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Relation	

Effect of sodium sulfate activator on compressive strength and hydration of fly ash–cement pastes

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Abstract

In the study, the effect of 4% sodium sulfate (Na_2SO_4) as an activator on cement pastes with 0, 20, and 40% fly ash replacements and a low water-to-cementitious materials ratio of 0.30 was investigated. The investigation was conducted to evaluate the effectiveness of the technique for the utilization of fly ash in developing sustainable concrete. The use of Na_2SO_4 decreased setting times of the fresh pastes and increased compressive strength of the hardened pastes up to 28 days irrespective of fly ash replacement. The use decreased $Ca(OH)_2$ content in the hardened pastes irrespective of fly ash replacement. Meanwhile, it increased $Ca(OH)_2$ consumption by the pozzolanic reaction of fly ash and content of calcium silicate and aluminate hydrates in the hardened fly ash-cement pastes. Consequently, the use of Na_2SO_4 negatively affected cement hydration in the hardened cement pastes without fly ash, while the use accelerated ettringite formation and pozzolanic reaction of fly ash in the hardened pastes.

Keywords: Compressive strength; Hydration; Setting time; Thermal gravimetric analysis; X-ray diffraction.

Conflict of interest

The authors declare no conflict of interest.

Introduction

Fly ash is known as a green material that is used to replace Portland cement in concrete in the modern and sustainable construction industry (Zachar 2011; Hemalatha and Ramaswamy 2017; Hemalatha and Sasmal 2019). The use of fly ash in the concrete leads to several benefits such as replacing natural materials (i.e. limestone and clay) used for Portland cement manufacture, reducing CO_2 emissions, air pollutant, waste, and cost of concrete, and improving the later-age strength and durability of concrete (Shi and Day 1995; Baert et al. 2008; Camões et al. 2015; Hemalatha and Ramaswamy 2017). The improvement is attributed to the pozzolanic reaction of fly ash that consumes $Ca(OH)_2$ formed from cement hydration and generates secondary hydration products (Mehta 1987; Bui et al. 2016; Hemalatha and Ramaswamy 2017). Nevertheless, the pozzolanic reaction of fly ash in cement concrete is extremely slow at early ages (Feldman et al. 1990; Lam et al. 2000; Baert et al. 2008). The slow pozzolanic reaction results in lower early-age strength and slower strength development of the cement concrete with fly ash when compared with that of cement concrete without fly ash (Qian et al. 2001; Durán-Herrera et al. 2011; Bui et al. 2017). Baert et al. (2008) concluded that compressive strength of concrete at early ages significantly decreases with increases in the fly ash replacement. Lam et al. (2000) also observed that fly ash replacement negatively affects the compressive strength of fly ash–cement pastes up to the age of 28 days. However, the negative effect was insignificant when pastes exhibited low water-to-cementitious materials ratios (w/cms) (Lam et al. 2000).

Recently, a chemical activation via the use of several chemical activators was proposed to promote the pozzolanic reaction of fly ash and eliminate low early-age strength of fly ash concretes (Shi and Day 1995; Lee et al. 2003). Sodium hydroxide, sodium carbonate, water glass, and sodium sulfate are the most widely used chemical activators due to their availability and economic benefits (Shi et al. 2006). It was reported that sulfate activators are extremely effective for fly ash–cement paste when the Portland cement content exceeded 20% (Shi et al. 2006). Shi and Day (1995) added sodium sulfate (Na_2SO_4) to lime-fly ash pastes with water-to-cement ratios in the range of 0.35 – 0.375. The addition increased the pozzolanic reactivity of fly ash, thereby increasing the strength of the pastes moist-cured at 50 °C. When the Na_2SO_4 activator was used in the range of 3 – 5% of the mass of lime-fly ash cement, the improvement in strength at the ages corresponding to 90 and 180 days was significant (Shi and Day 1995). However, high curing temperature is potentially limited in a few practical situations. Therefore, Shi (1996) investigated the effect of Na_2SO_4 on setting time and strength development of lime-fly ash pastes cured at 23 °C. The addition of Na_2SO_4 to the lime-fly ash pastes with a water-to-solid ratio of 0.35 slightly decreased their initial setting time, significantly decreased final setting time, and significantly increased their strength development (Shi 1996). Significant increases in the compressive strength up to 28 days by the addition of 3% Na_2SO_4 to lime-fly ash mortars with a water-to-cement ratio of 0.46 was also indicated in the study by Qian et al. (2001). In addition to lime-fly ash mortars, the addition of 3% Na_2SO_4 was especially effective in increasing the strength from 3 to 28 days for the cement paste with 30% fly ash replacement (Qian et al. 2001). Lee et al. (2003) reported that low $Ca(OH)_2$ content and high amount of ettringite (AFt) were observed following the addition of 1% Na_2SO_4 to cement pastes with 40% fly ash replacement and a w/cm of 0.485. Thus, their compressive strength increased at early ages (i.e. at the ages of 1, 3, and 7 days) and even at later ages (i.e. at the age of 28 days) (Lee et al. 2003). The increase was also observed in the pastes activated via 0.5 and 2% Na_2SO_4. However, the effect of 4% Na_2SO_4 on increases in the strength at 28 days is not shown (Lee et al. 2003). Briefly, most existing studies focused on increasing the strength of the blended cements (i.e. lime-fly ash and fly ash–cement) with w/cms in the range of 0.35 – 0.485 via the use of Na_2SO_4 from 1 to 5% of the mass of cementitious materials. There is a paucity of studies on the effect of Na_2SO_4 on hydration (i.e. cement hydration and pozzolanic reaction of fly ash) in the fly ash–cement pastes with w/cms lower than 0.35.

The purpose of the present study involved evaluating the effectiveness of the use of Na_2SO_4 on fresh and hardened properties, and hydration of cement pastes with 0, 20, and 40% fly ash replacements and a low w/cm of 0.30. In addition to setting time and compressive strength up to the age corresponding to 28 days, contents of $Ca(OH)_2$, and calcium silicate and aluminate hydrates were analyzed by thermal gravimetric analysis in order to deeply understand the cement hydration and pozzolanic reaction of fly ash in the hardened pastes with 0 and 4% Na_2SO_4. The main phases detected via X-ray diffraction were also investigated.

Research significance

The utilization of fly ash in the concrete production has been recently promoted towards developing sustainability in construction. The sulfate activation on pozzolanic reactivity of fly ash in the blended cements with w/cms higher than 0.35 has been investigated in order to expand its application. The motivation of the present study is the applicability of sulfate activation to the fly ash-cement pastes with a w/cm lower than 0.35. It is expected that a high volume of fly ash resulting from a low w/cm could be activated by the use of Na_2SO_4. The effect of sulfate activator on hydration in the cement pastes with and without fly ash could be clarified more in the present study.

Experiments

1. Materials

Portland cement conforming to TCVN 2682:2009 (Vietnamese Standard 2009) and Class-F fly ash conforming to TCVN 10302:2014 (Vietnamese Standard 2014) were used as cementitious materials in the study. The physical properties and chemical compositions of the cement and fly ash are listed in Table 1. Tap water without any impurities as per TCVN 4506:2012 (Vietnamese Standard 2012) was used to mix the cement and fly ash. Sodium sulfate (Na_2SO_4) was used as a sulfate activator and was expected to accelerate the pozzolanic reaction of fly ash.

2. Mixture proportion

A low w/cm corresponding to 0.30 was used to produce a paste with sufficient strength and also utilize the high volume of Class-F fly ash towards developing sustainable construction. The pastes were designated as Fa0, Fa20, and Fa40 with 0, 20, and 40% replacements of cement by fly ash, respectively. The amount of Na_2SO_4 with 4% mass of cementitious materials was kept constant for all mixture proportions. The amount was based on that in a previous study (Lee et al. 2003). Additionally, pastes with 0% Na_2SO_4 was prepared for reference purposes. Table 2 summarizes the mass proportions of all pastes in the present study.

3. Mixing procedure

First, Na_2SO_4 with a pre-weighed dosage was added to the mixing water until all sodium compounds dissolved in water to form a chemical solution. Second, Portland cement and fly ash were thoroughly blended in dry form at an extremely slow speed in a mixer to obtain an acceptably homogenous mixture. Subsequently, a chemical solution or only water was added to the dry mixture, and the mixture was mixed at a low speed for 30 s and then at a medium speed for 90 s prior to testing the setting times of the pastes and casting specimens.

4. Setting time test

The setting times of all the fresh pastes were tested by using a 1 mm^2 section Vicat needle as per TCVN 6017:1995 (Vietnamese Standard 1995). The setting time test was done one time for each mixture proportion. The initial setting time was defined as the time elapsed between the initial contact of water and cement and time when the penetration of Vicat needle was at 36±1 mm. Furthermore, final setting time was calculated as the time elapsed between the initial contact of water and cement and time when the needle sank into the paste at 0.5 mm.

5. Specimen preparation and curing condition

After mixing, the pastes were cast in 50-mm cube-shaped moulds for strength measurements. Following casting, the placing surfaces of specimens were covered with polyethylene sheets and cured at temperature corresponding to 29±1 °C and relative humidity corresponding to 90±5%, which are nearly identical to those in the practical curing condition for concrete structures in Vietnam. All specimens were demoulded 24 h after casting and cured at a temperature corresponding to 29±1 °C and relative humidity corresponding to 90±5% until the designated test ages.

6. Test procedures

Compressive strength of hardened pastes

To assess the effectiveness of sulfate activator on the strength of the hardened pastes, their compressive strengths at the ages of 1, 3, 7, and 28 days were measured via a compression machine. The compressive strength of each mixture proportion at each age corresponded to the average value of three cubic specimens. It means that the compressive strength test was repeated three times for each mixture proportion at each age.

Hydration products of the pastes

To evaluate the effect of sulfate activator on hydration in the pastes, thermal gravimetric analysis and X-ray diffraction test were applied to the aforementioned pastes. The samples for thermal gravimetric analysis and X-ray diffraction test were collected from cubic specimens used for the compressive strength tests at the ages corresponding to 3 and 28 days. The samples were immersed in acetone to avoid any further hydration and were subsequently dried in a vacuum desiccator. Subsequently, the samples were ground into powders with a size of less than 150 μm prior to testing. It is noted that each test was carried out one time for each mixture proportion at each age.

Thermal gravimetric analysis

Thermal gravimetric analysis was applied to determine the $Ca(OH)_2$ content in the hardened pastes by using simultaneous differential thermal analysis and thermal gravimetry (Shimadzu DTG-60H). The $Ca(OH)_2$ content was calculated from the mass of the paste powder after ignition and mass loss from the dehydration of $Ca(OH)_2$ and that from the decomposition of calcium carbonate on heating. The temperature range for the thermal gravimetric analysis corresponded to 20–1000 °C at a rate of 20 °C /min.

In addition to measuring the $Ca(OH)_2$ content, the content of calcium silicate and aluminate hydrates including AFt, calcium silicate hydrate (C–S–H), and gehlenite hydrate (C_2ASH_8) was also computed. The content of the calcium silicate and aluminate hydrates was calculated in the study based on the mass loss between 20 and 420 °C and mass of the paste powder after ignition that was based on a previous study (Chaipanich and Nochaiya 2010).

X-ray diffraction

In the study, X-ray diffraction (XRD) was used to identify phase changes in the powders prepared from the hardened pastes. The XRD patterns were acquired via a Bruker D2 Phaser. A test was performed with CuKα radiation and with a 2theta angle scan ranging from 5 to 65 ° at a rate of 5 °/min. Specifically, EVA program software was used to analyze the test data.

Results and discussion

Setting time of fresh pastes

Effects of fly ash replacement and Na_2SO_4 on setting time including initial and final setting times of the fresh pastes are shown in Fig. 1. With respect to the initial setting time, fly ash delayed the setting times of the fresh pastes with 0% Na_2SO_4 for 55 min while it delayed the setting times of those with 4% Na_2SO_4 from 25 to 35 min. With respect to the final setting time, fly ash also delayed the setting time of fresh pastes with 0% Na_2SO_4 from 40 to 65 min while it delayed the setting time of fresh pastes with 4% Na_2SO_4 from 40 to 60 min. The delay in the setting time of the pastes due to the presence of fly ash was also observed in a few previous studies (Ravina and Mehta 1986; Durán-Herrera et al. 2011; Huang et al. 2013). This was potentially owing to decreases in the amount of Portland cement that was replaced by Class-F fly ash in the fly ash–cement pastes. When compared with the fresh pastes with 20% fly ash replacement, the initial setting time of those with 40% fly ash replacement was slightly higher or nearly identical. Meanwhile, the final setting time of the fresh pastes with 40%

fly ash replacement was accelerated more regardless of Na_2SO_4. Naik and Singh (1997) explained that the acceleration of the setting time was due to the low gypsum content in the paste with low cement and high fly ash contents (Naik and Singh 1997). The lower gypsum content in the fresh pastes with 40% fly ash replacement than that in the fresh pastes with 20% fly ash replacement might affect their setting time, leading to the slightly higher or nearly identical initial setting time and lower final setting time.

As shown in Fig. 1, Na_2SO_4 decreased the initial setting time from 5 to 35 min and the final setting time from 45 to 50 min in fresh pastes with 0, 20, and 40% fly ash replacements. The decreases in the setting time due to the use of Na_2SO_4 was also observed in the lime-fly ash cement paste cured at 23 °C and in blended cement pastes with a high volume of calcined clay pozzolan as reported in existing studies (Shi 1996; Boakye et al. 2017). Kumar and Rameswara Rao (1994) indicated that the type and concentration of SO_4^{2-} ions significantly affected the setting time of the cement paste because they contributed to the solubility of cement compounds (Kumar and Kameswara Rao 1994). Therefore, decreases in setting time of the fresh pastes with 4% Na_2SO_4 when compared with that of the fresh pastes with 0% Na_2SO_4 is potentially due to the acceleration of the dissolution of calcium ions in the cement paste irrespective of fly ash replacement.

Compressive strength of hardened pastes

Effects of Na_2SO_4 on the compressive strength of the hardened pastes with 0, 20, and 40% fly ash replacements at the ages corresponding to 1, 3, 7, and 28 days are shown in Figs. 2 (a), (b), and (c), respectively. Generally, Class-F fly ash decreases the compressive strength of cement/concrete mixtures and especially at early ages (Sahmaran and Yaman 2007; Baert et al. 2008; Durán-Herrera et al. 2011; Bui et al.

2017). With respect to specimens with 0% Na_2SO_4, the compressive strength of almost all the hardened fly ash–cement pastes (Fa20 and Fa40) was lower than that of the plain cement paste (Fa0) at 1 and 3 days. Additionally, increases in the fly ash replacement decreased the compressive strength at early ages (i.e. at the ages of 1 and 3 days). The aforementioned tendency was also reported in a previous study by Baert et al. (2008). Decreases in the compressive strength were attributed to the slow pozzolanic reaction of fly ash at early ages (Durán-Herrera et al. 2011). However, the compressive strength of the Fa20 specimen with 0% Na_2SO_4 was slightly higher and that of the Fa40 specimen with 0% Na_2SO_4 was nearly identical to that of the Fa0 specimen at 7 days. The increase in compressive strength of the Fa20 and Fa40 specimens with 0% Na_2SO_4 could be due the formation of AFt as a hydration product of the fly ash at early ages and the space-filling effect by fly ash particles (Berry et al. 1990). At 28 days, the compressive strength of the Fa40 specimen with 0% Na_2SO_4 was slightly higher than that of the Fa20 specimen and even higher than that of the Fa0 specimen at 28 days. Durán-Herrera et al. (2011) also indicated that the difference in compressive strength between the fly ash concrete and reference concrete without fly ash decreased with time (Durán-Herrera et al. 2011). This was potentially due to the pozzolanic reaction of fly ash that proceeded in the aforementioned cement paste at the 28 days.

A previous study observed that the use of Na_2SO_4 from 1 to 4% of the mass of cementitious materials significantly increased the compressive strength of the fly ash–cement system with a w/cm of 0.485 at early ages (i.e. at 1 and 3 days) (Lee et al. 2003). However, the increase was not observed at later ages (i.e. after 7 days) when the use of Na_2SO_4 exceeded 2% of the mass of cementitious materials (Lee et al. 2003). In the study, when compared with the hardened cement pastes with 0% Na_2SO_4, the compressive strength of the Fa0 specimen with 4% Na_2SO_4 was slightly higher at the ages corresponding to 1, 3, and 7 days and significantly at the age corresponding to 28 days as shown in Fig. 2 (a). The slightly higher compressive strengths of the Fa20 and Fa40 specimens with 4% Na_2SO_4 were also observed at 1 day and significantly at 3, 7, and 28 days as shown in Figs. 2 (b) and (c), respectively. Evidently, the use of 4% Na_2SO_4 increased the compressive strength of the hardened cement pastes at early ages and also at later ages irrespective of fly ash replacement. The reason for the increase is explained in further detail in the section on hydration products of the pastes.

As shown in Figs. 2 (a), (b), and (c), the gain in compressive strength of the Fa20 and Fa40 specimens with 4% Na_2SO_4 was more significant than that of the Fa0 specimen from the age of 1 to 7 days. This implies that the use of Na_2SO_4 effectively resulted in a higher increase in compressive strength of the Fa20 and Fa40 specimens when compared with that of the Fa0 specimen at early ages.

Hydration products of the pastes

$Ca(OH)_2$ content

Effects of fly ash replacement and Na_2SO_4 on the $Ca(OH)_2$ content in the hardened pastes at the ages corresponding to 3 and 28 days are shown in Figs. 3 (a) and (b), respectively. Generally, the $Ca(OH)_2$ content in cement pastes containing fly ash is lower than that in plain cement paste without fly ash (Lam et al. 2000; Sakai et al. 2005; Bui et al. 2015, 2016, 2017, 2018). As shown in Figs. 3 (a) and (b), decreases in the $Ca(OH)_2$ content at the ages corresponding to 3 and 28 days in the Fa20 and Fa40 specimens when compared with that in the Fa0 specimen irrespective of the use of Na_2SO_4 are attributed to the partial replacement of Portland cement by Class-F fly ash. Additionally, the $Ca(OH)_2$ content was low with increases in the fly ash replacement.

With respect to the hardened pastes with 0% Na_2SO_4, the $Ca(OH)_2$ content in the Fa0, Fa20, and Fa40 specimens increased until 28 days. The increase in the $Ca(OH)_2$ implied that the cement hydration in all specimens proceeded until 28 days. The tendency was also observed in the Fa0 specimen with 4% Na_2SO_4. However, a slight decrease in $Ca(OH)_2$ content from the age of 3 to 28 days in the Fa20 and Fa40 specimens with 4% Na_2SO_4 is shown in Figs. 3 (a) and (b). The decrease in $Ca(OH)_2$ content with time potentially indicated the progress of the pozzolanic reaction of fly ash in the Fa20 and Fa40 specimens with 4% Na_2SO_4.

When compared with the hardened fly ash–cement pastes with 0% Na_2SO_4, $Ca(OH)_2$ contents in the hardened pastes with 4% Na_2SO_4 were lower at the ages corresponding to 3 and 28 days. The decrease in the $Ca(OH)_2$ contents up to 28 days in the hardened cement pastes with 40% fly ash replacement via the addition of 1% Na_2SO_4 was also observed in a previous study (Lee et al. 2003). The decrease indicates that the pozzolanic reaction of fly ash in Fa20 and Fa40 specimens was accelerated via the use of Na_2SO_4. Figs. 3 (a) and (b) also show the decrease in the $Ca(OH)_2$ contents in the hardened cement paste with 0% fly ash replacement via using Na_2SO_4. The use of Na_2SO_4 increased alkali concentration of pore solution in the hardened cement pastes with 0% fly ash replacement, resulting in limiting cement hydration. This was also found in the hardened cement paste with 0% fly ash replacement naturally injected by alkali solution from the age of 1 month (Bui et al. 2015). It was concluded that the use of Na_2SO_4 negatively affected cement hydration in the hardened pastes without fly ash.

$Ca(OH)_2$ consumption by the pozzolanic reaction of fly ash

It is assumed that cement hydration in the cement pastes with 20 and 40% fly ash replacements was identical to that in the plain cement paste with 0% fly ash replacement

(Bui et al. 2016, 2018). Therefore, the $Ca(OH)_2$ consumption by the pozzolanic reaction of fly ash in the cement pastes is calculated by Eq. (1) as follows:

$$Ca(OH)_2 \text{ consumption} = Ca(OH)_{2\ \text{plain cement paste}}\,(c/(c+f)) - Ca(OH)_{2\ \text{fly ash–cement paste}} \quad (1)$$

where,

$Ca(OH)_2$ consumption: $Ca(OH)_2$ consumption by the pozzolanic reaction of fly ash in the Fa20 or Fa40 specimen (%)

$Ca(OH)_{2\ \text{plain cement paste}}$: $Ca(OH)_2$ content in the Fa0 specimen (%)

$Ca(OH)_{2\ \text{fly ash–cement paste}}$: $Ca(OH)_2$ content in the Fa20 or Fa40 specimen (%)

(c/(c+f)): mass ratio of cement in cementitious materials including Portland cement and Class-F fly ash (= 0.8 for the Fa20 specimen and = 0.6 for the Fa40 specimen)

Figure 4 (a) shows the effects of Na_2SO_4 on the $Ca(OH)_2$ consumption via the pozzolanic reaction of fly ash in the hardened pastes with 20 and 40% fly ash replacements at the ages corresponding to 3 and 28 days. It is observed that the $Ca(OH)_2$ consumption increased until 28 days irrespective of the fly ash replacement and the use of Na_2SO_4, and this was due to the pozzolanic reaction of fly ash. Increases in the fly ash replacement increased the $Ca(OH)_2$ consumption due to the pozzolanic reaction of fly ash in the hardened pastes. This was also compatible with the results of a previous study (Bui et al. 2015).

With respect to the Fa20 specimen, the $Ca(OH)_2$ consumption in the hardened pastes with 4% Na_2SO_4 increased by 3.35 and 51.1% at the ages corresponding to 3 and 28 days, respectively, when compared with that in the hardened pastes with 0% Na_2SO_4. With respect to the Fa40 specimen, the $Ca(OH)_2$ consumption in the hardened pastes with 4% Na_2SO_4 increased by 28.3 and 55.8% at the ages corresponding to 3 and 28 days, respectively, when compared with that in the hardened pastes with 0% Na_2SO_4. The increase in the $Ca(OH)_2$ consumption indicated that the pozzolanic reaction of the fly ash–cement pastes was accelerated via the use of Na_2SO_4. Comparing the $Ca(OH)_2$ consumption between the Fa20 and Fa40 specimens, the normalization is also shown in Fig. 4 (b). For the hardened pastes with 0% Na_2SO_4, the $Ca(OH)_2$ consumption in the Fa40 specimen, in which the fly ash content was twice as much as that in the Fa20 specimen, was 1.51 and 1.46 times as much as that in the Fa20 specimen at the ages corresponding to 3 and 28 days, respectively. For the hardened pastes with 4% Na_2SO_4, the $Ca(OH)_2$ consumption in the Fa40 specimen, in which the fly ash content was twice as much as that in the Fa20 specimen, was 1.87 and 1.50 times as much as that in the Fa20 specimen at the ages corresponding to 3 and 28 days, respectively. A comparison of the $Ca(OH)_2$ consumption between the Fa20 and Fa40 specimens indicated that the use of Na_2SO_4 was effective in accelerating the pozzolanic reaction of fly ash in the Fa40 specimen when compared with that in the Fa20 specimen at an early age (i.e. at 3 days) and at later age (i.e. at 28 days).

Content of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8

The contents of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8 in the Fa0, Fa20, and Fa40 specimens at the ages corresponding to 3 and 28 days are shown in Figs. 5 (a) and (b), respectively. The content of calcium silicate and aluminate hydrates in the Fa0, Fa20, and Fa40 specimens increased until 28 days. This indicated that the content of the hydrates increases with time, thereby leading to increases in the compressive strength up to 28 days of the hardened pastes as shown in Fig. 2. However, fly ash decreased the content of calcium silicate and aluminate hydrates in the hardened pastes irrespective of curing age and the use of Na_2SO_4. This tendency was also observed in an extant study (Chaipanich and Nochaiya 2010). This was potentially due to decreases in the amount of C–S–H that decreased compressive strength of the Fa20 and Fa40 specimens when compared with that of the Fa0 specimen as shown in Fig. 2. As shown in Figs. 5 (a) and (b), increases in the fly ash replacement decrease the content of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8.

As shown in Figs. 5 (a) and (b), 4% Na_2SO_4 increases the content of calcium silicate and aluminate hydrates in hardened pastes irrespective of fly ash replacement and curing age. This confirms that the use of Na_2SO_4 positively contributed to the formation of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8 in the pastes.

Furthermore, the gain in the content of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8 from 3 to 28 days in Fa0 specimens with 0 and 4% Na_2SO_4 corresponded to 17.5 and 14.1%, respectively. The gain in the content of calcium silicate and aluminate hydrates from 3 to 28 days in Fa20 specimens with 0 and 4% Na_2SO_4 corresponded to 23.0 and 25.2%, respectively. Furthermore, the gain in the content of calcium silicate and aluminate hydrates from 3 to 28 days in Fa40 specimens with 0 and 4% Na_2SO_4 corresponded to 41.3 and 29.4%, respectively. This indicated that the gain in the content of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8 in the fly ash cement pastes increased more significantly from 3 to 28 days when compared with that in the plain cement paste irrespective of the use of Na_2SO_4. This was potentially due to the formation of secondary C–S–H from the pozzolanic reaction of fly ash.

X-ray diffraction

Figures 6, 7, and 8 show the XRD patterns of the Fa0, Fa20, and Fa40 specimens with 0 and 4% Na_2SO_4 at ages corresponding to 3 and 28 days, respectively. With respect to the pastes with 0% Na_2SO_4, the main phases in all the Fa0, Fa20, and Fa40 specimens corresponded to monosulfoaluminate, portlandite ($Ca(OH)_2$), and calcite ($CaCO_3$). It is considered that AFt in the pastes with 0% Na_2SO_4 converted to monosulfoaluminate after the age of 3 days, thereby leading to the absence of AFt peak in the Fa0, Fa20, and Fa40 specimens. Furthermore, with respect to the pastes with 4% Na_2SO_4, the main phases in all the Fa0, Fa20, and Fa40 specimens corresponded to AFt, $Ca(OH)_2$, and $CaCO_3$. The presence of AFt after the addition of Na_2SO_4 was also observed in the lime-low calcium fly ash pastes and in the fly ash–cement pastes as reported in the previous studies (Shi 1996; Lee et al. 2003). The production of AFt in the hardened fly ash–cement pastes with 4% Na_2SO_4 was explained via the following mechanism: (1) when Na_2SO_4 was added to the paste, it reacted with $Ca(OH)_2$ formed from cement hydration to form gypsum and sodium hydroxide that increased the pH value in the paste; (2) the gypsum reacted with unreacted tri-calcium aluminate to produce AFt; (3) when the pastes exhibited sufficient pH value, the glassy surface layer of fly ash particles began to corrode and the chains of the Si-O-Si and Al-O-Al links also began to break, and thus the pozzolanic reaction of fly ash proceeded. Briefly, the use of Na_2SO_4 promoted the formation of AFt and accelerated the pozzolanic reaction of fly ash in the hardened cement pastes. Thus, the decrease in the $Ca(OH)_2$ content, increases in the $Ca(OH)_2$ consumption via the pozzolanic reaction of fly ash, and content of calcium silicate and aluminate hydrates including AFt, C–S–H, and C_2ASH_8 are shown in Figs. 3, 4, and 5, respectively, thereby resulting in significant increases in the compressive strength of the fly ash–cement pastes as shown in Fig. 2. Similarly, the addition of Na_2SO_4 also produced AFt in the hardened cement paste without fly ash and increased the pH value in the aforementioned paste. The increase in the pH value partially hindered the cement hydration at early ages in the paste, thereby leading to decreases in $Ca(OH)_2$ content as shown in Fig. 3.

The presence of peaks of AFt in the Fa40 specimens was weaker than those in Fa0 and Fa20 specimens irrespective of the use of Na_2SO_4. This indicated that the amount of AFt was minor, and this was due to the lower $Ca(OH)_2$ content in the Fa40 specimens when compared with that in the Fa0 and Fa20 specimens as shown in Fig. 3. A comparison of Figs. 6, 7, and 8 indicates that the peak of $Ca(OH)_2$ in the Fa20 and Fa40 specimens is weaker than that in the Fa0 specimens. This was due to the lower $Ca(OH)_2$ content in the specimens when compared with that in the Fa0 specimens as shown in Fig. 3.

4. Conclusions

Effects of Na_2SO_4 activator with 4% mass of cementitious materials on setting time, compressive strength, and hydration of fly ash–cement pastes with a low w/cm of 0.30 were investigated experimentally in the study. The following conclusions are obtained from the study:

The use of Na_2SO_4 accelerated the dissolution of calcium ions in the fresh pastes irrespective of fly ash replacement, thereby decreasing the initial and final setting times of the fresh pastes.

The use of Na_2SO_4 positively affected the formation of ettringite detected via X-ray diffraction analysis in the hardened cement paste without fly ash although it negatively affected the cement hydration at an early age (i.e. at 3 days) which was not found in the previous studies. However, the negative effect was negligible at later ages, thereby resulting in significant increases in the compressive strength at 28 days.

The use of Na_2SO_4 accelerated the pozzolanic reaction of a high volume of fly ash in the hardened cement paste with a low w/cm in addition to promoting the ettringite formation, thereby resulting in significant increases in the compressive strength at early ages (i.e. at 3 and 7 days) and also up to 28 days for the hardened pastes.

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Data Availability Statement

All data, models, and code generated or used during the study appear in the submitted article.

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