

**EFFECT OF FLY ASH IN SOUTHEAST ASIA ON THE
PROPERTIES OF CONCRETE**



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ผลกระทบของถ้ำลอยในเอเชียตะวันออกเฉียงใต้ต่อสมบัติของคอนกรีต



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ชว ชว วิน : ผลกระทบของเถ้าลอยในเอเชียตะวันออกเฉียงใต้ต่อสมบัติของคอนกรีต. (EFFECT OF FLY ASH IN SOUTHEAST ASIA ON THE PROPERTIES OF CONCRETE) อ.ที่ปรึกษาหลัก : รศ. ดร.วิฑิต ปานสุข, อ.ที่ปรึกษาร่วม : Dr.รุ่งริ วัฒนพรพรม

ในปัจจุบันวัสดุปอซโซลานถูกนำมาใช้ในส่วนผสมคอนกรีตเพื่อเสริมสร้างความทนทาน การประยุกต์ใช้เถ้าลอย (FA) เป็นวัสดุประสานอย่างแพร่หลายสามารถส่งผลให้มีความทนทานเพิ่มขึ้นในการใช้งานด้านวิศวกรรมโยธาของเรา ถึงแม้ว่าเถ้าลอยจะเป็นทั้งวัสดุทางการเกษตรหรือผลพลอยได้จากการผลิตในภาคอุตสาหกรรมและมีการใช้งานอย่างแพร่หลาย ทั้งในการพัฒนาวัสดุซีเมนต์และคอนกรีตมาหลายทศวรรษ แต่ทว่าการใช้เถ้าลอยยังคงมีความท้าทายในเชิงปฏิบัติ ความท้าทายดังกล่าวคือความแปรปรวนและความแตกต่างของเถ้าลอย วัสดุปอซโซลานที่แตกต่างกันมีสมบัติที่แตกต่างกันดังนั้นจึงทำให้สมบัติของคอนกรีตแตกต่างกันไปด้วยในเอเชียตะวันออกเฉียงใต้เถ้าลอยถูกใช้ในการผลิตคอนกรีตโดยแทนที่ปูนซีเมนต์ในลักษณะของวัสดุปอซโซลาน อย่างไรก็ตามปัจจุบันแทบจะไม่มีข้อกำหนดเกี่ยวกับการใช้เถ้าลอยระหว่างประเทศ การศึกษานี้จะประเมินความทนทานของวัสดุซีเมนต์หลังจากการผสมเถ้าลอยห้าประเภทในสัดส่วนที่แตกต่างกันจากสามประเภท ได้แก่ เถ้าลอยจากพม่า เมียนมาร์ ไทย และอินโดนีเซีย เพื่อนำไปใช้ในการเป็นแนวทางการใช้งานเถ้าลอยระหว่างประเทศ ในการศึกษาจะมีการสำหรับสร้างแบบจำลองทางคณิตศาสตร์ โดยเถ้าลอยแต่ละประเภทจะนำมาถูกใช้เพื่อแทนที่ปูนซีเมนต์ปอร์ตแลนด์ 15% โดยมีอัตราส่วนน้ำต่อวัสดุประสานเท่ากับ 0.54 นอกจากนี้งานวิจัยนี้จะดำเนินการศึกษาทั้งการทดลองและการวิเคราะห์เชิงตัวเลขเพื่อที่จะได้ข้อมูลเชิงลึกที่คิดว่าสำหรับประเมินปัจจัย ที่มีผลต่อการควบคุมความแตกต่างของเถ้าลอยที่ส่งผลต่อความทนทาน โดยในการศึกษาจะมีการประเมินผลกระทบขององค์ประกอบทางเคมีและสมบัติทางกายภาพของเถ้าลอย เถ้าลอยที่ได้มาจากทั้งห้าแหล่งที่แตกต่างกัน ถูกประเมินเพื่อศึกษาผลกระทบขององค์ประกอบทางเคมีและสมบัติทางกายภาพของเถ้าลอย โดยจะผสมปูนซีเมนต์ผสมและเถ้าลอยถูกผสมและเพื่อประเมินการไหล กำลังอัดของมอร์ตาร์ ความหนาแน่น และปริมาตรโพรง ความสามารถในการต้านทานต่อคลอไรด์ สัมประสิทธิ์การแพร่ของคลอไรด์ (D_a) และการต้านทานต่อคาร์บอนชั้นหลังจาก 7, 28 และ 91 วัน และระดับของการทำปฏิกิริยา เนื่องจากองค์ประกอบทางเคมีของเถ้าลอยในแต่ละประเทศแตกต่างกันเล็กน้อย การทำปฏิกิริยาทางเคมีกับปูนซีเมนต์จึงแตกต่างกันน้อยมาก ดังนั้นความทนทานของมอร์ตาร์ที่ผสมเถ้าลอยที่มีความละเอียดสูงจะมีในระยะแรกจะความทนทานที่คิดว่า สำหรับเถ้าลอยชนิดที่มีความละเอียดมากกว่านอกจากนั้นแบบจำลองอายุการใช้งานที่ใช้ Life365 จะถูกใช้เพื่อคาดการณ์อายุการใช้งานของปูนซีเมนต์เถ้าลอยผสม ผลการทดลองถูกนำมาวิเคราะห์เชิงสถิติโดยใช้การวิเคราะห์เชิงผันแปร (ANOVA) และการวิเคราะห์ความไวกับการลดอายุเชิงเส้น การวิเคราะห์บ่งชี้ว่ากลไกทางเคมีและกายภาพของโครงสร้างหลายขนาดคือปัจจัยหลักและทั้งระดับของการทำปฏิกิริยาของปูนซีเมนต์เถ้าลอยผสมและโพรงคือปัจจัยที่ดีที่ส่งผลต่อความทนทาน

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Thwe Thwe Win : EFFECT OF FLY ASH IN SOUTHEAST ASIA ON THE PROPERTIES OF CONCRETE . Advisor: Assoc. Prof. Dr. WITHIT PANSUK, Ph.D. Co-advisor: Dr. Rungrawee Wattanapornprom, Ph.D.

A wide use of fly ash (FA) as a supplementary cementitious material (SCM) can result in an enhancement in its durability performance in our civil engineering applications. Although FA is either agricultural or industrial by-product and is abundant for use in cement and concrete works for many decades now, the utilization of FA still has a practical challenge. The challenge is due to variability and their heterogeneity. In Southeast Asia, fly ash is used in concrete production replacing cement as a pozzolanic material. However, there are few standard guidelines for using fly ash across the region. This study evaluates the durability of cementitious materials after the including of five types of fly ash in different mix proportions from three countries, Myanmar, Thailand, and Indonesia. For the mathematical model, each type is used to replace ordinary Portland cement in 15 % with a water-to-binder ratio of 0.54. Moreover, this work is to perform both experimental and numerical studies to have a better insight for controlling the different FA, reflecting its durability. FA from five different sources were assessed to investigate the impacts on its chemical composition and physical properties. The blended FA-cement systems were also prepared and evaluated on its flow, compressive strength of mortar, hardened porosity, ability to resist chloride penetration, apparent chloride diffusivity coefficients (D_a), and carbonation resistance after 7, 28, and 91 days, and degree of reaction. Because the chemical composition of each country's fly ash is slightly different, their chemical reaction with cement is marginally different. Thus, the durability performances of the mortar are better for finer fly ash types at an early age. The service life model using Life365 was performed to predict the service life of blended FA-cement system. The experimental results were statistically analyzed using analysis of variance (ANOVA) and sensitivity analysis with linear regression. The analyses indicate that chemo-physical mechanisms of multi-scale structures are the main factors, and both degree of reaction of blended FA-cement systems and its hardened porosity are among the most positive factors influencing its durability.

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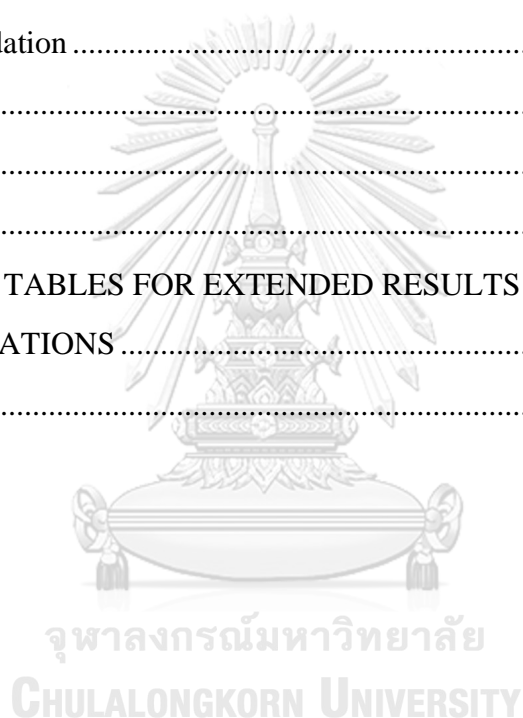
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CHAPTER 1

INTRODUCTION

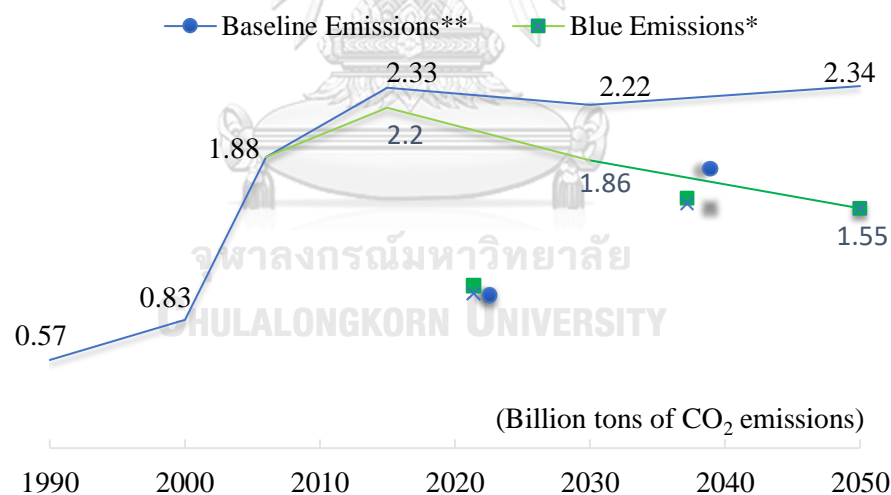
1.1 Background

In many decades, concrete is used as a structural material in construction work such as dam, bridge, pavement, building frame and in many different structures throughout the world. Concrete which plays a vital role of the main building of structure is widely used with the development of economy and population. Durability, low cost, good in compression, ability to fire resistance, general availability, and freedom of applicability into any design made this material obviously satisfactory. However, the production of concrete also takes many expensive with it a huge environmental cost. Concrete as a construction material is a manufactured product, essentially consisting of cement, aggregates, water, chemical and mineral admixtures [1]. Among these materials, cement is one of the crucial materials of concrete work, which reacts with H₂O and blends the aggregates together. Therefore, cement industry is one of the most important primary industries in the globe.

A lot of energy is consumed by manufacturing of cement clinker from limestone and chalk consuming process in industry. 95% cement clinker contains in Ordinary Portland cement which is mostly used cement type. Clinker is manufactured by heating limestone with temperatures over 950°C. Concrete creation is an energy-escalated measure in which energy addresses 20 to 40% of absolute creation costs. The majority of the energy utilized is as fuel for the creation of concrete clinker and power for granulating the crude materials and completed cement [2]. Global cement manufacture increased steadily over this period, with total annual production fluctuating around 1 billion tons until the 1990s [3], and then rapidly increasing to nearly 4.1 billion tons in 2020, with most of the growth occurring in developing countries.

Nowadays, developing countries depend mainly on the coal power stations and also involve in important improvement of infrastructures that requires the extensive concrete usage. Cement manufacture is one of the major sources of CO₂ emissions in the world and leads to manufacture the huge amounts of CO₂ released

into the atmosphere in the process which create many damaging. High quantity content of cement leads to an increment in greenhouse gases emission, which is extremely related to global warming. The second largest used invention is cement in the world after water, and also the second largest source of anthropogenic carbon dioxide (CO₂) emissions, after power generation. Present cement manufacture provides 4 – 7% of the CO₂ emission all over the world, with the supply of 1 ton of cement generating from 600 to 800 kg of CO₂ [4]. In the saddest-case situation rapid city growing in developing countries including Myanmar, Thailand and Indonesia may substantially enhance cement need with assessments that cement manufacture could be 10–15% of worldwide CO₂ emissions in next decade [5]. A less reduction of cement manufacture could result in substantial environmental advantages in terms of CO₂ emission. The predicted trend of worldwide CO₂ emission by cement plants from 1990 to 2050 is demonstrated in Figure 1.



*Blue emissions: Future emissions by considering application of mitigation technologies and policies.

**Baseline emissions: Expected emissions without applying any mitigation actions.

Figure 1: Compressive Global CO₂ emission by cement industries

In contrast, one ton of cement production requires approximately 2.8 tons of raw materials especially limestone, having fuel and other materials. Cement

manufacturing generates not only CO₂ emission but also 5 to 10 % of dust, i.e., cement production does a dust-having airstreams totally around 6000 to 14000 m³. Generally, cement manufacturing led to a increase in cost of energy, requirements to reduce CO₂ emissions, mitigation of additional environmental problems and the supply of raw materials in sufficient qualities and quantities.

Therefore, a reasonable solution for these problems to reduce carbon emission and low embodied energy is via replacing cement the substitution of larger portions of the cement by supplementary cementitious materials without sacrificing its mechanical and durability properties. Industrial wastes like blast furnace slag, fly ash and silica fume are being applied as supplementary cement replacement materials. In addition, agricultural wastes, for instance, rice husk ash, wheat straw ash, and sugarcane bagasse ash are also being utilized pozzolanic materials as partial cement replacement material.

Many researchers have been studying the utilization of different mineral admixtures which are used to replace in cement for mass concrete structures are developing in construction materials mainly due to the consideration of cost reducing, energy decreasing, environmental invention and maintenance of sources [6].

Fly ash as a pozzolanic material, an industrial by-product of the burning of pulverized coal, is the most widely used in construction industry. As per ASTM C-618, fly ash is divided into Class F and Class C fly ashes which are normally used as supplementary cementitious materials for the purpose of concrete through either pozzolanic or hydraulic activities, or both. Anthracite or bituminous coal provide a low calcium content fly ash which is a real pozzolanic material, having silica and alumina and iron oxide display in active amounts. Fly ash with high calcium content fly ash come from lignite or subbituminous coal which has the sufficient calcium content and has minor hydraulic cementitious value without cement. Fly ash possess siliceous or siliceous and aluminous material which when is mixed with Portland cement and water, react with the calcium hydroxide released by the hydration of Portland cement to form more calcium-silicate hydrates (C-S-H) gel and calcium-aluminate hydrates (C-A-H), increasing the long-term strength of concrete, reducing the permeability of cement system, and thus improve concrete density [7].

Therefore, the pozzolanic reaction is the main essential effect of fly ash, which used as a cement substituting material in concrete by considering the mechanical and durability properties of infrastructures of concrete. The secondary hydration of fly ash produces more hydrated gel which fill in the capillary pore in concrete, it successfully improves to concrete strength [8]. Such pozzolanic materials have a very beneficial factor in decrease the heat of hydration in early ages and greatly reduces the heat cracks in massive concretes which display one of the most important problems in such cases. Therefore, the utilization of fly ash is used widely in massive concrete work such as dams project and concrete bridge infrastructure in which long term strength is considered [9]. Some of these interesting effects are because of physical properties and pozzolanic properties of fly ash [10].

The use of fly ash as a partial replacement of cement in concrete is believed to be useful by many reasons. In regard of environment, the cement replacement reduces the depletion of natural resources used for cement production. It also reduces the energy used for clinkerization, then reduces the gases emitted to the environment, especially CO₂. Although some properties of fly ash blended concrete, such as initial strength, carbonation and freezing and thawing resistance, have been observed to be poorer than the concrete without fly ash, the utilization of fly ash to partially replace cement enhances numerous properties of concrete specially durability properties such as enhancing workability and pumpability, developing long-term strength, reducing temperature, reducing shrinkage, improving resistance against chloride-induced steel corrosion, increasing sulfate resistance, reducing risk due to alkali-aggregate reaction, etc [11-14]. A proper using fly ash based on the type of construction work and the service environment that the located construction structure is considered to be most rational. Though there have been many studies, showing the excellent benefit of fly ash usage in concrete, fly ash has still not been effectively used in most countries until now due to many reasons.

Almost all fly ash produced in Thailand is used as a partial replacement of cement for both quality improvement and cost reduction of concrete. Thailand is quite possibly the best nations in respect of the successful utilization of fly ash in concrete industry. Moreover, in Myanmar, the use of fly ash as a cement substitution material is also abundant in recent years. It is estimated that in recent years, the significant

increase of coal usage in power generation, especially in Indonesia, approximately 8.31 million tons of fly ash is manufactured in 2019 with 5% per year increase [15]. About 3 million tons of fly ash is produced annually from electricity generation using coal in Thailand during the past 10 years [16].

Among the Southeast Asia nations, fly ash is the generally utilized pozzolan in these regions. Some countries, for example, Thailand uses many sources of fly ash both local and neighboring countries. However, the appropriate guideline in utilizing fly ash across the nation are restricted. Therefore, fly ash from a new source need to be tested before its successful application in civil engineering work. Moreover, although some works have been made to characterize the fly ash, it did not mention the proper guidelines about how to select the fly ash. Thus, a further experiment about fly ash from different sources is necessary in this research. It is very important to study the effects of fly ash on properties of fresh and hardened concrete, such as durability aspects and to provide the proper way to select the fly ash in this research study.

1.2 Statement of problem

Variations in the combustion process and unreliable chemical composition of coal sources result in variability in the chemical, physical and mineralogical properties of precursor fly ash. Thus, the major challenge in design of infrastructures is the variability of performance of concrete and other material properties of concrete resulting from different sources of fly ash. Thus, understanding the distinct properties of the fly ash as the concrete precursor and correlating these properties with the development of durability properties of concrete is essential at the real application stage.

The applications of fly ash in cement system are still insufficient even though some researchers have been studied to characterize the material properties of fly ash, and it is difficult to provide a vital understanding of a unified pozzolanic reaction of fly ash due to its essential heterogeneity and variability. This research is intended to make some contributions to propose the effects of fineness and calcium oxide content in fly ash, focusing on five sources of fly ash from different countries. Furthermore,

the empirical data from laboratory test will provide how to select the fly ash from different sources and replacement level to optimize a concrete mix for engineering field. Hence, this systematic guideline will be extremely useful that provides the information to the user about benefits of using fly ash, construction difficulties that using fly ash can create and helpful measures when problems do occur and to build a model that are available across the country in the future study.

1.3 Objective of the Study

The objective of this research is to investigate the performance of fly ash from different sources. There is a limitation of standard guidelines for using fly ash across the nation. Chemical reaction of fly ash with cement is expected to be a little bit different since the chemical composition of each country's fly ash is slightly different. Thus, before using fly ash, engineers has to test fly ash from a new source. In addition to, this research addresses issues included in the selection of fly ash source properly. In this study, the durability performance of fly ash-cement composite and service life of concrete structure was assessed by application of fly ash across the country. The results of this investigation will be useful as the guideline for the engineer, the trend about the usage of fly ash across the country and the easily exchange of the fly ash between each country.

The specific objectives are in the following:

- To evaluate the chemical composition and physical properties of fly ash from different sources affecting durability performances of mortar.
- To provide the guidelines based on the experimental data for on-site application and for developing the numerical model that simulates the hydration of concrete incorporating fly ash in the future research.

1.4 Scope of the Study

For the scope of this research, various parameters are studied to achieve the objectives as follows:

- a. Materials
 - Type of cement: Ordinary Portland cement (OPC) type 1
 - Type of fly ash: Class F Myanmar fly ash, Class F and Class C Thailand fly ash, and Class F and Class C Indonesia fly ash
- b. Paste mixtures
 - Water to binder ratio: 0.44, 0.54 and 0.64
 - Amount of fly ash: 0%, 10%, 20% and 30% by weight of cement
 - Curing time: 28 days and 90 days
- c. Mortar mixtures
 - Water to binder ratio: 0.54
 - Amount of fly ash: fly ash content from second-degree polynomial equation
 - Curing time: 7 days, 28 days and 90 days
- d. Experimental programs
 - Compressive strength of paste
 - Heat flow and heat release
 - Calcium hydroxide content
 - Compressive strength, chloride concentration of mortar, porosity and accelerated carbonation
 - Reaction degree of fly ash
- e. Service life prediction

1.5 Outlines of thesis

Totally five chapters involve in this thesis research which are presented below.

Chapter 1 mentions introduction, statement of problem, objectives, and scope of research work.

Chapter 2 presents a brief literature review related to this study, including fly ash and its engineering properties, chemical reaction involving fly ash (pozzolanic reaction) and simplified calculation of reaction degree of fly ash.

Chapter 3 illustrates the detail applications of experimental work in this research.

Chapter 4 discusses and analyzes about the obtained results.

Chapter 5 expresses conclusions and recommendation for future research



CHAPTER 2

LITERATURE REVIEW

2.1 Introducing to supplementary cementitious materials

Nowadays, additional cementitious materials (SCMs) are commonly employed as a pozzolanic material to partially replace Portland cement in concrete production. Rice husk ash (RHA), silica fume (SF), palm oil fuel ash (POFA), ground granulated blast furnace slag (GGBS), sugarcane bagasse ash (SCBA), metakaolin (MK), as well as fly ash are examples of SCMs (FA). SCMs have pozzolanic and/or cementitious capabilities, regardless of their origin, chemical composition, or physical features. Based on published reports, books, and academic journal publications, Table 1 depicts the essential point about their chemical and physical features. The degree to which SCMs are reactive, pozzolanic, and/or cementitious is influenced by the chemical composition, mineralogy, morphology, and physical properties of these materials, which affects the qualities of concrete.

SCMs can improve the concrete's fresh, mechanical, and transport qualities, as well as its long-term durability. Beyond the performance benefits of concrete containing SCM, their inclusion is also encouraged by their great ability to minimize the environmental responsibilities of concrete in terms of energy use, greenhouse gas emissions, waste disposal, and natural resource use. SCM has been used successfully as a partial replacement for cement in concrete for decades and is largely regarded as a sturdy, long-lasting, and sustainable structural material. Ready-mix, precast, and prestressed concretes, as well as mortars and grouts, all use SCMs. Bridges, roads, highway barriers, walkways, buildings, huge concrete constructions, tunnels, and underground infrastructure are some of the civil engineering applications of concrete containing SCMs.

This chapter also briefly discusses the environmental benefits associated with the use of SCMs. In particular, this research work illustrates the role of fly ash from different sources and their resistance to chloride ingress, porosity, carbonation process, degree of reaction and service life prediction. Therefore, this chapter presents a brief overview of certain SCMs, including, RHA, SF, POFA, GGBS, SCBA, MK and FA.

2.1.1 Rice husk ash

During the milling of paddy rice harvested from the fields, the rice industry produces millions of tons of rice husk. RHA is a byproduct of consuming rice husk at temperatures ranging from 800 to 900 degrees Celsius in biomass plants that use rice husk as a source of energy [17]. RHA can also be found in large quantities in many places of the world. Rice husk ash contains a high percentage of silica, roughly 90%. Silica in its amorphous form can be used as a pozzolan. Ground rice husk ash can be created and used as a pozzolanic material with correct burning and grinding. Fine granulation can achieve high RHA even at higher consumption temperatures with some crystalline production of silica [18].

Many researchers showed that the concrete could achieve considerably improvement by using RHA with pozzolanic activity [17]. RHA supports to improve the pozzolanic reactivity of cement. This pozzolanic reactivity mentions to the high substance of amorphous silica and to an extremely huge surface area represented by the porous structures of the particles. The fineness of the RHA likewise contributes to the reactivity by giving a higher surface area to a improved reaction. The reactive RHA is used to make high-quality concrete with lower Ca(OH)_2 and greater resistance to accelerated chloride penetration in mortars. RHA can be utilized up to 20% as SCM without impacting the strength and durability of concrete, according to research, due to its pozzolanic character [19]. Another study on the improvement of high-strength concrete found that adding 10–30 percent RHA to the mix might boost compressive strength up to 80 MPa [20].

2.1.2 Silica fume

In electric curve heaters, silica fume is a byproduct of the production of elemental silicon or silicon alloys. When high-purity quartz is reduced to silicon at roughly 2000°C, silicon dioxide fume is produced, which oxidizes and condenses at low temperatures to form silica fume. Silica fume particles are spherical and very tiny, with an average size of 0.1 – 0.3 μm [21]. SF is an ultrafine material that is used for the pozzolanic effect in concrete. Silica fume containing more than 78% SiO_2 in amorphous form is suitable for use in the cement and concrete industries. Because of

incredibly fine particle size and low bulk density, the handling and transportation of the material is mostly carried out in the form of slurry or a pelletized item [22].

Silica fume is widely known to improve the early strength and durability of concrete and produce a high-strength concrete because of a significant enhancement attained on interfacial zone of cement paste-aggregate. SF is often used in two different ways such as a cement replacement and an additive material to improve concrete properties. Sun and his colleagues (Sun et al.) [23] found that adding 20–30 wt% SF could increase the compressive strength, splitting tensile strength, and early strength. Nevertheless, although SF contributes mostly to concrete strength and chemical resistance, it can also increase concrete water consumption and plastic shrinkage these issues have been the subject of extensive research. SF and FA have been combined in ternary cement systems by some researchers [24, 25]. They found increases in the compressive strength of FA concrete with the addition of SF at all ages. Fly ash is a supportable substitution of Portland cement that is known for its slow pozzolanic reaction, leading to lower concrete strength at early periods. However, when SF is added, high early strength can be improved in concrete.

Thomas et al. [26] reported the excellent durability of concrete with the incorporation of both FA and SF. The early strength of concrete development and sorptivity of concrete with the incorporation of both FA and SF was reported by Barbhuiya et al. [27]. Therefore, using silica fume in combination with fly ash to boost the early strength of concrete containing FA is an intriguing alternative, and numerous researchers have lately done studies using a mixture of the two by-products.

2.1.3 Palm oil fuel ash

Pozzolanic materials derived from agricultural waste are gaining popularity as a result of their ability to improve the qualities of blended cement concrete while also reducing environmental concerns. POFA is a by-product obtained from a small power station that uses palm fiber, shells, and empty fruit bunches as a fuel and burns it at temperatures between 800 and 1000 degrees Celsius to generate energy during the palm oil extraction process. POFA is also a suitable pozzolanic material since it has a high percentage of silica (50–70%) and is widely utilized [17, 28].

Research presents that POFA can be used as a pozzolan in normal and high strength concrete [17]. In addition, partial replacement of cement with POFA supports

to improve the durability performance of concrete. Concrete containing 20% POFA has a 28-day compressive strength fulfilling the strength necessity for high-strength concrete studied by Safiuddin et al. [29]. Furthermore, due to the pozzolanic mechanism of POFA, Johari et al. [30] discovered that using POFA reduces early mechanical attributes while maintaining strength at a later age that is nearly equal to control specimens.

2.1.4 Ground granulated blast furnace slag

Because of remarkable growing in urbanization and industrialization, by-products from industries are turning into an increasing concern for recycling and waste management. Ground granulated blast furnace slag (GGBS), a by-product is obtained from the blast-furnaces of iron and steel industries. Blast-furnaces are fed with controlled combination of coke, iron-ore, limestone, and worked at a temperature of around 1,450 – 1,550°C. GGBS is one such pozzolanic material which can be used as a cementitious ingredient in either cement or concrete composites [31].

GGBS is used as a cement replacement, and replacement percentage could be up to 85 percent depending upon the applications. Generally, 50 percent is used in most applications. Higher substitution rates up to 85 percent are utilized in expert applications, for example, in aggressive environmental conditions and to decrease heat of hydration. In lend-blend concrete GGBS can be used at 70 percent substitution stages. ASTM C 989 defines three strength grades as Grade 80, 100 and 120 of slag, depending upon their relative compressive strength when blended with an equal mass of Portland cement. The most common admixtures in concrete are Grades 100 and 120 [32].

Reactivity of GGBS relies on content of glass, chemical composition, fineness of the slag, alkali concentration of the reacting scheme, and temperature changes during the beginning stages of hydration development. The compressive strength of concrete including replacement levels of 0–80 % GGBS reported by Khatib and Hibbert [33]. During the early stages of hydration, there was a decrease in compressive strength as the GGBS content increased. When compared to concrete without GGBS, the content of GGBS was quite useful at 40 and 60 percent replacement after 28 days and up to something like 90 days compressive strength. It is noted that the strength reduction is observed at 80 % GGBS at all ages. Huang and

Yeih [34] investigated the diffusivity of chloride ions through high-strength concrete containing slag and found ranging from 2.53×10^{-14} to $9.84 \times 10^{-4} \text{ m}^2 / \text{s}$ for compressive strengths between 62.5 and 91.1 MPa. According to Cheng et al. [35] showed that a higher GGBS percentage produced structure denser and prevented concrete from water penetration and resulted in lower coulombs passed in the rapid chloride penetration test.

2.1.5 Sugarcane bagasse ash

Sugarcane bagasse ash, a pozzolanic substance, is a by-product of the sugar industry that is discarded as garbage, resulting in severe environmental deterioration [36]. SCBA is generally found under uncontrolled burning conditions in boilers of the cogeneration measures. Subsequently, the ash may contain black particles because of the content of carbon and crystalline silica, when burning happens under high temperature above 800°C or for a prolonged time frame. In general, silica (SiO_2) present in an amorphous form is the main component of SCBA [37].

Mahima investigated the quick chloride permeability test of SCBA blended concrete and compared it to FA blended concrete [36]. It is interested to note that the improvement of durability performance was found for SCBA blended concrete when compared with FA blended concrete which shows a good pozzolanic characteristic of SCBA than FA [36].

2.1.6 Metakaolin

Metakaolin is an amorphous aluminosilicate that is a highly reactive natural pozzolan that is made by calcining high-purity kaolinite clay mineral at temperatures ranging from 500°C to 900°C [21]. The major ingredients of metakaolin are silicon dioxide and alumina oxide, but the composition varies depending on the kaolin wellspring. According to ASTM C 618, MK is classed as Class N (raw or calcined natural pozzolan) [38]. MK is a pozzolanic material, which reacts with the CaOH_2 produced from Portland cement hydration and forms calcium silicate hydrate (CSH) and calcium-aluminate-hydrate (CAH). MK also contains alumina that reacts with CaOH_2 to produce alumina-containing phases. The reactivity of metakaolin is reliant

on the quantity of kaolinite controlled in the original clay material, mineralogical composition of the metakaolin, handling temperature of the calcined materials, and the surface area of metakaolin.

Daman presented that concrete with up to 25% metakaolin reaches a similar or greater compressive strength compared to conventional concrete [21]. Dhinakaran et al. investigated that the rapid chloride permeability test result decreased when cement replaced with MK substitution up to 10%. It was seen that the total charge passing value of the concrete containing 15% MK replacement marginally increased contrasted with the 10% MK. As a result, the chloride permeability of all concrete mixtures containing MK were much lower than that the control mixture [39].

In recent decades, pozzolans or using of SCMs has strongly become in the concrete industry because of their better long-term performances. Therefore, worries over the plentiful availability of the conventional SCMs guided to perception about other sustainable sources as pozzolanic materials [17]. Researchers have used sustainable sources of SCMs including such as RHA, SF, POFA, GGBS, SCBA, MK, and FA in the construction of normal, high-strength, and lightweight concretes; nevertheless, the use of these economical SCMs has been limited to particular qualities, and there is a limited literature on SCMs.

The literature work illustrates that pozzolanic reactivity of RHA refers to the high presence of amorphous silica and to an exceptionally huge surface area represented by the porous structures of the particles. The fineness of the RHA additionally benefits in the reactivity by offering a higher surface area for a better reaction. Even at an early stage, SF concrete outperformed FA concrete in the manufacturing of high strength and high-performance concrete. Furthermore, the investigation into the potential use of POFA as an SCM revealed that POFA is a useful pozzolanic material with a high silica content. The mechanical and durability qualities of GGBS were observed to improve with age, depending on the replacement percentage. SCBA shows high pozzolanic activity, which is generally related with the formation of huge amounts of amorphous silica. MK was discovered to have low workability and to develop early age strength as well as long term strength. Due to the delayed pace of pozzolanic reaction, FA improves later-life strength.

Table 1: Chemical and physical composition of supplementary cementitious materials

[21, 28, 37, 40, 41]

	RHA	SF	POFA	GGBS	SCBA	MK	FA (F)	FA (C)
SiO ₂ , %	93.2	>85	63.6	30-40	80.8	50.6-74.3	37-62.1	11.8-46.4
Al ₂ O ₃ , %	0.4	0-1.1	1.5	6-19.3	5.1	17.8-46.9	15.3-35.6	2.6-20.5
Fe ₂ O ₃ , %	0.1	0-2	1.5	0.1-2.5	1.6	0.5-1.2	2.6-24.8	1.4-15.6
CaO, %	1.1	0-0.8	7.6	29-43.7	3.1	0-3.4	0.5-19.3	21.2-62.9
MgO, %	0.1	0-4.5	3.9	0-19	-	0.1-0.3	0-5.4	0.1-6.1
Na ₂ O, %	0.1	0-1.3	0.1	0-1.2	-	0.1-0.3	0.1-7.9	0.2-2.8
K ₂ O, %	1.3	0-1.3	6.9	0.3-0.5	6.3	0.2-1.1	0.1-7.8	0.3-9.3
SO ₃ , %	0.9	0-1.3	0.2	1-4	1.5	0-0.03	0-4.9	0.9-12.9
LOI, %	3.7	0-2.8	9.6	0.1-1.7	0.4	1-2.6	0.2-32.8	0.1-11.7
Specific gravity, g/cm ³	2.23	2.2-2.3	2.25	2.85-2.95	2.53	2.2-2.6	1.3-2.9	1.3-2.9
Surface area, m ² /kg	14000	13000-30000	11800	350-650	495	-	300-500	300-500

2.1.7 Fly ash

Fly ash is a well-known pulverized-fuel ash that is created electrostatically or mechanically from coal-fired power plant exhaust gases. It is plenty of used pozzolanic material all over the world. Coal is crushed and blown into the combustion chamber of the boiler, in which it suddenly ignites, generating heat and a molten mineral residue. The heat from the evaporator is removed by boiler tubes, which cools the flue gas and makes the liquid mineral waste to solidify and create ash. The bottom

ash, which contains coarse particles, settles in the bottom of the combustion chamber, while the finer ash particles float in the flue flow. Particulate emission control equipment, such as electrostatic precipitators, remove fly ash before the flue gas is exhausted.

Fly ash particles has both solid spheres and hollow spheres. However, Portland cement have solid irregular particles. Fly ash has major constituents and minor constituents. Silicate glass, which contains silica, alumina, iron, and calcium, is a significant constituent, whereas magnesium, sulfur, sodium, potassium, and carbon are minor constituents of fly ash. The relatively (specific gravity) of fly ash is typically between 1.9 and 2.4, compared to 3.15 for cement, and its color is gray or tan [42]. Fly ash reacts with calcium hydroxide $(CaOH)_2$ which generated from cement hydration to produce calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (CAH). This is primary reaction when fly ash used as a cement replacement material.

Coal-Fired Power Plants

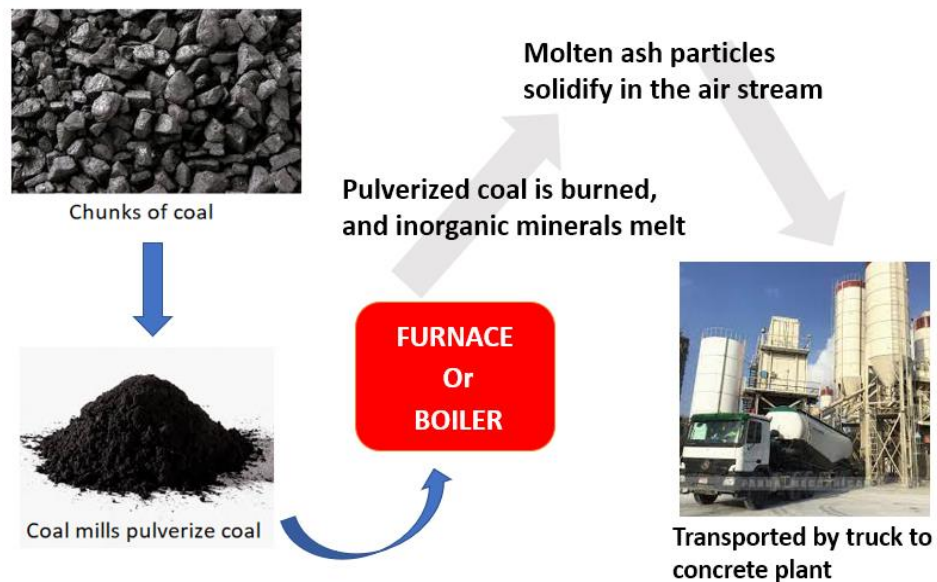


Figure 2: Fly ash come from coal fired power stations

2.2 Classification of fly ash

Fly ash and fly ash blended concrete have different criteria in different nations. Most countries have standard fly ash standards for use in cement, concrete, and other similar purposes. The following are the fly ash classification requirements of the most popular coal combustion product producers (American, European, Canadian, Japanese, Chinese, and Thai standards).

Table 2: Standards related to fly ash classification in different countries

No.	Title of the standard	Relevant country	References
1	ASTM C618: Specification for coal fly ash and raw or calcined natural pozzolan for use in concrete	ASTM International	[38]
2	BS EN 450-1: Fly ash for concrete. Definition, specifications, and conformity criteria	British and European standard	[43]
3	CSA A3000: Cementitious materials compendium	Canadian standard	[40]
4	JIS A 6201: Supplementary cementitious materials fly ash	Japanese standards association	[44]
5	GB/T 1596: Fly ash used for cement and concrete	Chinese standard	[45]
6	TIS 2135: Standard specification for coal fly ash	Thai Industrial Standards	[46]

2.2.1 American standard

ASTM C 618 categorizes fly ash into two kinds based on its chemical composition: Classes C and F. In Class C fly ash, the sum of the three main ingredients ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) must be a minimum of 50%, whereas in Class F fly ash, the sum must only be a minimum of 70%. The classification of fly ash materials according to ASTM C 618 is shown in Table 3. The ASTM C 311 standard process is used to test a fly ash product and give results that may be compared to ASTM C 618 standards. CaO content in Class F fly ash normally ranges from 1 to 12%, whereas CaO content in Class C fly ash is typically greater than 20. Class F fly ash is “normally formed from burning anthracite or bituminous coal,” whereas Class

C fly ash is “normally produced from lignite or sub-bituminous coal,” according to ASTM C 618. The two classifications of fly ash are defined by ASTM C 618 based solely on the coal source and chemical component. Class F fly ash can be used at replacement levels of 15% to 25% by weight of cementitious material and Class C fly ash can be applied at replacement percentages of 15% to 40% by weight of cementitious material [47]. Although there are physical property requirements for using fly ash in concrete, the requirements do not differentiate between different types of fly ash. The differences in the constituents for any fly ash have not been shown to relate with the qualities of fresh and hardened concrete, therefore classification based on coal source and the total of the three main constituents was found to be insufficient.

Key points regarding ASTM C 618 include the following:

- The oxides of the ash are determined during routine QC of fly ash using ASTM C618. Routine QC tests do not determine the mineralogical composition.
- While ASTM C311 determines the amount of calcium oxide in a fly ash characterization test, the ASTM C 618 standard does not consider the quantity of calcium oxide in the classification.
- Only the retention of 45 m sieve based on ASTM C618 is governed by routine QC of fly ash. The actual distribution of fly ash particle size is rarely known.

Table 3: Requirements for chemical compositions and physical properties of fly ash classification according to ASTM C 618

Chemical Requirements	Class		
	N	F	C
(SiO ₂) + (Al ₂ O ₃) + (Fe ₂ O ₃), min %	70	50	50
(CaO), %	report only	18.0 max.	>18.0
(SO ₃), max %	4.0	5.0	5.0
Moisture content, max %	3.0	3.0	3.0
LOI, max %	10.0	6.0 ^A	6.0
^A The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.			
Physical Requirements	N	F	C
Fineness: Amount retained when wet-sieved on 45 µm (No. 325) sieve, max %	34	34	34

Strength activity index: ^A With Portland cement, at 7 days, min % of control	75 ^B	75 ^B	75 ^B
With Portland cement, at 28 days, min % of control	75 ^B	75 ^B	75 ^B
Water requirement, max % of control	115	105	105
Soundness: ^C Autoclave expansion or contraction, max %	0.8	0.8	0.8
<p>^AThe compressive strength of concrete containing fly ash or natural pozzolan should not be measured using the strength activity index with Portland cement. The mass of fly ash or natural pozzolan provided for the strength activity index test with Portland cement is not considered to be the acceptable proportion for the concrete to be utilized in the work. The required qualities of the concrete and other ingredients of the concrete are determined by testing, and the optimum amount of fly ash or natural pozzolan for any individual project is determined by testing. The strength activity index with Portland cement is a measure of reactivity with a specific cement that varies based on the fly ash or natural pozzolan source as well as the cement.</p> <p>^B Specification compliance is determined by meeting the 7-day or 28-day strength activity index.</p> <p>^C If the cementitious material in the project combination will comprise greater than 20% fly ash or natural pozzolan by mass, the test specimens for autoclave expansion must contain that amount. In circumstances where the water to cementitious material ratios is low, for as in block or shotcrete combinations, excessive autoclave expansion is quite important.</p>			

2.2.2 European standard

The European Union Standards, BS EN 450-1 for Fly Ash in Concrete, classify fly ashes based on loss on ignition and particle fineness, as shown in Table 4. The rationale behind this classification is that variations in fineness of fly ash from a particular source affect concrete strength and water content, and variations in LOI cause color variations and issues when attempting to entrain air for frost-resistant concrete, according to Sear (2009) [48]. In addition to the standard terms of LOI, there is a note that the amount of LOI can affect the efficiency of air entraining admixtures used to produce durability performance of concrete [49].

The European Standard BS EN 206 and a complementary U.K. Standard BS 8500 propose significant changes in the use of fly ash additives to concrete mixtures. Type I and Type II additions are the two types of additions. A Type I addition is an

inert filler or pigment, while a Type II addition is pozzolanic or latent hydraulic. The EN 206 standard establishes specific criteria for a Type II addition of EN 450 fly ash, allowing for partial consideration of fly ash in the presence of cement in the mix utilizing the k-value concept, which Sear is researching (2005) [50]. The expression "water to cement ratio" should be replaced by a water/(cement + k* addition) ratio, according to BS EN 206-1. 5.2.5.2. The addition may be included toward the cement content requirement. For OPC I 32.5, the k-value is 0.2, and for OPC I 42.5, it is 0.4. It is permissible to use up to 25% fly ash by weight (cement + ash) as a cementitious material. To put it another way, the fly ash/cement ratio must not exceed 33% of the overall weight. Any extra ash is assumed to be used as an inert filler (Type I addition).

Table 4 : Limits of European standard for fly ash Classification

Property	Category	Requirement
Loss on Ignition, LOI	A	< 5.0 %
	B	2.0 % - 7.0 %
	C*	4.0 % - 9.0%
Fineness remains on sieve 45 μm	N	$\leq 40\%$ and a limit of + 10% on the supplier's declared mean value permitted
	S	$\leq 12\%$

* Category C ash is not permitted in UK concrete due to a 7.0 % limit set by BS8500.

2.2.3 Canadian standard

The CSA A 3000 specification, published by the Canadian Standards Association, classifies fly ash according to its lime content (percent of calcium oxide, CaO). As a result, fly ash can be divided into three types: Type F, Type CI, and Type CH, which denote low, intermediate, and high calcium content, respectively. It does not consider the coal type in fly ash classification.

Table 5 displays the different types of fly ash in Canada, as well as the overall calcium content requirements, expressed in percent by weight as CaO. Except for the percent limit of the LOI, Manz found no additional variances in requirements for various kinds of fly ash [51]. The amount of CaO in Type F fly ash has now been reduced to 15%. Thomas et al. discovered that fly ashes with a very high calcium concentration ($>25\%$) altered concrete characteristics in a different way than ordinary fly ashes. They discovered that the total calcium content of fly ashes might be used as a good foundation for categorizing them [52].

Table 5: Classification of fly ash according to Canadian standard

Type	CaO, %	LOI, %
F	≤ 15	max: 8
CI	15 – 20	max: 6
CH	≥ 20	max: 6

The CSA and ASTM specifications have an overlap across the categories, but for most part, there exists a correlation between the CaO content and the sum of SiO_2 , Al_2O_3 and Fe_2O_3 , as illustrated in Figure 3 [6].

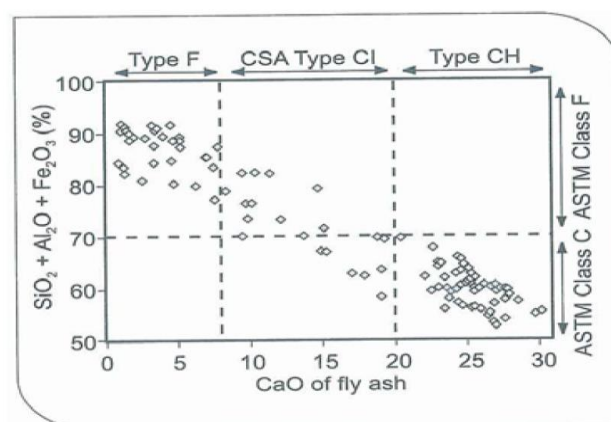


Figure 3: Comparison of CSA A3001-03 and ASTM C618-05 specifications for North American fly ash sources

2.2.4 Japanese standard

Fly Ash is utilized in Concrete is classified as Types I, II, III, and IV by the Japan Industrial Standard, JIS A 6201, on the basis of the following criteria [53]:

- Type I fly ash is defined as high-quality fly ash with a LOI of less than 3.0% and a Blaine fineness of more than 5000 cm²/g.
- The majority of JIS A 6201-qualified fly ash is classed as Type II.
- Fly ash with a high LOI of 5.0 to 8.0 percent is classified as Type III.
- Type IV is defined as a low Blaine fineness value range of 1500 to 2500 cm²/g.

A minimum percentage of flow value ratio which is the ratio of flow of fly ash content in cement relative to conventional Portland cement is shown in JIS standard. Table 6 shows the test procedures and standards for categorizing fly ash according to Ishikawa (2007).

Table 6: Fly ash for use in concrete according to Japanese standard

Item		Type I	Type II	Type III	Type IV
Loss on Ignition, LOI %		≤ 3	≤ 5	≤ 8	≤ 5
Fineness	Residue on 45 um sieve (mesh sieving method, %)	≤ 10	≤ 40	≤ 40	≤ 70
	Specific Surface area (cm ² /g), (Blaine method)	≥ 5000	≥ 2500	≥ 2500	≥ 1500
Flow value ratio (%)		≥ 105	≥ 95	≥ 85	≥ 75
Activity index (%)	Material age 28 days	≥ 90	≥ 80	≥ 80	≥ 60
	Material age 91 days	≥ 100	≥ 90	≥ 90	≥ 70
Density (g/cm ³) (specific gravity)		≥ 1.95			

Silicon dioxide: SiO ₂ (%)		≥ 45.0
Hygroscopic moisture (%)		≤ 1.0
Homogeneity in quality: Not to exceed values of submitted samples	Blaine method (cm ² /g)	≥ ± 450
	Mesh Sieving method (%)	≥ ± 5

2.2.5 Chinese standard

Chinese standard, GB/T 1596, considered coal type and simply stated as low fly ash, F and high fly ash, C with the latter possessing of 10% CaO content. The grade for fly ash classified with the limit of 1.0% free calcium oxide, CaO content for type F and 4.0% for type C.

Table 7: Chinese fly ash classification standard

Type of test	Grade		
	I	II	III
max %, SO ₃	3.0	3.0	3.0
max %, free CaO (Type F/ Type C)	1.0/4.0	1.0/4.0	1.0/4.0
max %, moisture	1.0	1.0	1.0
max %, LOI	5.0	8.0	15.0
max %, Fineness remains on sieve 45 μm	12.0	25.0	45.0

2.2.6 Thai standard

Quality of fly ashes is classified by their chemical composition and physical properties into 3 classes as in the following.

- (i) First class is suitable for extremely high-quality concrete.

(ii) Second class is suitable for control concrete and is divided in to 2 types.

(a) Type A has low CaO content

(b) Type B has high CaO content

(iii) Third class is fly ashes those have lower quality than the first and second class fly ashes. The third class fly ash is suitable for mass concrete, dam, and low-quality concrete. Thai standard (TIS 2135) for fly ashes is shown in Table 8 and Table 9.

Table 8: Chemical composition of fly ash according to Thai standard

Item	Properties	Requirement			
		First class	Second class		Third class
			Type A	Type B	
1	SiO ₂ , min %	30.0	30.0	30.0	30.0
2	CaO, %	-	Less than 10	Not less than 10	-
3	SO ₃ , max %	5.0	5.0	5.0	5.0
4	Moisture content, max %	3.0	3.0	2.0	3.0
5	LOI content, max %	6.0 ¹⁾	6.0 ¹⁾	6.0 ¹⁾	12.0

Note: ¹⁾ If satisfactory performance records or laboratory test results are provided, the use of fly ash with up to 12 % LOI may be permitted.

Table 9: Physical properties of fly ash according to Thai standard

Item	Properties	Requirement			
		First class	Second class		Third class
			Type A	Type B	
1	Fineness (select a method) The amount retained on a 45- μ m-mesh sieve, max. % Or Blaine fineness, min./ cm ² /g	10 6000	50 2300	55 2000	65 1600

2	Strength activity index with OPC type I	85	70	70	60
	7 days, min. % of the control	95	75	75	70
	28 days, min. % of the control	100	85	85	75
	91 days, min. % of the control				
3	Water requirement, max. % of the control	102	105	105	108
4	Autoclave expansion, max. %	0.8	0.8	0.8	0.8

2.2.7 Notable studies of relevance to classification of fly ash

The resulting pozzolanic activity index findings from test procedures according to American, Brazilian, and British standards were compared and connected with the chemical composition and physical features of the pozzolans, according to Gava et al. [54, 55]. The findings of several test procedures were shown to have little correlation with the real performance of pozzolans in mortars. Type of cement, cement replacement level, water reduction admixtures, and water to cement (w/c) ratio are all important parameters that influence the performance of a pozzolan when used as a cement replacement material in mortar and concrete work. Other investigations have confirmed that existing methodologies do not allow for proper evaluation, and that current categories may make pozzolans inappropriate for use.

To summarize, fly ash properties vary greatly depending on the source, and current classification methods do not correspond to the actual performance of fly ash cement concrete. In addition to, the literature indicates adequate facts that current specifications for using fly ash in Portland cement concrete are not sufficient from a performance standpoint. At the same time, it is noted that standard specifications are essentially prescriptive; therefore, they are confined to the class of fly ash and area. These standards did not state about how to select fly ash from different sources properly. The selection of fly ash as a cement replacement material also should involve verification using the standard tests to ensure that the desired results are attained. When constructing a concrete mixture including fly ash, more focus should

be placed on the performance criteria. It provides inspiration to investigate the effects of fly ash on concrete durability across geographies.

Table 10: Limits of standards for chemical composition and physical properties of fly ash

Constituent	ASTM C618	BS EN 450-1	CSA A3000	JIS A6201	GB/T 1956	TIS 2135
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ , min, %	Class: F, 50 C, 50	≥ 70	– ^a	– ^a	– ^a	– ^a
SiO ₂ , %	– ^a	– ^a	– ^a	≥ 45	– ^a	30
SO ₃ , max, %	5	≤ 3	5	– ^a	3	5
CaO, %	Class: F, 18 max. C, > 18	– ^a	Type: F, ≤ 15 CI, 15-20 CH, ≥ 20	– ^a	– ^a	Class: 1, – ^a 2, Type: A, less than 10 B, not less than 10 3, – ^a
Free CaO, max, %	– ^a	≤ 2.5	– ^a	– ^a	Type: F, 1 C, 4	– ^a
Fineness remains on sieve 45 μm	34	Category: N, ≤ 40% S, ≤ 12%	34	Type: I, ≤ 10 II, ≤ 40 III, ≤ 40 IV, ≤ 7	Grade: I, 12 II, 25 III, 45	Class: 1, 6 2, Type: A, 6 B, 6 3, 12
LOI, max, %	6	Category: A, < 5 B, 2 – 7 C, 4 – 9	Type: F, 8 CI, 6 CH, 6	Type: I, ≤ 3 II, ≤ 5 III, ≤ 8 IV, ≤ 5	Grade: I, 5 II, 8 III, 15	Class: 1, 10 2, Type: A, 50 B, 55 3, 65

^aNot taken into consideration.

2.3 Information of fly ash source in Southeast Asia countries

Nowadays, a byproduct, fly ash (FA) are growing abundantly in many Southeast Asia countries. It is estimated that approximate annual of the high consumption of fly ash rate across these countries are summarized in Table 11.

In Myanmar, the largest source of fly ash can be found in Tigyit power plant located in South-west Shan State and the amount of using fly ash is still low. There is a scarcity of information related to its beneficial usage in the civil engineering applications. As expected, in next decades, there will be increase coal-fired thermal power plant and a large amount of fly ash use in construction industries.



Figure 4: Tigyit coal-fired power plant in Myanmar

Indonesia is one of the biggest coal exporters in the planet, and the total of coal production and the export has expanded at a yearly average rate of over 10% since 2000 [56]. Indonesia has roughly in excess 85 coal-fired power stations. These power stations provide to million tons of fly ash consistently. In Indonesia, coal ash such as fly ash is predicted reaching 10.8 million tons in the year 2020 [57]. This information shows that Indonesia has an abundance resource of coal fly ash. The

amount of fly ash used in Indonesia is still very low amount around 0.47%. The largest coal fly ash source was mainly produced by Paiton coal power plant located in East Java province, Indonesia.

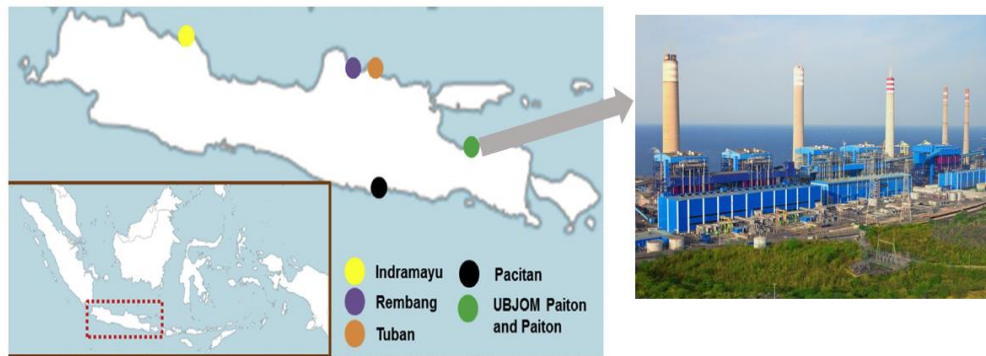


Figure 5: Paiton coal-fired power plant in Indonesia

Mae Moh, Lampang province, in northern Thailand, is the largest local source of fly ash. Lignite is used in Mae Moh, whereas anthracite and bituminous coals make up the bulk portion of imported coals. Approximate annual of the amount of fly ash and bottom ash produced is 4 million tons annually [58]. The utilization of fly ash as a pozzolanic material in concrete works in Thailand is approximately annual 1.8 million tons (45% of the total output of fly ash). It should be mentioned that the Electricity Producing Authority of Thailand's Mae Moh generating facility produces about 95% of the total fly ash (EGAT) [59].

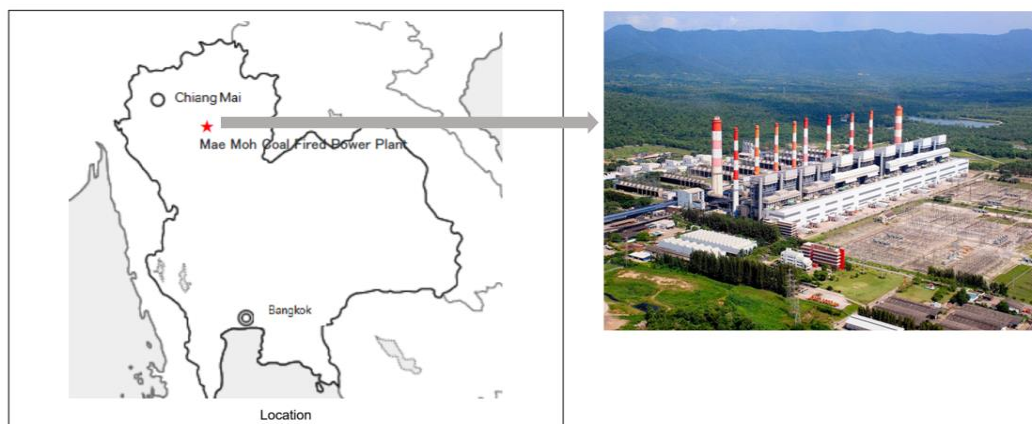


Figure 6: Mae Moh coal-fired power plant in Thailand

Coal-fired electric power plants were first built in Malaysia in 1987, and there are currently about seven coal-fired electric power plants in the country. It is recorded that the rate of fly ash production in Malaysia reached approximately 6.8 million tons annually from those power stations [60]. Approximately 42.6% of the total produced fly ash was applied as a cementitious material in concrete works and the remaining amounts of 57.2% of the total fly ash were disposed in landfills [61]. The largest local fly ash source located in Tanjung Bin coal power plant, Johor, Malaysia. It is noted that Tanjung Bin coal fired thermal power station is the first private coal-fired plant in Malaysia and biggest coal fired power plant in Southeast Asia [62].

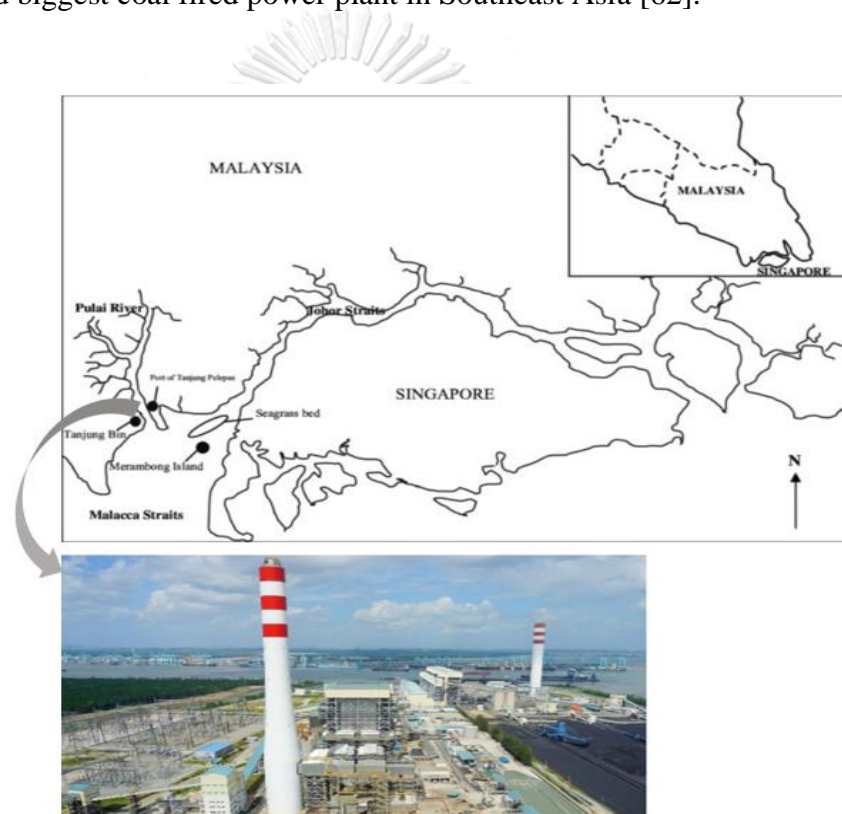


Figure 7: Tanjung Bin coal fired thermal power station in Malaysia

Vietnam is one of the Southeast Asia countries which has a high coal potential. The most abundant coal in Vietnam is anthracite with the reserve of approximately 3.4 billion tons and 90% of the total anthracite reserve is observed in Quang Ninh province, the northern part of Vietnam [63]. Currently, Vietnam is the biggest anthracite coal exporter in the globe, representing 13% of the world market [63]. A large amount of fly ash is produced about 12.2 million tons from Vietnam's coal power plants and utilized only 4 million tons (30% of the total produced fly ash)

[64]. The largest coal-fired power plant in Vietnam is Pha Lai coal-fired thermal power plant which use anthracitic coal and is in Hai Duong which is in northern part of Vietnam.



Figure 8: Pha Lai coal fired thermal power station in Vietnam

Table 11: Estimated fly ash production and utilization in different countries

Country	Amount of production (million tons/year)	Amount of utilization (%/year)
Indonesia	10.8	0.47
Thailand	4	45
Malaysia	6.8	42.6
Vietnam	3.4	30

2.4 Fly ash usage in many sectors

Many research works have been performed in goal to increase the using fly ash in various sectors since it is not considered as hazardous waste in 30 years ago [60, 65]. Figure 9 illustrates many countries across the worldwide use this deposit waste which convert into beneficial product as a replacement material to another industrial resource, process or use [60]. Fly ash usage can be classified into three classes of application such as low, medium and high technology application.

Since fly ash possess oxide-rich material, it is widely used as a raw material in construction work and many different industries [66]. At this time, the fly ash was effectively use in enhancing the construction material and suitable to be used in

agriculture area to improve the soil properties too [65]. Some large countries like India, China, US and EU used the fly ash in many sectors such as brick production, ceramics production, road construction, concrete manufacturing and other applications as displayed in Figure 10 [67]. Concrete production is the most important areas of using fly ash, either in conventional concrete or in geopolymer concrete.

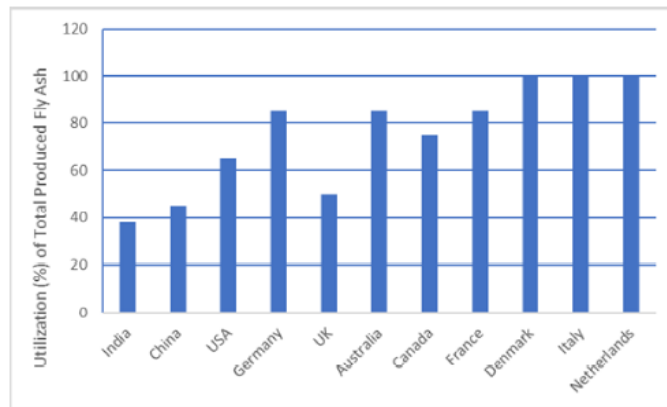


Figure 9: Utilization rate of total produced fly ash in different countries

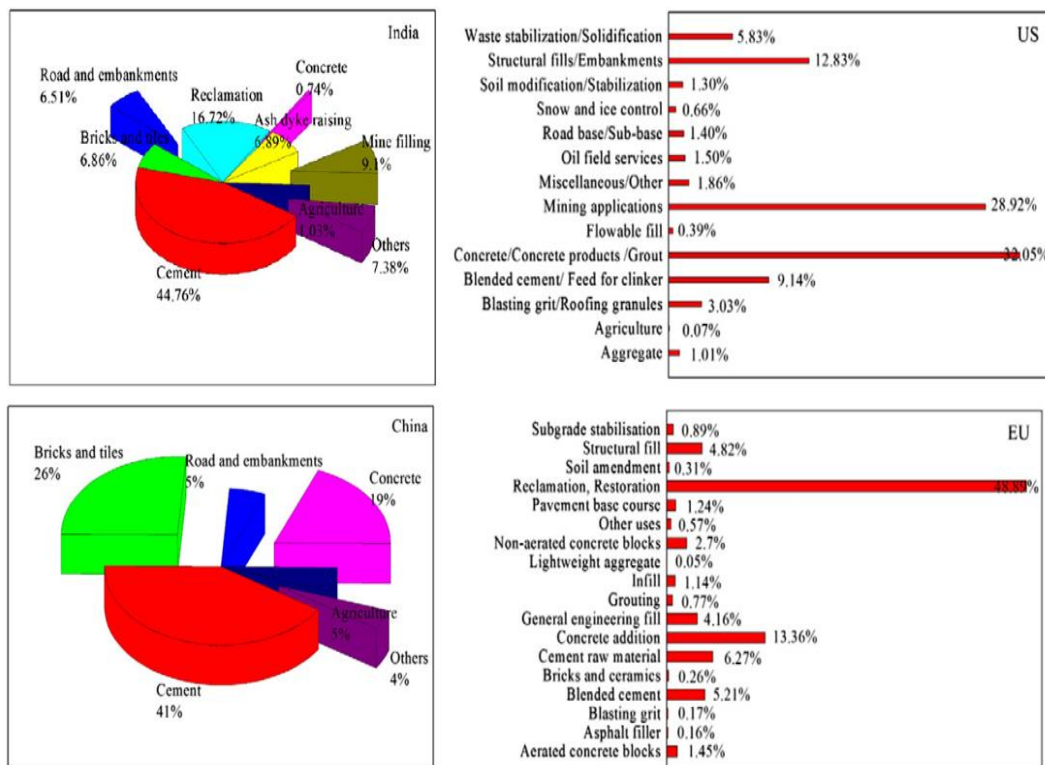


Figure 10: Utilization of fly ash in China, India, US as well as EU

2.4.1 Fly ash usage in building construction

In the civil work field, the use of fly ash has grown as a result of expanding technology, while also improving construction quality and environmental quality. It is not a new technology. At present, due to the content of SiO_2 and Al_2SiO_3 is almost the same with Portland cement, cement industries used fly ash as a pozzolanic material for producing of Portland Pozzolana Cement [61]. The production of extra calcium silicate hydrate gel begins in the glassy phase of fly ash and calcium hydroxide, resulting in greater density and strength [68].

Although fly ash can be used to replace up to 75% of the cement weight, there are only a few standards that govern its use, such as ASTM C 618 and EN 450-1 [38, 43]. The geopolymer concrete including fly ash can be provided as a new cement substitute in the building and construction materials field [69]. This concrete mixture made some concrete with high compressive strength, low creep, good acid resistance and low shrinkage [70].

Normally fly ash was used both in blended cement to product in-situ concrete mixture and in high strength precast and prestressed concrete application. The utilization of fly ash in high strength precast and prestressed concrete has been limited due to having slow strength development at early age [71]. Replacing normal aggregates with fly ash can be used in an artificial lightweight aggregates manufacturing by using sintered (fired) and unfired (cold bonded) processing methods [71].

2.4.2 Fly ash usage in road and embankment construction

Using fly ash in road and embankment construction has a lot of advantages compared to parent method. Fly Ash may be applied in road construction for filling activities, stabilizing and constructing subbase or base [70, 71].

Fly ash can be used as a fill material in embankment construction. The well-compacted fly ash presented good shear strength when compared with normal soils used in earth-fill operation. Fly ash also has ability to resist permeability and even moisture-density curve, therefore, to improve embankment application, backfilling and land construction, the fly ash usage considered as a desirable material [72].

Fly ash combined with lime, is applied to stabilize the subgrade to reduce plasticity, and improve workability of weak soils [71]. Soil mixed with fly ash and lime will increase California Bearing Ratio (CBR), increased (84.6%) when compared with fly ash alone to soil [73]. Fly ash is used either with lime or Portland cement, and aggregate for base and subbase courses for pavements work [71]. Even though containing 50% Class C fly ash mixture gained strength more slowly at the beginning, this mixture help a good alternative for paving [74].

2.4.3 Fly ash usage in masonry work and other application

Among the sector of using fly ash, it developed top 3 in the fired, unfired, and steam cured bricks manufacturing [67]. Fly ash bricks have several advantages more than the conventional burnt clay bricks [75]. Fly ash ranges between 40% and 70% can be utilized in brick production and the fly ash brick is technically acceptable, economically feasible and environment friendly. Fly ash also utilized in high-flexural strength ceramics production including railroad ties, fence posts, electric line insulators and others suitable usage [71].

2.5 Properties of concrete containing fly ash

2.5.1 Effect of fly ash on compressive strength

Many researchers published the utilization of fly ash in cementitious matrices which used to maintain the durability of concrete structures and also to apply more sustainable concrete [18]. However, there is a double effect when replacing cement with fly ash by considering carbonation.

A. K. Saha remarked that the performance of concrete by replacing various levels of fly ash as 0%, 10%, 20%, 30%, 40% by mass of cement. The concrete specimens including 20% fly ash showed a rapid strength improvement from 7 to 90 days of water curing, and concrete strength with 30% and 40% fly ash was improved strongly from 7 to 180 days of curing time [11].

P. Chindapasirt et al. examined the combined effect of complex admixture of palm oil fuel ash (POA) and fly ash (FA) in cement on the strengthen the mortar at the long age of 90 days, which are 102–103% of that of control mortar at the same age

[18, 28, 76]. The low early strengths and later age strength development are the general effect of pozzolanic materials on concrete.

F. Moghaddam et al. showed that the compressive strength of concrete decrease when the increasing of fly ash content over 20% at both 7 and 28 days. However, due to the slow pozzolanic reaction between the fly ash and calcium hydroxide released from cement hydration, the strength will continue to increase at long term curing for the mixes incorporation fly ash [9].

Naik et al. investigated that the effect of three sources of pozzolanic material such as the fly ash on the strength development of concrete. The development strength of the fly ash mixtures concrete was observed significantly at the age of 91 days. The compressive strength of concrete with the source F1 fly ash have the highest strength for the mixture, followed by FA2 and FA3 [77].

Kiattikomol et al. studied to determine the completely different shapes, sizes, and chemical composition of ground coarse fly ashes, from five different sources in Thailand. The results showed that the improvement of strength of mortar including fly ash mostly depends on the main factor, which is the fineness of fly ash, not the chemical composition. The development rates of compressive strength were not the same with the different physical and chemical properties [78].

FA reacts with calcium hydroxide which generates during the hydration of cement produce the calcium-silicate-hydrate (C-S-H) gel. The C-S-H gel can improve the microstructure of the cement paste; meaningly, its porosity is reduced. This is well known as a pozzolanic reaction of FA [6, 42]. Therefore, FA can be ubiquitously used today as the replacement of cementing materials due to its pozzolanic nature. It has been used in concrete at replacement levels from 15 % to 25 % by weight of cement ingredient [6]. However, when replacing cement with FA in a large percentage, its hydration reactions are apparently delayed and early-age performance characteristics (especially within 1 to 3 days) of reacting product are deteriorated. This is because its pozzolanic reaction takes place at later ages. In terms of the cost efficiency, having better early-age performance characteristics are valuable to perform rather than having better later-age performance characteristics [79, 80]. The use of optimum content depends widely on the application, specific limitation, the properties of the FA, the climate and geographic location, and type of cement used. However, for mass

concrete application, to control the temperature rise of the cementing structure is critical. To delay the heat release from early hydration reactions allows the structure having no thermal cracks. Whereas, FA has been used with higher replacement levels ranging from 30 % to 50 % in mass concrete structures such as foundations, bridges, and dams [6]. Recently, research has illustrated that high replacement levels from 40 % to 60 % can be applied in concrete production with good durability and mechanical properties [81]. Performance characteristics of the blended FA cementing system improves a long-term strength development because a well workability of fresh FA-cement system consumes less water content when compared to plain system having the same slump. This means that, at a given slump, FA-cement system can flow and consolidate better than the plain system when being vibrated. Better consolidation of the fresh mixture results in reducing its segregation.

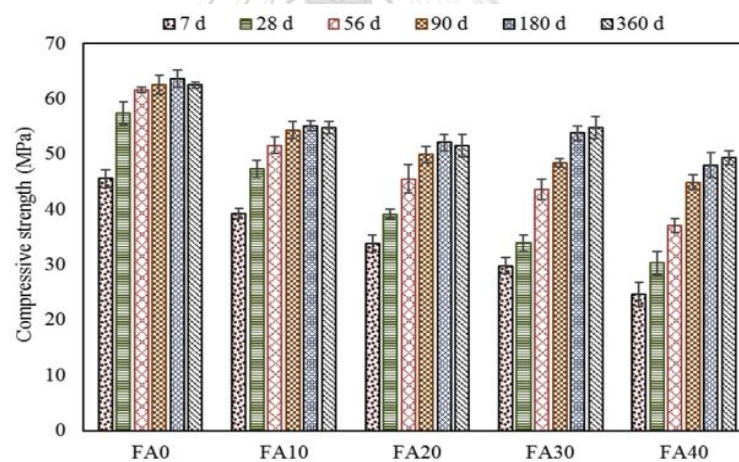


Figure 11: Compressive strength of concrete with fly ash

Table 12: Comparison of compressive strength from literature review

References	Compressive strength development
A.K.Saha [11]	30%-40% FA concrete strength increased gradually up to 180 days owing to the pozzolanic reaction.

P. Chindapasirt et al. [18, 28, 76]	The use of the blend of FA and POA produce high strength mortars due to the synergic effect.
F. Moghaddam et al. [9]	The strength of blended cement paste with finer grade FA showed higher strength than the coarser grade FA at replacement level (20% and 40%).
Naik et al. [77]	The effect of source of FA was significant on the strength development of concrete due to the differences in the reactivity of fly ashes obtained from different sources.
Kiattikomol et al. [78]	The strength development of ground coarse fly ash-cement mortar mostly depends on the main factor, which is the fineness of fly ash, not the chemical composition.

2.5.2 Effect of fly ash on chloride concentration

The durability of concrete is one of the most importance as it controls the performance of reinforced concrete structures during their running life. Chloride make corrosion in infrastructure is one of the major durability concerns, causing billions of dollars to be spent globally in repairs and maintenance of reinforced concrete structures.

In 2008, P. Chindapasirt et al presented that the results of chloride penetration test of mortar incorporation supplementary cementitious materials exposed to 3% NaCl solution for 30 days exposure time are illustrated in Figure 12 [18]. Because of the reducing $\text{Ca}(\text{OH})_2$ and improving the permeability of mortar, replacing cement with pozzolanic materials remarkably improve the ability to resist chloride concentration [18]. Weerdt et al. investigated that using NaCl solution instead of seawater can be evaluated the performance of concrete structure in marine conditions by chloride concentration testing [82].

The cement-fly ash composites were reported to improve early-age properties in term of reduced porosity leading to denser matrix [83]. Durdzinski et al. reported the high-calcium fly ash generated from a coal power plant and observed that the fly ash had different chemical compositions. The researchers also found that when casting fresh concrete mixture, the fly ash with different chemical compositions and particle size distribution or degree of fineness led to different resistance to chloride

ion penetration. This is also the cases when different fly ash lots are all produced in the same power plant [84, 85]. Meaningfully, our specification standard of fly ash that normally classifies only its chemical composition between Class F and Class C seems not to differentiate the quality of fly ash properly. However, FA has a significant influence on increasing the sustainability of our concrete infrastructure. For example, the incorporation of FA improved the resistance of chloride penetration in mortar, as reported by many researchers [28, 84, 85] . Remarkably, beyond the 60-day studied period, replaced blended cement mortar with 40% FA reduced its chloride diffusion coefficient value by approximately 85 % when compared the plain mortar (0% FA). It exhibited that the blended mortar having FA decreased the chloride diffusion coefficient for all testing periods [12].

Moreover, the durability and service life of infrastructure strongly depend on its material transport properties such as sorptivity, permeability, and diffusivity which are measured by the microstructural characteristics of cementing systems. It is known that the porosity and pore size distribution are two important parameters of the microstructure of hydrated cement system that significantly influence durability of final product [86]. Therefore, FA widely used to reduce the porosity of blended cement system in civil engineering applications. Kumar et al. (2021) [87] presented the effect of curing age on the porosity of blended cement system containing coal FA, waste eggshell powder, and steel fiber as a partial replacement of cement [88-91]. Tested results indicate that increase in long time water curing, decrease the porosity of concrete and compressive strength increased with a combined mix of 35% FA, 6% eggshell powder, and 0.75% steel fibers. Nakamura et al. (2021) [92] investigated the strength development of blended cement system containing coal FA by three-dimensional visualization of porosity distribution. Results exhibited the porosity of microstructure of cementing systems produced by the moisture ratio played an important role for the strength development. P. Chindaprasert et al. [93, 94] reported that the incorporation of FA and its fineness significantly affected on the total porosity and pore size of blended cement systems having FA.

However, the civil engineering applications of blended FA-cementing materials continue having a practical challenge due to a wide variability and heterogeneity of FA. When many researchers [44, 95] studied the wide variation of

FA, their results showed that when mixing cement with FA having different chemical compositions led to changes in compressive strengths, pore-size distribution, and its ability to resist chloride concentration even though such FA came from the same power plant. This is due to the combustion condition, surrounding environmental conduction during firing, and composition of the raw feed [96, 97]. Wang et al. (2019, 2020) [98, 99] investigated that FA which have the same class in cement systems and in alkaline conditions. It was observed that even though the FA had the same material properties, the reactivities of FA could be different from lot-to-lot.

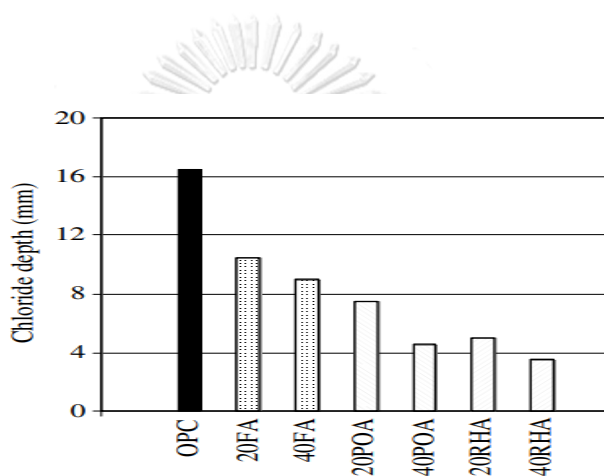


Figure 12: Chloride depths after 30 days immersion in 3% NaCl solution

Table 13: Comparison of chloride concentration and porosity from literature review

References	Chloride concentration resistance
P. Chindaprasirt et al. [18]	Replacing cement with FA significantly increase good resistance to chloride penetration, due to reducing $\text{Ca}(\text{OH})_2$ and improving the permeability of mortar.
Weerdt et al. [82]	Leaching, found in the outer 10–20mm both for seawater exposure and for NaCl solution had a much stronger influence on the chloride ingress. Thus, chloride ingress in marine exposed concrete can be assessed using NaCl solutions.
Durdzinski et al. [44, 84]	Cementitious pastes with high calcium FA which come from the same power plant found varying chloride resistance.
Malheiro et al. [12]	Incorporation of FA decreases the chloride diffusion coefficient for all periods studied.

Kumar et al. [87-91]	The porosity of concrete including the combined mix of fly ash, eggshell powder and steel fiber decreased with the increase in water curing age.
P. Chindaprasert et al. [93, 94]	The cement pastes having the classified FA observed in lower total porosity and capillary porosity than those with the original FA.

2.5.3 Effect of fly ash on accelerated carbonation

For determining carbonation resistance of cement–fly ash composite, it can be explained that the secondary hydration reaction of cement–fly ash composite consumes partially amount of $\text{Ca}(\text{OH})_2$ phase. Reduced $\text{Ca}(\text{OH})_2$ phase results in decreased carbonation resistance of the final product. The long-term concrete performance is now in concern. Hence, reduced carbonation resistance of the cement–fly ash composite is one of the primary challenges limiting the utilization of fly ash in cementitious material. As discussed, because of anthropogenic climate change, the large amount of greenhouse gas introduced into our atmosphere. This may cause faster carbonation reaction to our concrete structure, leading to shorter service life. CO_2 penetrates through concrete pores and dissolves in the pore solution. It is then changed into carbonic acid H_2CO_3 which reacts with the highly alkaline components such as $\text{Ca}(\text{OH})_2$ and C-S-H gel generated from cement hydration process and produces calcium carbonate (CaCO_3). This effect leads to reduce the pH value of concrete, causing carbonation reduced a lot of good reinforced concrete structures. The carbonation of concrete can be evaluated by acceleration carbonation test [100, 101].



Replacing sand with fly ash in concrete tested under severe condition provide increasing carbonation resistance compared to parent concrete reported by many researchers [102, 103]. To make sure the durability of reinforced concrete structures, the carbonation depth of fly ash as a partial replacement of cement in concrete should be less than thickness of concrete cover which is normally 20mm. The cement matrix

neutralization process which leads to decrease of pH level in concrete ranges from 13 to below 9, reduces the chemical protection of steel. Therefore, steel corrosion can start when the pH value reduces under around 9.5. Ho and Lewis investigated the effect of accelerated carbonation on cementitious materials cured under 4 % CO₂ concentration with a chamber temperature controlled at 20 °C and 50 % relative humidity for 60 days. Their results indicated that such concentrated CO₂ condition could result in faster carbonation. Only a week under the carbonation chamber was predicted to be equal to about one year under the normal condition [104]. Increased CO₂ concentration in today atmosphere leads to increased rate of carbonation significantly. There are many factors to affect the carbonation process, especially binder content and porosity content, CO₂ concentration, temperature, humidity and curing age [105].

Therefore, when fly ash are used to be a kind of pozzolanic material to replace for cement, the content of Ca(OH)₂ is considered to measure as a main factor in concrete which is determined by thermogravimetric analysis (TGA) [106, 107]. The main objective of TGA method is to evaluate the loss masses that are attributed to different compounds, which appear in different temperature and to describe the reactivity of the pozzolanic mixture, mainly in terms of the study of the hydration reaction products [108].

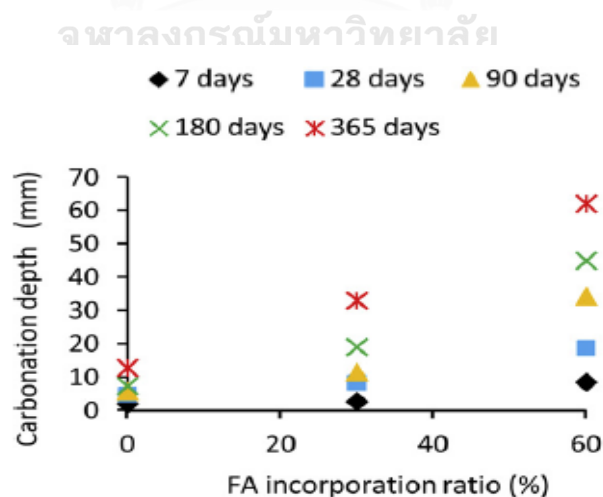


Figure 13: Effect of the incorporation of FA on the carbonation depth of concrete over time

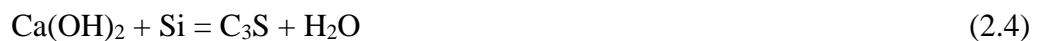
Table 14: Comparison of accelerated carbonation from literature review

References	Carbonation
D. Zhang et al. [102, 103]	Substituting fine aggregate with fly ash can improve the carbonation resistance of concrete when compared with conventional concrete.
Lewis et al. [104]	For 25 MPa compressive strength, concrete including fly ash carbonated 50% faster than the control concrete.

2.6 Pozzolanic reaction

The use of fly ash as SCM provides the key advantage in concrete which not only reduces the amount of non-durable calcium hydroxide (lime or portlandite), but also it is transformed into calcium silicate hydrate (CSH) in the process, which is the strongest and most durable portion of the paste in concrete. The paste is the key to durable and sustainable concrete [109].

To generate the same binder (CSH) as cement, both Class C and Class F fly ashes react in concrete in similar ways they have “pozzolanic reaction” with the lime (calcium hydroxide) released by the hydration of cement. The hydration of ordinary Portland cement (OPC) and the chemical reactions involved in the pozzolanic reactions are shown in equations 2.3 and 2.4, respectively [109].



2.7 Assessment of the degree reaction of fly ash

It is necessary to determine the pozzolanic reaction of FA to optimize using this material because this chemical reaction can be one of the factors changing its overall performance. There are several methods including selective dissolution [98, 110, 111], scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) [44], image analysis (IA) [112], and quantitative X-ray diffraction (QXRD) [44, 113]. This pozzolanic test to determine the degree of reaction of cement paste with

SCMs using isothermal calorimetry and thermogravimetric analysis (TGA) was performed before and showed a promising analysis [114-116].

Many researchers proposed several pozzolanic tests to determine the pozzolanic material and quantify their reactivity which are the main components for engineering practices. The pozzolanic test method was performed by using isothermal calorimetry to measure the heat release of mix fly ash and $\text{Ca}(\text{OH})_2$ at temperature 40°C and pH level 13.5 [117]. The modification of this test method has been reported using the different conditions such as 50°C , a different liquid-to-solid ratio, and no added sulfate or carbonate [116]. The aim of this pozzolanic test was to measure heat release and $\text{Ca}(\text{OH})_2$ consumption of mix fly ash and $\text{Ca}(\text{OH})_2$ and use these parameters to “classify” the pozzolanic materials. It is important to differentiate the response in a pozzolanic test, such as the heat release or $\text{Ca}(\text{OH})_2$ content from the degree of reaction of fly ash. Therefore, the heat release or $\text{Ca}(\text{OH})_2$ content can be measured to be a degree of reaction of fly ash in cementitious systems [116].

The degree of reaction of SCMs in cementitious pastes can be interesting to determine because of the filler effect of the SCMs and low degree of reaction process. The backscatter electron image analysis (BSE/IA), X-ray diffraction (XRD) coupled with Rietveld analysis and the thermal gravity analysis (TGA) could be used to measure the reaction degree of SCMs. However, it is difficult to quantify the unreacted mineral admixture by XRD due to including large amount of amorphous phases in mineral admixtures. Many researchers reported that the reaction degrees of fly ash in cementitious paste were reported by selective dissolution method. The objective of this method is dissolving the hydration products and unhydrated cement and leaving the unreacted fly ash [118]. The amount of unreacted mineral admixture and further its reaction degree could be directly determined by this method. The pozzolanic reaction of the fly ash consumes $\text{Ca}(\text{OH})_2$ released from cement hydration to produce CSH gel. Therefore, the consumption of $\text{Ca}(\text{OH})_2$ has been used as a measure for the degree of reaction of fly ash. The quantification of the fly ash in fly ash blended cements is an important parameter to understand the effect of the fly ash on the hydration of cement (OPC) and on the microstructural development [112].

In 2010, Haha et al. proposed the use of a selective dissolution technique based on EDTA/NaOH, diluted NaOH solution, the portlandite content and by

backscattered electron image analysis to determine the fly ash reaction in cementitious system. The amount of fly ash determined by selective dissolution using EDTA/NaOH is observed to be reported with a significant possible error as different assumptions lead to large differences in the evaluation of fly ash reacted [110].

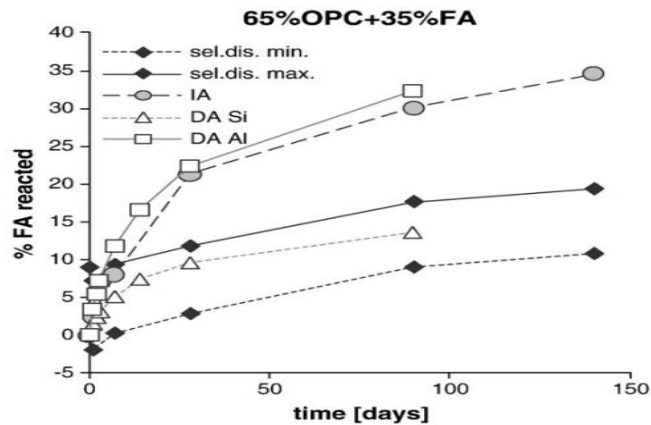


Figure 14: The % FA reaction determined by image analysis (IA), FA dissolution in 0.5 mol/l NaOH (DA) and selective dissolution using EDTA/NaOH

Pane and Hansen [119] investigated the degree of reaction in cement pastes incorporation SCMs at different temperature by combining the use of isothermal calorimetry and thermogravimetric analysis (TGA). Ramanathan et al. used the same test procedure to determine SCMs reaction in cementitious pastes. This was achieved by comparing the heat release and $\text{Ca}(\text{OH})_2$ consumption in cementitious pastes with the corresponding values from a pozzolanic test [106].

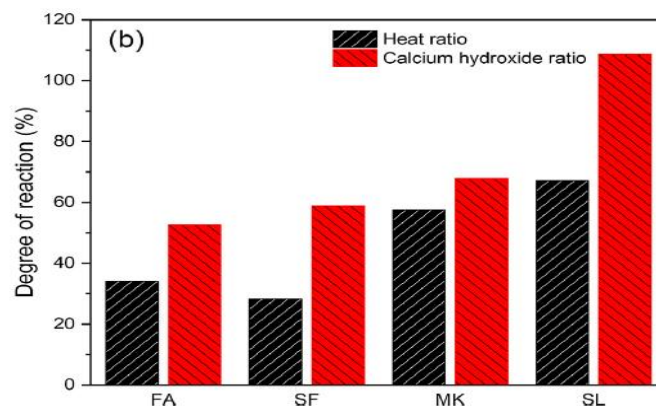


Figure 15: Degree of reaction of SCMs with $w/cm = 0.5$ at 50°C

Table 15: Comparison of pozzolanic test with selective dissolution method

References	Method	Process	Advantages	Disadvantages
Haha et al. [98, 110, 111]	Selective Dissolution Test	<ul style="list-style-type: none"> - Mix cement and FA with water. - After curing, added into dissolving solvent (EDTA/NaOH) 	<ul style="list-style-type: none"> - Can determine the amount of unreacted FA correctly. 	<ul style="list-style-type: none"> - Cannot work for all SCMs. - Difficult to measure the residue % for high calcium FA due to dissolved too much into acid.
Pane and Hansen [114, 116, 119]	Pozzolanic Test	<ul style="list-style-type: none"> - Mix FA and CaOH with 0.5M KOH - After mixing, Placed into an Isothermal Calorimeter and TGA 	<ul style="list-style-type: none"> - Can produce the relationships between heat release and CaOH consumption. - Less time consuming. 	<ul style="list-style-type: none"> - Difficult to calibrate.

2.8 Service life prediction

The service of reinforced concrete infrastructures mainly depends on the durability performance of concrete. Concrete made of traditional Portland cement is considered as a durable material for the non-aggressive condition. However, being a heterogeneous porous material, concrete is sensitive to degradation in aggressive exposures such as in the marine conditions, underground and in exposure to chemicals. In such environments, concrete undergoes early deterioration effect which finally decreases the service life of structures and require expensive repair and maintenance cost. Corrosion of reinforced steel directly impacts on strength, durability, and serviceability of reinforced concrete structures. This is the main durability problem in the concrete structures. For example, in the U.S. alone, more

than 18 billion dollars was spent annually to repair and maintain those infrastructure [120]. Nevertheless, good resistance against aggressive exposures can be accomplished by choice of materials and their proper mix proportioning without increasing the cost of concrete production and further maintenance. Therefore, the use of fly ash as a partial replacement of cement in concrete can enhance the ability to resist chloride penetration in the marine conditions and develop the durability properties of concrete by its pozzolanic reaction and particle packing effects. Chloride surface concentration of cementing system was reported to be one of the most important factors to develop the service life of any reinforced concrete structures in the aggressive environment [12, 36, 121]. The durability performance of bagasse ash blended concrete, and its service life prediction are investigated by Mahima et. al. [36]. Accelerated durability test results were related with the parameters impact on the long-term performance of the concrete. The service lives of reinforced concrete for various cover depths were predicted by Pradip et.al. in 2018 [121]. They reported that the fly ash blended cement in concrete for marine infrastructure has not only been observed structurally sound but also offers significant environmental benefits in terms of improved durability.

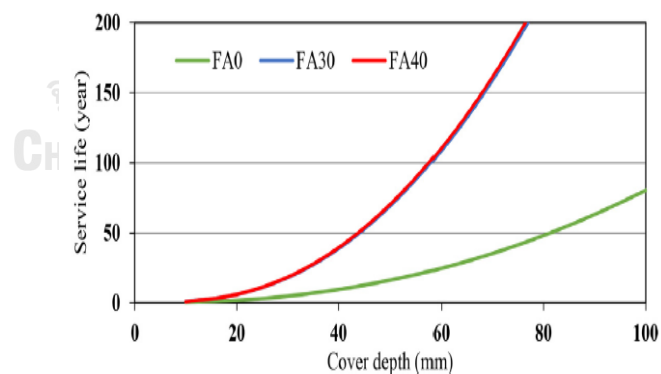


Figure 16: Variation of service life of concrete containing fly ash with cover depth

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

In the coming century, it is necessary to maintain the durability of infrastructures which keep their required performances over the long term. Because structural concrete undergoes deteriorated structures due to expected environmental and load conditions, a lot of money spent to maintain them in every year. Engineers are also attempting to develop a more durable concrete structure to decrease the maintenance costs. Among the various measures being explored, the use of supplementary cementitious materials (SCMs) is one of the most promising and possible approaches. Recently, to improve the concrete performance, the pozzolan materials are used in the concrete mixture in each country. However, with the different properties of the materials, the hardened concrete properties become differ. Among the Southeast Asia countries, fly ash is the mostly used pozzolan in this area. However, the proper guideline in using fly ash across the country are limited. Thus, a further experiment about fly ash from different sources is necessary. Moreover, the service life of infrastructures mainly depends on the durability of concrete. The service life model using Life365 was performed to predict the service life of blended FA-cement system.

3.2 Procedure of the study

In this chapter, the necessary materials, apparatus and tools, and testing methods are described. The flow chart of this research is expressed as follows.

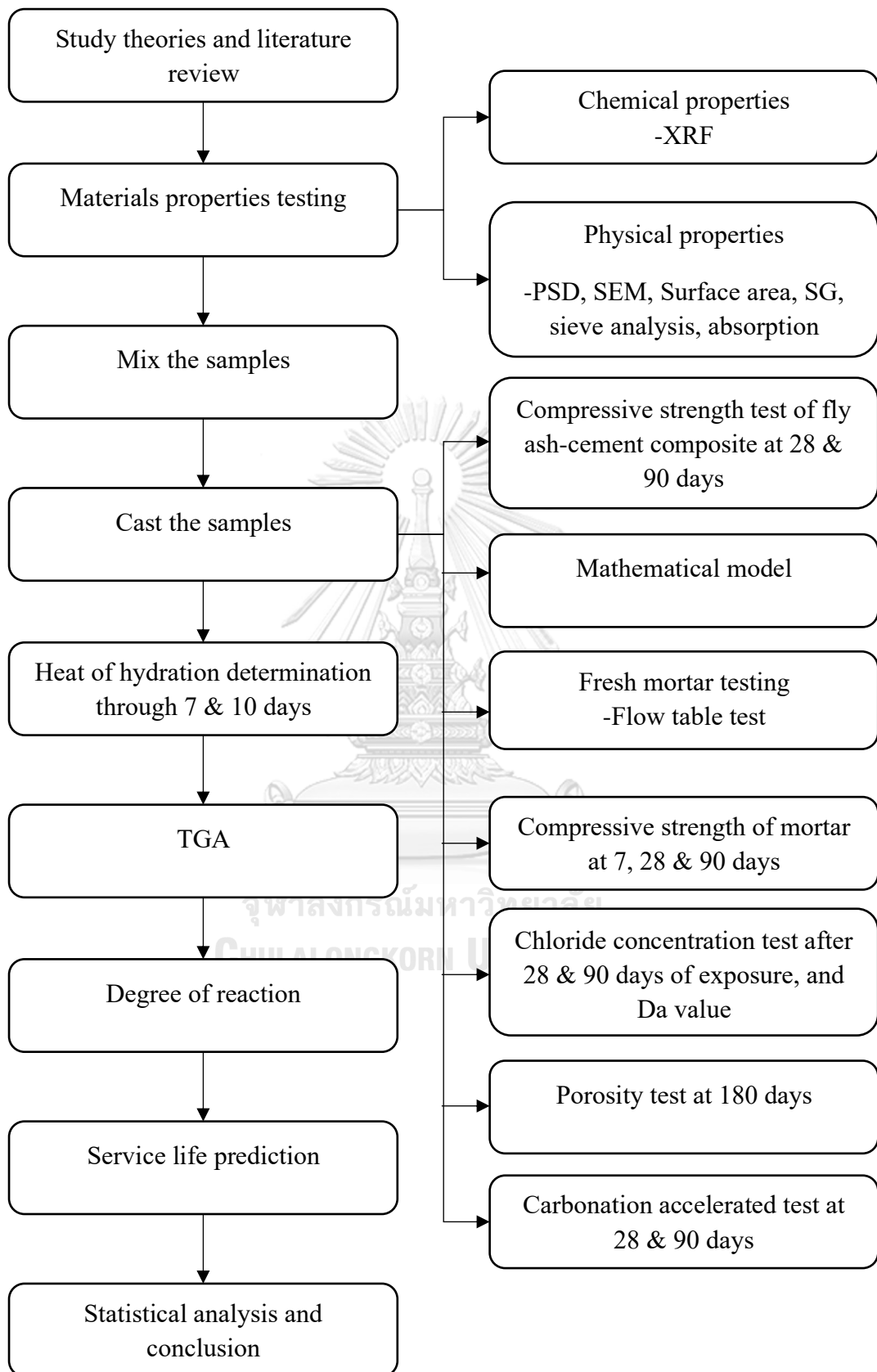


Figure 17: Flow chart of the study

3.3 Materials

Ordinary Portland cement Type I (OPC) as per ASTM C150 [122] was procured from SCG company, Thailand. Water used for all experimental studies was deionized water. River sand having a specific gravity of 2.62, water absorption of 0.65 %, and fineness modulus of 2.96 was obtained from Saraburi, Thailand. The river sand was used as fine aggregate for mortar preparation. Fly ash, as the SCM, was procured from three different countries including Myanmar, Thailand, and Indonesia. Fly ash was collected from five different coal power plants, namely Myanmar class F (FA1), Thailand class F (FA2), Thailand class C (FA3), Indonesia class F (FA4), and Indonesia class F (FA5). Epoxy, reagent-grade NaCl, AgNO₃, and H₂SO₄ were lab-graded and used in the chloride concentration test. Methyl orange (C₁₄H₁₄N₃NaO₃S), and phenolphthalein (C₂₀H₁₄O₄) were lab-graded and used in the accelerated carbonation test.

3.4 Chemical properties of materials

It is noted that the chemical composition of fly ash as a cement replacing material play an important role in the durability properties of concrete. Significant variation in the chemical composition of the different fly ash was observed in Table 4.1, particularly, the content of SiO₂, Al₂O₃, CaO, Fe₂O₃ and alkali oxide content. The chemical composition of fly ash used for fly ash blended concrete may slightly differ even though they obtained from the same coal-fired power station. In order to account for the variations in the chemical composition of the different fly ash, the chemical properties of materials were evaluated by using XRF to analyze in term of quantity analysis of cement and fly ash.

3.5 Physical properties of cement and fly ash

3.5.1 Particle size distribution (PSD)

The particle size distribution of the raw fly ash has been identified as influencing the compressive strength of concrete, with an increase of finesses leading to an increase compressive strength. The particle size distribution can be measured by using Laser particle size analyzer. It can see in Figure 18.



Figure 18: Laser particle size analyzer machine

3.5.2 SEM analysis

SEM analysis was taken with Scanning Electron Microscope and Energy Dispersive X-Ray machine shown in Figure 19 to determine the behavior of the specimens such as particles shape, cement paste and the interfacial transition zone (ITZ) at micro-structure level. Before the process of scanning images, the small particles were coated with diamond paste (conducting material) to prevent the damages from cutting.

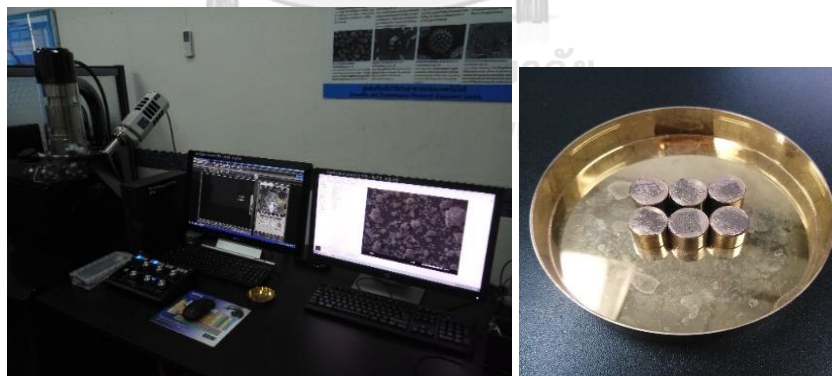


Figure 19: SEM and Energy Dispersive X-Ray machine

3.5.3 Blain fineness test

Fineness is an important parameter of cement and fly ash. It refers to the size of particles and directly affects the strength of concrete. According to ASTM C204 [123], the fineness of materials was obtained by using Blaine air permeability

apparatus. The specific surface area of materials is a value which showing the fineness.

3.5.4 Specific gravity test

The aim of this test is to evaluate the weight per unit volume of the materials. The specific gravity of cement and fly ash was tested by using Le Chatelier flask according to ASTM C188 [124]. The specific gravity of great Portland cement should be in the range of 3.15 and 3.2. The ranges of specific gravity of fly ash have between 1.9 and 2.4 compared to 3.15 for cement.

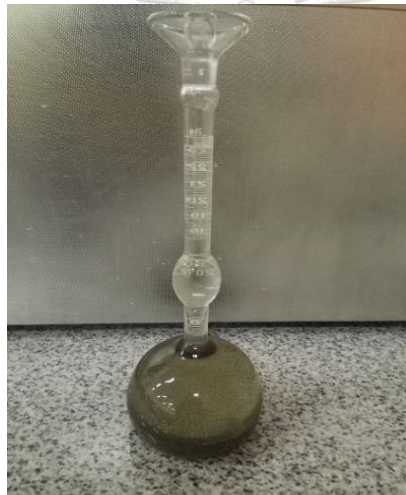


Figure 20: Performance test: specific gravity of cement

3.6 Physical properties of fine aggregate

Aggregates are a collective term for the mineral materials like sand, gravel and crushed stone that are utilized with a binding medium (such as water, bitumen, Portland cement, lime, etc.) to produce compound materials, for example, asphalt concrete and Portland cement concrete. Natural aggregates are generally classified as fine and coarse aggregates. The following tests are performed for aggregates.

1. Sieve Analysis of Aggregate Test
2. Specific Gravity Test
3. Water Absorption Test

3.6.1 Sieve analysis

Determining of the grading of materials is necessary to use for concreting work. Aggregate includes various grading sizes. This test is necessary for checking where the aggregate meets the requirements and controlling the quality of mixture of aggregates. As the grading of aggregates affects not only the workability of concrete, but also the cost of concrete, it is important to select on appropriate materials and maintain the constant particle distribution during the construction of the structure. This test is performed according to ASTM C 136 [125]. The requirement of standard sieves for aggregates are “no. 4, 8, 16, 30, 50, 100 and 200”. The process of sieve analysis was applied with mechanical sieve shaker as shown in Figure 21.



Figure 21: Mechanical sieve shaker

3.6.2 Specific gravity and water absorption of aggregates

The objective of this test is to determine the specific gravity and absorption of aggregates for use in concrete. The specific gravity of aggregates which is used in this test is estimated on the basis of weight of saturated surface-dry is required for determining the mix proportion of concrete based on the weight of saturated-surface-dry of aggregates. The saturated-surface-dry aggregate is defined as the aggregate whose pores are completely filled with water but have no water adhering to the outside surface. The aggregates lose all uncombined water when it is dried at a

temperature of $110 \pm 5^\circ\text{C}$ for an enough period. These tests are carried out according to ASTM C128 [126] for fine aggregate. Figure 3.6 shows the performance of specific gravity of fine aggregate.



Figure 22: Performance test (a) saturated surface dry of fine aggregate and (b) specific gravity of fine aggregate

3.7 Preparation Methods

In both cement and fly ash–cement paste, water-to-binder ratios (w/b) of 0.44, 0.54, and 0.64 were used. In the cement pastes, the OPC was replaced with five types of fly ash (FA1, FA2, FA3, FA4, and FA5) at the replacement percentages of 0, 10, 20 and 30 % by weight of the cement. For testing the heat release and TGA, the paste samples were prepared. The binder component consisted of 85 % OPC and 15 % fly ash on a mass basis. Their weight and a water-to-binder ratio (w/b) was 0.54. This proportion was obtained using a curvilinear regression analysis. The paste preparation began with dry-mixing the OPC powder and fly ash homogenously and then adding water. The paste mixing was discontinued after the paste was homogenous¹². For testing the flow, compressive strength, chloride resistance, porosity and carbonation resistance, mortar samples with 15% fly ash replacement level were prepared. The sand-to-binder ratio of 1:2.75 by weight and the w/b of 0.54 were used as per ASTM C109 [127]. The mortar mixing proportions used are given in Table 16. The flow values of fresh mortars were assessed, and fresh mortars were then casted in cylindrical molds for compressive strengths, chloride ion penetration resistance, and

carbonation resistance at different ages [127]. The fresh samples were covered with a polyethylene sheet for curing. After curing for 24 h, the samples were demolded and submerged in saturated-lime solution until testing [114]. Testing procedure of fly ash – cement paste can be seen in Figure 23.

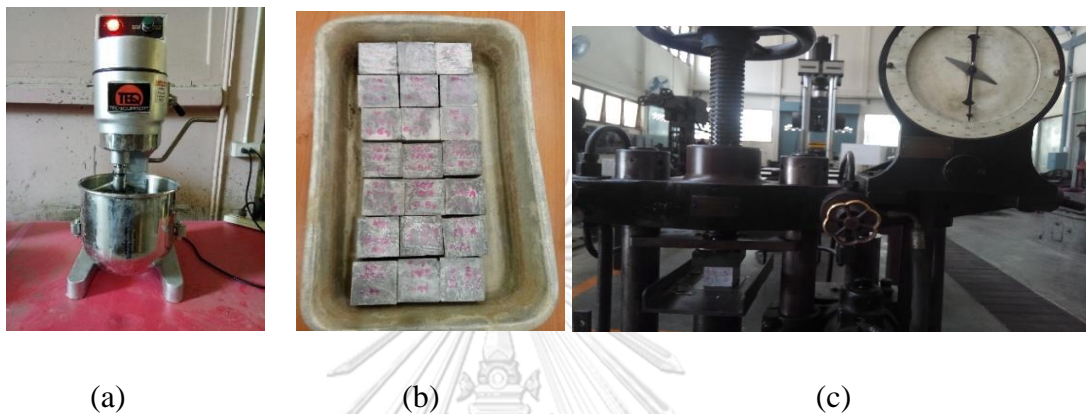


Figure 23: Test procedure (a) mixing the materials (b) hardened paste samples (c) compression test

3.8 Mathematical model

The equation models were applied to provide the proper percentage of cement paste with fly ash. The model of compressive strength can be evaluated as the following equation:

First Degree Polynomial Equation (Linear Equation)

$$\Sigma Y = b_0 + b_1 \Sigma X \quad (3.1)$$

Second Degree Polynomial Equation (Quadratic Equation)

$$\Sigma Y = b_0 + b_1 \Sigma X + b_2 \Sigma X^2 \quad (3.2)$$

Third Degree Polynomial Equation (Cubic Equation)

$$\Sigma Y = b_0 + b_1 \Sigma X + b_2 \Sigma X^2 + b_3 \Sigma X^3 \quad (3.3)$$

Where, Y is the corresponding strength at 28 days and 90 days, X is the replacement percentage of fly ash and b_0 , b_1 , b_2 , b_3 are the constant obtained by using the curvilinear regression analysis.

In analysis of curvilinear regression, the result of compressive strength of pastes needed to check which equation is convenient to use among linear, quadratic and cubic models by using coefficient of determination, R^2 . R^2 determine of how well the goodness of best fit line performs. The higher the value of R^2 , the more useful the model. R^2 takes on values between 0 and 1, where 1 shows a sufficient fit and a very consistent model for future forecasts. A value of zero, on the other hand, shows that the model fails to accurate model the data set. The values of R^2 can be got by using statistical software.

Table 16: Mortar mixing proportions (kg/m³)

Mix	OPC	FA	Sand	Water
OPC	525.0	0.0	1443.0	283.0
FA1	446.25	78.75	1443.0	283.0
FA2	446.25	78.75	1443.0	283.0
FA3	446.25	78.75	1443.0	283.0
FA4	446.25	78.75	1443.0	283.0
FA5	446.25	78.75	1443.0	283.0

3.9 Isothermal Calorimetry and TGA Analysis

Isothermal calorimetry method was performed to evaluate on the heat release of the early-age hydration reaction of paste mixtures having 15 % fly ash. The method was followed as per ASTM C1702 [128]. 60 g of pastes were mixed for 5 min using a mechanical stirrer. 10 g of the pastes were then placed in glass vials and inserted in the isothermal calorimeter's channels. The temperature was set at 25°C and 40°C. The heat release data were then collected for 7 days. All tested samples were discontinued

after testing for 7 days. Immediately, approximately 60 mg of the hardened samples were then placed for testing the TGA. The rate of temperature rise of TGA was set at 10 °C/min to 1000 °C under N₂ condition. The thermogravimetry-differential scanning calorimetry (TG-DSC) profiles for all mixtures were reported. Triplicated samples were performed for each test. The content of Ca(OH)₂ presented calculated using a tangent method [107]. The Ca(OH)₂ phase decomposes in the temperature ranging between 400 °C and 550 °C. The corresponding masses (*M*) were calculated from TGA results. Eq. (3.4) can be used to measure Ca(OH)₂ content (CH):

$$Ca(OH)_2 = \frac{74.1}{18.0} \times \frac{M_{start}^s - M_{end}^s}{M_c} \quad (3.4)$$

where CH represents Ca(OH)₂ content of hydrated cement; M_{start}^s represents the initial mass of sample ; M_{end}^s represents the final mass of sample (assumed at the end of the test); and M_c represents the initial mass of the cement paste. The multiplied factor ($\frac{74.1}{18.0}$) represents the molar mass ratio of Ca(OH)₂ (equaling 74.1) and H₂O (equaling 18.0).



(a)

(b)

Figure 24: (a) TAMAIR isothermal calorimeter, (b) TGA, TA instrument

3.10 Durability performance of fly ash-cement system

3.10.1 Compressive strength of mortar

The purpose of this test is to evaluate the compressive strength of (1:2.75) mortar composed of the cement and sand. Based on ASTM C1437 [129], the flow table test of mortar with different sources of fly ash are tested by using water to cement ratio (0.54). The cube specimens (50 mm) were performed according to ASTM C109. They were evaluated at the curing time of 7, 28 and 90 days. Each compressive strength result was the average value of three specimens.

3.10.2 Chloride concentration test

To study the chloride ion diffusion mechanism, the mortar mixtures were prepared and tested, as per ASTM C1556 [130]. After cured for 28 days, the hardened samples were removed and coated with epoxy on the top surface as well as around the cylindrical body. One side of the top surface was left without epoxy coating for analyzing one-dimensional chloride ion penetration. After the epoxy was hardened, the epoxy-coated mortar samples were submerged in 3 % NaCl solution for 30 and 90 days. Fresh NaCl solution was replenished weekly. Chloride ion penetration resistance test was measured by cutting the exposed mortar samples in half. The AgNO₃ solution with 0.1 M concentration was then applied on the surface of exposed samples to see their appearance change [93]. The gray color indicates the depth of chloride ion that can penetrate because of the reaction between AgNO₃ and chloride ion. The average chloride ion penetration depth value was reported after measuring the samples 10 times. Moreover, after exposed for 90 days, the samples were oven-dried overnight and ground into powder from different depth levels [130]. Six depth levels of samples were analyzed including 0–5, 5–10, 10–15, 15–20, 20–25, and 25–30 mm. Then, approximately 2.5 g of each powdered sample was used to evaluate the acid-soluble chloride ion concentration. The powdered samples were dissolved in 30 ml H₂SO₄ with 100 ml water and then three drops of C₁₄H₁₄N₃NaO₃S indicator were added and then stirred for 1 h. Subsequently, the sample was titrated with AgNO₃ using an automated titrator (Titrator Excellence T5, Mettler-Toledo) to determine the

chloride ion concentration at each depth. For measuring the D_a value, Fick's second law was applied as shown in Eq. (3.5). The results are based on the triplicated tests.

$$C(x,t) = C_s - \left[(C_s - C_i) \times \operatorname{erf} \left(\frac{x}{\sqrt{4D_a t}} \right) \right] \quad (3.5)$$

where $C(x,t)$ represents the mass percentage of chloride ion concentration at a depth x and time t ; C_s represents the predicted mass percentage of chloride ion concentration on mortar surface; C_i represents the percentage of initial chloride ion concentration of the mortar measured before exposure; and erf represents the error function.

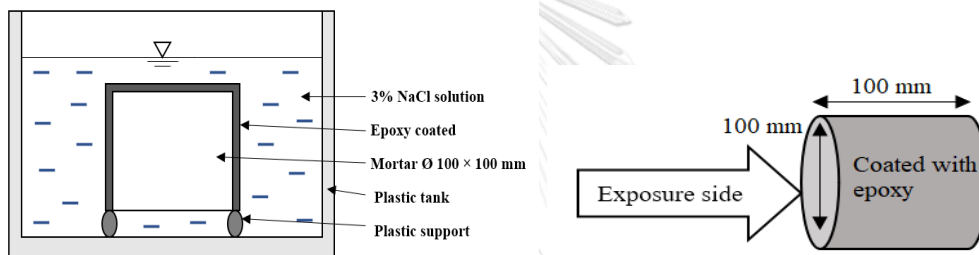


Figure 25: Specimen kept in 3% NaCl solution for Cl^- testing

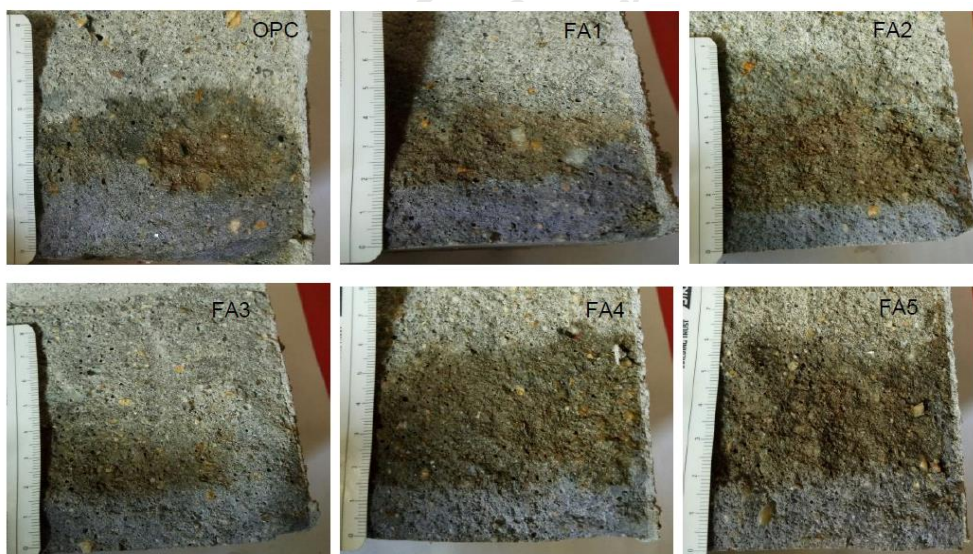


Figure 26: Measurement of the Cl^- penetration depth

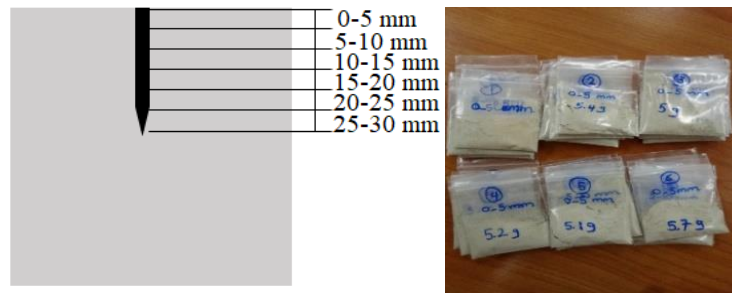


Figure 27: Drilling depth and powder samples for Cl^- concentration



Figure 28: Measuring the total Cl^- content

3.10.3 Porosity test

As aforementioned, because porosity of cementing system is one of the most important microstructural performance relating to its durability, measuring the hardened porosity of blended fly ash cement system was performed. The porosity of blended cement mortar with fly ash can be determined by measuring the total amount of water from the saturated samples. $10 \times 10 \times 10$ cm cube specimens were casted and cured for 180 days. After being oven dried at 105°C until a stable mass loss was measured, the specimens were immersed in water allowing water penetrating fully into their voids. It is noted that all the physically bonded and capillary water in the cementitious pastes had evaporated at this temperature of 105°C . The masses of saturated and dried specimens were measured using a weight scale with an accuracy of 0.01 g. Triplicated specimens were performed for each test. The porosity values were calculated as the following Eq. (3.6) [131].

$$p = \frac{M_w - M_d}{v \times \rho} \quad (3.6)$$

where p is the porosity, M_w is the mass of the saturated specimen in g, M_d is the mass of the dried specimen in g, v is the specimen volume in cm^3 , and ρ is the density of water at 20°C in g/cm^3 .

3.10.4 Accelerated carbonation test

After the mortar specimens were cured under saturated-lime solution for 28 and 90 days, hardened specimens were coated with epoxy leaving one top surface uncoated. This attributes to one-directional exposure of carbonation. The specimens were kept in the laboratory environment for 24 h for epoxy hardening. Then, the epoxy-coated specimens were transferred to the accelerated carbonation chamber and tested for 28 days. The CO_2 concentration in the chamber was set at 4 %. Higher concentration of CO_2 results in higher rate of carbonation reaction. The temperature inside the chamber was set at $40 \pm 2^\circ\text{C}$, and the relative humidity was set at $50 \pm 5\%$. Then, the specimens were removed from the chamber and split using a cutting machine. The carbonation depths were measured using $\text{C}_{20}\text{H}_{14}\text{O}_4$ solution [12, 132]. This $\text{C}_{20}\text{H}_{14}\text{O}_4$ solution is colorless at pH below 9.3 and changes to pink color when pH is higher than 9.3. In general, the pH levels of the pore solution of OPC mortar range from 11 to 13. When the carbonation of OPC takes place, this leads to the reduction of pH due to the formation of CaCO_3 . After carbonated, the color of non-carbonated region of the sample is pink; in contrast, the color of their carbonated region is unchanged. Data reported for each sample represent the average value from 32 measurements using a Vernier caliper. Each side of the specimen was measured 8 times from corner to corner. Three samples were tested for measurement.



Figure 29: Preparing specimens for accelerated carbonation



Figure 30: Specimens placed in carbonation chamber

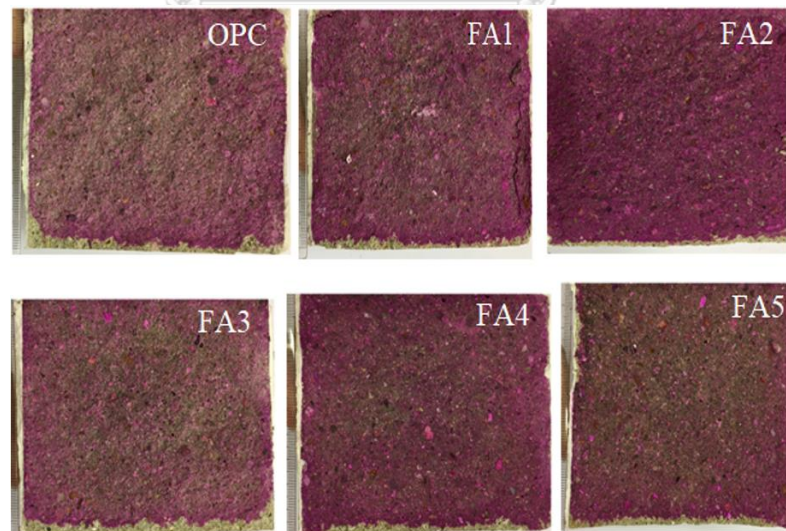


Figure 31: Measuring the carbonation depth

3.10.5 Pozzolanic test on fly ash

Pozzolanic test method [116] was used to determine the heat release and the content of $\text{Ca}(\text{OH})_2$ of the fly ash. This method was chosen due to its relative simplicity and its ability to produce two differing metrics which are the heat release and calcium hydroxide consumption. Reagent grade $\text{Ca}(\text{OH})_2$ and fly ash were mixed at a mass ratio 3:1 with 0.5 M KOH (liquids to solid ratio of 0.9). Mixing was done for five minutes using a mechanical stirrer and the test procedure was equal to that in literature [116]. Immediately after mixing, nearly 10 g of sample was slowly moved into a glass calorimeter ampoule and kept into an isothermal calorimeter (TAMAIR, TA instruments) maintained at temperature $40 \pm 0.05^\circ\text{C}$. The heat flow data from the calorimeter was collected for a period of 10 days after signal stabilization. Heat flow and heat release normalized to fly ash mass were determined.

3.10.6 Calculation of degree of reaction of fly ash

Fly ash degree of reaction in the cementitious pastes was determined by calculating the ratio of the response of the cementitious paste to that of the pozzolanic system as shown in Eq. (3.7).

$$\alpha = \frac{Q_{cem}}{Q_{poz}} \quad (3.7)$$

where α is the degree of reaction, Q_{cem} is the heat release (J/g fly ash) in the cementitious pastes at 7 days, and Q_{poz} is the heat release (J/g fly ash) in the pozzolanic test at 10 days. For fly ash – cement pastes, a filler effect of 5% was assumed while calculating heat release and $\text{Ca}(\text{OH})_2$ produced by cement hydration [114]. The heat release for fly ash in the cementitious pastes were calculated using Eq. (3.8).

$$Q_{FA} = \frac{Q_{cementitious} - Q_{control} \times f \times (1 - R)}{R} \quad (3.8)$$

Where, Q_{FA} is the heat release by fly ash (J/g fly ash), $Q_{cementitious}$ is the heat release in fly ash – cement paste (J/g cementitious), $Q_{control}$ is the heat release in the reference cement paste (J/g cement) and R is the fly ash mass replacement percentage.

Therefore, the pozzolanic test are investigated using isothermal calorimetry and TGA to determine the degree of reaction of fly ash and using this method could result in easier ways to measure degree of reaction of SCMs. The objective of such efforts is to link the pozzolanic test response to long-term concrete properties and durability, potentially through the determination of degree of reaction [133].

3.11 Service life prediction

Due to the corrosion of steel reinforcement, the deterioration process in reinforced concrete structure can be classified into four periods with respect to exposure time. These four periods include initiation period, propagation period, acceleration period, and deterioration period. This study considered the time between construction and the time for the first repair as the service life of structure. The time required for the chloride ion from the external source entering in the concrete and accumulating enough in the vicinity of the surface of embedded steel. After the accumulation of chloride ion within this region is progressing, the pH value of pore solution of concrete in this region is decreasing. The high pH value ranging around 12 to 13 allows a passivated layer to form and the passivated layer acts as a protection of the embedded steel from corrosion. Once the pH value is reduced and the passivated layer is disappeared.

The corrosion is initiated. This period is called as initiation period. The initial period is a function of quality of concrete, clear cover to main steel, chloride threshold concentration, and exposure conditions such as surrounding temperature and pressure. Next, the time required for adequate corrosion occurring and then causing an unacceptable level of damage to the building or structural element can be called as propagation period. The service life of concrete is determined as the sum of the corrosion initiation period and the steady propagation period. Lastly the acceleration period and deterioration period are when the structure rapidly become weaken and its strength performance reduced fast until the point that the structure is unable to withstand the external loads.

The service life of concrete structures can be effectively predicted based on exposure conditions and material characteristics. In this study, Life-365 software [134] was performed for predicting the service life of structure and allowed to predict

in both one dimensional and two-dimensional chloride ion penetration. This model approached based on Fick's second law, similarly to the D_a calculation. Diffusion mechanisms of chloride ion penetration depends on both exposure time and environmental temperature. To calculate the service life, the required input parameters such as mix proportion characteristics, diffusion rate at 28 days (D_{28}), diffusion decay index (m), maximum surface chloride level (C_s), chloride threshold to initiate corrosion of steel (C_t), clear cover to reinforcement, temperature profile for the whole year, and propagation period were inputted in the software.

3.12 Statistical analysis

Prior to performing the statistical analyses using Minitab software (Minitab, LLC), the Shapiro–Wilk test was performed to determine the normality of sample data. Levene's test was also performed to check the equal variances of the data. Two sample t-test analysis was then conducted for assessing the sample data with two data groups. Meanwhile, ANOVA was assessed for data more than two data groups. Null hypothesis (H_0) and alternative hypothesis (H_a) of the data groups were described in the following equations:

$$\text{Null hypothesis (H}_0\text{): } \mu_1 = \mu_2 = \dots = \mu_a \quad (3.9)$$

$$\text{Alternative hypothesis (H}_a\text{): } \mu_i \neq \mu_j \text{ for some } i \neq j \quad (3.10)$$

From these analyses, the 95 % confidence interval was. On one hand, if H_0 were rejected (p -value < 0.05), we could conclude the existence of a statistically significant different (at the 5 % level) among the mean values of group populations. Whereas, if H_0 were not rejected (p -value ≥ 0.05), there was no statistically significant effect existing at the 5 % level among the mean values of group populations.

After analyzing the ANOVA, resulting parameters which were statistically significant different on the D_a were then further analyzed their sensitivity analyses. The regression analyses were used the data that are fit a linear regression to the model response and using beta coefficients (β) as direct measures of sensitivity of each parameter. The coefficient of determination that is used in this linear regression is set to be greater than 60 %; otherwise, the analysis of such parameters is neglected. The β

value can be normally assessed of effect size, quantifying the magnitude of the effect of one variable on another. If the β value is large, this can represent larger effect can be influence on the D_a value of the blended fly ash -cement systems.



CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Chemical and physical properties of materials

As shown in Table 17, the chemical composition of FA2 contains 0.797 % CaO, which is less than the other types of fly ash. However, the total content of SiO₂, Al₂O₃, and Fe₂O₃ is 93.44 %, which is higher than the rest. The total content of SiO₂, Al₂O₃, and Fe₂O₃ of FA3 was 55.3 %, which is lower than the minimum value of 70 % as specified for pozzolanic material (Class F fly ash) as per ASTM C618. However, the CaO content of FA3 exhibited the highest value. Therefore, the least value of total content of SiO₂, Al₂O₃ and Fe₂O₃ was observed. The general physical characteristics of materials (OPC and fly ash) include the Blaine surface area or degree of fineness²² [123] and specific gravity [124]. The fineness of OPC was 3764 cm²/g, which is lower than that of FA2, FA4, and FA5. This is because the density of OPC is higher than those of FA2, FA4, and FA5. The fineness of FA5 increased further when compared with that of the other types of fly ash. Their particle size distribution curves are shown in Fig. 32. Their mean particle sizes (ranked from smaller to larger) are FA5 5.68 μm, FA4 14.7 μm, OPC 17.2 μm, FA2 17.9 μm, FA3 27.5 μm, and FA1 31.9 μm.

Table 17: Chemical composition and physical properties of OPC and FA

[%]	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	LOI	Specific gravity (g/cm ³)
OPC	17.8	4.4	3.0	61.1	0.9	4.14	0.34	0.26	-	1.9	3.1
FA1	50.3	19.6	3.3	9.9	2.2	0.68	-	2.25	73.2	1.4	2.2
FA2	73.8	17.7	1.9	0.8	0.3	0.20	0.39	0.71	93.4	1.8	2.1
FA3	27.4	15.8	12.1	21.6	2.3	6.92	1.70	2.02	55.3	0.2	2.4
FA4	51.7	23.4	14.0	4.2	1.5	1.84	0.53	1.15	89.1	0.3	2.5
FA5	35.5	14.8	17.8	16.7	6.8	1.82	1.33	1.13	68.1	0.3	2.9

The particle size distributions are shown in Figure 32. Their mean particle sizes are FA5 5.68 μm , FA4 14.7 μm , OPC 17.2 μm , FA2 17.9 μm , FA3 27.5 μm , and FA1 31.9 μm . The particle microstructures under SEM are depicted in Figure 33. As in Figure 33, the cementitious particle has an irregular shape with many smaller particles attached to it, and the microstructure of all types of fly ash are spherical particles.

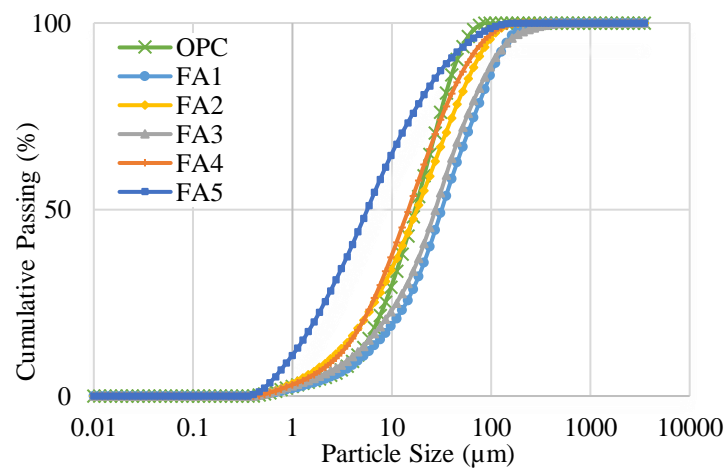


Figure 32: Particle size distribution of materials

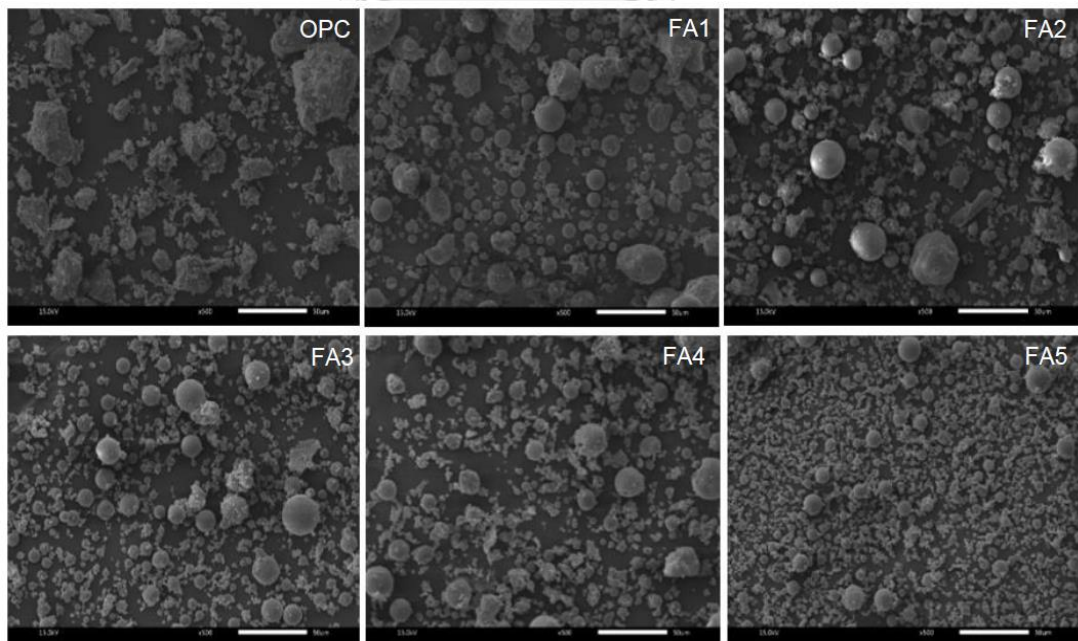
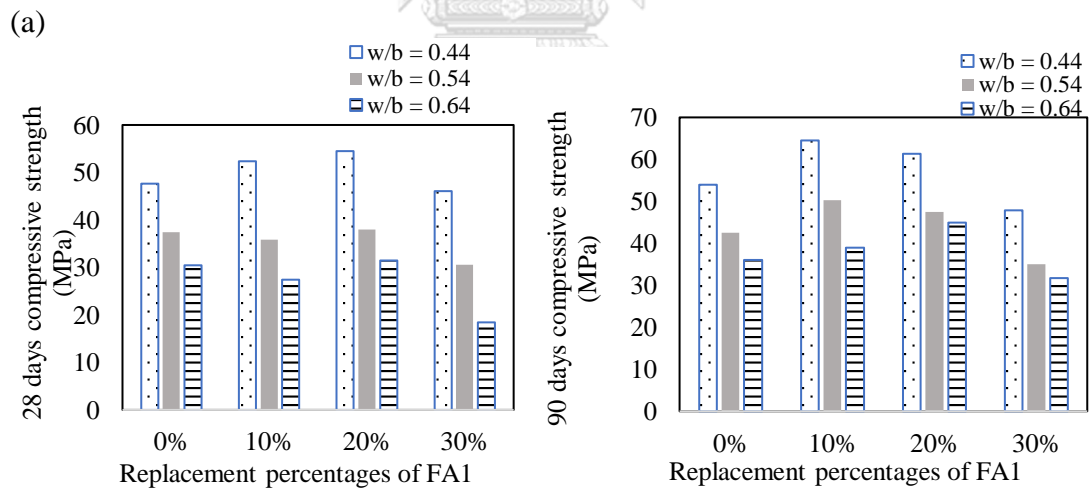


Figure 33: Particle microstructure (SEM) of materials

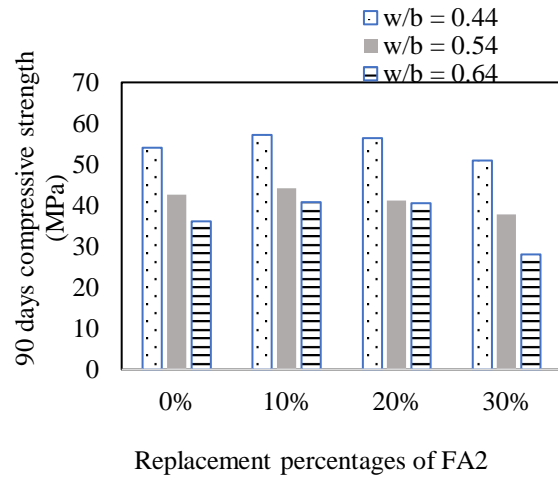
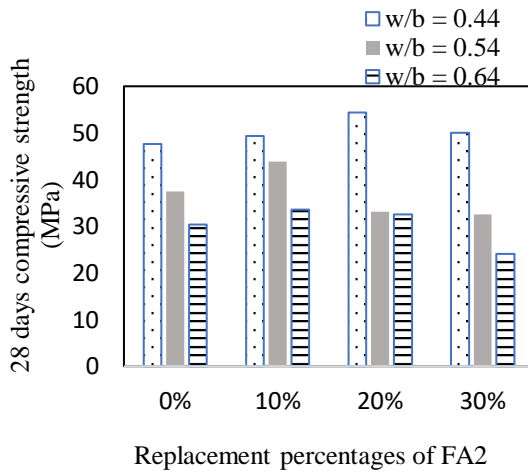
4.2 Compressive strength of fly ash-cement paste

This section reports the experimental results on the compressive strengths of the cementitious paste containing 0, 10, 20, and 30 % of fly ash with w/b of 0.44, 0.54, and 0.64, respectively. The strength values of the cement paste replaced with fly ash after 28 days and 90 days water curing is shown in Figure 34. The results also show the influence of replacing portions of cement with fly ash in terms of the compressive strength. Increasing the fly ash content over 20 % decreases the compressive strength. Moreover, the higher the w/b in the paste, the weaker the cement. Therefore, H₂O content can be decreased by replacing it with fly ash in the cement paste. The increase in the amount of fly ash reduced the early strengths [42].

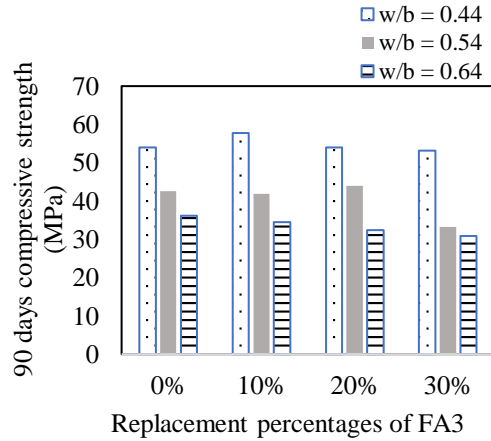
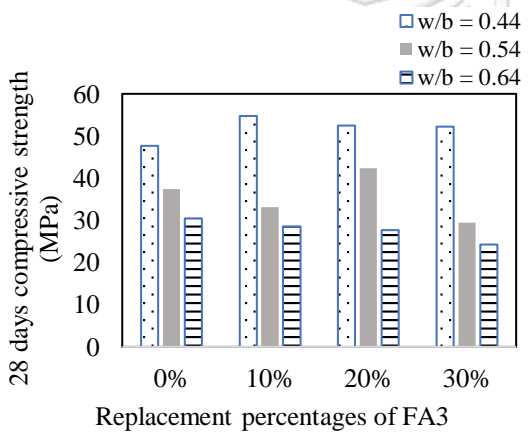
The optimal replacing portions of cement with fly ash is needed to assess and this portion is analyzed in Section 4.2.1. As demonstrated in literature, cementitious pastes with fly ash exhibited remarkably different results, even though they come from the same powerplant [95].



(b)

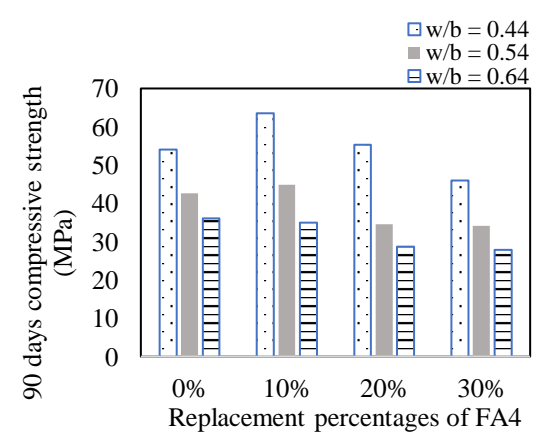
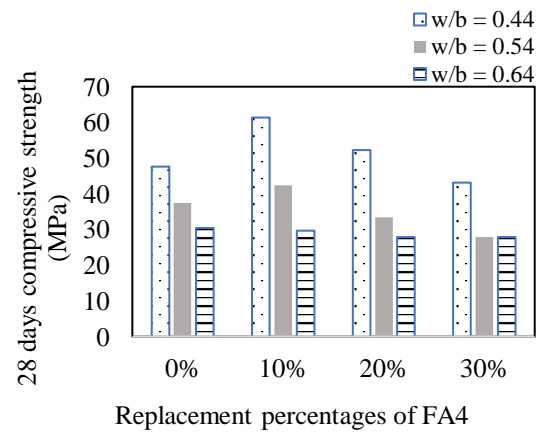


(c)



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CHULALONGKORN UNIVERSITY

(d)



(e)

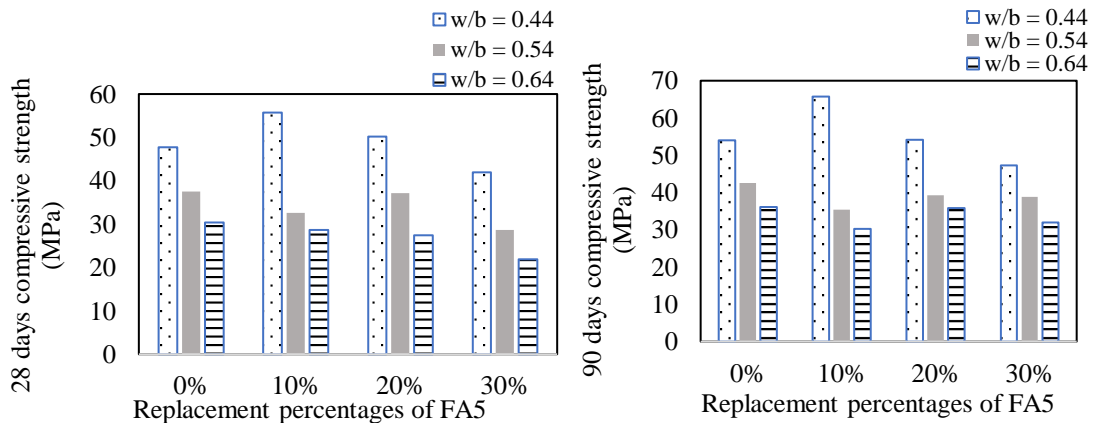


Figure 34: 28 days and 90 days compressive strength of fly ash-cement composite (a) FA1, (b) FA2, (c) FA3, (d) FA4 and (e) FA5

4.2.1 Mathematical modelling

In analysis of curvilinear regression, the result of compressive strength of mortars are needed to check which equation is convenient to use among linear, quadratic and cubic models by using coefficient of determination R^2 . The coefficient of determination R^2 measure of how well the goodness of best fit line performs. The values of R^2 can be got by using SPSS software.

The quadratic model (second degree polynomial equation) and cubic model (third degree polynomial equation) is convenient to use for this case because the values of R^2 are near to 1 which is strong and best fit data. However, the higher degree of polynomial equation can cause overflow, therefore the second degree of polynomial equation (quadratic model) are used in this research. Moreover, w/b 0.44 is reliable to use because the compressive strength results of fly ash-cement pastes with w/b 0.44 are greater than that of fly ash-cement pastes with w/b 0.54 and w/b 0.64.

By using curvilinear regression, the following second-degree polynomial equations (quadratic model) (4.1) -(4.10) of FA1, FA2, FA3, FA4 and FA5 at 28 days and 90 days can be obtained using variable proportion of fly ash. Coefficient of determination R^2 were 0.927, 0.997, 0.897, 0.999, 0.922 at 28 days, and 0.929, 0.853, 0.912, 0.865, 0.915 at 91 days, respectively.

$$y_{(28, FA1)} = 47.26 + 95.85x - 328.50x^2 \quad (4.1)$$

$$y_{(90, FA1)} = 54.18 + 157.79x - 597.49x^2 \quad (4.2)$$

$$y_{(28, FA2)} = 45.93 + 104.69x - 333.28x^2 \quad (4.3)$$

$$y_{(90, FA2)} = 53.99 + 53.93x - 212.49x^2 \quad (4.4)$$

$$y_{(28, FA3)} = 47.22 + 110.73x - 354.50x^2 \quad (4.5)$$

$$y_{(90, FA3)} = 53.53 + 72.24x - 284.86x^2 \quad (4.6)$$

$$y_{(28, FA4)} = 50.31 + 84.02x - 323.21x^2 \quad (4.7)$$

$$y_{(90, FA4)} = 54.85 + 109.70x - 474.25x^2 \quad (4.8)$$

$$y_{(28, FA5)} = 48.67 + 119.10x - 482.25x^2 \quad (4.9)$$

$$y_{(90, FA5)} = 56.18 + 73.59x - 334.50x^2 \quad (4.10)$$

The second-degree polynomial mathematical analysis method using the fly ash content is proposed to calculate the strength of the blended cement paste. Moreover, it can be seen that the proper percentages of fly ash as cement replacement are 14.59%, 15.71%, 15.62%, 13.00%, 12.35% for 28 days strength and 13.20%, 12.69, 12.68, 11.57, 11.00% for 91 days strength of FA1, FA2, FA3, FA4 and FA5, respectively which are approximately 15%. According to the above equation, the compressive strength of fly ash-cement paste can be predicted using a variable proportion of fly ash at initial and long-term strength.

In the above test, FA4 and FA5 showed the characteristics of general fly ash, but FA1, FA2 and FA3 showed different characteristics from general fly ash. The reason for this is that there is a difference in the particle sizes and the difference in the content of Silica (SiO_2) and Alumina (Al_2O_3) in the case of Class F, and the Calcium Oxide (CaO) in the case of Class C.

It is noted that the replacement level is one of the important recommendations in optimizing the concrete mix design with fly ash. Replacement levels of fly ash are categorized as a low replacement ($\leq 15\%$), moderate replacement (15%-30%), high replacement (30%-50%) and very high replacement ($\geq 50\%$). The obtained test results

on fly ash FA1, FA2 and FA3 showed that it had moderate replacement levels with a compressive strength 54.25 MPa, 54.15 MPa and 55.87 MPa. For the low replacement levels of FA4 and FA5 including 13% and 12.35% fly ash, the compressive strength was found 55.77 MPa and 56.02 MPa. Therefore, it can be determined that the fly ash FA1, FA2 and FA3 can be used to reduce cement consuming to improve concrete strength while FA4 and FA5 can be considered with moderate replacement levels and reducing water-binder ratio to achieve the high strength concrete at 28 days.

4.3 Heat flow and heat release of fly ash-cement pastes

The heat flow of cement–fly ash pastes at 25 °C and 40°C up to 7 days are plotted in Figures 35 (a) and (b), respectively. Whilst Figures 36 (a) and (b) show the cumulative heat release of cement pastes containing fly ash at 25 °C and 40°C tested for 7 days, respectively. The results show that the heat flow and the amount of heat release which measured by isothermal conduction calorimetry are influenced by the replacement of fly ash in cement. It should be noted here that the heat flow tests of all systems were also performed at the temperature of 25°C but the curve patterns show no significant difference. Therefore, this work determined the test at 40°C to be suitably predict the performance of blended FA-cement systems in tropical region.

OPC shows a higher peak height (the maximum magnitude of the heat flow) compared to cement pastes containing fly ash from different sources. Replacing 15 % FA results in the reduction of the maximum magnitude of the heat flow by approximately 8 % to 10 %. One of the reasons for this occurrence may be due to the dilution effect of cement with low C₃S available when replacing cement with FA [135]. Cement pastes which are replaced with FA evaluated from the highest to the lowest heat release are: OPC > FA1 > FA3 > FA2 > FA5 > FA4. The heat release values of blended FA-cement paste varies between 198 J/g and 214 J/g.

In general, the heat release increases when the temperature increases. One of the reasons is due to the increase in the rates of the hydration and pozzolanic reactions at higher temperature. As expected, the blended FA-cement systems release less heat than the OPC system. Replacing a portion of OPC with FA leads to the reduction of increase of heat release. This is possibly due to the secondary hydration reaction of

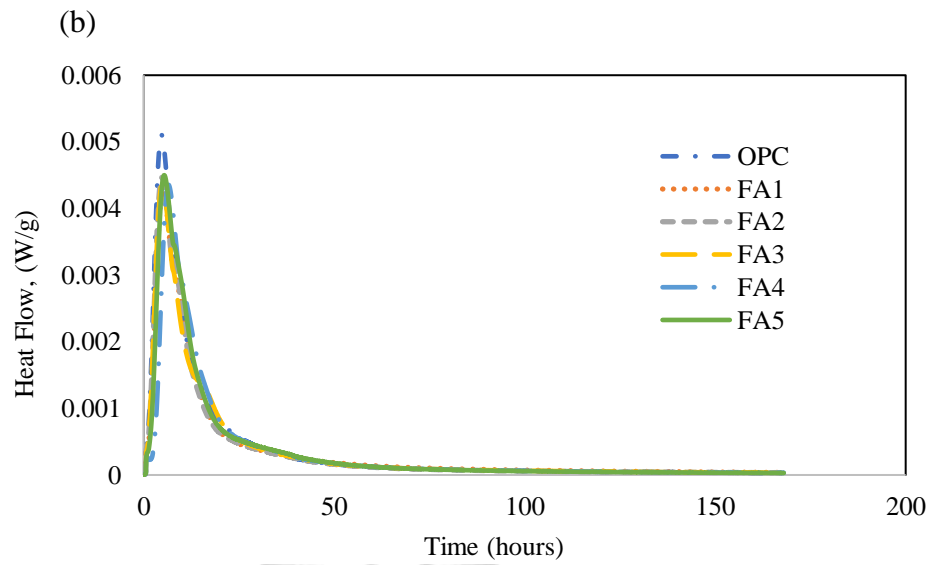
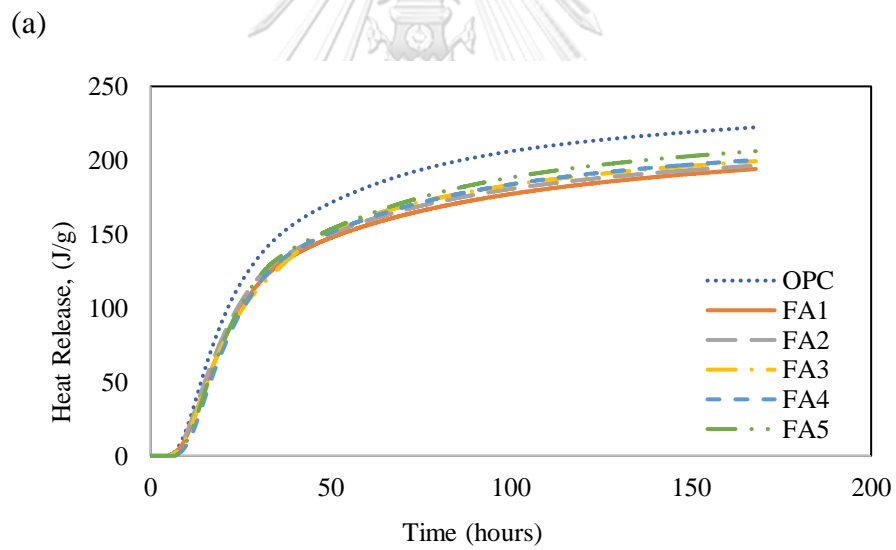


Figure 35: Heat flow of fly ash-cement pastes at (a) 25°C and (b) 40°C



(b)

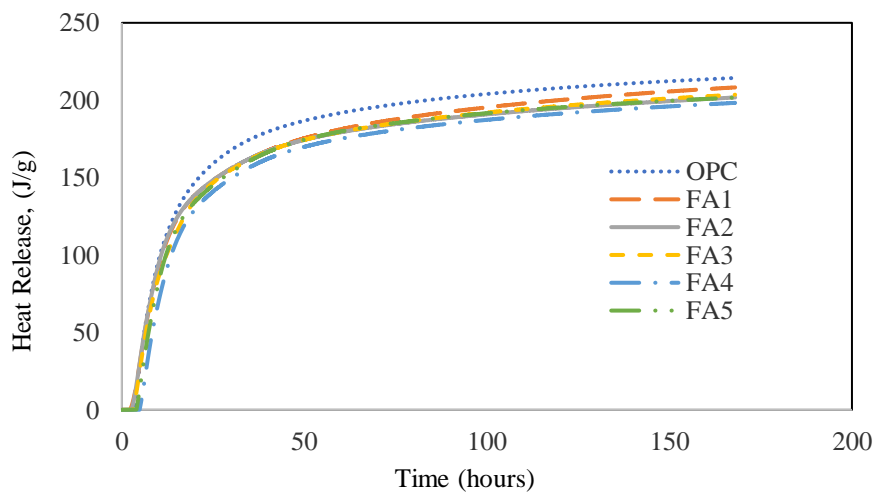


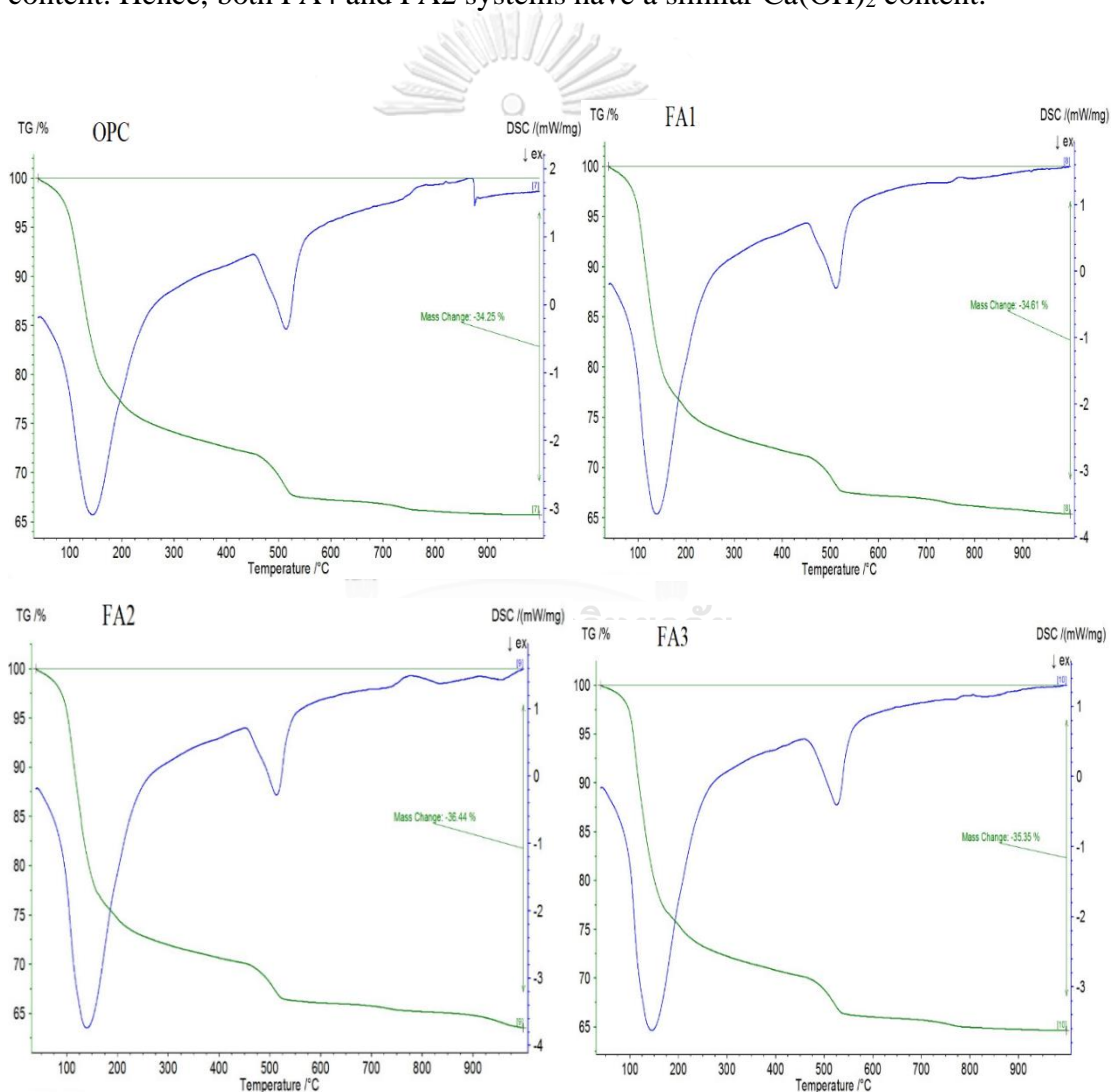
Figure 36: Heat Release after 7 days for fly ash-cement pastes at (a) 25°C and (b) 40°C

4.4 TGA analysis and calcium hydroxide content in fly ash-cement pastes

The TGA is a common measurement used to evaluate the $\text{Ca}(\text{OH})_2$ content in fly ash-cement composite. The content of $\text{Ca}(\text{OH})_2$ is one of the key factors that can influence on the hydration mechanisms. It can be described by the pozzolanic reactions and $\text{Ca}(\text{OH})_2$ obtained by the hydration of cement [136]. Figs. 37 and 38 show the TG-DSC profiles of cement-fly ash composites measured after 7 days. The TG-DSC profile represents the hydration behavior of hydrating cementitious pastes, related to a steady positive temperature gradient. The gradient of the profile represents the mass loss for each cement paste. The TG/DSC profile represents endothermic decomposition in four different stages: (1) dehydration of pore water, (2) $\text{Ca}(\text{OH})_2$ decomposition, (3) CaCO_3 decomposition, and (4) C-S-H breakdown. The peak in the TG/DSC profile represents the mass attributing to the dehydroxylation of $\text{Ca}(\text{OH})_2$ phase. It is reportedly contributed to the region at high temperature levels ranging between 400 °C and 450 °C [111].

Fig. 39 shows the calculated $\text{Ca}(\text{OH})_2$ content cement pastes containing fly ash from different sources. The $\text{Ca}(\text{OH})_2$ phase is formed during hydration reaction of dicalcium silicate (C_2S) phase and tricalcium silicate (C_3S) phase. The $\text{Ca}(\text{OH})_2$ content in cement paste containing fly ash is significantly lower than the OPC, which

is due to the slow pozzolanic reaction of fly ash. It is surprising to note that the Ca(OH)_2 content of fly ash-cement pastes maintained at 40°C is remarkably lower than that of fly ash-cement pastes maintained at 25°C . This is presumably due to the increase of Ca/Si ratio in the C-S-H gel as the temperature increases [111]. The lowest Ca(OH)_2 content was observed in the FA1-cement system. The FA5 system has the highest degree of fineness, but the FA3 system has the highest CaO content and the lowest specific surface area. Therefore, their Ca(OH)_2 contents are not different. The FA4 particle is coarser than the FA2 particle, but the FA4 system contains higher CaO content. Hence, both FA4 and FA2 systems have a similar Ca(OH)_2 content.



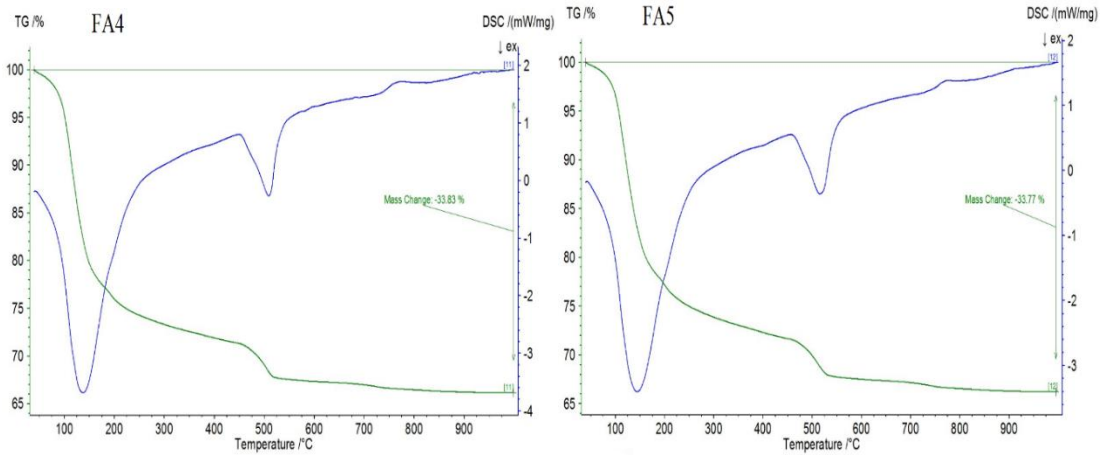
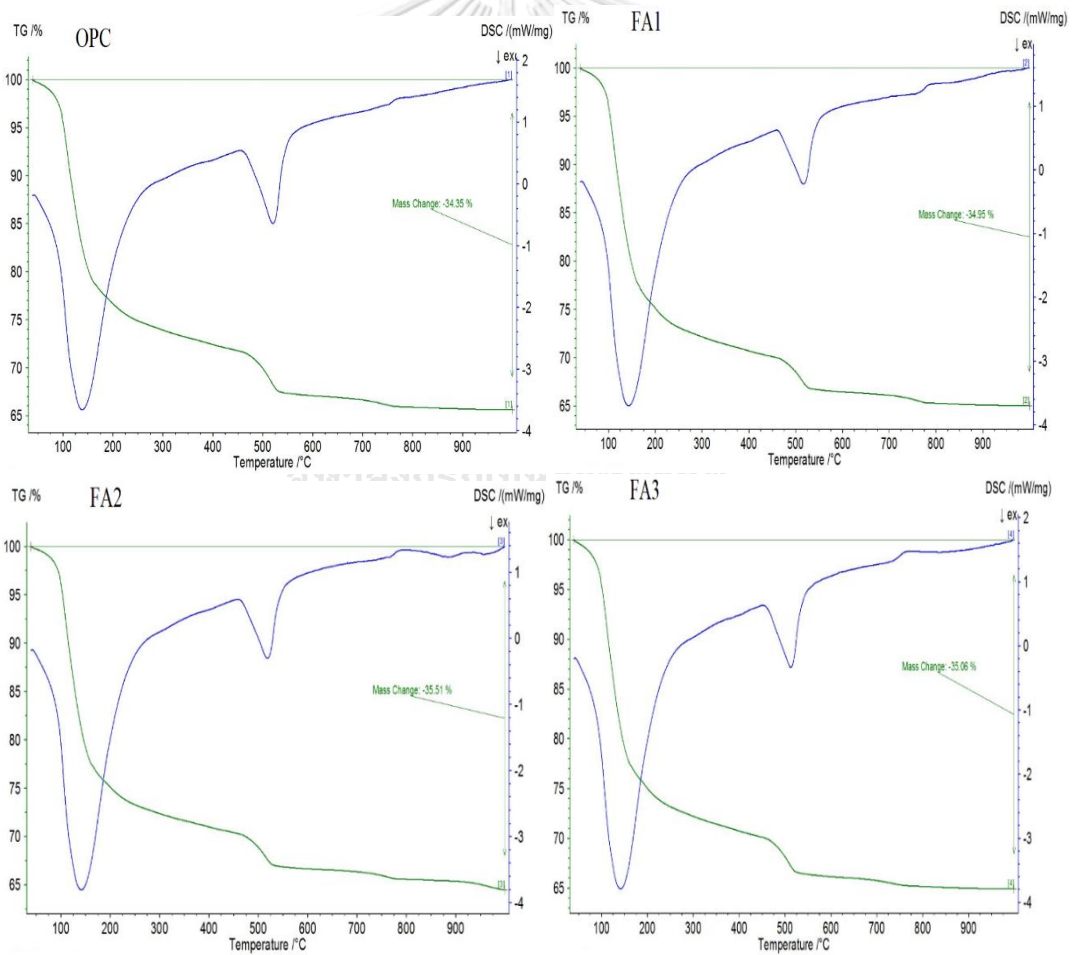


Figure 37: Thermogravimetric analysis (TGA) of cement pastes with fly ash at 25°C



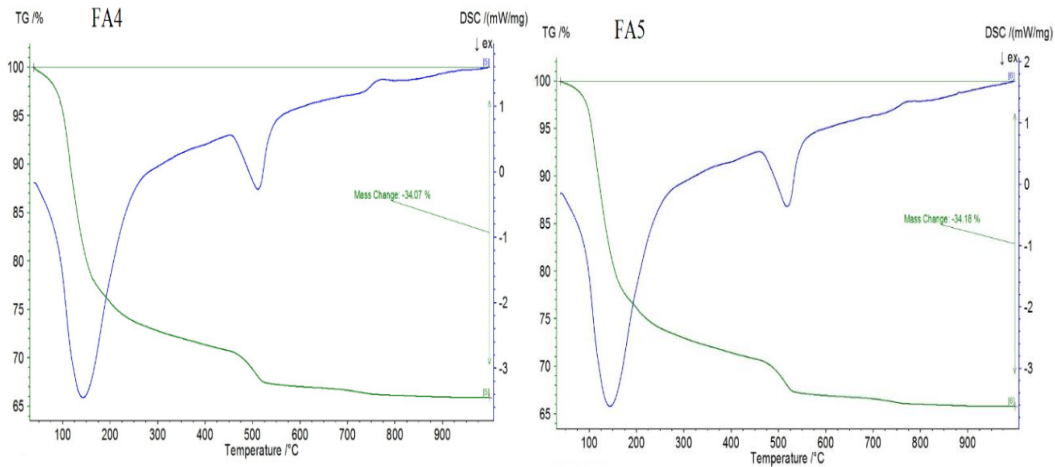


Figure 38: Thermogravimetric analysis (TGA) of cement pastes with fly ash at 40°C

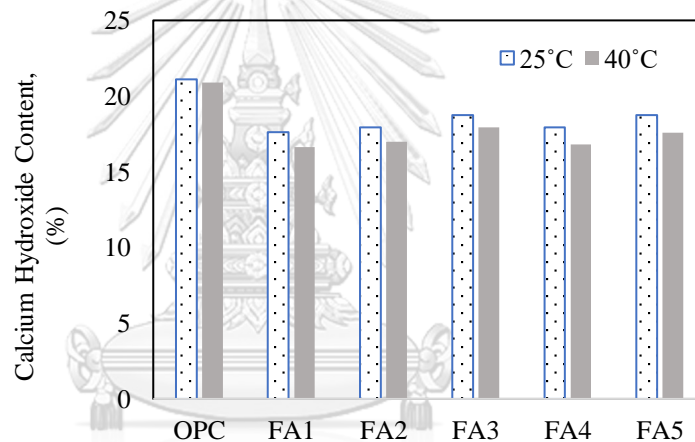


Figure 39: Calcium hydroxide content for cement pastes with fly ash at 25°C and 40°C

4.5 Flow and compressive strength of mortar

The influence of the fresh mortars containing 15 % fly ash on flow values is shown in Fig. 40. The flow values of all mortars range between 76 and 113 %. The highest flow value of the FA5 was seen. This is likely due to the higher amount of finer fly ash particles per unit mass, consequently leading to the increase of lubricant effect compared to coarser particles. It is reported that the use of good quality silica-rich fly ash (spherical morphology and high degree of fineness) results in reduced water demand of cement mixture [6]

The 7-, 28-, and 90-day compressive strengths of the mortars containing 15 % fly ash from different sources are shown in Fig. 41. The 7, 28, and 90-day compressive strengths of OPC are 37.0, 42.6 and 43.0 MPa, respectively. The compressive strengths of the OPC increase rapidly at the first 28 days but not much increase at 90 days. The compressive strength development of the OPC mortar during 7 and 28 days is higher than the mortars containing fly ash. Whereas, the 90-day compressive strengths of the mortars containing fly ash are similar to or higher than the OPC. Consequently, the fly ash from different sources only little reacts for the first 7 days because the pozzolanic reaction from fly ash begins to react at longer time.

The highest 90-day compressive strength value was observed for the FA5, followed by the FA4, FA3, FA2, and FA1. This is because the FA5 has the highest degree of fineness as shown in Table 4.1. Significant increases of the compressive strengths of mortars containing fly ash were apparently observed when the mortars were cured for 90 days. This is because of the slower pozzolanic reaction in the cement-fly ash composite. Therefore, the rate of pozzolanic reaction of fly ash depends on the type and amount of the amorphous silicate phase and its fineness. The CaO content in fly ash is likely one of the best indicators of how it will perform with cementitious material for the early-age performance of concrete (i.e., 28-days or less) [6, 137], although other minor constituents such as alkalis (Na_2O and K_2O), residual carbon (LOI), and SO_3 can also influence the properties of fly ash. The FA5 has the highest degree of fineness and highest CaO content (16.7 %), and this results in the highest compressive strength at 90 days. It is believed that fly ash with higher degree of fineness allows its particle to easily dissolve into silicate ions in the alkali solution and fly ash with a lower CaO content can increase the likelihood that the silicate ion dissolves into the solution based on chemical conversion. The FA1 is coarser than the FA2 but has higher CaO content. Therefore, both have similar compressive strengths at 90 days. According to Schlorholtz et al. [95], although fly ash for different batches were obtained from the same power plant, the performance of final product of fly ash-cement composite can be remarkably different.

Because fly ash is a pozzolan, its reaction to cement delivers enhanced concrete quality through the pozzolanic reactions. Pozzolanic materials react with

Ca(OH)_2 phase and H_2O to form compounds with cementitious properties. Two hydrated phases produced from cement hydration are C–S–H and Ca(OH)_2 , of which C–S–H phase is the main contributor to the later-age concrete strength. Mineral admixtures such as fly ash comprising amorphous (glassy) silica that can react with Ca(OH)_2 compound forms additional C–S–H phase. The additional C–S–H phase consequently resulting in improved mechanical properties. The increasing in later-age strength is the typical performance characteristic of pozzolans owing to the pozzolanic reaction [13]. Fly ash (generally having the secondary hydration reaction, when tested with calorimeter) yields gel-form products. These gel-form products fill the micro-pores in the interfacial transition zone between binder and aggregate, thus increasing the density.

Therefore, based on the chemical composition and fineness of fly ash, the results of compressive strength can be varied from different regions or countries. When performing ANOVA method, p -value = 0 was observed, which represents the significant influence of its fineness on the compressive strength of the mortar. The improvement of compressive strength with longer curing times and fineness can be explained from the influence of the factors on the strength of the cement mortar with fly ash.

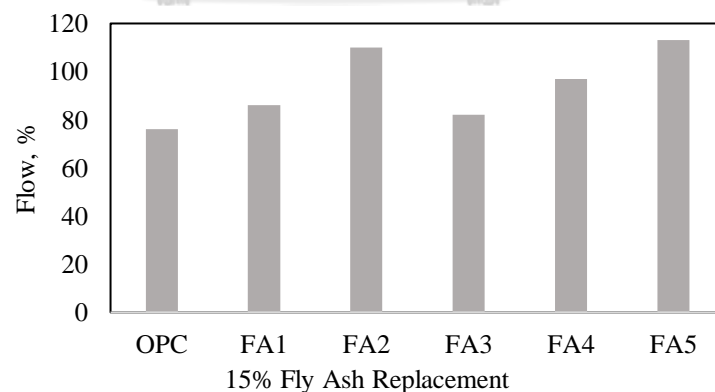


Figure 40: Flow of the mortar including fly ash from different sources

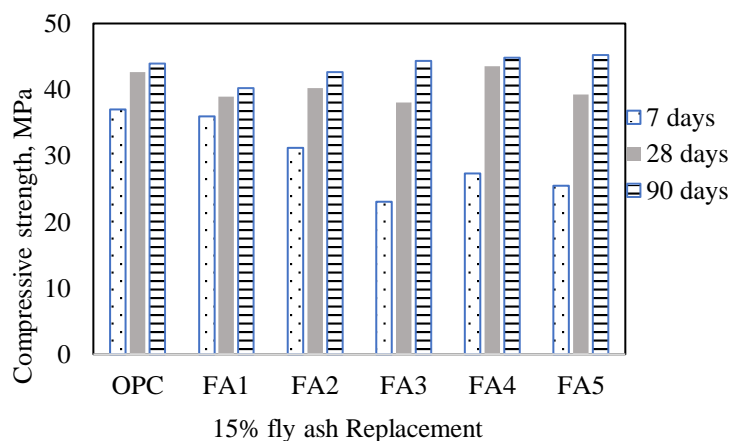


Figure 41: Compressive strength of mortar containing fly ash from different sources

4.6 Chloride concentration

The effects of cement mortars containing fly ash from different sources on the chloride ion penetration depth exposed under NaCl solution for 30 and 90 days are shown in Fig. 42. Results indicate that the chloride ion penetration depths of the mortars exposed for 90 days are significantly higher than the mortars exposed for 30 days. The OPC mortars exposed for 90 days have almost 5 times higher in chloride ion penetration depths than the mortars exposed for 30 days. Whereas, the mortars containing 15 % FA exposed for 90 days are roughly 4 times higher in chloride ion penetration depths than the mortars exposed for 30 days. The use of pozzolanic materials effectively promote the resistance to chloride ion penetration. A significantly lower chloride ion penetration depth was observed in the FA2. The FA2 has a stronger initial pozzolanic reaction than the other fly ash that allows less chloride ion penetrating. Among the types of fly ash, the FA2 and FA5 are the most effective, followed by the FA4, FA3, FA1, and OPC. This is due to the different degrees of fineness of their particle. As shown in Table 4.1, FA2 and FA5 have higher degrees of fineness, from which it can be inferred that FA2 and FA5 have smaller particle compared to the other types of fly ash. Thus, the smaller particle can act as an inert filler inside the mortar matrix and results in increased its density and reduced number of interconnecting voids [11]. Consequently, the chloride ion is blocked.

Fig. 43 shows the effect of total chloride ion concentration on the different sources of fly ash in mortar exposed to 3 % NaCl solution for 90 days. Results

indicate the OPC mortar has a higher chloride ion concentration than the mortars containing fly ash from different sources at the same depth. Therefore, the presence of fly ash in the fresh state of cement mixture and the final hydrating state can improve the microstructure of capillary pore in concrete through its physical manner, chemical revolution, and pozzolanic reaction [137]. As observed from the analysis, the chloride ion concentration at the top surface section (0–5 mm) cannot be measured for all samples owing to the evaporation of water in chloride salt solution from the exposed surface and the higher porosity and pore diameter [138]. Therefore, the chloride ion concentration at the 0–5 mm section is not used to calculate the D_a value.

Chloride ion continuously transports into the matrix by the combined effects of capillary sorption and diffusion mechanism [34, 139]. The maximum values of the chloride ion concentration are all the samples at the 5–10 mm section. At the deeper sections, the chloride contents decrease. It is shown that there is no chloride ion penetrating (chloride content = 0) in the 20–25 mm section for the FA3, FA4, and FA5, and in the 25–30 mm section for the OPC and FA1. Meaningly, chloride ion cannot penetrate through these regions when exposed to NaCl solution for 90 days. This is because of the varying rates of pozzolanic reaction between the different sources of fly ash. At the 5–10 mm and 15–20 mm sections, the FA3 exhibited the least chloride content. This is because it contains the highest CaO content (= 21.6 %).

The D_a values of mortars containing fly ash after 90 days of exposure in 3 % NaCl solution are shown in Fig. 44. Results indicate that the D_a values are in the range of 1.37×10^{-11} and 7.22×10^{-12} m²/s. The D_a value of the OPC mortar is significantly higher than mortars containing fly ash. This may be due to the higher porosity and more capillary pores in the OPC specimens. These parameters allow more chloride ion transferring into the matrix. The lowest D_a value of 4.44×10^{-12} m²/s was observed in the FA3. It can be assumed that chloride ion diffusion mechanism is influenced by both the binding capacity and pore structure.

The reaction between fly ash and alkaline solution in the cementitious system may differ even for fly ash of the same class and similar material properties [98]. Fly ash from different sources have different chemical compositions, leading to different effects on the resistance of chloride ion penetration.

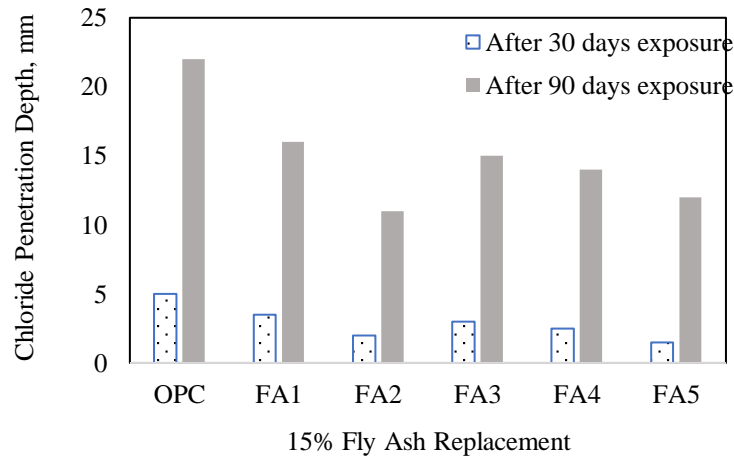


Figure 42: Comparison of chloride penetration depths on the different sources of fly ash after 30 days and 90 days

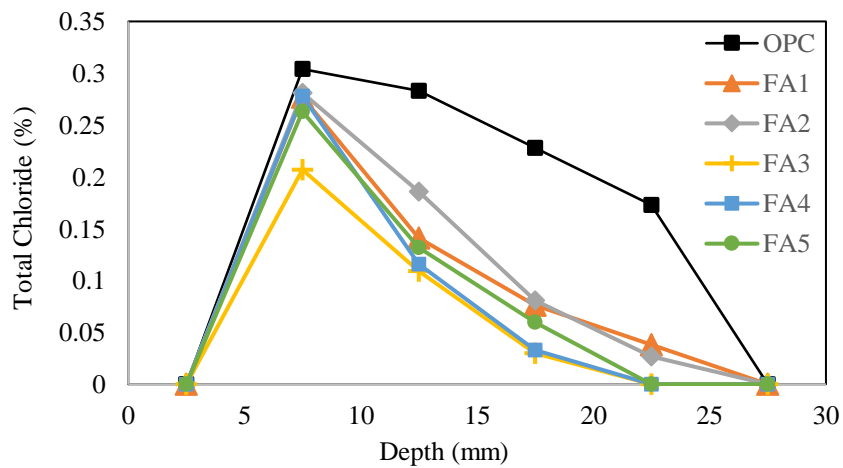


Figure 43: Comparison of the total chloride content on the different sources of fly ash after 90 days exposure

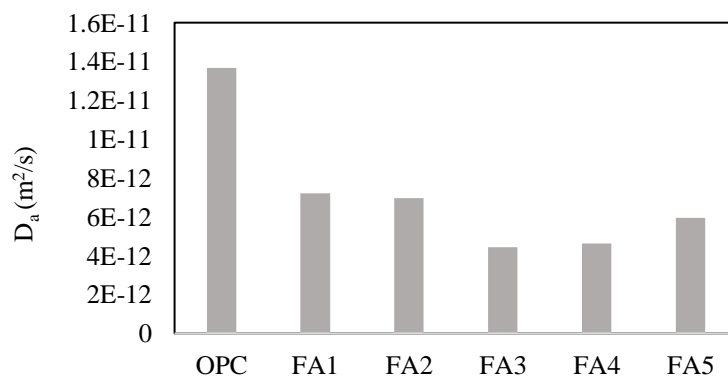


Figure 44: D_a values of mortar with fly ash

4.7 Porosity results

The hardened porosity of incorporation of fly ash in blended cement systems after 180 days are shown in Figure 45. Results indicate that when the blended fly ash-cement systems with w/b value of 0.54, their porosity values are between 0.25 and 0.37. The test results also indicate that the FA1 and FA2 have the same regarding porosity results. It seems that the FA2 has a higher flow value and a lower mean particle size but the FA1 has a lower flow value and a higher mean particle size. The FA5 has the 38 % and 16 % higher flow value when compared with the flow value in the FA3 and FA4, respectively. But the mean particle size of the FA5 has a lower value. Moreover, the FA3 has a greater mean particle size and a lower flow value; however, the reverse is true in the FA4. Therefore, the FA3, FA4 and FA5 which have a similar porosity. Moreover, the OPC system has greater values of 180-day porosity. Due to the formation of additional C-S-H in the blended FA-cement systems, their porosity decreases by 20-29 %.

It can also be seen from Figure 45; the incorporation of fly ash significantly decreases the hardened porosity of the blended fly ash-cement systems when compared to the OPC system even though the flow values of the blended fly ash-cement systems are higher than that of the OPC. The results are in accordance with several studies [135, 140, 141]. Therefore, the particle size of SCMs plays a vital role of the cement hydration process of blended cement system. Moreover, the water demand can be reduced resulting in better durability performance of final products. Its service life can be apparently prolonged. This will be discussed in Section 4.10.

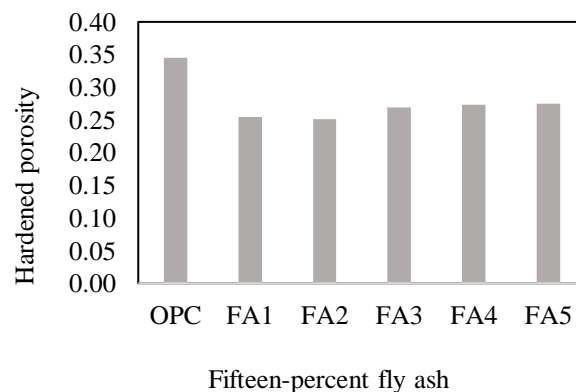


Figure 45: Hardened porosity test result with 15% fly ash

4.8 Carbonation depth

The influences of mortars containing different fly ash cured under water for 28 and 90 days on carbonation depth are shown in Fig. 10. Results indicate that all the mortars cured in water for 28 days have higher carbonation depths than the mortars cured for 90 days. The FA3 cured for 28 and 90 days have the highest carbonation depths, despite of a smaller permeability. This is due to the consumption of Ca(OH)_2 , lower pH, and changes in the microstructures³⁴. At 28 days, the FA1, FA2, and FA4 mortar specimens exhibited smaller carbonation depths than the FA3, FA5, and OPC. The reason may be the lower consumption of Ca(OH)_2 in the FA1, FA2, and FA4. The carbonation depths of mortars are differed even within the same class of fly ash. As discussed, the reaction of fly ash with Ca(OH)_2 phase leads to faster carbonation. The pH levels of pore solution of concrete normally range from 11 to 13 because it includes basic compounds like NaOH , KOH , and Ca(OH)_2 . When the moisture in the mortar reacts with CO_2 and forming H_2CO_3 , further reaction between H_2CO_3 and Ca(OH)_2 progresses yielding CaCO_3 . This effect leads to the removal of calcium consumed in the formation of C–S–H gel, which in turn decreases the mortar's pH (nearly 8–9). This leads to increase the permeability³⁴. It should be noted here that many related factors also influence on the carbonation of fly ash–cement composite such as the pore system of hardened specimens, type of fly ash attributed to pozzolanic reaction, surrounding temperature, and relative humidity condition (for dissolution of Ca(OH)_2).

There are two effects on the carbonation resistance when fly ash presents in the cementitious materials. On one hand, fly ash enhances the formation of C–S–H gel. A large amount of C–S–H gel results in decreased porosity and increased density. This results in improved carbonation resistance. On the other hand, the pozzolanic reaction of fly ash consumes more Ca(OH)_2 produced from cement hydration. This has the negative impact on the carbonation resistance of concrete^{35, 36}. Because the C–S–H gel forms at the longer time, a sufficient curing period for the pozzolanic reaction progressing is needed.

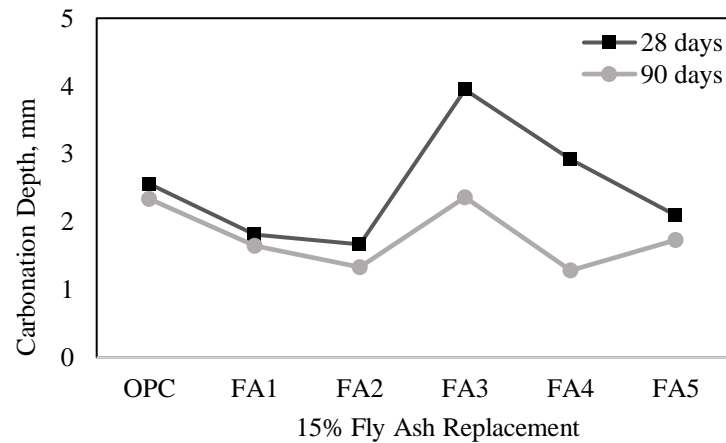


Figure 46: Comparison of carbonation depths on the different sources of fly ash after curing age 28 days and 90 days

4.9 Heat release of fly ash

Figure 47 shows the cumulative heat release of fly ash from different sources at 40°C. The heat release is measured using isothermal calorimetry for fly ashes are mixed with $\text{Ca}(\text{OH})_2$ at temperature 40°C. The order of the heat release from highest to lowest at 10 days is $\text{FA5} > \text{FA1} > \text{FA3} > \text{FA4} > \text{FA2}$. FA1 and FA3 have a similar fineness air permeability, and therefore, they show similar behavior with the heat release falling in a narrow range of 21.38 J/g to 21.6 J/g at 10 days. FA2 and FA4 have the lower heat release than the other types of fly ash, probably due to the low CaO content in these fly ashes. The highest heat release value was observed in FA5. This is due to the highest values of fineness in fly ash as illustrated in SEM image. Moreover, The main contributing factors in fly ash include the high specific surface area and the high solubility of the aluminosilicate to increase heat release [142].

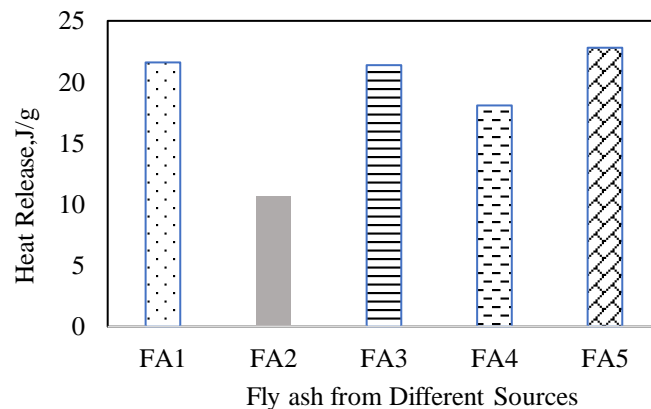


Figure 47: Heat release after 10 days for all tested fly ashes at 40°C

4.10 Degree of reaction of fly ash

Figure 48 exhibits the pozzolanic reaction degrees of fly ash at temperature of 40°C. The details of the method can be found in [106]. Results indicate that the degree of reaction of fly ash values range from 2.6 % to 6.5 %. the degree of reaction of fly ash values arranges from greatest to lowest using the heat ratio which is the ratio of heat release of fly ash in the cementitious pastes to the heat release from the pozzolanic test are $FA2 > FA1 > FA3 > FA5 > FA4$. It should be noted here that the FA2 has the highest pozzolanic reactivity, but the FA4 is less reactive than the other types of fly ash. This may be due to assumptions regarding the filler effect factor. This could also occur because the reaction is incomplete in the pozzolanic test. Additionally, Ramanathan et al. [106] investigated the determination of the degree of reaction of SCMs using pozzolanic test. Their results indicated that the value of degree of reaction of SCMs could be greater than 100, and negative values could occur due to the filler effect. As reported in [98], the reactivities of different fly ash were varied even though the fly ash had similar material properties and chemical compositions. Moreover, the reactivities of fly ash were reported to depend on their mineralogical composition such as mullite content. Therefore, further statistical analysis is required to perform and discussed in Section 4.11.

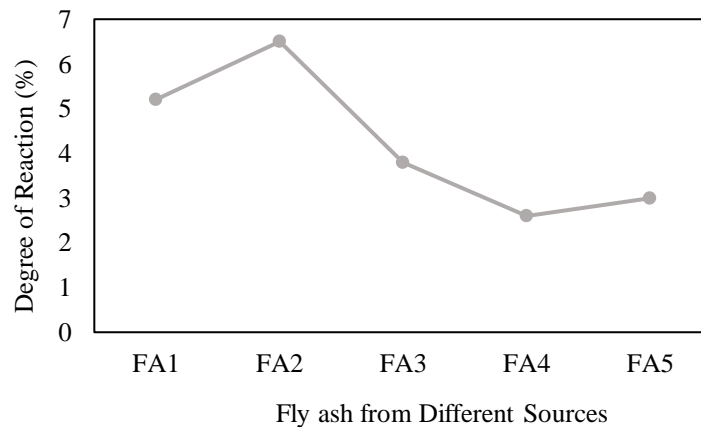


Figure 48: Degree of reaction of fly ash from different sources at 40°C

4.11 Service life

To estimate the service life of reinforced concrete structure, Life 365 software was applied based on Fick's second law of diffusion which has been widely used and recommended by previous research [36, 143]. In this study, severe exposure environment (directly exposed to marine tidal zone) and average annual temperature profile of the tropical location (Florida, USA) were inputted. Chloride threshold value was set at 0.05% by weight of concrete for the black steel and concrete cover was considered at 60 mm as suggested in the manual, and the w/b value was set at 0.54 as per mix proportion in Table 16. All these parameters were applied as constant for the OPC and blended FA-cement systems. Additionally, the effect of w/b values of 0.54 and 0.44 on service life was determined to assess the influence of water content. Both w/b values are generally used in mix proportions. Furthermore, the performance of parameters including diffusion coefficient (D_{28}) and diffusion decay index (m) were also included (see Table 22 and Table 23). Both parameters are required for predicting a proper service life of concrete structure.

The initiation period of blended systems containing fly ash was observed to be longer when compared to the OPC system. Tables 22 and 23 show the influence on service life of concrete structures when the w/b values of the mixture are at 0.54 and 0.44, respectively. For same replacement percentage of fly ash at 15 %, a change in w/b value was observed to remarkably influence on service life of concrete. Lower w/b results in longer service life values for all systems. It should be noted that the

propagation period is fixed at 6 years because in this work there is no change in embedded steel type or surrounding conditions (only the matrix of cement system assumingly is changed). When service life values of the systems having w/b values of 0.54 and 0.44, the longer service life values for both w/b values were clearly observed for concrete containing fly ash. Therefore, water content can decrease by replacing cement with fly ash in concrete in order to prolong the service life. It should be noted that considerable enhancement in the durability was found for concrete including fly ash compared to the OPC concrete. This is also due to the presence of pozzolanic characteristics of fly ash.

Moreover, Figure 49 shows the influence of w/b value on the service life of fly ash -cement concrete for the similar exposure condition and replacement level. Results indicate that with decrease in the w/b value of the blended fly ash -cement systems, the service life of concrete is changed significantly. The service life of blended concrete containing fly ash is much longer than that of OPC concrete with the same w/b value. Test results showed that the blended fly ash -cement systems having w/b value of 0.54 have the estimated service life is longer about 8 % compared to the OPC and by about 13 % for system having w/b value of 0.44. There is a slight difference between the results of concrete with different sources of fly ash, due to the difference between the experimental values of the D_{28} of the different types of fly ash concretes has very small amount and the same value of diffusion decay constant (m) is considered in the calculation for the mix proportions.

Service life prediction of this study is compared with those predicted by Mahima et al. [36]. Whilst the prediction models of these studies are based on concrete mixture proportions and concrete cover depth, their results differ from the results of this work. The time to initiate corrosion in reinforcing steel was approximately 6.6 years and 16.4 years for 20% fly ash replacement concrete with 30 mm and 50 mm concrete cover depth, respectively and the w/b value at 0.45, and 32 years for concrete including fly ash with 50 mm cover depth as presented by Nath et al. [143] . However, in this study, the prediction of initiation period of 15% fly ash replacement concrete with 60 mm cover depth is observed the estimated range from 4.0 to 5.0 years for the w/b value of 0.54 and from 5.9 to 7.3 years for the w/b value of 0.44, respectively. The shorter service life herein is because of the consideration of

mix proportions (such as lower % fly ash replacement, presence of coarse aggregate), cover depth, type of galvanized steel, and the D_a value.

Table 18: Influence of fly ash on service life (having w/b value of 0.54)

Specimens	D_{28} ($\times 10^{-11}$ m^2/s)	m	Ct % wt. concrete	Initiation period (Years)	Propagation period (Years)	Service life (Years)
OPC	1.72	0.2	0.05	4.2	6	10.2
FA1	1.72	0.32	0.05	4.8	6	10.8
FA2	1.72	0.32	0.05	4.9	6	10.9
FA3	1.72	0.32	0.05	5.0	6	11.0
FA4	1.72	0.32	0.05	4.0	6	10.0
FA5	1.72	0.32	0.05	4.6	6	10.6

Table 19: Influence of fly ash on service life (having w/b value of 0.44)

Specimens	D_{28} ($\times 10^{-12}$ m^2/s)	m	Ct % wt. concrete	Initiation period (Years)	Propagation period (Years)	Service life (Years)
OPC	9.91	0.2	0.05	5.8	6	11.8
FA1	9.91	0.32	0.05	6.9	6	12.9
FA2	9.91	0.32	0.05	7.1	6	13.1
FA3	9.91	0.32	0.05	7.3	6	13.3
FA4	9.91	0.32	0.05	5.9	6	11.9
FA5	9.91	0.32	0.05	6.8	6	12.8

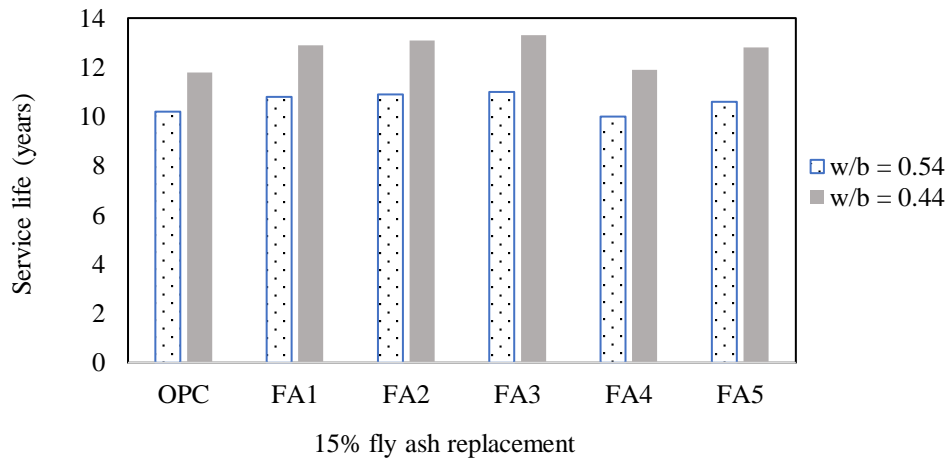


Figure 49: Service life of blended fly ash concrete with different w/b values

4.12 Statistical analysis of the results

All tested results of total 270 data (from 6 different mixtures for different experimental testing and triplicated samples each test) were statistically analyzed by ANOVA. The statistical analysis of the compressive strength, chloride ion penetration resistance, and carbonation resistance of cement–fly ash composites are summarized in Table 20. Results indicate that for the compressive strength, changes of heat release, mortar flow, fineness of fly ash particle, and CaO content can significantly influence on its mortars' compressive strengths. For the chloride ion penetration resistance, the heat release, mortar flow, and fineness of fly ash particle have a significant influence on the D_a value, whereas, the CaO has no significant effect on the D_a value. For the carbonation test, changing the heat release of paste, mortar flow, and fineness of fly ash particle significantly influence on carbonation properties, while CaO content of fly ash does not. The results of both chloride ion penetration resistance and the carbonation resistance exhibited conformed results of which the CaO content of different fly ash has not significantly different.

In this work, ANOVA was first performed to find out the significant level of the design parameters to the durability performance (herein resistance to chloride ion; D_a) of the blended fly ash -cement systems. From statistical analysis, all results of % CaO, particle size porosity, degree of reaction of fly ash and chloride diffusion considering the factors such as flow, particle size, flow of fresh mixture, degree of

reaction of blended fly ash -cement paste, and hardened porosity at 180 days are shown in Table 21. The analyses exhibited that all listed parameters significantly influence on the D_a value because the p-value is less than 0.05. This means CaO content of fly ash used, particle size of fly ash, flow of fresh mixture, degree of reaction of blended fly ash -cement system, and hardened porosity can have the impact on durability of structure. Therefore, all parameters were then further analyzed using sensitivity analysis. For this analysis, results indicate that only three parameters including % CaO, Degree of reaction of blended system, and hardened porosity can directly effect on the D_a . As shown in the β value in Table 21, the porosity has roughly greater impact on D_a than the degree of reaction and % CaO by 36 % and 535 %, respectively. This can represent that the two keys performance parameters of the systems having different fly ash are degree of reaction and hardened porosity of the blended systems; whereas chemical composition of fly ash (% CaO) has the slight impact, and particle size and flow (under the normal fresh mixture) are trivial. For promoting the durability of cement system, the key factor is replacing cement with fly ash. More specifically, selecting the fly ash type that can have a high pozzolanic reactions (that is Type-F fly ash) to the blended system and has good lubricant properties to control less porosity of hardened blended system is the key. The effect on the degree of reaction of fly ash is chemical properties in micro scale and the porosity is the physical properties in macro scale. These chemo-physical mechanisms of multi-scale structures mainly hinder the chloride ion to penetrating into the matrix in multi scales, resulting in the great improvement of durability of the blended fly ash -cement system.

Table 20: ANOVA statistical analysis

ANOVA	Source	p-value
Compressive strength	Heat release	**
	Curing ages	**
	Fineness	**
	CaO (%)	**

	Porosity	**
Chloride concentration	Heat release	*
	Testing ages	**
	Fineness	*
	CaO (%)	*
	Porosity	**
Accelerated carbonation	Heat release	**
	Curing ages	**
	Fineness	**
	CaO (%)	**
	Porosity	**

** = Apparently significant; * = Slightly significant

Table 21: ANOVA and β results summary

ANOVA	Source	p-value	$\beta (\times 10^{-13})$
D_a	% CaO	**	1.29
	Particle size	**	-
	Flow	**	-
	Degree of reaction	**	6.03
	Porosity	**	8.20

** = Apparently significant; * = Slightly significant; - = Not significant / Negligible

From the statistical analysis, it can be recommended that:

- In term of the fresh properties and mechanical properties, the wide variation of different fly ash properties including chemical composition and degree of fineness seem not easy to control. This is because the chemical composition and fineness are significantly affected on both fresh and mechanical properties.
- Apparently, for the durability properties for both chloride ion penetration and carbonation resistance, statistical analysis of numerous tested samples confirms that the fineness of fly ash particle is more likely important than chemical composition. To improve the durability of final product, it is better to find and screen fly ash to have smaller particle.
- The fineness of fly ash particle can also be controlled by using a wet or dry grinding process. However, it is required to perform feasibility analysis because the grinding process can be costly³⁷⁻³⁹.
- It is seen that Class F and Class C fly ash classified following ASTM C618² is important and useful for determining its fresh and mechanical properties, but unlikely proper to adopt for the long-term durability performance. It is believed that the durability performance is significantly impacted by microstructure (attributed to the degree of fineness of fly ash particle), rather than the chemical composition which likely impact much on its fresh and mechanical properties.

4.13 Overall performance of each type of fly ash

To sum up overall results, as it can be observed in Table 25, the highest flow value was found in FA5 fly ash. This is due to it contains lower LOI (meaningly lower carbon content) per unit mass. It can be seen that the conventional samples without fly ash display a high compressive strength at the early age. However, with including fly ash the long age compressive strength of mortar gradually increases, which is due to the slow pozzolanic reaction of fly ash over a longer period. After 90 days of curing the compressive strength was 45.22 MPa for the samples with FA5 fly ash which is higher than the other types of fly ash mortar strength. The lowest value

of compressive strength was observed in FA1. This is because the small size fly ash particles along with a high surface area and high amount of amorphous silica content impact the pozzolanic reaction and thus increment of strength [11]. Thus, the amount of chloride content in FA2 and FA5 samples has a lower value compared to other types of fly ash. Pozzolanic reaction enhances the formation of C–S–H gel. A large amount of C–S–H gel results in increased density. Results of chloride diffusion test were correlated with the parameters influencing the long-term performance of the fly ash blended concrete. It was observed that FA3 fly ash samples exhibited lowest chloride diffusion coefficient (D_a value). Therefore, the service life years of reinforced concrete structure including FA3 fly ash is higher than that of other types of fly ash. On the other hand, FA3 fly ash sample has a higher carbonation depth. This is due to the consumption of $\text{Ca}(\text{OH})_2$, lower pH, and changes in the microstructures. In addition, the pozzolanic reaction of fly ash consumes more $\text{Ca}(\text{OH})_2$ produced from cement hydration. This has the negative impact on the carbonation resistance of concrete [103]. Because the C–S–H gel forms at the longer time, a sufficient curing period for the pozzolanic reaction progressing is needed. Replacing OPC with fly ash results in reduced heat release by about 7 % to 13 %. This is believed to occur from the slow pozzolanic reaction of fly ash constituent. The use of fly ash contributes to the filler effect (an increase in the cement degree of reaction due to the physical presence of the fly ash), but can also result in the retardation of cement hydration due to release of aluminum as the fly ash dissolves [115]. It is noticeable that FA2 has the highest pozzolanic reactivity, but the FA4 is less reactive than the other types of FA. This may be due to assumptions regarding the filler effect factor [114]. This could also occur because the reaction is incomplete in the pozzolanic test. Results show that even among fly ashes of the same type, there is considerable difference in the pozzolanic reactivities, likely due to differences in amorphous content, chemical composition and fineness, leading to different reactivities. Thus, blending fly ash with OPC results in complicate system.

As the degree of reaction values increase, the incorporation of FA1 and FA2 have a higher compressive strength at the early age 7 days. At testing temperature 40°C , the calcium hydroxide content of FA3 is slightly higher than that of other fly ashes, and thus, it is the greatest carbonation depth among these five fly ashes.

Moreover, it can be inferred that the service life of containing FA4 is lower than that of other types of fly ash, as the degree of reaction of fly ash decreased. There is an increase in the porosity content with an increase in workability for including FA5.

After long wet curing, the spherical fly ash particles were replaced by ettringite due to the pozzolanic reaction of fly ash. The ettringite needles enter in the vacant space of the blended fly ash-cement system. Consequently, the pozzolanic reaction of fly ash contentiously fills the voids between the aggregates by the ettringite needles which are longer. Thus, blended fly ash concrete provide a denser binder matrix compared to the parent concrete [11].

Table 22: Overall performance of each type of fly ash

		OPC	FA1	FA2	FA3	FA4	FA5
Workability	Flow (%)	76	86	110	82	97	113
Compressive Strength, (MPa)	28°C, water curing, 7 days	37.02	35.97	31.2	23.02	27.34	25.51
	27°C, water curing, 28 days	42.64	38.98	40.22	38.06	43.56	39.24
	27°C, water curing, 90 days	43.95	40.21	42.67	44.36	44.84	45.22
Porosity (%)	After 180 curing days,	34.53	25.41	25.13	26.86	27.25	27.46
Chloride Penetration Depth, (mm)	After 30 days exposure	5	3.5	2	3	2.5	1.5
	After 90 days exposure	22	16	11	15	14	12
Total Chloride Content (%), After 91 days exposure	0-5 mm (depth)	0	0	0	0	0	0
	5-10 mm	0.304	0.277	0.281	0.207	0.278	0.263
	10-15 mm	0.283	0.141	0.186	0.109	0.116	0.132
	15-20 mm	0.228	0.076	0.081	0.03	0.033	0.06
	20-25 mm	0.173	0.038	0.027	0	0	0
	25-30 mm	0	0	0	0	0	0

D_a value (m^2/s)	After 90 days exposure	1.367 5E-11	7.221 8E-12	6.951 3E-12	4.437 9E-12	4.623 2E-12	5.955 E-12
Carbonation Depth, (mm), After 28 days, CO ₂ 4%, 4°C, RH 50%	28°C, water curing, 28 days	2.56	1.806	1.665	3.946	2.918	2.091
	28°C, water curing, 90 days	2.34	1.64	1.33	2.36	1.28	1.73
Heat Release in Cementitious Pastes, J/g	Testing Temperature, 25°C	222.3 3	194.1 3	196.4 0	199.3 8	200.2 5	206.1 8
	Testing Temperature, 40°C	214.3 9	208.2 9	201.7 8	203.5 5	198.2 9	201.7 5
Heat Release in Pozzolanic test, J/g	Testing Temperature, 40°C	-	21.60	10.69	21.38	18.09	22.81
CH content in Cementitious Pates, %	Testing Temperature, 25°C	21.09	17.61	17.95	18.74	17.92	18.75
	Testing Temperature, 40°C	20.89	16.64	16.99	17.95	16.82	17.58
Reaction Degree of fly ash, %	Testing Temperature, 40°C	-	5.2	6.5	3.8	2.6	3.0
Service Life (years)	w/c = 0.54	10.2	10.8	10.9	11	10	10.6
	w/c = 0.44	11.8	12.9	13.1	13.3	11.9	12.8

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 General

The current utilization of fly ash worldwide has a practical challenge because of its heterogeneity and wide variation from source to source. The need to better control fly ash quality can promisingly promote the utilization of fly ash in cement and concrete industry. The results in this study could be concluded that:

- Fly ash from five different sources could be used as the SCM to have higher compressive strength over the long curing time and good resistance to chloride ion penetration.
- The compressive strengths of mortars at different ages could be statistically influenced by changes of heat release, mortar flow, fineness of fly ash particle, and CaO content.
- Long-term durability properties like chloride ion penetration resistance and carbonation resistance tended to be affected by fly ash particle size, but not chemical composition.

are as follows:

- The incorporation of FA in blended systems exhibited lower total porosity than the OPC because of a good pozzolanic performance of FA and subsequently enhancing in the pore refinement.
- Using the pozzolanic test results, the degree of reaction of different sources of FA was determined using heat ratio at 40°C. The different sources of FA had different reactivities even though they had the similar material properties.
- The corrosion initiation period was observed to be delayed with the replacement of cement by FA and prolonged service life of marine infrastructures was observed with the partial replacement of FA. Therefore, the incorporation of FA in concrete produced effective and sustainable concrete to improve the serviceability subjected to the rich chloride conditions.
- In addition, FA from different sources that can offer a high pozzolanic reactions to the blended system and offer the fresh mixtures for easy

consolidation, leading to less porosity of hardened systems can minimize the chloride ion penetrating to its matrix. Both chemo-physical mechanisms of multi-scale structures significantly improve its durability.

It is suggested here that the grinding process should be adopted for increasing degree of fineness of fly ash particle. The outcome of this study offers a deep technical value differentiating between effects of fineness of fly ash particle and its chemical composition such that the cement manufacturers, concrete producers, coal powerplants can realize and optimize their process parameters to achieve good product quality. Further investigation programs focusing on serviceability of these cement-fly ash composites, life cycle assessment, and cost feasibility analysis comparing between sorting a proper fly ash source and implementing the industrial grinding process are required. This work offers the in-dept insight to mitigate the practical challenge of using FA in our today's infrastructure. The on-going research programs includes assessing the effects of grinding process to the particle size of FA, consequently, impacting on hardened performance of blended FA-cement system is under investigation.

5.2 Conclusions

In the current study, it can be concluded that the chemical composition and physical properties of fly ash remarkably influence the mechanical and durability performance results. Furthermore, properties of fly ash are different depending on the source. Therefore, fly ash from a new source has to be tested before its application. In practical engineering, the results of chloride concentration and CO₂ concentration can be used to improve the accuracy of evaluation the durability of the concrete structure under harsh environmental conditions and the service life prediction of fly ash blended concrete could facilitate to be examined to ensure its durability enhancement in the structures specifically exposed to severe environment.

- ❖ Moreover, the goal of this research was to provide proper guideline on how to select the fly ash from different sources. Therefore, we can select fly ash from different sources based on the value of fineness in the fly ash particles and the

content of CaO referred to as oxide level or calcium content. CaO content is an indicator of the type of reaction the fly ash undergoes in a concrete mixture as a pozzolanic or hydraulic. It is also an indicator of how it can improve concrete durability.

- Normally, <10 percent calcium content fly ash is low calcium fly ash and >20 percent calcium content fly ash is high calcium fly ash.
- The higher fineness value and calcium content influences the compressive strength, accelerated carbonation, and also determines the ability of fly ash to control the chloride diffusion that have an impact on the service life of reinforce concrete structures.

The guidelines developed under this study were based largely on empirical data available from laboratory tests and literature review.

5.3 Recommendation

Future work should be considered to achieve a better understanding of the long-term performance of different fly ash cement concrete and their practical using in engineering works. This is important before blended fly ash concrete can be widely accepted in commercial products as structural parts. Thus, the following recommendations offer some insights on the future research that can be accepted to enhance and optimize the findings of this study:

- ❖ Based on this research, the test results of this study can provide reference for the evaluation of the structural durability of reinforced concrete exposed to severe environmental conditions and facilitate the actual use of fly ash from a new source. Among the different sources of fly ash, FA3 can be considered for reinforced concrete structures in the marine environmental conditions to solve the durability problems. Thus, the service life value can be improved more for concrete having FA3 compared to other types of fly ash. FA5 fly ash has a higher compressive strength after long-wet age curing. The replacement cement with FA4 reduced the heat release of hydration process rather than the

other types of fly ash. It has a extremely benefit when use in massive concrete structure, for case in gravity dam applications.

- ❖ The effect of fly ash from different sources on the durability properties of concrete is the most important in this study because of their significant heterogeneity and variability. There are several methods to measure the degree of reaction of fly ash thus it should be selected the proper method for the further engineering practices.
- ❖ In addition, for future research, we recommend that although this study has been investigated to characterize the material properties of fly ash, that information is still insufficient, and it should provide a vital understanding of a unified pozzolanic reaction model that considers various types of materials to predict and optimize the performance of fly ash blended cement concrete.
- ❖ Due to the limitation of application of fly ash and the reaction between Ca(OH)_2 and fly ash, the hydration of concrete including fly ash is much more complex when compared with conventional concrete. Thus, we should create a numerical model that simulates the hydration of concrete incorporating fly ash for future study. The production of Ca(OH)_2 in cement hydration and its consumption in the reaction of fly ash is considered in order to develop a numerical model. The model can be verified through comparison of the experimental results of this study. To validate the model, multiple checks, including the experiments on the early-stage temperature rise and the evolution of chemically bound water should be performed for verification in the future research. In addition, due to the slow pozzolanic reactions of fly ash also limit their application in engineering work, high temperature curing should be employed to accelerate the pozzolanic reaction of fly ash.

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APPENDIX A
SPECIFICATION TABLES FOR EXTENDED RESULTS

Table A.1. Compressive strength of fly ash-cement paste for FA1

FA1	w/c = 0.44		w/c = 0.54		w/c = 0.64	
	28 days	91 days	28 days	91 days	28 days	91 days
0%	47.68	54.02	37.47	42.58	30.41	36.1
10%	52.32	64.48	35.84	50.23	27.47	38.98
20%	54.54	61.35	37.93	47.48	31.52	44.93
30%	46.04	47.91	30.61	35.08	18.44	31.78

Table A.2. Compressive strength of fly ash-cement paste for FA2

FA2	w/c = 0.44		w/c = 0.54		w/c = 0.64	
	28 days	91 days	28 days	91 days	28 days	91 days
0%	47.68	54.02	37.47	42.58	30.41	36.1
10%	49.31	57.16	43.82	44.15	33.62	40.81
20%	54.35	56.37	33.16	41.2	32.57	40.61
30%	50.03	51.01	32.57	37.82	24.13	28.06

Table A.3. Compressive strength of fly ash-cement paste for FA3

FA3	w/c = 0.44		w/c = 0.54		w/c = 0.64	
	28 days	91 days	28 days	91 days	28 days	91 days
0%	47.68	54.02	37.47	42.58	30.41	36.1

10%	54.74	57.81	33.16	41.86	28.51	34.53
20%	52.45	53.96	42.38	43.95	27.66	32.44
30%	52.19	53.17	29.43	33.16	24.33	30.8

Table A.4. Compressive strength of fly ash-cement paste for FA4

FA4	w/c = 0.44		w/c = 0.54		w/c = 0.64	
	28 days	91 days	28 days	91 days	28 days	91 days
0%	47.68	54.02	37.47	42.58	30.41	36.1
10%	61.41	63.57	42.38	44.86	29.63	34.92
20%	52.19	55.33	33.35	34.53	27.86	28.65
30%	43.16	45.91	27.86	34.14	27.84	27.86

Table A.5. Compressive strength of fly ash-cement paste for FA5

FA5	w/c = 0.44		w/c = 0.54		w/c = 0.64	
	28 days	91 days	28 days	91 days	28 days	91 days
0%	47.68	54.02	37.47	42.58	30.41	36.1
10%	58.73	65.67	32.57	35.32	28.65	30.21
20%	50.23	54.09	37.11	39.24	27.47	35.84
30%	41.99	47.26	28.65	38.85	21.91	31.92

LIST OF PUBLICATIONS

Journal articles

1. **Thwe Thwe Win**, Rungrawee Wattanapornprom, Lapyote Prasittisopin, Withit Pansuk, Phoonsak Pheinsusom: *Effects of fineness and calcium-oxide content in fly ash on early-age and hardening performance of cement–fly ash composite. (In peer-review process)*
2. **Thwe Thwe Win**, Rungrawee Wattanapornprom, Lapyote Prasittisopin, Withit Pansuk, Phoonsak Pheinsusom: *Effects of fly ash on the durability properties of concrete and service life prediction. (In peer-review process)*

Conference papers

1. **Thwe Thwe Win**, Rungrawee Wattanapornprom, Withit Pansuk: *Development of mathematical models for predicting the compressive strength of fly Ash blended cement paste from different sources. The 32nd KKHTCNN Symposium on Civil Engineering, KAIST, Daejeon, South Korea, October 24-26, 2019.*
2. **Thwe Thwe Win**, Rungrawee Wattanapornprom, Withit Pansuk: *Effect of fly ash in Southeast Asia on the properties of mortar, The 10th International Conference on Bridge Maintenance, Safety and Management (IABMAS), Hokkaido University, Sapporo, Japan, 2020.*

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AWARD RECEIVED

1. 2015 WFK-TPC (Techno Peace Corps) Project: "Study on Hot Weather Concrete Replaces the Pozzolan and Slag Powder, Myanmar", National Research Foundation (NRF), South Korea.
2. ASEAN Scholarship Program, Chulalongkorn University, Thailand.
3. The 90th Anniversary Chulalongkorn University Scholarship, Thailand.