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Strength and microstructural characteristics of chemically activated fly ash–cement systems

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Abstract

The use of fly ash as a cement replacement material increases the long-term strength and durability of concrete. Despite these great benefits, the use of fly ash is limited due to the low early strength of fly ash concrete. To eliminate this problem, many studies have been conducted on accelerating the pozzolanic properties of fly ash. The study reported below investigated the strength and microstructural characteristics of fly ash–cement systems containing three kinds of activators—Na_2SO_4, K_2SO_4, and triethanolamine—to accelerate the early strength of fly ash mortars. Through the use of thermal gravity analysis, it was demonstrated that the activators not only decreased or maintained the amount of $Ca(OH)_2$ products, but also increased the production of ettringite at early ages. X-ray diffraction, scanning electron microcopy, and mercury intrusion porosimetry also confirmed that in the early curing stages of fly ash–cement pastes containing activators, large amounts of ettringite were formed, resulting in a reduction in the pore size ranging from 0.01 to 5 μm. The research results support the supposition that the addition of small amounts of activators is a viable solution for increasing the early-age compressive strength of fly ash concrete.

Keywords: Fly ash; Activator; Pore size distribution; Compressive strength; Hydration products

1. Introduction

For several decades, the concrete and cement industry has routinely incorporated fly ash into cement as a partial cement replacement. Fly ash improves concrete properties, lowers the costs of concrete production, and is ecologically beneficial [1]. Moreover, large volumes of fly ash in concrete mixtures may improve durability and reduce heat of hydration.

Despite these benefits, practical problems in the field application of fly ash remain. At early ages, the strength of concrete containing high volumes of fly ash as a partial cement replacement is much lower than that of control concrete; this is due to the slow pozzolanic reaction of fly ash [2]. To address this issue, research has focused on the following methods to accelerate the pozzolanic reactivity of fly ash: (1) increasing its fineness [3]; (2) elevating the curing temperature [4]; and (3) the use of chemical activators [5–15]. Several studies have reported that use of chemical activators, specifically sulfate activation and alkali activation, effectively accelerates the pozzolanic reaction of fly ash. Gypsum ($CaSO_4{\cdot}2H_2O$) and sodium sulfate (Na_2SO_4) have been used to study sulfate activation [5–10], and NaOH and $Ca(OH)_2$ and others have been used to study alkali activation [10–15].

Previous research has determined that the sulfate activation mechanism is as follows: (1) incorporating sulfate activators into fly ash-cement pastes accelerates the depletion of $Ca(OH)_2$ at early ages [6–8]; (2) the amount of ettringite (AFt) produced in fly ash cement pastes containing activators increases at early ages by breaking down the glass phases in an elevated alkaline environment [5–9]; (3) the addition of sulfate activators into fly ash-cement pastes changes the pore distribution, resulting in smaller pore size and lower porosity [9,10]; and (4) the addition of activators increases the early-age strength of fly ash mortar; however, later-age strength is not increased when compared to fly ash mortar without activators [5,8,9].

Most research works have focused on accelerating the pozzolanic reactivity of fly ash by adding two sulfate chem-

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icals: gypsum and Na_2SO_4. Few studies on the use of other sulfate activators, such as K_2SO_4, for activating fly ash have been done, however, and only limited study has been conducted on the effect of different levels of activators in order to improve the strength development of fly ash mortar. This study addresses this issue and investigates the effects of two sulfate activators, Na_2SO_4 and K_2SO_4, and an organic activator, triethanolamine, on the development of strength of fly ash mortars and microstructure of fly ash–cement pastes through the quantitative analysis of $Ca(OH)_2$, ettringite, and porosity with curing time.

2. Experimental work

2.1. Materials

Type I Portland cement and low-calcium fly ash produced in coal-fired electric power stations in South Korea were used as cementitious materials. The physical characteristics and chemical compositions of the materials are shown in Table 1. Washed river sand with a specific gravity of 2.51 was used as fine aggregate.

Eight chemical compounds selected from nonorganic and organic materials were pretested to determine the activators applicable to this study. Two sulfate activators, Na_2SO_4 and K_2SO_4, and an organic activator, triethanolamine, were chosen for the activation of the pozzolanic reaction of fly ash. Previous testing found that these compounds developed the early strength of fly ash mortar and fly ash–cement pastes more effectively than other chemical compounds.

2.2. Mix proportions of pastes and mortars

Mortars were prepared with a water-to-cementitious materials (cement + fly ash) ratio of 0.485 and a fine aggregate-to-cementitious materials ratio of 2.45. Fly ash mortars contained 40% fly ash by weight of cementitious materials and variable amounts of chemical activators. A control mortar sample without fly ash and activators was also prepared.

Fly ash–cement pastes with water-to-cementitious materials ratio of 0.4 were prepared for thermal gravity analysis (TGA), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and mercury intrusion porosimetry (MIP) testing. The pastes contained 40% fly ash and 1.0% Na_2SO_4, 1.0% K_2SO_4, or 0.03% triethanolamine by weight of cementitious materials.

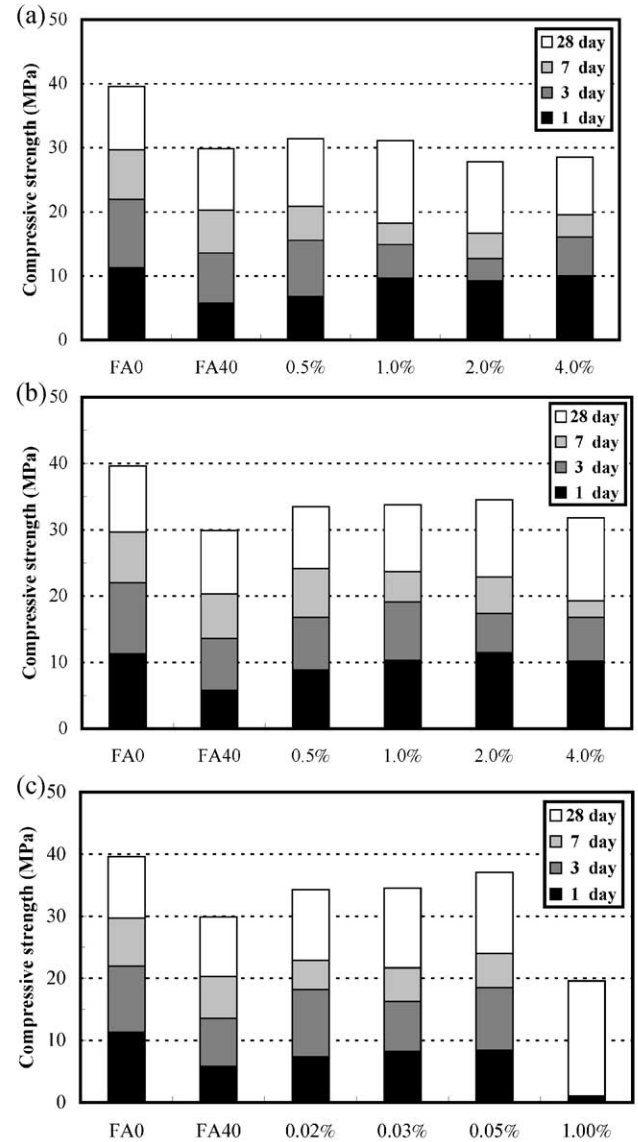

Fig. 1. Compressive strength of chemically activated fly ash mortars: (a) with Na_2SO_4, (b) with K_2SO_4, (c) with triethanolamine.

2.3. Preparation specimens and test methods

Paste and mortar cubes, $10 \times 10 \times 10$ cm, were cast into steel. All specimens were unmolded 24 h after casting and then cured in a water bath at 20 °C until testing. In order to verify the effectiveness of the activators on the strength of

Table 1
Physical characteristics and chemical compositions of cement and fly ash

Materials	Physical characteristics		Chemical compositions (%)						
	Specific gravity	Blaine fineness (cm^2/g)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition
Cement	3.15	3450	20.68	5.16	3.02	62.42	4.71	2.42	1.36
Fly ash	2.10	4350	57.09	24.66	10.50	2.58	1.37	0.94	3.02

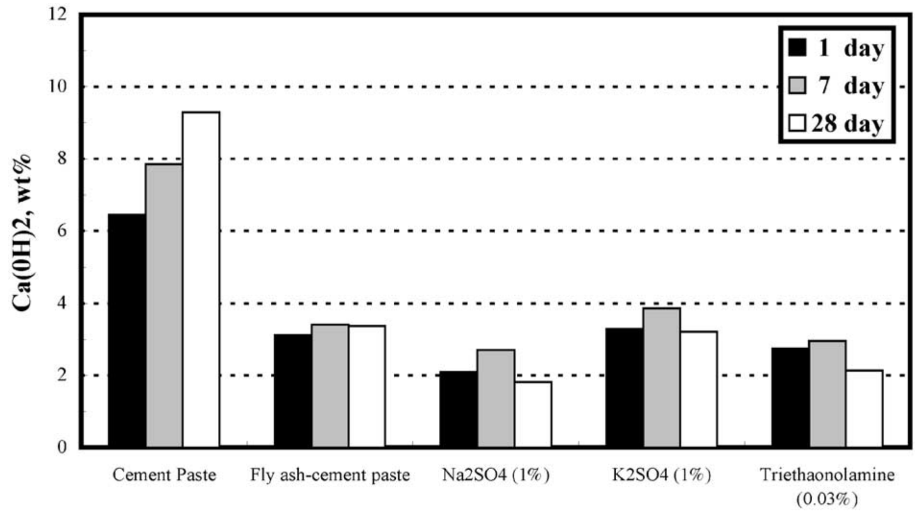

Fig. 2. Amount of $Ca(OH)_2$ of cement paste, fly ash–cement paste, and chemically activated fly ash–cement pastes at 1, 7, and 28 days.

mortars, their compressive strengths were measured at 1, 3, 7, and 28 days.

Paste specimens were crushed into small pieces and then soaked in acetone for more than 7 days to stop further hydration. In order to determine the influence of activators on hydration products and microstructure of fly ash–cement pastes, the samples were freeze-dried and stored in a sealed container for use in TGA, XRD, and SEM.

To determine the amount of $Ca(OH)_2$ produced in samples, it was separated from the hydrates at 450–500 °C. The amount of ettringite produced was measured from the peak of heat absorption in a temperature range between 130 and 160 °C through TGA. Freeze-dried fly ash–cement pastes were ground and analyzed using XRD. SEM was used to observe the morphology of fly ash–cement pastes. MIP with a maximum mercury intrusion pressure of 420 MPa was employed to evaluate the pore size distribution of fly ash–cement paste samples.

3. Results and discussion

3.1. Effect of activators on strength development of mortar

The effects of the three activators on the strength development of control mortar and fly ash mortars are shown in Fig. 1. At day 1, the compressive strength of the mortar without fly ash (FA0) was almost twice as high as

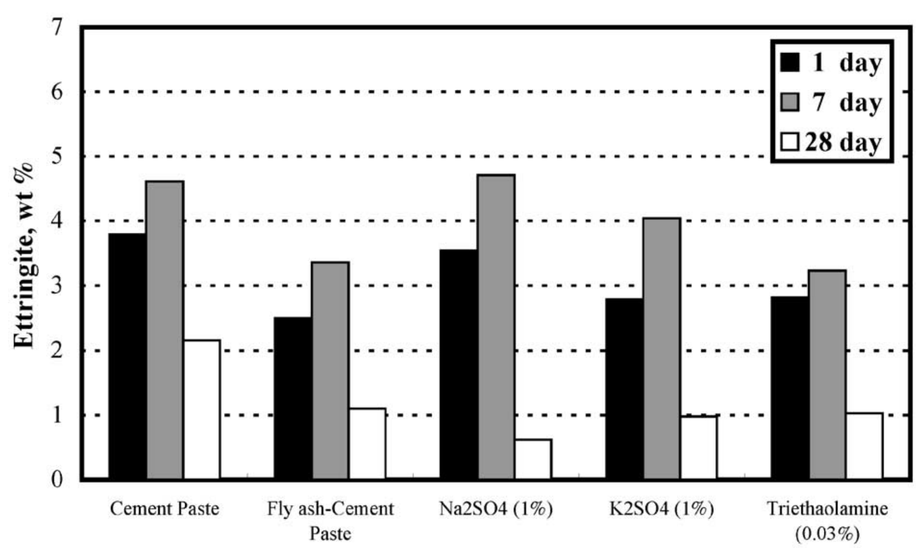

Fig. 3. Amount of ettringite of cement paste, fly ash–cement paste, and chemically activated fly ash–cement pastes at 1, 7, and 28 days.

that of the fly ash mortar without activators (FA40), while the 28-day strength of FA0 was about 24% higher than that of FA40.

The strength of fly ash mortars with more than 1% of Na_2SO_4 increased considerably at 1 day, while 0.5% Na_2SO_4 only slightly increased the strength of fly ash mortar compared with FA40. The strength of FA40 with 1% Na_2SO_4 was about 70% higher than that of FA40 at 1 day but was the same strength of FA40 at 28 days.

Both 1- and 28-day strengths of K_2SO_4-activated fly ash mortars were greater than those measured in FA40. At 1 day, the strength of 2.0% K_2SO_4-activated mortars reached that of FA0 but was about 15% lower than that of FA0 at 28 days. Compared with other two activators, K_2SO_4 was the most effective in the strength development at early ages (see Fig. 1).

The 1-day strength of the mortars including a small amount of triethanolamine was lower than that of mortars with other activators. In particular, the compressive strength of FA40 with 1% triethanolamine was significantly lower at early ages. The rate of strength gain increased thereafter, and the 28-day strength of mortar with 0.03% triethanolamine was similar to that of mortar with 1% K_2SO_4.

To conduct a microstructural study of the fly ash–cement pastes, the amounts of activators incorporated into the samples were as follows: 1% for Na_2SO_4, 1% for K_2SO_4, and 0.03% for triethanolamine. These levels were chosen with respect to their success in strength development and cost-effectiveness.

3.2. $Ca(OH)_2$ and ettringite production

TGA was used to determine the amounts of $Ca(OH)_2$ present in the samples at 1, 7, and 28 days, as shown in Fig. 2. The amount of $Ca(OH)_2$ in cement pastes with no fly ash continuously increased until 28 days. Cement pastes containing 40% fly ash had nearly 50% less $Ca(OH)_2$ than cement pastes without fly ash. The addition of Na_2SO_4, K_2SO_4, and triethanolamine resulted in similar trends in the production of $Ca(OH)_2$ to cement pastes containing 40% fly ash. Note that the amount of $Ca(OH)_2$ in fly ash–cement pastes decreased after 7 days, easily explained by the fact that fly ash originally had less CaO in chemical composition and, in addition, the pozzolanic activity of fly ash significantly consumed $Ca(OH)_2$ beyond 7 days. Among the three activators, Na_2SO_4 was the most effective in decreasing the level of $Ca(OH)_2$.

TGA was also used to determine the amount of ettringite produced in the samples. As shown in Fig. 3, Na_2SO_4 and K_2SO_4 increased the production of ettringite in fly ash–cement pastes at early age—a result of the sulfate

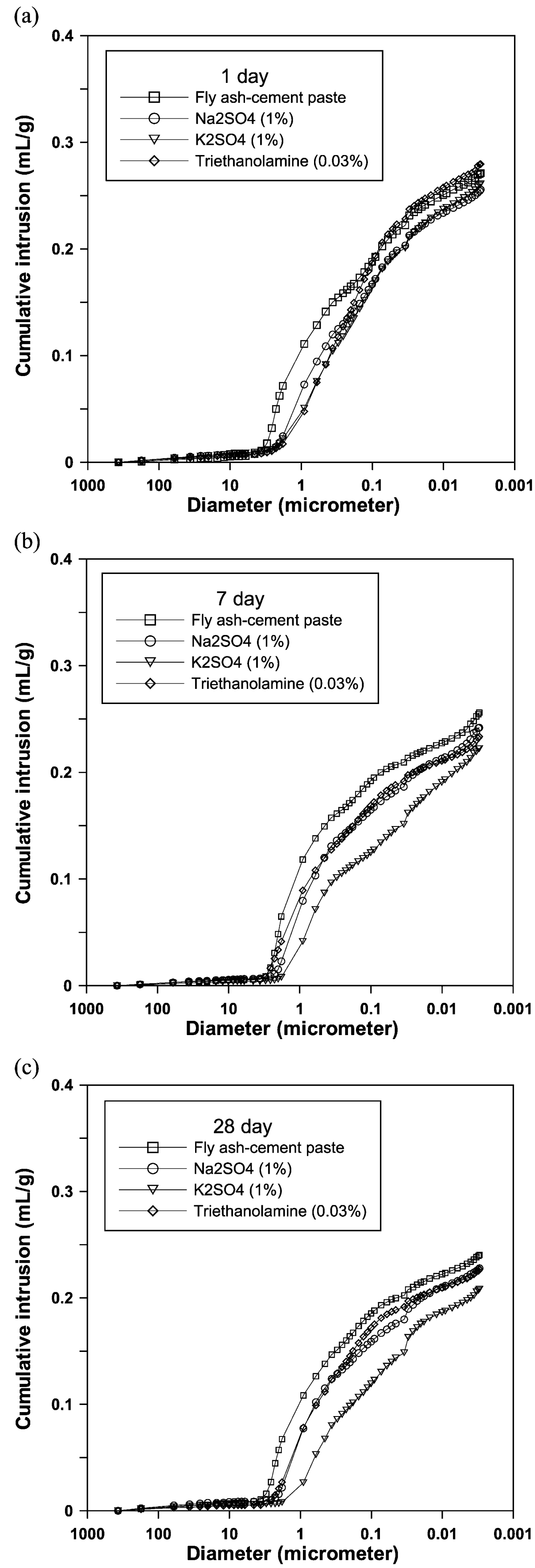

Fig. 4. Accumulated porosity of chemically activated fly ash–cement pastes: (a) 1 day, (b) 7 days, (c) 28 days.

reaction between SO_4^{2-} and C_3A. The production of ettringite was maximized at 7 days, then tapered off as the ettringite was transferred to the monosulfate, C_4AH_{13}, and C_2ASH_8 [2]. Clearly, Na_2SO_4 and K_2SO_4 influenced the production of ettringite, contributing to the improvement of the early compressive strength of fly ash–cement mortars. The addition of triethanolamine, however, had little effect on the production of ettringite, although it also improved the early compressive strength of the samples. Other microstructural factors must be responsible for improving the early compressive strength of samples containing triethanolamine.

3.3. Pore size distribution

The accumulated porosity was measured using MIP. As shown in Fig. 4, cement pastes containing 40% fly ash with activators had fewer accumulated pores with a diameter ranging from 0.01 to 5 μm than fly ash–cement pastes with no activators. The cumulative porosity of fly ash–cement pastes with 1% K_2SO_4 was almost the same as fly ash–cement paste with either 1% Na_2SO_4 or 0.03% triethanolamine at 1 day, but was lowered at 7 and 28 days. As previously noted, the production of calcium silicate hydrate (C–S–H) and C_2ASH_8 was accelerated by ettringite and C_3S at early ages of hydration and, consequently, the accumulated porosity was reduced and the compressive strength increased. As K_2SO_4 was the most effective activator in reducing porosity, it follows that it should also be the most effective in improving early-age strength.

3.4. XRD analysis of hydration products

Fig. 5 shows the XRD patterns of the fly ash–cement pastes at 1, 3, 7, and 28 days. For the fly ash–cement pastes with no activator, a small ettringite peak was observed at 9.1° (2θ) (see Fig. 5a). In the XRD patterns of the fly ash–cement pastes with activators shown in Fig. 5b–d, the diffraction peak due to the production of ettringite was present at early ages up to 7 days. Over time, the ettringite was transferred to monosulfate and other products; therefore, little ettringite remained at 28 days. $Ca(OH)_2$, the main hydration product, appeared at 18° (2θ). Its peak of XRD was the highest at 3 days but was reduced

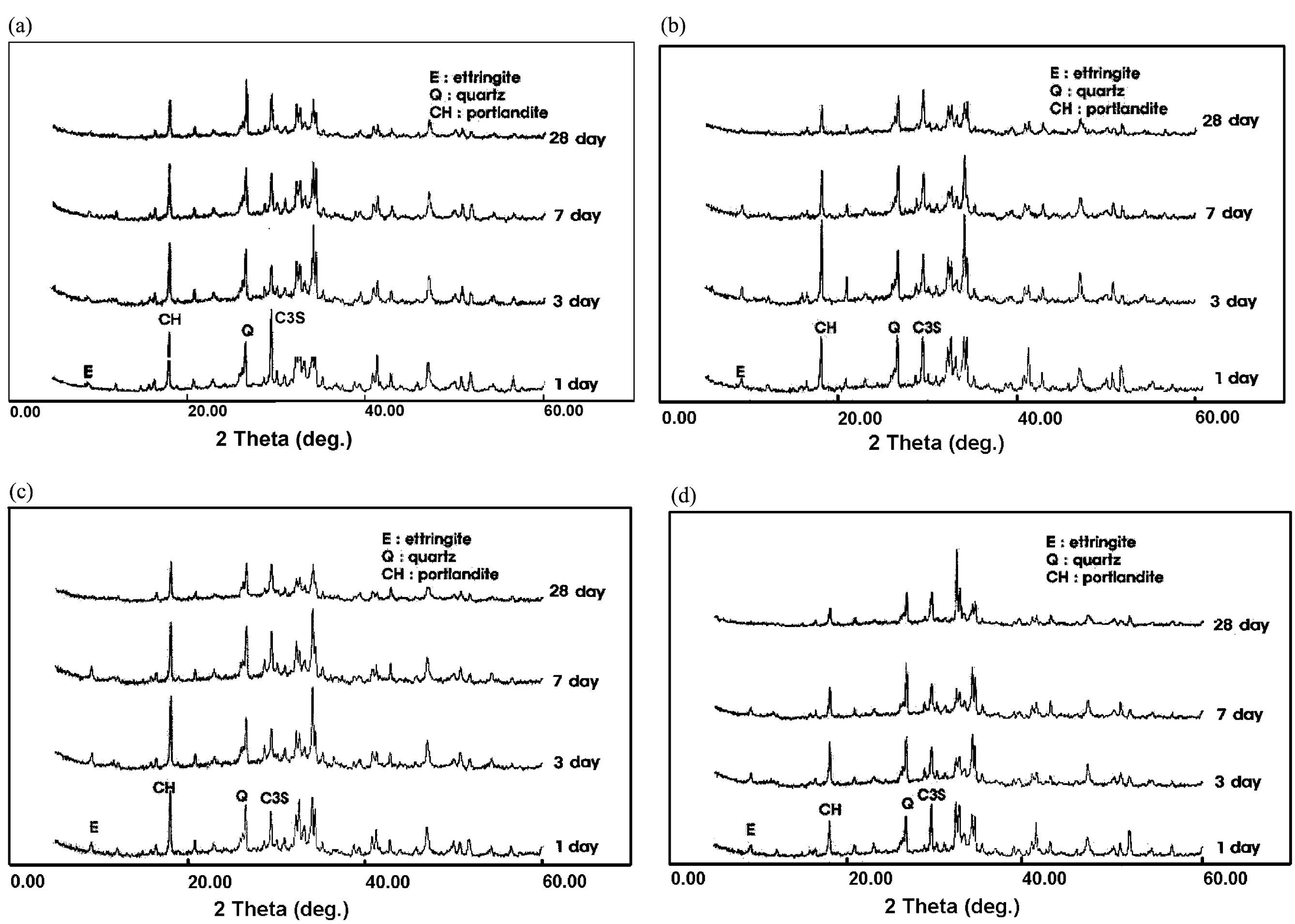

Fig. 5. XRD patterns of chemically activated fly ash–cement pastes: (a) No activator, (b) with Na_2SO_4 (1%), (c) with K_2SO_4 (1%), (d) with triethanolamine (0.03%).

thereafter by the pozzolanic reaction. These results, consistent with the research of Shi [8] and Poon et al. [9], indicate that the slight accelerated consumption of $Ca(OH)_2$ and the formation of ettringite contributed to the strength of the fly ash–cement pastes containing sulfate activators. XRD supports the theory that the large amount of ettringite produced at early ages of hydration may result in the high early strength of the fly ash mortar or concrete containing activators.

3.5. SEM observation of microstructure

Fig. 6 shows SEM pictures of hydration products—C–S–H, ettringite, and $Ca(OH)_2$—at 3 days. In fly ash–cement pastes containing no activator, the hydrates were mostly C–S–H and monosulfate, and the development of microstructure was delayed due to pozzolanic activity (see Fig. 6a); however, in pastes containing either Na_2SO_4 or K_2SO_4, SO_3^{2-} ions supplied by the activators created needle-like hydration products, i.e., ettringite-sized 1–5 μm in diameter. Other alkali compounds and crystallized mullite also appeared on the surface of $Ca(OH)_2$, as shown in Fig. 6b and c. The morphology of the fly ash–cement pastes with triethanolamine was similar to that of the fly ash–cement pastes with sulfate-type activators, but the amounts of ettringite were relatively less than those of the others, as shown in Fig. 6d.

4. Conclusions

The following conclusions may be drawn from this study:

(1) The addition of activators, such as Na_2SO_4, K_2SO_4, and triethanolamine, in mortar samples containing fly ash accelerated the strength development of these samples at early ages, but their strengths were comparable to strength of fly ash mortar sample without activators at 28 days. Of these activators, K_2SO_4 was the most effective in increasing the early strength of fly ash mortars.

(2) XRD and TGA analyses showed that at 3 and 7 days, the amount of $Ca(OH)_2$ of fly ash–cement pastes containing activators decreased slightly or was comparable to cement pastes without activators and, in addition, decreased even further a little bit thereafter. In contrast,

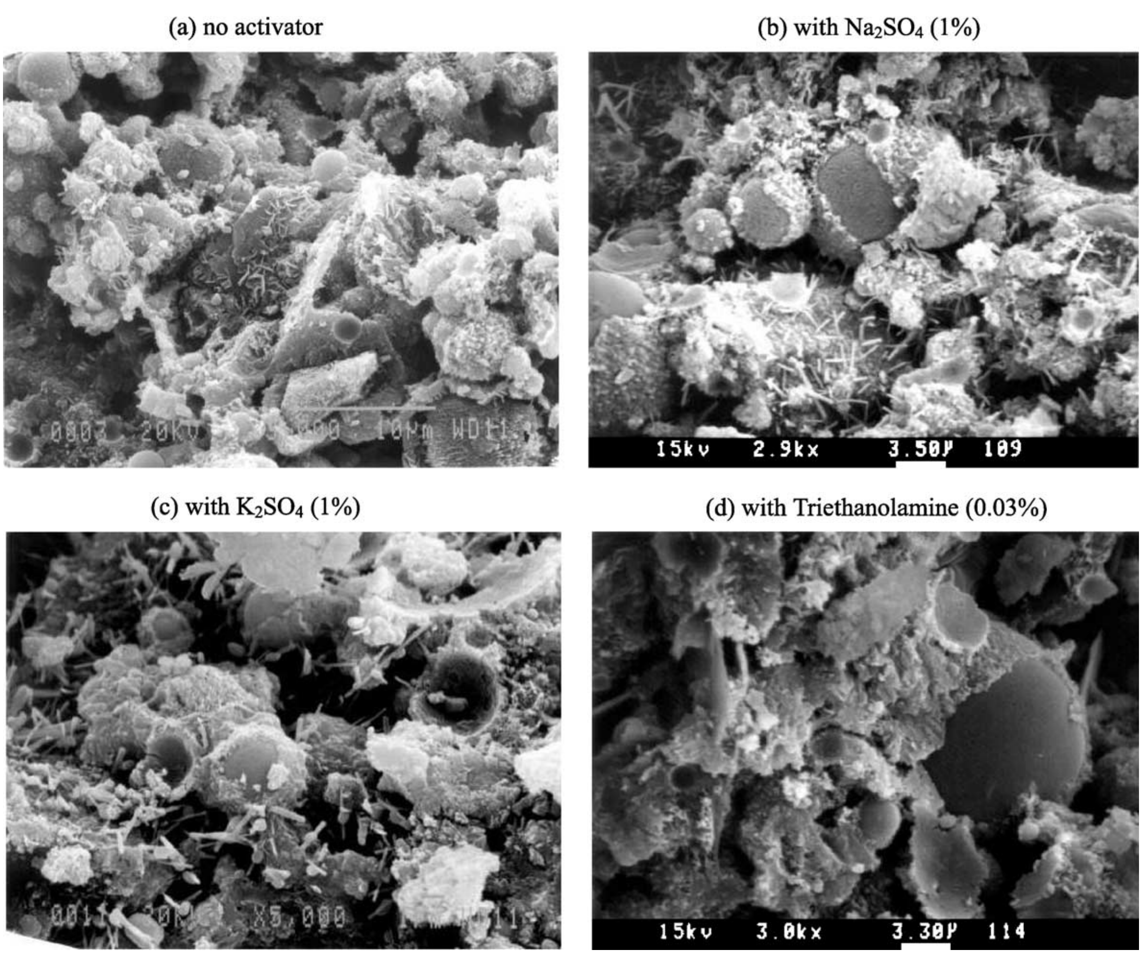

Fig. 6. SEM pictures of chemically activated fly ash–cement pastes at 3 days.

the activators increased production of ettringite during early ages of hydration. Na_2SO_4 was the most effective in accelerating the consumption of $Ca(OH)_2$ and increasing the amount of ettringite in fly ash–cement pastes, offering a reasonable explanation why mortar samples with Na_2SO_4 showed higher compressive strength at early ages.

(3) The addition of activators resulted in increasing the volume of smaller pores and lowering the total porosity for the fly ash–cement pastes. K_2SO_4 was the most effective in reducing the pore size and the total porosity. This is one of the major causes of the enhancement of the early strength of fly ash mortar with activators.

(4) Further investigation is needed to quantify the effects of activators on the development of microstructure and strength of fly ash–cement systems at early and later ages with respect to the their dosage level and curing method.

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