

## KINETICS OF HYDRATION OF TRICALCIUM SILICATE IN PRESENCE OF CALCIUM CHLORIDE BY THERMAL METHODS

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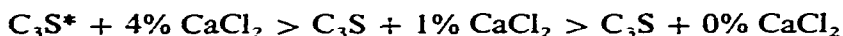
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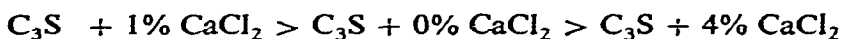
### ABSTRACT

Thermal methods were applied to investigate the influence of  $\text{CaCl}_2$  on the hydration of tricalcium silicate from a few minutes to a month. Both TGA and DTA methods showed a good correlation for the estimation of  $\text{Ca}(\text{OH})_2$  at different degrees of hydration.

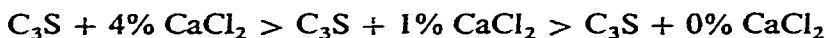
In presence of  $\text{CaCl}_2$  the dormant period was reduced, and with 5% it was reduced from 4 to 2 h. The extent of hydration at 6 h in terms of estimated  $\text{Ca}(\text{OH})_2$  was in the order



and at 30 days



In terms of the disappearance of  $\text{C}_3\text{S}$ , however, the extent of hydration at 6 h or 30 days was in the order



These results indicate that in presence of higher percentages of  $\text{CaCl}_2$ ,  $\text{C}_3\text{S}$  hydrates to form C-S-H\* with a higher  $\text{CaO}/\text{SiO}_2$  ratio.

Thermal curves showed an endothermic effect at 550 to 590°C during the dormant period in samples hydrated with  $\text{CaCl}_2$ . This could be attributed to the formation of a surface complex of chloride on the  $\text{C}_3\text{S}$  surface in presence of water. An intense exothermic effect which appeared at the acceleratory period is ascribed to an interaction of the chemisorbed chloride on the C-S-H surface as well as to the presence of chloride in the interlayer spaces. Adsorption of chloride may play a more important role than the "compound or free  $\text{CaCl}_2$ " mechanisms for acceleration.

### INTRODUCTION

In concrete practice, accelerating admixtures are used in small quantities to shorten the time of setting and to increase the rate of early strength development. The accelerating effectiveness<sup>1,2</sup> of anions is in the order of  $\text{Cl}^- > \text{S}_2\text{O}_3^{2-} > \text{SO}_4^{2-} > \text{NO}_3^-$

\*The following nomenclature used in cement chemistry will be followed where necessary: C =  $\text{CaO}$ , S =  $\text{SiO}_2$ , A =  $\text{Al}_2\text{O}_3$ , and H =  $\text{H}_2\text{O}$ .

and that for cations,  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{Zn}^{2+}$ . Calcium chloride acts as a very efficient accelerator and, being cheap, is the most widely recognized admixture of this type.

Millar and Nichols in 1885 published the first patent on the accelerating influence of  $\text{CaCl}_2$  on cements<sup>3</sup>. Candlot in 1886 described in a publication that the use of  $\text{CaCl}_2$  solutions up to 50 g/l increased the strength of cement<sup>4</sup>. Since then, extensive data have been published about the effect of  $\text{CaCl}_2$  on the properties of cement and concrete. Vollmer<sup>5</sup> prepared an annotated bibliography of the publications pertaining to the effect of  $\text{CaCl}_2$  on concrete, covering the years 1885 to 1952. In the years 1952 to 1969, interest has increased in this subject, as is evidenced by a number of publications and discussions in conferences. A survey of the literature indicates that most of the published data relate to the engineering properties of concrete, and comparatively less attention has been paid to the basic understanding of the accelerating mechanism of  $\text{CaCl}_2$ .

According to earlier concepts,  $\text{CaCl}_2$  facilitates strength development in cement by forming a complex compound with the tricalcium aluminate phase, which implies thereby that  $\text{CaCl}_2$  does not have any influence on the hydration of  $\text{C}_3\text{S}$  phase. This explanation was generally accepted because  $3\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ , analogous to calcium sulfoaluminate hydrate, was identified in hydrating cements containing  $\text{CaCl}_2$ .

Sloane *et al.* found some evidence that the hardening of pure calcium silicates is accelerated<sup>6</sup> by  $\text{CaCl}_2$ . This important observation has been confirmed recently by others<sup>7-26</sup>. It is now widely recognized that, in cements, accelerators greatly influence the hydration kinetics of the silicate phases.

In recent years thermoanalytical techniques have attained recognition as being valuable tools in cement chemistry for investigating the rate and mechanism of reactions, for quantitatively evaluating the products and for detecting the presence of new compounds<sup>27,28</sup>. These techniques have not yet been applied systematically to follow the hydration of  $\text{C}_3\text{S}$  in presence of  $\text{CaCl}_2$ . The object of the present investigation is to examine the influence of different amounts of  $\text{CaCl}_2$  on the progress of hydration of  $\text{C}_3\text{S}$  from a few minutes to about 30 days by means of DTA, TGA, and X-ray methods, in order to seek new evidence that might provide further insight into the role of accelerators in cements.

## EXPERIMENTAL

### *Materials*

The tricalcium silicate sample used in the present work was made available by the Portland Cement Association, U.S.A., and had the following composition expressed as per cent ignited basis.

*Chemical:* CaO, 73.88;  $\text{SiO}_2$ , 26.17;  $\text{Al}_2\text{O}_3$ , 0.08; free CaO (ASTM), 0.18; free CaO (Franke), 0.46. *Mineralogical:*  $\text{C}_3\text{S}$ , 99.33;  $\text{C}_2\text{S}$ , 0.00;  $\text{C}_3\text{A}$ , 0.21; CaO (Franke), 0.46. *Fineness:* Blaine 3310  $\text{cm}^2/\text{g}$ .

Calcium chloride hexahydrate of analytical reagent quality was used as the accelerating admixture. Because the solid was very deliquescent, solutions of required concentrations could not be prepared directly by weighing and dissolving in water. Hence, approximately 15%  $\text{CaCl}_2$  solution was prepared and the exact concentration was determined by argentometric method. Dilutions were then made to obtain any required concentration.

#### *Sample preparation*

The hydration of  $\text{C}_3\text{S}$  was studied by mixing it with double-distilled water at a water to silicate ratio of 0.5. The hydration was carried out in tightly covered polyethylene containers rotated continuously over rollers. At specified intervals of time, varying between 15 minutes and 1 month, each sample was ground in cold ethyl alcohol, placed in a desiccator, and continuously evacuated for 24 h using liquid air in the trap. Care was taken throughout to prevent contamination with  $\text{CO}_2$ .

A similar method was followed for the hydration experiments in presence of different concentrations of  $\text{CaCl}_2$ . The solution/silicate (vol./wt.) ratio was kept at 0.5. This could be achieved with 1, 4 or 5%  $\text{CaCl}_2$  (with respect to  $\text{C}_3\text{S}$ ) by adding 10 ml each of 2, 8 or 10%  $\text{CaCl}_2$  solution, respectively, to 20 g of  $\text{C}_3\text{S}$ .

The reaction was carried out at a temperature of  $70 \pm 1^\circ\text{F}$ .

#### ANALYSIS

Differential Thermal Analysis (DTA) was carried out using DuPont 900-Thermal Analyser. This unit utilizes platinum holders, and in this work platinum *vs.* platinum-rhodium (13%) thermocouples were used for differential and sample temperature measurements. The reference material was ignited  $\alpha\text{-Al}_2\text{O}_3$  and the rate of heating was  $20^\circ\text{C}/\text{min}$ . In each run, 50 mg of the sample passing through 100-mesh sieve was packed with moderate pressure. Thermograms were obtained in air, in continuous vacuum or in a continuous flow of nitrogen at a pressure of 1.5 in. The sensitivity of the differential temperature on the y-axis was 0.004 mV/in. for most of the experiments, with a sample temperature on the x-axis registering 2 mV/in. The cold junction was kept at  $0^\circ\text{C}$  with crushed ice. In experiments, especially those involving samples with higher  $\text{CaCl}_2$  content, refractory cups, placed in the standard platinum sample holders, were used. Otherwise the sample tended to some extent to fuse and stick to the container and the thermocouple, and it was not easy to remove it. Many samples were run in duplicate and the results showed good reproducibility.

Calcium hydroxide, formed at different periods of hydration, was estimated by determining the endothermal area of dehydration. A comparison was made between the values using the planimeter and by weighing the cut-out area. In the latter method the thermograms were transferred onto a high quality vellum paper by reproducing them by Xerox method. The values obtained by planimeter were less reproducible and hence the Xerox reproduction method was used throughout.

Thermogravimetric analysis (TGA) of the samples was obtained by the standard

Stanton thermobalance at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The  $\text{H}_2\text{O}$  lost due to  $\text{Ca}(\text{OH})_2$  decomposition was estimated between the temperature at which the curve showed deviation from linearity and the temperature at which it levelled off. Generally this occurred between  $450$  and  $550^{\circ}\text{C}$ , and it was not always sharp.

X-ray diffraction powder photographs were taken with a Nonius Guinier quadruple-focusing camera. Most of the results were obtained by a Hilger and Watts diffractometer using  $\text{CuK}\alpha$  source.

## RESULTS

Fig. 1 presents the DTA curves of  $\text{C}_3\text{S}$  hydrated for 5, 15 and 30 min, 1, 2, 3, 4, 6, 8, 10, and 12 h, and 1, 3, 7 and 30 days. For shorter periods of hydration, there is almost a complete absence of any endothermic effect at low temperatures (below  $300^{\circ}\text{C}$ ); an effect is more discernible at 8 h, and its intensity increases continuously up to 30 days. Another feature of the low temperature curves is the emergence of a small endothermic effect at about  $260^{\circ}\text{C}$  which becomes apparent at 3 days. There is

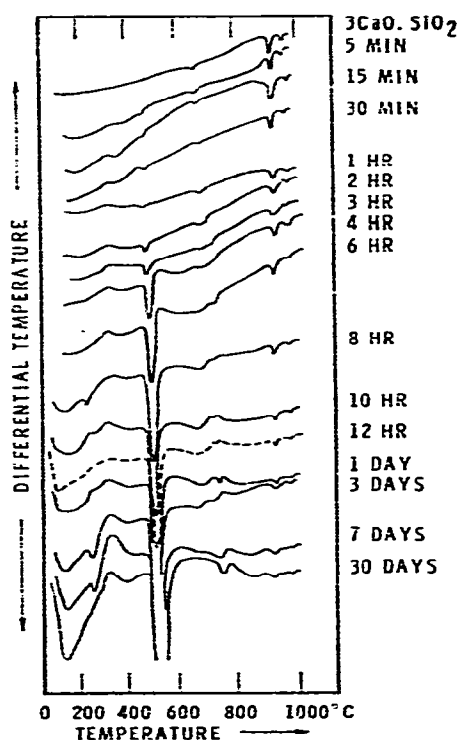


Fig. 1. Rate of hydration of  $3\text{CaO}\cdot\text{SiO}_2$  by DTA.

also an indication of an endothermic valley occurring between  $340$  and  $480^{\circ}\text{C}$ ; it does not have a well defined peak temperature. A slight enhancement of the peak intensity can be seen after longer periods of hydration. At 5, 15, and 30 min of hydration, an unmistakable endothermic effect of low intensity is observed at about  $480^{\circ}\text{C}$ , which

becomes more evident at 1, 2 and 3 h. There is a rapid increase in the intensity of this peak at 4 h and it is still growing at 30 days. The peak temperature of this effect shifts slightly toward higher temperatures with the progress of hydration. There are irregular, poorly defined thermal effects of small magnitude between 640 and 800°C in samples hydrated for 2 h or more. In addition, two endothermic effects exist in all samples at 930 and 980°C, the former being of higher intensity.

Fig. 2 shows the DTA curves of  $C_3S$  hydrated in the presence of 1%  $CaCl_2$  obtained at different times. The two low-temperature endothermic effects below 300°C are evident in these samples also, although at any comparable period the

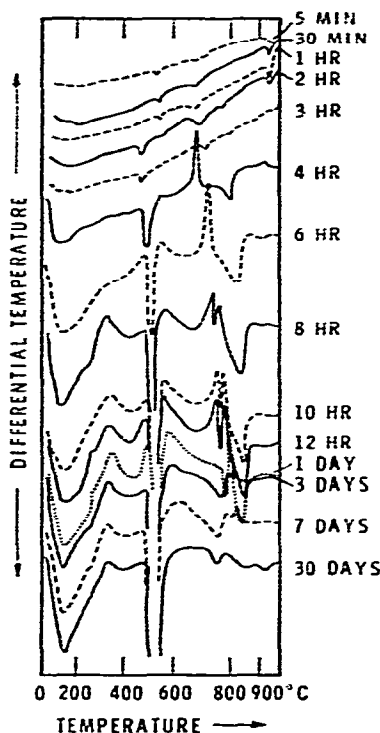


Fig. 2. Rate of hydration of  $3CaO \cdot SiO_2$  in presence of 1%  $CaCl_2$  by DTA.

amplitude of these effects is greater than that found in samples in Fig. 1. The broad endothermic valley between 340 and 480°C is also much more pronounced than that for  $C_3S$  hydrated without  $CaCl_2$ . The intensity of this endothermic valley decreases with the progress of hydration. This series shows that up until 2 h, there is an additional endothermic peak at about 550°C, not detected in corresponding samples in Fig. 1. The small endothermic effect at 480°C, which occurred previously at 5, 15, or 30 min, or 1 h (Fig. 1) is absent, and only at 2 h does this peak become evident. At 4 h this peak is manifest as an intense endothermic effect. From this period onward, the intensity steadily increases up to 30 days. A remarkable feature of this series is the sudden emergence of an intense exothermic effect at about 690°C after 4 h of hydration. This peak shifts towards higher temperatures at later times. At 8 h, in addition

to this peak, a second exothermic peak develops at about  $760^{\circ}\text{C}$ . This peak seems to persist, though with decreasing intensity, up to at least 7 days, after which time it is not obvious. Another interesting feature is the existence of an intense endotherm in the range from  $800$  to  $840^{\circ}\text{C}$  following the exothermal effect. After 1 day it is absent.

In Fig. 3, thermograms of  $\text{C}_3\text{S}$  hydrated in the presence of 4%  $\text{CaCl}_2$  are shown. As before, the curves exhibit two low-temperature endothermal effects of high intensity. There is also an endothermal valley (below  $400^{\circ}\text{C}$ ) which is less pronounced except in a few samples. The endothermic peak at  $570^{\circ}\text{C}$ , which corresponds to the

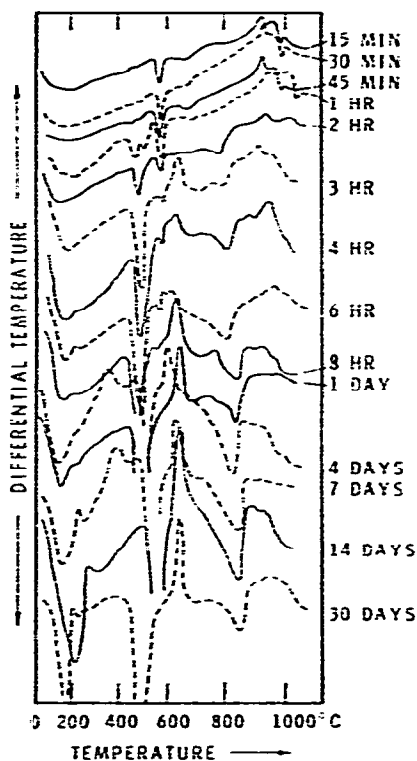


Fig. 3. Rate of hydration of  $3\text{CaO}\cdot\text{SiO}_2$  in presence of 4%  $\text{CaCl}_2$  by DTA.

$550^{\circ}\text{C}$  effect of Fig. 2, appears at 15 min but with a much greater intensity. The intensity of this effect is greatest at 1 h, decreases thereafter and is not detectable at 1 day and after. Two additional endotherms in the form of a doublet appear at 1 h in the temperature range  $450$  to  $550^{\circ}\text{C}$ , but at 2 h and thereafter only a single endotherm is noticeable in this range. The rate of development of this endothermal peak area is pronounced between 2 and 3 h. When this peak was compared to the corresponding peaks in the previous series, it was seen that the peak appeared earlier and with more intensity in this series than previously. At 1 day, after the intensity had decreased with respect to the samples hydrated with 1%  $\text{CaCl}_2$  and of samples  $\text{C}_3\text{S} + 0\%$   $\text{CaCl}_2$ ,  $\text{C}_3\text{S} + 1\%$   $\text{CaCl}_2$ , and  $\text{C}_3\text{S} + 4\%$   $\text{CaCl}_2$  cured for 30 days, the peak for the 4%  $\text{CaCl}_2$  has the least intensity. In samples hydrated with 4%  $\text{CaCl}_2$  the sudden onset of exo-

thermic peak occurs at 3 h. This exotherm at 640°C appears as a hump at 4 h and 6 h, and is sharper at later stages of hydration. A large endothermic inflection between 810 and 850°C is also evident in samples cured for 3 h or more.

TGA has shown certain features common to those of DTA curves. Increases in intensity of curves at low temperatures corresponded with greater weight losses. It was not always possible, however, to realize sharp inflections corresponding to various thermal effects registered by DTA.

## DISCUSSION

### Hydration of $3\text{CaO}\cdot\text{SiO}_2$

Methods such as those involving determination of the quantities of non-evaporable water, calcium hydroxide, residual  $\text{C}_3\text{S}$ , and also electrical conductivity, heats of hydration, or strength, have been adopted to follow the hydration of  $\text{C}_3\text{S}$ . In this work the quantity of  $\text{Ca}(\text{OH})_2$  was estimated at different stages of hydration of  $\text{C}_3\text{S}$ , with or without  $\text{CaCl}_2$ , by DTA and TGA techniques. These methods served as a reasonable basis for investigating the accelerating influence of  $\text{CaCl}_2$ , and were particularly suitable for assessing the dormant period and degree of hydration within a particular series. These results, in conjunction with X-ray methods, enabled an over-all picture of the relative degrees of hydration of  $\text{C}_3\text{S}$ .

Fig. 4 shows the DTA peak areas of the endothermic effects due to  $\text{Ca}(\text{OH})_2$

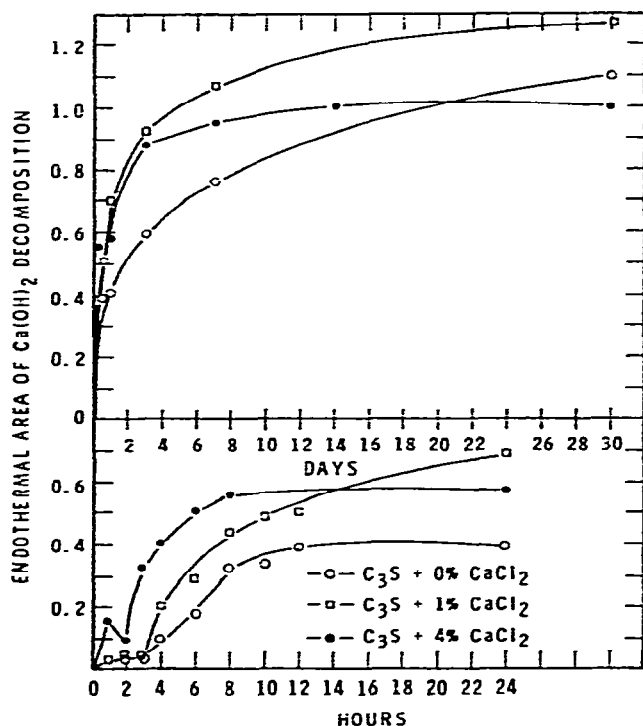


Fig. 4. Estimation of  $\text{Ca}(\text{OH})_2$  at different periods of hydration of  $3\text{CaO}\cdot\text{SiO}_2$  by DTA.

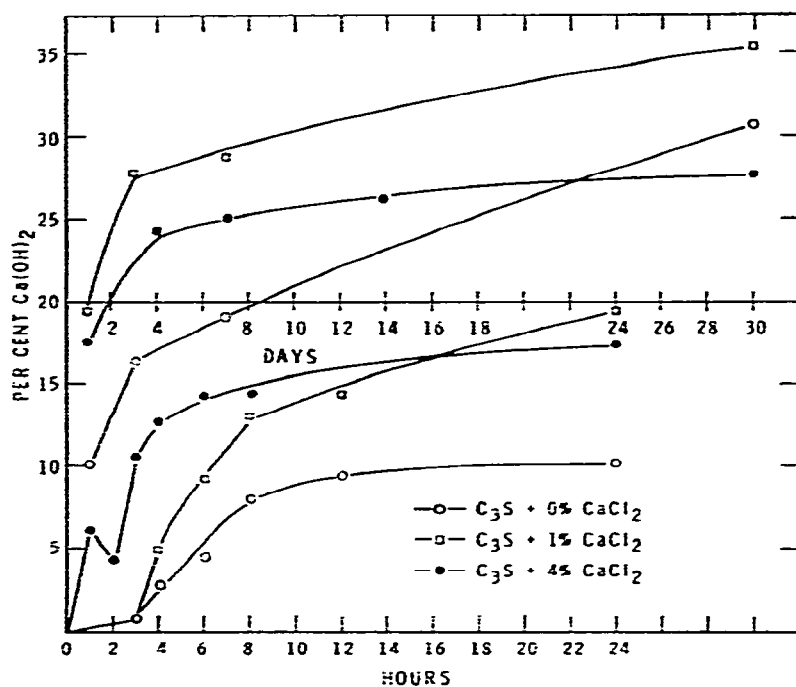


Fig. 5. Percentage  $\text{Ca(OH)}_2$  formed at different periods of hydration of  $3\text{CaO}\cdot\text{SiO}_2$  determined by TGA.

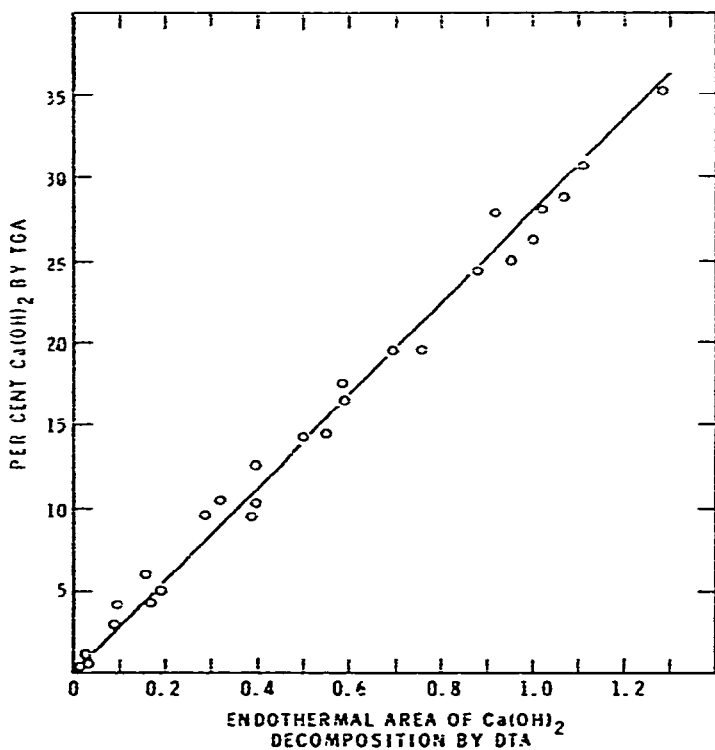


Fig. 6. Comparative estimation of  $\text{Ca(OH)}_2$  by TGA and DTA methods.



decomposition at hydration periods ranging from 1 h to 30 days. Fig. 5 refers to the percentage  $\text{Ca(OH)}_2$  determined by TGA at various stages of hydration. A comparison of the TGA and DTA methods of estimation of  $\text{Ca(OH)}_2$  indicates a linear relationship (Fig. 6).

Thermograms of pure  $\text{C}_3\text{S}$ , as well as of  $\text{C}_3\text{S}$  cured at earlier times, indicate three endothermic peaks at about 680, 930, and 970–980°C, the one at 930°C being of highest intensity (Fig. 1). The transitions in the  $\text{C}_3\text{S}$ , *viz.*  $\alpha \rightarrow \beta$  in the triclinic form, triclinic  $\rightarrow$  monoclinic, and monoclinic  $\rightarrow$  trigonal forms, may respectively explain these effects<sup>29</sup>. The intensity of these peaks diminishes with the progress of hydration.

The two low-temperature endothermic peaks below 300°C, which seem to merge into one in many instances denote the expulsion of loosely- as well as firmly-bound water from the C–S–H product. The increase in intensity of this effect with time is due to larger amounts of C–S–H being formed with the progress of hydration. Results of TGA are also in accord with these observations.

An endothermic valley between 340 and 480°C, which is more evident in some samples than others, may represent the dehydration effect of  $\text{Ca(OH)}_2$  when it is present in a non-crystalline form, and also the evolution of firmly-bound  $\text{H}_2\text{O}$  from C–S–H<sup>30</sup>. In Fig. 6 the area of this valley is not taken into consideration for plotting DTA peak areas. A better fit of many points into a linear relationship may be expected if these values are also taken into account.

A very small endothermic effect at about 480°C, which appeared immediately after hydration began, and became more evident at 1 h and after, may be attributed to the dehydration of crystalline  $\text{Ca(OH)}_2$ . Small amounts of  $\text{Ca(OH)}_2$  are present initially due to hydration of  $\text{C}_3\text{S}$  as well as to the hydration of free CaO present in the original silicate sample. These were undetected by X-ray method. At 4 h a pronounced increase in the amount of  $\text{Ca(OH)}_2$  is evident; there is more than a 200% increase over the amount present at 3 h (Fig. 4). According to DTA and TGA results, the first 3 h should be reckoned as the dormant period during which very small amounts of  $\text{Ca(OH)}_2$  are formed. The period between 3 and 8 h (approximately) may be termed as an acceleratory stage during which about 25 per cent of all the  $\text{Ca(OH)}_2$  produced up to 30 days is formed. After 8 h  $\text{Ca(OH)}_2$  continues to form but at relatively slower rates.

With the progress of hydration, small thermal effects are discernible between 640 and 800°C, especially at longer periods of hydration. They may represent loss of water from the C–S–H<sup>31</sup> and decarbonation of very small amounts of  $\text{CaCO}_3$  that might have formed in those samples.

#### *Hydration of $3\text{CaO} \cdot \text{SiO}_2$ in presence of 1% $\text{CaCl}_2$*

The comparative rates of hydration of  $\text{C}_3\text{S}$  with or without 1%  $\text{CaCl}_2$  may be studied from Figs. 1, 2, 4, and 5. In presence of  $\text{CaCl}_2$ , certain interesting features are indicated in the thermograms, which have not been reported before in literature.

The two low-temperature (below 300°C) endothermic effects exhibited by some samples in the hydrated  $\text{C}_3\text{S}$  (Fig. 1) are not well defined in this series. The intensity of

this effect is small in the early stages, becomes larger at 4 h, and increases continuously with hydration. A comparison of the magnitude of this effect with that hydrated to corresponding periods without  $\text{CaCl}_2$  (Fig. 1) indicates that more hydration takes place in samples hydrated in presence of  $\text{CaCl}_2$ , assuming that C-S-H gels formed in these specimens are of nearly the same composition.

Samples hydrated in the presence of 1%  $\text{CaCl}_2$  show an additional endotherm at  $550^\circ\text{C}$  up to 2 h that is not observed in those hydrated in the absence of  $\text{CaCl}_2$  (Figs. 1 and 2). This endotherm is not evident at later periods; in  $\text{C}_3\text{S}$  samples hydrated with 4%  $\text{CaCl}_2$ , it is accentuated (Fig. 3). This peak is ascribed to the presence of a complex of  $\text{CaCl}_2$  on the surface of the hydrating  $\text{C}_3\text{S}$  during the induction period. Evidence for this was obtained through many experiments which are to be described in another paper.

At 2 h, evidence of  $\text{Ca}(\text{OH})_2$  is seen by a peak at  $480^\circ\text{C}$ , the magnitude of which does not seem to increase at 3 h. But at 4 h a great increase in intensity of this effect is noted. In the so-called dormant period below 4 h, hydration seems to take place, but only to a small extent. It appears that with 1%  $\text{CaCl}_2$ , the dormant period is about the same as that without  $\text{CaCl}_2$ , but the reaction is accelerated much more from the end of this period. For example, at 4 h  $\text{C}_3\text{S}$  hydrated in 1%  $\text{CaCl}_2$  has about double the amount of  $\text{Ca}(\text{OH})_2$  that is present in  $\text{C}_3\text{S}$  hydrated without  $\text{CaCl}_2$ .

Maximum acceleration in hydration is observed between 3 and 8 h. Of the estimated total  $\text{Ca}(\text{OH})_2$  at 30 days, about 33% is formed within the 5 h of hydration between 3 and 8 h.

The much more pronounced endothermal valleys observed in most of the samples before the onset of the dehydration peak of crystalline  $\text{Ca}(\text{OH})_2$ , shows a likelihood of more non-crystalline  $\text{Ca}(\text{OH})_2$  forming in  $\text{C}_3\text{S}$  hydrated in presence of 1%  $\text{CaCl}_2$  than that without  $\text{CaCl}_2$  (Figs. 1 and 2). In this temperature range, however, C-S-H also dehydrates, and hence it is difficult to assess the relative contributions of these two effects.

A remarkable feature of these thermograms is the onset of an intense exothermic peak at 4 h at a temperature of  $690^\circ\text{C}$ . Whenever present in a sample, this exothermal effect is always followed by a large endothermal dip at about 800 to  $840^\circ\text{C}$ . This seems to be caused by chemisorbed chloride contained on the C-S-H surface, and possibly also by chloride ions in its interlayer positions. Some evidence was obtained for this in experiments and will be described in another publication.

It is interesting to observe that in presence of  $\text{CaCl}_2$ ,  $\text{C}_3\text{S}$  does not exhibit the high temperature endothermic effects at  $930$  and  $980^\circ\text{C}$  in most of the samples, and that an exothermal effect is registered in some samples in the range from  $950$  to  $1000^\circ\text{C}$ . It seems that the high temperature crystalline transitions of  $\text{C}_3\text{S}$  are modified in the presence of  $\text{Cl}^-$  ions.

Another distinct feature of the DTA curves of this series is the development of a second exothermic effect ranging from  $760$  to  $790^\circ\text{C}$ . It is more pronounced in samples hydrated for 8, 10, or 12 h, but after longer periods of hydration, this peak diminishes in intensity. The peak is ascribed to the crystallization effect of the high

surface, low lime C-S-H product formed in the presence of 1%  $\text{CaCl}_2$ . It is known that CSH(I), a low  $\text{CaO/SiO}_2$  ratio hydrate, gives a large exothermic peak around  $800^\circ\text{C}$ . Collepardi *et al.*<sup>20</sup> have reported that  $\text{C}_3\text{S}$  hydrated in low concentrations of  $\text{CaCl}_2$  forms C-S-H of high specific surface — about three times higher than that hydrated only in water.

#### *Hydration of $3\text{CaO}\cdot\text{SiO}_2$ in presence of 4% $\text{CaCl}_2$*

Some of the thermal effects in this series are more intense at earlier times of hydration than the corresponding ones hydrated in presence of 1%  $\text{CaCl}_2$  (Figs. 3, 4, and 5). The endothermic effects caused by a surface complex of chloride on hydrating  $\text{C}_3\text{S}$ , occur as a higher intensity endotherm, and persist until 8 h in the range from  $570$  to  $590^\circ\text{C}$ . Its presence at later periods cannot be confirmed due to the masking effect of the exotherm. The low temperature endothermic curve below about  $400^\circ\text{C}$  continues right up to the temperature of onset of dehydration of  $\text{Ca(OH)}_2$ . The resultant endotherm seems to be larger than the corresponding effect for hydrated  $\text{C}_3\text{S}$  in presence of 0 or 1%  $\text{CaCl}_2$  solution, showing thereby that more water is held in these products.

No  $\text{Ca(OH)}_2$  peak is observed till 45 min; at 1 h the endothermic effect suddenly emerges. At 2 h, the peak due to  $\text{Ca(OH)}_2$  decreases slightly, possibly because the excess of  $\text{Ca(OH)}_2$  was being incorporated in the C-S-H product, with some combining with  $\text{CaCl}_2$  at the surface. It is likely that the degree of hydration, in terms of  $\text{C}_3\text{S}$  consumed, is greater at 2 than at 1 h. The doublet at 1 h may represent the formation of some non-crystalline  $\text{Ca(OH)}_2$ . A sudden increase in the rate of formation of  $\text{Ca(OH)}_2$  occurs between 2 and 3 h. Evidently more heat would be developed in this period than between 1 and 2 h, and the acceleration of the reaction would also be relatively more. An exothermic effect also develops at 3 h at a temperature of  $640^\circ\text{C}$ . Interestingly enough, of the total lime estimated at 30 days, about 50% of the  $\text{Ca(OH)}_2$  is formed within the first 6 h of hydration.

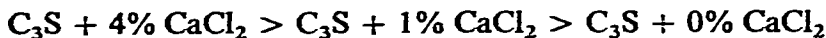
In terms of the amount of  $\text{Ca(OH)}_2$  formed,  $\text{C}_3\text{S}$  with 4%  $\text{CaCl}_2$  hydrates to the greatest extent in the first 12–16 h, after which time it is exceeded by  $\text{C}_3\text{S}$  with 1%  $\text{CaCl}_2$ , and is exceeded in about 22–24 days by the  $\text{C}_3\text{S}$  hydrated with 0%  $\text{CaCl}_2$ . The hydration reaction of  $\text{C}_3\text{S}$  in presence of 4%  $\text{CaCl}_2$  seems to be almost completed within about 15 days, judging by the estimated amount of  $\text{Ca(OH)}_2$  (Figs. 4 and 5). At 30 days, in terms of  $\text{Ca(OH)}_2$  formed, the extent of hydration with  $\text{C}_3\text{S}$  plus 1%  $\text{CaCl}_2$  is greater than  $\text{C}_3\text{S}$  plus 0%  $\text{CaCl}_2$ , which is greater than  $\text{C}_3\text{S}$  plus 4%  $\text{CaCl}_2$ .

The larger endothermic effect at  $810$  to  $850^\circ\text{C}$ , following the exothermic effect, is present along with the exothermic effect from 3 h to 30 days. The endothermic effects representing  $\text{C}_3\text{S}$  transitions beyond  $900^\circ\text{C}$  are absent.

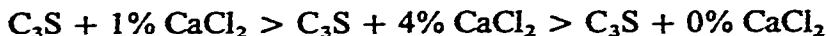
In presence of 5%  $\text{CaCl}_2$ , the initial endothermic peak, during the induction period, as well as the exothermic peak, in the acceleratory period, appear at an earlier stage of hydration.

*Degree of hydration by the rate of disappearance of  $C_3S$*

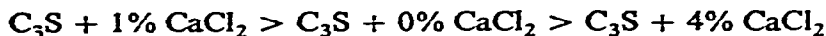
If the amount of  $Ca(OH)_2$  represents the degree of hydration of  $C_3S$ , then at 6 h the rates of the hydration are in the order



whereas at 24 h



and at 30 days



It was of interest to compare these results with X-ray data.

X-ray diffractograms of the samples are shown in Figs. 7 and 8. The diffractogram of pure  $C_3S$  is also given as it enables a better qualitative comparison of the various peaks in the hydrating system.

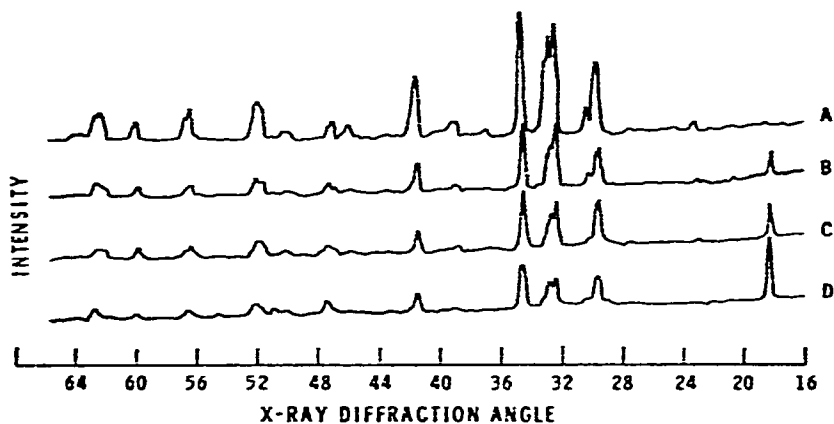


Fig. 7. X-ray diffraction tracings of  $C_3S$  hydrated for six hours; A,  $C_3S$ ; B,  $C_3S + 0\% CaCl_2$ ; C,  $C_3S + 1\% CaCl_2$ ; D,  $C_3S + 4\% CaCl_2$ .

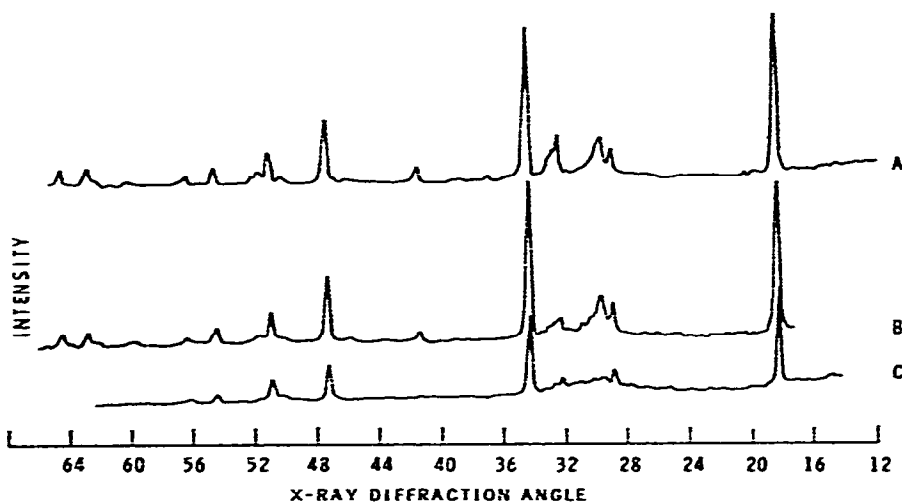
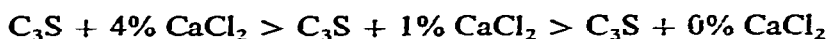


Fig. 8. X-ray diffraction tracings of  $C_3S$  hydrated for 30 days; A,  $C_3S + 0\% CaCl_2$ ; B,  $C_3S + 1\% CaCl_2$ ; C,  $C_3S + 4\% CaCl_2$ .

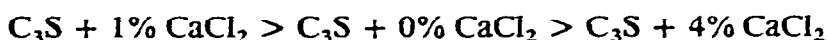
The results show that at 6 h of hydration,  $C_3S$  hydrated in presence of 4%  $CaCl_2$  has the maximum amount of lime; this agrees with DTA-TGA observations. Also at this period, more  $C_3S$  has disappeared in samples hydrated with 4%  $CaCl_2$ . Comparison of the  $Ca(OH)_2$  peaks, when  $C_3S$  is hydrated with 0%  $CaCl_2$  and when hydrated with 1%  $CaCl_2$ , shows slightly more  $Ca(OH)_2$  being formed with 1%  $CaCl_2$ . More  $C_3S$  has disappeared in  $C_3S$  hydrated with 1%  $CaCl_2$ . DTA-TGA results also indicate higher lime contents in  $C_3S$  with 1%  $CaCl_2$ .

At 1 day the sample hydrated with 1%  $CaCl_2$  shows a more intense  $Ca(OH)_2$  peak than either  $C_3S$  hydrated with 0 or 4%  $CaCl_2$ . The DTA-TGA results also show the same trend (Figs. 4 and 5). At this period, however,  $C_3S$  hydrated with 0%  $CaCl_2$  shows less  $Ca(OH)_2$  than that with 4%  $CaCl_2$ . X-ray data also indicate that at 1 day, more  $C_3S$  has hydrated in presence of 4%  $CaCl_2$ . A comparison of the diffractograms of  $C_3S$  hydrated in presence of 1 or 4%  $CaCl_2$  demonstrates that though with 1%  $CaCl_2$  more lime is formed at 1 day, in fact more  $C_3S$  has disappeared from the samples with 4%  $CaCl_2$ . The excess lime formed in presence of 4%  $CaCl_2$  should be present in C-S-H as a product with higher CaO/SiO<sub>2</sub> ratio. Some  $Ca(OH)_2$  may also have formed a surface complex with  $CaCl_2$ .

At 30 days of hydration, the  $Ca(OH)_2$  peak is least intense in  $C_3S$  hydrated with 4%  $CaCl_2$ , and there is almost a complete absence of  $C_3S$  (Fig. 8). This should mean that  $C_3S$  has almost completely hydrated in 30 days; this is also indicated by TGA-DTA data. In 30 days,  $C_3S$  hydrated in 0 or 1%  $CaCl_2$  shows some unhydrated  $C_3S$ , more being present in 0%  $CaCl_2$ . X-ray data suggest that at 30 days, the degree of hydration in terms of  $C_3S$  disappearance would be



whereas according to the  $Ca(OH)_2$  formed



This difference can easily be explained by the formation of a high CaO/SiO<sub>2</sub> hydrated product, especially in the  $C_3S$  with 4%  $CaCl_2$  sample. Hence, it is possible that in presence of  $CaCl_2$  the degree of hydration is always greater after a induction period. It has been shown by conduction calorimeter that the intensity of the peaks in  $C_3S$ - $CaCl_2$ -H<sub>2</sub>O system increases with  $CaCl_2$  concentration<sup>17</sup>.

A comparison of X-ray data for  $C_3S$  hydrated in water at 6 h, 1 day, or 30 days shows an increase in the  $Ca(OH)_2$  contents as hydration progresses, with a corresponding decrease in  $C_3S$  contents. In presence of 1%  $CaCl_2$ , a steady decrease of  $C_3S$  peaks and an increase of  $Ca(OH)_2$  is observed with time. With 4%  $CaCl_2$ , however, there is only a small increase in  $Ca(OH)_2$  between 6 h and 1 day, which corresponds with DTA-TGA results. At 30 days, more  $Ca(OH)_2$  forms and there is almost a complete absence of  $C_3S$ . X-ray data for  $C_3S$  with 4%  $CaCl_2$  hydrated for 60 days shows similar behaviour to the data for the sample hydrated for 30 days, revealing that no further hydration is effected in this period.

Many of the samples were heated to 900°C and subjected to X-ray studies. In general, those containing more  $Ca(OH)_2$  also showed more CaO in the heated samples.

In the hydrated samples no attempts have been made to identify the lines due to C-S-H because of interference effects at 3.07, 2.8 and 1.8 Å.

#### CONCLUSIONS

The rate of hydration of tricalcium silicate was increased and the dormant period reduced as the amount of admixed  $\text{CaCl}_2$  was increased. With higher percentages of  $\text{CaCl}_2$ , the C-S-H product seemed to have a higher  $\text{CaO}/\text{SiO}_2$  ratio. The dormant period and the acceleration of hydration were apparently influenced by the adsorbed chloride. Evidence for the formation of adsorbed complexes was obtained in a series of experiments and is discussed in another paper.

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