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EARLY MICROSTRUCTURE DEVELOPMENT OF ACTIVATED LIME-FLY ASH PASTES

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ABSTRACT

The effect of activators Na_2SO_4 and $CaCl_2$ on early microstructure development of lime-fly ash pastes was examined. The control lime-fly ash pastes did not show a significant strength up to 28 days. The addition of 4% Na_2SO_4 increased both the early and later strengths of lime-fly ash pastes significantly. $CaCl_2.2H_2O$ (4%) was less effective at 3 and 7 days, but more effective at 28 days than Na_2SO_4. Scanning electron microscope observation and X-ray diffraction analysis indicated that very limited amount of C-S-H, ettringite (AFt) and monosulphoaluminate (AFm) formed in the control pastes even at 28 days. C-S-H and AFt filled most spaces between fly ash particles in the Na_2SO_4 activated pastes at 3 days, and the structure became denser with time. $CaCl_2$ activated pastes also exhibited a dense structure at 3 days, in which most voids between fly ash particles were filled with C-S-H and the solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ ($X<1$ and $Y<2$). The amount of the solid solution increased drastically from 7 to 28 days, which resulted in a denser structure and a higher strength than Na_2SO_4 activated pastes.

INTRODUCTION

Fly ash is being increasingly used in concrete because it lowers the cost and improves some properties of concrete. However, the replacement of portland cement with fly ash, especially in high volume, decreases the early strength of concrete.

Fly ash contributes to the strength of concrete in three ways: (1) by reduction of water requirement for a given slump; (2) by increase of volume of paste thereby improvement of workability and (3) by pozzolanic reaction between fly ash and $Ca(OH)_2$ [1]. The first two aspects are beneficial to the early strength. Thus, the decrease of the early strength of concrete containing fly ash is attributed to the slow pozzolanic reaction between fly ash and $Ca(OH)_2$.

Different means have been investigated to accelerate the pozzolanic reaction between fly ash and $Ca(OH)_2$ thereby to increase the early strength of the concrete containing fly ash. Increasing fineness of fly ash apparently increases the pozzolanic reactivity of fly ash and the early strength of the concrete containing fly ash [2-4]. Elevating curing temperature is

TABLE 1
Composition and Some Physical Properties of Fly Ash [14]

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
57.8	23.0	3.5	9.9	1.5	0.3	2.3	0.5	0.5

Glass	Quartz	Mullite	Hematite	Density (kg/m^3)	Blaine Fineness (m^3/kg)	% Pass 45 um
83.9	4.1	10.2	1.4	2000	280	74

also beneficial to the early strength development of fly ash concrete [5-6], but is limited for many applications. Little work has been done on the chemical activation of the reactivity of fly ash [7-9]. Extensive studies have indicated that the addition of chemical activators can effectively accelerate or improve the pozzolanic reactivity of natural pozzolans [10-13]. In a preliminary study [9], it was found that the reactivity of fly ash could be significantly increased by the addition of Na_2SO_4 and $CaCl_2$. This study examines the effect of chemical activators Na_2SO_4 and $CaCl_2$ on early microstructure development of lime-fly ash pastes at room temperatures.

Experimentation

Raw Materials. One subbituminous fly ash from Sundance, Alberta, Canada, was used in this study. The chemical composition, mineral composition and some physical properties of the fly ash are given in Table 1. According to ASTM C618, this fly ash belongs to Type F. Scanning electron microscope (SEM) observation, as shown in Figure 1, indicated that the fly ash consisted of smooth spherical particles.

A commercial hydrated high calcium lime was blended with fly ash to test the pozzolanic reactivity of fly ash. Chemical reagents Na_2SO_4 and $CaCl_2.2H_2O$ were used as activators.

Preparation of Specimens. Pozzolanic reactivity of the fly ash was determined by blending 80% fly ash and 20% hydrated lime in mass. A water to solid ratio of 0.35 was used to pro-

FIG. 1.
SEM observation of fly ash particles.

duce a paste with a normal consistency. Activators Na_2SO_4 and $CaCl_2.2H_2O$, whose dosage was 4% based on the mass of lime-fly ash blend, were dissolved into mixing water first, then mixed with the lime-fly ash blend for five minutes by hand. Pastes were cast into glass vials 25 mm diameter and 50 mm high, and placed in a fog room at a temperature of 23°C for curing. These specimens were demoulded quickly when they showed a certain strength, and then put back into the fog room and cured until testing ages were attained.

Setting Times. Setting times were determined by following ASTM C191.

Strength Tests. At every testing age, four specimens were taken out from the fog room. Ends of each specimen were polished to make the two bearing surfaces flat and parallel. Three specimens were used for compressive strength tests and the other one for microstructural examination. An average strength from the three specimens is presented. The coefficient of variation of these results is less than 10%.

Preparation of Specimens for SEM Observation and X-Ray Diffraction (XRD) Analysis. A freeze-drying technique was used to arrest the hydration of lime-fly ash pastes and to dry them for the purpose of SEM observation and XRD analysis. The 4th cylinder was cut into small fragments and then freeze-dried to remove evaporable water in the lime-fly ash pastes. The freeze-drying procedures were described previously [15]. The dried fragments were stored in sealed containers and used for later SEM observation and X-ray diffraction analysis.

SEM Observation and Powder XRD Analysis. A Cambridge stereoscan 150 Scanning Electron Microscope was employed to observe the morphology of the raw fly ash particles and the microstructure of lime-fly ash pastes. Micrographs were taken of areas showing typical morphology for different samples at magnifications ranging from 20X to 100,000X.

Freeze-dried lime-fly ash pastes were ground and tested using a Philips X-ray diffractometer. Hydration products were identified with the help of the characteristics peak database from the Powder Diffraction File of the International Centre for Diffraction data, together with the SEM observation.

Experimental Results

Setting Times. The control lime-fly ash paste exhibited a long setting time, as shown in Table 2. The addition of Na_2SO_4 or $CaCl_2$ to lime-fly ash paste did not show an obvious

TABLE 2

Effect of Activators on the Setting Times of Lime-Fly Ash Pastes at Room Temperatures

Paste	Setting Time (h:m)	
	Initial	Final
Control	7:45	60:05
+ 4% Na_2SO_4	7:20	26:05
+ 4% $CaCl_2.2H_2O$	5:40	26:00

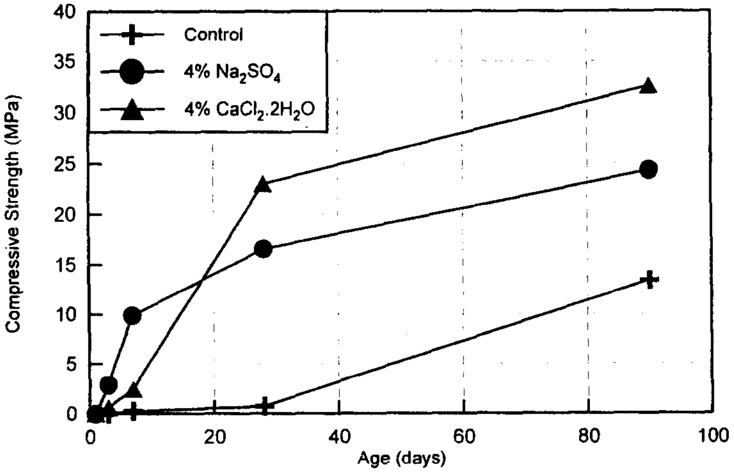


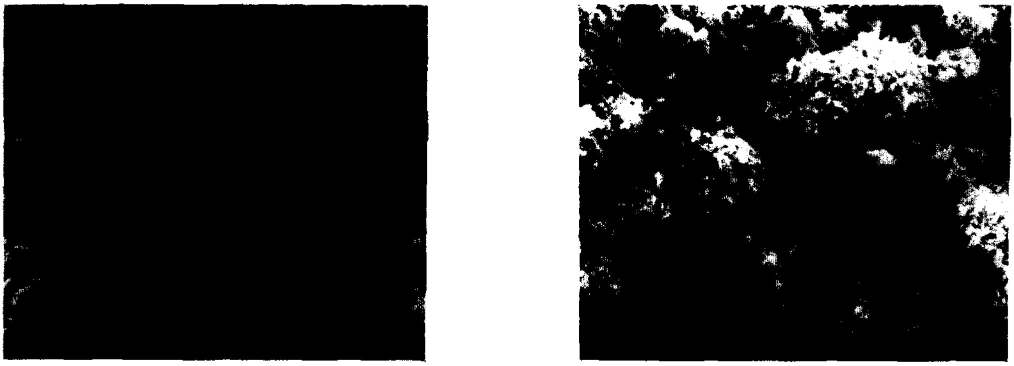
FIG. 2.
Effect of Activators on Strength Development of Lime-Fly Ash Pastes at 23°C

effect on the initial setting time, but shortened the final setting time from approximately 60 to 26 hours.

Compressive Strength. Figure 2 shows the effect of chemical activators on strength development of lime-fly ash pastes at 23°C. The control lime-fly ash paste exhibited no measurable strength up to 3 days, a strength of approximately 1 MPa at 7 and 28 days, and 13 MPa at 90 days. Na_2SO_4 activated paste also exhibited no measurable strength at 1 day, but gave 3 MPa at 3 days, 10 MPa at 7 days and 19 MPa at 28 days. $CaCl_2$ activated paste showed no strength at 1 day, and only one third of the strength of Na_2SO_4 activated pastes at 3 and 7 days, but 23 MPa at 28 days. This meant that $CaCl_2$ was very effective in increasing the strength of lime-fly ash pastes at later ages

SEM Observation. The microstructure of lime-fly ash pastes hydrated for 3 days is shown in Figure 3. For the control pastes (Figure 3-a), all fly ash particles appeared to be slightly etched but far separated. Only very small amount of coagulated gel, needles and hexagonal plates precipitated on the surface of fly ash particles. In the Na_2SO_4 activated pastes (Figure 3-b), all fly ash particles in the pastes were covered by coagulated gel and needles, which were interlocked. $CaCl_2$ activated pastes appeared to be less dense than the Na_2SO_4 activated pastes, but most spaces between fly ash particles were filled by foil-like gel and hexagonal plates (Figure 3-c).

Figure 4 shows the microstructure of the control lime-fly ash pastes at 28 days. Compared with the structure at 3 days (Figure 3-a), all fly ash particles were more etched, but still far separated (Figure 4-a). It seemed that more coagulated gel, needles and bigger hexagonal plates precipitated on the surface of fly ash particles (Figure 4-a). The fracture surface of the Na_2SO_4 activated pastes cured for 28 days showed a dense structure (Figure 4-b). Overlapped needles could be identified on the fracture surface, while coarse needles were clearly observed in air voids (Figure 4-c). Occasionally, very few hexagonal plates could also be observed in air voids in the Na_2SO_4 activated pastes. The fracture surface of the $CaCl_2$ activated pastes appeared to be much denser than that of the Na_2SO_4 activated pastes (Figure 4-



(a) Control Pastes (b) Na_2SO_4 Activated Pastes

(c) $CaCl_2$ Activated Pastes

FIG. 3.
SEM observation of lime-fly ash pastes cured for 3 days.

d). The morphology of hydration products could not be identified on the fracture surface, but a large amount of big hexagonal plates were observed in air voids in the $CaCl_2$ activated pastes.

XRD Analysis. Figure 5 shows the XRD patterns of lime-fly ash pastes cured for 3, 7 and 28 days. The hydration products were identified in combination with the SEM observations. C-S-H gel was the main hydration product in the three pastes. The addition of activator changed the other hydration products.

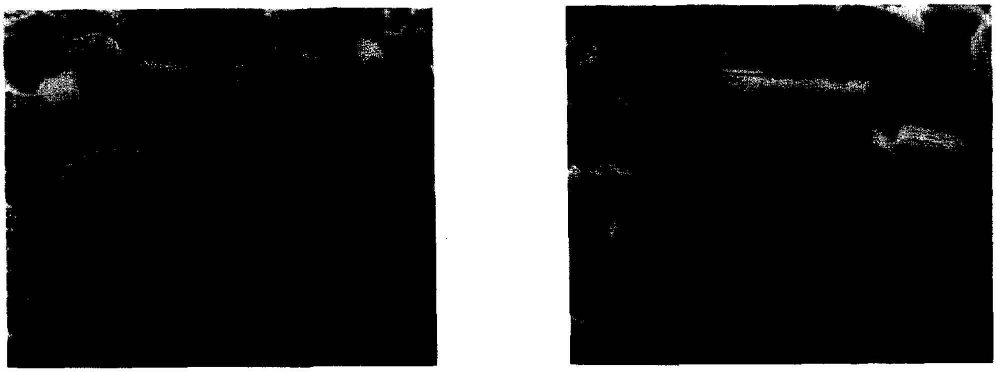
In addition to C-S-H, ettringite (AFt) and AFm were detected in the control pastes. Weak diffraction peaks indicated that the amount of AFt was minor and no observable change happened from 3 to 28 days. While AFm diffraction peaks were intensified from 3 to 28 days. Unreacted hydrated lime was also detected and its diffraction peaks seemed unchanged from 3 to 28 days.

When 4% Na_2SO_4 was added, strong AFt diffraction peaks were observed at 3 days and diminished slightly with time. Very weak AFm diffraction peaks were identified at 3 days, and diminished with time and disappeared at 28 days. Diffraction peaks of unreacted hydrated lime were weaker than those in the control pastes and diminished slightly with time.

(a) Control Pastes

(b) Fracture Surface of Na_2SO_4 Activated Pastes

(c) Products in Voids of Na_2SO_4 Activated Pastes



(d) Fracture Surface of $CaCl_2$ Activated Pastes

(e) Products in Voids of $CaCl_2$ Activated Pastes

FIG. 4.
SEM observation of lime-fly ash pastes cured for 28 days.

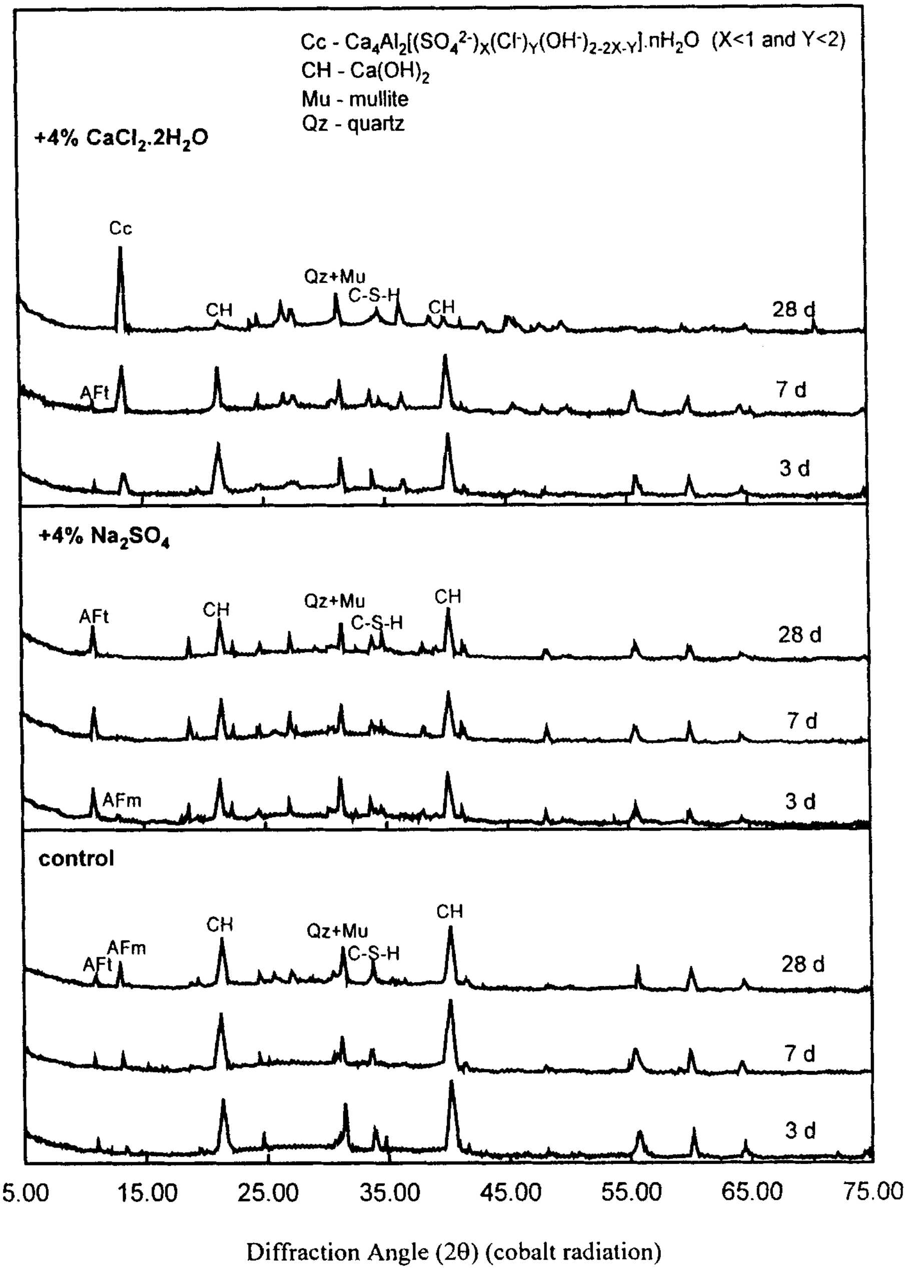


FIG. 5.
XRD patterns of lime-fly ash pastes at different ages.

In the $CaCl_2$ activated pastes, diffraction peaks similar to those of AFm were identified and were intensified from 3 to 28 days. According to the compositionof this paste, these diffraction peaks might belong to a solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ (X<1 and Y<2). As time proceeded, the intensity of these diffraction peaks increased significantly and the portion of SO_4^{2-}, Cl^- and OH^- changed with time. Weak AFt diffraction peaks appeared at 3 and 7 days, but disappeared at 28 days. The other interesting fact was that diffraction peaks of hydrated lime slightly diminished from 3 to 7 days, and almost disappeared at 28 days.

Discussion

The addition of Na_2SO_4 significantly increased both early and later strengths of lime-fly ash pastes. $CaCl_2$ was less effective at 3 and 7 days, but more effective at 28 days than Na_2SO_4. A suggested activation mechanism of lime-fly ash pastes by Na_2SO_4 and $CaCl_2$ can be briefly described in the following paragraphs.

The early pozzolanic reaction between lime and fly ash depends upon the dissolution of fly ash. The addition of Na_2SO_4 to lime-fly ash pastes increases the alkalinity of the solution and the dissolution of fly ash at initial stages, which accelerates the pozzolanic reaction between lime and fly ash [15]. At the same time, a large amount of AFt is also formed due to the added SO_4^{2-}. The accelerated initial pozzolanic reaction and the formation of AFt induce high early strength of the lime-fly ash paste. As time proceeds, pozzolanic reaction continues and pastes become stronger.

The introduction of $CaCl_2$ decreases the solubility of $Ca(OH)_2$ and pH of lime-fly ash pastes due to the common ion effect [16], which decreases the dissolution of fly ash, but favour the formation of the solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ ($X<1$ and $Y<2$). The formation of the solid solution would speed up the dissolution of fly ash particles and the pozzolanic reaction, which enhances the strength of lime-fly ash pastes at 3 and 7 days. As curing time increases, the amount of the solid solution increases significantly, which results in a denser structure and a higher strength than Na_2SO_4 activated pastes.

Conclusions

1. The addition of Na_2SO_4 or $CaCl_2$ did not affect the initial setting time, but shortened the final setting time of lime-fly ash pastes.
2. No pastes showed measurable strengths at 1 day. Both Na_2SO_4 and $CaCl_2$ activated pastes showed much higher strength than control pastes from 3 to 28 days. Na_2SO_4 activated pastes had a much higher strength than $CaCl_2$ activated pastes at 3 and 7 days, but the former had a lower strength than the latter at 28 days.
3. C-S-H, AFt and AFm were the identified hydration products in the control lime-fly as pastes. The addition of Na_2SO_4 resulted in the formation of a large amount of AFt in addi-tion to C-S-H. The presence of $CaCl_2$ caused the formation of a solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ ($X<1$ and $Y<2$) instead of AFt.
4. The addition of Na_2SO_4 raised the alkalinity of pore solutions, accelerated initial pozzolanic reaction and resulted in the formation of AFt, which gave the high early strength of the lime-fly ash paste. While the presence of $CaCl_2$ decreased the alkalinity of the solution but favoured the formation of a solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ ($X<1$ and $Y<2$). The drastic increase of the solid solution resulted in a denser structure and a strength higher than Na_2SO_4 activated pastes at 28 days.

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