A NOVEL LOW – CARBON RECYCLED ASPHALT

PAVEMENT – FLY ASH GEOPOLYMER

AS A PAVEMENT MATERIAL



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วัสดุเถ้าถอยจีโอโพลิเมอร์คาร์บอนต่ำสำหรับใช้เป็นวัสดุงานทาง



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วิทยานิพนธ์นี้ศึกษาความเป็นไปได้ของการประชุกต์ใช้เถ้าลอย (fly ash, FA) จีโอโพลิเมอร์ ้ปรับปรุงผิวทางแอสพัลต์รี่ ไซเคิล (recycled <mark>asp</mark>halt pavement, RAP) เพื่อใช้เป็นวัสดุผิวทางที่ยั่งยืน การศึกษาประกอบด้วยงานทดสอบด้านวิศ<mark>วก</mark>รรมและสิ่งแวดล้อม 3 ส่วน เพื่อให้ครอบคลมความ ต้องการสำหรับใช้เป็นวัสดุชั้นพื้นทาง (base) และชั้นรองพื้นทาง (subbase) การทดสอบในส่วน แรกเป็นการศึกษาการพัฒนากำลังของ RAP-FA จีโอโพลิเมอร์ การสังเคราะห์ RAP-FA จีโอโพลิ เมอร์ใช้สารละลายโซเดียมไฮครอกไ<mark>ซค์ (</mark>NaOH) <mark>และ</mark>สารละลายโซเดียมซิลิเกต (Na₋SiO₂) เป็นสาร กระตุ้น ส่วนผสม RAP-FA เตรียม<mark>ขึ้นจ</mark>ากการผส<mark>ม R</mark>AP, FA และน้ำ เพื่อใช้เป็นวัสดุควบคุมใน การศึกษาอิทธิพลของสารกระต<mark>ุ้นต่</mark>อกำลังของ RAP-F<mark>A จี</mark>โอโพลิเมอร์ การทคสอบในส่วนที่สอง เป็นการศึกษาอิทธิพลของวัฏ<mark>จักร</mark>เปียกสลับแห้ง (wetting-drying cycles : w-d cycle) ต่อกำลังและ การเปลี่ยนแปลงโครงสร้างจุลภาคของ RAP-FA จีโอโพลิเมอร์และส่วนผสม RAP-FA กำลังของ ส่วนผสม RAP-FA แล<mark>ะ RAP-FA จีโอโพลิเมอร์ตรวจวัดด้</mark>วยเ<mark>ครื่อ</mark>งทุดสอบกำลังอัดแรงเดียว ผล การทดสอบ X-ray diffraction (XRD) และ scanning electron microscopy (SEM) ใช้ในการ วิเคราะห์การเปลี่ยนแปล<mark>งของกำลังอัดและ โครงสร้างจุลภาคของส่</mark>วนผสม RAP-FA และ RAP-FA ้จีโอโพลิเมอร์ ที่วัฏจักรเปียกสล<mark>ับแห้งต่าง ๆ การทุดสอบในส่ว</mark>นสุดท้ายเป็นการศึกษาการชะละลาย ของโลหะหนักด้วยวิธี Toxicity Characteristic Leaching Procedure (TCLP) ผลทดสอบที่ได้นำมา เปรียบเทียบกับมาตรฐานสากลเพื่อยืนยันความเสี่ยงต่อการใช้ส่วนผสม RAP-FA และ RAP-FA จีโอโพลิเมอร์เป็นวัสดุงานทาง ผลทดสอบกำลังอัดแกนเดียวแสดงให้เห็นว่าส่วนผสม RAP-FA สามารถใช้เป็นวัสดุงานทางได้ เนื่องจากมีกำลังอัดเพียงพอตามความต้องการของกรมทางหลวง ชนบทและกรมทางหลวง กำลังอัคของส่วนผสม RAP-FA เพิ่มขึ้นเมื่อเวลาเพิ่มขึ้น เนื่องจาก ปฏิกริยาทางเคมีระหว่างแคลเซียมและแมกนีเซียมที่มีปริมาณมากใน RAP และซิลิกาและอลูมินาที่ มีปริมาณมากใน FA ก่อให้เกิดแคลเซียม-อลูมิเนต-ซิลิเกต-ไฮเดรต (Calcium Aluminate Silicate Hydrate, C-A-S-H) (ดังที่พบได้จากผลทดสอบ XRD และ SEM) ผลจาก XRD และ SEM ในช่วง 7 ้วันแรกของการบ่มที่อุณหภูมิห้อง พบว่าการใช้เฉพาะสารละลายโซเดียมไฮดรอกไซด์ในการ สังเคราะห์ RAP-FA จีโอโพลิเมอร์ให้ผลิตภัณฑ์จีโอโพลิเมอร์ไรเซชั่น (N-A-S-H) ในปริมาณต่ำ ้ด้วยเหตุนี้ RAP-FA จิโอโพลิเมอร์ที่อัตราส่วน NaOH/Na2SiO3 = 100:0 จึงมีกำลังอัดต่ำกว่า

้ส่วนผสม RAP-FA การเพิ่มอายุบ่มและอุณหภูมิในการบ่มทำให้สารละลายโซเดียมไฮครอกไซค์ ้สามารถละลายซิลิกาและอลูมินาจาก FA ในการทำปฏิกิริยาจิโอโพลิเมอร์ไรเซชันได้มากส่งผลให้ ้ กำลังอัดเพิ่มขึ้น ซิลิกาที่ความพร้อมในการทำปฏิกิริยาในโซเดียมซิลิเกตทำปฏิกิริยากับซิลิกาและ อลูมินาจาก FA และสร้างเจล N-A-S-H ร่วมกับกับ C-S-H และ C-A-H ซึ่งเกิดจากปฏิกิริยาของ RAP กับ FA ดังนั้น กำลังอัดที่อายบ่ม 7 วัน ของ RAP-FA จีโอโพลิเมอร์จึงมีค่าเพิ่มขึ้นตามการ ลดลงของ NaOH/Na2SiO3 ทั้งการบ่มที่อุณหภูมิห้องและที่ 40 องศาเซลเซียส ผลการทดลองความ ้คงทนแสดงให้เห็นว่า UCS ของส่วนผสม RAP-FA มีค่าเพิ่มขึ้นเมื่อเพิ่มจำนวนวักจักรเปียกแห้ง เพิ่มขึ้น จนถึงวัฏจักรที่ 6 ผลการวิเคราะห์ XRD และ SEM แสดงให้เห็นว่าการเปียกสลับแห้ง ในช่วง 6 วัฏจักรแรกช่วยเร่งปฏิกิริยาเคมีร<mark>ะห</mark>ว่างแคลเซียมใน RAP และซิลิกาและอลูมินาในเด้า ลอย ส่งผลให้เกิดการเพิ่มขึ้นของ C-A-S<mark>-H</mark> ในขณะที่ การแตกร้าวในระดับมหภากและจุลภาค เกิดขึ้นเมื่อวัฏจักรการเปียกสลับแห้งมาก<mark>ก</mark>ว่า 6 และส่งผลให้กำลังอัดของ RAP-FA จีโอโพลิเมอร์ ิลดลง RAP-FA จีโอโพลิเมอร์มีความคง<mark>ท</mark>นมาก<mark>ขึ</mark>้นตามปริมาณ NaOH ที่เพิ่มขึ้น ซึ่งก่อให้เกิดการ เชื่อมโยงของโครงสร้างอลูมิโน-ซิลิ<mark>เกต</mark>โพลิเมอร์<mark>ที่มี</mark>ความเสถียรสูง ผลทคสอบ TCLP แสดงให้ เห็นว่าส่วนผสม RAP-FA และ RAP-FA จิโอโพลิเมอร์สามารถใช้เป็นวัสดุงานทางที่ปราศจาก ความเสี่ยงด้านสภาพแวดล้อมน<mark>อก</mark>จากนี้จีโอโพลิเมอร์ย<mark>ังช่ว</mark>ยลดการชะละลายโลหะหนักที่มีอยู่ใน RAP และ FA (RAP-FA) งานวิจัยจึงยืนยันความเป็นไปได้ในการใช้ส่วนผสม RAP-FA และ RAP-FA จีโอโพลิเมอร์เป็นวัสดุงานทาง (ทางเลือกหนึ่ง) และยังเป็นการส่งเสริมการประยุกต์ใช้ วัสดุรีไซเคิลในงานก่อส<mark>ร้าง</mark>ถน<mark>นที่ยั่งยืน</mark>



สาขาวิชา<u>วิศวกรรม โยธา</u> ปีการศึกษา 2559

MENGLIM HOY : A NOVEL LOW – CARBON RECYCELD ASPHALT PAVEMENT – FLY ASH GEOPOLYMER AS A PAVEMENT MATERIAL. THESIS ADVISOR : PROF. SUKSUN HORPIBULSUK, Ph.D., 201 PP.

SRENGTH/FLY ASH GEOPOLYMER/RECYCLED ASPHALT PAVEMENT/ MICROSTRUCTURE/HEAVY METALS/DURABILITY

This thesis studies the feasibility of using fly ash (FA) geopolymer to stabilize recycled asphalt pavement (RAP) to be a pavement material. Liquid alkaline activator (L), a mixture NaOH and Na₂SiO₃ was used to synthesis RAP-FA geopolymer, while RAP-FA blend, a mixture of RAP, FA, and water, was prepared as a control material. The investigation consists of three main laboratory engineering programs to cover requirements for the base/subbase material. First, the strength development of these materials was investigated. Second, a durability against wetting-drying (w-d) cycles of these materials was studied. The strength characteristic of these materials was determined by unconfined compression strength (UCS) test. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses is used to analyze the UCS and microstructural changes of these materials. Finally, the leachability of the heavy metals is measured by Toxicity Characteristic Leaching Procedure (TCLP) to verify the risk of using the stabilized pavement materials. The UCS results show that RAP-FA blend can be used as a base course material as its UCS meets the strength requirement specified by road authorities, Thailand. The UCS of RAP-FA blend increases with time because the reaction between high calcium in RAP and the silica

and alumina in FA form Calcium Aluminate Silicate Hydrate (C-A-S-H). At 7 days and room temperature curing, XRD and SEM analyses show that low geopolymerization products in RAP-FA geopolymer are detected when only NaOH is used as L, hence its UCS is lower than of RAP-FA blend. With increasing curing time and temperature, NaOH solution dissolves more silica and alumina from FA in the geopolymerization reaction, hence the UCS development. The highly soluble silica from Na2SiO3 incorporates with leached silica and alumina from FA into a N-A-S-H gel and co-exists with C-A-S-H, hence the UCS values of RAP-FA geopolymer increase with decreasing NaOH/Na2SiO3 ratio. The durability test results show the UCS of these materials increase with increasing the number of w-d cycles (C), reaching its peak at 6 w-d cycles. The microstructural analyses indicate the increased UCS of these materials is due to stimulation of the chemical reaction during w-d cycles leading to generate more C-A-S-H and N-A-S-H. The macro- and micro-cracks when C > 6 cause strength reduction of these materials. A better durability performance is observed when RAP-FA geopolymers are prepared with higher NaOH content that can be attributed to formation of a stable cross-linked alumino-silicate polymer structure. TCLP results demonstrated that there is no environmental risk for both RAP-FA blends and RAP-FA geopolymers in road construction. Moreover, the geopolymer binder reduces the leaching of heavy metal in RAP-FA mixture. This research study confirms the viability of using RAP-FA blends and RAP-FA geopolymers as an alternative stabilized pavement material.

School of <u>Civil Engineering</u> Academic Year 2016

Student's Signature Advisor's Signature

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SYMBOLS AND ABBREVIATIONS

3D	=	Three dimensions
AASHTO	=	American Association of State Highway and
		Transportation official
Al ₂ O ₃	=	Aluminum oxide
ASTM	=	American Society for Testing and Material
BDL	=	below detection limit
C&D	=	construction and demolition
CaO	=	calcium oxide
CBR	=	California Bearing Ratio
CO_2	=	carbon dioxide
COD	=	chemical oxygen demand
DOH	=	department of highway
EPA	=7,5	environmental protection agency
FA	= '0/18	environmental protection agency fly ash hematite
Fe ₂ O ₃	=	hematite
HMA	=	hot-mix asphalt
K ₂ O	=	potassium oxide
kPa	=	kilo Pascal
L	=	liquid alkaline activator
LOI	=	loss of ignition

SYMBOLS AND ABBREVIATIONS (Continued)

М	=	a monovalent cation such as K+ or Na+
М	=	molar
MgO	=	magnesium oxide
MCL	=	maximum contaminate level
M _R	=	resilient modulus
n	=	degree of poly-condensation
NA	=	not analyzed
Na ₂ O	=	sodium oxide
Na ₂ SiO ₃	=	sodium silicate solution
NaOH	=	sodium hydroxide solution
ND	=	not detect
°20	=	2 theta
°C	=	degree Celsius
OLC	E.	optimum liquid content
OWC	= 151518	optimum water content
РАН	=	polycyclic aromatic hydrocarbons
PC	=	Portland cement
pН	=	potential of Hydrogen ion
RAP	=	recycled asphalt pavement
SEM	=	scanning electron microscope
SiO ₂	=	silicon dioxide
SO ₃	=	sulfur trioxide

SYMBOLS AND ABBREVIATIONS (Continued)

Toxicity characteristic leaching procedure TCLP = unconfined compression strength UCS =WC water content = X-Ray Diffraction XRD =X-Ray Fluorescence XRF = 1, 2, 3, or higher Ζ = dry unit weight Υ_{dmax} =

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CHAPTER I

INTRODUCTION

1.1 Background

Thailand is recognized as one of the fastest growing and most successful developing countries, among ASEAN countries as well as in the world. Within the national's economic expansion and progress, the huge demands of road infrastructure constructions have increased remarkably (DOH, 2012; Nikomborirak, 2004).

In the meantime, a significant expansion in the availability and good quality of natural materials such as high quality rock and other good natural aggregates for use in road construction is observed. These cause the good quality of virgin materials supply very costly and time consuming to achieve and it may vanish natural landscapes and existing ecological values. Furthermore, local sources are needed to minimize the transportation costs. High cartage costs make construction projects more expensive when there are not available natural materials nearby the construction site, the quarry products are transported from distant regional sources.

Moreover, transporting materials over long distances also add significantly to the carbon footprint of road construction and increase road wear (VicRoads, 2011). Therefore, it demanded the immediate attention of not only Thailand's government, but also all over the globe and forced them to look for alternative construction materials. Recycled materials can be used as alternative materials to supplement the use of virgin quarry materials (Hendriks & Pietersen, 2000; Sherwood, 2001). Sustainable infrastructure is a key initiative in many developed and developing countries. Research on the usage of alternative sustainable materials is at the forefront of many governments, researches, and pavement industries worldwide. The utilization of recycled materials derived from construction and demolition waste (C&D waste) materials is growing all over the world. The most recent research conducted using recycled materials into construction applications were reported that a particular amount of these recycled materials can be used in footpath, road, and pavement base and subbase application, which considered as environmentally friendly construction (Arulrajah et al., 2013; Arulrajah et al., 2015; Disfani et al., 2011; Galvin et al., 2014; Hu et al., 2014; Park, 2003).

Using recycled materials in appropriate applications can contribute significantly towards making prime non-renewable rock resources last longer, has a significant impact on the sustainability of the scarcity of virgin materials and the reduction of the construction debris disposed of the landfill as well as the decreases construction cost of highway pavements (Disfani et al., 2011; Hajj et al., 2009; Hoyos et al., 2011; Puppala et al., 2011; VicRoads, 2011; Wartman et al., 2004).

Thailand, in recent year, government has been strongly encouraging all departments to reuse the recycle materials in concerned with the environmental pollution issues. However, there is a low rate of application of recycled aggregates in construction of pavement base and subbase due to the limitation of laboratory investigations as well as construction guidelines. Therefore, based on sustainable civil engineering construction, the authors are being researched extensively on the recycled materials and investigated their performance via laboratory evaluation in order to ensure these recycled materials meet specification requirements.

1.2 Problem statement

As the result of the reform on the implementation of national multi-year large public infrastructure projects, the rehabilitation and reconstruction of the exist roadways have been observed. Recycled Asphalt Pavement (RAP), a combination of both aggregates and aged bituminous additives, is obtained from spent asphalt extracted from roads that have reached the end of their design life (Arulrajah et al., 2013; Rahman et al., 2014).

A huge amount of RAP is produced due to the road pavement rehabilitation and reconstruction of existing roadways annually in Thailand (Suebsuk et al., 2014). As pavement materials predominantly consist of crushed rock and aggregate there is significant opportunity to utilize RAP as an alternative material for pavement base or subbase products. However, if alternative materials are to be used in road construction they have to be classified and meet specification requirement in the same way that classification systems and specifications have been drawn up for roadmaking materials already in use (Sherwood, 2001). Although most RAP can be used as a total substitute for natural aggregates or blend with other alternative materials, the RAP blends do not often meet the minimum local base/subbase material requirements (Arulrajah et al., 2013; Cosentino et al., 2003; Locander, 2009; Taha, 2003; Teha et al., 1999). Cement is used in road construction for the last century and it was found by many researchers that cement-stabilized RAP has shown a greater mechanical strength, which meet the requirements of pavement base/subbase applications. On the other hand, in the term of environment, it is not considered as an environmentally friendly solution due to the production of Portland Cement (PC) emits a very large amount of greenhouse gas – carbon dioxide (CO_2), which can be a serious threat to the global environment.

From the perspective of environment, the resource conservative challenge is a global concern that committed to save energy and reduce greenhouse gas emission by managing materials more efficiently and sustainably. Thus, a low carbon stabilization method is very interesting in road construction. Davidovits introduced a new green cementing agent, an inorganic aluminosilicate material synthesized by alkaline activation of materials rich in alumina (Al₂O₃) and silica (SiO₂), which known as geopolymer (Davidovits, 1991, 2002, 2005). Geopolymer is usually made of alkaliactivated aluminosilicate materials such as fly ash, slag, rice hush ash and bottom ash and was reported to produce low CO₂ emission and energy consumption (Palomo et al., 1999). Besides all the positive environment impact of geopolymer, it also provides good mechanical performances in some applications. The clear evidence is the most recent research conducted using geopolymer to stabilize natural soils to develop green building materials such as masonry products. It was reported that geopolymer based materials possess higher compressive strength and durability against sulfate than cement based materials (Sukmak et al., 2014; Sukmak et al., 2013a; Sukmak et al., 2013b). Furthermore, Suksiripattanapong et al. (2015) and Horpibulsuk et al. (2015) successfully stabilized water treatment sludge using fly ash based geopolymer to develop sustainable non- and bearing masonry units. It was demonstrated that the strength and durability of sludge-geopolymer masonry units is significantly higher than sludge-cement masonry units.

Therefore, this research tends to evaluate the possibility of using geopolymer to stabilize RAP to be a sustainable stabilized pavement material. Since abundant of fly ash is generated from power plants each year in Thailand and its high percentage of amorphous silica and alumina, it is suitable as a precursor for making geopolymer (Chindaprasirt et al., 2009; Rattanasak & Chindaprasirt, 2009). This study is a significant impact as utilization of recycled materials is environmental concern as well as sustainable development, which helping to green the nation's infrastructures by making roadways more durable, conserving natural resources, decreasing energy use, and reducing greenhouse gas emissions.

1.3 Research objectives and scope

With the huge ever-increasing amount of stockpile RAP material, the search for potential of using this material as alternative recycling application is intensified. In order to use the alternative materials (recycled materials) such as RAP and fly ash in the road construction, an evaluation in the field and laboratory have to be fully conducted.

The scope of the study is limited to the feasibility of using FA-geopolymer stabilized RAP as subbase and base material in road construction. This research focus on geotechnical and geoenvironmental laboratory experimental programs in order to clarify this novel chemical stabilization method meet the specified requirements of stabilized pavement materials.

The three main objectives of this research is to address as following outlines:

- 1. To investigate the strength development of RAP-FA geopolymer as a lowcarbon stabilized pavement material.
- 2. To study the effect of wetting-drying (w-d) cycles on the compression strength and microstructure property of RAP-FA geopolymer.

3. To study the engineering and environmental characteristics of RAP-FA geopolymer as a low-carbon stabilized pavement material.

1.4 Structure of dissertation

This thesis consists of six chapters and divides according to the following outlines:

Chapter I is the introduction part that presents the objective and scope of the study.

Chapter II presents the literature review of the recent research papers involves with engineering properties, influential factors, and characteristics of geopolymer treated recycled materials as a pavement application. The aspects of geotechnical and geoenvironmental application of geopolymer are also concluded in this chapter.

Chapter III present the study of the possibility of using FA-geopolymer to stabilized RAP as a low-carbon stabilized pavement material. The basic engineering properties of RAP and FA materials are presented. Besides, the study is mostly focuses on the various influential factor on the unconfined compression strength (UCS) development include liquid alkaline activator (L) content, NaOH/Na₂SiO₃ ratio, FA content, and heat condition (temperature and duration). The UCS development of RAP-FA geopolymer and RAP-FA blend (without L) are analyzed via the most sophisticated science tools such as Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analyses.

Chapter IV presents the study of the durability of RAP-FA geopolymer and RAP-FA blend against wetting-drying (w-d) cycles, which is simulated as one of the most destructive actions that can induce damage to infrastructures such as highways and pavements. This chapter aims to investigate the ability of these materials to retain their stability, integrity and to maintain adequate short-term as well as long-term strength capacity to provide sufficient resistance to severe climatic conditions.

Chapter V presents the engineering and environmental laboratory evaluation of RAP-FA geopolymer and RAP-FA blend which provides a basis for assessing clearly the viability of using these materials in road pavement application.

Chapter VI concludes the research work and provides the suggestion as well as recommendation as one of the road construction guidelines for the road decision maker.

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CHAPTER II

LITERATURE REVIEW

2.1 Introduction

This chapter presents the literature on the use of RAP as a pavement base layer in the road construction application. First, a brief introduction regarding to the specification of pavement structures and engineering properties of RAP is presented. Those engineering properties of RAP that are of particular interest when RAP is incorporated in the pavement base application include gradation, bearing strength, compacted density, moisture content, permeability, and durability (Chesner et al., 1997).

Structural properties of RAP and RAP-Virgin Aggregates blends use as a base course are also included in this chapter. Improvements in highway design, which required higher quality of pavement base structure properties have caused the researchers to find other stabilized methods for heavy load road construction. The chemical stabilization, Portland cement (PC) treated granular aggregates is one of the most extensively used techniques and practices are reflected in this chapter.

As the environmental issue is a severe global concern, the trend to replace the PC product with a low-carbon chemical stabilized method, which known as geopolymer are then presented. This part provides an overview of the geopolymer chemistry and its application as well as fly ash based geopolymer. A mechanical theorems of fly based geopolymer stabilized recycled materials is included.

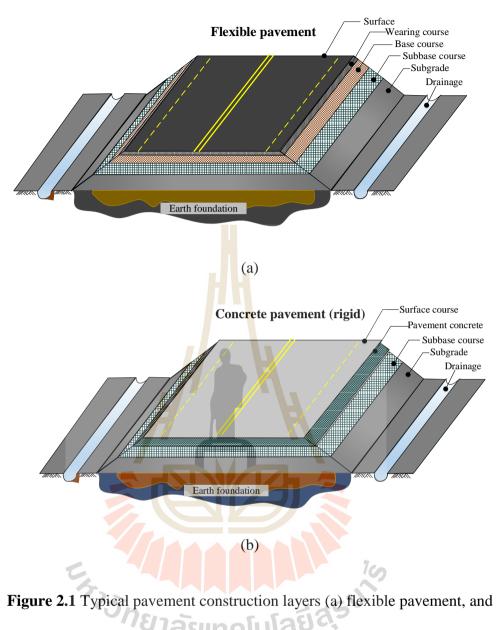
Finally, this chapter also includes the overall concepts of the major environmental concerns which play a vital role in the planning, construction, rehabilitation, and maintenance of highways.

2.2 Specification for pavement construction

Collins et al., (1993) recently conducted a survey of specifications in use for aggregates and shown that the specification of pavement structure in most of the countries did not differ significantly in fundamental principles. All countries use similar (but not identical) tests to determine suitability and adopt a layer technique for road construction as shown in Figure 2.1.

In general, difference country has completely independent highway authority under the Department of Highway or Department of Rural Road. Thailand, however national road authorities' specification has adopted from the great influence of international standards, namely the American Association of State Highway and Transportation Officials (AASHTO) and the American Society of Testing Materials (ASTM). Both international standards have issued specifications for subbase and base materials.

The specification covers the quality and grading of the following materials for use in the construction of subbase, base, and surface courses: sand-clay mixtures, gravel, stone or slag screenings, sand, crusher-run coarse aggregate consisting of gravel, crushed stone, or slag combined with soil mortar, or any combination of these materials. Those size gradation requirements for soil-aggregate materials for AASHTO and ASTM are demonstrated in Table 2.1 and Table 2. 2, respectively. The base course material shall conform to one of the gradation as specified.



(b) concrete pavement (rigid) (not to scale) (Sherwood, 2001).

2.3 RAP properties and characteristic

When virgin materials, alternative materials, and recycled materials such as RAP use as pavement subbase and base aggregates, there are the varieties of those material characteristics affecting the aggregate behavior include mineralogy, particle size distribution, particle shape, surface texture, angularity, durability (soundness, abrasion resistance), and other engineering properties (Tutumluer, 2013).

Standard	Percentage by weight passing square-mesh sieves						
US sieve	LL < 35			LL < 30			
size	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6	Class 7
4-in	-	100	-	-	-	-	
3-in	-	95–100	AA	-	-	-	-
21/2-in	100	-	<i>[</i> **\	-	-	-	-
2-in	95–100	-		100	-	-	-
1½-in	-	-		90–100	100	-	-
1-in	-	-1			95–100	-	100
3/4-in	-			50–90	-	100	-
No. 4	30–65	J		30–50	30–70	30–65	-
No. 8	-				-	-	25–55
No. 200	3–15	3–15	20max.	3–12	3–15	3–12	5-12
Note: Class 3 materials shall consist of bank or pit run material.							

 Table 2.1 Gradation requirements for aggregate and soil-aggregate subbase, base, and surface courses (AASTHO-M147-65, 2012).

Since RAP may be obtained from different numbers of existed or old pavement layer, resource, and the number of times pavement resurfaced, hence its quality as well as characteristic can be varied. In order to reuse the RAP material in the pavement application, the physical engineering properties as well as index properties of this RAP material have to be classified. Some of the engineering properties of RAP that are of particular play out during construction when it used in pavement application are reflected as follows:

2.3.1 Gradation

The particle size distribution of milled or crushed RAP may vary to some extent, depending on the type of equipment used to produce the RAP, the type of aggregate in the pavement, and whether any underlying base or subbase aggregate has been mixed in with the reclaimed asphalt pavement material during the pavement removal. The gradation of milled RAP is generally finer and denser than that of the virgin aggregates. Crushing does not cause as much degradation as milling; consequently, the gradation of crushed RAP is generally not as fine as milled RAP, but finer than virgin aggregates crushed with the same type of equipment.

The gradation for milled RAP is governed by the spacing the teeth and speed of the pulverizing unit (Chesner et al., 1997). This means that the gradation of RAP can be desired depend on engineer designers (i.e. wider tooth spacing and higher speed result in larger particle sizes and coarser gradation). RAP thus can be readily processed to satisfy gradation requirements for granular base and subbase specification set forth by local authorities.

In general, RAP particles range from those composed of largely amount of the virgin coarse aggregate of asphalt concrete matrix, vary of fine aggregate and mineral fines, asphalt cement as well as bituminous additives (Arulrajah et al., 2014; Hoppe et al., 2015; Hoyos et a., 2011; Rahman et al., 2014). A cold milling machine was used to remove the asphalt pavement for resurfacing in the cold in-place recycling process is depicted in Figure 2.2. Table 2. 2 Gradation requirements for soil-aggregate materials

Sieve Size	Weight percent passing square mesh sieves					
(Square		Туј	Type II			
Opening)	А	В	С	D	Е	F
2-in. (50-mm)	100	100	-	-	-	-
1-in. (25-mm)	-	75–95	100	100	100	100
3/8-in. (9.5-mm)	30–65	40–75	50-85	60–100	-	-
No.4 (4.75-mm)	25–55	30–60	35–65	50-85	55-100	70–100
No.10 (2.0-mm)	15–40	20–45	25–50	40–70	40–100	55-100
No.40 (425-µm)	8–20	15–30	15–30	25–45	20–50	30–70
No.200 (75- µm)	2–8	5–15	5–15	8–15	6–15	8–15

(ASTM-D1241, 2015).



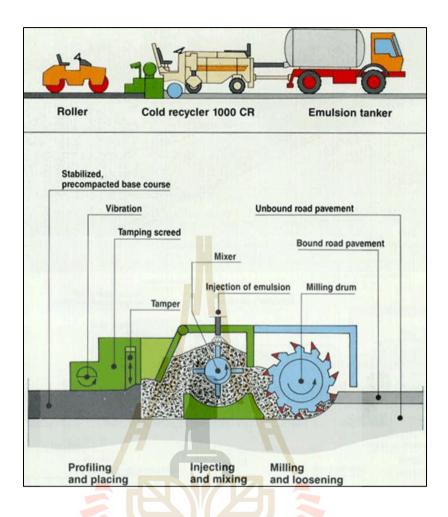


Figure 2.2 Cold In-Place (CIP) recycling process (Kandhal & Mallick, 1998).

2.3.2 Strength and stiffness

A study of utilization of construction and demolition debris under traffic-type loading in base and subbase applications by Bennert et al. (2000) reported that 100% RAP has higher stiffness, higher Resilient Modulus (M_R) values, and lower shear strengths than dense-graded aggregate base course materials. Although 100% RAP is stiffer than the dense-graded base course, several studies demonstrated that its relatively high M_R values accumulates the large permanent strain (Dong & Huang, 2013; Hoppe et al., 2015). MaGrrah (2007) and Locander (2009) have confirmed that as the quantity of RAP increase, the shear strength decreases and below the required level. Teha et al. (2002); MaGrrah (2007); Dong and Huang (2013) recommended that 100% RAP should not be used as a base or unbound base applications unless blended with other virgin aggregates or stabilized with cement. This contributed to RAP itself does not produce a product of adequate (deficient strength).

The bearing capacity of RAP – Aggregate blends is significantly depend on the proportion of RAP to those conventional aggregate while the original RAP may exhibit a lower bearing capacity than conventional granular aggregate bases (Chesner et al., 1997; Taha. et al., 2002). Furthermore, the bearing capacity decreases with increasing RAP content. The California Bearing Ratio (CBR) values have been shown to decrease almost directly with increasing RAP contents, and it reduced below the expected for conventional granular base when the amount of RAP exceeds approximately 20-25 percent (Arulrajah et al., 2014; Ayan, 2011; Hanks & Magni, 1989; Senior et al., 1994). Furthermore, many researchers (Cosentino et al., 2012; McGarrah, 2007; Ooi et al., 2010; Schaefer et al., 2008) have reported a similar conclusion that RAP blended with virgin aggregate and/or recycle aggregates be limited to maximum 50% by weight.

2.3.3 Compaction characteristic

Currently the author conducted the compaction test on the studied RAP material and found that the dry unit weights of virgin 100% RAP are insensitive to water content. Several researchers (Arulrajah et al., 2014; Osinubi et al., 2012; Saride et al., 2014; Senior et al., 1994) reported that the compacted density of RAP–Aggregate blend tends to decrease with increasing RAP content.

These characteristics are playing a significant role during construction, which affecting the workability of the mixture and controlling the degree of compaction (density) and pore structure of the layer. In addition, these have impacted on the layer strength, stability (resistance to deformation), and modulus (stiffness) properties that are relevant to the performance and design of pavement application (Hoppe et al., 2015).

2.4 Potential stabilization methods

Typical stabilization methods available for use RAP incorporate with granular aggregates as a pavement subbase or base course in road construction have been illustrated. Those selected viable stabilization techniques include physical and mechanical improvement (compaction, geotextile, polymer geocell, and improving grading deficiencies), chemical and cementitious method (including hydraulic, pozzolanic materials, cement, cement-fiber, etc.).

Grading is one of the most important factors affecting the stabilization process. RAP is generally classified as well-graded or poorly-graded material with mostly coarse aggregate and deficient in fines aggregated, thus it is difficult to compact (Hoppe et al., 2015).

Improving grading deficiency can be done by blended with fine soil, mineral fines, or others ash. This method is playing a vital role to enhance the workability and strength of the material when fine particles create an internal pore structure in the compacted material through capillary suction. However, if sufficient fines are predominant in RAP blended, this may provide adequate chemical stabilization.

Chemical and cementitious stabilization method are required where application needs higher strength level and/or in case of lack of fines content. Most of the studies conducted on stabilized RAP can be achieved by using calcium base chemical such as PC, pozzolanic fly ash, and other pozzolans with lime, cement kiln dust, and other activator.

A study cement stabilization of reclaimed asphalt pavement aggregates for road bases and subbases by Taha. et al. (2002) indicated that the optimum moisture content, maximum dry density, and unconfined compressive strength will generally increase as virgin aggregate and cement contents increase. The authors claimed the conclusion that a 100% RAP can be successfully utilized as a conventional base material if stabilized with cement rather than blending the RAP with only virgin aggregate. The similar researches were also concluded that 100 % RAP does not meet the CBR and repeated load triaxial test requirements to qualify as an unbound subbase material in Australia unless RAP blended with recycled asphalt concrete (RCA) with 15% RAP content (Arulrajah et al., 2013; Arulrajah et al., 2014).

Taha (2003) repeated the similar study to evaluate of cement kiln dust stabilized RAP. It was observed that higher strength and stiffness were gained with increasing cement kiln dust, which similar trends as those cement-stabilized RAP. Ganne (2010) evaluated the possibility of using PC and self-cementing fly ash (FA) to stabilize Texas RAP. Three RAP materials were collected from different sites and blended with varying percentage of virgin aggregate materials. Thereafter, RAP-Base blends were mixed with PC or FA, which PC varied in different amounts. The author demonstrated that the optimal performance was provided by the 75% RAP blend stabilized with PC at 4%, while at 7% of FA mixture exhibited excessive volume changes in the wet-dry test.

In recent study, Puppala et al. (2011) have evaluated the resilient moduli (M_R) response of moderately cement-treated RAP aggregates. The experimental results

performed on cement-treated RAP mixtures showed that the percentage of M_R increase with respect to the moderate cement treatment of the RAP. Moreover, it is reaching significantly high levels at 4% cement dosage used. This research demonstrated that RAP can be effectively used as a base material to support pavement infrastructure.

The preliminary investigation of characterization of cement-fiber-treated RAP aggregates were studied by Hoyos. et al. (2011) concluded that the cement-fiber-treated RAP can be used as a base/sub-base applications. The research also reported that the inclusion of a 0.15% by weight dosage of alkali-resistance glass fibers, however, appears to have only limited beneficial effects on the stiffness response of 4% cement-treated RAP. From engineering test results, fiber dosage effects should be further investigated.

The blends of 50% RAP and 50% lime-rock can be effectively stabilized when the asphalt liquid emulsion used as an activator (Cosentino et al., 2012). It was recommended that the asphalt binder content of a blend stabilized with asphalt emulsion not exceed 3.5% by weight. When PC is used as a stabilizer, excessive application of this stabilizer can cause the brittle behavior of base material, hence its content should not exceed 2% by weight.

The satisfactory performance of a novel polymeric alloy geocell infilled with RAP was introduced by Thakur (2010) who conducted an experimental study on geocell-reinforced RAP base and confirmed by the experimental program using cyclic plate testing (Thakur et al., 2012). It is very interesting to notice that 100% RAP can be used as an effective base course material in road construction when it used with geocell confinement. The geocell-reinforced RAP bases also can improve creep deformation behavior as compared with the unreinforced base (Thakur et al., 2013). However, the availability of those geocell still limited in some developing countries such as Thailand.

2.5 Geopolymer: chemistry and application

Geopolymers are basically synthesized by alkali-activated aluminosilicate of a base material, natural or by-product, which is rich in alumina and silica with a metal hydroxide solution at moderate temperatures (Davidovits., 1989). It is formed through a complex multi-phase chemical process involving a series of dissolution, diffusion, polycondensation and hardening (Davidovits., 2005).

Since early 1978, Davidovits introduced a new geopolymer technique known as geopolymer and geopolymerization technology, there has been tremendous attracted most of the researchers all over the globe to investigate in a variety of aspects of its synthesizing process and various physio-mechanical and durability properties.

Geopolymer technology, developed in the last few decades is an environmental impact on advancement which is promised to provide a cleaner and environmentally friendly alternative to traditional ordinary Portland cements (Palomo et al., 1999; Thockhom et al., 2012). Recent years, the pioneering techniques are very sophisticated and the comprehensiveness of the chemistry, synthesis and manufacturing of geopolymers has improved to such an extent that commercialization of geopolymers as a green technology. These are expected one of the best possible in the near future for recycling both natural aluminosilicate like metakaolin and industrial wastes include as fly ash, silica fume, blast furnace slag, sludge, rice hush ash and bottom ash etc. into mechanically strong and highly durable construction materials. Many previous researches as well as recently publish papers have reported that a novel binder (fly ash based geopolymers) shown very good physical and mechanical properties, which in some cases are better than those of traditional stabilized method such as Portland cements (Chindaprasirt et al., 2010; Chindaprasirt et al., 2007; Chindaprasirt et al., 2009; Horpibulsuk et al., 2015; Sukmak et al., 2013a; Sukmak et al., 2013b). Furthermore, the large scale use of fly ash as a basic starting material in producing geopolymer can be a significant impact on good economic and environmental benefits (Suksiripattanapong et al., 2015a).

Several advantages of geopolymer application are described in this chapter. Compared with ordinary PC, newly developed inorganic binder geopolymers possess more advantages and good characteristics. Studies have shown that the production of 1 ton PC releases approximately 1 ton of carbon dioxide gas into the atmosphere everywhere in the world, which is one of a major reasons for global warming (Davidovits., 2013). On the other hand, the production of geopolymer cement is manufactured in a different way from PC. Davidovits. (1994) reported that about 60% less energy is required, and 80–90% less CO₂ is generated in the production of geopolymer cement comparing with the production of PC.

Geopolymer products do not require extremely high-temperature treatment of the limestone. Thermal processing of natural aluminosilicate at elevated temperature (600 to 800°C) or natural processing (man-made) aluminosilicate such as fly ash at relatively low temperature provides suitable geopolymer raw materials. This contributes to a significant reduction in energy consumption and CO_2 emission.

Geopolymer preparation is a simple preparation technique and very similar to the preparation of PC. It can be synthesized simply by preparing a blend of aluminosilicate reactive materials and strongly alkaline solution and cured at room temperature. A strength development is observed in a short period. These properties, hence make geopolymers suitable for application in many fields of industry include civil engineering. Some geopolymer binders have been tested and proven to be successful in construction, transportation, and infrastructure applications (Li., 2011). Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high early compressive strength, low shrinkage, acid resistance, fire resistance, low thermal conductivity and have low CO₂ emission (Davidovits., 1994a; Lyon et al., 1997). Some current building construction components such as bricks, ceramic tiles, cement, and other pavement application could be replaced by geopolymer products.

It is evident from the literature that geopolymers have emerged as a possible technological solution for effective stabilization and immobilization of toxic materials. Davidovits. (1994c) first began to investigate the possibilities of using commercial geopolymeric products to immobilize heavy metal in the early 1990s. The leachate results for geopolymerization on various mine tailing showed that 90% of heavy metal ions can be tightly solidified in a 3D geopolymer framework. The molecular structure of a geopolymer is similar to that zeolites, which their performances have excellent abilities to adsorb and solidify toxic chemical wastes, such as heavy metal ions and nuclear residues (Van Jaarsveld et al., 1997; Van Jaarsveld et al., 1999).

2.5.1 Mechanism of geopolymerization

The first development of alkali activated binders had a major contribution in the 1940s with the work of Purdon (1940). Purdon used blast furnace slag with sodium hydroxide to produce the binders and published that when activated with an alkaline solution, blast furnace slag could achieve high compressive strength. Glukhovskij et al., (1983) developed a new type of binders that were named as "soilcement". The soil-cement was obtained from ground aluminosilicate mixed with rich alkali industrial wastes. In the 1970s, Davidovits with a background in mineralogy and geochemistry, has extensively researched on geopolymer structure. Thereafter, the author has developed and patented a novel binder by using of metakaolin alkali activation and named it as "geopolymer". This the development of this new binder material was based on alkali activation used to synthesis inorganic materials. There are several types of inorganic materials that can be used, for instance fly ash, bottom ash, rice husk ash, steel slag and other commercial alumino-silicate material.

According to Davidovits, Geopolymerization is a complex multiphase exothermic reaction involving a series of independent and simultaneous steps consisting of dissolution-reorientation-solidification reactions. These theories are very similar to zeolite synthesis. A highly alkaline solution is used to leach the alumina (Al₂O₃) and silica (SiO₂) atoms in the source material to dissolve and form a 3dimensional polymeric structure consisting of –Si-O-Al-O- bonds. The chemical structures of geopolymer (Poly(sialates)) can be expressed as an empirical equation, proposed by Davidovits.

$$M_n[-(SiO_2)_z - AlO_2]_n.wH_2O$$

Where, M is the alkaline element or a monovalent cation such as potassium, sodium or calcium; "n" is the degree of polycondensation or polymerization; and "z" is 1, 2, 3, or higher, which connected by a symbol "–" indicates the presence of a bond.

Davidovites proposed that geopolymers have amorphous to semicrystalline 3D alumino-silicate structures. Three typical structures of geopolymer are: the Poly(sialate) type (-Si-O-Al-O-), the Poly(sialate-siloxo) type (-Si-O-Al-O-Si-O-), and the Poly(sialate-disiloxo) type (-Si-O-Al-O-Si-O-), as shown in Figure 2.3.

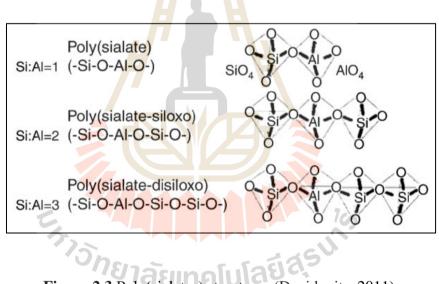


Figure 2.3 Poly(sialates) structures (Davidovits, 2011).

2.5.2 Scientific tools and mineral geopolymer concept

Geopolymeric compounds are either crystalline or non-crystalline (amorphous or glassy structure). Crystalline Poly(sialate) (-SiO-Al-O-)_n and Poly(sialate-siloxo) (-SiO-O-Al-O-Si-O-)_n result from hydrothermal setting conditions, whereas hardening at ambient temperature induces amorphous or glassy structures (Davidovits, 2011).

During the microscopic examination or microstructural analysis, the structural of material is studied under magnification. The properties of the materials determine how they will perform under a given application, and these properties are dependent on the material's structure. The following are the tools of chemical analyzer.

An X-Ray Fluorescence (XRF) analyzer is proven scientific instrument for analyzing chemical properties of material in a broad range of industries and applications. It works by exposing samples to be measured to be a beam of primary X-rays. The XRF application is written by an Oxford Instrument organization that the atoms of the sample absorb energy from the X-rays, become temporarily excited and then emit secondary X-rays. Each chemical element emits X-rays at a unique energy.

By measuring the intensity and characteristic energy of the emitted X-Rays, and XRF analyzer can provide qualitative and quantitative analysis regarding the thickness and composition of the material being tested (Oxford-Instruments.com, 2015). A schematic of the work processing of XRF analyzer, which used to analyze the chemical composition of the material is represented Figure 2.4 and a photo of the XRF analyzer instruments is depicted in Figure 2.5, respectively.



Figure 2.4 A schematic of the work processing of XRF analyzer

(Oxford-Instruments.com, 2015).



Figure 2.5 X-Ray Fluorescence analyzer instrument.



Figure 2.6 Brucker's X-Ray Diffraction D2-Phaser instrument.

X-Ray Diffraction (XRD) analysis: the X-Ray Diffraction technique is a rapid analytical method used for phase identification of crystalline solids or crystalline mineral and can provide information on unit cell dimensions (Klug & Alexander, 1954; Moore & Reynolds, 1989). The XRD tool is illustrated in Figure 2.6.

The XRD application was descripted by Thockhom et al. (2012) that when a crystalline mineral is exposed to X-Ray of a particular wavelength, the layers of atoms diffract the rays and produces a pattern of peaks, which is characteristic of the mineral. The horizontal scale (diffraction angle) of a typical XRD pattern gives the crystal lattice spacing, and the vertical scale (peak height) measures the intensity of the diffracted ray. When the powder specimen being X-Rayed contains more than one mineral, the intensity of characteristic peaks from the individual minerals is proportional to their amount. The XRD analyses were done on the powder samples, which were compacted in a Cu X-Ray tube. The XRD traces were obtained by scanning at $0.1^{\circ}(2\theta)$ per min and at steps of $0.05^{\circ}(2\theta)$.

The degree of disorder in a geopolymer can be inferred from observations of the way it diffraction of X-Ray to form a diffraction pattern. In the non-crystalline state, diffraction of X-Rays results in a broad diffuse halo rather than sharp diffraction peaks (Davidovits, 2011). Their structure cannot be investigated from XRD alone, SEM provides better insight into the molecular framework.

For an instant, the 2θ max diffraction angle (maximum of the halo) in the non-crystalline state is in the range of the major diffraction peak in the crystalline state. This illustrated with the diffraction patterns of ordered, crystalline SiO₂ (cristobalite) and non-crystalline SiO₂ displayed in Figure 2.7 (Hemmings & Berry, 1987).

A scanning electron microscopy (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. SEM is a type of electron microscope which work very effectively in microanalysis of inorganic materials. It is used to produce images of a sample by scanning it with a focused beam of electrons. The electrons interact with the atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position combines with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The common SEM model is detection of secondary electron emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends on specimen topography.

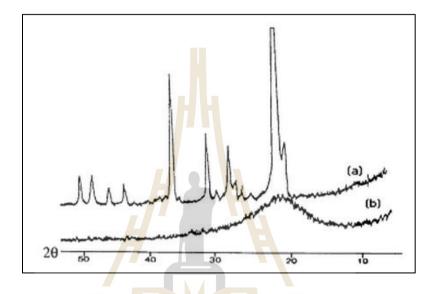


Figure 2.7 XRD patterns of (a) crystalline, and (b) non-crystalline SiO₂

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(Hemmings & Berry, 1987).

Samples for SEM have to be prepared to withstand the vacuum conditions and high energy beam of electrons, and have to be of a size that will fit on the specimen stage. Samples are generally mounted rigidly to a specimen holder or stub using a conductive adhesive.

The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitative or semiquantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD) (Clarke & Eberhardt, 2002; Echlin et al., 2013; Egerton, 2006; Goldstein et al., 2012).

Laboratory testing faculty, Suranaree University of Technology (SUT) has a complete system of SEM which also offers Energy Dispersive X-Ray Spectroscopy (EDS) capabilities. Figure 2.8 shows an SEM instrument that performed at high magnifications, generates high-resolution images and precisely measures in Nano-scale features and objects.



Figure 2.8 Scanning electron microscope instrument (JEOL JSM-6010LV device).

Use of SEM/EDX, XRD further helps to obtain a clear understanding of the performance of geopolymer prepared with sodium hydroxide solution and sodium silicate solution. These studies will ultimately provide a better scientific understanding of geopolymerization process and helps in developing realistic prediction model.

2.6 Engineering properties and characteristics of fly ash geopolymer

A brief review of existing literature on fly ash geopolymers theories and applications are presented in this part. It covers past to recent understanding of manufacturing, mechanical and durability properties of fly ash geopolymer binders.

2.6.1 Production of fly ashes

The term of fly ash is often used to describe any pulverized fuel ash, which is comprised of fine particulate material precipitated from the stack gases of industrial furnaces burning solid fuels. Fly ash is one of the solid residue composed of the fine particles that are driven out of the boiler with flue gases in coal-fired power plants. Fly ash is produced by the combustion of finely ground coal injected at high speed with a stream of hot air into the furnace ground at electricity generating power plants (Davidovits, 2011).

The chemical components of fly ashes are varied considerably and depend on the source and manufacturing process of the coal being burned, but all fly ashes contain three main chemical components include substantial amounts of silicon dioxide (SiO₂) (both amorphous and crystalline), aluminum oxide (Al₂O₃) and calcium oxide (CaO). According to American Society Testing and Materials (ASTMC618, 2012), fly ash is divided into two distinct categories as shown in Table 2.3. In Thailand, Fly ash from the Mae Moh power plant has been extensively studied by many researchers and an indication of its chemical components disclosed in Table 2.4.

Among many possible aluminosilicate source materials, fly ash has attracted maximum attention to the global researchers because of its abundant availability as wastes from thermal power plants around the world. For instance, the total about 4.0 million tons of fly ash and bottom ash are produced annually from power plants in Thailand was reported by Chindaprasirt et al., (2009). However, approximately only 1.8 million tons of fly ash is used a pozzolanic material in the concrete industry.

The utilization of fly ash in the effective way is still a limitation which required research to solve the problem. Recent years, most of the research on geopolymers have used fly ash as the starting material and tried to improve the strength development of fly ash geopolymers (Palomo et al., 2007; Phoo-ngernkham et al., 2013). As results, the application of fly ash geopolymers have been encouraging.

Type of Fly ash	Description
Low-calcium fly ash – Class F	CaO content less than 10%
	Usually produced from anthracite and
E	bituminous coals
High-calcium fly ash – Class C	CaO content greater than 10%
^{ักย} าลัยเทค	Usually produced from sub-bituminous
	and lignite coals.

Table 2.3 Main categories of fly ashes (ASTM-C618, 2012).

Chemical components	Range values (%)
SiO ₂	20 - 55
Al ₂ O ₃	5 - 40
Fe ₂ O ₃	1 – 15
CaO	1 – 35
SO ₃	0+ - 10
MgO	0+ - 5
(Na ₂ O+K ₂ O)	0.5 - 2.5

Table 2.4 Typical properties of fly ash in Thailand (Tangtermsirikul et al., 2005).

2.6.2 Fly ash geopolymer synthesis

Theoretically, many kinds of aluminosilicate material can be used as a base material to produce geopolymer binder. The utilization of metakaolin in the synthesis of geopolymer proved useful for research purposes, but its processing cost is relatively higher (Thockhom et al., 2012). On the other hand, in the abundance of quantity, the solid waste material generated from thermal power plants, fly ash containing a large amount of silica and alumina. Hence it has full potential to be used as one of the base material for producing geopolymer binder at relatively lower cost (Lee & Van Deventer, 2002).

The fly ash geopolymer is prepared by a mixture of reactive aluminosilicate source and alkaline activator with a temperature curing. The most common alkaline activator studied by many researchers is the alkali hydroxide solution, alkali silicate solution, or a mixture of sodium hydroxide solution (NaOH) and sodium silicate solution (Na₂SiO₃) (Chindaprasirt. et al., 2009; Weerdt, 2011). The geopolymerization reaction has occurred since the blended ingredients producing an alumino-silicate cementitious compound in the final polycondensation geopolymer product which are very complex and still not fully understood (see Figure 2. 9).

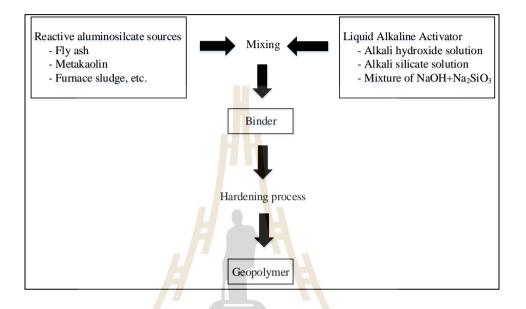


Figure 2. 9 Process of geopolymer production.

It should be noted that the strength of fly ash geopolymer significantly influence by a ratio of NaOH/Na₂SiO₃ with a variety of NaOH concentrations. Chindaprasirt. et al. (2009) conducted the comparative study on the characteristic of fly ash and bottom ash geopolymer with an illustration of Figure 2.10 indicated that an increasing NaOH concentration of the activator results in enhanced compressive strength. However, as a higher concentration of alkali hydroxide activation can be considered to be not so user friendly due to the highly corrosive of the alkali hydroxide activators and higher heat release associated with their dissolution to form concentrated (Weerdt, 2011). It was reported that a mixture NaOH and Na₂SiO₃ solution might be preferred, therefore the focus of this report is a moderate concentration of NaOH (10M) used in this research.

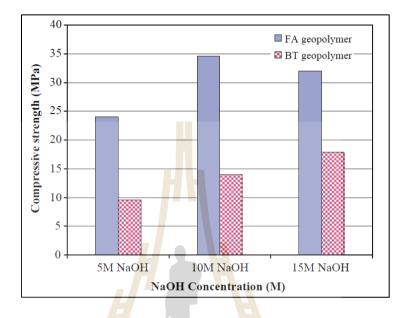


Figure 2.10 Compressive strength of geopolymer mortar (Chindaprasirt. et al., 2009).

The process of geopolymerization is similar to the zeolitization process except for the full crystallization (Fernández-Jiménez et al., 2005). Murayama et al., (2002) describes the zeolitization, first by a dissolution of Si^{4+} and AL^{3+} from the reactive aluminosilicate, followed by a condensation step of silicate and aluminate ions where the aluminosilicate gel precipitates, and final crystallization of the zeolite occurs. In geopolymers, this full crystallization is slowed down dramatically due to the relatively low water to solid ratio and the high concentration of OH^- . The first model, a general mechanism for the alkali activation of materials, primarily comprising silica and reactive alumina, was proposed by Glukhovsky (1959). The Glukhovsky model divides the whole process into three stages (1) destruction-coagulation (2) coagulation-condensation and (3) condensation-crystallization. In a recent study, other authors such as Fernández-Jiménez et al., (2005) have adopted and expanded on the Glukhovsky's theories and applied the existing knowledge of zeolite synthesis to explain greater detail in the formation of alkaline inorganic polymer. Later on, the authors slightly modified the model by collaborate with Duxson and colleagues and have published the geopolymer technology: the current state of art. Duxson et al. (2007) provided a more elaborated model with a graphic description to explain the whole geopolymerization process as shown in Figure 2.11.

Initial stage, alkaline solution comes in contact with the solid particles and causes the amorphous component to dissolve. During the dissolution process, the high concentration of OH⁻ in the system is releasing and breaking down the Si-O-Si, Si-O-Al and Al-O-Al bonds to form the vitreous glass phase and Si-OH and Al-OH groups (most likely monomers). This mechanism governs the dissolution of solid particles and forms a complex mixture of silicate, aluminate and aluminosilicate species. These monomers inter-react to form dimers, which in turn interact with another monomer to form trimmers, tetramers and so on.

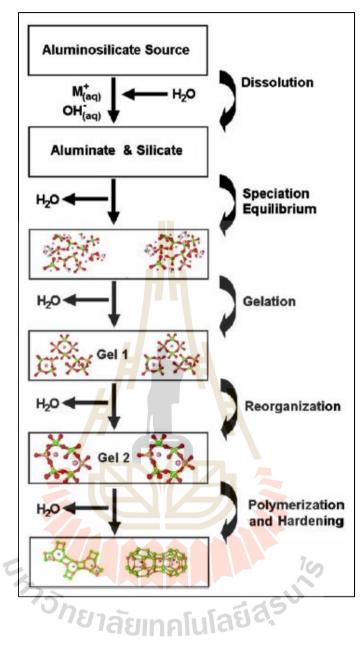


Figure 2.11 Conceptual model for geopolymerization (Duxson et al., 2007).

The solution quickly over-saturates, due to the fast dissolution of the glass at high pH and it will precipitate an aluminosilicate gel. This first gel type formed and intermediate reaction product (denominated Gel 1, Figure 2.11) which is rich in aluminum. This can be attributed to higher aluminum concentration in the solution during the early stages of the process as Al-O bonds are weaker than Si-O in

the reactive aluminosilicate powder (Fernández-Jiménez et al., 2006). As the reaction continues more Si-O of the initial source go into solution, raising the silicon concentration in the solution and in the zeolite precursor gel phase, Gel 2. During the gelation process, the water which was used during the dissolution is released. Hence, water plays the role of reaction medium and resides within the pores of the gel. The system continues to rearrange and reorganize in the process of reorganization from Gel 1 to Gel 2, and the connectivity of the gel network increases. This results in the formation of a 3D aluminosilicate network or known as polymerization and hardening process of geopolymers.

Recently, this gel is known to be a product containing large numbers of zeolite-like nanocrystals. Fernández-Jiménez. and Palomo. (2009) studied the nanostructure and microstructure of fly ash geopolymer have confirmed this hypothesis that many cementitious systems made from inorganic polymers are observed to contain small amounts of perfectly crystallized zeolites such as chabazite-Na, analcime, Linde A and so on.

2.6.3 Strength development of fly ash geopolymer

The geopolymer technology provides a new good and green solution to the utilization of fly ash. Geopolymeric reaction usually relies on the chemical reaction between alkaline activator solution and aluminosilicate source. Recent studies conducted by Riahi and Nazari (2012) and Khater et al., (2012) indicated that the compressive strength of geopolymer depends on the type of aluminosilicate starting materials and its fineness. Fly ash from Mea Moh power plant station was reported that it is suitable as a precursor for making good geopolymer since it contains a high percentage of amorphous silica and alumina (Chindaprasirt. et al., 2010; Chindaprasirt. et al., 2007; Chindaprasirt. et al., 2009; Sinsiri et al., 2012).

Factors affecting of strength development of fly ash based geopolymer is still not completely understand even though many researchers (Komnitsas & Zaharaki, 2007; Van Jaarsveld et al., 2003; Xu et al., 2000) have shown that the compressive strength of geopolymer is dependent upon several factors include the gel phase strength, the ratio of the gel phase/undissolved Al-Si particles, the hardening process of the undissolved Al-Si particle sizes, the nature of amorphous geopolymer or the amount of crystallinity, and the surface reaction between the gel phase and the undissolved Al-Si particles.

Komnitsas and Zaharaki (2007) added that factors such as the %CaO, %K₂O and the type of alkali have a significant effect on compressive strength. Moreover, the significance of the molar Si/Al ratio and a complex reaction between the mineral aggregate surface and the concentration of sodium silicate solution also correlated with compressive strength. Xu and Van Deventer (2002) indicated that when an aggregate such as granular sand is added to the geopolymer mixture, the geopolymerization of its natural miners can enhance the compressive strength.

Wang et al., (2005) and Granizo et al., (2007) have proven experimentally that the alkali activation solution containing Na₂SiO₃ and NaOH used to generate geopolymer results in higher mechanical strength compared to the activation with only NaOH. A similar study on effects of NaOH concentrations of physical and electrical properties of high calcium fly ash geopolymer paste conducted by Hanjitsuwan. et al. (2014) has proved the previous work (Kangar, 2011; Rattanasak & Chindaprasirt, 2009; Van Jaarsveld & Van Deventer, 1999) that the increase in the NaOH concentration in the geopolymer system can enhance the ability of leaching of silica and alumina from the fly ash particles in the solution, hence the compressive strength is increased. This attributed to a dense and strong geopolymer matrix when the aluminosilicate source material came into contact with the alkali solution. In addition, the amount of calcium content of fly ash based geopolymer as well as the water/fly ash ratio have a significant impact on compressive strength (Van Jaarsveld et al., 2003).

Kumar et al., (2005) have shown that mechanically activated fly ash geopolymer exhibited higher compressive strength due to the formation of a compact microstructure which is strongly affected by the alkaline activator added to the system.

Miller et al., (2005) investigated the effect of curing temperature and time on the flexural properties of geopolymer based on class C fly ash. The result shown that the curing regime has a highly significant impact on both physical and chemical properties of fly ash based geopolymers. For instance, the increase in mere synthesis temperature provides a sufficient to increase the level of long-range ordering in geopolymeric binders (Duxson et al., 2007).

Fernández-Jiménez et al. (2005) proposed a descriptive model for the alkali activation of fly ash as shown in Figure 2.12. It was reported that when fly ashes are submitted to the alkaline solution, a dissolution process of the Al and Si occurs. Initially, alkali attack occurs on the spherical surface of the fly ash particles exposing small spheres inside.

Consequently, the dissolution and reaction products are generated both inside and outside the fly ash particles, until the ash particles are completely or almost completely consumed. Thockhom et al. (2012) concluded that the activation of fly ashes may be considered as a zeolitization in which the last phase does not occur. The experimental conditions led to very fast dissolution and condensation reactions. But this process becomes slow when the hardening takes place.

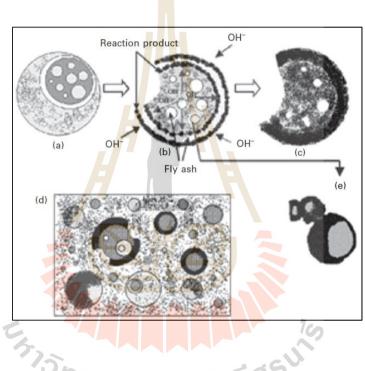


Figure 2.12 Descriptive model of fly ash geopolymer mechanism (Fernandez-Jimenez et al., 2005).

The alkaline activator with soluble silica has been proved to increase the extent of geopolymerization reaction compared to alkaline solution that contains only sodium hydroxide (Thockhom et al., 2012). It has also been reported by some authors that increasing silicate content beyond certain maximum limits also decreases the rate of geopolymerization. The choice of curing temperature and curing time is an important aspect of the strength development in geopolymers. Higher curing temperature and longer curing time were proved to result in higher compressive strength (Palomo. et al., 1999). However, it is reported that increasing curing temperature above 100°C does not affect the properties of geopolymer significantly.

2.6.4 Durability of fly ash geopolymer

Durability is assessed in terms of physical changes, residual alkalinity and strength, weight changes, microstructural and mineralogical changes. In other word, durability can be defined as the ability of the materials to retain their stability and integrity in order to maintain adequate long-term residual strength when subject to a climatic change (Dempsey & Thompson, 1967). Durability of pavement material, hence has a significant influence on its service behavior, service life design, and safety in which impact the sustainable development of national infrastructures. When exposed to aggressive environments, the deterioration of pavement applications takes place in a variety of physical and/or chemical processes.

The durability performance of underground structures is usually investigated through many ways include sulfate attack, chloride-induced corrosion, atmospheric carbonation, alkali silica reaction (ASR), resistance to elevated temperatures, freeze-thaw attack, and wetting-drying cycles attack (Kupwade-Patil et al., 2013).

A durability of fly ash based geopolymer structural concrete in the marine environment was studied by Reddy et al., (2012). The authors have analyzed and compared between fly ash based geopolymer concrete (GPC) and ordinary Portland concrete (OPC) and concluded that the GPC is more homogeneous and wellbonded. Moreover, GPC possessed high early compressive strengths and the splitting tensile strengths relative to OPC.

Bakharev (2005) investigated the durability of geopolymer materials manufactured using class F fly ash and alkaline activators when exposed to a sulfate environment. It was found that the stability of geopolymer samples depended on the type of activator, samples preparation and concentration, and type of cation in the sulfate media. Furthermore, it was observed that the formation of ettringite was occurred when sodium silicate used as activator resulted in a loss of strength. On the other hand, in magnesium sulfate solution, the diffusion of Mg and Ca in the surface layer of geopolymers was detected, which improved the strength of the specimens. Bakharev concluded that the best performance in different sulfate solution was observed when sodium hydroxide was used as alkaline activator for making geopolymer and cured at elevated temperature.

Moreover, geopolymer prepared with sodium hydroxide shown a more stable structure than specimen prepared using sodium silicate or a mixture of sodium and potassium hydroxide solutions. The good performance of geopolymer materials against sulfate solution was attributed to a more stable cross-linked aluminosilicate polymer structure. A similar conclusion was made by Ariffin et al., (2013) who studied the comparison durability of geopolymer concrete and ordinary Portland cement concrete (OPC). Further, results showed that the performance of geopolymer concrete when exposed to 2% sulfuric acid solution in a long-term was superior to OPC. An experimental investigation of the performance of fly ash based geopolymer mortar specimens in magnesium sulfate solution was conducted by Thokchom et al., (2010). A mixture of sodium hydroxide solution and sodium silicate solution was used as an alkaline activator. The authors concluded that residual compressive strength showed some fluctuation during the period of the exposure and after the exposure the specimen with the highest Na₂O content shown relatively high retained strength.

Various tests such as compressive strength, apparent porosity, water sorptivity, water absorption, etc. and mineralogical investigation with the help of XRD, microstructural analysis employing SEM and pore structure study by MIP, have been carried out to investigate the durability of fly ash geopolymer mortar specimens in sulfuric acid solution (Thokchom et al., 2009a; 2009b). The results demonstrated that geopolymer materials are highly resistance to sulfuric acid.

Besides, the mechanical and mineralogical properties of the construction materials, the durability of materials under severe climatic condition is playing an important role to evaluate in situ the use of those materials as a pavement construction material (Aldaood et al., 2014). Allam and Sridharan (1981) and Sobhan and Das (2007) reported that wetting-drying cycles simulate as climatic conditions, weather changes over geological ages is considered to be one of the most destructive actions that can induce damage to infrastructures such as highways and pavements.

The effects of these cycles are severely affecting on the engineering properties of materials, crack propagation and as a result, mechanical strength reduction and stability failure occur (Al-Obaydi et al., 2010; Al-Zubaydi, 2011).

Recently, Suksiripattanapong et al. (2015) and Horpibulsuk et al. (2015) successfully stabilized water treatment sludge using fly ash based geopolymer to develop sustainable non- and bearing masonry units. It was illustrated that the geopolymer is more effective than Portland cement in stabilizing the water treatment sludge with high alum content. The strength and durability of sludge-geopolymer masonry units is significantly higher than sludge-cement masonry units. As a continuous work, a recent study, durability against wetting-drying cycles of water treatment sludge-fly ash (WTS-FA) geopolymer and water treatment sludge-cement and silty clay-cement systems were studied by Horpibulsuk et al. (2015). The outcome from this research indicates that WTS-FA geopolymer masonry units have a longer service life than clay-cement masonry units, which confirmed that the possibility of using geopolymer product will improve not only the strength but also durability.

2.7 Environmental and Economical consideration

A broad range of environmental regulation has been established concern with highway projects, which have the potential to result in significant social, environmental, and economic impacts (Brockenbrough, 2009). Those most of the environmental departments as well as the court rule makings suggest the urgent need to consider potential effects of global climate change or well known as global warming and related ecological impacts.

Brockenbrough (2009) wrote about the impacts of highway projects in the highway engineering handbook, which published by McGraw-Hill. The author divided the impact into two items, temporary (short-term effects that occur during

construction of a facility) and permanent (long-term effects resulting from the operation of a facility). Both short-term and long-term impacts can be direct, indirect, or cumulative. All these effects caused by an action that occur during the time and the place of the road construction, the result from the direct of increase of land use or resource. In additional to the disturbance of land, environmental impacts such as the effect of alteration of the chemical substances, acid, and dissolve metal loading the ground water (Viadero et al., 2008).

The following discussion is intended to provide an overview of the principal effects which must be considered in evaluating the environmental impacts of road construction projects.

From a positive point of view, Sherwood (2001) who studied on the alternative materials in road construction suggested that materials bound with bitumen or cement are not likely to present any serious environmental problems for two reasons. First, it's attributed to the condensation of the layer which the particles are encapsulated by bitumen or cement layer. Hence, the low rate of water passes into the individual particles. Second, bound materials are mainly used in the upper layers of the road structure in layers that are thin compared with the thicknesses of the underlying layers and they are not in a permanently wet condition. A similar statement was also addressed by Hoyos. et al. (2011) that base or subbase layer would not be directly exposed to extreme weather cycles. Apart from the fact that the rate of leaching out is also likely to be low.

However, the lower layers of the road structure may require considerable volumes of material for a long distance. Due to the large volumes of pavement or embankment materials, especially recycled or waste materials, even if its concentration is low, it can be a sources of contaminates that reach the environment either through leaching, run-off transport or aerial transport (Dawson., 2008b). The possibility amount of leaching variously depend on materials used in the various layers, condition and wear resistance of the surface layers, the influence of water or run-off movement to drainage (Arulrajah et al., 2015).

It is a significant impact when reuse of the recycled materials or waste material in term of resource management and environmental concerns. Use waste or recycle materials in highway construction; however, may contain traces of toxic compounds that could leach out and pollute source of public water supply. The possibility of the contaminates depends on the concentration of the toxic substance, the quantity of material being used and the readiness with which it can be brought into solution (Sherwood, 2001). A range of heavy metals and other pollutants include oil and/or organic micro-contaminants may consist in those alternative materials which recommend to test to ascertain feasibility of road construction application (Apul et al., 2002; Baldwin et al., 1997; Dawson et al., 2006; Hill, 2004; Lindgren, 1998; Olsson, 2005).

Jandov'a (2006) conducted a field experiment located in Czech to study the pollutant leaching from road construction materials which containing potentially harmful chemicals. Water was collected 1.5 m beneath the road surface by seeping down from the road surface through the embankment and pavement foundation formed of slag. The test was carried out by using the device as illustrated in Figure 2.13.

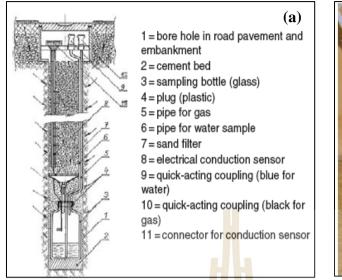




Figure 2.13 (a) Seeping water sampler in road embankment, and (b) Sampling bottle (Sytchev, 1988 modified in Jandov´a, 2006).

Legret et al., (2005) analyzed percolating water through two core samples containing 10% and 20% of reclaimed asphalt pavement. The authors also conducted static batch tests and column leaching tests on site to evaluate the leaching selected heavy metals and PAH from reclaimed asphalt pavement. The data of leaching tests for water having passed through an asphalt contained recycled components, are given for comparison in Table 2.5.

Chemical Characterization	Jandov´a (2006)	Legret et al. (2005)			
(µg/l except pH)	Slag under asphalt	10%RAP	20%RAP		
Ph	6.99	6.9	6.9		
Cu	9.8	20	21		
Cr	14.9	5	8		
Cd	<0.1	1.6	1.0		
Ni	30.7	11	11		
Zn	16.0	250	317		
Pb	4.3	BDL	BDL		
Anthracene	0.0001	BDL	BDL		
Benzo(a)anthracene	0.0004	NA	NA		
Benzo(a)pyrene	0.0012	BDL	BDL		
Benzo(b)fluoranthene	0.0006	BDL	BDL		
Benzo(ghi)perylene	0.0005	BDL	BDL		
Benzo(k)fluoranthene	0.0009	BDL	BDL		
Dibenzo(ah)anthracene	0.0001	0.0001 BDL			
Fluoranthene	0.0021	0.035	0.035		
Indeno(123cd)pyrene	0.0007	BDL	BDL		
Naphthalene	0.0006	NA	NA		
Phenanthrene	0.0008	NA	NA		
Pyrene	0.0019	NA	NA		
Chrysene	0.0008	NA	NA		
Acenaphthylene	0.0001	NA	NA		
Acenaphthene	0.0002	NA	NA		
Fluornene	0.0003	NA	NA		

 Table 2.5 Leaching of pollutants from road construction containing recycled materials.

Note: BDL = below detection limit, NA = not analyzed

Sadler et al., (1999) also found significant PAH concentrations in the soil beneath the asphalt due to water reaching the environment through leaching from asphalt surfaces. In additional to PAH, heavy metals were observed by Kriech (1990, 1992) who carried out the leaching experiment tests on standard hot-mix asphalt.

The road construction composes of multi-layer with different types of materials which is not isolated, but open to physical, chemical, and biological interaction with its environments. Chemical reactions in the road construction, thus occur and adjacent soil systems commonly involve the solid and the liquid phases (Dawson., 2008a). The author reported that the wearing course of a road is not an impervious layer which the rainfall can infiltrate into the road structure. Pollutants included in the multi-component system of road construction (matrix of road materials) can eventually be made soluble.

The problem could arise, however, where embankments are constructed close to ground water sources and/or the drainage from the road embankments discharges directly to the river (source of public water supply) as pollution of the water may seriously affect aquatic life (Sherwood, 2001). For instance, run-off can bring organic and inorganic compounds to road shoulder materials will discharge down the slopes and into the drains provided at the bottom of the road embankment. Some infiltration and seepage from the road surface will occur in the road structure which lead to chemical reaction with materials in the various road layers and the underlying soil. These phenomena can be depicted by the Figure 2.14 which adapted from Dawson. (2008a) and Arulrajah et al. (2015).

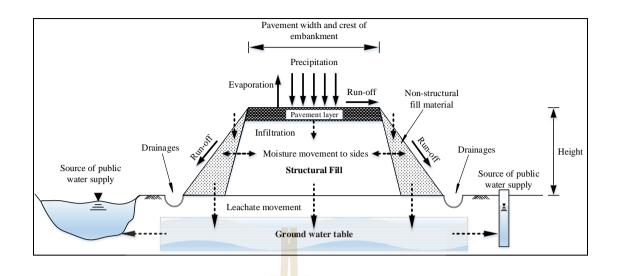


Figure 2.14 A schematic diagram of water flow balance and possible contaminate targets (not to scale).

Leachate will seep into the groundwater table, hence if doubt exists about the water pollution arising from the use of substantial amounts of alternative materials, recycle materials, and waste materials in road construction, the necessity for the environmental testing analysis should be undertaken. The inclusion in this chapter, the potential contamination concerns related to the use of RAP in the base and subbase applications that may not typically associated with the use of RAP in HMA also discussed. The significant concerns are fundamentally related to the leaching of contaminates resulting from RAP itself and the pulverization of the binder or additive materials when used to stabilize RAP material. Those contaminates include pH, polycyclic aromatic hydrocarbons (PAH), and a variety of metals (aluminum, cadmium, chromium, lead, silver, and selenium) will discuss as follow:

2.7.1 pH contaminates concerns

A dual channel pH conductivity mater following to ASTM D1287-91 (ASTM-D1287-91, 2002) was used to read the pH of free water in soaked 100% RAP and cement-treated RAP samples (Hoyos et al., 2008; Hoyos. et al., 2011). The neutral pH values (approximately 6 to 7) of 100% RAP were found while the pH readings from cement-treated RAP and cement-treated RAP with fiber tend to increase with an increase in cement dosage (pH values are approximately 10 to 11 for both 2% and 4% of cement inclusion). This trend is attributed to the formation of the soluble calcium hydroxide or portlandite during the hydration reactions of cement-RAP goes into solution. However, according to benchmarks mandated by the U.S. Environmental Protection Agency (EPA) for storm-water sampling, pH values should be in the range of 6 to 9 (EPA, 2005).

The leachate assessment study of four recycled materials include RAP, reclaimed concrete material (RCM), fly ash (FA), and foundry sand (FS) for the Minnesota Department of Transportation (Mn/DOT) found that pH levels in RAP leachate are 7.57 and 9.67 for unsaturated leachate tests and batch tests, respectively (Gupta et al., 2009; Kang et al., 2011).

Kang et al. also measured the pH values when FA were used to stabilize RAP+RCM and indicated that pH values are as low as 9.7 and as high as 10.99 for the blends of (5% FA + 25% RAP + 70% RCM) and (15% FA + 75% RAP + 10% RCM), respectively. The authors concluded that inorganic desorption and dissolution from FA are dependent on pH. Li at al. (2008) studied the utilization of RAP with 10% Class C FA for a road base construction reported that leachate from this blend ranged from 6.9 to 7.5. Edil, Tinjum, and Benson (2012) investigated the characterization of RCA and RAP behavior when the blend used as unbound base without being stabilized. The authors found the unbound RAP samples leachate pH values between 6.5 and 8.5.

In recent study, Arulrajah et al. (2014) evaluated the effects of RCA on the RAP performance. This research article indicated that samples composed of 50% RAP and 50% RCA had a pH of 11.37, which insignificantly lower than that for 100% RCA. However, pH values for the blends much higher than an average pH level of 7.6 in 100% RAP samples. The authors concluded that this increase in pH was the result of the soluble calcium hydroxide being formed during the chemical reaction (hydration reaction) in RCA, which similar to the previous research conducted by Hoyos et al., (2011).

2.7.2 Chemical Oxygen Demand (COD)

Hoyos et al., (2008; 2011) performed COD analyses in according with ASTM D1252 (ASTM-D1252, 2006) and found COD values of approximately 60 mg/L, lower than the U.S. Environmental Protection Agency's (EPA, 2005) stormwater sampling benchmark of 120 mg/L. Found that the COD values dropped with the addition of 2% and 4% PC Type I. This reduction was said to be attributable to the reduction of the fine materials coming in from the RAP materials as a result of the addition of the cementitious material.

2.7.3 Polycyclic Aromatic Hydrocarbons (PAH)

Shediy et al. (2012) performed the laboratory batch leaching tests on RAP samples by using both toxicity characteristic leaching procedure (TCLP) fluid and deionized water. The results shown that PAH levels (ace naphthalene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene) very close to or below the U.S. EPA drinking water standards. Townsend (1998) and Brantley and Townsend (1999) have confirmed that PAH levels of RAP below drinking water standards in laboratory leaching tests.

2.7.4 Metal contaminate concerns

In recent years, several studies have been conducted leaching tests in the concern of metals contamination resulting from the use of RAP as base/subbase applications, to determine the potential environmental effects of using of RAP.

Leaching tests of RAP following EPA Method 131 with both TCLP fluid and deionized water were performed in a recent study (Shedivy et al., 2012). The results shown that all metals except manages and arsenic were below the maximum contaminate level (MCL) concentration for drinking water. Edil et al. (2012) reported that concentrations of arsenic, selenium, and antinomy were slightly higher than the U.S. EPA MCL for drinking water. Furthermore, the leachate of referenced material (Class 5 virgin aggregate) provided similar concentrations. Hence, the author assumed that the values of these concentrations attributed strongly to leachate of asphalt binder.

Kang et al. (2011) concluded that up to 5% FA could be stabilized 75% RAP with 20% aggregate and have insignificant substantial leaching of metals except aluminum. Moreover, the additional of RAP and aggregate amount leading to drop pH and leaching of aluminum from FA to perform the formation of amorphous Al(OH₃) (aluminum hydroxide) and CaAl₂(OH)₈ + 6H₂O.

The authors addressed that mixtures containing 15% FA resulted in considerable leachate concentration, hence it was predicted that with increased residence time may result in leaching above the U.S. EPA drinking water standards and further investigation should be undertaken.

2.8 Summary

The widely great detail literature reviews, including existing theories and applications of RAP and fly ash geopolymer are illustrated in this chapter. It covers all from the past to recent research publications. It's not only concern with the engineering properties and engineering construction application, but also the perspectives of the environmental and sustainable development are included. The structure of this chapter (literature review) is summarized and demonstrated as the following:

Initially, the basic properties and characteristic of RAP is briefly descripted. Furthermore, both existing traditional and modern potential stabilization methods are reviewed. A newly geochemical binder known as geopolymer is introduced. Geopolymer technology offers a facile approach for fly ash utilization. The preparation and formation, and properties of the fly ash based geopolymer products depend heavily on alumino-silicate source of fly ash, alkali activators, curing conditions (heat and temperature). Then, the green technology of using fly ash geopolymer for construction applications is reported by many researchers. The literature, lastly concluded by the environmental testing system to assess the possibility of toxicity or contaminate in which derive from the RAP utilization in the underground structures. All in all, based on the review of literatures, it is observed that there are still knowledge gaps in the current understanding of properties of fly ash based geopolymer composites for their proper applications in construction such as the stabilization of fly ash geopolymer with the recycle material include RAP. This shortcoming, hence encouraging the authors to develop a novel green chemical technology stabilization method by using recycled asphalt pavement – fly ash geopolymer as a low carbon stabilized pavement material.

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CHAPTER III

STRENGTH DEVELOPMENT OF RECYCLED ASPHALT PAVEMENT – FLY ASH GEOPOLYMER

3.1 Introduction

Recycle Asphalt Pavement (RAP) is obtained from spent asphalt extracted from roads that reached the end of their design life (Arulrajah et al., 2014; Rahman et al., 2014). RAP is predominantly a combination of aggregates and aged bituminous additives and is an ideal aggregate for pavement application. RAP has successfully been reused as a construction material in road bases, road subbase, asphalt concrete aggregates, embankments and backfills (Arulrajah et al., 2013; Hoyos et al., 2011; Puppala et al., 2011). The utilization of RAP materials in civil engineering infrastructure works has led to significant environmental benefits, as well as a vast reduction of construction and demolition debris being disposed to landfills.

RAP is increasingly becoming a popular material in unbounded base and subbase applications due to its lower cost comparing to that of natural quality aggregates. The sustainable usage of RAP also leads to significant economical savings for the construction of new highway pavements (Hajj et al., 2010).

Large quantities of RAP are however not taken up whole-heartedly by construction industry, due to their often low mechanical strength and stiffness characteristics (Cosentino et al., 2003; Locander, 2009; Maher et al., 1997; Taha., 2003; Teha et al., 1999).

Though some efforts have been made do blend RAP with other higher quality natural or recycled material in pavements base/subbase applications, these RAP blends often do not meet the minimum local road authorities specified requirements (Arulrajah et al., 2013; Taha. et al., 1999). Saride et al., (2015) evaluated fly ash (FA) stabilized RAP, with different percentages of FA replacement contents. The authors reported that in the short-term (curing periods of 1 day and 7 days), the Unconfined Compression Strength (UCS) and resilient modulus (M_R) values increased with an increase in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content with up to 30% replacement, thereafter further increases in FA content is investigation showed that 7-day UCS values (maximum 1497 kPa) did not meet the strength requirements specified for base materials.

The utilization of RAP substitution in Virgin Aggregate (VA) stabilized by FA have been evaluated by (Saride et al., 2015) whom reported that RAP:VA = 80:20 with 40% FA mix satisfies the strength, stiffness, and California Bearing Ratio requirements for low volume roads. (Mohammadinia et al., 2016) recently evaluated the behavior of geopolymer stabilized RAP with FA and blast furnace slag precursors and reported that geopolymer stabilized RAP, with 7 days of curing, could only meet subbase requirements.

Several researchers have reported that the performance of cement stabilized RAP satisfied the requirements of pavement base/subbase applications (Hoyos et al., 2011; Puppala et al., 2011; Suebsuk et al., 2014; Teha et al., 2002). Cement-stabilized RAP is however not considered as an environmentally friendly material, as the production Portland Cement (PC) contributes significantly to global warming. The energy-intensive process for the production of PC emits a large amount of greenhouse gas – carbon dioxide (CO₂) into the atmosphere (Joseph Davidovits., 1994, 2002, 2013). Joseph Davidovits. (2013) demonstrated that the production of 1 ton of PC clinker directly products about 0.55 tons of CO₂ and requires the combustion of carbon-fuel, which results in an additional 0.40 tons of CO₂. The production of 1 ton of PC releases approximately 1 ton of CO₂.

These shortcomings have led to an attempt to explore novel low carbon stabilization methods. Geopolymer is an inorganic aluminosilicate material synthesized by alkaline activation of materials rich in alumina (Al₂O₃) and silica (SiO₂) and is considered as a green cementing agent. Geopolymerization involves the chemical reaction of alumino-silicate oxides by alkaline activation, yielding the polycondensation of the material in the three-dimensional silico-aluminate structure (Davidovits, 1991; Zhang et al., 2010). Three typical structures of geopolymer are: Poly (silicate) type (-SiO-Al-O-), the Poly (sialate-siloxo) type (-Si-O-Al-O-Si-O-) and the Poly (sialate-disiloxo) type (-Si-O-Al-O-Si-O-).

Geopolymer is made of alkali-activated aluminosilicate materials such as metakaolin, fly ash, slag, rice husk ash and bottom ash as well as other commercial materials rich in high percentage of silica and alumina. Geopolymers are reported to produce low CO₂ emission and energy consumption (Palomo et al., 1999). In Thailand, power plants produce a total output of 4.0 million tons of FA and bottom ash annually. However, only approximately 1.8 million tons of FA is used as a pozzolanic material in the concrete industry (Chindaprasirt et al., 2009) with the balance being stockpiled as waste materials. Since FA contains a high percentage of amorphous silica and alumina, it is suitable as a precursor for manufacturing geopolymers (Rattanasak & Chindaprasirt, 2009). Geopolymer has in recent years been used to stabilized natural soils to develop green building materials such as masonry products. It was reported that geopolymer based materials possess higher compressive strength and durability against sulfate than cement based materials (Sukmak et al., 2015; Sukmak et al., 2013a; Sukmak et al., 2013b). Recently, (Suksiripattanapong et al., 2015) and (Horpibulsuk et al., 2015) successfully stabilized water treatment sludge using FA geopolymer to develop sustainable non-structural and bearing masonry units. It was illustrated that the geopolymer is more effective than PC in stabilizing the water treatment sludge with high alum content. The strength and durability of sludge-geopolymer masonry units is significantly higher than sludge-cement masonry units.

The RAP stabilized with FA-geopolymer for pavement applications is currently limited due to the lack of laboratory and field evaluation of this material. This research aims to study the possibility of using geopolymer to stabilized RAP as a stabilized pavement material. An extensive site of laboratory experimental programs was carried out to investigate the strength development of RAP-FA geopolymer. The RAP-FA geopolymer samples were prepared using modified Proctor compaction energy. UCS is used as an indicator to evaluate strength development is this research. The role of various influence factor on UCS development is examined via Scanning Electron Microscopy, and X-Ray Diffraction analyses.

The various influential factors studied in this research included liquid alkaline activator (L) content, NaOH/Na₂SiO₃ ratio, FA content, and heat condition (temperature and duration). This study has significant impacts on pavement applications by using RAP stabilized with FA-geopolymer binder, a sustainable alternative to ordinary PC, in pavement base and subbase course.

3.2 Materials and methods

3.2.1 Recycled Asphalt Pavement (RAP)

RAP, collected from a milled asphalt pavement stockpile in Nakhon Ratchasima province, Thailand was used in this research. A cold milling machine was used to remove the asphalt pavement for resurfacing in the cold in-place recycling process. The low water content (WC) of RAP (less than 0.3%) was detected. The gradation of air-dried RAP was determined by a sieve analysis in accordance with (ASTM-D422-63, 2007) and is shown in Figure 3.1.

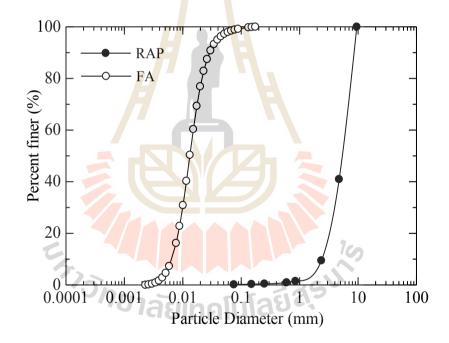


Figure 3.1 Grain size distribution of RAP and FA.

The RAP contains approximately 99.8% coarse-grained particles (retained on No. 200 sieve). The specified gravity of RAP is 2.7. The RAP is classified as poorly graded sand (SP) according to the Unified Soil Classification System (USCS) (ASTM-D2487-11, 2011). The maximum size of RAP is approximately 10 mm. The

modified Proctor compaction test was performed to determine the maximum dry unit weight (γ_{dmax}) and Optimum Water Content (OWC) of RAP in accordance with (ASTM-D1557-12, 2012). The γ_{dmax} and OWC values of RAP are 17.5 kN/m^3 and 4.1%, respectively. California Bearing Ratio (CBR) test followed the (ASTM-D1883-07, 2007) was carried out on RAP samples under the modified Proctor compaction effort at OWC and soaked for 4 days. Water absorption and swelling after 4 days of soaking were also measured. The soaked CBR values is approximately 10 to 15%, while water absorption and swelling values are 6.8% and 0.2%, respectively. These values indicated that this RAP is not suitable for base and subbase materials, as specified by the Department of Highways (DOH), Thailand (DOH, 2000). This research thus aims to study the possibility of using FA-geopolymer to stabilized RAP to meet the specified requirements of stabilized pavement material. The miner and chemical compositions of RAP, obtained by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses, are depicted in Table 3.1 and Figure 3.2, respectively. The predominant mineral components in RAP are calcite-magnesium and dolomite. The main chemical composition detected in RAP is 41.93% CaO and 36.11% MgO. This high CaO in RAP can react with silica and alumina in FA for a suitable pozzolanic reaction.

3.2.2 Fly Ash (FA)

FA was obtained from Mae Moh power plant, which is the largest lignite power plant of Electricity Generating Authority of Thailand (EGAT) in the northern region of Thailand. Table 3.1 summarizes the chemical compositions of FA using XRF analysis. The major components are 39.12% SiO₂, 20.51% Al₂O₃, 5.83% Fe₂O₃, and 12.41% CaO. Based on (ASTM-C618-12, 2012), FA was classified Class

C as the total chemical composition of SiO₂+Al₂O₃+Fe₂O₃ was greater than 50% and CaO greater than 10%. Figure 3.1 shows the grain size distribution curve of FA, which was obtained by laser particle size analysis. The specific gravity of FA is 2.50. The peaks of main amorphous phases including calcium sulfate, quartz, calcite, mulite, and hematite are detected by XRD pattern in region of 15-40°20 as presented in Figure 3.2. The morphology of RAP and FA obtained by SEM is shown in Figure 3.3. It indicates that the FA particles are fine and spherical whereas the RAP particles are irregular in shape.

Chemical formula	RAP (%)	FA (%)
SiO ₂	3.11	39.12
Al ₂ O ₃	4.73	20.51
Fe ₂ O ₃	0.10	5.83
CaO	41.93	12.41
MgO	36.11	2.49
SO3	0.89	0.49
K ₂ O	0.04	1.53
LOI	N.D.	0.41

Table 3.1	Chemical	composition	of	RAP	and	FA.

Note: N.D. = not detected.

3.2.3 Sample preparation

The liquid alkaline activator (L) was a mixture of sodium silicate (Na_2SiO_3) type CR 53, which was composed of Na_2O (14.50 – 16.50%) and SiO_2 (31.50 – 34.00%) by weight, and sodium hydroxide (NaOH) solution with a 10 molar concentration. The mixing was started by preparing the required NaOH content with distilled water. Na_2SiO_3 was then added and thoroughly mixed into the solution. A 10 M concentration was selected based on previous research (Chindaprasirt. et al., 2009), which reported that 10 M concentration was the optimum NaOH concentration for FA geopolymer.

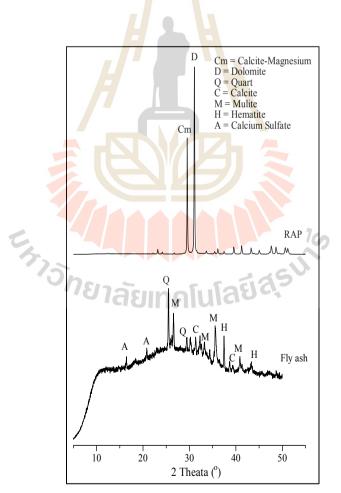
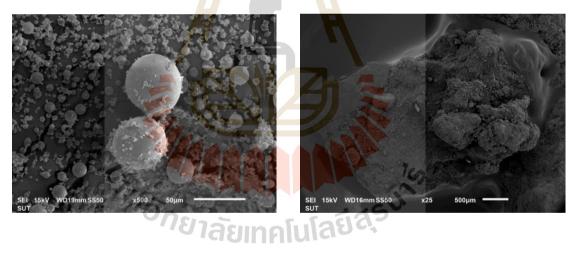


Figure 3.2 X-Ray Diffraction (XRD) pattern of RAP and FA.

The RAP-FA geopolymer was a combination of RAP, FA, and L (NaOH+Na₂SiO₃). The NaOH/Na₂SiO₃ ratios studied were 100:0, 90:10, 60:40, and 50:50. The RAP-FA blend, which is a mixture of RAP, FA, and water, is prepared as a control material to compare effect of L on strength development. FA replacement ratios were 10%, 20%, and 30% by weight of RAP for both RAP-FA geopolymers and RAP-FA blends.

The mixing procedure started with mixing air-dried RAP and FA for 5 min and then the mixture was separated into tow portion. One mixture was then mixed with L for RAP-FA geopolymer and the other was mixed with water for RAP-FA blends for additional 5 minutes to ensure the homogeneous.



(a) FA

(b) RAP

Figure 3.3 SEM image of: (a) FA and (b) RAP.

The mixtures were next compacted under the modified Proctor effort followed the ASTM Method B (ASTM-D1557-12, 2012). The test cylinder molds are 101.6 mm in diameter and 116.3 mm in height. Once the compaction curves were obtained, the RAP-FA geopolymer samples at each NaOH/Na₂SiO₃ ratio were prepared at Optimum Liquid alkaline activator Content (OLC) and the RAP-FA blend samples were prepared at Optimum Water Content (OWC) for UCS tests. The samples were dismantled, wrapped within vinyl sheet and then cured at both room temperature (RT) and 40°C for 7 days and 28 days. The test under 40°C was to simulate an average pavement temperature in Thailand (Phetchuay et al., 2014).

The UCS tests were undertaken in accordance with (ASTM-D1557-12, 2012) using a 100 kN compression machine with a strain rate of 0.5%/min. The samples were soaked in water for 2 hours and then were air-dried for 1 hour prior to UCS test according to the specification of the Department of Highways, Thailand (DOH, 2000). The mean UCS values were obtained by testing the triplicated samples to ensure the consistency.

X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses were performed to investigate the microstructural development of RAP-FA geopolymer and RAP-FA blends. The small fragments were taken from the broken portion of the UCS samples and then frozen at -195°C by immersion in liquid nitrogen for 5 min and coated with gold before SEM (JEOL JSM-6410 device) analysis (Sukmak. et al., 2013a). The XRD analyses were done on the powder samples, which were compacted in a Cu X-ray tube. The XRD traces were obtained by scanning at 0.1°(20) per min and at steps of 0.05°(20).

3.3 Results and discussion

3.3.1 Compaction test

Figure 3.4 shows the relationships between dry unit weight (γ_d) and WC of the compacted RAP-FA blends and between total unit weight and L content of the compacted RAP-FA geopolymers at various NaOH/Na₂SiO₃ ratios. The γ_d of 100% RAP (without FA) are insensitive to WC (Figure 3.4a). On the other hand, the γ_d of RAP and FA blends is sensitive to WC and γ_{dmax} is at OWC. The γ_{dmax} tends to increase with increasing FA replacement ratios.

However, the FA replacement ratio up to 20% insignificantly affects the compaction curve of RAP and FA blend as seen that the compaction curves of RAP + 20% FA and RAP + 30% FA blends are similar (Figure 3.4a). The FA replacement at optimal content can improve its compactability as a filler, hence the increase in dry unit weight is evident on comparison of the compaction curves of the 100%RAP and RAP+10%FA samples in Figure 3.4a. However, excessive FA content absorbs more water, hence resulting reduction in compactability.

The compaction curves of RAP-FA geopolymer are dependent on the ratio of NaOH/Na₂SiO₃ and FA replacement ratio. For a particular FA replacement ratio, the OLC providing the maximum unit weight is found to be the same for all NaOH/Na₂SiO₃ ratios. For instance, the OLC values are 7%, 8%, 9% for RAP+10%FA, RAP+20%FA, and RAP+30%FA geopolymers, respectively as shown in Figure 3.4(b-d). The optimum NaOH/Na₂SiO₃ ratio providing the highest maximum total unit weight of RAP-FA geopolymer is dependent upon the FA replacement ratio; i.e., it is 100:0, 90:10, and 50:50 for 10%, 20%, and 30% FA replacement, respectively. It is also noticed that for a particular NaOH/Na₂SiO₃ ratio,

the total unit weight of RAP-FA geopolymer increases when FA replacement ratio increases from 10% to 20%; however, it decreases when the FA replacement ratio increases to 30%.

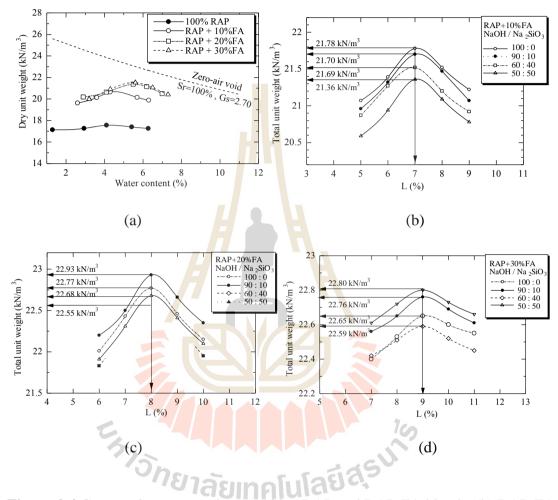


Figure 3.4 Compaction test results: (a) 100% RAP and RAP-FA blends, (b) RAP-FA

geopolymer with 10% FA, (c) RAP-FA geopolymer with 20% FA,

and (d) RAP-FA geopolymer with 30% FA.

3.3.2 Unconfined Compression Strength (UCS) test

Figure 3.5 summarizes the UCS results of the RAP-FA blend and RAP-FA geopolymer (RAP + 20% FA and RAP + 30%FA) for various NaOH/Na₂SiO₃ ratios (100:0 to 50:50), curing times (7 and 28 days), and curing temperatures (RT and 40°C). The UCS development of geopolymer relies on the reaction between the precursor and alkali activator and heat condition of samples (Phoo-ngernkham et al., 2014; Somna et al., 2011; Sukmak. et al., 2013b). It is noted that the UCS values of both RAP-FA blend and geopolymer increase with increasing curing time and temperature (see Figure 3.5a-b). This result is also similar to the previous research that reported on strength development of cement-stabilized RAP (Suebsuk et al., 2014; Taha et al., 2002).

Figure 3.5a shows that the 7-day UCS values of RAP-FA blends (at 20%FA and 30% FA) are higher than RAP studied by Saride et al. and greater than the strength requirement specified by the Thailand national road authorities in which UCS > 1,724 kPa and UCS > 2,413 kPa for low and high volume roads, respectively (DOH, 2000; DRR, 2013). At early stage of geopolymerization (7 days), the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ = 100:0 is lower than that of RAP-FA blends for both FA replacement ratios of 20% and 30% at RT cuing. However, the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ < 10:90 is higher than that of RAP-FA blends and the UCS values of RAP-FA geopolymers increase when NaOH/Na₂SiO₃ ratio is decreased. This implies that the input of Na₂SiO₃ can enhance the short-term strength of RAP-FA geopolymer, which is an advantage for applications that require high early strength.

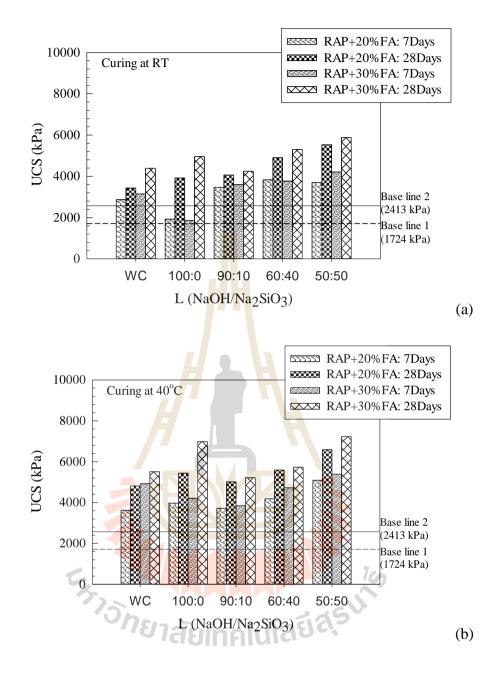


Figure 3.5 Compressive strength of RAP-FA blends and RAP-FA geopolymer cured at 7 days and 28 days and (a) at RT and (b) at 40°C.

For the same NaOH/Na₂SiO₃, the 30% FA-RAP geopolymer exhibits higher UCS than the 20% FA-RAP geopolymer, despite the gradation of 30% FA-RAP being finer than that of 20% FA-RAP. This is because the UCS of RAP-FA geopolymers is mainly governed by the degree of chemical reactions, in that higher FA contents results in higher silica and alumina contents for the geopolymerization reaction.

3.4 Microstructural analyses

The XRD patterns of RAP-FA blends samples cured for 7 days and 28 days at RT and 40°C are shown in Figure 3.6. The RAP-FA blend samples consist of the amorphous phase and broad hump between 23 and 35°20, which indicate the anhydrous carbonate mineral composed of high calcium magnesium carbonate from the RAP material (Chesner et al., 1998). By comparing Figure 3.2 (RAP) and Figure 3.6 (RAP-FA), the FA replacement in the RAP-FA blend generates new chemical silica- and alumina-rich products, inclusive of mulite, gypsum, ladradorite, malladrite, and margarite. This high amount of calcium and magnesium of RAP and high amount of silica and alumina of FA result in the chemical reaction to form Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H) similar to the hydration of Portland cement (Cristelo et al., 2012; Hanjitsuwan et al., 2014). Consequently, the UCS of RAP-FA blends increases with increasing curing time (see Figure 3.5).

Besides the XRD results, SEM analysis is also performed on the samples to confirm the growth of cementitious products of RAP-FA blend and RAP-FA geopolymer over time. The SEM images of RAP-FA blend samples cured for 7 days and 28 days at RT and 40°C are illustrated in Figure 3.7. The dense cementation

matric due to the chemical products from the reaction between silica and alumina (in FA) and CaO and MgO (in RAP) binds the RAP and FA particles together, which confirms the XRD results. Consequently, the densification of compacted RAP-FA blends with increasing temperature and curing time are observed, resulting in UCS development.

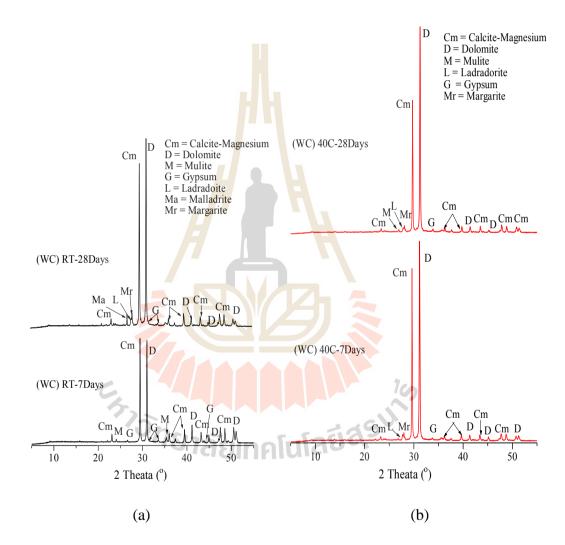
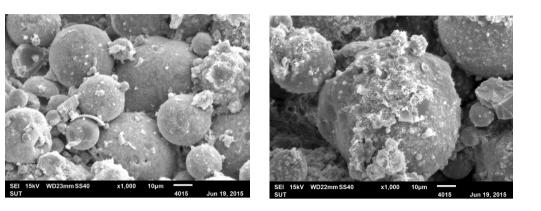


Figure 3.6 XRD patterns of RAP-FA blend samples cured for 7 days and 28 days at (a) RT condition and (b) 40°C condition.

Figure 3.8 shows the XRD patterns of RAP-FA geopolymers at NaOH//Na₂SiO₃ ratios of 100:0 and 50:50 cured for 7 days and 28 days at RT and 40°C. The XRD patterns of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 cured for 7 days at RT are similar to those of RAP-FA blends in that the presence of a large amount of dolomite and calcite-magnesium is indicated by the broad hump around 25-35°20 (Figure 3.8a and 3.8c). The geopolymerization products, sodium alumino silicate hydrate (N-A-S-H) phases formed as a result of the alkaline activation are also detected at longer curing time and higher temperature. The products are started by the dissolution of FA particles in which the original mineralogy is significantly modified (Davidovits et al., 2014).

Figure 3.8 shows the decrease of the main amorphous silica and alumina phases of FA, which are consumed to react with alkaline activation (NaOH/Na₂SiO₃) (compare Figure 3.2 and Figure 3.8). This results in new geopolymerization species including nepheline, ladradorite, and muscovite as observed at the broad hump between 27-30°20 in the XRD patterns of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratios of 100:0 cured for 28 days at RT (Figure 3.8a) as well as 7 days and 28 days at 40°C (Figure 3.8b).



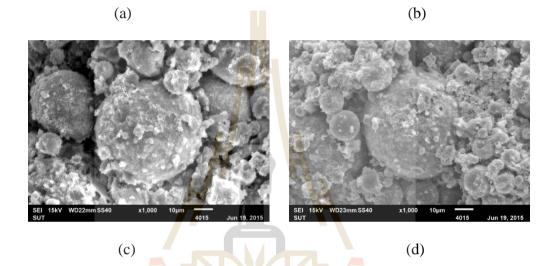


Figure 3.7 SEM images of RAP-FA blend samples cured for (a) 7 days at RT condition, (b) 7 days at 40°C condition, (c) 28 days at RT condition, and (d) 28 days at 40°C condition.

Similar XRD patterns are observed for RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratios of 50:50 (Figure 3.8c-d). These new nanocrystalline phases create cementitious systems, which are associated with the strength enhancement. The Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H) co-exist with geopolymerization products, Sodium Alumino-Silicate Hydrate (N-A-S-H gel), therefore enhanced UCS of the RAP-FA geopolymer as also reported by (Phoongernkham et al., 2014; Somna et al., 2011). Even with the coexistence of pozzolanic products and geopolymerization products, the 7-day UCS of RAP-FA geopolymer at NaOH:Na₂SiO₃ = 100:0 is lower than that of RAP-FA blend at RT curing (see Figure 3.5a).

This low geopolymerization products are early curing time might be attributed to two main reasons. Guo et al., (2010) reported that when FA based geopolymer materials is cured at ambient temperature of around 25°C, the strength development is rather slow. The other reason is concerned with the alkaline activator via a chargebalancing role with aluminum, which incorporated into geopolymerization binders (FA filters) (Criado et al., 2007; Cristelo et al., 2012; Duxson et al., 2005; Fernández-Jiménez et al., 2005; Provis et al., 2005).

With a very high NaOH content (NaOH/Na₂SiO₃ = 100:0), the chargebalancing is unstable and hence slower strength development. However, when the cured temperature of FA-geopolymer increase from the ambient temperature to higher temperature (40°C), NaOH can dissolve more silica and alumina from FA to generate more geopolymerization reaction and resulted in the strength development.

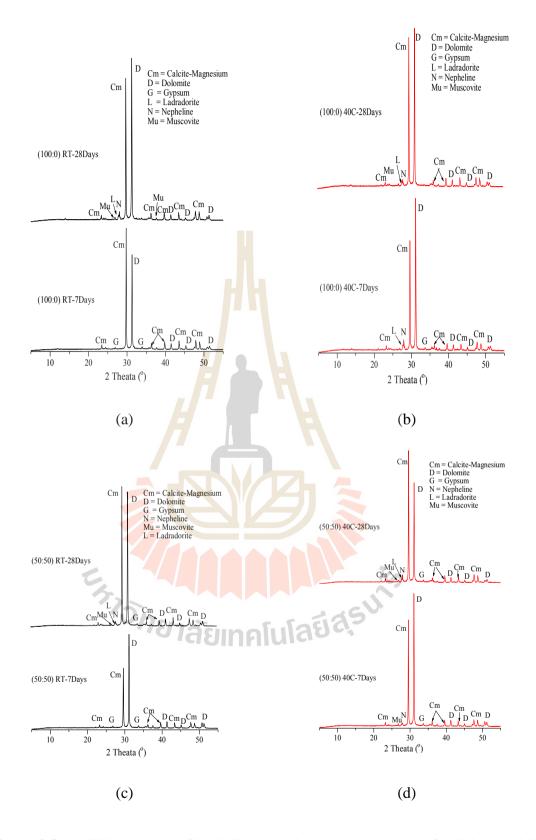


Figure 3.8 XRD patterns of RAP-FA geopolymer samples cured for 7 days and 28 days at different NaOH/Na₂SiO₃ ratios and heat condition.

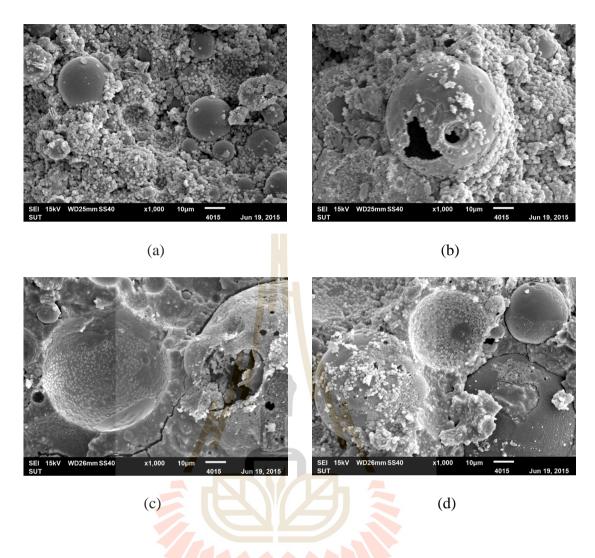


Figure 3.9 SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 cured for (a) 7 days at RT condition, (b) 7 days at 40°C condition, (c) 28 days at RT condition, and (d) 28 days at 40°C condition.

This is attributed to a raised alkalinity, derived from the loss of water due to the almost immediate formation of C-S-H and C-A-H phases (Chindaprasirt et al., 2007; Pangdaeng et al., 2014) and the acceleration of geopolymerization reaction due to heat temperature (Horpibulsuk et al., 2015; Sukmak. et al., 2015; Sukmak. et al., 2013a). It is evident that the higher UCS values of RAP-FA geopolymer at the NaOH/Na₂SiO₃ ratio of 100:0 are obtained as curing time increases from 7 to 28 days and/or curing temperature from RT to 40°C (Figure 3.5a-b).

The growth of geopolymerization products with various NaOH/Na₂SiO₃ ratios, curing time and temperature is demonstrated by SEM images (Figure 3.9 and Figure 3.10 for NaOH/Na₂SiO₃ ratios of 100:0 and 50:50, respectively). Figure 3.9a shows the SEM image of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 (without Na₂SiO₃) cured for 7 days at RT.

The roughly smooth and spherical surface of FA is clearly observed, which indicates that no perceptible reaction or less alkali reaction and confirms the slow reaction of NaOH and FA. In other words, even with an addition of NaOH, the unreacted and/or partially reacted FA particles are more and the matrices look rather loose (compare Figure 3.7a with Figure 3.9a), which is similar to the previous publication (Hanjitsuwan et al., 2014). The SEM (Figure 3.7a and Figure 3.9a) and XRD (Figure 3.6a and Figure 3.8a) results confirm the lower UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ = 100:0 and room temperature curing than the RAP-FA blend. However, with increasing curing time and temperature, the NaOH solution can dissolve more silica and alumina from FA, which can generate more geopolymerization products.

The alkali activation begins at a point on the FA surface and then expands to form a larger hole. Consequently, geopolymerization products are generated both inside and outside the shell of the sphere, until the FA particle is completely or almost completely consumed (Fernández-Jiménez & Palomo, 2009). The effect of temperature and curing time on UCS development is clearly evident by comparing Figure 3.9b-d with 3.9a. Etched holes on the FA surface and the cementitious products are more with increasing curing time and temperature. Therefore, their UCS sharply increases with temperature and curing time.

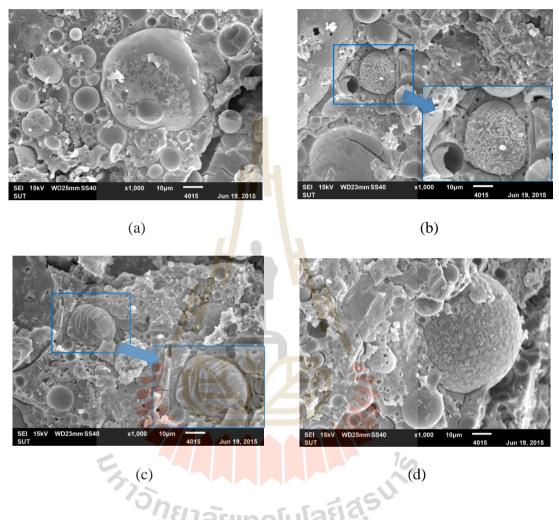


Figure 3.10 SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 50:50 cured for (a) 7 days at RT condition, (b) 7 days at 40°C condition, (c) 28 days at RT condition, and (d) 28 days at 40°C condition.

Figure 3.10(a-b) show the SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 50:50 at the early age (7 days) and at RT and 40°C curing. Once the source of alumino-silicate material comes into contact with alkali solution, the leaching of both silica and alumina started to generate the geopolymerization products (Van Jaarsveld & Van Deventer, 1999). Although the presence of small amounts of zeolites has a beneficial effect on mechanical property enhancement, the large zeolites formation can have a detrimental effect on the geopolymerization gel and mechanical performance. When sodium silicate is used, the presence of silica in the sodium silicate retards the zeolite formation rate, moreover, the highly soluble silica incorporated with leached silica and alumina into the N-A-S-H gel (Criado et al., 2007; Fernández-Jiménez, & Palomo, 2005).

The geopolymerization products in the samples with NaOH/Na₂SiO₃ = 50:50 are more than those with NaOH/Na₂SiO₃ = 100:0 for the same curing time and temperature. The more alumino-silicate gel on FA surface indicates the immediate formation of N-A-S-H phases (Figure 3.10a-b). The growth of geopolymerization products with time and temperature increased are clearly detected around FA particles and the pores (Figure 3.10c-d) in which the geopolymerization products are a well-formed Si-O-Al and Si-O-Si three dimensional structures.

The laboratory test results indicate the viability of using RAP-FA blends as a pavement base course in which their UCS values meet the minimum strength requirement specified by national road authorities. The early and long term strength and durability of the RAP-FA base course can be improved by FA based geopolymer. The higher Na₂SiO₃ content enhances the short-term UCS of RAP-FA geopolymer for both RT and 40°C curing, which is advantageous for applications required high early strength. In addition to the engineering impact, the RAP-FA and RAP-FA geopolymer are a low-carbon pavement base course compared to the traditional PC stabilized RAP commonly used worldwide.

3.5 Conclusion

A series of laboratory experiments were conducted to ascertain the strength development of RAP-FA geopolymer as a sustainable stabilized pavement course in this study. The influencing factors studied are mixing ingredients (FA content, L content and NaOH/Na₂SiO₃ ratio) and heat condition (temperature and duration). The strength development is analyzed via Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) results. The conclusions arising from this study are as follows:

1. The dry unit weight of RAP-FA blends increases with increasing FA replacement ratio and water content until OWC. The FA replacement ratios excessive of 20% insignificantly alter the water-density relationship.

- 2. The compaction curves of RAP-FA geopolymer depend on the NaOH/Na₂SiO₃ ratio and FA replacement ratio. For a particular FA replacement ratio, the OLC values providing the maxim unit weight are found at NaOH/Na₂SiO₃ ratio of 100:0, 90:10, and 50:50 for 10%, 20%, and 30% FA replacement ratios, respectively.
- 3. The 7-days UCS of the compacted RAP-FA blend (without L) at OWC meets the strength requirements for base course specified by Thailand national road authorities for both RT and 40°C cuing and for both 20% and 30% FA replacement. The UCS improves insignificantly when the FA replacement ratio exceeds 20%, indicating this to be optimal. The UCS ratio decreases and are higher than those of the compacted RAP-FA blends at the same curing time and FA replacement ratio when the NaOH/Na₂SiO₃ ratio are less than 90:10.
- 4. The XRD and SEM analyses of RAP-FA geopolymers and RAP-FA blends show that the high amount of calcium and magnesium of RAP and high amount of silica and alumina of FA form C-S-H and C-A-H. The growth of C-S-H and C-A-H products over the time is observed and hence the UCS of RAP-FA blends increases with time.
- 5. The silica present in sodium silicate is highly soluble, hence the higher Na₂SiO₃ content in liquid alkaline activator results in faster geopolymerization reaction and more geopolymerization (N-A-S-H gel). Both N-A-S-H and C-S-H from CaO and MgO (in RAP) and silica and alumina (in FA) fill the pores to make the RAP-FA structure dense. Consequently, the UCS increase as the NaOH/Na₂SiO₃ ratio decrease.

- 6. Without Na₂SiO₃ (NaOH/ Na₂SiO₃ = 100:0), the geopolymerization reaction of the FA-geopolymer cured at room temperature is slow; hence the 7-day UCS of RAP-FA blend is higher than RAP-FA geopolymer. With increasing curing time and temperature, the XRD and SEM analyses show that the NaOH solution is able to dissolve more silica and alumina from the FA for geopolymerization reaction. As such, the UCS of RAP-FA geopolymer NaOH/ Na₂SiO₃ = 100:0 increases with time and temperature increased.
- 7. The outcome of this research confirms the potential of suing FA stabilized RAP as pavement base course where its UCS values meet the minimum strength requirement specified by the Thailand national road authorities.

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CHAPTER IV

DURABILITY STUDY OF RECYCLED ASPHALT PAVEMENT – FLY ASH GEOPOLYMER

4.1 Introduction

Sustainable infrastructure is a key strategic initiative in many developed and developing countries. Research on the usage of alternative sustainable materials is at the forefront of many governments, researchers, and pavement industries worldwide (Lindsey, 2011). The usage of recycled materials and waste by-products in civil infrastructure enables a more durable alternative to quarried materials resulting in conservation of natural resources, decreased energy use, and reduced greenhouse gas emission.

In recent years, extensive research works on innovative and environmentally friendly solutions have resulted in the applications of green technologies in pavement construction, which have led to more efficient use of natural resources and recycled materials (Moreno et al., 2012).

Several researchers have investigated the usage of fly ash (FA) in civil infrastructure applications such as production of geopolymer cement and concrete (Assi et al., 2016; Mo et al., 2016), geopolymer stabilized expansive soil (Sharma & Sivapullaiah, 2016), stabilization of soft clays (Phetchuay et al., 2016) and treatment of marginal lateritic soil as a pavement base/subbase layers (Phummiphan et al., 2016; Phummiphan et al., 2015).

Several geotechnical researchers have evaluated recycled waste materials as an alternative construction material in civil infrastructure applications. Surplus clay and FA were used for developing a sustainable lightweight cellular cemented construction material (Neramitkornburi et al., 2015). Waste carpet fibers were used to increase the strength and reduce the swelling pressure of expansive soils (Mirzababaei et al., 2013a, 2013b). Calcium Carbide Residue (CCR), a waste by-product of the acetylene gas production process, has been established as a green soil stabilizer (Horpibulsuk et al., 2011; Kampala et al., 2013), to develop non-bearing masonry units (Horpibulsuk et al., 2014), and stabilized subgrade materials (Phetchuay et al., 2014).

From a geoenvironmental perspective, FA based geopolymer is an environmentally friendly additive for improving the mechanical and durability characteristics of problematic soils (Sukmak et al., 2013a; Sukmak et al., 2013b). Water treatment sludge, FA, and rice husk ash have furthermore been used to manufacture sustainable geopolymer masonry units (Horpibulsuk et al., 2015; Nimwinya et al., 2016; Suksiripattanapong et al., 2015b; Suksiripattanapong et al., 2015a). The strength and durability of sludge geopolymer masonry units.

Meanwhile, roads are a central component of many nation's infrastructure and present a wide array of opportunities for the usage of vast quantities of recycled materials. Recycled Asphalt Pavement (RAP), is obtained from spent asphalt extracted from roads that have reached the end of their design life (Arulrajah et al., 2014; Rahman et al., 2014). RAP contains asphalt binder (3–7%) and aggregates (93–97%) by weight (Han & Thakur, 2015), and is an ideal recycled material for reuse in

pavement applications. RAP often exhibits low strength and stiffness performances; hence chemical stabilization of RAP is used extensively for developing bound pavement base/sub-base material (Hoyos et al., 2011; Saride et al., 2015a).

An evaluation of FA-stabilized RAP as pavement base/sub-base material has been investigated by (Saride et al., 2014) whom reported that the unconfined compression strength (UCS) and resilient modulus (M_R) properties can be improved by FA replacement. However, the 7-day UCS of RAP was reported to be lower than the strength requirement specified for pavement base materials. Further studies on the mechanical and microstructural properties of a stabilized RAP, Virgin Aggregate (VA) and FA blend as a pavement base/sub-base (Saride et al., 2015b; Saride et al., 2015a) indicated that RAP:VA = 80:20 with 40% FA replacement satisfied the strength, stiffness, and California Bearing Ratio requirements for low volume roads.

Mohammadinia et al. (2016) explored a sustainable stabilization solution for RAP by using FA and blast furnace slag geopolymers and reported that 7-day strength of geopolymer stabilized RAP could meet pavement subbase specification requirements.

Hoy et al., (2016a) have evaluated the strength development of RAP-FA geopolymers and RAP-FA blends as sustainable stabilized pavement base/sub-base materials, in which up to 80% RAP was used as aggregates. Liquid alkaline activator (L), a mixture of sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH), was used to activate the alumino-silicate FA to produce FA-geopolymer binder, while RAP, FA, and water (RAP-FA blend) were mixed as a control material. The authors reported that both the RAP-FA blends and RAP-FA geopolymers could be used in

pavement base applications as the strength requirements met the specifications of the Department of Highways, Thailand.

Besides strength and environmental requirements as investigated previously, the durability of RAP-FA blends and RAP-FA geopolymer under server climatic conditions is a crucial parameter when used in road construction applications. The study on durability of RAP-FA blends and RAP-FA geopolymers is however still in its infancy. Dempsey and Thompson (1967) defined durability as the ability of the materials to retain their stability and integrity and to maintain adequate long-term residual strength to provide sufficient resistance to climate condition.

Cyclic wetting-drying (w-d) test, simulates weather changes over a geological age, and is considered to be one of the most appropriate simulation that can induce damage to pavement materials (Allam & Sridharan, 1981; Sobhan & Das, 2007). Al-Obaydi et al., (2010) and Al-Zubaydi (2011) indicated that after repeated w-d cycles, crack propagation would occur, resulting in severe effects on the engineering properties of the materials, particularly in terms of their residual strength and stability.

This research attempts to study the durability of RAP-FA blend and RAP-FA geopolymer when subjected to cyclic wetting-drying tests. The changes in material properties, microstructure and mineralogy during cyclic w-d tests were examined. The change in materials' strength/physical properties were examined using unconfined compressive strength (UCS) and weigh loss tests, while the mineralogical and microstructural changes were examined by the application of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses at various repeated w-d cycles.

The outcomes of this research will have significant impact on construction guidelines and specifications for using RAP-FA blends and RAP-FA geopolymers in road construction applications. Furthermore, it will promote the utilization of recycled and waste materials worldwide.

4.2 Materials and methods

4.2.1 Materials

In this research, RAP samples were collected from a mill asphalt pavement stockpile in Nakhon Ratchasima province, Thailand. The gradation and the engineering properties of air-dried RAP are shown in Figure 4.1 and Table 4. 1, respectively. The chemical and mineral composition of RAP, obtained by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analyses, are presented in Table 4.2 and Figure 4.2, respectively.

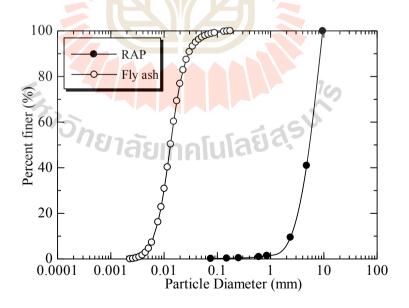


Figure 4.1 Grain size distribution of RAP and FA.

The XRD analyses indicated that the predominant mineral components in RAP were calcite-magnesium and dolomite, while the XRF results indicated that the main chemical composition in RAP were 41.93% CaO and 36.18% MgO. This high CaO in RAP can react with silica and alumina in FA for an enhanced pozzolanic reaction. The irregular shape of RAP particles covered by amorphous asphalt binder, obtained by SEM analysis, is presented in Figure 4.3a.

Geotechnical parameters	Values	Test method
USCS classification	SP	ASTM-D2487-11
D ₁₀ (mm)	2.50	_
D ₃₀ (mm)	4.20	_
D ₅₀ (mm)	5.30	_
D ₆₀ (mm)	6.10	_
Cu	2.44	_
C _c	1.16	~ -
Specific gravity (G _s)	2.70	ASTM-D1883-07
CBR (%)	10-15	ASTM-D557-12
Water absorption (%)	6.80	_
Swelling ratio (%)	0.20	_
Maximum dry unit weight from	17.50	ASTM-D1557-12
modified compaction test (kN/m ³)		
Optimum water content from	4.10	ASTM-D1557-12
modified compaction test (%)		

 Table 4. 1 Geotechnical Properties of Recycled Asphalt Pavement.

FA used in this study was obtained from Mae Moh power plant, the largest lignite power plant in the northern region of Thailand. The grain size distribution curve of FA, obtained by a laser particle analyzer, is also shown in Figure 4.1. The specific gravity of FA was 2.50. Table 4.2 summarizes the chemical composition of FA using XRF analysis. FA was composed mainly of 40.13% SiO₂, 20.51% Al₂O₃, 583% Fe₂O₃, and 12.45% CaO. In accordance with ASTM C 618 (ASTM-C618-12, 2012), FA was classified as Class C because the total chemical composition of SiO₂+Al₂O₃+Fe₂O₃ was greater than 50% and CaO greater than 10%.

The peaks of main amorphous phases, including calcium sulfate, quartz, calcite, mulite, and hematite were detected by XRD analysis in region of 15- $40^{\circ}2\theta$ as demonstrated in Figure 4.2. The SEM image in Figure 4.3b indicated that variety sizes of FA particles were in fine and spherical shape.

Chemical formula	RAP (%)	FA (%)
SiO ₂	3.11	39.12
Al ₂ O ₃	4.73	20.51
Fe ₂ O ₃	101010.10	5.83
CaO	41.93	12.41
MgO	36.11	2.49
SO ₃	0.89	0.49
K ₂ O	0.04	1.53
LOI	N.D.	0.41

Table 4.2 Chemical composition of RAP and FA.

Note: N.D. = not detected.

Liquid alkaline activator (L) is a mixture of sodium silicate (Na₂SiO₃), which is composed of Na₂O (14.50 – 16.50%) and SiO₂ (31.50 – 34.00%) by weight, and sodium hydroxide (NaOH) solution with a 10 M concentration. A 10 M concentration was selected based on previous research outcomes (Chindaprasirt et al., 2009), which studied on the strength of fly ash geopolymer mortar and reported that 10 M concentration was the optimum NaOH concentration for FA geopolymer. A higher concentration of NaOH may affect the human health.

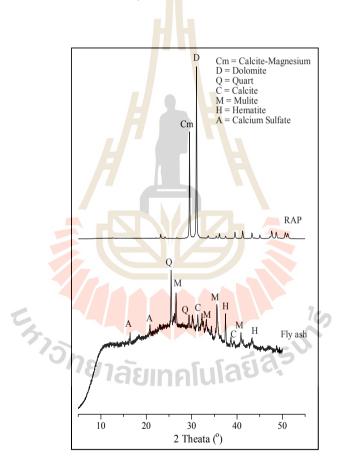


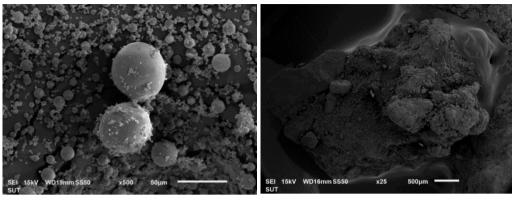
Figure 4.2 X-Ray Diffraction (XRD) pattern of RAP and FA.

4.2.2 Sample preparation

The NaOH/Na₂SiO₃ ratios studied were 100:0, 90:10, 60:40, and 50:50. The RAP-FA geopolymer was a combination of RAP, FA, and L (NaOH+Na₂SiO₃). The RAP-FA blend, which was a mixture of RAP, FA, and water, was prepared as a control material to compare the effect of L on strength development. Based on a previous study (Hoy et al., 2016a), FA replacement ratio at 20% by weight of RAP was reported to be optimal. This ratio was hence selected for evaluating the durability of RAP-FA geopolymer and RAP-FA blend.

The mixing procedure started with mixing air-dried RAP and FA for 5 min, after which the mixture was divided into two portions. Once was activated by L for producing RAP-FA geopolymer and the other was mixed with water for an additional 5 min to ensure homogeneity. The mixture was next compacted in a cylindrical mold (101.6 mm in diameter and 116.3 mm in height) under the modified Proctor energy (ASTM-D1557-12, 2012) for the Unconfined Compression Strength (UCS) test. The samples were dismantled, wrapped within vinyl sheet and then cured at room temperature (RT) ($20 - 25^{\circ}$ C) for 7 days and 28 days.

UCS is considered as one of the most important design parameters in road construction and earthwork applications (Yarbaşı et al., 2007). The UCS of the samples was determined in accordance with ASTM D 1633 (ASTM-D1633, 2007) using a compression machine with a strain rate of 0.5%/min. The samples after 7 and 28 days of curing soaked in water for 2 hours and then were air-dried for 1 hour prior to UCS test according to the specifications of the Department of Highways, Thailand (DOH, 2000). The water absorption of 28 days cured samples was also measured every one hour during soaking.



(a)

(b)

Figure 4.3 SEM image of: (a) FA and (b) RAP.

4.2.3 Wetting and drying (w-d) test

Standard wetting and drying test methods for compacted soil-cement mixture (ASTM-D559/D559M-15, 2015) was adopted for the sample preparations. 28-day samples were selected for wetting and drying (w-d) tests and were submerged in potable water at room temperature for 5 hours. They were then dried in an oven at 70°C for 42 hours and air-dried for 1 hour. This procedure constitutes one w-d cycle (48 h). The weight loss of the samples was recorded by weighting at each w-d cycle. At the targeted w-d cycles, the samples again were immersed in water for 2 hours and then air-dried for at least 1 hour prior to the UCS test. The UCS of the samples were measured at 1, 3, 6, 9, 12, 15, and 20 w-d cycles and compared with that of the samples without w-d cycle to investigate the effect of w-d cycles on the UCS.

4.2.4 Mineralogical and microstructural analyses

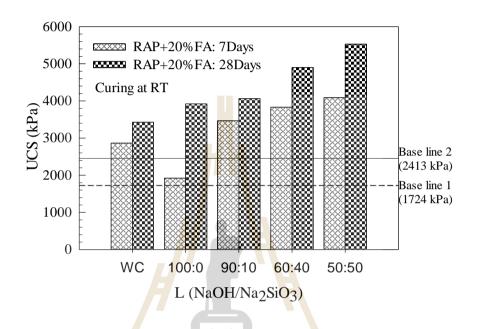
The micro-structure change of RAP-FA geopolymer and RAP-FA blend samples was examined using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to indicate the mineralogical and microstructural changes before and after the w-d cycles. Small fragments were taken from the broken portion of the UCS samples and separated into two portions. One was frozen at -195°C immersion in liquid Nitrogen for 5 minutes and coated with gold for SEM analysis using JEOL JSM-6400 device (Sukmak et al., 2013a). The other portion was air-dried and further processed to produce finer than 75 μ m powder for XRD analysis. The traces were obtained by scanning at 0.1°(20) per min and at steps of 0.05°(20).

4.3 **Results and discussion**

4.3.1 Unconfined Compression Strength (UCS)

Figure 4.4 summarizes the UCS results of RAP+20%FA blend and RAP+20%FA geopolymer at all NaOH/Na₂SiO₃ ratios (100:0 to 50:50) at the curing times of 7 days and 28 days. It clearly indicates that the UCS values of both the RAP+20%FA blend and RAP+20%FA geopolymer increase with curing time. This is notably similar to previous studies on strength development of cement-stabilized RAP (Suebsuk et al., 2014; Teha et al., 2002) and FA-stabilized RAP (Saride et al., 2015b; Saride et al., 2015a). The 7-day UCS value of RAP+20%FA blend was greater than the strength requirement specified by the Thailand national road authorities in which UCS > 1,724 kPa and UCS > 2,413 kPa for both low and high volume roads, respectively (DOH, 2000; DRR, 2013). Hoy et al. (2016a) explained that the UCS of RAP-FA blend increased with time due to the growth of Calcium Silicate Hydrate (C-

S-H) and Calcium Aluminate Hydrate (C-A-H) resulted from the chemical reaction between a high amount of calcium in RAP and high amount of silica and alumina in FA.





geopolymer cured for 7 days and 28 days at room

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temperature condition.

The strength development of RAP-FA geopolymers on the other hand, depends on alumino-silicate FA, liquid alkaline activator ($L = NaOH/Na_2SiO_3$ ratios) and heat condition (temperature and duration). The early strength gains of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 100:0 (without Na₂SiO₃) is relatively slow. However, its UCS increases remarkably with time (Figure 4.4). The higher Na₂SiO₃ content results in faster geopolymerization reactions and more geopolymer products (N-A-S-H gels). Hence, the UCS of RAP-FA geopolymer is higher than that of RAP-FA blend when NaOH/Na₂SiO₃ < 90:10. The highest and lowest UCS values of RAP-FA geopolymer were found at NaOH/Na₂SiO₃ ratios of 50:50 and 100:0, respectively.

4.3.2 Strength after wetting-drying process

The durability against wetting-drying (w-d) cycles was performed on RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 as well as RAP+20%FA blend after 28 days of curing to investigate the effect of NaOH/Na₂SiO₃ ratio on the strength, mineralogical, and microstructural properties.

The UCS of RAP+20%FA blend and RAP+20%FA geopolymer at various number of w-d cycles, *C* is presented in Figure 4.5. The UCS of RAP+20%FA blend and RAP+20%FA geopolymer evidently increases with increasing *C*, up to C = 6 and then decreases when C > 6. Previous research, which investigated the effect of w-d cycles on strength development of an FA stabilized with lime and gypsum, also indicated the strength increase due to the development of cementitious compounds during the w-d process (Sivapullaiah & Moghal, 2010). The UCS of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 increase sharply after the first w-d cycle and is much higher than that of compacted RAP+20%FA blend for all *C* tested. Although the RAP+20%FA geopolymer sample with NaOH/Na₂SiO₃ = 50:50 possesses higher UCS than the sample with NaOH/Na₂SiO₃ = 100:0 within the first 2 w-d cycles, it as lower UCS when C > 6.

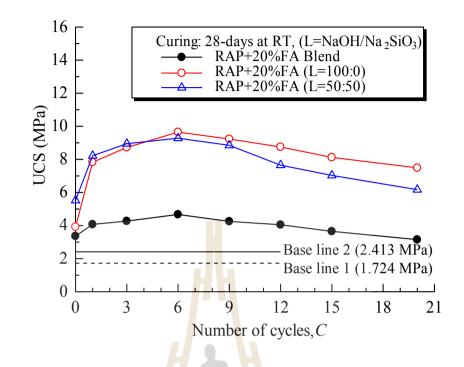


Figure 4.5 Relationship between strength and number of w-d cycles of RAP+20%FA blend and RAP+20%FA geopolymers.

Figure 4.6 shows the relationship between water absorption and soaking time of RAP+20%FA geopolymer and RAP+20%FA blend after 28 days of curing. Evidently, the water absorption of RAP+20%FA blend and RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 is very low and lower than 1% for all tested *C*. Kuosa and Niemeläinen (2013) reported that the water absorption for pavement materials is normally < 1%.

The water absorption of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 50:50 and RAP+20%FA blend are similar and noticeably much lower than that RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 100:0. The high water absorption of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 100:0 is possibly due to the cracks developed by a higher heat temperature generated by higher NaOH content during the wetting-drying processes.

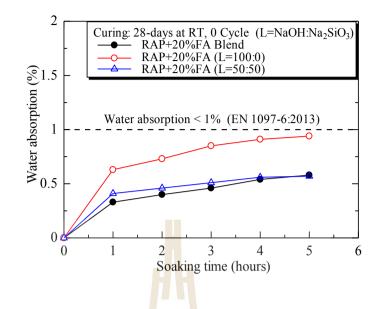


Figure 4.6 Relationship between water absorption and soaking time of

RAP+20%FA blend and RAP+20%FA geopolymers.

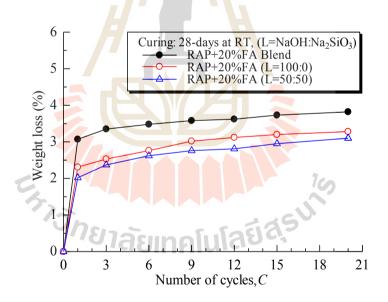


Figure 4.7 Relationship between weight loss and number of w-d cycles of RAP+20%FA blend and RAP+20%FA geopolymers.

The relationship between the weight loss of RAP+20%FA geopolymer and the RAP+20%FA blend versus number of w-d cycles, *C* is illustrated in Figure 4.7. The weight loss of both RAP+20%FA geopolymer and RAP+20%FA blend remarkably increase within the first w-d cycle and thereafter gradually increase with an increase in *C*. It is noted that the weight loss of RAP+20%FA geopolymer for both NaOH/Na₂SiO₃ ratios is lower than that blend sample due to the stronger RAP-FA bonding structure.

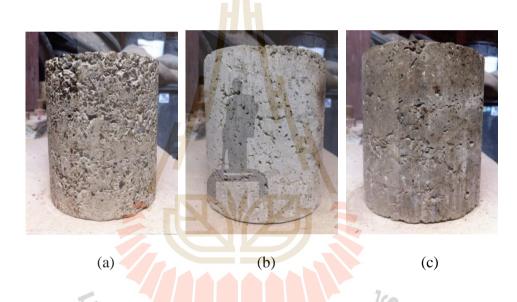


Figure 4.8 Photos of (a) RAP+20%FA blend, (b) RAP+20%FA geopolymer (NaOH/Na₂SiO₃ = 100:0), and (c) RAP+20%FA geopolymer (NaOH/Na₂SiO₃ = 50:50) at C = 20.

The effect of cyclic w-d cycles on the external surface of the RAP+20%FA blend and RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 is evident in

Figure 4.8a, b, and c, respectively at a particular C = 20. Large macrocracks and surface deterioration on the RAP+20%FA blends are clearly observed, which leads to strength loss. On the other hand, Figure 4.8b obviously shows the minimum cracks on the surface of the RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 100:0, while more cracks are observed for NaOH/Na₂SiO₃ = 50:50 (Figure 4.8c). This implies that the sample at NaOH/Na₂SiO₃ = 100:0 has stronger RAP-FA bonding structure than the sample at NaOH/Na₂SiO₃ = 50:50. From the cyclic w-d results and the photos, it is evident that RAP+20%FA blend provides a fairly good durability when subjected to w-d cycles. FA geopolymer can enhance the durability of RAP-FA material, especially for the sample at NaOH/Na₂SiO₃ = 100:0.

4.3.3 Mineralogical and microstructural changes

The XRD patterns of RAP+20%FA blend at various *C* are shown in Figure 4.9. Without w-d cycle (C = 0), the RAP+20%FA blend (Figure 4.9a) contains the amorphous phases of Calcium Magnesium as the predominant minerals in RAP as well as new cementitious minerals (Silica- and Alumina-products), such as Anorthite, Diopsite, Ladradorite, and Ettringite. These new minerals are formed when RAP is mixed with FA (RAP-FA blend), as evidenced by comparing Figure 4.3 (RAP) and Figure 4.9a (RAP-FA). In other words, the chemical reaction between the high amount of silica and alumina of FA and high amount of Calcium of RAP results in the formation of Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-

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A-H), similar to the hydration of Portland cement (Cristelo et al., 2012; Hanjitsuwan et al., 2014), that can enhance the strength development.

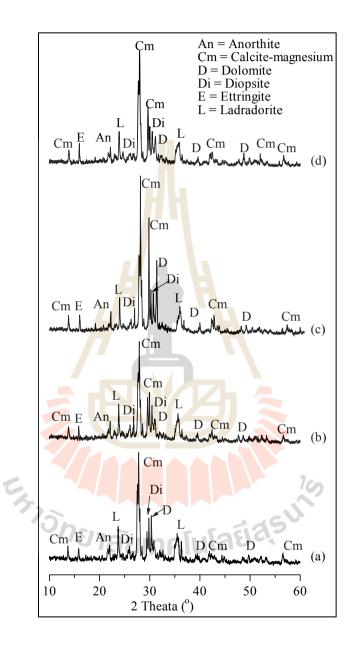
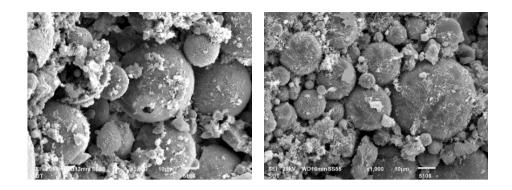


Figure 4.9 XRD patterns of RAP+20%FA blend samples at:

(a) C = 0, (b) C = 1, (c) C = 6, and (d) C = 12.

The increase in peaks corresponded to Anorthite, Diopsite, and Ladradorite with increasing *C* to 6 is observed by comparing Figure 4.9b (*C* = 1) with Figure 4.9c (*C* = 6), that indicates the increase of C-S-H and C-A-H. Drying at 70°C for w-d test evidently enhances the cementitious products (C-A-S-H) (Brue et al., 2012; Jiang & Yuan, 2013); i.e., an increased temperature results in a faster moisture diffusivity of the cementitious materials and hence cement hardening (Drouet el al., 2015; Jooss & Reinhardt, 2002; Wang et al., 2016). The same is however not true for *C* > 6. The temperature affects the water physical properties (density and surface tension) (Wu et al., 2014) and causes the coarsening of the pore structure in relation to Ettringite dissolution and C-S-H alteration (Brue et al., 2012).

The XRD patterns of RAP+20%FA blend in Figure 4.9d indicates the presence of Ettringite and the decreased intensity of Anorthite and Diopsite minerals when the samples are subjected to 12 w-d cycles. Ettringite is a hydrous mineral that exhibits expansive behavior upon wetting (Celik & Nalbantoglu, 2013; Little et al., 2009) and makes the RAP-FA blends potentially volumetrically unstable (Aldaood et al., 2014; Rahmat & Kinuthia, 2011). As result, the strength reduction of RAP+20%FA blend was observed.



(a)



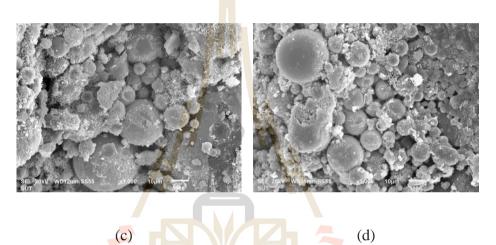


Figure 4.10 SEM images of RAP+20% FA blend samples at:

(a) C = 0, (b) C = 1, (c) C = 6, and (d) C = 12.

Besides the XRD results, SEM images of RAP+20%FA blend at various *C* are illustrated in Figure 4.10. The growth of C-S-H and C-A-H gels inner and on the spherical surface of FA with increasing C (C = 0 to 6, see Figure 4.10a-c) is observed while reduction in cementitious gel at the C = 12 (Figure 4.10d) is detected, which confirms the XRD results.

Figure 4.11 and 4.12 presents the XRD patterns of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 and various w-d cycles, respectively. As a result of the alkaline activation, new geopolymerization products inclusive of Albite, Nepheline, and Analcime are observed at the broad hump between $22-33^{\circ}20$ in the XRD pattern of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 100:0 (Figure 4.11a) and at NaOH/Na₂SiO₃ = 50:50 (Figure 4.12a) for *C* = 0. Albite and Analcime contribute to the strength enhancement of the geopolymer matrix once FA is activated by NaOH (Chen & Brouwers, 2010; Kupwade-Patil & Allouche, 2013).

A good performance of geopolymer was observed when the precursor was in contact with the alkaline activator at curing temperature of $40-75^{\circ}$ C (Chindaprasirt et al., 2007; Pangdaeng et al., 2014; Sukmak et al., 2013b). Therefore, the C-S-H and C-A-H from the RAP-FA blend co-exist with the geopolymer products (N-A-S-H) and contribute to the additional strength development of the RAP+20%FA geopolymers within the first 6 w-d cycles as presented in Figure 4.5. the silica present in sodium silicate is highly soluble and consequently incorporated immediately into the N-A-S-H formation, hence more geopolymerization products are detected in the XRD patterns of RAP+20%FA geopolymer sample at NaOH/Na₂SiO₃ = 50:50 (Figure 4.11b and c) compared with those at NaOH/Na₂SiO₃ = 100:0 (Figure 4.12b and c). Consequently, the UCS values of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ = 50:50 are higher than those at NaOH/Na₂SiO₃ = 100:0 within the first 6 w-d cycles (see Figure 4.5).

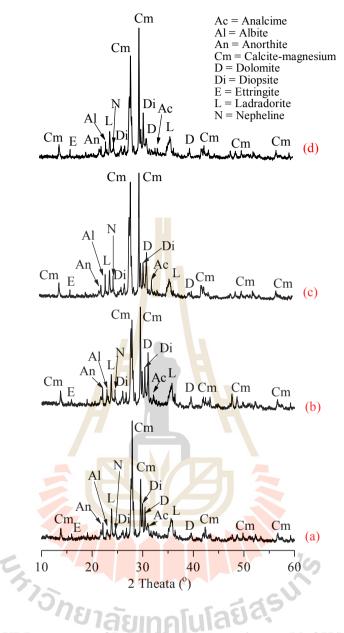


Figure 4.11 XRD patterns of RAP+20%FA geopolymer (NaOH/Na₂SiO₃ = 100:0)

samples at: (a) C = 0, (b) C = 1, (c) C = 6, and (d) C = 12.

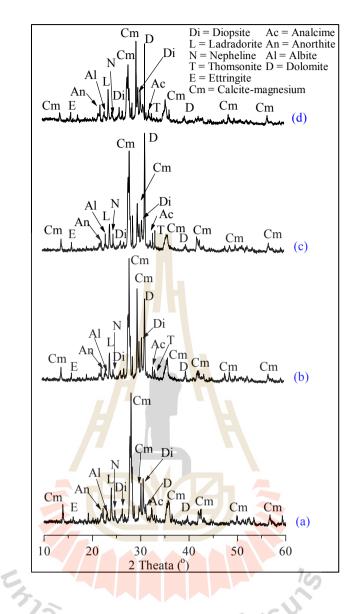


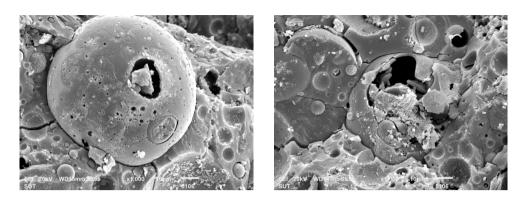
Figure 4.12 XRD patterns of RAP+20% FA geopolymer (NaOH/Na₂SiO₃ = 50:50) samples at: (a) C = 0, (b) C = 1, (d) C = 6, and (d) C = 12.

The SEM images of RAP+20%FA geopolymer at NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 (Figure 4.13 and 4.14) were examined to support the XRD results. Morphology change of RAP+20%FA geopolymer samples was observed at different w-d cycles. With increasing w-d cycles, the NaOH solution could dissolve more silica and alumina from both inside and outside of FA shell to generate the

geopolymerization products (comparing Figure 4.13b-c with 13a and Figure 4.14b-c with 14a) and results in strength development. The geopolymerization products in the sample at NaOH/Na₂SiO₃ = 50:50 are more than those in the samples at NaOH/Na₂SiO₃ = 100:0 for C < 6.

For C > 6, at a particular C = 12, the micro-cracks are clearly observed in RAP+20%FA geopolymer samples (Figure 4.13d and 4.14d) along with high amount of cementitious products (Figure 4.11d and 4.12d). The decrease in water content (absorbed in wetting state) during drying process increases suction forces until the tensile stress is equal to the cohesion (Aldaood et al., 2014); and thereby results in the crack formation and degradation on the external surface of the samples as shown in Figure 4.8. Hence, formation of significant external surface cracks results in internal micro-cracks (Figure 4.13d) leading to a strength loss.

It is noted that the samples at NaOH/Na₂SiO₃ = 50:50 (Figure 4.14d) has more micro-cracks than the sample at NaOH/Na₂SiO₃ = 100:0 (Figure 4.13d). Consequently, the rate of strength reduction of the sample at NaOH/Na₂SiO₃ = 50:50 is higher than that of the sample at NaOH/Na₂SiO₃ = 100:0 when C > 6. This indicates that the RAP+20%FA geopolymer with NaOH/Na₂SiO₃ = 100:0 has higher durability against w-d cycles than that with NaOH/Na₂SiO₃ = 50:50. This finding is similar to previous studies (Bakharev, 2005a, 2005b) reported that the FA geopolymer material prepared by sodium hydroxide solution as an activator exhibited better performance compared with the materials prepared with sodium silicate and potassium hydroxide solution. The high durability is attributed to the formation of stable cross-lined alumino-silicate polymer structure.



(a)



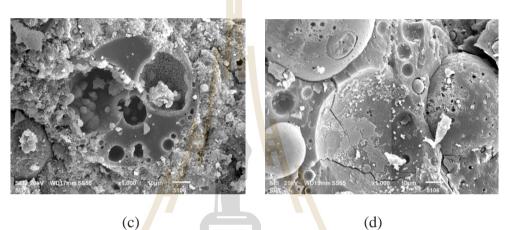
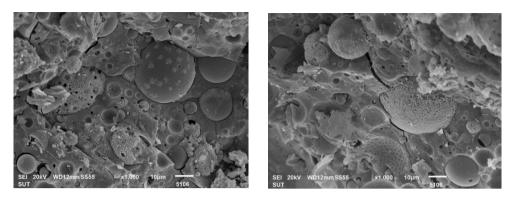


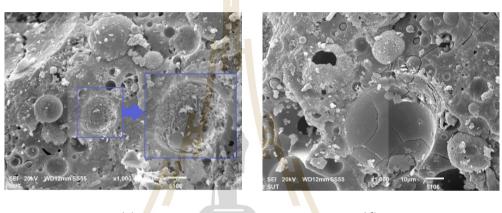
Figure 4.13 SEM images of RAP+20% FA geopolymer (NaOH/Na₂SiO₃ = 100:0) samples at: (a) C = 0, (b) C = 1, (c) C = 6, and (d) C = 12.

From a geotechnical engineering perspective, besides having a high UCS, the RAP-FA blend exhibits good durability against w-d cycles, that can be attributed to the growth of C-S-H and C-A-H during the w-d processes. The short-term and long-term UCS and durability of the RAP-FA material can be improved significantly with the FA geopolymer that is advantageous for applications requiring high durability properties. The RAP-FA geopolymer is found to be durable and with a positive impact on the environment that enables its application in sustainable civil engineering infrastructures.



(a)





(c)

(d)

Figure 4.14 SEM images of RAP+20% FA geopolymer (NaOH/Na₂SiO₃ = 50:50)

samples at: (a) C = 0, (b) C = 1, (c) C = 6, and (d) C = 12.

4.4 Conclusion

The present study investigated the durability of the RAP-FA blend and RAP-FA geopolymer as a sustainable pavement material. The outcome of this research is to promote the use of recycled waste material in road construction, with economic and environmental benefits. The following conclusions can be drawn from this study: When subjected to w-d cycles, the UCS of RAP+20%FA blend increases with increasing the number of w-d cycles (*C*) up to 6 cycles and then decrease. The XRD and SEM analyses indicated that for C < 6, the w-d cycles increase the strength of RAP+20%FA blend due to the growth of C-S-H and C-A-H due to the chemical reaction between high amount of calcium in RAP with high amount of silica and alumina in FA. With C > 6, large cracks due to the loss of moisture content during drying stage, lead to reduction in UCS of RAP+20%FA blend. However, even with the strength reduction after C = 6, its 20-days cycle UCS value is still greater than the minimum strength requirement specified by Thailand national road authorities.

The short-term and long-term strength as well as durability of the RAP-FA base material can be improved significantly by FA geopolymerization. As a result of alkaline activator, the w-d cycles strongly enhance the degree of geopolymerization reactions, generating more geopolymer products (N-A-S-H gels). The XRD and SEM analyses of RAP+20%FA geopolymer when C < 6 indicate that the N-A-S-H phases increase with an increase in *C* and co-exist with C-S-H and C-A-H that results in a significant strength increase of RAP+20%FA geopolymer.

Similar to the RAP-FA blend, the developed large cracks at C > 6 cause reduction in UCS values in the RAP-FA geopolymer. The external surface cracks and micro-cracks in the samples are larger for lower NaOH contents. Therefore, the strength reduction of the samples at NaOH/Na₂SiO₃ = 50:50 is higher than the sample at NaOH/Na₂SiO₃ = 100:0. In other words, the RAP-FA geopolymer with higher NaOH content evidently exhibits better durability performance that can be attributed to the formed stable cross-lined alumino-silicate polymer structure. From an environmental perspective, this study confirms the potential use of the RAP-FA blend and RAP-FA geopolymers as a sustainable pavement base material, with high durability performance. The use of these recycled materials furthermore results in significant energy saving and reduction in greenhouse gas emission.

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CHAPTER V

TOXIC LEACHING INVESTIGATION OF RECYCLED ASPHALT PAVEMENT – FLY ASH GEOPOLYMER

5.1 Introduction

Highway construction is an important aspect in infrastructure construction in many developed and developing countries. Highway construction however consumes a large amount of natural aggregates, particularly in their pavement base/subbase layers. As a result, the quantities and gravel pits are increasingly exploited as a source of pavement materials, which notably leads to subsequent devastating of natural environmental resources.

The urgent need for new environmentally friendly solutions has made researchers explore new alternative materials that reduce energy consumption, and greenhouse gas emissions. Sustainable strategies increasingly pursued which have less environmental impact and which will lead to more efficient use of natural resources (Moreno et al., 2012). An important environmental strategy increasing sought by the pavement designer and road construction industry is the use of recycled materials in pavement base/subbase.

Several researchers have in recent years investigated the usage of recycled and/or waste materials as the substitutes for natural quality materials in the civil infrastructure applications, such as in pavements base/sub-base, footpaths and embankments application. Materials such as recycled glass (Disfani et al., 2012; Grubb et al., 2006; Wartman et al., 2004), melamine debris (Donrak et al., 2016), recycled concrete aggregate (Poon & Chan, 2006; Tam, 2009), recycled asphalt pavement (RAP) (Arulrajah et al., 2013; Puppala et al., 2011; Suebsuk et al., 2014), and various other forms of recycled construction and demotion (C&D) materials (Arulrajah et al., 2012) have been recently evaluated for embankment, pavement, footpath, and pipe-bedding applications (Rahman et al., 2014).

Calcium carbide residue is a by-product of the acetylene production process and has been established as binder for soil stabilization (Horpibulsuk et al., 2012; Horpibulsuk et al., 2011; Kampala et al., 2013; Phetchuay et al., 2016; Phummiphan et al., 2016). Water treatment sludge and fly ah have been used to manufacture sustainable geopolymer masonry units (Horpibulsuk et al., 2015; Suksiripattanapong et al., 2015b; Suksiripattanapong et al., 2015a).

Recently, Hoy et al., (2016) reported on the novel low-carbon geochemical stabilization of RAP for pavement base/subbase applications, namely with a Recycled Asphalt Pavement – Fly Ash geopolymer (RAP-FA geopolymer). A large amount of RAP, of up to 80% could be used as a coarse aggregate. A liquid alkaline activator (L), a mixture of sodium hydroxide solution (NaOH) and sodium silicate solution (Na₂SiO₃), was used to synthesis the RAP-FA geopolymer, while for the RAP-FA blend, a mixture of RAP, FA, and water was prepared as a control material to investigate the effect of L on strength development. Both the RAP-FA blend and RAP-FA geopolymer products were found to be viable in pavement base application as their Unconfined Compression Strength (UCS) results were greater than the minimum strength requirement specified by the Department of Highway, Thailand.

Though the utilization of recycled waste materials in highway construction can be considered as having significant impacts on resource management, the hazardous compounds that can leach out and pollute the water resource should also be considered (Dawson., 2009). A range of heavy metals and other pollutions including oil and/or organic micro-contaminants may be present in the recycled material and should be ascertained for pavement base applications (Apul et al., 2002; Dawson et al., 2006; Hill, 2004; Olsson, 2005).

Sherwood. (2001) studied the usage of alternative materials in road construction and indicated that contamination depends on the concentration of the toxic substance and the quantity of material being used. Sherwood. (2001) furthermore reported that water pollution could arise where embankments were constructed close to the ground water sources and when drainage from the road embankments discharges directly into a watercourse, resulting in serious impacts on aquatic life. Similar works by Dawson. (2009); Disfani et al. (2012); and Arulrajah. et al. (2015) on the flow water balance in road construction revealed that the infiltration and seepage from the road surface would occur in the road structure, which will lead to chemical reaction with materials in the various road layers and the underlying soil. This phenomenon can be illustrated in Figure 5.1.

Literature (Gupta et al., 2009; Legret et al., 2005) showed that there was the potential leaching of contaminants resulting from RAP itself as well as the pulverization of the binder or additives used to stabilize RAP in road construction applications. The contamination is primarily related to pH, Polycyclic Aromatic Hydrocarbons (PAH), and variety of metals. A dual channel pH conductivity meter was used to read the pH of free water by soaking 100% RAP and cement-treated RAP

samples (Hoyos et al., 2008; Hoyos et al., 2011). The neutral pH values of approximately 6 to 7 of 100% RAP were found while the pH of cement-treated RAP and cement-treated RAP with fiber tends to increase with an increase in cement dosage. (Li et al., 2008) studied the utilization of RAP with 10% of class C fly ash for a road base construction and reported that leachate from this blend raged from 6.9 to 7.5.

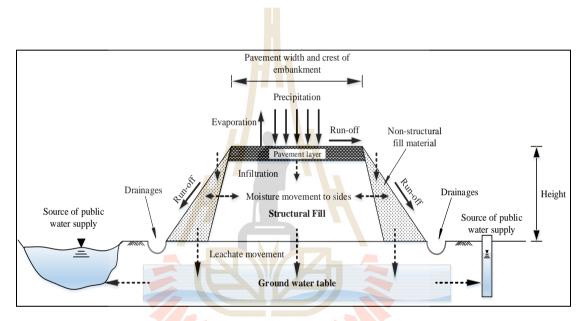


Figure 5.1 A schematic diagram of water flow balance and possible contaminate targets (not to scale).

Kang et al. (2011) studied the leachate assessment of various recycled materials, including Reclaimed Concrete Aggregate (RCA), FA, and RAP. It was found that pH levels in RAP leachate were7.57 and 9.67 for unsaturated leachate tests and batch tests, respectively. When FA was added in RAP + RCA, the pH values were 9.7 and 10.99 for the 5%FA + 25%RAP + 70%RCA and 15%FA + 75%RAP + 10%RCA. The authors concluded that when up to 5% of FA content was used, an insignificant substantial leaching of metals apart from aluminum took place.

Moreover, the mixtures containing 15%FA resulted in considerable leaching of metals as the residence time increased.

Shedivy et al., (2012) performed laboratory batch leachate tests on RAP by using both Toxicity Characteristic Leaching Procedure (TCLP) fluid and deionized water. The results showed that the PAH levels included acenaphthalene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(ghi)perylene which were very close to the U.S. EPA drinking water standards.

Though suitable mechanical properties of RAP-FA blend (Li et al., 2009; Mohammadinia et al., 2016; Wen et al., 2010) and RAP-FA geopolymer (Hoy et al., 2016) have been previously reported by several authors, the limited knowledge of the environmental risks of these materials remain as primary barriers to their reuse in pavement applications. Therefore, in this research, the most reliable leachate tests to estimate the contaminant concentration in the seepage water (Susset & Grathwohl, 2011), which provide information about the impacts on groundwater in the life cycled of the projects (Hellweg et al., 2005) were undertaken to cover the knowledge gap on possible environmental risks of using RAP-FA blend and RAP-FA geopolymer in road work application. The outcomes of this research will facilitate the move toward increased usage of recycled material worldwide in pavement base/subbase applications.

5.2 Materials and sample preparation

5.2.1 Materials

RAP samples, obtained from a mill asphalt pavement stockpile in Nakhon Ratchasima province, Thailand were used in this research. The gradation and the basic engineering properties of air-dried RAP is shown in Figure 5.2 and Table 5.1, respectively. The asphalt content in RAP aggregates is approximately 4 to 6% by weight. The mineral and chemical composition of RAP, obtained by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses, are presented in Figure 5.3 and Table 5.1, respectively.

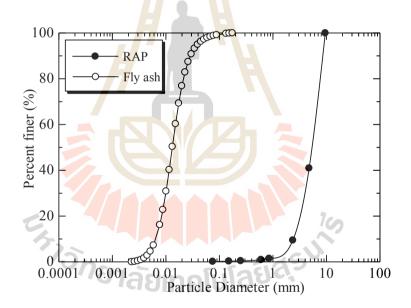


Figure 5.2 Grain size distribution of RAP and FA.

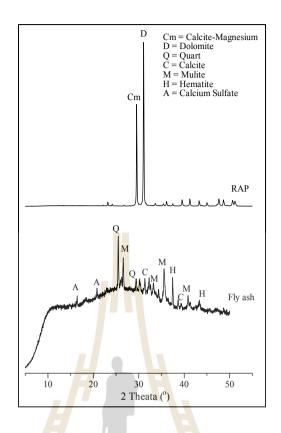


Figure 5.3 X-Ray Diffraction (XRD) pattern of RAP and FA.

The predominant mineral components in RAP are calcite-magnesium and ladradorite. The main chemical composition detected in RAP is 41.93% CaO and 36.11% MgO. This high percentage amount of calcium and magnesium in RAP can react with the high percentage amount of silica and alumina in FA for a stable pozzolanic reaction. The hazardous substance content of RAP detected by TCLP test is shown in Table 5.3.

Geotechnical parameters	Values	Test method
USCS classification	SP	ASTM-D2487-11
D ₁₀ (mm)	2.50	_
D ₃₀ (mm)	4.20	_
D ₅₀ (mm)	5.30	_
D ₆₀ (mm)	6.10	_
Cu	2.44	_
Cc	1.16	_
Specific gravity (G _s)	2.70	ASTM-D1883-07
CBR (%)	10-15	ASTM-D557-12
Water absorption (%)	6.80	_
Swelling ratio (%)	0.20	_
Maximum dry unit weight from	17.50	ASTM-D1557-12
modified compaction test (kN/m ³)	, · · ·	\$
Optimum water content from	4.10	ASTM-D1557-12
modified compaction test (%)	ย่สุรุง	

Table 5.1 Geotechnical Properties of Recycled Asphalt Pavement.

FA used in this study was obtained from the largest powerplant, Mae Moh power plant in the northern region of Thailand. The grain size distribution curve of FA and chemical composition, obtained by laser particle size and XRF analysis, are shown in Figure. 5.1 and Table 5.2, respectively. FA is composed mainly of 40.10% SiO₂, 20.12% Al₂O₃, 6.48% Fe₂O₃, and 12.68% CaO. Therefore, in accordance with

ASTM C 618 (ASTM-C618, 2012), it is classified as Class C, high calcium fly ash (CaO > 10%).

The peaks of main amorphous phase, including calcium sulfate, quartz, calcite, mulite, and hematite are detected by X-Ray Diffraction (XRD) analysis in the region of 15-40°2θ as demonstrated in Figure 5.3. The fine and spherical morphology of FA particles and irregular shape of RAP particle obtained by Scanning Electron Microscopy (SEM) analysis, are presented in Figure 5.4.

Chemical formula	RAP (%)	FA (%)
SiO ₂	3.11	39.12
Al ₂ O ₃	4.73	20.51
Fe ₂ O ₃	0.10	5.83
CaO	41.93	12.41
MgO	36.11	2.49
SO ₃	0.89	0.49
Na ₂ O	N.D.	0.67
K ₂ O	0.04	1.53
LOI	N.D.	0.41

 Table 5.2 Chemical composition of RAP and FA.

Note: N.D. = not detected.

The liquid alkaline activator (L) is a mixture of sodium silicate (Na₂SiO₃) type CR 53, which is composed of Na₂O (14.50-16.50%) and SiO₂ (31.50-34.00%) by weight, and sodium hydroxide (NaOH) solution with a 10 M concentration. A 10 M concentration was selected based on the previous research (Chindaprasirt et al., 2009), which studied on the strength development of fly ash geopolymer mortar and indicated that 10 M concentration was the optimum NaOH content. In addition, a high concentration of NaOH used may affect the human hazard.

	Samples of acid leachate extraction (mg/L)				
	Samples of actu reachate extraction (mg/L)				
	100%RAP	RAP-FA	RAP-FA	RAP-FA	
Parameter		blend	geopolymer	geopolymer	
			(NaOH/Na ₂ SiO ₃ =	(NaOH/Na ₂ SiO ₃ =	
		E V	100:0)	50:50)	
рН	5.12	5.59	7.59	7.44	
Arsenic	<0.01	<0.01	BDL	BDL	
Cadmium	BDL	BDL	BDL	BDL	
Chromium	<0.05	<0.05 JNA	<0.05	<0.05	
Copper	BDL	BDL	BDL	BDL	
Lead	BDL	BDL	BDL	BDL	
Mercury	BDL	BDL	BDL	BDL	
Nickel	< 0.05	0.051	< 0.05	<0.05	
Zinc	1.348	0.657	BDL	BDL	
Note: BDL = Below Detection Limit					

Table 5.3 Leachate analysis of 100% RAP, RAP+20% FA blend, and geopolymer.

5.2.2 Sample preparation

The RAP-FA geopolymer was a combination of RAP, FA, and L (NaOH + Na₂SiO₃). The NaOH/Na₂SiO₃ ratios studied were 100:0, 90:10, 60:40, and 50:50. The RAP-FA blend, which is a mixture of RAP, FA, and water, was prepared as a control material to compare the effect of L on strength development and environmental risk. According to a previous study (Hoy et al., 2016), FA replacement ratios at 20% by weight of RAP were reported to be the optimal proportion. This ratio was then fixed in this investigation for both RAP-FA geopolymer and RAP-FA blends. The mixing procedure started with mixing air-dried RAP and FA for 5 min and then the mixture was divided into two portions. One was activated by for RAP-FA geopolymer and the other was mixed with water for an additional 5 min to ensure the homogenous mixing.

5.3 Experimental program

5.3.1 Compaction test

The compaction test was performed under the modified Proctor procedure according to the ASTM Method B (ASTM-D1557, 2012) to determine the water content, dry unit weight, and total unit weight of 100% RAP, RAP-FA blend, and RAP-FA geopolymer at various NaOH/Na₂SiO₃ ratios as well as the mixtures. The cylindrical mold was 101.6 mm in diameter and 116.3 mm in height. Once the compaction curves were obtained, the RAP-FA geopolymer samples at each NaOH/Na₂SiO₃ ratio were prepared at Optimum Liquid alkaline activator Content (OLC) and the RAP-FA blend samples were prepared at Optimum Water Content (OWC) for UCS tests.

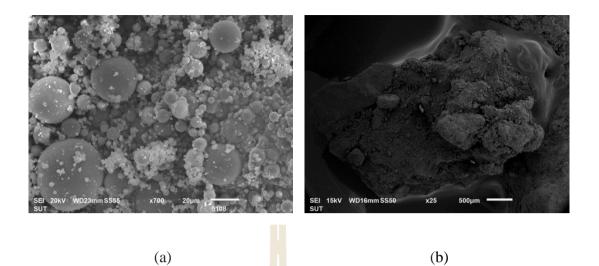


Figure 5.4 SEM image of: (a) FA and (b) RAP.

5.3.2 Unconfined Compression Strength (UCS) test

The unconfined compression strength (UCS) of the samples was measured in accordance with ASTM D 1633 (ASTM-D1633, 2007) using a compression machine with a strain rate of 0.5%/min. The samples were dismantled from the cylindrical molds, then wrapped within a vinyl sheet and cured at room temperature for 7 days and 28 days. When the samples reached the pre-planned curing conditions, they were soaked in water for 2 h and then were air-dried for 1 h prior to UCS tests according to the specification of the Department oh Highway, Thailand (DOH, 2000).

5.3.3 Scanning Electron Microscopy (SEM)

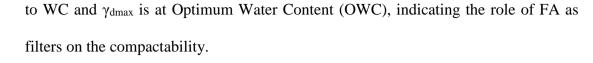
Scanning Electron Microscopy (SEM) analysis was performed to investigate the UCS development of RAP-FA geopolymer and RAP-FA blend. The small fragments were taken from the broken portion of the UCS samples and then frozen at -195° C by immersion in liquid nitrogen for 5 min and coated with gold prior to conducting SEM (JEOL JSM – 6400 device) analysis (Sukmak et al., 2013a).

5.3.4 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test is the method prescribed by the US EPA guidelines to determine if the solid waste is hazardous (Townsend, 1998). The TCLP tests were assessed on 100% RAP, RAP + 20% FA blend, and RAP + 20% FA geopolymer at the NaOH/Na₂SiO₃ ratios of 100:0 and 50:50 for different types of heavy metal. (Napia et al., 2012) studied the leaching of heavy metals from solidified waste and indicated that the leachability reduced when sample age increased. Thus, in this study the early 7 days cured samples were crushed to smaller particles of <9.5 mm for the leachate tests. The crushed sample was extracted using an acetic acid solution (pH = 4) in a volume with a solid to liquid ratio of 1:20. The mixture was agitated for 18 h in the extraction vessels, which were rotated in an end-over-end manner at 30 rpm. The leachate was then filtered through a 0.45-µm membrane filter to remove suspended solids and divided into two portions. One portion was used for a pH measurement, and the other was used for the determination of the metals present in the leachate by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The average values form each extraction were obtained by testing in triplicated samples to ensure the data consistency (Asavapisit et al., 2005).

5.4 Results and discussion

Figure 5.5 shows the relationships between dry unit weight (γ_d) and water content (WC) of the compacted 100% RAP, RAP + 20%FA blend, and between total unit weight (γ_t) and L content of the compacted RAP + 20%FA geopolymer at various NaOH/Na₂SiO₃ ratios. It was observed that the γ_d of 100% RAP (without FA) is not sensitive to WC (Figure 5.5a) while γ_d of RAP + 20%FA blend tends is more sensitive



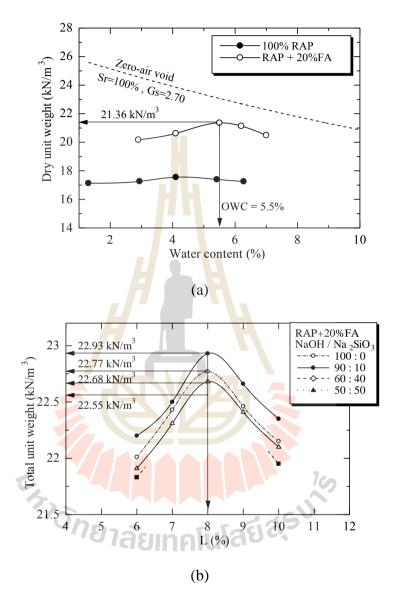


Figure 5.5 Compaction test results: (a) 100% RAP and RAP+20% FA blends,(b) RAP+20% FA geopolymer with 20% FA.

Although the γ_{dmax} of RAP + 20%FA geopolymer is dependent on NaOH/Na₂SiO₃ ratio, the OLC providing the maximum total unit weight (γ_{tmax}) is found to be the same for all NaOH/Na₂SiO₃ ratios (Figure 5.5b). The optimum NaOH/Na₂SiO₃ ratio of 90:10 provides the highest γ_{tmax} of RAP + 20%FA geopolymer, while the lowest γ_{tmax} is found at NaOH/Na₂SiO₃ ratios of 50:50.

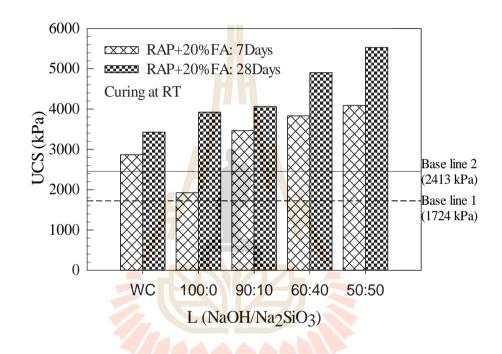


Figure 5.6 Compressive strength of RAP+20%FA blends and RAP+20%FA geopolymer cured for 7 days and 28 days at RT condition.

Figure 5.6 summarizes the UCS results of the RAP + 20%FA blend and RAP + 20%FA geopolymer for various NaOH/Na₂SiO₃ ratios (100:0 to 50:50) at the ages of 7 days and 28 days. It is clearly indicated that the UCS values of both RAP + 20%FA blend and RAP + 20%FA geopolymer increase with increasing curing time, which is similar to the previous studies on strength development of cement treated RAP (Suebsuk et al., 2014; Taha et al., 2002).

In addition, the stress-strain behavior of 7 days cured samples of RAP + FA blend and RAP + 20%FA geopolymer is presented in Figure 5.7. It is noted that the 7-day UCS value of RAP + 20%FA blend is greater than the strength requirement specified by the Thailand national road authorities in which UCS > 1724 kPa and UCS > 2413 kPa for low and high volume roads, respectively for cement stabilized materials (DOH, 2000; DRR, 2013).

Recent studies (Phoo-ngernkham et al., 2014; Somna et al., 2011; Sukmak et al., 2013b) have reported that the UCS development of geopolymer relies on the chemical reaction (geopolymerization reaction) between the precursor and alkali activator and heat condition (cured temperature and duration) of samples. At the onset of geopolymerization, the UCS of RAP + 20%FA geopolymer at NaOH/Na₂SiO₃ ratio = 100:0 cured for 7 days is lower than that of RAP + 20%FA blend. However, the UCS development of RAP+20%FA geopolymer is remarkable and the 28-day UCS is greater than that compacted RAP + 20%FA blend (Figure 5.6). The UCS values of RAP-FA geopolymers (all NaOH/Na₂SiO₃ ratios) increase as the Na₂SiO₃ content increases and are higher than those of the compacted RAP + 20%FA blend. This indicates that the input of Na2SiO₃ can enhance the short-term strength of RAP-FA geopolymer which is advantageous for some applications required high early strength.

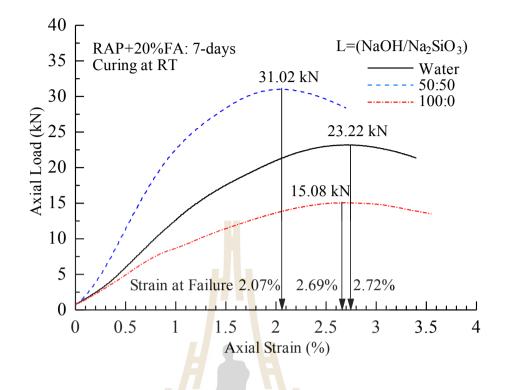
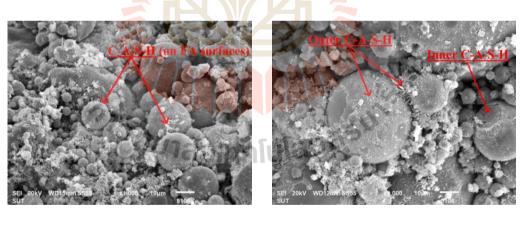


Figure 5.7 UCS Stress-Strain behavior of selected samples from 7-days RAP+20%FA blend and RAP+20%FA geopolymer.



(a)

(b)

Figure 5.8 SEM images of RAP+20%FA blend samples cured for (a) 7 days and (b) 28 days at RT condition.

In recent years, Scanning Electron Microscopy (SEM) has been proven to be a sophisticated scientific tool for developing models to ascertain the structure of the various cementitious gel formations. The microstructure morphology of the RAP + 20%FA blend and RAP + 20%FA geopolymer samples were investigated by SEM analysis. The SEM images of RAP + 20%FA blend samples cured for 7 and 28 days are illustrated in Figure 5.8. The main reaction products formed are Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H) gels whose composition of Ca/Si and Ca/Al ratios are detected by the SEM analysis. This finding has been found a model proposed by Glasser (1990) whose studies on cements, from micro- to macro-structures that C-A-S-H products generated by the nature of the anion in the solution form the reaction in the early stage of hydration, and in particular with regard to paste setting from high calcium.

The growth of C-A-S-H gels of RAP + 20%FA blend over time (see Figure 5.8a and b) can be attribute to the high amount of calcium and magnesium in RAP and the high amount of silica and alumina in FA (detected by XRD and XRF analyses depicted in Figure 5.3 and Table 5.2, respectively). This results in chemical products in the form of C-S-H and C-A-H similar to the hydration of Portland cement (Cristelo et al., 2012; Hanjitsuwan et al., 2014). Consequently, the UCS of RAP + 20%FA blend increases with increasing curing time (see Figure 5.6).

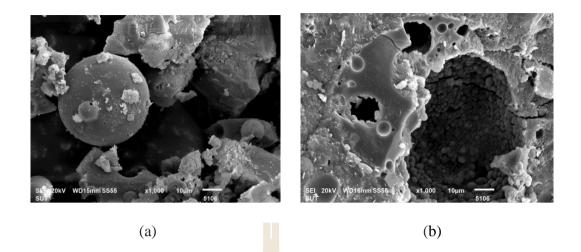


Figure 5.9 SEM images of RAP+20%FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 cured for (a) 7 days and (b) 28 days at RT condition.

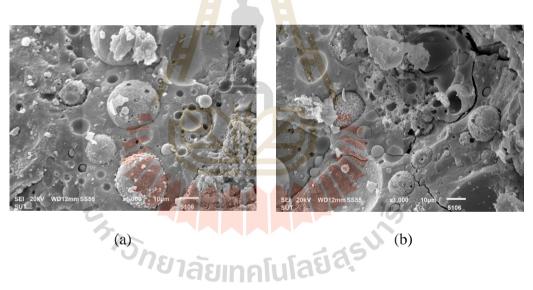


Figure 5.10 SEM images of RAP+20%FA geopolymer samples at NaOH/Na₂SiO₃

ratio of 50:50 cured for (a) 7 days and (b) 28 days at RT condition.

Figure 5.9a shows the SEM images of RAP + 20%FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 (without Na₂SiO₃) cured for 7 days. The roughly smoot and spherical surface of FA is clearly observed, which indicates the unreacted or partial alkali reaction between NaOH and FA and hence the low UCS of RAP + 20%FA geopolymer at early 7 days. This contributes to the low rates of the strength development when FA-geopolymer material is cured at ambient temperature of around 25°C (Guo et al., 2010). Fernández-Jiménez. and Palomo. (2009) studied the nanostructure of FA geopolymer and reported that when alkali activators came into contact with an aluminosilicate source, such as FA, the geopolymerization reactions began at a point on the FA surface and then expanded to form a larger hole until both the inside and outside of the spherical FA particle shell, was completely or almost completely consumed. Figure 5.9b demonstrates a clear evidence that with increasing curing time, NaOH solution can dissolve more silica and alumina from FA to raise alkalinity and accelerate the geopolymerization reaction. Consequently, the UCS of RAP + 20%FA geopolymerization at NaOH/Na₂SiO₃ = 100:0 increase remarkably.

Fernández-Jiménez. and Palomo. (2005) and Criado et al., (2007) reported that when sodium silicate was used as an alkaline activator, the highly soluble silica incorporated with leached silica and alumina from a alumino-silicate source to form the N-A-S-H gel and zeolite formation.

The SEM images of RAP + 20%FA geopolymer with NaOH/Na₂SiO₃ = 50:50 in Figure 5.10 clearly indicate that geopolymerization products (N-A-S-H gels) generated are more than those with NaOH/Na₂SiO₃ = 100:0 for the same curing time. Furthermore, the growth of formation of N-A-S-H gel and zeolite products with time is clearly detected around FA particles (comparing Figure 5.10a and b); hence, strength development over time.

Contaminant	Drinking water	Threshold for solid	Hazardous waste
	standards (EPA,	inert waste (EPA,	designation (Wartman et
	1999) (mg/L)	2009) (mg/L)	al., 2004) (mg/L)
Arsenic	0.05	0.35	5.0
Barium	2.0	35.0	100.0
Cadmium	0.005	0.1	1.0
Chromium	0.1	2.5	5.0
Lead	0.015	0.5	5.0
Mercury	0.002	0.05	0.2
Selenium	0.05	0.5	1.0
Silver	0.05	5.0	5.0
	6		10

Table 5.4 Comparison of TCLP data analysis with U.S. EPA Requirements.

Form environmental perspective, recycled material or solid inert waste material can be accepted in field applications, even due to rainfall or storm water events, if RAP-FA blends and RAP-FA geopolymer will not pose any risk to the ground water tables or water stream beyond. Therefore, in order to use the RAP-FA blends as well as RAP-FA geopolymer in road construction, the environmental risk assessment needs to be ascertained. Table 5.3 shows the leachate analysis of 100%RAP, RAP + 20%FA blend, and RAP + 20%FA geopolymer by using acetic leachate extraction. According to benchmark mandated by the U.S. Environmental Protection Agency (EPA) for storm-water sampling, pH values should be in the range of 6 to 9 (EPA, 2005). Leachate pH results show that pH level in 100% RAP is 5.12 and 5.59 for RAP + 20%FA blend. When FA-geopolymer is sued to stabilized RAP, pH values are 7.59 and 7.44 for RAP + 20%FA geopolymer at the NaOH/Na₂SiO₃ ratios of 100:0 and 50:50, respectively. These results indicate that all pH levels of 100% RAP and the mixtures are within allowable limits.

Table 5.4 presents the prescribed limits for drinking water and the threshold for hazardous waste defined by the U.S. Environmental Protection Agency (EPA, 1999, 2009). Wartman et al. (2004) reported that a material is designed as a hazardous waste in according to U.S. EPA if any detected metal is present I concentrations > 100 times the drinking water standards. Based on this criterion, the comparison of TCLP results between Table 5.4 and Table 5.3 indicated that all metal contaminates are within acceptable limits. Furthermore, TCLP results show that FA-geopolymer has effectiveness in reducing the leachability of metal concentrations (Arsenic and Zinc) (see Table 5.3). This is attributed to the net negative charge in the three-dimensional framework of SiO₄ and AlO₄ tetrahedral of FA-geopolymer, which is mainly composed of SiO₂, Al₂O₃, and Fe₂O₃, and is balanced by the exchangeable caption (Cheng & Bishop, 1992; Napia et al., 2012; Peralta et al., 1992). In other words, the metal ion uptake could mainly be contributed to the ion-exchanged reaction in the micro-porous minerals of zeolite (Erdem et al., 2004).

From an engineering perspective, the research results indicate that RAP is mechanically and economically viable for use in pavement base applications, when it is stabilized with 20% of FA. Furthermore, the early and long term strength and durability of RAP-FA base course can be improved with FA based geopolymer binder. The higher Na₂SiO₃ used in L can enhance the short-term UCS of RAP + 20%FA geopolymer, which is advantageous for applications required for high early strength gain. The laboratory test results indicate that besides good mechanical properties of RAP-FA blend and RAP-FA geopolymer, these materials provide a positive environmental impact as environmental test results show no significant risk to the ground water or stream water line. Moreover, FA-geopolymer stabilization of RAP material can effectively reduce metal concentrations, which is advantageous for some strict guidelines of using recycled or waste materials in road applications

5.5 Conclusion

This research attempts to promote the use of large quantities of RAP in pavement base applications. The geotechnical engineering and geoenvironmental laboratory evaluations were conducted in this research to ascertain the viability of using RAP-FA blend and RAP-FA geopolymer as a sustainable stabilized pavement course.

The outcomes of this research confirms the potential use of large amounts of RAP, up to 80% as a pavement base material, when treated with 20% FA (by weight of RAP) where the UCS of the blend meets the minimum strength requirement specified by the Thailand national road authorities. The SEM analysis of RAP-FA blend indicates the formation of Calcium Aluminate (Silicate) Hydrate (C-A-(S)-H), which is due to the chemical reaction between the high amount of calcium and magnesium of RAP and high amount of silica and alumina of FA. Furthermore, the short-term and long-term UCS of RAP-FA base can be improved with FA-geopolymer binder.

The geopolymerization products (N-A-S-H gel) are detected by SEM analysis of RAP-FA geopolymer. When a higher content of sodium silicate is used in L, its highly soluble silica can rapidly accelerate the leachate of silica and alumina form FA to generate the growth of N-A-S-H gel. Consequently, the coexistence of N-A-S-H and C-A-S-H from CaO and MgO (in RAP) and silica and alumina (in FA) results in the increase in UCS of RAP-FA geopolymer as the NaOH/Na₂SiO₃ ratio decreases. However, without Na₂SiO₃ (NaOH/Na₂SiO₃ = 100:0), SEM analysis shows the low geopolymerization products present in the RAP-FA geopolymer system. Moreover, with prolonged curing time, the NaOH solution is able to dissolve more silica and alumina from FA for geopolymerization reaction. Hence, the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ = 100:0 increases with time.

From an environmental perspective, the TCLP results indicate that both RAP + 20%FA blend and RAP + 20%FA geopolymer can be safely used in sustainable pavement base applications, as these materials pose no significant environmental and leaching hazard compounds into soil, surface and ground water resources.

In addition, the leachability of heavy metals was reduced when FAgeopolymer used to stabilized RAP, which is advantageous for some strict guidelines of using recycled or waste materials in road applications. This study indicates that both RAP-FA blend and RAP-FA geopolymer can be considered as environmentally friendly stabilized pavement material alternative to Portland cement, which will encourage the researchers and end-users worldwide to increase the utilization of recycled and waste material in diverse civil infrastructure, especially in road construction field leading to numerous environmental benefits.

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CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summarization

Over the last decades, Thailand has made remarkable progress in social and economic development, moving from a low-income country to an upper-income country in less than a generation. Therefore, Thailand has been one of the widely cited development success stories, with sustainable strong growth and impressive poverty reduction. However, average growth has slowed in progress due to the world economic crisis over the last few years. The government, hence has embarked on an ambitious reform program to raise Thailand's long-term growth path and achieve high-income status. The reforms strongly address on competiveness, effective human resources, and economic stability in the sustainable environmental way. Progress on reforms has already been made on the implementation of multi-year large public infrastructure projects. Theoretically, the development of transportation system has been the key driver of economic growth and poverty reduction.

Hence, the rehabilitation and reconstruction of the exist roadways that reached their designed life have been observed. Recycled Asphalt Pavement (RAP), therefore is generated in the huge amount annually. Meanwhile, a vast demand of new construction of highways that links between the cities is dramatically increased. Highway construction however consumes a large amount of natural quality aggregates, particularly in their pavement base/subbase layers. As a result, the quarries and gravel pits are increasingly exploited as a source of pavement materials, which notably leads to subsequent devastating of natural environmental resources. Other important subjects must also be taken into account in considering the future environmental impact of construction and building materials. Over the last few decades, the depletion of fossil fuels and the virgin raw materials, and the looming crisis of climate change from greenhouses emission brought a change in how the world thinks about its waste. In the recent year, concern has been growing about resource efficiency and the environmental impact of material consumption. An important environmental strategy increasingly sought by the road construction industry is the use of the recycled materials such as RAP in pavement base/subbase layers.

From the geotechnical perspective, the utilization of 100% RAP in road pavement applications is however not recommended due to its low strength and stiffness properties. Hence, chemical stabilization of RAP is extensively used for developing bound pavement base/subbase material. Although Portland cement has been successively used to stabilized recycled materials, the production of Portland cement is widely known as a serious cause of global warming. These shortcomings have led to new research efforts aimed at exploring novel green cementitious and cost-effective stabilization methods to stabilized RAP for producing pavement base/subbase materials.

Geopolymer technology, developed in the last few decades, is an environmental impact on advancement which is promised to provide a cleaner and environmentally friendly alternative to traditional Portland cements. Geopolymers are basically synthesized by alkali-activated aluminosilicate of a base material, natural or by product, which is rich in alumina and silica with a metal hydroxide solution at moderate temperatures. In Thailand, power plants generated an enormous amount of fly ash (FA) annually and without proper utilization, FA is considered as a solid waste. Furthermore, improper disposal of FA brings the danger of the release of toxic elements. Since FA contains a high percentage of amorphous silica and alumina, it is suitable as a precursor for manufacturing geopolymers.

The fast-growing knowledge in turn results in many modification methods to significantly improve the production and the performances of the FA based geopolymers. All these would justify the thought that production of FA based geopolymer is a cleaner process with improved natural resource efficiency. However, the real reactions occurred in the process are very complicated and remain elusive especially when FA based geopolymer used to stabilized recycled material such as RAP.

The present work is motivated by the geoenvironmental perspective, which strongly focus on the green technology, has led to an attempt to study the possibility of using geopolymer to stabilized RAP as a sustainable pavement base/subbase material. The investigation is strongly focus on the laboratory experimental programs, which divided into three main areas in order to typically cover requirements for the choice of a base/subbase material.

Firstly, an extensive suite of laboratory experimental programs was strongly carried out to investigated the strength development of RAP-FA geopolymer, while RAP-FA blend was prepared as a control material. Liquid alkaline activator (L), a mixture of sodium silicate solution (Na₂SiO₃) and sodium hydroxide solution (NaOH), was used to activated the alumino-silicate FA to produce FA-geopolymer binder, whereas RAP, FA, and water were mixed as a RAP-FA blend.

Besides strength requirement study, the durability of RAP-FA blends and RAP-FA geopolymers under severe climatic conditions is a crucial parameter when used in road construction projects. The study on durability of RAP-FA blend and RAP-FA geopolymers is however still in its infancy. A simulation of weather changes over a geological age namely wetting-drying (w-d) cycles is considered to be one of the most appropriate cause of pavement materials damage. This research attempts to study the durability of RAP-FA blend and RAP-FA geopolymer when subjected to cyclic wetting-drying tests.

Unconfined compressive strength (UCS) test is used as an indicator to evaluated strength development with and without subject to w-d test. The changes in the physical property of RAP-FA blends and RAP-FA geopolymers at various cyclic w-d cycles were examined by weight loss tests. The role of various influence factors on UCS development is examined via scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. Furthermore, the applications of SEM and XRD analyses were also used to investigate the microstructural and mineralogical changes of both RAP-FA blend and RAP-FA geopolymer at various cyclic w-d cycles test.

Though the utilization of recycled waste materials in highway construction can be considered as having significant impacts on resource management, the hazardous compounds that can leach out pollute the water resource should also be considered. A range of heavy metals and other pollutions including oil and/or organic microcontaminants may be present in the recycled material and should be ascertained for pavement base applications. Finally, the environmental assessment is undertaken to verify the risk of using the recycled waste material stabilized by the geochemical stabilizer in road work application. In this research, the most reliable leachate test was carried out using Toxicity Characteristic Leaching Procedure (TCLP) test prescribed by the US Environmental Protection Agency (EPA) guidelines to estimate the contaminant concentration in the seepage water, which provide information about the impacts on groundwater in the life cycle of the road construction projects.

The outcomes of this research is to promote the use of recycled waste materials in road construction, with economic and environmental benefits. The following conclusions can be drawn from this study:

FA replacement at optimal content can improved the compactability of RAP-FA blends as a filler and hence the increase in maximum dry unit weight is noted by a comparison of the compaction curves of the 100% RAP and RAP + 10% FA samples. However, the excessive FA content absorbs more water and hence the reduction in compactability as seen by slight increase in dry unit weight when FA is greater than 20%. The compaction curves of RAP-FA geopolymer depend on the NaOH/Na₂SiO₃ ratio and FA replacement ratio.

The 7-day UCS of the compacted RAP-FA blend (without L) at optimal water content meets the strength requirement for base course specified by Thailand national road authorities for both room temperature (RT) and 40°C curing and for both 20% and 30% FA replacement. The UCS improves insignificantly when the FA replacement ratio exceeds 20%, indicating this to be the optimal blend. The UCS values of RAP-FA geopolymer increase as the NaOH/Na₂SiO₃ ratio decreases and are higher than those of the compacted RAP-FA blends at the same curing time and FA replacement ratio when the NaOH/Na₂SiO₃ ratios are less than 90:10. The XRD and SEM analyses of RAP-FA geopolymers and RAP-FA blends indicate that the high amount of Calcium and Magnesium of RAP and high amount of Silica and Alumina of FA form Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H). The growth of C-S-H and C-A-H products over the time is observed, hence the UCS values of RAP-FA blends increase with time.

The silica present in sodium silicate is highly soluble, hence the higher Na₂SiO₃ content in liquid alkaline activator results in faster geopolymerization reactions and more geopolymerization products (N-A-S-H gel). Both N-A-S-H and C-S-H from the reaction between CaO and MgO (in RAP) and Silica and Alumina (in FA) fill the pores to make the RAP-FA structure dense. Consequently, the UCS is increases as the NaOH/Na₂SiO₃ ratio decreases.

Without Na₂SiO₃ (NaOH/Na₂SiO₃ = 100:0), the geopolymerization reaction of the FA-geopolymer cured at RT is slow; hence the 7-day UCS of RAP-FA blend is higher than that of RAP-FA geopolymer. With increasing curing time and temperature, the XRD and SEM analyses show that the NaOH solution is able to dissolve more Silica and Alumina from FA for geopolymerization reaction. As such, the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ = 100:0 increases with time and temperature increased.

When subjected to w-d cycles, the UCS of RAP+20%FA blend increased with increasing the number of w-d cycles (*C*) up to 6 cycles and then decrease. The XRD and SEM analyses indicated that for C < 6, the w-d cycles increase the strength of RAP+20%FA blend due to the growth of C-S-S and C-A-H due to the continues chemical reactions between high amount of Calcium Oxide in RAP with high amount of Silica and Alumina in FA. With C > 6, large cracks due to the loss of moisture content during drying stage, lead to reduction in UCS of RAP+20%FA blend. However, even with the strength reduction after C = 6, its 20-days cycles UCS value is still greater than the minimum strength requirement specified by Thailand national road authorities.

The short-term and long-term strength as well as durability of the RAP-FA base material can be improved by FA geopolymerization. As a result of alkaline activator, the w-d cycles strongly enhance the degree of geopolymeric reactions, generating more geopolymer products. The XRD and SEM analyses of RAP+20%FA geopolymer when C < 6 indicate that the N-A-S-H phases increases with an increase in *C* and co-exist with C-A-S-H that results in a strength increase of RAP+20%FA geopolymer.

Similar to the RAP-FA blend, the developed large cracks at C > 6 cause reduction in UCS values in the RAP-FA geopolymer. The external surface cracks and micro-cracks in the samples are larger for lower NaOH contents. Therefore, the strength reduction of the samples at NaOH/Na₂SiO₃ = 50:50 is higher than the sample at NaOH/Na₂SiO₃ = 100:0. In other words, the RAP-FA geopolymer with higher NaOH content evidently exhibits better durability performance that can be attributed to the formed stable cross-linked alumino-silicate polymer structure.

From an environmental perspective, the TCLP results indicate that both RAP+20%FA blend and RAP+20%FA geopolymer can be safely used in sustainable pavement base applications, as these materials pose no significant environmental and leaching hazard into soil, surface and ground water sources. In addition, the leachability of heavy metals was reduced when FA-geopolymer used to stabilized

RAP, which is advantages for some strict guidelines of using recycled or waste materials in road applications.

To sum up, this study indicates that both RAP-FA blend and RAP-FA geopolymer can be considered as an environmentally friendly stabilized pavement material, which will encourage the researchers and end-users worldwide to increase the utilization of recycled material leading to numerous environmental benefits.

6.2 **Recommendation for future work**

Geopolymer preparation is a simple preparation technique and very similar to the preparation of Portland cement. It can be synthesized simply by preparing a blend of aluminosilicate materials and strongly alkaline solution and cured at room temperature. A strength development is observed in a short time. These properties, hence make geopolymers suitable for application in many fields of industry include civil engineering. Geopolymer technology offers a good benefit to use the waste material such ash fly ash, which containing a high amount of silica and alumina.

For the practical applications of fly ash based geopolymer, mechanical properties including compressive strength and flexural strength as well as durability such as wet-dry cycles, freeze-thaw cycles, and thermal testing should be comprehensively investigated.

From geoenvironmental perspective, considering the low cost, low-carbon solution and low energy usage in the application of cementitious additives treated recycled waste material, fly ash based geopolymer can be used as cement to stabilized aggregates and regarded as possible alternative green materials to Portland cement. In addition, fly ash based geopolymer has also been used to adsorb and immobilized toxic metals and it shows better performance than those Portland cement.

Though evident has been proofed in the application of fly as based geopolymer stabilized RAP regarding to mechanical strength, durability, and leachability of heavy metals in this research work, there exists several issues and some issues are required further study and proposed below for future work.

The alter Si/Al ratios of reactants, alkali-activator, curing conditions, and the addition of slag, calcium carbide residue, rice hush ash, bottom ash, and other aluminosilicate materials can be impacted on the mechanical properties of the geopolymer. The change of Si/Al ratios, alkali solution, and adding other aluminosilicate sources may lead to the different geopolymeric gel, including N-A-S-H gel, C-A-H, C-S-H, and C-A-S-H gel. These gels can influence the final structure of geopolymer production.

Therefore, to control the production and to improve the performances of fly ash based geopolymer, the reaction mechanisms in each step should be uncovered in more details. Advancing in the science and sophisticate technology such as thermodynamics, kinetics, identifications of intermediates and insights into the geopolymer structure and the degree to which the three dimensional structure of geopolymer are required.

With recently, in most cases, fly ash based geopolymer are merely produced at laboratory scale with empirical formulations. To manufacturing and using the fly ash based geopolymer stabilized recycled waste materials on a large-scale are encouraging and need further input and endeavor.

APPENDIX A

PUBLICATIONS

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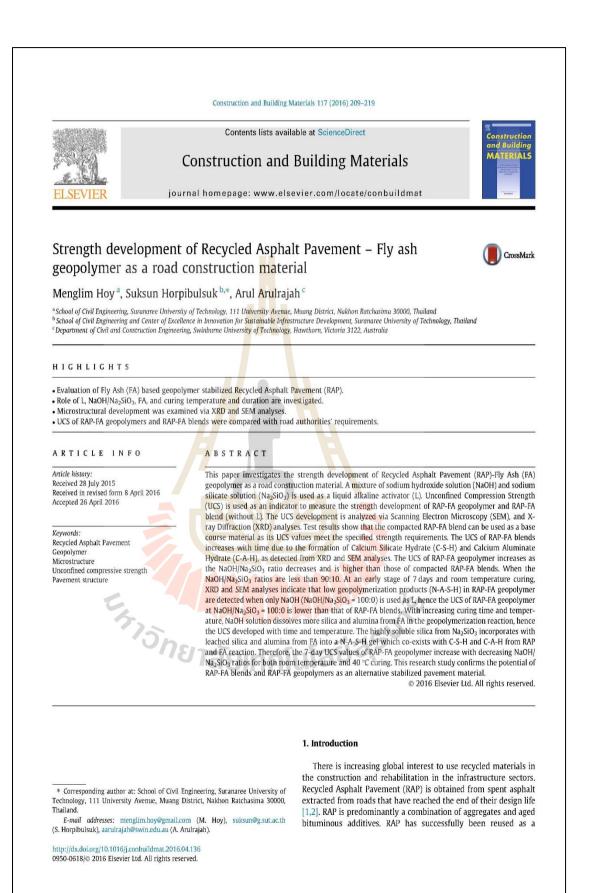
List of Publications

INTERNATIONAL JOURNAL PAPERS

- Hoy, M., Horpibulsuk, S., & Arulrajah, A. (2016). Strength development of Recycled Asphalt Pavement – Fly ash geopolymer as a road construction material. Construction and Building Materials, 117, 209-219.
- Hoy, M., Horpibulsuk, S., Rachan, R., Chinkulkijniwat, A., & Arulrajah, A. (2016).
 Recycled asphalt pavement fly ash geopolymers as a sustainable pavement base material: Strength and toxic leaching investigations. Science of The Total Environment, 573, 19-26.
- Hoy, M., Rachan, R., Horpibulsuk, S., Arulrajah, A., & Mirzababaei, M. (2017).
 Effect of wetting-drying cycles on compressive strength and microstructure of recycled asphalt pavement – Fly ash geopolymer. Construction and Building Materials, 144, 624-634.

INTERNATIONAL CONFERENCE PAPER

- Menglim Hoy, Suksun Horpibulsuk, and Arul Arulrajah. (2015). Effects of NaOH/Na2SiO3 ratios on strength development of recycled asphalt pavement – fly ash geopolymer. International Conference 5th GEOINDO 2015, Geology, Geotechnology, and Mineral Resources of INDOCHINA, November 23-24, Khon Kaen, Thailand.
- Menglim Hoy, Suksun Horpibulsuk, and Arul Arulrajah. (2016). Evaluation of fly ash based geopolymer stabilized recycled asphalt pavement as a sustainable pavement material. International Conference on Sustainable and Renewable Energy Engineering, May 5-7, 2016 in Seoul.



construction material in road bases, road subbase, asphalt concrete aggregates, embankments and backfills [3–5]. The utilization of RAP materials in civil engineering infrastructure works has led to significant environmental benefits, as well as a vast reduction of construction and demolition debris being disposed to landfills.

RAP is increasingly becoming a popular material in unbound base and subbase applications due to its lower cost compared to that of natural quality aggregates. The sustainable usage of RAP also leads to significant economical savings for the construction of new highway pavements [6]. Large quantities of RAP are however not taken up whole-heartedly by industry, due to their often low strength and stiffness characteristics [3,7–11]. Though some efforts have been made to blend RAP with other higher quality natural or recycled materials in payement base/subbase applications. these RAP blends often do not meet the minimum local road authorities specified requirements [4,8]. Saride et al. [12] evaluated fly ash stabilized RAP, with different percentages of fly ash (FA) replacement contents. The authors reported that in the shortterm (curing periods of 1 day and 7 days), the Unconfined Compression Strength (UCS) and resilient modulus (M_R) values increased with an increase in FA content with up to 30% replacement, thereafter further increases in FA content resulted in a decrease in the UCS and M_R values. This investigation showed that 7-day UCS values (maximum 1497 kPa) did not meet the strength requirements specified for base materials. The utilization of RAP substitution in Virgin Aggregate (VA) stabilized by FA have been evaluated by Saride et al. [13] whom reported that RAP: VA = 80:20 with 40% FA mix satisfies the strength, stiffness, and California Bearing Ratio requirements for low volume roads. Mohammadinia et al. [14] recently evaluated the behavior of geopolymer stabilized RAP with FA and blast furnace slag precursors and reported that geopolymer stabilized RAP, with 7 days of curing, could only meet subbase requirements.

Several researchers have reported that the performance of cement stabilized RAP satisfied the requirements of pavement base/subbase applications [3,10,15–17]. Cement-stabilized RAP is however not considered as an environmentally friendly material, as the production of Portland Cement (PC) contributes significantly to global warming. The energy-intensive process for the production of PC emits a large amount of greenhouse gas – carbon dioxide (CO₂) into the atmosphere [18–23]. Davidovits [20] demonstrated that the production of 1 ton of PC clinker directly produces about 0.55 tons of CO₂ and requires the combustion of carbon-fuel, which results in an additional 0.40 tons of CO₂. The production of 1 ton of PC releases approximately 1 ton of CO₂.

These shortcomings have led to an attempt to explore novel low carbon stabilization methods. Geopolymer is an inorganic aluminosilicate material synthesized by alkaline activation of materials rich in alumina (Al_2O_3) and silica (SiO₂) and is considered as a green cementing agent. Geopolymerization involves the chemical reaction of alumino-silicate oxides by alkaline activation, yielding the polycondensation of the material in the three-dimensional silico-aluminate structure [21,24]. Three typical structures of geopolymer are: Poly (sialate) type (-SiO-Al-O-), the Poly (sialate-silox) type (-SiO-Al-O-), the Poly (sialate-silox) type (-SiO-Al-O-).

Geopolymer is made of alkali-activated aluminosilicate materials such as FA, slag, rice husk ash and bottom ash. Geopolymers are reported to produce low CO_2 emission and energy consumption [25]. In Thailand, power plants produce a total output of 4.0 million tons of FA and bottom ash annually. However, only approximately 1.8 million tons of FA is used as a pozzolanic material in the concrete industry [26] with the balance being stockpiled as waste materials. Since FA contains a high percentage of amorphous silica and alumina, it is suitable as a precursor for manufacturing geopolymers [27]. Geopolymer has in recent years been used to stabilize natural soils to develop green building materials such as masonry products. It was reported that geopolymer based materials possess higher compressive strength and durability against sulfate than cement based materials [28–30]. Recently, Suksiripattanapong et al. [31] and Horpibulsuk et al. [32] successfully stabilized water treatment sludge using fly ash based geopolymer to develop sustainable non-structural and bearing masonry units. It was illustrated that the geopolymer is more effective than PC in stabilizing the water treatment sludge with high alum content. The strength and durability of sludge-geopolymer masonry units is significantly higher than sludge-cement masonry units.

The RAP stabilized with FA based geopolymer for pavement applications is currently limited due to the lack of laboratory and field evaluation of this novel material. This research aims to study the possibility of using geopolymer to stabilize RAP as a sustainable stabilized pavement material. An extensive suite of laboratory experimental programs was carried out to investigate the strength development of RAP-FA geopolymer. The RAP-FA geopolymer samples were prepared using modified Proctor compaction energy. UCS is used as an indicator to evaluate strength development in this research. The role of various influence factors on UCS development is examined via Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) analyses. The various influential factors studied in this research included liquid alkaline activator (L) content, NaOH/Na2SiO3 ratio, FA content, and heat condition (temperature and duration). This study has significant impacts on pavement applications by using RAP stabilized with FAgeopolymer binder, a sustainable alternative to ordinary PC, in pavement base and subbase courses.

2. Materials and methods

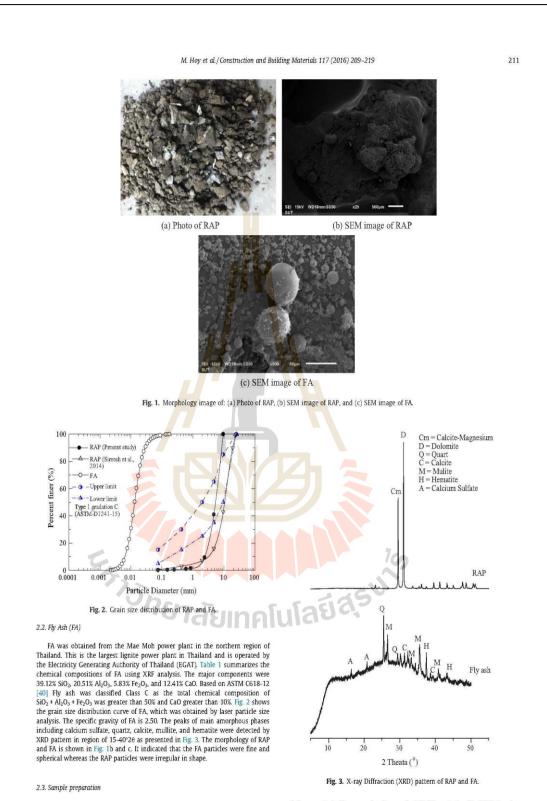
2.1. Recycled Asphalt Pavement (RAP)

RAP, collected from a milled asphalt pavement stockpile in Nakhon Ratchasima province, Thailand was used in this research. A cold milling machine was used to remove the asphalt pavement for resurfacing in the cold in-place recycling process. Fig. I a shows a photo of RAP from the stockpile. The low water content of RAP (less than 0.3%) was detected. The gradation of air-dried RAP was determined by a sieve analysis in accordance with ASTM-D422-63 [33] and is shown in Fig. 2. The cold in-place recycling process used a narrow tooth spacing milling drum with a lower speed and therefore result in the maximum size of approximately 10 mm. The RAP contains approximately 99.8% coarse-grained particles (retained on No. 200 sieve). The specified gravity of RAP is 2.7. The RAP is classified as poorly graded sand (GP) according to the Unifed Soil Classification System (USCS) [34].

(SP) according to the Unified Soil Classification System (USCS) [34]. The gradation of the RAP was compared with that specified for base materials (ASTM-D1241-15] [35] and AASTHO-M147-65] [36] and is shown in Fig. 2. It is noted that RAP gradation does nor meet the specification requirements. Although this gradation specification is used for unstabilized base materials in several countries, it is however not applied to stabilized materials in India and Thailand. For instance, Sardation specification is used for unstabilized base material. The modified Proctor compaction test was performed to determine the maximum dry unit weight (Y_{dmax}) and Optimum Water Content (OWC) of RAP in accordance with ASTM D 1557-12, 2012 [37]. The Y_{dmax} and OWC values of RAP were 17.5 kN/m² and 4.1%, respectively. California Bearing Ratio (CBR) test followed the ASTM D 1883-07 [38] was carried out on RAP samples under the modified Proctor compaction effort at OWC and soaked for 4 days. Water absorption and swelling after 4 days of Soaking were also measured. The soaked CBR value was approximately 10–15%, while water absorption and swelling values were 6.8% and 0.2%, respectively. These values indicate that this RAP did not meet the requirements for base and subbase materials, as specified by the Department of Highways (DOH), Thailand [39].

Spectime by the Department of rightways (DOH), finalitating 159. This research aims to study the stabilization of RAP with FA-geopolymer to meet the specified requirements for stabilized pavement material. The mineral and chemical compositions of RAP, obtained by X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) analyses, are depicted in Fig. 3 and Table 1, respectively. Since the RAP (consisting of aggregates and aged bituminous additives) was removed by a cold milling machine, the amorphous asphalt was not fully covered by aggregates, as presented in Fig. 1a. Hence, the predominant mineral components in RAP were calcite-magnesium and dolomite. The main chemical composition detected in RAP was 41.93% CaO and 36.11% MgO. This high CaO in RAP can react with silica and alumina in FA for a suitable pozzolanic reaction.

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The liquid alkaline activator (L) was a mixture of sodium silicate (Na₂SiO₃) type CR 53, which was composed of Na₂O (14.50–16.50%) and SiO₂ (31.50–34.00%) by weight, and sodium hydroxide (NaOH) solution with a 10 M concentration. The

mixing was started by preparing the required NaOH content with distilled water. $Na_2 SiO_3$ was then added and thoroughly mixed into the solution. A 10 M concentration was selected based on previous research [26], which reported that 10 M

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Table 1 Chemical composition of RAP and FA

Chemical formula (%)	RAP	FA
SiO ₂	3.11	39.12
Al ₂ O ₃	4.73	20.51
Fe ₂ O ₃	0.10	5.83
CaO	41.93	12.41
MgO	36.11	2.49
SO ₃	0.89	0.49
Na ₂ O	N.D.	0.67
K ₂ O	0.04	1.53
LOI	N.D.	0.41

The UCS tests were undertaken in accordance with ASTM D1633 [42] using a 100 kN compression machine with a strain rate of 0.5%/min. The samples were soaked in water for 2 h and then were air-dried for 1 h prior to UCS test according to the specification of the Department of Highways, Thailand [39]. The mean UCS values were obtained by testing triplicate samples, to ensure testing consistency.

X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses were performed to investigate the microstructural development of RAP-FA geopolymer and RAP-FA blends. The small fragments were taken from the broken portion of the UCS samples and then frozen at –195 °C by immersion in liquid nitrogen for 5 min and coated with gold before SEM (JEOL JSM-6400 device) analysis [29]. The XRD analyses were done on the powder samples, which were compacted in a Cu X-ray tube. The XRD traces were obtained by scanning at 0.1°(20) per min and at steps of 0.05°(28).

3. Result and discussion

3.1. Compaction test

concentration was the optimum NaOH concentration for FA geopolymer. Based on the authors' unpublished leachate test results, the leached hazardous materials was also within the US and Australian specifications, indicating the safe environment for using this geopolymer.

The RAP-FA geopolymer was a combination of RAP, FA, and L (NaOH + Na₂SiO₃). The NaOH/Na₂SiO₃ ratios studied were 100:0, 90:10, 60:40, and 50:50. The RAP-FA blend, which was a mixture of RAP, FA, and water, was prepared as a control material to compare effect of L on strength development. FA replacement ratios were 10%, 20%, and 30% by weight of RAP for both RAP-FA geopolymers and RAP-FA blends. The mixing procedure started with mixing air-dried RAP and FA for 5 min. The mixing procedure started with L for RAP-FA geopolymer or water for RAP-FA blends for additional 5 min. The mixtures were next compacted under molds were 101.6 mm in diameter and 116.3 mm in height. Once the compaction curves were obtained, the RAP-FA geopolymer samples at each NaOH/Na₃SiO₃ ratio were prepared at Optimum liquid alkaline activator Content (OLC) and the RAP-FA blend samples were gismantled, wrapped within vinyl sheet and then cured at both room temperature (RT) (20-25 °C) and 40 °C for 7 days and 28 days. The test under 40 °C was to simulate average payement temperatures in Thailand [41].

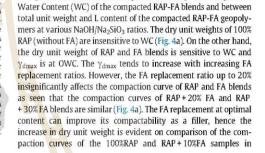


Fig. 4 shows the relationships between dry unit weight and

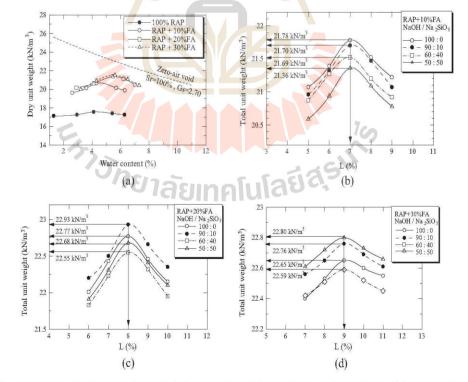


Fig. 4. Compaction test results: (a) 100% RAP and RAP-FA blends, (b) RAP-FA geopolymer with 10%FA, (c) RAP-FA geopolymer with 20%FA, and (d) RAP-FA geopolymer with 30%FA.

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Fig. 4a. However, excessive FA content absorbs more water, hence the resulting reduction in compactability.

The compaction curves of RAP-FA geopolymers are dependent on the ratio of NaOH/Na₂SiO₃ and FA replacement ratio. For a particular FA replacement ratio, the maximum unit weights of RAP-FA geopolymer are dependent on the NaOH/Na₂SiO₃ ratios, while, the OLC providing the maximum unit weight is found to be the same at all NaOH/Na₂SiO₃ ratios. For instance, the OLC values are 7%, 8%, 9% for RAP + 10%FA, RAP + 20%FA, and RAP + 30%FA geopolymers, respectively as shown in Fig. 4(b-d). The optimum NaOH/Na₂SiO₃ ratio providing the highest maximum total unit weight of RAP-FA geopolymer is dependent upon the FA replacement ratio; i.e., it is 100:0, 90:10, and 50:50 for 10%, 20%, and 30% FA replacement, respectively. It is also noticed that for a particular NaOH/Na₂SiO₃ ratio, the total unit weight of RAP-FA geopolymer increases when FA replacement ratio increases from 10% to 20%; however, it decreases when the FA replacement ratio increases to 30%.

3.2. Unconfined Compression Strength (UCS) test

Fig. 5 summarizes the UCS results of the RAP-FA blend and RAP-FA geopolymer (RAP + 20% FA and RAP + 30%FA) for various NaOH/ Na₂SiO₃ ratios (100:0–50:50), curing times (7 and 28 days), and curing temperatures (RT and 40 °C). The UCS development of geopolymer relies on the reaction between the precursor and alkali activator (geopolymerization reaction) and heat condition (cured temperature and duration) of samples [28,43,44]. It is noted that the UCS values of both RAP-FA blends and RAP-FA geopolymers increase with increasing curing time and temperature (see Fig. 5a and b). This result is also similar to that reported in previous research on the strength development of cement-stabilized RAP

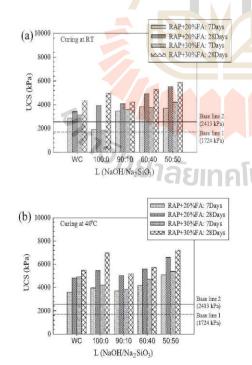


Fig. 5. Compressive strength of RAP-FA blends and RAP-FA geopolymer cured at 7 days and 28 days and (a) at Room Temperature and (b) at 40 °C.

[15,17]. Fig. 5(a) shows that the 7-day UCS values of RAP-FA blends (at 20%FA and 30% FA) are higher than RAP results reported by Saride et al. and greater than the strength requirement specified by the Thailand national road authorities in which UCS > 1724 kPa and UCS > 2413 kPa for low and high volume roads, respectively [39,45]. At the early stage of geopolymerization (7 days), the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ = 100:0 (without Na₂SiO₃) is lower than that of RAP-FA blends for both FA replacement ratios of 20% and 30% at RT curing. However, the UCS of RAP-FA geopolymer at NaOH/Na₂SiO₃ < 10:90 is higher than that of RAP-FA blends and the UCS values of RAP-FA geopolymers increase when NaOH/ Na₂SiO₃ ratio is decreased. This implies that the input of Na₂SiO₃ can enhance the short-term strength of RAP-FA-FA geopolymer, which is an advantage for anplications that require high early strength.

For the same NaOH/Na₂SiO₃, the 30% FA-RAP geopolymer exhibits higher UCS than the 20% FA-RAP geopolymer, despite the gradation of 30% FA-RAP being finer than that of 20% FA-RAP. This is because the UCS of RAP-FA geopolymers is mainly governed by the degree of chemical reactions, in that higher FA contents results in higher silica and alumina contents for the geopolymer-ization reaction.

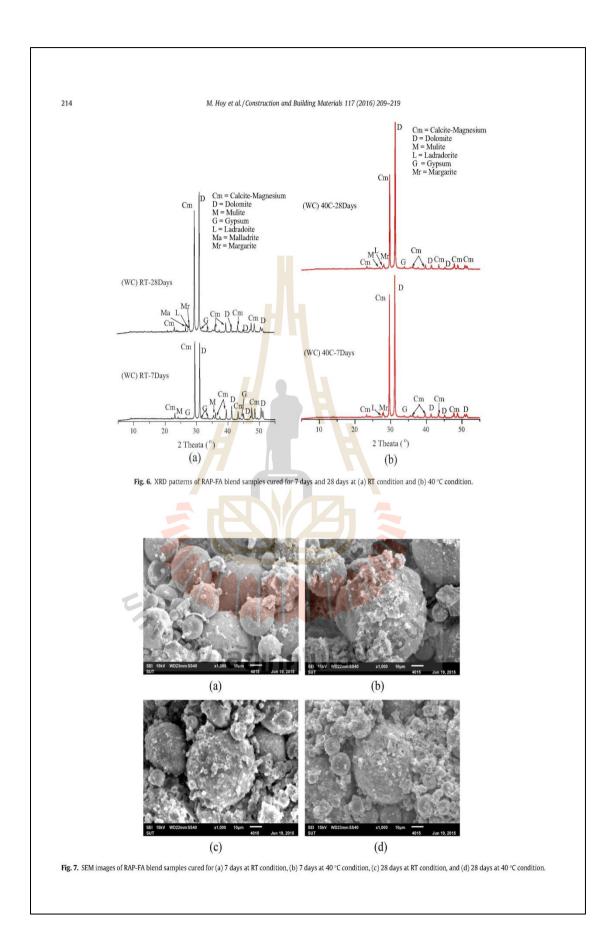
3.3. Microstructural analyses

The XRD patterns of RAP-FA blend samples cured for 7 days and 28 days at RT and 40 °C are shown in Fig. 6. The RAP-FA blend samples consist of the amorphous phase and the board hump (peak) between 23 and 35°20, which indicates the anhydrous carbonate mineral to be composed of high calcium magnesium carbonate from the RAP material [46]. By comparing Fig. 2 (RAP) and Fig. 6 (RAP-FA), the FA replacement in the RAP-FA blend generates new chemical silica- and alumina-rich products, inclusive of mulite, gypsum, ladradorite, malladrite, and margarite. The high amount of calcium and magnesium of RAP and high amount of silica and alumina of FA result in the chemical reaction to form Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H), similar to the hydration of Portland cement [47,48]. Consequently, the UCS of RAP-FA blends increases with increasing curing time (see Fig. 5).

Besides the XRD results, SEM analysis is performed on the samples to confirm the growth of cementitious products of RAP-FA blend and RAP-FA geopolymer over time. The SEM images of RAP-FA blend samples cured for 7 days and 28 days at RT and 40 °C are illustrated in Fig. 7. The dense cementation matrix due to the chemical products from the reaction between silica and alumina (in FA) and CaO and MgO (in RAP) binds the RAP and FA particles together, which confirms the XRD results. Consequently, the densification of compacted RAP-FA blends with increasing temperature and curing time are observed, resulting in UCS development.

Fig. 8 shows the XRD patterns of RAP-FA geopolymer samples at NaOH/Na2SiO3 ratios of 100:0 and 50:50 cured for 7 days and 28 days at RT and 40 °C. The alumina phases are present in the geopolymerization products such as nepheline and muscovite, which are observed at the broad hump between 27 and 30°20 in Fig. 8a for RAP-FA geopolymer samples cured for 28-days at RT and Fig. 8b for the samples cured for 28-days at 40 °C. The XRD patterns of RAP-FA geopolymer samples at NaOH/Na2SiO3 ratios of 100:0 and 50:50 cured for 7 days at RT are similar to those of RAP-FA blends in that the presence of a large amount of dolomite and calcite-magnesium is indicated by the broad hump around 25-35°20 (Fig. 8a and c). The geopolymerization products, sodium alumino silicate hydrate (N-A-S-H) phases formed as a result of the alkaline activation are also detected at longer curing time and higher temperature. The products are started by the dissolution of FA particles in which the original mineralogy is significantly modified [49]. Fig. 8 shows the decrease of the main amorphous

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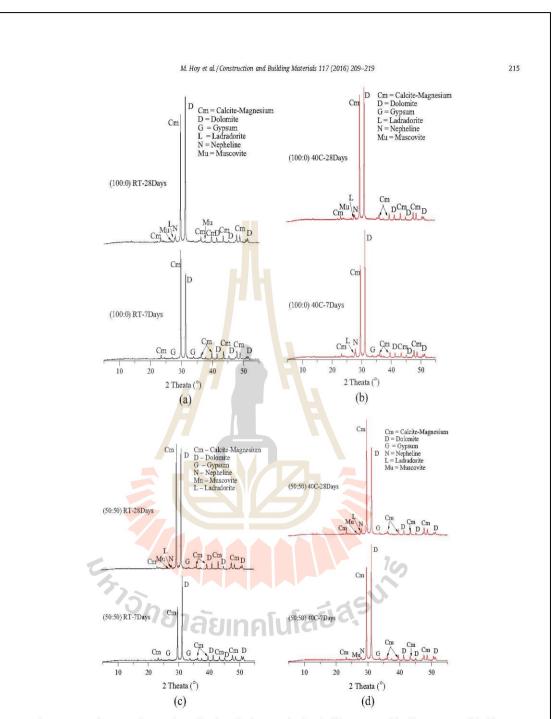


Fig. 8. XRD patterns of RAP-FA geopolymer samples cured for 7 days and 28 days at NaOH/Na₂SiO₃ ratio of (a) 100:0 at RT condition, (b) 100:0 at 40 °C condition, (c) 50:50 at RT condition, and (d) 50:50 at 40 °C condition.

silica and alumina phases of FA, which are consumed to react with alkaline activation (NaOH/Na₂SiO₃) (compare Figs. 2 and 8). This results in a new geopolymerization matric including nepheline, ladradorite, and muscovite as observed at the broad hump between 27 and 30°2 θ in the XRD patterns of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratios of 100:0 cured for 28 days at RT

(Fig. 8a) as well as 7 days and 28 days at 40 °C (Fig. 8b). Similar XRD patterns are observed for RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratios of 50:50 (Fig. 8c and d). These new nanocrystalline phases create cementitious systems, which are associated with the strength enhancement. The C-S-H and C-A-H co-exist with geopolymerization products, therefore enhanced UCS of the

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RAP-FA geopolymer as also reported by [43,44]. Even with the coexistence of pozzolanic products and geopolymerization products, the 7-day UCS of RAP-FA geopolymer at NaOH:Na₂-SiO₃ = 100:0 is lower than that of RAP-FA blend at RT curing (see Fig. 5a).

The low geopolymerization products at early curing time might be attributed to two main reasons. Guo et al. [50] reported that when FA-geopolymer material is cured at ambient temperature of around 25 °C, the strength development is rather slow. The other reason is concerned with the alkaline activator via a chargebalancing role with aluminium, which incorporated into geopolymerization binders (FA filter) [47,51-54]. With a very high NaOH content (NaOH/Na₂SiO₃ = 100:0), the charge-balancing is unstable and hence slower strength development. However, when the cured temperature of FA-geopolymer increases from the ambient temperature to higher temperature (40 °C), the strength gain is evident. This is attributed to a raised alkalinity, derived from the loss of water due to the almost immediate formation of C-S-H and C-A-H phases [47,55,56] and the acceleration of geopolymerization reaction due to heat temperature [29,30,32]. It is evident that the higher UCS values of RAP-FA geopolymer at the NaOH/ Na2SiO3 ratio of 100:0 are obtained as curing time increases from 7 to 28 days and/or curing temperature increases from RT to 40 °C (Fig. 5a-b).

The growth of geopolymerization products with various NaOH/ Na₂SiO₃ ratios, curing time and temperatures is demonstrated by SEM images (Figs. 9 and 10 for NaOH/Na₂SiO₃ ratios of 100:0 and 50:50, respectively). Fig. 9(a) shows the SEM image of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 (without Na₂-SiO₃) cured for 7 days at RT. The roughly smooth and spherical surface of FA is clearly observed, which indicates that no perceptible reaction or less alkali reaction and confirms the slow reaction of NaOH and FA. In other words, even with an addition of NaOH, the unreacted and/or partially reacted FA particles are more and the matrices look rather loose (compare Figs. 7a with 9a), which is similar to the previous publication [48]. The SEM (Figs. 7a and 9a) and XRD (Figs. 6a and 8a) results confirm the lower UCS of RAP-FA geopolymer at NaOH/Na2SiO3 = 100:0 and RT curing than the RAP-FA blend. However, with increasing curing time and temperature, the NaOH solution can dissolve more silica and alumina from FA. The alkali activation begins at a point on the FA surface and then expands to form a larger hole. Consequently, geopolymerization products are generated both inside and outside the shell of the sphere, until the FA particle is completely or almost completely consumed [57]. The effect of temperature and curing time on UCS development is clearly evident by comparing Fig. 9b-d with a. Etched holes on the FA surface and the cementitious products are more with increasing curing time and temperature. Therefore, their UCS sharply increases with temperature and curing time.

Fig. 10(a-b) show the SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 50:50 at the early age (7 days) and at RT and 40 °C curing. Once the source of alumino-silicate material comes into contact with an alkali solution, the leaching of both silica and alumina started to generate the geopolymerization products in the samples with NaOH/Na₂SiO₃ = 50:50 are more than those with NaOH/Na₂SiO₃ = 50:50 are more than those with NaOH/Na₂SiO₃ = 100:0 for the same curing time and temperature. The more alumino-silicate gel on FA surface indicates the immediate formation products with time and temperature increased are clearly detected around FA particles and the pores (Fig. 10c-d) in which the geopolymerization products are a well-formed Si-O-Al and Si-O-Si three dimensional structure.

The laboratory test results indicate the viability of using RAP-FA blends as a pavement base course in which their UCS values meet the minimum strength requirement specified by national road authorities. The early and long term strength and durability of

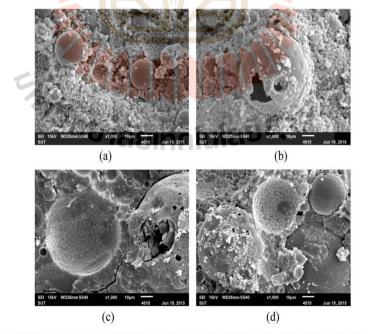


Fig. 9. SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 100:0 cured for (a) 7 days at RT condition, (b) 7 days at 40 °C condition, (c) 28 days at RT condition, and (d) 28 days at 40 °C condition.

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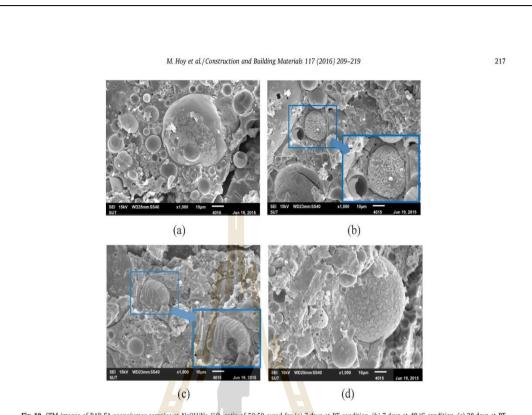


Fig. 10. SEM images of RAP-FA geopolymer samples at NaOH/Na₂SiO₃ ratio of 50:50 cured for (a) 7 days at RT condition, (b) 7 days at 40 °C condition, (c) 28 days at RT condition, and (d) 28 days at 40 °C condition.

the RAP-FA base course can be improved by FA based geopolymer. The higher Na₂SiO₃ content enhances the short-term UCS of RAP-FA geopolymer for both RT and 40 °C curing, which is advantageous for applications required high early strength. In addition to the engineering impact, the RAP-FA blends and RAP-FA geopolymers are low-carbon pavement base course materials compared to the traditional PC stabilized RAP commonly used worldwide.

According to Department of Highways (DOH), Thailand, as well as road authorities in Australia and other countries, the UCS is the specified design parameter and as such it is used for comparison purposes. However, stiffness properties such as resilient modulus and permanent strain are also important to understand the material performance and are used for a mechanistic design. This stiffness property study is thus recommended for further study, which is extensive enough for a separate publication.

4. Conclusion

A series of laboratory experiments were conducted to ascertain the strength development of RAP-FA geopolymer as a sustainable stabilized pavement course in this study. The influence factors studied are mixing ingredients (FA content, L content and NaOH/Na₂SiO₃ ratio) and heat condition (temperature and duration). The strength development is analyzed via Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) results. The conclusions arising from this study are as follows:

(1) FA replacement at optimal content can improve the compactability of RAP-FA blends as a filler and hence the increase in maximum dry unit weight is noted by a comparison of the compaction curves of the 100%RAP and RAP + 10% FA samples. However, the excessive FA content absorbs more water and hence the reduction in compactability as seen by slight increase in dry unit weight when FA is greater than 20%.

- (2) The compaction curves of RAP-FA geopolymer depend on the NaOH/Na₂SiO₃ ratio and FA replacement ratio. For a particular FA replacement ratio, the OLC values providing the maximum unit weight are found at NaOH/Na₂SiO₃ ratios of 100:0, 90:10, and 50:50 for 10%, 20%, and 30% FA replacement ratios, respectively.
- (3) The 7-day UCS of the compacted RAP-FA blend (without L) at OWC meets the strength requirement for base course specified by Thailand national road authorities for both RT and 40 °C curing and for both 20% and 30% FA replacement. The UCS improves insignificantly when the FA replacement ratio exceeds 20%, indicating this to be the optimal blend. The UCS values of RAP-FA geopolymer increase as the NaOH/Na₂SiO₃ ratio decreases and are higher than those of the compacted RAP-FA blends at the same curing time and FA replacement ratio when the NaOH/Na₂SiO₂ ratios are less
- than 90:10.
 (4) The XRD and SEM analyses of RAP-FA geopolymers and RAP-FA blends indicate that the high amount of calcium and magnesium of RAP and high amount of silica and alumina of FA form Calcium Silicate Hydrate (C-S-H) and Calcium Aluminate Hydrate (C-A-H). The growth of C-S-H and C-A-H products over the time is observed, hence the UCS values of RAP-FA blends increases with time.
- (5) The silica present in sodium silicate is highly soluble, hence the higher Na₂SiO₃ content in liquid alkaline activator results in faster geopolymerization reactions and more geopolymerization products (N-A-S-H gel). Both N-A-S-H and C-S-H from the reaction between CaO and MgO (in

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RAP) and silica and alumina (in FA) fill the pores to make the RAP-FA structure dense. Consequently, the UCS increases as the NaOH/Na2SiO3 ratio decreases.

- (6) Without Na2SiO3 (NaOH/ Na2SiO3 = 100:0), the geopolymerization reaction of the FA-geopolymer cured at room temperature is slow; hence the 7-day UCS of RAP-FA blend is higher than that of RAP-FA geopolymer. With increasing curing time and temperature, the XRD and SEM analyses show that the NaOH solution is able to dissolve more silica and alumina from FA for geopolymerization reaction. As such, the UCS of RAP-FA geopolymer at NaOH/ Na2SiO3 = 100:0 increases with time and temperature increased.
- (7) The outcome of this research confirms the potential of using FA stabilized RAP as pavement base course where its UCS values meet the minimum strength requirement specified by the Thailand national road authorities. The short-term and long-term UCS and durability of the RAP-FA base course can be improved by FA-based geopolymer. Both RAP-FA blends and RAP-FA geopolymers are an environmentally friendly stabilized pavement material.

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BIOGRAPHY

Mr. Menglim Hoy was born on April 12, 1989 in Kampong Cham province, Cambodia. He earned his double Bachelor's degrees, which one was in Business Administration specialized in Business-Economic from National University of Management in 2011 and another was in Civil Engineering from Norton University in 2012. Both universities were located in Phnom Penh, Cambodia. Soon after graduated, he worked for Advancing Engineering Consultants Ltd, the US company based in Cambodia as a junior civil engineer. In 2013, he has been awarded a SUT-Ph.D. Scholarship for ASEAN (5-year) Program in academic year 2013-2018, study in the School of Civil Engineering, Suranaree University of Technology, Thailand. During his Ph.D. study, he conducted a research and wrote his dissertation under the supervision of Prof. Dr. Suksun Horpibulsuk. He has been awarded a 6-month research scholarship financed by the Austrian Federal Ministry of Science, Research and Economy for his oversea research under the supervisor of Univ. Prof. Dr. Ronald Blab at Vienna University of Technology from November 2016 to April 2017. He has published 3 leading international journal papers and 2 international conference papers. He has been rewarded a best presentation winner of International Conference on Sustainable and Renewable Energy Engineering, Seoul, South Korea, May 5-7, 2016. His expertise and research filed are in the area of the geochemical stabilization of recycled materials and the microstructural analysis.