Action Time-Effect and Mechanism of Low-Calcium Fly Ash in Cement-Based Composites

Na Yan 1, Qingqing Tang 1, Ying Zhang 1 and Guowen Sun 1,2,*

1 School of Materials Science and Engineering, Shijiazhuang Tiedao University, Shijiazhuang 050043, China; yanna1833279026@163.com (N.Y.); tangabc0987654321@163.com (Q.T.); 15613346876@163.com (Y.Z.)
2 State Key Laboratory of Mechanical Behavior and System Safety of Traffic Engineering Structures, Shijiazhuang Tiedao University, Shijiazhuang 050043, China
* Correspondence: sunguowen_2003@163.com or sungw@stdu.edu.cn

Abstract: This study was conducted in order to investigate when low-calcium fly ash plays a physical or chemical effect and what is the chemical effect proportion of low-calcium fly ash. Two types of low-calcium fly ash and quartz powder, with similar fineness as active and inert admixtures, were used as materials in this study. Under different water/binder ratios and hydration ages, the effects of the different types of admixtures and their dosages on the flexural and compressive strength of the composites were studied. X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption methods, in addition to an assessment of the degree of hydration of the fly ash, were employed to observe the hydration products at different ages, the microstructures of the hydration products, as well as their surface areas and pore size distributions. The results show that during the hydration period of 28 days, the low-calcium fly ash has a micro-aggregate filling physical effect. However, after 56 days, the hydration degree of fly ash begins to exceed 1%. This illustrates that the low-calcium fly ash has both the pozzolanic activity effect and micro-aggregate filling effect. In contrast, the low-calcium fly ash hydrated for 90 days is still dominated by the physical filling effect.

Keywords: low-calcium fly ash; micro-aggregate effect; pozzolanic activity effect; time-effect; mechanism of action

1. Introduction

A large amount of low-calcium fly ash is produced in China, and its quality is unstable. In order to maximize its utilization in practical engineering, in the past several years, a number of studies have been carried out including investigations into the morphological, micro-aggregate and pozzolanic activity effects of fly ash in cement-based materials [1–13]. Most of these studies focused on its chemical effects and the activation of its chemical activity. However, in terms of its chemical activity, there are few studies which have focused on the effect of different types of fly ash, the conditions under which low-calcium fly ash has a physical or chemical effect, and what proportion of low-calcium fly ash is responsible for the chemical effect when it occurs. On the other hand, the findings from previous research regarding its time-effects differ, and some of the findings are even contradictory. Pipat et al. [14] claimed that the reaction degree of C₃S at 7 days was 80% with slow growth, while the amount involved in the reaction of C₂S was less than 50% in the early stage. They also assessed the growth potential of the late reaction degree by using the XRD full-spectrum method (Rietveld method) in the composite cementitious material system. Lam et al. [15] tested the hydration degree of pure cement and fly ash in the composite cementitious material by the determination of chemically bound water and the hydrochloric acid selective dissolution test, respectively, whereas the hydration degree of the cement in the composite cementitious material was calculated by the conceptual fitting of the effective water/binder ratio. The results showed that the hydration degree of fly ash in the high-volume fly ash system was low, and the hydration degree of cement.
increased alongside the increase in fly ash content. Wang et al. [16] observed that the degree of the pozzolanic reaction of fly ash was higher than 20% at day 1 by assessing the change in calcium hydroxide content in the hydration products of cementitious materials. Hu et al. [17] found that the pozzolanic reaction degree of fly ash was not greater than 2% at 28 days. Wang et al. [18] thought that the FA was partly involved in the pozzolanic reaction in the hydrated fly ash-cement (FC) paste at 30 days, but at 120 days, a large amount of FA was consumed. Kien et al. [19] studied the induction period of the early and late mortar strength of low-calcium fly ash at low temperature (5 °C) and at normal temperature (20 °C) by adding chemical mixtures including sodium thiocyanate (NaSCN), diethanolamine (DEA) and glycerol (Gly). Results showed that at 28 days, the three chemical accelerators played a significant role in coagulation during the early induction of low-calcium fly ash. Kunal et al. [20] quantitatively studied the change in Si and Al content in the hydration products at 7 days and 90 days by using nuclear magnetic resonance. Results showed that C (N)-A-SH gel increased with increase curing age. Sakai et al. [21] studied the reaction of cement clinker with fly ash in the dosage range of 20% to 60% at 365 days. Results showed that fly ash promoted the reaction of C$_3$S but inhibited the hydration of C$_2$S and C$_4$AF in the long-term. Lam [15] believed that high-volume fly ash pastes underwent a lower degree of fly ash reaction, and in the pastes with 45% to 55% fly ash, more than 80% of the fly ash remained unreacted after 90 days of curing.

Therefore, it is very important to study the time-effect of low-calcium fly ash during the strength evolution process in cement-based composites. Through this investigation, we were able to answer some key questions, including what effect plays a dominant role and when it works. Clarifying the relationship between the physical and chemical actions of fly ash will allow for facilitation of targeted excitation. This study has significant theoretical and practical interest for the application of high-volume low-calcium fly ash and activation time-effect. To eliminate experimental error according to the cement mortar strength test method (ISO method), the evolution law of the compressive and flexural strength of the composite cementitious mix containing fly ash and ground fine quartz powder are systematically studied by the contrast method, and the hardened paste microstructure evolutions are characterized using X-ray diffraction, scanning electron microscopy and nitrogen adsorption techniques to investigate its time-effect and mechanism.

2. Materials and Methods

2.1. Raw Materials

In order to eliminate experimental error, the main raw materials were the reference cement used for the concrete admixture performance test, ISO standard sand and two types of low-calcium fly ash produced by Jinyu concrete mixing plant. The chemical composition of the two kinds of fly ash are shown in Table 1. Quartz powder was made by grinding pure quartz sand such that its fineness was similar to the fly ash. The mixture proportions of the composite cementitious material in the experiment are shown in Table 2, in which F, Q and C represent the mixed low-calcium fly ash, the ground quartz powder and the reference cement, respectively.

| Table 1. The chemical composition of fly ash (%) |
|-----------------------------------------------|
|      | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | SO$_3$ | NaO$_{equi}$ |
| F$_1$(I) | 58.10   | 30.20       | 4.32       | 1.54 | 2.82 | 0.50    | 3.20        |
| F$_2$(II) | 57.85   | 28.32       | 3.89       | 1.43 | 2.74 | 0.48    | 3.65        |
Table 2. Composition of binders (%/wt).

| Sample | Composition |
|--------|-------------|
|        | Cement | Fly Ash | Quartz Powder |
| C      | 100    | -      | -             |
| F₁     | 90     | 10     | -             |
| F₂     | 80     | 20     | -             |
| F₁     | 70     | 30     | -             |
| F₂     | 50     | 50     | -             |
| F₁     | 90     | 10     | -             |
| F₂     | 80     | 20     | -             |
| F₂     | 70     | 30     | -             |
| Q      | 90     | -      | 10            |
| Q      | 80     | -      | 20            |
| Q      | 70     | -      | 30            |
| Q      | 50     | -      | 50            |

2.2. Experimental Method

The mechanical properties of cement mortar were tested according to Chinese standards GB/T 17671-1999. A side of the 40 mm × 40 mm × 160 mm test block was placed on the supporting cylinder of the bending tester, and the flexural strength was measured by evenly adding the load on the non-forming surface at a rate of 50 N/s ± 10 N/s until it broke. The semi-prismatic block, after measuring the bending resistance, was put on the press and evenly loaded at the rate of 2400 N/s ± 200 N/s until it was destroyed, and the compressive strength was recorded. The compressive strength and flexural strength of the tested mortar were measured at 3, 7, 14, 28, 56, 90 and 180 days, respectively, to accurately estimate the time-effect of fly ash in cement-based materials. The binder/sand ratio by weight was 1.3 and the water/binder ratio was 0.45.

2.3. Instrumentation and Testing Conditions

Scanning electron microscopy (SEM) was performed using a Hitachi SU8010 field-emission scanning electron microscope at an accelerating voltage of 5.0 kV. The samples were treated with a Hitachi MC1000 gold spraying instrument to prevent generation of accumulated charge when the incident electron beam hits the sample, which could affect the image quality.

X-ray diffraction analysis (XRD) was carried out on a Bruker AXS D8, with Cu Ka radiation and a step size of 0.02° between 5° and 80°.

Nitrogen adsorption analysis (BET) was conducted using a V-Sorb2800 automatic specific surface area and porosity analyzer. After drying and degassing, the samples were placed in liquid nitrogen. By adjusting different test pressures, the adsorption capacity of the mortar test block for nitrogen was measured, and then the adsorption and desorption isotherms were drawn to analyze the pore distribution and specific surface area.

3. Results and Discussion

3.1. Impact of Fly Ash Content on the Fluidity of Mortar

The effect of fly ash on the properties of fresh concrete depends on the particle morphology, also termed the “morphological effect”. At room temperature (20 °C), Lawrence et al. [22] found that the hydration rate of cement paste decreased with increasing fly ash content. In this process, the particle morphology of fly ash creates a dilution effect [23] on the mortar. The present research studies the effects of fly ash on the workability of cement-based materials with dosages of 0%, 10%, 20%, 30% and 50%. The results of the slump flow tests are shown in Figures 1 and 2. It can be observed in Figure 1 that when the ratio of water to cement is 0.45, with an increase in mineral admixture content, the slump flow of mortar increases. As shown in Figure 2, compared to the control cement
paste, when the concentration of mineral admixture is 30%, the slump flow of mortar with the addition of low-calcium fly ash is better than that of mortar with the addition of quartz powder. This is mainly because when compared to the spherical particles of fly ash, quartz powder contains polygonal particles [24]. Under the same water/binder ratio and total quantity of paste conditions, the larger the friction between the particles, the lower the fluidity of the mortar.

![Graph showing the slump flow of mortars](image)

**Figure 1.** Comparison of the slump flow of mortars made of FA and Q.

![Images of slump flow tests](image)

(a) F10, (b) Q30 and (c) F130.

**Figure 2.** Slump flow of mortars (a) F10, (b) Q30 and (c) F130.
3.2. Development of Mortar Strength under Standard Curing Conditions

When the water/binder ratio is 0.45, the effect of different dosages of low-calcium fly ash and quartz powder on the flexural and compressive strength of mortars are shown in Figure 3. In order to eliminate error and allow the test results to be comparable, the flexural and compressive strength of the mortar with a water/binder ratio of 0.45 are considered as the object of study. When the water/binder ratio exceeds 0.45, with increasing $F_1$ and $Q$ content, the slurry is prone to segregation and bleeding. The flexural and compressive strength development of the $F_1$ and $F_2$ mortars are almost similar, as shown in Figure 3a–d. From Figure 3a,c, it can be seen that the flexural strength decreases with the increase in fly ash content within 7 days, whereas the strength increases after 7 days but decreases when the content reaches 50%. It can be seen from Figure 3b,d that the compressive strength decreases with increasing fly ash content within 28 days.

![Figure 3a](image1)
![Figure 3b](image2)
![Figure 3c](image3)
![Figure 3d](image4)
![Figure 3e](image5)
![Figure 3f](image6)

Figure 3. Cont.
3.3. Effect of Low-Calcium Fly Ash and Ground Quartz Powder on the Microstructure of Hardened Pastes

In order to reveal the time-effect and the mechanism of action of low-calcium fly ash, the hardened cement paste was doped with different concentrations of low-calcium fly ash and quartz powder at a water/binder ratio of 0.45. Pastes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption. The symbols F1, Q and C represent hardened cement paste doped with first-class low-calcium fly ash and quartz powder, as well as the pure cement hardened paste, respectively.

3.3.1. XRD Analysis

The XRD patterns of the hardened paste with water/binder ratio of 0.45 at different curing ages were measured. The results are shown in Figure 4a–d, where CH and Q represent calcium hydroxide (Ca(OH)2) and silica (SiO2), respectively.
From Figure 4a, it can be seen that the intensity of the CH peaks of the 30% F and Q groups are almost the same, which indicates that there is no chemical reaction for the low-calcium fly ash at 14 days. However, at 28 days, the CH peak intensity of the F group is slightly lower than that of the Q group, suggesting that the low-calcium fly ash begins to undergo the pozzolanic reaction, as shown in Figure 4b. The XRD patterns of pastes with different dosages of fly ash at the same curing age of 28 days are compared in Figure 4c. It can be observed that the CH peak value of the pure cement hardened paste sample is the highest. When the content of low-calcium fly ash is 10%, the change in the CH diffraction peak is very minor; comparatively, when its dosage reaches 30%, the CH peak value decreases significantly. One reason for this is that the relative content of cement decreases, which results in the reduction CH formation. Another reason is the secondary pozzolanic reaction with fly ash. To further confirm the physical and chemical effects of fly ash, XRD patterns (Figure 4d) of the paste with the addition of 30% F at different ages were compared, showing that the diffraction peak of CH does not change much between 7 days and 14 days. However, the peak of CH begins to decrease at 28 days and continues to decrease significantly at 56 days. These findings confirm that the pozzolanic activity effect of fly ash occurs after the age of 28 days.
3.3.2. Morphology Analysis

The micro-morphology of specimens with the addition of 30% F and Q at a water/binder ratio of 0.45, used for standard curing for 7 days and 28 days, are shown in Figure 5. It can be seen from Figure 5a,b that in the hardened paste of pure cement at 7 days, the formation C-S-H gel is not compact and the structure is loose, while when the age reaches 28 days, a large number of compact and dense C-S-H gels form with crossing of plate-like CH forms, which makes the structure of the paste relatively compact.

![Micrographs of the hardened pastes with F and Q at different curing ages](image)

**Figure 5.** Micrographs of the hardened pastes with F and Q at different curing ages (a) hardened paste of pure cement at 7 d; (b) hardened paste of pure cement at 28 d; (c) hardened paste with F at 7 d; (d) hardened paste with F at 28 d; (e) hardened paste with Q at 7 d; (f) hardened paste with Q at 28 d.
The SEM micrograph of the harden paste with 30% F at 7 days is shown in Figure 5c. It can be seen that the structure of the entire hardened paste is relatively homogeneous and dense [27], and the surface of the fly ash is smooth with its surroundings and surface areas covered with some short rods and irregular C-S-H gels, indicating that low-calcium fly ash plays a micro-aggregate physical filling effect at 7 days. On the surface of the paste with the same amount of quartz powder, some C-S-H gels are attached (Figure 5e). However, as quartz powder is irregular and polygonal, this leads to the loose accumulation of hydration products compared to those of fly ash particles. At 28 days, a large amount of plate-like CH can be observed in Figure 5d. The low-calcium fly ash particles are surrounded by a large number of hydration products, and the interface between the cement matrix and fly ash is closely linked. In addition, some pits begin to appear on the surface of the fly ash, supporting that low-calcium fly ash begins to participate in the hydration reaction (i.e., the pozzolanic reaction), but the physical filling effect is still dominant. For the paste with the addition of quartz powder at the same age (Figure 5f), there are a large number of clusters of C-S-H gels on the surface of quartz powder, and the degree of its tightness is significantly improved compared to that which was cured for 7 days.

3.3.3. Effect of Fly Ash and Quartz Powder on the Pore Structure of Hardened Pastes

The adsorption/desorption curves and differential pore size distribution curves of hardened cement pastes at water/binder ratio of 0.45 are shown in Figures 6 and 7. From Figure 6, it can be seen that the nitrogen adsorption capacity of F and Q samples increases with increasing relative pressure and curing age. The adsorption capacity increases from 45 mL/g to 57 mL/g when the curing age increases from 7 days to 28 days (Figure 6a). One reason is that the pore structure of the hardened paste, and the interface between the pure cement and fly ash, are improved [28]. The second reason is that the low-calcium fly ash reacts with the calcium hydroxide of the cement hydration product, leading to an increase in the amount of formed C-S-H gels, thus resulting in an increase in adsorption [29]. In addition, the F adsorption/desorption curves are similar, indicating that there is no obvious change in the pore morphology of the hardened paste when F is added into the cement. The adsorption/desorption curve of the Q specimen at 3 days is evidently different from those at other ages. When the relative pressure P/P₀ is in the range of 0–0.8, the adsorption curve is almost parallel with the X axis, indicating that no adsorption is occurring. This is caused by the hydration of the Q samples. Namely, as quartz powder is an inert mineral admixture, when it replaces a portion of the cement, the cement hydration rate slows down before 3 days of age, and the gel holes are less aggregated. The adsorption/desorption curve increases with the increase in hydration age, especially at 28 days, indicating that cement hydration is promoted in the later stage, and the pore structure changes greatly with the addition of quartz powder. In contrast, the adsorption/desorption curves of the hardened pure cement paste are almost identical compared with those without admixtures at 3, 7 and 28 days (Figure 6c), indicating that the pore structures of hydration are very similar. The adsorption capacity of the C group is up to 800 mL/g, indicating that the hydration rate of this group is higher than that of the F and Q groups.

The specific surface areas obtained by nitrogen adsorption are given in Table 3. Here, the specific surface areas of the F and Q groups are similar at 3 and 7 days which indicates that the effects of low-calcium fly ash and quartz powder are similar. However, the specific surface area of the Q group specimens is smaller than that of F specimens at 28 days, suggesting that the amount of gel pores in the F specimens increases; that is, the peak value shifts to the left and the most probable aperture decreases, thus, the pore structure is further refined for the whole paste (Figure 7a). For the C specimen, the specific surface area increases with increasing curing age to a much larger extent than that of the F and Q groups, such that many gel pores are formed for the C sample at the age of 3 days. In addition, from Figure 7c, the peak values of the pore size of the C specimen are much higher than those of the F and Q specimens, and the C specimen also has two pore distribution zones, which
are a 2–3 nm gel pore and a 10–30 nm capillary zone. Likewise, the F and Q specimens also have two pore distribution zones, a gel pore of 2–2.5 nm and a capillary zone of 10–90 nm.

**Figure 6.** Isothermal nitrogen adsorption/desorption curves of the hardened pastes with (a) F1, (b) Q and (c) C at different ages.

**Figure 7.** Distribution of different pores in the hardened pastes with (a) F1, (b) Q and (c) C at different ages.

**Table 3.** F, Q, and C pore specific surface area (m²/g).

| Curing Age (d) | F1 Specific Surface Area | Q Specific Surface | C Specific Surface |
|---------------|--------------------------|--------------------|--------------------|
| 3             | 11.5905                  | 11.2080            | 15.8466            |
| 7             | 14.5362                  | 14.1271            | 17.5558            |
| 28            | 18.5235                  | 15.9949            | 20.9049            |

In summary, based on the results for the amount of adsorption/desorption, the surface area and the pore structure of samples, before the hydration age of 7 days, low-calcium fly ash and quartz powder play the same role in cement-based composites—namely, the physical filling of the micro-aggregate. At an age of 28 days, the adsorption capacity, specific surface area and pore size distribution of the F specimen are obviously higher than those of the Q specimen, demonstrating that the low-calcium fly ash plays a pozzolanic activity effect in the cement-based composites.

3.3.4. Hydration Degree of Fly Ash

According to the guide of the ACI Committee 211 [30], the degree of the hydration reaction of fly ash (α_f) in blended pastes was tested by the selective dissolution method and calculated by the following formula [31]:

\[
α_f = 1 - \frac{R_b - m_{900}/m_0 \cdot (1 + f_p \cdot LOI_P + f_c \cdot LOI_C) \cdot f_c R_c}{m_{900}/m_0 \cdot (1 + f_p \cdot LOI_P + f_c \cdot LOI_C) \cdot f_p R_p}
\]
where, $R_b$, $R_p$ and $R_c$ are the percentages of the insoluble residue of sample, unreacted fly ash and cement by mass, respectively; $m_0$ and $m_{900}$ are the weights of the initial dried sample and the amount of sample at a temperature of 900 °C, respectively; $f_c$ and $f_p$ represent the mass fractions of cement and fly ash in the blend; $LOI_c$ and $LOI_p$ represent the losses on ignition of cement and fly ash, respectively; and the formula $(1 + f_p \cdot LOI_p + f_c \cdot LOI_c)$ takes into account any further impact of loss on ignition. The obtained values for the reaction of fly ash ($\alpha_f$) in the blended paste with a water/binder ratio of 0.45 are presented in Figure 8. It can be observed that the $\alpha_f$ value decreases with increasing F dosage at the same curing age (e.g., $\alpha_f$ at $f_p = 30\%$ is almost double the $\alpha_f$ at $f_p = 50\%$). Of course, the reaction degree of F increases substantially with curing age (i.e., $\alpha_f = 1.05$ at 7 days and $\alpha_f = 8.46$ at 90 days for $f_p = 30\%$). However, the reaction degree of F is very low at 28 days (i.e., $\alpha_f = 3.89$ at $f_p = 30\%$ and $\alpha_f = 2.57$ at $f_p = 50\%$). It can also be further confirmed that fly ash is responsible for the main physical function at 28 days. After 56 days, the hydration degree of fly ash begins to exceed 3%. This illustrates that the low-calcium fly ash is important in both the pozzolanic activity effect and micro-aggregate filling effect. In contrast, the low-calcium fly ash in the hydrated paste at 90 days is dominated by the physical filling effect, according to the hydration results in Figure 8.

![Figure 8. Reaction degree of fly ash in blended pastes.](image)

**4. Conclusions**

(1) The slump flow and the workability of the paste with low-calcium fly ash increases with increasing dosage, which is attributed to the morphological effect of low-calcium fly ash.

(2) At the same dosage of mineral admixture, at an age of 14 days, the flexural and compressive strength of mortars with low-calcium fly ash and quartz powder have a similar trend of development, which means that before 28 days, the low-calcium fly ash in the cement-based composite material only has a micro-aggregate physical filling effect. The flexural strength and compressive strength of the specimens with added fly ash are slightly higher than those of the specimens incorporating ground fine quartz powder at 28 days. At 56 days of age, the flexural and compressive strength of the former approaches, if not exceeds, the latter, indicating that the low-calcium fly ash in the cement-based composite material produces a pozzolanic effect at 28 days.

(3) The results of XRD, SEM and nitrogen adsorption analyses verify that low-calcium fly ash mainly plays a role in the physical filling of micro-aggregates within the first 28 days. The activation of low-calcium fly ash activity comes to effect only after 28 days. At the later stage of hydration (especially after 56 days), low-calcium fly ash plays a role in both the pozzolanic activity effect and micro-aggregate filling effect.
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