Exploring ASEAN Fly Ash for Enhancing Cement Hydration and Service Life Prediction of Portland Cement Mortar

Thwe Thwe Win\textsuperscript{1},\textsuperscript{a} Ranrawee Wattanapornprom\textsuperscript{2b}, Lapyote Prasittisopin\textsuperscript{1c},\textsuperscript{*}, Withit Pansuk\textsuperscript{2d}, and Phoonsak Pheinsusom\textsuperscript{2e}

\textsuperscript{1} Architectural Technology Research Unit, Department of Architecture, Faculty of Architecture, Chulalongkorn University, Bangkok 10330, Thailand
\textsuperscript{2} Department of Civil Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: \textsuperscript{a}thwethwewin2991@gmail.com, \textsuperscript{b}runrawee.w@gmail.com, \textsuperscript{c}lapyote.p@chula.ac.th (Corresponding author), \textsuperscript{d}withit.p@chula.ac.th, \textsuperscript{e}dr.phoonsak@gmail.com

Abstract. The durability of cementitious materials can be improved with the widespread utilization of fly ash (FA). Although FA has been available for use in cement and concrete industries for decades, there is still a practical barrier associated with its application. The difficulty stems from its wide variety and heterogeneity. The purpose of this research is to conduct both experimental and numerical investigations to achieve a better understanding of managing the variation of FA, which reflects its durability. The chemical properties and particle size distribution of FA from five distinct sources in ASEAN region were analyzed. In addition, the degree of reactivity, flow, toughened porosity, and apparent chloride diffusivity coefficients of blended FA-cement systems were studied (\(D_a\)). The Life365 service life model was executed. Using analysis of variance (ANOVA) and sensitivity analysis using linear regression, the experimental outcomes were statistically examined. Having a 15% FA replacement level resulted in a roughly 70% decrease of the \(D_a\) value, extending its serviceability by around 13%. The chemo-physical processes in multi-scale structures were shown to be the most important element by statistical analysis, and the degree of response in blended FA-cement systems and its toughened porosity were found to be among the most beneficial aspects affecting its durability.

Keywords: Fly ash, porosity, degree of reaction, chloride diffusion, service life, cement.
1. Introduction

Utilization of supplementary cementitious materials (SCMs) as a pozzolanic material has increased in cement and concrete works over the past several decades due to its ability to reduce material production costs, create energy savings, lower carbon dioxide emissions, improve durable and sustainable concrete, and use fewer natural resources [1, 2]. A byproduct of combustion of either pulverized coal or agricultural waste, fly ash (FA), is an SCM that can be used to raise the level of quality of cementing material. One of the most significant factors affecting the fresh and hardened properties of blended cementing systems is the many chemo-physical properties of FA [2-5]. When calcium hydroxide is formed during cement hydration, and FA interacts with it, calcium-silicate-hydrate (C-S-H) gel is formed. By diminishing its porosity, the CSH gel can improve the microstructure of cement paste. This is a well-known example of an FA pozzolanic reaction [5]. Due to its pozzolanic characteristics, FA can be widely used today to replace cementing materials. It has replaced from 15–25% of the binder in concrete [5].

However, when FA is used to replace cement in a significant amount, the hydration reactions appear to be delayed, and the early-age performance characteristics of the reacting product (especially within 1–3 days) are lost. This is due to the fact that its pozzolanic reaction occurs at older ages. Better performance qualities at an earlier age are more cost-effective than those at a later age [6, 7]. The use of optimum content is greatly influenced by the application, particular restrictions, FA properties, geographic location, climate, and cement type. Controlling the cementing structure’s temperature rise, however, is essential for the application of mass concrete. By postponing the heat release from early hydration reactions, the temperature rise can be controlled. Due to the delayed heat release, the early-age thermal fractures on the structural concrete surface were decreased. In contrast, FA has been utilized in mass concrete constructions such as foundations, bridges, and dams with replacement amounts between 30% and 50% [5]. Recent studies have demonstrated that concrete with high mechanical and long-lasting qualities may be produced with replacement amounts of 40–60% [8]. Because the fresh cement mixture containing FA typically uses less water to have the same slump values as the plain mixture, the performance attributes of the mixed FA cementing system enhance the development of long-term strength. This suggests that the FA-cement system may flow and can be compacted more efficiently than the plain system at a given slump when vibrated. Improved consolidation of the innovative mixture reduces segregation, which is reflected in smaller pores in the macrostructure. FA has a substantial effect on enhancing long-term performance. For instance, many researchers found that adding FA to mortar increased its resistance to chloride penetration. [9-11]. Durdziński et al. [12] described the evaluation of the resilience of mixed FA-cement mortar in the presence of chloride and carbon dioxide in harsh environments. Remarkably, when compared to plain mortar (0% FA), blended cement mortar that had been replaced with 40% FA reduced its D₃ value by about 85% after the 60 days of study. It showed that the mortar that had been mixed with FA decreased the D₃ value throughout all testing periods [13].

Additionally, the sorptivity, permeability, and diffusivity of infrastructure—material transport parameters measured by the microstructural features of cementing systems—have a substantial effect on its durability and service life. The durability of the completed product is greatly influenced by two essential elements of the hydrated cement system: porosity and pore size distribution [14]. FA is frequently used in civil engineering applications to reduce the porosity of blended cement systems. Kumar et al. [15] showed how the curing age affects the porosity of a hybrid cement system made with eggshell powder, steel fiber, and coal FA as a partial cement substitute. According to test results, the combination of 35% FA, 6% eggshell powder, and 0.75% steel fibers increased compressive strength while decreasing concrete porosity as water curing age increased. Nakamura et al. [16] investigated the strength development of a blended coal FA-cement system by visualizing porosity distribution in three dimensions and concluded the strength development was significantly impacted by the moisture ratio-induced porosity of the microstructure of the cementing systems. Moreover, the amount of FA present and how fine its particle was had a significant impact on the total porosity and pore size of blended cement systems[17, 18].

Nevertheless, because FA has such a wide range of variability and inhomogeneity, applying it to blended FA-cementing materials in civil engineering remains a difficult practical challenge. When many researchers [10, 19-21] studied despite the fact that FA varied widely in chemical composition and came from the same power plant, their findings revealed that mixing cement with FA caused changes in pore-size distribution, compressive strength, and the chloride resistivity due to combustion conditions, ambient environment conditions during the fire, and the raw feed composition [22, 23]. Wang et al. [24, 25] studied FA, which belonged to the same category in both alkaline and cement systems. Their findings suggested that although it had the same physical characteristics as other materials, FA reactivities widely varied from lot to lot.

The pozzolanic reaction of blended FA-cement system is important to understand because it has a significant impact on the system's general properties. Image analysis (IA), quantitative X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and selective dissolution are a few techniques to assess the level of pozzolanic reaction. The results of this pozzolanic test, which used isothermal calorimetry and thermogravimetric analysis (TGA) to measure how well cement paste reacted with SCMs, were good. [1, 26, 27]. Furthermore, the strength, serviceability, and durability of reinforced concrete structures are directly impacted by corrosion of
reinforced steel. Without a doubt, this is the main issue with the durability of concrete structures. The durability of concrete has a major impact on how long reinforced concrete structures last. For instance, more than 18 billion dollars were spent annually in the U.S. alone on infrastructure maintenance and repair [28]. Therefore, it has been proposed that a crucial consideration in determining the service life of reinforced concrete buildings in harsh conditions is the chloride diffusion coefficient of the cementing system [13, 29, 30]. Service life is extended as a result of lower chloride surface concentration. The significance of the research is providing an in-depth comprehension of cement hydration affecting the chloride penetration performance of cement with different sources of FA, such that the concerns on different FA obtained that can result in durability of concrete properties can be mitigated.

2. Materials and Methods

2.1. Materials

Table 1. Chemical and physical properties of OPC and FA.

<table>
<thead>
<tr>
<th>%</th>
<th>OPC</th>
<th>FA1</th>
<th>FA2</th>
<th>FA3</th>
<th>FA4</th>
<th>FA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>17.9</td>
<td>50.4</td>
<td>73.8</td>
<td>27.4</td>
<td>51.7</td>
<td>35.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.45</td>
<td>19.7</td>
<td>17.7</td>
<td>15.8</td>
<td>23.5</td>
<td>14.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.10</td>
<td>3.31</td>
<td>1.92</td>
<td>12.2</td>
<td>14.1</td>
<td>17.9</td>
</tr>
<tr>
<td>CaO</td>
<td>61.2</td>
<td>9.91</td>
<td>0.81</td>
<td>21.7</td>
<td>4.22</td>
<td>16.8</td>
</tr>
<tr>
<td>MgO</td>
<td>0.91</td>
<td>2.23</td>
<td>0.32</td>
<td>2.31</td>
<td>1.52</td>
<td>6.81</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.15</td>
<td>0.69</td>
<td>0.21</td>
<td>6.93</td>
<td>1.85</td>
<td>1.83</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.35</td>
<td>-</td>
<td>0.40</td>
<td>1.72</td>
<td>0.54</td>
<td>1.32</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.27</td>
<td>2.26</td>
<td>0.72</td>
<td>2.01</td>
<td>1.16</td>
<td>1.14</td>
</tr>
<tr>
<td>SiO₂ + Al₂O₃ + Fe₂O₃</td>
<td>73.4</td>
<td>93.4</td>
<td>55.4</td>
<td>89.3</td>
<td>68.4</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>1.92</td>
<td>1.42</td>
<td>1.83</td>
<td>0.22</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td>Class per ASTM C618</td>
<td>-</td>
<td>F</td>
<td>F</td>
<td>C</td>
<td>F</td>
<td>C</td>
</tr>
<tr>
<td>Specific gravity (g/cm³)</td>
<td>3.10</td>
<td>2.20</td>
<td>2.10</td>
<td>2.40</td>
<td>2.50</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Ordinary Portland cement (OPC) of grade 42.5 cement that satisfies the specifications of ASTM C150 [31] was procured locally. Five different FA were accumulated from coal power plants in Myanmar, Thailand, and Indonesia: FA1 from Myanmar, FA2 and FA3 from Thailand, and FA4 and FA5 from Indonesia. Table 1 displays the loss on ignition (LOI), oxide composition as established by X-ray fluorescence analysis, and physical characteristics of the OPC and FA as determined by ASTM C618 standard [32]. Figure 2 illustrates the findings of the particle size distribution obtained through laser diffraction. OPC 17.2 µm, FA1 31.9 µm, FA2 17.9 µm, FA3 27.5 µm, FA4 14.7 µm, and FA5 5.68 µm are their average particle sizes. In contrast to the other FA, the FA5 has extremely fine particles, it is noted. De-ionized water was used throughout the entire study. To determine apparent chloride diffusivity coefficient (Dₐₐ) value, laboratory-grade NaCl, AgNO₃, H₂SO₄, methyl orange, and epoxy resin were utilized. The fine aggregate proportion used in the mortar mix was described. According to ASTM C128 [33] and ASTM C136 [34], fine aggregate has a fineness modulus of 2.95, a specific gravity of 2.61, and a water absorption of 0.66%.

2.2. Proportions, Mixing, and Curing

Cement pastes with 15% FA and a water-to-binder ratio (w/b) of 0.54 for cementitious pastes were mixed for investigating heat of hydration. Although the replacement level is low, in our earlier research, 15% by weight of cement was the optimum replacement level for FA from a variety of sources in ASEAN, which could produce the highest compressive strengths [20]. Curvilinear regression analysis was used to determine the best ratio [20]. Sand-to-binder weight ratio for mortar preparation was 1:2.75, and w/b was 0.54 for chloride diffusion of mortar. Table 2 provides the associated mortar mix design. The necessary amount of water was added after the materials had been dry mixed uniformly in a mechanical mixer. The mixture was continued until it reached a consistent consistency [35]. Following the completion of mixing, the flow table test per ASTM C1437 [36] was performed to evaluate the mortar workability. For the 100-mm cubic molds for the porosity test [37] and standard cylinders for the chloride diffusion [38], the fresh mortars were cast. To prevent moisture loss, a polyethylene covering sheet was placed over the cast specimens. After 24 hours, the specimens were removed from the molds and immersed in water for 180 days [39]. All experiments have been performed in laboratory condition at the controlled temperature of 23°C.

Fig. 1. Outline of the test program.

2.3. Experimental Testing and Analysis

As aforementioned, many involved parameters can significantly influence the chloride resistant characteristics
of blended cementing system containing FA. Five parameters experimentally assessed in this work include:

- % CaO in FA composition,
- particle size of FA,
- degree of reaction of blended system,
- flow of fresh mixture, and
- porosity of hardened system.

The outline of the test program is given in Fig 1. The goal is to investigate the effects of five parameters enlisted above on the $D_s$ value of hardened systems having five different FA from three different ASEAN countries. Their durability is assessed including $D_s$ value, and then service life prediction of are determined. The statistical analysis with sensitivity analysis is performed to rank the importance of the parameters relating to the $D_s$ value.

- Porosity Test

As previously detailed, the porosity of the blended FA cement system was measured because it is one of the most crucial characteristics relating to its durability. The total amount of water from the saturated samples can be used to calculate the porosity of blended cement mortar with FA. 180 days were needed for the cube specimens of 100 × 100 × 100 mm to cure at 23°C. The specimens were oven dried at 105°C until a constant mass loss was seen, and then immersed in water to allow water to entirely fill their gaps. At this 105°C, all physically bound and capillary water in the pastes had evaporated. A scale that is accurate to 0.01 g was used to measure the weights of the saturated and dry samples. Each test involved three duplicate samples. Eq. (1) was used to calculate the porosity values.

$$p = \frac{M_w - M_d}{v \times \rho}$$

where $p$ represents porosity, $M_w$ represents the mass of saturated sample in g, $M_d$ represents the mass of the dry sample in g, $v$ represents the paste volume in cm³, and $\rho$ represents the water density at 20°C in g/cm³.

- Pozzolanic Test on FA

To establish the extent of FA reactivity, the pozzolanic test method was used. This approach was used because it was relatively easy to use and could find the heat release [3]. To maintain a liquid to solid ratio of 0.9, lab-grade Ca(OH)₂ and coal FA were mixed in a mass ratio of 3:1 in 0.5 M KOH solution. Using a mechanical stirrer, sixty grams of paste were mixed for five minutes as instructed in the test procedure [25]. About 10 g of the sample were added to a glass calorimeter ampoule and kept in an isothermal calorimeter (TAM Air, TA instruments) that was retained at a temperature of 40 ± 0.05°C after mixing. Following signal stabilization, the calorimeter’s heat flow data was recorded up to 10 days. Each test involved three duplicate samples. A determination was made of heat flow and heat release normalized to FA amount.

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

<table>
<thead>
<tr>
<th>Mix</th>
<th>OPC</th>
<th>FA1</th>
<th>FA2</th>
<th>FA3</th>
<th>FA4</th>
<th>FA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>525</td>
<td>446</td>
<td>446</td>
<td>446</td>
<td>446</td>
<td>446</td>
</tr>
<tr>
<td>FA</td>
<td>-</td>
<td>79</td>
<td>79</td>
<td>79</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>Sand</td>
<td>1443</td>
<td>1443</td>
<td>1443</td>
<td>1443</td>
<td>1443</td>
<td>1443</td>
</tr>
<tr>
<td>Water</td>
<td>283</td>
<td>283</td>
<td>283</td>
<td>283</td>
<td>283</td>
<td>283</td>
</tr>
</tbody>
</table>

- Isothermal Calorimetry of Blended Cement

To measure the heat released from the inclusion of blended FA/cement paste, isothermal calorimetry in accordance with ASTM C186 [17] was used. First, a mechanical stirrer was used for mixing 60 g of paste for five minutes. Homogenous pastes of approximately 10 g were kept in a glass ampoule and stored at 40 ± 0.05°C in an isothermal calorimeter. Heat release data were created after 7 days. The ratio of the blended FA-cement paste's response to that of the pozzolanic system, as given in Eq. (2) [25], was calculated to determine the degree of FA reactions:

$$\alpha = \frac{Q_{FA}}{Q_{poe}}$$

where $\alpha$ represents the degree of reaction, $Q_{FA}$ represents the FA heat release in J/g in the cementitious pastes after 7 days, whereas $Q_{poe}$ represents the heat release in the pozzolanic test after 10 days. When estimating heat release [40], a filler effect of 5% was used for blended FA-cement pastes. Using Eq. (3) [25], their heat release was determined.

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

where $Q_{FA}$ represents the heat release by FA in J/g, $Q_{cementitious}$ represents the heat release in cement paste including FA in J/g, $Q_{control}$ represents the heat release in the reference cement paste in J/g, and $R$ represents the % of FA replacement.

Isothermal calorimetry was used to investigate the pozzolanic test in order to ascertain the level of FA reaction, and using this method may produce a more straightforward way to measure the level of SCM reaction. Such a test's goal is to establish a link between the pozzolanic test response and the durability and long-term performances of concrete, possibly by measuring the degree of reaction.

- $D_s$ Analysis

The ASTM C1556 standard [38] was followed for conducting the $D_s$ test. Cast cylindrical test specimens having a 100 mm diameter and a 75 mm thickness were
used. Alkaline ions were prevented from leaching from the cast specimens by curing them in a solution saturated with lime. The cured specimens were taken out after a 28-day water curing period in controlled temperature of 23°C. The top and bottom of the dried cylinders were cut into two 25 mm-thick slices. The initial chloride content test was conducted using the first disc, and the chloride diffusion was assessed using the other two discs. Only the top surface of the test specimens was left exposed for the investigation of chloride ion diffusion in one dimension after epoxy resin had been applied to all test specimens' surfaces (from the top surface to the interior). By submerging in a 3% sodium chloride solution, which appears to be equal to the chloride concentration in sea water, the specimens had been subjected to chloride ions for 90 days. Specimens were taken out after immersion and dried in an oven for two days. After that, six layers of specimens were ground into powder at 5 mm intervals to create the specimens. According to ASTM C1152, acid-soluble chloride was utilized to compute each layer’s total chloride concentration [41]. To determine the amount of chloride that is acid-soluble in the powder specimen, the potentiometric titration method was used. The average values from three-disc specimens were used to calculate the amount of chloride in each layer. Using a non-linear regression analysis with a least-squares fit to the total chloride concentration profile, as provided in Eq. (4), the \( D_a \) value of each specimen was established.

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

where \( C(x,t) \) represents the chloride concentration considered at depth \( x \) and exposure period \( t \) in mass\%, \( C_i \) represents the anticipated chloride concentration at the interface between the exposure solution and sample surface using the regression analysis technique in mass\%, \( C_s \) represents the concentration of chloride in the sample prior to immersion in the exposure solution in mass %, \( x \) represents the distance from the exposure surface in meters, \( t \) represents the contact time in seconds, and \( \text{erf} \) is the error function.

- **Service Life Prediction**

Based on the length of exposure, the deterioration process in reinforced concrete structures may be divided into four phases due to the corrosion of steel reinforcement. One of these four processes is the initiation stage. The other three are the propagation stage, the acceleration stage, and the decomposition stage [28]. The service life of a structure was determined by this study using the interval between construction and the first repair. The amount of time needed for the chloride ion from an external source to enter the concrete and build up sufficiently close to the surface of embedded steel. The pH level of the pore solution of concrete drops dropping as the accumulation of chloride ions within this area progresses. The formation of a passivated layer, which protects the embedded steel from corrosion, is made possible by the high pH range of 12 to 13. Once the passivated layer is removed and the pH level is lowered. The corrosion has already begun. The initiation period refers to this time frame. The initial period depends on the transparent cover over the primary steel, the chloride threshold concentration, the quality of the concrete, and exposure conditions such as temperature and pressure. The propagation period is the time required for enough corrosion to build up to cause improper destruction to a building or structural part. To determine the service life of concrete, the corrosion start period and the steady propagation period are added together. Finally, the deterioration and acceleration phases are when the structure rapidly deteriorates, weakens, and loses strength to the point where it is unable to support external loads.

Based on exposure circumstances and material properties, calculating the service life of concrete buildings is achievable. In this investigation, the Life-365 program [42] was utilized to predict both one-dimensional and two-dimensional chloride ion penetration as well as the service life of a structure. Fick’s second law is the basis for this model’s approach, just like the \( D_a \) calculation. Both exposure duration and ambient temperature have an impact on the diffusion mechanisms of chloride ion penetration. The essential input data were loaded into the program to calculate the service life, including diffusion rate at 28 days (\( D_28 \)), diffusion decay index (m), maximum surface chloride level (\( C_0 \)), chloride threshold to commence steel corrosion (\( C_t \)), the mix percentage characteristics, temperature distribution for the entire year, transparent cover to reinforcement, and propagation time.

- **Statistical Analysis**

To examine the impact of experimental parameters on porosity, FA reaction intensity, and chloride diffusion coefficient, analysis of variance (ANOVA) was used. Furthermore, it was determined which factor had the greatest impact on each response variable. To investigate the sample data with two data groups and more than two data groups, an ANOVA was used. The following is the definition of statistical hypotheses:
Null hypothesis ($H_0$): $\mu_1 = \mu_2 = \ldots = \mu_n$ (5)

Alternative hypothesis ($H_a$): $\mu_i \neq \mu_j$ for some $i \neq j$ (6)

The 95% confidence interval was employed in the study. If $H_0$ is rejected, there is a statistically significant difference between the group population means at the 5% level ($p$-value ≤ 0.05). Alternatively, if $H_0$ were not rejected ($p$-value > 0.05), there would be no statistically significant difference at the 5% level between the group population averages.

Following an analysis of the ANOVA, sensitivity analyses were conducted on the parameters that had statistically significant differences on the $D_a$ parameter. Beta coefficients ($\beta$), which are direct measures of each parameter's sensitivity, were used in the regression analyses to fit the data to the response of the model. The coefficient of determination for this linear regression is specified to be more than 60%; however, the analysis of such parameters is excluded. Effect size can be evaluated by calculating the $\beta$ value, which quantifies how much one variable has an impact on another. The factor may have a greater impact on the $D_a$ value of the blended FA-cement systems if the $\beta$ value is high.

3. Results and Discussions

3.1. Flow Value and Porosity

Figure 3 shows the impact of replacing from OPC to 15% FA with a fixed w/b value of 0.54 on the flow of fresh mortar. According to the results, the flow values for each mortar range from 76% to 113%. Within these flow values, all recently cast mortars could be used. Compared to the other types of FA, the FA5 has a better or comparable flow. When compared to coarser particles (OPC, FA1, FA2, FA3, and FA4), these effects increase the lubricant effect, and lower carbon content results in less water absorption. Utilizing FA of sufficient quality, low carbon content, and high fineness can reduce the water requirement of blended FA-cement systems [3].

![Fig. 3. Test results for flow of mortar.](image)

![Fig. 4. Test results for hardened porosity.](image)

After 180 days, Fig. 4 displays the hardened porosity of FA inclusion in cement mixtures. For mixed FA-cement systems with a w/b ratio of 0.54, the range of porosity values is 0.25 to 0.37. The porosity measurements for FA1 and FA2 are the same. In contrast to FA1, which has a lower flow value and a larger average particle size, FA2 has a higher flow value and a smaller average particle size. This may be the effects of LOI and chemical composition. FA5 has a flow value that is 38% bigger than FA3 and 16% more than FA4. However, FA5 has a lower mean particle size. In addition, comparing FA3 with FA4, FA3 has a larger mean particle size and a lower flow value, which possesses the opposite qualities. FA3, FA4, and FA5 have comparable porosity as a result. Moreover, the OPC system has higher porosity values after 180 days. The formation of further C-S-H decreases the porosity of blended FA-cement by 20–29%. Figure 4 indicates that despite the blended FA-cement systems having greater flow values than the OPC systems, the supplement of FA greatly diminishes the porosity of the blended FA-cement systems in comparison to the OPC system. The results are consistent with other investigations [2, 43, 44]. Consequently, the hydration process of blended cement systems depends critically on the particle size of SCMs. In addition, water consumption may be decreased, leading in improved durability performance of finished goods. Apparently, its service life is extendable. This will be discussed in Section 3.6.

3.2. Heat Release of Blended FA-Cement Systems

Figure 5 illustrates the heat flows of blended FA-cement systems at 40 °C for up to 7 days. It should be mentioned that heat flow experiments were also done on all systems at 23 °C; however, there is no notable difference in the curve patterns. This concluded the adoption of blended FA-cement systems in tropical locations may be reliably predicted by the test at 40 °C. The cumulative heat release of cement pastes containing FA at 40 °C after 7 days of testing is represented in Fig. 6. According to the isothermal conductance calorimetry data, FA substitution in cement may have an impact on the quantity of heat released and the heat flow. The OPC
system has a greater peak height (the greatest magnitude of the heat flow) than the blended systems comprised of FA from various sources. Approximately 8 to 10% of the maximum amount of the heat flow is reduced when 15% of the FA is replaced. One of the causes of this phenomenon may be the diluting impact of cement with low C₃S content when cement is replaced with FA [2]. OPC > FA1 > FA3 > FA2 > FA5 > FA4 are the cement pastes that are replaced by FA, ranked from highest to lowest heat release. Combined FA-cement paste heat release values range between 198 and 214 J/g.

In general, as the temperature rises, so does the rate of heat release. Increased rates of hydration and pozzolanic reactions at higher temperatures are one of the causes. The FA-cement systems emit less heat than the OPC system, as predicted. Replacement of a part of OPC with FA reduces the rise in heat emissions. Furthermore, due to the hydration reaction that happens when FA is mixed with cement, more hydration heat is released by the system with the finer FA than the system with the coarser FA.

**Fig. 5.** Heat flow of blended FA-cement systems at 40˚C.

**Fig. 6.** Cumulative heat release after 7 days for blended FA-cement systems at 40˚C.

### 3.3. Heat Release from Pozzolanic Test

Figure 7 shows the total quantity of heat generated by FA from various sources at 40 °C. Isothermal calorimetry, as calculated in Eqs. (2) and (3), is used at 40 °C to evaluate the heat release when FA is combined with Ca(OH)₂ [3]. From greatest to least, the order of heat release at 10 days is FA5 > FA1 > FA3 > FA4 > FA2. A similar level of fineness exists in FA1 and FA3. At 10 days, the heat emission from these systems falls within a limited range, between 21.4 and 21.6 J/g. In comparison to the other FA classes, FA2 and FA4 have the lowest heat release, which is most likely caused by their low CaO content. FA5 exhibited the greatest heat release value. As demonstrated in Fig. 2, the maximum fineness values are found in FA5 with a moderate CaO component. Also, The increase in heat release is believed to be primarily caused by the FA's large specific surface area and high aluminosilicate solubility [45].

**Fig. 7.** Heat release after 10 days for FA at 40˚C.

### 3.4. Degree of Reaction of FA

The degrees of pozzolanic reaction of FA at a temperature of 40 °C are depicted in Fig. 8. The method's specifics are available at [22]. According to the findings, the degree of reactivity of FA levels ranges between 2.6% and 6.5%. According to the heat ratio, which compares the amount of heat generated by FA in cementitious pastes to the amount of heat released by the pozzolanic test, FA2 is higher than FA1, FA3, FA5, and FA4. It is clear that FA4 is the least reactive of the FA types, while FA2 has the highest pozzolanic reactivity. This may be the result of presumptions concerning the filler effect factor. This may also appear if the response to the pozzolanic test is incomplete. In addition, the pozzolanic test for
determining the degree of reactivity of SCMs[22]. According to their findings, the degree of activation of SCMs can be higher than 100, and filler can cause values to be lower. Despite comparable material qualities and chemical compositions, the reactivities of various FA differed, according to [20]. Moreover, it was observed that the reactivities of FA depend on [4]their mineralogical composition, such as their mullite concentration. Consequently, statistical analysis is necessary, as detailed in Section 3.7. It should be noted here that many research studies advocated that the in terms of concrete construction, the early-age performance is more important than the later-age performance which represents lower life cycle costs [46, 47].

3.5. $D_s$ Analysis

After 90 days of exposure to NaCl solution, Fig. 9 exhibits the influence of $D_s$ values on mixed cement mortar with varied FA. The results show that the cement replacement with FA exhibits higher resistance to chloride diffusion than the OPC system. This may be owing to the OPC system’s high porosity and huge number of capillary pores. These factors facilitate the entry of chloride ions into the mortar matrix. The $D_s$ value of the OPC system falls by 50% to 69% when 15% FA is substituted. Owing to the extra-pozzolanic reaction of the FA and the process of pore structure refinement, the chloride diffusion resistance of mortars containing FA has been observed to be much greater. Within the mixed FA-cement systems alone, the $D_s$ values might vary by 19% compared to the OPC. FA3 had the lowest possible $D_s$ value ($4.44 \times 10^{-12}$ m$^2$/s). Chloride diffusion activity is presumed to be affected by both the pore structure and chloride binding capacity.

The reactivity between FA and an alkaline solution in blended FA-cement systems may vary despite the identical material qualities of FA from the same class [48]. Because of the different physical and chemical characteristics of these FA, as well as their pozzolanic reaction, the mortar’s chloride resistance varies. In addition, the outcome can be altered by a variety of other variables, such as the specimen preparation procedure and drilling, as well as the uniformity of FA.

![Graph showing $D_s$ values of mortar with FA](image_url)

Fig. 9. $D_s$ values of mortar with FA.

### 3.6. Service Life

Many studies have employed and suggested Fick's second law of diffusion. [28, 29], was used with Life 365 software to predict how long a building made of reinforced concrete would last in the chloride intensive environments.

The study’s inputs included a severe exposure environment (direct exposure to the marine tidal zone) and the tropical region's annual average temperature profile (Florida, US). According to the manual’s guidelines, concrete cover is assumed at 60 mm and chloride threshold value was established at 0.05% by weight of concrete for the black steel, and the w/b value was decided at 0.54 as per the mix design in Table 1. For the OPC and FA-cement blended systems, all of these characteristics remained the same. In order to investigate the influence of water content, it was also examined how w/b values of 0.54 and 0.44 affected service life. In most cases, mixing proportions employ both the w/b values. The performance of measures like the diffusion decay index ($m$) and the diffusion coefficient after 28 days ($D_{28}$) is shown (see Tables 3 and 4). To anticipate the service life of structural concrete, both components must be present. Note that the $D_{28}$ of concrete changed by w/b, not %FA. The obtained $D_s$ values from Fig. 9 mainly changed the initiation period in the calculation. Their calculations were given in Eqs. (7) and (8).

$$ D_{28} = 1 \times 10^{-12.06+2.4w/cm} $$  \hspace{1cm} (7)

$$ m = 0.2 + (%FA/50 + %slag/70) $$  \hspace{1cm} (8)

The initiation time for blended systems with FA is shown to be longer than that of the OPC system. The impacts on the service life of structural concrete at w/b ratios of 0.54 and 0.44, respectively, are illustrated in Tables 3 and 4. For the same replacement level 15%, changes in w/b value were shown to significantly affect the service life of concrete. All systems have longer service lives as a result of reduced w/b. The propagation period is established at 6 years since the implanted steel type and environmental factors are constant (only the matrix of the cement system is changed). It was obvious, the concrete with FA had longer service lives for both w/b values when the service life values of systems with w/b values of 0.54 and 0.44 were compared. In order to increase the service life of structural concrete, the water content can be decreased by substituting FA for cement. It should be highlighted that the durability of concrete containing FA was significantly enhanced compared to OPC concrete. This is also attributable to the pozzolanic properties of FA.

In addition, Fig. 10 illustrates, under the same exposure circumstances and replacement levels, the effect of the w/b value on the service life of FA-cement concrete. The results show that the durability of concrete changes a lot when the w/b ratio of mixed FA-cement systems goes down. When the same w/b ratio is used for both OPC and blended concrete, the durability of blended
concrete with FA is much better than that of OPC concrete. The blended FA-cement systems with a w/b value of 0.54 have a projected service life that is around 8% longer than the OPC and roughly 13% longer than the system with a w/b value of 0.44. Since the experimental D_{50} values of the different kinds of FA concrete are so close to each other and the same diffusion m value is used to figure out the mix proportions, the results of concrete made with different kinds of FA are not that different.

Table 3. The effect of FA on service life (w/b = 0.54).

<table>
<thead>
<tr>
<th>Samples</th>
<th>OPC</th>
<th>FA1</th>
<th>FA2</th>
<th>FA3</th>
<th>FA4</th>
<th>FA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{50} (x 10^{-11} m^2/s)</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>m</td>
<td>0.2</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Ct %wt.</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Initiation period (Years)</td>
<td>4.2</td>
<td>4.8</td>
<td>4.9</td>
<td>5.0</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Propagation period (Years)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Service life (Years)</td>
<td>10.2</td>
<td>10.8</td>
<td>10.9</td>
<td>11.0</td>
<td>10.0</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The predictions of this study for service life are contrasted with those made by Mahima et al. [25]. Although the concrete mixture proportions and concrete cover depth served as the foundation for prediction models of earlier studies, findings of those studies diverged from those of this one. According to Nath et al. [26], for 20% FA containing structural concrete with 30 mm and 50 mm thickness cover, the period to commence corrosion in reinforcing steel was around 6.6 years and 16.4 years, respectively. In this study, however, for a w/b value of 0.54 and a w/b value of 0.44, respectively, the expected range for the estimate of the beginning time of 15% FA substitute concrete with 60 mm cover thickness is 4.0–5.0 years and 5.9–7.3 years, respectively. Due to mix proportions (such as a lower percentage of FA replacement and the inclusion of coarse aggregate), cover thickness, sort of galvanized steel, and the D_{50} value, the service life presented here is reduced. Although FA type can be different, the effects of service life is more dependent on the w/c and the presence of FA in cement mixtures. Hence, this study can be inferred that the early-age properties can significantly depend on the FA type, but not for the durability one.

Table 4. The effect of FA on service life (w/b = 0.44).

<table>
<thead>
<tr>
<th>Samples</th>
<th>OPC</th>
<th>FA1</th>
<th>FA2</th>
<th>FA3</th>
<th>FA4</th>
<th>FA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{50} (x 10^{-11} m^2/s)</td>
<td>9.91</td>
<td>9.91</td>
<td>9.91</td>
<td>9.91</td>
<td>9.91</td>
<td>9.91</td>
</tr>
<tr>
<td>m</td>
<td>0.2</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Ct %wt.</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Initiation period (years)</td>
<td>5.8</td>
<td>6.9</td>
<td>7.1</td>
<td>7.3</td>
<td>5.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Propagation period (years)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Service life (years)</td>
<td>11.8</td>
<td>12.9</td>
<td>13.1</td>
<td>13.3</td>
<td>11.9</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Fig. 10. Serviceability of mixed FA concrete with various w/b values.

Table 5. Results summary for ANOVA and β.

<table>
<thead>
<tr>
<th>ANOVA</th>
<th>Source</th>
<th>p-value</th>
<th>β (x 10^{-13})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO%</td>
<td>**</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>Particle size</td>
<td>**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Degree of reaction</td>
<td>**</td>
<td>6.03</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>**</td>
<td>8.20</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions

The study presented experimentally assessing the influence of FA from various sources in ASEAN on flow, particle size, flow of a fresh mixture, degree of reactivity of blended FA-cement paste, and hardened porosity. Also, service lives of FA mortar systems were numerically predicted. The conclusions can be made as follows:

- When FA was added to blended systems, the overall porosity went down compared to OPC. This was because FA had better pozzolanic performance, which led to better pore refinement.
- Based on the findings of the pozzolanic test, the degrees of reactivity of various sources of FA with comparable material characteristics exhibited varied reactivities.
- By replacing 15% FA the D_s value was significantly decreased almost 70%.
- The predicted service life was longer up to 13% with 15% FA replacement. When FA was added to concrete, it made the concrete stronger and more useful in situations where there was a lot of chloride.
- FA from different sources gave the mixed system a strong pozzolanic reaction at the microscale level and made it easy to consolidate the fresh mixes. This led to less porosity in the hardened systems, which can stop chloride ions from getting into the matrix at the macroscale level. Both chemo-physical methods and multiscale structures boost their endurance greatly.
- Porosity can be the key to influence durability the most. The FA degree of reaction and %CaO can also impacted on durability mainly affected hydration and pozzolanic reactions. While the particle size and flow of fresh mortar was less sensitive to durability.

This work provides comprehensive knowledge for overcoming the practical challenges of implementing FA in existing mortar. 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.

Acknowledgement

The authors would like to thank Dr. Warangkana Saengsoy, SIIT, Thammasat University, Thailand, and the Research and Innovation Center, SCG, Thailand, for their collaboration and support.

Funding Source

This research was funded financially by the Asian Scholarship Program and The Second Century Fund (C2F) from Chulalongkorn University.

Conflicts of Interest

The authors of this study declare that they don't know of any financial or personal conflicts that could have affected the research presented here.

Data Availability

This article has all the information that was found or analyzed during this investigation.

References


Thwe Thwe Win was born in Allakapa Village, Myinmu Township, Sagaing Division, Myanmar in 1992. She received the B.Eng. degree in civil engineering from Technological University Sagaing, Myanmar in 2013, M.Eng. degree in civil engineering from Mandalay Technological University, Myanmar in 2016 and she earned the Ph.D. in civil engineering in Chulalongkorn University, Bangkok, Thailand, from 2018 to present.

From 2016 to 2018, she worked as a concrete engineer in Sika Myanmar Company Limited. She has been a postdoc researcher with Department of Architecture, Chulalongkorn University. She is the author of two international conference papers. Her research interests include predicting the life-span behaviour and performance of concrete structure, sustainability and construction building materials.

Dr. Win got a scholarship award for excellence in 2015 WFK-TPC (Techno Peace Corps) Project: “Study on Hot Weather Concrete Replaces the Pozzolan Powder, Myanmar”, and the graduate scholarship program for ASEAN countries at Chulalongkorn University.

Rungrawee Wattanapornprom was born in Bangkok, Thailand in 1987. She received the B.Eng. in civil engineering from Chulalongkorn University, Bangkok and the B.B.A., in construction management from Sukhothai Thammathirat Open University, Nonthaburi, Thailand, in 2009. In 2012, she received M.Sc. in technopreneurship and innovation management from Chulalongkorn University, Thailand and D.Eng. in civil engineering from the University of Tokyo, Japan, in 2016.

From 2009 to 2012, she was an engineer in the product development department in Concrete Product and Aggregate Company Co. Ltd (CPAC) under Siam Cement Group (SCG), Thailand. From 2016 to 2018, she was a postdoctoral researcher at the University of Tokyo, Japan. From 2018 to 2019, she was a postdoctoral researcher in the Innovative Construction Materials Research Unit of Chulalongkorn University. She is currently a managing director at Print A-Like Co. Ltd and an innovation and marketing consultant at Thaioccean Industries Co., Ltd, Thailand. Her research interests include the innovation of construction materials, durability of concrete and recycled materials on concrete properties.
Lapyote Prasittisopin was born in Bangkok, Thailand in 1983. He earned B.S. degree in chemical engineer from Chulalongkorn University, Bangkok in 2006, M.S degree in material science and Ph.D. in civil engineering from Oregon State University, USA in 2012. He also earned LL.B. degree in Law from Sukhothai Thammathirat Open University, Thailand in 2021.

From 2007 to 2012, he was a research and teaching assistant with the School of Wood Science and Engineering, College of Forestry and School of Civil Engineering and Construction Management, College of Engineering at Oregon State University. After graduating, he was working in O.H. Hinsdale Wave Research Laboratory, USA and Siam Research and Innovation company, Siam Cement Group, Thailand. He is now an assistant professor with Department of Architecture, Chulalongkorn University. He held 12 patents and published more than 50 technical articles. His research interests include materiality, sustainability, materiality, and architectural engineering.

Withit Pansuk was born in Bangkok, Thailand in 1981. He received the B.Eng. in civil engineering from Chulalongkorn University, Thailand, in 2002 and the M.Eng. and Ph.D. in structural engineering from Hokkaido University, Japan, in 2007.

From 2008, he was a lecturer in civil engineering at the Faculty of Engineering, Chulalongkorn University. Since 2021, he has been a full professor with Civil Engineering Department, Faculty of Engineering, Chulalongkorn University. He is one of the founding members of the Center of Excellence in Innovative Construction Materials of Chulalongkorn University. His research interests include protection of construction materials, design, and construction of 3-D printed structures and investigation of infrastructures by UAVs & Big Data Analysis.

Phoonsak Pheinsusom was born in Bangkok, Thailand in 1961. He received the B.Eng. in civil engineering from Chulalongkorn University, Thailand, in 1983 and the M.Eng. and Ph.D. in civil engineering from Tokyo University, Japan, in 1988.

From 1991 to present, he was an associate professor with the Civil Engineering Department, Faculty of Engineering, Chulalongkorn University. His research interests include structural engineering, building and bridge design.