Article

Investigation of Fineness and Calcium-Oxide Content in Fly Ash from ASEAN Region on Properties and Durability of Cement–Fly Ash System

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Abstract. Fly ash is a ubiquitously used pozzolan in cementitious material. Its technical knowledge has been widely studied for several decades and seems very well-established. However, a practical challenge currently exists. Different fly ash, even in different batches produced from similar power plant, has a wide variation of properties. To better control the wide variation of properties, this study aims to assess the effects of cementitious mixtures containing different fly ash properties (degree of fineness and CaO content) on heat release, flow, compressive strength, chloride ion penetration resistance, and carbonation resistance. Results from statistical analysis of 270 tested data of fly ash in various ASEAN countries indicate that the fineness of fly ash particle influences on the compressive strength, chloride ion penetration resistance, and carbonation resistance. Whereas, the CaO content of fly ash only statistically impacts on the compressive strength, but not on the chloride ion penetration resistance and carbonation resistance. To reduce the current practical challenge of the wide variation of cement–fly ash composite properties, their durability properties can be improved by adding smaller fly ash particle in cement system. The control of fly ash production by delivering its optimal degree of fineness is more important than selecting the optimal CaO content of fly ash. The study offers a deep technical value differentiating between effects of its fineness and CaO content such that the fly ash producers and consumers can realize and offer the optimized fly ash for good product quality.

Keywords: Fly ash, fineness, calcium oxide, early-age, durability, supplementary cementing material.

1. Introduction

Cementitious material is the widely used construction material. Its production normally consumes a large amount of natural resource and generated a significant portion of greenhouse gas globally. There have been many attempts to save costs, conserve energy, minimize the utilization of natural resource, reduce greenhouse gas from its production, and conserve the environment. These promoted the intensive research and development programs of mineral admixtures as supplementary cementitious materials (SCMs) [1]. Fly ash is one type of SCMs that can be obtained from different industrial and agricultural by-products (in this work, coal fly ash was used). It is known that the coal fly ash has a solid morphology, while fly ash from agricultural waste may have hollow morphology. According to the classification of ASTM C618, there are two categories of fly ash [2]. These include Class F and Class C fly ash. Class F fly ash, normally produced from burning bituminous coal (anthracite), contains a large portion of silicate compound. The silicate compound generally attributes to the later-age strengths of cementitious material. For Class C fly ash, it is typically produced from burning subbituminous coal (lignite). It consists of a great portion of CaO. The CaO content performs as hydraulic cementitious properties and typically attributes to the early-age strength. Type F fly ash has a low calcium content which requires a source of alkali or lime to react and form cementitious hydrates. It is the true pozzolanic material. Type C fly ash has a high calcium content which react more rapidly than low calcium content fly ash and harden when mixed with water due to the formation of cementitious hydration products. Such fly ash possesses both pozzolanic and hydraulic properties [1]. Thomas et al. investigated that the fly ashes including very high calcium content influenced properties of concrete in a different manner than traditional fly ashes. They determined that the total calcium content could be used as a reasonable basis for classifying fly ashes [1]. Because numerous studies focusing on the influences of fly ash in cementitious materials have been performed for several decades, the understanding of its mechanisms and its effects on performance of cementitious systems is well-defined.

However, regarding its production and industrial utilization, a current practical challenge exists. This is because of a large variation from source to source and even in different batches produced from the same powerplant. When producing concrete containing fly ash, this practical challenge results in an inconsistent quality of final product (even the color). For ready-mixed concrete application, when casting concrete for a large concrete structure such as foundation and sub-structure, often the ready-mixed concrete mixtures are manufactured from different lots at the same batching plant or from different batching plants nearby the construction site. It is found that fresh concrete mixtures containing fly ash do not have the same performance and the same color making the heterogeneity or inconsistency in casted concrete mixtures. The inconsistency among different fresh mixtures for casting each section of large concrete structure leads to the difficulty to control its quality. Durdzinski et al. investigated the high-calcium fly ash generated from a coal power plant and observed that the fly ash had different chemical compositions [3, 4]. 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. Meaningly, 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.

The incorporation of SCMs enhances the durability performance of final products. Rukzon and Chindaprasirt studied the use of ternary cement blends with coal fly ash and palm oil fuel fly ash with chemical admixture to improve performance of cement–fly ash composite [5]. The cement–fly ash composite was reported to have improved strength performance in term of reduced porosity, and consequently leading to denser matrix [6]. This led to better long-term performance. As a result, fly ash as the SCM can offer benefits for better and sustainable cementitious solution.

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 $Ca(OH)_2$ phase [7]. Reduced $Ca(OH)_2$ 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. This carbonation reaction to concrete can be assessed following an accelerated carbonation test. Ho and Lewis [8] investigated the effect of accelerated carbonation on cementitious materials cured under 4 % CO_2 concentration with a chamber temperature controlled at 20 °C and 50 % relative humidity for 60 days. Their results indicated that such concentrated CO_2 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. Increased CO_2 concentration in today atmosphere leads to increased rate of carbonation significantly. Carevic et al. [9, 10] assessed the accelerated carbonation test of cementitious materials with different curing periods. The authors indicated that the carbonation process of concrete mixtures could be affected by many involved parameters

such as their constituents, microstructure, temperature, CO_2 concentration, and curing conditions.

As aforementioned, the standard specification ASTM C618 classifies fly ash into two classes regarding the chemical composition. However, discussed literatures indicated that the particle size or fineness of fly ash could directly affect its performance. This work aims to investigate on the performance of cement–fly ash composite when its properties including degree of fineness and CaO content are varied. Tested specimens containing fly ash from five different sources were evaluated on (1) heat release by isothermal calorimeter and thermogravimetric analysis (TGA), (2) flow and compressive strength of mortar, (3) chloride ion penetration and apparent chloride diffusion coefficient (D_a) value, and (4) carbonation resistance of mortar. For the heat release and TGA tests, after measuring all the tests, the $Ca(OH)_2$ content for each system is then calculated. For the compressive strengths, the samples were replaced with different fly ash at 15 % and tested at 7, 28, and 90 days. It should be noted here that although ASTM standard suggests 20% replacement level is the minimum level, from our research data, the compressive strength test for different percent replacement levels (up to 30 %) from five different sources of fly ash have been assessed, optimized, and curved-fitted to get the optimal percent replacement level used in this publication. The chloride ion penetration resistance of saturated samples cured under NaCl solution for 30 days and 90 days after casting. The influences of the 28- and 90-day mortars containing fly ash from different sources on the carbonation resistance of cement–fly ash composite were evaluated. After performing and collecting the tested data of total 270 cementitious mixtures, all the test data results were inputted into the statistical software. The large number of mixtures tested can ensure that the statistical interpretation is validated and presented properly.

Since there is a lack of studies of fly ash obtained from different sources or different countries, the result of this study is a novel finding to our understanding of different fly ash properties (namely, degree of fineness and CaO content) influencing on its fresh, mechanical properties, and durability performance from different sources. The source parameters may affect the overall outcomes of cthe mixtures. It should be noted that other physical properties and chemical compositions such as Loss on Ignition (LOI) and alkalinities of coal fly ash and agricultural fly ash were assessed and will be reported in the future publication. The agricultural fly ash normally has higher LOI value so the study to investigate the effects of LOI on products' properties of both agricultural and coal fly ash will be meaningful. The outcome of this study offers in-depth technical information, leading to reduce the mentioned practical challenge of using fly ash in cement, especially in a very large-scale project. When fly ash properties are better controlled and apparently sorted out, the quality of final product can be better controlled. The sorting system and pre-processing of fly ash can be recommended properly for acquiring more durable and sustainable concrete solution. Additionally, this document can provide as a guideline to utilize fly ash in construction applications for cement manufacturers, coal power plants, and concrete producers.

2. Materials and Methods

2.1. Materials

Ordinary Portland cement Type I (OPC) as per ASTM C150 [11] 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 C (FA5). The obtained LOI value, chemical composition of OPC and fly ash using X-ray fluorescence analysis, and their physical characteristics in accordance with the ASTM C618 standard are shown in Table 1. Figures 1 and 2 show their particle size distribution curves obtained from laser diffraction analyzer (Mastersizer 2000, Malvern Panalytical Ltd) and the particle microstructure obtained from scanning electron microscopy (SEM) respectively. Epoxy, reagent-grade NaCl, $AgNO_3$, and H_2SO_4 were lab-graded and used in the chloride concentration test. Methyl orange $(C_{14}H_{14}N_3NaO_3S)$, and phenolphthalein $(C_{20}H_{14}O_4)$ were lab-graded and used in the accelerated carbonation test.

Table 1. Chemical compositions and physical properties of cement and fly ash from different sources.

%	OPC	FA1	FA2	FA3	FA4	FA5
SiO_2	17.80	50.30	73.80	27.40	51.70	35.50
Al_2O_3	4.29	19.60	17.70	15.80	23.40	14.80
Fe_2O_3	2.97	3.33	1.94	12.10	14.00	17.80
CaO	61.10	9.93	0.80	21.60	4.24	16.70
MgO	0.87	2.20	0.31	2.26	1.53	6.78
SO_3	4.14	0.68	0.19	6.92	1.84	1.82
Na_2O	0.34	-	0.39	1.70	0.53	1.33
K_2O	0.26	2.25	0.71	2.02	1.15	1.13
$SiO_2 + Al_2O_3 + Fe_2O_3$	-	73.23	93.44	55.30	89.10	68.10
LOI	1.9	1.4	1.8	0.2	0.3	0.3
Class per ASTM C618	-	F	F	C	F	C
Specific gravity (g/cm^3)	3.1	2.2	2.1	2.4	2.5	2.9
Blaine surface area (cm^2/g)	3764	3395	4654	3131	4315	5475

2.2. Preparation Methods

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. 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 homogenous [12].

For testing the flow, compressive strength, chloride resistance, 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 [13]. The mortar mixing proportions used are given in Table 2. 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 [13]. 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 [14].
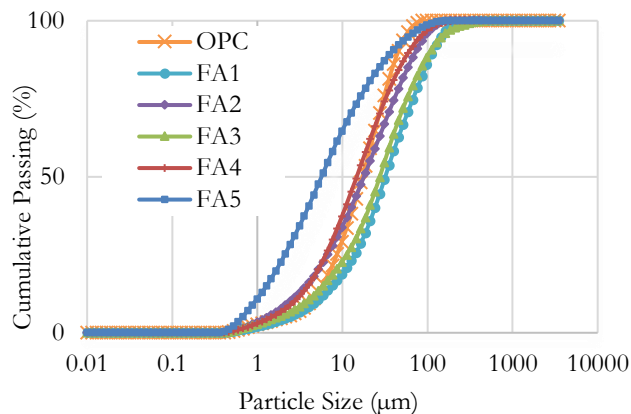

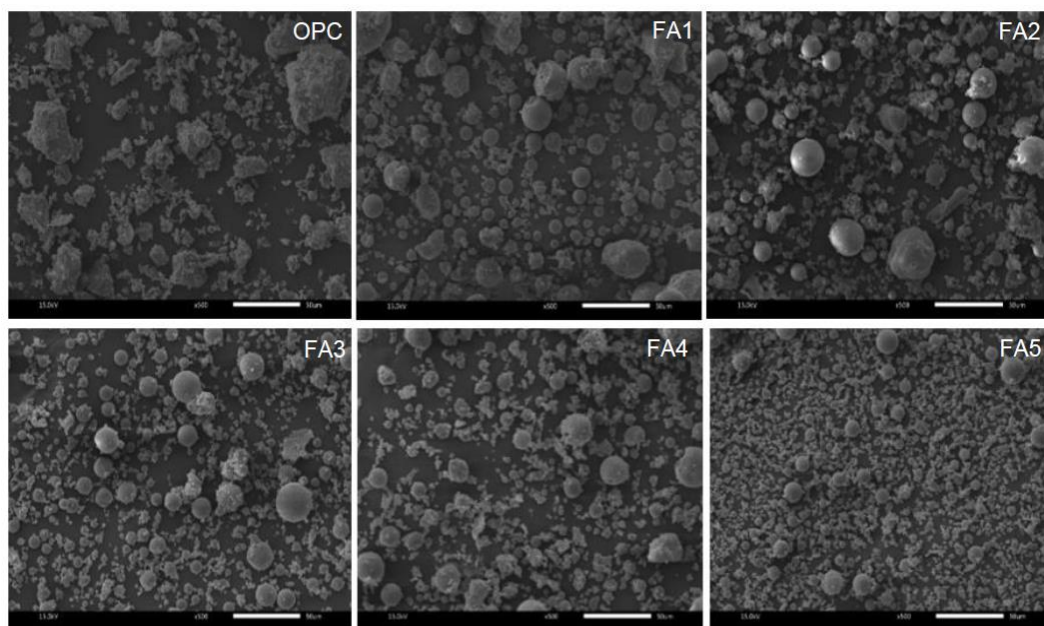Fig. 1. Particle size distribution of OPC and fly ash from different sources.

Fig. 2. Microstructure of cement and fly ashes under scanning electron microscope SEM.

Table 2. Mortar mixing proportions (in kg/m³).

Mix	OPC	Fly ash	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

2.3. 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 [15]. 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. 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 N_2 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 [16]. 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. (1) can be used to measure $Ca(OH)_2$ content (CH):

$$CH(\%) = \frac{74.1}{18.0} \times \frac{M_{start}^s - M_{end}^s}{M_c} \times 100 \qquad (1)$$

where CH represents $Ca(OH)_2$ content of hydrated cement; M_{start}^s represents the initial mass of sample recorded during the TGA; M_{end}^s represents the final mass of sample (assumed at the end of the test); and M_c represents the initial (anhydrous) mass of the cement in the TGA sample. The multiplied factor ($\frac{74.1}{18.0}$) represents the molar mass ratio of $Ca(OH)_2$ (equaling 74.1) and H_2O (equaling 18.0).

2.4. Flow and Compressive Strength

After preparing the fresh mortar mixtures, their flow values were measured using the flow table, as per ASTM C1437 [17]. For the compressive strength test, all hardened mortar samples were tested at 7, 28, and 90 days using a compression testing machine ASTM C109. The reported values were the average values from triplicated samples. Their error bars represent the standard deviations of tested data.

2.5. Chloride Concentration and D_a Value

To study the chloride ion diffusion mechanism, the mortar mixtures were prepared and tested, as per ASTM C1556 [18]. 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 $AgNO_3$ solution with 0.1 M concentration was then applied on the surface of exposed samples to see their appearance change [19]. The grey colour indicates the depth of chloride ion that can penetrate because of the reaction between $AgNO_3$ 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 [18]. Six depth

levels of samples were analysed 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 H_2SO_4 with 100 ml water and then three drops of $C_{14}H_{14}N_3NaO_3S$ indicator were added and then stirred for 1 h. Subsequently, the sample was titrated with $AgNO_3$ 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. (2). The results are based on the triplicated tests. Their error bars represent the standard deviations of tested data.

$$C(x,t) = C_s - \left[(C_s - C_i) \times erf \left(\frac{x}{\sqrt{4D_a t}} \right) \right] \qquad (2)$$

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.

2.6. 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 ± 0.1%. Higher concentration of CO_2 results in higher rate of carbonation reaction [9]. The temperature inside the chamber was set at 20 ± 2 °C, and the relative humidity was set at 50 ± 5 %. Then, the specimens were removed from the chamber and split using a compression machine into two halves. The carbonation depths were measured using $C_{20}H_{14}O_4$ solution [20, 21]. This $C_{20}H_{14}O_4$ 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. The mean value was

shown, and the error bar represents the standard deviations.

2.7. 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:

$$H_0: \mu_1 = \mu_2 = \mu_3 = \ldots. = \mu_a$$
$$H_a: \mu_i \neq \mu_j \text{ for some i} \neq \text{j}$$

The 95 % confidence interval was used for all analyses. 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 $\geq$ 0.05), there was no statistically significant effect existing at the 5 % level among the mean values of group populations [22].

3. Results and Discussions

3.1. Characteristics of Cement and Fly Ash

As shown in Table 1, the chemical composition of FA2 contains 0.797 % CaO, which is less than the other types of fly ash. However, the total content of SiO_2, Al_2O_3, and Fe_2O_3 is 93.44 %, which is higher than the rest. The total content of SiO_2, Al_2O_3, and Fe_2O_3 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 SiO_2, Al_2O_3 and Fe_2O_3 was observed. The general physical characteristics of materials (OPC and fly ash) include the Blaine surface area or degree of fineness [23] and specific gravity [24]. 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. 1.

3.2. Heat Release and TGA analysis

The heat flow and (cumulative) heat release of cement–fly ash composites cured for 7 days at 25 °C are shown in Fig. 3 and Fig. 4. Results indicate that partial replacement of cement with fly ash influences on the amount of heat release. The heat release of OPC paste is higher than the FA5, FA4, FA3, FA2, and FA1, respectively. The heat values of cementitious pastes range from 194 to 222 J/g. 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 TGA is a common measurement used to evaluate the $Ca(OH)_2$ content in fly ash–cement composite. The content of $Ca(OH)_2$ is one of the key factors that can influence on the hydration mechanisms. It can be described by the pozzolanic reactions and $Ca(OH)_2$ obtained by the hydration of cement [25]. Figure 5 shows the TG-DSC profiles of cement–fly ash composites measured after 7 days. The TG-DSC profile represents the hydration behaviour 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) $Ca(OH)_2$ 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 $Ca(OH)_2$ phase [26].
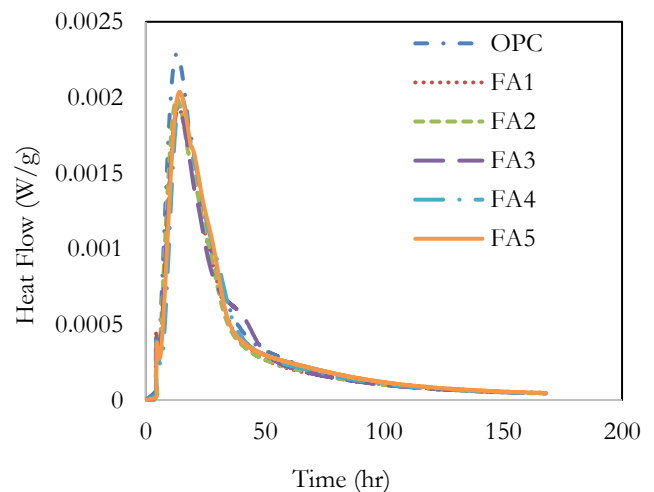

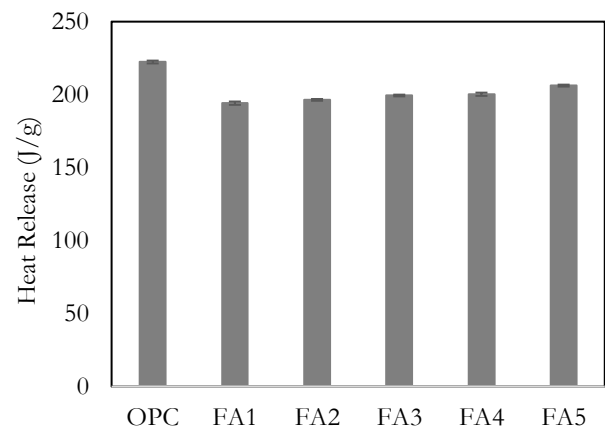Fig. 3. Heat flow of cement pastes with/without fly ash from different sources.

Fig. 4. Heat release of cement pastes with/without fly ash from different sources.

Figure 6 shows the calculated $Ca(OH)_2$ content cement pastes containing fly ash from different sources.

The Ca(OH)$_2$ phase is formed during hydration reaction of dicalcium silicate (C$_2$S) phase and tricalcium silicate (C$_3$S) phase. The Ca(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. 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.

3.3. Flow and Compressive Strength of Mortar

The influence of the fresh mortars containing 15 % fly ash on flow values is shown in Fig. 7. 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 [1].

The 7-, 28-, and 90-day compressive strengths of the mortars containing 15 % fly ash from different sources are shown in Fig. 8. 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 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) [27], although other minor constituents such as alkalis (Na$_2$O and K$_2$O), 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. 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 [28].

Pozzolanic materials react with Ca(OH)$_2$ phase and H$_2$O 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 [27]. The increasing in later-age strength is the typical performance characteristic of pozzolans owing to the pozzolanic reaction [29]. 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.
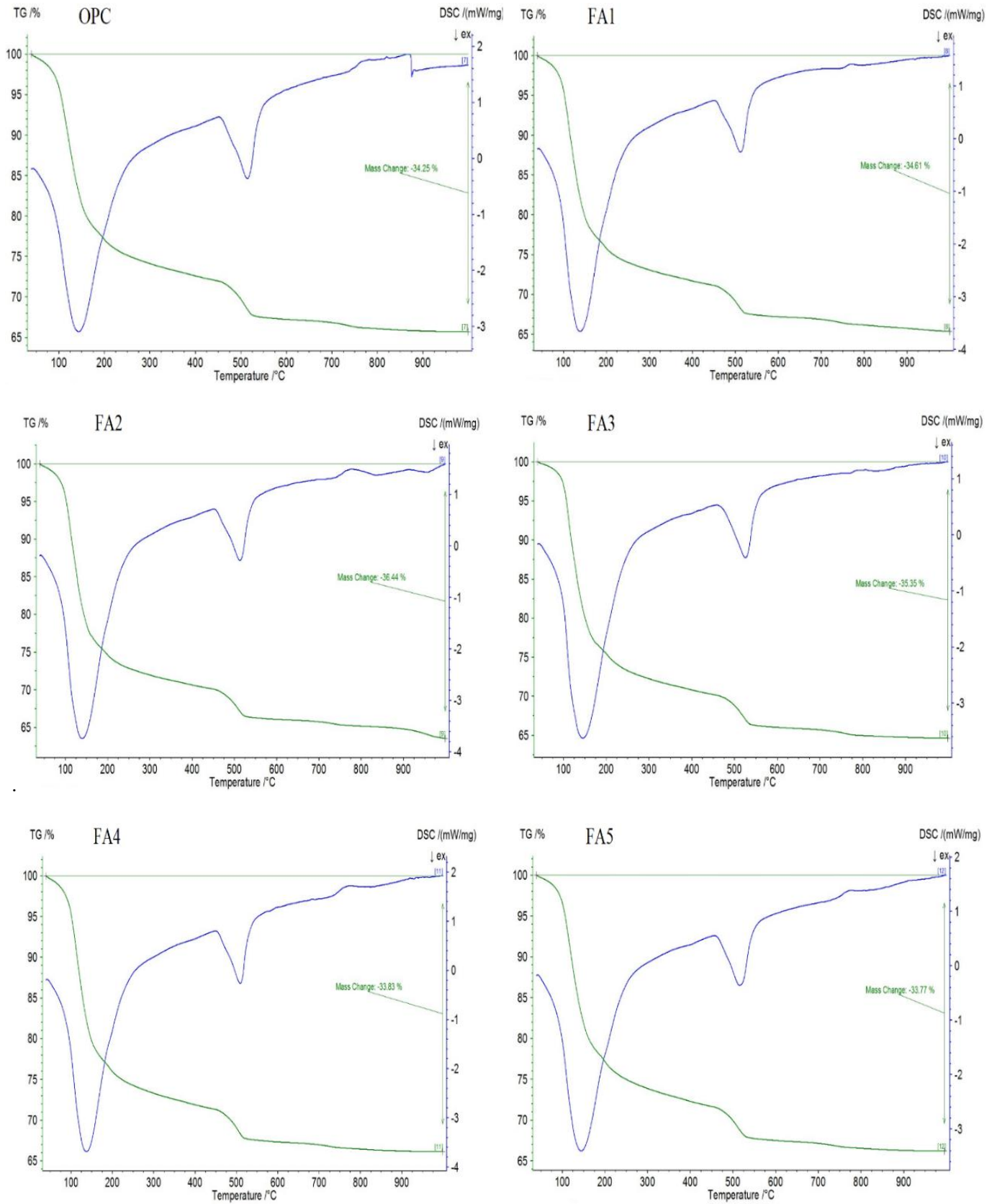
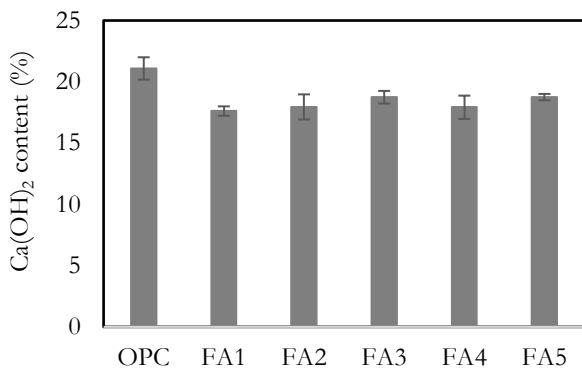Fig. 5. TGA of cement pastes with/without fly ash from different sources.

Fig. 6. Ca(OH)$_2$ content for cement pastes with/without fly ash from different sources.
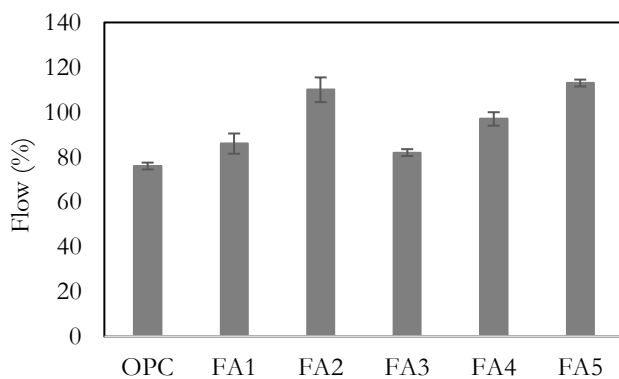

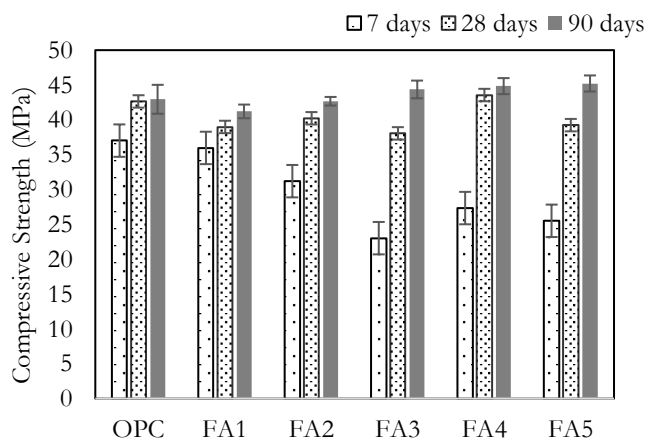Fig. 7. Flow of cement mortars with/without fly ash from different sources.

Fig. 8. Compressive strength of cement mortars with/without fly ash from different sources.

3.4. Chloride Ion Penetration Depth and D$_a$ Value

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. 9. 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 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 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 [30]. Consequently, the chloride ion is blocked.

Figure 10 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 [27]. 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 [31]. 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 [32, 33]. 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 %) [27].

The D$_a$ values of mortars containing fly ash after 90 days of exposure in 3 % NaCl solution are shown in Fig. 11. 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 [34].

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 [35]. Fly ash from different sources have different chemical compositions, leading to different effects on the resistance of chloride ion penetration.
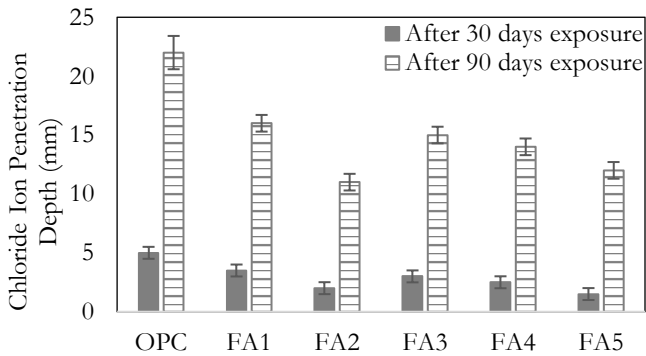

Fig. 9. Chloride ion penetration depth of cement mortars with/without fly ash from different sources and exposed for 30 and 90 days.
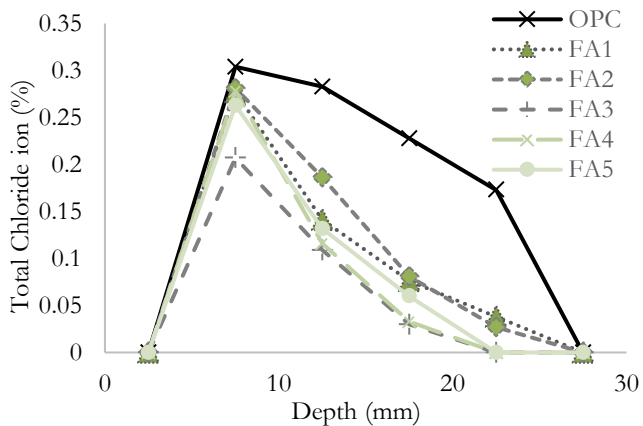

Fig. 10. Total chloride ion concentration of cement mortars with/without fly ash from different sources and exposed for 90 days.
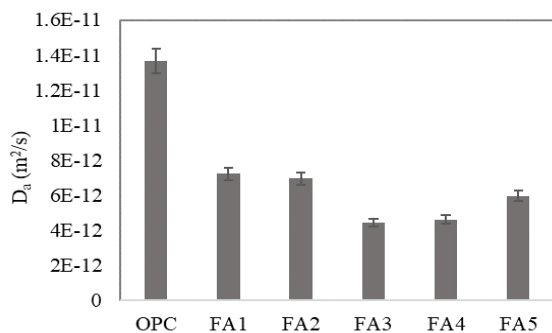

Fig. 11. D_a values of mortar cement mortars with/without fly ash from different sources.

3.5. 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. 12. 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 microstructures [36]. 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 permeability [36]. 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 [7, 37]. Because the C–S–H gel forms at the longer time, a sufficient curing period for the pozzolanic reaction progressing is needed.
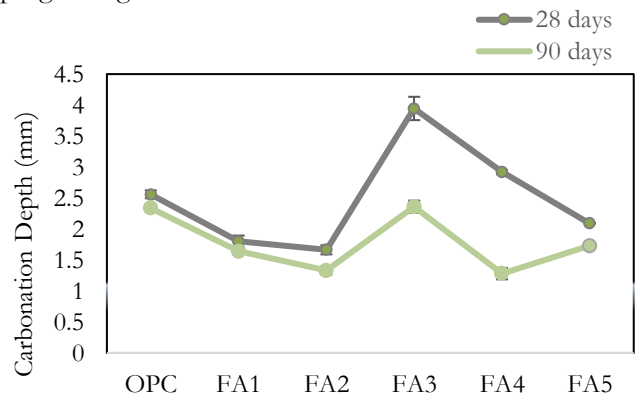

Fig. 12. Carbonation depth on of 28- and 90-day cement mortars with/without fly ash from different sources.

3.6. Statistical Analysis and Recommendation

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 3. 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.

Table 3. ANOVA results summary.

ANOVA	Source	p-value
Compressive strength	Heat release	*
	Flow	*
	Fineness	*
	CaO (%)	*
Chloride ion penetration resistance	Heat release	*
	Flow	*
	Fineness	*
	CaO (%)	-
Carbonation resistance	Heat release	*
	Flow	*
	Fineness	*
	CaO (%)	-

* = Significant; - = Not significant

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 costly [38-40].

- It is seen that Class F and Class C fly ash classified following ASTM C618 [2] 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. Conclusions

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.

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.

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Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

All data generated or analysed during this study are included in this published article.

References

[1] M. Thomas, "Optimizing the use of fly ash in concrete," Portland Cement Association Skokie, IL, vol. 5420, 2007.

[2] *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, ASTM C618, ASTM International, West Conshohocken. 2005.

[3] P. T. Durdziński, "Hydration of multi-component cements containing cement clinker, slag, calcareous fly ash and limestone," EPFL, 2016.

[4] P. T. Durdziński, et al., "A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste," *Cement and Concrete Research*, vol. 73, pp. 111-122, 2015.

[5] S. Rukzon and P. Chindaprasirt, "Strength and chloride resistance of blended Portland cement mortar containing palm oil fuel ash and fly ash," *International Journal of Minerals, Metallurgy and Materials*, vol. 16, no. 4, pp. 475-481, 2009.

[6] L. Prasittisopin, and I. Sereewatthanawut, "Effects of seeding nucleation agent on geopolymerization process of fly-ash geopolymer," *Frontiers of Structural and Civil Engineering*, vol. 12, no. 1, pp. 16-25, 2018.

[7] Q. Zhao, et al., "Long-age wet curing effect on performance of carbonation resistance of fly ash concrete," *Construction and Building Materials*, vol. 127, pp. 577-587, 2016.

[8] D. Ho and R. Lewis, "Carbonation of concrete incorporating fly ash or a chemical admixture," *Special Publication*, vol. 79, pp. 333-346, 1983.

[9] V. Carević, I. Ignjatović, and J. Dragaš, "Model for practical carbonation depth prediction for high volume fly ash concrete and recycled aggregate concrete," *Construction and Building Materials*, vol. 213, pp. 194-208, 2019.

[10] D. Zhang, et al., "Carbonation performance of concrete with fly ash as fine aggregate after stress damage and high temperature exposure," *Construction and Building Materials*, vol. 242, p. 118125, 2020.

[11] *Standard Specification for Portland Cement*, ASTM C150, ASTM International, West Conshohocken, 2005.

[12] *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*, ASTM 305, ASTM International, West Conshohocken, 2014.

[13] *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)*, ASTM C109, ASTM International, West Conshohocken, 2005.

[14] *Standard Specification for Mixing Room; Moist Cabinets; Moist Rooms; and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes*, ASTM C511, ASTM International, West Conshohocken, 2019.

[15] *Standard Test Method for Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry*, ASTM C1702, ASTM International, West Conshohocken, 2010.

[16] T. Kim and J. Olek, "Effects of sample preparation and interpretation of thermogravimetric curves on calcium hydroxide in hydrated pastes and mortars," *Transportation Research Record*, vol. 2290, no. 1, pp. 10-18, 2012.

[17] *Standard Test Method for Flow of Hydraulic Cement Mortar*, ASTM C1437, ASTM International, West Conshohocken, 2011.

[18] *Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion*, ASTM C1556, Annual Book of American Society for Testing Materials Standards, 4, 2004.

[19] P. Chindaprasirt, C. Jaturapitakkul, and T. Sinsiri, "Effect of fly ash fineness on compressive strength and pore size of blended cement paste," *Cement and Concrete Composites*, vol. 27, no. 4, pp. 425-428, 2005.

[20] R. Malheiro, et al., "Durability of fly ash eco-friendly cement mortars in severe environment," *Procedia Manufacturing*, vol. 46, pp. 122-130, 2020.

[21] *Products and systems for the protection and repair of concrete structures. Test methods. Determination of carbonation depth in hardened concrete by the phenolphthalein method*, British Standard, BS EN 14630, 2006.

[22] L. Prasittisopin and D. Trejo, "Performance characteristics of blended cementitious systems incorporating chemically transformed rice husk ash,"

Advances in Civil Engineering Materials, vol. 6, no. 1, pp. 17-35, 2017.

[23] *Standard Test Method for Fineness of Hydraulic Cement by Air-Permeability Apparatus*, ASTM C204, ASTM International, West Conshohocken, 2011.

[24] *Standard Test Method for Density of Hydraulic Cement*, ASTM C188, ASTM International, West Conshohocken, 2007.

[25] M. Anjos, et al., "Evaluation of hydration of cement pastes containing high volume of mineral additions," *European Journal of Environmental and Civil Engineering*, vol. 23, no. 8, pp. 987-1002, 2019.

[26] T. Wang, et al., "Experimental investigation of pozzolanic reaction and curing temperature-dependence of low-calcium fly ash in cement system and Ca-Si-Al element distribution of fly ash-blended cement paste," *Construction and Building Materials*, vol. 267, p. 121012, 2021.

[27] M. Uysal and V. Akyuncu, "Durability performance of concrete incorporating Class F and Class C fly ashes," *Construction and Building Materials*, vol. 34, pp. 170-178, 2012.

[28] S. Schlorholtz, K. Bergeson, and T. Demirel, "Monitoring of fluctuations in the physical and chemical properties of a high-calcium fly ash," MRS Online Proceedings Library Archive, vol. 113, 1987.

[29] E. Sakai, et al., "Hydration of fly ash cement," *Cement and Concrete Research*, vol. 35, no. 6, pp. 1135-1140, 2005.

[30] A. K. Saha, "Effect of class F fly ash on the durability properties of concrete," *Sustainable Environment Research*, vol. 28, no. 1, pp. 25-31, 2018.

[31] P. Van den Heede, C. Thiel, and N. De Belie, "Natural and accelerated carbonation behaviour of high-volume fly ash (HVFA) mortar: Effects on internal moisture, microstructure and carbonated phase proportioning," *Cement and Concrete Composites*, vol. 113, p. 103713, 2020.

[32] E. Poulsen and L. Mejlbro, *Diffusion of Chloride in Concrete: Theory and Application*. CRC Press, 2010.

[33] G. Meira, et al., "Chloride penetration into concrete structures in the marine atmosphere zone–Relationship between deposition of chlorides on the wet candle and chlorides accumulated into concrete," *Cement and Concrete Composites*, vol. 29, no. 9, pp. 667-676, 2007.

[34] T. Sumranwanich and S. Tangtermsirikul, "A model for predicting time-dependent chloride binding capacity of cement-fly ash cementitious system," *Materials and Structures*, vol. 37, 6, pp. 387-396, 2004.

[35] T. Wang and T. Ishida, "Multiphase pozzolanic reaction model of low-calcium fly ash in cement systems," *Cement and Concrete Research*, vol. 122, pp. 274-287, 2019.

[36] D. Ramachandran, S. Uthaman, and V. Vishwakarma, "Studies of carbonation process in nanoparticles modified fly ash concrete," *Construction and Building Materials*, vol. 252, p. 119127, 2020.

[37] M. Montemor, et al., "Corrosion behaviour of rebars in fly ash mortar exposed to carbon dioxide and chlorides," *Cement and Concrete Composites*, vol. 24, no. 1, pp. 45-53, 2002.

[38] J. Paya, et al., "Mechanical treatment of fly ashes. Part I: Physico-chemical characterization of ground fly ashes," *Cement and Concrete Research*, vol. 25, no. 7, pp. 1469-1479, 1995.

[39] J. Zhao,, et al., "Ultrafine grinding of fly ash with grinding aids: Impact on particle characteristics of ultrafine fly ash and properties of blended cement containing ultrafine fly ash," *Construction and Building Materials*, vol. 78, pp. 250-259, 2015.

[40] L. Prasittisopin and D. Trejo, "Characterization of chemical treatment method for rice husk ash cementing materials," *Special Publication*, vol. 294, pp. 1-14, 2013.

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