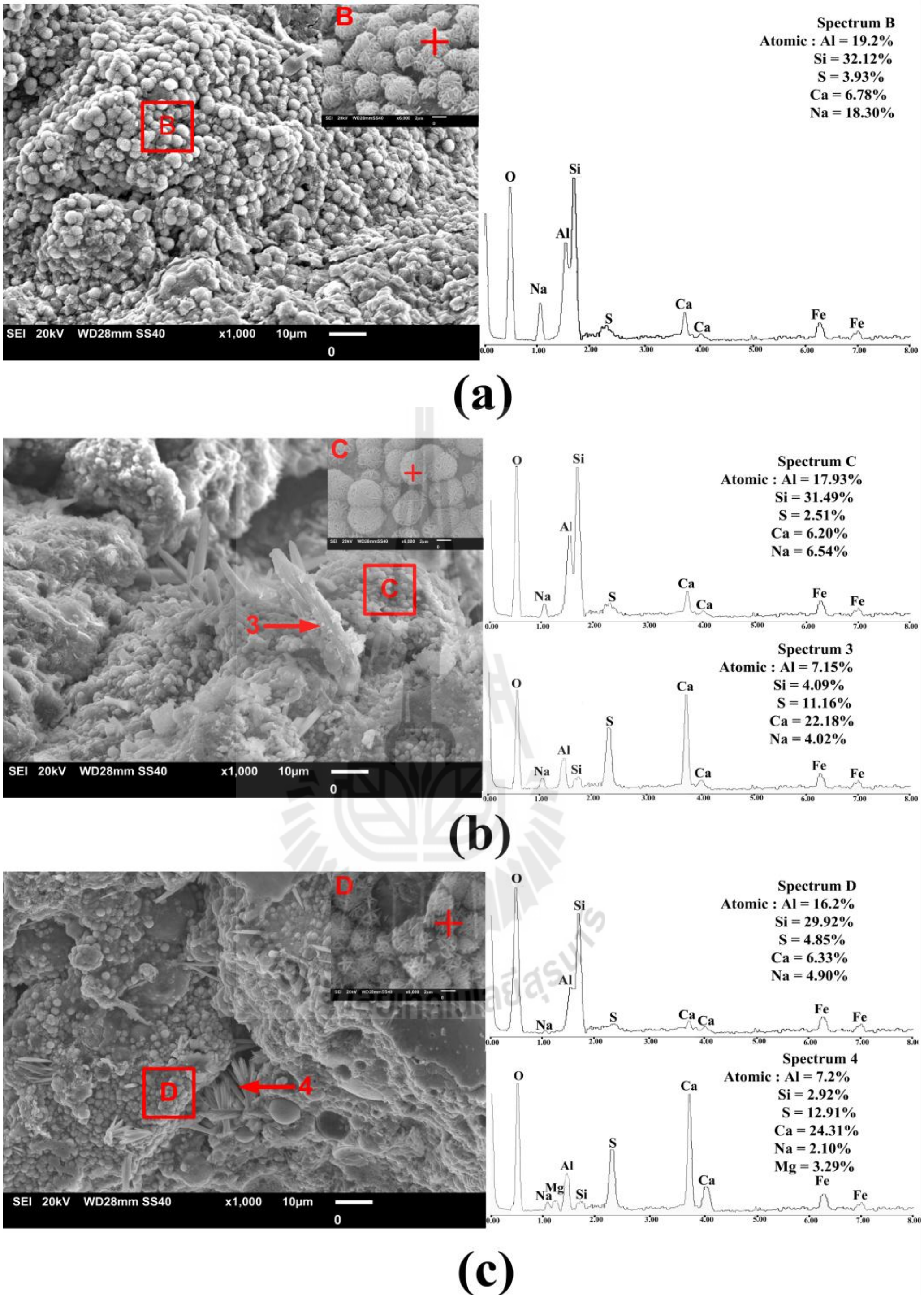


Figure 5.12 SEM image of clay-FA geopolymer a) unexposed to a sulfate solution at 28 days, b) exposed to 5% sodium sulfate at 240 days and c) exposed to 5% magnesium sulfate at 240 days.

5.5 Discussion

5.5.1 Compaction and optimum moisture content

The gradation and specific gravity control the shape of compaction curve. The grain size distribution (Figure 5.2) and specific gravity of the silty clay and FA are similar; therefore, the compaction curve of the clay-FA geopolymer and the silty clay is essentially the same (Figure 5.3). The maximum dry unit weight of the compacted clay-cement samples is higher than that of both clay-FA geopolymer and silty clay because of higher specific gravity of PC. Generally, the increase in maximum dry unit weight is associated with the decrease in the OMC and liquid limit, which is different from this case. The OMC of clay-cement is higher than that of clay-FA geopolymer but is close to that of silty clay. Horpibulsuk et al. (Horpibulsuk et al. 2006) also reported this characteristic of cement stabilized coarse- and fine-grained soils. The decrease in the repulsion between diffused double layers and the increase in the edge-to-face contacts between clay sheets are from the adsorption of Ca^{2+} ions onto the clay particle surface (Chew et al. 2004; Locat et al. 1990). The clay particles therefore flocculate, which increase in the plastic limit with an insignificant change in the liquid limit (Table 5.2). Since the OMC of low swelling clays is mainly controlled by the liquid limit (Horpibulsuk et al. 2008; Horpibulsuk et al. 2007; Nagaraj et al. 2006), the OMCs of the silty clay and the clay-cement samples are almost the same.

The influence of state of moisture content on the compressive strength of clay-cement is shown by Figure 5.4 that the moisture content at1.2OMC provides the highest 28-day strength which complies with the finding of Horpibulsuk et al. (Horpibulsuk et al. 2010). Beyond this state of content, the strength decreases due to the decrease in water/content ratio (Chindaprasirt et al. 2007; Collepardi 2003; Glasser et al. 1995). While the lower water content is not sufficient for hydration (Chindaprasirt et al. 2007).

In general, when the soil is compressed to a higher dry unit weight, a higher strength is attained. The same is not always true for chemical stabilized soil. The 28-day strength of clay-FA geopolymer is up to 1.2 times higher than that of clay-cement (Figure 5.5) even though the weight of clay-FA geopolymer is lower because of lower specific gravity of FA. Pacheco-Torgal et al. (Yang et al. 1996) also showed that for the same water/binder ratio, geopolymers attain a higher mechanical strength than Portland cement. This high strength with low unit weight is an advantage of using the geopolymer as a cementitious material over the cement.

5.5.2 Durability against sulphate

Ettringite is a component of the hydration products of ordinary Portland cement. In the normal setting reactions of cement, ettringite develops in the course of early hydration (“primary” or early ettringite formation, EEF). This process occurs homogeneously and immediately. The volume changes arising due to the formation of this low-density phase (d=1.77g/cm^3) are readily accommodated while the cement is still plastic; therefore, it does not cause any significant localized disruptive action. When ettringite is formed later, after several months or years, (delayed ettringite formation, DEF) in the cement paste, this can cause a disruptive effect if it occurs heterogeneously in the very rigid paste (Collepardi 2003; Lauer 1990).

One of the ways that DEF related damage can occur in cement pastes is from the externally available sulphates such as the sulphates present in water or soil environments. In addition to the permeability of the cement paste, the conditions such as the high sulphate environment and the presence of water collectively favor the DEF formation resulting in the disruptive effect (Lauer 1990). The damage is known to cause by several chemical processes in which sulphate reacts with CH, CSH and CAH phases in cement, causing decalcification and expansion in the paste (Sata et al. 2012).

When exposed to sulphate solutions, both clay-cement and clay-FA geopolymer systems show the formation of new sulphate-containing phases proving that some sort of sulphate attack has taken place in both systems. It is clear from XRD results that, the formation of gypsum and ettringite in the clay-cement system is associated with the disappearance of CAH, CH and CSH phases. Sulphates react with calcium and aluminate ions as follows:

$$6Ca^{+2} + 3SO_4^{-2} + 2H_2O \text{ ----> } Ca(SO_4)_2.2H_2O$$

$$6Ca^{+2} + 2Al(OH)_4^{-1} + 4OH^{-1} + 3SO_4^{-2} + 26H_2O \text{ ----> }$$
$$Ca_6[Al(OH)_6]_2.(SO4)_2.26H_2O$$

The expansion caused by the formation of ettringite, crystallization of gypsum and decalcification of CSH phases are the reasons for the observed damage in the clay-cement samples (Chindaprasirt et al. 2007; Glasser et al. 1995). The pH of the clay-cement system which is around pH 12.5 is usually due to the presence of $Ca(OH)_2$,. When Ca^{+2} ions are consumed by the above reaction (Lauer 1990), the pH gradually decreases with the continuous exposure to sulphates.

The extent of the physical damage caused by sulphate attack and the change in pH in the clay-cement system seems to depend on the type of sulphate source. As shown by the compressive strength results, the damage caused by magnesium sulphate is greater than that of sodium sulphate. Also, the samples exposed to magnesium sulphate show a slower decrease in pH than that of sodium sulphate. One possible reason is when magnesium sulfate reacts with the cement paste, in addition to ettringite and gypsum, it forms brucite (as detected in XRD patterns). Brucite helps mainline the pH of clay-cement system at a level closer to 10.5 at which ettringite phase still remain stable because pH is an important factor controlling the stability of ettringite (Collepardi 2003).

Similar chemical processes seem to take place in the clay-FA geopolymer system too. Phases such as ettringite, gypsum and brucite are detected during the exposure to sulphate environments. However, the extent of damage appears to be considerably smaller than what have been noted with the clay-cement system. One difference in the two systems is the source of calcium. In the clay-FA geopolymer system, the only source of calcium is from fly ash which is limited in quantity and therefore the ettringite formation is not sustainable. Unlike cement hydration products, the Na-Al-Si network structure of geopolymer is less susceptible to sulphate attack. Thus, this study shows that silty clay can be successfully used as a composite material in the production of clay-FA geopolymer bricks with strong resistance to sulphate attack.

5.6 Conclusions

The following conclusions can be drawn from this study.

(1) Both clay-FA geopolymer and clay-cement systems are susceptible to sulphate attacks. The mechanism of degradation is primarily related to the formation of ettringite, gypsum and brucite.

(2) The source of sulphate has an impact on the sulphate attack on cementitious systems. Exposure to Magnesium sulphate causes more degradation than sodium sulphate in both clay-FA geopolymer and clay-cement systems. In magnesium sulphate environment, the formation of ettringite, gypsum and brucite are more evident than that in the sodium sulphate environment.

(3) The clay-fly ash geopolymer is less susceptible to sulphate attack than the clay-cement system. In the clay-FA geopolymer system, calcium from fly ash is limited in quantity and therefore the ettringite formation is not sustainable. In addition, the Na-Al-Si network structure of geopolymer is less susceptible to sulphate attack.

(4) Silty clay-high calcium fly ash geopolymers can be considered as a good composite material to be used as building products in Northeast Thailand.

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CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and conclusions

This thesis consists of three main objectives. The first is to investigate the possibility of using a silty clay as a raw material to develop a clay–fly ash geopolymer. The silty clay is used as fine aggregates and fly ash (FA) is used as a pozzolanic material. A liquid alkaline activator, L is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH). The second is to understand the strength development with different ingredients, specimen sizes, and heating conditions for the manufacturing of clay–FA geopolymer. The studied factors are FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio, molding moisture content, specimen size, heat temperature and duration. The third is to investigate the durability characteristics of the clay-fly ash geopolymer against sodium and magnesium sulphate attack. The conclusions can be drawn as follows:

6.1.1 Chapter 3: Strength development in clay-fly ash geopolymer

This chapter illustrates the possibility of using the silty clay as fine aggregates and FA as a pozzolanic material to develop geopolymer at FA/clay ratio of 0.3. The optimum ingredient for manufacturing the clay–FA geopolymer is the Na_2SiO_3/NaOH ratio of 0.7 and the L/FA ratio of 0.6. The Na_2SiO_3/NaOH ratio required for the clay–FA geopolymer is less than that of the FA geopolymer because the clay has high cation absorption ability and then absorbs some of the input NaOH. For a given Na_2SiO_3/NaOH content, the strength increases with increasing the liquid alkaline activator. The excess input alkaline activator causes the precipitation at very early stage before the condensation process in geopolymerization. The overheating (very high temperature) and excess heat duration cause the micro-cracks on the specimens; hence strength reduction.

6.1.2 Chapter 4: Factors influencing strength development in clay–fly ash geopolymer.

The strength development with influential factors for the manufacturing of clay–fly ash geopolymer is presented in this chapter. The studied factors are FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio, molding moisture content, specimen size, heat temperature and duration. The optimum Na_2SiO_3/NaOH ratio for manufacturing clay-FA geopolymer is 0.7 for all FA/clay ratios, L/FA ratios and specimen sizes tested. This Na_2SiO_3/NaOH ratio is thus considered as constant for making clay–FA geopolymer. The optimum L/FA ratio decreases as the FA/clay ratio increases. The optimum L/FA ratio is 0.6 for FA/clay ratio of 0.3 and is 0.5 for FA/clay ratio of 0.7. The molding moisture content providing the highest strength is at 1.0OMC for FA/clay ratio of 0.3, 0.8OMC for FA/clay ratio of 0.5, and 0.6OMC for FA/clay ratio of 0.7. The optimum ingredient (Na_2SiO_3/NaOH ratio, L/FA ratio and moisture content) is irrespective of specimen size. The larger specimens with higher weight require higher heat temperature and longer duration for the geopolymerization development. The heat energy per weight (E/W) concept integrates the role of heat temperature, duration and specimen weight on the geopolymerization. The specimens with high FA/clay ratio require low E/W. The optimum heat energy per weight is approximately 8.5 ^{o}C h/g for FA/clay ratios of 0.3 and 0.5 and 7.57 ^{o}C h/g for FA/clay ratio of 0.7. The relationship between strength and E/W is very useful for production industry to estimate the heat temperature and duration to attain the target strength for the required weight in making clay–FA geopolymer brick.

6.1.3 Chapter 5: Durability of clay-fly ash geopolymer against sodium sulphate and magnesium sulphate solution

This chapter examines the resistance ability of two different cementitious systems prepared using silty clay as a major component against 5% sodium sulfate and 5% magnesium sulfate solutions. The two cementitious systems are clay - Portland cement and clay- high calcium fly ash geopolymer. The clay–fly ash geopolymer is a mixture of silty clay and fly ash (FA) at optimum moisture content (OMC) and FA/clay ratio of 0.3 by dry soil mass. A liquid alkaline activator (L) is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH) at Na_2SiO_3/NaOH of 0.7 and L/FA ratio of 0.6. For the clay - Portland cement system, a cement/clay ratio of 0.3 by dry soil mass and the molding moisture content providing the highest strength at 1.2OMC are used. Results show that the 28-day strength of the clay-FA geopolymer is up to 1.2 times higher than that of clay-cement. The physical performance of clay-FA geopolymer when exposed to sulphate solution is better than that of clay-cement. While the geopolymer phase is prominent in the clay-fly ash geopolymer system, gypsum and ettringite phases are present in both systems especially in the clay-cement system. The exposure to magnesium sulphate solution causes more degradation in both clay-FA geopolymer and clay-cement system than the exposure to sodium sulphate. Overall, clay-high calcium fly ash geopolymers show better resistance to sulphate attack than clay-cement mixtures.

6.2 Recommendations for future work

- This study used only fly ash as a pozzolanic material. The other pozzolanic materials such as rice husk ash, bagasse ash, metakaolin can be considered for further study.
- NaOH was used as alkali for leaching Si and Al in this study. Further work can be done using other waste calcium-rich materials such as the calcium carbide residue and slag.
- It would be useful to study a possibility of manufacturing clay-fly ash geopolymer under low temperature by using hybrid geopolymer such as cement-geopolymer.
- This thesis only investigates the sulphate resistance of clay-fly ash geopolymer. The acid resistance of clay-fly ash geopolymer should be further studied.

APPENDIX A

PUBLICATIONS

List of Publications

INTERNATIONAL JOURNAL PAPERS

Sukmak P., Horpibulsuk S., and Shen S.L., **Strength development in clay–fly ash geopolymer,** Construction and Building Materials 40 (2013) pp.566-574.

Sukmak P., Horpibulsuk S., Shen S.L., Chindaprasirt P., and Suksiripattqanapong C., **Factors influencing strength development in clay-fly ash geopolymer**, Construction and Building Materials 47 (2013) pp. 1125-1136.

NATIONAL CONFERENCE PAPERS

สุขสันติ์ หอพิบูลสุข และ ปฏิมาพร สุขมาก (2556) **พฤติกรรมด้านกำลังอัดของดินเหนียวเถ้าลอยจีโอโพลิเมอร์:วัสดุก่อสร้างเขียว** การประชุมวิชาการวิศวกรรมโยธาแห่งชาติ ครั้งที่ 18. มหาวิทยาลัยเชียงใหม่. วันที่ 8-10 พฤษภาคม 2556 (บทความรับเชิญ)

Construction and Building Materials 47 (2013) 1125–1136

Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Factors influencing strength development in clay–fly ash geopolymer

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HIGHLIGHTS

- Strength and microstructure tests of clay–FA geopolymer.
- Role of liquid alkaline activator, clay/FA ratio and moisture on strength.
- Explain role of heat temperature and duration on strength.
- Analyze strength of the clay–FA geopolymer.
- Suggest a relationship between strength and heat energy per weight.

ARTICLE INFO

Article history:
Received 12 February 2013
Received in revised form 23 May 2013
Accepted 29 May 2013

Keywords:
Geopolymer
Strength
Microstructure
Silty clay
Fly ash
Heat energy per weight

ABSTRACT

This paper investigates the strength development with different ingredients, specimen sizes, and heating conditions for the manufacturing of clay–fly ash geopolymer. A silty clay is used as fine aggregates and fly ash (FA) is used as a pozzolanic material. A liquid alkaline activator (L) is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide solution (NaOH). The studied factors are FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio, molding moisture content, specimen sizes, heat temperature and duration. The optimum ingredients for clay–FA geopolymer are Na_2SiO_3/NaOH ratio of 0.7 for all FA/clay ratios, L/FA ratios and specimen sizes tested. This Na_2SiO_3/NaOH ratio is thus considered as constant for making clay–FA geopolymer. The optimum L/FA ratio decreases as the FA/clay ratio increases. The optimum L/FA ratio is 0.6 for FA/clay ratio of 0.3 and is 0.5 for FA/clay ratio of 0.7. The molding moisture content providing the highest strength is at 1.0OMC for FA/clay ratio of 0.3, 0.8OMC for FA/clay ratio of 0.5, and 0.6OMC for FA/clay ratio of 0.7. The optimum ingredient (Na_2SiO_3/NaOH ratio, L/FA ratio and moisture content) is irrespective of sample size. The larger specimens with higher weight require higher heat temperature and longer duration for the geopolymerization development. The heat energy per weight (E/W) concept can integrate the role of heat temperature, duration and specimen weight on the geopolymerization. The specimens with high FA/clay ratio require low E/W. The optimum heat energy per weight is approximately 8.5 °C h/g for FA/clay ratios of 0.3 and 0.5 and 7.57 °C h/g for FA/clay ratio of 0.7. The relationship between strength and E/W is very useful for production industry to estimate the heat temperature and duration to attain the target strength for the required weight in making clay–FA geopolymer brick.

1. Introduction

The construction cost and serviceability of a building is mainly dependent upon production process, transportation and durability of construction and building materials. The selection of materials, taken into account the affordability and durability is therefore necessary. Clay-based bricks are mostly used in the northeastern region of Thailand as a construction and building material. These bricks are a mixture of cement and clay and therefore are sensitive to the climate change (collapse and swelling with the change in moisture content). The manufacturing of Portland cement causes greenhouse effects and global warming. The development of a new cementing agent with low carbon dioxide release is considered an attractive issue. Commercial

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http://dx.doi.org/10.1016/j.conbuildmat.2013.05.104

Table 1
Chemical composition of fly ash and silty clay using X-ray fluorescence (XRF).

Chemical composition (%)	Clay	FA
SiO_2	20.10	39.18
Al_2O_3	7.55	22.64
Fe_2O_3	32.89	15.45
CaO	26.15	11.3
MgO	0.47	1.69
SO_3	4.92	4.29
Na_2O	NA	1.81
K_2O	3.17	2.03
LOI	3.44	1.61

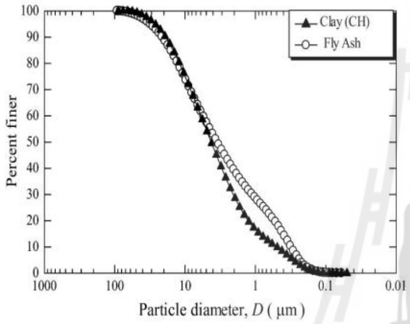
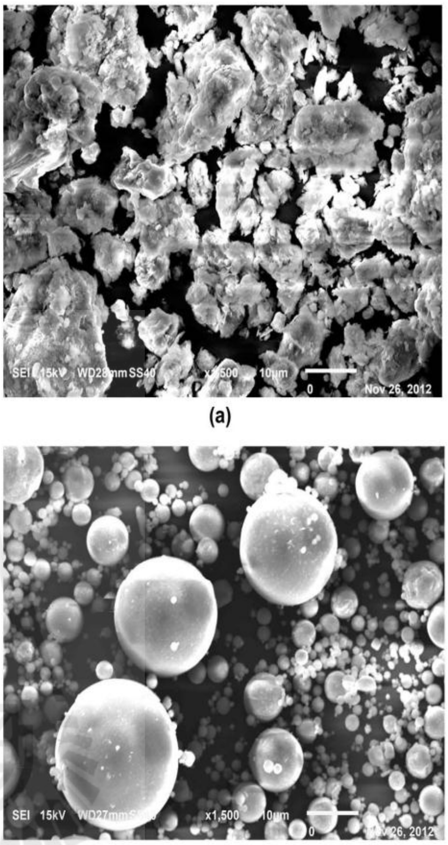


Fig. 1. Grain size distribution of clay and FA.



(a)

(b)

Fig. 2. SEM image of: (a) silty clay and (b) FA.

and industrial utilization of alkali-activated alumino-silicate cements, known as 'geopolymers' has becoming well-known over the past several decades because of their high performance (high strength and durability) and environmentally maintainable alternative to the ordinary Portland cement [1]. Geopolymers belong to a group of materials with increased interest due to low CO_2 emission and energy consumption. The hardening process of geopolymers at ambient temperature results in materials with ceramic-like properties, such as resistance against acids and high temperatures. The silica rich materials such as clay or kaolin [2], fly ash, and bottom ash [3] can be used as a source material to react with liquid alkaline activator. The commonly used liquid alkaline activator is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide (NaOH). Fly ash (FA) obtained from coal-fired electricity generation provides the greatest opportunity for commercial utilization of this technology due to the plentiful worldwide supply [4,5].

Recently, Sukmak et al. [6] investigated the possibility of using FA as a raw material and silty clay as aggregates to develop the clay–FA geopolymer brick. The liquid alkaline activator (L) was a mixture of Na_2SiO_3 and NaOH. The suitable ingredient for the clay–FA geopolymer is Na_2SiO_3/NaOH ratio of 0.7 and L/FA ratio of 0.6, which are lower than those of FA geopolymer. The research was limited to specific FA/clay ratio of 0.3, molding moisture content and specimen size. The present work is thus to investigate strength development with different ingredients (FA/clay ratio, Na_2SiO_3/NaOH, L/FA ratio, and molding moisture content), specimen weights, and heating conditions (curing temperature and duration). The microstructure of specimens was examined by the scanning electron microscope (SEM) to illustrate the effect of the geopolymerization products on the strength development. The outcome of this result is possibly applied to other clay–FA geopolymer.

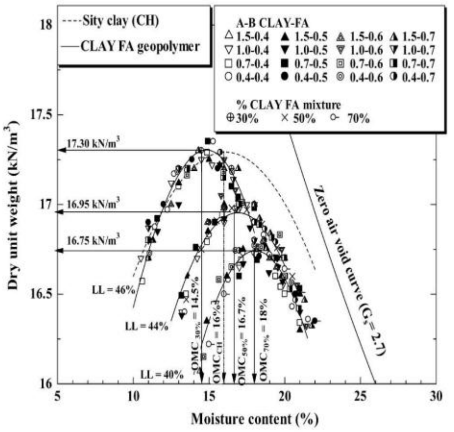


Fig. 3. Plots of dry unit weight versus molding moisture content of clay and clay–FA geopolymer for FA/clay ratios of 0.3, 0.5, and 0.7.

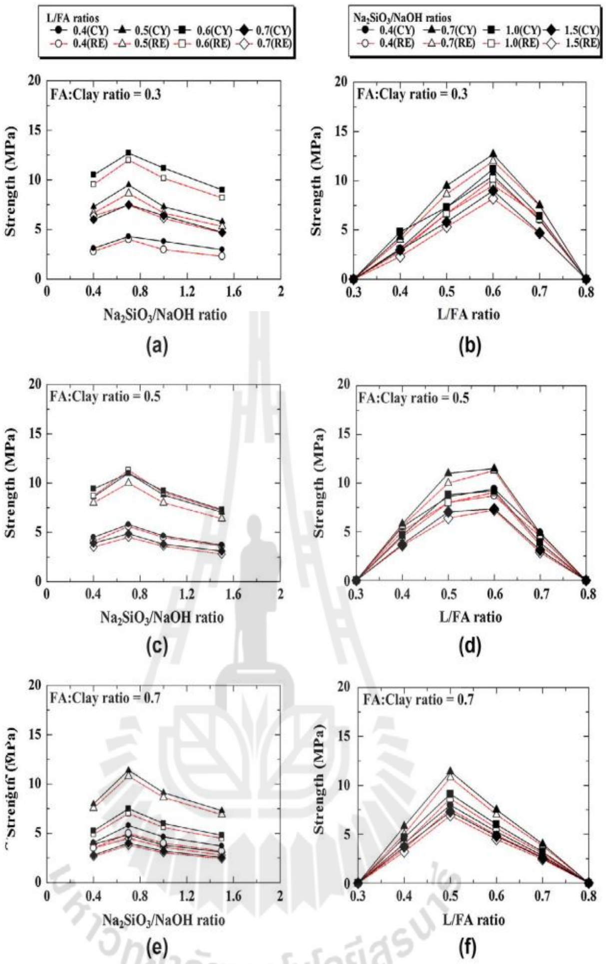


Fig. 4. The 28 day compressive strengths of clay–geopolymer.

2. Materials and methods

2.1. Materials

The studied soil is silty clay collected at a depth of 3–4 m from the Suranaree University of Technology campus in Nakhon Ratchasima, Thailand. The specific gravity is 2.70. The soil is weathered from claystone, which consists of clay, silt and sand [7]. Its liquid and plastic limits are approximately 54% and 28%, respectively. The soil contains 2%, 45% and 53% of sand, silt and clay, respectively. The natural moisture content is 5.3%. This clay is classified as high plasticity (CH), according to the Unified Soil Classification System (USCS). The free swell test result reveals that the clay is a low swelling type with a free swell ratio (FSR) of 1.0. The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum moisture content (OMC) of 16%, and maximum dry unit weight (γ_{dmax}) of 17.3 kN/m^3.

FA was acquired from the Mae Moh power plant in the northern region of Thailand. Table 1 illustrates the chemical composition of FA using X-ray fluorescence (XRF). Total amount of the major components (SiO_2, Al_2O_3 and Fe_2O_3) are 77.27%; therefore, in accordance with ASTM C 618, it is classified as class F fly ash. Figs. 1 and 2 show the grain size distribution curve and SEM photos of FA, compared with those of the silty clay, respectively. The silty clay's grain size distribution is similar to the FA's. The FA particles are fine and spherical whereas the clay particles are irregular in shape. Although the grain size distribution of both clay and FA is approximately the same, FA shows higher reactivity with the liquid alkaline in the development of geopolymer [6]. The liquid alkaline activator (L) is a mixture of Na_2SiO_3, consisting of 9% Na_2O and 30% SiO_2 by weight, and NaOH with a concentration of 10 molars.

2.2. Sample preparation

The clay–FA geopolymer specimen is a combination of silty clay, FA, liquid alkaline activator (Na_2SiO_3 and NaOH), and tap water. The FA/clay ratios of 0.3, 0.5, and 0.7; Na_2SiO_3/NaOH ratios of 0.4, 0.7, 1.0, and 1.5; L/FA ratios of 0.4, 0.5, 0.6, and 0.7 were used. The clay, FA, and L were thoroughly mixed with water to conduct the modified compaction test. Having obtained the compaction curves, the clay–FA–L–water mixture at the moisture contents between 0.6 and 1.2 OMC was statically compressed in a cylindrical mold with 50 mm in diameter and 100 mm in height and in a rectangular mold with 230 mm in length, 90 mm in width, and 75 mm in height. The compression was performed by a manual hydraulic jack. According to this procedure, all the specimens for different molding water contents have the same compression (modified Proctor) energy per volume. Practically, the OMC value at any compaction energy can be easily and rapidly approximated from the one known at a particular energy [8–10]. The specimens were dismantled, wrapped within vinyl sheet and stored in ambient temperature (27–30 °C) for 24 h, and then cured at 55 to 140 °C for 24 to 168 h.

The symbols for clay–FA geopolymer specimens are shown as follows:

$\underline{A} - \underline{B}$ CLAY – FA – $\underline{C}$ – $\underline{D}$OMC($\underline{CY}$ or $\underline{RE}$)

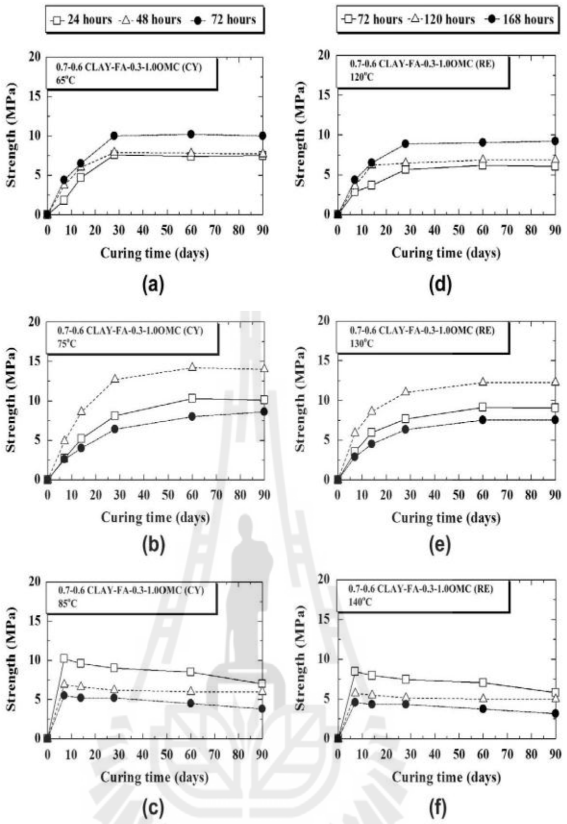


Fig. 5. Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.3 at different heat conditions.

where <u>A</u> is the Na_2SiO_3/NaOH ratio, <u>B</u> is the L/FA ratio, <u>C</u> is the FA/clay ratio, <u>D</u> is the state of moisture content (0.6, 0.8, 1.0, and 1.2 times), and (<u>CY</u> or <u>RE</u>) is small (cylindrical) or large (rectangular) specimens.

2.3. Methods

Compressive strengths of clay–FA geopolymer specimens were measured after 7, 14, 28, 60, and 90 days of curing in accordance with ASTM D 1633. The reported results were the average of at least five specimens in order to obtain reliable test results. In most cases, the results under the same testing condition were reproducible with a low standard deviation, *SD* ($SD/\bar{x} < 10\%$, where $\bar{x}$ is the mean strength value).

The clay–FA geopolymer specimens were carefully broken and small fragments were taken from the center for microstructure test. The SEM specimens were frozen at −195 °C by immersion in liquid nitrogen for 5 min and evacuated at a pressure of 0.5 Pa at −40 °C for 5 days [11–13]. All specimens were coated with gold before SEM (JOEL JSM-6400) analysis.

3. Results

Fig. 3 depicts the plots of dry unit weight versus molding moisture content of clay–FA geopolymer samples with different ingredients compared with those of clay and clay–FA mixtures (FA/clay ratios of 0.3, 0.5, and 0.7), under modified Proctor energy. For a given FA/clay ratio, the compaction curves of both clay–FA mixtures and clay–FA geopolymers are approximately the same for all Na_2SiO_3/NaOH and L/FA ratios. The maximum dry unit weight for compacted clay–FA mixture of 0.3 is slightly higher than that of compacted silty clay. However, for FA/clay ratios greater than 0.3, the clay–FA mixtures possess lower maximum dry unit weight than the compacted clay. The decrease in maximum dry unit weight is associated with the increase in OMC. The OMCs of the clay–FA mixtures and clay–FA geopolymers are almost the same.

The 28 day strength of clay–FA geopolymers at OMC with different ratios of Na_2SiO_3/NaOH, L/FA and FA/clay, and specimen dimensions are illustrated in Fig. 4. The small specimens were heated at 75 °C for 48 h while the large specimens were heated at 130 °C for 120 h. The result shows that the relationship between strength versus Na_2SiO_3/NaOH ratio and L/FA ratio for a given FA/clay ratio exhibits similar pattern with almost the same maximum strength, regardless of specimen sizes (weight). The maximum compressive strengths for both specimen dimensions are at Na_2SiO_3/NaOH ratio of 0.7 for all L/FA and FA/clay ratios. For a given Na_2SiO_3/NaOH ratio, the strength increases with increasing L/FA ratio until its optimum value and then tends to decrease. The strength is null at very low and high L/FA ratios of 0.3 and 0.8. The optimum L/FA ratio for the highest strength varies between 0.5 and 0.6 and tends to reduce with the increase in FA/clay ratio. It is 0.6 for FA/clay ratio of 0.3 and is 0.5 for FA/clay ratio of 0.7. These results identify that the optimum Na_2SiO_3/NaOH ratio is 0.7 for all FA/clay ratios, L/FA and specimens as well as the L/FA ratios of less than 0.3 and greater than 0.8 are not suitable to manufacture the clay–FA geopolymer.

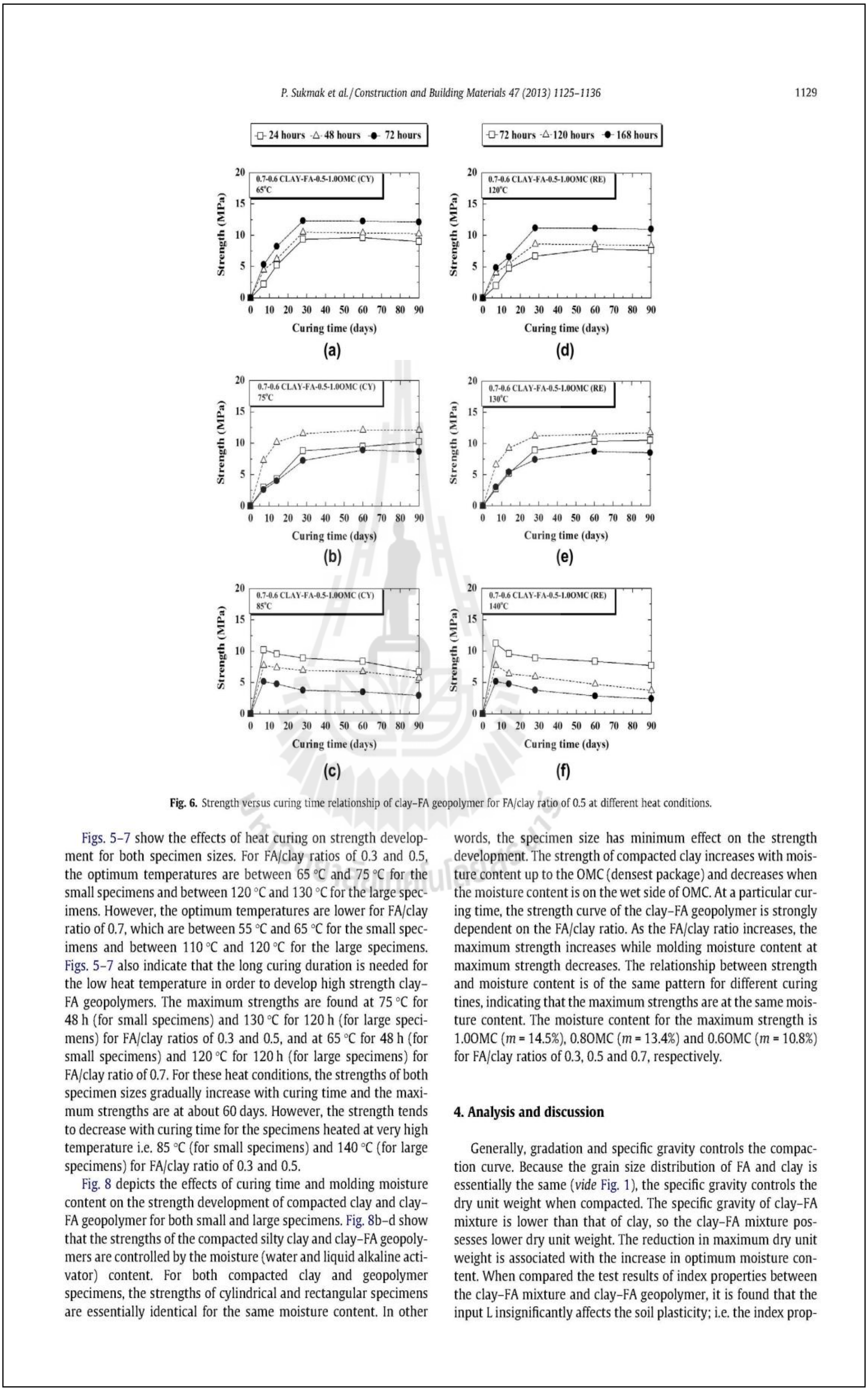


Fig. 6. Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.5 at different heat conditions.

Figs. 5–7 show the effects of heat curing on strength development for both specimen sizes. For FA/clay ratios of 0.3 and 0.5, the optimum temperatures are between 65 °C and 75 °C for the small specimens and between 120 °C and 130 °C for the large specimens. However, the optimum temperatures are lower for FA/clay ratio of 0.7, which are between 55 °C and 65 °C for the small specimens and between 110 °C and 120 °C for the large specimens. Figs. 5–7 also indicate that the long curing duration is needed for the low heat temperature in order to develop high strength clay–FA geopolymers. The maximum strengths are found at 75 °C for 48 h (for small specimens) and 130 °C for 120 h (for large specimens) for FA/clay ratios of 0.3 and 0.5, and at 65 °C for 48 h (for small specimens) and 120 °C for 120 h (for large specimens) for FA/clay ratio of 0.7. For these heat conditions, the strengths of both specimen sizes gradually increase with curing time and the maximum strengths are at about 60 days. However, the strength tends to decrease with curing time for the specimens heated at very high temperature i.e. 85 °C (for small specimens) and 140 °C (for large specimens) for FA/clay ratio of 0.3 and 0.5.

Fig. 8 depicts the effects of curing time and molding moisture content on the strength development of compacted clay and clay–FA geopolymer for both small and large specimens. Fig. 8b–d show that the strengths of the compacted silty clay and clay–FA geopolymers are controlled by the moisture (water and liquid alkaline activator) content. For both compacted clay and geopolymer specimens, the strengths of cylindrical and rectangular specimens are essentially identical for the same moisture content. In other words, the specimen size has minimum effect on the strength development. The strength of compacted clay increases with moisture content up to the OMC (densest package) and decreases when the moisture content is on the wet side of OMC. At a particular curing time, the strength curve of the clay–FA geopolymer is strongly dependent on the FA/clay ratio. As the FA/clay ratio increases, the maximum strength increases while molding moisture content at maximum strength decreases. The relationship between strength and moisture content is of the same pattern for different curing tines, indicating that the maximum strengths are at the same moisture content. The moisture content for the maximum strength is 1.0OMC ($m = 14.5\%$), 0.8OMC ($m = 13.4\%$) and 0.6OMC ($m = 10.8\%$) for FA/clay ratios of 0.3, 0.5 and 0.7, respectively.

4. Analysis and discussion

Generally, gradation and specific gravity controls the compaction curve. Because the grain size distribution of FA and clay is essentially the same (*vide* Fig. 1), the specific gravity controls the dry unit weight when compacted. The specific gravity of clay–FA mixture is lower than that of clay, so the clay–FA mixture possesses lower dry unit weight. The reduction in maximum dry unit weight is associated with the increase in optimum moisture content. When compared the test results of index properties between the clay–FA mixture and clay–FA geopolymer, it is found that the input L insignificantly affects the soil plasticity; i.e. the index prop-

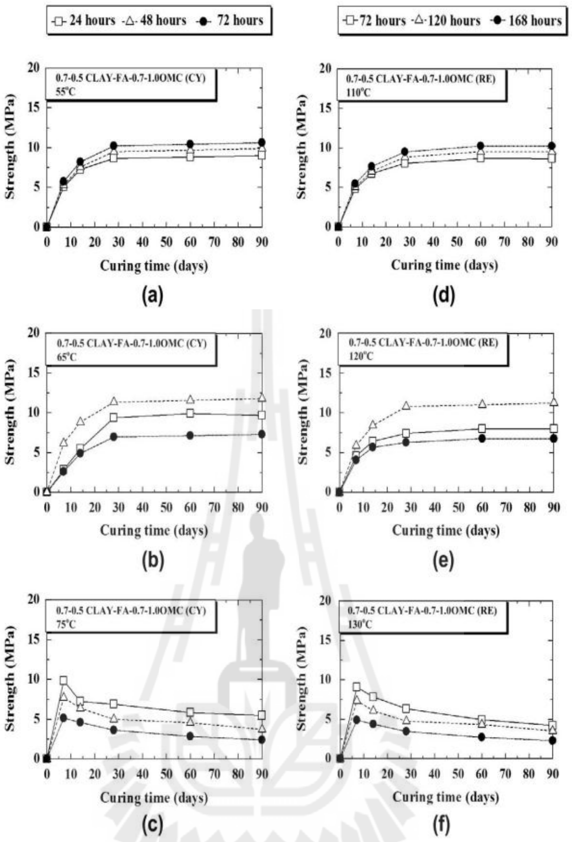


Fig. 7. Strength versus curing time relationship of clay–FA geopolymer for FA/clay ratio of 0.7 at different heat conditions.

erties of clay–FA mixture and clay–FA geopolymer are identical for the same FA/clay ratio (*vide* Table 2). Because the liquid limit controls the compaction curve [8,10,12], the compaction curves of compacted clay–FA mixture and clay–FA geopolymer are essentially identical for the same FA/clay ratio (Fig. 3).

The strength development in clay–FA geopolymer specimen is controlled by four factors; namely, L, heat condition, FA/clay ratio and molding moisture content. For both specimen sizes, at a particular Na_2SiO_3/NaOH ratio and curing condition, the compressive strength increases rapidly with L/FA ratio until a maximum value. Beyond this value, the compressive strength decreases with L/FA ratio. It is of interest to note that the optimum L/FA ratio is dependent upon FA replacement (FA/clay ratio) and irrespective of specimen size. It is approximately 0.6 for FA/clay ratio of 0.3 and 0.5 for FA/clay ratio of 0.7. It is a fact that the clay contains alumino-silicate layers with both external and internal negative layer surfaces as indicated by its relatively high CEC of 31.5 meq/100 g clay. The negative layers act as a huge anion and a swarm of positively charged cations (such as Na, K, Ca, and Mg) [14–16]. When the clay content decreases (FA/clay ratio increases), the negative layer surfaces decrease. In addition to the reduction in negative surfaces, the increase in FA/clay ratio increases the alumino-silicate for the geopolymerization reaction [17,18]. Sukmak et al. [6] showed the leaching results of SiO_2 and Al_2O_3 in the clay and FA using the X-ray fluorescence (XRF). The clay exhibited the leaching capacity of SiO_2 and Al_2O_3 less than the FA because the silica and alumina in FA are mostly amorphous. Both the reduction in negative surfaces and the increase in amorphous alimino-silicate result in the decrease in L required for the cation exchange and the increase in the degree of the geopolymerization reaction. Consequently, the optimum L/FA ratio decreases as FA/clay ratio increases.

It is now to examine the effect of the heat conditions on the strength development. For all Na_2SiO_3/NaOH and L/FA ratios, the heat temperature and the duration required for the geopolymerization are dependent upon the specimen dimension and FA/clay ratio. With larger specimen size (weight) and lower FA/clay ratio, the higher temperature and longer duration are required to attain the highest strength. Sukmak et al. [6] depicted the effect of the heat condition on the microstructure of clay–FA geopolymer specimens at a particular FA/clay ratio. For a very high temperature, the clay–FA geopolymer experienced a substantial loss of moisture. The loss of moisture played a major part in obtaining a crack-free geopolymer. Consequently, the rapid drying during curing should be avoided, while curing at a lower relative humidity was preferable. For low temperature, the heat duration stimulated the geopolymerization reaction as shown by the increase in the geopolymerization products. However, the heat duration is not always positive. The excess heat duration also caused the microcracks on the specimen structure. In this study, it is found that the excess temperature is strongly dependent upon the specimen size and FA/clay ratio. For FA/clay ratios of 0.3 and 0.5, it is 85 °C for the small specimen and 140 °C for the large specimen. For

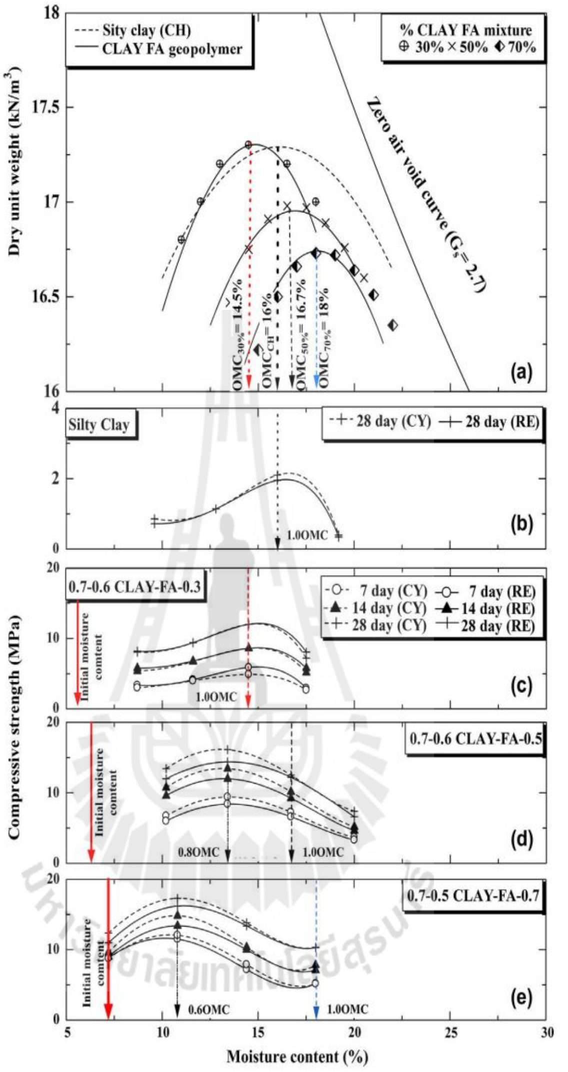


Fig. 8. Role of curing time and molding moisture content on the strength development of clay–FA geopolymer.

FA/clay ratio of 0.7, it is 75 °C for the small specimen and 130 °C for the large specimen.

The combined effect from the heat temperature and duration was taken into account by the heat energy parameter [6]. The heat energy is the product of heat temperature and duration. At low heat temperature, even though the temperature and duration are different, the strength at a given curing time and weight is practically identical as long as the heat energy is the same. The strength increases with the heat energy up to a certain level and then decreases. It is found from this investigation that the heat energy is not the controlled parameter for different specimen sizes. In other words, the specimen weight must be taken into consideration. The larger specimens with higher weights require higher energy for the geopolymerization development. Consequently, the heat energy per weight, E/W is thus proposed as a key parameter controlling the strength development. Fig. 9 shows the applicability of E/W for FA/clay ratios of 0.3, 0.5 and 0.7. Even with different specimen weights and heat conditions, the strength development for both 7 and 14 days is governed by the E/W and FA/clay ratio. Higher degrees of correlation of 0.80 are found for both curing times. For FA/clay ratios of 0.3 and 0.5, the optimum E/W (providing the highest strength) is approximately 8.5 °C h/g for both curing times. It is approximately 7.57 °C h/g for FA/clay ratio of 0.7. This result shows that the optimum E/W increases as FA/clay ratio decreases. For better understanding of the role of FA content on the required E/W, the test data of the FA geopolymer (no clay) is compared in the Figure. It is shown that the optimum E/W for FA geopoplymer is lower than that of clay–FA geopolymers. This is a fact that silica and alumina in FA are mostly amorphous and therefore the heat energy required for geopolymerization reaction is lower. Beyond this optimum value, the specimens shrink and crack due to the loss of pore fluid, which results in the strength reduction.

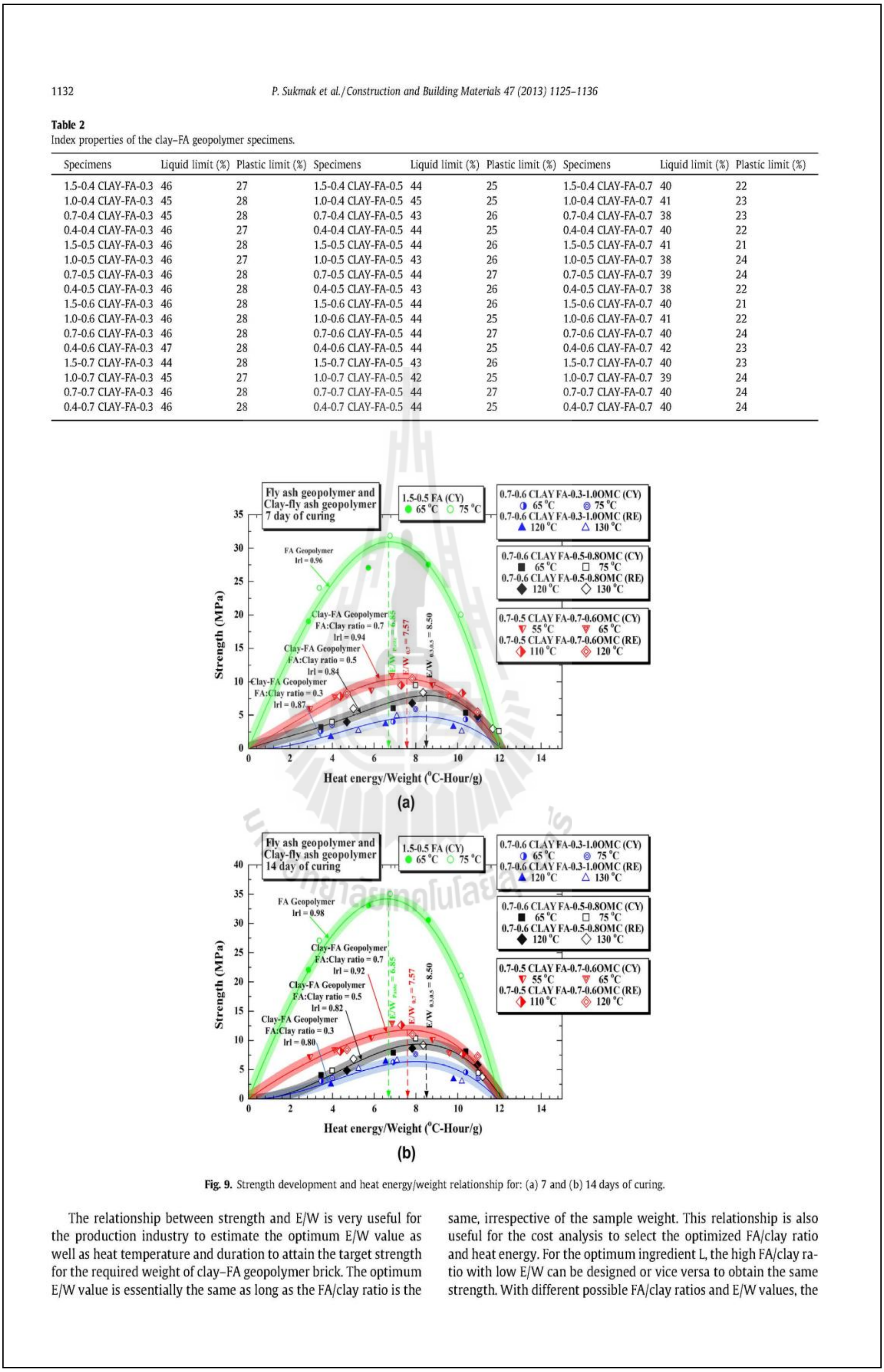
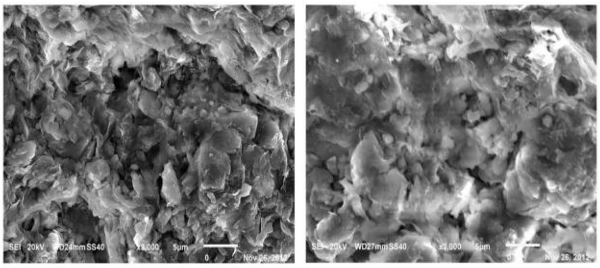


Table 2
Index properties of the clay–FA geopolymer specimens.

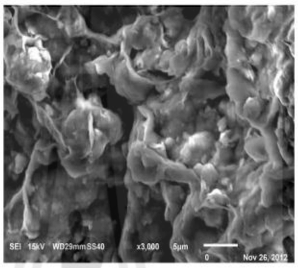
Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)	Specimens	Liquid limit (%)	Plastic limit (%)
1.5-0.4 CLAY-FA-0.3	46	27	1.5-0.4 CLAY-FA-0.5	44	25	1.5-0.4 CLAY-FA-0.7	40	22
1.0-0.4 CLAY-FA-0.3	45	28	1.0-0.4 CLAY-FA-0.5	45	25	1.0-0.4 CLAY-FA-0.7	41	23
0.7-0.4 CLAY-FA-0.3	45	28	0.7-0.4 CLAY-FA-0.5	43	26	0.7-0.4 CLAY-FA-0.7	38	23
0.4-0.4 CLAY-FA-0.3	46	27	0.4-0.4 CLAY-FA-0.5	44	25	0.4-0.4 CLAY-FA-0.7	40	22
1.5-0.5 CLAY-FA-0.3	46	28	1.5-0.5 CLAY-FA-0.5	44	26	1.5-0.5 CLAY-FA-0.7	41	21
1.0-0.5 CLAY-FA-0.3	46	27	1.0-0.5 CLAY-FA-0.5	43	26	1.0-0.5 CLAY-FA-0.7	38	24
0.7-0.5 CLAY-FA-0.3	46	28	0.7-0.5 CLAY-FA-0.5	44	27	0.7-0.5 CLAY-FA-0.7	39	24
0.4-0.5 CLAY-FA-0.3	46	28	0.4-0.5 CLAY-FA-0.5	43	26	0.4-0.5 CLAY-FA-0.7	38	22
1.5-0.6 CLAY-FA-0.3	46	28	1.5-0.6 CLAY-FA-0.5	44	26	1.5-0.6 CLAY-FA-0.7	40	21
1.0-0.6 CLAY-FA-0.3	46	28	1.0-0.6 CLAY-FA-0.5	44	25	1.0-0.6 CLAY-FA-0.7	41	22
0.7-0.6 CLAY-FA-0.3	46	28	0.7-0.6 CLAY-FA-0.5	44	27	0.7-0.6 CLAY-FA-0.7	40	24
0.4-0.6 CLAY-FA-0.3	47	28	0.4-0.6 CLAY-FA-0.5	44	25	0.4-0.6 CLAY-FA-0.7	42	23
1.5-0.7 CLAY-FA-0.3	44	28	1.5-0.7 CLAY-FA-0.5	43	26	1.5-0.7 CLAY-FA-0.7	40	23
1.0-0.7 CLAY-FA-0.3	45	27	1.0-0.7 CLAY-FA-0.5	42	25	1.0-0.7 CLAY-FA-0.7	39	24
0.7-0.7 CLAY-FA-0.3	46	28	0.7-0.7 CLAY-FA-0.5	44	27	0.7-0.7 CLAY-FA-0.7	40	24
0.4-0.7 CLAY-FA-0.3	46	28	0.4-0.7 CLAY-FA-0.5	44	25	0.4-0.7 CLAY-FA-0.7	40	24

Fig. 9. Strength development and heat energy/weight relationship for: (a) 7 and (b) 14 days of curing.

The relationship between strength and E/W is very useful for the production industry to estimate the optimum E/W value as well as heat temperature and duration to attain the target strength for the required weight of clay–FA geopolymer brick. The optimum E/W value is essentially the same as long as the FA/clay ratio is the same, irrespective of the sample weight. This relationship is also useful for the cost analysis to select the optimized FA/clay ratio and heat energy. For the optimum ingredient L, the high FA/clay ratio with low E/W can be designed or vice versa to obtain the same strength. With different possible FA/clay ratios and E/W values, the

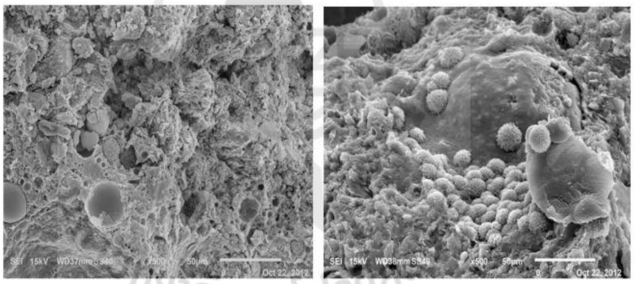


(a) m = 12.8% (0.8OMC) **(b) m = 16% (OMC)**



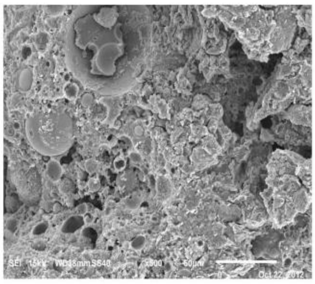
(c) m = 19.2% (1.2OMC)

Fig. 10. SEM images of compacted clay for: (a) $m = 12.8\%$, (b) $m = 16\%$ and (c) $m = 19.2\%$.



(a) 0.7-0.6 CLAY-FA-0.3
m = 11.6% (0.8OMC)

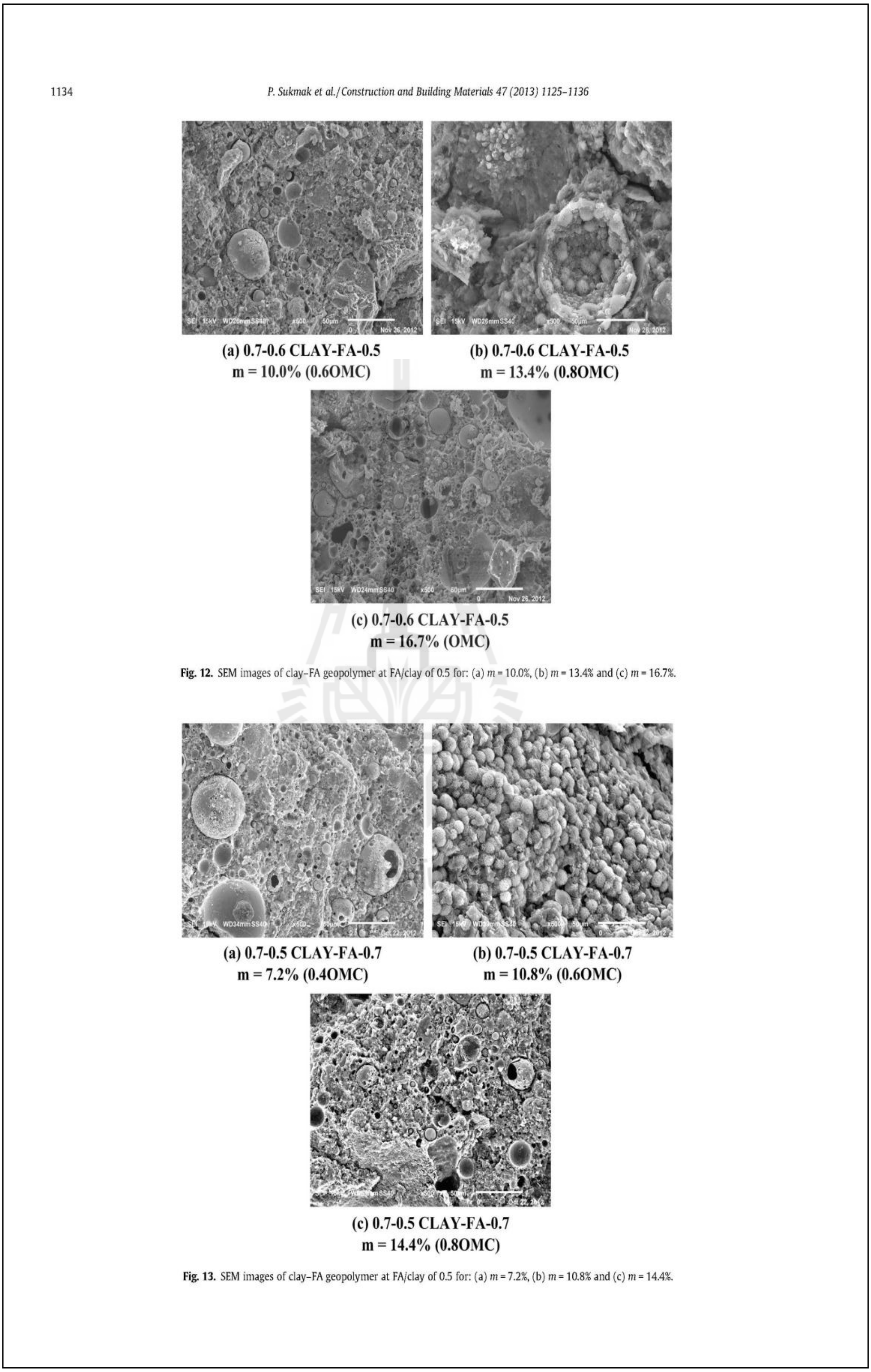
(b) 0.7-0.6 CLAY-FA-0.3
m = 14.5% (OMC)



(c) 0.7-0.6 CLAY-FA-0.3
m = 17.4% (1.2OMC)

Fig. 11. SEM images of clay–FA geopolymer at FA/clay of 0.3 for: (a) $m = 11.6\%$, (b) $m = 14.5\%$ and (c) $m = 17.4\%$.

cost optimization can be performed. For a selected brick weight, the required heat energy is then estimated; hence the duration for a specific heat temperature. The manufacturing of geoploymer bricks at E/W values beyond the optimum value is not recommended even with high strength. This is because micro-crack in the brick might cause the low durability. The formulation of the



(a) 0.7-0.6 CLAY-FA-0.5
m = 10.0% (0.6OMC)

(b) 0.7-0.6 CLAY-FA-0.5
m = 13.4% (0.8OMC)

(c) 0.7-0.6 CLAY-FA-0.5
m = 16.7% (OMC)

Fig. 12. SEM images of clay–FA geopolymer at FA/clay of 0.5 for: (a) $m = 10.0\%$, (b) $m = 13.4\%$ and (c) $m = 16.7\%$.

(a) 0.7-0.5 CLAY-FA-0.7
m = 7.2% (0.4OMC)

(b) 0.7-0.5 CLAY-FA-0.7
m = 10.8% (0.6OMC)

(c) 0.7-0.5 CLAY-FA-0.7
m = 14.4% (0.8OMC)

Fig. 13. SEM images of clay–FA geopolymer at FA/clay of 0.5 for: (a) $m = 7.2\%$, (b) $m = 10.8\%$ and (c) $m = 14.4\%$.

proposed relationship is on sound principle and developed from two weights of the geopolymer specimens. The relationship can be further refined with the analysis of more data for different specimen weights, temperatures and durations.

The effect of molding moisture content on the strength development of compacted clay and clay–FA geopolymer is being illustrated. For compacted silty clay, the clay structure, which is governed by molding moisture content, mainly controls the strength [13]. Fig. 10 shows the SEM photos of the compacted specimen under the modified Proctor energy at different moisture contents ranging from (0.8–1.2)OMC. On the wet side of optimum (*vide* Fig. 10c), a dispersed structure is likely to develop because the quantity of pore water is sufficient to develop a complete double layer of the ions that are attracted to the clay particles. As such, the clay particles and clay clusters easily slide over each other when sheared and results in low strength. On the dry side of optimum (*vide* Fig. 10a), there is not sufficient water to develop a complete double-layer; thus, the distance between two clay platelets is small enough for van der Waals type attraction to dominate. Such an attraction leads to flocculation with more surface to edge bonds; thus, more aggregates of platelets lead to compressible flows, which make up the overall structure. At the OMC, the structure results from a combination of these two characteristics (*vide* Fig. 10b). Under this condition, the compacted specimen exhibits the highest strength (*vide* Fig. 8b).

Unlike the compacted clay, the strength of the clay–FA geopolymer is contributed from two components: mechanical and chemical. Because the geopolymer specimens were prepared at the same compression energy per volume (modified Proctor), the mechanical component is mainly governed by the soil densification, where the OMC provides the densest packing. At very low moisture content, the L is not sufficient for geopolymerization reaction because it is taken by the clay particles for developing the soil structure. With increasing moisture content (densification), the clay and FA particles come closer due to the water lubrication and thus the gopolymerization reaction can be better developed. As such, the strengths of each ingredient increase with molding moisture content up to the highest values and the highest strengths of clay–FA geopolymer specimens are not at the OMC. The contribution from the chemical component (geopolymerization) decreases with the excessive molding moisture content due to the reduction in L concentration. The moisture content providing the highest strength is thus the combination of these two components. Figs. 11–13 show the SEM photos of the clay–FA geopolymers cured for 60 days, at different molding moisture contents for FA/clay ratios of 0.3, 0.5 and 0.7 respectively. The geopolymerization products are clearly seen at OMC, 0.8OMC and 0.6OMC for FA/clay ratios of 0.3, 0.5 and 0.7, respectively, which are associated with the highest strength. Geopolymerization products produced are clearly observed around FA particles and in the pores. The geopolymer gel is in a form of colloid with different sizes ranging from less than 1 μm to about 20 μm. As more gel is formed, it overwhelms clay and FA particles and forms a continuous mass of gel resulting in a relatively dense alumino-silicate and strong bond among clay particles [19].

5. Conclusions

This paper investigates the effect of ingredients (FA/clay ratio, Na_2SiO_3/NaOH ratio, L/FA ratio), molding moisture content, specimen sizes, and heating conditions (heat temperature and heat duration) on the strength development in clay–fly ash geopolymer. The following conclusions are drawn.

(1) The FA replacement reduces liquid limit and dry unit weight of the clay, although the particle size distribution of FA and clay is almost the same. The compaction curves of clay–FA mixture and clay–FA geopolymer for the same clay–FA ratio are identical because the L insignificantly affects the index properties for the same FA/clay ratio.

(2) The NaOH leaches the silicon and aluminum in amorphous phase of FA and the Na_2SiO_3 acts as a binder. In this study, the liquid alkaline activator (L) is a mixture of Na_2SiO_3, consisting of 9% Na_2O and 30% SiO_2 by weight, and NaOH with a concentration of 10 molars. With this condition, the Na_2SiO_3/NaOH ratio of 0.7 can be considered as constant for the manufacturing of clay–FA geopolymer.

(3) The optimum L/FA ratio is dependent upon only the FA replacement (FA/clay ratio). When the clay content decreases (the FA/clay decreases), the L required for the reaction decreases. It is approximately 0.6 for FA/clay ratio of 0.3 and 0.5 for FA/clay ratio of 0.7.

(4) The relationship between strength and E/W is proposed. The optimum E/W at the highest strength is approximately 8.50 °C h/g for FA/clay ratios of 0.3 and 0.5 and approximately 7.57 °C h/g for FA/clay ratio of 0.7. The relationship is very useful for production industry to estimate the heat temperature and duration to attain the target strength for the required weight of clay–FA geopolymer brick.

(5) The molding moisture content for the highest strength is the combination of mechanical and chemical components. The mechanical component is governed by the soil densification, where the OMC provides the densest packing. The contribution from the chemical component (geopolymerization) decreases with increasing the molding moisture content due to the reduction in L concentration. At very low moisture content, the L is not sufficient for geopolymerization reaction because it is taken by the clay particles for developing the soil structure, hence low strength is obtained. The moisture contents for the highest strength are 1.0OMC, 0.8 OMC and 0.6 OMC for FA/clay ratios of 0.3, 0.5 and 0.7, respectively.

Acknowledgements

The first author is grateful to the Thailand Research Fund for Ph.D. study financial support under the Ph.D. Royal Jubilee program. The authors acknowledge the financial support from the Higher Education Research Promotion and National Research University Project of Thailand, Office of Higher Education Commission. Financial support, facilities and equipment provided from the Suranaree University of Technology are very much appreciated.

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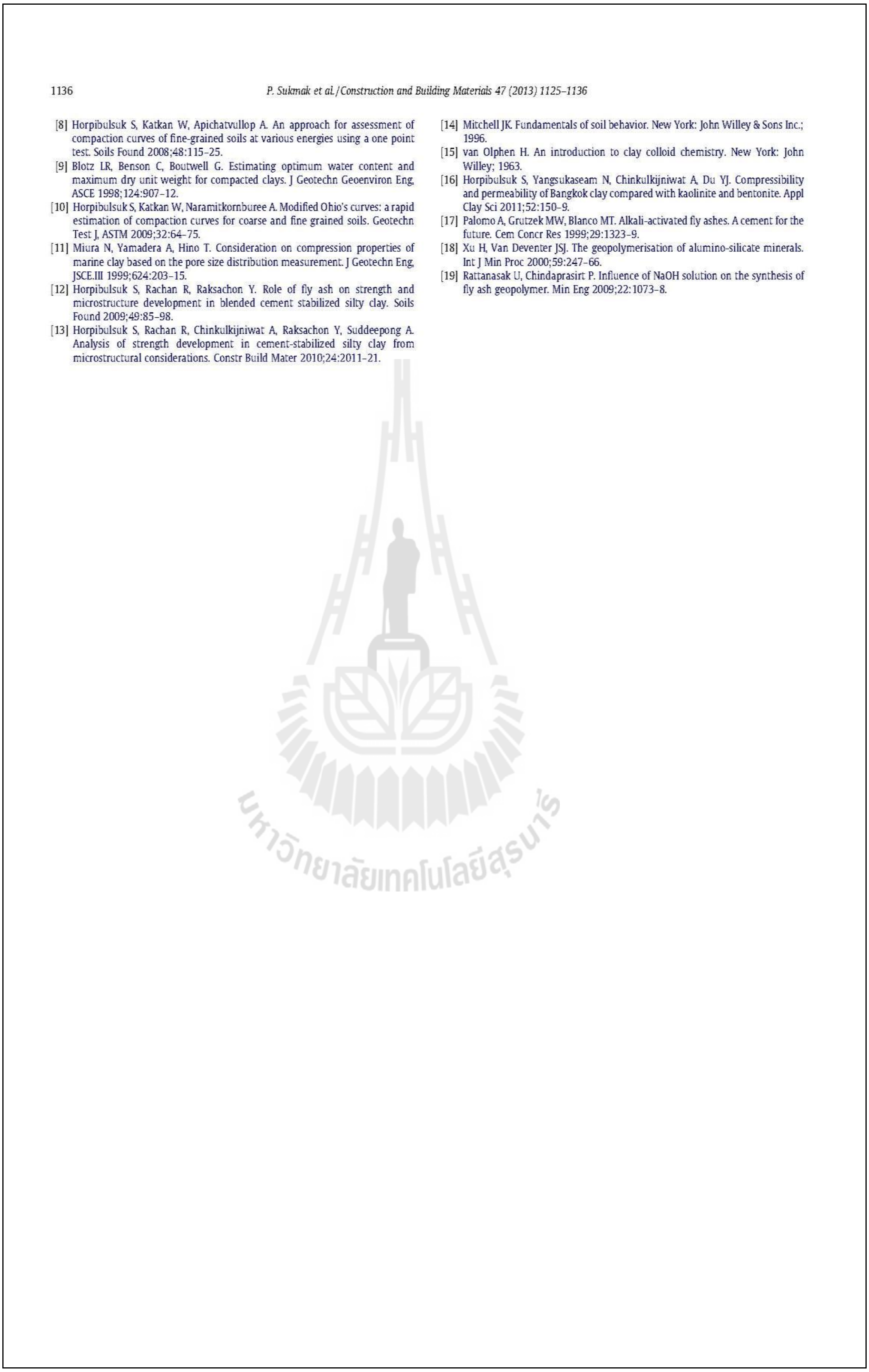

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BIOGRAPHY

Miss Patimapon Sukmak was born in April 1987 in Nakhon Ratchasima, Thailand. She obtained her Bachelor’s degree in Civil Engineering from the School of Civil Engineering, Suranaree University of Technology in 2008. Then, she has been awarded a Royal Golden Jubilee (RGJ) Ph.D. Program Scholarship from the Thailand Research Fund (TRF) in 2008 for her Ph.D. study in the School of Civil Engineering, Suranaree University of Technology. During her Ph.D. study (2009-2012), she has worked as a teaching assistant for Surveying Laboratory and Applied Mechanics Laboratory. She has visited the School of Arts and Sciences, Australian Catholic University, New South Wales, Australia for her oversea research under the supervision of Dr. Pre De Silva from March 25, 2013 to September 22, 2013. She has published 2 international ISI journal papers and 1 keynote lecture in 18th National Convention in Civil Engineering, Chiang Mai, Thailand.