SOIL STABILIZATION BY CALCIUM CARBIDE RESIDUE AND FLY ASH BASED GEOPOLYMER

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ปูนซีเมนต์เป็นวัสดุโดยทั่วไปที่ใช้ในการใช้ปรับปรุงดินทั้งสภานะไม่อิ่มตัวด้วยน้ำ และอิ่มตัวด้วยน้ำ เนื่องจากหาได้ง่าย และสมเหตุสมผลด้านราคาค่าใช้จ่าย จากการที่ราคาต่อหน่วยที่สูง และการใช้พลังงานสูงในกระบวนการผลิตปูนซีเมนต์ เป็นเหตุให้มีความต้องการหาวัสดุทางเลือกชนิดอื่นแทนที่ซีเมนต์ จีโอโพลิเมอร์เป็นวัสดุเชื่อมประสารที่เป็นมิตรกับสิ่งแวดล้อม และมีประสิทธิภาพที่ดีกว่าปูนซีเมนต์ งานวิจัยนี้มีจุดมุ่งหมายที่จะศึกษาพัฒนาการใช้เถ้าลอยจีโอโพลิเมอร์เพื่อปรับปรุงปัญหาของ ดินเหนียวปนดินตะกอนไม่อิ่มตัวด้วยน้ำและดินเหนียวที่ตกตะกอนในน้ำทะเล โดยใช้กากแคลเซียมคาร์ไบด์ซึ่งเป็นวัสดุเหลือทิ้งจากโรงงานผลิตก๊าซอะเซทิลีนมีแคลเซียมเป็นองค์ประกอบหลักเป็นวัสดุผสมเพิ่มช่วยเร่งปฏิกิริยาจีโอโพลิเมอร์ไลซ์เซชั่น วิทยานิพนธ์นี้ประกอบด้วย 2 บทหลัก (บทที่ 3 และ 4)

บทที่ 3 ศึกษาการใช้กากแคลเซียมคาร์ไบด์เป็นสารอัลคาไลน์ ร่วมกับเถ้าลอยปรับปรุงคุณสมบัติทางวิศวกรรมของดินเหนียวปนดินตะกอนเพื่อใช้เป็นวัสดุคันทาง ตัวแปรที่ศึกษาได้แก่ อัตราส่วนโซเดียมซิลิเกตต่อน้ำ ปริมาณเถ้าลอย อายุบ่ม อุณหภูมิการบ่ม และสภาวะแช่น้ำ สำหรับปริมาณกากแคลเซียมคาร์ไบด์ร้อยละ 7 จากศึกษาการพัฒนากำลังอัดโดยการทดสอบกำลังอัดแกนเดียว พบว่ากากแคลเซียมคาร์ไบด์ชะล้าง ซิลิกอนและอลูมินัมในรูปอสัณฐานในเถ้าลอย และถูกทำปฏิกิริยาโดยสารละลายโซเดียมซิเกต กำลังสูงสุดที่สภาวะแช่น้ำของดินเหนียว-เถ้าลอยจีโอโพลิเมอร์ พบที่อัตราส่วนสารละลายโซเดียมซิเกตต่อน้ำที่ 0.6 และอัตราส่วนเถ้าลอยร้อยละ15 โดยอัตราส่วนเหมาะสมของสารละลายโซเดียมซิลิเกตสามารถประมาณได้จากค่าคุณสมบัติพื้นฐาน กำลังอัดที่ 7 วันที่สภาวะแช่น้ำที่จุดเหมาะสมสามารถผ่านมาตรฐานของวัสดุคันทางของกรมทางหลวง

บทที่ 4 เป็นศึกษาการพัฒนากำลังอัดแกนเดียว และปริมาณคาร์บอนฟุตพรินต์ของกากแคลเซียมคาร์ไบด์ และเถ้าลอยปรับปรุงดินเหนียวที่ตกตะกอนในน้ำทะเล Coode Island Silt (CIS) สารละลายอัลคาไลน์ที่ใช้เป็นส่วนผสมของสารละลายโซเดียมซิลิเกต และโซเดียมไฮดรอกไซด์ ตัวแปรที่ศึกษาได้แก่ อัตราส่วนสารละลายโซเดียมซิลิเกตต่อสารละลายโซเดียมไฮดรอกไซด์ ความเข้มข้นของสารละลายโซเดียมไฮดรอกไซด์ อัตราส่วนสารอัลคาไลน์ต่อเถ้าลอย ปริมาณความชื้นเริ่มต้น ปริมาณเถ้าลอย ปริมาณกากแคลเซียมคาร์ไบด์ อายุบ่ม และอุณหภูมิการบ่ม พบว่าดินเหนียว CIS ที่ปรับปรุงมีค่ากำลังอัดแกนเดียวขึ้นกับค่าปริมาณเถ้าลอย และความเข้มข้นของสารละลาย

โซเดียมไฮดรอกไซด์ บทบาทของกากแคลเซียมคาร์ไบด์ต่อกำลังอัดแกนเดียวของดินเหนียว CIS ปรับปรุงด้วยเถ้าลอยจีโอโพลิเมอร์ สามารถแบ่งได้ 3 ช่วง ได้แก่ inactive, active และ quasi-inert ที่บริเวณช่วง active พบที่ปริมาณกากแคลเซียมคาร์ไบด์ร้อยละ 7 ถึง 12 ซึ่งเป็นช่วงแนะนำให้ใช้งาน ปริมาณคาร์บอนฟุตพรินต์ของดินเหนียวปรับปรุงด้วยจีโอโพลิเมอร์ พบว่าต่ำกว่ากรณีปรับปรุงด้วยซีเมนต์ที่ค่ากำลังอัดเท่ากัน การลดปริมาณคาร์บอนฟุตพรินต์ที่กำลังสูงแสดงให้เห็นประโยชน์ของการใช้เถ้าลอยจีโอโพลิเมอร์ซึ่งเป็นมิตรกับสิ่งแวดล้อมเป็นวัสดุทางเลือกในการปรับปรุงดินเหนียวแทนที่ซีเมนต์ ประโยชน์ที่ได้จากวิทยานิพนธ์นี้ได้แก่ สามารถสร้างประโยชน์จากการใช้กากแคลเซียมคาร์ไบด์ด้านอื่นนอกจากใช้เป็นวัสดุถมดิน และลดปริมาณการปล่อยก๊าซคาร์บอนของกระบวนการผลิตปูนซีเมนต์

สาขาวิชา วิศวกรรมโยธา ลายมือชื่อนักศึกษา ____________________________
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CHAYAKRIT PHETCHUAY : SOIL STABILIZATION BY CALCIUM
CARBIDE RESIDUE AND FLY ASH BASED GEOPOLYMER. THESIS
ADVISOR : PROF. SUKSUN HORPIBULSUK, Ph.D., 159 PP.

STRENGTH/COODE ISLAND SILT/SILTY CLAY/CCR /GEOPOLYMER

Portland cement is commonly used for soil improvement in both unsaturated and saturated states because it is readily available at reasonable cost. The high unit cost and energy intensive process for the production of Portland cement are the driving forces for the constant need within the industry to seek alternative cementitious binders. Geopolymer is an environmentally friendly cementing agent and better engineering performance than ordinary Portland cement. The main objective of this research is to investigate the viability of using Fly Ash (FA) based geopolymer to stabilize unsaturated collapsible silty clay and saturated marine clay. Calcium Carbide Residue (CCR), by-products from acetylene gas, is used as a calcium-rich additive to stimulate the geopolymerization reaction. This thesis consists of two main chapters (Chapter III and IV).

Chapter III investigates the viability of using CCR as an alkaline activator and FA as a precursor to improve the engineering properties of an unsaturated silty clay to facilitate its usage as stabilized subgrade material. The influential factors studied are Na_2SiO_3/water ratio, FA replacement ratio, curing time, curing temperature and soaking condition. Strength development is investigated via the Unconfined Compression Strength (UCS) test. Results show that CCR dissolves the silicon and aluminum in amorphous phase of FA and the Na_2SiO_3 acts as a binder. The maximum soaked UCS of the FA geopolymer stabilized silty clay is found at Na_2SiO_3/water ratio of 0.6 and FA replacement ratio of 15%. The optimal Na_2SiO_3/water ratio is approximated from index test, which is a very practical approach. The 7-day soaked UCS at the optimal ingredient meets the strength requirement for subgrade materials specified by the local national road authority.

Chapter IV investigates UCS development and the carbon footprint of Calcium Carbide Residue (CCR) and Fly Ash (FA based) geopolymer stabilized marine Coode Island Silt (CIS). The liquid alkaline activator used is a mixture of sodium silicate solution (Na_2SiO_3) and sodium hydroxide (NaOH). The influential factors studied are Na_2SiO_3/NaOH ratio, NaOH concentration, L/FA ratio, initial water content, FA content, CCR content, curing temperature and curing time. The UCS of stabilized CIS was found to be strongly dependent upon FA content and NaOH concentration. The optimal ingredient providing the highest UCS is found to be dependent on water content. The role of CCR on UCS of FA geopolymer stabilized CIS can be classified into three zones: inactive, active and quasi-inert. The active zone where CCR content is between 7% and 12% is recommended in practice. The carbon footprints of the geopolymer stabilized soils are lower than those of cement stabilized soil at the same strengths. The outcome of this thesis would divert significant quantity of CCR from landfills and considerably reduce carbon emissions due to Portland cement production.

School of Civil Engineering Student's Signature ____________________

Academic Year 2015 Advisor's Signature ____________________

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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

FA = Fly ash

OWC = optimum water content

CCR = calcium carbide residue

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

CIS = Coode Island Silt

CG = spent coffee grounds

OLC = optimum liquid content

CHAPTER I

INTRODUCTION

1.1 Statement of problems

Problematic soils are mainly swelling and collapsible soils and soft marine clays, which significantly need the soil improvement. Silty clay in the northeastern region of Thailand is a problematic unsaturated soil, which cannot use for constructional material due to its high swelling. One of the extensively used techniques for the improvement of problematic soil in relatively dry states is the compaction of the in situ soil, mixed with cement slurry. An advantage of this technique is that adequate strength can be achieved in a short time. The effects of some influential factors (i.e., water content, cement content, curing time, and compaction energy) on the microstructure and engineering characteristics of cement-stabilized soils have been extensively researched (Horpibulsuk and Miura, 2001; Horpibulsuk et al. 2003, 2004a, b, 2005, 2006, 2010a, b, 2011b)

The marine clay named Coode Island Silt (CIS) in the Yarra Delta, eastern part of Melbourne Central Business District, is of poor geotechnical properties and classified as a problematic soil. This soft (undrained shear strength in the range of 5-30 kPa) and highly compressible clay imposes geotechnical constraints on the design and performance of infrastructure works. An extensive deposit of CIS extends up to a depth of 30 m. Regardless of the magnitude of the applied loads, total and differential settlements in the range of 500-700 mm were expected for shallow foundation supported structures built on CIS (Ervin, 1992). The traditional engineering solution is deep foundation (pile) to transfer loads through the soft clay to deeper and stiffer layers. However, this solution is always expensive and may not suit to low to medium load bearing structures.

Several ground improvement techniques dealing with soft soil foundation have been developed over the past 30 years (Bouazza et al., 2006; Bergado et al., 2003; Du et al., 2013 and 2014; Chai et al., 2014; Bo et al., 2015; Wu et al., 2015). In situ deep mixing (DM) is an effective means. The DM method has been developed during last over two decades primarily to effect columnar inclusions into the soft ground to transform such whole soft ground to composite ground. The DM technology was simultaneously developed in Sweden and Japan using quicklime as a hardening agent. Later on, ordinary Portland cement slurry was used. Portland cement is commonly used as a cementing agent because it is readily available at reasonable cost. The influential factors, controlling the field strength of deep mixing columns such as penetration and withdrawal rates, water to cement ratio, and rate of blade rotation were extensively investigated by Horpibulsuk et al., (2004a) (Ariake clay, Japan) and Horpibulsuk et al. (2011b and 2012c) (Bangkok clay, Thailand).

The 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 and development of recycled construction materials derived from waste materials with low carbon dioxide release is considered 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 (J. Davidovits 1991).

Geopolymers are a group of cementitious materials that has garnered increasing interest as an alternative stabilizing agent (Sukmak et al. 2013a; Zaliha et al. 2014) to replace portland cement. Specifically, fly ash-based geopolymers were reported to leave essentially no carbon footprint relative to portland cement (Hicks 2010). The chemical process to produce geopolymers involves the co-polymerization of alumina and silica components whereby aluminosilicate-rich materials are dissolved by highly alkaline solutions such as sodium hydroxide (NaOH). Sodium silicate (Na_2SiO_3) can further increase the strength of the geopolymer (Palomo et al. 1999) because of the gel-like product derived from the aluminosilicate-sodium silicate reaction (Xie and Xi 2001). Calcium carbide residue (CCR) is a by-product of the acetylene production process that contains mainly calcium hydroxide, $Ca(OH)_2$. CCR is $Ca(OH)_2$-rich materials can be utilized together with waste pozzolanic materials, such as fly ash, biomass ash and rice husk ash to develop a cementitious material. Moreover, CCR produces high alkaline (pH = 12) when it reacts with water (Horpibulsuk et al., 2012, 2013). Consequently, this thesis attempts to study the possibility of using calcium carbide residue and geopolymer to develop strength of silty clay and soft clay for using as construction and pavement materials.

1.2 Objectives of the study

1.2.1 To investigate a possibility of using CCR as a liquid alkaline instead of sodium hydroxide solution (NaOH) in geopolymer process to improve the strength of silty clay

1.2.2 To investigate a possibility of using FA and CCR based geopolymer to improve the strength of soft marine clay.

1.3 Structure of presentation

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

Chapter II presents the review of previous research on calcium carbide residue and characterization of geopolymer. The aspects of the science and application of geopolymer are also renewed and presented.

Chapter III presents the study on a possibility of using CCR as a liquid alkaline instead of sodium hydroxide solution (NaOH) in geopolymer process to improve the strength of problematic silty clay. The soil used in this study is high plasticity (CH) types classified by Unified Soil Classification System (USCS), which was collected from Nakhon Ratchasima, Thailand. The comparison of liquid alkaline ratios, fly ash content, temperature condition and duration of curing on the compressive strength between the unsoaked and soaked condition are revealed.

Chapter IV attempts to examine the viability of using FA and CCR based geopolymers as a sustainable binder to improve strength of soft marine CIS. The

Unconfined Compressive Strength (UCS) is used as a practical indicator to investigate the strength development. The influential factors studied include liquid alkaline activator, L content, L/FA ratio, FA content, water content, curing time, curing temperature and CCR content. Moreover, the carbon footprints of FA and CCR based geopolymers stabilized CIS are calculated and compared with those of cement stabilized CIS at the same UCS values practically used in the soil improvement. The outcome of this research campaign the usage of FA-CCR geopolymer as a sustainable soil stabilizer alternative to high carbon Portland cement, which benefits in term of engineering, economic and environmental perspectives.

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

1.4 References

Berg, L.G, Remiznikova, V.I, Vlasov, V.V. 1968. **Nature of the interaction of kaolinite with some bases**. Stekloobraznye Sistemy i Materialy 11 (1):10 - 13.

Bergado, D.T., Sasanakul, I., Horpibulsuk, S., 2003. **Electro-Osmotic Consolidation of Soft Bangkok Clay Using Cooper and Carbon Electrodes with PVD**. Geotechnical Testing Journal, ASTM, Vol.26, No.3, doi: 10.1520/GTJ11309J.

Bo, M.W., Arulrajah, A., Horpibulsuk, S. and Leong, M., 2015a. **Quality management of prefabricated vertical drain materials in mega land reclamation projects: A case study.** Soils and Foundations, Vol.55, No.4, pp.895-905. doi: 10.1016/j.sandf.2015.06.019.

Bo, M.W., Arulrajah, A., Sukmak, P. and Horpibulsuk, S. 2015b. **Mineralogy and geotechnical properties of Singapore marine clay at Changi, Soils and Foundations,** Vol.55, No.3, pp.600-613.

Bouazza, A., Haque, A., Kwan, P.S., 2006. **Chapman G. Strength improvement of cement treated Coode Island Silt by mixing method**. Australian Geomechanics, Vol. 41 p. 101-106.

Chai, J.C., Horpibulsuk, S., Shen, S.L. and Carter, J.P., 2014. **Consolidation analysis of clayey deposits under vacuum pressure with horizontal drains**. Geotextiles and Geomembranes, Vol.42, pp.437-444.

Davidovits, J. 1991. **Geopolymers**. Journal of Thermal Analysis and Calorimetry 37(8):1633-1656.

Davidovits, J. and Davidovics, M.. 2008. **Geopolymer: Room-Temperature Ceramic Matrix for Composites.** Proceedings of the 12th Annual Conference on Composites and Advanced Ceramic Materials: Ceramic Engineering and Science Proceedings: John Wiley & Sons, Inc. p 835-841.

Du, Y. J., Wei, M. L., Jin, F., Liu, Z. B. 2013. **Stress-train relation and strength characteristics of cement treated zinc-contaminated clay,** Engineering Geology, 167, 20-26.

Du, Y. J., Horpibulsuk, S., Wei, M. L., Liu, M. L. 2014**. Modeling compression behavior of cement treated zinc contaminated clayey soils**. Soils and Foundations, 54(5), 1018-1026.

Ervin, M. C., 1992. **Engineering properties of Quaternary age sediments of the Yarra Delta, Engineering Geology of Melbourne.**

Horpibulsuk, S., 2001. **Analysis and Assessment of Engineering Behavior of Cement Stabilized Clays.** Saga University, Saga, Japan (Ph.D. dissertation).

Horpibulsuk, S., Bergado, D.T., Lorenzo, G.A., 2004a. **Compressibility of cement admixed clays at high water content.** Geotechnique 54 (2), 151–154.

Horpibulsuk, S., Chinkulkijniwat, A., Cholaphatsorn, A., Suebsuk, J., and Liu, M.D. (2012c). **Consolidation behavior of soil cement column improved ground**. *Computers and Geotechnics,* Vol.43, pp.37-50.

Horpibulsuk, S., Katkan, W., Sirilerdwattana, W., Rachan, R., 2006. **Strength development in cement stabilized low plasticity and coarse grained soils: laboratory and field study**. Soils and Foundations 46 (3), 351–366.

Horpibulsuk, S., Kumpala, A., Katkan, W., 2008. **A case history on underpinning for a distressed building on hard residual soil underneath nonuniform loose sand**. Soils and Foundations 48 (2), 273–291.

Horpibulsuk, S., Liu, M.D., Liyanapathirana, D.S., Suebsuk, J., 2010a. **Behavior of cemented clay simulated via the theoretical framework of the structured cam clay model.** Computers and Geotechnics 37 (1–2), 1–9.

Horpibulsuk, S., Miura, N., 2001. **A new approach for studying behavior of cement stabilized clays**. In: Proceedings of the 15th International Conference on Soil Mechanics and Geotechnical Engineering, vol. 3, pp. 1759–1762.

Horpibulsuk, S., Miura, N., Nagaraj, T.S., 2003. **Assessment of strength development in cement–admixed high water content clays with Abrams' law as a basis.** Geotechnique 53 (4), 439–444.

Horpibulsuk, S., Miura, N., Koga, H., Nagaraj, TS., 2004a. **Analysis of strength development in deep mixing – a field study.** Ground Improve 8(2):59–68.

Horpibulsuk, S., Miura, N., Bergado, D.T., 2004b. **Undrained shear behavior of cement admixed clay at high water content.** Journal of Geotechnical and Geoenvironmental Engineering, ASCE 30 (10), 1096–1105.

Horpibulsuk, S., Miura, N., Nagaraj, T.S., 2005. **Clay–water/cement ratio identity of cement admixed soft clay**. Journal of Geotechnical and Geoenvironmental Engineering, ASCE 131 (2), 187–192.

Horpibulsuk, S., Phetchuay, C., **Chinkulkijniwat, A., 2012a. Soil stabilization by calcium carbide residue and fly ash**. Journal of Materials in Civil Engineering, ASCE 24 (2), 184–193.

Horpibulsuk, S., Phochan, W., Suddeepong, A., Chinkulkijniwat, A., Liu, M.D., 2012b. **Strength development in blended cement admixed saline clay**. Applied Clay Science 55, 44–52.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., Cholaphatsorn, A. 2013. **Strenth development in silty clay stabilized with calcium carbide residue and fly ash**. Soil and Foundations 53, 477-486.

Horpibulsuk, S., Rachan, R., Chinkulkijniwat, A., Raksachon, Y., Suddeepong, A., 2010b. **Analysis of strength development in cement-stabilized silty clay based on microstructural considerations**. Construction and Building Materials 24, 2011–2021.

Horpibulsuk, S., Rachan, R., Raksachon, Y., 2009. **Role of fly ash on strength and microstructure development in blended cement stabilized silty clay**. Soils and Foundations 49 (1), 85–98.

Horpibulsuk, S., Rachan, R., Suddeepong, A., 2011a. **Assessment of strength development in blended cement admixed Bangkok clay**. Construction and Building Materials 25 (4), 1521–1531.

Horpibulsuk, S., Rachan, R., Suddeepong, A., Chinkulkijniwat, A., 2011b. **Strength development in cement admixed Bangkok clay: laboratory and field investigations.** Soils and Foundations 51 (2), 239–251.

Horpibulsuk, S., Shibuya, S., Fuenkajorn, K., Katkan, W., 2007. **Assessment of engineering properties of Bangkok clay.** Canadian Geotechnical Journal 44 (2), 173–187.

Ikeda, K.. 1998. **Consolidation of mineral powders by the geopolymer binder technique for materials use.** Journal of the Mining and Materials Processing Institute of Japan 114 497-500.

Jaarsveld, J. Van, Deventer, J. Van, Lorenzen, L. 1998. **Factors affecting the immobilization of metals in geopolymerized fly ash**. Metallurgical and Materials Transactions B 29:283-291.

Kawasaki, T., Niina, A., Saitoh, S., Suzuki, Y., and Honjo, Y. (1981). "**Deepmixing method using cement hardening agent.**" Proc., 10th Int. Conf. on Soil Mechanics and Foundation Engineering, Southeast Asian Geotechnical Soc., Bangkok, 721–724.

Kehew, E. A. (1995). **Geology for engineers and environmental scientists,** 2nd Ed., Prentice Hall, Englewood Cliffs, NJ, 295–302.

Kitazume, M., Yamazaki, H., and Tsuchida, T. (2000). "**Recent soil admixture stabilization techniques for port and harbor constructions in Japan—**

Deep mixing method, premix method, light-weight method.” Proc., Int. Seminar on Geotechnics in Kochi, ISGK 2000, Kochi, Japan, 23–40.

Khoury, N.N. and Zaman, M.M. 2007. **Environmental effects of aggregate stabilized with cementation materials.** Journal of Materials in Civil Engineering 180(1):41-48.

Mohapatra, R. and Rao, JR. 2001. **Some aspects of characterisation, utilisation and environmental effects of fly ash.** Journal of Chemical Technology & Biotechnology 76:9-26.

Phair, J.W. 2001. **Compositional effects and microstructure of fly ash-based geopolymers**. PhD Thesis, Department of Chemical Engineering, University of Melbourne, Victoria, Australia.

Rajasekaran, G. 2005. **Sulphate attack and ettringite formation in the lime and cement stabilized marine clays.** Ocean Engineering 32(8–9):1133-1159.

Sukmak, P., Horpibulsuk, S., Shen, S-L. 2013a. **Strength development in clay–fly ash geopolymer**. Construction and Building Materials 40(0):566-574.

Sukmak, P., Horpibulsuk, S., Shen, S-L, Chindaprasirt, P, Suksiripattqanapong, C. 2013b. **Factors influencing strength development in clay-fly ash geopolymer**. Construction and Building Materials 40:1125-1136.

Wu, H.N., Shen, S.L., Ma, L., Yin, Z.Y., Horpibulsuk, S., 2015. **Evaluation of the strength increase of marine clay under seawall construction: a case study.** Marine Georesources & Geotechnology, Vol.33, pp.532-541.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Compacting in-situ soil mixed with cement slurry are an extensively used soil improvement technique for problematic soil that are in relatively a dry state. And in situ deep mixing (DM) is an effective for soft soil. An advantage of these technique is that adequate strength can be achieved in a short time. Portland cement is commonly used as a cementing agent because it is readily available at reasonable cost. The high unit cost and energy intensive process for the production of Portland cement are the driving forces for the constant need within the industry to seek alternative cementitious binders. The cement manufacturing process emits CO_2 into the atmosphere, which accounts for 5% of the total CO_2 released into the air (Horpibulsuk et al., 2013). The development of a new cementing agent with low carbon dioxide release is thus considered as an interesting issue. Commercial and industrial utilization of alkali-activated aluminosilicate cements, known as ‘geopolymers’ has increasingly 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 (Davidovits, 1991). 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 (Buchwald and Kaps 2002), fly ash, and bottom ash (Davidovits et al., 1999) can be used as a precursor to react with the liquid alkaline activator. Fly Ash (FA) 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). Even though geopolymer has been recently used in building concrete application, its usage in geotechnical application has been very limited.

The focus of the current research is to carry out an in-depth investigation on the effectiveness of geopolymer technique. The review commences with a brief review of problematic soil (silty clay, soft CIS and CG). After that a brief review of properties and previous research of CCR that use as alkaline activator and additive for geopolymer in chapter III and IV.

2.2 Problematic soil

2.2.1 Silty clay

Soil in northeast Thailand generally consists of two layers. The upper layer (varying from 0 to 3 m thickness) is wind-blown and has been deposited over several decades. It is clayey sand or silty clay with low to moderate strength (12 < N < 20, where N is the standard penetration number). This upper soil is problematic because it is sensitive to changes in water content (Horpibulsuk et al., 2008). Its collapse behavior as a result of wetting is illustrated by Kohgo et al. (1970); and Kohgo and Horpibulsuk (1999). The lower layer is residual soil that is weathered from claystone and consists of clay, silt, and sand (Udomchore, 1991). It possesses very high strength (generally N > 30) and very low compressibility

2.2.2 Coode island silt

Coode Island Silt (CIS) is one of the four youngest formed sedimentary formations in the Melbourne geological region of the Yarra Delta. The extent of the Yarra Delta is shown in Figure 2.1. CIS is widespread throughout the lower Yarra Delta region and is present beneath much of South Melbourne, Port Melbourne and Footscray (Ervin, 1992).

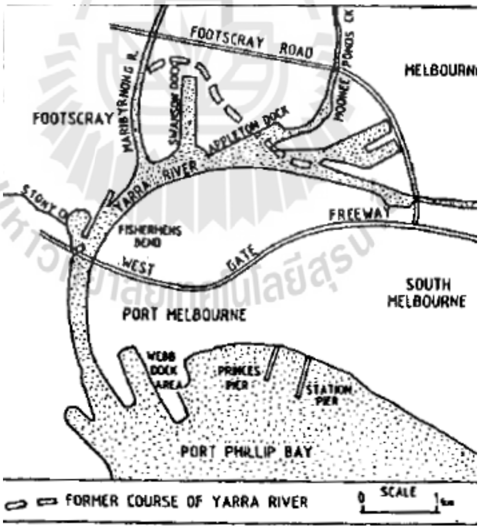


Figure 2.1 Distribution of Yarra Delta (from Ervin, 1992)

The existence of a soft (undrained shear strength in the range of 5-30 kPa) and highly compressible layer of marine sediment, Coode Island Silt (CIS), in the Yarra

Delta imposes geotechnical constraints on the design and performance of infrastructure works. An extensive deposit of CIS extends up to a depth of 30 m. Regardless of the magnitude of the applied loads, total and differential settlements in the range of 500-700 mm were expected for shallow foundation supported structures built on CIS (Ervin, 1992).

2.3 Calcium carbide residue

To improve economic and environmental impacts, some waste $Ca(OH)_2$-rich materials can be utilized together with waste pozzolanic materials, such as fly ash, biomass ash and rice husk ash to develop a cementitious material. Calcium carbide residue (CCR) is a by-product of the acetylene production process that contains mainly calcium hydroxide, $Ca(OH)_2$. Between 1995 and 1998, the demand for calcium carbide for the production of acetylene gas in Thailand was 74,000 t (Tanalapasakul, 1998). This demand is continuously increasing each year. Due to its highly basic pH, CCR has been little utilized and was typically gone to a disposal area in the form of slurry. After being sundried for a few days, the slurry form changes to a dry form.

Its production is described in the following equation:

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

From Eq., it can be seen that 64 g of calcium carbide (CaC_2) provides 26 g of acetylene gas (C_2H_2) and 74 g of CCR in the form of $Ca(OH)_2$.

Jaturapitakkul and Roongreung (2003) have introduced a cementitious material that is a mixture of CCR and rice husk ash. The cementing property was identified as a pozzolanic reaction between the two materials, and no Portland cement was included in the mixture. Consoli et al. (2001) have reported on the possibility of using CCR and fly ash to stabilize non-plasticity silty sand. For clayey soils, which have a high content of natural pozzolanic materials, stabilization by using CCR is very effective. Horpibulsuk et al. (2012a) and Kumpala and Horpibulsuk (2013) explained the possible mechanism controlling the engineering properties of CCR stabilized clay based on macro- and micro-scale observations. The optimum water content (OWC) of the stabilized clay exhibits the highest strength because it engenders the densest packing and highest cementitious products. Strength improvement for a particular curing time is classified into three zones: active, inert and deterioration (vide Fig. 2.1).

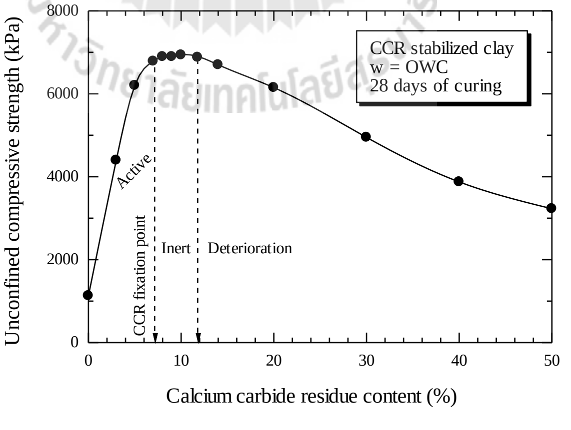


Figure 2.2 Improvement zones (Horpibulsuk et al., 2011c).

The data were obtained from an unconfined compression test under unsoaked condition on CCR-stabilized samples at optimum water content. In the active zone, strength increases remarkably with increased CCR content. All the input $Ca(OH)_2$ is consumed by the natural pozzolanic material in the soil to produce a pozzolanic reaction. This active zone can be determined from the CCR fixation point, which is obtained simply from the index test. CCR fixation is defined as the CCR content at which the plasticity index of the CCR-clay mixture changes insignificantly with the CCR input. Strength development in the inert zone tends to slow down; the incremental gradient becomes nearly zero and does not make any further significant improvement. A decrease in strength, which appears when the CCR content is in the deterioration zone, is caused by unsoundness due to free lime. This free lime [$Ca(OH)_2$] is clearly observed by the thermal gravity analysis (TGA) (Horpibulsuk et al., 2012a). Even with the high unsoaked strength in the active zone (Fig. 1), Kumpala et al. (2013a, 2013b) found that the wet-dry cycled strength of stabilized clay was considered insufficient according to recommendations by the ACI (1990) and the U.S. Army Corps of Engineers (2004). The input of FA (as a CCR replacement) may improve the strength of CCR stabilized clay when the CCR content is in excess of the active zone (i.e., in inert and deterioration zones) where natural pozzolanic material in the soil is not in sufficient quantities to react with the $Ca(OH)_2$. In the inert zone, the input FA enhances strength. The FA improves the densification and the pozzolanic reactive capacity. For the short-term, the strength increase is mainly caused by the packing effect because the pozzolanic reaction is a time-dependent process. The highest short-term strength is thus associated with the highest maximum dry unit weight. Over the time, a higher FA content is needed for the pozzolanic reaction; therefore, the optimal FA content increases. Improvement in the deterioration zone is not recommended in practice, even with the input of FA. Unsoundness due to the free lime content hinders the strength development by pozzolanic reactions. The soaked strength is generally lower than the unsoaked strength because the absorbed water increases repulsive forces. Even though the strengths of the stabilized clay are strongly dependent upon the CCR and FA contents, the ratio of soaked strength to unsoaked strength is almost equal. Most of the ratios vary between 0.45 and 0.65 with an average of 0.55. (Horpibulsuk et al., 2013)

2.4 Geopolymer

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).

2.5 Chemistry of geopolymer

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 2.2 (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).

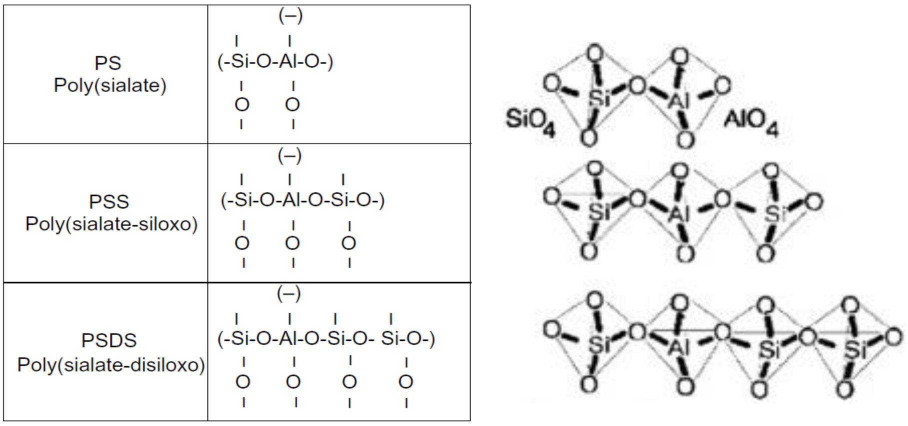


Figure 2.3 The types of polysialates (Davidovits 1988a).

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:

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

$$\Big\downarrow \text{(1)}$$

$$\text{Al–Si material}_{(s)} + [M_z\,(\text{AlO}_2)_x\,(\text{SiO}_2)_y \cdot nM\text{OH} \cdot m\text{H}_2\text{O}]\text{ gel} \qquad (2.2)$$

$$\Big\downarrow$$

$$\text{Al–Si material}_{(s)} + [M_a\,((\text{AlO}_2)_a\,(\text{SiO}_2)_b)\; nMOH \cdot m\text{H}_2\text{O}] \qquad (2.3)$$

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.

2.6 Geopolymer Development

Geopolymer cements develop through a series of several distinct reaction processes from initial pozzolanic activation to final microstructure development. The benefits of using pozzolans as a matrix binder for agglomeration is that they tend to be economical, environmentally-friendly, more absorbent of liquids and produce a highly durable product (Jiminez et al. 2005). The major processes are dissolution of the aluminosilicate species within a highly basic, alkaline environment, polymerization of the dissolved minerals into short-lived structural gel, precipitation of formed hydration products similar to natural zeolites and final hardening of the matrix by excess water exclusion and the growth of crystalline structures (Petermann et al. 2010). Figure 2.3 illustrates the overall polymerization process in alkali-activated geopolymers.

2.6.1 Dissolution

Dissolution occurs immediately upon contact between the alkaline solution and the pozzolanic material and allows for ionic interface between species and the breaking of covalent bonds between silicon, aluminum and oxygen atoms. Similarly to PCC, this process generates rapid and intense heat and is directly proportional to the pH level of the activating solution. The rate of dissolution is relevant to the amount and composition of the ashes and the pH of the activating solution (Jiminez et al. 2006: Xie and Xi. 2001:Petermann et al. 2010).

2.6.2 Polymerization

The polymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals, resulting in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. The formed gel product contains alkaline cations which compensate for the deficit charges associated with the aluminum-for-silicon substitution (Xie and Xi. 2001:Petermann et al. 2010). An intermediate, aluminum-rich phase is first formed which then gives way to a more stable, silicon-rich three-dimensional gel product of form Q^4(nAl), which is dependent upon curing conditions and activator type (Jiminez et al. 2006:Petermann et al. 2010).

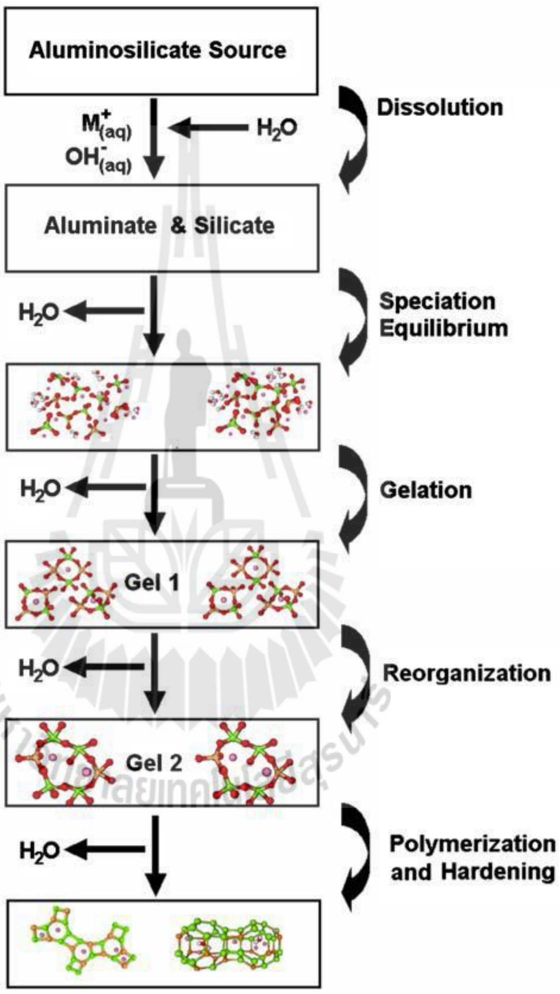


Figure 2.4 Geopolymer Development Model (Vijaya Rangan).

2.6.3 Growth

During this process, the slow growth of crystalline structures become evident as the nuclei of the polymerized gel reaches critical size. The matrix crystallinity is relative to the rate by which precipitation occurs: fast reactions between alkali and ash do not allow time for growth of a well-structured crystalline environment (representative of typical zeolites). Therefore, most hardened geopolymer cements are referred to as zeolitic precursors rather than actual zeolites. The final product of geopolymerization is an amorphous, semi-crystalline cementitious material. (Petermann et al. 2010).

2.7 Hydration reaction characteristics

Within these process intervals, themodynamic and kinetic parameters become vital to gel formation and reaction degree. Several factors directly influence the degree of reaction (α) observed in a mixed geopolymer paste and either enhance or detract from the polymerization process and subsequent phases that strictly define the formed cementitious properties of the hardened cement. The activation reaction rate as well as the chemical composition of the reaction products depends on several factors such as the particle size distribution and the mineral composition of the precursor fly ash (Jiminez et al. 2006). A fly ash material used in a study (by Xie and Xi) contained a high fraction of reactive oxides which reacted significantly with a waterglass (Na_2SiO_3) activator, leading to a high strength within a short time and under relatively lower temperatures (Williams PJ et al. 2002). Likewise, alkaline activator type, concentration of activators, ratios of solids to liquids and curing temperatures and time are all relevant in the characterization of geopolymer cements and the mechanical properties attained. In practice, no matter which method is used, the selection of proper activators is the most important part of the technology (Williams PJ et al. 2002 :Petermann et al. 2010).

2.8 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.

2.9 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).

In 1974, Kaolinite and other clays were initially utilized in as fillers for the encapsulation of radioactive wastes right into a monolithic solid. Davidovits primarily 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)**.**

2.9.1 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:

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

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°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.

2.10 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 2.4).

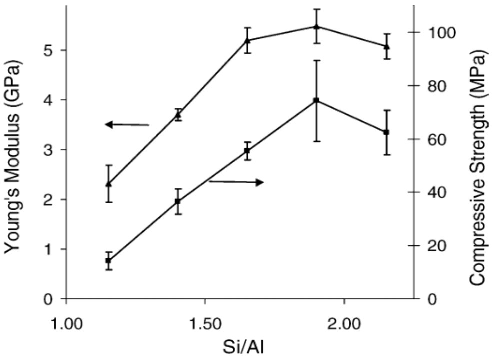


Figure 2.5 Young’s moduli (▲) and ultimate compressive strengths (■) of geopolymers. (Duxson et al. 2005).

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 2.5 and 2.6).

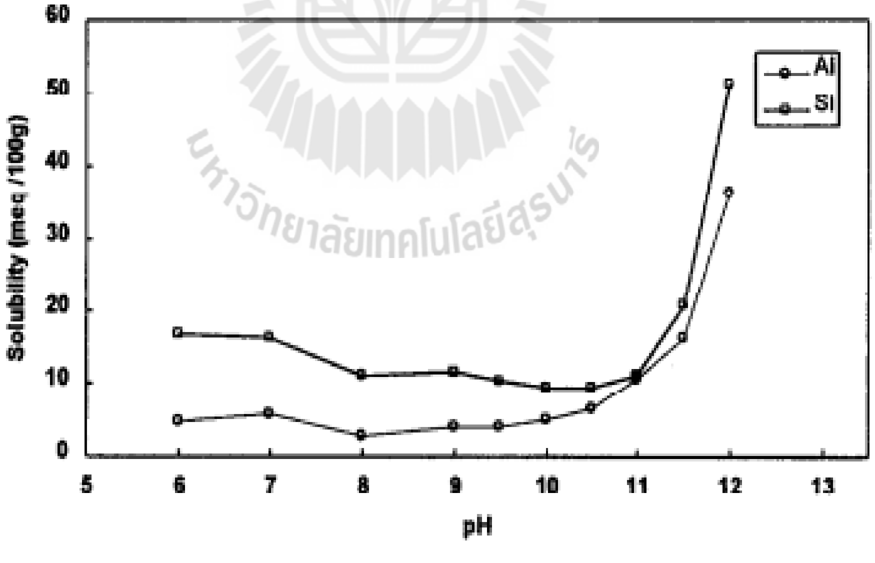


Figure 2.6 Dissolution of Al Si from metakaolin as a function of pH over a 5 h period (Phair and Van Deventer 2001).

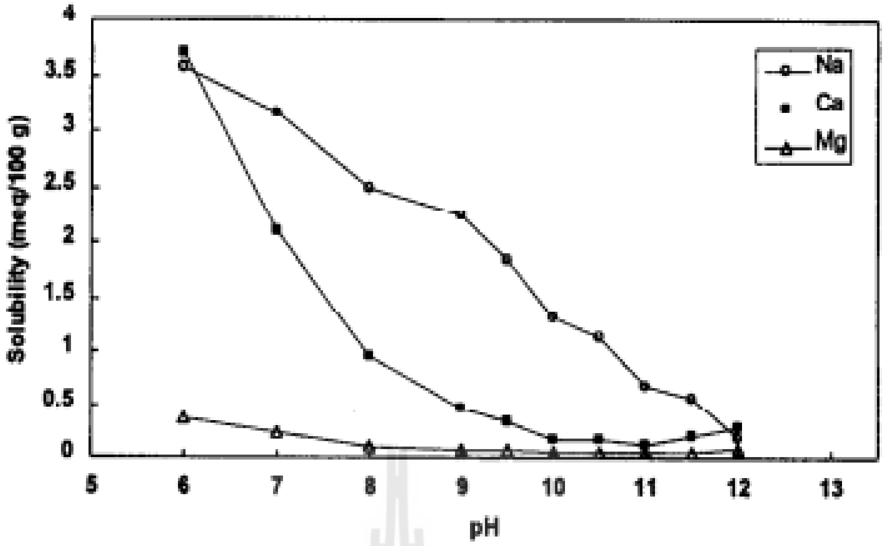


Figure 2.7 Dissolution of Na, Ca, and Mg metakaolin as a function of pH over a 5 h period. Ti and Fe concentration were negligible (Phair and Van Deventer 2001).

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 2.7, 2.8 and 2.9).

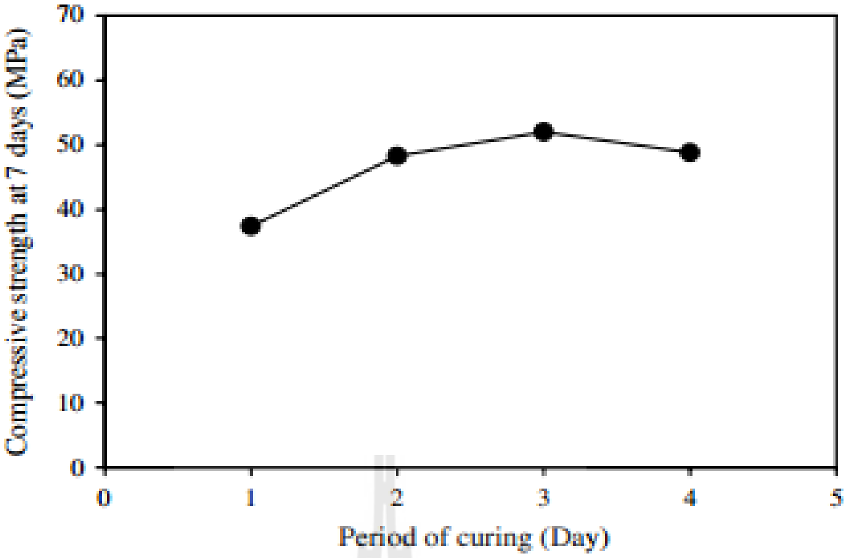


Figure 2.8 Duration of heat curing and strength cured at 60°C with delay time (Chindaprasirt et al. 2007).

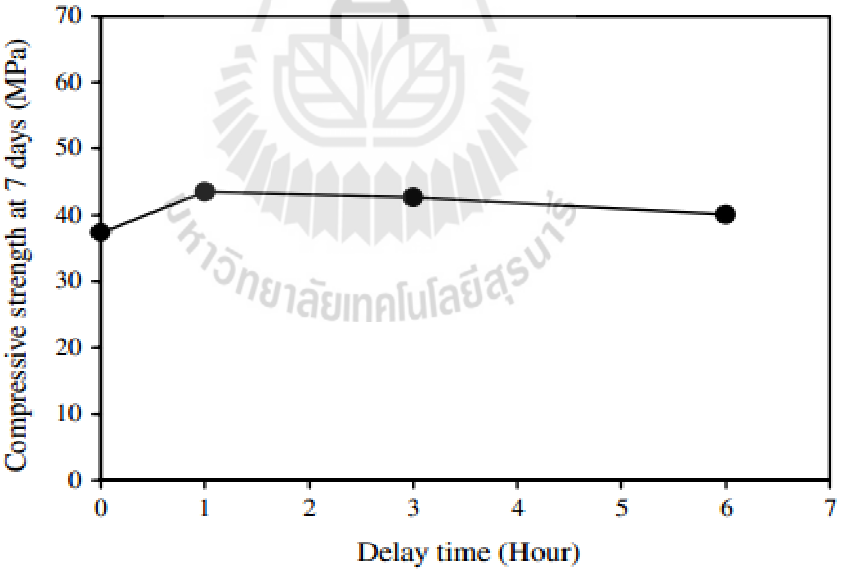


Figure 2.9 Strength and delay time of geopolymer mortar with 60°C heat curing for 24 h (Chindaprasirt et al. 2007).

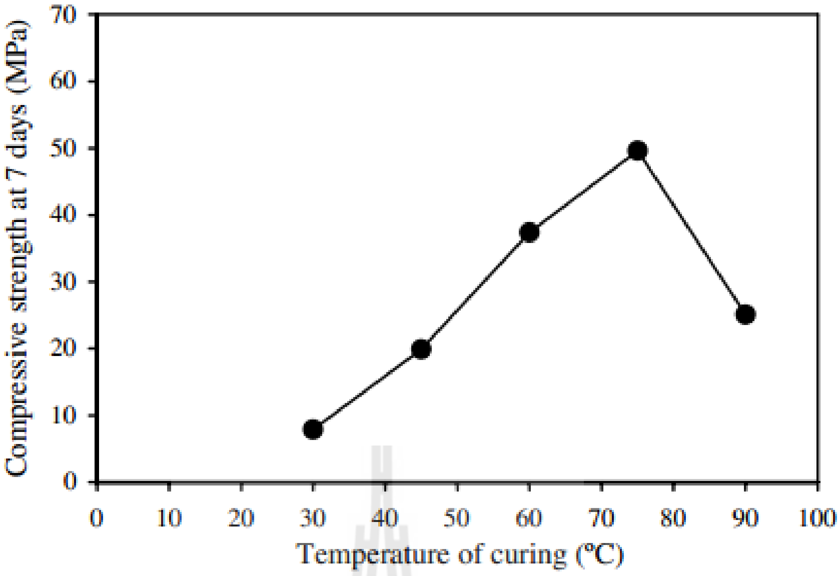


Figure 2.10 Strength and temperature of curing of geopolymer with no delay time before curing (Chindaprasirt et al. 2007).

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 2.10 and 2.11).

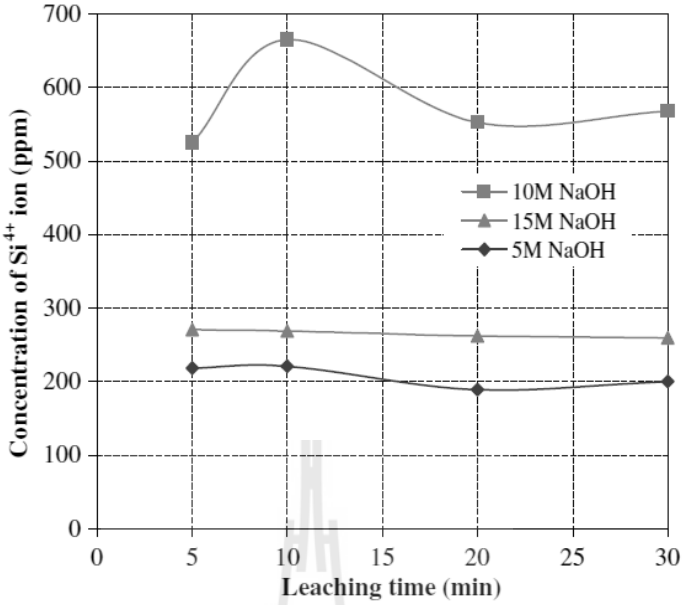


Figure 2.11 Si^{4+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH (Rattanasak and Chindaprasirt 2009).

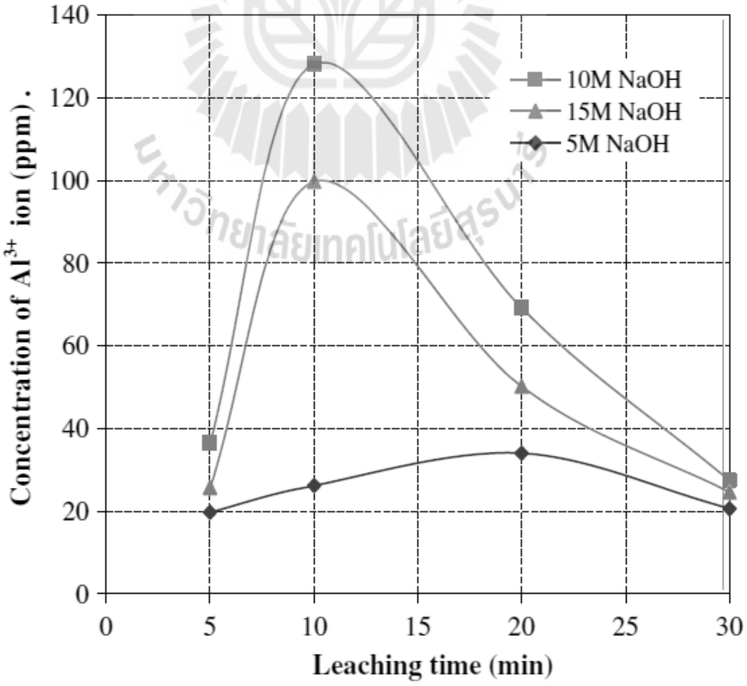


Figure 2.12 Al^{3+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH (Rattanasak and Chindaprasirt 2009).

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.

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.

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.

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 2.12).

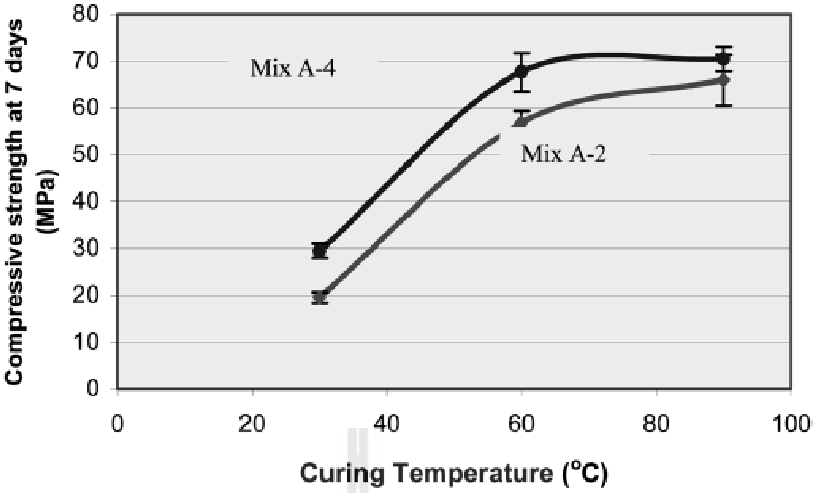


Figure 2.13 Effect of curing temperature on compressive strength (Hardjito et al. 2004).

- 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 2.13).

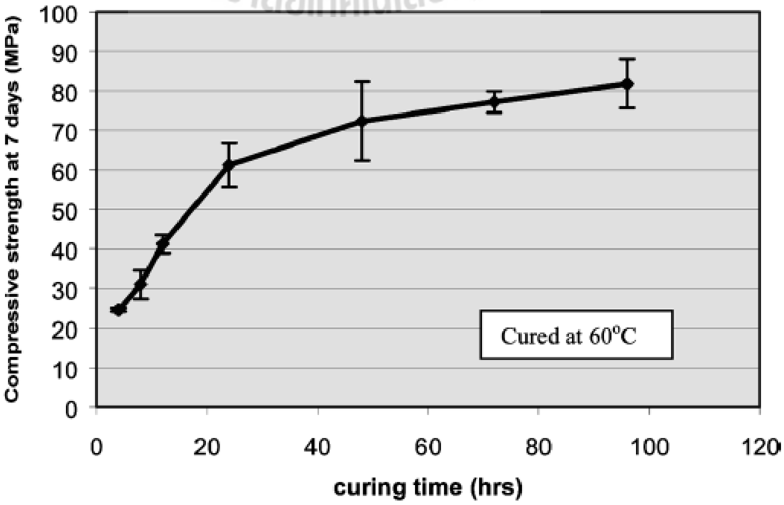


Figure 2.14 Influence of curing time on compressive strength (Hardjito et al. 2004).

- 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 2.13).

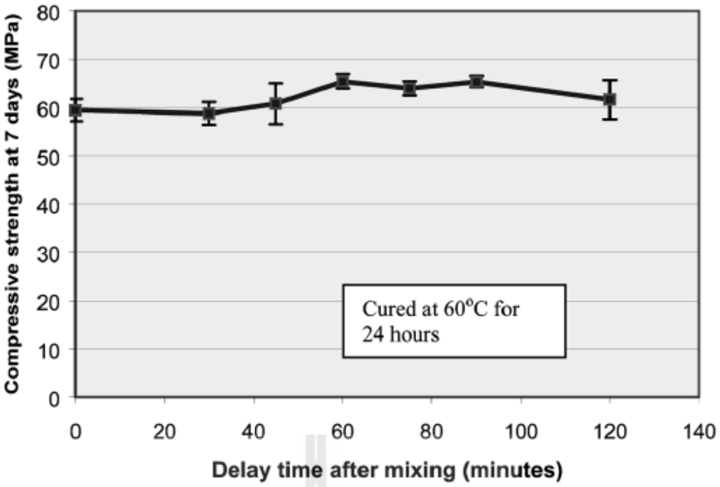


Figure 2.15 Influence of delay time on compressive strength (Hardjito et al. 2004).

- 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 2.15).

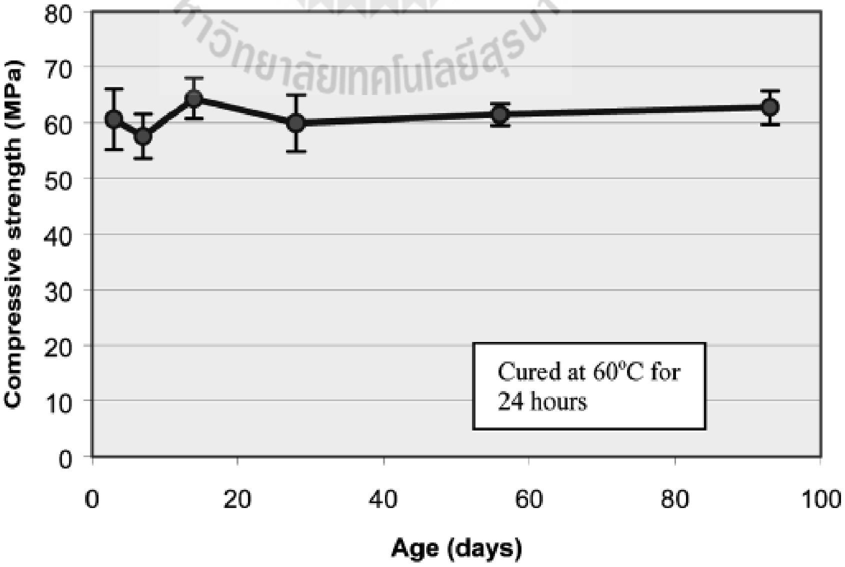


Figure 2.16 Compressive strength at different ages (Hardjito et al. 2004).

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 2.16 and 2.17).

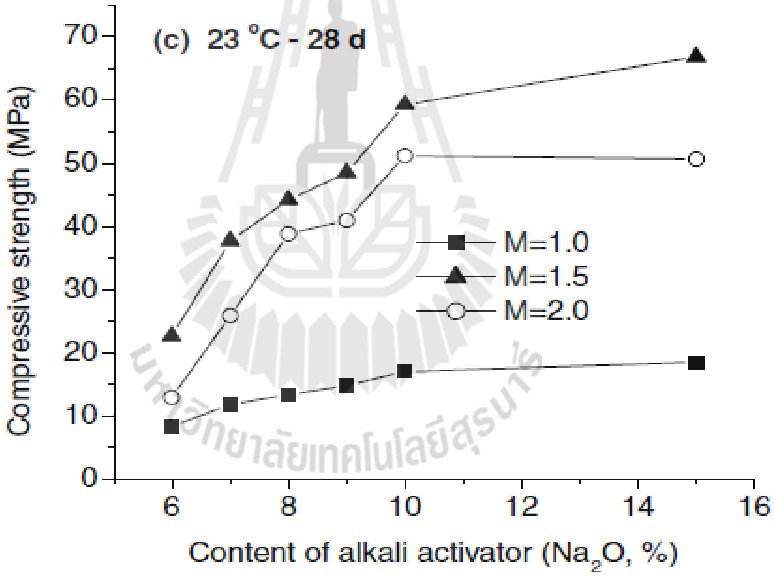


Figure 2.17 Effects of modulus (M) and content of the mixed alkali activator on the compressive strength of fly ash geopolymer cured at room temperature of 23°C for 28 days (Guo et al. 2010).

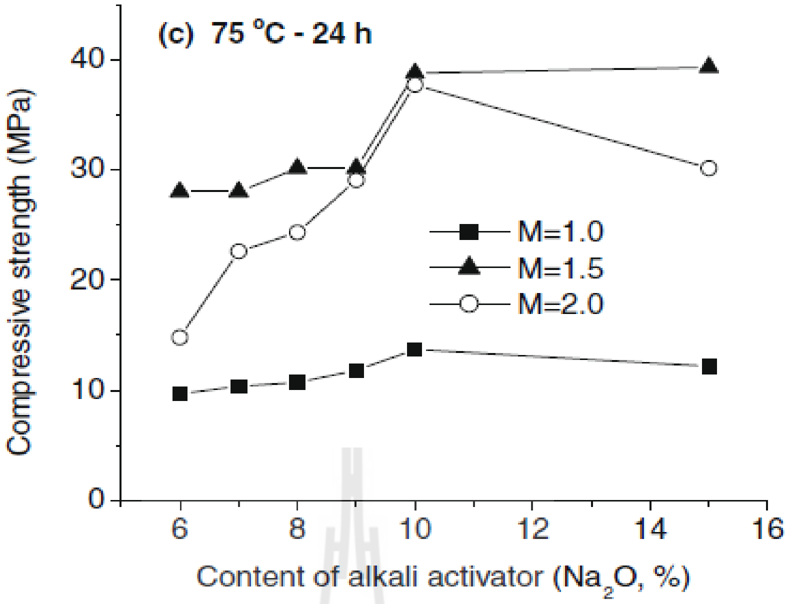


Figure 2.18 Effects of modulus (M) and content of the mixed alkali activator on the compressive strength of fly ash geopolymer cured at room temperature of 75°C for 4, 8, and 24 h (Guo et al. 2010).

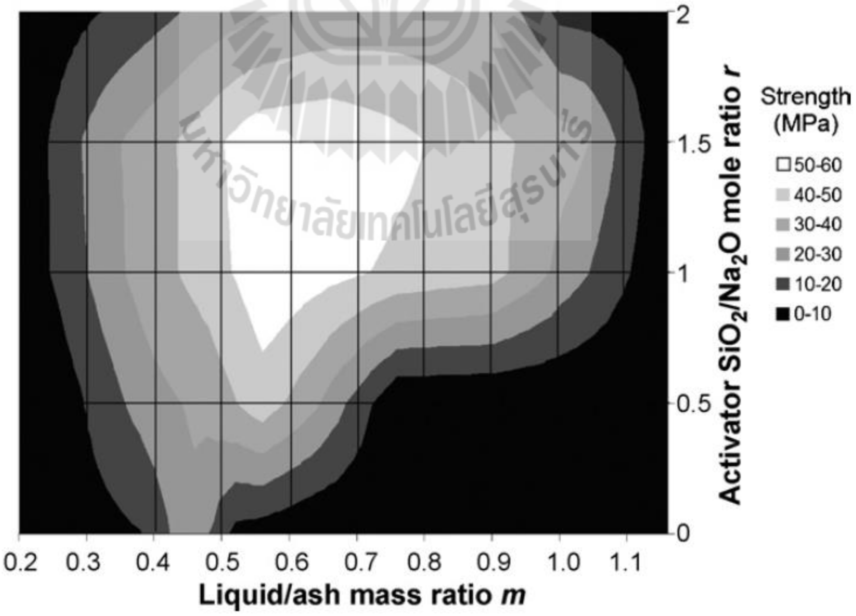


Figure 2.19 Contour plot of compressive strength data for all samples (Provis et al. 2009)

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 2.18).

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 2.19).

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 2.20, 2.21 and 2.22).

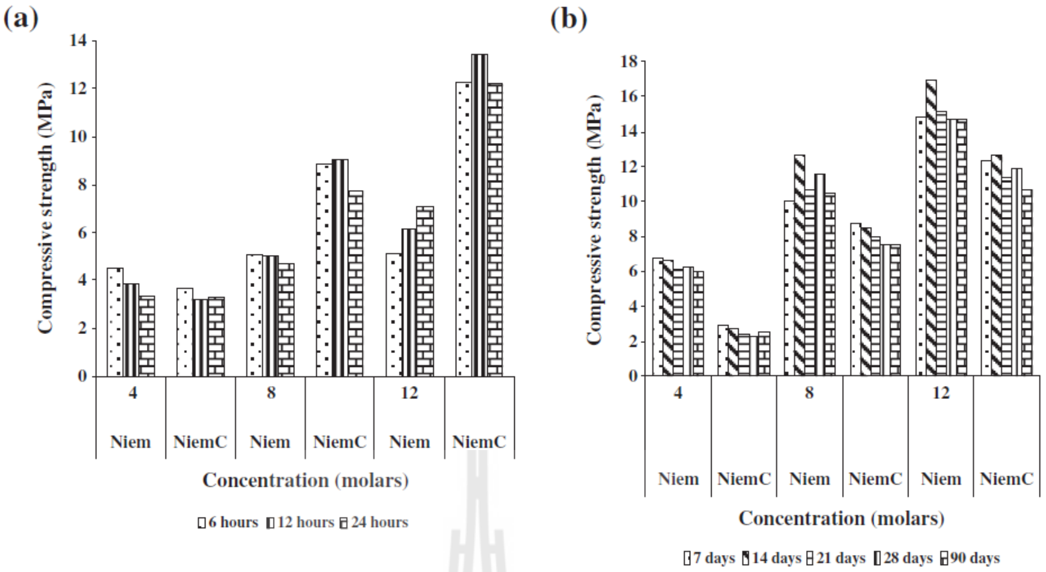


Figure 2.20 Summary of compressive strength of samples cured at (a) 120°C and (b) 40°C (Diop et al. 2011).

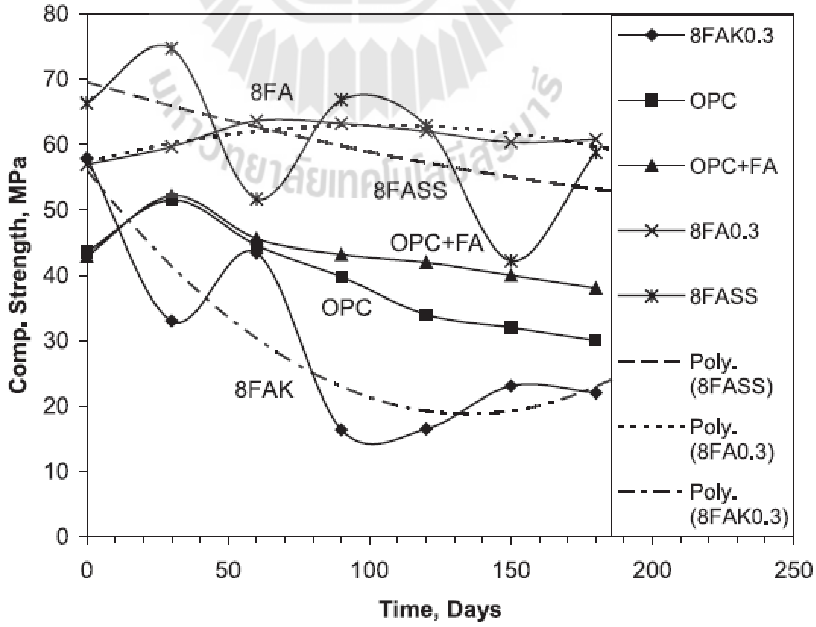


Figure 2.21 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to 5% sodium sulfate solution (Bakharev 2005a).

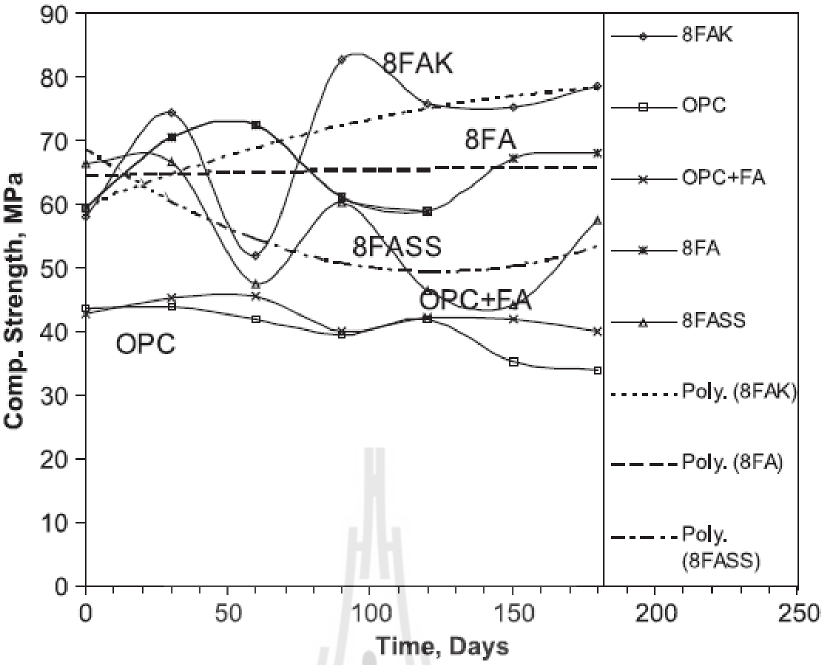


Figure 2.22 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to 5% magnesium sulfate solution (Bakharev 2005a).

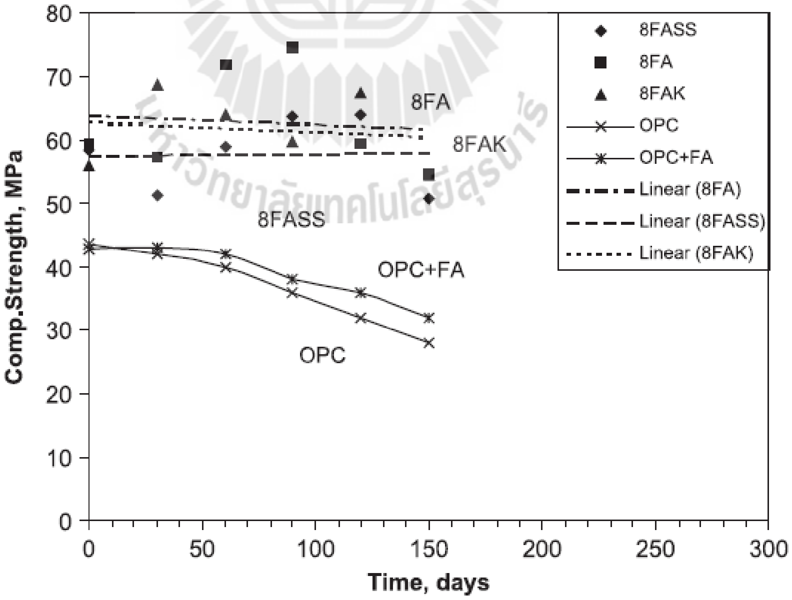


Figure 2.23 Compressive strength evolution of the geopolymer and Portland cement specimens exposed to a solution of 5% sodium sulfate+5% magnesium sulfate (Bakharev 2005a).

2.11 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 2.22 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).

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 2.24 - 2.27) 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 2.24 and 2.25) offer a summary of the distribution of numerous constituent phases with an increase of local detail being provided in Figure. 2.26 and 2.27.

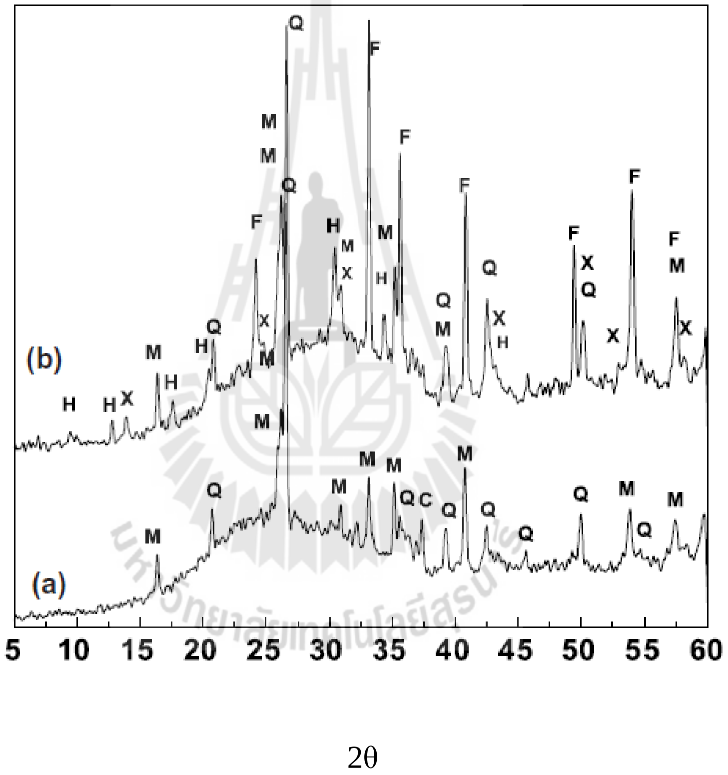


Figure 2.24 XRD spectra (a) un-reacted fly ash; (b) alkali-activated fly ash 20 h at 85°C Q=Quartz; M= Mullite; F=Hematite; C=CaO; H=Herschelite; X=Hydroxysodalite (Fernandez Jiminez et al. 2004).

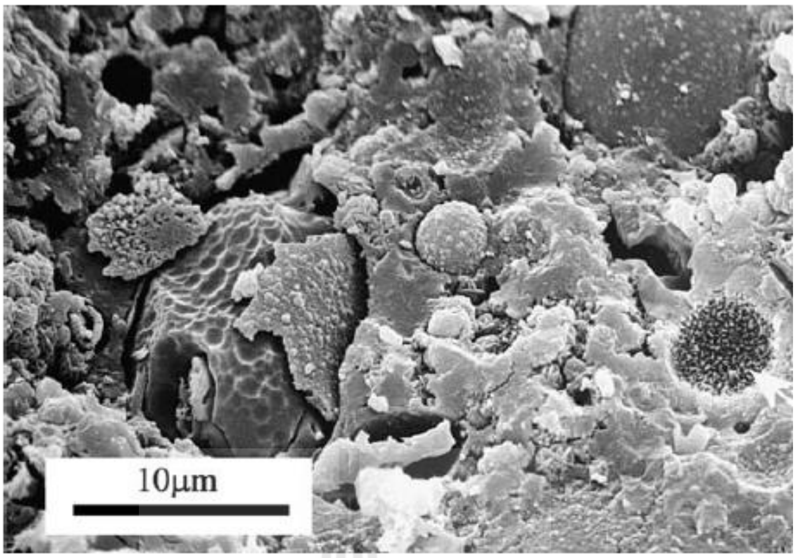


Figure 2.25 SEM micrograph of fracture surface of alkali-activated PFA geopolymer. Fe_2O_3 is arrowed (Jiminez et al. 2004).

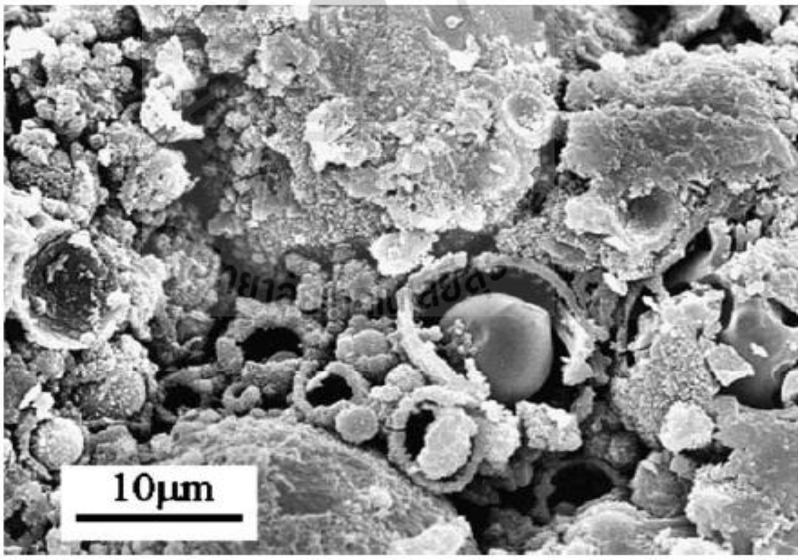


Figure 2.26 SEM micrograph of fracture surface of alkali-activated PFA geopolymer (Jiminez et al. 2004).

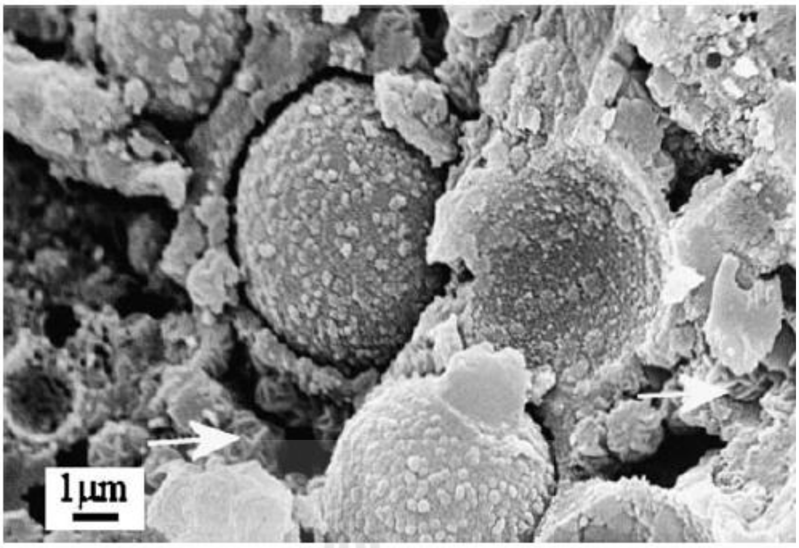


Figure 2.27 SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing PFA particle with reaction shells and also unidentified spherical assemblages (arrowed) (Jiminez et al. 2004)

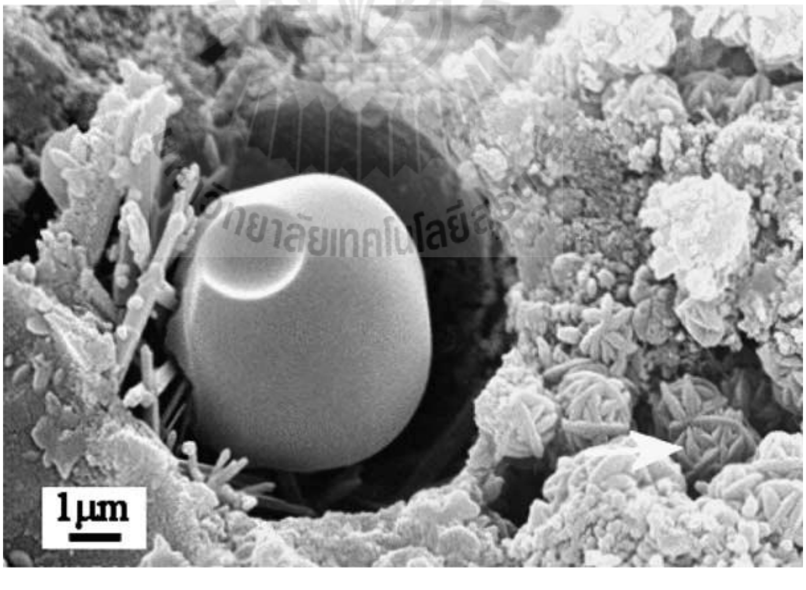


Figure 2.28 SEM micrograph of fracture surface of alkali-activated PFA geopolymer showing considerably eroded PFA particle and also unidentified spherical assemblages (arrowed) (Jiminez et al. 2004).

2.12 The new information obtained from this thesis

The thesis attempts to study the possibility of using calcium carbide residue fly ash and geopolymer stabilized the silty clay, soft clay and spent coffee grounds to develop engineering properties and then, presents the factors influencing strength development. The factors are different ingredients (CCR content, fly ash/clay ratio, Na_2SiO_3/water ratio, Na_2SiO_3/NaOH ratio, Liquid alkaline/fly ash ratio, and moisture content), specimen weights, and heating conditions (40 ºC curing temperature and room temperature). The outcome of this work would provide choices and be beneficial for the production of construction materials in the problem soil areas and thus lead to the reduction in the cement consumption and environmental problems.

2.13 References

ACI, 1990. **State-of-the art report on soil cement**, ACI 230.1R-90. ACI Materials Journal 87 (4), 23.

Alonso S, and Palomo A. 2001a. **Alkaline Activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio**. Materials Letters 47:55-62.

Alonso S, and Palomo A. 2001b. **Calorimetric study of alkaline activation of calcium hydroxide-metakaolin solid mixtures.** Cement and Concrete Research 31:25-30.

Arulrajah A, Maghoolpilehrood F, Disfani MM, Horpibulsuk S. 2014b. **Spent coffee grounds as a non-structural embankment fill material: engineering and environmental considerations.** *Journal of Cleaner Production*, 72, pp. 181-186.

Bakharev T. 2005a. **Durability of geopolymer materials in sodium and magnesium sulfate solutions**. Cement and Concrete Research 35(6):1233-1246.

Bakharev T. 2005b. **Geopolymeric materials prepared using Class F fly ash and elevated temperature curing.** Cement and Concrete Research 35(6):1224-1232.

Barbosa VFF, and MacKenzie KJD. 2003a. **Synthesis and thermal behaviour of potassium sialate geopolymers**. Materials Letters 57(9–10):1477-1482.

Barbosa VFF, and MacKenzie KJD. 2003b. **Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate**. Materials Research Bulletin 38(2):319-331.

Barbosa VFF, MacKenzie KJD, and Thaumaturgo C. 1999. **Synthesis and characterization of sodium polysialate inorganic polymer based on alumina and silica.** In: Davidovits, J., Davidovits, R., James, C. (Eds.), Proceedings of the 2nd International Conference on Geopolymer '99, Saint Qunentin, France, June 30-July 2.65-78.

Barbosa VFF, MacKenzie KJD, and Thaumaturgo C. 2000. **Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymer**s. International Journal of Inorganic Materials 2(4):309-317.

Bergna HE, and Roberts WO. 2006. **Colloidal Silica: Fundamentals and Applications**. CRC Press, New York.

Baudet, B., Stallebrass, S., 2004. **A constitutive model for structured clays**. Geotechnique 54 (4), 269–278.

Cheng T, and Chiu J. 2003. **Fire resistant geopolymer produced by granulated blast furnace slag**. Minerals Engineering 16:205-210.

Chindaprasirt P, Kanchanda P, Sathonsaowaphak A, and Cao H. 2007. **Sulfate resistance of blended cements containing fly ash and rice husk ash.** Construction and Building Materials 1356-1361.

Ching SL, Yusoff MS, Aziz HA, Umar M. 2011. **Influence of impregnation ratio on coffee ground activated carbon as landfill leachate adsorbent for removal of total iron and orthophosphate**. *Desalination*, 279(1), pp. 225-234.

Cioffi R, Maffucci L, and Santoro L. 2003. **Optimization of geopolymer synthesis by calcination and polycondensation of a kaolinitic residue**. Resources, Conservation and Recycling 40(1):27-38.

Consoli, N.C., Rotta, G.V., Prietto, P.D.M., 2000. **Influence of curing under stress on the triaxial response of cemented soil**. Geotechnique 50 (1), 99–105.

Consoli, N.C., Prietto, P.D.M., Carroro, J.A.H., Heineck, K.S., 2001. **Behavior of compacted soil-fly ash-carbide lime mixture.** Journal of Geotechnical and Geoenvironmental Engineering, ASCE 127 (9), 774–782.

Davidovits J. 1976. **Solid phase synthesis of a mineral blockpolymer bylow temperature polycondensation of aluminosilicate polymers**, IUPAC International Symposium on Macromolecules Stockholm; Sept. ;Topic III, New Polymers of high stability.

Davidovits J. 1979. **Synthesis of new high temperature geo-polymers for reinforced plastics/composites.** SPE PACTEC 79 Society of Plastic Engineers, Brookfield Center.151-154.

Davidovits J. 1984. **Synthetic mineral polymer compound of the silicoaluminates family and preparation process.** US Patent 4,472,199.

Davidovits J. 1988a. **Geopolymer chemistry and properties.** In: Davidovits, J., Orlinski, J. (Eds.), Proceedings of the 1st International Conference on Geopolymer ’88, vol. 1, Compiegne, France, 1-3 June.25-48.

Davidovits J. 1988b. **Long term durability of hazardous toxic and nuclear waste disposals**. In: Davidovits, J., Orlinski, J. (Eds.), Proceedings of the 1st International Conference on Geopolymer ’88, vol. 1, Compiegne, France, 1-3 June.125-134.

Davidovits J. 1988c. **Soft Mineralurgy and Geopolymers**. In: Davidovits, J., Orlinski, J. (Eds.), . Proceedings of the 1st International Conference on Geopolymer ’88, vol 1, Compiegne, France, 1-3 June:19-23.

Davidovits J. 1999. **Chemistry of geopolymeric systems. Terminology.** In Proceedings of 99 geopolymer conference 1:9-40.

Davidovits J. 2005a. **Geopolymer chemistry and sustainable development**. The poly (sialate) terminology: a very useful and simple model for the promotion and understanding of green-chemistry. In: Proceedings of geopolymer conference 1:9-15.

Davidovits J. 2005b. **Geopolymer chemistry and sustainable development**. The poly(sialate) terminology: a very useful and simple model for the promotion and understanding of green-chemistry. In: Proceedings of 2005 geopolymer conference. 1:9-15.

Davidovits J, and Sawyer J. 1985. **Early high strength mineral polymer.** US Patent 4.509.958.

DH-S, 1990. Soil cement base. **Standards for Highway Construction.** Department of Highways (in Thai).

Diop MB, Grutzeck MW, and Molez L. 2011. **Comparing the performances of bricks made with natural clay and clay activated by calcination and addition of sodium silicate.** Applied Clay Science 54(2):172-178.

Dombrowski K, Buchwald A, and Weil M. 2007. **The influence of calcium content on the structure and thermal performance of fly ash based geopolymers.** Journal of Materials Science 42:3033-3043.

Duxson P, Ferna´ndez-Jime´nez A, Provis JL, Lukey GC, Palomo A, and Van Deventer JSJ. 2007a. **Geopolymer technology: the current state of the art.** Journal of Materials Science 42:2917-2933.

Duxson P, Lukey GC, and Van Deventer JSJ. 2006. **Nanostructural design of multifunctional geopolymeric materials.** p 203-214.

Duxson P, Lukey GC, and Van Deventer JSJ. 2007b. **Physical evolution of Na-geopolymer derived from metakaolin up to 1000 C.** Journal of Materials Science 42:3044-3054.

Duxson P, Mallicoat SW, Lukey GC, Kriven WM, and Van Deventer JSJ. 2007c. **The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers.** Colloids and Surfaces A Physicochemical and Engineering Aspects 292(1):8-20.

Duxson P, Provis JL, Lukey GC, Mallicoat SW, Kriven WM, and Van Deventer JSJ. 2005. **Understanding the relationship between geopolymer composition, microstructure and mechanical properties.** Colloids and Surfaces A Physicochemical and Engineering Aspects 269 (1-3):47-58.

Ervin M. C. 1992. **Engineering properties of Quaternary age sediments of the Yarra Delta**, Engineering Geology of Melbourne.

Fernandez-Jimenez A, and Palomo A. 2003. **Characterisation of fly ashes. Potential reactivity as alkaline cements.** Fuel 82:2259-2265.

Fernandez-Jimenez A, and Palomo J. 2005. **Composition and microstructure of alkali activated fly ash binder: effect of the activator**. Cement and Concrete Research 35:1984-1992.

Fernandez-Jimenez A, Palomo J, and Criado M. 2005. **Microstructure development of alkali activated fly ash cement: A descriptive model.** Cement and Concrete Research 35:1204-1209.

Fernandez-Jimenez A, Palomo J, and Puertas F. 1999. **Alkali activated slag mortars. Mechanical strength behaviour.** Cement and Concrete Research 29:1313-1321.

Fernandez-Jimenez A, Palomo J, Sobrados I, and Sanz J. 2006. **The role played by reactive alumina content in the alkaline activation of fly ashes**. Microporous and Mesoporous Materials 91:111-119.

Fernandez Jiminez AM, Lachowski EE, Palomo A, and Macphee DE. 2004. **Microstructural characterisation of alkali-activated PFA matrices for waste immobilisation.** Cement and Concrete Composites 26(8):1001-1006.

Fletcher RA, Mackenzie KJD, Nicholson CL, and Shimada S. 2005. **The composition range of alumino silicate geopolymers.** Journal of the European Ceramic Society 25:1471-1477.

Gomes T, Pereira JA, Ramalhosa E, Casal S, Baptista P. 2013. **Effect of fresh and composted spend coffee grounds on lettuce growth, photosynthetic**

pigments and mineral composition., *Agroingeniería VII and Iberian Congress of Horticultural Science*, Madrid.

Grutzeck MW, and Siemer DD. 1997. **Zeolites synthesised from class F fly ash and sodium aluminate slurry.** Journal of American Ceramic Society 80(9):2449-2458.

Guo X, Shi H, and Dick WA. 2010. **Compressive strength and microstructural characteristics of class C fly ash geopolymer**. Cement and Concrete Composites 32(2):142-147.

Hardjito D, Wallah SE, Sumajouw DMJ, and Vijaya Rangan B. 2004. **On the Development of Fly Ash-Based Geopolymer Concrete.** ACI Materials Journal 101(6):467-472.

Herrin, M., Mitchell, H., 1961. Lime–soil mixtures. Bulletin No.304, **Highway Research Board National Academy of Sciences, Research,** Washington, D.C.

Horpibulsuk, S., 2001. **Analysis and Assessment of Engineering Behavior of Cement Stabilized Clays.** Saga University, Saga, Japan (Ph.D. dissertation).

Horpibulsuk, S., Miura, N., 2001. **A new approach for studying behavior of cement stabilized clays. In: Proceedings of the 15th International Conference on Soil Mechanics and Geotechnical Engineering**, vol. 3, pp. 1759–1762.

Horpibulsuk, S., Miura, N., Nagaraj, T.S., 2003. **Assessment of strength development in cement–admixed high water content clays with Abrams' law as a basis.** Geotechnique 53 (4), 439–444.

Horpibulsuk, S., Bergado, D.T., Lorenzo, G.A., 2004a. **Compressibility of cement admixed clays at high water content.** Geotechnique 54 (2), 151–154.

Horpibulsuk, S., Miura, N., Bergado, D.T., 2004b. **Undrained shear behavior of cement admixed clay at high water content.** Journal of Geotechnical and Geoenvironmental Engineering, ASCE 30 (10), 1096–1105.

Horpibulsuk, S., Miura, N., Nagaraj, T.S., 2005. **Clay–water/cement ratio identity of cement admixed soft clay.** Journal of Geotechnical and Geoenvironmental Engineering, ASCE 131 (2), 187–192.

Horpibulsuk, S., Katkan, W., Sirilerdwattana, W., Rachan, R., 2006. **Strength development in cement stabilized low plasticity and coarse grained soils: laboratory and field study.** Soils and Foundations 46 (3), 351–366.

Horpibulsuk, S., Shibuya, S., Fuenkajorn, K., Katkan, W., 2007. **Assessment of engineering properties of Bangkok clay**. Canadian Geotechnical Journal 44 (2), 173–187.

Horpibulsuk, S., Kumpala, A., Katkan, W., 2008. **A case history on underpinning for a distressed building on hard residual soil underneath nonuniform loose sand**. Soils and Foundations 48 (2), 273–291.

Horpibulsuk, S., Rachan, R., Raksachon, Y., 2009. **Role of fly ash on strength and microstructure development in blended cement stabilized silty clay**. Soils and Foundations 49 (1), 85–98.

Horpibulsuk, S., Liu, M.D., Liyanapathirana, D.S., Suebsuk, J., 2010a. **Behavior of cemented clay simulated via the theoretical framework of the structured cam clay model**. Computers and Geotechnics 37 (1–2), 1–9.

Horpibulsuk, S., Rachan, R., Chinkulkijniwat, A., Raksachon, Y., Suddeepong, A., 2010b. **Analysis of strength development in cement-stabilized silty clay**

based on microstructural considerations. Construction and Building Materials 24, 2011–2021.

Horpibulsuk, S., Rachan, R., Suddeepong, A., 2011a. **Assessment of strength development in blended cement admixed Bangkok clay**. Construction and Building Materials 25 (4), 1521–1531.

Horpibulsuk, S., Rachan, R., Suddeepong, A., Chinkulkijniwat, A., 2011b. **Strength development in cement admixed Bangkok clay: laboratory and field investigations.** Soils and Foundations 51 (2), 239–251.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., 2012a. **Soil stabilization by calcium carbide residue and fly ash**. Journal of Materials in Civil Engineering, ASCE 24 (2), 184–193.

Horpibulsuk, S., Phochan, W., Suddeepong, A., Chinkulkijniwat, A., Liu, M.D., 2012b. Str**ength development in blended cement admixed saline clay.** Applied Clay Science 55, 44–52.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., Cholaphatsorn, A. 2013. **Strenth development in silty clay stabilized with calcium carbide residue and fly ash**. Soil and Foundations 53, 477-486.

Hos JP, McCormick PG, and Byrne LT. 2002. **Investigation of a synthetic aluminosilicate inorganic polymer.** Journal of Materials Science 37(11):2311-2316.

Ikeda K. 1998. **Consolidation of mineral powders by the geopolymer binder technique for materials use.** Journal of the Mining and Materials Processing Institute of Japan 114 497-500.

Ivanova I, Aiello R, Nagy JB, Crea F, Derouane EG, Dumont N, Nastro A, Subotic B, and Testa F. 1994. **Influence of cations on the physicochemical and structural properties of aluminosilicate gel precursors:II**. Multinuclear magnetic resonance characterization Microporous Materials 3(3):245-257.

Jaturapitakkul, C., Roongreung, B., 2003. **Cementing material from calcium carbide residue-rice husk ash.** Journal of Materials in Civil Engineering, ASCE 15 (5), 470–475.

Jiminez AMF, Lachowski EE, Palomo A, and Macphee DE. 2004. **Microstructural characterisation of alkali-activated PFA matrices for waste immobilisation**. Cement & Concrete Composites 26:1001-1006.

Kamon, M., Bergado, D.T., 1992. **Ground improvement techniques**. In Proceedings of the 9th Asian Regional Conference on Soil Mechanics and Foundation Engineering, vol. 2, pp. 526–546.

Kasama, K., Ochiai, H., Yasufuku, N., 2000. **On the stress–strain behaviour of lightly cemented clay based on an extended critical state concept.** Soils and Foundations 40 (5), 37–47.

Khale D, and Chaudhary R. 2007. **Mechanism of geopolymerization and factors influencing its development: a review**. Journal of Materials Science 42:729-746.

Khalil MY, and Merz E. 1994. **Immobilisation of intermediate-level wastes in geopolymers**. Journal of Nuclear Materials 211:141-148.

Khoury NN, and Zaman MM. 2007. **Environmental effects of aggregate stabilized with cementation materials.** Journal of Materials in Civil Engineering 180(1):41-48.

Komnitsas K, and Zaharaki D. 2007. **Geopolymerisation: A review and prospects for the minerals industry.** Minerals Engineering 20(14):1261-1277.

Kohgo Y, Tamrakar SB, Tang HG. 1970. **Investigations on the mechanical properties of typical soils distributed in northeast Thailand for the construction of irrigation facility**. Technical Report, Japan International Research Center for Agricultural Sciences; p. 222.

Kohgo Y, Horpibulsuk S. 1999. **Simulation of volume change behavior of yellow soil sampled from Khon Kaen City in Northeast Thailand.** In: Proceedings of the 11th Asian regional conference on soil mechanics and geotechnical engineering, Soul, Korea, p. 141–4.

Kondamundi N, Mohapatra SK, Misra M. 2008. **Spent coffee ground as a versatile source of green energy.** *Journal of Agriculture and Food Chemistry*, 56, 11757-11760.

Kumar S, Kumar R, Alex TC, Bandopadhyay A, and Mehrotra SP. 2005. **Effect of mechanically activated fly ash on the properties of geopolymer cement**. Proceedings of the World Congress Geopolymer Saint Quentin, France, 28 June-1 July:113-116.

Kumpala, A., Horpibulsuk, S., 2013. **Engineering properties of calcium carbide residue stabilized silty clay**. Journal of Materials in Civil Engineering, ASCE 25 (5), http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000618.

Kumpala, A., Horpibulsuk, S., Chinkulkijniwat, A., Shen, S.L., 2013a. **Engineering properties of recycled cemented clay as fill and pavement materials**. Construction and Building Materials 46, 203–210.

Kumpala, A., Horpibulsuk, S., Prongmanee, N., Chinkulkijniwat, A., 2013b. **Influence of wet-dry cycles on compressive strength of calcium carbide residue-fly ash stabilized clay**. Journal of Materials in Civil Engineering, ASCE

Lee WK. 2002. Solid-gel interactions in geopolymers. PhD Thesis, **Department of Chemical Engineering, University of Melbourne**, Australia.

Lee WKW, and Van Deventer JSJ. 2002. **The effects of inorganic salt contamination on the strength and durability of geopolymers**. Colloids and Surfaces A: Physicochemical and Engineering Aspects 211(2–3):115-126.

Liu, M.D., Indraratna, B., Horpibulsuk, S., Suebsuk, J., 2012. **Variations in strength of lime treated soft clays.** Ground Improvement 165 (4), 217–223.

Luz Granizo M, Blanco-Varela MT, and Mart´ınez-Ramı´rez S. 2007. **Alkali activation of metakaolins: parameters affecting mechanical, structural and microstructural properties**. Journal of Materials Science 42:2934-2943.

MacKenzie KJD, Brew D, Fletcher R, Nicholson C, Vagana R, and Schmu¨cker M. 2006. **Advances in understanding the synthesis mechanisms of new geopolymeric materials**. Ceramic Transactions 195:187-199.

McCormick AV, Bell AT, and Radke CJ. 1989. **Multinuclear NMR investigation of the formation of aluminosilicate anions.** Journal of Physical Chemistry 93(5):1741-1744.

Miller NA, Stirling CD, and Nicholson CL. 2005. **The relationship between cure conditions and flexural properties in flyash-based geopolymers.** Proceedings of the World Congress Geopolymer, Saint Quentin, France, 28 June-1 July:121-122.

Minaŕková M, and Škvára F. 2005. **Fixation of heavy metals in geopolymeric materials based on brown coal fly ash**. In: Davidovits, J. (Ed.), K. Komnitsas, D. Zaharaki / Minerals Engineering 20 (2007) 1261-1277 1275 Proceedings of the World Congress Geopolymer, Saint Quentin, France, 28 June-1 July, .45-49.

Miura, N., Horpibulsuk, S., Nagaraj, T.S., 2001. **Engineering behavior of cement stabilized clay at high water content**. Soils and Foundations 41 (5), 33–45.

Mussatto SI, Machado EMS, Martins S, Teixeira JA. 2011. P**roduction, composition and application of coffee and its industrial residues.** *Food and Bioprocess Technology*, 4(5), pp. 661.

Nagaraj, T.S., Miura, N., Yamadera, A., Yaligar, P., 1997. **Strength assessment of cement admixed soft clays—Parametric study.** in Proceedings of the International Conference on Ground Improvement Techniques, pp. 379–386.

Palomo A, Fernández-Jiménez A, Kovalchuk G, Ordoñez LM, and Naranjo MC. 2007. **Opc-fly ash cementitious systems: Study of gel binders produced during alkaline hydration**. Journal of Materials Science 42(9):2958-2966.

Palomo A, Grutzek M, and Blanco M. 1999. **Alkali-activated fly ashes. A cement for the future. .** Cement and Concrete Research 29:1323-1329.

Panagiotopoulou C, Kontori E, Perraki T, and Kakali G. 2007. **Dissolution of aluminosilicate minerals and by-products in alkaline media**. Journal of Materials Science 42:2967-2973.

Panias D, Giannopoulou I, and Perraki T. 2007. **Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers.Colloids Surf A**. 301:246-254.

Petermann JC, Saeed A, and Hammond MI. 2010. **Alkali-activated geopolymers: A literature review.** Air force research laboratory materials and manufacturing directorate.

Perera DS, Blackford MG, Vance ER, Hanna JV, Finnie KS, and Nicholson CL. 2004. **eopolymers for the immobilization of radioactive waste**. proceedings of the Materials Research Society Symposium:607-612.

Phair JW. 2001. **Compositional effects and microstructure of fly ash-based geopolymers.** PhD Thesis, Department of Chemical Engineering, University of Melbourne, Victoria, Australia.

Phair JW, and Van Deventer JSJ. 2001. **Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers**. Minerals Engineering 14(3):289-304.

Phair JW, Van Deventer JSJ, and Smith JD. 2000. **Mechanism of polysialation in the incorporation of zirconia into fly ash-based geopolymers.** Industrial and Engineering Chemistry Research 39(8):2925-2934.

Pinto A. 2004. **Alkali-activated metakaolin based binders**. PhD Thesis University of Minho.

Prakash, K., Sridharan, A., 2004. **Free swell ratio and clay mineralogy of finegrained soils**. Geotechnical Testing Journal, ASTM 27 (2), 220–225.

Provis JL, Lukey GC, and Van Deventer JSJ. 2005. **Do geopolymers actually contain nanocrystalline zeolites?** A reexamination of existing results. Chemistry of Materials 17:3075-3085.

Provis JL, and Van Deventer JSJ. 2007. **Geopolymerisation kinetics. 1. In situ energy-dispersive X-ray diffractometry.** Chemical Engineering Science 62:2309-2317.

Provis JL, Yong CZ, Duxson P, and van Deventer JSJ. 2009. **Correlating mechanical and thermal properties of sodium silicate-fly ash geopolymers**. Colloids and Surfaces A: Physicochemical and Engineering Aspects 336(1–3):57-63.

Puertas F, and Fernandez-Jimenez A. 2003. **Mineralogical and microstructural characterisation of alkali-activated fly ash/slag pastes**. Cement and Concrete Research 25:287-292.

Puertas F, Martinez-Ramirez S, Alonso S, and Vasquez T. 2000. Alkaliactivated fly ash/slag cement. **Strength behaviour and hydration products.** Cement and Concrete Research 30:1625-1632.

Purdon A. 1940. **The action of alkalis on blast furnace slag**. Journal Society of Chemical Industry 59:191-202.

Rahier H, Ban Melle V, Biesemans M, Wastiels J, and Wu X. 1996. **Low temperature synthesized aluminosilicate glasses. Part I. Low temperature reaction stoichiometry and structure of a model compound.** Journal of Mater Sci 31:71-79.

Rahier H, Simons W, Van Mele B, and Biesemans M. 1997. **Low-temperature synthesized aluminosilicate glasses: Part III Influence of the composition of the silicate solution on production, structure and properties**. Journal of Materials Science 32(9):2237-2247.

Rattanasak U, and Chindaprasirt P. 2009. **Influence of NaOH solution on the synthesis of fly ash geopolymer**. Minerals Engineering 22(12):1073-1078.

Silva PD, Sagoe-Crenstil K, and Sirivivatnanon V. 2007. **Kinetics of geopolymerization: Role of Al2O3 and SiO2.** Cement and Concrete Research 37(4):512-518.

Singh PS, Bastow T, and Trigg M. 2005. **Structural studies of geopolymers by 29Si and 27Al MAS-NMR.** Journal of Materials Science 40:3951-3961.

Stevenson M, and Sagoe-Crentsil K. 2005. **Relationship between composition, structure and strength of inorganic polymers: part 1 metakaolinderived inorganic polymers.** Journal of Materials Science 40:2023-2036.

Swaddle TW. 2001. **Silicate complexes of aluminum(III) in aqueous systems.** Coordination Chemistry Reviews 219-221, 665-686.

Swanepoel J, and Strydom Appl Geochem C. 2002. **Utilization of fly ash in a geopolymeric material**. 17(11):43-48.

Swanepoel JC, Strydom CA, and Smit JP. 1999. **Safe disposal of brine water in fly-ash geopolymeric material.** Proceedings of the 2nd International Conference on Geopolymer '99, Saint Qunentin, France, June 30-July 2:253-267.

Tanalapasakul, A., 1998. **Document from M Thai Industrial Company Limited.** M Thai Industrial Co., Ltd., Samutsakorn, Thailand.

Tatsuoka, F. and Kobayashi, A., 1983. **Triaxial strength characteristics of cement-treated soft clay.** In: Proceedings of the 8th European Conference on Soil Mechanics and Foundation Engineering, pp. 421–426.

Teixeira-Pinto A, Fernandes P, and Jalali S. 2002. **Geopolymer manufacture and application - main problems when using concrete technology**. Proceedings of the International Conference on Geopolymers, 28-29 October, Melbourne, Australia.

Terashi, M., Tanaka, H., Okumura, T., 1979. **Engineering properties of lime treated marine soils and DMM.** In: Proceedings of the 6th Asian Regional Conference on Soil Mechanics and Foundation Engineering, vol. 1, pp. 191–194.

Terashi, M., Tanaka, H., Mitsumoto, T., Niidome, Y., Honma, S., 1980. **Fundamental of lime and cement treated soils.** Report of Port and Harbour Research Institute 19 (1), 33–62 (in Japanese).

Thompson, M.R., 1966. **Lime reactivity of Illinois soil. Journal of Soil Mechanics and Foundation Division**, ASCE 92 (5), 67–92.

Udomchore V. 1991. **Origin and engineering characteristics of the problem soils in the Khorat Basin.** Northeastern Thailand, D.Tech. Dissertation, Asian Institute of Technology.

U.S. Army Corps of Engineers 2004. **Soil Stabilization for Pavements**. TM 5- 822-14/AFJMAN32/1019.,⟨http://www.wbdg.org/ccb/DOD/UFC/ufc_3_250_11.pdf⟩ (accessed 1607.2006).

Van Deventer JSJ, Provis JL, Duxson P, and Lukey GC. 2007. **Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products**. Journal of Hazardous Materials 139(3):506-513.

Van Jaarsveld JGS. 2000. **The physical and chemical characterisation of fly ash based geopolymers.** PhD Thesis, Department of Chemical Engineering, University of Melbourne, Australia.

Van Jaarsveld JGS, and Van Deventer JSJ. 1999. **Effect of the alkali metal activator on the properties of fly-ash based geopolymers.** Industrial and Engineering Chemistry Research 38(10):3932-3941.

Van Jaarsveld JGS, Van Deventer JSJ, and Lorenzen L. 1997. **The potential use of geopolymeric materials to immobilise toxic metals: Part I.** Theory and applications. Minerals Engineering 10:659-669.

Van Jaarsveld JGS, Van Deventer JSJ, and Lorenzen L. 1998. **Factors affecting the immobilization of metals in geopolymerized fly ash.** Metallurgical and Materials Transactions B 29:283-291.

Van Jaarsveld JGS, Van Deventer JSJ, and Lukey GC. 2002. **The effect of composition and temperature on the properties of fly ash- and kaolinite**. Chemical Engineering Journal 89(1-3):63-73.

Van Jaarsveld JGS, Van Deventer JSJ, and Lukey GC. 2003. **The characterisation of source materials in fly ash-based geopolymers**. Materials Letters 57(7):1272-1280.

Vijaya Rangan B. **Fly Ash-Based Geopolymer Concrete.** Available at: http://www.yourbuilding.org/display/yb/Fly+Ash Based+Geopolymer+Concrete

Wang H, Li H, and Yan F. 2005. **Synthesis and mechanical properties of metakaolinite-based geopolymers.** Colloids and Surfaces A - Physicochemical and Engineering Aspects 268:1-6.

Wang S-D, and Scrivener K. 1995. **Hydration products of alkali activated slag cement**. Cement and Concrete Research 25:561-571.

Williams PJ, Biernacki JJ, Walker LR, Meyer HM, Rawn CJ, and Bai J. 2002. **Microanalysis of Alkali-Activated fly ash-CH pastes**. Cement and Concrete Research 32:963-972.

Xie Z, and Xi Y. 2001. **Hardening mechanisms of an Alkaline-Activated class F fly ash.** Cement and Concrete Research 31:1245-1249

Xu H. 2001. **Geopolymerisation of aluminosilicate minerals.** PhD Thesis, Department of Chemical Engineering, University of Melbourne, Australia.

Xu H, and Van Deventer JSJ. 1999. **The geopolymerisation of natural alumino-silicates.** In Proceedings of the 2nd International Conference on Geopolymer '99, Saint Qunentin, France, June 30-July 2:43-64.

Xu H, and Van Deventer JSJ. 2000a. **Ab initio calculations on the fivemembered alumino-silicate framework rings model: implications for dissolution in alkaline solutions.** A Computers and Chemistry 24(391-404).

Xu H, and Van Deventer JSJ. 2000b. **The geopolymerisation of aluminosilicate minerals**. International Journal of Mineral Processing 59(3):247-266.

Xu H, and Van Deventer JSJ. 2002. **Microstructural characterisation of geopolymers synthesized from kaolinite/stilbite mixtures using XRD**, MAS-NMR, SEM/EDX, TEM/EDX and HREM. Cement and Concrete Research 32(1705-1716).

Xu H, Van Deventer JSJ, and Jannie S. 2002. **Geopolymerisation of multiple minerals**. Minerals Engineering 15:1131-1139.

Yip CK. 2004. **The role of calcium in geopolymerisation.** PhD Thesis, The University of Melbourne, Australia.

Yip CK, and Van Deventer JSJ. 2001. **Effect of granulated blast furnace slag on geopolymerisation.** In: CD-ROM Proceedings 6th World Congress of Chemical Engineering Melbourne, 23-27 September, Australia.

Yin, J.H., Lai, C.K., 1998. **Strength and stiffness of Hong Kong marine deposit mixed with cement.** Geotechnical Engineering Journal 29 (1), 29–44.

Zaharaki D, Komnitsas K, and Perdikatsis V. 2006. **Factors affecting synthesis of ferronickel slag based geopolymers**. In: Agioutantis, Z., Komnitsas, K. (Eds.), Proceedings of the 2nd International Conference on Advances in Mineral Resources Management and Environmental Geotechnology, Chania, Crete, Greece, 25-27 September, pp. 63-68.

Zillur Rabbi, A.T.M., Kuwano, J., Deng, J., Boon, T.W., 2011. **Effect of curing stress and period on the mechanical properties of cement-mixed sand**. Soils and Foundations 51 (4), 651–661.

Zhihua P, Dongxu L, Jian Y, and Nanry Y. 2002. **Hydration products of alkali-activated slag red mud cementitious material**. 32:357-362.

Zhihua P, Dongxu L, Jian Y, and Nanry Y. 2003. **Properties and microstructure of the hardened alkali-activated red mud-slag cementitious material**. Cement and Concrete Research 33:1437-1441.

CHAPTER III

CALCIUM CARBIDE RESIDUE AS A LIQUID ALKALINE FOR CLAY-FA GEOPOLYMER

3.1 Statement of problem

The chemical stabilization is one of the extensively used soil improvement techniques. The resistance of compression and consequent strength development increase with increasing curing time. Portland cement is commonly used for this stabilization. A high unit cost and energy intensive process of Portland cement are, however, the driving forces for the alternative cementitious additives. More importantly, the cement manufacturing process emits CO_2 into the atmosphere, which accounts for 5% of the total CO_2 released into the air. (Horpibulsuk et al., 2013)

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 (a mixture of sodium silicate solution and sodium hydroxide solution). 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 (Van Jaarsveld et al. 1998; Mohapatra and Rao 2001).

To improve economic and environmental impacts, some waste $Ca(OH)_2$-rich materials can be utilized together with waste pozzolanic materials, such as fly ash, biomass ash and rice husk ash to develop a geopolymer. Calcium carbide residue (CCR) is a by-product of the acetylene production process that contains mainly calcium hydroxide, $Ca(OH)_2$. Between 1995 and 1998, the demand for calcium carbide for the production of acetylene gas in Thailand was 74,000 t (Tanalapasakul, 1998). This demand is continuously increasing each year. The dissociation of $Ca(OH)_2$ leads to an increase in the pH values of the pore water. Strong bases dissolve the silica and alumina from the clay particles (a natural pozzolanic material) in a manner similar to the reaction between a weak acid and a strong base. The hydrous silica and alumina then gradually react with the calcium ions (pozzolanic reaction), which hardens with time. The variations in the strength and durability of CCR-stabilized soils under various influential factors such as CCR content and curing time have been studied and reported by Horpibulsuk et al. (2013), Kumpala and Horpibulsuk (2013) and Kumpala et al. (2013).

This chapter attempts to study the possibility of using CCR as a liquid alkaline instead of sodium hydroxide solution (NaOH) in geopolymer process to improve the strength of problematic silty clay in northeast Thailand. The unconfined compressive strength was used as a practical indicator to investigate strength development. The effects of liquid alkaline activator, fly ash content, state of water content, soaking condition, curing temperature and curing time on the strength development in the stabilized clay are illustrated.

3.2 Materials and methods

3.2.1 Soil sample

The soil sample is silty clay that was collected from the Suranaree University of Technology campus in the Nakhon Ratchasima province of Thailand at a depth of 3 m. It is a problematic soil, which is sensitive to changes in water content (Horpibulsuk et al., 2008). Fig. 3.1 shows the grain size distribution of the silty clay. It is composed of 2% sand, 43% silt and 55% clay. The average grain size, D_{50}, of the clay is 0.004 mm and the specific gravity is 2.76. The liquid and plastic limits are approximately 61% and 22%. Based on the Unified Soil Classification System (USCS), the clay is classified as high plasticity (CH). During sampling, the groundwater disappeared. The natural water content was 10%. The soil swelling potential of the tested clays was investigated by the free swelling test proposed by Prakash and Sridharan (2004) because it is simple and predicts dominant clay mineralogy of soils satisfactorily (Horpibulsuk et al., 2007). The free swell ratio, FSR, is defined as the ratio of equilibrium sediment volume of 10 g of oven-dried soil passing through a 425 μm sieve in distilled water (V_d) to that in carbon tetra chloride or kerosene (V_k). The clay is classified as low swelling with a free swell ratio (FSR) of 1.4. The Cation Exchange Capacity (CEC) is 27.6 meq/100 g. The chemical composition of the silty clay is shown in Table 3.1. The sum of SiO_2, Al_2O_3 and Fe_2O_3 is 60.54%, which is considered as high for pozzolanic reaction.

3.2.2 Binder

CCR from the Sai 5 Gas Product Co., Ltd. and FA from the Mae Moh power plant in the north of Thailand were used in this study. The CCR was oven-dried at 100°C for 24 h and was then ground using a Los Angeles abrasion machine. Both the CCR and FA were passed through a no. 40 sieve (425 μm). The specific gravity values are 2.32 and 2.39 for CCR and FA, respectively. Table 3.1 shows the chemical composition of both the FA and CCR compared with that of hydrated lime. The 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 C FA in accordance with ASTM C 618. Table 3.1 summarizes the chemical composition of hydrated lime and CCR using X-ray fluorescence (XRF). The oxides were obtained from weight loss at temperatures lower than 800 °C. The weight loss of the samples at a temperature of greater than 800 °C was used to determine the loss of ignition (LOI). The CaO contents are 90.13% and 70.78% for hydrated lime and CCR, respectively. This result is in agreement with the XRD pattern (Horpibulsuk et al., 2012a). The XRD pattern of the CCR is similar to that of hydrated lime, indicating that the $Ca(OH)_2$ is a main component of CCR. The high $Ca(OH)_2$ and CaO contents of the CCR indicate that it can react with pozzolanic material and produce a cementitious material. The grain size distribution of the FA and the CCR compared with that of the silty clay is shown in Figure 3.1. The curves were obtained from laser particle size analysis. The D_{50} of the FA is 0.0035 mm, which is close to that of the clay, and the D_{50} of the CCR is 0.01 mm (2.5 times larger than that of the clay).

The morphology of the silty clay and the FA is shown in Figure 3.2. The FA particles are normally fine and spherical while the clay and CCR particles are irregular in shape. The sodium silicate solution (Na_2SiO_3) contains 9% Na_2O and 30% SiO_2 by weight. Water was added to clay for possible compaction in proportion to Na_2SiO_3 content.

3.2.3 Methods

The silty clay was passed through a 2-mm sieve to remove the coarser particles. It was air-dried for at least 3 days and then the water content was adjusted for the compaction test. At least five compaction points were generated. The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum water content, OWC of 18% and maximum dry unit weight, γ_{dmax} of 16.9 kN/m^3. The modified Proctor energy was performed on this stabilized clay to study its engineering properties for pavement bases and subbases. It was shown that the stabilized clay compacted under the modified Proctor energy exhibited higher strength than that under the standard Proctor energy (Horpibulsuk et al., 2010b).

Having obtained the compaction curve, the air-dried clay was thoroughly mixed with CCR, FA and Na_2siO_3/water ratio compacted at OWC under the modified Proctor energy. This OWC provides higher strength than other molding water contents at the same compaction energy (Horpibulsuk et al., 2012a). The CCR content was 7%, which is the representative of the active zones. The FA contents were from 0% to 20% by weight of dry soil. In this study, the Na_2SiO_3/water ratios were 0.2, 0.6, 1.0 and 1.4 by weight. The liquid and plastic limits of the geopolymer-stabilized samples were determined immediately after thorough mixing. The index tests were finished within 15 min after mixing. After thoroughly mixing clay, the clay-CCR-FA–Na_2SiO_3 mixture was statically compressed in a cylindrical mold with 38 mm in diameter and 76 mm in height, and then cured at 40°C and the room temperature. The 40°C temperature was used to simulate heat on pavement in Thailand. 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. An unconfined compression (UC) test was run on the samples after 7, 14, 28 and 60 days of curing. Two sets of test sample were prepared for the unsoaked and soaked conditions. For the soaked condition, the samples were submerged under tap water for 2 hours according to the specification of the Department of Highways, Thailand, DH-S 204/2533 (DH-S, 1990). The rate of vertical displacement for the UC test was fixed at 1 mm/min. The testing program is summarized in Table 3.2. For each curing time and combination of water content, CCR content and FA content, at least five samples were tested under the same conditions to check for the test consistency. In most cases, the results under the same testing condition were reproducible with low mean standard deviation, SD ($SD / x < 10\%$, where x is mean strength value).

Table 3.1 Chemical properties of silty clay, fly ash, CCR and hydrated lime. (Horpibulsuk et al., 2013)

Chemical composition (%)	Silty clay	Fly Ash	CCR	Hydrated lime
CaO	26.15	30.24	70.78	90.13
SiO_2	20.10	47.51	6.49	1.29
Al_2O_3	7.55	13.14	2.55	0.24
Fe_2O_3	32.89	6.66	3.25	0.49
MgO	0.47	N.D.	0.69	0.22
SO_3	4.92	N.D.	0.66	0.86
Na_2O	ND	0.41	N.D.	N.D.
K_2O	3.17	1.63	7.93	3.3
LOI	3.44	0.42	1.35	1.21

N.D. = not detected.

Table 3.2 Summary of the testing program.

Test	Binder			Water content (%)	Curing temp. (°C)	Curing time (days)
	CCR (%)	FA (%)	Na_2sio_3/Water By weight			
Index properties	7	0, 5, 10, 15,20	0.2, 0.6, 1.0, 1.4	-		
Compaction	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	-		
UC test (soaked condition)	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	OWC	ambient, 40	7, 14, 28, 60
UC test (unsoaked condition)	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	OWC	ambient, 40	7, 14, 28, 60
	7	0, 5, 10, 15	0.2, 0.6, 1.0, 1.4	0.8,1.2,1.4OWC	ambient, 40	7

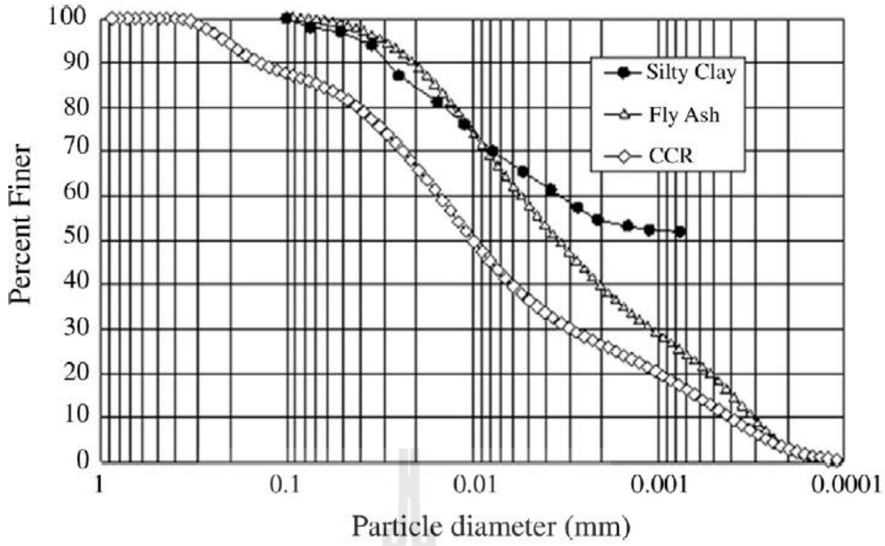
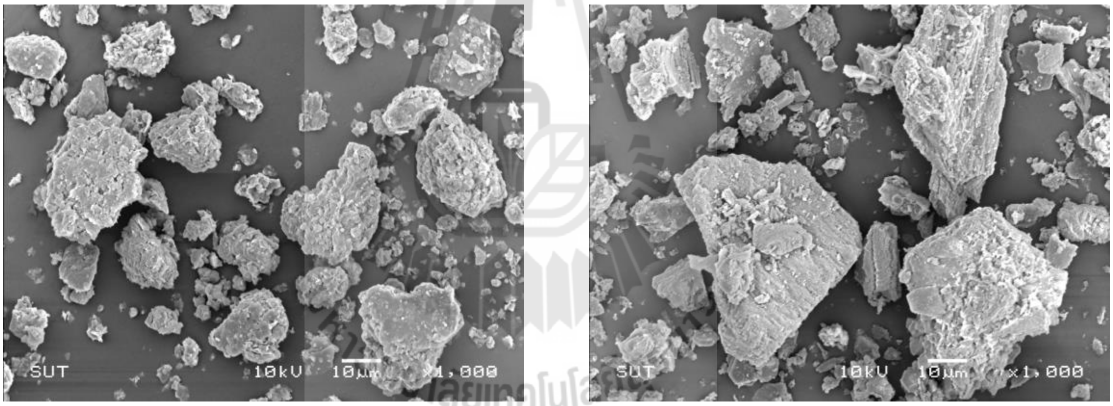
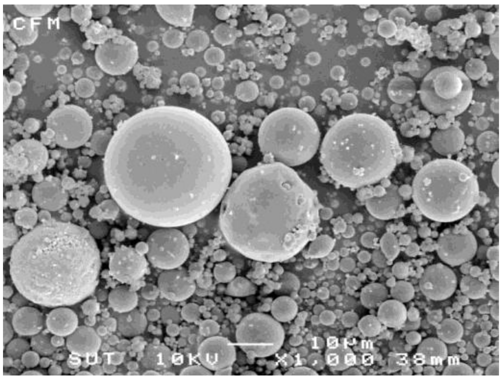


Figure 3.1 Grain size distribution of the clay, CCR and FA.



(a) Silty Clay

(b) CCR



(c) Fly Ash

Figure 3.2 Scanning Electron Microscope (SEM).

3.3 Results

Figure 3.3 shows typical compaction for the geopolymer stabilized clay without FA for different Na_2SiO_3/water ratios. The maximum dry unit weight, ($\gamma_{d,\ max}$), increases with increasing Na_2SiO_3/water ratio. This increase in $\gamma_{d,max}$ is associated with an decrease in optimum liquid content (OLC). Figures 3.4 and 3.5 show typical compaction curves of geopolymer stabilized clay with various Na_2SiO_3/water and FA ratios. The maximum dry unit weight of geopolymer-stabilized clay increases with increasing Na_2SiO_3/water ratio. When the Na_2SiO_3/water ratio is greater than 1.0, the dry unit weight decreases. The geopolymer-stabilized clay samples show lower $\gamma_{d,max}$ than the compacted clay sample (16.9 kN/m^3) because the CCR and FA have a lower specific gravity than the clay.

Even though their OLC values are different, the maximum strengths of all the stabilized clay samples occur approximately at their OLC (maximum dry unit weight) [Figure 3.6]. This characteristic is the same as that of cement-stabilized silty clay, as illustrated by Horpibulsuk et al. (2009, 2010b).

Table 3.3 shows the change in index properties of the geopolymer-stabilized clay with and without FA. As the FA content increases, the plastic limit (PL) of the stabilized clay insignificantly changes with Na_2SiO_3/water ratio while the liquid limit (LL) decreases significantly, resulting in a sharp decrease in the plasticity index (PI).

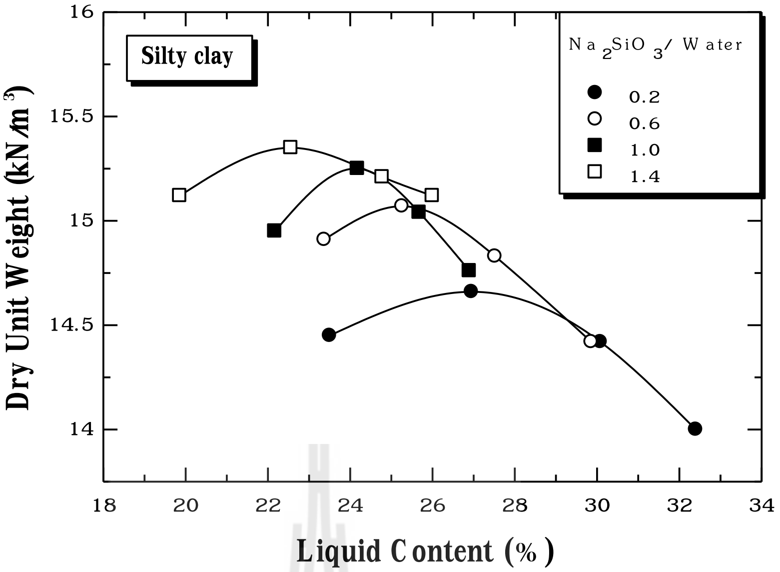


Figure 3.3 Compaction curves of CCR-stabilized clay for difference Na2SiO3/water ratios.

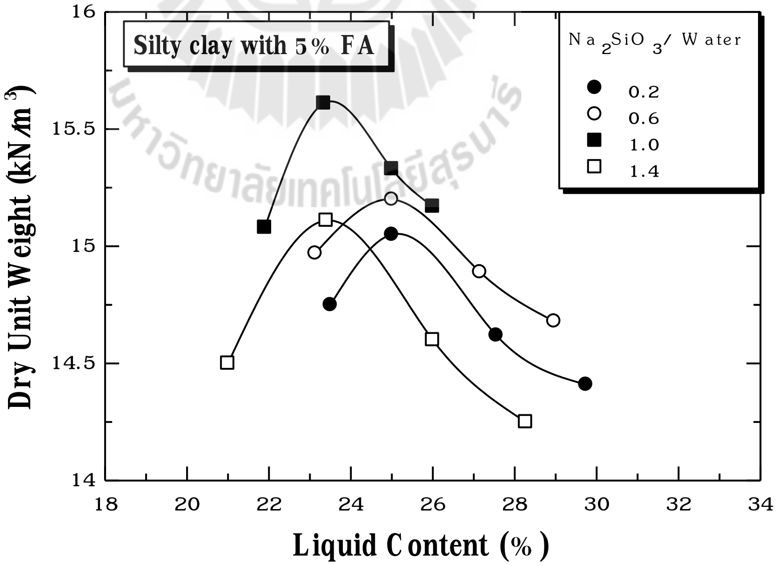


Figure 3.4 Compaction curves of CCR-and FA-stabilized clay for different Na2SiO3/water ratios.

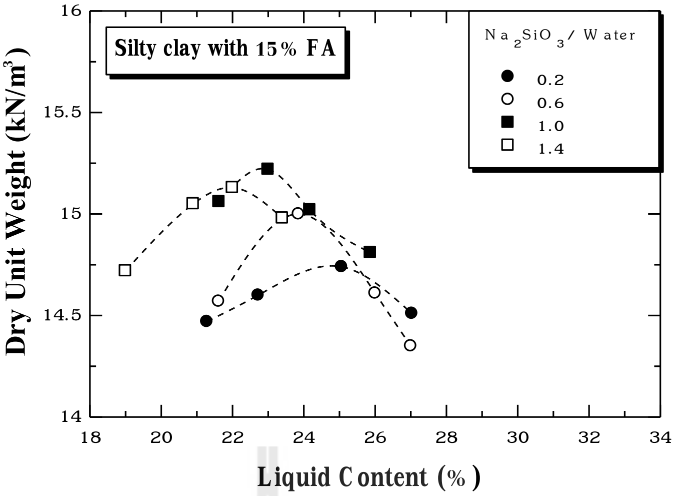


Figure 3.5 Compaction curves of CCR-and FA-stabilized clay for different Na_2SiO_3/water ratios.

Table 3.3 Index properties of the CCR-stbilized clay for different FA and Na2SiO3/water ratios.

Sample	Na_2SiO_3/water	Liquid limit (%)	Plastic limit (%)	PI	OLC	$\Upsilon_{d,max}$
Silty clay	0.2	70	22	48	27	14.7
	0.6	47	22	25	25	15.1
	1.0	40	22	18	24	15.3
	1.4	35	22	13	23	15.3
Silty clay+5%FA	0.2	62	23	39	25	15.0
	0.6	46	23	23	25	15.2
	1.0	39	22	17	23	15.6
	1.4	36	22	14	23	15.1
Silty clay+10%FA	0.2	57	23	34	25	14.7
	0.6	47	23	24	25	15.0
	1.0	41	23	18	23	15.4
	1.4	37	23	14	23	15.1
Silty clay+15%FA	0.2	56	24	32	25	14.7
	0.6	46	24	22	25	15.0
	1.0	43	23	20	23	15.2
	1.4	41	23	18	22	15.1
Silty clay+20%FA	0.2	55	25	30	25	14.5
	0.6	45	25	20	26	14.7
	1.0	44	25	19	23	15.1
	1.4	41	25	16	23	14.8

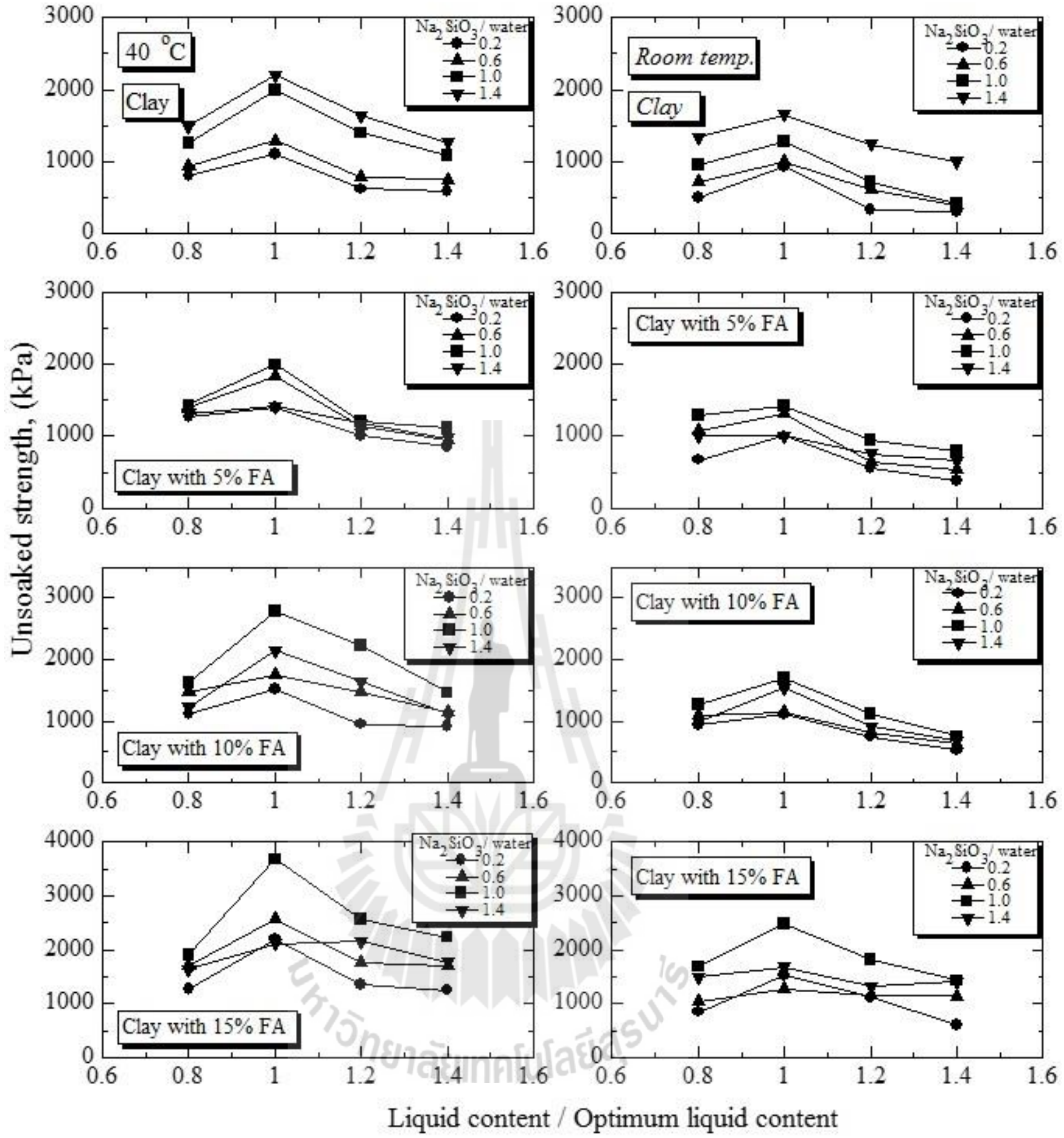


Figure 3.6 Unsoaked strengths of CCR-FA- Na_2SiO_3/water stabilized clay for difference liquid content/OLC.

The unsoaked strengths of the stabilized clay samples for different Na_2SiO_3/water ratios and curing times at the OLC are shown in Fig. 3.7 for 40°C and room temperature curing. Strength development is significantly dependent on the Na_2SiO_3/water ratio. The strength increases sharply as the Na_2SiO_3/water ratio increases up to the optimal value and then decreases as the Na_2SiO_3/water ratio increases. The optimum Na_2SiO_3/water ratios is 1.4 and 1.0 for geopolymer stabilized clay with and without FA, respectively. The strength at 40 °C is higher than the strength at room temperature.

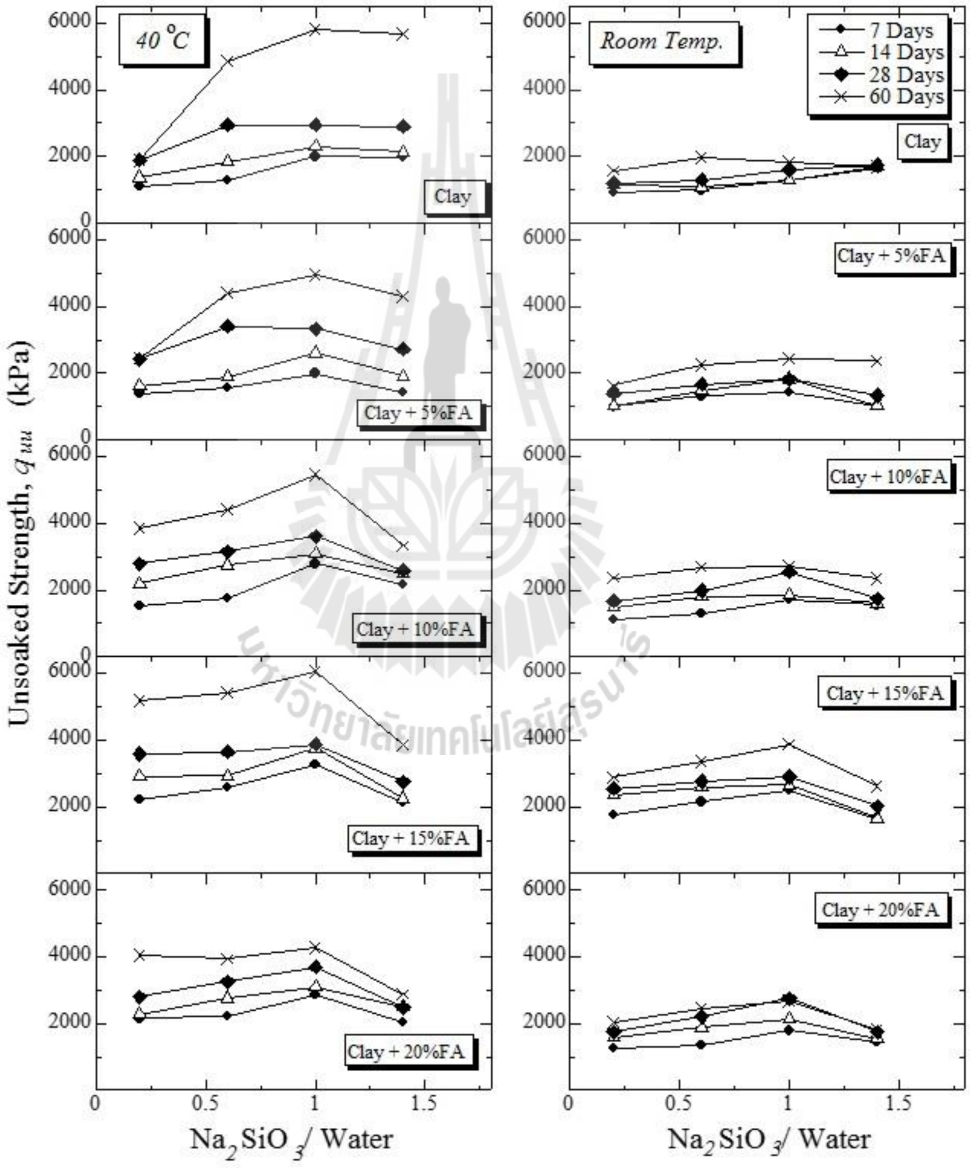


Figure 3.7 Unsoaked strengths of CCR-FA stabilized clay for different Na_2SiO_3/water ratios.

Figure 3.8 shows relationship between Unsoaked strength and FA contents with constant Na_2SiO_3/water ratios. The maximum strengths for all curing times and both curing temperatures are found at 15% FA replcamentsThere exists two types of strength decevelopment with FA. The 40°C curing provides higher strength than the room temperature curing, showing the effect of curing temperature.

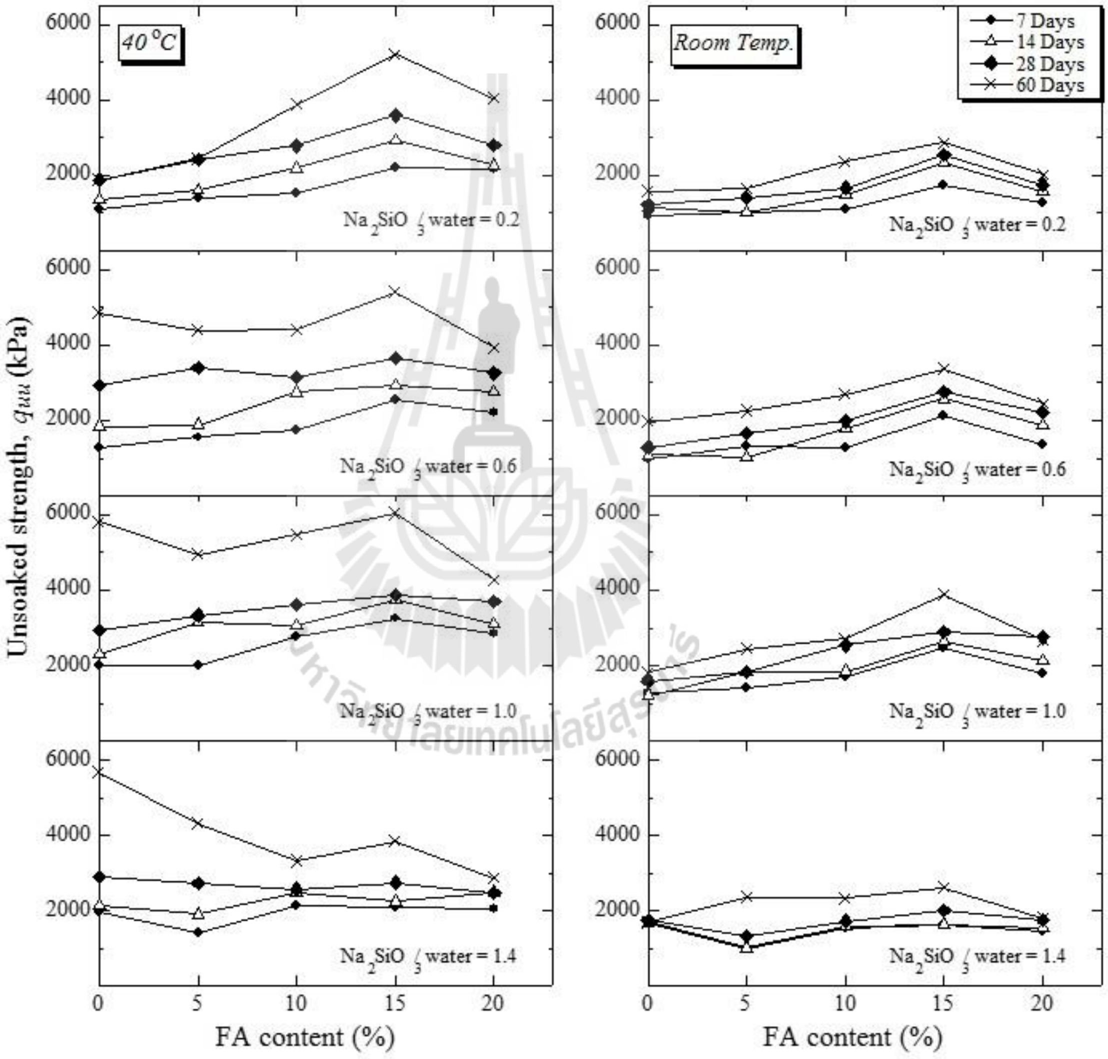


Figure 3.8 Unsoaked strengths of geopolymer stabilized clay for different FA replacement ratios.

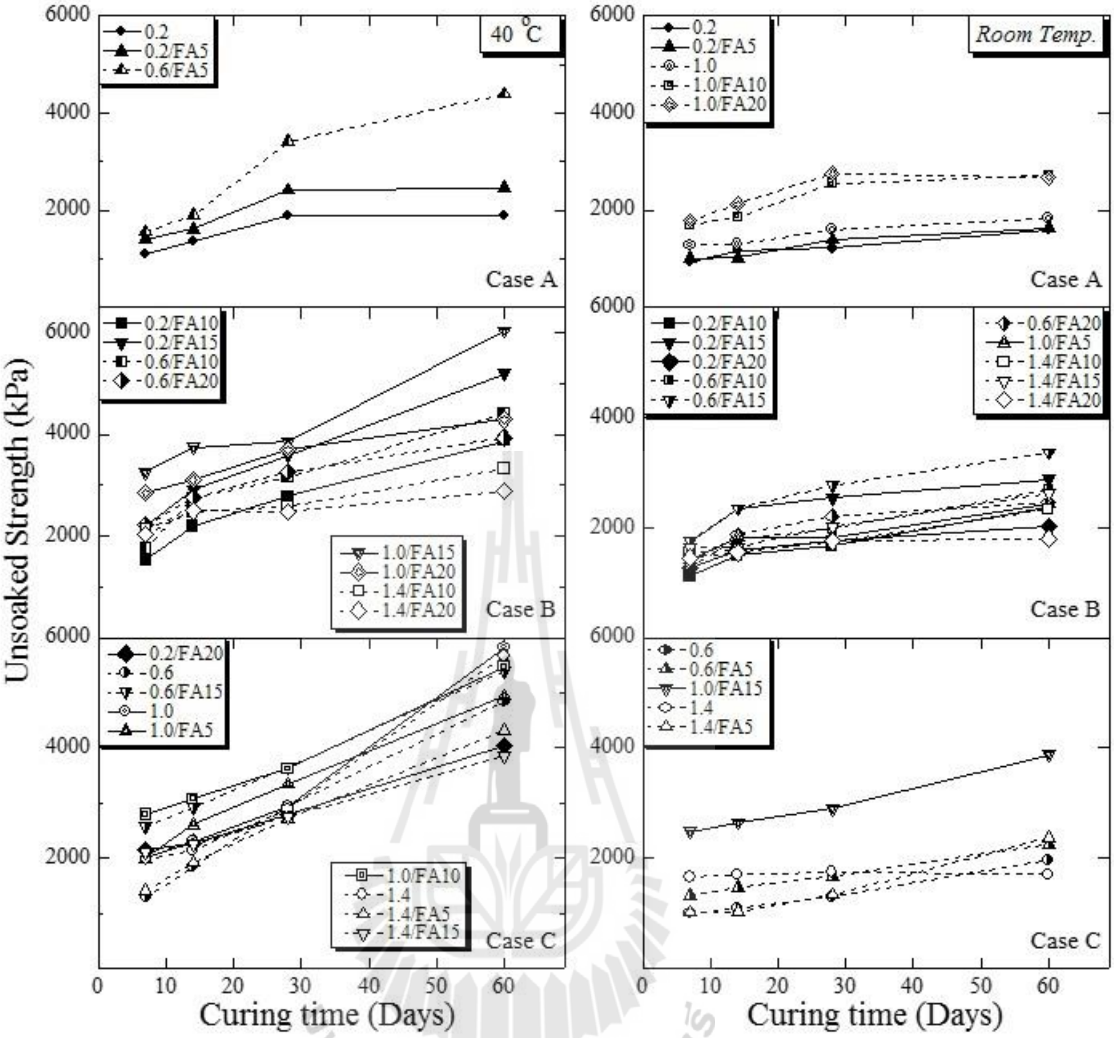


Figure 3.9 Unsoaked strengths of CCR-FA and Na_2SiO_3/water stabilized clay for different curing times.

Figure 3.9 shows a relationship between Unsoaked strength and curing time for different FA replacement ratios at constant Na_2SiO_3/water ratios. The result of same Na_2SiO_3/water ratios can be divided into 3 groups. First, the strength significantly increases with curing time up to 14 days after that strength increase becomes insignificant. This first group is found for 5% FA and 10% FA replacement ratios.

Second, the strength increases significantly after 28 days (namely FA15). Third, the strength linearly increases with curing time.

Table 3.4 Soaked strength of CCR-FA and Na_2SiO_3/water stabilized clay

		7Days		14Days		28Days		60Days	
Description	Na_2SiO_3/water	40 C°	RT	40 C°	RT	40 C°	RT	40 C°	RT
clay	0.2	0	0	0	0	990	1205	1485	1300
clay + 5%FA		0	0	773	773	1101	928	1628	1375
clay + 10%FA		1454	1052	1514	1265	1698	1694	2332	1804
clay + 15%FA		2166	1732	2258	1812	2241	1856	2345	1924
clay + 20%FA		2004	1178	2105	1356	1988	1590	2014	1651
clay	0.6	0	0	0	0	0	0	689	1120
clay + 5%FA		0	0	447	433	954	988	1598	1303
clay + 10%FA		1728	1354	1802	1874	1650	1745	2544	1924
clay + 15%FA		2154	1658	2269	2000	2345	2458	3120	2578
clay + 20%FA		2100	1254	2187	1578	2095	1687	2245	1767
clay	1.0	0	0	0	0	0	0	0	0
clay + 5%FA		0	0	0	0	0	0	0	0
clay + 10%FA		0	0	0	0	0	0	0	0
clay + 15%FA		0	0	0	0	0	0	0	0
clay + 20%FA		0	0	0	0	0	0	0	0
clay	1.4	0	0	0	0	0	0	0	0
clay + 5%FA		0	0	0	0	0	0	0	0
clay + 10%FA		0	0	0	0	0	0	0	0
clay + 15%FA		0	0	0	0	0	0	0	0
clay + 20%FA		0	0	0	0	0	0	0	0

Table 3.4 shows the soaked strength of geopolymer stabilized clay. The soaked strengths are lower than the unsoaked strengths. The soaked strengths at 40^{o}C curing are null for Na_2SiO_3/water ratios greater than 1.0 for all curing times even though the unsoaked strengths are highest at these ratios. The stable samples at these high

Na_2SiO_3/water ratios under the water immersion are found only for high curing time and at room temperature curing. The highest soaked strengths are found for the geopolymer stabilized samples at Na_2SiO_3/water ratio of 0.6 for different FA replacement ratios. The optimum FA replacement ratio is at 15% and the 40^oC curing time provider higher soaked strength than the room temperature curing.

Figure 3.10 shows the soaked strength development with time for the geopolymer stabilized clay for Na_2SiO_3/water ratios of 0.2 and 0.6 and different FA replacement ratios. The strength development of the geopolymer stabilized samples with the 40^oC is insignificant compared with that with the room temperature. For the room temperature curing, the strength sharply increases for curing times lower than 28 days and becomes insignificant for curing times greater than 28 days.

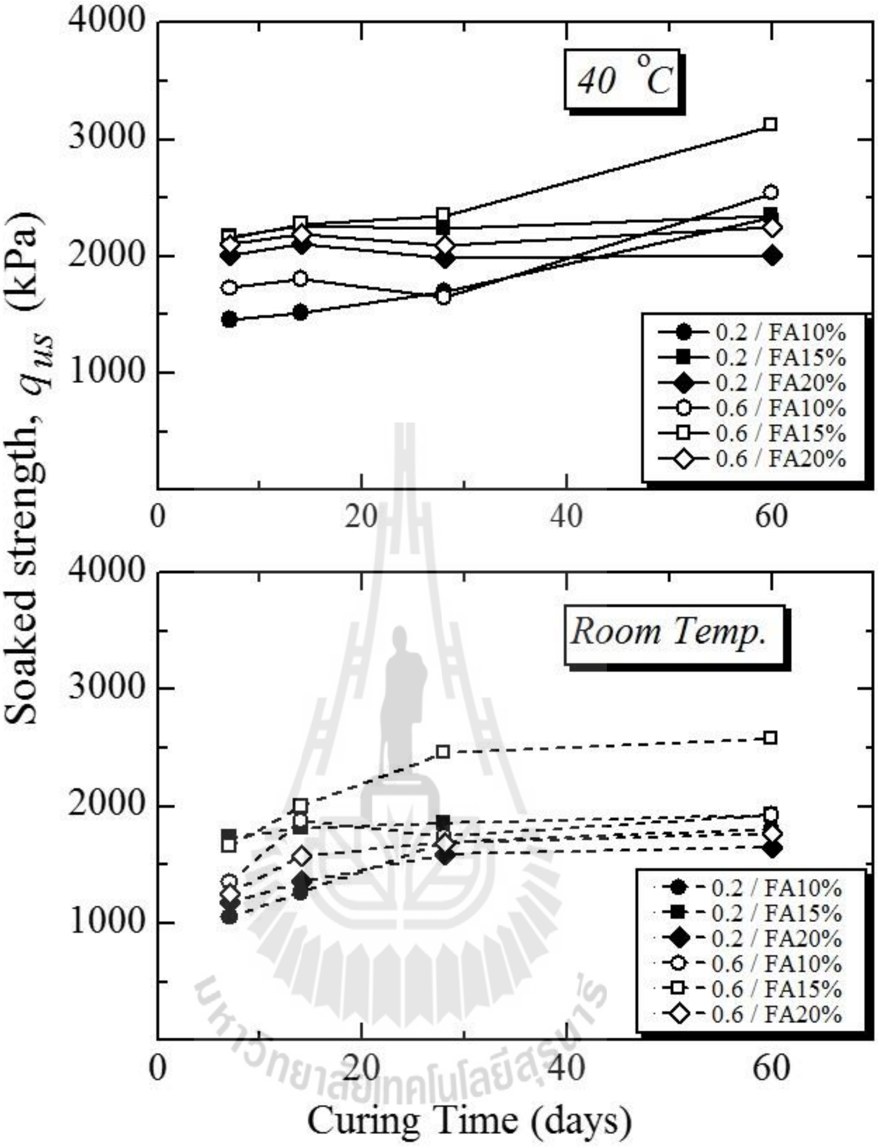


Figure 3.10 Soaked strengths of CCR-FA and Na_2SiO_3/water stabilized clay for different curing times.

Figure 3.11 presents the relationship between soaked strengths of geopolymer stabilized clay and FA replacement ratio. The strength increases as the FA increases up to optimum at 15% FA replcament ratio. Final strength of 0.2 Na_2SiO_3/water ratio at 40^{o}C is close to that at room temperature but strength of 0.6 Na_2SiO_3/water ratio at 40 ^{o}C is lower than that at room temperature.

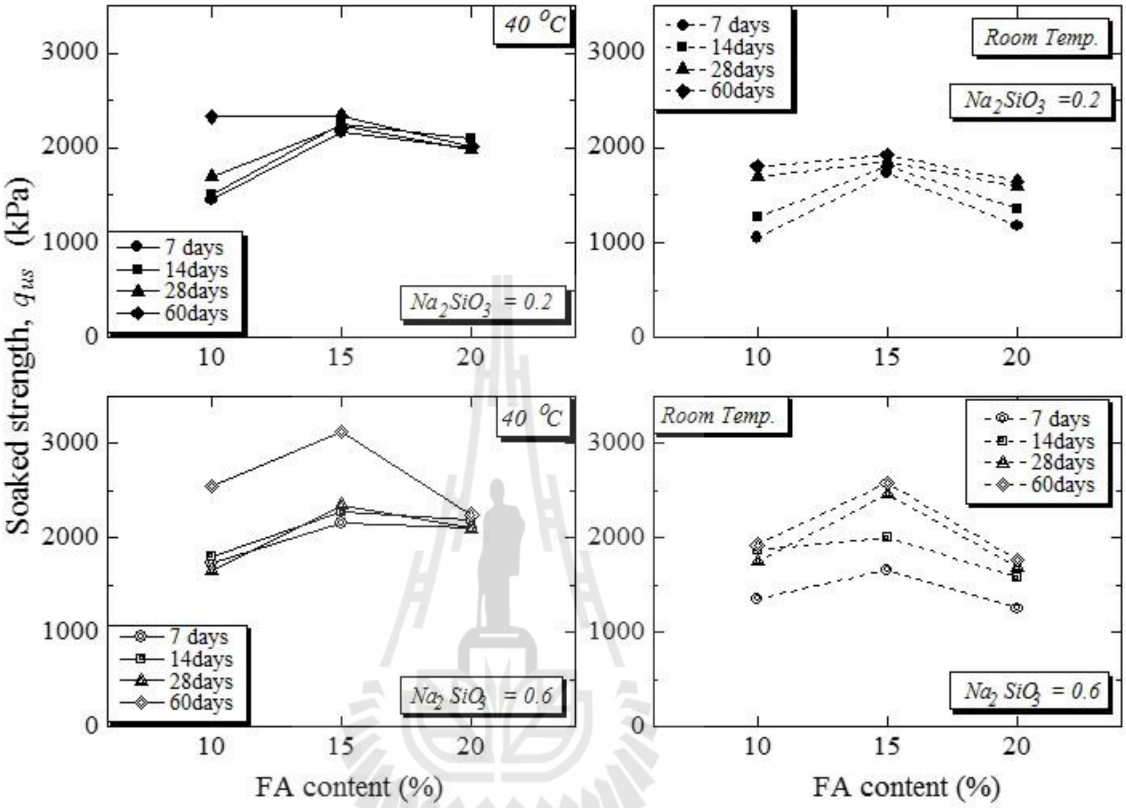


Figure 3.11 Soaked strengths of geopolymer stabilized clay for different FA replacement ratios.

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 that shows in

Figure 3.12 and 3.13. The compaction curves of the clay–FA Na_2sio_3 are significantly changed with the input liquid activator. This is because the liquid activators change the index properties of the clay and FA mixture and interrupt flocculation reaction between clay and CCR.

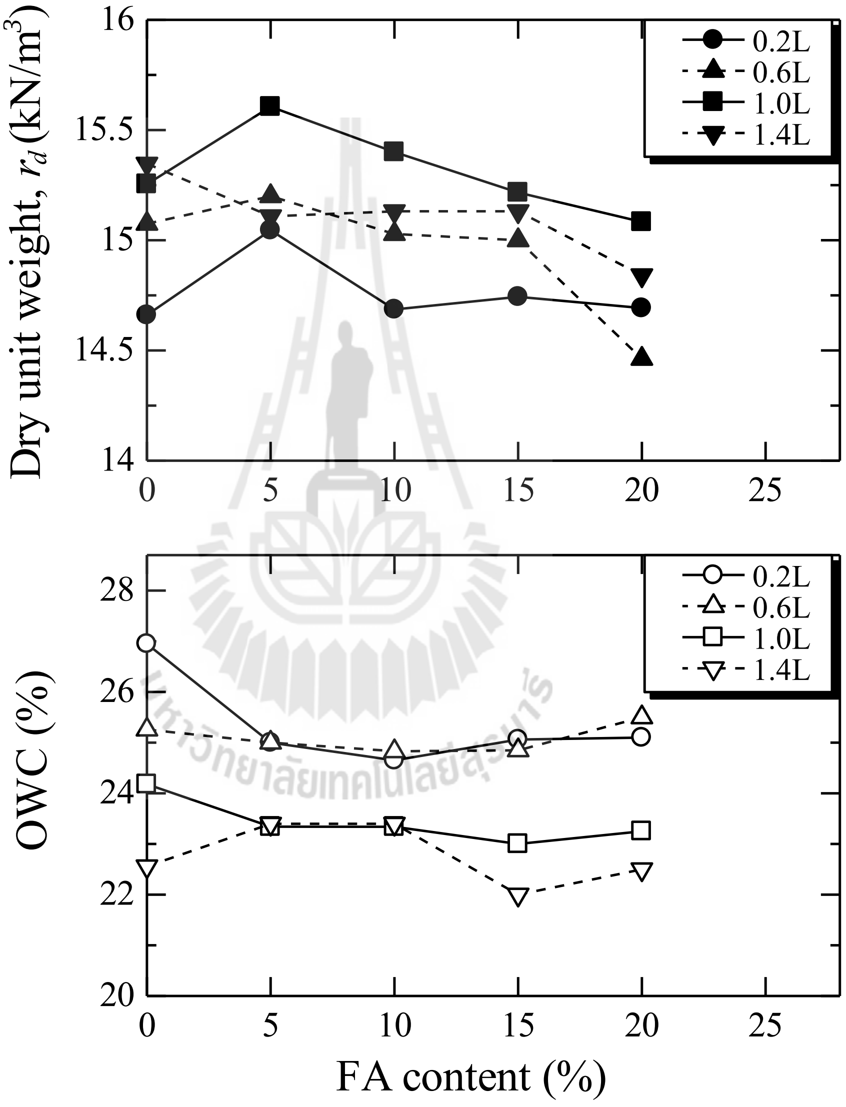


Figure 3.12 Dry unit weigth and OWC of CCR- Na2SiO3/water stabilized clay for different FA.

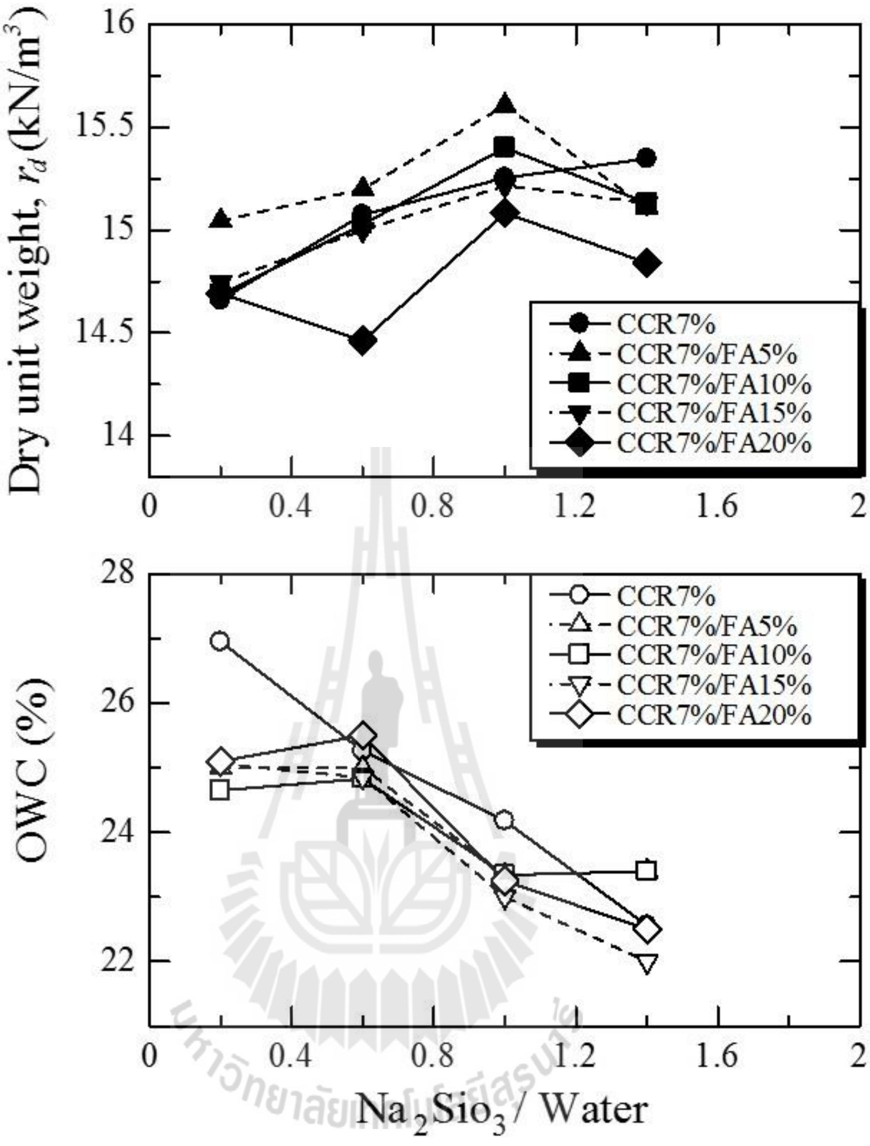


Figure 3.13 Dry unit weight and OWC of CCR- Na2SiO3/water stabilized clay for different L.

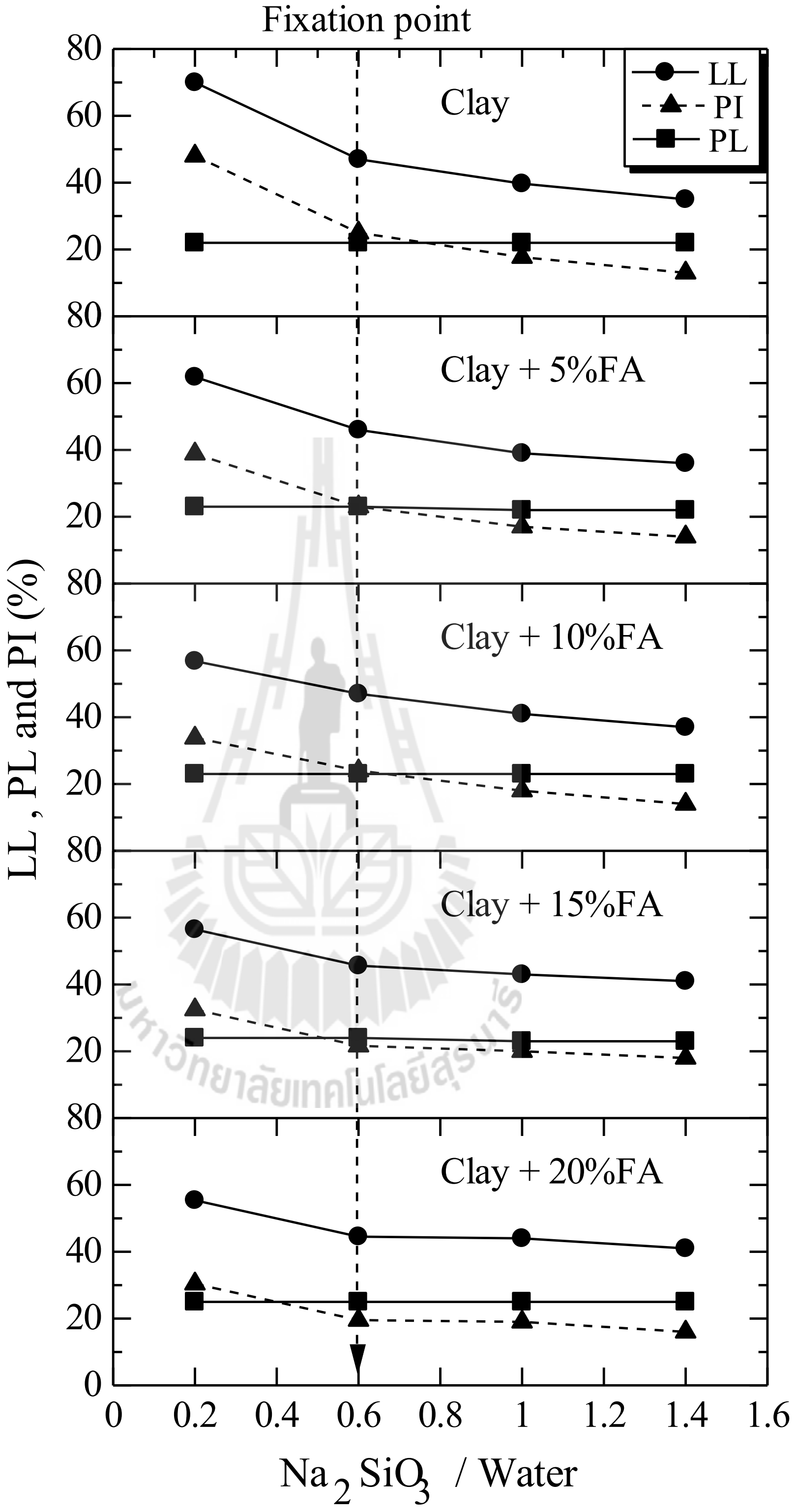


Figure 3.14 LL, PL and PI of CCR- Na_2SiO_3-clay mixtures for different Na_2SiO_3/water ratios.

The strength development in the clay-FA Na_2sio_3 specimen is controlled by four factors; namely, cation exchange, liquid activator, heat and pozzolanic reaction. In the present work, the liquid activator is the mixture of sodium silicate solution (Na_2SiO_3) water and CCR. The high pH environment from CCR 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/water ratios to provide the maximum unsoaked and soaked strength for Clay–FA Geopolymer specimens are different. They are 1.0 and 0.6 for the unsoaked strengths and soaked strength, respectively. Na_2SiO_3 itself can harden at room temperature so, when it is mixed with clay, the unsoaked strength increases with Na_2SiO_3. The Na_2SiO_3 is sensitive to water; thus the high amount of Na_2SiO_3 cause unstable to the samples under soaking condition. The optimum Na_2SiO_3/water providing the highest soaked strength is found at 0.6, which is the transition PI for all mixtures (*vide* Figure 3.14). This is implies that the transitional PI can be used in practice to determine the optimum Na_2SiO_3/water ratio. The decrease in PI is due to the compression in diffusion double layer resulted from the cation exchange. The insignificant change in PI after transitional PI shows that Na_2SiO_3 is in excess the requirement for geopolymerization reaction. As such, the unsoaked strength increases with Na_2SiO_3 due to the hardening of Na_2SiO_3. The effect of added FA on the strength development is shown in Figures 3.9 and 3.10. SiO_2 and Al_2O_3 in FA are in amorphous phase and can be effectively reacted with CCR and Na_2SiO_3. As such, the strength increases with FA replacement ratio. However, the excess FA of greater than 15% is not meaningless because the excess FA surrounds the CCR particles and obstructs the geopolymerization reaction. The 40oC curing provides higher unsoked and soaked strengths than the room temperature curing. This implies that the geopolymer stabilized clay can be applied as subbase/base materials in practice. The soaked strengths are lower than unsoaked strength for all ingredients and curing conditions. The lower strength is due to two main factors: degradation of Na_2SiO_3 and repulsive forces due to water absorption. At Na2SiO3/water lowers than 1.0, the effect of degradation of Na_2SiO_3decreases as Na_2SiO_3/water ratio decreases. It is more or less insignificant when the Na_2SiO_3/water ratios are lower than 1.0 where Na_2SiO_3 is optimal for the geopolymerization reaction.

Kumpala and Horpibulsuk (2013) conducted water absorption and oedometer soaking tests. It was found that water absorption increased with immersion time, which was associated with an increase in vertical swelling and swelling pressure. The swelling pressure is the pressure applied to the samples until the vertical swell becomes null. This swelling pressure induces repulsion between the cemented clay particles. Consequently, the soaked strength is lower than the unsoaked strength.

Horpibulsuk et al. (2013) found that even though the strength development in both the soaked and unsoaked samples depends on the CCR and FA contents, the ratio of the soaked strength to unsoaked strength is almost the same for all the CCR and FA contents Most of the ratios vary between 0.45 and 0.65, with an average of 0.55 (vide Fig. 3.15). Figure 3.16 shows the strength ratio for the geopolymer stabilized clay for both curing temperatures. Compared with the test data by Kumpala and Horpibulsuk (2013), the strength ratios for geopolymer stabilized clay (0.6-0.95 for 40^oC temperature and 0.75-1.0 for room temperature) are higher than those the CCR stabilized clay (0.45-0.65). This shows the advantage of the geopolymer stabilized clay in term of durability against wet-dry cycles. In other words, the cementation bonding due to chemical reaction from geopolymer effectively prevents reduce repulsive forces between the clay particles.

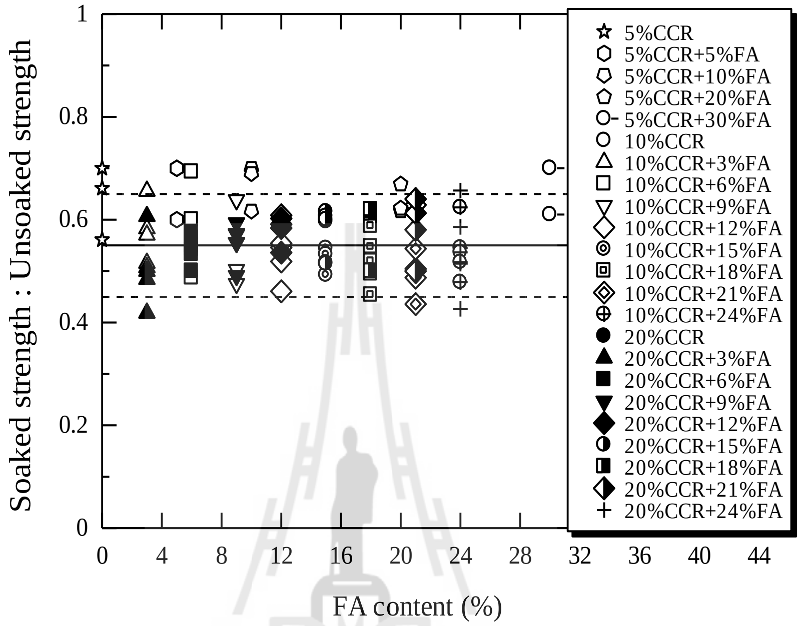


Figure 3.15 Strength ratio of the CCR stabilized clay with different FA content. Horpibulsuk et al. (2013)

Scanning Electron microscopy (SEM) image is a useful tool for monitoring the microstructural development over time of the cementitious matrix generated as a result of the alkali activation of fly ash (Horpibulsuk et al., 2009: 2010b, Du et al., 2014). Figure 3.17 and 3.18 show a comparison of microstructure of two clay-FA geopolymer samples at Na_2SiO_3/water ratios of 0.6 (optimal) and 1.4, respectively. Figure 3.17 shows the chemical attack (alkaline dissolution) at some points on the surface of FA particles (positions A and B). The lower images show the magnified FA particles at positions A and B. Many holes on the FA surface (refer to point A) caused by chemical attack are observed and exposes smaller particles.

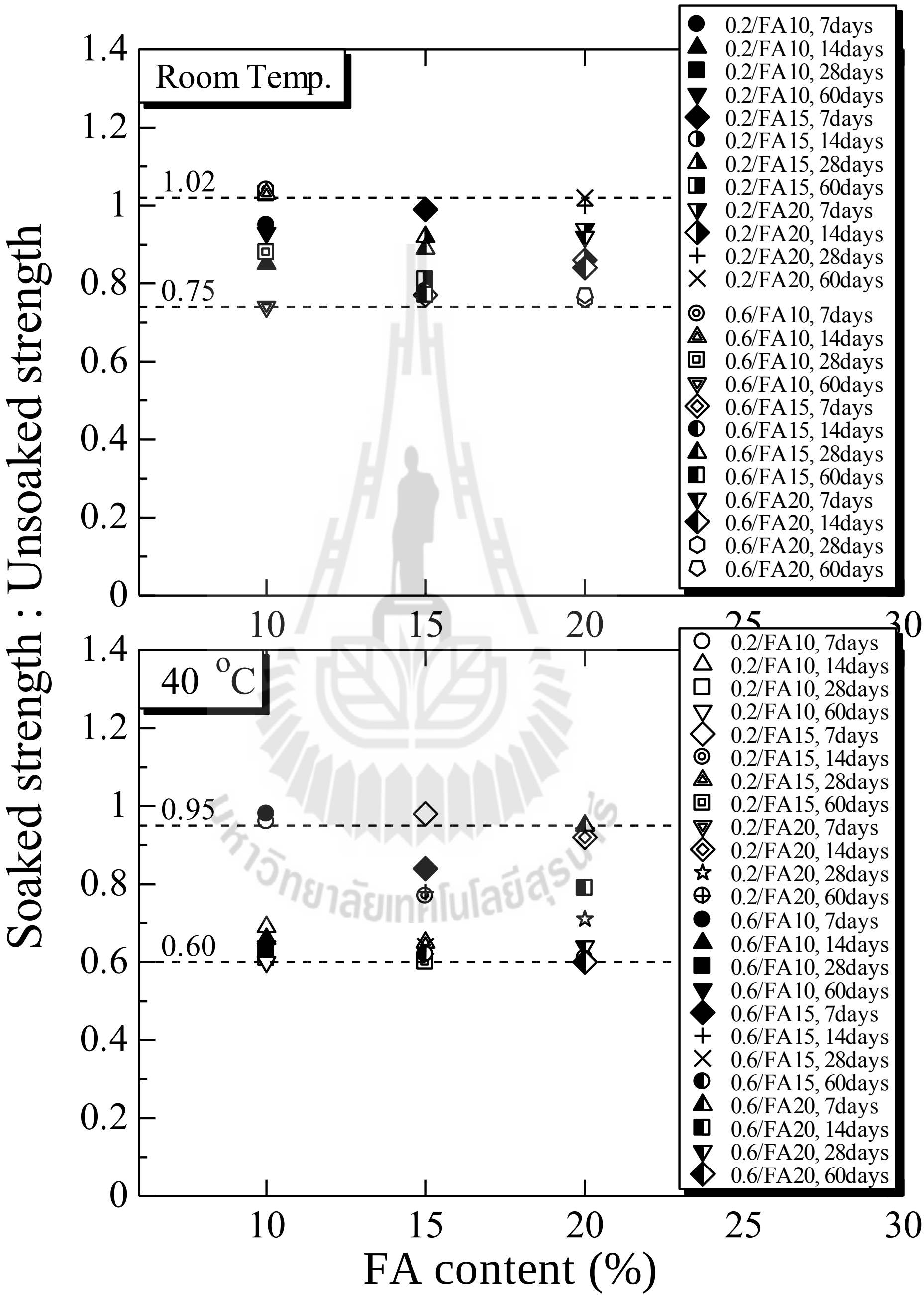


Figure 3.16 Strength ratio of the geopolymer stabilized clay with different FA content.

The holes are partially filled with other smaller size ash particles (refer to point B).The alkaline solution contacts the smaller particles housed inside the larger spheres and the interior space of the latter starts to fill up with reaction product, forming a dense matrix. Figure 3.18 shows the microstructure of the sample with high Na_2SiO_3/water ratio of 1.4. The lower image presents the magnified FA particle at position A where the excessive (unreacted) Na_2SiO_3 is clearly seen on FA particle. Therefore, the samples with Na_2SiO_3/water ratio of 0.6 shows higher soaked strength while the samples with Na_2SiO_3/water ratio of 1.4 show zero soaked strength due to lower cementation bonding. Figure 3.19 shows SEM image of the clay-FA geopolymer samples with Na_2SiO_3/water ratio of 0.6 and cured at room temperature after 60 days of curing. The effect of temperature curing on the strength development is illustrated by comparing Figure 3.19 with Figure 3.17. The geopolymerization products and etching on the surface are seen to be more evident at a higher curing temperature. The effect of temperature curing on early strength of clay-FA geopolymer is depicted in Figure 3.20. The etching on the FA surface is clearly shown for 40 ^{o}C curing after 7 days of curing while Na_2SiO_3 is still abundant on the FA surface. The role of FA on strength development is shown in Figure 3.21, which shows the SEM image of the clay-FA geopolymer cured for 60 days with and without FA. The structure of the clay–geopolymer is a result of the coagulation of sodium silicate. The geopolymerization products are less because the silica and alumina in the soil are mostly in crystal phase. Therefore, the strength of clay–geopolymer is caused by the coagulation of clay particles. Due to the clay swelling pressure, these unstable structures of clay–geopolymer collapses and the soaked strength is nullified. In practice, the subgrade improvement begins with the mixing in-situ soil with FA to attain the laboratory design soil:FA ratio requirement. The liquid alkaline activator, which is a mixture of CCR, water and Na_2SiO_3, is then mixed with the soil-FA mixture. Subsequently, compaction is undertaken on the clay-FA geopolymer. The subgrade stabilization time by geopolymer is more or less the same as that by cement. The stabilization cost of geopolymer stabilized soil varies from countries to countries due to varying labor, gasoline and facility cost and tax policy even though the energy consumption and raw materials are approximately the same. From both engineering and environmental perspectives, the geopolymer stabilized soil, a novel sustainable subgrade material, is more advantage than the conventional cement stabilized clay.

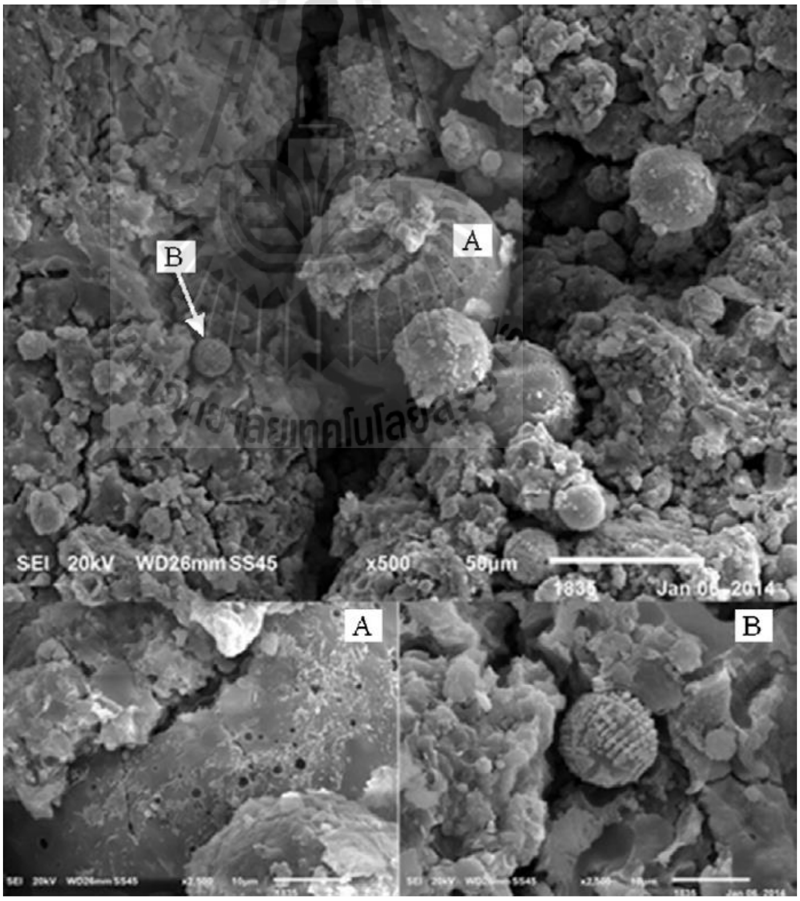


Figure 3.17 SEM images of clay-FA geopolymer at Na_2SiO_3/water ratio = 0.6, FA = 15%, 40 °C curing after 60 days of curing.

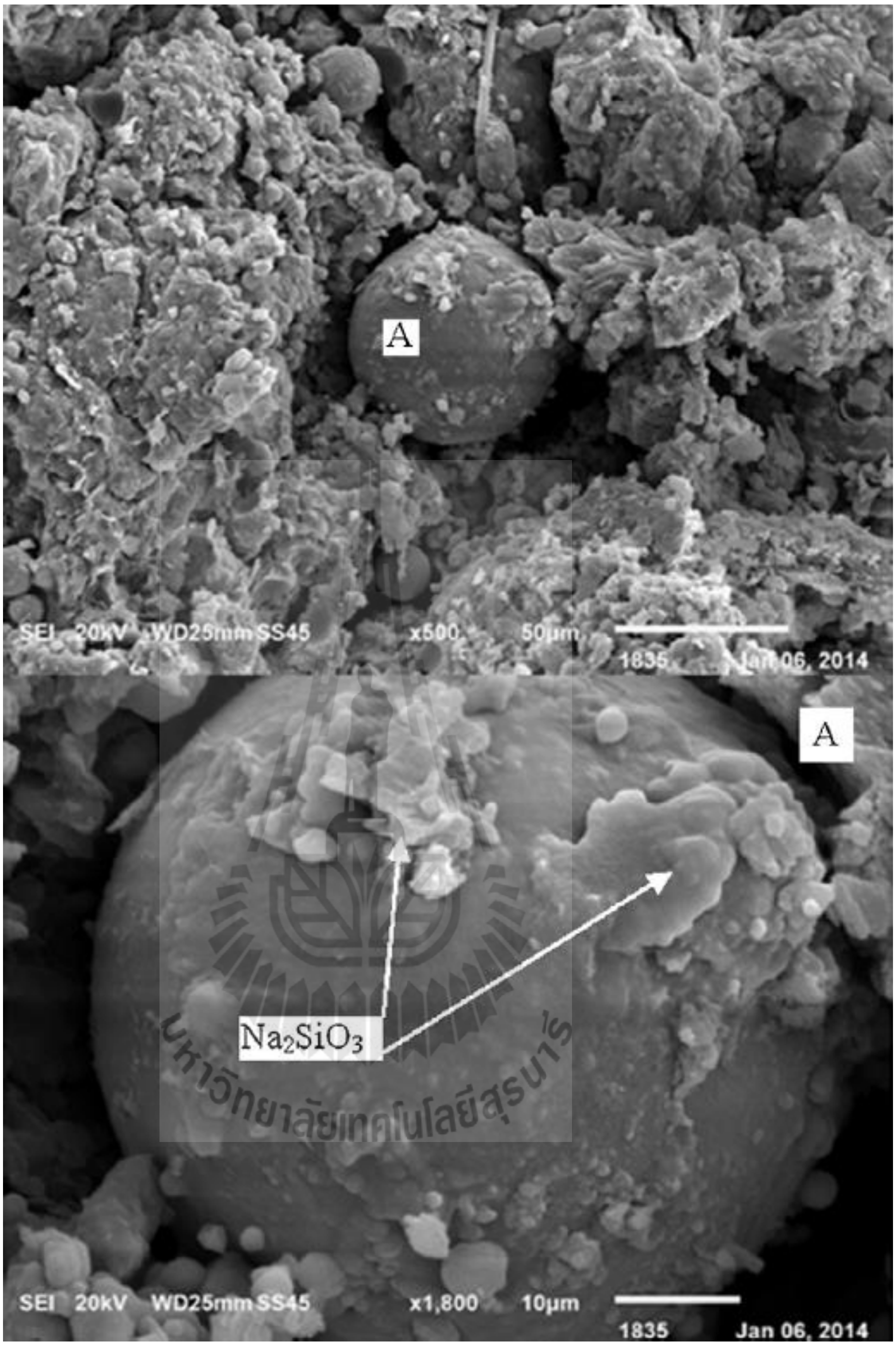


Figure 3.18 SEM images of clay-FA geopolymer at Na2SiO3/water = 1.4, FA = 15%, 40 °C curing after 60 days of curing.

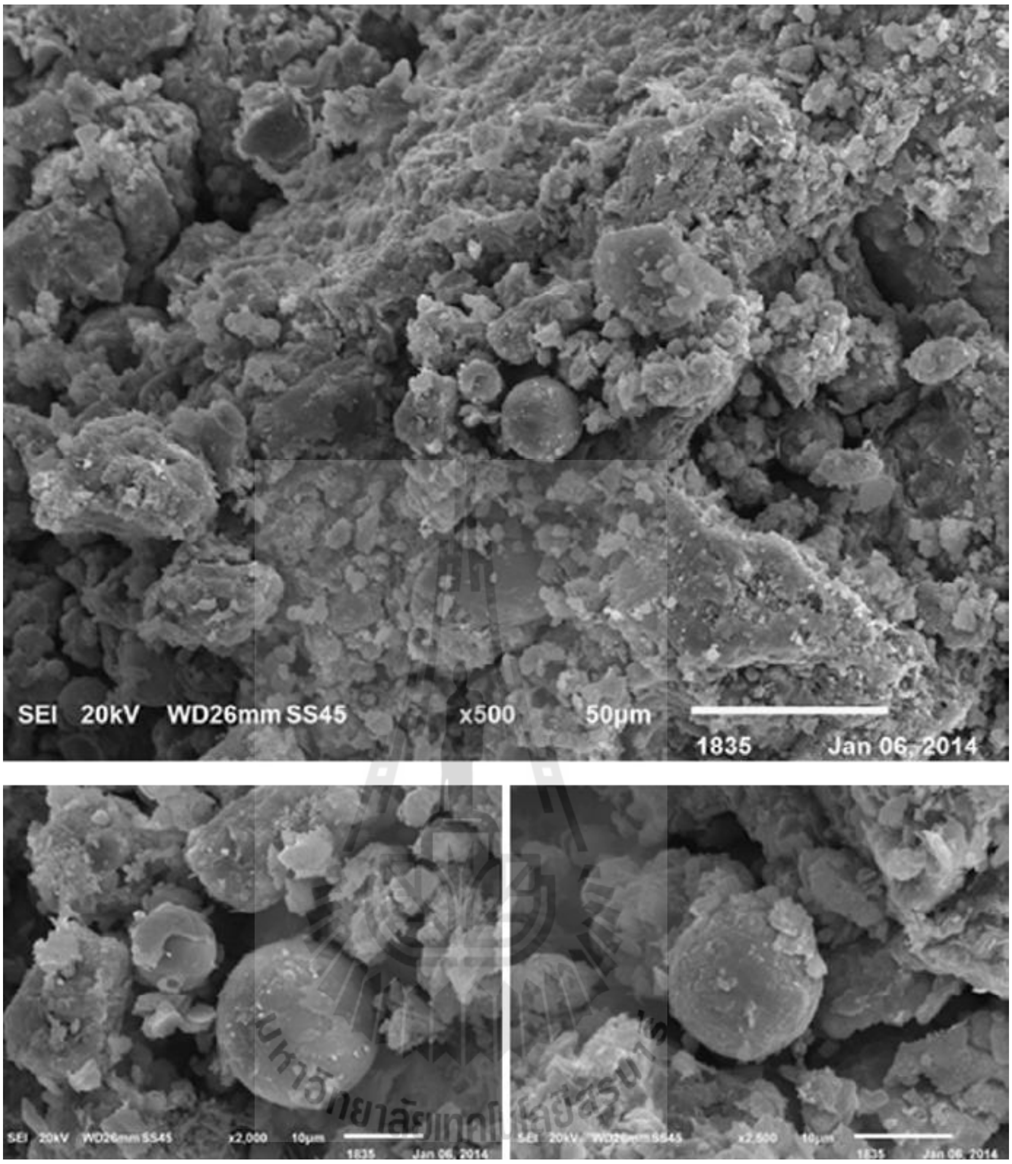
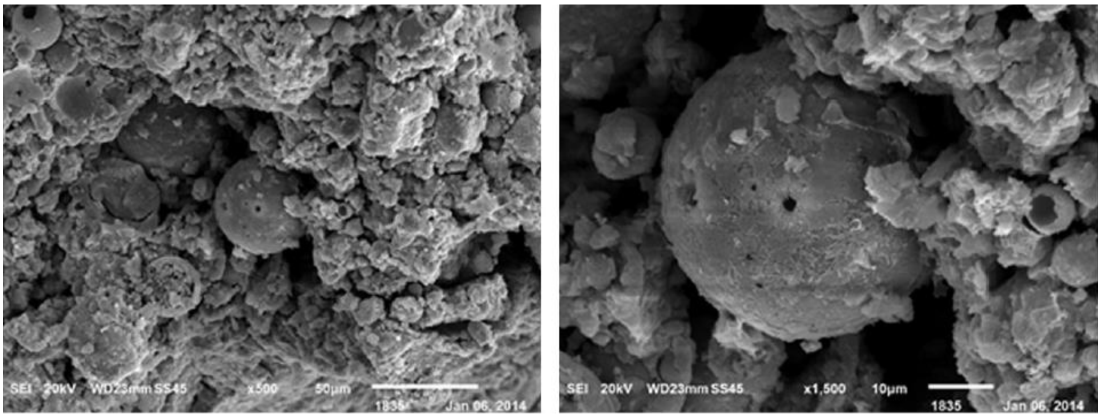
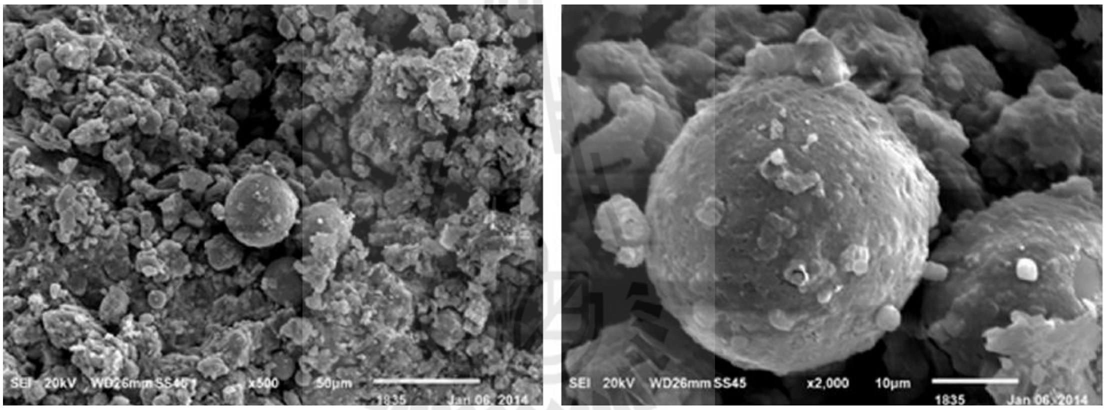


Figure 3.19 SEM images of clay-FA geopolymer at Na_2SiO_3/water = 0.6, FA = 15, room temperature curing after 60 days of curing.

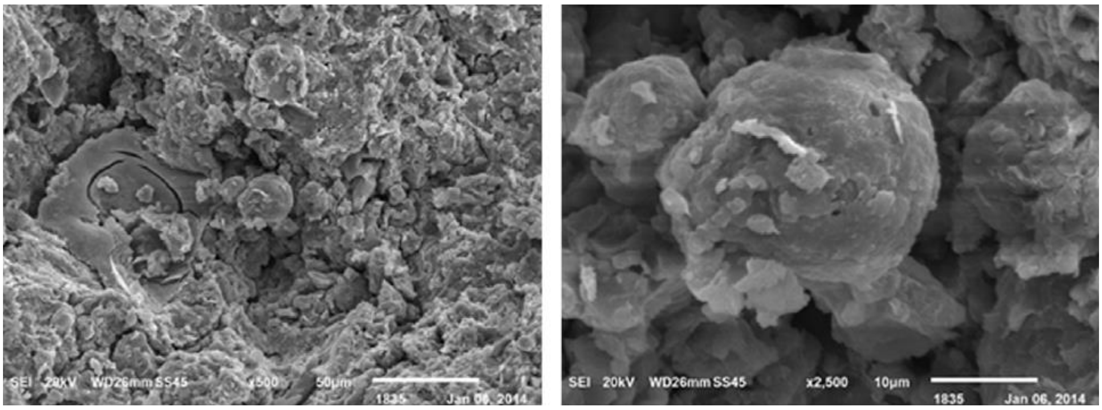


(a) Cured at 40 °C

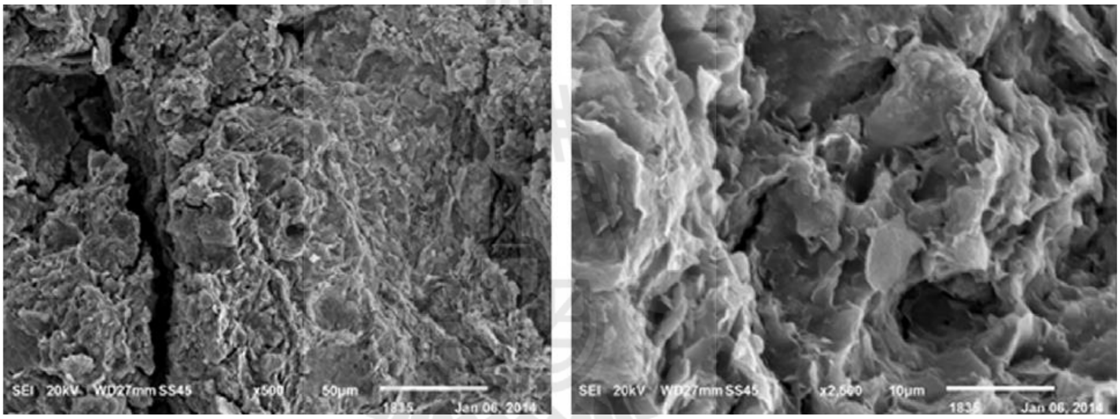


(b) Cured at room temperature

Figure 3.20 SEM images of geopolymer after 7 days of curing, Na_2SiO_3/water = 0.6 and FA = 15%: (a) cured at 40 °C and (b) cured at room temperature.



(a) Clay-FA geopolymer cured at 40 ^{o}C



(b) Clay-FA geopolymer cured at room temperature

Figure 3.21 SEM images for Na_2SiO_3/water = 0.6 after 60 days of curing (a) clay-FA geopolymer cured at 40 ^{o}C and (b) clay–geopolymer cured at room temperature.

3.5 Conclusions

This chapter deals with the analysis of strength development in geopolymer stabilized clay by using CCR as a liquid alkaline. A possible mechanism controlling strength development is presented. The following conclusions can be drawn:

(1) The input of Na_2SiO_3/water ratio affects the optimum liquid content and maximum dry unit weight of the clay-FA geopolymer. The optimal Na_2SiO_3/water ratio provides the highest unsoaked strength and maximum dry unit weight.

(2) The optimal Na_2SiO_3/water ratio providing highest soaked strength is found at the fixation point, which is the threshold limit from large to small reduction in PI and is equal to 0.6 for this clay-FA geopolymer. The optimal FA replacement ratio is 15%. Curing at 40 ^{o}C provides higher strength than room temperature curing, indicating the possibility of using this clay-FA geopolymer as a pavement subgrade material. The 7-day soaked strength meets the strength requirement for subgrade materials specified by Department of Rural Roads, Thailand.

(3) SEM images are useful to explain the role of influential factors on strength development in clay-FA geopolymer. The alkaline dissolution occurs on the surface of FA particles, resulting in many holes on the FA surface and smaller particles. The alkaline solution contacts the smaller particles housed inside the larger spheres and forms a dense matrix.

(4) CCR traditionally destined for landfill can be used in a sustainable manner as an alternative alkaline activator to develop geopolymer subgrade materials. The outcome of this research enables the production of road subgrade materials, which

consequently will reduce Portland cement consumption and associated environmental problems.

3.6 References

Buchwald, A., Kaps, Ch. 2002. **Property controlling influences on the generation of geopolymeric binders based on clay**. Geopolymer 2002 (Melbournd Australia).

Davidovits, J., Buzzi, L., Rocher, R., Gimeno, D., Marini, C., Tocco, S. 1999. **Geopolymeric cement based on low cost geologic material,** results from the European Research project GEOCIS-TEM. In: Davidovits et al., editors. Proceedings of the second international conference geopolymere 99:83-96.

DH-S, 1990. Soil cement base. **Standards for Highway Construction**. Department of Highways (in Thai).

Du, YJ., Jiang, NJ., Liu, SY., Jin, F., Singh, DN., Puppala, A. 2014. **Engineering properties and microstructural characteristics of cement solidified zinc-contaminated kaolin clay.** Can Geotech J ;51:289–302.

Gurtug, Y., Sridharan, A. 2002. **Prediction of compaction characteristics of fine-grained soils**. Geotechnique 52(10):761-763.

Horpibulsuk, S., Kumpala, A., Katkan, W., 2008. **A case history on underpinning for a distressed building on hard residual soil underneath nonuniform loose sand**. Soils and Foundations 48 (2), 273–291.

Horpibulsuk, S., Rachan, R., Raksachon, Y., 2009. **Role of fly ash on strength and microstructure development in blended cement stabilized silty clay**. Soils and Foundations 49 (1), 85–98.

Horpibulsuk, S., Liu, M.D., **Liyanapathirana, D.S., Suebsuk, J., 2010a. Behavior of cemented clay simulated via the theoretical framework of the structured cam clay model.** Computers and Geotechnics 37 (1–2), 1–9.

Horpibulsuk, S., Rachan, R., Chinkulkijniwat, A., Raksachon, Y., Suddeepong, A., 2010b. **Analysis of strength development in cement-stabilized silty clay based on microstructural considerations**. Construction and Building Materials 24, 2011–2021.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., Cholaphatsorn, A. 2013. **Strenth development in silty clay stabilized with calcium carbide residue and fly ash**. Soil and Foundations 53, 477-486.

Kumpala, A., Horpibulsuk, S., 2013. **Engineering properties of calcium carbide residue stabilized silty clay.** Journal of Materials in Civil Engineering, ASCE 25 (5), http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000618.

Kumpala, A., Horpibulsuk, S., Chinkulkijniwat, A., Shen, S.L., 2013a. **Engineering properties of recycled cemented clay as fill and pavement materials**. Construction and Building Materials 46, 203–210.

Kumpala, A., Horpibulsuk, S., Prongmanee, N., Chinkulkijniwat, A., 2013b. **Influence of wet-dry cycles on compressive strength of calcium carbide residue-fly ash stabilized clay.** Journal of Materials in Civil Engineering, ASCE

Mohapatra, R., Rao, JR. 2001. **Some aspects of characterisation, utilisation and environmental effects of fly ash**. Journal of Chemical Technology & Biotechnology 76:9-26.

Nagaraj, T.S., Miura, N., Yamadera, A., Yaligar, P., 1997. Strength assessment of cement admixed soft clays—Parametric study. in Proceedings of the International Conference on Ground Improvement Techniques, pp. 379–386.

Piyapanuwat, R. and Asavapisit, S. 2011. **Performance of lime-BHA solidified plating sludge in presence of Na_2SiO_3 and Na_2CO_3**. Journal of Environmental Management. 92: 2222-2228.

Prakash, K., Sridharan, A., 2004. **Free swell ratio and clay mineralogy of finegrained soils.** Geotechnical Testing Journal, ASTM 27 (2), 220–225.

Tanalapasakul, A., 1998. **Document from M Thai Industrial Company Limited.** M Thai Industrial Co., Ltd., Samutsakorn, Thailand.

Shi, C., Day, R.L. 1993. **Chemical activation of blended cements made with lime and natural pozzolans.** Cem. Concr. Res. 23, 389-1396

Shi, C., Day, R.L. 2000. Pozzolanic reaction in the presence of chemical activators Part I. reaction kinetics. Cem. Concr. Res. 30, 51-58

Van Jaarsveld, J., Van Deventer, J., and Lorenzen, L. 1998. **Factors affecting the immobilization of metals in geopolymerized fly ash**. Metallurgical and Materials Transactions B 29:283-291.

CHAPTER IV

STRENGTH DEVELOPMENT IN SOFT MARINE CLAY STABILIZED BY FLY ASH AND CALCIUM CARBIDE RESIDUE BASED GEOPOLYMER

4.1 Statement of problem

Recycling and utilizing of waste material is a significant contribution to environment and sustainable development. Calcium Carbide Residue (CCR) and Fly Ash (FA) are waste industry by-products from acetylene gas and power plant production, respectively. This chapter investigates strength development in CCR and FA based geopolymer stabilized Coode Island Silt (CIS), a soft and highly compressible clay, for ground improvement application such as in-situ deep mixing (DM). The influential factors studied are Na_2SiO_3/NaOH ratio, NaOH concentration, L/FA content, initial water content (LL), FA content, CCR content, curing temperature and curing time. Moreover, the UCS and carbon footprints of FA and CCR based geopolymers stabilized CIS are finally compared with those of cement stabilized CIS. The outcome of this research would divert significant quantity of CCR from landfills and considerably reduce carbon emissions due to Portland cement production.

4.2 Materials and methods

4.2.1 Materials

Coode Island Silt (CIS)

Coode Island Silt (CIS) sample was collected from the Port Melbourne area at a depth of 3-5 m. CIS consists of 4% sand, 29% silt and 67% clay. The specific gravity and organic content are 2.60 and 2.5%, respectively. Liquid Limit (LL) and Plastic Limit (PL) are approximately 65% and 32%, respectively. Based on the Unified Soil Classification System (USCS), the CIS is classified as highly plastic (CH). The basic properties are shown in Table 4.1. The grain size distribution and chemical compositions of CIS obtained from hydrometer analysis and X-ray Fluorescence (XRF) analysis are shown in Figure 4.1 and Table 4.2, respectively.

Fly ash (FA)

FA was obtained from Boral (Australia) Company limited. Table 4.2 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) of FA is 94.40% while the CaO content is 1.68%; therefore, it is classified as Class F.

Calcium carbide residue (CCR)

The CCR was oven-dried at 100 ^{o}C for 24 h and was then ground using a Los Angeles abrasion machine. The CCR was passed through a No. 40 sieve (425 μm). The specific gravity value is 2.32. Table 4.2 summarizes the chemical composition of CCR. The high $Ca(OH)_2$ and CaO contents of the CCR indicate that it can react with FA and produce a cementitious material (Palomo et al., 1999). The grain size distribution of the CCR compared with that of the CIS is shown in Figure 4.1. The curves were obtained from laser particle size analysis, which is applicable for materials that react with water. The average grain size (D_{50}) of CCR is 0.01 mm.

Liquid alkaline activator (L)

The liquid alkaline activator (L) is a mixture of Na_2SiO_3, which consists of 9% Na_2O and 30% SiO_2 by weight, and NaOH.

4.2.2 Sample Preparation and Testing

The testing program is summarized in Table 4.3.

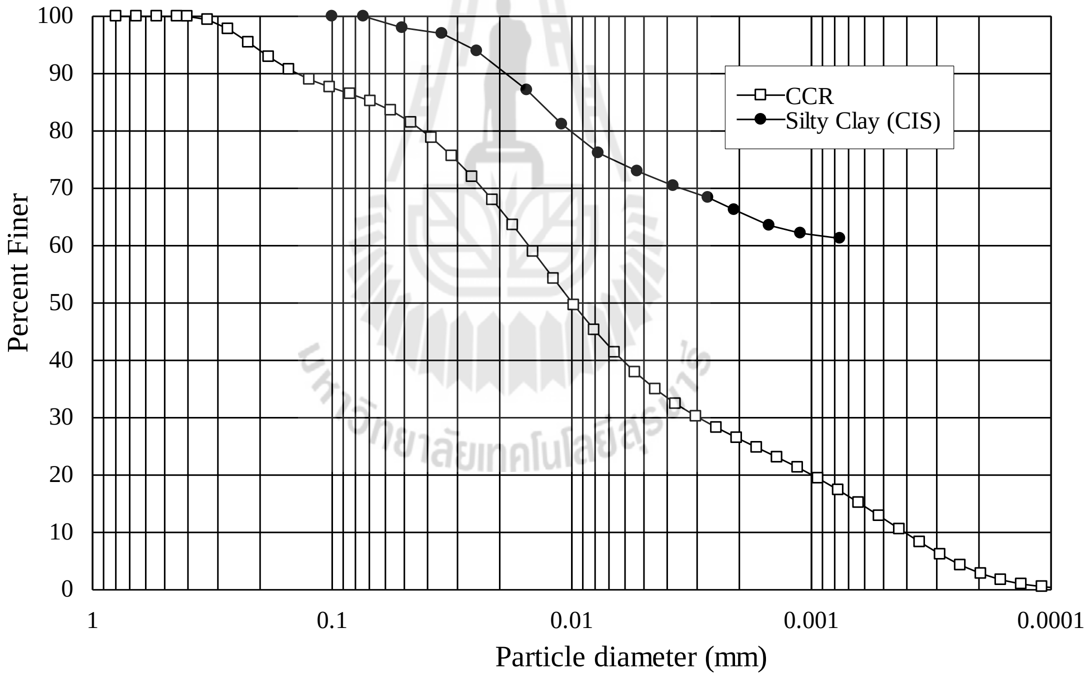


Figure 4.1 Grain size distribution of clay and CCR.

Table 4.1 Basic properties of CIS.

Properties	**Characteristics**
Liquid limit, LL (%)	65%
Plastic limit, PL (%)	32%
Plasticity index, PI (%)	33%
Grain size distribution	Clay 67%, Silt 29%, Sand 4%
Organic content	2.50%
Specific gravity, Gs	2.6
P.H.	7.25

Table 4.2 Chemical properties of CIS, fly ash and CCR.

Chemical composition (%)	**CIS**	**Fly Ash**	**CCR**
Al_2O_3	12.760	25.116	7.141
SiO_2	66.953	66.879	19.413
SO_3	7.893	0.984	1.230
Cl	0.576	0.030	0.056
K_2O	1.387	1.831	0.721
CaO	5.642	1.689	69.540
TiO_2	1.179	0.949	0.675
Cr_2O_3	0.010	0.005	0.006
MnO_2	0.022	0.058	0.065
Fe_2O_3	3.523	2.406	1.041
CuO	0.026	0.004	0.030
ZnO	0.005	0.006	N.D.
PbO	0.010	0.004	0.013
SrO	0.013	0.019	0.044
Rb_2O	N.D.	0.004	0.017
ZrO_2	N.D.	0.015	0.007

N.D. = none detected

Table 4.3 Summary of the testing program.

		UC test1	UC test2	UC test3	UC test4	UC test5	UC test6
NaOH	(molar)	3, 6, 9, 12, 15, 18	12	3, 6, 12, 18	12	12	
Na_2SiO_3: NaOH	(L)	70:30	90:10, 80:20, 70:30, 60:40	70:30	70:30	70:30	-
Alkaline content	(L/FA)	1	0.5, 1.0, 1.5, 2.0	1	1	1	-
FA	(%)	35	35	25, 35, 45	35	35	-
CCR	(%)	-	-	-	0, 3, 6, 9, 12, 15	0,12	-
Cement	(%)	-	-	-	-	-	15, 20, 25 30, 35, 45
Water content of LL	(%)	1.0, 1.5, 2.0	1.0, 1.5, 2.0	1	1	1	1
Curing temp.	(°C)	40	40	40	40	25	25
Curing time	(days)	3,7, 14, 28	3, 7, 14, 28	7	3, 7, 14, 28	7	7

4.2.2.1 FA geopolymer stabilized CIS

The FA geopolymer binder was a combination of FA and liquid alkaline activator (Na_2SiO_3 and NaOH). The FA contents were 25, 35 and 45% by weight of dry soil. The Na_2SiO_3/NaOH ratios were 90:10, 80:20, 70:30 and 60:40. The concentrations of NaOH were 3, 6, 9, 12, 15 and 18 molars. The L/FA ratios were 0.5, 1.0, 1.5 and 2.0. The initial water content (*w*) of the CIS varied from 1 to 2 times LL. The CIS and FA were mixed for 5 minutes in a mixer to ensure homogeneity of the mixture. The mixer was stopped and the mixture was mixed with the liquid alkaline activator (L) for an additional 5 minutes. The uniform CIS-FA-L mixtures were transferred to cylinder molds of 38 mm in diameter and 76 mm in height for UCS test. The FA geopolymer stabilized CIS samples were dismantled, wrapped within vinyl sheet and then heated at 40^{o}C (Phetchuay et al., 2014). The 40 ^{o}C temperature was used to simulate an average heat temperature in countries with a tropical climate, including Australia and Thailand. UCS tests were carried out on the samples after 3, 7, 14 and 28 days of curing in accordance with ASTM C69-09. For each curing time and ingredient, at least five samples were tested under the same conditions to assure test result consistency. In most cases, the results under the same testing condition were reproducible with low mean standard deviation, SD (SD/$\bar{x}$ < 10%, where $\bar{x}$ is mean strength value).

4.2.2.2 CCR-FA geopolymer stabilized CIS

The FA content was fixed at 35% by weight of dry soil and the Na_2SiO_3/NaOH ratio, concentration of NaOH, L/FA ratio and water content were fixed at the optimal ingredient for the FA geopolymer stabilized CIS while the CCR contents were varied to investigate the influence of CCR on UCS development. The

CCR contents were 3, 6, 9, 12 and 15%. The uniform CIS-CCR-FA-L mixtures were transferred to cylinder molds of 38 mm in diameter and 76 mm in height for UCS test. The samples were subsequently cured at 40°C. UCSs of CIS-FA-CCR geopolymer sample were measured after 3, 7, 14 and 28 days of curing.

4.2.2.3 Cement stabilized CIS

The cement contents tested were 15, 20, 25, 30, 35 and 45% by weight of dry soil. The initial water content of the CIS at 1.0 times LL. The CIS-cement mixtures were transferred to cylinder molds of 38 mm in diameter and 76 mm in height and then cured at 25°C. UCSs of cement stabilized samples were measured after 7 days of curing.

4.3 RESULTS AND DISCUSSION

4.3.1 Strength of FA geopolymer stabilized CIS

Figure 4.2 shows the relationship between 7-day UCS versus concentration of NaOH at Na_2SiO_3/NaOH ratio = 70:30, FA = 35%, L/FA = 1 and w = LL. The silica and alumina ions from FA were leached by alkaline activator for the geopolymerization reaction. A higher NaOH concentration results in higher leached silica and alumina ions and hence the UCS increases with increasing NaOH concentration. The increase of UCS with NaOH concentration in geopolymeric system was also noted by other researchers (Allahverdi and Khani, 2009; Hardjito et al., 2004; Yunfen et al., 2009; Guo et al., 2010). It is noted that the NaOH concentration of 12% is designated as alkaline fixation point and the UCS gradually increases when NaOH is greater than the alkaline fixation point.

The effect of FA content on 7-day UCS of the FA geopolymer stabilized CIS at Na_2SiO_3/NaOH ratio = 70:30 and *w* = LL for various NaOH concentrations is shown in Figure 4.3. The SiO_2 and Al_2O_3 in FA are in amorphous phase and can effectively react with NaOH and Na_2SiO_3. As such, the UCS of the clay-FA geopolymer increases as the FA content increases. A higher NaOH concentration dissolves more silica and alumina oxide from FA and hence stronger geopolymerization reaction with sodium silicate solution.

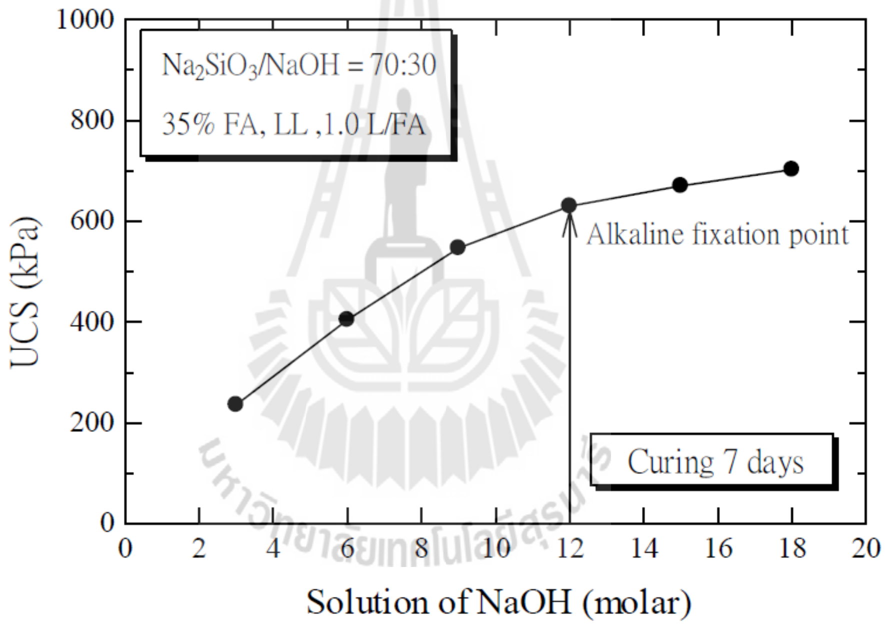


Figure 4.2 Effect of solution of NaOH on compressive strength.

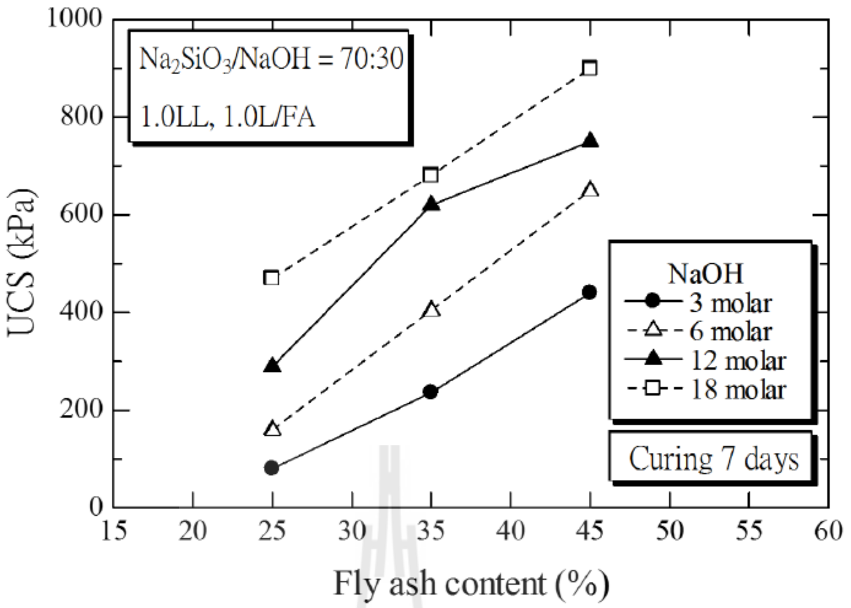


Figure 4.3 Effect of fly ash content on compressive strength.

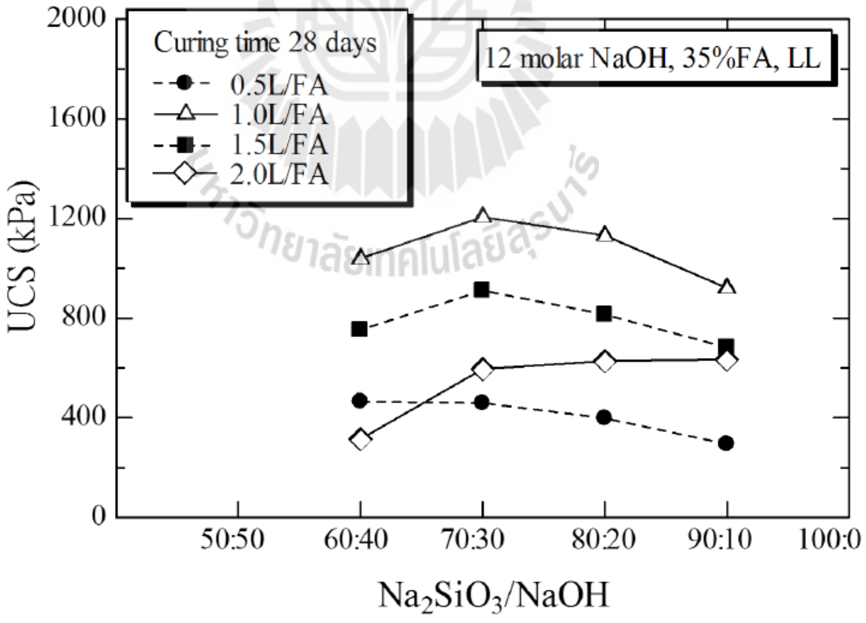


Figure 4.4 Effect of liquid alkaline activator.

Table 4.4 summarizes the UCS values of FA geopolymer stabilized CIS for various initial water contents, curing times, Na_2SiO_3/NaOH ratios and L/FA ratios at 35%FA. For a particular curing time, Na_2SiO_3/NaOH ratio and L/FA ratio, the maximum UCS of FA geopolymer stabilized CIS is found at w = LL. The optimum ingredient providing the maximum UCS at w = LL is Na_2SiO_3/NaOH ratio = 70:30 and L/FA ratio = 1.0 for all curing times tested. The effect of Na_2SiO_3/NaOH ratio on the UCS development in the FA geopolymer stabilized CIS at w = LL is shown in Figure 4.4. The optimal Na_2SiO_3/NaOH ratio providing the maximum UCS tends to increase with increasing L/FA ratio. For example, at L/FA ratio = 0.5, the optimum Na_2SiO_3/NaOH = 60:40 whereas at L/FA = 2, the optimum Na_2SiO_3/NaOH = 90:10.

The UCS versus L/FA ratio relationship of FA geopolymer stabilized CIS at various water contents and curing times for 12 molar NaOH (alkaline fixation point) is shown in Figure 4.5. The UCS increases with increasing the curing time for all Na_2SiO_3/NaOH ratios and water contents tested. For a given L/FA ratio and curing time, LL provides the highest strength. The higher water content causes the larger spacing between clay particles (Horpibulsuk et al. 2011) and dilutes the concentration solution of NaOH, which results in the strength reduction (Suksiripattanapong et al., 2015). At LL, the UCS decreases significantly when L/FA ratio is greater than the optimum value of 1.0. Whereas at higher water content (water content > LL), the UCS gradually increases with L/FA ratio without the distinct peak. This implies that the clay with higher water content needs more alkalinity to produce optimal pH environment to dissolve silicon and aluminum in the amorphous phase of FA.

Table 4.4 Test result. (12 molar NaOH, 35%FA)

Description	**Na_2SiO_3: NaOH**	**3 Days**				**7 Days**				**14 Days**				**28 Days**			
		L/FA= 0.5	**L/FA= 1.0**	**L/FA= 1.5**	**L/FA= 2.0**	**L/FA= 0.5**	**L/FA= 1.0**	**L/FA= 1.5**	**L/FA= 2.0**	**L/FA= 0.5**	**L/FA= 1.0**	**L/FA= 1.5**	**L/FA= 2.0**	**L/FA= 0.5**	**L/FA= 1.0**	**L/FA= 1.5**	**L/FA= 2.0**
1.0LL	90:10	115	305	134	128	172	431	248	225	255	649	364	356	295	921	683	635
	80:20	146	308	184	172	184	454	289	277	319	755	428	388	399	1132	815	628
	70:30	131	321	158	110	225	610	326	239	409	850	478	382	460	1206	911	596
	60:40	126	195	107	48	249	469	230	137	462	683	414	222	466	1040	753	315
1.5LL	90:10	100	122	118	136	126	173	178	187	86	291	302	277	100	401	376	374
	80:20	65	92	96	132	98	185	196	248	95	253	485	409	114	546	533	525
	70:30	62	104	104	143	82	217	222	225	98	341	524	437	124	641	605	570
	60:40	48	96	97	100	69	195	224	214	102	491	462	432	127	632	568	511
2.0LL	90:10	31	53	41	36	38	73	71	54	42	109	163	161	57	147	220	218
	80:20	17	37	40	38	20	61	150	48	41	73	287	153	55	99	387	206
	70:30	19	28	32	44	32	52	135	72	0	129	204	210	0	175	275	283
	60:40	16	28	35	47	25	41	72	78	0	0	181	226	0	0	245	305

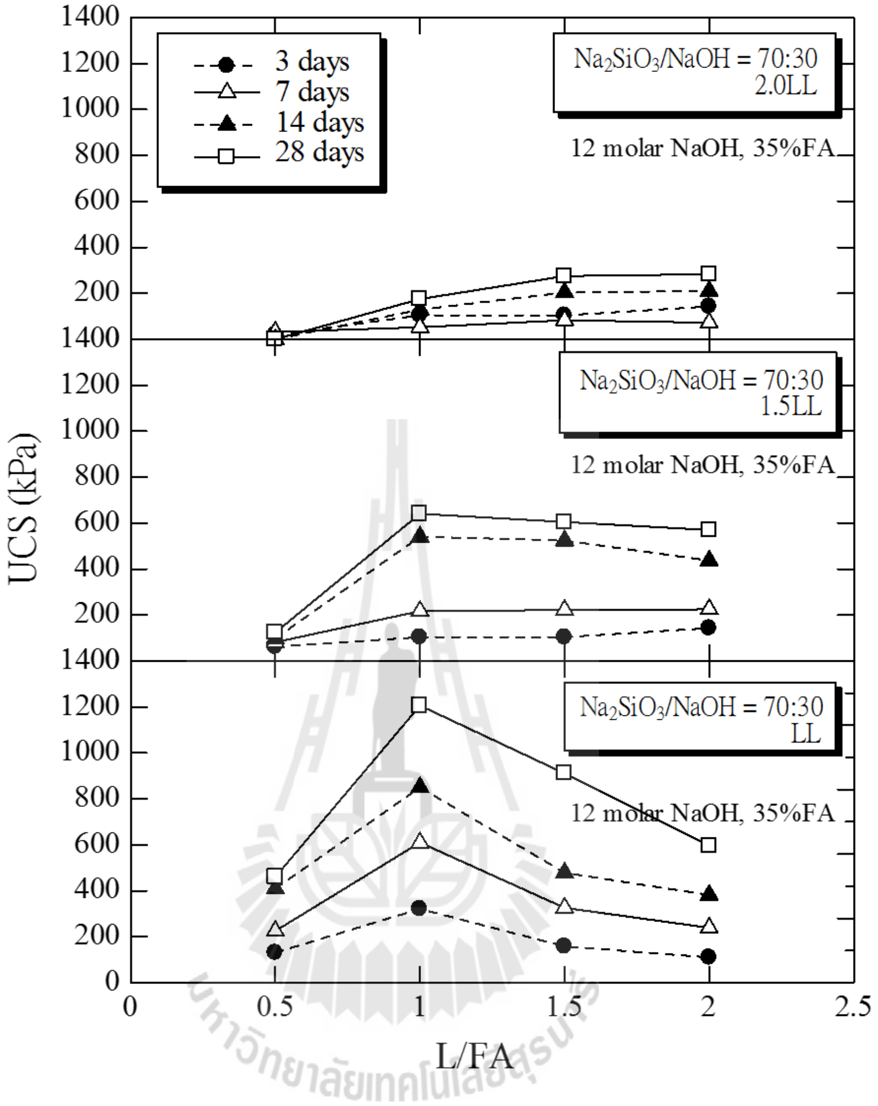


Figure 4.5 Effect of liquid alkaline activator / Fly ash at different LL.

The typical UCS development with curing time for the FA geopolymer stabilized CIS with various initial water contents, NaOH concentrations, Na_2SiO_3/NaOH ratios and L/FA ratios at 35% FA is shown in Figure 4.6. The strength development with curing time (days) in natural logarithmic scale can be expressed as a linear variation. The 28-day UCS was taken for the examination of the normalized characteristic, as previously done by Horpibulsuk et al. (2003, 2009, 2011a, 2011b, 2012b). Although the UCS values are different for different NaOH concentrations, Na_2SiO_3/NaOH ratios, L/FA ratios and water contents, the normalized strength, UCS_D/UCS_{28} is essentially the same where UCS_D is the UCS at any curing time and UCS_{28} is the 28-day UCS. The normalized strength of the geopolymer stabilized CIS is also compared with that of the cement stabilized clays (data from Horpibulsuk et al., 2011a) in Figure 4.7. It is evident that the normalized behavior is similar to that of cement stabilized clays and presented in the form:

$$UCS_D/UCS_{28} = 0.269 \qquad \text{for } 3 < D < 28 \text{ days} \qquad (4.1)$$

with a high correlation of 0.897. The proposed equation is useful to predict the target UCS value for 35% FA at any curing time when 28-day UCS is known.

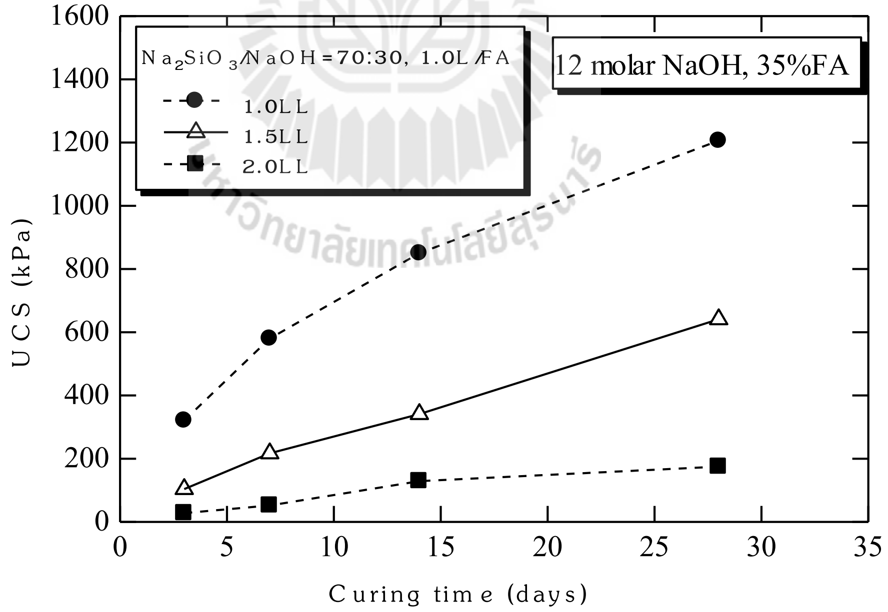
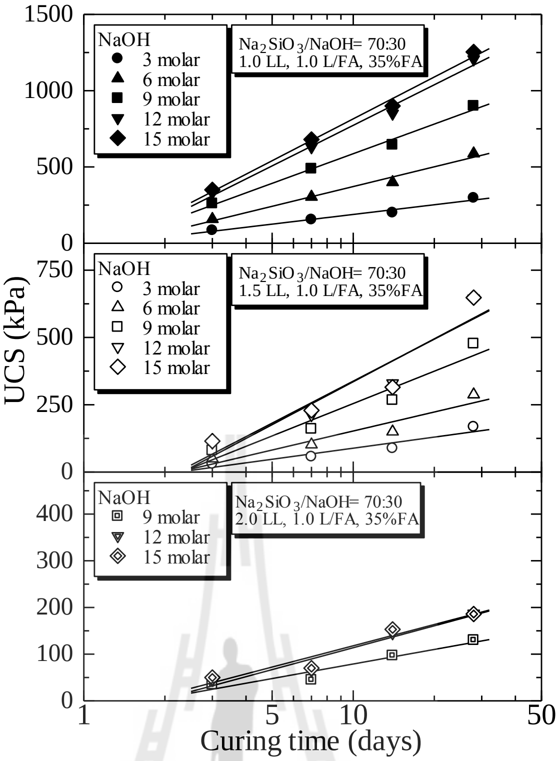
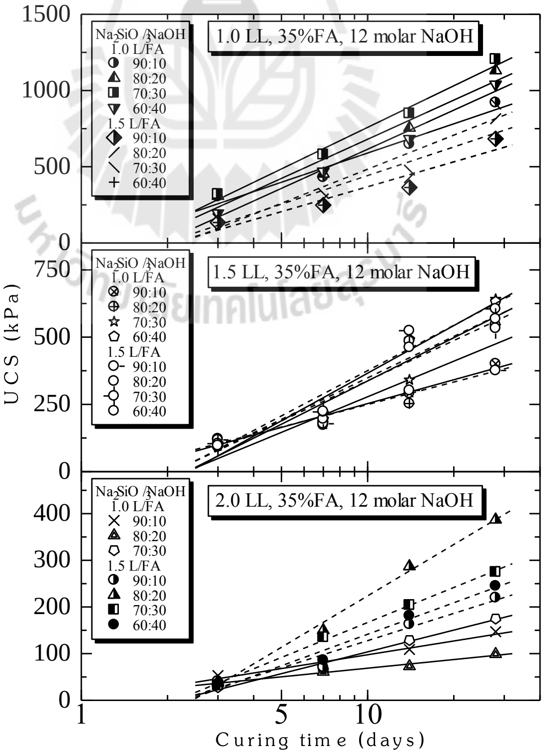


Figure 4.6 Effect of curing time on compressive strength.


NaOH
3 molar
6 molar
9 molar
12 molar
15 molar
Na2SiO3/NaOH= 70:30
1.0 LL, 1.0 L/FA, 35%FA
1.5 LL, 1.0 L/FA, 35%FA
2.0 LL, 1.0 L/FA, 35%FA
UCS (kPa)
Curing time (days)
1500
1000
500
0
750
500
250
400
300
200
100
1
5
10
50


Na2SiO3/NaOH
1.0 L/FA
90:10
80:20
70:30
60:40
1.5 L/FA
1.0 LL, 35%FA, 12 molar NaOH
1.5 LL, 35%FA, 12 molar NaOH
2.0 LL, 35%FA, 12 molar NaOH
UCS (kPa)
Curing time (days)
1500
1000
500
0
750
500
250
400
300
200
100
1
5
10

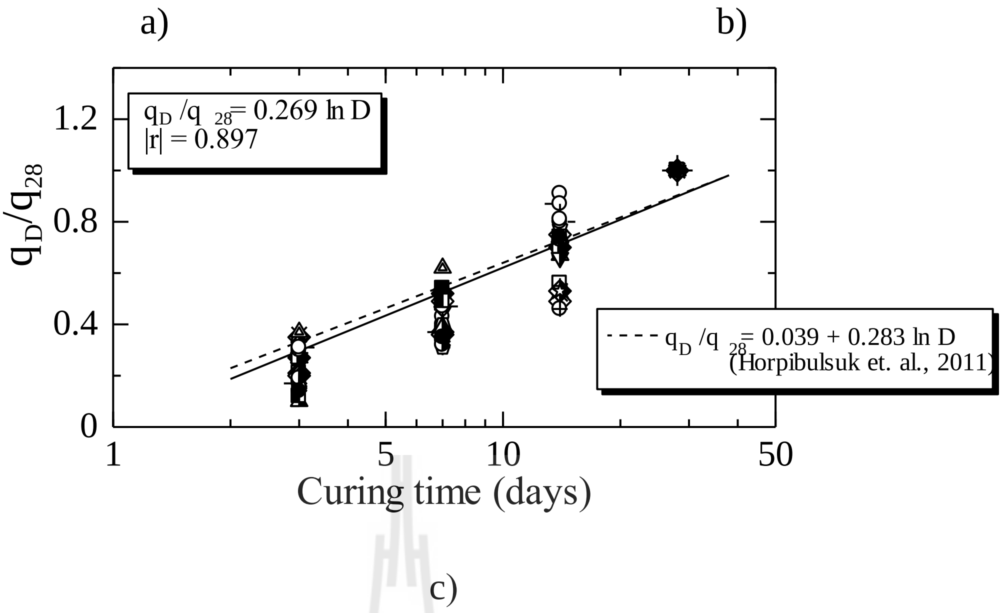


Figure 4.7 Strength development with time for different NaOH, LL, ratio of Na_2SiO_3/NaOH, L/FA and their generalization

4.3.2 Strength of FA-CCR geopolymer stabilized CIS

The role of CCR on UCS development in FA-CCR geopolymer stabilized CIS is shown in Figure 4.8. The UCS development is classified into three zone (inactive, active and quasi-inert zones). For CCR content less than 7%, the UCS decreases with increasing CCR content while for CCR content more than 12%, the UCS slightly incareses with increasing CCR content. The CCR contents between 7 and 12% are regarded as active zone and significantly improve the UCS of the FA-CCR geopolymer stabilized CIS. The addition of a sufficient quantity of Ca^{2+} to FA based geopolymers in the form of calcium hydroxide can lead to the formation of phase separated Al-substitute calcium silicate hydrate (C-(A)-S-H) and geopolymer (N-A-S-H) gel (Yip et al., 2005 and 2008; Granizo et al., 2002; and Xu and Van Deventer, 2005). Moreover, Ca^{2+} is capable of acting as charge-balancing cation within the geopolymeric binding structure (Li et al., 2010). The role of Ca^{2+} more prevalent at relatively low alkalinity condition system while the dissolution of $Ca(OH)_2$ is hindered when the OH- concentration is high. As such, the insignificant strength gain is noted when CCR content greater than 12%. Therefore, the practical optimum mix of CCR is in the active zone. The UCS versus curing time relationship of CIS-FA-CCR geopolymer at LL, 35% FA and 12M NaOH is shown in Figure 4.9. Strength development over curing time is noticed for all CCR contents tested. The gradient after 14 days of curing of the relationship for 12% CCR is highest.

The effect of temperature curing is shown in Figure 4.10, which depicts the strength comparison of FA and FA-CCR geopolymer stabilized CIS between 25^{o}C and 40^{o}C. The UCS of FA-CCR geopolymer stabilized CIS is higher than that of the FA geopolymer stabilized CIS at the same temperature, NaOH concentration (12 molar), L/FA ratio (1.0), Na_2SiO_3/NaOH ratio (70:30) and water content (w = LL). In addition, the UCS of FA-CCR geopolymer stabilized CIS at 25^{o}C is close to that of FA geopolymer stabilized CIS at 40^{o}C, showing the effectiveness of CCR in term of engineering and economic perspectives. Van Deventer and co-workers suggested that the presence of calcium in solid waste material will provide extra nucleation sites for precipitation of dissolved species and cause rapid hardening (Van Deventer et al., 2007; Lee and Van Deventer, 2002). Moreover, MacKenzie et al. (2007) suggested that $Ca(OH)_2$ is incorporated into the geopolymer network.

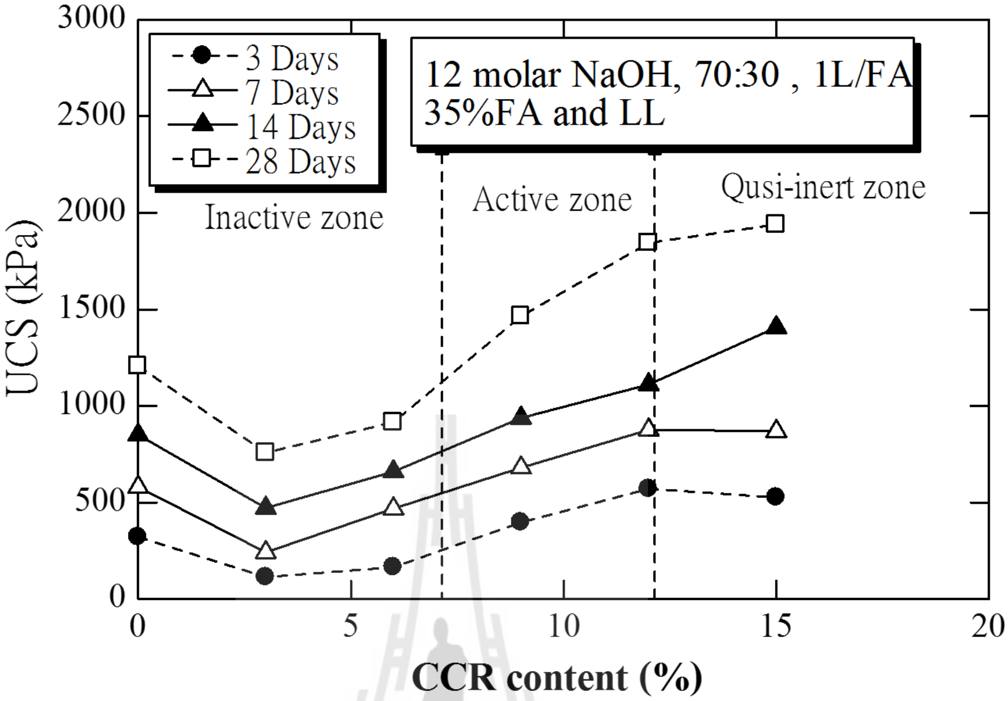


Figure 4.8 Effect of CCR content on compressive strength.

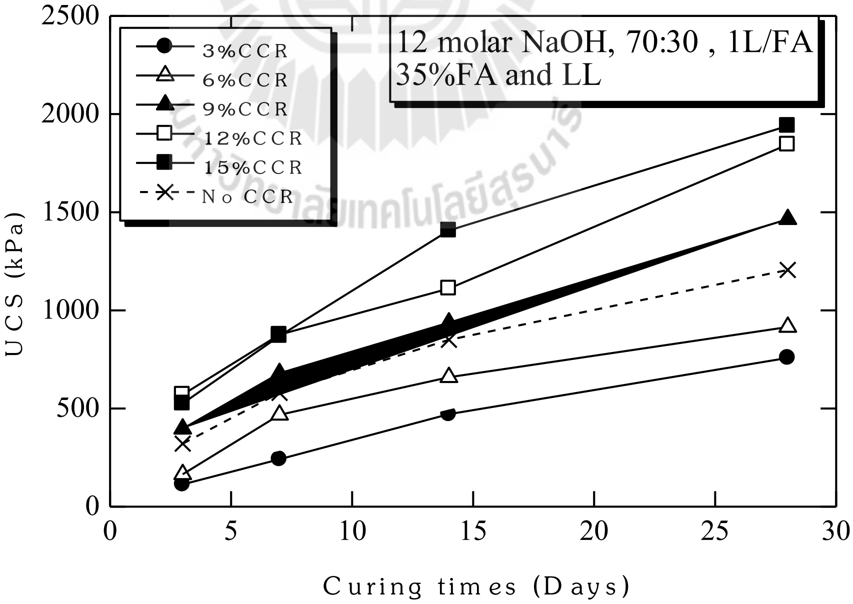


Figure 4.9 Effect of curing times content on compressive strength.

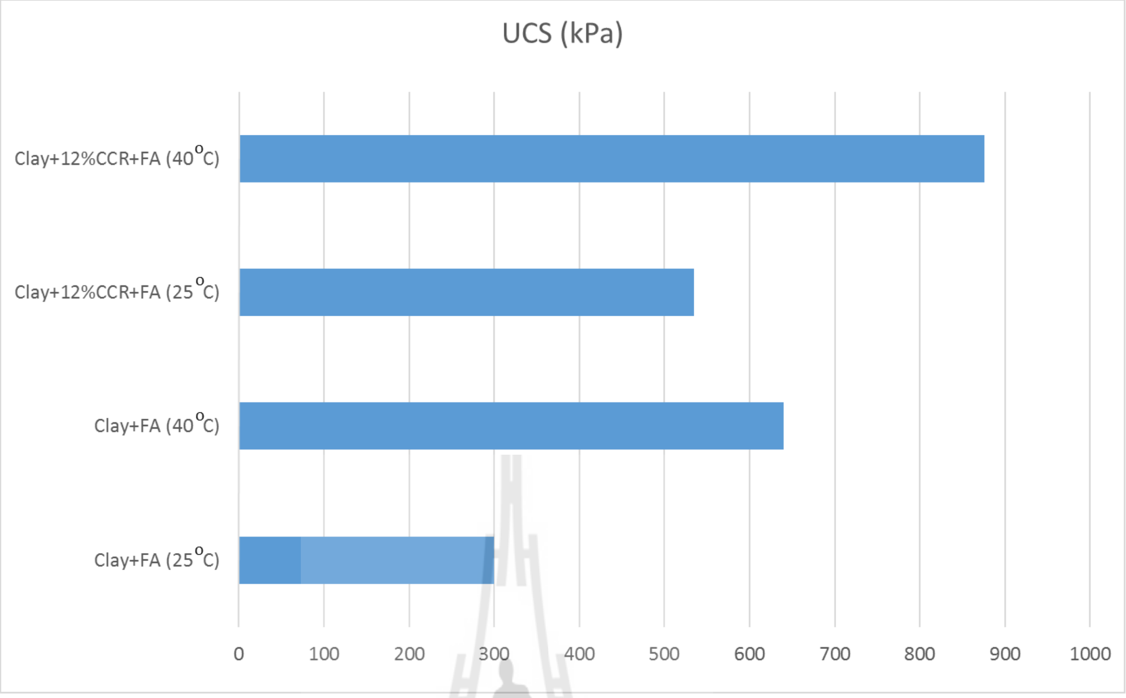


Figure 4.10 The effect of temperature on strength at LL

Temujin et al. (2009) is also concluded that noticeable a mounts of crystalline or poorly crystalline C-S-H phase is usually formed at high Ca concentrations. They investigated the hardening mechanism for samples with calcium-rich additives and cured at ambient temperature. For low amount of calcium hydroxide, the additive will react with sodium silicate or sodium hydroxide solution to precipitate amorphous or poorly ordered crystalline calcium silicate hydrate or calcium aluminosilicate hydrate phases causing a water deficiency in the alkaline mixture, which will raise its alkalinity. The higher alkalinity of the dissolution medium allows higher dissolution of existing aluminosilicates and thus a greater rate of polycondensation-geopolymerization. If hardening occurs with this mechanism, then there will be contribution to mechanical strength from both the precipitated compound and the geopolymeric gel.

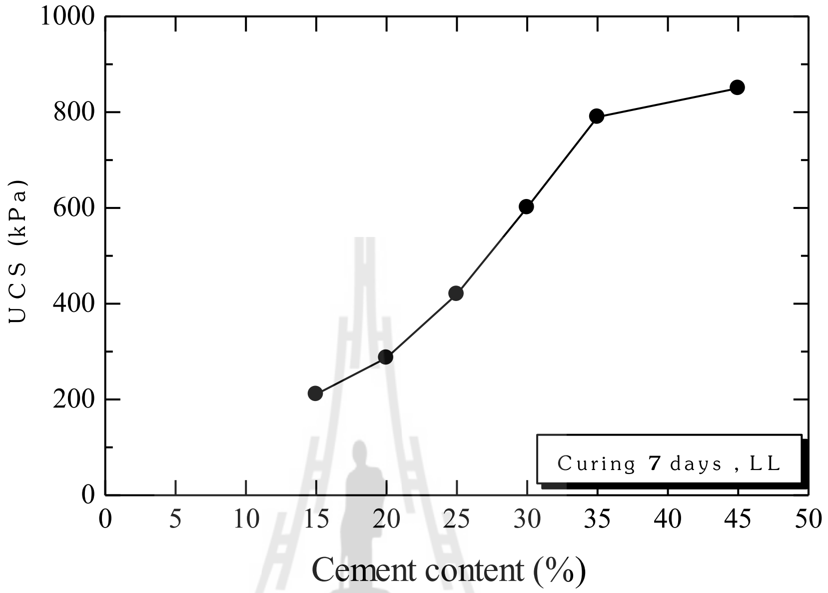


Figure 4.11 The relationship between cement content and strength at liquid limit**.**

4.3.3 Carbon footprint evaluation

The relationship between cement content and strength at liquid limit in Figure 4.11 was calculated carbon footprint to compare with geopolymer stabilized soil and CCR-geopolymer stabilized soil. The Functional Unit, defined as CO_2-e emitted (kg CO_2-e/ton), is the unit constant, used in this study to undertake the environmental assessment between Original Portland Cement (OPC) and geopolymer binders. The CO_2 emission of cement stabilized soil and geopolymer stabilized soil, which associated with the mining, processing and manufacturing of raw materials and cement production was examined. Table 4.5 shows the comparison mix design between cement-stabilized soil, geopolymer-stabilized soil and CCR-geopolymer stabilized soil at various strength. The emission factors of materials are presented in Table 4.6 (presented factor in solid state of NaOH and Na_2SiO_3). It is found that the NaOH is the highest emission factor for the geopolymer. Fly ash has the lowest emission factor. And this paper was defined the emission factor of CCR = 0.007 kg CO_2-e/ton that same as emission factor of fly ash because CCR also use the energy spending relating to milling and grinding, drying, and transport. Figure 4.12 shows the total CO_2-e of cement geopolymer and CCR-geopolymer. From the calculation show that the emission CO_2-e of geopolymer binders (FA, Na_2SiO_3 and NaOH) are 176 and 200 kg CO_2-e/ton compared with the emission CO2-e of cement of 215 and 258 kg CO_2-e/ton at strength 400 kPa and 600 kPa, respectively. The emission CO_2-e of cement is greater than geopolymer which is about 18%. Adding of CCR increase strength of geopolymer stabilized clay about 33% but it not significantly changes in CO_2 emission. The CO2 footprint of CCR-geopolymer stabilized clay was approximately 30% less than comparable cement stabilized clay: much less than geopolymer concrete that McLellan et al. (2011) investigated over Australian geopolymer concrete and found an estimate 44-64% reduction in greenhouse gas emissions over OPC. The key factors that led to the higher than expected is high water content of soft clay that use high content of liquid alkaline to produce cementation bond. The outcome of this research is consequently significant from engineering, economic and environmental perspectives.

Table 4.5 Mixture proportions of cement, geopolymer and CCR-geopolymer binders for dry soil of 1 ton at various strength.

Material	geopolymer		CCR & geopolymer	Cement		
	400 (kPa)	600 (kPa)	800 (kPa)	400 (kPa)	600 (kPa)	800 (kPa)
Fly ash (kg)	350	350	350	-	-	-
Sodium hydroxide (kg)	18.95	37.9	37.9	-	-	-
Sodium silicate (kg)	105.35	105.35	105.35	-	-	-
Calcium carbide Residue (kg)	-	-	42	-	-	-
Cement (kg)	-	-	-	250	300	350

Table 4.6 The emission factor of material.

Material	Emission factor (kg CO_2-e/ton)	Key References
Fly ash (kg)	0.007	(McLellan et al., 2011)
Sodium hydroxide (kg)	1.915	(Turner and Collins, 2013)
Sodium silicate (kg)	1.514	(Turner and Collins, 2013)
Calcium carbide residue (kg)	0.007	
Cement (kg)	0.86	(McLellan et al., 2011)

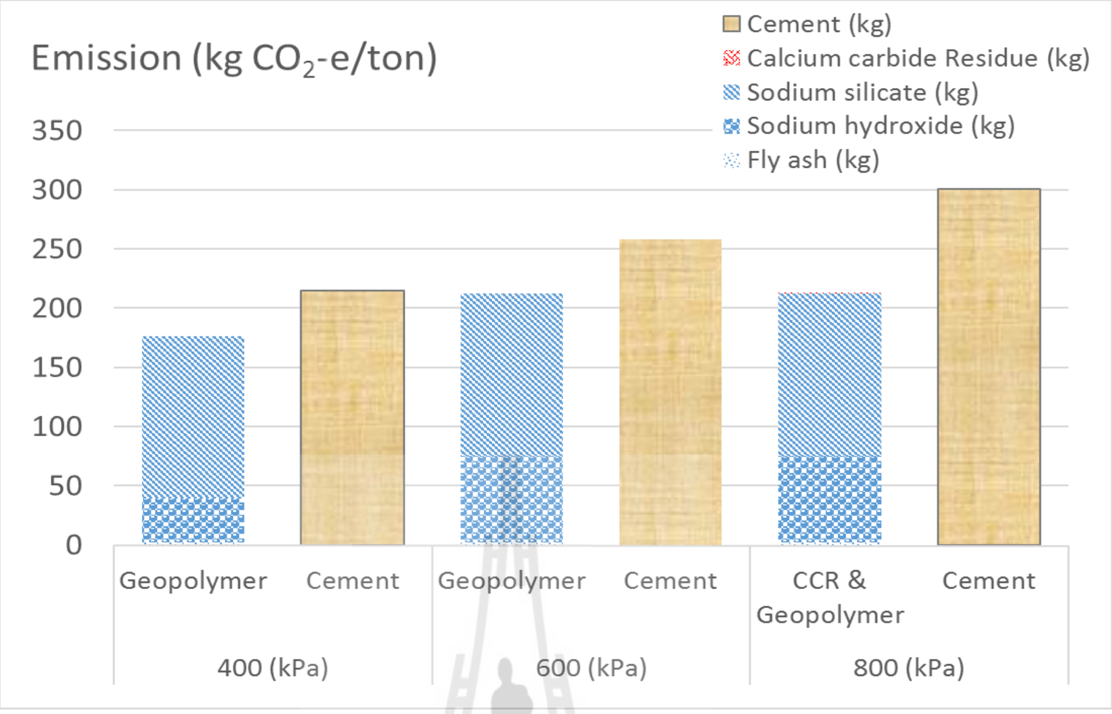


Figure 4.12 The total CO_2-e of cement, geopolymer and CCR-geopolymer

4.4 Conclusions

The feasibility of utilizing CCR and FA produce geopolymer binder to stabilize CIS. Specifically, the effect of NaOH concentration, L/FA content, several of LL, FA content, CCR content, temperature and curing time on strength was investigated. Based on the experimental results, the following major conclusions can be drawn.

1. Increase NaOH concentration result in higher strength until 12 molars (Alkaline fixation point) after that strength is nearly zero and does not make any further significant improvement.

2. Inclusion of FA-geopolymer helps improve the strength of treated clay. In the current experiment, the optimum of alkaline ratio (Na_2SiO_3: NaOH) and L/FA content are 70:30 and 1.0, respectively. The liquid limit at 1.0LL produces highest strength.

3. Addition of CCR improves mechanical properties of the fly ash based geopolymers cured at ambient temperature. The effectiveness of CCR stabilization in CIS-FA geopolymer can be classified into three zones: inactive, active and quasi-inert. It is important to select a mixing proportion that lies in the active zone to ensure an effective treatment.

4. The maximum strength of clay FA-geopolymer is 600 kPa that can replace 30% cement at curing 7 days. The maximum strength of clay CCR and FA-geopolymer is 800 kPa that can replace with 35% cement at curing 7 days.

5. The CO_2 footprint of geopolymer stabilized soil was approximately 18% less than comparable cement stabilized soil at the same strength.

6. Addition of CCR increases strength about 33% of geopolymer stabilized soil but the CO_2 emission of CCR-geopolymer stabilized soil was not significant change and approximately 30% less than comparable cement stabilized cement stabilized soil at the same strength.

4.5 References

Allahverdi, A., Khani, EN., 2009. **Construction wastes as raw materials for geopolymer binders.** Int J Civil Eng 7(3):154–60.

Bergado, D.T., Anderson, L.R., Miura, N., Balasubramaniam, **A.S. Soft ground improvement in lowland and other environment. ASCE Press,** New York.

Bergado, D.T., Sasanakul, I., Horpibulsuk, S., 2003. **Electro-Osmotic Consolidation of Soft Bangkok Clay Using Cooper and Carbon Electrodes with PVD**. Geotechnical Testing Journal, ASTM, Vol.26, No.3, doi: 10.1520/GTJ11309J.

Bo, M.W., Arulrajah, A., Horpibulsuk, S. and Leong, M., 2015. **Quality management of prefabricated vertical drain materials in mega land reclamation projects: A case study.** Soils and Foundations, Vol.55, No.4, pp.895-905. doi: 10.1016/j.sandf.2015.06.019.

Bouazza, A., Haque, A., Kwan, P.S., 2006. Chapman G. **Strength improvement of cement treated Coode Island Silt by mixing method.** Australian Geomechanics, Vol. 41 p. 101-106.

Bouazza, A., Kwan, P.S., Chapman, G., 2004. **Strength properties of cement treated Coode Island Silt by mixing method.** Geotechnical Engineering for Transportation Projects ASCE 1421-1428.

Buchwald, A., Kaps, Ch., 2002. **Property controlling influences on the generation of geopolymeric binders based on clay.** Geopolymer (Melbournd Australia).

Chai, J.C., Horpibulsuk, S., Shen, S.L. and Carter, J.P., 2014. **Consolidation analysis of clayey deposits under vacuum pressure with horizontal drains**. Geotextiles and Geomembranes, Vol.42, pp.437-444.

Davidovits, J., Buzzi, L., Rocher, R., Gimeno, D., Marini, C., 1999. Tocco S. **Geopolymeric cement based on low cost geologic material, results from the European Research project GEOCIS-TEM. In: Davidovits et al., editors**. Proceedings of the second international conference Geopolymere ’99; p. 83–96.

Davidovits, J., 1991. Geopolymers. **J Therm Anal Calorim** 37(8):1633–56.

Du, Y. J., Horpibulsuk, S., Wei, M. L., Liu, M. L. 2014. **Modeling compression behavior of cement treated zinc contaminated clayey soils**. Soils and Foundations, 54(5), 1018-1026.

Du, Y. J., Wei, M. L., Jin, F., Liu, Z. B. 2013. **Stress-train relation and strength characteristics of cement treated zinc-contaminated clay**, Engineering Geology, 167, 20-26.

Ervin, M. C., 1992. **Engineering properties of Quaternary age sediments of the Yarra Delta**, Engineering Geology of Melbourne.

Granizo, M.L., Alonso, S., Blanco-Varela, M.T., 2002. **Palomo A. Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction**, J. Am. Ceram. Soc. 85 (1) 225–231.

Granizo, M.L., Alonso, S., Blanco-Varela, M.T., 2002. Palomo A. **Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction**. J. Am. Ceram. Soc. 85 (1) 225–231.

Guo, X., Shi, H., Dick, WA., 2010. **Compressive strength and microstructural characteristics of class C fly ash geopolymer**. Cem Concr Compos 32:142–7.

Hardjito, D., Wallah, SE., Sumajouw, DMJ., Rangan, BV., 2004. **On the development of fly ash-based geopolymer concrete**. ACI Mater J 101(6):467–72.

Horpibulsuk, S., Miura, N., and Nagaraj, T.S., 2003. **Assessment of strength development in cement-admixed high water content clays with Abrams' law as a basis.** Geotechnique, Vol.53, No.4, pp.439-444.

Horpibulsuk, S., Miura, N., Koga, H., Nagaraj, TS., 2004. **Analysis of strength development in deep mixing – a field study.** Ground Improve 8(2):59–68.

Horpibulsuk, S., Rachan, R., Raksachon, Y., 2009. **Role of fly ash on strength and microstructure development in blended cement stabilized silty clay**. Soils and Foundations 49 (1), 85–98.

Horpibulsuk, S., Rachan, R., Suddeepong, A., 2011a. **Assessment of strength development in blended cement admixed Bangkok clay**. Construction and Building Materials 25 (4), 1521–1531.

Horpibulsuk, S., Rachan, R., Suddeepong, A., Chinkulkijniwat, A., 2011b. **Strength development in cement admixed Bangkok clay: laboratory and field investigations.** Soils and Foundations 51 (2), 239–251.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., 2012a. **Soil stabilization by calcium carbide residue and fly ash**. Journal of Materials in Civil Engineering, ASCE 24 (2), 184–193.

Horpibulsuk, S., Phochan, W., Suddeepong, A., Chinkulkijniwat, A., Liu, M. D., 2012b. **Strength development in blended cement admixed saline clay**. Applied Clay Science 55, 44–52.

Horpibulsuk, S., Chinkulkijniwat, A., Cholaphatsorn, A., Suebsuk, J., and Liu, M.D. (2012c), "**Consolidation behavior of soil cement column improved ground**", *Computers and Geotechnics*, Vol.43, pp.37-50.

Horpibulsuk, S., Phetchuay, C., Chinkulkijniwat, A., Cholaphatsorn, A., 2013. **Strength development in silty clay stabilized with calcium carbide residue and fly ash**. Soils Found 53:477–86.

Kampala, A., Horpibulsuk, S., Chinkulkijniwat, A., 2013. **Shen SL. Engineering properties of recycled calcium carbide residue stabilized clay as fill and pavement materials**. Constr Build Mater 46:203–10.

Kampala, A., Horpibulsuk, S., Prongmanee, N., Chinkulkijniwat, A., 2014. **Influence of wet-dry cycles on compressive strength of calcium carbide residue-fly ash stabilized clay.** J Mater Civ Eng ASCE 26:633–43.

Kampala, A., Horpibulsuk, S., 2013. **Engineering properties of calcium carbide residue stabilized silty clay.** J Mater Civ Eng ASCE 25(5):632–44.

Lee, W., Van Deventer, J., 2002. **The effect of ionic contaminants on the early age properties of alkali-activated fly ash based cements**. Cement Concrete Res. 32 577–584.

Li, C., Sun, H., Li, L., 2010. A review: **The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements.** Cem. Concr. Res. 40 1341–1349.

MacKenzie, K., Smith, M., Wong, A., 2007. **A multinuclear MAS NMR study of calcium-containing aluminosilicate inorganic polymers**. J. Mater. Chem. 17 5090–5096.

McLellan, B.C., Williams, R.P., Lay, J., Van Riessen, A., Corder, G.D., 2011. **Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement.** J. Clean. Prod. 19 (9-10) 1080-1090.

Mohapatra, R., Rao, JR., 2001. **Some aspects of characterisation, utilisation and environmental effects of fly ash**. J Chem Technol Biotechnol 76(1):9–26.

Palomo, A., Grutzeck, MW., Blanco, MT., 1999. **Alkali activated fly ashes: a cement for the future**. Cement and Concrete Research 29(8):1323-1329.

Phetchuay, C., Horpibulsuk, S., Suksiripattanapong, C., Chinkulkijniwat, A., Arulrajah, A., Disfani, M.M., 2014. **Calcium carbide residue: alkaline activator for clay-fly ash geopolymer,** Constr. Build. Mater. 69 285–294.

Phoo-ngernkham, T., Hanjitsuwan, S., Horpibulsuk, S., Poowancum, A. and Chindaprasirt, P., 2015. **Rapid setting fly ash geopolymers with calcium rich additives as alternative repair material**. Journal of Cleaner Production (Tentatively accepted for publication).

Phummiphan, I., Horpibulsuk, S., Sukmak, P., Chinkulkijniwat, A., Arulrajah, A., and Shen S.L. (2015), "**Stabilization of marginal lateritic soil using high**

calcium fly ash based geopolymer”, *Road Materials and Pavement Design* (Accepted for publication on 3 December 2015)

Shen, S.L., Wang, Z.F., Horpibulsuk, S. and Kim, Y.H. 2013a. **Jet grouting with a newly developed technology: The twin-jet method**. Engineering Geology 152(1), 87-95.

Shen, S.L., Wang, Z.F., Yang, J. and Ho, C.E., 2013b. **Generalized approach for prediction of jet grout column diameter.** Journal of Geotechnical and Geoenvironmental Engineering, doi: 10.1061/(ASCE)GT.1943-5606.0000932.

Shen, S.L., Wang, Z.F., Sun, W.J., Wang, L.B., Horpibulsuk, S., 2013b. **A field trial of horizontal jet grouting using the composite-pipe method in the soft deposit of Shanghai.**Tunn.Undergr. Sp. Tech. 35, 142-151.

Suksiripattanapong, C., Horpibulsuk, S., Chanprasert, P., Sukmak, P., Arulrajah, A., 2015. **Compressive strength development in fly ash geopolymer masonsy units manufactured from water treatment sludge**. Constr. Build. Mater. 82 20-30.

Temuujin, J., Van Riessen, A., Williams, R., 2009. **Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes**. J. Hazard. Mater. 167 82–88.

Turner, L.K., Collins, F.G., 2013. **Carbon dioxide equivalent (CO2-e) emissions: a comparison between geopolymer and OPC cement concrete**. Constr. Build. Mater. 43 125–130.

Van Deventer, J., Provis, J., Duxson, P., Luckey, G.C., 2007. **Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products**. J. Hazard. Mater. A139 506–513.

Van Jaarsveld, J., Van Deventer, J., Lorenzen, L., 1998. **Factors affecting the immobilization of metals in geopolymerized fly ash**. Metall Mater Trans B 29(1):283–91.

Vichan, S., Rachan, R., Horpibulsuk, S., 2013. **Strength and microstructure development in Bangkok clay with calcium carbide residue and biomass ash**. ScienceAsia 39:186–93.

Wu, H.N., Shen, S.L., Ma, L., Yin, Z.Y., Horpibulsuk, S., 2015. **Evaluation of the strength increase of marine clay under seawall construction: a case study**. Marine Georesources & Geotechnology, Vol.33, pp.532-541.

Xu, H., Van Deventer, J.S.J., 2005. **The geopolymerisation of alumino-silicate minerals.** Int. J. Miner. Process. 59 247–266. 1688–1697.

Yip, C.K., Lukey, G.C., Deventer, J.S.J., 2005. **The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation**, Cem. Concr. Res. 35 1688–1697.

Yip, C.K., Lukey, G.C., Provis, J.L., Deventer, J.S.J., 2008. **Effect of calcium silicate sources on geopolymerisation**, Cem. Concr. Res. 38 554–564.

Yip, C.K., Lukey, G.C., Provis, J.L., Van Deventer, J.S.J., 2008. **Effect of calcium silicate sources on geopolymerisation.** Cem. Concr. Res. 38 554–564.

Yip, C.K., Lukey, G.C., Van Deventer, J.S.J., 2005. **The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation.** Cem. Concr. Res. 35 1688–1697.

Yunfen, H., Dongmin, W., Wenjuan, Z., Hongbo, L., Lin, W., 2009. Effect of activator and curing mode on fly ash-based geopolymer. J Wuhan Univ Technol Mater Sci Ed 24(5):711–5.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and conclusions

This thesis consists of two main objectives. The first is to investigate a possibility of using Calcium Carbide Residue (CCR) as a liquid alkaline instead of sodium hydroxide solution (NaOH) in geopolymer process to improve the strength of problematic silty clay. The second attempts to examine the viability of using Fly Ash (FA) and CCR based geopolymers as a sustainable binder to improve strength of soft marine clay, namely CIS. The conclusions can be drawn as follows:

5.1.1 Calcium Carbide Residue: A Liquid Alkaline for Clay-FA Geopolymer

5.1.1.1 The role of Na_2SiO_3 /water on the compaction curves

The input of Na_2SiO_3/water ratio affects the optimum liquid content and maximum dry unit weight of the clay-FA geopolymer. The optimal Na_2SiO_3/water ratio provides the highest unsoaked strength and maximum dry unit weight.

5.1.1.2 The role Na_2SiO_3/NaOH ratio FA and curing on soaked strength of clay–FA geopolymer

The optimal Na_2SiO_3/water ratio providing highest soaked strength is found at the fixation point, which is the threshold limit from large to small reduction in PI and is equal to 0.6 for this clay-FA geopolymer. The optimal FA replacement ratio is 15%. Curing at 40 °C provides higher strength than room temperature curing, indicating the possibility of using this clay-FA geopolymer as a pavement subgrade material. The 7-day soaked strength meets the strength requirement for subgrade materials specified by Department of Rural Roads, Thailand.

5.1.1.3 SEM analysis

SEM images are useful to explain the role of influential factors on strength development in clay-FA geopolymer. The alkaline dissolution occurs on the surface of FA particles, resulting in many holes on the FA surface and smaller particles. The alkaline solution contacts the smaller particles housed inside the larger spheres and forms a dense matrix.

5.1.2 Strength development in soft marine clay stabilized by fly ash and calcium carbide residue based geopolymer

5.1.2.1 The role of NaOH and FA content on UCS

A higher NaOH concentration can leach higher silica and alumina from FA for geopolymerization reaction for a particular FA content. For a particular NaOH concentration, the higher FA content results in higher consumed silica and alumina oxides. As such, the increase in both NaOH concentration and FA content in the geopolymeric system at a specific Na_2SiO_3/NaOH, Liquid Alkaline Activator (L) content and water content improves significantly the UCS.

5.1.2.2 The role of L/FA on UCS

For a particular NaOH concentration, the optimal Na_2SiO_3/NaOH providing the highest UCS is governed by L/FA; i.e., a higher FA content (lower L/FA) requires a more NaOH content for leaching silica and alumina; hence, the optimal Na_2SiO_3/NaOH decreases with FA content. The increase in L/FA initially improves the UCS of the FA geopolymer but when the L/FA is excessive of the optimal value, the UCS decreases due to the precipitation at very early stage before the poly-condensation process in geopolymer. The optimal L/A is dependent upon the initial water content; i.e., the optimal L/FA increases with water content as the high water content dilutes NaOH concentration. The results show that the optimal ingredient providing the maximum UCS for w = LL is L/FA = 1 and Na_2SiO_3/NaOH = 70:30.

5.1.2.3 The normalized equation for approximating UCS

The UCS development with time of FA geopolymer with various ingredients of water content, Na_2SiO_3/NaOH, L/FA and NaOH concentration can be normalized by 28-day UCS, similar to that of cement stabilized clays. The proposed normalized equation is useful for approximating UCS at any curing time within 28 days. The proposed equation is on sound principles and can be refined by more test data.

5.1.2.4 The role of CCR on UCS development

The role of CCR on UCS development in FA geopolymer stabilized CIS is classified into three zones: inactive, active and quasi-inert. The CCR contents between 7 and 12% are in the active zone where significant UCS development is evident. The dissolution of $Ca(OH)_2$ concentration is hindered when CCR content exceeds the active zone. As such, the rate of UCS development decreases in CCR increases in the quasi-inert zone. The 12% CCR addition can improve UCS up to approximately 1.5 times of the original value.

5.1.2.5 Carbon footprint evaluation

The difference in CO_2 footprints between FA geopolymer stabilized CIS and cement stabilized CIS increases as the UCS increases. The emission CO_2-e of FA geopolymer stabilized CIS is 22%, 23% and 43% lower than that of cement stabilized CIS at UCS of 400 kPa, 600 kPa and 800 kPa, respectively. This shows the benefit of FA-CCR geopolymer as a green and strong binder alternative to Portland cement.

5.2 Recommendations for future work

- The strength and microstructure of CCR and FA-geopolymer stabilized soils presented in this research can be used as fundamental for further study on other calcium-rich additive by-products such as steel slag.
- Advanced microstructural tests such as synchrotron X-ray diffraction are recommended for further investigation on time-dependent geopolymerization mechanism and products.

APPENDIX A

LIST OF PUBLICATIONS

List Of Publications

INTERNATIONAL JOURNAL PAPERS

Phetchuay, C., Horpibulsuk, S., Suksiripattanapong, C., Chinkulkijniwat, A., Arulrajah, A., and Disfani, M. M. (2014). **Calcium carbide residue: Alkaline activator for clay-fly ash geopolymer.** *Constr. Build. Mater*., 69(20), 285–294.

Phetchuay, C., Horpibulsuk, S., Arulrajah, A., Suksiripattanapong, C., Udomchai, A. (2016). **Strength development in Soft Marine Clay stabilized by fly ash and Calcium carbide residue based geopolymer**. *Applied Clay Science* (Tentatively accepted for publication).

INTERNATIONAL CONFERENCE PAPERS

Phetchuay, C., Horpibulsuk, S., Arulrajah, A., Suksiripattanapong, C., (2015). **Calcium carbide residue as alkaline activator for clay-fly ash geopolymer.** *The 41st Congress on Science and Technology of Thailand (STT41)*, November 6 - 8, Suranaree University of Technology, Nakhonratchasima, Thailand.

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Calcium carbide residue: Alkaline activator for clay–fly ash geopolymer

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HIGHLIGHTS

- Industrial by-product: Calcium Carbide Residue (CCR).
- A green geopolymer subgrade using CCR as alkaline activator.
- Strength and microstructural analysis of CCR–FA based geopolymer.
- Role of heat temperature and curing on strength development.

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ABSTRACT

Calcium Carbide Residue (CCR) and Fly Ash (FA) are waste by-products from acetylene gas and power plant production, respectively. The liquid alkaline activator studied in this research is a mixture of sodium silicate solution (Na_2SiO_3), water and CCR. The primary aim of this research is to investigate the viability of using CCR, a cementitious waste material, as an alkaline activator and FA as a precursor to improve the engineering properties of a problematic silty clay to facilitate its usage as stabilized subgrade material. The influential factors studied are Na_2SiO_3/water ratio, FA replacement ratio, curing time, curing temperature and soaking condition for a fixed CCR content of 7%. Strength development is investigated via the unconfined compression test. Scanning Electron Microscopy (SEM) observation is used to explain the role and contribution of influential factors on strength development. CCR dissolves the silicon and aluminum in amorphous phase of FA and the Na_2SiO_3 acts as a binder. The maximum soaked strength of the clay-FA geopolymer is found at Na_2SiO_3/water ratio of 0.6 and FA replacement ratio of 15%. The optimal Na_2SiO_3/water ratio is approximated from index test, which is a very practical approach. The clay-FA geopolymers with 40 °C curing exhibit higher strength than those with room temperature curing, indicating the possibility of using clay-FA geopolymer for pavement subgrade applications. The 7-day soaked strength at the optimal ingredient meets the strength requirement for subgrade materials specified by the local national road authority. CCR is found to be a sustainable alkaline activator for geopolymer stabilized subgrade materials, which will result in the diversion of significant quantities of this by-product from landfills.

1. Introduction

Chemical stabilization is an extensively used soil improvement technique for road embankments and pavement applications. The resistance of compression and consequent strength development of stabilized materials increases with an increase in curing time. Portland cement is commonly used as a cementing agent for this stabilization [1–6]. The stabilization commences with mixing of the soil in a relatively dry state with cement and water specified for compaction. The compaction effort from rollers is needed to remove air from the soil (to increase degree of saturation) and to make soil particles slip over each other and move into a densely packed state. The high unit cost and energy intensive process for the production of Portland cement are the driving forces for the constant need within the industry to seek alternative cementitious additives. The cement manufacturing process emits CO_2 into the atmosphere, which accounts for 5% of the total CO_2 released into

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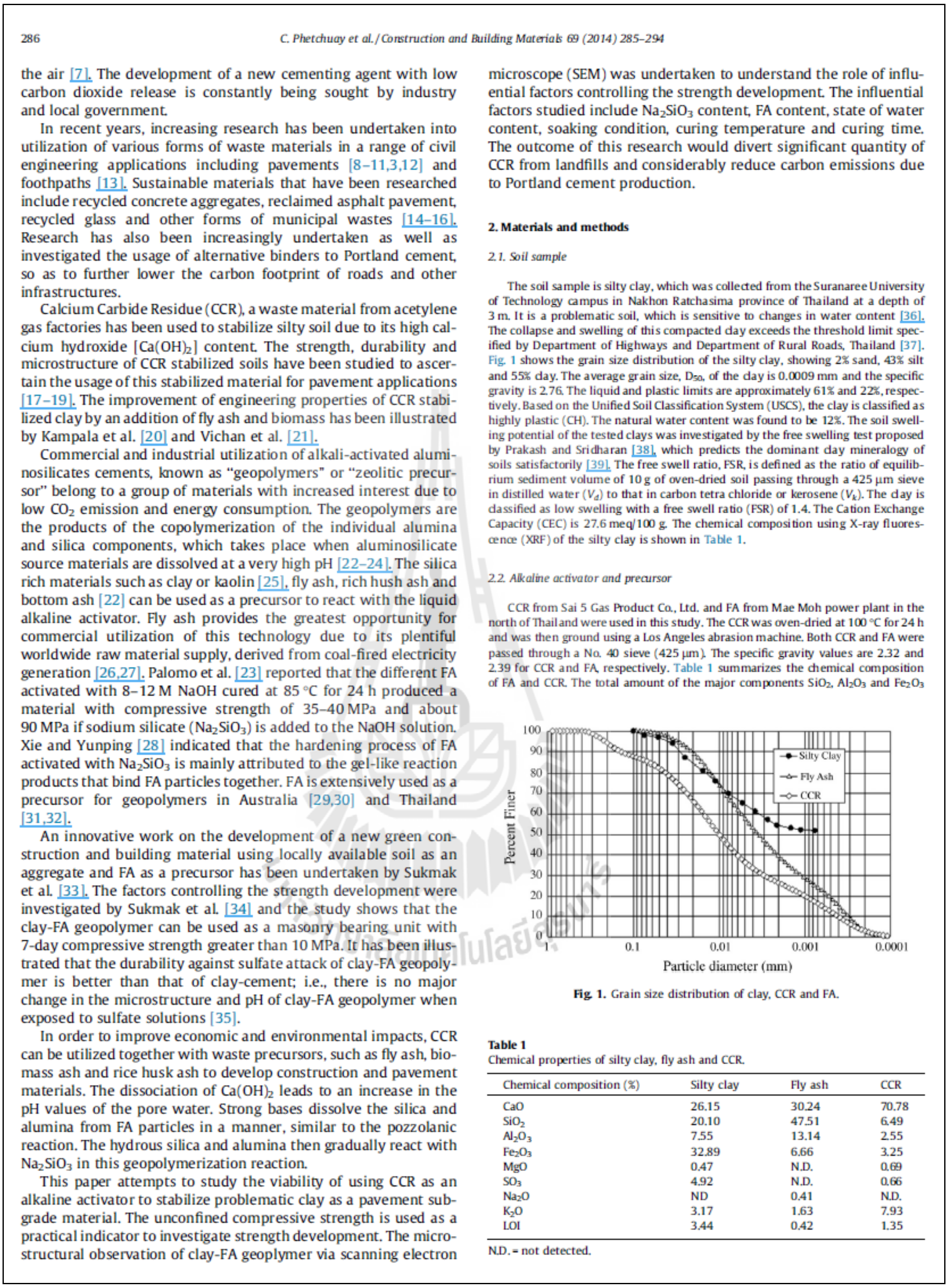


the air [7]. The development of a new cementing agent with low carbon dioxide release is constantly being sought by industry and local government.

In recent years, increasing research has been undertaken into utilization of various forms of waste materials in a range of civil engineering applications including pavements [8–11,3,12] and foothpaths [13]. Sustainable materials that have been researched include recycled concrete aggregates, reclaimed asphalt pavement, recycled glass and other forms of municipal wastes [14–16]. Research has also been increasingly undertaken as well as investigated the usage of alternative binders to Portland cement, so as to further lower the carbon footprint of roads and other infrastructures.

Calcium Carbide Residue (CCR), a waste material from acetylene gas factories has been used to stabilize silty soil due to its high calcium hydroxide [$Ca(OH)_2$] content. The strength, durability and microstructure of CCR stabilized soils have been studied to ascertain the usage of this stabilized material for pavement applications [17–19]. The improvement of engineering properties of CCR stabilized clay by an addition of fly ash and biomass has been illustrated by Kampala et al. [20] and Vichan et al. [21].

Commercial and industrial utilization of alkali-activated aluminosilicates cements, known as “geopolymers” or “zeolitic precursor” belong to a group of materials with increased interest due to low CO_2 emission and energy consumption. The geopolymers are the products of the copolymerization of the individual alumina and silica components, which takes place when aluminosilicate source materials are dissolved at a very high pH [22–24]. The silica rich materials such as clay or kaolin [25], fly ash, rich hush ash and bottom ash [22] can be used as a precursor to react with the liquid alkaline activator. Fly ash provides the greatest opportunity for commercial utilization of this technology due to its plentiful worldwide raw material supply, derived from coal-fired electricity generation [26,27]. Palomo et al. [23] reported that the different FA activated with 8–12 M NaOH cured at 85 °C for 24 h produced a material with compressive strength of 35–40 MPa and about 90 MPa if sodium silicate (Na_2SiO_3) is added to the NaOH solution. Xie and Yunping [28] indicated that the hardening process of FA activated with Na_2SiO_3 is mainly attributed to the gel-like reaction products that bind FA particles together. FA is extensively used as a precursor for geopolymers in Australia [29,30] and Thailand [31,32].

An innovative work on the development of a new green construction and building material using locally available soil as an aggregate and FA as a precursor has been undertaken by Sukmak et al. [33]. The factors controlling the strength development were investigated by Sukmak et al. [34] and the study shows that the clay-FA geopolymer can be used as a masonry bearing unit with 7-day compressive strength greater than 10 MPa. It has been illustrated that the durability against sulfate attack of clay-FA geopolymer is better than that of clay-cement; i.e., there is no major change in the microstructure and pH of clay-FA geopolymer when exposed to sulfate solutions [35].

In order to improve economic and environmental impacts, CCR can be utilized together with waste precursors, such as fly ash, biomass ash and rice husk ash to develop construction and pavement materials. The dissociation of $Ca(OH)_2$ leads to an increase in the pH values of the pore water. Strong bases dissolve the silica and alumina from FA particles in a manner, similar to the pozzolanic reaction. The hydrous silica and alumina then gradually react with Na_2SiO_3 in this geopolymerization reaction.

This paper attempts to study the viability of using CCR as an alkaline activator to stabilize problematic clay as a pavement subgrade material. The unconfined compressive strength is used as a practical indicator to investigate strength development. The microstructural observation of clay-FA geoplymer via scanning electron microscope (SEM) was undertaken to understand the role of influential factors controlling the strength development. The influential factors studied include Na_2SiO_3 content, FA content, state of water content, soaking condition, curing temperature and curing time. The outcome of this research would divert significant quantity of CCR from landfills and considerably reduce carbon emissions due to Portland cement production.

2. Materials and methods

2.1. Soil sample

The soil sample is silty clay, which was collected from the Suranaree University of Technology campus in Nakhon Ratchasima province of Thailand at a depth of 3 m. It is a problematic soil, which is sensitive to changes in water content [36]. The collapse and swelling of this compacted clay exceeds the threshold limit specified by Department of Highways and Department of Rural Roads, Thailand [37]. Fig. 1 shows the grain size distribution of the silty clay, showing 2% sand, 43% silt and 55% clay. The average grain size, D_{50}, of the clay is 0.0009 mm and the specific gravity is 2.76. The liquid and plastic limits are approximately 61% and 22%, respectively. Based on the Unified Soil Classification System (USCS), the clay is classified as highly plastic (CH). The natural water content was found to be 12%. The soil swelling potential of the tested clays was investigated by the free swelling test proposed by Prakash and Sridharan [38], which predicts the dominant clay mineralogy of soils satisfactorily [39]. The free swell ratio, FSR, is defined as the ratio of equilibrium sediment volume of 10 g of oven-dried soil passing through a 425 μm sieve in distilled water (V_d) to that in carbon tetra chloride or kerosene (V_k). The clay is classified as low swelling with a free swell ratio (FSR) of 1.4. The Cation Exchange Capacity (CEC) is 27.6 meq/100 g. The chemical composition using X-ray fluorescence (XRF) of the silty clay is shown in Table 1.

2.2. Alkaline activator and precursor

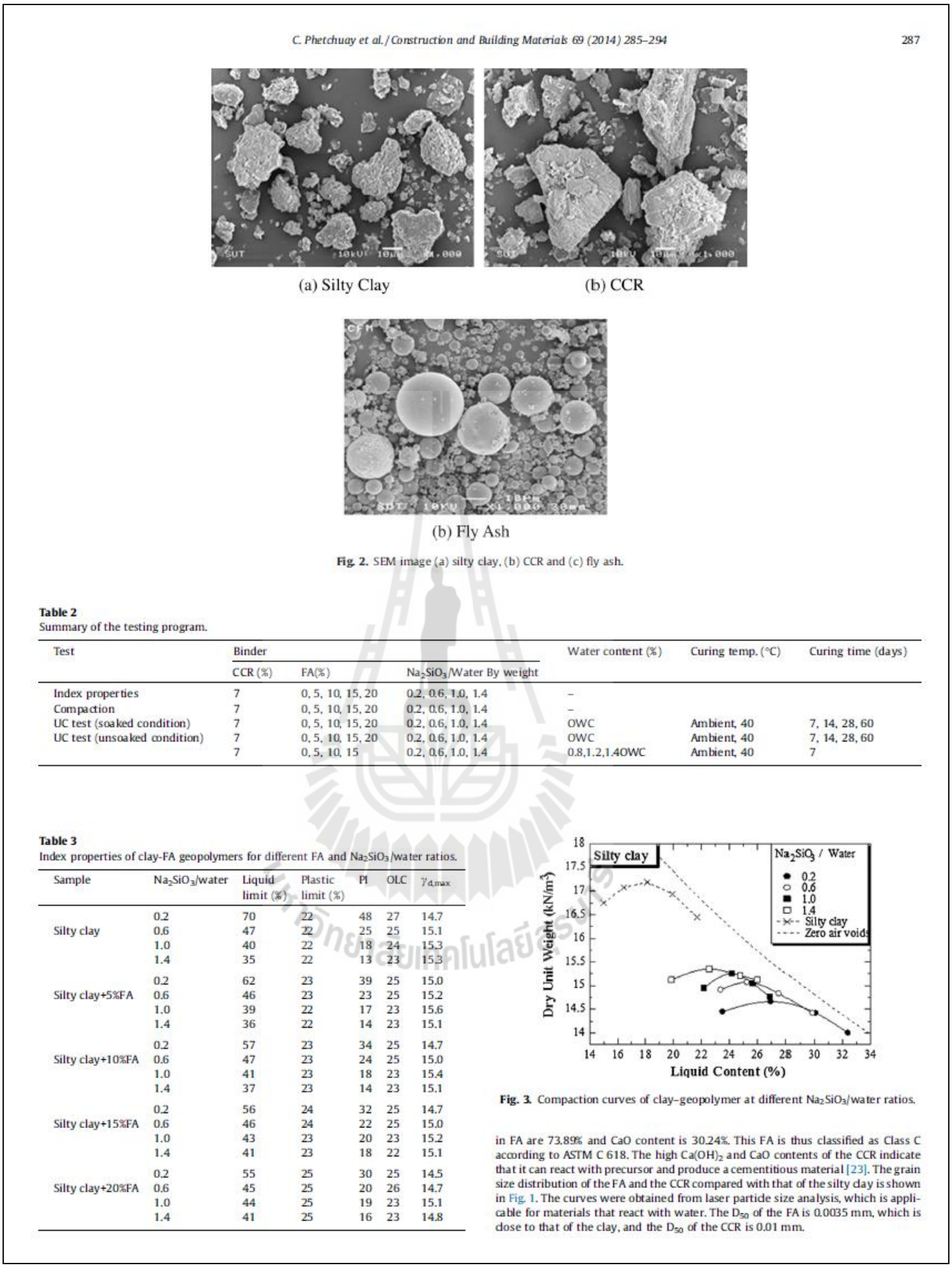
CCR from Sai 5 Gas Product Co., Ltd. and FA from Mae Moh power plant in the north of Thailand were used in this study. The CCR was oven-dried at 100 °C for 24 h and was then ground using a Los Angeles abrasion machine. Both CCR and FA were passed through a No. 40 sieve (425 μm). The specific gravity values are 2.32 and 2.39 for CCR and FA, respectively. Table 1 summarizes the chemical composition of FA and CCR. The total amount of the major components SiO_2, Al_2O_3 and Fe_2O_3

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

Table 1
Chemical properties of silty clay, fly ash and CCR.

Chemical composition (%)	Silty clay	Fly ash	CCR
CaO	26.15	30.24	70.78
SiO_2	20.10	47.51	6.49
Al_2O_3	7.55	13.14	2.55
Fe_2O_3	32.89	6.66	3.25
MgO	0.47	N.D.	0.69
SO_3	4.92	N.D.	0.66
Na_2O	ND	0.41	N.D.
K_2O	3.17	1.63	7.93
LOI	3.44	0.42	1.35

N.D. = not detected.



(a) Silty Clay (b) CCR

(b) Fly Ash

Fig. 2. SEM image (a) silty clay, (b) CCR and (c) fly ash.

Table 2
Summary of the testing program.

Test	Binder			Water content (%)	Curing temp. (°C)	Curing time (days)
	CCR (%)	FA(%)	Na_2SiO_3/Water By weight			
Index properties	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	–		
Compaction	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	–		
UC test (soaked condition)	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	OWC	Ambient, 40	7, 14, 28, 60
UC test (unsoaked condition)	7	0, 5, 10, 15, 20	0.2, 0.6, 1.0, 1.4	OWC	Ambient, 40	7, 14, 28, 60
	7	0, 5, 10, 15	0.2, 0.6, 1.0, 1.4	0.8,1.2,1.4OWC	Ambient, 40	7

Table 3
Index properties of clay-FA geopolymers for different FA and Na_2SiO_3/water ratios.

Sample	Na_2SiO_3/water	Liquid limit (%)	Plastic limit (%)	PI	OLC	$\gamma_{d,max}$
Silty clay	0.2	70	22	48	27	14.7
	0.6	47	22	25	25	15.1
	1.0	40	22	18	24	15.3
	1.4	35	22	13	23	15.3
Silty clay+5%FA	0.2	62	23	39	25	15.0
	0.6	46	23	23	25	15.2
	1.0	39	22	17	23	15.6
	1.4	36	22	14	23	15.1
Silty clay+10%FA	0.2	57	23	34	25	14.7
	0.6	47	23	24	25	15.0
	1.0	41	23	18	23	15.4
	1.4	37	23	14	23	15.1
Silty clay+15%FA	0.2	56	24	32	25	14.7
	0.6	46	24	22	25	15.0
	1.0	43	23	20	23	15.2
	1.4	41	23	18	22	15.1
Silty clay+20%FA	0.2	55	25	30	25	14.5
	0.6	45	25	20	26	14.7
	1.0	44	25	19	23	15.1
	1.4	41	25	16	23	14.8

Fig. 3. Compaction curves of clay–geopolymer at different Na_2SiO_3/water ratios.

in FA are 73.89% and CaO content is 30.24%. This FA is thus classified as Class C according to ASTM C 618. The high $Ca(OH)_2$ and CaO contents of the CCR indicate that it can react with precursor and produce a cementitious material [23]. The grain size distribution of the FA and the CCR compared with that of the silty clay is shown in Fig. 1. The curves were obtained from laser particle size analysis, which is applicable for materials that react with water. The D_{50} of the FA is 0.0035 mm, which is close to that of the clay, and the D_{50} of the CCR is 0.01 mm.

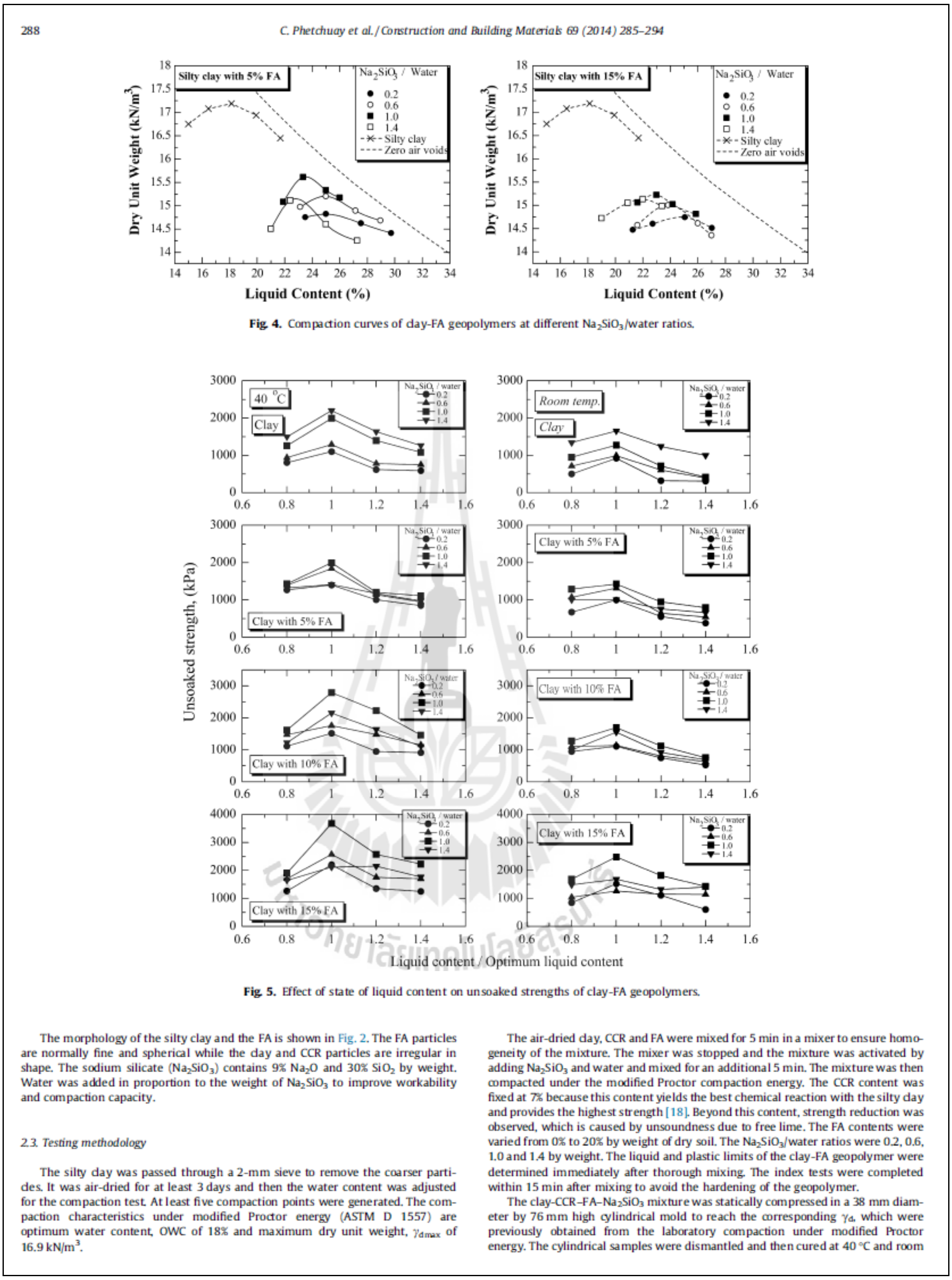


Fig. 4. Compaction curves of clay-FA geopolymers at different Na$_2$SiO$_3$/water ratios.

Fig. 5. Effect of state of liquid content on unsoaked strengths of clay-FA geopolymers.

The morphology of the silty clay and the FA is shown in Fig. 2. The FA particles are normally fine and spherical while the clay and CCR particles are irregular in shape. The sodium silicate (Na_2SiO_3) contains 9% Na_2O and 30% SiO_2 by weight. Water was added in proportion to the weight of Na_2SiO_3 to improve workability and compaction capacity.

2.3. *Testing methodology*

The silty clay was passed through a 2-mm sieve to remove the coarser particles. It was air-dried for at least 3 days and then the water content was adjusted for the compaction test. At least five compaction points were generated. The compaction characteristics under modified Proctor energy (ASTM D 1557) are optimum water content, OWC of 18% and maximum dry unit weight, γ_{dmax} of 16.9 kN/m^3.

The air-dried clay, CCR and FA were mixed for 5 min in a mixer to ensure homogeneity of the mixture. The mixer was stopped and the mixture was activated by adding Na_2SiO_3 and water and mixed for an additional 5 min. The mixture was then compacted under the modified Proctor compaction energy. The CCR content was fixed at 7% because this content yields the best chemical reaction with the silty clay and provides the highest strength [18]. Beyond this content, strength reduction was observed, which is caused by unsoundness due to free lime. The FA contents were varied from 0% to 20% by weight of dry soil. The Na_2SiO_3/water ratios were 0.2, 0.6, 1.0 and 1.4 by weight. The liquid and plastic limits of the clay-FA geopolymer were determined immediately after thorough mixing. The index tests were completed within 15 min after mixing to avoid the hardening of the geopolymer.

The clay-CCR–FA–Na_2SiO_3 mixture was statically compressed in a 38 mm diameter by 76 mm high cylindrical mold to reach the corresponding γ_d, which were previously obtained from the laboratory compaction under modified Proctor energy. The cylindrical samples were dismantled and then cured at 40 °C and room

Table 4
Soaked strength of clay-FA geopolymers (kPa).

Description	Na_2SiO_3/water	7Days		14Days		28Days		60Days	
		40 °C	RT	40 °C	RT	40 °C	RT	40 °C	RT
Clay		0	0	0	0	990	1205	1485	1300
Clay + 5%FA		0	0	773	773	1101	928	1628	1375
Clay + 10%FA	0.2	1454	1052	1514	1265	1698	1694	2332	1804
Clay + 15%FA		2166	1732	2258	1812	2241	1856	2345	1924
Clay + 20%FA		2004	1178	2105	1356	1988	1590	2014	1651
Clay		0	0	0	0	0	0	689	1120
Clay + 5%FA		0	0	447	433	954	988	1598	1303
Clay + 10%FA	0.6	1728	1354	1802	1874	1650	1745	2544	1924
Clay + 15%FA		2154	1658	2269	2000	2345	2458	3120	2578
Clay + 20%FA		2100	1254	2187	1578	2095	1687	2245	1767
Clay		0	0	0	0	0	0	0	0
Clay + 5%FA		0	0	0	0	0	0	0	0
Clay + 10%FA	1.0	0	0	0	0	0	0	0	0
Clay + 15%FA		0	0	0	0	0	0	0	0
Clay + 20%FA		0	0	0	0	0	0	0	0
Clay		0	0	0	0	0	0	0	0
Clay + 5%FA		0	0	0	0	0	0	0	0
Clay + 10%FA	1.4	0	0	0	0	0	0	0	0
Clay + 15%FA		0	0	0	0	0	0	0	0
Clay + 20%FA		0	0	0	0	0	0	0	0

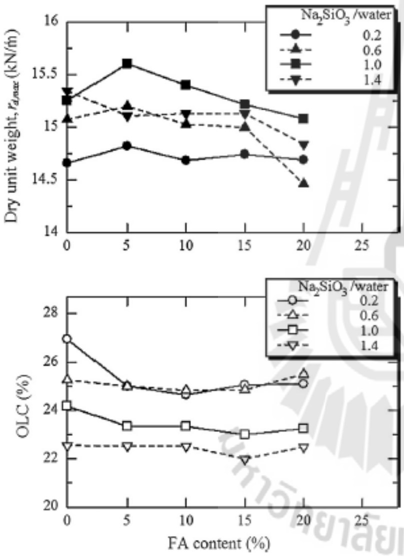


Fig. 6. Dry unit weight and OLC of clay-FA geopolymers for different FA replacement ratios.

temperature (27–30 °C). 40 °C temperature was used to simulate an average heat temperature on pavement subgrades in countries with a tropical climate, including Thailand. Unconfined Compression (UC) tests were carried out on the samples after 7, 14, 28 and 60 days of curing under both unsoaked and soaked conditions. For the soaked condition, the samples were submerged under tap water for 2 h according to the specification of the Department of Highways, Thailand, DH-S 204/2533 (DH-S, 1990) [40]. The rate of vertical displacement for the UC test was fixed at 1 mm/min. The testing program is summarized in Table 2. For each curing time and ingredient, at least five samples were tested under the same conditions to assure test result consistency. In most cases, the results under the same testing condition were reproducible with low mean standard deviation, *SD* ($SD/\overline{x} < 10\%$, where $\overline{x}$ is mean strength value).

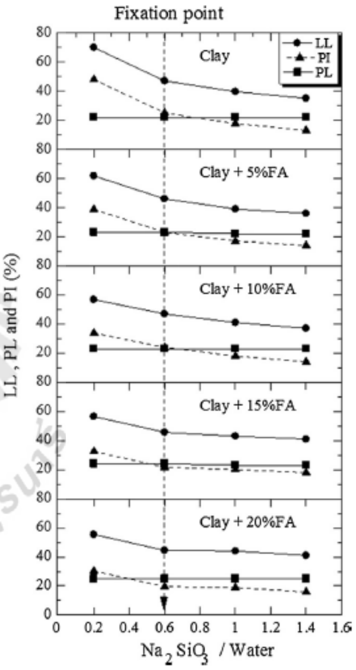


Fig. 7. Relationship between index properties and Na_2SiO_3/water ratio.

3. Results

Table 3 shows index properties of the clay-FA geopolymer with different ingredients. The plastic limit (PL) of the clay-FA geopolymer changes insignificantly with Na_2SiO_3/water ratio while the

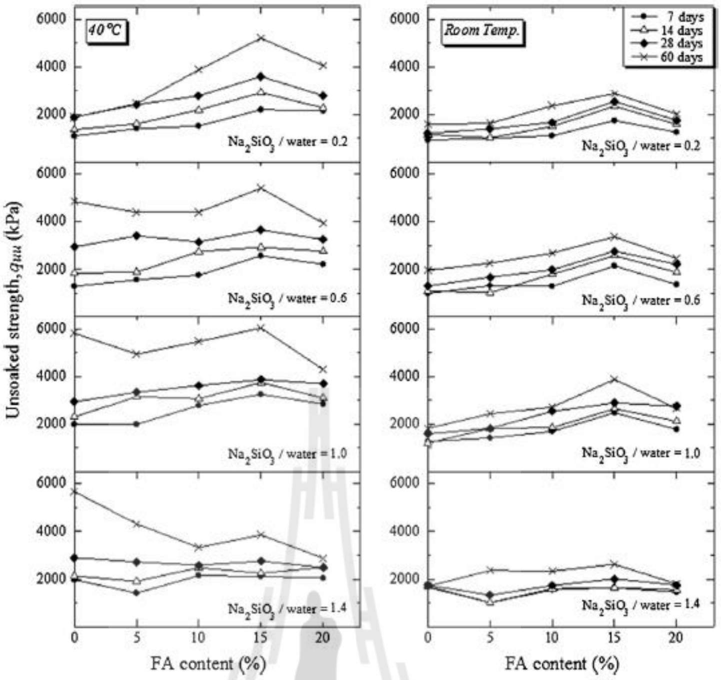


Fig. 8. Effect of FA replacement on unsoaked strengths of clay-FA geopolymers.

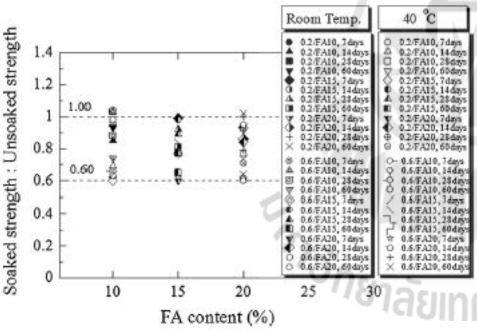


Fig. 9. Strength ratio of clay-FA geopolymers with different FA contents.

liquid limit (LL) decreases significantly, resulting in a sharp decline in the plasticity index (PI) with increasing Na_2SiO_3/water ratio and FA replacement. However, the effect of FA replacement on the change in PI is comparatively lower than that of Na_2SiO_3/water ratio.

Fig. 3 shows typical compaction curves (relationships between dry unit weight and liquid content with different Na_2SiO_3/water ratios) of clay–geopolymer (without FA). The maximum dry unit weight ($\gamma_{d,max}$) increases with increasing Na_2SiO_3/water ratio. This increase in $\gamma_{d,max}$ is associated with an decrease in optimum liquid content (OLC). Fig. 4 shows typical compaction curves of clay-FA geopolymer with various Na_2SiO_3/water ratios for FA replacement ratios of 5% and 15%. $\gamma_{d,max}$ of clay-FA geopolymer increases with increasing Na_2SiO_3/water ratio. However, when the Na_2SiO_3/water ratio is greater than 1.0, $\gamma_{d,max}$ decreases. The compacted clay-FA

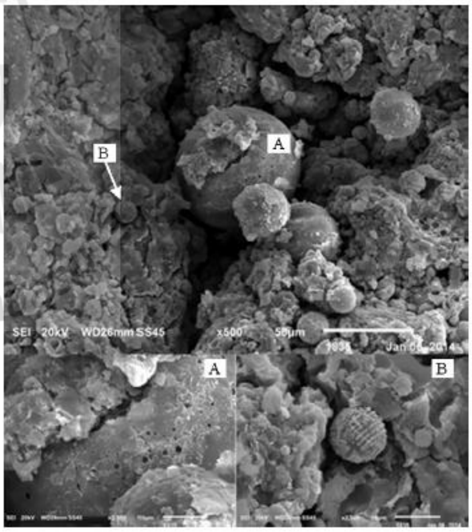


Fig. 10. SEM images of clay-FA geopolymer at Na_2SiO_3/water ratio = 0.6, FA = 15%, 40 °C curing after 60 days of curing.

geopolymers show lower $\gamma_{d,max}$ than the compacted clay (16.9 kN/m^3) because the CCR and FA have a lower specific gravity than the clay.

Fig. 5 shows the relationship between 7-day unsoaked strength and state of liquid content for different Na_2SiO_3/water ratios. Even though the OLC values are different for different ingredients (*refer to* Figs. 3 and 4), the maximum unsoaked strengths of all test clay-FA geopolymers are approximately at their OLC (maximum dry unit weight) for both curing temperatures. This relationship is the same as that of cement-stabilized silty clay, reported previously by Horpibulsuk et al. [16,41]. The OLC is thus recommended for this stabilization. At OLC, the strength development is dependent on the Na_2SiO_3/water ratio. The strength increases as the Na_2SiO_3/water ratio increases up to the optimal value and then decreases as the Na_2SiO_3/water ratio increases. The Na_2SiO_3/water ratios of 1.4 and 1.0 provide the highest strength for clay-FA geopolymers without and with FA, respectively for all curing times. These values correspond to γ_{dmax}. In other words, the densification controls the unsoaked strength. The maximum unsoaked strengths for both curing temperatures are found at 15% FA replacement ratio. The samples cured at 40 °C show higher strength than those cured at room temperature, indicating the effect of temperature.

Table 4 summarizes the soaked strengths of clay-FA geopolymers for various FA replacement ratios, curing times and Na_2SiO_3/water ratios for both curing temperatures. The soaked strengths are significantly lower than the unsoaked strengths. All test clay-FA geopolymers for various FA replacement ratios and curing times at Na_2SiO_3/water ratios of 1.0 and 1.4 show zero soaked strength. The soaked strengths at 40 °C curing are null for Na_2SiO_3/water ratio of 1.0 even though the unsoaked strengths are highest. The highest soaked strengths are found for the clay-FA geopolymers at Na_2SiO_3/water ratio of 0.6 for different FA replacement ratios and both curing temperatures. The optimal FA replacement ratio is at 15% and the 40 °C curing provides higher soaked strength than the room temperature curing. The strength development after 7 days of curing of the geopolymers cured at the 40 °C curing is insignificant when compared with that at the room temperature curing. For the room temperature curing, the strength sharply increases for curing times lower than 28 days and becomes insignificant for curing times greater than 28 days.

4. Result analysis and discussion

It has been reported that the liquid limit controls the compaction characteristics of the low swelling clays [42–45]. Because the input of Na_2SiO_3 decreases the liquid limit of the clay-FA geopolymer significantly, OLC of the clay-FA mixture decreases with increasing Na_2SiO_3/water ratio. The decrease in OLC is associated to the increase in the maximum dry unit weight as shown in Fig. 6. The input of FA slightly amends the liquid limit. Consequently, the OLC and γ_{dmax} are essentially the same even with the increase in FA replacement ratio.

The high pH environment from CCR dissolves silicon and aluminum in the amorphous phase of FA while the sodium silicate solution (Na_2SiO_3) acts as a binder. The optimal Na_2SiO_3/water ratio providing the maximum unsoaked and soaked strength for clay-FA geopolymer specimens is different. This is 1.0 for the unsoaked strengths and 0.6 for the soaked strength. The unsoaked strength is dependent upon the densification.

Fig. 7 shows the relationship between index properties and Na_2SiO_3/water ratio for various FA replacement ratios. Liquid limit is defined as water content at which soil begins to behave as liquid material and begin to flow while the plastic limit is at which soil begins to behave as plastic material. When the Na_2SiO_3 is added into clay-FA-CCR mixture, the flocculation and the coagulate aggregation of the clay-FA-CCR particles occur, which are caused by the chemical reaction between SiO_2, Al_2O_3, $Ca(OH)_2$ and Na_2SiO_3. The flocculation and the coagulate aggregation reduce the liquid limit while insignificantly affects the plastic limit. The insignificant change in plastic limit due to the flocculation and the coagulate aggregation has also been reported [46–48]. The Na_2SiO_3/water fixation point, which is the threshold limit from large to small reduction in PI, is found at 0.6 for all FA replacement ratios tested. The insignificant change in PI indicates that the Na_2SiO_3 content is excessive for the requirements for a chemical reaction. It is noted that the optimal Na_2SiO_3/water ratio providing the maximum soaked strength is also found at fixation point. This implies that the fixation point can be used in practice to determine the optimal Na_2SiO_3/water ratio.

The effect of FA replacement on the strength development of the clay-FA geopolymers at OLC is shown in Fig. 8. SiO_2 and Al_2O_3 in FA are in amorphous phase and can effectively react with CCR and Na_2SiO_3. As such, the strength increases with FA replacement ratio. However, the addition of FA content greater than 15% is ineffective possibly because excessive FA surrounds the CCR particles and obstructs the chemical reaction between CCR grain and water, resulting in lesser dissociation of $Ca(OH)_2$ to dissolve the silica and alumina from FA; hence, lesser geopolymerization products. It is evident that curing at 40°C provides higher unsoaked and soaked strengths than room temperature curing (*refer to* Table 4). The maximum 7-day soaked strength of clay-FA geopolymers is found to be 2154 kPa at Na_2SiO_3/water ratio of 0.6 and FA replacement ratio of 15%, which is greater than the specification for the Department of Rural Roads, Thailand (i.e., 1750 kPa) for

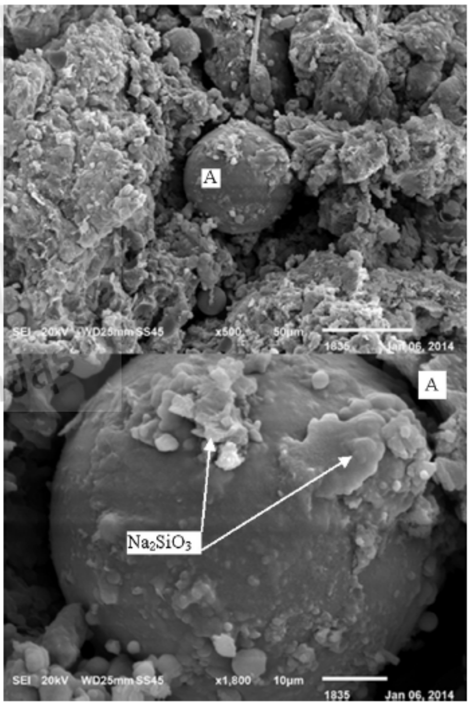


Fig. 11. SEM images of clay-FA geopolymer at Na_2SiO_3/water = 1.4, FA = 15%, 40 °C curing after 60 days of curing.

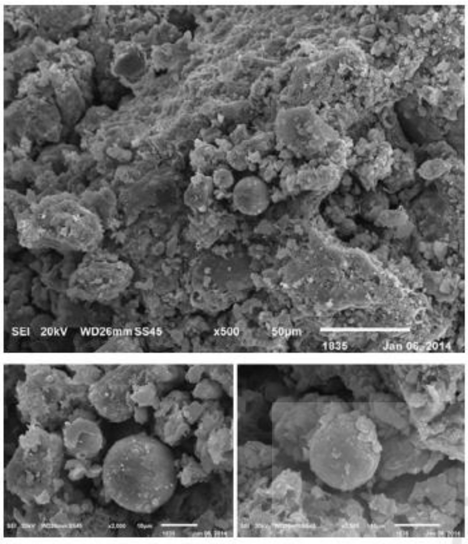


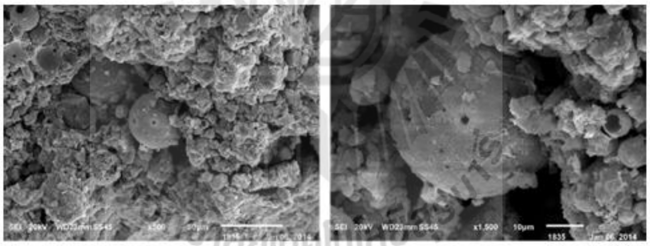
Fig. 12. SEM images of clay-FA geopolymer at Na_2SiO_3/water = 0.6, FA = 15, room temperature curing after 60 days of curing.

stabilized subgrade materials. This implies that the clay-FA geopolymer can be applied in road subgrade applications. The soaked strengths are lower than unsoaked strength for all ingredients and curing conditions. Kampala and Horpibulsuk [16] conducted water absorption and oedometer soaking tests and found that water absorption is associated with an increase in vertical swelling and swelling pressure. This swelling pressure induces repulsion between the cemented clay particles leading to the lower soaked strength. Due to relatively high repulsion and low chemical bond, the samples with Na_2SiO_3/water ratios of 1.0 and 1.4 exhibit zero soaked strength.

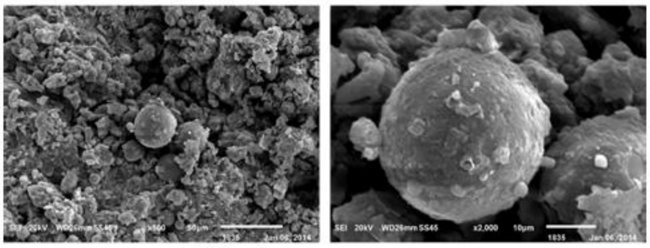
Kampala and Horpibulsuk [18] reported that even though the strength development in both the soaked and unsoaked samples depends on the CCR and FA contents, the ratio of the soaked strength to unsoaked strength is almost similar for all the CCR and FA contents. Most of the ratios vary between 0.45 and 0.65, with an average of 0.55. Fig. 9 shows the strength ratio for the clay-FA geopolymers for both curing temperatures. The ratios between 0.6 and 1.0 with an average of 0.8 are found for clay-FA geopolymer at Na_2SiO_3/water ratios between 0.6 and 0.2 for both curing temperatures and all curing times tested.

Scanning Electron microscopy (SEM) image is a useful tool for monitoring the microstructural development over time of the cementitious matrix generated as a result of the alkali activation of fly ash [49–51]. Figs. 10 and 11 show a comparison of microstructure of two clay-FA geopolymer samples at Na_2SiO_3/water ratios of 0.6 (optimal) and 1.4, respectively. Fig. 10 shows the chemical attack (alkaline dissolution) at some points on the surface of FA particles (positions A and B). The lower images show the magnified FA particles at positions A and B. Many holes on the FA surface (*refer to* point A) caused by chemical attack are observed and exposes smaller particles. The holes are partially filled with other smaller size ash particles (*refer to* point B). The alkaline solution contacts the smaller particles housed inside the larger spheres and the interior space of the latter starts to fill up with reaction product, forming a dense matrix. Fig. 11 shows the microstructure of the sample with high Na_2SiO_3/water ratio of 1.4. The lower image presents the magnified FA particle at position A where the excessive (unreacted) Na_2SiO_3 is clearly seen on FA particle. Therefore, the samples with Na_2SiO_3/water ratio of 0.6 shows higher soaked strength while the samples with Na_2SiO_3/water ratio of 1.4 show zero soaked strength due to lower cementation bonding.

Fig. 12 shows SEM image of the clay-FA geopolymer samples with Na_2SiO_3/water ratio of 0.6 and cured at room temperature

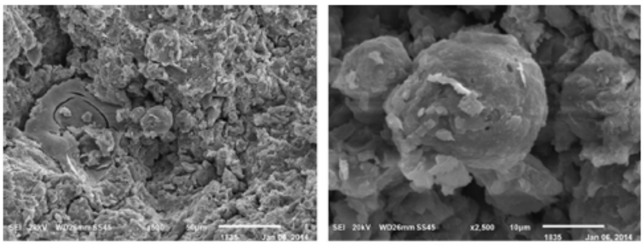


(a) Cured at 40 °C

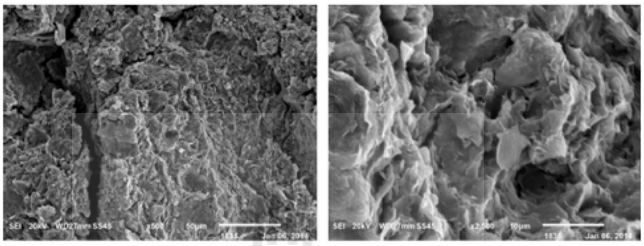


(b) Cured at room temperature

Fig. 13. SEM images of geopolymer after 7 days of curing, Na_2SiO_3/water = 0.6 and FA = 15%: (a) cured at 40 °C and (b) cured at room temperature.



(a) clay-FA geopolymer cured at 40 °C



(b) clay-geopolymer cured at room temperature

Fig. 14. SEM images for Na_2SiO_3/water = 0.6 after 60 days of curing (a) clay-FA geopolymer cured at 40 °C and (b) clay–geopolymer cured at room temperature.

after 60 days of curing. The effect of temperature curing on the strength development is illustrated by comparing Fig. 12 with Fig. 10. The geopolymerization products and etching on the surface are seen to be more evident at a higher curing temperature. The effect of temperature curing on early strength of clay-FA geopolymer is depicted in Fig. 13. The etching on the FA surface is clearly shown for 40 °C curing after 7 days of curing while Na_2SiO_3 is still abundant on the FA surface.

The role of FA on strength development is shown in Fig. 14, which shows the SEM image of the clay-FA geopolymer cured for 60 days with and without FA. The structure of the clay–geopolymer is a result of the coagulation of sodium silicate. The geopolymerization products are less because the silica and alumina in the soil are mostly in crystal phase. Therefore, the strength of clay–geopolymer is caused by the coagulation of clay particles. Due to the clay swelling pressure, these unstable structures of clay–geopolymer collapses and the soaked strength is nullified.

In practice, the subgrade improvement begins with the mixing in-situ soil with FA to attain the laboratory design soil:FA ratio requirement. The liquid alkaline activator, which is a mixture of CCR, water and Na_2SiO_3, is then mixed with the soil-FA mixture. Subsequently, compaction is undertaken on the clay-FA geopolymer. The subgrade stabilization time by geopolymer is more or less the same as that by cement. The stabilization cost of geopolymer stabilized soil varies from countries to countries due to varying labor, gasoline and facility cost and tax policy even though the energy consumption and raw materials are approximately the same. From both engineering and environmental perspectives, the geopolymer stabilized soil, a novel sustainable subgrade material, is more advantage than the conventional cement stabilized clay.

5. Conclusions

This paper pertains to the analysis of strength development in clay-FA geopolymer by using CCR as an alkaline activator. This clay-FA geopolymer can be considered as a green pavement subgrade material where its strength meets the strength requirement specified by the national road authority in Thailand. The following conclusions can be drawn:

(1) The input of Na_2SiO_3/water ratio affects the optimum liquid content and maximum dry unit weight of the clay-FA geopolymer. The optimal Na_2SiO_3/water ratio provides the highest unsoaked strength and maximum dry unit weight.
(2) The optimal Na_2SiO_3/water ratio providing highest soaked strength is found at the fixation point, which is the threshold limit from large to small reduction in PI and is equal to 0.6 for this clay-FA geopolymer. The optimal FA replacement ratio is 15%. Curing at 40 °C provides higher strength than room temperature curing, indicating the possibility of using this clay-FA geopolymer as a pavement subgrade material. The 7-day soaked strength meets the strength requirement for subgrade materials specified by Department of Rural Roads, Thailand.
(3) SEM images are useful to explain the role of influential factors on strength development in clay-FA geopolymer. The alkaline dissolution occurs on the surface of FA particles, resulting in many holes on the FA surface and smaller particles. The alkaline solution contacts the smaller particles housed inside the larger spheres and forms a dense matrix.
(4) CCR traditionally destined for landfill can be used in a sustainable manner as an alternative alkaline activator to develop geopolymer subgrade materials. The outcome of this research enables the production of road subgrade materials, which consequently will reduce Portland cement consumption and associated environmental problems.

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References

[1] Chinkulkijniwat A, Horpibulsuk S. Field strength development of repaired pavement using the recycling technique. Q J Eng GeolHydrogeol 2012;45(2):221–9.
[2] Horpibulsuk S, Katkan W, Sirilerdwattana W, Rachan R. Strength development in cement stabilized low plasticity and coarse grained soils: Laboratory and field study. Soils Found 2006;46(3):351–66.
[3] Taha R, Al-Harthy A, Al-Shamsi K, Al-Zubeidi M. Cement stabilization of reclaimed asphalt pavement aggregate for road bases and subbases. J Mater CivilEng, ASCE 2002;14(3):239–45.
[4] Keshawarz MS, Dutta U. Stabilization of South Texas soils with fly ash. Fly Ash for Soil Improvement. Geotechnical Special Publication; 1993. p. 36.
[5] Du YJ, Li SL, Hayashi S. Swelling-shrinkage properties and soil improvement of compacted expansive soil, Ning-Lian Highway. China Eng Geol 1999;53:351–8.
[6] Du YJ, Wei ML, Jin F. Laboratory investigation on strength properties of cement stabilized zinc-contaminated clay. Eng Geol 2013;167(17):20–6.
[7] Horpibulsuk S, Phetchuay C, Chinkulkijniwat A, Cholaphatsorn A. Strength development in silty clay stabilized with calcium carbide residue and fly ash. Soils Found 2013;53:477–86.
[8] Akbulut H, Gurer C. Use of aggregates produced from marble quarry waste in asphalt pavements. Build Environ 2007;42:1921–30.
[9] Arulrajah A, Disfani MM, Horpibulsuk S, Suksiripattanapong C, Prongmanee N. Physical properties and shear strength response of recycled construction and demolition materials in unbound pavement base/subbase pavement. Constr Build Mater 2014;58:245–57.
[10] Huang WL, Lin DH, Chang NB, Lin KS. Recycling of construction and demolition waste via a mechanical sorting process. Resour Conserv Recycl 2002;37:23–37.
[11] Puppala AJ, Hoyos LR, Potturi AK. Resilient moduli response of moderately cement-treated reclaimed asphalt pavement aggregates. J Mater Civ Eng 2011;23(7):990–8.
[12] Arulrajah A, Ali MMY, Disfani MM, Horpibulsuk S. Recycled glass blends in pavement base/subbase applications: laboratory and field evaluation. J Mater Civil Eng, ASCE 2014;26(7):04014025.
[13] Arulrajah A, Ali MMY, Disfani MM, Piratheepan J, Bo MW. Geotechnical performance of recycled glass-waste rock blends in footpath bases. J Mater Civ Eng ASCE 2013;25(5):653–61.
[14] Reddy KR, Hettiarachchi H, Parakalla NS, Gangathulasi J, Bogner JE. Geotechnical properties of fresh municipal solid waste at Orchard Hills Landfill. USA Waste Manage 2009;29(2):952–9.
[15] Reddy KR, Gangathulasi J, Parakalla NS, Hettiarachchi H, Bogner JE, Lagier T. Compressibility and shear strength of municipal solid waste under short-term leachate recirculation operations. Waste Manage Res 2009;27(6):578–87.
[16] Zekkos DP, Bray JD, Kavazanjian JrE, Matasovic N, Rathje EM, Riemer MF. Unit weight of municipal solid waste. J Geotech Geoenviron Eng, ASCE 2006;132(10):1250–61.
[17] Horpibulsuk S, Phetchuay C, Chinkulkijniwat C. Soil stabilization by calcium carbide residue. J Mater Civ Eng 2012;24(2):184–93.
[18] Kampala A, Horpibulsuk S. Engineering properties of calcium carbide residue stabilized silty clay. J Mater Civ Eng ASCE 2013;25(5):632–44.
[19] Kampala A, Horpibulsuk S, Prongmanee N, Chinkulkijniwat A. Influence of wet-dry cycles on compressive strength of calcium carbide residue-fly ash stabilized clay. J Mater Civ Eng ASCE 2014;26:633–43.
[20] Kampala A, Horpibulsuk S, Chinkulkijniwat A, Shen SL. Engineering properties of recycled calcium carbide residue stabilized clay as fill and pavement materials. Constr Build Mater 2013;46:203–10.
[21] Vichan S, Rachan R, Horpibulsuk S. Strength and microstructure development in Bangkok clay with calcium carbide residue and biomass ash. ScienceAsia 2013;39:186–93.
[22] Davidovits J, Buzzi L, Rocher R, Gimeno D, Marini C, Tocco S. Geopolymeric cement based on low cost geologic material, results from the European Research project GEOCIS-TEM. In: Davidovits et al., editors. Proceedings of the second international conference Geopolymere, vol. 99; 1999. p. 83–96.
[23] Palomo A, Grutzeck MW, Blanco MT. Alkali activated fly ashes: a cement for the future. Cem Concr Res 1999;29(8):1323–9.
[24] Palomo A, Alonso S, Fernandez-Jimenez A, Sobrados I, Sanz J. Alkaline activation of fly ash. A NMR study of the reaction products J. Am Ceramic Soc 2004;87(6):1141–5.
[25] Buchwald A, Kaps Ch. Property controlling influences on the generation of geopolymeric binders based on clay, Geopolymer, 2002 (Melbournd Australia).
[26] Mohapatra R, Rao JR. Some aspects of characterisation, utilisation and environmental effects of fly ash. J Chem Technol Biotechnol 2001;76(1):9–26.
[27] Van Jaarsveld J, Van Deventer J, Lorenzen L. Factors affecting the immobilization of metals in geopolymerized fly ash. Metall Mater Trans B 1998;29(1):283–91.
[28] Xie Z, Yunping X. Hardening mechanisms of an alkaline-activated class F fly ash. Cem Concr Res 2001;31:1245–9.
[29] Rickard WDA, Williams R, Temuujin J, van Riessen A. Assessing the suitability of three Australian fly ashes as an aluminosilicate source for geopolymer in high temperature applications. Mater Sci Eng 2011;528:3390–7.
[30] Rickard WDA, Temuujin J, van Riessen A. Thermal analysis of geopolymer pastes synthesised from five fly ashes of variable composition. J Non-Cryst Solids 2012;388:1830–9.
[31] Chindaprasirt C, Chareerat T, Sirivivatnanon V. Workability and strength of coarse high calcium fly ash geopolymer. Cem Concr Compos 2007;29:224–9.
[32] Sata V, Sathonsaowaphak A, Chindaprasirt P. Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack. Cem Concr Compos 2012;34(5):700–8.
[33] Sukmak P, Horppibulsuk S, Shen S-L. Strength development in clay–fly ash geopolymer. Constr Build Mater 2013;40:566–74.
[34] Sukmak P, Horppibulsuk S, Shen S-L, Chindaprasirt P, Suksiripattqanapong C. Factors influencing strength development in clay–fly ash geopolymer. Constr Build Mater 2013;40:1125–36.
[35] Sukmak P, Silva P-D, Horpibulsuk S, Chindaprasirt P. Sulphate resistance of clay-Portland cement and clay-high calcium fly ash geopolymer. J Mater Civil Eng 2014. http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0001112.
[36] Horpibulsuk S, Kampala A, Katkan W. A case history on underpinning for a distressed building on hard residual soil underneath non-uniform loose sand. Soils Found 2008;48(2):267–86.
[37] Tanalapasakul A. Document from M Thai Industrial Company Limited. Samutsakorn, Thailand: M Thai Industrial Co., Ltd; 1998.
[38] Prakash K, Sridharan A. Free swell ratio and clay mineralogy of fine-grained soils. Geotech Test 2004;27(2):220–5.
[39] Horpibulsuk S, Shibuya S, Fuenkajorn K, Katkan W. Assessment of engineering properties of Bangkok clay. Can Geotech J 2007;44(2):173–87.
[40] DH-S. Soil cement base. Standards for Highway Construction. Department of Highways 1990. [in Thai].
[41] Horpibulsuk S, Rachan R, Raksachon Y. Role of fly ash on strength and microstructure development in blended cement stabilized silty clay. Soils Found 2009;49(1):85–98.
[42] Horpibulsuk S, Katkan W, Apichatvullop A. An approach for assessment of compaction curves of fine-grained soils at various energies using a one point test. Soils Found 2008;48(1):115–25.
[43] Horpibulsuk S, Katkan W, Naramitkornburee A. Modified Ohio's curves: a rapid estimation of compaction curves for coarse- and fine-grained soils. Geotech Test J ASTM 2009;32(1):64–75.
[44] Nagaraj TS, Lutenegger AJ, Pandian NS, Manoj M. Rapid estimation of compaction parameters for field control. Geotech Test J ASTM 2006;29(6):1–10.
[45] Gurtug Y, Sridharan A. Prediction of compaction characteristics of fine-grained soils. Geotechnique 2002;52(10):761–3.
[46] Horpibulsuk S, Yangsukaseam N, Chinkulkijniwat A, Du YJ. Compressibility and permeability of Bangkok clay compared with kaolinite and bentonite. Appl Clay Sci 2011;52:150–9.
[47] Sridharan A, Rao SM, Murthy NS. Liquid limit of montmorillonite soils. Geotech Test J ASTM 1986;9(3):156–9.
[48] Sridharan A, Rao SM, Murthy NS. Liquid limit of kaolinitic soils. Geotechnique 1988;38(2):191–8.
[49] Horpibulsuk S, Rachan R, Chinkulkijniwat A, Raksachon Y, Suddeepong A. Analysis of strength development in cement-stabilized silty clay from microstructural considerations. Constr Build Mater 2010;24(10):2011–21.
[50] Horpibulsuk S, Rachan R, Raksachon Y. Role of fly ash on strength and microstructure development in blended cement stabilized silty clay. Soils Found 2009;49(1):85–98.
[51] Du YJ, Jiang NJ, Liu SY, Jin F, Singh DN, Puppala A. Engineering properties and microstructural characteristics of cement solidified zinc-contaminated kaolin clay. Can Geotech J 2014;51:289–302.

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