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Activation of blended cements containing fly ash

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Abstract

This study has investigated the activation of reactivity of fly ash in different blended cements such as lime–fly ash, lime–fly ash–slag and Portland fly ash cements. Experimental results have indicated that the addition of Na_2SO_4 can significantly increase the strength of all these blended cements. The activation effect happens mainly during the first 3 to 7 days. The grinding of fly ash also increases its activity, but is not as effective as the addition of Na_2SO_4. On the other hand, the combination of grinding and the addition of Na_2SO_4 shows a much higher strength than a single activation method. Finally, this paper also discusses the feasibility of the addition of Na_2SO_4 in different cement and concrete products production processes.

Keywords: Fly ashes; Blended cements; Activation; Na_2SO_4

1. Introduction

Fly ash is a by-product during the coal power generation and consists mainly of SiO_2, Al_2O_3, Fe_2O_3 and CaO. According to ASTM C618 [1], fly ash belongs to Class F if it is $(SiO_2+Al_2O_3+Fe_2O_3)>70\%$, and belongs to Class C if it is $70\%>(SiO_2+Al_2O_3+Fe_2O_3)>50\%$. Usually, Class F fly ashes have a low content of CaO and exhibit pozzolanic properties, but Class C fly ashes contain up to 20% CaO and exhibit cementitious properties.

Most fly ashes in China belong to Class F and contain less than 5% CaO. Lime–fly ash mixtures have been widely used as masonry cement and for the production of blocks in China since the late 1950s. Different activation methods such as the addition of gypsum, grinding and elevated temperature curing are widely used in the production of blocks. However, the strength of lime–fly ash blocks is still much lower than Portland cement blocks. Most lime–fly ash block plants are closed now because of the low quality of the products.

Recently, Shi and his colleagues [2–8] have published a series of researches on the activation of reactivity of natural pozzolans and fly ashes. They found that Na_2SO_4 and $CaCl_2$ are the most effective activators to activate the potential activity of pozzolanic materials. A comparison based on strength and cost addition of Na_2SO_4 and $CaCl_2$ is much more effective than prolonged grinding of natural pozzolans or elevated curing temperature.

In this study, the focus was on the activation of activity of fly ash using Na_2SO_4. The purpose of this study was to try to find an effective and simple way to activate the activity of fly ash and to increase the utilization of fly ash in the production of blocks.

2. Experimentation

2.1. Raw materials

2.1.1. Fly ash

The fly ash used in this study was from Jiulongpo Power Plant in Chongqing City. Its chemical compositions and main physical properties are given in Tables 1 and 2. Some fly ash was also ground for 30 min in a lab ball mill in order to examine how the grinding increases the activity of the fly ash. Its specific density is 2560 kg/m^3 and specific surface area is 690 m^2/kg.

2.1.2. Blast furnace slag

Granulated blast furnace slag was obtained from Chongqing Iron and Steel Company. The basicity of the

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slag is 1.08. The slag was ground for 40 min in a lab ball mill. Its chemical composition is given in Table 1.

2.1.3. Portland cement

A Chinese GB Grade 525 Portland cement from Chongqing Cement Plant was used. The chemical composition of the cement is shown in Table 1.

2.1.4. Limes

Both quicklime and hydrated lime were used in this study. Quicklime was from Gele Mountain in Chongqing and was ground for 20 min. Hydrated lime was from the quicklime slaked in normal circumstance for 3 days.

2.1.5. Activators

Anhydrous sodium sulfate was used as the activator. Both gypsum and hemihydrate made in Chongqing were also used as activators in this study.

2.1.6. Sand

A fine sand from Yangtze River was used for making concrete. The modulus of the sand is 0.9. The standard sand which meets GB177-85 specification was used for standard mortar testing.

2.1.7. Coarse aggregate

Crushed limestone is used as the coarse aggregate and its maximum size is 15 cm.

2.2. Preparation of specimens and testing

The preparation and testing of mortar samples were conformed to GB177-85. When the standard sand is used, the sand–cement ratio is 2.5 and the water–cement ratio is 0.46. When the fine river sand is used, the sand–cement ratio is 2, and cement–water ratio is adjusted depending on the workability similar to the condition using standard sand. The water–cement ratio is 0.5 in most cases. The activator Na_2SO_4 was dissolved into water first then mixed with the dry materials. The mortar mixtures were cast into $4 \times 4 \times 16$ cm prisms and cured in a fog room at 20 ± 2°C.

When those mortar samples were strong enough for demolding, they were demolded and kept in the fog room for continued curing. At each testing age, three prisms were taken out for flexural strength test first, then compression tests were conducted on the six pieces of broken prisms.

Table 1
Chemical composition of raw materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
Fly ash	44.0	23.4	17.7	3.7	0.8	0.9	0.8	0.8	5.7
Slag	33.1	12.9	2.8	40.0	6.8		0.31	0.58	
Portland cement	21.97	6.72	3.43	58.36	2.13	2.24	0.85		

Table 2
Main physical properties of fly ash

Density (kg/m^3)	Blaine fineness (m^2/kg)	Retaining of 45 μm (%)	Water demand ratio (%)	Compressive strength ratio (%)
2330	440	29.4	94	77

Flexural strengths are not presented here. Presented compressive strengths were an average of results from six broken prisms.

There was some comparability on strength between the colloidal mortar using superfine sand and that using standard sand. The strength of the former is about 80–85% that of the latter.

3. Experimental results and discussions

3.1. Lime–fly ash blends

The strength experiment of lime–fly ash mortars is shown in Fig. 1. In the absence of an activator, the lime–fly ash (nonground) mortars did not exhibit any strength at 7 days and gave a strength of about 1 MPa at 28 days. After the fly ash was ground for 30 min in ball mill, the lime–fly ash mortars had no strength at 3 days, but a strength of about 1 MPa at 7 days and 2.3 MPa at 28 days.

When 3% Na_2SO_4 was added, the lime–fly ash (nonground) mortars gave a strength of 2.6 MPa at 7 days and approximately 9 MPa at 28 days. After the fly ash was ground, the lime–fly ash mortars gave a strength of 2.5 MPa at 3 days, 5.5 MPa at 7 days and approximately 12.5 MPa at 28 days.

Strength tests were also conducted on pure fly ash and fly ash with Na_2SO_4. Those materials did not show any strength at all. This means that the fly ash used does not have any cementitious properties. The grinding did increase the activity of the fly ash and the strength of lime–fly ash mortar. However, grinding is an energy-intensive process and needs complicated equipment. The addition of Na_2SO_4 increased the strength of the lime–fly ash mortars much more significantly than the grinding. Shi and Day [9] compared different activation methods based on the cost of per unit strength of materials, and concluded that the chemical activation method is the most effective. A chemical activator(s) can be added during the mixing process. It does not need any significant changes on current production line and can be easily accepted by the cement and concrete industry.

The other interesting factor is that the strength increase between 7 and 28 days was the same before and after the fly ash was ground. It indicates that the chemical activation effect happens mainly before 7 days. This is in agreement with the findings obtained by Shi [3] from lime–natural pozzolan blends. Of course, the combination of grinding and the addition of Na_2SO_4 gave higher strength than any

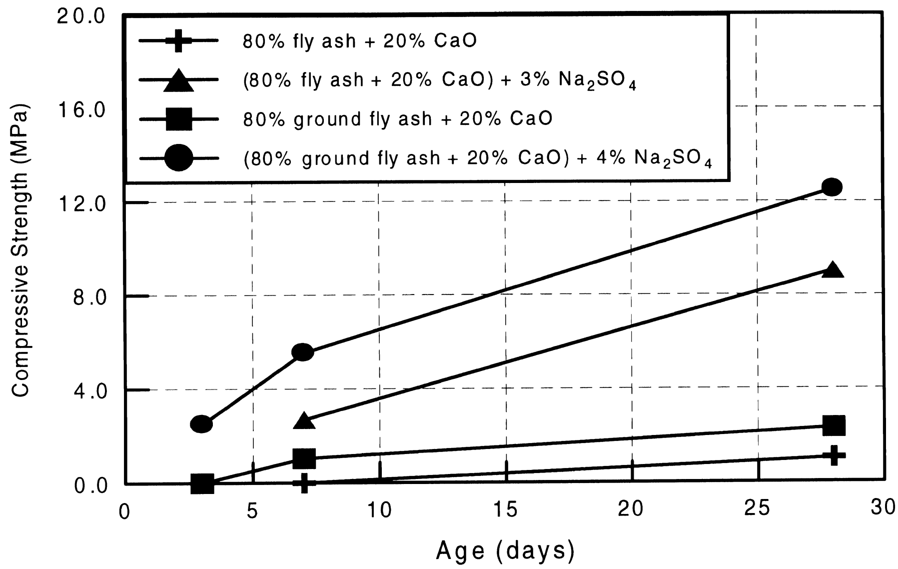


Fig. 1. Strength development of lime–fly ash mortars.

single activation process. This can be seen more obviously at 28 days than at 3 days.

3.2. Lime–fly ash–slag mixtures

Many studies have been conducted on the activation of slag [10–12]. Alkali-activated slag cements can give much higher strength than conventional Portland cement in the absence of lime and Portland cement. However, the hydration and strength development of alkali-activated slag are much more complicated than those of Portland cement because so many factors such as the nature and dosage of activator(s), source of slag, water to slag ratio, temperature, etc. The water to slag ratio and temperature can also affect the species in sodium silicate solution. Thus, the hydration and properties of sodium silicate-activated slag are very sensitive to these two factors [13]. Na_2SO_4 is not very effective to in activating the hydration of slag itself [14], but can increase the strength and change the structure of lime–slag blended cement very significantly [15].

In this study, some fly ash was replaced by ground granulated blast furnace slag in order to increase the strength of the cement. The strength development of

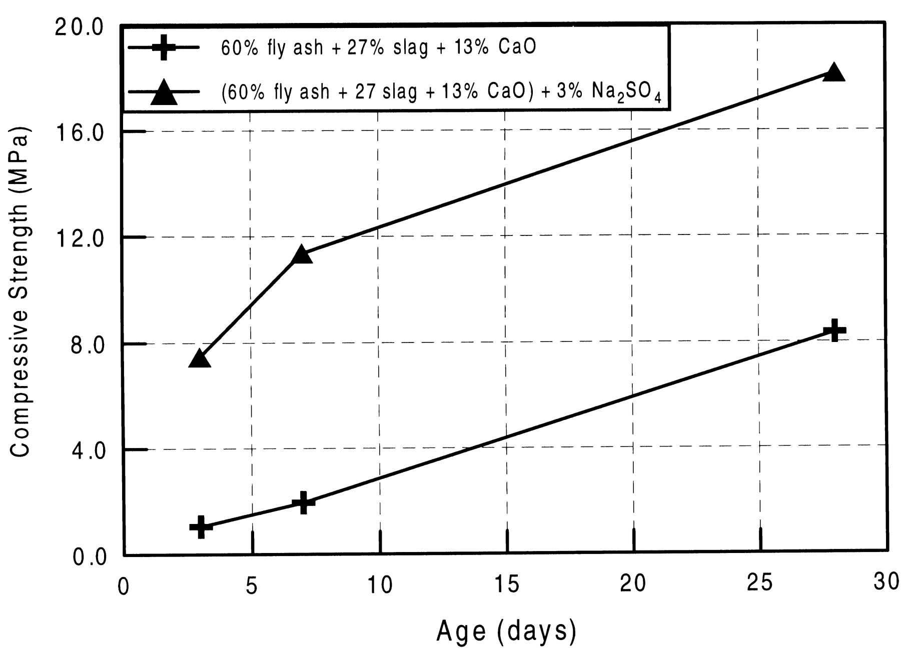


Fig. 2. Strength development of lime–fly ash–slag mortars.

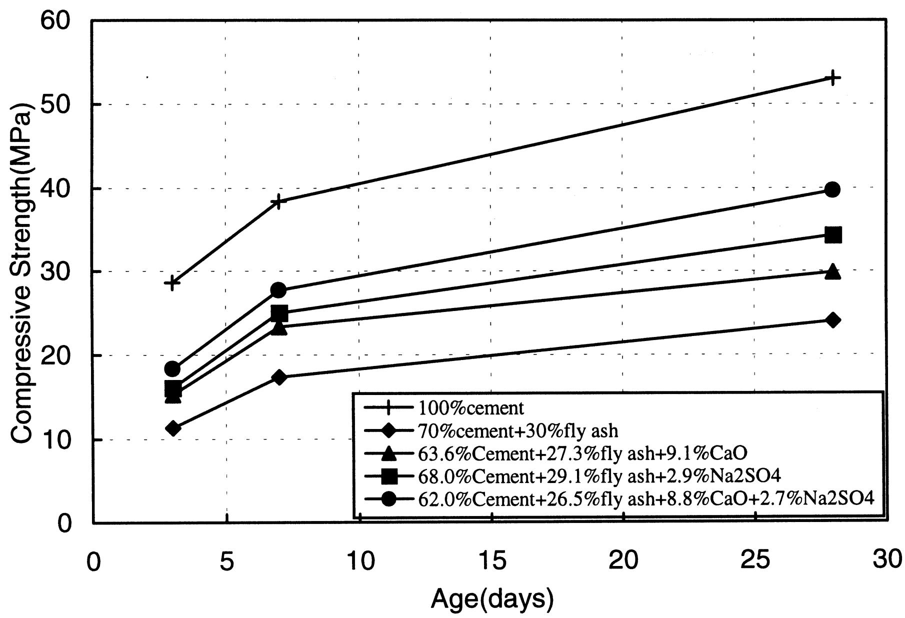


Fig. 3. Strength development of low volume fly ash Portland cement fly ash cement.

lime–fly ash–slag mortars is shown in Fig. 2. The replacement of fly ash with slag gave higher strengths from 3 to 28 days. The strength increase was much more obvious in the presence of 3% Na_2SO_4. It means that slag is much more sensitive to activator Na_2SO_4 than fly ash does. As for lime–fly ash mortars, the strength development trends of lime–fly ash–slag mortars in the presence and absence of Na_2SO_4 are very similar between 7 and 28 days. It further confirms that the activation effect of Na_2SO_4 happens mainly before 7 days.

3.3. Portland cement–fly ash–lime mixtures

Fly ash has been widely used to partially replace Portland cement in cement concrete. It can improve the later strength and durability of concrete and may decrease materials costs significantly. However, the obvious disadvantages of partial replacement of Portland cement with fly ash are longer times of setting and lower early strengths.

Fig. 3 shows the strength development of low volume fly ash Portland fly ash cement. When 30% Portland cement

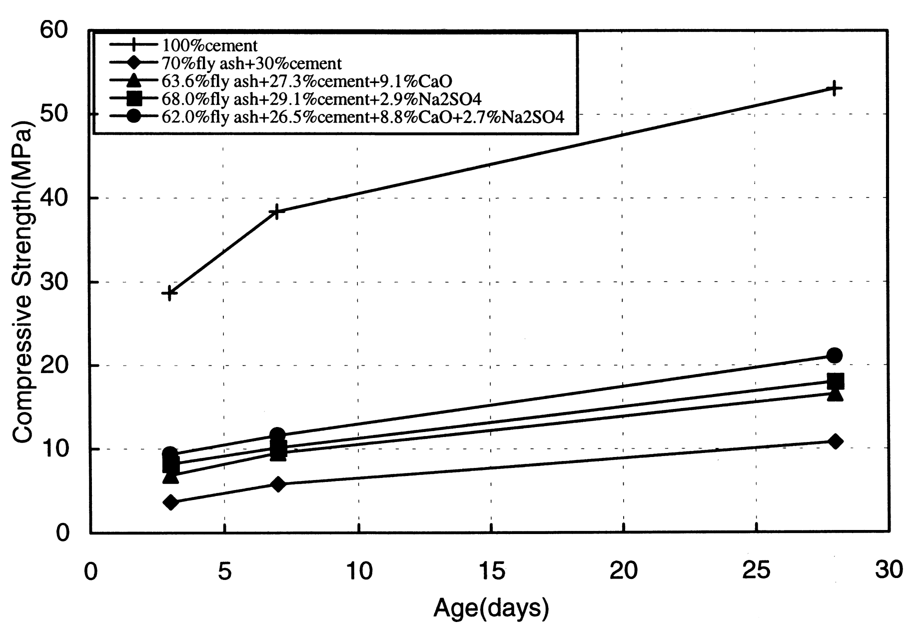


Fig. 4. Strength development of high volume fly ash Portland cement fly ash cement.

was replaced, the addition of 3% Na_2SO_4 increased the strength of the cement almost by 50% from 3 to 28 days. The addition of 9.1% CaO also increased the strength of the cement. The combination of Na_2SO_4 and CaO gave the highest strength from 3 to 28 days.

Fig. 4 shows the strength of high volume fly ash Portland fly ash cement. The strength of high volume fly ash Portland fly ash cement had lower strengths than low volume fly ash Portland fly ash cement. However, the effects of Na_2SO_4 and CaO on the strength development of the two cements are very similar. Since lime is much cheaper than Portland cement in China, there are technical and economical benefits to replace some Portland cement in Portland fly ash cement with quicklime.

3.4. Comparison of lime–fly ash and portland fly ash cement blocks

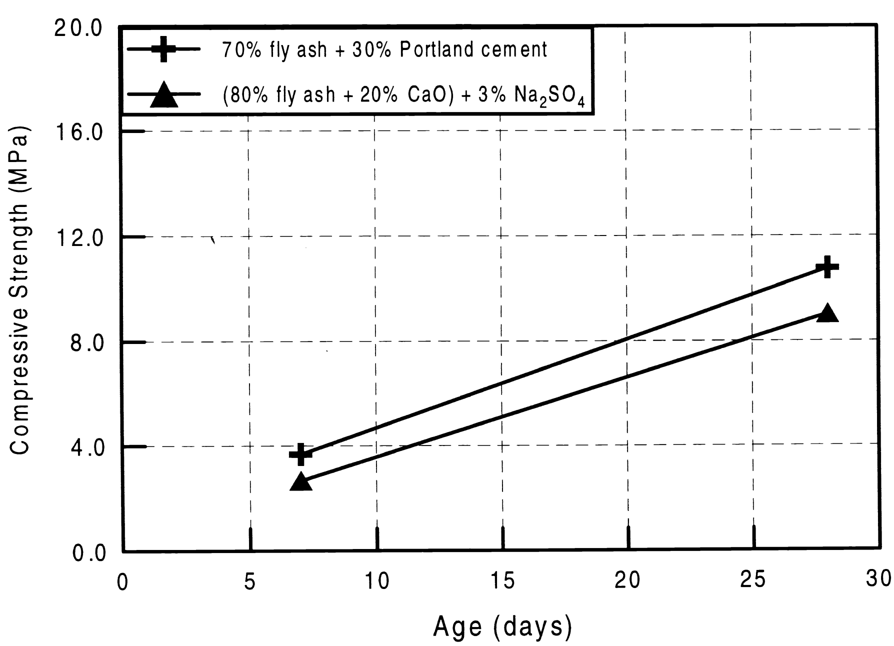
As stated above, Portland cement is much more expansive than lime and Na_2SO_4 in China, the replacement of Portland cement with lime and Na_2SO_4 is of practical significance. Fig. 5 is the comparison of strength development of lime–fly ash and Portland fly ash blocks. It can be seen that the strength of [(80% fly ash + 20 lime) + 3% Na_2SO_4] is only slightly lower than that of (70% fly ash + 30% Portland cement). Although no detailed cost calculations were conducted, it can be expected that the former binder is cheaper than the latter.

3.5. Activated lime–fly ash bricks/blocks

In China, a large quantity of land is being dug for the manufacture of clay bricks. Quality bricks or blocks cannot be manufactured by using traditional lime–fly ash blends. It can be expected that the quality from activated lime–fly ash blends should be much better. Fig. 6 shows the mixing proportions and strengths of blocks made from activated quicklime–fly ash cement. The cement used in this experiment was composed of 84% fly ash (raw fly ash), 13% calcium lime (the dosage of white lime is derived from CaO), and 3% Na_2SO_4. The compaction pressure was 20 MPa. The specimens have a size of $4 \times 4 \times 16$ cm and were cured in a fog room at 20°C. It can be seen that the compressive strength of the blocks was over 13 MPa, which is higher than the requirement of 10 MPa. The strength of blocks can be further improved by using ground fly ashes or a partial replacement of fly ash with slag. Thus, it is definitely feasible to use activated lime–fly ash cement to manufacture construction blocks. The ratio of compressive strength to flexural strength is about 6.

3.6. Activation mechanism of fly ashes by Na_2SO_4

It is well known that coal power plant fly ashes consist mainly of aluminosilicate glass. In the absence of an activator, when a lime–fly ash blended cement is mixed with water, $Ca(OH)_2$ in the blended cement hydrolyses first



(water to binder ratio =0.5, binder : river sand =1:2)

Fig. 5. Comparison of compressive strengths of Portland fly ash cement and lime–fly ash cement mortars.

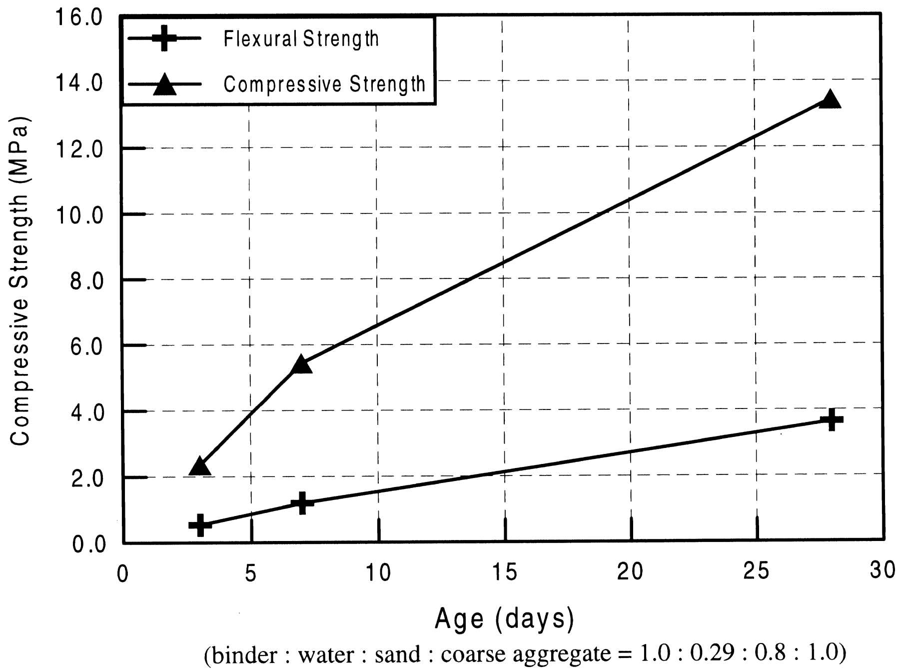


Fig. 6. Strength development of activated quicklime–fly ash blocks.

and the solution reaches a high pH value (approximately 12.5 at 20°C) very quickly (Eq. (1)):

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (1)$$

If a blended cement contains Portland cement instead of lime, on one hand, Portland cement always contains certain amounts of free lime; on the other hand, Portland cement hydrates very quickly when it comes into contact with water and releases lime.

Under the attack of OH^- in such a high pH solution, network modifiers, such as Ca^{2+}, K^+, Na^+, etc., in the fly ash are dissolved into the solution very quickly. Silicate or aluminosilicate network formers in fly ashes are also depolymerized and dissolved into the solution. When Ca^{2+} ions in solution contact these dissolved monosilicate and aluminate species, calcium silicate hydrate C-S-H and calcium aluminate hydrate C_4AH_{13} form.

Since the dissolution of aluminosilicate glass is the slowest process during the initial pozzolanic reaction, it determines the total pozzolanic reaction rate. After a certain period, the surface of fly ash particles is covered by precipitated hydration products; then the further reaction is controlled by the diffusion of OH^- and Ca^{2+} through the precipitated products and into the inner side of precipitated products. The later hydration is no longer a solution-precipitation reaction but a topochemical reaction.

When Na_2SO_4 is added, Na_2SO_4 reacts with $Ca(OH)_2$ first as expressed by Eq. (2):

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O\downarrow + 2NaOH \quad (2)$$

The reaction increases the pH of the solution, accelerates the dissolution of fly ashes and speeds up the pozzolanic reaction between $Ca(OH)_2$ and the fly ashes. At the same time, the introduction of Na_2SO_4 increases the concentration of SO_4^{2-} and results in the formation of more ettringite (AFt). The generation of AFt increases the solid volume by 164%, but the formation of C-S-H increases the solid volume by 17.5%. Thus, the generation of AFt densifies the structure and increases the early strength of hardened cement pastes very significantly [16]. Thus, the high early strength of the Na_2SO_4-activated pastes is attributed to two aspects: acceleration of early pozzolanic reaction and the formation of more AFt.

Thermodynamic calculation indicates that AFt is the stable phase below 70°C and AFm above 70°C [17]. High temperature curing may result in a lower strength development rate and lower ultimate compressive strength due to the formation of AFm.

4. Conclusions

The addition of Na_2SO_4 increased the strength of cement containing fly ash very significantly at early and later ages. Results from different types of cement confirmed that the activation effect happened mainly before 3 to 7 days.

The grinding of fly ash can also increase the activity of fly ash, but not as significant as the addition of Na_2SO_4. The combination of grinding and the addition of Na_2SO_4 gave higher strength than either the grinding or the addition of Na_2SO_4 alone.

Ground granulated blast furnace slag was much more sensitive to Na_2SO_4 than fly ash. The addition of CaO into Portland fly ash cement could also activate the potential activity of fly ash.

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