รายงานวิจัยฉบับสมบูรณ์

โครงการ การออกแบบส่วนผสมและสมบัติทางวิศวกรรมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง

โดย ผู้ช่วยศาสตราจารย์ ดร.ธนากร ภูเงินขำ

มีนาคม 2562

สัญญาเลขที่ MRG6080174

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และมหาวิทยาลัยเทคโนโลยีราชมงคลอีสาน

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ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

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งานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาวิธีการออกแบบส่วนผสมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง โดยใช้เถ้าลอยจากโรงไฟฟ้าแม่เมาะที่อยู่ในภาคเหนือของประเทศไทยเป็นวัสดุตั้งต้น สารละลายโซเดียมไฮดรอกไซด์และสารละลายโซเดียมซิลิเกตใช้เป็นสารละลายอัลคาไลน์ ปัจจัยที่ศึกษาประกอบด้วยความเข้มข้นสารละลายโซเดียมไฮดรอกไซด์ อัตราส่วนสารละลายอัลคาไลน์ต่อเถ้าลอย และขนาดอนุภาคของมวลรวมหยาบ โดยทดสอบกำลังรับแรงอัดที่ 28 วัน ของตัวอย่างส่วนผสมที่ถูกออกแบบ

การออกแบบส่วนผสมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูงได้อธิบายเป็นลำดับขั้นตอนซึ่งได้ดัดแปลงมาจากมาตรฐาน ACI ซึ่งผลการทดสอบกำลังรับแรงอัดที่ 28 วัน อยู่ระหว่าง 15-35 เมกะปาสคาล หลังจากทราบส่วนผสมที่ได้ดัดแปลงทำให้ทราบอัตราส่วนอัตราส่วนสารละลายอัลคาไลน์ต่อเถ้าลอยจากการทดลอง ซึ่งค่าค่ากำลังรับแรงอัดที่ใกล้เคียงกับผลทดสอบที่ต้องการ

คำหลัก: วัสดุอัลคาไลน์จากเถ้าลอยแคลเซียมสูง, ขั้นตอนการออกแบบส่วนผสม, กำลังอัดที่ต้องการ, สมบัติทางวิศวกรรม

ABSTRACT

Project Code:	MRG6080174
Project Title:	Mix Design Procedure and Engineering Properties of Alkali-Activated High Calcium Fly Ash Concrete
Investigator:	Assistant Professor Tanakorn Phoo-ngernkham, Ph.D.
Email Address:	Tanakorn.ph@rmuti.ac.th
Project Period:	2 years

This research focuses on developing a mix design methodology for alkali-activated high calcium fly ash concrete (AAHFAC). High calcium fly ash (FA) from Mae Moh power plant in northern Thailand was used as a starting material. Sodium hydroxide and sodium silicate were used as alkaline activator solutions (AAS). Many parameters viz., NaOH concentration, alkaline activator solution-to-fly ash (AAS/FA) ratio, and coarse aggregate size were investigated. The 28-day compressive strength was tested to validate the mix design proposed. The mix design methodology of the proposed AAHFAC mixes was given in step by step and it was modified from ACI standards. Test results showed that the 28-day compressive strength of 15-35 MPa were obtained. After modifying mix design of the AAHFAC mixes by updating the AAS/FA ratio from laboratory experiments, it was found that they met the strength requirement.

Keywords: Alkali-activated high-calcium fly ash, Mix design procedure, Strength requirement, Engineering properties.

บทสรุปผู้บริหาร

1. บทนำ

ปัจจุบันวัสดุอัลคาไลน์ได้รับความนิยมอย่างแพร่หลายในการพัฒนาเพื่อใช้เป็นทางเลือกของคอนกรีตปกติที่ผลิตจากปูนซีเมนต์ปอร์ตแลนด์ นอกจากนั้น ปัญหาสิ่งแวดล้อมที่น่าวิตกกังวล มีผลมาจากการปลดปล่อยก๊าซคาร์บอนไดออกไซด์สู่บรรยากาศในกระบวนการผลิตปูนซีเมนต์ ทำให้เกิดแรงกระตุ้นในการวิจัยและพัฒนาที่จะลดปัญหาดังกล่าวมากขึ้น เมื่อพิจารณาคุณสมบัติของวัสดุอัลคาไลน์ จะเห็นได้ว่า มีกำลังอัดที่สูงเทียบเท่าการใช้ปูนซีเมนต์ปอร์ตแลนด์เป็นวัสดุตั้งต้น อีกทั้งมีความทนต่ออุณหภูมิสูงและมีความทนทานต่อกรดและด่างสูง

วัสดุอัลคาไลน์เป็นวัสดุที่สามารถสังเคราะห์ได้จากวัสดุที่มีองค์ประกอบของซิลิกาและอะลูมินาเป็นหลัก เช่น เถ้าลอย ดินขาวเผา เป็นต้น และทำการกระตุ้นปฏิกิริยาด้วยสารละลายด่างสูง สำหรับในประเทศไทย นิยมใช้เถ้าลอยแคลเซียมสูง จากโรงไฟฟ้าแม่เมาะ จังหวัดลำปาง เป็นวัสดุตั้งต้น เถ้าลอยดังกล่าวมีองค์ประกอบของซิลิกา อะลูมินา และแคลเซียมเป็นหลัก และมีส่วนของอสัณฐานในองค์ประกอบทางแร่ ส่งผลให้สามารถเกิดปฏิกิริยาในสภาวะสารละลายด่างได้ดี จึงมีความเหมาะสมในการใช้เป็นวัสดุตั้งต้นในการผลิตวัสดุอัลคาไลน์ที่บ่มในอุณหภูมิปกติ แต่เป็นหนึ่งในเหตุผลที่ต้องมีการพัฒนาวัสดุอัลคาไลน์จากเถ้าลอยแคลเซียมสูงไปใช้ในงานก่อสร้างจริง

เมื่อพิจารณาถึงความเป็นไปได้ในการนำวัสดุอัลคาไลน์จากเถ้าลอยแคลเซียมสูงไปใช้ในงานก่อสร้างจริง พบว่า ค่อนข้างมีความซับซ้อนและยุ่งยาก อาจเนื่องจาก ไม่สามารถควบคุมคุณภาพให้ใกล้เคียงกันทุกส่วนผสมเมื่อมีการใช้วัสดุในการสังเคราะห์แตกต่างกันไป อีกทั้ง ยังไม่มีมาตรฐานการออกแบบส่วนผสมของวัสดุอัลคาไลน์เพื่อให้ได้กำลังอัดที่ต้องการ ในต่างประเทศมีความพยายามจะพัฒนาการออกแบบส่วนผสมของวัสดุอัลคาไลน์ แต่ยังคงเป็นการทดลองแบบแปรผันส่วนผสม แต่ยังคงไม่มีงานวิจัยที่พัฒนาการออกแบบส่วนผสมเหมือนกับการออกแบบส่วนผสมของคอนกรีตปกติ (ACI211.1-91 และ ACI211.4R-93) ซึ่งจะทำให้ได้ส่วนผสมที่ชัดเจนตามกำลังอัดที่ต้องการ ขณะเดียวกัน งานวิจัยล่าสุดในต่างประเทศได้มีการพัฒนาวิธีการออกแบบส่วนผสมวัสดุอัลคาไลน์ตามมาตรฐาน ACI โดยใช้เถ้าลอยแคลเซียมต่ำเป็นวัสดุตั้งต้นและบ่มด้วยความร้อน แต่เป็นไปได้ยากหากต้องการนำไปใช้ในงานก่อสร้างจริง ดังนั้น เพื่อให้วัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูงสามารถนำไปใช้ในงานก่อสร้างได้จริง งานวิจัยนี้จึงพัฒนาวิธีการออกแบบวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูงและบ่มที่อุณหภูมิปกติ ซึ่งข้อมูลจากงานวิจัยนี้จะเป็นข้อมูลที่สำคัญอย่างยิ่งในการใช้งานต่อไปในอนาคตของภาคอุตสาหกรรมก่อสร้างประเทศไทย

2. ความสำคัญของงานวิจัย

งานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาวิธีการออกแบบส่วนผสมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง การออกแบบส่วนผสมของวัสดุอัลคาไลน์คอนกรีตมีความซับซ้อนและไม่มีมาตรฐานสำหรับการออกแบบของวัสดุนี้ ดังนั้น งานวิจัยนี้จะทำให้วิธีการออกแบบส่วนผสมเพื่อให้ได้กำลังอัดของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูงเพื่อใช้งานในภาคอุตสาหกรรมต่อไป

3. ระเบียบวิธีวิจัย

การดำเนินงานวิจัยเกี่ยวกับการออกแบบส่วนผสมของของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง ประกอบด้วย

1) กำหนดขอบเขตงานวิจัย ดังนี้
   (1) แปรผันความเข้มข้นของสารละลายโซเดียมไฮดรอกไซด์ เท่ากับ 10 และ 15 โมลาร์
   (2) แปรผันอัตราส่วนของเหลวต่อวัสดุประสาน เท่ากับ 0.45, 0.50, 0.55 และ 0.60
   (3) แปรผันขนาดของมวลรวมหยาบ เท่ากับ 3/8, 1/2 และ 3/4 นิ้ว
2) ทดสอบคุณสมบัติพื้นฐานของวัสดุที่ใช้ในงานวิจัย ประกอบด้วย
   (1) ความถ่วงจำเพาะ หน่วยน้ำหนักและค่าการดูดซึมน้ำของเถ้าลอยที่ใช้ในงานวิจัย
   (2) ความถ่วงจำเพาะ หน่วยน้ำหนัก ค่าการดูดซึมน้ำ และขนาดคละของมวลรวมละเอียด
   (3) ความถ่วงจำเพาะ หน่วยน้ำหนัก ค่าการดูดซึมน้ำ และขนาดคละของมวลรวมหยาบ
3) ออกแบบส่วนของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง โดยมีขั้นตอนดังนี้
   (1) ขั้นตอนที่ 1 เลือกขนาดใหญ่สุดของมวลรวมหยาบ
   (2) ขั้นตอนที่ 2 หาปริมาณสารอัลคาไลน์และปริมาณช่องว่างที่ต้องใช้ในส่วนผสม
   (3) ขั้นตอนที่ 3 เลือกอัตราส่วนสารอัลคาไลน์ต่อวัสดุประสาน
   (4) ขั้นตอนที่ 4 คำนวณวัสดุประสานที่ต้องใช้ในส่วนผสมต่อลูกบาศก์เมตร โดยคำนวณจากปริมาณสารอัลคาไลน์ที่ได้จากขั้นตอนที่ 2
   (5) ขั้นตอนที่ 5 คำนวณปริมาณของมวลรวมละเอียดและมวลรวมหยาบทั้งหมดที่ต้องใช้ในส่วนผสม
   (6) ขั้นตอนที่ 6 คำนวณปริมาณของมวลละเอียดและมวลรวมหยาบ โดยอ้างอิงจากขั้นตอนที่ 5 โดยใช้อัตราส่วนมวลรวมหยาบต่อมวลรวมละเอียดเท่ากับ 70:30 จากปริมาณของมวลรวมทั้งหมดในส่วนผสมที่คิดเป็น 100%
   (7) ขั้นตอนที่ 7 คำนวณสารลดน้ำพิเศษ โดยเลือกใช้ 0.80-2.0% ของวัสดุประสาน ซึ่งปริมาณการเลือกใช้ขึ้นอยู่กับการทดสอบผสมและทดสอบหาค่ายุบตัวและการไหลแผ่ของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง
   (8) ขั้นตอนที่ 8 สรุปอัตราส่วนผสมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง
   (9) ขั้นตอนที่ 9 ทดสอบระยะเวลาการก่อตัวและการไหลแผ่ของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง
   (10) ขั้นตอนที่ 10 ทดสอบกำลังอัด โมดูลัสยืดหยุ่น และอัตราส่วนปัวซองของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูง เพื่อนำค่าที่ได้ไปคำนวณย้อนกลับและสร้างการออกแบบส่วนผสมของวัสดุอัลคาไลน์คอนกรีตจากเถ้าลอยแคลเซียมสูงต่อไปในขั้นตอนสุดท้ายของงานวิจัย

4. Output ที่ได้จากงานวิจัย

งานวิจัยนี้สามารถผลิตได้บทความวิจัยที่สืบค้นได้ในฐานข้อมูล ISI Web of Knowledge จำนวน 1 บทความ และที่สามารถสืบค้นได้ในฐานข้อมูล Scopus จำนวน 1 บทความ ดังมีรายชื่อบทความดังต่อไปนี้

1) **Tanakorn Phoo-ngernkham**, Chattarika Phiangphimai, Nattapong Damrongwiriyanupap, Sakonwan Hanjitsuwan, Jaksada Thumrongvut, Prinya Chindaprasirt (2018), "A Mix Design Procedure for Alkali-Activated High-Calcium Fly Ash Concrete Cured at Ambient Temperature". Advances in Materials Science and Engineering, 2460403: 1-13.

2) Prinya Chindaprasirt, **Tanakorn Phoo-ngernkham**, Sakonwan Hanjitsuwan, Suksun Horpibulsuk, Anurat Poowancum, Borwonrak Injorhor, (2018), "Effect of calcium-rich compounds on setting time and strength development of alkali-activated fly ash cured at ambient temperature". Case Studies in Construction Materials, 9(December 2018): 1-6.

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CHAPTER 1

INTRODUCTION

1.1 Background

Ordinary Portland cement is widely used for construction works in civilization of human society. However, the major problems associated with the Portland cement are its production, which is energy consuming and more significantly it releases very high volume of carbon dioxide into the atmosphere. At the same time the disposal of industrial wastes such as fly ash and other waste materials has become a big problem, it requires large areas of useful land and also has huge impact on the environment. Therefore, the need is emanated from further investigation into safe waste disposal and investigation into alternative to cement products with reduced environmental impacts. Alkali activated cement is now receiving more attention as an alternative binder for use as building material and is found to be one of the better alternatives in terms of reducing the global warming.

Alkali activated cement has been the subject of intense study because it is an environmentally friendly cementing agent, low energy consumption, low toxicity, stable at high temperature and high durability [1]. From the past, alkali activated concrete is certainly emerged as a novel construction material and has a huge potential to become a prominent construction product of good environmental sustainability [2]. Normally, this material is obtained from precursor materials containing silica and alumina such as fly ash, calcined kaolin or metakaolin activated with high alkali solutions [3-7]. The main reaction products is sodium aluminosilicate hydrate (N-A-S-H) gels for low calcium system. For the system with high calcium content, the main reaction products is calcium aluminosilicate hydrate (C-A-S-H) gels [6, 8]. However, both systems are considered as 'alkali activated materials'.

Fly ash is a widely used source material due to its low cost, abundance availability and greater potential for making alkali activated cements [9]. In Thailand, high calcium fly ash from Mae Moh power plant in the north of Thailand has been shown to be a good precursor materials in providing relatively high strength binder [10]. This is because of fly ash with high CaO content which is still contained high

SiO_2 and Al_2O_3 contents [11-16]. The usage of fly ash as a precursor material provides the greatest opportunity for commercial utilization of this technology due to the plentiful supply of the material worldwide [17, 18]. However, the strength development of alkali activated fly ash at ambient temperature condition is rather slow and relatively low strength is obtained [19, 20]. With the presence of calcium in the system, the reaction at ambient temperature is accelerated [21] and the reaction products contains both sodium aluminosilicate hydrate (N-A-S-H) and calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) [22]. The geopolymerization process can improve with temperature curing at around 40-70 ^{o}C and hence the strength development of alkali activated fly ash [10]. In order to put this material into real use, the improvement of strength development at ambient temperature curing is needed [19, 23]. The usage of calcium-rich materials as an additive can improve the strength development of alkali activated fly ash due to additional calcium silicate hydrate (C-S-H) which coexists with other products [24]. In addition, the reaction of calcium-rich materials with water generates heat from exothermic process at ambient temperature and thus helps enhance the geopolymerization process [19, 20].

Alkali activator solution is one of the most important factors affecting the strength development of alkali activated cement. Normally, sodium hydroxide and sodium silicate solutions are the most used as liquid activators because they are shown to be the most suitable activators in terms of availability and good mechanical properties [25]. Sodium hydroxide solution is commonly used for dissolution of Si^{4+} and Al^{3+} ions from precursor materials to form aluminosilicate material. While, sodium silicate solution contains soluble silicate species and thus is used to promote the condensation process of this material [26]. Also, it has been reported that the molarity of NaOH solution influences the leaching behavior of aluminates and silicates from fly ash. The influence of NaOH molarity and Na_2SiO_3 to NaOH ratios on the compressive strength of alkali activated fly ash. The common way to develop alkali activated fly ash concrete is to dry mix the solid constituents of 3 min followed by addition of liquid constituents of the mixture and wet mixing for another 4 min [27, 28], but Rattanasak and Chindaprasirt [29] noticed that mixing sequence has an effect on geopolymerization and final compressive strength of the alkali activated fly ash. A number of researchers [5, 30, 31] reported that the best mechanical performance of alkali activated fly ash are obtained with combinations of sodium silicate and sodium hydroxide solutions.

A few mix design methodologies have been proposed earlier for alkali activated concrete. Of them all, Lloyd and Rangan [32] were the first to propose a mix design methodology for alkali activated fly ash concrete. According to this method, density of alkali activated fly ash has been assumed as 2400 kg/m^3 and the total aggregates content was fixed at 80%. By deducting the total aggregates content from the assumed density of 2400 kg/m^3, the total mass of fly ash and alkaline activator solution was obtained. Consequently, the fly ash content was determined based on the activator solution to fly ash ratio. Further, individual sodium silicate and sodium hydroxide content were determined from the $Na_2SiO_3/NaOH$ ratio employed. Finally, the designed compressive strength and workability was determined by using water to alkali activated fly ash solid ratios. The main thing lacking in this method is that it doesn't take into consideration the specific gravity of materials used. Anuradha et al. [33] suggested a design procedure for different grade of alkali activated concrete by using Indian standards. In this method, fly ash content and activator solution to fly ash ratio was selected based on the strength required and by keeping fine aggregate percentage as constant. Later, correction to fine aggregate percentage was performed based on its zone. The activator solution content employed was observed to be excess for the corresponding strength reported. Ferdous et al. [34] proposed a mix design for fly ash based alkali activated concrete by considering the concrete density variability, specific gravity of the materials, air content, workability, and the strength requirement. The significant issue that arises in their design process could be the selection of activator solution to fly ash ratio, and also in determining the exact activator solution content with respect to the fly ash content. Development of alkali activated concrete requires suitable mix design to attain its desired strength and workability. Despite of the phenomenal research carried out in the area of alkali activated concrete there is only limited research available on its mix design, a proper and more rational mix design method for alkali activated concrete is still lacking. Even though researchers by Anuradha et al. [33] and Ferdous et al. [34] proposed their own mix design methodologies; they are all largely based by trial and error approach. Mix design and proportioning of alkali activated concrete become complex due to more variables being involved in it and there is no standard mix design method available for designing alkali activated concrete to date. According to Pavithra et al. [35], they are conducted on a mix design procedure for alkali-activated concrete with low calcium fly ash-based. From this experimental investigates found that the strengths were dependent on the alkali activator solution content. Also, its strength follow similar trend to that of normal concrete in the strength aspect. However, this work is still used the temperature curing for enhancing the strength development.

From the literature review, there is no research investigated on a mix design methodology for alkali-activated high calcium FA concrete. Therefore, in this research we attempt to make a new mix design methodology for alkali-activated high calcium FA concrete. Many parameters viz., NaOH concentration, alkaline activator solution-to-binder ratio, and coarse aggregate size have been investigated. An engineering properties i.e. setting time, compressive strength, flexural strength, modulus of elasticity, and Poisson ratio of the AAHFAC have been tested to understand behaviors for utilization this material in the future. The step by step of the mix design procedure for alkali-activated high calcium FA concrete will be explained in this paper. The outcome of this study would lay a foundation for the future use of alkali-activated high calcium FA concrete for manufacturing this material in construction work.

1.2 Objectives

In this research attempt will be made to propose mix design methodology for high calcium-based alkali activated concrete in a rational way. The activator solution is the costliest item among the raw materials involved in the production of high calcium-based alkali activated concrete. Also, by doing this, flexibility in the design mixes both on the strength requirement and desired activator solution point of view can be rendered. The essential features of the proposed method are the flexibility to select alkali activator solution to binder ratio, aggregate sizes and sodium hydroxide concentrations required for specific strength and to estimate the probable strength. Mix design and proportioning of alkali activated fly ash concrete is complex and there is no standard for mix design of this material. In addition, high calcium fly ash is abundance in Thailand. Therefore, the objectives of this research are to develop a mix design procedure to manufacture high calcium-based alkali activated concrete and to perform the parametric studies on engineering properties of high calcium-based alkali activated concrete.

1.3 Scope of research

The main scope of the proposed research is to develop the mix design methodology for high calcium-based alkali activated concrete in a rational way. Mix design method for High Calcium-based Alkali Activated Concrete are composed of various alkaline activator solution to binder ratios ranging from 0.5 to 0.7, sodium hydroxide concentrations ranging from 5 to 15 molar and coarse aggregate sizes ranging from 10 to 20 mm to estimate the probable strength. In the proposed mix design methodology, the materials volume and its specific gravity is also taken into account. The mix design methodology proposed has been given step-wise and the same has been verified with the help of an example in this research. Also, the parametric studies on engineering properties i.e. compressive strength, flexural strength, splitting strength, modulus of elasticity, and Poisson ratio of high calcium-based alkali activated concrete are also studied to understand and future utilization of this material.

CHAPTER 2
LITERATURE REVIEW

2.1 Alkali-activated cement

A historical background about important events in the field of alkali-activated binders is as follows. The development of alkali-activated binders had a major contribution in the 1940s with the work of Purdon [36]. The author used blast furnace slag activated with sodium hydroxide. According to the work, the process was developed in two steps. During the first one, liberation of silica aluminium and calcium hydroxide took place. After that, the formation of silica and alumina hydrates would happen as well as the regeneration of the alkali solution. His results led him to conclude that alkali hydroxides acted as catalysts, having proved that statement by leaching alkali hydroxides in the same amount as presented in the original mixture. However, Glukhovsky [37] concluded that it composed of aluminosilicate calcium hydrates similar to the ones of Portland cement and also of crystalline phases of analcite, a natural rock that would explain the durability of those binders.

A large part of the investigations about alkali-activated binders is related to the activation of blast furnace slag, known as Alkali-slag cement or Alkali-activated slag cement. Blast furnace slag is a by-product of iron production industry, having a high content of calcium which is due to the use of calcium carbonate in the calcination operations. Being a low performance cementitious material, it can achieve high compression strength when an alkaline activator is used. However, Glukhovsky [38] had already made crucial investigations about the activation of blast furnace slag: (a) identifying hydration products as being composed by calcium silicate hydrates and calcium and sodium aluminosilicate hydrates and (b) noticing that clay minerals when submitted to alkali-activation formed aluminium silicate hydrates (zeolite). In addition, Glukhovsky [38] reported that alkali activated cements can be classified into five main categories using the main cementitious components as a criterion as follow:

(1) Alkali activated slag-based cements

(2) Alkali activated pozzolan cements (including alkali activated fly ash cement, alkali activated metakaolin cement)

(3) Alkali activated lime-pozzolan/slag cements

(4) Alkali activated calcium aluminate blended cements, and

(5) Alkali activated Portland blended cements (hybrid cements).

Brief descriptions of the main characteristics of these alkali activated cements can readily be found in the literature [39, 40].

Investigations in the field of alkali activation had an exponential increase after the research results of the French author Davidovits [41] which developed and patented binders obtained from the alkali-activation of metakaolin, having named it after the term “geopolymer” in 1978. According to that author, the new binder is generated by an adjustment of the process used by the Roman and the Egyptians. Based on chemical and mineralogical studies he stated that the pyramid blocks were made of a mixture, with limestone sand, calcium hydroxide, sodium carbonate and water. According to his investigations, pyramid blocks were not made of calcium fossilized layers as it happens in natural stones, but oriented in a random manner as in an artificial binder. XRD diffraction patterns of pyramid specimens indicate that $CaCO_3$ is the major crystalline phase. However, an amorphous material composed of aluminosilicates and a zeolite like material were also found.

For the chemical designation of the geopolymer, Davidovits suggested that geopolymers are members of the family of inorganic polymers. The chemical composition of the geopolymer material is similar to natural zeolitic materials, but the microstructure is amorphous instead of crystalline [8, 9]. The polymerisation process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals, that results in a threedimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows [42]. The polysialate has the following empiric formulae:

$$M_n\left[-\left(SiO_2\right)_z-AlO_2\right]_n.wH_2O \tag{1}$$

Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or polymerisation; z is 1,2,3, or higher, up to 32.

Although these new binders have been named as alkaline cements or alkali-activated cements, this name is hardly peaceful, because of the foundings and designations introduced by Davidovits and on the other hand, due to the confusion over the name Portland cement. In fact, Portland cement also hardens in an alkaline environment. The same happens with the pozzolanic react ion, which means that the designation alkaline cement is not very accurate. Davidovits even calls Portland cement as alkali-activated calcium silicates.

Over the last few years that author has argued that the designation alkali-activated binders is confusing and may wrongly induce civil engineers. It makes them think it could generate alkali-silica reactions, suggesting other names such as geopolymer cement, geopolymeric cementitious compounds, geocements or poly(sialates). However, although Davidovits has some cause about the ambiguity of the name alkali-activated cement; it is not easy to accept the reason related to the fact that it may mislead engineers about the alkali-silica reaction. Besides, it is not granted that all alkali-activated binders are really geopolymers, nor even clear why some authors mentioned the pozzolanic reaction as being a geopolymeric one. The fact that alkali-activated binders could be considered pozzolanic cements is also raised. It is believed that the general rule is to use the name alkali-activated binders, and the name geopolymer should only be used when we are really in the presence of a geopolymer, a zeolite with amorphous to semi-crystalline characteristics.

2.2 Reaction mechanisms of alkali-activated cement

The exact reaction mechanism which explains the setting and hardening of alkali-activated binders is not yet quite understood, although it is thought to be dependent on the prime material as well as on the alkaline activator. According to Glukhovsky [38], it consists of a breakdown of the covalent bonds Si–O–Si and Al–O–Si, which happens when the pH of the alkaline solution raises. The majority of the proposed mechanisms indicate an initial phase of silica dissolution, followed by the phases of transportation and polycondensation [43]. According to Palomo et al.

[8], two models of alkali-activation could be established, the first one is the case of the activation of blast furnace slag (Si+Ca) with a mild alkaline solution, having C-S-H as the main reaction products. In the second model of alkali activation (Si + Al), the general example is the alkali-activation of metakaolin with medium to high alkaline solutions. The final product is characterized by a polymeric model and high mechanical strength. The former model has similarities with the zeolite formation process. Thus, it can be concluded that the activation of metakaolin gives rise to an amorphous polymer just like a zeolite. The alkali activation of fly ashes takes place through an exothermic process of dissolution, during which the breakdown of the covalent bonds Si–O–Si and Al–O–Al occurs. The products generated due to the destruction of fly ash start to accumulate for a period and finally a condensation of the produced structure in a poorly ordered structure with a high mechanical strength.

Alonso and Palomo [44] performed heat evolution tests over sodium hydroxide alkali-activated metakaolin, having identified several phase peaks. A first one due to the dissolution of metakaolin, followed by an induction period with a low heat release and, finally, a third exothermic peak related to the final structure formation and influenced by the concentration of the alkaline activator. According to Jaarsveld et al. [45], the geopolymer formation follows the same process of zeolites: (a) dissolution due to the hydroxide ions OH^-; (b) Orientation of the dissolved species; (c) condensation and hardening of the structure in an inorganic polymeric system.

Lee and Deventer [46] reported that one of the differences between the Portland cement binders and the alkali-activated ones is that in the first case it uses water with an initial neutral pH that slowly turns alkaline (12–13) as the hydration process undergoes a series of non-hydrated particles and several types of crystalline C-S-H gel. In the former case, strong alkali solutions are needed to start the dissolution process. In order to achieve good physical and chemical properties in the final product, it is necessary to add soluble silica (sodium silicate) but, as the initial pH is high, that prevents the coagulation and polymerization of the silicate. When the pH goes to less than 14 due to the dissolution of the prime materials, condensation occurs very quickly. Then a group of reactions of polysialatization, coagulation, colloid formation and hardening occurs in a final product of undissolved aluminosilicate species in an amorphous aluminosilicate structure. Xu et al. [47] studied mixtures of kaolin, sodium and potassium feldspars activated with water glass. He had reported that the geopolymerization is a three step process: dissolution of kaolin and feldspars forming a gel, condensation of the gel with the polymerization of Al and Si in three-dimensional structures in which the alkali metals compensate the electric charge of the aluminium. During the geopolymerization water acts as a reagent and also as a reaction process. The dissolution phase of Al–Si uses water, but the polymerization releases water.

For the hydration products within alkali-activated cement, several authors reported different results to different prime materials. Criado et al. [48] studied the activation of fly ashes having detected the hydration products hydroxisodalite and herschlite. Shi et al. [49] studied the alkali activation of blast furnace slag, having noticed the formation of C-S-H. Wang and Scrivener [50] confirmed that C-S-H gel is the main reaction product of alkali activation of blast furnace slag, having also noticed a low C/S ratio. That is probably due to the high pH solutions, which favors low Ca concentrations and high Si concentrations.

2.3 Alkali-activated fly ash

Fly ash is by-products obtained from the burning of coal at around temperature of around 1200–1300°C in pulverized coal combustion units in electricity power plants. During combustion, mineral impurities such as clay, feldspar, quartz and shale fuse and escape with the exhaust gases. Both Class F and Class C fly ashes as per ASTM C618 [51] can be used as cementing materials in alkali activated cements. Class F fly ash is required to have high content of SiO_2+ Al_2O_3+Fe_2O_3 of 70% minimum and is generally low in CaO (usually around the 3 to 5%). Class F fly ash has pozzolanic properties. Class C fly ash is a fly ash with a lower requirement of SiO_2+ Al_2O_3+ Fe_2O_3 content and usually contains a relatively high CaO content. Class C fly ash has some cementitious properties in addition to pozzolanic properties.

Factors such as particle size distribution, degree of verification and location of the glass diffraction maximum (which is related to the analytical CaO content) strongly affect both fresh and hardened properties of the resulting alkali activated cements/geopolymers [52]. Setting times of fly ash based geopolymers appear to be significantly quickened with increased CaO content [52] as shown in Figure 2.1.

For Class F fly ash, particularly coarse size fly ashes, the setting times of the alkali activated cement at temperature lower than 30°C is extended and can be longer than 1 day. Curing of alkali activated class F fly ash is therefore commonly carried out at high temperatures within the range of 40 to 90°C. At normal temperature, fresh Class F fly ash can be handled (placed, compacted and finished) up to two hours without indication of setting or evidence of degradation in the compressive strength [28].

The curing temperature has significant effect on the activation kinetics of class F fly ash based alkali activated cements [28]. At room temperature, the main reaction product of alkali activated fly ash is an amorphous aluminosilicate gel but is short range ordered. As temperature increases, a metastable intermediate Al-rich phase is formed at early stage which then evolves to a more stable Si-rich phase–zeolite precursor with time [8]. Zeolite crystallization may happen at long term as the final stage of alkali activated fly ash.

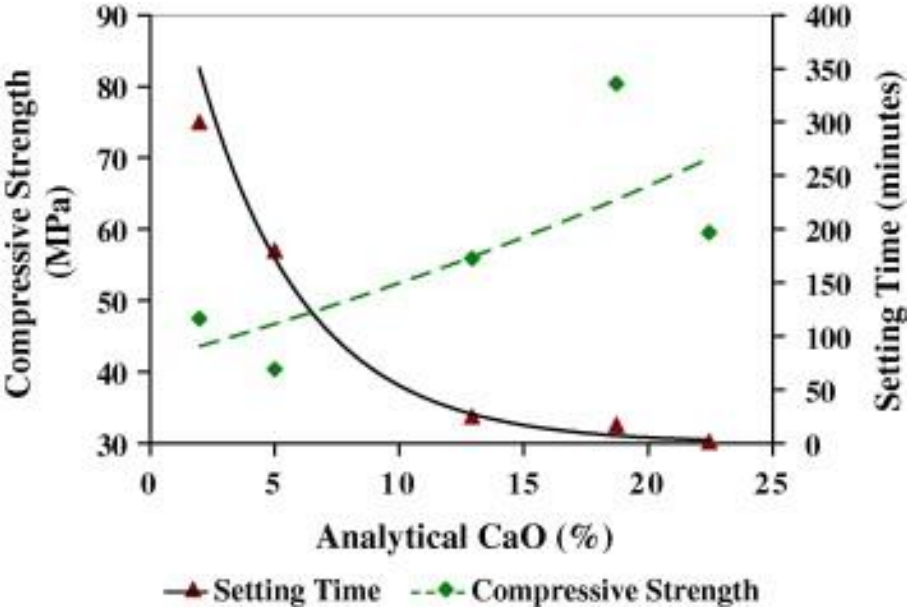


Figure 2.1 Influence of CaO content of fly ash on the setting time and compressive strength of fly ash based geopolymer [52]

When class C fly ash is used, calcium silicate hydrate (C-S-H), calcium aluminate silicate hydrate (C-A-S-H) and traces of calcium alumino silicate zeolite can be found [24]. The rapid formation of C-S-H has been attributed to the rapid setting characteristics of the alkali activated class C fly ash cement [53] which can be

1 to 2 hours at room temperature. Recent research [54] indicates that in addition to the calcium content, the SiO_2/Al_2O_3 has critical influence on the setting characteristics and the initial precipitation of C-A-S-H may be another key factor regulating the setting time. In the class C fly ash/NaOH/ sodium silicate system, the increases in both SiO_2 and Al_2O_3 shortens setting time as shown in Figure 2.2 due to the involvement of Ca^{2+} in the setting time with formation of C-A-S-H gel. The C-A-S-H gel is stable at high pH (over 12) environments and is, therefore, dominant in the setting process, whereas N-A-S-H gel formation is possible at lower pH (9–12) and is secondary in this system [54]. The strength of the class C fly ash/NaOH/sodium silicate system is also related to the amount of SiO_2 and Al_2O_3.

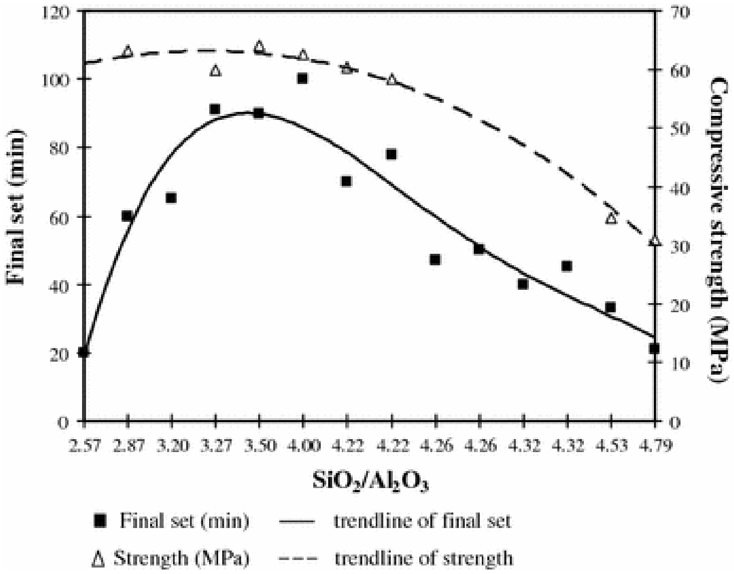


Figure 2.2 Final set and strength of class C fly ash/NaOH/sodium silicate cement with various SiO_2/Al_2O_3 ratios [54]

With regard to setting characteristics, the issues facing alkali activated Class C fly ash is short setting times (when rapid setting is not required), whereas, extended setting time is a concern for alkali activated Class F fly ash at room temperature. This can practically be resolved by blending with other pozzolans such as ground granulated blast furnace slag and selecting suitable activators. To adjust the setting characteristic of alkali activated fly ash, the use of accelerator and retarder are also practiced. Lee and Deventer [46] examined the incorporation of inorganic salt addition on the setting characteristics of KOH/sodium silicate activated class F fly ash pastes. Setting was accelerated by Ca and Mg salts through solid dissolution. The authors also found that potassium salts delayed setting only when the initial activated solution was low in soluble silicate. For class C fly ash, some of the normal accelerator and retarder are applicable. Addition of the proper amount of sucrose efficiently delays the setting time of alkali activated high calcium fly ash paste with no adverse effect on strength. Addition of 1 and 2% sucrose could delay final setting time from 130 min to 210 and 230 min, respectively [53]. On the other hand, addition of 1 and 2% $CaCl_2$ in the system could accelerate the setting with reduction of final setting times from 130 min to 60 and 45 min, respectively.

2.4 Alkaline Liquids

The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate [42]. The use of a single alkaline activator has been reported by Palomo et al. [8] and concluded that the type of alkaline liquid plays an important role in the polymerisation process. Reactions occur at a high rate when the alkaline liquid contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. Xu and van Deventer [9] confirmed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline liquid enhanced the reaction between the source material and the solution. Furthermore, they found that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution. Normally, sodium hydroxide and sodium silicate solutions are the most used as liquid activators because they are shown to be the most suitable activators in terms of availability and good mechanical properties. Phoo-ngernkham et al. [14] reported that the best mechanical performance of alkali-activated cement are obtained with combinations of sodium silicate and sodium hydroxide solutions.

2.5 Factor affecting the properties of alkali-activated concrete

Several factors have been identified as important parameters affecting the properties of alkali-activated concrete. Palomo et al. [8] concluded that the curing temperature was a reaction accelerator in alkali-activated fly ash-based, and significantly affected the mechanical strength, together with the curing time and the type of alkaline liquid. Higher curing temperature and longer curing time were proved to result in higher compressive strength. Alkaline liquid that contained soluble silicates was proved to increase the rate of reaction compared to alkaline solutions that contained only hydroxide. Van Jaarsveld et al. [45] concluded that the water content, and the curing and calcining condition of kaolin clay affected the properties of alkali-activated cement. However, they also stated that curing at too high temperature caused cracking and a negative effect on the properties of the material. In the manufacturing of alkali-activated fly ash concrete railway sleepers, it was reported that the alkali-activated fly ash concrete structural members could easily be produced using the existing current concrete technology without any significant changes. The engineering performances of the products were excellent, and the drying shrinkage was small. The use of alkali-activated fly ash composites to strengthen concrete structures as well as alkali-activated fly ash coating to protect the transportation infrastructures was studied. They reported that alkali-activated fly ash composites have been successfully applied to strengthen reinforced concrete beams. The performance of alkali-activated fly ash was better than the organic polymers in terms of fire resistance, durability under ultra violet light, and did not involve any toxic substances.

Aggregates are one of important factors on properties of alkali-activated cement. As mention, coarse aggregate will influence significantly the strength and structural properties of the concrete. For this reason, a coarse aggregate should be chosen that is sufficiently hard, free of fissures or weak planes, clean, and free of surface coatings. Coarse aggregate properties also affect aggregate-mortar bond characteristics and mixing water requirements. Smaller size aggregates have been shown to provide higher strength potential. For each concrete strength level, there is an optimum size for the coarse aggregate that will yield the greatest compressive strength per pound of cement. In general, the smallest size aggregate produces the highest strength. The use of the largest possible coarse aggregate is an important consideration if optimization of modulus of elasticity, creep, and drying shrinkage are important [55].

Also, ACI211.4R-93 [55] reported that the grading and particle shape of the fine aggregate are significant factors in the production of strength concrete. Particle shape and surface texture can have as great an effect on mixing water requirements and compressive strength of concrete as do those of coarse aggregate. The quantity of paste required per unit volume of a concrete mixture decreases as the relative volume of coarse aggregate versus fine material increases. Because the amount of cementitious material contained in strength concrete is large, the volume of fines tends to be high. Consequently, the volume of sand can be kept to the minimum necessary to achieve workability and compatibility. In this manner, it will be possible to produce higher strength concretes for a given cementitious material content. Fine aggregates with a fineness modulus (FM) in the ranges of 2.5 to 3.2 are preferable for high-strength concretes. Concrete mixtures made with a fine aggregate that has an FM of less than 2.5 may be “sticky” and result in poor workability and a higher water requirement. It is sometimes possible to blend sands from different sources to improve their grading and their capacity to produce higher strengths. If manufactured sands are used, consideration should be given to a possible increase in water demand for workability. The particle shape and the increased surface area of manufactured sands over natural sands can significantly affect water demand.

CHAPTER 3
EXPERIMENTAL DETAILS

3.1 PART A: Development of mix design procedure for alkali-activated high-calcium fly ash concrete cured at ambient temperature

3.1.1 Materials

The precursors used in this study is fly ash (FA) from lignite coal combustion. The FA is the by-product from the Mae Moh power plant in northern Thailand with a specific gravity of 2.65, mean particle size of 15.6 micron, and Blaine fineness of 4400 cm^2/g, respectively. Table 3.1 summarizes the chemical compositions of the FA used in the present experimental work. Note that the FA had sum of SiO_2+Al_2O_3+Fe_2O_3 at 60.96% and the CaO at 25.79%. Therefore, this FA was classified as class C FA as per ASTM C618 [51]. Fine aggregate is the local river sand (RS) with a specific gravity of 2.52 and fineness modulus of 2.20. While coarse aggregates are the crushed lime stone (LS) with various different average sizes of 7, 10, and 16 mm, respectively. Material properties of alkali-activated high calcium fly ash concrete (AAHFAC) ingredients are illustrated in Table 3.2.

Table 3.1 Chemical compositions of FA (by weight)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	31.32	13.96	15.64	25.79	2.94	2.93	2.83	3.29	1.30

Table 3.2 Material properties of the AAHFAC ingredients

Materials	Specific gravity	Fineness modulus	Absorption capacity (%)	Dry density (kg/m^3)
FA	2.65	-	-	-
RS	2.52	2.20	0.85	1585
7 mm LS	2.64	6.04	1.55	1420
10 mm LS	2.65	7.00	1.50	1405
16 mm LS	2.67	7.09	1.00	1400

Sodium hydroxide solution (NaOH) and sodium silicate solution (Na_2SiO_3) with 11.67% Na_2O, 28.66% SiO_2, and 59.67% H_2O were used as liquid activators. Example for the preparation of 10M NaOH, sodium hydroxide pellets of 400 gram was dissolved by distilled water of 1 liter and then allowed to cool down for 24 hours before use to avoid the uncontrolled acceleration of setting of alkali-activated binders [56-58].

3.1.2 Proposed method for designing alkali-activated high calcium fly ash concrete

In this paper, we propose a novel mix design methodology for alkali-activated high calcium fly ash concrete (AAHFAC) in a rational approach. It should be noted that the method is easy to use because it is based on the ACI211.4R-93 [55] with some modification. The parametric studies compose of different NaOH concentrations, alkaline activator solution (AAS) to binder ratios, and coarse aggregate sizes. Flow chart for mix design procedure in this study was illustrated in Figure 3.1. The step by step procedure is summarized as follows;

Step 1: Selection of the maximum size of coarse aggregate

This step is to select the maximum sizes of coarse aggregates for mixing the AAHFAC. Three different sizes of coarse aggregate have been investigated viz., 4.5-9.5 mm or average 7 mm, 9.5-12.5 mm or average 10 mm, and 12.5-20.0 mm or average 16 mm.

Step 2: Selection of the alkaline activator solution (AAS) content and air content

AAS content and air contents were based on the maximum coarse aggregate size as per ACI standards. Maximum AAS and percentage of air per cubic meter of concrete in this study were selected by using the slump condition of around 20 mm as per ACI standards. This condition is summarized in Table 3.3.

Table 3.3 Maximum water content and percentage of air per cubic meter of concrete [59]

Normal maximum size of aggregate (mm)	Maximum water content (kg/m^3)	Percentage of void (%)
10	225	3.0
12.5	215	2.5
20	200	2.0

Step 3: Adjustment of the alkaline activator solution (AAS) content due to percentage of void in fine aggregate

As per ACI211.4R-93 [55], a mixture of concrete has been recommended to use of fine aggregate with fineness modulus values from 2.4 to 3.2. However, particle shape and surface texture of fine aggregate has effect on its voids content, therefore, mixing water requirements may be different from the values given. As mentioned, the values for the required mixing water given are applicable when fine aggregate is used that has a void content of 35%. If not, an adjustment of water content must be added into the required water content. Therefore, this study will be calculated the AAS content due to percentage of void in fine aggregate in a similar way to Portland cement concrete. This adjustment can be calculated using Eq. (3.1);

$$AAS_{adjustment} = \left| \left\{ \left[1 - \left(\frac{\rho_{RS}}{S_G \rho_w} \right) \right] \times 100 \right\} - 35 \right| \times 4.75 \qquad (3.1)$$

Where $AAS_{adjustment}$ is an adjustment of the AAS content (kg/m^3), ρ_{RS} is density of fine aggregate in SSD condition (kg/m^3), S_G is specific gravity of fine aggregate, and ρ_w is density of water (kg/m^3).

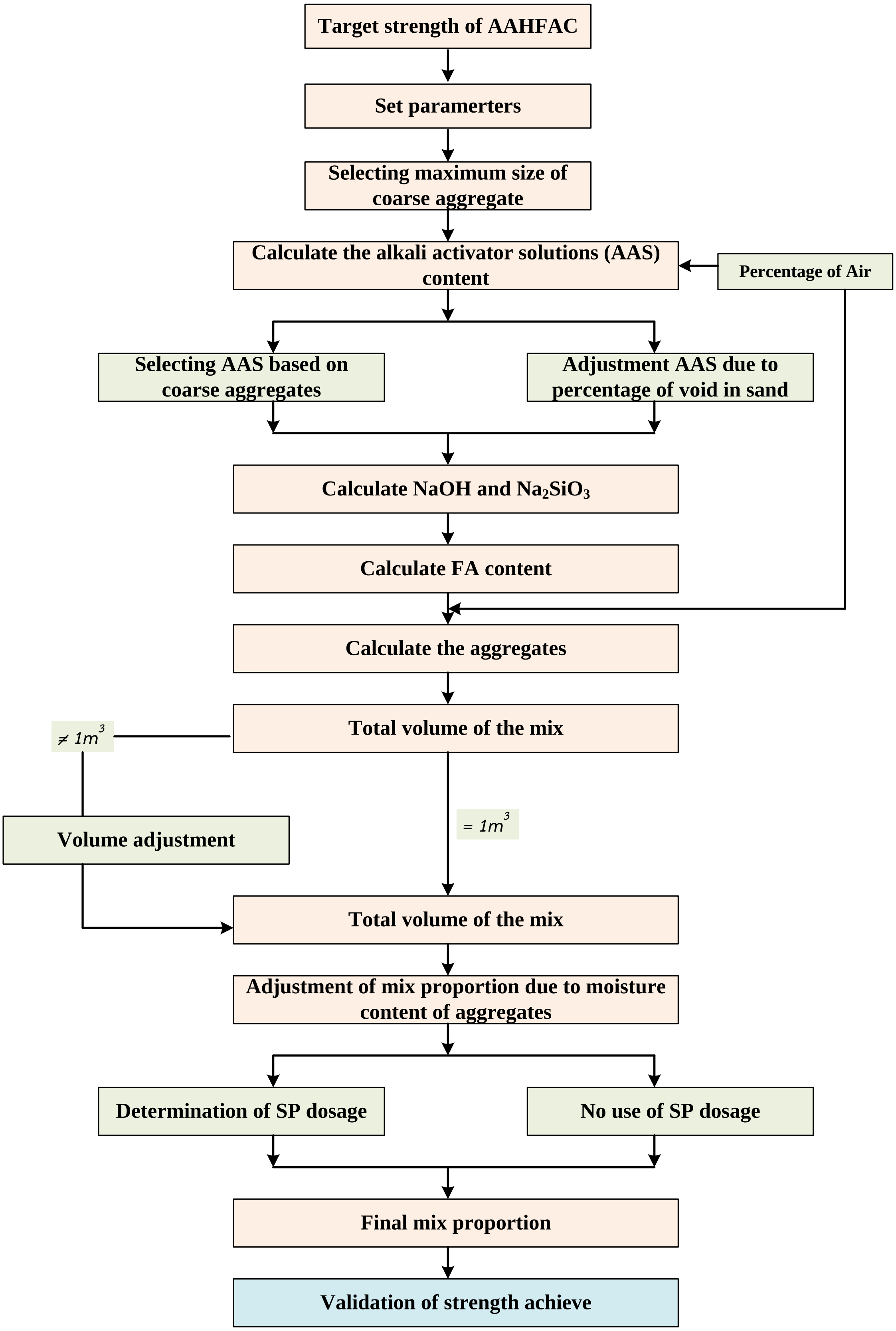


Figure 3.1 Flow chart for mix design procedure

Step 4: Selection of alkaline activator solution-to-fly ash (AAS/FA) ratio.

This research attempts in adopting the standard AAS-to-FA ratio curve of the AAHFAC before use. The minimum compressive strength could be determined from the relationship between 28-day compressive strength and AAS-to-FA ratio. Only the compressive strength of AAHFAC was considered as it is the requirement as per ACI211.4R-93 [55].

Step 5: Calculation of binder content

The weight of binder required per cubic of the AAHFAC could be determined by dividing the values of mixing the AAS content after an adjustment of the AAS content due to percentage of void in fine aggregate.

Step 6: Calculation of individual the AAS content (NaOH and Na_2SiO_3 solutions)

From the literature, NaOH and Na_2SiO_3 were found to be the commonly used alkali activators [32]. In this study, NaOH and Na_2SiO_3 have been selected as alkaline activator solutions. According to Table 4, the density of NaOH with different concentrations have been used for calculating the volume of AAS as per volume method. The individual mass of alkaline activator solutions content could be calculated using Eqs. (3.2) and (3.3);

$$Na_2SiO_3 = \frac{AAS}{\left[1+\dfrac{1}{\dfrac{Na_2SiO_3}{NaOH}}\right]} \tag{3.2}$$

$$NaOH = AAS - \frac{AAS}{\left[1+\dfrac{1}{\dfrac{Na_2SiO_3}{NaOH}}\right]} \tag{3.3}$$

Table 3.4 Density of NaOH solution with different concentrations

NaOH (Molar)	5M	10M	15M
Density (kg/m^3)	1200	1413	1430

Step 7: Calculation of fine and coarse aggregates

Mass of fine and coarse aggregates content is determined as per the absolute volume method. Let the percentage of fine aggregate in the total aggregate be 30% and that of the coarse aggregate be 70%. Fine and coarse aggregates content are determined using Eqs. (3.4) and (3.5).

$$M_{RS} = 0.3 S_{G(RS)} \left[1 - V_{FA} - V_{NaOH} - V_{Na_2SiO_3} - V_{air} \right] \times 1000 \tag{3.4}$$

$$M_{LS} = 0.7 S_{G(\mathrm{LS})} \left[1 - V_{FA} - V_{NaOH} - V_{Na_2SiO_3} - V_{air} \right] \times 1000 \tag{3.5}$$

where M_{RS} is mass of fine aggregate (kg), M_{LS} is mass of coarse aggregate (kg), $S_{G(RS)}$ is specific gravity of fine aggregate, $S_{G(\mathrm{LS})}$ is specific gravity of coarse aggregate, V_{FA} is volume of high calcium fly ash, V_{NaOH} is volume of NaOH, $V_{Na_2SiO_3}$ is volume of Na_2SiO_3, and V_{air} is volume of entrapped air.

Step 8: Calculation of super-plasticizer.

The AAS has the higher viscosity than tap water when used for making the AAHFAC. Hardjito and Rangan [28] reported that the dosage of super-plasticizer was effective for the range between 0.8 and 2% of binder content to improve the workability of alkali-activated binders concrete. Pavithra et al. [35] also claimed that the use of super-plasticizer dosage was found to have impact on behavior of fresh alkali-activated binders concrete, however, it was a little effect on strength and other properties. Therefore, to improve the workability of the AAFAC, a small amount of superplasticizer was incorporated in the mixture.

Step 9: Validation of strength attained with proposed mix design

The 28-day compressive strength obtained from testing will be verified with the target strength.

Step 10: Recalculation Step 4 by the strength obtained from Step 9.

After the 28-day compressive strength has been obtained from testing, all strengths will be recalculated in Step 4 for determining the strength requirement of the AAHFAC various with the AAS-to-FA ratio curve.

Step 11: Validation of strength achieved.

Compressive strength tests will be conducted in the laboratory using the mix design proposed above. When the designed mix satisfies the strength requirement, the final development of the AAHFAC can be made by employing the above design steps.

3.1.3 Manufacturing and testing of the AAHFAC

The laboratory experiments have been conducted to validate the proposed mix design proposed. Based on the AAHFAC trial mix, high calcium fly ash (FA) from Mae Moh power plant in northern Thailand is used as a stating material for making the AAHFAC. Constant NaOH/Na_2SiO_3 ratio is fixed at 1.0 in all mixes. The AAHFAC has been manufactured with different NaOH concentrations of 10 and 15 molar. Both fine and coarse aggregates in saturated surface (SSD) condition have been used for making the AAHFAC. Crushed lime stone with different average sizes of 7, 10, and 16 mm, respectively, are investigated. In this present work, mix design of the AAHFAC with slump at around 17.5-22.5 mm or average 20 mm has been controlled in order to ensure the workability of the AAHFAC.

For the mixing of the AAHFAC, fine and coarse aggregates were mixed together first for 60s. After that, NaOH solution was added in and then they were mixed again for 30s. After 30s, FA was added in and then the mixture was mixed for 60s. Right after, Na_2SiO_3 solution and super-plasticizer were added into a mixture and run the mixer again for a further 60s until becoming homogenous. The mix proportions of the AAHFAC is illustrated in Table 3.5.

Table 3.5 Mix proportion used in this study based on mix design procedure

Symbol	FA (kg/m^3)	NaOH (kg/m^3)		Na_2SiO_3 (kg/m^3)	Aggregates (kg/m^3)				SP (kg/m^3)
		10M	15M		7 mm LS	10 mm LS	16 mm LS	RS	
0.45AAS10M7mmLS	523	118	-	118	1124	-	-	459	5.2
0.45AAS10M10mmLS	500	113	-	113	-	1166	-	475	5.0
0.45AAS10M16mmLS	478	108	-	108	-	-	1211	490	4.8
0.50AAS10M7mmLS	470	118	-	118	1161	-	-	474	4.7
0.50AAS10M10mmLS	450	113	-	113	-	1201	-	489	4.5
0.50AAS10M16mmLS	430	108	-	108	-	-	1245	504	4.3
0.55AAS10M7mmLS	428	118	-	118	1191	-	-	487	4.3
0.55AAS10M10mmLS	409	113	-	113	-	1231	-	501	4.1
0.55AAS10M16mmLS	391	108	-	108	-	-	1273	515	3.9
0.60AAS10M7mmLS	392	118	-	118	1216	-	-	497	3.9
0.60AAS10M10mmLS	375	113	-	113	-	1255	-	511	3.8
0.60AAS10M16mmLS	359	108	-	108	-	-	1296	525	3.6
0.45AAS15M7mmLS	523	-	118	118	1126	-	-	460	5.2
0.45AAS150M10mmLS	500	-	113	113	-	1168	-	475	5.0
0.45AAS15M16mmLS	478	-	108	108	-	-	1212	491	4.8
0.50AAS15M7mmLS	470	-	118	118	1163	-	-	475	4.7
0.50AAS15M10mmLS	450	-	113	113	-	1203	-	490	4.5
0.50AAS15M16mmLS	430	-	108	108	-	-	1246	505	4.3
0.55AASB15M7mmLS	428	-	118	118	1193	-	-	487	4.3
0.55AAS15M10mmLS	409	-	113	113	-	1232	-	502	4.1
0.55AAS15M16mmLS	391	-	108	108	-	-	1274	516	3.9
0.60AASB150M7mmLS	392	-	118	118	1218	-	-	498	3.9
0.60AAS15M10mmLS	375	-	113	113	-	1257	-	512	3.8
0.60AAS15M16mmLS	359	-	108	108	-	-	1298	525	3.6

After mixing, the workability of the AAHFAC was tested using slump cone test as per ASTM C143 [60] as shown in Figure 3.2. Setting time of the AAHFAC was evaluated using method of penetration resistance as per ASTM C403/C403M-16 [61]. After that, a fresh AAHFAC was placed into a cylinder mold with 100 mm diameter and 200 mm height to measure the compressive strength, modulus of elasticity and Poisson’s ratio. Tests for the determination of the static chord modulus of elasticity and Poisson's ratio of the samples have been carried out as per ASTM C469 [62]. While the 75x75x300 mm^3 long beam was used to measure the flexural strength of the AAHFAC and they were calculated as per ASTM C78 [63]. Test setup for compressive strength, flexural strength, modulus of elasticity and Poisson’s ratio of the AAHFAC were illustrated in Figures 3.3 and 3.4. After curing, the AAHFAC samples were demoulded with the aid of slight tapping at the side of the mold at the age of 1 day and immediately wrapped with vinyl sheet to protect moisture loss and kept in the ambient room temperature. All samples of compressive strength, flexural strength, modulus of elasticity and Poisson’s ratio were tested at the age of 28 days curing of the AAHFAC. Five identical samples were tested for each mix and the average value was used as the test result.

(a) Fresh AAHFAC (b) Slump test

Figure 3.2 Fresh and slump test of the AAHFAC

Figure 3.3 Test setup for compressive strength, modulus of elasticity and Poisson’s ratio

Figure 3.4 Test setup for flexural strength

3.2 PART B: Study on effect of calcium-rich compounds on properties of alkali-activated high-calcium fly ash cured at ambient temperature

3.2.1 Introduction

In order to utilize the alkali-activated high calcium FA as a practical alternative repair material, research works have been directed towards the improvement of strength with the addition of additives [15] and nano-SiO_2 and nano-Al_2O_3 [11]. The research on the reduction of setting time of this binder is an important aspect that needs further investigation. The 7-day strength requirement of rapid hardening cementitious materials was 28.0 MPa as described in ASTM C928-13 [64], and the initial setting time and minimum strength requirements for repair binder were 30 minutes and 35.0 MPa, respectively as described in ASTM C881/C881M-14 [65]. The setting time and strength of the alkali-activated high calcium FA with the three additives were presented and compared. The FA used in this investigation was a high calcium FA from Mae Moh Power plant, which is extensively used in concrete and alkali-activated materials technology in Thailand. Three available additives were used: Portland cement (PC), calcium hydroxide (CH) and calcium oxide (CaO).

In addition, traditional repair material is based on epoxy resin, and the study indicated that the carbon footprint of this material is several times higher than that of alkali-activated materials [66, 67]. The use of alkali-activated high calcium FA as a repair material is, therefore, essential to the cleaner production particularly in the field of construction. The viability of usage of three available types of calcium-rich materials as additives in the development of a repair material using alkali- activated high calcium FA cured at ambient temperature has been reported in this paper. The outcome of this study should lay a foundation for the future use of alkali-activated high calcium FA binder as an alternative repair material in a sustainable manner.

3.2.2 Experimental procedure

The binder in this study is a mixture of high calcium FA and calcium additives. The FA was obtained from the Mae Moh power plant in northern Thailand,

and the chemical composition is summarized in Table 3.6. The FA mainly consisted of SiO_2, Al_2O_3, and CaO with some minor impurities. The sum of SiO_2, Al_2O_3, and Fe_2O_3 was 59.92%, and the CaO content was high at 25.79%; thus this FA can be grouped as Class C according to ASTM C618-15 [51]. The specific gravity, median particle size and Blaine fineness of FA were 2.61, 8.5 µm and 430 m^2/kg, respectively. The fine FA was shown to be very reactive and produced alkali-activated materials with high strength [68]. The alkali activators used in this study were 10M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 13.89% Na_2O, 32.15% SiO_2, and 53.96% H_2O. Previous studies on high calcium fly ash [22, 29] indicated that the use of NaOH with 10M concentration gave alkali-activated high calcium FA with high compressive strength. Therefore, 10M NaOH solution was selected for this study. The 10M NaOH was obtained by dissolving sodium hydroxide pellets in distilled water. The solution was left at ambient temperature until the excess heat had completely dissipated to avoid the uncontrolled acceleration of setting of alkali-activated materials as recommended by the previous studies [69]. The NaOH and Na_2SiO_3 solutions were mixed together prior to the mixing alkali-activated high calcium FA.

Table 3.6 Chemical compositions of FA and PC (by weight)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	30.32	13.96	15.64	25.79	2.94	2.93	2.83	4.29	1.30
PC	20.80	4.70	3.40	65.30	1. 50	0.40	0.10	2.70	0.90

Three additives viz., Portland cement (PC) Type I, calcium hydroxide (CH) and calcium oxide (CaO) powders were used to replace FA for making the alkali-activated material. Effect of calcium-rich compounds replacement on setting time and strength development of alkali-activated high calcium FA cured at ambient temperature was investigated and analyzed. The PC, CH and CaO powders were available commercial products in Thailand. The chemical composition of PC is summarized in Table 3.6. The PC powder consisted of 65.3% CaO. The properties of CH and CaO powders are summarized in Table 3.7. The mix proportions of alkali-activated high calcium FA with various replacement ratios of additives are presented in Table 3.8. The additive replacement ratios were 5, 10, and 15% by weight of FA. The liquid/binder (mixture of FA and additive) ratio of 0.60 and NaOH/ Na_2SiO_3 ratio of 2.0 were used in this study.

Table 3.7 The properties of CH and CaO powder

Materials	Density (g/cm^3)	Purity (%)	Appearance
CH	2.24	>95	White powder
CaO	3.30	>90	White powder

The binder (FA and additive) was dry-mixed for 1 min, and the alkali solution was then added and thoroughly mixed for an addition of 3 min. A total of 10 mixes of alkali-activated high calcium FA with calcium-rich compounds were prepared for setting time and compressive strength tests. The setting time of alkali-activated binder was tested using the Vicat apparatus as described in ASTM C191-13 [70]. The fresh alkali-activated binder was placed into 50x50x50 mm^3 cube molds and wrapped with a vinyl sheet to protect moisture loss. The alkali-activated binder samples were cured for 24 hours at ambient temperature of 25 °C and then demolded and immediately wrapped with a vinyl sheet and kept in 25 °C controlled room with the relative humidity of 50% until testing age. The compressive strengths of alkali-activated high calcium FA with calcium-rich compounds were tested at the ages of 7 and 28 days under ASTM C109/C109M-13 [71]. The reported results were the average of three tests.

After 28 day-compressive strength test, the samples from the middle portion were broken into small fragments for observing the growth of the reaction products via a low voltage scanning electron microscopy (LVSEM). The broken small fragments around 3-6 mm were placed on a brass stub sample holder with double stick carbon tape. The sample was dried using infrared light for 5 min and then coated with a layer of gold using a blazer sputtering coater. The micrographs were recorded at 1000x magnification.

Table 3.8 Mix proportions of alkali-activated high calcium FA paste

Mix No.	Mix symbol	FA (g)	PC (g)	CH (g)	CaO (g)	NaOH (g)	Na_2SiO_3 (g)
1	Control	100	-	-	-	20	40
2	5PC	95	5	-	-	20	40
3	10PC	90	10	-	-	20	40
4	15PC	85	15	-	-	20	40
5	5CH	95	-	5	-	20	40
6	10CH	90	-	10	-	20	40
7	15CH	85	-	15	-	20	40
8	5CaO	95	-	-	5	20	40
9	10CaO	90	-	-	10	20	40
10	15CaO	85	-	-	15	20	40

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PART A: Development of mix design procedure for alkali-activated high-calcium fly ash concrete cured at ambient temperature

4.1.1 Experimental results and discussion

Figures 4.1-4.6 show the test results of fresh and mechanical properties of the AAHFAC. According to Figure 4.1, the slump values are between 18-22 mm, therefore, mix design of the AAHFAC from Table 3.1 is in line the slump value at around 17.5-22.5 mm. As mentioned, the AAS and air contents based on the maximum size of the aggregate as per ACI standard could be taken for this study. Final setting time of the AAHFAC tends to obviously increase with increasing of AAS/FA ratio and NaOH concentration as illustrated in Figure 4.2. This result confirms to the previous studies [72, 73] that an increase of fluid medium content resulted in less particle interaction and increased the workability of the mixture. Hanjitsuwan et al. [74] and Rattanasak and Chindaprasirt [29] also explained that NaOH concentration is a main reason for leaching out of Si^{4+} and Al^{3+} ions, therefore, the time of setting tends to increase. However, different size of coarse aggregate is marginal changed in setting time of the AAHFAC.

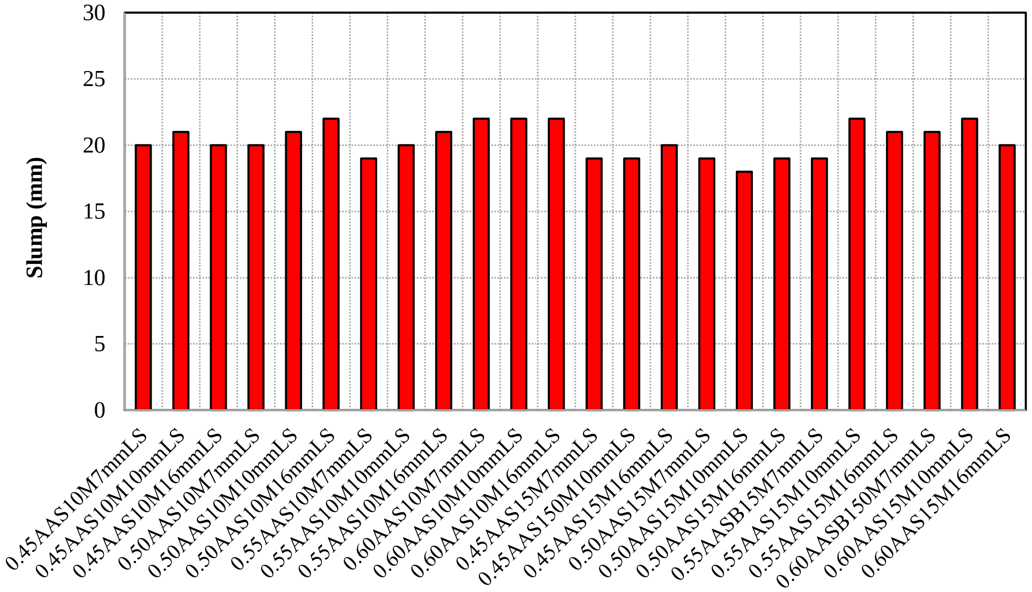


Figure 4.1 Slump of the AAHFAC

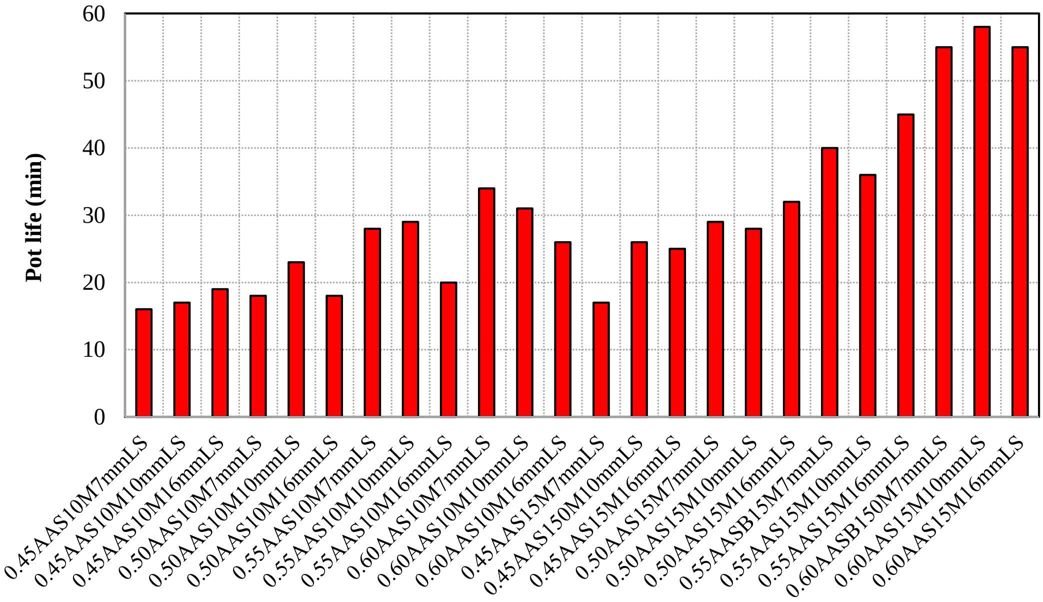


Figure 4.2 Pot life of the AAHFAC

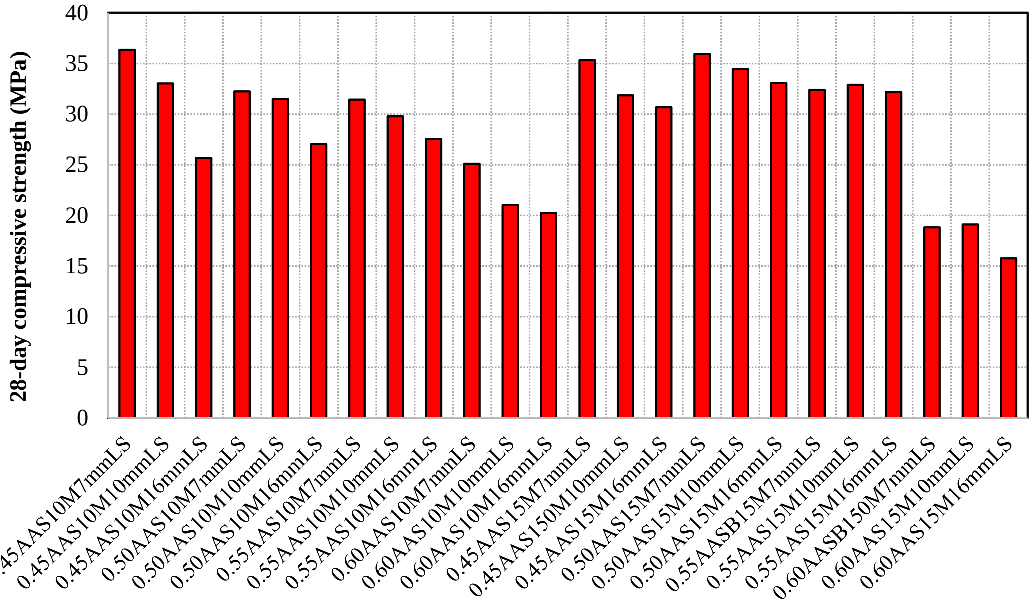


Figure 4.3 28-day compressive strength of the AAHFAC

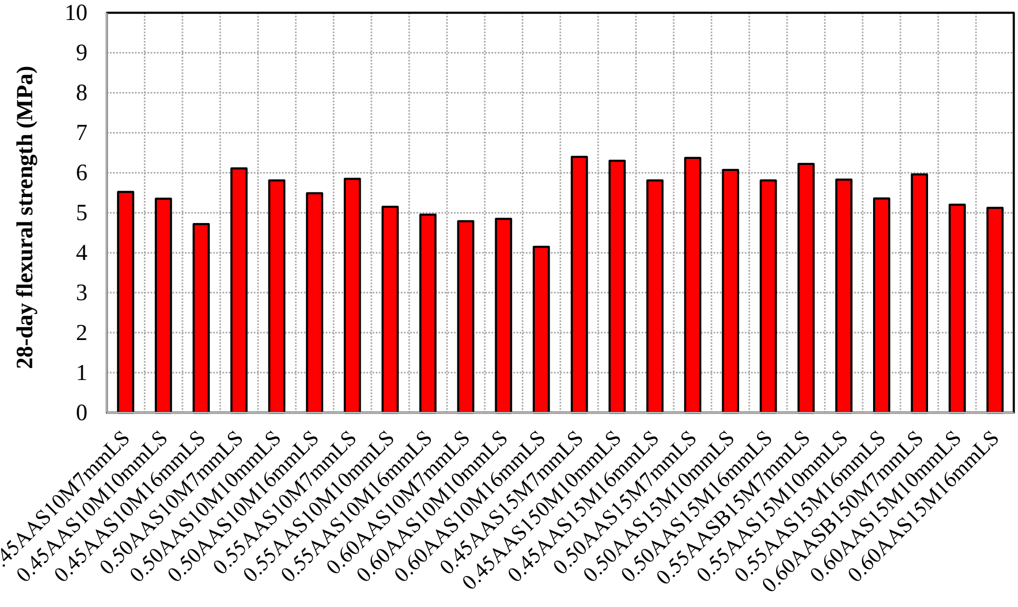


Figure 4.4 28-day flexural strength of the AAHFAC

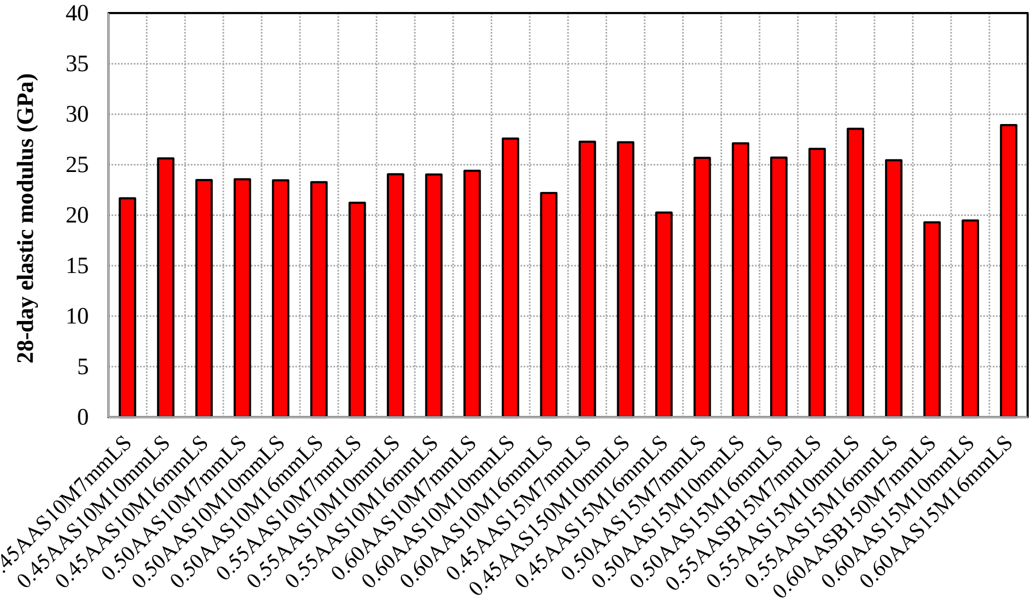


Figure 4.5 28-day elastic modulus of the AAHFAC

Test results of compressive strength, modulus of elasticity and Poisson’s ratio have been shown in Figures 4.3-4.4. It is found that the compressive and flexural strengths tend to increase with the increase of AAS/FA ratio and NaOH concentration, however, they are decreased with increasing coarse aggregate size. Sinsiri et al. [73] claimed that the excess of OH^- concentration in the mixture at high AAS/FA ratio causes in decreasing of strength development of the AAHFAC similar to in case of increasing water-to-cement ratio for Portland cement concrete. Also, the excess liquid solution could disrupt the polymerization process [72]. For effect of NaOH concentration, it is found that the increase in the leaching out of Si^{4+} and Al^{3+} ions from FA particles at high NaOH concentration could improve the N-A-S-H gel, and thus it gives high strength development of the AAHFAC [29]. Also, CaO oxide could react with silica and alumina from FA to form C-(A)-S-H gel which co-existed with N-A-S-H gel [12, 13, 15, 16, 75], resulting in an enhancement of strength. The short setting time of less than 60 minutes at ambient temperature with relatively high 28-day compressvie strengths of 16.0-36.0 MPa indicated the role of calcium in the system. Therefore, the AAHFAC could be used as alternative repair material as reported by several publications [14, 15, 58, 75-78]. There are many reasons such as high compressive strength [68], negligible drying shrinkage [79], low creep [80], good bond with reinforcing steel [81, 82], good resistance to acid and sulfate [2, 56] and fire resistance [83], and excellent bond with old concrete [15, 57, 75]. For effect of coarse aggregate size, the strength development tends to decrease with increasing of coarse aggregate size. Generally, the binder within the AAHFAC is an important factor on the strength development of matrix. This agrees with Pavithra et al. [35] that the increase in total aggregate with corresponding to decreasing of paste has an adverse effect on the strength development of low calcium fly ash geopolymer concrete.

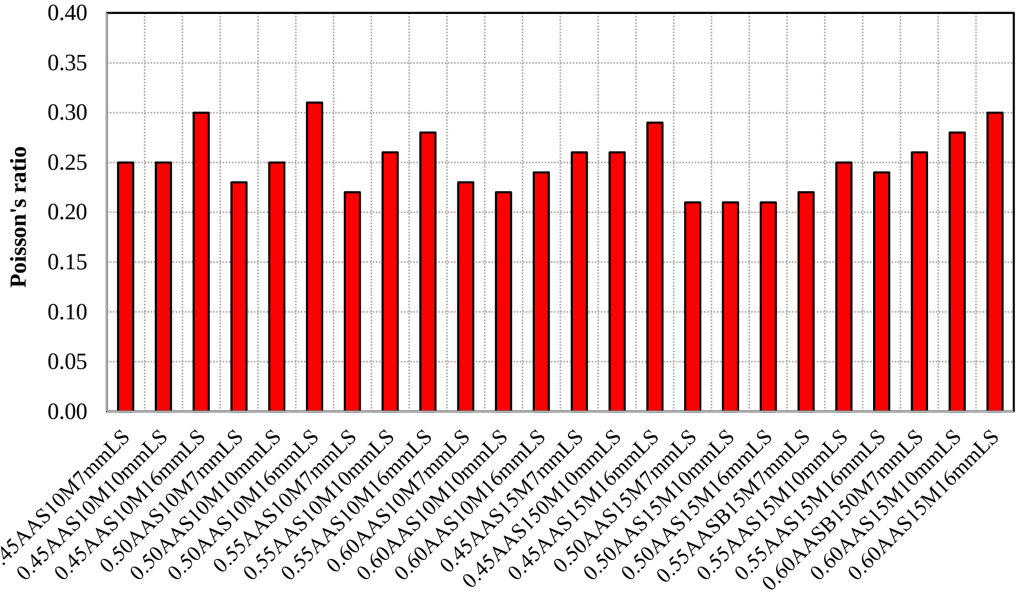


Figure 4.6 28-day Poisson’s ratio of the AAHFAC

The experimental results obtained for modulus of elasticity and Poisson's ratio of the AAHFAC mixes show an overall increase with the increase of compressive strength as shown in Figures 9-10, however, coarse aggregate size has influenced to modulus of elasticity and Poisson's ratio. Normally, it is well-known that the values of modulus of elasticity and Poisson's ratio of concrete depend on the stiffness of paste and aggregates [84]. The modulus of elasticity obtained from this study agrees with Nath and Sarker [85] that modulus of elasticity of geopolymer concrete with 28-day compressive strength of 25-45 MPa were between 17.4 and 24.6 GPa. While, modulus of elasticity of Portland cement concrete were between 25 and 35 GPa [85, 86]. According to Figure 10, the Poisson's ratio for all of the AAHFAC mixes are between 0.21 and 0.31. They show slightly higher than the values assigned for normal strength of Portland cement concrete which are between 0.11 and 0.21 [84]. The high Poisson’s ratios were associated with the mixes with large aggregate of 16 mm. For the mixes with smaller aggregates of 7 and 11 mm, the Poisson's ratios are between 0.21 and 0.27 similar to the previously reported values of inorganic polymer concrete between 0.23 and 0.26 and also in the same range as those of high strength concrete between 0.20 and 0.25 [84].

4.1.2 Verification of the mix design methodology using laboratory experiments

To develop the mix design methodology of the AAHFAC, some parameters from laboratory experiments should be updated before use. In order to support the basic principles of mix design, the relationship between 28-day compressive strength and AAS/FA ratio from laboratory experiments have been produced as shown in Figure 4.7. This AAS/FA ratio curve can be determined the minimum 28-day compressive strength of the AAHFAC similar to water-to-cement ratio curve of Portland cement concrete.

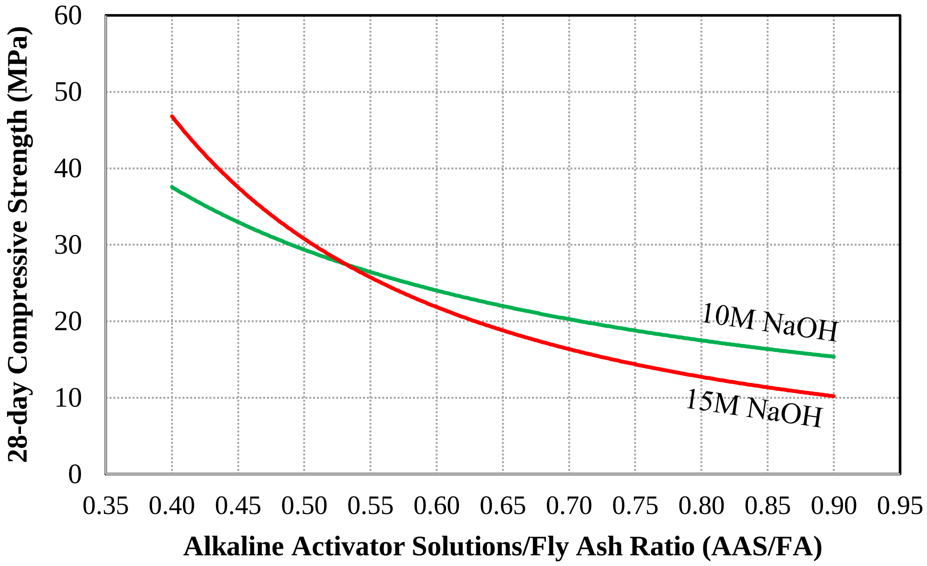


Figure 4.7 28-day compressive strength versus AAS/FA ratio curve

According to Tables 3.4 and Figures 4.1-4.6, the 24 different mixes of the AAHFAC were conducted to develop the mix design methodology. The 28-day compressive strength of the AAHFAC cured at ambient temperature ranging from 15-35 MPa were obtained by using the proposed mix design methodology. All obtained compressive strength of the AAHFAC mixes can be separated into 5 strength requirements viz., 15, 20, 25, 30, and 35 MPa, respectively. These obtained strength requirements of the AAHFAC will be used to recalculate in Step 4 for determining the strength requirement of the AAHFAC with various AAS/FA ratio (see Figure 4.7).

In order to verify the mix design procedure, an example design of the AAHFAC mix with target 28-day compressive strength of 30 MPa has been considered. The parameters are NaOH concentration of 10 molar, maximum aggregate size of 10 mm, and Na_2SiO_3/NaOH ratio of 1.0. Material properties of the AAHFAC ingredients are illustrated in Table 2. The step by step of the mix design procedure is explained as follows;

Step 1: Selection of the maximum coarse aggregate size.

This mix design of the AAHFAC has been selected the maximum coarse aggregate size of 10 mm for mixing the AAHFAC.

Step 2: Selection of AAS and air contents.

AAS and air contents are based on the maximum size of coarse aggregate, therefore, AAS content of 225 kg/m^3 and air content of 3.0% have been used as given in Table 3.3.

Step 3: Adjustment of AAS content due to percentage of void in fine aggregate.

Fine aggregate used in this example has a void of 37%, therefore, the value of adjustment could be calculated as follows;

$$AAS_{adjustment} = \left| \left\{ \left[1 - \left(\frac{1585}{2.52 * 1000} \right) \right] \times 100 \right\} - 35 \right| \times 4.75 = 10 \text{ kg/m}^3$$

Therefore, the AAS content after an adjustment of AAS content due to percentage of void in fine aggregate is 235 kg/m^3.

Step 4: Selection of AAS/FA ratio.

From Figure 4.7, for the minimum 28-day compressive strength of 30 MPa, it is found that the AAS/FA ratio of 0.50 is obtained when 10M NaOH was used as alkaline activator solution.

Step 5: Calculation of binder content.

$$FA\,content = \frac{AAS\,content}{AAS\,/\,\mathrm{FA}\,ratio} = \frac{235}{0.50} = 470\ \ \mathrm{kg/m^3}$$

Step 6: Calculation of NaOH and Na2SiO3 content.

The individual mass of NaOH and Na$_2$SiO$_3$ content could be calculated as follows;

$$Na_2SiO_3 = \frac{AAS}{\left[1+\dfrac{1}{\dfrac{Na_2SiO_3}{NaOH}}\right]} = \frac{235}{\left[1+\frac{1}{1}\right]} = 117.50\ \ \mathrm{kg/m^3}$$

$$NaOH = AAS - \frac{AAS}{\left[1+\dfrac{1}{\dfrac{Na_2SiO_3}{NaOH}}\right]} = 117.50 - \frac{235}{\left[1+\frac{1}{1}\right]} = 117.50\ \ \mathrm{kg/m^3}$$

Step 7: Calculation of fine and coarse aggregates.

$$M_{RS} = 0.3(2.52)\left[1-\frac{470}{2.65x1000}-\frac{117.5}{1413}-\frac{117.5}{1485}-\frac{3}{100}\right]\times 1000 = 477\ \ \mathrm{kg/m^3}$$

$$M_{LS} = 0.7(2.64)\left[1-\frac{470}{2.65x1000}-\frac{117.5}{1413}-\frac{117.5}{1485}-\frac{3}{100}\right]\times 1000 = 1164 \text{ kg/m}^3$$

Step 8: Calculation of super-plasticizer.

$$SP\,dosage = \left(\frac{1}{100}\right)\times 470 = 4.7 \text{ kg/m}^3$$

Step 9: Summarize of mix design.

Based on the mix design methodology of the AAHFAC mix, mix proportions of ingredients is concluded as follows;

FA= 470 kg/m^3
RS= 477 kg/m^3
LS= 1164 kg/m^3
NaOH= 117.5 kg/m^3
Na_2SiO_3= 117.5 kg/m^3
SP= 4.7 kg/m^3

Step 10: Validation of strength achieved.

After following the mix design of the AAHFAC mix, the AAHFAC samples for compressive strength test has been conducted on cylinder molds with 100 mm diameter and 200 mm height. After testing, it is found that 28-day compressive strength of the AAHFAC is 31.15 MPa. Therefore, the mix design of the AAHFAC above meets the strength requirement.

4.2 PART B: Study on effect of calcium-rich compounds on properties of alkali-activated high-calcium fly ash cured at ambient temperature

4.2.1 Effect of calcium-rich compounds on setting time of alkali-activated FA pastes

The setting time of alkali-activated high calcium FA [15, 56, 57, 87, 88] is normally faster than that of PC paste [89]. This fast setting of alkali-activated high calcium FA is an advantage for use as alternative repair material. The results of setting time tests of pastes with various additive contents are illustrated in Fig. 4.8. The initial and final setting times decreased with the increase in replacement level. They were 15-27 min and 26-47 min for FA-PC pastes, 10-25 min and 17-40 min for FA-CH pastes; and 5-19 min and 8-26 min for FA-CaO pastes. It was evident that the additives accelerated the setting of paste compared to that of the control paste (without additive) whose initial and final setting times were 30 and 58 min, respectively. The initial setting time of the control geopolymer was 30 min, which was the required value for repair binder as specified by ASTM C881/C881M-14 [65]. The initial setting times of pastes with the three additives were significantly reduced and met the requirement of ASTM standard. The alkali-activated high calcium FA with CaO exhibited the fastest setting time implying that the CaO had very high dissolution compared with those of PC and CH. The CaO has a generally higher potential of heat generation than CH [90].

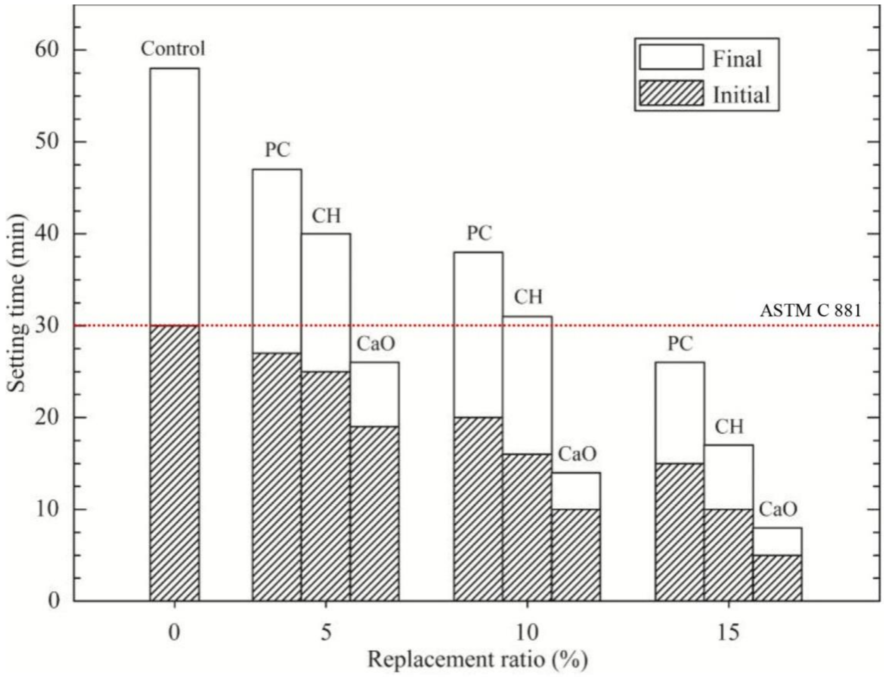


Figure 4.8 Setting time of alkali-activated high calcium FA pastes with different calcium-rich compounds

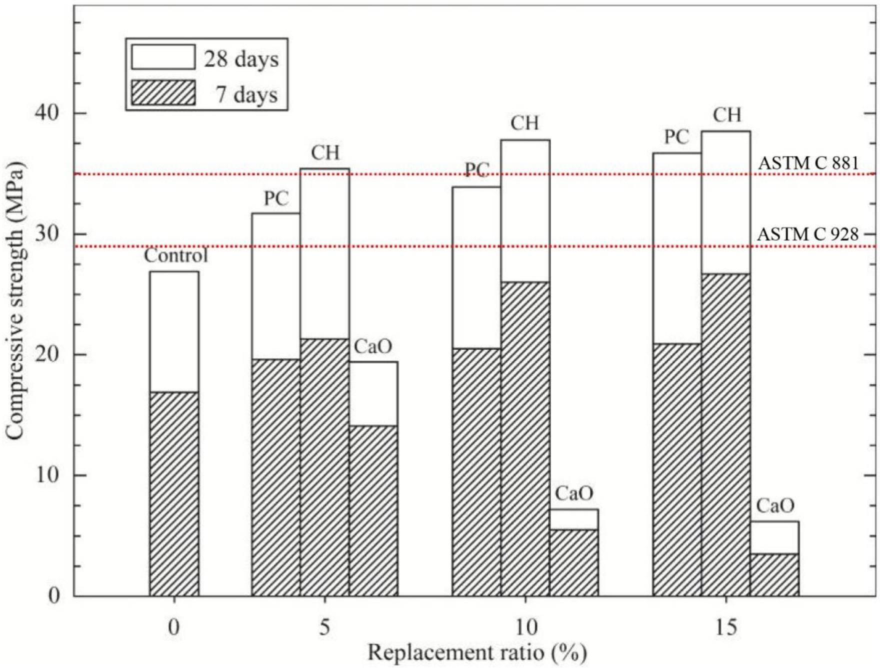


Figure 4.9 Compressive strength of alkali-activated high calcium FA pastes with different calcium-rich compounds

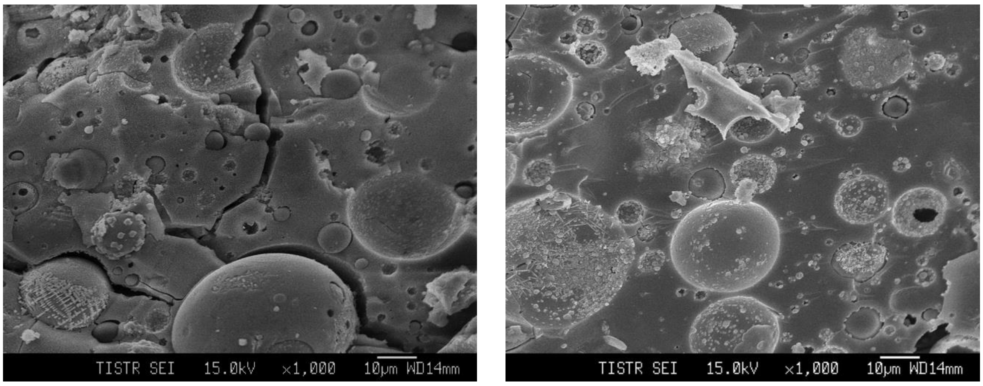
4.2.2 Effect of calcium-rich compounds on compressive strength of alkali-activated FA pastes

The increase in additive replacement ratio also controlled the strength development in alkali-activated high calcium FA. The results of compressive strength tests on pastes with different replacement ratios are illustrated in Fig. 4.9. The 7-day and 28-day strengths of FA-PC and FA-CH pastes increased with increasing replacement ratio. This was associated with the reduction in setting time. The readily available free calcium ions from PC and CH reacted with silica and alumina in FA, resulting in additional calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) within the matrix. The heat generated from the exothermic process due to calcium and water reaction also accelerated the reaction products. The coexistence of C-S-H, C-A-S-H and geopolymer product and generated heat resulted in rapid hardening and high strength. The combination of FA and CH as an additive is advantageous in term of setting time and strength.

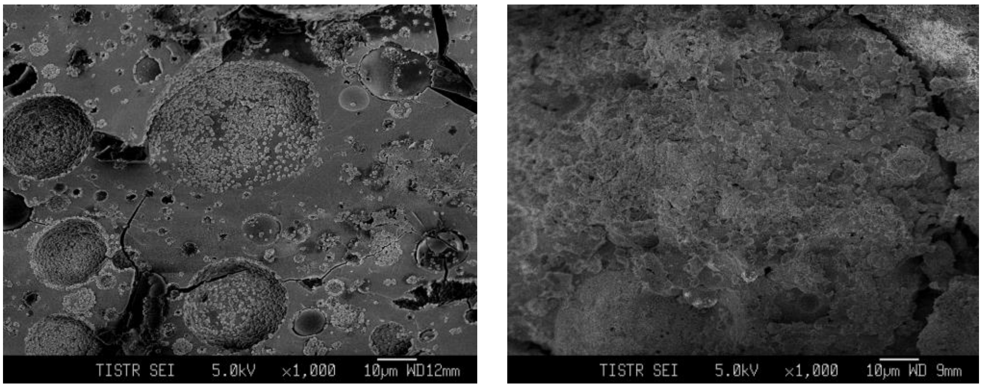
For the FA-CaO pastes, the 7-day and 28-day strengths decreased compared to those of control paste as the replacement ratio increased. In other words, the CaO replacement adversely affected the strength development. The 28-day compressive strengths of FA-CaO pastes were low between 6.2-19.4 MPa for CaO replacement ratios between 5-15%, while the strength of the control paste was 26.9 MPa. The strength reduction of FA-CaO pastes with the increase in replacement ratio was due to the speedy setting of paste resulting in a poor initial matrix framework, which hindered subsequent strength development. The hydration of CaO in alkali medium was incomplete and formed $Ca(OH)_2$ [91]. The hydration of CaO liberated a significant amount of heat and caused the expansion of alkali-activated high calcium FA samples. From the test results, the recommended additives for alkali-activated high calcium FA were PC and CH, which provided the maximum 28-day compressive strengths of FA geopolymer pastes (at 15% content) of 33.9 and 38.5 MPa for FA-PC and FA-CH pastes, respectively. For high early strength material, the 7-day strengths of both FA-PC and FA-CH pastes were slightly lower than 28.0 MPa requirement as specified by ASTM C928-13 [64]. In particular, the 7-day compressive strength of 27.0 MPa with 15% CH was very close to the requirement. The 28-day compressive strengths of FA-CH pastes with 5, 10 and 15% CH were 35.5, 38.0 and 39.0 MPa, which met the requirement of ASTM C881/C881M-14 [65] as a repair material. For the alkali-activated high calcium FA with PC additive, only the pastes with 15% PC with a compressive strength of 37.0 MPa met the 28-day strength requirement.

4.2.3 SEM analysis

The strength development can be explained by the condition of cementitious products via the SEM analysis. Figure 4.10 shows the fracture surfaces of pastes with different additives cured at ambient temperature for 28 days. The matrix of control, FA-PC, FA-CH pastes were dense with some non-reacted and/or partially reacted FA particles embedded in a continuous matrix. The differences in SEM images between these pastes and FA-CaO paste were noticeable. The control, FA-PC and FA-CH pastes were more homogeneous and denser than the FA-CaO paste. The matrix of FA-CaO paste was non-homogenous and loosely packed. Theses SEM photos agreed with the results of compressive strength tests on alkali-activated high calcium FA. The reaction products of this relatively fine alkali-activated FA at an ambient temperature of 25 ºC was reasonable. However, for lower ambient temperature and/or coarser fly ash, the setting and hardening of the FA paste could be a problem [92]. The typical increase in curing temperature is usually employed to ensure good reaction and adequate strength. Instead of heat curing, it is evident from this research that the use of PC and CH as additives can accelerate the reaction by forming additional C-S-H and C-A-S-H within the matrix, resulting in a homogeneous matrix. The reaction of PC and CH with water was an exothermal process and liberated heat, which also accelerated the reaction. The incorporation of CaO did not result in the same improvement of paste. The fast reaction of CaO induced the fast setting and this hindered subsequent strength development. It was reported that the strength of very fast setting cement is generally low at between 10-15 MPa [93]. The high compressive strength of FA-CH paste cured at ambient temperature is very attractive; however, the examination of a threshold CH replacement ratio for this high calcium FA is essential. This is because the excessive lime will disrupt the optimum gels binder structure [94] and hence the possible strength reduction.



(a) Control (b) 10PC



(c) 10CH (d) 10CaO

Figure 4.10 SEM of alkali-activated high calcium FA pastes with different calcium-rich compounds

4.2.4 Implications for use of alkali-activated FA as an alternative repair material

Table 4.1 shows the price of commercial repair material and alkali-activated high calcium FA binder based on Thailand market prices in the year 2018. According to Table 4.1, the total costs of alkali-activated FA pastes with PC, CH and CaO as an additive are about 8500, 88000, 46000 baht/m^3, respectively, whereas alkali-activated FA paste without calcium-rich compounds is about 8300 baht/m^3. Table 4.1 showed that the use of alkali-activated FA pastes with PC is more cost-effective than the use of alkali-activated FA pastes with CH and CaO as an additive. The price of alkali-activated materials is cheaper than that of commercial epoxy resin with the same mechanical properties (see Table 4.1). This agreed with works of Pacheco-Torgal et al. [77] and Phoo-ngernkham et al. [57]. Table 4.2 presents the emission factors of tested materials based on previous studies [95-97]. The emission factor of sodium silicate solution was the highest value whereas FA was the lowest value. Also, the production of alkali-activated materials using FA as the main precursor is to be a sustainable utilization in an alternative binder regarding engineering, economic and environmental perspectives with a low carbon footprint of alkali-activated materials comparable to the commercial epoxy resin as reported in Table 4.1. This is also confirmed with Habert et al. [66] and La Rosa et al. [67]. The outcome of this study is useful to enable the alkali-activated high calcium FA for use in repair applications commercially with FA as source material and CH and PC as an additive. For practical applications on a larger scale, the handling and disposal of generated waste and the possibility of reuse should be taken into consideration as well. The generated waste from this material can be handled the same way as ordinary Portland cement paste. It is not harmful to the environment and can also be used as recycled aggregate.

Table 4.1 Implications for use of alkali-activated FA as an alternative repair material based on test results

	Environmental indicator	**Economic indicator**	**Material properties**	
Mixture No #	**Carbon footprint (Total CO_2-e/t)**	**Price (Baht/m^3)**	**Initial setting time (min)**	**28-day compressive strength (MPa)**
Commercial epoxy A [13, 36]	12.00	156,000	10	45
Commercial epoxy B [13, 36]		65,000	15	60
Commercial epoxy C [13, 36]		93,000	15	40
Reference FA	0.250	8,300	30	27
FA+15%PC	0.348	8,500	15	37
FA+10%CH	0.286	88,000	16	38
FA+5%CaO	0.255	46,000	19	19

Table 4.2 The emission factors of tested materials [95-97].

Materials	Emission factor (t CO_2-e/ton)
Commercial epoxy	5.7000
Fly ash, FA (kg)	0.0070
Portland cement, PC (kg)	0.8200
Calcium hydroxide powder, CH (kg)	0.3740
Calcium oxide powder, CaO (kg)	0.1500
Sodium hydroxide, SH (kg)	1.0377
Sodium silicate, SS (kg)	1.5140

CHAPTER 5

CONCLUSIONS

5.1 Development of mix design procedure for alkali-activated high-calcium fly ash concrete cured at ambient temperature

In this study, the novel mix design methodology for alkali-activated high calcium fly ash concrete (AAHFAC) cured at ambient temperature in a rational way was proposed. From the review of mix design of alkali-activated binders concrete, there is no standard mix design method available for designing the AAHFAC. Some works have been investigated this area attempt to develop mix design methodology for alkali-activated low calcium fly ash. However, it is still used the temperature curing for enhancing the strength development of alkali-activated low calcium fly ash, but this is limited for construction work. To be useful in practice, alkali-activated binders concrete cured at ambient temperature has been conducted to solve this problem. In this study, a new mix design methodology for AAHFAC was modified from ACI standards. The step by step of the mix design procedure for the AAHFAC mixes have been explained in the earlier section. From laboratory experiments, the 28-day compressive strength of the AAHFAC cured at ambient temperature ranging from 15-35 MPa were obtained. After compressive strength was obtained, the alkaline activator solution-to-binder ratios were used to modify the mix design of the AAHFAC. Using modified mix design of the AAHFAC mix, it is found that the proposed mix design of the AAHFAC in this study meets the strength requirement. This mix design would lay a foundation for the future use of AAHFAC in construction industry.

5.2 Effect of calcium-rich compounds on properties of alkali-activated high-calcium fly ash cured at ambient temperature

This paper investigates the effects of the use of three calcium-rich materials (PC, CH, and CaO) on setting time and strength development of alkali-activated high calcium FA cured at ambient temperature. The incorporation of the three additives viz., Portland cement, calcium hydroxide and calcium oxide in alkali-activated high calcium FA resulted in the reduction in setting time, which is an essential requirement of repair material. The strengths of the mixes with PC and CH pastes were significantly improved compared with those of reference FA paste. The properties of FA-CH pastes were slightly better than that of FA-PC pastes. The 15% PC replacement and 5% CH replacement in alkali-activated high calcium FA met the strength requirement for repair material. Additional calcium ion from PC and CH reacted with silica and alumina from FA and formed the reaction products within the matrix, resulting in the additional strength development of pastes. However, the use CaO resulted in speedy setting and significant strength reduction. It is evident from this study that PC and CH can be incorporated into the high calcium fly ash geopolymer to produce reasonably fast setting mixtures with significant strength improvement complying with the strength requirement for repair material. Based on the experimental results obtained, the alkali-activated FA pastes with 15% PC, 5% CH, 10% CH and 15% CH are suitable for use as an alternative repair material.

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APPENDIX A

Paper entitled "A Mix Design Procedure for Alkali-Activated High-Calcium Fly Ash Concrete Cured at Ambient Temperature"

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Research Article

A Mix Design Procedure for Alkali-Activated High-Calcium Fly Ash Concrete Cured at Ambient Temperature

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Abstract

This research focuses on developing a mix design methodology for alkali-activated high-calcium fly ash concrete (AAHFAC). High-calcium fly ash (FA) from the Mae Moh power plant in northern Thailand was used as a starting material. Sodium hydroxide and sodium silicate were used as alkaline activator solutions (AAS). Many parameters, namely, NaOH concentration, alkaline activator solution-to-fly ash (AAS/FA) ratio, and coarse aggregate size, were investigated. The 28-day compressive strength was tested to validate the mix design proposed. The mix design methodology of the proposed AAHFAC mixes was given step by step, and it was modified from ACI standards. Test results showed that the 28-day compressive strength of 15–35 MPa was obtained. After modifying mix design of the AAHFAC mixes by updating the AAS/FA ratio from laboratory experiments, it was found that they met the strength requirement.

1. Introduction

Recently, alkali-activated binders have been widely studied to be used as a substitute for Portland cement. This is because they show great promise as an environmentally friendly binder, have high strength, are stable at high temperatures, and have high durability which are similar to those of Portland cement [1, 2]. From the past, alkali-activated binders are certainly emerged as a novel construction material and have a huge potential to become a prominent construction product of good environmental sustainability [3]. Alkali-activated binders are normally obtained from amorphous aluminosilicate materials such as fly ash, calcined kaolin, or metakaolin activated with high alkali solutions [4–8]. The sodium aluminosilicate hydrate (N-A-S-H) gel is the main reaction product for the low-calcium system, while calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) gels coexisted with sodium aluminosilicate hydrate (N-A-S-H) gel are the main reaction products for the high-calcium system [7, 9]. In Thailand, high-calcium fly ash (FA) from the Mae Moh power plant in the north of Thailand is a widely used starting material for making alkali-activated binders. High CaO content from this FA is very attractive for making alkali-activated binders because it can enhance the strength development when cured at ambient temperature [10–15]. This is why alkali-activated binders are needed to be used in practical works.

It is well known that alkali activator solution is one of the most important factors influencing the strength development of alkali-activated binders. From previous study on this area by Pimraksa et al. [16], they reported that sodium hydroxide and sodium silicate solutions were widely used as liquid activators because of availability and good mechanical properties. Panias et al. [17] claimed that sodium hydroxide solution is commonly used for the dissolution of Si^{4+} and Al^{3+} ions from FA to form aluminosilicate materials, whereas sodium silicate solution contains soluble silicate species and thus is used to promote the condensation process of alkali-activated binders [13]. Many researchers [6, 13, 18–20] reported that a combination of sodium silicate and sodium hydroxide solutions showed the best mechanical performance of alkali-activated binders.

To be useful in practice, a mix design methodology of alkali-activated binders has been studied. For example, Lloyd et al. [21] conducted a mix design methodology for alkali-activated low-calcium fly ash concrete. Ananda Kumar and Sankara Narayanan. [22] studied a design procedure for different grades of alkali-activated concrete by using Indian standards. In this method, fly ash content and activator solution-to-fly ash ratio were selected based on the strength requirement and by keeping the fine aggregate percentage as constant. Ferdous et al. [23] proposed a mix design for

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This research focuses on developing a mix design methodology for alkali-activated high-calcium fly ash concrete (AAHFAC). High-calcium fly ash (FA) from the Mae Moh power plant in northern Thailand was used as a starting material. Sodium hydroxide and sodium silicate were used as alkaline activator solutions (AAS). Many parameters, namely, NaOH concentration, alkaline activator solution-to-fly ash (AAS/FA) ratio, and coarse aggregate size, were investigated. The 28-day compressive strength was tested to validate the mix design proposed. The mix design methodology of the proposed AAHFAC mixes was given step by step, and it was modified from ACI standards. Test results showed that the 28-day compressive strength of 15–35 MPa was obtained. After modifying mix design of the AAHFAC mixes by updating the AAS/FA ratio from laboratory experiments, it was found that they met the strength requirement.

1. Introduction

Recently, alkali-activated binders have been widely studied to be used as a substitute for Portland cement. This is because they show great promise as an environmentally friendly binder, have high strength, are stable at high temperatures, and have high durability which are similar to those of Portland cement [1, 2]. From the past, alkali-activated binders are certainly emerged as a novel construction material and have a huge potential to become a prominent construction product of good environmental sustainability [3]. Alkali-activated binders are normally obtained from amorphous aluminosilicate materials such as fly ash, calcined kaolin, or metakaolin activated with high alkali solutions [4–8]. The sodium aluminosilicate hydrate (N-A-S-H) gel is the main reaction product for the low-calcium system, while calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) gels coexisted with sodium aluminosilicate hydrate (N-A-S-H) gel are the main reaction products for the high-calcium system [7, 9]. In Thailand, high-calcium fly ash (FA) from the Mae Moh power plant in the north of Thailand is a widely used starting material for making alkali-activated binders. High CaO content from this FA is very attractive for making alkali-activated binders because it can enhance the strength development when cured at ambient temperature [10–15]. This is why alkali-activated binders are needed to be used in practical works.

Table 1: Chemical compositions of FA (by weight).

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	31.32	13.96	15.64	25.79	2.94	2.93	2.83	3.29	1.30

Table 2: Material properties of the AAHFAC ingredients.

Materials	Specific gravity	Fineness modulus	Absorption capacity (%)	Dry density (kg/m^3)
FA	2.65	—	—	—
RS	2.52	2.20	0.85	1585
7 mm·LS	2.64	6.04	1.55	1420
10 mm·LS	2.65	7.00	1.50	1405
16 mm·LS	2.67	7.09	1.00	1400

It is well known that alkali activator solution is one of the most important factors influencing the strength development of alkali-activated binders. From previous study on this area by Pimraksa et al. [16], they reported that sodium hydroxide and sodium silicate solutions were widely used as liquid activators because of availability and good mechanical properties. Panias et al. [17] claimed that sodium hydroxide solution is commonly used for the dissolution of Si^{4+} and Al^{3+} ions from FA to form aluminosilicate materials, whereas sodium silicate solution contains soluble silicate species and thus is used to promote the condensation process of alkali-activated binders [13]. Many researchers [6, 13, 18–20] reported that a combination of sodium silicate and sodium hydroxide solutions showed the best mechanical performance of alkali-activated binders.

To be useful in practice, a mix design methodology of alkali-activated binders has been studied. For example, Lloyd et al. [21] conducted a mix design methodology for alkali-activated low-calcium fly ash concrete. Ananda Kumar and Sankara Narayanan. [22] studied a design procedure for different grades of alkali-activated concrete by using Indian standards. In this method, fly ash content and activator solution-to-fly ash ratio were selected based on the strength requirement and by keeping the fine aggregate percentage as constant. Ferdous et al. [23] proposed a mix design for fly ash-based alkali-activated binders concrete by considering the concrete density variability, specific gravity of the materials, air content, workability, and the strength requirement. Also, Lahoti et al. [24] studied the mix design factor and strength prediction of metakaolin-based geopolymer, but it was just a study on the basic properties of the geopolymer made from metakaolin which were not applicable for other raw materials such as fly ash and slag. There were few research studies conducted by Anuradha et al. [22] and Ferdous et al. [23] that used the trial-and-error approach for considering a mix design of alkali-activated binders. However, mix design and proportion of containing binders of alkali-activated concrete seem to be complex because more variables are being involved in it. Therefore, there is no standard mix design method available for designing alkali-activated binders concrete to date. According to the recent study, Pavithra et al. [25] studied a mix design procedure for alkali-activated low-calcium FA concrete. It is shown that its strength follows a similar trend to that of Portland cement concrete as per ACI standards. However, this work still used the temperature curing for enhancing the strength development. From the literature review, there is no research investigated on a mix design methodology for alkali-activated high-calcium FA concrete. Therefore, in this research, we attempt to make a new mix design methodology for alkali-activated high-calcium FA concrete. Many parameters, namely, NaOH concentration, alkaline activator solution-to-binder ratio, and coarse aggregate size, have been investigated. Engineering properties, that is, setting time, compressive strength, flexural strength, modulus of elasticity, and Poisson's ratio, of the AAHFAC have been tested to understand behaviors for utilizing this material in the future. The step-by-step procedure of the mix design for alkali-activated high-calcium FA concrete will be explained in this paper. The outcome of this study would lay a foundation for the future use of alkali-activated high-calcium FA concrete for manufacturing this material in construction work.

2. Experimental Details

2.1. Materials. The precursor used in this study is fly ash (FA) from lignite coal combustion. The FA is the byproduct from the Mae Moh power plant in northern Thailand with a specific gravity of 2.65, a mean particle size of 15.6 μm, and a Blaine fineness of 4400 cm^2/g, respectively. Table 1 summarizes the chemical compositions of the FA used in the present experimental work. Note that the FA had a sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ at 60.96% and CaO at 25.79%. Therefore, this FA was classified as class C FA as per ASTM C618 [26]. The fine aggregate is the local river sand (RS) with a specific gravity of 2.52 and a fineness modulus of 2.20, while coarse aggregates are the crushed lime stone (LS) with various different average sizes of 7, 10, and 16 mm, respectively. Material properties of alkali-activated high-calcium fly ash concrete (AAHFAC) ingredients are illustrated in Table 2.

Sodium hydroxide solution (NaOH) and sodium silicate solution (Na_2SiO_3) with 11.67% Na_2O, 28.66% SiO_2, and 59.67% H_2O were used as liquid activators. For example, for the preparation of 10 M·NaOH, sodium hydroxide pellets of 400 gram were dissolved by distilled water of 1 liter and then

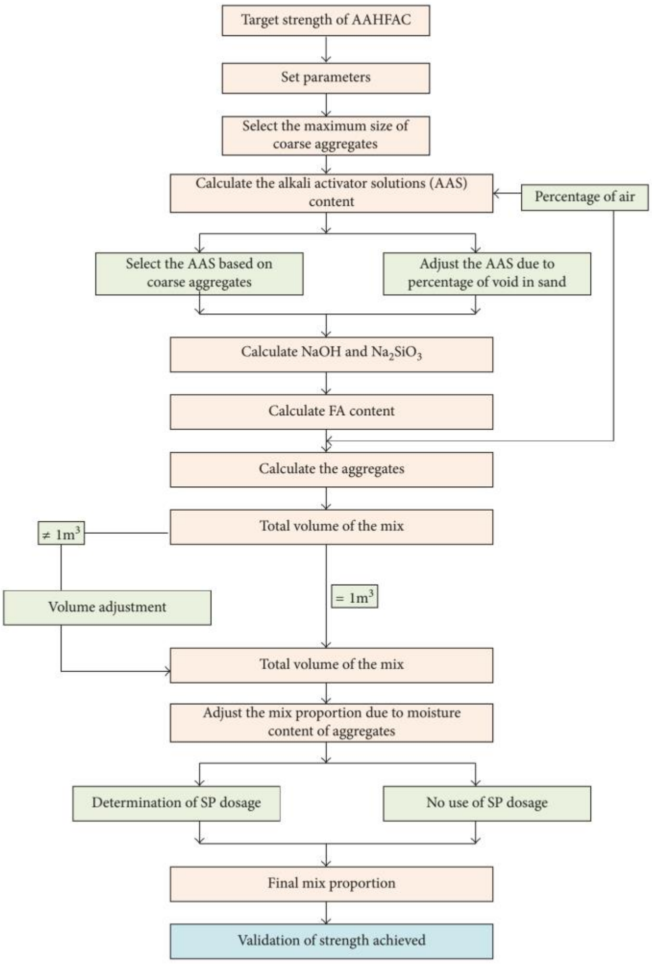

Figure 1: Flow chart for the mix design procedure.

allowed to cool down for 24 hours before use to avoid the uncontrolled acceleration of setting of alkali-activated binders [27–29].

2.2. Proposed Method for Designing Alkali-Activated High-Calcium Fly Ash Concrete. In this paper, we propose a novel mix design methodology for alkali-activated high-calcium fly ash concrete (AAHFAC) in a rational approach. It should be noted that the method is easy to use because it is based on the ACI 211.4R-93 [30] with some modification. The parametric studies are composed of different NaOH concentrations, alkaline activator solution- (AAS-) to-binder ratios, and coarse aggregate sizes. The flow chart for the mix design procedure in this study is illustrated in Figure 1. The step-by-step procedure is summarized as follows:

(1) Step 1: selection of the maximum size of the coarse aggregate

This step is to select the maximum sizes of coarse aggregates for mixing the AAHFAC. Three different sizes of coarse aggregates have been investigated, namely, 4.5–9.5 mm or average 7 mm, 9.5–12.5 mm or average 10 mm, and 12.5–20.0 mm or average 16 mm.

Table 3: Maximum water content and percentage of air per cubic meter of concrete [31].

Normal maximum size of the aggregate (mm)	Maximum water content (kg/m^3)	Percentage of void (%)
10	225	3.0
12.5	215	2.5
20	200	2.0

(2) Step 2: selection of the alkaline activator solution (AAS) content and air content

AAS content and air content were based on the maximum coarse aggregate size as per ACI standards. Maximum AAS and percentage of air per cubic meter of concrete in this study were selected by using the slump condition of around 20 mm as per ACI standards. This condition is summarized in Table 3.

(3) Step 3: adjustment of the alkaline activator solution (AAS) content due to percentage of void in the fine aggregate

As per ACI 211.4R-93 [30], a mixture of concrete has been recommended to use the fine aggregate with fineness modulus values from 2.4 to 3.2. However, particle shape and surface texture of the fine aggregate have an effect on its voids content; therefore, mixing water requirements may be different from the values given. As mentioned, the values for the required mixing water given are applicable when the fine aggregate is used that has a void content of 35%. If not, an adjustment of water content must be added into the required water content. Therefore, this study will calculate the AAS content due to percentage of void in the fine aggregate in a similar way to Portland cement concrete. This adjustment can be calculated using the following equation:

$$\mathrm{AAS}_{\mathrm{adjustment}} = \left| \left\{ \left[1 - \left(\frac{\rho_{\mathrm{RS}}}{S_{\mathrm{G}}\rho_{\mathrm{w}}} \right) \right] \times 100 \right\} - 35 \right| \times 4.75, \quad (1)$$

where $\mathrm{AAS}_{\mathrm{adjustment}}$ is an adjustment of the AAS content (kg/m^3), ρ_{RS} is the density of the fine aggregate in SSD condition (kg/m^3), S_{G} is the specific gravity of the fine aggregate, and ρ_{w} is the density of water (kg/m^3).

(4) Step 4: selection of alkaline activator solution-to-fly ash (AAS/FA) ratio

This research attempts in adopting the standard AAS-to-FA ratio curve of the AAHFAC before use. The minimum compressive strength could be determined from the relationship between 28-day compressive strength and AAS-to-FA ratio. Only the compressive strength of AAHFAC was considered as it is the requirement as per ACI 211.4R-93 [30].

(5) Step 5: calculation of binder content

The weight of the binder required per cubic meter of the AAHFAC could be determined by dividing the values of mixing the AAS content after an adjustment of the AAS content due to percentage of void in the fine aggregate.

(6) Step 6: calculation of individual mass of AAS content (NaOH and Na_2SiO_3 solutions)

Table 4: Density of NaOH solution with different concentrations.

NaOH (molar)	5 M	10 M	15 M
Density (kg/m^3)	1200	1413	1430

From the literature, NaOH and Na_2SiO_3 were found to be the commonly used alkali activators [21]. In this study, NaOH and Na_2SiO_3 have been selected as alkaline activator solutions. According to Table 4, the density of NaOH with different concentrations has been used for calculating the volume of AAS as per the volume method. The individual mass of alkaline activator solutions content could be calculated using the following equation:

$$\begin{aligned} \mathrm{Na_2SiO_3} &= \frac{\mathrm{AAS}}{\left[1 + \left(1/\left(\mathrm{Na_2SiO_3}/\mathrm{NaOH}\right)\right)\right]}, \\ \mathrm{NaOH} &= \mathrm{AAS} - \frac{\mathrm{AAS}}{\left[1 + \left(1/\left(\mathrm{Na_2SiO_3}/\mathrm{NaOH}\right)\right)\right]}. \end{aligned} \quad (2)$$

(7) Step 7: calculation of fine and coarse aggregates

The mass of fine and coarse aggregates content is determined as per the absolute volume method. Let the percentage of the fine aggregate in the total aggregate be 30% and that of the coarse aggregate be 70%. Fine and coarse aggregates content are determined using the following equation:

$$\begin{aligned} M_{\mathrm{RS}} &= 0.3S_{\mathrm{G(RS)}}\left[1 - V_{\mathrm{FA}} - V_{\mathrm{NaOH}} - V_{\mathrm{Na_2SiO_3}} - V_{\mathrm{air}}\right] \times 1000, \\ M_{\mathrm{LS}} &= 0.7S_{\mathrm{G(LS)}}\left[1 - V_{\mathrm{FA}} - V_{\mathrm{NaOH}} - V_{\mathrm{Na_2SiO_3}} - V_{\mathrm{air}}\right] \times 1000, \end{aligned} \quad (3)$$

where M_{RS} is the mass of the fine aggregate (kg), M_{LS} is the mass of the coarse aggregate (kg), $S_{\mathrm{G(RS)}}$ is the specific gravity of the fine aggregate, $S_{\mathrm{G(LS)}}$ is the specific gravity of the coarse aggregate, V_{FA} is the volume of high-calcium fly ash, V_{NaOH} is the volume of NaOH, $V_{\mathrm{Na_2SiO_3}}$ is the volume of Na_2SiO_3, and V_{air} is the volume of entrapped air.

(8) Step 8: calculation of superplasticizer dosage

The AAS has the higher viscosity than tap water when used for making the AAHFAC. Hardjito et al. [32] reported that the dosage of the superplasticizer was effective for the range between 0.8 and 2% of binder content to improve the workability of alkali-activated binder concrete. Pavithra et al. [25] also claimed that the use of superplasticizer dosage was found to have impact on behavior of fresh alkali-activated binder concrete; however, it had a little effect on strength and other properties. Therefore, to improve the workability of the AAHFAC, a small amount of the superplasticizer was incorporated in the mixture.

(9) Step 9: validation of strength attained with the proposed mix design

The 28-day compressive strength obtained from testing will be verified with the target strength.

(10) Step 10: recalculation of Step 4 by the strength obtained from Step 9

Table 5: Mix proportion used in this study based on the mix design procedure.

Mix	Symbol	FA (kg/m^3)	NaOH (kg/m^3)		Na_2SiO_3 (kg/m^3)	Aggregates (kg/m^3)				SP (kg/m^3)
			10 M	15 M		7 mm·LS	10 mm·LS	16 mm·LS	RS	
1	0.45AAS10M7mmLS	523	118	—	118	1124	—	—	459	5.2
2	0.45AAS10M10mmLS	500	113	—	113	—	1166	—	475	5.0
3	0.45AAS10M16mmLS	478	108	—	108	—	—	1211	490	4.8
4	0.50AAS10M7mmLS	470	118	—	118	1161	—	—	474	4.7
5	0.50AAS10M10mmLS	450	113	—	113	—	1201	—	489	4.5
6	0.50AAS10M16mmLS	430	108	—	108	—	—	1245	504	4.3
7	0.55AAS10M7mmLS	428	118	—	118	1191	—	—	487	4.3
8	0.55AAS10M10mmLS	409	113	—	113	—	1231	—	501	4.1
9	0.55AAS10M16mmLS	391	108	—	108	—	—	1273	515	3.9
10	0.60AAS10M7mmLS	392	118	—	118	1216	—	—	497	3.9
11	0.60AAS10M10mmLS	375	113	—	113	—	1255	—	511	3.8
12	0.60AAS10M16mmLS	359	108	—	108	—	—	1296	525	3.6
13	0.45AAS15M7mmLS	523	—	118	118	1126	—	—	460	5.2
14	0.45AAS150M10mmLS	500	—	113	113	—	1168	—	475	5.0
15	0.45AAS15M16mmLS	478	—	108	108	—	—	1212	491	4.8
16	0.50AAS15M7mmLS	470	—	118	118	1163	—	—	475	4.7
17	0.50AAS15M10mmLS	450	—	113	113	—	1203	—	490	4.5
18	0.50AAS15M16mmLS	430	—	108	108	—	—	1246	505	4.3
19	0.55AASB15M7mmLS	428	—	118	118	1193	—	—	487	4.3
20	0.55AAS15M10mmLS	409	—	113	113	—	1232	—	502	4.1
21	0.55AAS15M16mmLS	391	—	108	108	—	—	1274	516	3.9
22	0.60AASB150M7mmLS	392	—	118	118	1218	—	—	498	3.9
23	0.60AAS15M10mmLS	375	—	113	113	—	1257	—	512	3.8
24	0.60AAS15M16mmLS	359	—	108	108	—	—	1298	525	3.6

After the 28-day compressive strength has been obtained from testing, all strengths will be recalculated in Step 4 for determining the strength requirement of the AAHFAC with various AAS-to-FA ratios.

(11) Step 11: validation of strength achieved

Compressive strength tests will be conducted in the laboratory using the mix design proposed above. When the designed mix satisfies the strength requirement, the final development of the AAHFAC can be made by employing the above design steps.

2.3. Manufacturing and Testing of the AAHFAC. The laboratory experiments have been conducted to validate the proposed mix design. Based on the AAHFAC trial mix, high-calcium fly ash (FA) from the Mae Moh power plant in northern Thailand is used as a starting material for making the AAHFAC. Constant $NaOH/Na_2SiO_3$ ratio is fixed at 1.0 in all mixes. The AAHFAC has been manufactured with different NaOH concentrations of 10 M and 15 M. Both fine and coarse aggregates in saturated surface dry (SSD) condition have been used for making the AAHFAC. Crushed lime stone with different average sizes of 7, 10, and 16 mm, respectively, is investigated. In this present work, mix design of the AAHFAC with slump at around 17.5–22.5 mm or average 20 mm has been controlled in order to ensure the workability of the AAHFAC.

For the mixing of the AAHFAC, fine and coarse aggregates were mixed together first for 60 s. After that, NaOH solution was added, and then, they were mixed again for 30 s. After 30 s, FA was added, and then, the mixture was mixed for 60 s. Afterward, Na_2SiO_3 solution and superplasticizer were added into the mixture, and the mixture was mixed again for a further 60 s until becoming homogeneous. The mix proportions of the AAHFAC are illustrated in Table 5.

After mixing, the workability of the AAHFAC was tested using the slump cone test as per ASTM C143 [33] as shown in Figure 2. Setting time of the AAHFAC was evaluated using the method of penetration resistance as per ASTM C403/C403M-16 [34]. After that, a fresh AAHFAC was placed into a cylinder mold with 100 mm diameter and 200 mm height to measure the compressive strength, modulus of elasticity, and Poisson's ratio. Tests for the determination of the static chord modulus of elasticity and Poisson's ratio of the samples have been carried out as per ASTM C469 [35]. The 75 × 75 × 300 mm3 long beam was used to measure the flexural strength of the AAHFAC, and the flexural strength was calculated as per ASTM C78 [36]. The test setup for the compressive strength, flexural strength, modulus of elasticity, and Poisson's ratio of the AAHFAC is illustrated in Figures 3 and 4. After curing, the AAHFAC samples were demolded with the aid of slight tapping at the side of the mold at the age of 1 day and immediately wrapped with vinyl sheet to protect moisture loss and kept at the ambient room temperature. All samples of the compressive strength, flexural strength, modulus of elasticity, and Poisson's ratio were tested at the age of 28 days of curing of the AAHFAC. Five identical samples were tested for each mix, and the average value was used as the test result.

(a) (b)

Figure 2: Fresh AAHFAC (a) and slump test of the AAHFAC (b).

Figure 3: Test setup for compressive strength, modulus of elasticity, and Poisson's ratio.

Figure 4: Test setup for flexural strength.

3. Experimental Results and Discussion

Figures 5–10 show the test results of fresh AAHFAC and mechanical properties of the AAHFAC. According to Figure 5, the slump values are between 18 and 22 mm; therefore, mix design of the AAHFAC from Table 5 is in line with the slump value at around 17.5–22.5 mm. As mentioned, the AAS and air contents based on the maximum size of the aggregate as per the ACI standard could be taken for this study. The final setting time of the AAHFAC tends to obviously increase with the increase of AAS/FA ratio and NaOH concentration as illustrated in Figure 6. This result conforms to the previous studies [37, 38] that an increase of fluid medium content resulted in less particle interaction and increased the workability of the mixture. Hanjitsuwan et al. [39] and Rattanasak and Chindaprasirt [40] also explained that NaOH concentration is a main reason for leaching out of Si^{4+} and Al^{3+} ions; therefore, the time of setting tends to increase. However, different sizes of the coarse aggregate are marginal changed in the setting time of the AAHFAC.

Test results of the compressive strength, modulus of elasticity, and Poisson's ratio have been shown in Figures 7 and 8. It is found that the compressive and flexural strengths tend to increase with the increase of AAS/FA ratio and NaOH concentration; however, they are decreased with increasing coarse aggregate sizes. Sinsiri et al. [38] claimed that the excess OH^- concentration in the mixture at high AAS/FA ratio causes the decrease of strength development of the AAHFAC similar to that in case of increasing water-to-cement ratios for Portland cement concrete. Also, the excess liquid solution could disrupt the polymerization process [37]. For the effect of NaOH concentration, it is found that the increase in the leaching out of Si^{4+} and Al^{3+} ions from FA particles at high NaOH concentration could improve the N-A-S-H gel, and thus, it gives high strength development of the AAHFAC [40]. Also, CaO oxide could react with silica and alumina from FA to form C-(A)-S-H gel which coexisted with N-A-S-H gel [11, 12, 14, 15, 20], resulting in an enhancement of strength. The short setting time of less than 60 minutes at ambient temperature with relatively high 28-day compressive strengths of 16.0–36.0 MPa indicated the role of calcium in the system. Therefore, the AAHFAC could be used as an alternative repair material as reported by several publications [13, 14, 20, 29, 41–43]. There are many reasons such as high compressive strength [44], negligible drying shrinkage [45], low creep [46], good bond with reinforcing steel [47, 48], good resistance to acid and sulfate [3, 27], fire resistance [49], and excellent bond with old concrete [14, 20, 28]. For the effect of coarse aggregate size, the strength development tends to decrease with the increase of coarse aggregate size. Generally,

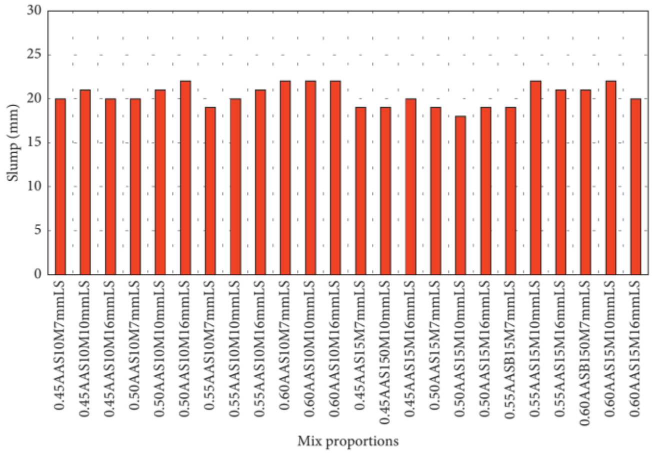

Figure 5: Slump of the AAHFAC

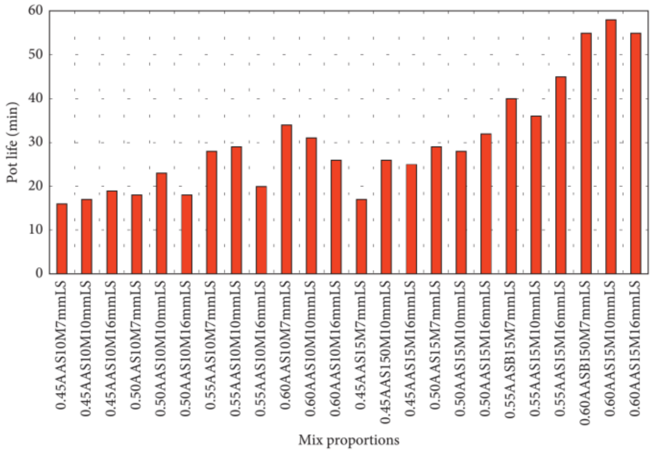

Figure 6: Pot life of the AAHFAC.

the binder within the AAHFAC is an important factor on the strength development of the matrix. This agrees with the findings of Pavithra et al. [25] that the increase in total aggregate corresponding to the decrease of paste has an adverse effect on the strength development of low-calcium fly ash geopolymer concrete.

The experimental results obtained for the modulus of elasticity and Poisson's ratio of the AAHFAC mixes show an overall increase with the increase of compressive strength as shown in Figures 9 and 10; however, the coarse aggregate size influenced the modulus of elasticity and Poisson's ratio. Normally, it is well known that the values of modulus of elasticity and Poisson's ratio of concrete depend on the stiffness of paste and aggregates [50]. The modulus of elasticity obtained from this study agrees with Nath and Sarker [51] that the modulus of elasticity of geopolymer concrete with 28-day compressive strength of 25–45 MPa was between 17.4 and 24.6 GPa, while the modulus of elasticity of Portland cement concrete was between 25 and 35 GPa [51, 52]. According to Figure 10, Poisson's ratio for

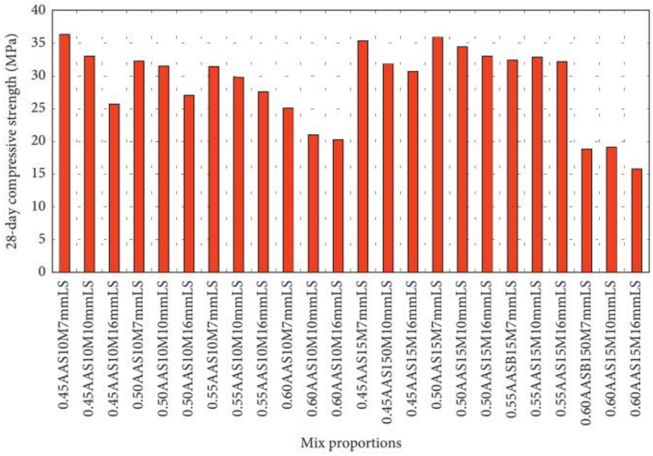

Figure 7: 28-day compressive strength of the AAHFAC.

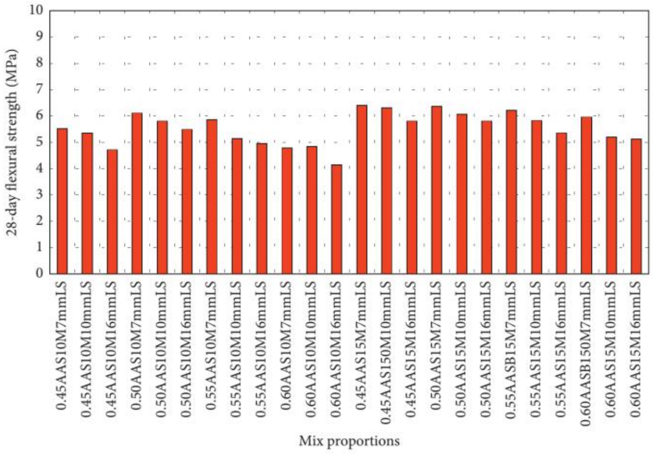

Figure 8: 28-day flexural strength of the AAHFAC.

all of the AAHFAC mixes is between 0.21 and 0.31. They show values slightly higher than the values assigned for normal strength of Portland cement concrete which are between 0.11 and 0.21 [50]. The high Poisson's ratios were associated with the mixes with large aggregates of 16 mm. For the mixes with smaller aggregates of 7 and 11 mm, Poisson's ratios are between 0.21 and 0.27 similar to the previously reported values of inorganic polymer concrete between 0.23 and 0.26 and also in the same range as those of high strength concrete between 0.20 and 0.25 [50].

4. Verification of the Mix Design Methodology Using Laboratory Experiments

To develop the mix design methodology of the AAHFAC, some parameters from laboratory experiments should be updated before use. In order to support the basic principles of mix design, the relationship between 28-day compressive strength and AAS/FA ratio from laboratory experiments has been produced as shown in Figure 11. The AAS/FA ratio curve can be determined for the minimum 28-day

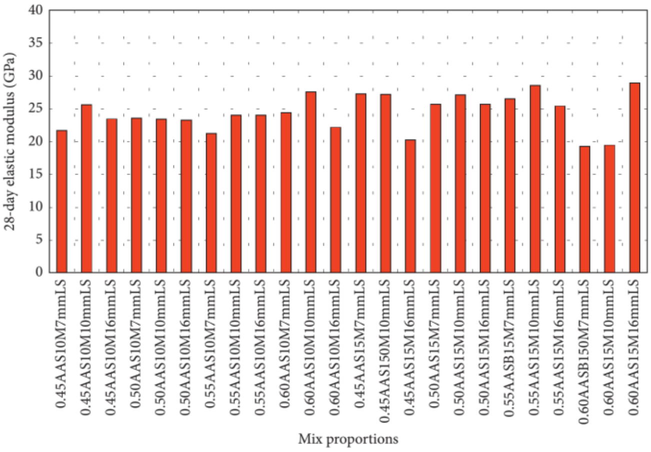

Figure 9: 28-day elastic modulus of the AAHFAC.

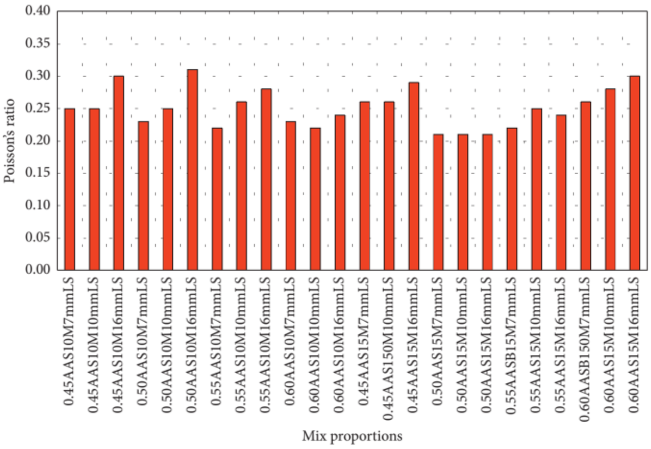

Figure 10: 28-day Poisson's ratio of the AAHFAC.

compressive strength of the AAHFAC similar to that of the water-to-cement ratio curve of Portland cement concrete.

According to Table 5 and Figures 5–10, the 24 different mixes of the AAHFAC were conducted to develop the mix design methodology. The 28-day compressive strength of the AAHFAC cured at ambient temperature ranging from 15 to 35 MPa was obtained by using the proposed mix design methodology. All obtained compressive strengths of the AAHFAC mixes can be separated into 5 strength requirements, namely, 15, 20, 25, 30, and 35 MPa, respectively. These obtained strength requirements of the AAHFAC will be used to recalculate in Step 4 for determining the strength requirement of the AAHFAC with various AAS/FA ratios (Figure 11).

In order to verify the mix design procedure, an example design of the AAHFAC mix with the target 28-day compressive strength of 30 MPa has been considered. The parameters are NaOH concentration of 10 M, maximum aggregate size of 10 mm, and Na_2SiO_3/NaOH ratio of 1.0. Material properties of the AAHFAC ingredients are

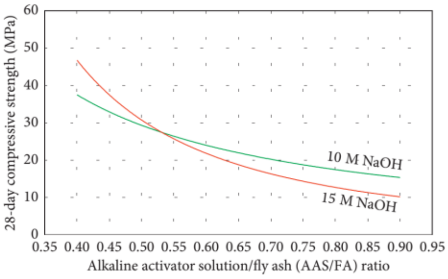

FIGURE 11: Twenty-eight-day compressive strength versus the AAS/FA ratio curve.

illustrated in Table 2. The step-by-step procedure of the mix design is explained as follows:

Step 1: selection of the maximum coarse aggregate size

This mix design of the AAHFAC has been selected the maximum coarse aggregate size of 10 mm for mixing the AAHFAC.

Step 2: selection of AAS and air contents

AAS and air contents are based on the maximum size of the coarse aggregate; therefore, AAS content of 225 kg/m^3 and air content of 3.0% have been used as given in Table 3.

Step 3: adjustment of AAS content due to percentage of void in the fine aggregate

The fine aggregate used in this example has a void of 37%; therefore, the value of adjustment could be calculated as follows:

$$\mathrm{AAS}_{\text{adjustment}} = \left|\left\{\left[1 - \left(\frac{1585}{2.52 * 1000}\right)\right] \times 100\right\} - 35\right| \times 4.75 = 10\ \mathrm{kg/m^3}. \tag{4}$$

Therefore, the AAS content after an adjustment of AAS content due to percentage of void in the fine aggregate is 235 kg/m^3.

Step 4: selection of AAS/FA ratio

From Figure 11, for the minimum 28-day compressive strength of 30 MPa, it is found that the AAS/FA ratio of 0.50 is obtained when 10 M·NaOH was used as alkaline activator solution.

Step 5: calculation of binder content

$$\text{FA content} = \frac{\text{AAS content}}{\text{AAS/FA ratio}} = \frac{235}{0.50} = 470\ \mathrm{kg/m^3}. \tag{5}$$

Step 6: calculation of NaOH and Na_2SiO_3 content

The individual mass of NaOH and Na_2SiO_3 content could be calculated as follows:

$$\begin{aligned}
\mathrm{Na_2SiO_3} &= \frac{\mathrm{AAS}}{[1 + (1/(\mathrm{Na_2SiO_3/NaOH}))]}\\
&= \frac{235}{[1 + (1/1)]} = 117.50\ \mathrm{kg/m^3},\\
\mathrm{NaOH} &= \mathrm{AAS} - \frac{\mathrm{AAS}}{[1 + (1/(\mathrm{Na_2SiO_3/NaOH}))]}\\
&= 117.50 - \frac{235}{[1 + (1/1)]} = 117.50\ \mathrm{kg/m^3}.
\end{aligned} \tag{6}$$

Step 7: calculation of fine and coarse aggregates

$$\begin{aligned}
M_{\mathrm{RS}} &= 0.3(2.52)\left[1 - \frac{470}{2.65 \times 1000} - \frac{117.5}{1413} - \frac{117.5}{1485} - \frac{3}{100}\right]\\
&\quad \times 1000 = 477\ \mathrm{kg/m^3},\\
M_{\mathrm{LS}} &= 0.7(2.64)\left[1 - \frac{470}{2.65 \times 1000} - \frac{117.5}{1413} - \frac{117.5}{1485} - \frac{3}{100}\right]\\
&\quad \times 1000 = 1164\ \mathrm{kg/m^3}.
\end{aligned} \tag{7}$$

Step 8: calculation of superplasticizer dosage

$$\text{SP dosage} = \left(\frac{1}{100}\right) \times 470 = 4.7\ \mathrm{kg/m^3}. \tag{8}$$

Step 9: summarization of mix design

Based on the mix design methodology of the AAHFAC mix, mix proportions of ingredients are concluded as follows:

$$\begin{aligned}
\mathrm{FA} &= 470\ \mathrm{kg/m^3},\\
\mathrm{RS} &= 477\ \mathrm{kg/m^3},\\
\mathrm{LS} &= 1164\ \mathrm{kg/m^3},\\
\mathrm{NaOH} &= 117.5\ \mathrm{kg/m^3},\\
\mathrm{Na_2SiO_3} &= 117.5\ \mathrm{kg/m^3},\\
\mathrm{SP} &= 4.7\ \mathrm{kg/m^3}.
\end{aligned} \tag{9}$$

Step 10: validation of strength achieved

After following the mix design of the AAHFAC mix, the AAHFAC samples were tested for compressive strength on cylinder molds with 100 mm diameter and 200 mm height. After testing, it is found that the 28-day compressive strength of the AAHFAC is 31.15 MPa. Therefore, the mix design of the AAHFAC above meets the strength requirement.

5. Conclusion

In this study, the novel mix design methodology for alkali-activated high-calcium fly ash concrete (AAHFAC) cured at ambient temperature in a rational way was proposed. From the review of mix design of alkali-activated binders concrete, there is no standard mix design method available for designing the AAHFAC. Some works have been investigated in this area in an attempt to develop mix design methodology for alkali-activated low-calcium fly ash. However, it still used the temperature curing for enhancing the strength development of alkali-activated low-calcium fly ash, but this is limited for construction work. To be useful in practice, alkali-activated binders concrete cured at ambient temperature has been used to solve this problem. In this study, a new mix design methodology for AAHFAC was modified from ACI standards. The step-by-step procedure of the mix design for the AAHFAC mixes has been explained in the earlier section. From laboratory experiments, the 28-day compressive strength of the AAHFAC cured at ambient temperature ranging from 15 to 35 MPa was obtained. After compressive strength was obtained, the alkaline activator solution-to-binder ratios were used to modify the mix design of the AAHFAC. Using the modified mix design of the AAHFAC mix, it is found that the proposed mix design of the AAHFAC in this study meets the strength requirement. This mix design would lay a foundation for the future use of AAHFAC in construction industry.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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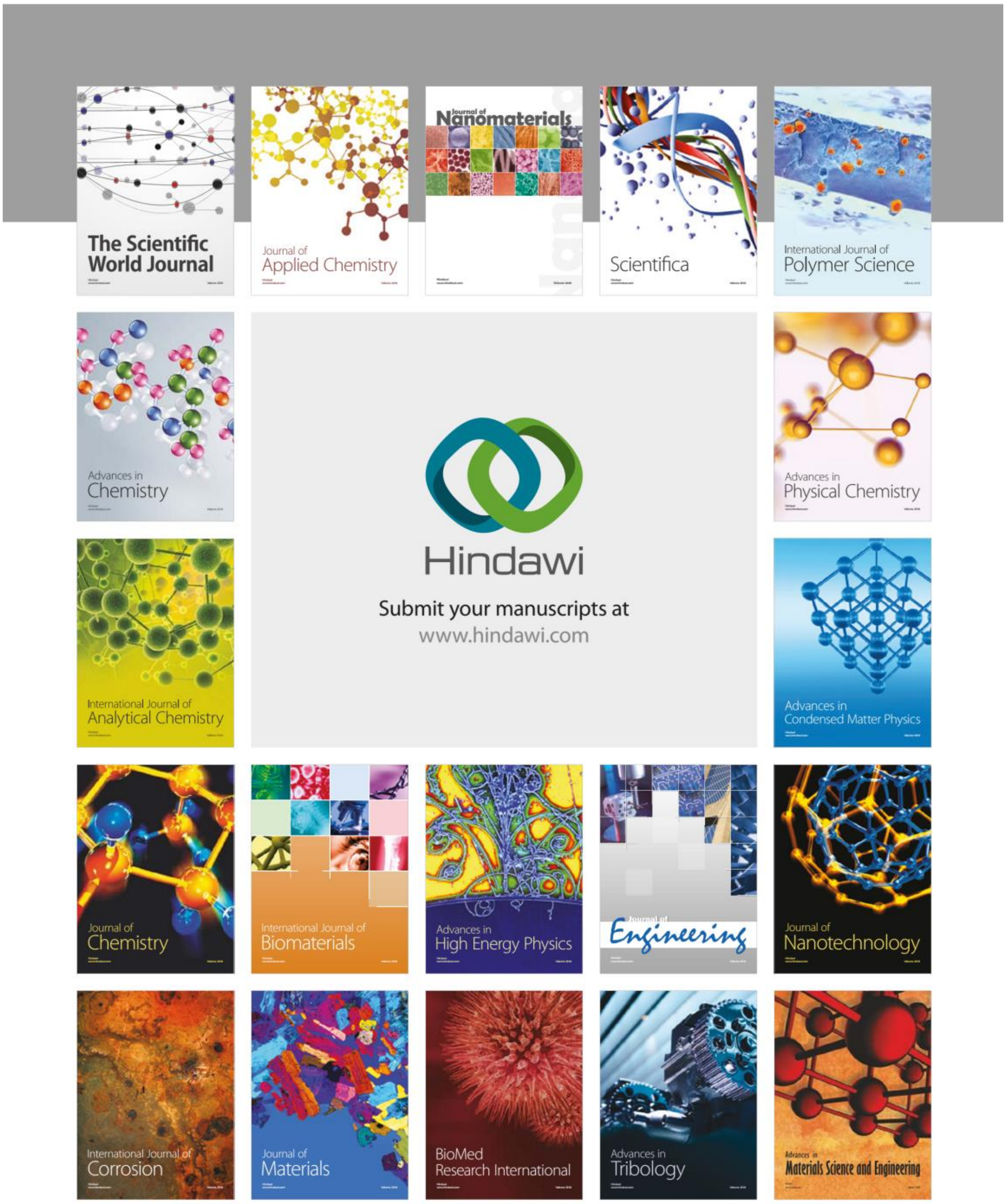

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APPENDIX B

Paper entitled “Effect of Calcium-Rich Compounds on Setting Time and Strength Development of Alkali-Activated Fly Ash Cured at Ambient Temperature”

Case Studies in Construction Materials
Volume 9, December 2018, e00198
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Case study

Effect of calcium-rich compounds on setting time and strength development of alkali-activated fly ash cured at ambient temperature

Prinya Chindaprasirt [a], [b], Tanakorn Phoo-ngernkham [c], Sakonwan Hanjitsuwan [d], Suksun Horpibulsuk [e], Anurat Poowancum [f], Borwonrak Injorhor [c]

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Abstract

This paper investigates the effect of calcium-rich compounds on setting time and compressive strength development of alkali-activated fly ash (FA) pastes. Three calcium-rich compounds viz., Portland cement (PC), calcium hydroxide (CH) and calcium oxide (CaO) were used as additives to replace FA at the dosages of 5, 10, and 15% by weight basis. Sodium hydroxide and sodium silicate solutions were used as alkali activator liquids in all mixtures. Alkali activator liquid/solid binder (FA and calcium-rich compound) ratio of 0.60, sodium silicate-to-sodium hydroxide ratio of 2.0 and curing at ambient temperature (25 °C) were used for all mixes. Test results showed that the setting time and compressive strength of alkali-activated FA depended on the type and content of calcium-rich compound. The incorporation of all three calcium additives resulted in the acceleration of setting time. Alkali-activated FA with CH and PC could improve the strength development; however, the use of CaO resulted in the compressive strength reduction. The 28-day compressive strengths of alkali-activated FA with 15% PC and 5%, 10% and 15% CH met the strength requirement for repair material as specified by ASTM standard. The alkali-activated FA with additives can thus be used as an alternative repair binding material.

Keywords

Alkali-activated fly ash; Calcium-rich compounds; Strength development; Alternative repair material

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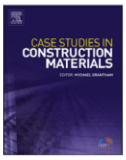

Case study

Effect of calcium-rich compounds on setting time and strength development of alkali-activated fly ash cured at ambient temperature

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ABSTRACT

This paper investigates the effect of calcium-rich compounds on setting time and compressive strength development of alkali-activated fly ash (FA) pastes. Three calcium-rich compounds viz., Portland cement (PC), calcium hydroxide (CH) and calcium oxide (CaO) were used as additives to replace FA at the dosages of 5, 10, and 15% by weight basis. Sodium hydroxide and sodium silicate solutions were used as alkali activator liquids in all mixtures. Alkali activator liquid/solid binder (FA and calcium-rich compound) ratio of 0.60, sodium silicate-to-sodium hydroxide ratio of 2.0 and curing at ambient temperature (25 °C) were used for all mixes. Test results showed that the setting time and compressive strength of alkali-activated FA depended on the type and content of calcium-rich compound. The incorporation of all three calcium additives resulted in the acceleration of setting time. Alkali-activated FA with CH and PC could improve the strength development; however, the use of CaO resulted in the compressive strength reduction. The 28-day compressive strengths of alkali-activated FA with 15% PC and 5%, 10% and 15% CH met the strength requirement for repair material as specified by ASTM standard. The alkali-activated FA with additives can thus be used as an alternative repair binding material.

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1. Introduction

At present, Portland Cement (PC) is the most widely used cementing material for construction works. However, its manufacturing process results in a significant amount of carbon dioxide (CO_2) emission [1,2]. Therefore, various eco-friendly cement has been widely studied. Promising alternative cement is alkali-activated materials [3]. Alkali-activated materials

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can be classified into two systems: low calcium system or geopolymer and high calcium system. Ordinarily low calcium system or geopolymer is an inorganic polymer made from silica and alumina source materials such as low calcium fly ash, calcined kaolin or metakaolin activated with medium to high alkali solutions, having sodium aluminosilicate hydrate (N-A-S-H) as the primary reaction products. For high calcium system, high calcium-based materials such as granulated blast furnace slag, high calcium fly ash activated with medium alkali solutions, having calcium silicate hydrate (C-S-H), calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) as the main reaction products [4,5]. Alkali-activated materials are being used as an alternative binder for construction works and some applications in concrete industry such as geopolymeric repair material made with steel slag [6], tungsten mine waste geopolymeric binder [7], ferro-fly ash geopolymer jacket [8], low calcium fly ash alkali-activated binders with ground granulated blast furnace slag [9,10], geopolymer masonry units manufactured from water treatment sludge [11] and usage of metakaolin-based geopolymer mortar to improvement of bond strength of Portland cement concrete pavement [12].

Recently, alkali-activated high calcium fly ash (FA) has been investigated for use as a repair material due to its advantage of reasonable setting time and hardening [8]. It has also been shown that alkali-activated high calcium FA could be used as an alternative commercial repair material with relatively high 28-day compressive and shear bond strengths comparable to those of expensive conventional repair materials [7,13,14]. However, the chemical compositions of source materials, alkali activators, and additives control the reaction degree within the matrix [15], and thus it affected the mechanical properties of alkali-activated high calcium FA. Therefore, the performance of alkali-activated high calcium FA as repair material should be studied in detail.

High calcium fly ash, a by-product from lignite coal burning from Mae Moh power station in northern Thailand, mainly consists of silica (SiO_2), alumina (Al_2O_3), and calcium oxide (CaO) along with other minor compounds [16]. According to ASTM C618-15 [17], high calcium or class C FA contains a high percentage of CaO with the minimum sum of the SiO_2+Al_2O_3+Fe_2O_3 content of 50%. This FA contains a high amount of amorphous phase and thus is suitable source material for making alkali-activated materials [18]. The high calcium content in FA influences the setting time of alkali-activated materials [19]. It is, therefore, one of the most promising source materials for sustainable utilization as source material in an alternative binder regarding engineering, economy and environment considerations [20].

It is known that the formation of the reaction products of alkali-activated FA-based at ambient temperature condition is slow and thus low strength is usually obtained [21,22]. Higher temperature curing around 40 to 75 °C can improve the evolution of the reaction products and the associated mechanical properties [16]. The heat curing process is only possible in precast concrete facilities. The use of alkali-activated FA-based in a wider application similar to that of ordinary concrete particularly curing at ambient temperature is a challenging task. It is significant from engineering and economic perspectives to develop a sufficiently high strength of alkali-activated FA-based under ambient curing temperature [15]. The additions of calcium-rich materials such as calcium oxide, calcium hydroxide, granulated blast furnace slag and PC to develop sufficiently high-early-strength of alkali-activated binder have been studied and reported in the literature [15,23]. Calcium-rich materials accelerate the setting of alkali-activated FA-based material [19] where additional calcium silicate hydrate (C-S-H) coexists with geopolymer products [24]. The total products improve the mechanical properties of the alkali-activated FA-based material. Besides, the calcium oxide from a calcium-rich material when reacted with water generates heat from the exothermic process at ambient temperature, and this generated heat accelerates the rate of reaction [21,22].

There are many types of calcium-rich materials, which can improve the strength development of alkali-activated FA-based material. Investigation on the effect of calcium on the properties of alkali-activated FA-based is limited to few calcium-rich materials [23,25]. Temuujin et al. [23] and Antiohos and Tsimas [26] investigated the strength improvement by adding a small amount of calcium compound in the alkali-activated FA-based material. They showed that the strength development of alkali-activated FA-based material depended on the type of calcium.

In order to utilize the alkali-activated high calcium FA as a practical alternative repair material, research works have been directed towards the improvement of strength with the addition of additives [13] and nano-SiO_2 and nano-Al_2O_3 [8]. The research on the reduction of setting time of this binder is an important aspect that needs further investigation. The 7-day strength requirement of rapid hardening cementitious materials was 28.0 MPa as described in ASTM C928-13 [27], and the initial setting time and minimum strength requirements for repair binder were 30 min and 35.0 MPa, respectively as described in ASTM C881/C881M-14 [28]. The setting time and strength of the alkali-activated high calcium FA with the three additives were presented and compared. The FA used in this investigation was a high calcium FA from Mae Moh Power plant, which is extensively used in concrete and alkali-activated materials technology in Thailand. Three available additives were used: Portland cement (PC), calcium hydroxide (CH) and calcium oxide (CaO).

In addition, traditional repair material is based on epoxy resin, and the study indicated that the carbon footprint of this material is several times higher than that of alkali-activated materials [1,29]. The use of alkali-activated high calcium FA as a repair material is, therefore, essential to the cleaner production particularly in the field of construction. The viability of usage of three available types of calcium-rich materials as additives in the development of a repair material using alkali- activated high calcium FA cured at ambient temperature has been reported in this paper. The outcome of this study should lay a foundation for the future use of alkali-activated high calcium FA binder as an alternative repair material in a sustainable manner.

2. Experimental procedure

The binder in this study is a mixture of high calcium FA and calcium additives. The FA was obtained from the Mae Moh power plant in northern Thailand, and the chemical composition is summarized in Table 1. The FA mainly consisted of SiO_2, Al_2O_3, and CaO with some minor impurities. The sum of SiO_2, Al_2O_3, and Fe_2O_3 was 59.92%, and the CaO content was high at 25.79%; thus this FA can be grouped as Class C according to ASTM C618-15 [17]. The specific gravity, median particle size and Blaine fineness of FA were 2.61, 8.5 μm and 430 m^2/kg, respectively. The fine FA was shown to be very reactive and produced alkali-activated materials with high strength [30]. The alkali activators used in this study were 10 M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 13.89% Na_2O, 32.15% SiO_2, and 53.96% H_2O. Previous studies on high calcium fly ash [31,32] indicated that the use of NaOH with 10 M concentration gave alkali-activated high calcium FA with high compressive strength. Therefore, 10 M NaOH solution was selected for this study. The 10 M NaOH was obtained by dissolving sodium hydroxide pellets in distilled water. The solution was left at ambient temperature until the excess heat had completely dissipated to avoid the uncontrolled acceleration of setting of alkali-activated materials as recommended by the previous studies [33]. The NaOH and Na_2SiO_3 solutions were mixed together prior to the mixing alkali-activated high calcium FA.

Three additives viz., Portland cement (PC) Type I, calcium hydroxide (CH) and calcium oxide (CaO) powders were used to replace FA for making the alkali-activated material. Effect of calcium-rich compounds replacement on setting time and strength development of alkali-activated high calcium FA cured at ambient temperature was investigated and analyzed. The PC, CH and CaO powders were available commercial products in Thailand. The chemical composition of PC is summarized in Table 1. The PC powder consisted of 65.3% CaO. The properties of CH and CaO powders are summarized in Table 2. The mix proportions of alkali-activated high calcium FA with various replacement ratios of additives are presented in Table 3. The additive replacement ratios were 5, 10, and 15% by weight of FA. The liquid/binder (mixture of FA and additive) ratio of 0.60 and NaOH/ Na_2SiO_3 ratio of 2.0 were used in this study.

The binder (FA and additive) was dry-mixed for 1 min, and the alkali solution was then added and thoroughly mixed for an addition of 3 min A total of 10 mixes of alkali-activated high calcium FA with calcium-rich compounds were prepared for setting time and compressive strength tests. The setting time of alkali-activated binder was tested using the Vicat apparatus as described in ASTM C191-13 [34]. The fresh alkali-activated binder was placed into 50 × 50 × 50 mm^3 cube molds and wrapped with a vinyl sheet to protect moisture loss. The alkali-activated binder samples were cured for 24 h at ambient temperature of 25 °C and then demolded and immediately wrapped with a vinyl sheet and kept in 25 °C controlled room with the relative humidity of 50% until testing age. The compressive strengths of alkali-activated high calcium FA with calcium-rich compounds were tested at the ages of 7 and 28 days under ASTM C109/C109M-13 [35]. The reported results were the average of three tests.

After 28 day-compressive strength test, the samples from the middle portion were broken into small fragments for observing the growth of the reaction products via a low voltage scanning electron microscopy (LVSEM). The broken small fragments around 3–6 mm were placed on a brass stub sample holder with double stick carbon tape. The sample was dried using infrared light for 5 min and then coated with a layer of gold using a blazer sputtering coater. The micrographs were recorded at 1000× magnification.

3. Results and discussion

3.1. Effect of calcium-rich compounds on setting time of alkali-activated FA pastes

The setting time of alkali-activated high calcium FA [13,36–39] is normally faster than that of PC paste [40]. This fast setting of alkali-activated high calcium FA is an advantage for use as alternative repair material. The results of setting time tests of pastes with various additive contents are illustrated in Fig. 1. The initial and final setting times decreased with the increase in replacement level. They were 15–27 min and 26–47 min for FA-PC pastes, 10–25 min and 17–40 min for FA-CH pastes; and 5–19 min and 8–26 min for FA-CaO pastes. It was evident that the additives accelerated the setting of paste compared to that of the control paste (without additive) whose initial and final setting times were 30 and 58 min, respectively. The initial setting time of the control geopolymer was 30 min, which was the required value for repair binder as specified by ASTM C881/C881M-14 [28]. The initial setting times of pastes with the three additives were significantly reduced and met the requirement of ASTM standard. The alkali-activated high calcium FA with CaO exhibited the fastest setting time implying that the CaO had very high dissolution compared with those of PC and CH. The CaO has a generally higher potential of heat generation than CH [41].

Table 1
Chemical compositions of FA and PC (by weight).

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	30.32	13.96	15.64	25.79	2.94	2.93	2.83	4.29	1.30
PC	20.80	4.70	3.40	65.30	1. 50	0.40	0.10	2.70	0.90

Table 2
The properties of CH and CaO powder.

Materials	Density (g/cm^3)	Purity (%)	Appearance
CH	2.24	>95	White powder
CaO	3.30	>90	White powder

Table 3
Mix proportions of alkali-activated high calcium FA paste.

Mix No.	Mix symbol	FA (g)	PC (g)	CH (g)	CaO (g)	NaOH (g)	Na_2SiO_3 (g)
1	Control	100	–	–	–	20	40
2	5PC	95	5	–	–	20	40
3	10PC	90	10	–	–	20	40
4	15PC	85	15	–	–	20	40
5	5CH	95	–	5	–	20	40
6	10CH	90	–	10	–	20	40
7	15CH	85	–	15	–	20	40
8	5CaO	95	–	–	5	20	40
9	10CaO	90	–	–	10	20	40
10	15CaO	85	–	–	15	20	40

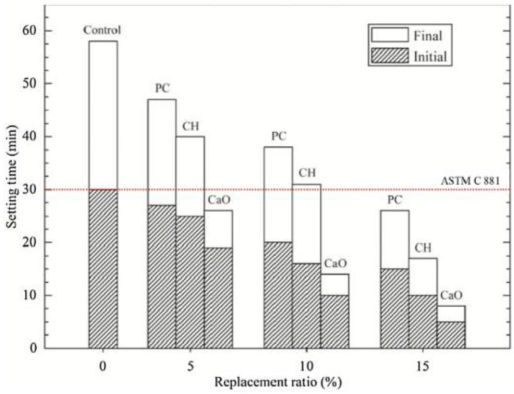


Fig. 1. Setting time of alkali-activated high calcium FA pastes with different calcium-rich compounds.

3.2. Effect of calcium-rich compounds on compressive strength of alkali-activated FA pastes

The increase in additive replacement ratio also controlled the strength development in alkali-activated high calcium FA. The results of compressive strength tests on pastes with different replacement ratios are illustrated in Fig. 2. The 7-day and 28-day strengths of FA-PC and FA-CH pastes increased with increasing replacement ratio. This was associated with the reduction in setting time. The readily available free calcium ions from PC and CH reacted with silica and alumina in FA, resulting in additional calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) within the matrix. The heat generated from the exothermic process due to calcium and water reaction also accelerated the reaction products. The coexistence of C-S-H, C-A-S-H and geopolymer product and generated heat resulted in rapid hardening and high strength. The combination of FA and CH as an additive is advantageous in term of setting time and strength.

For the FA-CaO pastes, the 7-day and 28-day strengths decreased compared to those of control paste as the replacement ratio increased. In other words, the CaO replacement adversely affected the strength development. The 28-day compressive strengths of FA-CaO pastes were low between 6.2–19.4 MPa for CaO replacement ratios between 5–15%, while the strength of the control paste was 26.9 MPa. The strength reduction of FA-CaO pastes with the increase in replacement ratio was due to the speedy setting of paste resulting in a poor initial matrix framework, which hindered subsequent strength development.

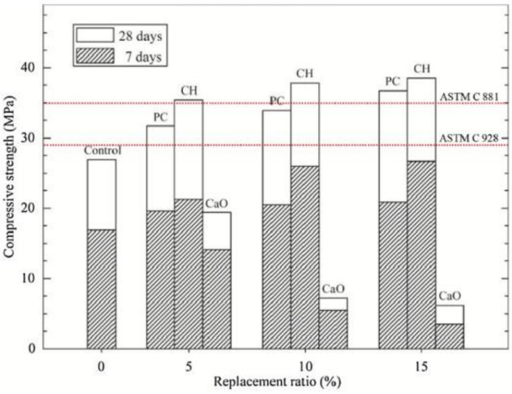
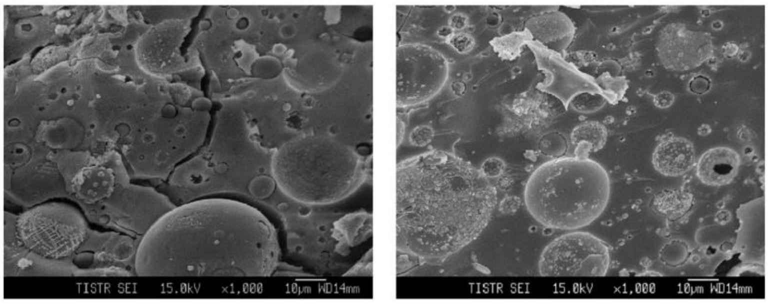
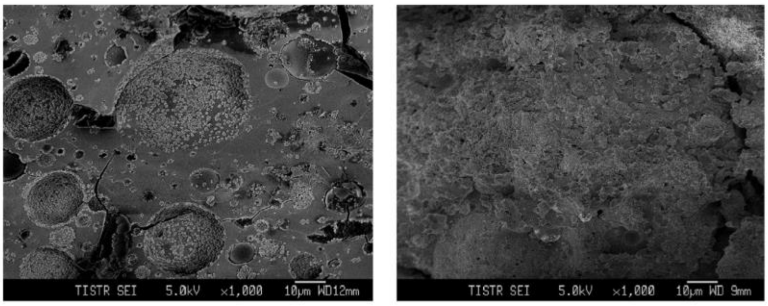


Fig. 2. Compressive strength of alkali-activated high calcium FA pastes with different calcium-rich compounds.

The hydration of CaO in alkali medium was incomplete and formed $Ca(OH)_2$ [42]. The hydration of CaO liberated a significant amount of heat and caused the expansion of alkali-activated high calcium FA samples. From the test results, the recommended additives for alkali-activated high calcium FA were PC and CH, which provided the maximum 28-day compressive strengths of FA geopolymer pastes (at 15% content) of 33.9 and 38.5 MPa for FA-PC and FA-CH pastes, respectively. For high early strength material, the 7-day strengths of both FA-PC and FA-CH pastes were slightly lower than 28.0 MPa requirement as specified by ASTM C928-13 [27]. In particular, the 7-day compressive strength of 27.0 MPa with 15%



(a) Control (b) 10PC



(c) 10CH (d) 10CaO

Fig. 3. SEM of alkali-activated high calcium FA pastes with different calcium-rich compounds.

Table 4
Implications for use of alkali-activated FA as an alternative repair material based on test results.

Mixture No #	Environmental indicator	Economic indicator	Material properties	
	Carbon footprint (Total CO_2-e/t)	Price (Baht/m^3)	Initial setting time (min)	28-day compressive strength (MPa)
Commercial epoxy A [13,36]	12.00	156,000	10	45
Commercial epoxy B [13,36]		65,000	15	60
Commercial epoxy C [13,36]		93,000	15	40
Reference FA	0.250	8300	30	27
FA+15%PC	0.348	8,500	15	37
FA+10%CH	0.286	88,000	16	38
FA+5%CaO	0.255	46,000	19	19

CH was very close to the requirement. The 28-day compressive strengths of FA-CH pastes with 5, 10 and 15% CH were 35.5, 38.0 and 39.0 MPa, which met the requirement of ASTM C881/C881M-14 [28] as a repair material. For the alkali-activated high calcium FA with PC additive, only the pastes with 15% PC with a compressive strength of 37.0 MPa met the 28-day strength requirement.

3.3. SEM analysis

The strength development can be explained by the condition of cementitious products via the SEM analysis. Fig. 3 shows the fracture surfaces of pastes with different additives cured at ambient temperature for 28 days. The matrix of control, FA-PC, FA-CH pastes were dense with some non-reacted and/or partially reacted FA particles embedded in a continuous matrix. The differences in SEM images between these pastes and FA-CaO paste were noticeable. The control, FA-PC and FA-CH pastes were more homogeneous and denser than the FA-CaO paste. The matrix of FA-CaO paste was non-homogenous and loosely packed. Theses SEM photos agreed with the results of compressive strength tests on alkali-activated high calcium FA. The reaction products of this relatively fine alkali-activated FA at an ambient temperature of 25 °C was reasonable. However, for lower ambient temperature and/or coarser fly ash, the setting and hardening of the FA paste could be a problem [43]. The typical increase in curing temperature is usually employed to ensure good reaction and adequate strength. Instead of heat curing, it is evident from this research that the use of PC and CH as additives can accelerate the reaction by forming additional C-S-H and C-A-S-H within the matrix, resulting in a homogeneous matrix. The reaction of PC and CH with water was an exothermal process and liberated heat, which also accelerated the reaction. The incorporation of CaO did not result in the same improvement of paste. The fast reaction of CaO induced the fast setting and this hindered subsequent strength development. It was reported that the strength of very fast setting cement is generally low at between 10–15 MPa [44]. The high compressive strength of FA-CH paste cured at ambient temperature is very attractive; however, the examination of a threshold CH replacement ratio for this high calcium FA is essential. This is because the excessive lime will disrupt the optimum gels binder structure [45] and hence the possible strength reduction.

3.4. Implications for use of alkali-activated FA as an alternative repair material

Table 4 shows the price of commercial repair material and alkali-activated high calcium FA binder based on Thailand market prices in the year 2018. According to Table 4, the total costs of alkali-activated FA pastes with PC, CH and CaO as an additive are about 8500, 88000, 46,000 baht/m^3, respectively, whereas alkali-activated FA paste without calcium-rich compounds is about 8300 baht/m^3. Table 4 showed that the use of alkali-activated FA pastes with PC is more cost-effective than the use of alkali-activated FA pastes with CH and CaO as an additive. The price of alkali-activated materials is cheaper than that of commercial epoxy resin with the same mechanical properties (see Table 4). This agreed with works of Pacheco-Torgal et al. [7] and Phoo-ngernkham et al. [36]. Table 5 presents the emission factors of tested materials based on previous studies [46–48]. The emission factor of sodium silicate solution was the highest value whereas FA was the lowest value. Also, the production of alkali-activated materials using FA as the main precursor is to be a sustainable utilization in an alternative

Table 5
The emission factors of tested materials [46–48].

Materials	Emission factor (t CO_2-e/ton)
Commercial epoxy	5.7000
Fly ash, FA (kg)	0.0070
Portland cement, PC (kg)	0.8200
Calcium hydroxide powder, CH (kg)	0.3740
Calcium oxide powder, CaO (kg)	0.1500
Sodium hydroxide, SH (kg)	1.0377
Sodium silicate, SS (kg)	1.5140

binder regarding engineering, economic and environmental perspectives with a low carbon footprint of alkali-activated materials comparable to the commercial epoxy resin as reported in Table 4. This is also confirmed with Habert et al. [1] and La Rosa et al. [29]. The outcome of this study is useful to enable the alkali-activated high calcium FA for use in repair applications commercially with FA as source material and CH and PC as an additive. For practical applications on a larger scale, the handling and disposal of generated waste and the possibility of reuse should be taken into consideration as well. The generated waste from this material can be handled the same way as ordinary Portland cement paste. It is not harmful to the environment and can also be used as recycled aggregate.

4. Conclusions

This paper investigates the effects of the use of three calcium-rich materials (PC, CH, and CaO) on setting time and strength development of alkali-activated high calcium FA cured at ambient temperature. The incorporation of the three additives viz., Portland cement, calcium hydroxide and calcium oxide in alkali-activated high calcium FA resulted in the reduction in setting time, which is an essential requirement of repair material. The strengths of the mixes with PC and CH pastes were significantly improved compared with those of reference FA paste. The properties of FA-CH pastes were slightly better than that of FA-PC pastes. The 15% PC replacement and 5% CH replacement in alkali-activated high calcium FA met the strength requirement for repair material. Additional calcium ion from PC and CH reacted with silica and alumina from FA and formed the reaction products within the matrix, resulting in the additional strength development of pastes. However, the use CaO resulted in speedy setting and significant strength reduction. It is evident from this study that PC and CH can be incorporated into the high calcium fly ash geopolymer to produce reasonably fast setting mixtures with significant strength improvement complying with the strength requirement for repair material. Based on the experimental results obtained, the alkali-activated FA pastes with 15% PC, 5% CH, 10% CH and 15% CH are suitable for use as an alternative repair material.

Conflict of interests

No conflict of interests regarding the publication of this paper.

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