# Characterization of Cement Pastes Incorporating Various Fly Ash Contents

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**Abstract.** Designing construction and building material containing recyclable resources have become a potential demand for sustainable development. The main objective of the research is to create fly ash cement paste (FCP), which incorporated various proportions of fly ash (FA) to replace Portland cement (PC) for ecological purposes. In this research, the dry density, compressive strength, water absorption, drying shrinkage, and chloride ion penetration (CIP) examinations were performed on mix designs assembled from various FA fractions (0, 20, 40, 60, and 80%) as a partial substitution of PC. Based on the laboratory findings, incorporating 20% FA in FCP formulations can achieve comparable bearing capacity at all cured ages as a reference mix. Among all FCP mixtures, specimens containing 20% FA exhibited the greatest compressive strength value of 70.92 MPa at 120 days, while the 80% FA samples exhibited the weakest load-carrying capacity of 39.28 MPa. The finding was consistent with the test results of the dry density and water absorption experiments since the optimized engineering characteristics may be attained by keeping the FA consumption below 20%. In addition, the ion charging conveyed across the FCP mixture can be mitigated by utilizing an adequate FA concentration (20%), contributing to an equivalent in resistivity compared to the reference mixture. The analysis findings also demonstrated a strong correlation between water absorption and CIP levels because a lower porosity value can lead to a denser framework and restrict chloride ions from migrating via the specimen. Besides, replacing the PC with high-volume FA was beneficial in reducing the drying shrinkage of the FCP. Overall, optimizing the FA content in FCP below 20% promotes ecological growth objectives while maintaining acceptable performance, highlighting the positive impact of proper FA utilization in achieving a balance between ecological considerations and desired engineering properties.

**Keywords:** Fly ash · Cement paste · Compressive strength · Drying shrinkage · Water absorption · Chloride ion penetration


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# 1 Introduction

Driven by globalization, a greater amount of greenhouse gas emissions in general and in particular carbon dioxide ($CO_2$) emissions are produced. These emissions account for climate change negatively around the world that push many countries, particularly Vietnam, to face planet warming and high sea level rise. Climate Central's report stated that, by 2050, the major land of the Red River and Mekong River Delta provinces in Vietnam will be sunk by seawater. Consequently, above 31 million local people in these areas may be influenced [1]. In order to decrease global warming and climate change, reducing $CO_2$ emissions is a priority task. Zhang and Wang [2] claimed that the building materials manufacturing stage with a 72.89% ratio is the main one to generate $CO_2$ emissions, which cement production attributed to 40.69%. Hence, to reduce $CO_2$ emissions in the construction industry, sustainable measures to replace cement with supplementary cementitious materials (SCM) are imperative event. Fly ash (FA) is a by-product generated during the burning of coal in a thermal power plant, also called SCM. It has a spherical shape with a particle size being generally finer than Portland cement (PC) and the major composition involves silica ($SiO_2$), ferric oxide ($Fe_2O_3$), and alumina ($Al_2O_3$) [3]. Therefore, FA widely uses to replace PC in concrete, mortar, and others. In particular, in Vietnam, the annual released FA amount is approximately 12.2 million tons but only 30% of this amount has been recycled [4]. To eliminate $CO_2$ emissions and limit environmental issues, a large remaining FA amount must be recycled and reused in several construction material productions. However, the use of a high volume of FA (at least 50%) in the mixture also releases some shortcomings. One drawback is to increase water absorption and reduces the durability of cement-based materials [5]. Moreover, by using the high volume of FA in cement paste, Park and Choi [6] find that the early compressive strength of samples can be achieved by increasing the fineness of FA particles.

Many studies have investigated the effect of FA on the construction material properties by using FA to partially replace cement in concrete and cement paste up to 50% and the ultra-high FA content (up to 80%) needs to be seriously considered to exploit the abundant FA source. Therefore, to clarify the role of FA, this study analyzed FA cement paste (FCP) characteristics by using the FA replacement from 20% up to 80% by mass along with a reference sample. Five cement paste samples with FA content of 0, 20, 40, 60, and 80% were set up. The experimental works like measuring and testing these samples are to define the influence of FA on dry density, compressive strength, drying shrinkage, water absorption, and chloride ion penetration (CIP) of the FCP. In addition, the correlation between dry density and compressive strength and the correlation between CIP and water absorption were analyzed.

# 2 Experimental Details

## 2.1 Materials and Mixture Proportions

The FCP samples used in this study were prepared using PC (type I) and low-calcium FA with specific gravities of 3.07 and 2.43, respectively. Table 1 shows the primary chemical compositions of PC and FA. According to ASTM C618 [7], FA with a CaO content of 5.46% and $SiO_2 + Al_2O_3 + Fe_2O_3$ content of 90.21% corresponds to class F.

**Table 1.** Characteristics of PC and FA

| Materials | Specific gravity | Compositions (% by mass) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $SO_3$ | Loss on ignition | Others |
| PC | 3.07 | 20.49 | 4.88 | 4.34 | 63.46 | 1.43 | 1.89 | 2.52 | 0.99 |
| FA | 2.43 | 57.14 | 16.12 | 16.95 | 5.46 | 0.43 | 0.38 | 2.34 | 1.18 |

Table 2 shows the mixture proportions of the FCP specimens fabricated that were used in the experiments in line with the scope of this study. The water-to-powder (w/p) ratio was selected at 0.3 after several preliminary trials, and five FA contents (0, 20, 40, 60, 80%) related to the PC replacement weight were used.

**Table 2.** Mixture proportions of FCP samples

| Mixtures | w/p | PC (wt. %) | FA (wt. %) | PC (kg/m$^3$) | FA (kg/m$^3$) | Water (kg/m$^3$) |
|---|---|---|---|---|---|---|
| C10F0 | 0.3 | 100 | 0 | 1597 | 0 | 479 |
| C8F2 | | 80 | 20 | 1244 | 311 | 467 |
| C6F4 | | 60 | 40 | 909 | 606 | 455 |
| C4F6 | | 40 | 60 | 591 | 886 | 443 |
| C2F8 | | 20 | 80 | 288 | 1153 | 432 |

## 2.2 Sample Preparation and Test Methods

PC and FA were mixed by a mechanical mixer for approximately 1 min to prepare FCP samples in the laboratory. And then, water was gradually added to this dry mixture, and it was continuously mixed for 5 min to obtain a homogeneous mixture. After that, FCP samples were cast for different test programs. The hardened FCP samples were checked for dry density and compressive strength at 28, 56, and 120 days of curing age according to the guidelines of ASTM C138 [8] and ASTM C109 [9], respectively, using the 50 × 50 × 50 mm cubic samples. The compressive strength test is crucial for assessing the strength and structural integrity of the hardened FCP samples, providing valuable insights into their durability and suitability for various applications. It is noted that to assess the dry density of the hardened FCP samples, a modified adaptation of ASTM C138, a standard commonly used for measuring the density of concrete, was employed. Given the similarities between FCP and concrete as cementitious materials, this standard was deemed suitable for evaluating the dry density of the FCP samples in this study [10]. The drying shrinkage of the FCP was measured on the 25 × 25 × 250 mm prismatic samples at 7, 14, 28, 56, and 120 days following the ASTM C596 [11]. The drying shrinkage test is of utmost importance as it enables the assessment of the potential volume change and the cracking tendency of FCP samples, aiding in determining their dimensional stability and long-term durability. The water absorption test was measured on 50 × 50 × 50 mm cubic samples at 28, 56, and 120 days in accordance with ASTM C1403 [12]. The water absorption test is essential for evaluating the porous nature of the FCP samples, allowing us to assess their resistance to water penetration and potential durability in various environments. The CIP test was performed at 28, 56, and 120 days following ASTM C1202 [13] using samples of 100 mm in diameter and 50 mm in thickness. The CIP test is of significant importance as it helps evaluate the resistance of FCP samples to chloride ion ingress, which is crucial for assessing their durability in chloride-rich environments and predicting their long-term performance. Finally, the relationship between CIP and water absorption was also analyzed.

## 3 Results and Discussion

### 3.1 Dry Density

Figure 1 summarizes the dry density among various FCP mix designs considering three stages of curing ages (28, 56, and 120 days). The addition of FA leads to the gradual drop in the dry density of the FCP mixture since the specific density of the FA particle is lower than that of the PC (see Table 1) and thereby, contributing to the reduced weight of samples. The curing age also plays a major role in the dry density of the hardened FCP mixtures as shown in the slight increase in all conditions. At the curing age of 28 days, the dry density of mix C10F0, C8F2, C6F4, C4F6, and C2F8 is 1926, 1917, 1871, 1790, and 1762 kg/m$^3$, respectively, while this value found in the 120 days circumstance is 1994, 1968, 1955, 1842, and 1814, respectively. The long-term development of hydrated products in the system contributes to the formation of denser structures, which in turn can impact the dry density of the material. This relationship between long-term hydration and density is an important factor to consider when analyzing the dry density of the samples [14]. Further investigations in the following discussions will clarify this mechanism.

### 3.2 Compressive Strength

Figure 2 illustrates how FA modification affected the load-bearing capacity of FCP. It was revealed that the FCP samples with 20% FA exhibited comparable compressive strength values concerning the standard samples with 0% FA once all curing processes were taken into account (FA00 mix). The no FA samples achieved the highest load-carrying performance throughout all curing ages. When more FA component (especially, at 60 and 80%) was added to the mixture, the strength of the FCP dropped gradually. For instance, the 28-day compressive strength value reduces from 67.14 to 30.33 MPa (54.83%) with a FA ratio ranging from 0 to 80% (C2F8 mixes), and greater strengths drop occurred from higher FA concentrations (C4F6 and C2F8 mixtures). However,

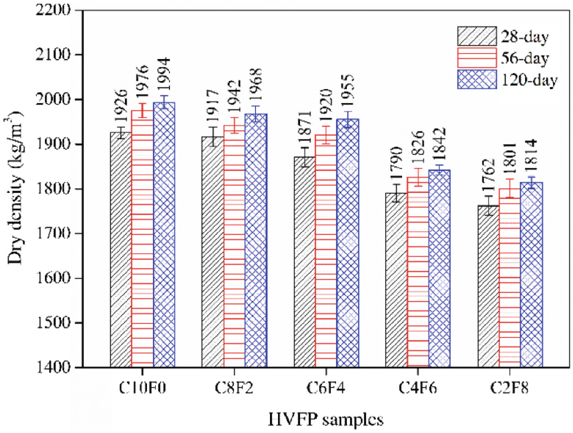


**Fig. 1.** Dry density of FCP samples

after a prolonged curing period, samples containing 20% FA experienced a 13.82% improvement in carrying capacity through 120 cured days, whereas a sample with 80% FA experienced a 29.5% increase. Furthermore, the results indicated that the compressive strength of FCP combinations had a mean difference throughout all samples of lower than 5%. As depicted in Fig. 3, the aforementioned strength drop may be attributable to the dry density of the mixture. The dry density and strength characteristics of FCP demonstrated a notable link, and low-density mixtures with higher porosity will acquire poor load-carrying ability. Besides, the compressive strength decreased significantly when the FA content was relatively high (from 60 to 80% by mass), as the pozzolanic activity was neglective in the initial stages, and using too much FA would impose a negative effect. In general, the FA supplementation under an accepted level (i.e., 20%) can promote the consumption of this by-product material while keeping the strength gain of paste at an acceptable level.

### 3.3 Drying Shrinkage

Figure 4 depicts the changes in length observed in different FCP samples over 120 days. Generally, the length variations increased during the curing period, especially in the initial 28 days. The length of the FCP samples exhibited fluctuations corresponding to the amount of FA used. Shrinkage in the solidified samples containing FA suffered greatly from the dry shrinkage. Particularly, the initial 7 day length change of the reference samples was about 13.3, 24.4, 87.7, and 106.4% higher than that of the FCP samples containing 20, 40, 60, and 80% FA addition, respectively. In a related manner, when compared to the reference C10F0 mix, the C2F8 sample demonstrated a significant decrease in length fluctuations, varying from 106.4 to 43.5% between 7 and 120 days. This research confirms that incorporating an appropriate amount of FA can achieve comparable levels of drying shrinkage to that of the full-use cement mixture. The reduced drying shrinkage observed in the FA-incorporated samples can be attributed to the lower moisture response of FA compared to cement. Specifically, the rapid formation of proper

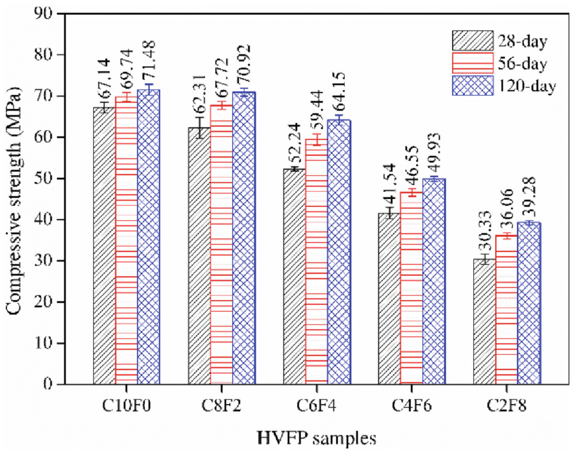


**Fig. 2.** Compressive strength of FCP samples

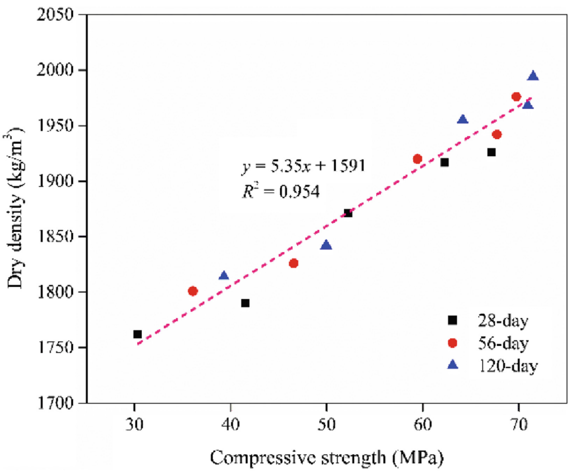


**Fig. 3.** Correlation between dry density and compressive strength of FCP samples

cement hydration products in the presence of FA leads to a more solid internal structure, which effectively restricts free water intrusion and evaporation. As a result, the drying shrinkage of the samples is reduced [14]. In order to further clarify the impact of FA on the electrokinetic properties of hydration products, it is important to note that the presence of FA can modify the surface charge and colloidal behavior of cement particles, potentially influencing the solidification process and resulting in a more compact internal structure that restricts water movement and reduces drying shrinkage [15].

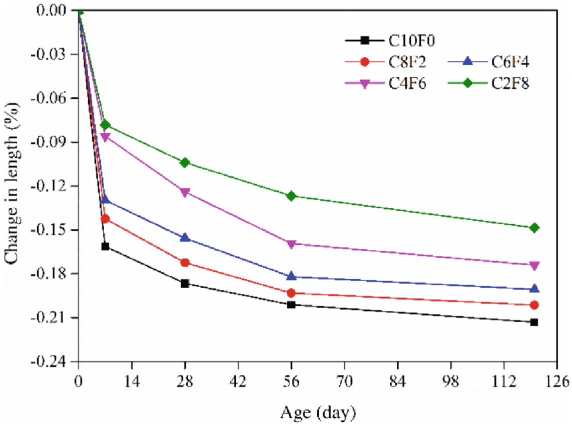


**Fig. 4.** Drying shrinkage of FCP samples

### 3.4 Water Absorption

Figure 5 presents the water absorption of the FCP specimens. While the rate of absorption in reference specimens was relatively low at 28 days (8.61%), this property was quite significant for the FCP samples within the FA group of 20–80%, ranging from 8.94 to 11.78%. As illustrated in Fig. 5, adding FA up to 60 and 80% may cause a looser structure due to the insufficient pozzolanic reaction, which enabled the C4F6 and C2F8 specimens to suffer from moisture penetration [16]. This trend is also spotted in the compressive strength characteristics of the samples (see Fig. 2). Considering the curing effect, at 56 days, the water absorption of the reference mix was 8.19%, while the 20–60% FA mix yielded a value of 8.63, 9.07, and 9.56%, respectively. The water absorption rate remained the equivalent tendency regardless of the required curing ages. The higher porosity observed in concrete with a high concentration of FA can be attributed to the slower pozzolanic reaction of FA particles compared to cement particles. FA, being pozzolanic in nature, requires additional time to react with water and form hydrates [17, 18]. This slower reaction rate leads to the formation of fewer hydration products compared to mixtures with lower FA content, such as C10F0 and C8F2. Consequently, the increased porosity in the concrete allows for the retention of more water, ultimately contributing to higher water absorption properties. Additionally, after a proper curing period, all specimens display a reduction in water absorption capacity. It was recognized that the rapid formation of hydrated product in the origin cement will cover such gaps occupied by mixing water, reducing the material's porosity. Generally, the incorporation of FA decreased the porosity and expedited the phase transformation when the proper reaction time was provided, especially after 120 days. In such circumstances, portlandite is absorbed by the pozzolanic reaction, which results in the creation of extra C-S-H and a reduction in the connectivity of the pore network [5]. This can be described as the permeability of the specimen gradually decreasing after the lengthened cure time.

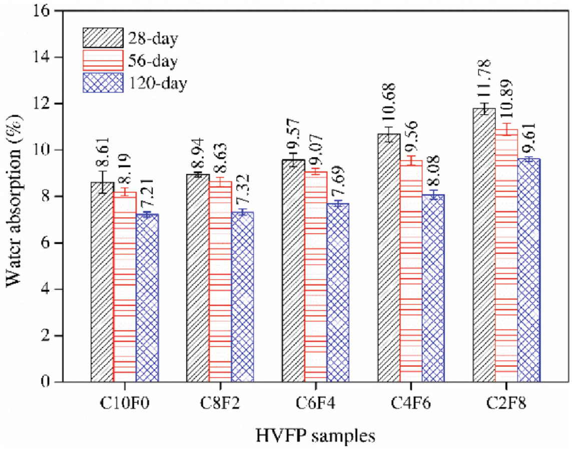


**Fig. 5.** Water absorption of FCP samples

## 3.5 Chloride Ion Penetration

Figure 6 displays the incremental charge density of chloride ions in the FCP samples. In general, the reference paste displayed a substantially low charge distribution at every hardening age when compared to the mixtures containing FA. The CIP value of the 28 day reference mix increased significantly from 449 to 546, 710, 873, and 1392 Coulombs for mixes C8F2, C6F4, C4F6, and C2F8, respectively. The evidence confirms that the ion charge transferred via the reference mixture was greater than that of the FA-enhanced mixtures. Additionally, the water absorption rate rises significantly as the FA content exceeded 20%, enabling a larger number of chloride ions to infiltrate the materials. Figure 7 illustrates a viable link between the ion stream paths and water absorption in FCP. In the reference mix (C10F0), the entire sample was believed to be shielded by the thicker microstructure in comparison to the FA sample due to the formation of a denser hydrated product [19], thus, greater CIP penetrating resistance can be ensured in the reference sample. However, samples with the appropriate amount of FA showed resistance to chloride ion migration after an extended hardening period. In particular, the C8F2, C6F4, C4F6, and C2F8 experienced a reduced CIP transmitting level of 23.8, 25.7, 25.6, and 29.9% at 120 days versus the 28 days age group. This chloride resistivity improvement can be attributed to the tough structural constraint resulting from enhanced tortuosity, which lowers the pore capillary system's conductance and decreases capillary surface adsorption [20]. The replacement of the internal pores with FA progressively reduces the size of the pores, thereby increasing the intricacy of the capillary network [21]. As a consequence, once FA quantity was given reasonable time to cure, chloride ionic dispersion was diminished.

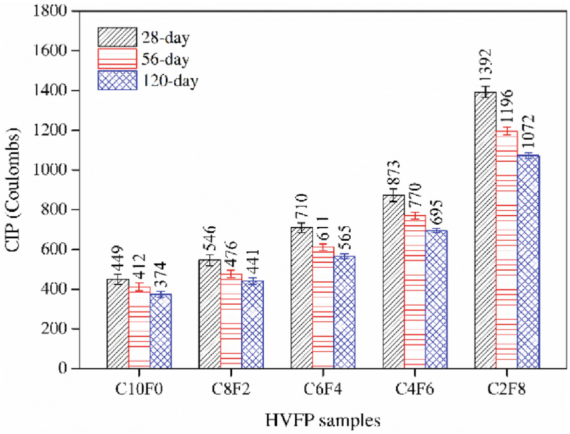


**Fig. 6.** CIP values of FCP samples

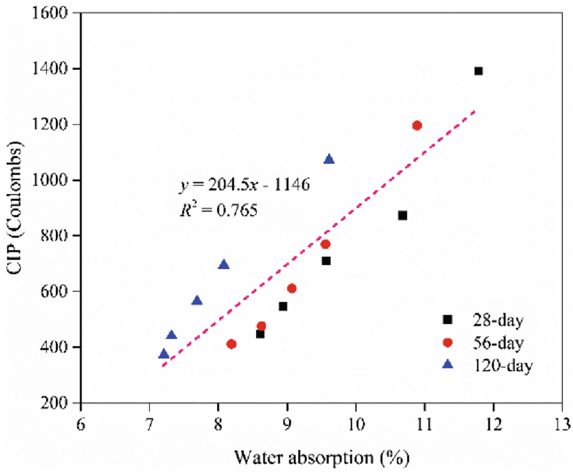


**Fig. 7.** Correlation between CIP and water absorption of FCP samples

## 4 Conclusions

This study aims to investigate the potential impacts of high-volume FA on the characteristic of FCP mixes. Based on the research analysis, the below conclusions can be drawn:

1. When the FA levels were maintained at an optimized level of ≤20%, the inclusion of FA can achieve the equivalent dry density to that of the reference mixture. At 28 days, the cement paste containing 20% FA had a dry density of around 1917 kg/m$^3$, whereas the 80% FA sample suffered a great drop to 1762 kg/m$^3$.

2. The addition of 20–80% FA reduced the bearing capacity of the FCP throughout all curing ages. The compressive strength of the FCP declined sharply as FA contents were designed at higher than 60%. At 120 days, the FCP sample containing 20% FA achieved the highest compressive strength (70.92 MPa) among all FA-modified mixtures, whereas the 80% FA sample experienced the lowest load-carrying ability (39.28 MPa).
3. The inclusion of more FA increased water absorption of FCP samples. This result was in line with the decline in the compressive strength value. On the other hand, using FA as a cement replacement, especially at high levels, remarkably reduced the drying shrinkage of the paste samples. After 120 days, the C2F8 sample obtained the lowest length change value of −0.15%, which was about 43.5% lower than that of the C10F0 sample.
4. The laboratory data suggest that by using an appropriate FA concentration of 20% by weight of cement, the ion charge conveyed across the specimen containing FA was comparable to the reference mix. This study also found that the water absorption and the CIP levels of FCP samples are strongly correlated because a reduced porosity value can prevent chloride ions from diffusing through the mixture.

In summary, the research results demonstrated that incorporating 20% FA represents the optimum level for ensuring the quality of mixes while promoting the consumption of industrial by-products.

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