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Effect of $CaCl_2$ on the hydration of tricalcium silicate

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The hydration of tricalcium silicate has been studied at 30° C in the presence and absence of 2 wt% $CaCl_2$ with a water:solid ratio of 0.8. Free lime determinations, X-ray diffraction analysis, thermal analysis, infra-red spectroscopy, scanning electron microscopy and zeta potential measurements were used for hydration studies. The results indicate that the accelerating action of $CaCl_2$ is due to higher diffusivity of chloride ions.

1. Introduction

When tricalcium silicate, $Ca_3SiO_5(C_3S)$, one of the major constituents of portland cement, is brought into contact with water, the hydration reaction starts [1]. The rate of the reaction and the relative amounts of hydration products formed are known to be dependent on several factors [2], e.g. temperature of hydration, surface area of the material, presence of admixtures and the water to solid ratio (W/S).

The use of chemical admixtures to give or to modify some particular properties of C_3S introduces further complications into the already complex $C_3S–H_2O$ system. The effect of various admixtures on the hydration of C_3S has been investigated by a number of investigators [2–19]. Calcium chloride acts as a very efficient accelerator and being cheap, it is the most widely recognized admixture of this type. Compared with many other complex admixtures, $CaCl_2$ is relatively simple in terms of its chemical and physical nature. However, there is not only much controversy regarding the actual mechanism of its action but also a persistent disagreement on its effects on concrete [15].

This paper describes the study of the effect of 2 wt% $CaCl_2$ on the hydration of C_3S.

2. Experimental details

2.1. Materials

C_3S was prepared by firing a stoichiometric mixture of calcium acetate and silica (acrosil) at 1350° C for 24 h. The BET surface area was $1.252\,m^2\,g^{-1}$ and the free lime was 1%. $CaCl_2$ (AR, Merck) was used as an accelerator.

2.2. Methods

C_3S was allowed to hydrate in polythene bags at different intervals of time at 30° C in the presence and absence of 2 wt% $CaCl_2$. The water to solid ratio was kept at 0.8. The hydration at different intervals of time was stopped with absolute alcohol.

The degree of hydration was determined by quantitative X-ray diffraction using 10 wt% MgO as an internal standard. The *d* values used for C_3S were 0.2776, 0.273 and 0.218 nm and for MgO, *d* was 0.210 nm. Free lime was determined by a modified Franke method [20].

Simultaneous differential thermal analysis (DTA), differential thermal gravimetric analysis (DTG) and thermal gravimetric analysis (TG) curves were obtained using a thermoanalyser. The rate of heating was maintained at $10°\,C\,min^{-1}$ from ambient temperature to 1000° C in atmospheric air.

Scanning electron microscope (SEM) pictures of C_3S hydrated in the presence and absence of $CaCl_2$ at 1 min and 24 h of hydration were obtained from the Institute für Gesteinshüttenkunde, TH, Aachen, W. Germany.

Infra-red (i.r.) spectra of C_3S hydrated at different intervals of time in the presence and absence of $CaCl_2$ in nujol mull were recorded using a Perkin-Elmer 621 spectrophotometer.

The electrophoretic velocity was measured by the technique used by Rastogi *et al.* [21]. The solvent used was methyl alcohol. From the value of electrophoretic velocity, the zeta potential values were calculated.

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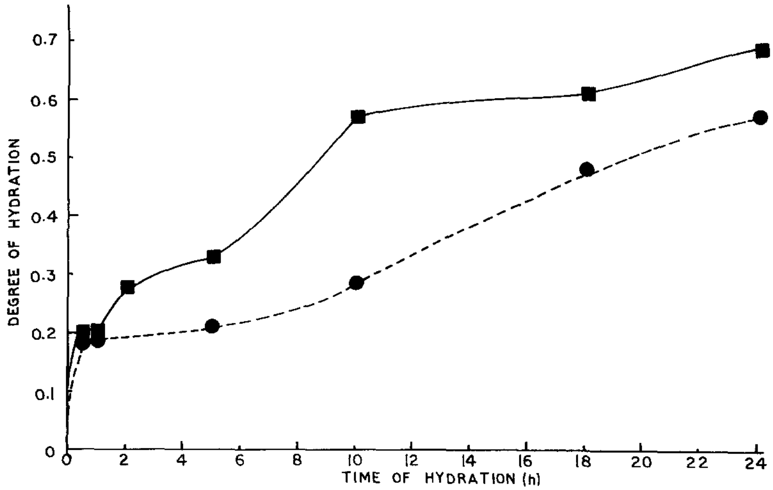


Figure 1 Variation of degree of hydration with time: ---●--- water, ——■—— 2 wt % $CaCl_2$.

3. Results and discussion

3.1. Degree of hydration

The variation of degree of hydration both in the absence and presence of $CaCl_2$ as determined by X-ray diffraction analysis is given in Fig. 1. From Fig. 1 it is clear that in the absence of $CaCl_2$, as soon as C_3S comes in contact with water, a small fraction of it is immediately hydrated and after this there is virtually no hydration until the induction period ($\approx$ 5 h) is over. After the induction period is over, the hydration accelerates with time and then becomes very slow at 24 h of hydration. It is believed that at later stages of hydration, the reaction becomes diffusion controlled. In the presence of 2 wt % $CaCl_2$, again a fraction of the C_3S is hydrated immediately after contact with water and then hydration remains practically constant during the induction period ($\approx$ 1 h). It is interesting to note that of course $CaCl_2$ reduces the induction period but during the early time of hydration i.e. up to the induction period, the degree of hydration is not affected by the $CaCl_2$. After the induction period is over, i.e. after 1 h, the hydration reaction again accelerates with time and becomes slow at or about 24 h of hydration. The overall effect of $CaCl_2$ is to reduce the induction period and increase the degree of hydration. However the data is always accompanied by a certain amount of experimental error, because of the uncertainty in the X-ray diffraction peaks and variation of the chemical composition of the calcium silicate hydrate during the progress of reaction.

The kinetic data on degree of hydration agree better with the equation of Jander [22]:

$$[1-(1-\alpha)^{1/3}]^2 = kt, \qquad (1)$$

where α is the degree of hydration at any time t and k is the apparent rate constant and includes the particle size and diffusion coefficient. A plot of $2 \log [1-(1-\alpha)^{1/3}]$ against $\log t$ gave two straight lines (Fig. 2). The intersection of the two lines gives the end of the induction period. Since Equation 1 is a diffusion-controlled equation, it can be said that the hydration of C_3S is a diffusion-controlled process. However it is difficult to conclude because Equation 1 is valid for particles only of the same size, whereas in the present study, particles of different sizes were present.

3.2. Free lime

The variation of free lime in the absence and presence of $CaCl_2$ is given in Fig. 3. From the curve, it is clear that in the presence of $CaCl_2$, more free lime is obtained and this value is nearly constant after 10 h of hydration, whereas without

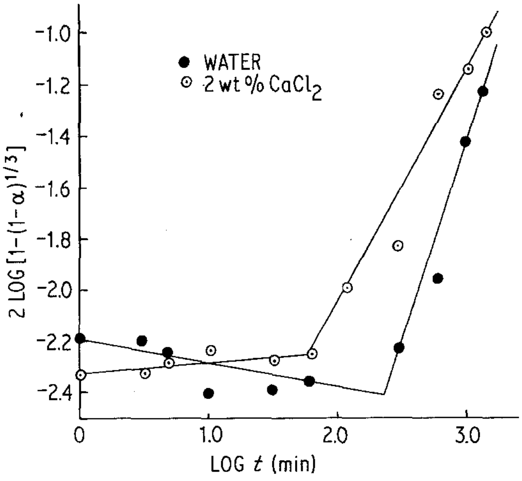


Figure 2 Test of Jander's equation.

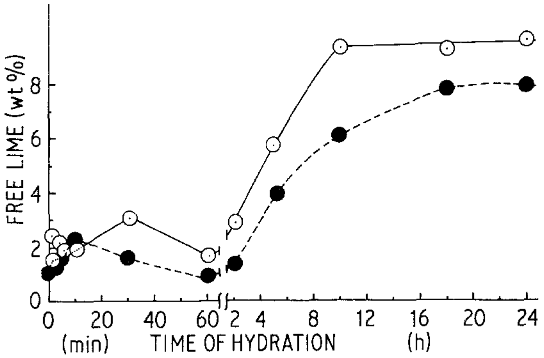


Figure 3 Variation of free lime in hydrating C_3S with time, - - -●- - - water, ——○—— 2 wt% $CaCl_2$.

$CaCl_2$, this continuously increases up to 24 h. This indicates that $CaCl_2$ accelerates the hydration.

The degree of hydration as determined by X-ray diffraction and the content of free lime as determined by an extraction method were used for the determination of the C/S ratio and the variation of this ratio is given in Table I. From the table it is clear that, the values of the C/S ratio are always less than 3 and vary with hydration time. The variation of C/S with hydration time may be due to changes in the relative amounts of different kinds of C–S–H. Using X-ray photoelectron analysis (ESCA) of the surface layers, Thomassin *et al.* [23] and Menetrier *et al.* [24] found that the C/S ratio in the early seconds of hydration is much lower than 3. The C/S values reported here are generally higher than the values reported in the literature. This may be due to the fact that the free lime determined by the extraction method is generally higher than that determined by any other technique and hence this will give a comparatively higher C/S value.

3.3. Thermal analysis

The product of hydration contains two components which lose water on heating: C–S–H, also called the tobermorite gel, and $Ca(OH)_2$. The first component loses water gradually in the range 60 to 260° C and the DTG peak appears at around 100° C. This peak occurs at 10 and 24 h of hydration, both in the presence and absence of $CaCl_2$. The absence of this peak below 10 h of hydration simply indicates that very little C–S–H is formed. A comparison of the magnitude of this effect with that for samples hydrated for corresponding periods of time without $CaCl_2$ indicates that more hydration takes place in samples hydrated in the presence of $CaCl_2$, assuming that C–S–H gels formed in these specimens are of nearly the same composition. A similar conclusion is obtained from the DTA peak appearing at about 150° C.

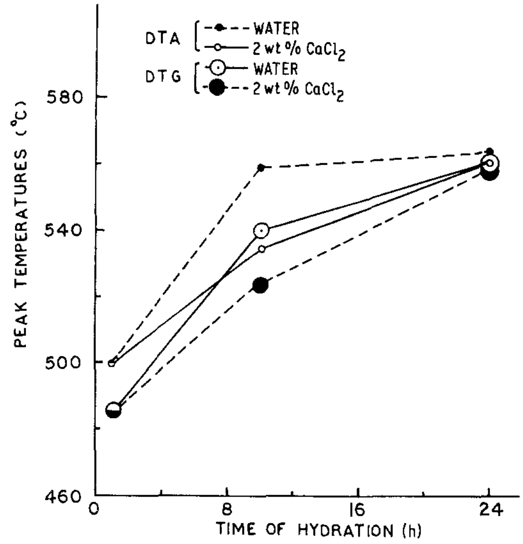


Figure 4 Shift of $Ca(OH)_2$ DTA and DTG peak.

The second peak appearing in the thermograms (DTG, DTA) indicates the decomposition of $Ca(OH)_2$, which is formed during hydration. In pure C_3S, the presence of a small peak indicates the hydration of free lime which is already present. The peak area increases with the time of hydration indicating that as the hydration proceeds, more $Ca(OH)_2$ is formed. The peak area in the presence of $CaCl_2$ is greater than the corresponding peak in the absence of $CaCl_2$, indicating the acceleration of C_3S hydration in the presence of $CaCl_2$.

The thermograms show a shift of the DTG and DTA second region peaks with increasing time of hydration. The shift in the peak temperatures in the presence and absence of $CaCl_2$ is indicated in Fig. 4. Both the DTG and DTA peaks shift to higher temperatures with increasing time of

TABLE I C/S ratio in C–S–H phase

Admixture (C/S)	C/S ratio values at varying times of hydration									
	1 min	3 min	5 min	10 min	30 min	1 h	5 h	10 h	18 h	24 h
0%	2.55	2.78	2.71	2.49	2.65	2.82	2.26	2.12	2.32	2.42
2 wt% $CaCl_2$	2.68	2.58	2.64	2.63	2.38	2.65	2.27	2.31	2.37	2.41

hydration. It appears that the shift is associated with the degree of hydration. However this shift in temperature is slightly lower in the presence of $CaCl_2$. These changes in peak temperature can be understood since, during the first hour of hydration, $Ca(OH)_2$ is formed at the surface of C_3S which decomposes quickly, but, as the time of hydration proceeds, more and more precipitation of $Ca(OH)_2$ takes place. This may have a different particle size, crystallinity and compactness. Due to these changes, the $Ca(OH)_2$ may be bonded differently at the surface of C_3S and C–S–H and with time diffuses into the bulk and hence a higher temperature is needed to decompose $Ca(OH)_2$. However, in the presence of $CaCl_2$, the particle size, crystallinity and compactness of $Ca(OH)_2$, because of rapid hydration, may be reduced. Further, due to the presence of $CaCl_2$ the rate of diffusion of $Ca(OH)_2$ in the bulk may also be reduced because chloride ions have more diffusive power and because of this more $Ca(OH)_2$ will be near the surface than the bulk and hence decomposition may take place at comparatively lower temperatures.

There is a slow weight loss at around 800° C and which is accompanied by a slight endothermic effect which is probably caused by the decomposition of small amounts of $CaCO_3$ obtained as a result of carbonation and also due to loss of water from C–S–H [25].

3.4. Scanning electron microscopy

The analysis of the SEM pictures as presented in Fig. 5 shows that as soon as C_3S comes into contact with water (1 min) hydration begins and C_3S grains are surrounded by some hydration products (Fig. 5a). In the presence of $CaCl_2$, the hydration products surrounding the C_3S grains increase (Fig. 5b). After 24 h of hydration in the absence of $CaCl_2$, the hydration products are in the form of compact needles (Fig. 5c), whereas in the presence of $CaCl_2$, the hydration products are granular in shape and less compact. These observations support the thermal decomposition studies.

3.5. Infra-red spectra

C_3S shows a broad absorption band in the 800 to 1200 cm^{-1} region. This feature is common to the spectra of most silicates [26] and is associated with a number of vibrational modes associated with Si–O linkages [27]. In the case of C_3S hydrated at different intervals of time, this band broadens and shifts to a higher frequency. The band intensities are also reduced. In the presence of $CaCl_2$, the band shifts more towards a higher frequency, indicating a higher degree of hydration. In the 3000 to 4000 cm^{-1} region, a band at around 3600 cm^{-1} indicates the presence of free OH, which is due to $Ca(OH)_2$. The intensity of this band increases with time and $CaCl_2$ content. This again shows that $CaCl_2$ accelerates the hydration. Since this band is at around 3600 cm^{-1}, this indicates that there is no hydrogen bonding in the OH group of $Ca(OH)_2$.

3.6. Zeta potential

Zeta potential values were obtained by measuring the electrophoretic velocities. The electrophoretic velocity, V_e, varies non-linearly with applied potential difference, $\Delta\phi$, as follows

$$V_e = L_{12}\Delta\phi + \tfrac{1}{2}L_{122}(\Delta\phi)^2. \qquad (2)$$

If $V_e/\Delta\phi$ is plotted against $\Delta\phi$, straight lines are obtained. Further, based on simplifying assumptions it is possible to express electrophoretic velocity as [21, 28]

$$V_e = \frac{D\zeta\Delta\phi}{6\pi\eta l} \qquad (3)$$

and

$$L_{12} = \frac{D\zeta}{6\pi\eta l} \qquad (4)$$

so that

$$\zeta = \frac{6\pi\eta l}{D} \times L_{12} \times 9 \times 10^4, \qquad (5)$$

where ζ is the zeta potential in V, $\Delta\phi$ is the applied potential difference, η is the coefficient of viscosity of the medium, l is the distance between the two electrodes, D is the dielectric constant of the medium, L_{12} is the electrophoretic coefficient and L_{12} is the higher order term.

The zeta potential values were calculated using Equation 5 and are given in Table II. From the table it is clear that the zeta potentials of all the samples are positive, showing that a positive charge exists on the surface of the particles. In the case of unhydrated C_3S, this may be due to non-stoichiometry of the compound, where a positive ion probably Ca^{2+} ions are in excess or it may be due to the partial hydration of C_3S in contact with air, which cannot be avoided. The zeta potential values in the absence of $CaCl_2$ are roughly constant up to 5 h, i.e., up to the induction period, and after the induction period is over, it decreases rapidly.

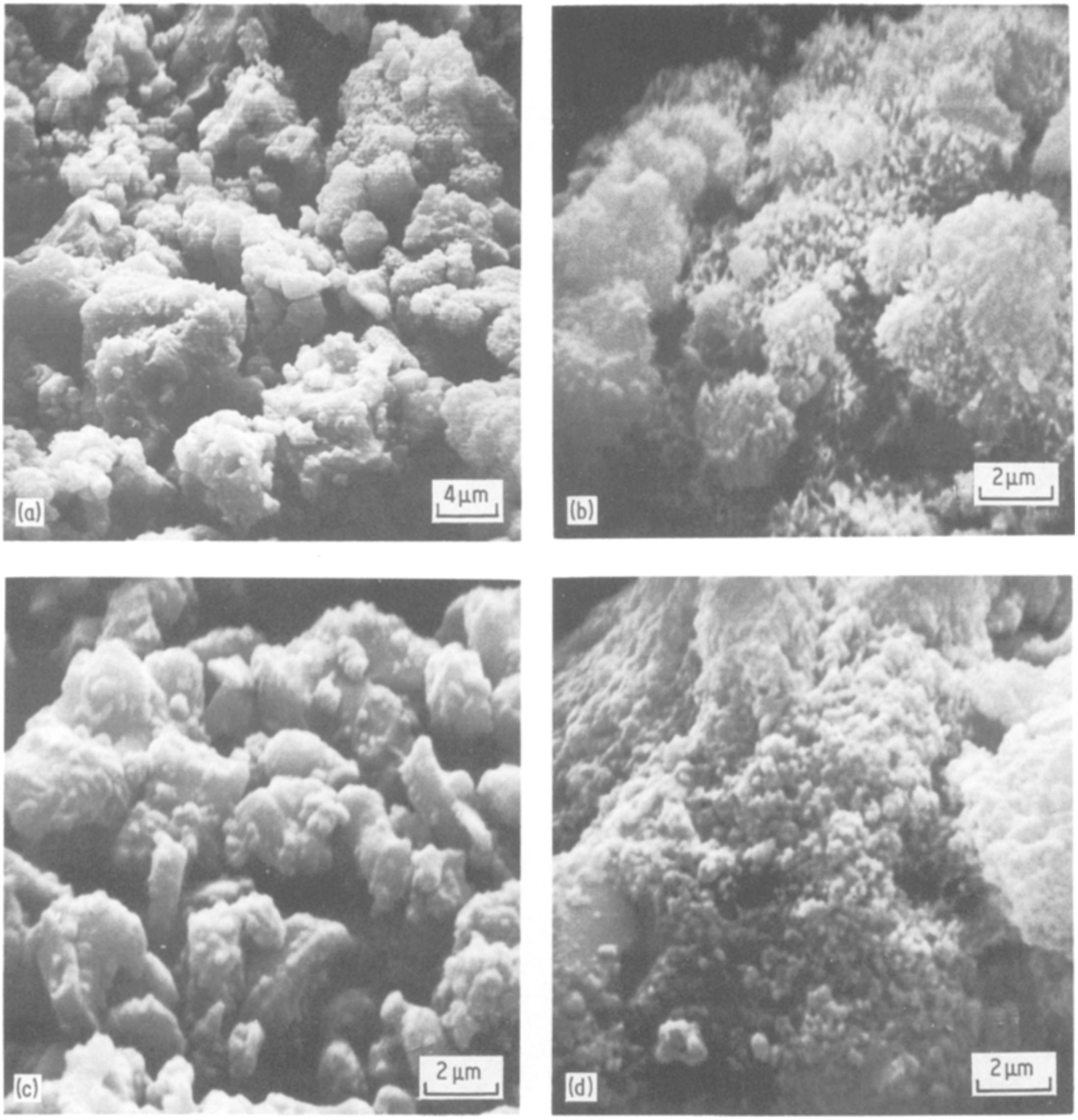


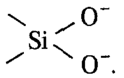
Figure 5 SEM photographs of C_3S hydrated for various lengths of time: (a) 1 min, (b) 24 h, (c) 1 min in 2 wt% $CaCl_2$ and (d) 24 h in 2 wt% $CaCl_2$.

TABLE II Zeta potential values

Time of hydration (h)	$CaCl_2$ (wt%)	Zeta potential (mV)
0.0	0	11.7
0.5	0	74.8
5.0	0	74.8
18.0	0	35.8
0.5	2	84.6
1.0	2	84.6
5.0	2	37.1
18.0	2	34.5

This can be understood since, as soon as C_3S comes in contact with water, the hydrolysis reaction starts and the calcium ions go into the solution, which rapidly becomes saturated or supersaturated with respect to calcium hydroxide [29, 30] leaving a silica-rich surface. Very little silica enters the solution [30]. Such a mode of dissolution would be expected from the orthosilicate structure of the anhydrous C_3S [31, 32] since the breaking of two bonds mobilizes calcium whereas the breaking of four bonds would be needed to release silicic acid.

Since the total hydrolysis of C_3S must necessarily release orthosilicate species and since the other dominant silicate species at the early stages of hydration is disilicate, the surface layer must consist of two molecular mass silicates. The surface of the hydrated C_3S at the early stages can be represented as [33]



Since in the solution near the negatively charged solid interface, Ca^{2+} and possibly $CaOH^+$ ions are present, they are adsorbed at the surface making it positive and hence cause an increase in the zeta potential. The adsorption or, in other words, the coating of the ions, may act as a membrane as pointed out by Double *et al.* [34, 35] and others [36] and would not allow further hydration of C_3S during the induction period. As time passes, and so-called membranes of ions is broken in a random fashion due to internal pressure. As a result of this rupturing, fresh C_3S surface comes in contact with water and the hydration reaction accelerates, precipitation of $Ca(OH)_2$ and C–S–H takes place and the concentration of the adsorbed positive ions decreases. This causes a decrease in the zeta potential.

In the presence of $CaCl_2$, the value of the zeta potential is maximum for the sample hydrated for 30 min and is higher than that of the sample hydrated for 30 min in the absence of $CaCl_2$. This value decreases very slowly up to 1 h of hydration, i.e., up to the induction, period, after which it decreases rapidly. These results indicate that the Ca^{2+} ions of the $CaCl_2$ are probably also adsorbed on the surface of the hydrated C_3S thus causing an increase in the zeta potential values. The values are maximum during the induction period after which it decreases with the acceleration of the reaction. Since $CaCl_2$ acts as an accelerator for the hydration the zeta potential values decrease more rapidly for samples with $CaCl_2$ than those without $CaCl_2$.

The accelerating action of $CaCl_2$ on the hydration of C_3S is probably due to the fact that Cl^- ions have a smaller ionic size and a greater tendency to diffuse inside the so-called membranes compared with OH^- ions and hence an increase in the internal pressure takes place more quickly. This causes an early rupturing of the so-called membrane and hence an acceleration of hydration.

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