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Pozzolanic reaction in the presence of chemical activators
Part I. Reaction kinetics

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Abstract

This study has examined the effect of activators (Na_2SO_4 and $CaCl_2$) on pozzolanic reaction kinetics in a lime-pozzolan blend, which consists of 80% ground volcanic ash and 20% hydrated lime, at 23, 35, 50, and 65°C. The addition of 4% Na_2SO_4 increased both the early and later strengths of lime-pozzolan pastes from 23 to 65°C. The presence of 4% $CaCl_2 \cdot 2H_2O$ decreased the early strength but increased the later strength at 23°C, and increased both the early and later strengths of the paste from 35 to 65°C. Measurement of free $Ca(OH)_2$ in hardened pastes indicated that the presence of Na_2SO_4 and $CaCl_2$ accelerated the consumption of $Ca(OH)_2$. A fair linear correlation could be established between measurable compressive strength and the degree of reaction of $Ca(OH)_2$ regardless of activators. Kinetic analyses using modified Jander's equation suggest that the pozzolanic reaction process in the lime-pozzolan pastes could be divided into three phases: Phase I, controlled by the pozzolanic reaction rate; Phase II, controlled by the diffusion of reactants through a layer of porous hydration products; and Phase III, controlled by the diffusion of reactants through a layer of dense hydration products

Keywords: Pozzolan; Activator; $Ca(OH)_2$; Reaction; Kinetics

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1. Introduction

Lime-pozzolan cement is one of the earliest building materials widely used for all kinds of construction. One obvious disadvantage of lime-pozzolan cements is their long setting time and slow strength development. In practice, it is important for cement to reach satisfactory strengths within a short period of time. Different attempts have tried to activate the potential reactivity of natural pozzolans and to increase the strength of pozzolan-containing cement or concrete [1–5]: (a) calcination of natural pozzolans, (b) acid treatment of natural pozzolans, (c) prolonged grinding of natural pozzolans, (d) elevated temperature curing of pozzolan-containing cement paste and concrete, and (e) the addition of alkalis to pozzolan-containing cement paste and concrete. However, some methods are too expensive to be used practically, and some do not show a significant efficacy. Prolonged grinding of natural pozzolans and elevated temperature curing of lime-pozzolan pastes are most often used.

In previous studies [6–8], it has been found that the addition of proper activators can increase the strength of lime-pozzolan cements significantly, and Na_2SO_4 and $CaCl_2$ are very effective activators. A comparison based on strength development and cost indicates that the addition of Na_2SO_4 or $CaCl_2$ is much more effective than prolonged grinding of natural pozzolans or elevated temperature curing of lime-pozzolan pastes [9].

The objectives of this study are to examine the hydration kinetics and to explain hydration mechanism of lime-pozzolan cement in the presence of Na_2SO_4 and $CaCl_2$ through the measurement of strength development, pozzolanic reaction rate, and hydration products of the lime-pozzolan cement pastes at 23, 35, 50, and 65°C.

2. Methods

2.1. Raw materials

A ground volcanic ash from Bolivia was used. Its chemical analysis and some physical properties are presented in Table 1. X-ray diffraction (XRD) analysis, as shown in Fig. 1, indicates that biotite $[K(Fe,Mg)_3AlSiO_3O_{10}(OH)_2]$, quartz ($SiO_2$), and plagioclase ($0.35Na_2AlSi_3O_8 \cdot 0.65CaAl_2Si_2O_8$) are the detected crystalline substances in the volcanic ash. A

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Table 1
Chemical composition and some physical properties of the ground volcanic ash

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	IL	Density (kg/m^3)	Blain fineness (m^2/kg)
66.48	15.41	0.66	10.29	0.31	0.23	1.39	5.64	5.10	2410	291

IL, loss on ignition.

diffuse band between 20 and 40° (2θ) is due to the presence of aluminosilicate glass, which is similar to that observed from low calcium fly ashes [10–12].

A commercial hydrated high calcium lime that meets ASTM C141 specifications was utilized. The ground natural pozzolan was blended with the lime 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. Activators were added by dissolving them into the mixing water before mixing. The dosage of Na_2SO_4 or $CaCl_2 \cdot 2H_2O$ was 4% based on the mass of the lime-pozzolan blends.

2.2. Preparation of specimens

The specimen preparation was performed at room temperature. Prior to mixing, however, mixing water containing activator (if any), lime-pozzolan blends, and mixing apparatus were heated so that the initial temperature of the pastes was close to the designed curing temperature. The water to the blended material ratio was 0.5. The pastes were cast into 25-mm diameter and 50-mm height vials, capped, and then placed into water baths having temperature of 23, 35, 50, and 65 ± 2°C.

2.3. Compressive strength test

The glass vials were stripped when specimens were strong enough and demoulded specimens were put back into the baths for further curing. This process was done very quickly and did not substantially affect the curing process. Strengths were tested in compression from 1 to 270 days. At every testing age, four specimens were taken out 1 h before the testing time to cool. The ends of these specimens were polished to make the two bearing surfaces flat and parallel. The strength results reported are an average of the three specimens. The coefficients of variation of these results are less than 10%.

2.4. Drying of samples

At every testing age, one specimen was used for the determination of free lime content, XRD analysis, and scanning electron microscope (SEM) observation of microstructure of hydration products. The specimen was crashed to small pieces and then freeze-dried. The small fragments were placed in a bath of liquid nitrogen to be frozen. After 2 to 3 min in the bath, these fragments were carefully moved to a vacuum freeze-drying apparatus for 24 h to remove all free water, and were stored in sealed containers for these tests. The free lime contents are reported here in Part I. XRD analysis of hydration products and SEM observations of microstructure will be discussed in Part II [13].

2.5. Determination of free lime content

The progress of the pozzolanic reaction between lime and pozzolans can easily be monitored by measuring free $Ca(OH)_2$ in the mixtures at different ages. The methods to determine $Ca(OH)_2$ content in hardened cement pastes can be classified into three groups: quantitative XRD analysis, thermal analysis (thermogravimetry and derivative thermogravimetry), and chemical extraction. Some $Ca(OH)_2$ exists in hardened cement concrete in amorphous form, which can not be identified by XRD analysis [14]. This will cause lower results than the actual values. Some loosely combined Ca^{2+} can be extracted during the chemical extraction process and can give higher results. A comparison indicates that thermal analysis gives the most accurate results [15]. Thus, thermogravimetry was employed in this study.

The free lime content was determined using freeze-dried fragments and a Du Point 1090 thermal analyzer. The weight loss due to the dehydration of $Ca(OH)_2$ was graphically calculated on recorded thermogravimetric curves. Then, free

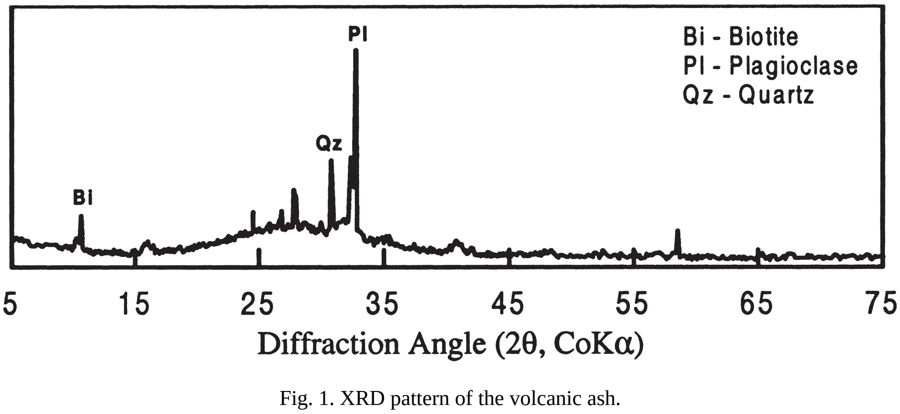


Fig. 1. XRD pattern of the volcanic ash.

$Ca(OH)_2$ content was back-calculated based on the weight loss [9].

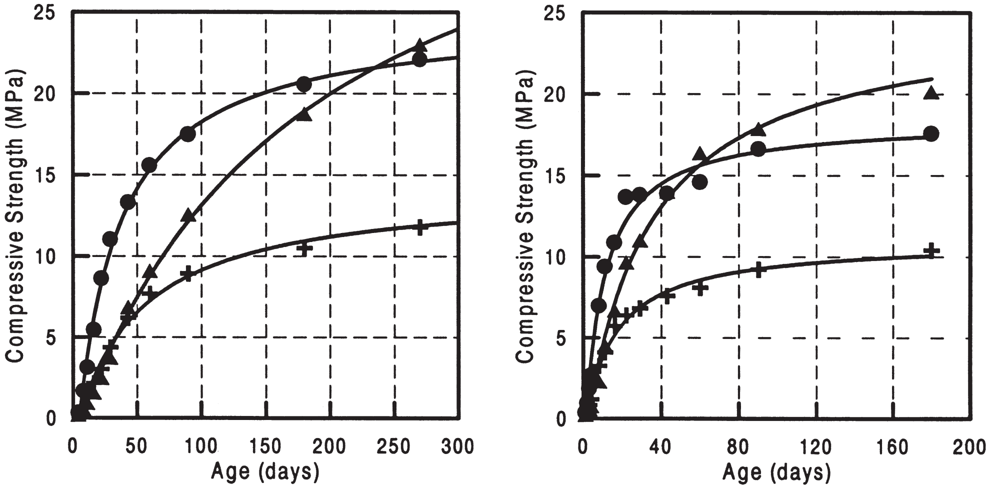
3. Experimental results and discussions

3.1. Strength development at different temperatures

Fig. 2 shows the strength development of lime-pozzolan pastes without activators (control), with 4% Na_2SO_4 and 4% $CaCl_2 \cdot 2H_2O$ cured at 23, 35, 50, and 65°C. All these pastes at different temperatures exhibited a rapid initial strength gain and a much slower later strength gain. At 23°C, the presence of Na_2SO_4 significantly increased the early strength of the lime-pozzolan pastes (Fig. 2a), while $CaCl_2$-activated pastes exhibited a slightly lower strength at early ages but a higher strength than the control pastes at later ages, even higher than the Na_2SO_4-activated pastes after approximately 8 months of curing. Based on the magnitude of strength of the three lime-pozzolan pastes, the effect of activators on strength gain at different temperatures could be divided, for descriptive purposes, into three stages:

Stage I, Na_2SO_4-activated pastes $>$ control pastes $>$ $CaCl_2$-activated pastes

Stage II, Na_2SO_4-activated pastes $>$ $CaCl_2$-activated pastes $>$ control pastes



(a) at 23°C

(b) at 35°C

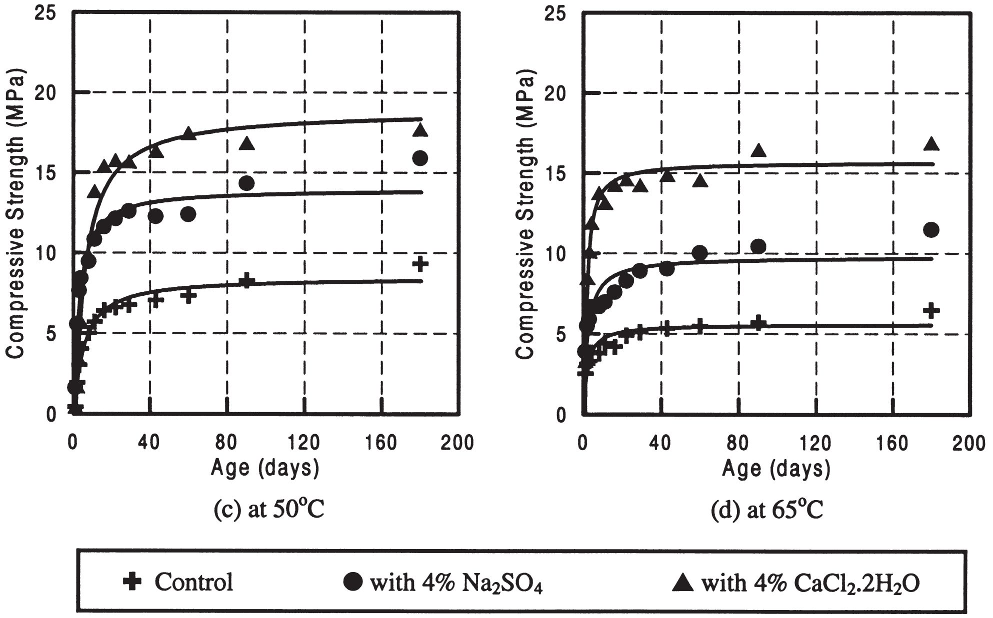


Fig. 2. Strength development of lime-natural pozzolan pastes cured at different temperatures.

Table 2
Stage length of lime-pozzolan pastes at different temperatures (days)

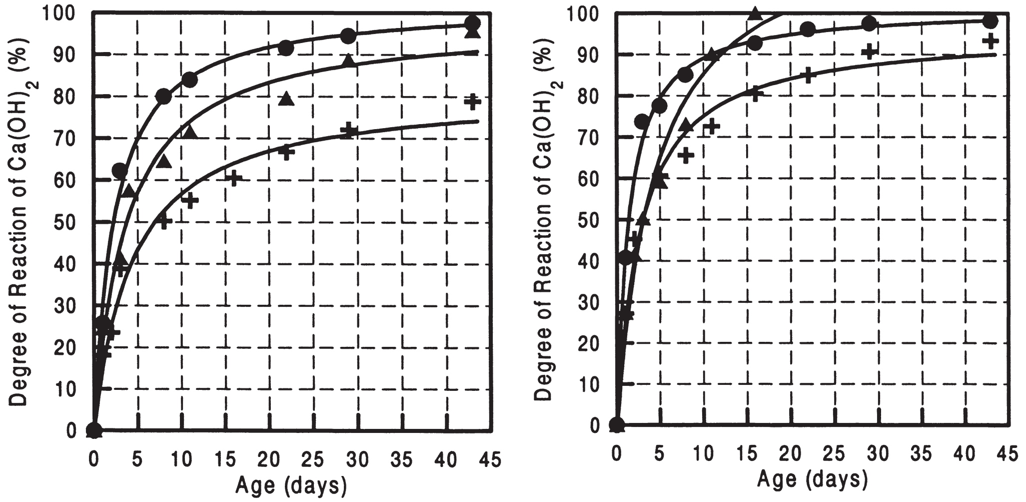
	Temperature (°C)			
	23	35	50	65
Stage I	0–34	0–1	0	0
Stage II	34–220	1–60	0–7	0–1.2
Stage III	>220	>60	>7	>1.2

Stage III, $CaCl_2$-activated pastes > Na_2SO_4-activated pastes > control pastes

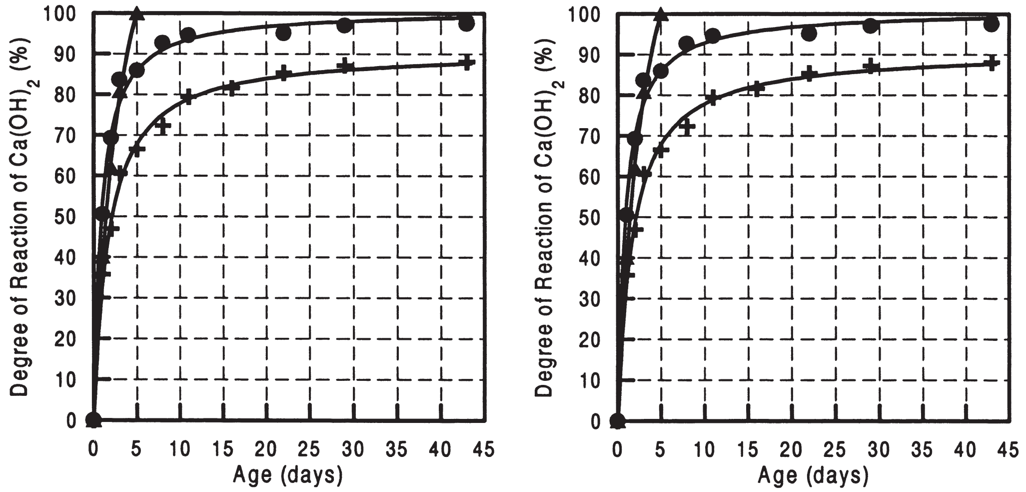
Table 2 summarizes the length of each stage of these pastes at different temperatures. The lengths of Stages I and II decrease and Stage III increases as the curing temperature elevates. Stage III appears after 220 days of curing at 23°C, but after only after 1.2 days of curing at 65°C. Stage I does not exist at 50°C and above. The increase in temperature appears to be more sensitive to the pastes with an activator, particularly $CaCl_2$-activated pastes, than to the control pastes. This can be attributed to the higher apparent activation energy of the pastes with an activator than the control pastes as discussed in a previous study [8].

3.2. Degree of reaction of $Ca(OH)_2$ in lime-pozzolan pastes

Fig. 3 shows the reacted percentage of $Ca(OH)_2$ in the three pastes cured at 23, 35, 50, and 65°C. $Ca(OH)_2$ in the



(a) at 23°C (b) at 35°C



(c) at 50°C (d) at 65°C

✚ Control ● with 4% Na_2SO_4 ▲ with 4% $CaCl_2.2H_2O$

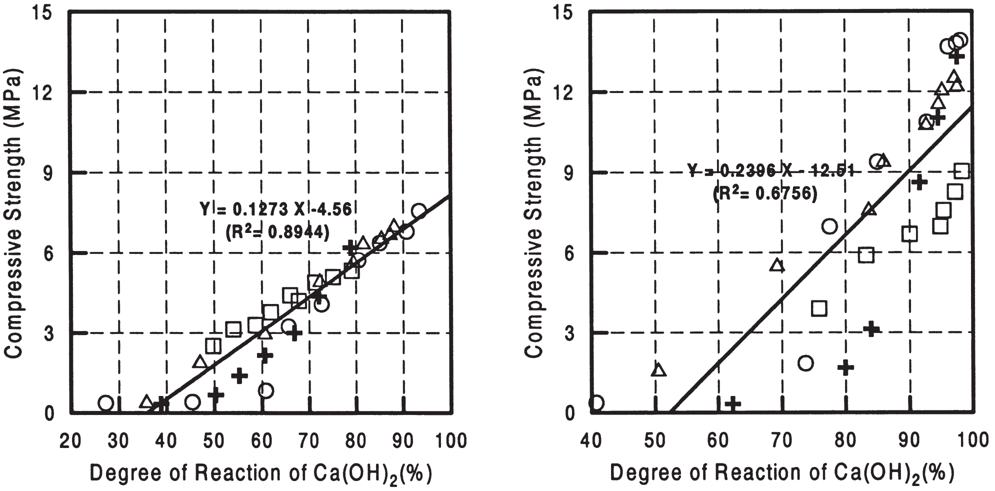
Fig. 3. The degree of reaction of $Ca(OH)_2$ in lime-natural pozzolan pastes cured at different temperatures.

control pastes was consumed very quickly during initial period, and then much more slowly thereafter. The tendencies for the consumption of $Ca(OH)_2$ in Na_2SO_4-activated pastes were the same as the control pastes. However, $Ca(OH)_2$ in Na_2SO_4-activated pastes was consumed more quickly than that in control pastes during the initial rapid reaction stage. It can be concluded that the addition of Na_2SO_4 accelerated the early pozzolanic reaction. But a small amount of $Ca(OH)_2$ still could be detected in Na_2SO_4-activated pastes at later stages regardless of curing temperatures; however, the remaining $Ca(OH)_2$ in Na_2SO_4-activated pastes was less than that in the control pastes.

At 23°C, the consumption of $Ca(OH)_2$ in $CaCl_2$-activated pastes was similar to that in the control or Na_2SO_4-activated pastes within the testing period. As the curing temperature elevated, the $Ca(OH)_2$ in $CaCl_2$-activated pastes vanished very quickly: 16 days at 35°C, 5 days at 50°C and 2 days at 65°C.

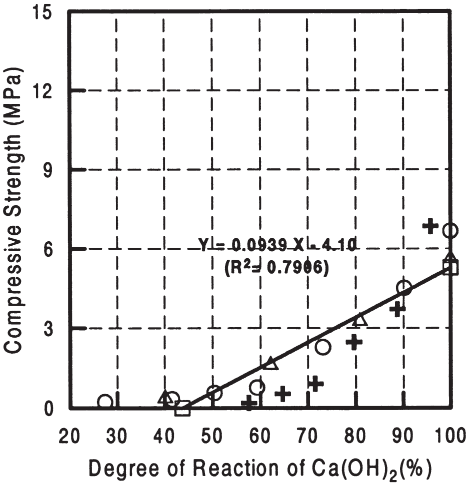
3.3. Correlation between compressive strength and the degree of reaction of $Ca(OH)_2$

Fig. 4 is the plot of compressive strength vs. the degree of reaction of $Ca(OH)_2$ for the control and Na_2SO_4- and $CaCl_2$-activated pastes cured at different temperatures. Generally speaking, the measurable compressive strength and the degree of reaction of $Ca(OH)_2$ for the three pastes at different temperatures could be correlated with fair linear relationships. The variation in the degree of reaction of



(a) Control Pastes

(b) Na_2SO_4 Activated Pastes



(c) $CaCl_2$ Activated Pastes

✚ cured at 23°C ○ cured at 35°C Δ cured at 50°C cured at 65°C

Fig. 4. Correlation between compressive strength and the degree of reaction of $Ca(OH)_2$ in lime-natural pozzolan pastes cured at different temperatures.

$Ca(OH)_2$ corresponding to the first measurable strength and the slope of these linear relationships might be attributed to the formation of different hydration products as discussed in Part II [13].

3.4. Kinetic analysis

Kondo et al. [16] have classified a reaction process based on the reaction grade N using a modified Jander's equation [see Eq. (1)]:

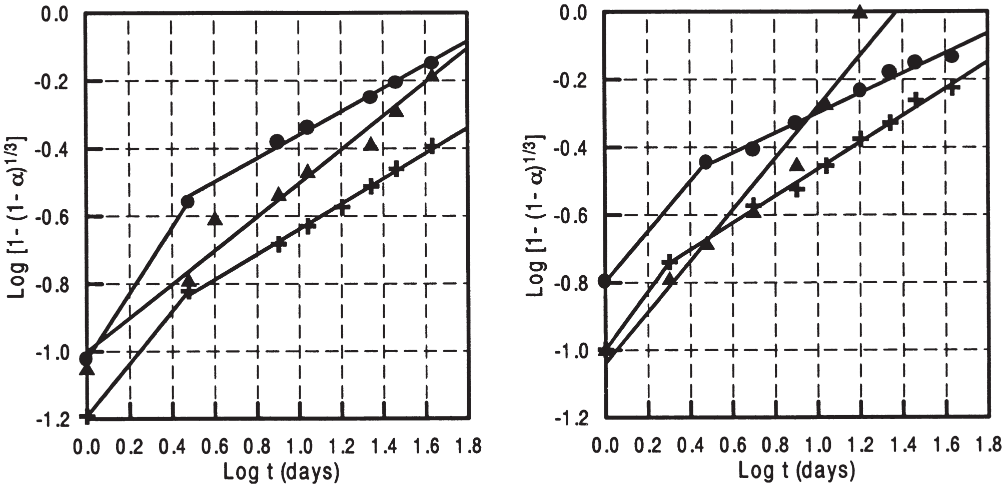
$$(1-\sqrt[3]{1-\alpha})^N = Kt \qquad (1)$$

where α is the reaction degree; K is the reaction constant; t is the reaction time; and N is the reaction grade.

1. If the reaction is controlled by the reaction occurring on the surface of grains, or by the dissolution of reactants or the precipitation of reaction products, then $N \leqslant 1$.
2. If the reaction is controlled by the diffusion of reactants through a layer of porous reaction products, then $1 < N \leqslant 2$.
3. If the total reaction is controlled by the diffusion of reactants through a layer of dense reaction products, then $N > 2$.

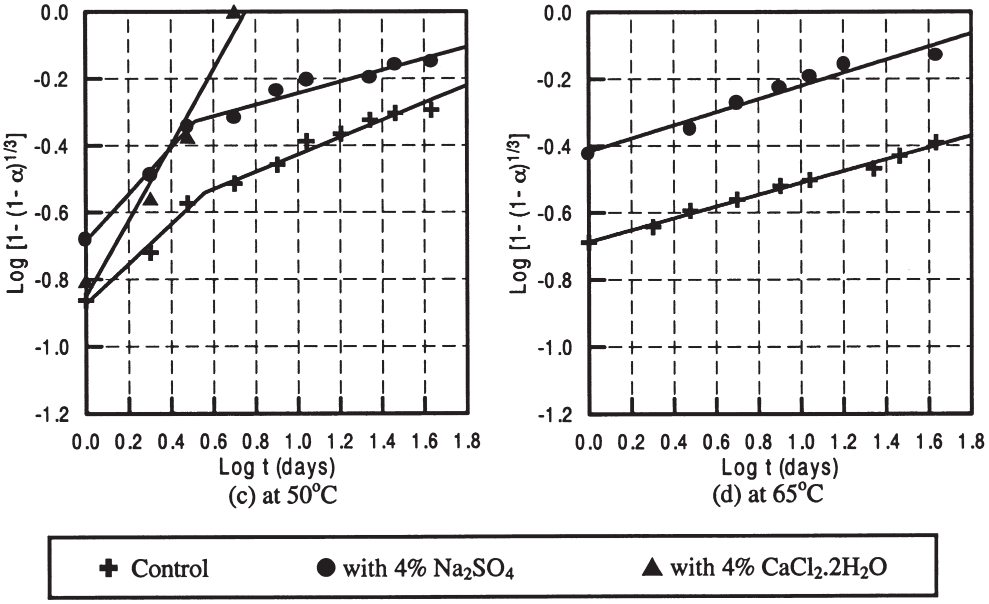
Fig. 5 is the plot of Eq. (1) in log-scale using the degree of reacted $Ca(OH)_2$ as shown in Fig. 2. The slopes of these straight lines are the reaction grade N. Table 3 lists the grade N and phase period of pozzolanic reactions that took place in the three pastes at different temperatures.

For the control pastes, Phase I was not detected regardless of curing temperatures. This means that Phase I completed before the determination of free lime in this study. From 23 to



(a) at 23°C

(b) at 35°C



(c) at 50°C

(d) at 65°C

Fig. 5. Pozzolanic reaction kinetics in lime-natural pozzolan pastes cured at different temperatures.

Table 3
Reaction grade *N* and phase period of the three pastes at different temperatures

		Phase I ($N \leqslant 1$)		Phase II ($2 \geqslant N > 1$)		Phase III ($N > 2$)	
Curing temperature	Paste	*N*	Period	*N*	Period	*N*	Period
23°C	Control	N/A	N/A	1.28	3 days	2.90	>3 days
	+ 4% Na_2SO_4	N/A	N/A	1.02	3 days	2.68	>3 days
	+ 4% $CaCl_2 \cdot 2H_2O$	N/A	N/A	N/A	N/A	2.01	>1 day
35°C	Control	N/A	N/A	1.16	3 days	2.53	>3 days
	+ 4% Na_2SO_4	N/A	N/A	1.36	3 days	3.40	>3 days
	+ 4% $CaCl_2 \cdot 2H_2O$	N/A	N/A	1.51	21 days	N/A	N/A
50°C	Control	N/A	N/A	1.69	3 days	3.87	>3 days
	+ 4% Na_2SO_4	N/A	N/A	1.43	3 days	5.81	>3 days
	+ 4% $CaCl_2 \cdot 2H_2O$	0.89	0–7 days	N/A	N/A	N/A	N/A
65°C	Control	N/A	N/A	N/A	N/A	5.68	>1 day
	+ 4% Na_2SO_4	N/A	N/A	N/A	N/A	5.11	>1 day
	+ 4% $CaCl_2 \cdot 2H_2O$	<0.89	<2 d	N/A	N/A	N/A	N/A

N/A , not applicable.

50°C, pozzolanic reactions in the control pastes behaved in the same way: Phase II ended after approximately 3 days of curing and Phase III started thereafter. As curing temperature increased to 65°C, only Phase III could be identified.

From 23 to 65°C, the trend of pozzolanic reactions in the Na_2SO_4-activated pastes was very similar to that in the control pastes except for some offset of the reaction degree. This means that the addition of Na_2SO_4 accelerated the consumption of lime or the pozzolanic reaction rate mainly during the first day.

Based on the measurement of free lime content, it could be seen that the introduction of $CaCl_2$ had a significant effect on the pozzolanic reaction in the lime-pozzolan pastes. There was only one phase detected during each of the curing regimes: Phase III at 23°C, Phase II at 35°C, and Phase I at 50 and 65°C. The reaction grade *N* decreased with curing temperature. Although the grade *N* at 65°C was not given, it was certainly less than that at 50°C (0.89) because all $Ca(OH)_2$ was consumed within the first 2 days. Thus, the addition of $CaCl_2$ significantly alters the pozzolanic reaction behavior, especially at elevated temperatures. At 50°C and above, *N* is less than 1 and the total pozzolanic reaction is controlled by the dissolution of reactants. The dissolution of $Ca(OH)_2$ should be much faster than that of a natural pozzolan. Thus, the total pozzolanic reaction in $CaCl_2$-activated pastes is controlled by the dissolution of the natural pozzolan at elevated temperatures.

4. Conclusions

This study has investigated the strength development and lime consumption of lime-natural pozzolan pastes in the presence of 4% Na_2SO_4 or $CaCl_2 \cdot 2H_2O$ at 23, 35, 50, and 65°C. The following conclusions can be drawn based on the experimental results:

1. The addition of 4% Na_2SO_4 increased both the early and later strength of lime-pozzolan cement pastes from 23 to 65°C. The addition of 4% $CaCl_2 \cdot 2H_2O$ lowered the early strength but increased the later strength at 23°C, and increased both the early and later strengths from 35 to 65°C.
2. The presence of Na_2SO_4 accelerated the early consumption of $Ca(OH)_2$, but showed the same trend as control pastes except for some offset for the degree of reaction of $Ca(OH)_2$ from 23 to 65°C. There was always some free $Ca(OH)_2$ present in both the control and Na_2SO_4-activated pastes up to 43 days. The effect of $CaCl_2$ on the consumption of $Ca(OH)_2$ was drastic and temperature-dependent. Some $Ca(OH)_2$ could be detected in 43-day-old $CaCl_2$-activated pastes at 23°C but $Ca(OH)_2$ vanished very quickly as curing temperature was elevated to 35°C or above.
3. A fair linear relationship could be observed between measurable compressive strength and the degree of reaction of $Ca(OH)_2$ for all these lime-pozzolan pastes. The addition of Na_2SO_4 or $CaCl_2$ changed the initially measurable strength and the slope of the linear relationship. This may be attributed to the change in hydration products.
4. Kinetic analyses based on the degree of reaction of $Ca(OH)_2$ indicated that the pozzolanic reaction process in lime-pozzolan pastes could be divided into three phases: Phase I, controlled by the pozzolanic reaction rate; Phase II, controlled by the diffusion of reactants through a layer of porous hydration products; and Phase III, controlled by the diffusion of reactants through a layer of dense products. The addition of Na_2SO_4 mainly accelerated the consumption of lime during the first day and did not affect pozzolanic reaction thereafter, while the introduction of $CaCl_2$ had a significant effect on pozzolanic reaction over the testing period.

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