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**A STUDY OF THE MICROSTRUCTURE AND
HYDRATION CHARACTERISTICS OF TRICALCIUM
SILICATE IN THE PRESENCE OF
CALCIUM CHLORIDE**

by

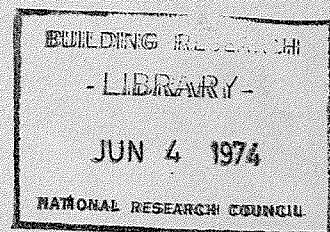
A. Traetteberg, V. S. Ramachandran and P. E. Grattan-Bellew

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ANALYZED

A STUDY OF THE MICROSTRUCTURE AND HYDRATION
CHARACTERISTICS OF TRICALCIUM SILICATE IN
THE PRESENCE OF CALCIUM CHLORIDE

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(Communicated by P. J. Sereda)
(Received Nov. 29, 1973)

ABSTRACT:

The morphological and hydration characteristics of tricalcium silicate treated with 0, 2 and 5 per cent calcium chloride were followed by employing Scanning Electron Microscopy (SEM), Differential Thermal Analysis (DTA), and X-ray diffraction techniques. The water:solid ratios used were either 0.5 or 0.3. In terms of $\text{Ca}(\text{OH})_2$ estimation CaCl_2 accelerated hydration, except with 5 per cent CaCl_2 at a 0.3 w/s ratio. The maximum amount of $\text{Ca}(\text{OH})_2$ and calcium silicate hydrate was formed at 2 per cent CaCl_2 and a w/s ratio of 0.5. Except at very early times, the rate of reaction was slower at 0.3 w/s with or without CaCl_2 compared with the corresponding samples at 0.5 w/s.

On observe les caractéristiques morphologiques et d'hydratation du silicate tricalcique en présence de 0 pour cent, 2 pour cent et 5 pour cent de chlorure de calcium au moyen de la microscopie électronique à grille, de l'analyse thermique différentielle et de techniques de diffraction de rayons X. Le rapport eau/solide est de 0.5 ou de 0.3. En termes d'évaluation de $\text{Ca}(\text{OH})_2$, le CaCl_2 accélère l'hydratation, sauf pour 5 pour cent de CaCl_2 et un rapport eau/solide de 0.3. La formation maximale de $\text{Ca}(\text{OH})_2$ et d'hydrate de silicate de calcium résulte de 2 pour cent de CaCl_2 et d'un rapport eau/solide de 0.5. Après trois mois, le degré d'hydratation, en termes de formation d'hydrate de silicate de calcium, est très semblable dans pâtes lorsque le rapport eau/solide est de 0.3. En comparaison des échantillons correspondants lorsque le rapport eau/solide est de 0.5, la réaction est plus lente pour un rapport eau/solide de 0.3 avec ou sans CaCl_2 , sauf au tout début.

Introduction

Much attention has been directed to studies of the hydration of $3\text{CaO} \cdot \text{SiO}_2$ in terms of the physical, chemical and mechanical properties, as this phase constitutes the major component in portland cement.

The chemical composition and morphology of the hydrated tricalcium silicate change with the period of hydration and also depend on the nature of the starting material, the specific surface, the history of the sample, the water:silicate ratio, and the temperature and condition of curing. The morphology of hydrated C_3S^* has been described variously as needles, fibres, cigar-shaped sheets, plates, crumpled sheets or foils, tabulated structure, thin sheets, spicules, spherulitic particles, and rosettes. It is thus obvious that there is some difficulty in defining the morphological features of the hydrating C_3S with reliability because of the variation in the starting material, the preparation techniques and the methods of examination. It has been recognized therefore that for comparative purposes a sequential study of the hydration from the first few minutes to a specific period yields a more reasonable basis for comparison (1, 2, 3).

Calcium chloride is a well known accelerating admixture used in concrete. Various mechanisms have been proposed to explain its accelerating influence, but there is no general agreement on this question (4, 5). No systematic work has been reported on the effect of CaCl_2 on C_3S , in terms of the sequential behaviour with respect to microstructure and kinetics of hydration. It was thought, therefore, that a systematic and sequential investigation on the hydration of C_3S at a water:solid ratio of 0.3 or 0.5, using 2 and 5 per cent CaCl_2 , should be carried out to examine the mechanism of acceleration by following the progressive development of the microstructure and hydration products.

Experimental

Materials

The tricalcium silicate sample was supplied by Tetrattech International,

* Standard cement nomenclature is used: $\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{H}=\text{H}_2\text{O}$
and w/s = water:solid ratio by weight

San Diego: the chemical analysis was as follows: CaO = 73.5 per cent; SiO_2 = 26.0 per cent; MgO = 0.5 per cent; insolubles = 0.1 per cent. X-ray diffraction results showed it to be practically free from CaO . The surface area of the specimen was found to be $0.45\text{m}^2/\text{g}$ using N_2 as the adsorbate.

Calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) of reagent grade supplied by Fisher Scientific Co., was used as the admixture. It is assayed at a minimum purity of 99.0 per cent, expressed as $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Double-distilled water was used.

Preparation of Samples

In all, six series of C_3S pastes were prepared as follows. The first three series were made at a water/solid ratio of 0.5 with 0, 2 and 5 per cent CaCl_2 on the C_3S basis. The last three series were made at a water/solid ratio of 0.3 with 0, 2 and 5 per cent CaCl_2 . The hydration was carried out in sealed plastic containers rotated continuously on rollers for a specified period. Hydration was stopped by treating the specimens with cold acetone and then by vacuum-drying using a liquid nitrogen trap. All the preparations were made at a temperature of $70 \pm 1^\circ\text{F}$. The reaction products were examined after hydration periods of 2, 4, 6 and 8 hours, 1, 3, 7, 14 and 30 days and 3 and 6 months. The samples were ground finely for X-ray and DTA examination and were fractured for the electron-microscopic study.

Methods of Investigation

Scanning Electron Microscopy (SEM):- A Cambridge Stereoscan Mark 2A equipment was used. The specimens were given a conductive coating by evaporating a layer of carbon and gold.

X-ray Diffraction:- The X-ray examinations were carried out with a Debye-Scherrer camera. Microdensitometer traces were made from the powder photographs. These traces could be used for identifying different phases and also for assessing the relative amounts of calcium hydroxide formed.

Differential Thermal Analysis (DTA):- This analysis was carried out in air using a DuPont 900 thermal analyser. The heating rate was $20^\circ\text{C}/\text{min}$. A constant quantity of 50 mg was used in each experiment.

Results

Hydration at a w/s = 0.5

$\text{C}_3\text{S} + 0$ per cent CaCl_2

No significant changes in the microstructure could be observed in the early periods of hydration in samples prepared at a w/s ratio of 0.5. The only indication was the formation of gel-like products on the surface of C_3S particles at 8 hours. A clearer picture emerged at 1 day, by which time a considerable amount of gel formation, hexagonal plates and prisms were evident. Figure 1a represents the over-all microstructure at 1 day. The

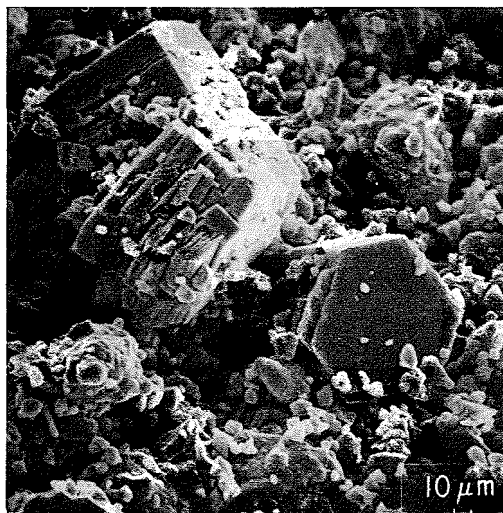


FIG. 1a
Paste of C_3S (w/s = 0.5),
hydrated 1 day

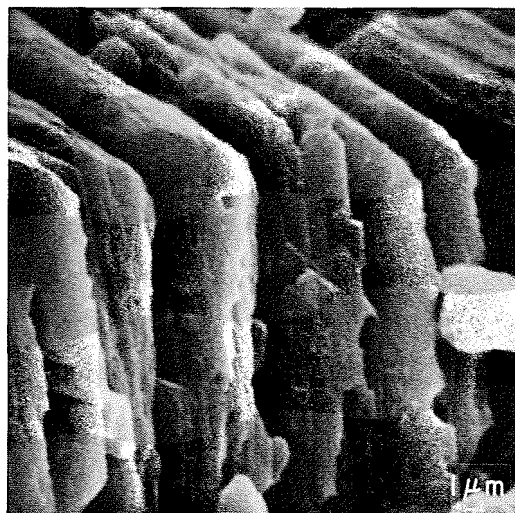


FIG. 1b
A region in the C_3S paste,
hydrated for 1 day (w/s = 0.5)

hexagonal plates formed parallel to each other and seemed to grow into hexagonal prisms (Figures 1a and b). At this stage there was no indication of the definite growth of needles. At 7 days there was evidence of an intergrowth of needles between the hexagonal plates (Figures 1c and d). The needle-like reaction product appeared in the 14-day sample as a layer around the C_3S grains and around some hexagonal plates. During hydration up to 6 months the mesh of needles developed to a more coarse structure which together with the plates constituted an apparently tightly bound microstructure.

Thermograms of $\text{C}_3\text{S} + 0$ per cent CaCl_2 show a progressive development of endothermal peaks between 400 - 500°C. At one day and later there

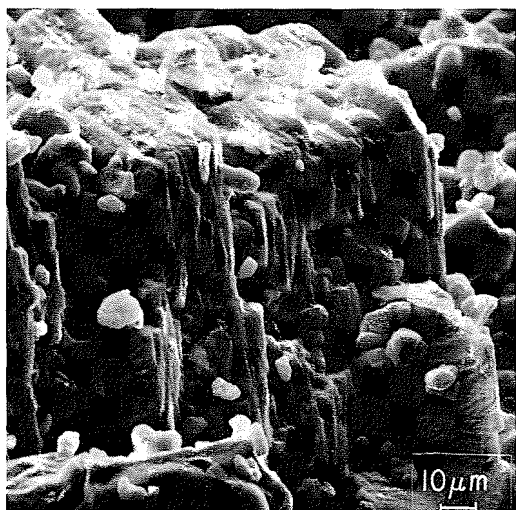


FIG. 1c
Paste of C_3S ($w/s = 0.5$)
hydrated 7 days

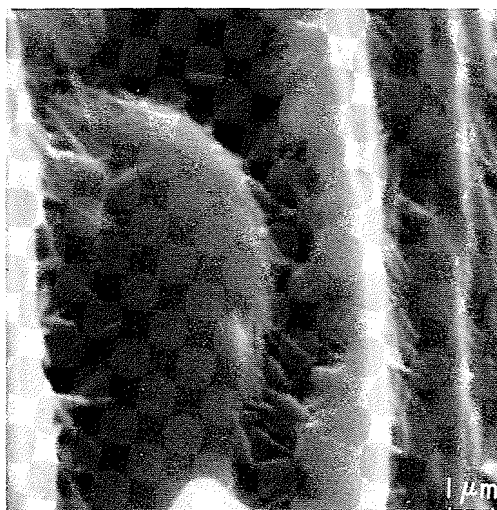


FIG. 1d
A magnified portion of a region
from FIG. 1c, 7-day paste
($w/s = 0.5$)

was also an endothermal peak at about 700°C (Figure 2a). The X-ray patterns showed that the C_3S peak at 2.78 \AA decreases with the progress of hydration. The peak at 4.9 \AA for $\text{Ca}(\text{OH})_2$ could be discerned at 8 hours.

$\text{C}_3\text{S} + 2$ per cent CaCl_2

Some change in the surface structure of the C_3S grains was observed after 4 hours' hydration. The needle-like surface layer as well as crumpled foils appeared clearly in the 6-hour sample (Figure 3a). At this period the sample without CaCl_2 was not very definitive. A few parallel plates could be distinguished after 8 hours, but were seen more distinctly in the 1-day specimen. They did not appear to have a hexagonal outline as did the sample without CaCl_2 . The layered structure developed during continued hydration to a dense matrix, intermixed with grains of rounded particles covered with hydration product. Figures 3b and c illustrate inter-granular bondings, and Figure 3d shows a representative example of the over-all morphology at 3 months. The main reaction products are coarser needles and layered sheets.

Thermal curves show more intense endothermal peaks at 100 to 200°C and at 400 to 500°C than those observed for $\text{C}_3\text{S} + 0$ per cent CaCl_2 paste (Figure 2b). Also additional exothermal and large endothermal peaks were

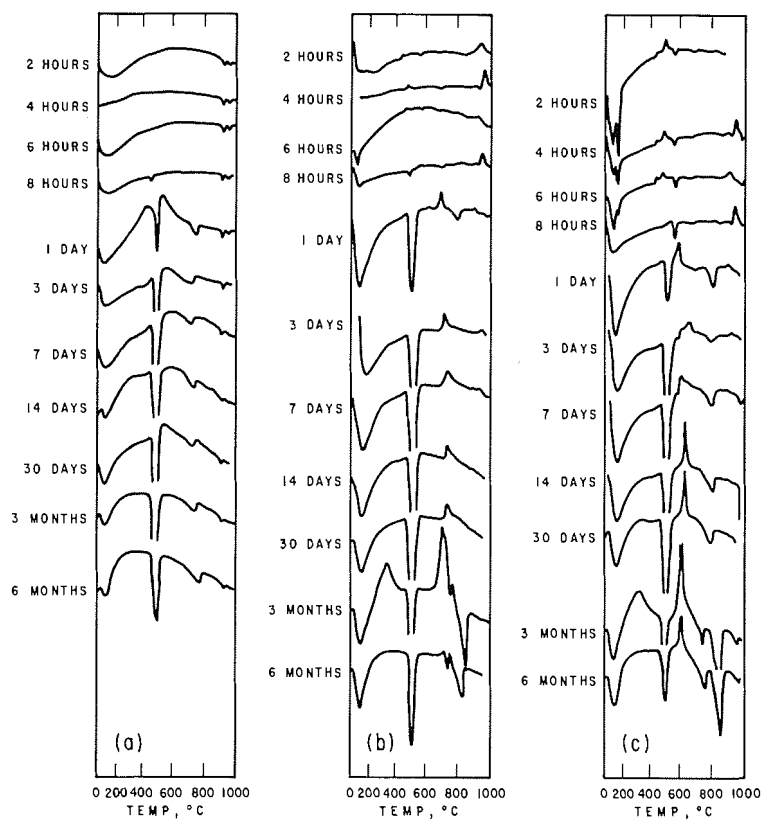


FIG. 2

Thermograms of a) pastes of C_3S , b) pastes of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$ and c) pastes of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$, all with w/s ratio of 0.5.

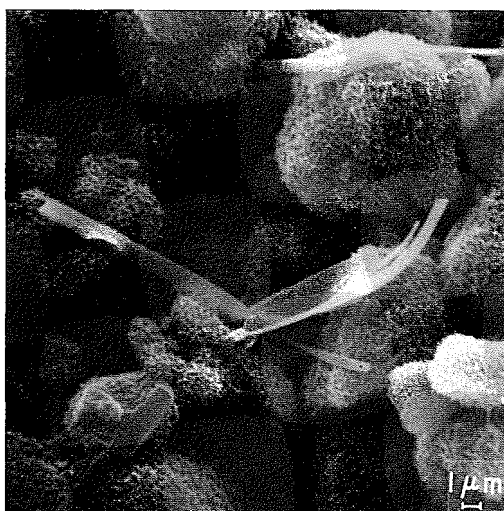


FIG. 3a

Paste of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$
(w/s = 0.5) hydrated 6 hours

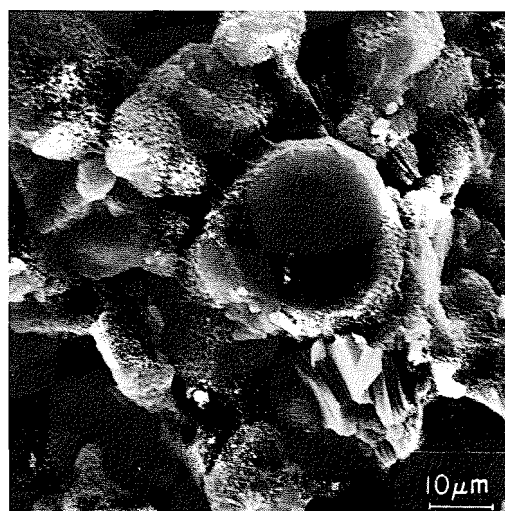


FIG. 3b

Paste of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$
(w/s = 0.5), hydrated 14 days

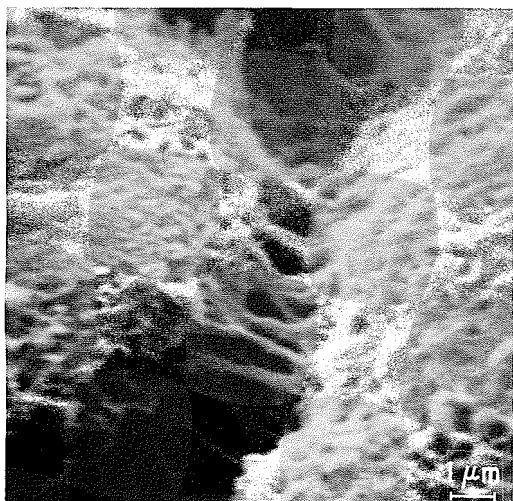


FIG. 3c

Paste of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$
(w/s = 0.5), hydrated 14 days

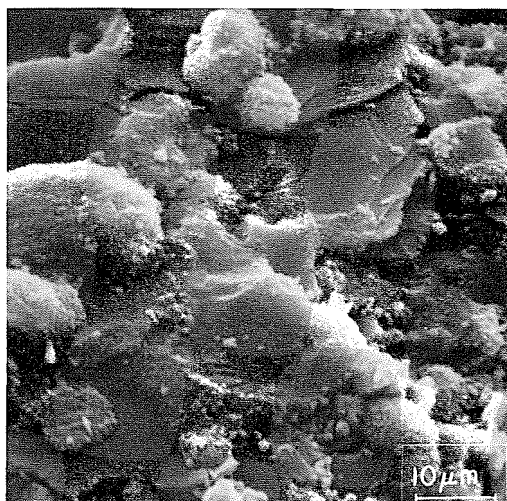


FIG. 3d

Paste of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$
(w/s = 0.5), hydrated 3 months

observed beyond 500°C . A small endothermal peak emerged at 6 hours at about 550°C . X-ray diffraction results indicated more $\text{Ca}(\text{OH})_2$ formation and more hydration for $\text{C}_3\text{S} + 2$ per cent CaCl_2 samples.

$\text{C}_3\text{S} + 5$ per cent CaCl_2

The surface reaction was more obvious in this paste at very early stages than in the previous examples; smaller particles seemed to have grown on the surface of larger ones. The rough surface structure of the grains to-

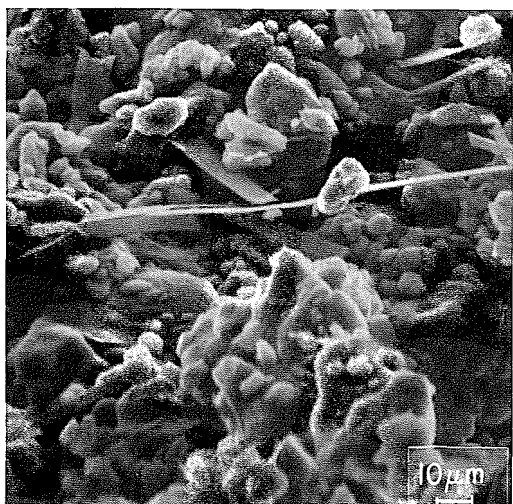


FIG. 4a

Paste of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$
(w/s = 0.5) hydrated 6 hours

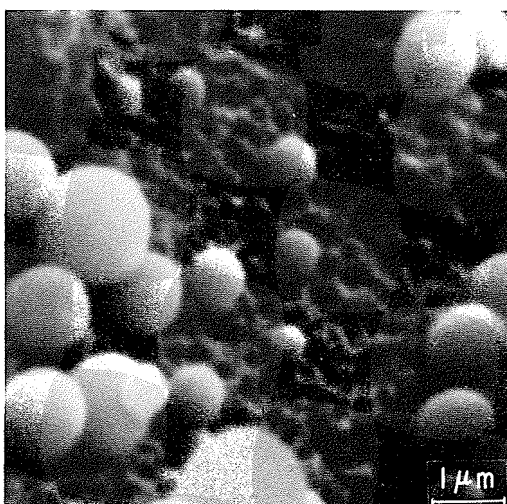


FIG. 4b

A region in the paste of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$ (w/s = 0.5) hydrated 8 hours

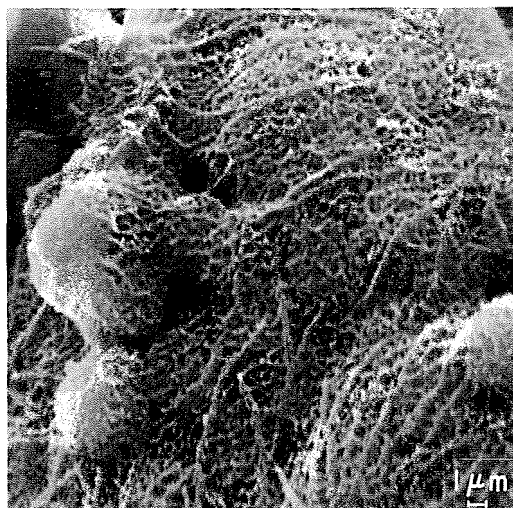


FIG. 4c
Paste of C_3S + 5% CaCl_2
(w/s = 0.5), hydrated 3 days

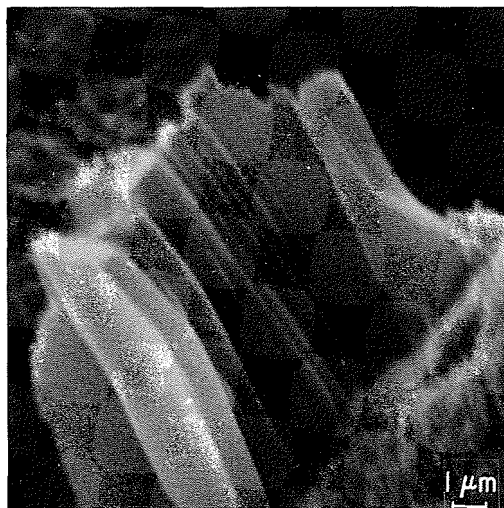


FIG. 4d
A region in the paste of C_3S + 5%
 CaCl_2 (w/s = 0.5) hydrated 7 days

gether with some sheets or foils was evident in the 6-hour sample (Figure 4a). In the 8-hour sample occasional formation of spherical particles was observed (Figure 4b). In the 1- and 3-day samples veins grow out of the hydrating C_3S particles covering the underlying needle-structure (Figure 4c). The growth of crumpled sheets can also be observed in the 7-day samples (Figure 4d). The dense matrix of columnar structure was also evident at 7 days of hydration. Further hydration of this series gave a similar microstructure to

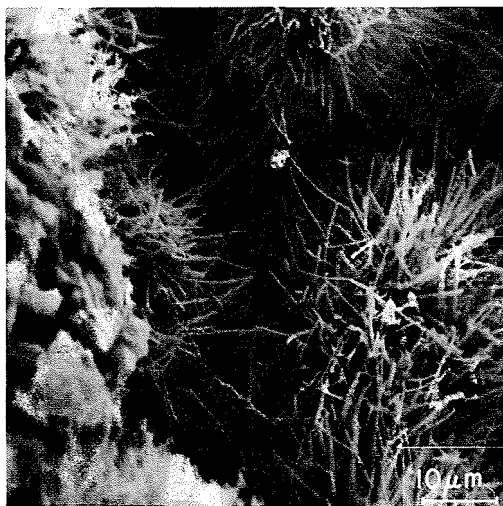


FIG. 4e
A region in the paste of C_3S + 5%
 CaCl_2 (w/s = 0.5) hydrated 6 months

that of C_3S + 2 per cent CaCl_2 paste, but with an apparently more open matrix. The 6-month sample of this paste exhibited, at some locations, a very well developed needle-structure that was not seen in other samples of C_3S paste (Figure 4e).

Thermograms of the samples treated with 5 per cent CaCl_2 are shown in Figure 2 (c). The thermograms show some features different from either C_3S + 0 per cent CaCl_2

or $\text{C}_3\text{S} + 2$ per cent CaCl_2 . At 2 hours an exothermal effect followed by an endothermal peak is observed in the 450 to 550°C region. In general the endothermal peaks at about 450 to 500°C appear to be of less intensity than those with 2 per cent CaCl_2 . Exothermal peaks developed at about 550°C from 1 day onward. The X-ray patterns indicate that at 1 month less $\text{Ca}(\text{OH})_2$ formed at 5 per cent CaCl_2 than at 2 per cent CaCl_2 .

Pastes at $w/s = 0.3$

$\text{C}_3\text{S} + 0$ per cent CaCl_2

The C_3S paste with a w/s ratio of 0.3 exhibited the needle-like network coating on the C_3S grains at 1 day of hydration, (Figures 5a and b). The platy structure could not be distinguished until 3 days, and the hexagonal shape did not appear as obviously as in the sample with the higher water content. The structure at later stages of these two paste hydrations showed similar features.

The qualitative nature of the thermograms of $\text{C}_3\text{S} + 0$ per cent CaCl_2 samples at a w/s ratio of 0.3 are similar to those prepared at w/s ratio of 0.5 (Figures 2a and 6a). The main difference is the intensities of the endothermal peaks at about 400 to 450°C, they are slightly larger for the 0.3 w/s

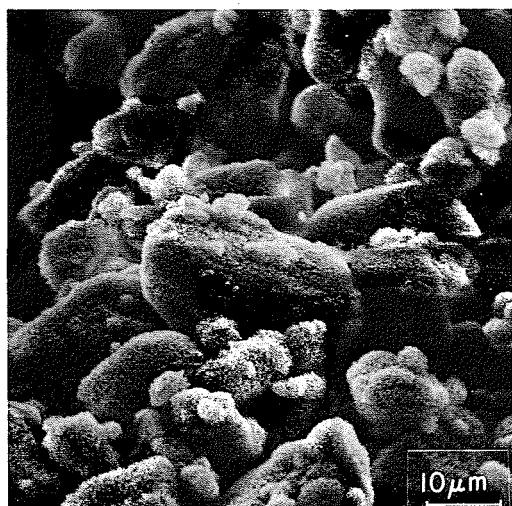


FIG. 5a
Paste of $\text{C}_3\text{S} + 0\%$ CaCl_2
($w/s = 0.3$), hydrated 1 day

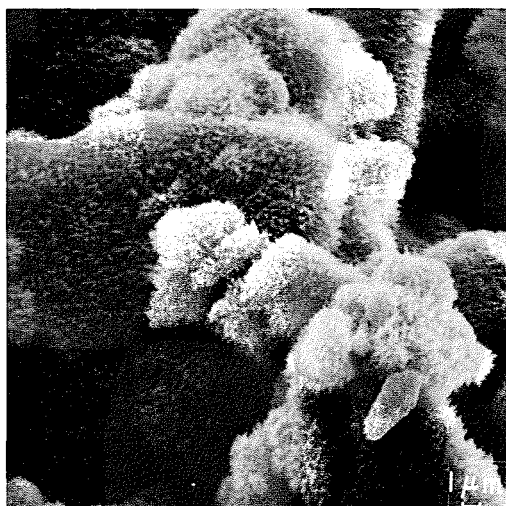


FIG. 5b
Paste of $\text{C}_3\text{S} + 0\%$ CaCl_2
($w/s = 0.3$), hydrated 1 day

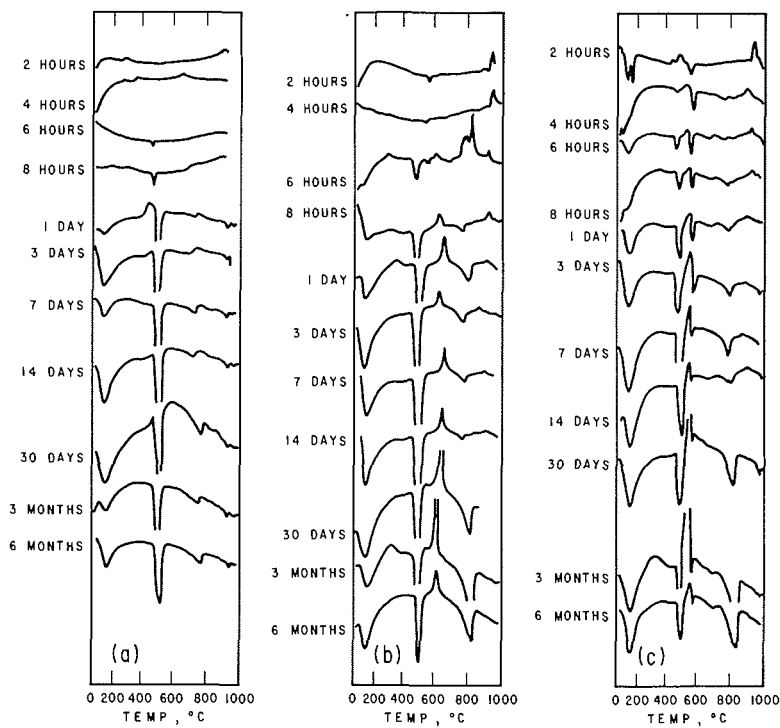


FIG. 6

Thermograms of a) pastes of C_3S , b) pastes of $\text{C}_3\text{S} + 2\%$ CaCl_2 and c) pastes of $\text{C}_3\text{S} + 5\%$ CaCl_2 , all with w/s ratio of 0.3.

paste at 14 and 30 days but at 3 months the sample at 0.3 w/s has less lime than that at 0.5 w/s. The X-ray diffractograms indicate less formation of $\text{Ca}(\text{OH})_2$ in the hydrated C_3S at 0.3 w/s than in the $\text{C}_3\text{S} + 0$ per cent CaCl_2 at w/s = 0.5.

$\text{C}_3\text{S} + 2$ per cent CaCl_2

A reaction on the surface of the C_3S grains seemed to have started in the early stages of hydration, i.e., 2 and 4 hours. The 6-hour sample exhibited a needle-like surface layer as well as crumpled foils and showed similar microstructure to $\text{C}_3\text{S} + 2$ per cent CaCl_2 at a w/s ratio of 0.5. A platy structure could be discerned after 8 hours' hydration. The paste at 14 days showed a more dense, striated structure than that for $\text{C}_3\text{S} + 2$ per cent CaCl_2 at a w/s ratio of 0.5. In addition microcracks were developed at the lower w/s ratio (Figure 7).

Thermograms indicate that the addition of 2 per cent CaCl_2 to C_3S intensifies the endothermal peak in the region of 500°C (Figures 6a and b). However, the endothermal peaks for the samples prepared at w/s ratio of 0.5 are more intense than the corresponding samples prepared at a 0.3 w/s ratio. The pastes with CaCl_2 exhibited additional exothermal and endothermal peaks. An endothermal peak that could not be observed with $\text{C}_3\text{S} + 0$ per cent CaCl_2 appeared at 550°C at 2 hours.

X-ray diffraction indicates less formation of $\text{Ca}(\text{OH})_2$ and more unhydrated C_3S than in $\text{C}_3\text{S} + 2$ per cent CaCl_2 at a w/s ratio of 0.5.

$\text{C}_3\text{S} + 5$ per cent CaCl_2

The surface features of the $\text{C}_3\text{S} + 5$ per cent CaCl_2 paste with a w/s ratio of 0.3 showed more clearly the hydration products at early stages than the one with 0.5 w/s ratio. In the 6-hour sample sheets were observed along with the hydrated C_3S grains. The 8-hour sample seemed to consist of two different reaction products, one with initial hydration products on the surface and the other appearing as sheets, or veins, growing between or on the surface of the grains (Figure 8a). The growth of plates into a tabular structure could be observed at 7 days (Figure 8b). The microstructure became more dense at later stages than in the 0.5 w/s paste. The grains seemed to be smaller than those in the other pastes.

Thermograms for the system show distinct differences between $\text{C}_3\text{S} + 0$ per cent CaCl_2 and $\text{C}_3\text{S} + 2$ per cent CaCl_2 . Double endothermal peaks appear at 2 hr below 200°C . Also an endothermal and an exothermal peak appear below 500°C at 2 hours' hydration that are not observed for $\text{C}_3\text{S} + 0$

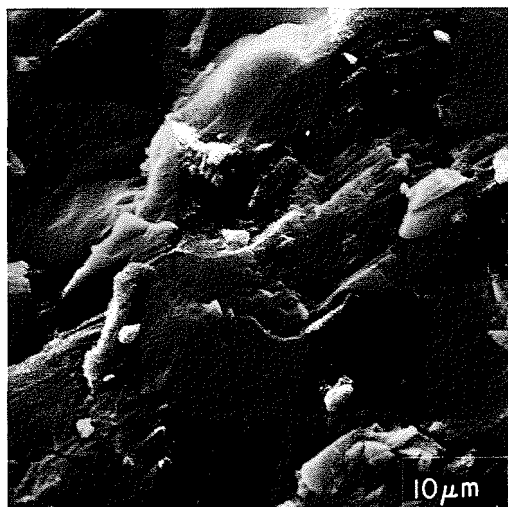


FIG. 7
Paste of $\text{C}_3\text{S} + 2\%$ CaCl_2
(w/s = 0.3) hydrated 14 days

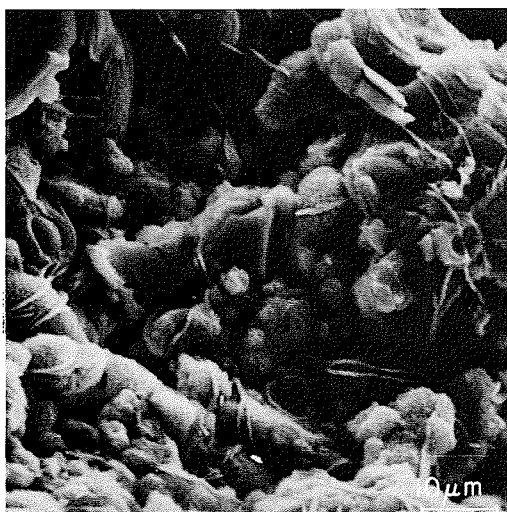


FIG. 8a

Paste of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$
(w/s = 0.3) hydrated 8 hours

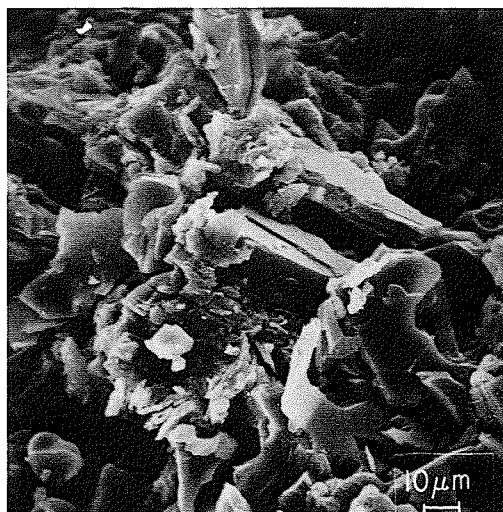


FIG. 8b

Paste of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$
(w/s = 0.3) hydrated 7 days

per cent CaCl_2 or $\text{C}_3\text{S} + 2$ per cent CaCl_2 . The endothermal peaks in the region of 400 to 450°C are less intense than those for $\text{C}_3\text{S} + 2$ per cent CaCl_2 at later periods but the exothermal peaks (500 to 550°C) appear to be more intense in $\text{C}_3\text{S} + 5$ per cent CaCl_2 samples. It may also be observed that the areas of the peaks at 400 to 450°C for 0.5 w/s ratios are higher than those prepared at a 0.3 w/s ratio (Figures 6a and b). The X-ray patterns for the three series with w/s ratios of 0.3 do not show very pronounced differences. Less hydration in terms of $\text{Ca}(\text{OH})_2$ is indicated in this paste compared with $\text{C}_3\text{S} + 5$ per cent CaCl_2 at w/s = 0.5 .

Discussion

C_3S pastes at a w/s of 0.5 with 0 , 2 and 5 per cent CaCl_2

The unhydrated C_3S exhibits two endothermal peaks in the temperature range 900 to 1000°C caused by reversible phase transitions (6). The intensities of these effects decrease with the progress of hydration (Figure 2a). The formation of $\text{Ca}(\text{OH})_2$ is denoted by the endothermal effect at about 450°C and it appears at about 8 hours. The dehydration of C-S-H phase is represented by the peak below 200°C and by another around 800°C (4). Decarbonation of CaCO_3 may also represent the peak at about 800°C . In Figure 9 a plot of

the endothermal area for the decomposition of Ca(OH)_2 as a function of the period of hydration shows some interesting features. Up to about 7 days the rate of formation of Ca(OH)_2 is relatively rapid and subsequently the rate decreases to a great extent. Microstructural studies did not reveal the presence of Ca(OH)_2 at 8 hours but at 1 day hexagonal plates and prisms could be observed.

Typical lines at 4.9 \AA of Ca(OH)_2 could also be discerned in the X-ray diffractograms at this stage. In this study there is a definite

indication that the tabular masses represent mainly Ca(OH)_2 with some engulfed C-S-H product. The clear cleavage characteristics as well as microprobe studies seem to confirm this fact (7, 8). Though the C_3S hydrated to a good extent after 1 and 3 days, no indication could be found for a fibrous structure representing the C-S-H gel. At 7 days the fibers appear on the C_3S grains as well as between the hexagonal plates of Ca(OH)_2 (Figure 1d). Possibly some of the C-S-H gel particles grow as needles and interlock the plates of Ca(OH)_2 , thus acting as a bridge between the hexagonal plates. At some places in the system Ca(OH)_2 may possibly grow around the hydrating C_3S particles thus enveloping them as indicated in Figure 1c. Whether this is similar to the tabular structure described by Ciach et al (1) is not clear. With time and diffusion of water the C_3S particles hydrate, grow into fibers and interconnect the Ca(OH)_2 plates. Some of the cavities in the interior of

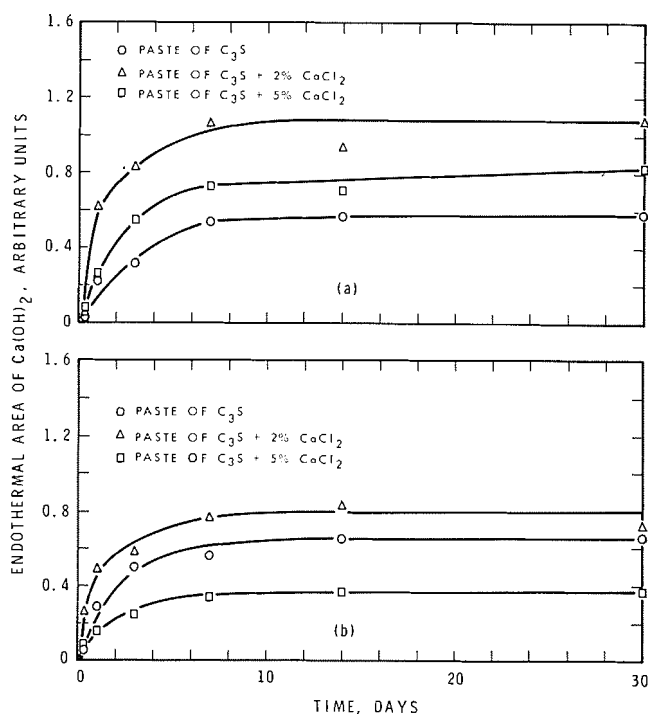


FIG. 9
Endothermal areas for Ca(OH)_2
decomposition as a function of
hydration time, a) pastes with w/s
ratio 0.5, b) pastes with w/s ratio 0.3

the hexagonal plates may represent the original sites where the C_3S particles resided. Pseudo-hexagonal plates composed of interlocking fibers have been reported by Ciach et al (1) in samples etched with glycol. This feature may indicate that $\text{Ca}(\text{OH})_2$ may contribute to strength in cements (8) and it is perhaps analogous to the bond developed by hydrated C-S-H and aggregates. Prolonged hydration of the C_3S resulted in the development of a needle-like structure as a coating on the unhydrated C_3S grains and on the conglomerates of hexagonal plates.

Addition of 2 per cent CaCl_2 resulted in the formation of the acicular product of C-S-H at an earlier period than the sample without the chloride. Some crumpled sheets or foils are also observed in the 6-hour sample, and they probably denote the formation of C-S-H (I) and C-S-H (II) -like products (Figure 3a). The 8-hour sample clearly shows the presence of $\text{Ca}(\text{OH})_2$ in the microstructure, thermograms and the X-ray diffraction pattern. The microstructural examinations of CaCl_2 -treated samples (Figure 3c) show clearly the bonding of grains by fibers. The higher degree of hydration with 2 per cent CaCl_2 is evident from the larger amount of $\text{Ca}(\text{OH})_2$ formed at different stages of hydration (Figure 9a). In the CaCl_2 -treated samples the foil-like product was not dominant in contrast with the observations of other workers (5, 9). It is probable that it can be induced by dispersing the hydrated material. There is a general indication that addition of CaCl_2 results in an increase in the C-S-H formation as evident from the endothermal effects below 200°C (Figure 2b). At 3 months more hydration seems to have taken place with 2 per cent CaCl_2 than without it.

The formation of a surface complex of CaCl_2 with the hydrating C_3S is difficult to confirm, but there is a possibility of this formation in the form of a featureless and continuous product developed between the hydrated grains in the 6-hour sample (Figure 3a). The possible surface complex in the early stage of hydration is indicated by a small endothermal peak at about 560°C (Figure 2b). The exothermal peak at 700°C , followed by an endothermal peak at about 800°C , has been attributed to the surface complex of chloride with C-S-H or the interlayer chloride (5) or both. No indication of the complex of chloride with C-S-H could be seen in the diffraction patterns, either

because it was amorphous or because it was present in small amounts or both.

With 5 per cent CaCl_2 hydrated products of C_3S at 6 hours consist of thin sheets or foils and fibers probably representing a mixture of C-S-H (I) and C-S-H (II) -type products. At 8 hours spherical particles were seen (Figure 4b). This may represent CaCO_3 or $\text{Ca}(\text{OH})_2$ (10, 11). In the DTA thermograms the endothermal peak representing the surface complex appears fairly early and is more intense than that observed for C_3S + 2 per cent CaCl_2 . The onset of exothermal peak takes place at 1 day at about 600°C along with a large endothermal peak at about 800°C (Figure 2c). Earlier work suggests that these peaks represent the dehydration of the chloride C-S-H complex (5). The coarse vein-like structure appearing at 1 day, and more clearly at 3 days is peculiar to CaCl_2 -treated C_3S and it may perhaps be due to a CaCl_2 -C-S-H complex (Figure 4c). X-ray results do not show any evidence for a complex formation. However, the results show that at 3 months slightly more C_3S has hydrated with 2 per cent CaCl_2 than with 5 per cent CaCl_2 .

The micrograph in Figure 4e represents only a special feature at a particular location. This shows that at certain pore regions there may be space available for C-S-H needles to grow freely in the paste. Such an observation in hydrating portland cement paste may be mistaken for the presence of ettringite.

The $\text{Ca}(\text{OH})_2$ estimation at various stages of hydration shows the amounts in the order C_3S + 2 per cent $\text{CaCl}_2 > \text{C}_3\text{S}$ + 5 per cent $\text{CaCl}_2 > \text{C}_3\text{S}$ + 0 per cent CaCl_2 (Figure 9).

C_3S pastes at a w/s 0.3 with 0, 2 and 5 per cent CaCl_2

At early periods of hydration C_3S hydrates faster at a w/s ratio of 0.3 than at 0.5. This is probably facilitated by the early supersaturation and nucleation.

Figure 9b clearly shows that at a w/s of 0.3 and with the addition of CaCl_2 the amount of $\text{Ca}(\text{OH})_2$ formed is generally less than in the corresponding samples prepared with a w/s ratio of 0.5. However, in the pure C_3S

pastes at 0.3 or 0.5 w/s ratio the contents of Ca(OH)_2 are not much different. X-ray results show that the pastes obtained at a w/s = 0.3 generally contain more unhydrated C_3S at later stages compared with the samples prepared at a w/s ratio of 0.5. The accelerating action of CaCl_2 at 0.3 w/s ratio does not seem to be as pronounced as at 0.5 w/s ratio.

Thermograms of 0.3 w/s series of C_3S show an endothermal peak for Ca(OH)_2 at 6 hours but this phase is not detected up to 3 days by microscopy. It is possible that Ca(OH)_2 has been covered with C-S-H reaction products and it may also be partly in an amorphous form. In the C_3S paste, C-S-H phase is formed on the C_3S particles (Figure 5a and b). Due to the low w/s ratio crystallization and full development of the hexagonal phase was somewhat inhibited, thus the hexagonal morphology could not be distinguished.

Addition of 2 per cent CaCl_2 results in the accelerating of reaction as evident from thermograms (Figures 2a and b, and 6b). The fibrous structure was indicated at an earlier period than in the 0.5 w/s paste. Foils were also observed in this paste. The rate of hydration with 2 per cent CaCl_2 is higher at a w/s 0.5 than at 0.3. The CaCl_2 complexes are also indicated (Figure 6b).

At 1 day and beyond there is more Ca(OH)_2 in the 2 per cent CaCl_2 paste than in the 5 per cent CaCl_2 one. After 7 days the amount of Ca(OH)_2 is about constant up to 30 days for all three mixtures. The Ca(OH)_2 estimation is in the order $\text{C}_3\text{S} + 2 \text{ per cent } \text{CaCl}_2 > \text{C}_3\text{S} + 0 \text{ per cent } \text{CaCl}_2 > \text{C}_3\text{S} + 5 \text{ per cent } \text{CaCl}_2$, and C_3S left unhydrated is estimated to be about the same in the three mixtures. This leads to the conclusion that at 5 per cent CaCl_2 C-S-H with a high C/S ratio is probably formed. This is possible because it is known that even without acceleration C_3S paste formed at a lower w/s ratio has a C-S-H product with a higher ratio of C/S (12, 13).

The special vein-like structure developed at 0.3 w/s at 8 hours (Figure 8a). The endothermal peak at 550 to 600°C may correspond to this complex (Figure 6c). The veins seem to be absent at later stages of hydration, and hence it is reasonable to assume that they are only intermediate products containing chloride.

All the foregoing results show changes in the rate of hydration and the microstructural details of C_3S hydrated to different extents with the addition of 2 or 5 per cent CaCl_2 . Certain microstructural details seem to lend support to the existence of chloride complex in this system. The initial complex formed in the C_3S at the accelerating period may modify the surface and activate it through complex changes viz., permeability, dispersibility, adhesive force of the initial layer on C_3S , and the nucleating or reaction centre. At later stages chloride ions seem to be strongly adsorbed and possibly it may be included in the C-S-H lattice in interstitial positions, or by replacement of OH groups or in the interlayer positions.

Conclusion

This study has revealed some important differences in the microstructure of C_3S paste due to different w/s ratio and the presence of CaCl_2 . In the hydration of C_3S at a water:solid ratio of 0.5 the reaction products formed are $\text{Ca}(\text{OH})_2$ and calcium silicate hydrate, probably in different shapes. Also the $\text{Ca}(\text{OH})_2$ grows as parallel hexagonal plates and prisms and is suggested to constitute the platy or layered morphology. There is also evidence that needles of C-S-H phase grow between hexagonal plates and interlock them. Thus a portion of $\text{Ca}(\text{OH})_2$ phase may participate in the strength development in C_3S pastes. At a lower water/solid ratio of 0.3 no clearly defined hexagonal plates of $\text{Ca}(\text{OH})_2$ are formed. The needle-shaped hydrated products appear earlier and the hydration rate is higher at earlier periods.

Calcium chloride accelerates the hydration of C_3S both at high and low w/s ratios, the influence being greater at a higher water content. The chloride appears to promote the formation of a higher CaO/SiO_2 hydrated product, especially at a lower w/s ratio. There is indication of a possible chloride complex in the hydrating C_3S system.

With increasing amounts of CaCl_2 it seems the hexagonal feature of the calcium hydroxide crystals becomes less distinct. In the CaCl_2 -containing pastes both the foil-like C-S-H (I) phase and the fibrous C-S-H (II) phase are indicated. Generally the presence of CaCl_2 influences the morphological features in the early stages of hydration but not as much in the later periods.

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