

THE INFLUENCE OF HIGH-VOLUME FLY ASH CONTENT ON MECHANICAL PROPERTIES OF CEMENT PASTE

ẢNH HƯỞNG CỦA HÀM LƯỢNG TRO BAY CAO ĐẾN CÁC TÍNH CHẤT CƠ LÝ CỦA HỒ XI MĂNG

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Abstract - Investigation into the reuse of industrial by-products for producing eco-friendly construction materials has still received much attention from research scholars around the world. This study investigates the influence of fly ash (FA) content as a cement replacement on the fresh and hardened properties of cement paste. FA was used to substitute Portland cement at different levels of 0 – 80% by weight. Results show that, increasing the FA content resulted in better flowability and longer setting time of the mixtures. However, the samples with higher FA content exhibited lower compressive strength and higher water absorption. Importantly, the inclusion of FA reduced the drying shrinkage of the hardened paste. At 28 days, the 80% FA samples had values of compressive strength, water absorption, and change in length of about 45.2, 136.82, and 55.7% of the corresponding values of the FA-free sample. Thus, the quantity of FA should be selected based on specific application purposes.

Key words - High-volume fly ash; cement paste; flowability; setting time; water absorption; compressive strength; drying shrinkage

1. Introduction

Reducing carbon emissions is a vital task in order to reduce global warming and climate change trends. It was reported that cement production discharges approximately 9.5% of total global human CO₂ emissions [1–3]. Indeed, cement production still increases all over the world, and it is estimated that the CO₂ emission from the cement industry will also increase [4, 5]. One of the attempts to reduce CO₂ emissions is to use by-product materials. A previous study reported that concrete containing by-products of up to 30% could satisfy both national and international requirements [6]. Fly ash (FA) is a by-product generated from thermal power plants, which is also known as a supplementary cementitious material (SCM). Commonly, FA has a spherical shape with a particle size of less than 0.075 mm, and the major chemical components of FA are silica, alumina, iron oxide, and calcium [7]. Based on the chemical compositions, FA is generally classified into two classes, including classes F and C, in which class F has more than 70% (by weight) of SiO₂ + Al₂O₃ + Fe₂O₃. So far, FA has been widely used to replace Portland cement in concrete, mortar, and paste samples [8, 9]. It is reported that the annual amount of FA discharge is around 900 million [10], and approximately 35% of this amount has been recycled [11]. In Vietnam, the annual amount of FA discharged is about 12.2 million, whereas only 30% of such amount has been treated as

Tóm tắt - Việc nghiên cứu tái sử dụng phụ phẩm công nghiệp để sản xuất vật liệu xây dựng thân thiện với môi trường rất được quan tâm bởi nhiều nhà nghiên cứu trên thế giới. Nghiên cứu đánh giá các ảnh hưởng của hàm lượng tro bay (FA) dùng như một phụ gia khoáng thay thế xi măng đến các tính chất kỹ thuật của hồ xi măng. FA được sử dụng thay thế xi măng poóc lăng từ 0 – 80% theo khối lượng. Kết quả cho thấy, tăng hàm lượng FA làm cho hỗn hợp có khả năng chảy tốt hơn nhưng thời gian đông kết lâu hơn. Tuy nhiên, các mẫu chứa nhiều FA hơn có cường độ chịu nén thấp hơn và độ hút nước cao hơn. Việc thêm FA làm giảm đáng kể độ co khô của hồ xi măng. Ở 28 ngày, các mẫu chứa 80% FA có giá trị cường độ chịu nén, độ hút nước và độ thay đổi chiều dài bằng khoảng 45,2%, 136,8% và 55,7% so với các giá trị tương ứng của mẫu không có FA. Do đó, tùy vào mục đích ứng dụng cụ thể mà chọn hàm lượng FA hợp lý.

Từ khóa - Hàm lượng tro bay cao; hồ xi măng; độ lưu động; thời gian đông kết; độ hút nước; cường độ chịu nén; độ co khô

either SCM or other purposes [12, 13]. The remaining amount is generally used as landfilling, which causes many environmental problems. Therefore, finding suitable ways to treat the abundant FA is extremely important for a cleaner environment.

To reduce the CO₂ emission and limit the above-mentioned environmental problems, a high amount of FA has been employed in the production of various construction materials (i.e., concrete, mortar, and paste). The addition of FA in these mixtures is governed by cement hydration and the pozzolanic between cement hydrates and FA particles. The products of pozzolanic reactions such as C–S–H and C–A–H could enhance concrete properties [14, 15]. Besides, the use of a high volume of FA in concrete could also enhance the workability and drying shrinkage of concrete considerably. Nevertheless, the excess content of FA not only leads to a reduction in early-strength evolution but also negatively affects other mechanical properties as well as induces a porous microstructure [6, 16]. Nath and Sarker [17] previously reported that the drying shrinkage of concrete containing 30 – 40% FA was smaller than that of concrete without FA inclusion. At the age of 28 days, 45% FA replacement caused lower porosity as well as pore size of concrete [18]. A recent study on the use of high-volume FA (up to 50%) in cement pastes found that the early compressive strength of paste samples can be achieved by

increasing the fineness of FA particles [19]. Besides, Tan et al. [20] indicated that the compressive strength as well as the microstructure of paste samples containing up to 50% FA could be improved by using wet ground cement.

Literature review shows that almost previous studies used FA to partially replace cement in both cement paste and concrete up to 50%, and there is a limited study using a higher FA content of above 50%. Thus, to fill the gap in the literature on the use of high-volume FA in cement paste systems, this study utilized the high-volume of FA substitution up to 80% in cement paste systems. The effects of high-volume FA on flowability, setting time, water absorption, compressive strength, and drying shrinkage of the cement pastes were extensively investigated through experimental works. It is well-known that the characteristics of raw materials greatly influence the performance of final products. Therefore, the use of locally available raw materials (i.e., cement and FA) is meaningful.

2. Materials and experimental programs

2.1. Materials

The paste samples used in this study were prepared using blended Portland cement of grade 40 (Figure 1a) and FA of class F (Figure 1b) with specific gravities of 3.07 and 2.43, respectively.

Table 1. Chemical composition of cement and FA

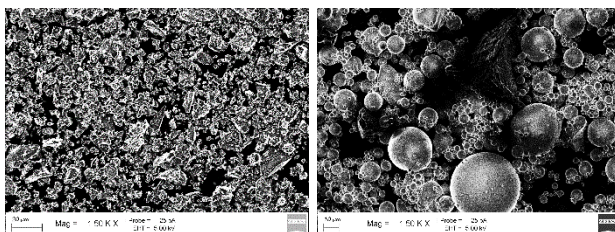
Compositions (wt.%)	Cement	FA
SiO ₂	22.4	44.8
Al ₂ O ₃	5.4	21.5
Fe ₂ O ₃	4.1	19.0
MgO	2.0	1.6
CaO	55.7	1.7
SO ₃	2.4	1.1
Loss on ignition	2.6	2.3
Others	5.4	8.0



(a) Cement

(b) FA

Figure 1. Raw materials used in the study



(a) Cement

(b) FA

Figure 2. SEM micrographs of cement and FA

The primary chemical compositions, scanning electron micrographs (SEM), and X-ray diffraction (XRD) patterns

of these powders are presented in Table 1, Figure 2, and Figure 3, respectively. Besides, it is noted that the strength activity index of FA at 28 days was 89.3% in comparison to the cement's strength. Local tap water was used as mixing water.

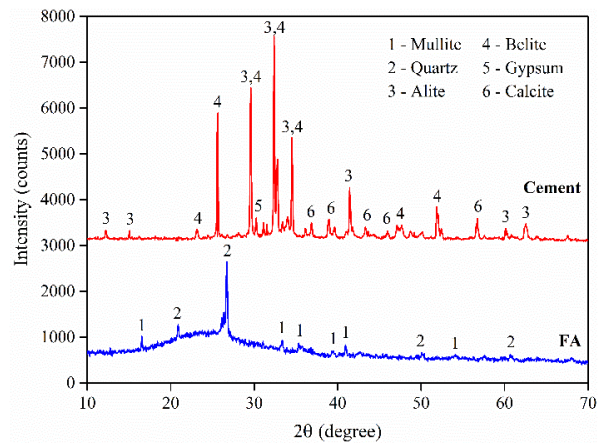


Figure 3. XRD patterns of cement and FA

2.2. Mix design and proportions

In line with the scope of the study as mentioned in the previous section and to see a clear influence of FA in the cement paste mixtures, FA was used to partially replace cement by 0, 20, 40, 60, and 80% by weight. To prepare the paste samples for the experimental programs, the quantity of cement, FA, and water was calculated as shown in Table 2. Several preliminary trials were performed for selecting the water/powder (w/p) ratio of 0.3.

Table 2. Mix proportions of paste samples

Mix ID	FA content (%)	w/p	Material proportions (kg)		
			Cement	FA	Water
F00	0	0.3	25	0	7.5
F20	20		20	5	7.5
F40	40		15	10	7.5
F60	60		10	15	7.5
F80	80		5	20	7.5

Note: w/p = water/powder

2.3. Samples preparation and test methods

To prepare the paste samples in the laboratory, cement and FA were first mixed in a mechanical mixer for 1 min. Water was then gradually added to the dry mixture and mixing continued for 5 min to obtain a homogeneous mixture. After that, the fresh paste mixtures were checked for flowability and setting time following the guidelines of ASTM C230 [21] and ASTM C191 [22], respectively. Finally, the fresh mixture was poured into molds of different sizes to prepare the samples for water absorption, compressive strength, and drying shrinkage tests. In detail, the water absorption test was measured on 50×50×50mm at 7 and 28 days in accordance with ASTM C1403 [23]. The test of compressive strength was performed on the 50×50×50 mm cubic samples at 7, 14, and 28 days following ASTM C109 [24]. Drying shrinkage of the paste was recorded on the 25×25×285 prismatic samples at 0, 3, 7, 14, and 28 days according to ASTM C596 [25].

3. Results and discussion

3.1. Flowability

The flow diameter of the cement paste was measured and is presented in Table 3. It can be seen that the higher FA content resulted in greater flowability of the fresh mixture. This result is consistent with the result found in the previous study [26]. In this study, the flow diameter of the cement paste mixtures ranged from 17.5 to 27.5 cm. Whereas, the reference mixture (F00) had the lowest flow diameter value of 17.5 cm, followed by the mixtures with FA content from 20 to 80%. In detail, the flow diameters of the mixtures containing 20, 40, 60, and 80% were 21.5, 22.5, 25.0, and 27.5 cm, respectively. The results confirmed that FA affected the mixture's flowability significantly. The reason for the increase in the flowability of the mixture is due to the spherical shape of FA particles (see Figure 2b), which reduces the frictional force between the particles. Another reason is that the lower particle density of FA in comparison with cement causes more paste content for a fixed binder, thus enhancing the flow of paste mixtures [26, 27]. This is considered one of the main advantages of FA for substituting Portland cement.

Table 3. Flowability and setting time of paste mixtures

Mix ID	FA content (%)	Flow diameter (mm)	Initial setting (min)	Final setting (min)
F00	0	175	130	150
F20	20	215	158	180
F40	40	225	229	255
F60	60	250	305	365
F80	80	275	392	438

3.2. Setting time

The initial and final setting times of the cement pastes containing 0 – 80% FA are presented in Table 3. It can be seen that the replacement of cement by FA led to an increment in both initial and final setting times. This result is consistent with the result found in the literature [28]. The reference mixture (F00) with no FA content was initially set at 130 min after mixing, while the mixtures with 20, 40, 60, and 80% FA had initial setting times of 158, 229, 305, and 392 min, respectively. The final setting times of all mixtures showed the same trend as the initial setting times. The final setting times recorded for the F00, F20, F40, F60, and F80 mixtures were 150, 180, 255, 365, and 438 min, respectively. The longer setting time of the mixture with a higher FA content is mainly due to the slow pozzolanic reaction of FA in comparison with the hydration of cement [29]. Furthermore, the addition of FA provides more SiO₂ (see the chemical compositions of FA in Table 1), which increases the SiO₂/Al₂O₃ ratio, resulting in a higher setting time of the mixture as reported in the previous study [30].

3.3. Water absorption

The water absorption of the paste samples is presented in Figure 4. It could be observed that the water absorption decreased with an increase in the curing period. As a result, the water absorption of all paste samples in the study ranged from 11.34% to 16.07% at 7 days and from 8.61% to 11.78%

at 28 days. Thus, all of the samples incorporating FA exhibited higher water absorption levels than the samples without FA addition (F00) at all curing ages and the water absorption rates increased with increasing FA content in the samples. This increment is due to the porous structure of paste samples because the reaction of FA particles with cement hydrate products occurs slowly as reported in the previous study [31, 32]. Furthermore, inactive FA particles play a role as fine aggregate, resulting in an increase in total surface area, which absorbs more water [33].

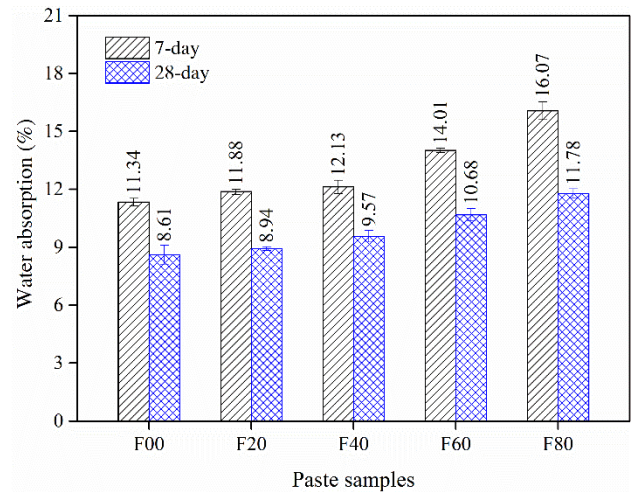


Figure 4. Water absorption of paste samples

3.4. Compressive strength

Figure 5 illustrates the development in compressive strength of the paste samples. As observed, the compressive strength increased with the curing period. This may be attributable to both the continuous hydration of cement and the pozzolanic reaction of FA. In addition, it was found that the F00 sample achieved the highest values of compressive strength at all curing ages. For instance, the compressive strength of the F00 samples at 7, 14, and 28 days were 57.15, 60.66, and 67.14 MPa, respectively. Increasing the FA content in the samples caused a reduction in the compressive strength of the pastes. After 28 days, the samples containing 20, 40, 60, and 80% FA gained compressive strength values of 62.31, 52.24, 41.54, and 30.33 MPa, which were about 92.8, 77.8, 61.9, and 45.2% as compared to the compressive strength of the FA-free sample at the same age, respectively. A similar finding was previously reported by some researchers [34–36]. As already mentioned, the inclusion of FA resulted in a slow chemical reaction in the paste samples. A previous study also indicated that the presence of FA caused a delay of Ca(OH)₂ formation, resulting in slow hydration of C₃S and consequently reducing the sample's strength [37].

Besides, it could be observed from Figure 5 that there was a significant reduction in the compressive strength of the samples containing up to 60 and 80% FA. In this case, with the excessive FA content, mixing water (see Table 2) may not be enough for further chemical reactions. Some FA particles might play as a fine aggregate to fill the void of paste samples. However, FA particles had a spherical shape with a porous structure (see Figure 2b), therefore, reducing the compressive strength of the paste samples.

Moreover, the replacement of cement with a high volume of FA reduced the formation of portlandite, hindering the pozzolanic reaction and thus resulting in the decline of the compressive strength of paste samples [26, 36].

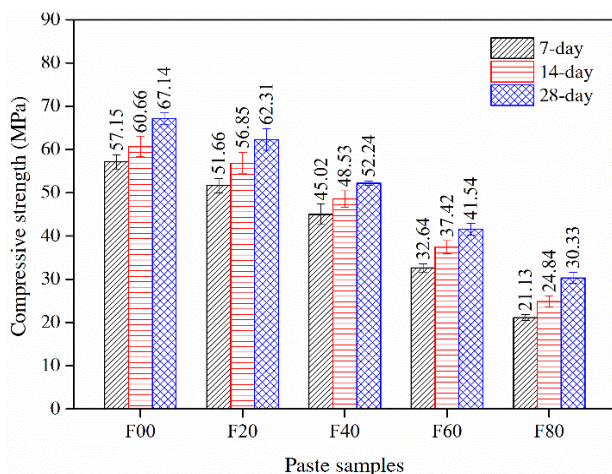


Figure 5. Compressive strength of paste samples

3.5. Drying shrinkage

The drying shrinkage of the paste samples is evaluated through the change in length as presented in Figure 6. For all cement paste samples, the change in length increased with curing time. The length change significantly increased from 0 to 7 days, then it slightly increased from 7 to 28 days. This is because from 0 to 7 days, the hydration of cement occurs strongly, which causes a significant change in length. From 7 to 28 days, the chemical reaction (i.e., cement hydration and pozzolanic reaction) in the samples happens slowly, resulting in a small change in length at this age. From Figure 6, it can be observed that the lowest change in length was found in the F80 mixture, its change in length at 3, 7, 14, and 28 days were -0.0408%, -0.0782%, -0.0926%, and -0.1040%, respectively. While the highest change in length values was found for the reference mixture with no FA. The change in length of the F00 samples at 3, 7, 14, and 28 days were -0.1212%, -0.1614%, -0.1786%, and -0.1866%, respectively. Overall, the use of FA to replace cement could bring a positive effect in reducing the drying shrinkage of paste samples. The samples with higher FA content exhibited lower drying shrinkage. Atiş [38, 39] indicated that the lower drying shrinkage of the mixture with high FA content is due to lower hydration heat and unreacted FA particles can play as an aggregate, which reduces the drying shrinkage. In addition, Lee et al. [40] suggested that the reduction in dry shrinkage of the paste sample could be attributed to the dilution effect when replacing cement with FA. In other words, FA slows down the hydration reaction, which also leads to a slow pozzolanic reaction between FA particles and $\text{Ca}(\text{OH})_2$ generated from cement hydration. On the other hand, when the water/binder ratio is fixed, the addition of FA reduces the lime content in the mixture, resulting in a reduced rate of hydration and thus lowering dry shrinkage in the paste samples. As a result, using FA to replace cement is considered an effective solution for reducing the drying shrinkage of paste samples.

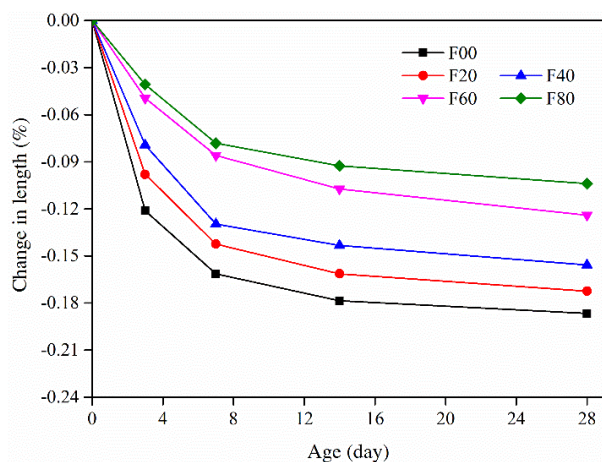


Figure 6. Drying shrinkage of paste samples

4. Conclusions

The influence of FA used as a cement substitution on the mechanical properties of cement paste was evaluated in this study. Based on the experimental outcomes, the following findings can be noted:

1. Increasing the FA content resulted in better flowability and longer setting time of the paste mixtures. The flow diameter and final setting time of the mixtures with 20 – 80% FA were in the respective ranges of 21.5 – 27.5 cm and 180 – 438 min while those of the FA-free mixtures were 17.5 cm and 150 min, respectively.

2. The water absorption of the cement paste was raised proportionally with the FA content in the samples. At 28 days, water absorption values of the samples incorporating 20 – 80% FA ranged from 8.94% to 11.78%, which was about 0.3 – 3.2% higher than that of the no FA sample.

3. The inclusion of higher FA content caused the samples to lower compressive strength at all curing ages. The 28-day compressive strength values of 67.14, 62.31, 52.24, 41.54, and 30.33 MPa were recorded for the samples with 0, 20, 40, 60, and 80% FA content. As a result, the compressive strength of the cement paste declined remarkably at the FA content of above 40%.

4. It is important to note that the incorporation of FA took advantage of reducing the drying shrinkage of the hardened cement paste. The higher the FA content, the lower the drying shrinkage of the sample. The change in length of the samples with 0, 20, 40, 60, and 80% FA recorded at 28 days were -0.1866, -0.1724, -0.1557, -0.1240, and -0.1040%, respectively. At relatively high FA content (i.e., 60% and 80%), the drying shrinkage of the samples reduced significantly.

Based on the experimental results, the quantity of FA could be properly selected for specific application purposes. On the other hand, the performance of the paste samples should be further evaluated at long-term ages. The solution for shortening the setting time of the paste mixture needs also to be investigated in future studies to promote the application of high-volume FA paste in real practice.

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