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# Pozzolanic reaction in the presence of chemical activators
# Part II. Reaction products and mechanism

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## Abstract

This paper has dealt with the pozzolanic reaction products and mechanism in lime–pozzolan cement pastes in the presence of $Na_2SO_4$ and $CaCl_2$. X-ray diffraction (XRD) analysis indicated that the hydration products in control lime–natural pozzolan pastes were calcium silicate hydrate (C-S-H) and $C_4AH_{13}$. The addition of $Na_2SO_4$ to lime–natural pozzolan paste accelerated the pozzolanic reaction and resulted in the formation of AFt, instead of $C_4AH_{13}$, which endorsed the paste a higher strength compared with the control pastes. The introduction of 4% $CaCl_2{\cdot}2H_2O$ decreased the pH of lime–pozzolan pastes, but favoured the formation of the solid solution of $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$–$C_3A{\cdot}CaCl_2{\cdot}10H_2O$. As the curing temperature was raised from 23°C to 65°C, it accelerated the reaction rates in all these pastes. The hydration products in the control and the $CaCl_2$ activated pastes did not change with temperature, but AFm appeared in the $Na_2SO_4$ activated pastes when temperature was above 50°C. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Pozzolan; $Ca(OH)_2$; Pozzolanic reactions; Activator; Microstructure; Hydration products

## 1. Introduction

The addition of proper activators accelerates the pozzolanic reactions and increases the strength of lime–pozzolan cements [1–5]. The first part of this study has investigated the effects of $Na_2SO_4$ and $CaCl_2$ on strength development, pozzolanic reaction rate, and the relationship between strength and consumed lime [5]. It has been found that the addition of 4% $Na_2SO_4$ increases both the early and later strength of the cement from 23°C to 65°C. The addition of 4% $CaCl_2{\cdot}2H_2O$ lowers the early strength but increases the later strength at 23°C, and increases both the early and later strength of the cement from 35°C to 65°C. The presence of $Na_2SO_4$ accelerates early consumption of $Ca(OH)_2$, but shows the same trend as control pastes except some offset in the degree of reaction of $Ca(OH)_2$ from 23°C to 65°C. $Ca(OH)_2$ can still be detected in both the control and $Na_2SO_4$ pastes after 43 days of hydration. The effect of $CaCl_2$ on the consumption of $Ca(OH)_2$ is drastic and temperature-dependent. $Ca(OH)_2$ can be detected in $CaCl_2$ activated pastes after 43 days of hydration at 23°C, but vanished very quickly as the curing temperature elevates. No $Ca(OH)_2$ can be detected in the $CaCl_2$ activated pastes after 3 days of hydration at 65°C.

The purposes of this study are to examine the hydration products and to explore pozzolanic reaction mechanism in the presence of $Na_2SO_4$ and $CaCl_2$.

## 2. Experimentation

### 2.1. Raw materials and preparation of specimens

The raw materials and preparation of specimens have been described in Part I [5].

### 2.2. Powder X-ray diffraction (XRD) analysis

Freeze-dried lime–natural pozzolan pastes, as described in Part I, were pulverized by manual grinding with an agate mortar and analyzed using a Phillips X-ray diffractometer. Hydration products were identified with the help of the characteristic peak database from the Powder Diffraction File of the Joint Committee on Powder Diffraction

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Standards, together with scanning electron microscope (SEM) observations.

### 2.3. SEM observation

A Cambridge stereoscan 150 SEM was employed to observe the microstructure and morphology of hardened lime–pozzolan pastes. The surface of the sample was extensively viewed before photographs were taken of representative areas. Micrographs were taken of areas showing typical morphology for different samples at magnifications ranging from 20× to 100,000×.

### 2.4. pH measurement

The effect of $Na_2SO_4$ and $CaCl_2$ dosage on the pH of $Ca(OH)_2$ saturated solution was measured at 23°C. Different amounts of $Na_2SO_4$ and $CaCl_2$ were dissolved in distilled water first, then mixed with $Ca(OH)_2$ powder at a water to $Ca(OH)_2$ powder ratio of 2.5, which was the same as used

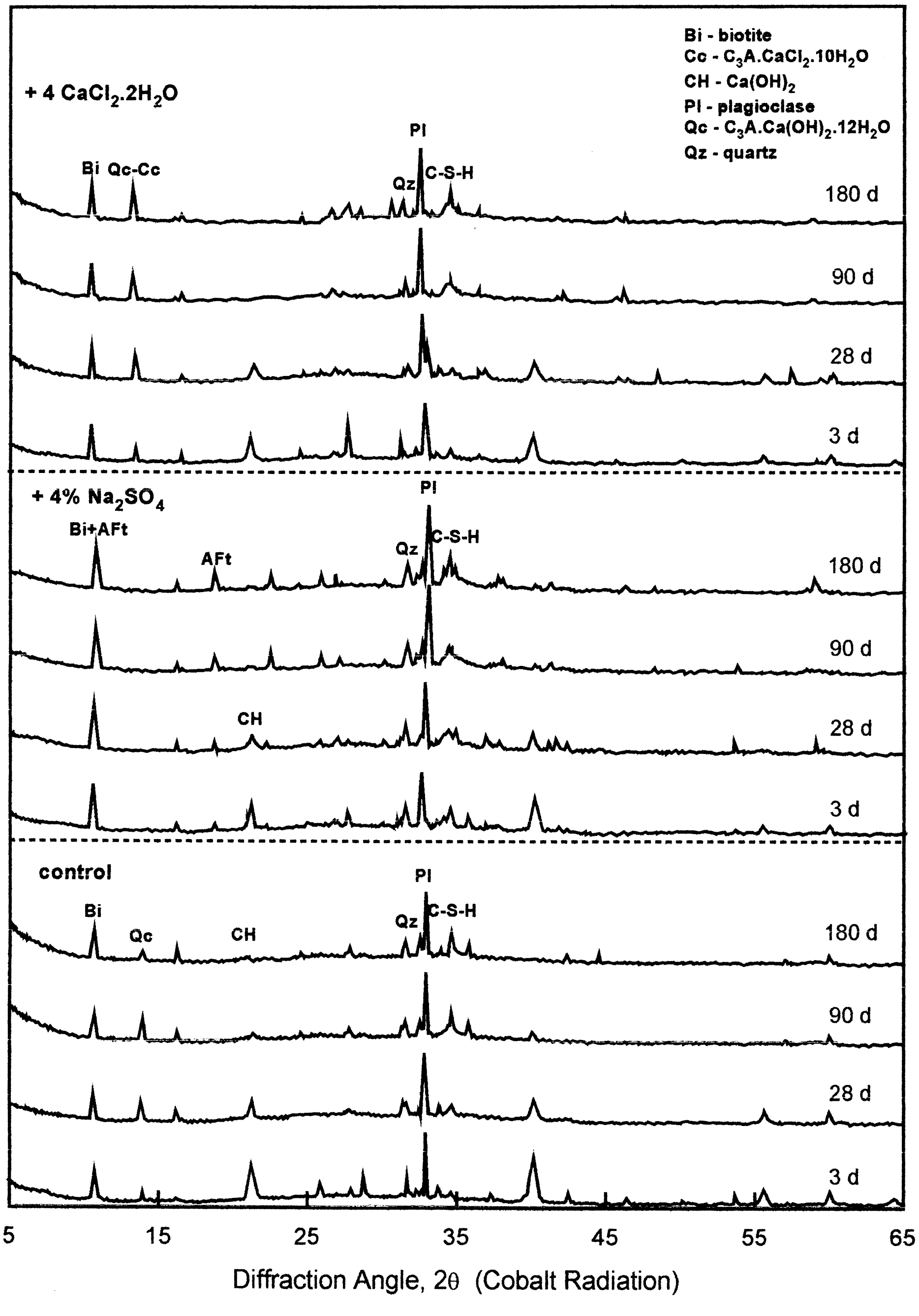
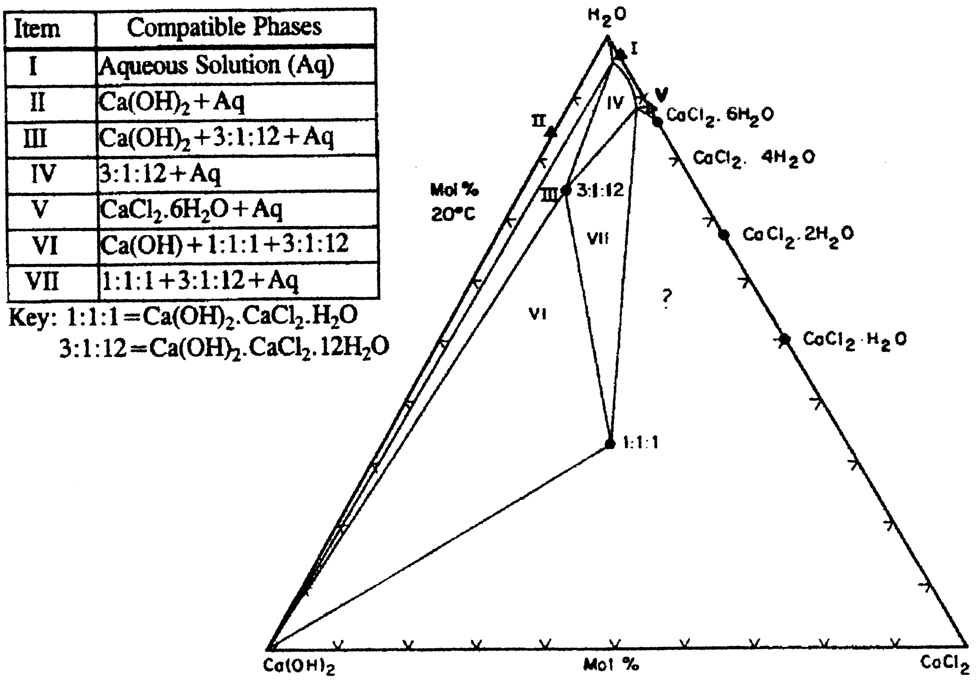


Fig. 1. XRD analysis of lime–natural pozzolan pates cured at 23°C.



| Item | Compatible Phases |
|---|---|
| I | Aqueous Solution (Aq) |
| II | $Ca(OH)_2+Aq$ |
| III | $Ca(OH)_2+3{:}1{:}12+Aq$ |
| IV | $3{:}1{:}12+Aq$ |
| V | $CaCl_2.6H_2O+Aq$ |
| VI | $Ca(OH)+1{:}1{:}1+3{:}1{:}12$ |
| VII | $1{:}1{:}1+3{:}1{:}12+Aq$ |

Key: $1{:}1{:}1=Ca(OH)_2.CaCl_2.H_2O$
$3{:}1{:}12=Ca(OH)_2.CaCl_2.12H_2O$

Fig. 2. Phase diagram of $CaCl_2-Ca(OH)_2-H_2O$ system at 20°C [10].

for the preparation of lime–pozzolan pastes. The $Ca(OH)_2$ slurries were sealed in plastic bottles and shaken everyday. The slurries were filtered after 7 days of reaction. The pH of the filtrate was measured using an 805 MP Fisher Acunet pH meter.

## 3. Experimental results and discussion

### *3.1. XRD analysis of hardened lime–pozzolan pastes*

Fig. 1 shows the XRD patterns of hardened lime–pozzolan pastes at 23°C. $C_4AH_{13}$ ($d$ = 7.4 A) was identified in the control pastes. Because the biotite in the natural pozzolan has its strongest peak at $d$ = 9.7 A, which is similar to that of $C_3A{\cdot}3CaX{\cdot}nH_2O$, the identification of AFt in the control pastes based on XRD analysis was difficult since the $SO_3$ content of the natural pozzolan was only about 0.9%. Extensive SEM observations indicated that very limited amount of AFt could be identified at early ages.

As age proceeded, the intensity of diffraction peaks of $C_4AH_{13}$ increased, reaching a maximum at 90 days and decreasing thereafter. A diffuse band around $d$ = 3.04 A may be attributed to calcium silicate hydrate (C-S-H), the diffuse band became larger and sharper with time. Free $Ca(OH)_2$ decreased with time and disappeared after 180 days of hydration.

In the $Na_2SO_4$ activated pastes, the presence of a peak at $d$ = 5.5 A confirmed the formation of AFt. The diffraction peaks of AFt were intensified with time. The diffuse band of C-S-H at $d$ = 3.04 A was sharper than that in control pastes. The diffraction peaks of $Ca(OH)_2$ in the $Na_2SO_4$ activated pastes weakened more quickly at early ages but were much similar to those in the control pastes between 90 and 180 days.

The XRD patterns of the $CaCl_2$ activated pastes were similar to those in the control pastes but a peak at $d$ = 7.7 A was identified in the $CaCl_2$ activated pastes instead of at 7.4 A in the control pastes. This difference may be attributed to the replacement of $Ca(OH)_2$ in $C_4AH_{13}$ by $CaCl_2$ and the formation of a solid solution of $C_4AH_{13}-C_3A{\cdot}CaCl_2{\cdot}10H_2O$. The peak at $d$ = 7.7 A was strong even at 1 day, and increased with time until 180 days.

As the curing temperature elevated from 23°C to 65°C, it did not change the nature of products in the control and $CaCl_2$ activated pastes except for some difference in the intensities of diffraction peaks of the reaction products. At higher temperatures, the diffraction peaks of hydration products became stronger. However, the peaks of $Ca(OH)_2$ weakened more quickly with temperature increase. As for the $Na_2SO_4$ activated pastes, the XRD patterns at 35°C were the same as those at 23°C, however, AFm appeared at 50°C and 65°C in addition to those peaks appearing at 23°C and 35°C.

### *3.2. Reactions between $Ca(OH)_2$ and $Na_2SO_4$ or $CaCl_2$*

When $Na_2SO_4$ solution is mixed with $Ca(OH)_2$, they react as follows [6]:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2NaOH. \quad (1)$$

This reaction results in a higher alkaline solution than the $Ca(OH)_2$ saturated solution. Although no data are available about the effect of $CaSO_4 \cdot 2H_2O$ and NaOH on the dissolution rate of $Ca(OH)_2$, it is well known that they significantly decrease the solubility of $Ca(OH)_2$ [5].

In $CaO-CaCl_2-H_2O$ system, two oxychlorides $3CaO \cdot CaCl_2 \cdot 15H_2O$ and $CaO \cdot CaCl_2 \cdot 2H_2O$ exist [7–10]. The former forms at high $CaO/CaCl_2$ ratios when temperature is below 38.9°C. The higher the temperature is, the lower the critical ratio of $CaO/CaCl_2$ ratio is for $3CaO \cdot CaCl_2 \cdot 15H_2O$ to exist [6]. According to the phase diagram of the $CaO-CaCl_2-H_2O$ system as shown in Fig. 2, $Ca(OH)_2$ is the only detected phase in the studied mixture of hydrated lime:$CaCl_2 \cdot 2H_2O$:water = 20:4:50 ($CaO$:$CaCl_2$:$H_2O$ = 21.05:4.32:74.62) when pozzolan in the blend is not taken into account. This is in agreement with the XRD analysis of the mixture.

The dissolution of $Ca(OH)_2$ is a very sluggish process. The addition of a small amount of $CaCl_2$ decreases the solubility of $Ca(OH)_2$, but increases the dissolution rate of $Ca(OH)_2$ significantly [8]. It is the dissolution rate, rather than the solubility of $Ca(OH)_2$, that affects the rate of pozzolanic reaction in the lime–pozzolan pastes.

### 3.3. Effect of activators on the pH of $Ca(OH)_2$ saturated solutions

Fig. 3 shows the effect of $Na_2SO_4$ and $CaCl_2 \cdot 2H_2O$ dosage on the pH of $Ca(OH)_2$ saturated solution. The addition of 4% $Na_2SO_4$ raised the pH value from 12.50 to 12.75. The dissolution rate and solubility of $Ca(OH)_2$ may be decreased due to the increase in the alkalinity of the solution. $CaCl_2$ showed an obvious negative effect on the pH values of the solution — the presence of 4% $CaCl_2 \cdot 2H_2O$ decreased the pH value of the of saturated $Ca(OH)_2$ solution from 12.50 to 11.75.

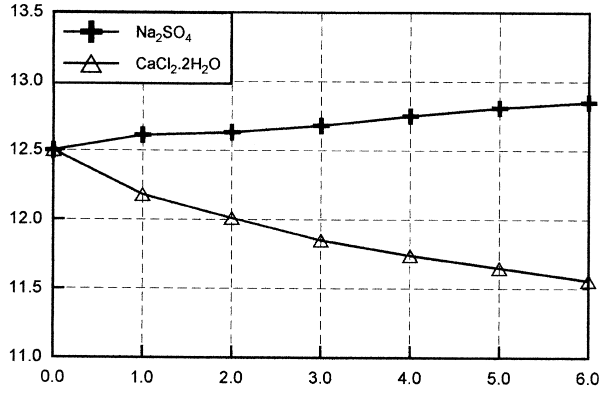


Fig. 3. Effect of activator dosage on the pH of saturated $Ca(OH)_2$ solution.

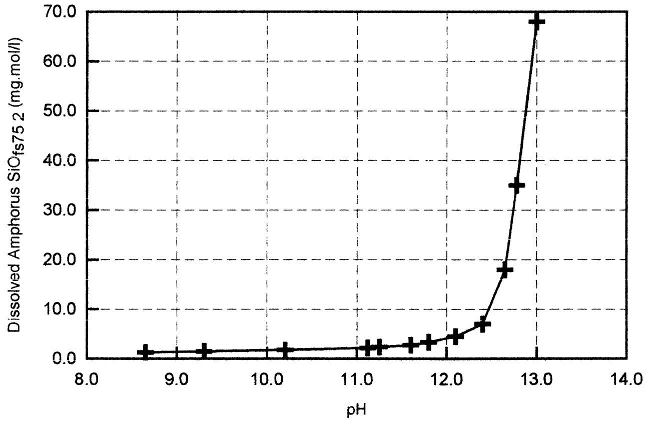


Fig. 4. Effect of pH on the dissolution of amorphous $SiO_2$ [11].

### 3.4. Effect of pH on the dissolution of pozzolans

Fig. 4 shows the effect of pH on the dissolution of amorphous $SiO_2$. There is an abrupt rise in dissolution at about pH = 12.5 at room temperature; after this point, the dissolution of amorphous $SiO_2$ increases very steeply with pH.

Usually, natural pozzolans consist of siliceous or aluminosilicate glass. According to their structure, it can be inferred that pH will have a similar effect on the dissolution of natural pozzolans as that on the amorphous $SiO_2$. The presence of Al increases the dissolution of natural pozzolans due to the lower bonding energy of Al–O bond compared to that of Si–O bond.

### 3.5. Pozzolanic reaction mechanism

#### 3.5.1. Lime–pozzolan blend

In the absence of an activator, when a lime–pozzolan blend is mixed with water, $Ca(OH)_2$ in the blend hydrolyses first and the solution reaches a high pH value (approximately 12.5 at 20°C) very quickly [Eq. (2)]:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- . \qquad (2)$$

Under the attack of $OH^-$ in such a high pH solution, network modifiers, such as $Ca^{2+}$, $K^+$, $Na^+$, etc., in the pozzolan are dissolved into the solution very quickly. Silicate or aluminosilicate network formers in the pozzolan are also depolymerized and dissolved into the solution. However, a larger fraction of network modifiers are dissolved into the solution than network formers due to the lower bond energy of network modifiers. Depolymerized monosilicate and aluminate species enter the solution as follows in Eq. (3) and Eq. (4):

$$\equiv Si - O - Si \equiv +3OH^- \rightarrow [SiO(OH)_3]^- \qquad (3)$$

$$\equiv Si - O - Al \equiv +7OH^- \rightarrow [SiO(OH)_3]^- + [Al(OH)_4]^- . \qquad (4)$$

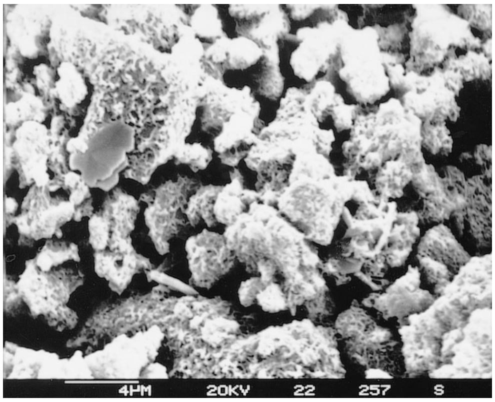


Fig. 5. SEM observation of control lime–pozzolan paste hydrated for 3 days.

When $Ca^{2+}$ ions contact these dissolved monosilicate and aluminate species, C-S-H and calcium aluminate hydrate $C_4AH_{13}$ form [Eq. (5,6)]:

$$Y[SiO(OH)_3]^- + XCa^{2+} + (Z - X - Y)H_2O + (2X - Y)OH^- \rightarrow C_X - S_Y - H_Z \tag{5}$$

$$2[Al(OH)_4]^- + 4Ca^{2+} + 6H_2O + 6OH^- \rightarrow C_4AH_{13}. \tag{6}$$

Although lime–pozzolan pastes do not show a significant strength after 3 days at 23°C, SEM observation shows that all pozzolan particles are coated by a layer of grape-like C-S-H gel (see Fig. 5). The chemical composition of C-S-H varies with the local concentration of reactants and reaction conditions [12].

Because dissolved monosilicate species diffuse much more quickly than dissolved aluminate species, and a higher concentration of $Ca^{2+}$ is needed for the formation of calcium aluminate hydrates than for hydrated calcium silicates, hydrated calcium aluminates precipitate away from pozzolan particles and hydrated calcium silicates precipitate around the pozzolan particles [12]. Fig. 5 also shows precipitation of the hexagonal plate, $C_4AH_{13}$, on the outside surface of C-S-H.

In the presence of sulphate ions, AFt forms first. Because the $SO_3$ content of the natural pozzolan is low, AFt transforms to AFm very quickly. These reactions can be expressed as follows in Eq. (7) and Eq. (8):

$$2[Al(OH)_4]^- + 3SO_4^{2-} + 6Ca^{2+} + 4OH^- + 26H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \tag{7}$$

$$6Ca^{2+} + 2[Al(OH)_4]^- + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 10OH^- \rightarrow 3[3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O] + 5H_2O. \tag{8}$$

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 pozzolan 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. Based on the kinetic analysis and hydration product analyses, it seems that a rise in curing temperature does not affect the hydration process, but the hydration rate [5].

### *3.5.2. Lime–pozzolan–$Na_2SO_4$ system*

When $Na_2SO_4$ is added, the reaction between $Ca(OH)_2$ and $Na_2SO_4$, as expressed by Eq. (1), happens first. The reaction increases the pH of the solution, accelerates the dissolution of pozzolans, and speeds up the pozzolanic reaction between $Ca(OH)_2$ and the pozzolan. The kinetic analyses in Part I [5] have indicated that the acceleration occurs mainly when reaction is controlled by the dissolution of the natural pozzolan. At the same time, the introduction of $Na_2SO_4$ increases the concentration of $SO_4{}^{2-}$ and results in the formation of more AFt than in the control pastes.

The properties of related hydration products in lime–pozzolan pastes are listed in Table 1. The calculation, as shown in Table 2, indicates that 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 lime–pozzolan pastes very significantly [13]. 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.

Table 1
Properties of related reaction products [15]

| Formula | Abbreviation | Molar mass (g/mol) | Crystal form | Density ($g/cm^3$) |
|---|---|---|---|---|
| $CaO \cdot SiO_2 \cdot 1.5H_2O$ | $C\text{-}S\text{-}H_{1.5}$ | 143 | Fibre bundles | 2.0–2.2 |
| $4CaO \cdot Al_2O_3 \cdot 13H_2O$ | $C_4AH_{13}$ or<br>$C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ | 560 | Hexagonal plate | 2.02 |
| $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ | $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ | 1254 | Needle | 1.73 |
| $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ | $C_3A \cdot CaSO_4 \cdot 12H_2O$ | 622 | Hexagonal plate | 1.99 |
| $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ | $C_3A \cdot CaCl_2 \cdot 10H_2O$ | 561 | Hexagonal plate | 2.03[a] |

[a] From JCPDS file 19-201 and 19-202.

Table 2
Relevant pozzolanic reactions

| Reactants | Products | Solid volume change (cm$^3$) |
|---|---|---|
| $Ca(OH)_2+SiO_2+0.5H_2O$ | $CaO{\cdot}SiO_2{\cdot}1.5H_2O$ | 10.16 (17.5%) |
| $4Ca(OH)_2+Al_2O_3+9H_2O$ | $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ | 102.76 (58.9%) |
| $6Ca(OH)_2+Al_2O_3+3Na_2SO_4$ (sol.)$+29H_2O$ | $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O+6NaOH$ (sol.) | 395.03 (164.2%) |
| $4Ca(OH)_2+Al_2O_3+Na_2SO_4$ (sol.)$+9H_2O$ | $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O+2NaOH$ (sol.) | 138.09 (79.2%) |
| $6Ca(OH)_2+2Al_2O_3+3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ | $3[3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O]+2H_2O$ | −70.02 (−7.0%) |
| $3Ca(OH)_2+Al_2O_3+CaCl_2$ (sol.)$+7H_2O$ | $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$ | 134.92 (95.4%) |

Monosulphoaluminate (AFm) was identified at 50°C and 65°C in the $Na_2SO_4$ activated pastes. Thermodynamic calculation indicates that AFt is the stable phase below 70°C and AFm above 70°C [14]. Due to the variation of the concentration of reactants and environmental conditions, it is possible for AFm to form directly or from the conversion of AFt below 70°C in the $Na_2SO_4$ activated pastes [Eq. (9,10)]:

$$2[Al(OH)_4]^- + SO_4^{2-} + 4Ca^{2+} + 6H_2O + 4OH^- \rightarrow C_3A \cdot CaSO_4 \cdot 12H_2O \tag{9}$$

$$6Ca(OH)_2 + 2Al_2O_3 + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightarrow 3[3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O] + 2H_2O. \tag{10}$$

The direct formation of AFm increases the solid volume by 79.2%, but the conversion of AFt to AFm decreases the solid volume by 7.0%. This means the $Na_2SO_4$ activated pastes will exhibit a lower strength at higher temperatures. This is in agreement with the results reported in Part I [5].

### *3.5.3. Lime–pozzolan–$CaCl_2$ system*

$CaCl_2$ was widely used as an accelerator for Portland cement concrete. However, in spite of great effort, the detailed action mechanism of $CaCl_2$ on the hydration of cement is still obscure [15]. Various explanations have been offered from time to time; none of them would be able to explain all the effects of $CaCl_2$ in concrete. Based on the experimental results described above and published results in the literature, the action mechanism of $CaCl_2$ in lime–pozzolan system can be summarized as follows.

After the mixing of lime–pozzolan blend with $CaCl_2$ solution, $Ca(OH)_2$ dissolves first. The presence of $CaCl_2$ accelerates the dissolution of $Ca(OH)_2$, but reduces the pH of the solution. The drop of pH retards and reduces the dissolution of the pozzolan. Compared with the control pastes, the solution in the $CaCl_2$ activated pastes has a higher concentration of $Ca^{2+}$ but a lower concentration of dissolved monosilicate and aluminate species, which result in the formation of $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ very quickly [Eq. (11)]:

$$2[Al(OH)_4]^- + 2Cl^- + 3Ca^{2+} + 4OH^- + 4H_2O \rightarrow C_3A \cdot CaCl_2 \cdot 10H_2O. \tag{11}$$

Since $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ and $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ have the same crystal structure, a solid solution of $C_3A{\cdot}CaCl_2{\cdot}10H_2O–C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ can form very easily. This is why only one set of peaks, corresponding to the solid solution of $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O–C_3A{\cdot}CaCl_2{\cdot}10H_2O$, appear in the diffraction patterns. XRD analysis in Fig. 1 has confirmed that the diffraction peaks of the solid solution of $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O–C_3A{\cdot}CaCl_2{\cdot}10H_2O$ in the $CaCl_2$ activated pastes are much stronger than those of $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ in the control pastes. SEM observation also indicates that much more and larger hexagonal plates can be observed in the $CaCl_2$ activated pastes than in the control pastes.

Since 1 mol of $Al_2O_3$ requires 4 mol of CaO to form $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ and 3 mol to form $C_3A{\cdot}CaCl_2{\cdot}10H_2O$, more lime is consumed than for the formation of C-S-H. Since the concentration of dissolved monosilicate and aluminate species is lower than that in the control pastes, the depletion of $Ca(OH)_2$ in the $CaCl_2$ activated pastes was very similar to that in the control pastes at 23°C and 35°C at early ages. The formation of the solid solution $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O–C_3A{\cdot}CaCl_2{\cdot}10H_2O$ consumes dissolved monosilicate and aluminate species. Also, the solid solution precipitates far away from pozzolan particles. Thus, the dissolution of the pozzolan and the precipitation can continue at a high rate. As shown in Table 2, the formation of $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ increases the solid volume much more than C-S-H, even more than $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$. It can be expected that the $CaCl_2$ activated pastes will give a denser structure and a higher

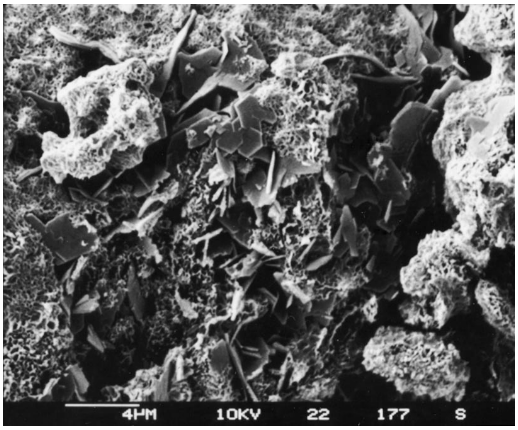


Fig. 6. Hexagonal plate bridge in lime–natural pozzolan pastes ($CaCl_2$ activated paste after 28 days of curing at 35°C).

strength than the control pastes after a certain period of time. Of course, some C-S-H also forms at the same time. The solid solution bridges the C-S-H surrounding the pozzolan particles and reinforces the pastes (as shown in Fig. 6). As the structure of $CaCl_2$ pastes is further densified, the $CaCl_2$ activated pastes exhibit a higher strength than the $Na_2SO_4$ activated pastes. Unetched surface of pozzolan particles in the $CaCl_2$ pastes can even be observed even at 180 days. The increase in curing temperature accelerates the dissolution of the pozzolan and the formation of reaction products in the $CaCl_2$ activated pastes more significantly than those in the control or $Na_2SO_4$ activated pastes. This may explain why the $CaCl_2$ activated pastes exhibit higher strengths than the control or $Na_2SO_4$ activated pastes at higher temperatures.

## 4. Conclusions

$C_4AH_{13}$ and C-S-H were the main hydration products in the control lime–pozzolan pastes. A solid solution of $C_3A \cdot Ca(OH)_2 \cdot 12H_2O - C_3A \cdot CaCl_2 \cdot 10H_2O$ rather than $C_4AH_{13}$ formed in the $CaCl_2$ activated pastes. The increase in the curing temperature accelerated the reaction rate but did not show an effect on the hydration products in these pastes. AFt, instead of $C_4AH_{13}$, was identified at 23°C and 35°C, and AFt and AFm at 50°C and 65°C in the $Na_2SO_4$ activated pastes.

The addition of $Na_2SO_4$ to lime–pozzolan paste increased the alkalinity of the solution, accelerated the dissolution of the natural pozzolan and the pozzolanic reactions at initial stages. AFt forms in the $Na_2SO_4$ activated pastes due to the presence of $Na_2SO_4$. The higher early strength of $Na_2SO_4$ activated pastes was attributed to both the accelerated pozzolanic reaction and the formation of AFt. As temperature increased to over 35°C, AFm appeared and resulted in a lower strength.

The introduction of 4% $CaCl_2 \cdot 2H_2O$ decreased the pH values of the solution, and retarded the dissolution of the pozzolan, but accelerated the dissolution of $Ca(OH)_2$. The higher concentration of $Ca^{2+}$ but lower concentration of dissolved pozzolan resulted in the formation of the solid solution of $C_3A \cdot Ca(OH)_2 \cdot 12H_2O - C_3A \cdot CaCl_2 \cdot 10H_2O$. The formation of the solid solution consumed dissolved pozzolan and it precipitates far away from pozzolan particles. Thus, the dissolution of the pozzolan and the precipitation continued at a high rate. Also, the formation of the solid solution increases the solid volume much more than C-S-H, even more than $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$. The $CaCl_2$ activated pastes formed a denser structure and exhibited a higher strength than the control or the $Na_2SO_4$ pastes after a certain period of time. The increase in curing temperature accelerated the dissolution of the pozzolan and the formation of reaction products in the $CaCl_2$ activated pastes more significantly than those in the control or $Na_2SO_4$ activated pastes.

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