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Comparison of different methods for enhancing reactivity of pozzolans

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Abstract

This paper compares three methods for the activation of pozzolanic reactivity of a natural pozzolan: (1) prolonged grinding of natural pozzolans (mechanical method), (2) elevated temperature curing of cement pastes containing a pozzolan (thermal method), and (3) use of chemical activators such as Na_2SO_4 and $CaCl_2$ (chemical method). The pozzolanic reactivity of natural pozzolans was evaluated using a mixture of 80% natural pozzolan and 20% hydrated lime. Several parameters such as $Ca(OH)_2$ consumption rate, strength development, ultimate compressive strength and cost were compared. All three activation methods accelerated both the pozzolanic reaction and strength development rates of the lime–pozzolan pastes. However, mechanical activation did not show a significant effect on the ultimate strength, while thermal activation decreased the ultimate strength and chemical activation (addition of 4% Na_2SO_4 or $CaCl_2{\cdot}2H_2O$ based on the mass of lime–pozzolan blends) increased the ultimate strength of lime–pozzolan mixtures significantly. The application of mechanical or thermal activation techniques needs extra equipment and energy, and thus increases materials costs significantly. Chemical activators can be added during the grinding of the natural pozzolan or during the mixing of concrete containing a pozzolan, so the requirement of extra equipment is minimal. Although the addition of chemical activator(s) increases the total material costs, the cost per unit strength development decreases. Based on current test results, chemical activation is the most efficient and feasible method for the activation of natural pozzolans.

Keywords: Pozzolan; Chemical activators; Grinding; Thermal treatment; Strength

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1. Introduction

Natural pozzolans have been widely used as substitutes for Portland cement in many applications because of their advantageous properties which include cost reduction, reduction in heat evolution, decreased permeability, alkali–aggregate expansion control, increased chemical resistance, reduced concrete drying shrinkage and the improvement of the properties of fresh concrete [1]. However, the most obvious disadvantage for the replacement of Portland cement with natural pozzolans is that early strength is normally decreased.

Several techniques have been tried to improve the pozzolanic reactivity of natural pozzolans, which include calcination [2–4], acid treatment [5–7], prolonged grinding [8,9], elevated temperature curing [1,10,11] and the use of chemical activators [12,13]. It has been found that the effect of calcination on the reactivity of the pozzolan depends on the combination of the two effects: an activation depending on the reactivity of the vitreous, zeolite and clay phase, and a disactivation depending on the decrease of specific surface area and soluble fraction and the increase of crystalline fraction [4]. Acid treatments result in the formation of gels on the surface of pozzolans and increase reactivity [5,7]; however, this technique is only suitable for low-calcium pozzolans [7]. Prolonged grinding of pozzolans and elevated temperature curing of concrete containing a natural pozzolan can increase reactivity, but their effects are minor. Often, concrete cured at elevated temperatures exhibits lower strengths at later ages. The addition of chemicals to concrete containing pozzolans can increase the pozzolanic reaction rate, strength development rate and ultimate strengths significantly. Although some chemicals such as caustic alkalis are very effective, they are expensive, dangerous and not practically feasible.

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Table 1
Summary of activation methods used for lime–pozzolan cements containing 20% hydrated lime and 80% ground natural pozzolan

Batch	Activator	Curing temperature (°C)	Blaine fineness of pozzolan (m^2/kg)	Effect examined
A	none	50	291	control
B	4% Na_2SO_4[a]	50	291	chemical activation
C	4% $CaCl_2 \cdot 2H_2O$[a]	50	291	chemical activation
D	none	23	291	thermal activation
E	none	65	291	thermal activation
F	none	50	385	mechanical activation
G	none	50	554	mechanical activation

[a] Based on the mass of lime–pozzolan blends.

Previous work has detailed how prolonged grinding of natural pozzolans (mechanical activation), elevated temperature curing of lime–pozzolan pastes (thermal activation) and the addition of 4% (based on the weight of lime–pozzolan blend) Na_2SO_4 or $CaCl_2 \cdot 2H_2O$ (chemical activation) affect pozzolanic reactivity of the natural pozzolans [14–16]. The objective of the current paper is to compare the efficacy of three activation methods as measured by (1) $Ca(OH)_2$ consumption rate (pozzolanic reaction rate), (2) strength development, (3) ultimate compressive strength and (4) cost.

2. Experimentation

2.1. Materials

A volcanic ash (natural pozzolan) from Bolivia was used in this study. The ash was ground to different Blaine finenesses in a ceramic jar. The characteristics of the ash have been described in earlier work [14–16]. A commercial hydrated high calcium lime, which meets ASTM C141 specifications, was utilized for the evaluation of pozzolanic reactivity of the ground natural pozzolan in a mass proportion of 80% and 20%. Chemical reagents Na_2SO_4 and calcium chloride flake ($CaCl_2 \cdot 2H_2O$) were used as chemical activators.

Seven batches, noted as A, B, C, D, E, F and G, were designed to compare the efficacy of the chemical, thermal and mechanical activation methods. The mixing proportions and curing conditions for the seven batches are summarized in Table 1. Since the properties of Batch A have been thoroughly reported in previous work [14–16], it was used as a reference material in this study. Batches B and C were designed to examine the effects of chemical activation, Batches D and E to examine the thermal activation, and Batches F and G to examine the mechanical activation.

2.2. Preparation of specimens

Mixing and specimen preparation were carried out at room temperature. Raw materials were heated to make the initial temperature of the mixtures close to the curing temperatures if the specimens were to be cured at elevated temperatures. After casting into glass vials ($\emptyset 25 \times 50$ mm), the specimens were placed into water baths having temperatures of 23°C, 50°C and 65°C, respectively. The glass vials were stripped very quickly when these specimens had hardened significantly. The demolding process was very quick so that the effect on the curing process was minimal.

2.3. Strength testing and measurement of free $Ca(OH)_2$

At designated testing age from 1 to 28 days, three specimens were used to measure compressive strength. Ends of these specimens were polished to make the two bearing surfaces flat and parallel. If the strength of a specimen differed by more than 10% from the average of the three specimens, the strength value was discarded, and one more specimen was tested. The strength results presented are averages of three specimens whose strengths differed less than 10% from the average of the three specimens.

At the same time, one companion specimen was crushed and soaked in 2-propanol for 3 weeks to stop further hydration and to apply a gentle first drying procedure, the sample was then freeze-dried and used to determine the content of free $Ca(OH)_2$ by Du Pont thermogravimetric analysis in a flowing nitrogen atmosphere at a heating rate of 20°C/min from ambient temperature to 950°C. Sample size was approximately 40 mg. The content of free $Ca(OH)_2$ was back-calculated based upon the mass loss due to the dehydration of $Ca(OH)_2$ determined by a graphical technique [17].

3. Experimental results and discussion

3.1. Pozzolanic reaction rate

The pozzolanic reaction rates, as measured by reduction in free $Ca(OH)_2$ in different mixtures are plotted in Fig. 1. The results from Batch B, compared with Batch A, indicated that the addition of Na_2SO_4 accelerated the pozzolan reaction mainly before 3 days, but the pozzolanic reaction slowed thereafter. The percentage of reacted $Ca(OH)_2$ in Batch B was higher than that in Batch A at all times. The addition of 4% $CaCl_2 \cdot 2H_2O$ showed a very significant

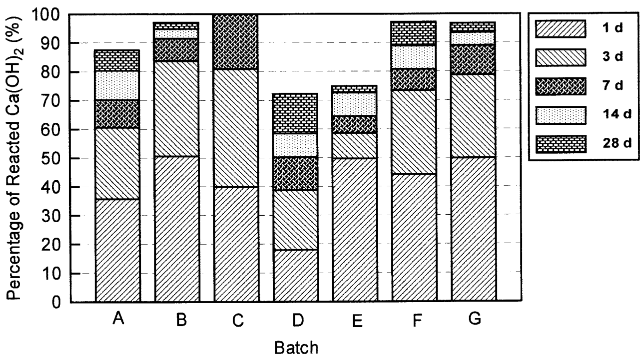

Fig. 1. Percentage of reacted $Ca(OH)_2$ in different batches at different ages.

acceleration effect (Batch C), and all $Ca(OH)_2$ was consumed at 7 days of hydration.

The decrease in curing temperature from 50°C to 23°C (Batch A vs. Batch D) slowed down the pozzolanic reaction rate during the first 3 days, but resulted in a higher rate thereafter. However, the amount of $Ca(OH)_2$ consumed over 28 days at 23°C was still lower than that at 50°C. An increase in curing temperature from 50°C to 65°C (Batch A vs. Batch E) accelerated the pozzolanic reaction rate during the first day, but slowed down the reaction rate thereafter and caused a lower percentage of consumed $Ca(OH)_2$ in the overall testing period. It seems that accelerated pozzolanic reaction during early stages at high temperatures retards further pozzolanic reactions.

The increase in the fineness of the natural pozzolan appeared to accelerate the pozzolanic reaction during the first 3 days (Batch A vs. Batches F and G). The finer the natural pozzolan, the more pronounced the acceleration effect is.

3.2. Strength development

The compressive strengths of different batches at different ages are summarized in Table 2. In order to have a better understanding of how different activation techniques affect strength development, strengths of Batch A at different ages were regarded as 100% and strengths of the six batches relative to Batch A are plotted in Fig. 2. Na_2SO_4 activation (Batch B) increased the strength by 150% at 1 day. Its relative strength decreased thereafter, but was still 75% to 90% higher than the control. $CaCl_2$ activation (Batch C) showed a strength similar to the control at 1 day, but was 100% to 150% higher than the control thereafter.

Table 2
Compressive strength of different batches at different ages

Age	Compressive strength of different batches at different ages (MPa)						
(days)	A	B	C	D	E	F	G
3	3.03	7.65	3.35	nil	3.3	4.71	6.98
7	5	9.46	9.82	0.67	3.79	6.53	8.88
28	6.76	12.58	15.68	4.37	5.1	7.62	9.77
90	8.28	14.32	16.85	8.94	5.72	10.37	11.91

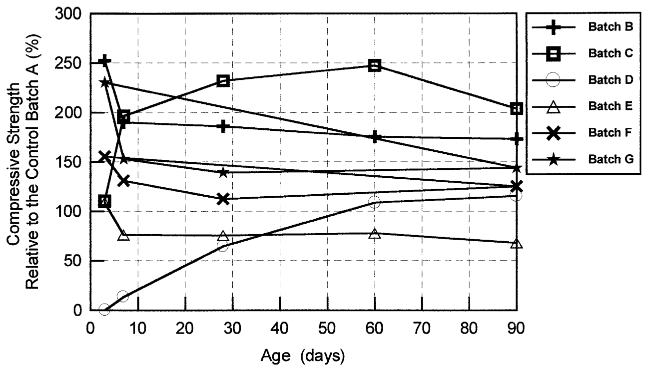

Fig. 2. Relative strength development of different batches.

Batch D did not show measurable strength at 3 days at 23°C, the strength developed slowly with time and was only 10% higher at 60 days and 20% higher at 90 days than the control. The increase in curing temperature from 50°C to 65°C slightly increased the strength at 3 days (Batch E), but decreased the strength by 20% to 25% thereafter compared with the control. It seems that temperature has a very significant effect on the strength development of lime–pozzolan mixtures. This may be contributed to the high hydration activation energy.

Prolonged grinding of the natural pozzolan increased the strength by 50% to 130% at 3 days (Batches F and G), but only 10% to 50% thereafter. The finer the natural pozzolan, the higher the strength of lime–pozzolan cements.

3.3. Strength development rate

It has been shown that the strength development of hardened cement pastes and concrete materials obeys the strength–age relationship [16, 18–20]:

$$S = S_{\infty}\frac{K_T(t-t_0)}{1+K_T(t-t_0)}$$

where: S = compressive strength (MPa); S_{∞} = ultimate compressive strength at $t=\infty$ (MPa); K_T = strength development rate constant at curing temperature T (day^{-1}); t = actual curing time at temperature T (days); t_0 = theoretical initial hardening time (days). By using this equation, the strength development rate constant and the ultimate strength of these batches can be predicted.

The strength development rate constants K_T of those batches prepared with different activation methods relative to the control batch are shown in Fig. 3. The addition of 4% Na_2SO_4 almost doubled the constant, but the introduction of 4% $CaCl_2{\cdot}2H_2O$ somewhat decreased the constant at this temperature (50°C). Previous study [21] has indicated that the presence of 4% $CaCl_2{\cdot}2H_2O$ increased the apparent activation energy greatly and these pastes give a much higher strength development rate constant at higher temperature than the pastes without a chemical activator. Batch D showed the lowest value (only about 20% of the control), and reflected how the curing temperature affected the

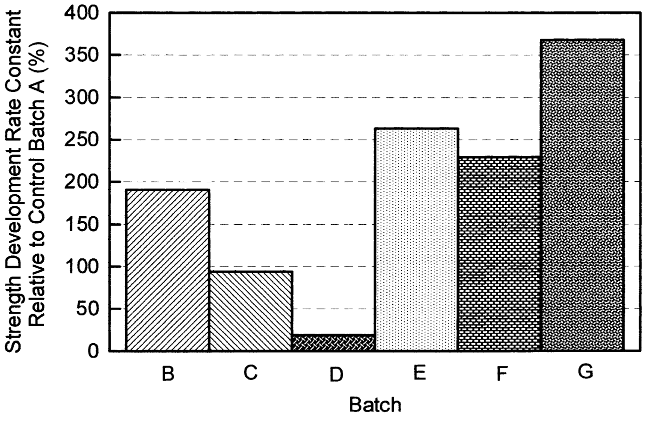

Fig. 3. Comparison of strength development rate constant of different batches.

strength development. Among these batches, Batch G showed the highest strength development rate constant (about 3.7 times as high as the control).

3.4. Ultimate strength

Fig. 4 shows the estimated ultimate compressive strengths of these batches relative to the control batch. The introduction of 4% Na_2SO_4 increased the ultimate strength by about 70% and 4% $CaCl_2{\cdot}2H_2O$ by about 125%. Thus, the use of chemical activators increases the ultimate strength significantly. The ultimate strength of Batch D was about 70% higher than Batch A, but Batch E was only about 70% of the control. This means that the ultimate strength of the lime–pozzolan pastes is very sensitive to the curing temperature. The higher the curing temperature, the lower the ultimate compressive strength of lime–pozzolan pastes. Batches F and G showed a slightly higher ultimate compressive strength than the control; the increase in the Blaine fineness of the pozzolan does not have a significant influence on the ultimate strength of the lime–pozzolan pastes.

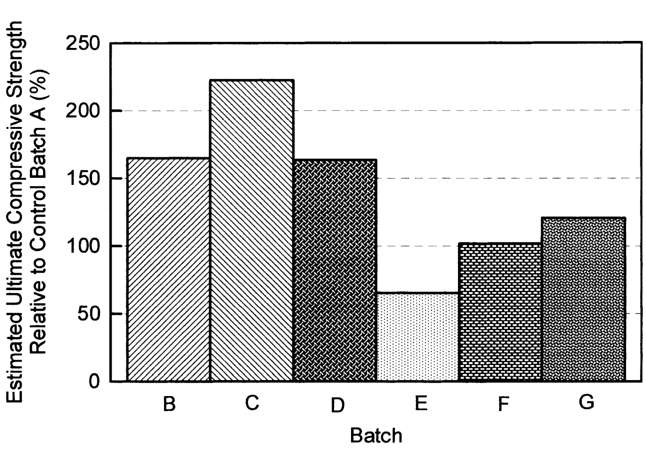

Fig. 4. Comparison of estimated ultimate compressive strength of different batches.

Table 3
Cost of raw materials

No.	Material	Cost (US$/ton)
1	natural pozzolan (estimated transportation and grinding costs)	25.00
2	hydrated lime	60.00
3	Na_2SO_4	150.00
4	$CaCl_2{\cdot}2H_2O$	120.00
5	80% natural pozzolan + 20% hydrated lime	32.00
6	[80% natural pozzolan + 20% hydrated lime] + 4% Na_2SO_4	38.00
7	[80% natural pozzolan + 20% hydrated lime] + 4% $CaCl_2{\cdot}2H_2O$	36.80

3.5. Cost calculations

Table 3 lists the market prices of these raw materials and the cost of the studied mixtures based on these raw materials. The addition of Na_2SO_4 or $CaCl_2{\cdot}2H_2O$ slightly increases the cost of lime–pozzolan cements. However, the addition of Na_2SO_4 or $CaCl_2$ can increase the strength of lime–pozzolan pastes significantly. Fig. 5 compares the ratio of cost/strength of materials for Batches A, B and C cured at 50°C based on strength. Batch B (Na_2SO_4-activated mixtures) exhibited a much higher strength, or a much lower unit strength cost than that of the control batch at early ages. Although the difference decreased with time, the unit strength cost of Batch B was still about 60% lower than that of the control at 180 days.

Batch C exhibited a unit strength cost similar to that of the control at 1 day. However, it decreased with time very quickly and was lower than that of Batch B after 7 days of hydration. It did not change significantly with time after approximately 20 days of hydration, but was still lower than that of Batch B even at 180 days.

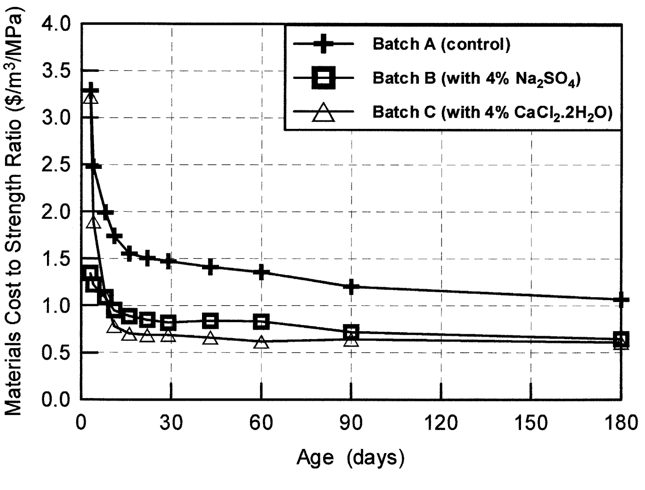

Fig. 5. Materials cost to strength ratio of Batches A, B and C cured at 50°C.

4. Discussions

The enhancement of pozzolanic reactivity using chemical activators accelerated the pozzolanic reaction and strength development rates, and increases the ultimate strength of lime–pozzolan pastes. Elevated temperature curing and prolonged grinding of the natural pozzolan can also increase the strength development, but elevated temperature curing decreases the ultimate strength and prolonged grinding of the natural pozzolan does not show a significant effect on the ultimate strength of lime–natural pozzolan pastes.

Elevated temperature curing needs additional equipment and is usually suitable for precast products. It also consumes a significant amount of energy. Prolonged grinding of natural pozzolan also consumes extra energy and reduces grinding productivity. It is stated [21] that the increase of each 10 m^2/kg Blaine fineness increases grinding energy cost by 10%. Although the addition of Na_2SO_4 or $CaCl_2$ increases the cost of raw materials, the cost per unit strength decreases. The other significant advantage of chemical activation is that the chemical activators can be added either during the grinding of the natural pozzolan or the mixing of concrete mixtures. The requirements for additional equipment and modification of production procedure are very minimal. Thus, the addition of a proper chemical activator is the most economical and simple means to activate the pozzolanic reactivity of pozzolans. According to the previous study [18], Na_2SO_4 is most suitable for the applications where elevated temperature curing is mild or is not feasible, and $CaCl_2$ appears to be most efficient above 50°C. Detailed examination of durability in particular situations is necessary prior to use of these activators.

5. Conclusions

Based on the results obtained in this study, the following conclusions can be drawn:

(1) The prolonged grinding of the natural pozzolan (mechanical activation) and elevated temperature curing of the lime–pozzolan mixtures (thermal activation) accelerates the pozzolanic reactions mainly during the first 1 to 3 days. However, chemical activation shows a much more significant acceleration effect than mechanical or thermal activation.

(2) All three activation methods accelerate the strength development rates of lime–pozzolan mixtures. Mechanical activation of the natural pozzolan does not show a significant effect on ultimate strength, and thermal activation decreases the ultimate strength. The chemical activation method significantly increases the ultimate strength of lime–pozzolan mixtures.

(3) Prolonged grinding of natural pozzolans or elevated temperature curing of lime–pozzolan pastes costs extra energy and increases costs. Although the addition of Na_2SO_4 or $CaCl_2$ increases the cost of raw materials, the cost per unit strength decreases. The other significant advantage is that Na_2SO_4 or $CaCl_2$ can be added during the grinding of the natural pozzolan or the blending of lime–natural pozzolan cement pastes. The requirements for additional equipment or production modifications are minimal. Thus, chemical activation is the most efficient and practical method to activate the potential reactivity of pozzolans. Durability issues surrounding the use of a particular activator in a particular environment must be addressed prior to the implementation phase of a project.

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