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POSSIBLE STATES OF CHLORIDE IN THE HYDRATION
OF TRICALCIUM SILICATE IN THE PRESENCE
OF CALCIUM CHLORIDE

BY

V. S. RAMACHANDRAN

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Possible states of chloride in the hydration of tricalcium silicate in the presence of calcium chloride

V.S. RAMACHANDRAN ⁽¹⁾

Calcium chloride may be present in the free, adsorbed or interlayer state in hydrating tricalcium silicate. Attempts have been made to study these states to correlate some of the physical, chemical and mechanical properties.

Calcium chloride is a well-known accelerator in concrete practice. Most published data, however, relate to its influence on the engineering properties of concrete rather than to understanding of the basic mechanism. Early workers believed that the interaction of the $C_3A^{(1)}$ phase of cement with $CaCl_2$ was responsible for acceleration and strength development. Only recently have studies recognized the predominant role of $CaCl_2$ in the hydration of silicate phases of cement [1-21].

Several explanations have been offered for the action of $CaCl_2$. The possibility that a complex calcium oxychloride hydrate is formed, promoting hydration in some way, was proposed by Candlot [22], Koyanagi [23], Kallauner [24], Kleinlogel [25] and Tenoutasse [26]. It should be recognized that in the system $CaO-CaCl_2-H_2O$ two oxychlorides of composition $3 CaO \cdot CaCl_2 \cdot 16H_2O$ and $CaO \cdot CaCl_2 \cdot 2H_2O$ exist [27-30]. The former is stable at $CaCl_2$ concentrations of 18 per cent or more, and the latter at 34 per cent or more.

In actual practice the concentration of $CaCl_2$ used is much lower than the above figures, and on these grounds the possibility of formation of calcium

oxychloride complexes has generally been discounted. In addition, application of techniques such as X-ray, dynamic differential and conduction calorimetry, electron microscopy and chemical analysis has not revealed the presence of such complexes in hydrating cements [3, 4, 9, 11, 14, 31, 32].

In the absence of any evidence of a complex compound between $Ca(OH)_2$ and $CaCl_2$ in hydrating cements it is suggested that $CaCl_2$ acts catalytically [4, 10, 20, 24, 32]. The exact mechanism through which this action takes place, however, is still obscure. Addition of $CaCl_2$ to a hydrating cement is known to reduce the alkalinity of the aqueous phase. It is thus believed that by a reduced pH the system would attempt to compensate by liberating more lime through increased rate of hydrolysis of C_3S [3, 4, 31, 33]. Acceleration can also be brought about in an environment of higher pH values and it is doubtful whether acceleration is based on pH effects only.

Any proposed mechanism should recognize that calcium chloride, in addition to modifying the hydration kinetics of C_3S , affects chemical composition, physical and mechanical properties of the system at various stages of hydration. These manifest themselves in terms of induction period, initial and final set, CaO/SiO_2 ratio of the hydrated silicate, surface area, microstructure, pH of the aqueous phase, shrinkage, strength and resistance to sulphate attack and freezing-thawing. It is extremely unlikely that any one mechanism could explain all these effects,

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⁽¹⁾ The following nomenclature used in cement chemistry will be followed where necessary : C = CaO , S = SiO_2 , A = Al_2O_3 and H = H_2O .

and a combination of factors may be involved, depending on the experimental conditions and period of hydration.

In studying the kinetics of hydration of C_3S in the presence of $CaCl_2$ by thermal methods, there was evidence of various states of chloride, including complexes [34]. This evidence led to a new series of experiments the results of which are now presented with a discussion of the possible mechanism.

EXPERIMENTAL

Materials

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

Chemical	
CaO	= 73.88
SiO ₂	= 26.17
Al ₂ O ₃	= 0.08
	100.13
Free CaO (ASTM)	= 0.18
Free CaO (Franke)	= 0.46
Mineralogical	
C ₃ S	= 99.33
C ₂ S	= 0.00
C ₃ A	= 0.21
CaO (Franke)	= 0.46
	100.00

Fineness = Blaine 3310 sq cm/g

Calcium chloride hexahydrate of analytical reagent quality was used as the accelerating admixture. As the solid is deliquescent, solutions of required concentrations could not be prepared directly by weighing and dissolving in water. Approximately 15 per cent $CaCl_2$ solution was therefore prepared and the exact concentration determined by the argentometric method. Dilutions were made to any required concentration.

Sample Preparation

Hydration of C_3S was studied by mixing it with double-distilled water at a water-silicate ratio of 0.5. Hydration was carried out in tightly-covered polyethylene containers rotated continuously over rollers. At specified intervals, varying between 15 minutes and 1 month, each sample was ground, placed in a desiccator and continuously evacuated for 24 hours, using liquid air in the trap. Care was taken throughout to prevent contamination with CO_2 .

A similar method was followed for the hydration experiments in the presence of different concentrations of $CaCl_2$. The solution-silicate (volume/weight) ratio was kept at 0.5. This could be achieved with 1, 4 and 5 per cent $CaCl_2$ (with respect to C_3S) by adding 10 cc each of 2, 8 and 10 per cent $CaCl_2$ solution, respectively, to 20g of C_3S . The reaction was carried out at a temperature of $70 \pm 1^\circ F$.

Analysis

Differential thermal analysis (DTA) was carried out using the Du Pont 900-Thermal Analyser. This

unit utilizes platinum holders and platinum vs platinum-rhodium (13 per cent) thermocouples were used for differential and sample temperature measurements. The reference material was ignited $\alpha-Al_2O_3$ and the rate of heating was $20^\circ C/min$. In each run 50 mg of the sample was passed through a 100-mesh sieve and packed with moderate pressure. Thermograms were obtained in air, 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 sample temperature on the X axis at 2 mV/in. Cold junction was maintained at $0^\circ C$ with crushed ice. Refractory cups placed in the standard platinum sample holders were used in the experiments, especially those involving samples with higher $CaCl_2$ content. Otherwise, the sample tended to fuse to some extent 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. Thermogravimetric analysis (TGA) of the samples was obtained by the standard Stanton thermobalance at a heating rate of $10^\circ C/min$. X-ray diffraction results were obtained by a Hilger diffractometer using CuK_α source.

Experiments were also carried out to determine the chloride content of solutions leached with absolute alcohol or water. The method consisted of adding 5 cc 10 per cent $CaCl_2$ solution to 10g C_3S in a polyethylene container, rotating it on rollers for different periods, removing it and grinding it in cold absolute alcohol. The sample was continuously washed over a filter paper with alcohol or water and the leachate collected in a standard flask enclosed in a chamber. Each gram of hydrated sample was washed with about 100 cc alcohol or water and this is referred to as leaching in the following text. The solid material left on the filter paper was dried in vacuum for 24 hours and subjected to DTA examination in air, vacuum or nitrogen. Due precaution was taken to prevent carbonation of the sample.

The chloride content in the leachate was estimated by the argentometric method, using standard solutions of silver nitrate and ammonium thiocyanate, with ferric alum as the indicator [26]. A blank series was also run by leaching pure C_3S after hydration to corresponding periods.

RESULTS AND DISCUSSION

Good correlation of DTA and TGA results was obtained for the estimation of $Ca(OH)_2$ at any stage of hydration. Comparison of estimated $Ca(OH)_2$ and the rate of disappearance of C_3S indicated that with higher $CaCl_2$ content the C-S-H product had a higher CaO/SiO_2 ratio than that formed without $CaCl_2$.

The addition of $CaCl_2$ in amounts of 1 to 5 per cent increased the rate of hydration of C_3S profoundly, especially early in the experiment. A considerable amount of hydration within a few hours must significantly influence even the nature of hydration products. Hence, an understanding of the hydration reactions in the earlier periods should hold the key to the effective action of $CaCl_2$ on the hydration of C_3S .

In addition to an intensification of certain endothermal effects in the presence of $CaCl_2$, significant new developments are observed, viz., an endothermal

effect between 550 and 560 °C, one or two intense exothermic effects in the temperature range 600 to 800 °C, an endothermal peak of large magnitude at 800 to 850 °C, depletion of peaks due to phase transitions and an emergence of a new exothermic effect in the high temperature regions.

A further investigation was made to examine the possible causes of these thermal effects and their role in the accelerating action of CaCl_2 .

Surface Complex of Chloride during the Dormant Period

The endothermic effect at 550 to 560 °C can be observed when C_3S is placed in a CaCl_2 solution even for a few minutes. This has not been reported before. The possibility that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in the free state is responsible can be discounted because pure $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ does not exhibit an endothermic effect at 550 to 560 °C and the effect at 750 °C represents fusion (fig. 1, curve 1). Calcium chloride is highly soluble in ethyl alcohol and this solvent was used to leach out free chloride from the C_3S hydrated for an hour in the presence of calcium chloride. In the leached sample the endothermal effect persists (fig. 1, curves 2 and 3), and this means that free chloride is not responsible for the endothermal effect. Leaching of the sample with water, however, eliminates the effect (fig. 1, curve 4). An additional endothermal effect also develops at 495 °C, obviously due to the formation of $\text{Ca}(\text{OH})_2$ as a result of hydration of C_3S during leaching.

Fig. 1. — Thermal curves of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{SiO}_2$ hydrated for 1 hour in presence of 5% CaCl_2

- (1) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
- (2) $3\text{CaO} \cdot \text{SiO}_2$ hydrated for 1 hour in 5% CaCl_2
- (3) 2 leached with alcohol
- (4) 2 leached with water.

Chemical analysis of Cl^- in alcohol or water-leached sample reveals that almost 100 per cent of the chloride is removed by water, whereas alcohol extracts only about 94 per cent from a sample hydrated for 1 hr (fig. 2).

Calcium hydroxychloride shows an endothermic effect at about 550 to 600 °C [35, 36]. A preparation of calcium hydroxychloride formed by reacting

CaO with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was subjected to DTA and the curve showed a peak at 600 °C. As free calcium hydroxychloride is not expected to be present under low CaCl_2 concentrations prevailing at 1 hr, it is very probable that the endothermal effect at 550 to 560 °C is the result of an adsorption complex of chloride and H_2O formed on the hydrating C_3S surface in the dormant period. It is possible that this has a composition similar to calcium hydroxychloride. TGA shows a small loss in weight corresponding to the endothermal effect for this complex.

Fig. 2. — Estimation of chloride content in hydrating C_3S in 5% CaCl_2 solution.

Formation of the adsorbed chloride complex could not be detected before by X-ray or calorimetric techniques because of the small quantities involved and the nature of the complex. Previous workers estimated the amount of chloride in the water-leached samples and found that water extracted all chloride ions. This was taken as evidence that no complex of CaCl_2 formed. The present work has shown that leaching with water, in fact, decomposes this complex, whereas alcohol removes only free CaCl_2 without interfering with the chloride complex, C_3S or $\text{Ca}(\text{OH})_2$.

Surface adsorption in the C_3S - CaCl_2 - H_2O system, as a prelude to accelerating action, was investigated by a few more experiments. Tricalcium silicate was hydrated in water for 3 hr while still in the so-called dormant period. The sample was vacuum-dried and one part hydrated in water, the other with 5 per cent CaCl_2 . The results are shown in figures 3 and 4. Acceleration of the formation of $\text{Ca}(\text{OH})_2$ seems to take place within 1 hr in water. This, together with 3 hr of prehydration, is equivalent to the period for acceleration if C_3S is directly treated with water. It may indicate that in the dormant period it is the state of the solid phase that significantly contributes to the reaction.

In the presence of 5 per cent CaCl_2 the pretreated sample exhibits an endothermal effect corresponding to the surface chloride complex for 1 hr. At 2 hr acceleration of hydration is evident. In C_3S directly exposed to 5 per cent CaCl_2 the dormant period is 2 hr and a surface complex exists before acceleration (fig. 5). These results confirm that a surface complex forms at any stage during the dormant period and is a prelude to the accelerating stage.

Fig. 3. — Hydration behaviour of pre-hydrated $3\text{CaO} \cdot \text{SiO}_2$ with 5 % CaCl_2 .

Fig. 4. — Hydration of $3\text{CaO} \cdot \text{SiO}_2$ prehydrated for 3 hours.

Fig. 5. — Effect of leaching with alcohol on the exothermal behaviour of $3\text{CaO} \cdot \text{SiO}_2$ hydrated in presence of 5 % CaCl_2 .

Chemisorbed Chloride Layer on the Surface of C-S-H and Chloride in the Interlayer Space

The emergence of an intense exothermic peak in the DTA curve of C_3S always coincides with the onset of acceleration during hydration in the presence of varying amounts of CaCl_2 (fig. 5). It was first thought that this could be due to crystallization of the dehydrated C-S-H to β -wollastonite or β - C_2S . The CSH (I) product is known to give an exothermic peak of large magnitude, but this occurs at temperatures beyond 800°C . Tobermorite gel, or CSH (II), shows only very small exothermal dents at temperatures beyond 850°C .

Further experiments indicated that it is very unlikely the exothermal effect is only a crystallization effect of dehydrated CSH (I) or CSH (II). Samples of tricalcium silicate were hydrated in water or in 5 per cent CaCl_2 and the resultant products washed with water or alcohol. Figure 5 refers to C_3S hydrated with 5 per cent CaCl_2 for different lengths of time and washed with absolute alcohol. Figure 6 represents the thermal behaviour of samples washed with water. A blank experiment was also conducted by hydrating C_3S without CaCl_2 for different periods of time and subsequently washing each with excess water (fig. 7). This set of curves was obtained at a sensitivity different from those reported earlier and cannot be directly compared. A sudden acceleration effect and the emergence of the exothermic effect at 2 hr was, however, observed in C_3S hydrated in 5 per cent CaCl_2 (fig. 5). Washing with absolute alcohol has no effect on either the exothermal effect or the $\text{Ca}(\text{OH})_2$ peak. Samples of hydrated C_3S not treated with alcohol were identical to those reported in figure 5 and are not shown separately. Washing with water eliminated the exothermic peak in all samples (fig. 6). The blank runs of samples of C_3S hydrated in water for different lengths of time

and washed with excess of water did not exhibit any spurious effect that could interfere with or annul the exothermal effect (fig. 7).

The samples described in figures 5 and 6, leached with absolute alcohol or water, were analysed for chloride content. By knowing the total chloride content in the sample before extraction and that present in the extract the percentage of unextractable chloride could be calculated. Figure 2 gives the relative extraction effects of alcohol and water. At 2 hr, during which period the reaction is already accelerated, all the chloride is extracted by water, whereas about 56 per cent of the chloride is unextracted by alcohol. At 4 hr, however, even with water, 14 per cent chloride is unextracted and with alcohol the value increases to 87 per cent. At 24 hr and 168 hr alcohol extracts negligible amounts of chloride. At 168 hr water can extract only 78 per cent of the chloride, even with excess of water.

These results may mean that there is less CaCl_2 in the free state as hydration proceeds. Within 4 hr a major proportion of chloride may be strongly chemisorbed by the C-S-H product and hence not be removable by alcohol leaching. It is calculated that freshly formed C-S-H in CaCl_2 has a large surface area of over $200\text{ m}^2/\text{g}$ and has both electrostatic and van der Waal's forces. There is evidence that the C-S-H has a positive-charged surface [37], and this should encourage Cl^- ions to be avidly adsorbed. The exothermic peak in the acceleratory period may represent some sort of interaction of the chloride ions on the C-S-H surface. The emergence of this peak coincides with acceleration and formation of a high surface area C-S-H product.

It may be reasoned that $\text{C}_2\text{H}_5\text{OH}$ does not extract free CaCl_2 even if it is present in large quantities; being larger than the H_2O molecule, it cannot penetrate all the pores in the C-S-H phase. It is quite

Fig. 6. — Effect of leaching with water on the exothermal behaviour of $3\text{CaO} \cdot \text{SiO}_2$ hydrated in presence of 5% CaCl_2 .

Fig. 7. — Effect of leaching with water on the thermograms of $3\text{Ca} \cdot \text{OSiO}_2$ hydrated in water to different periods.

Fig. 8. — Thermal behaviour of hydrated $3\text{CaO} \cdot \text{SiO}_2$ treated with CaCl_2 .

- (1) C_3S hydrated 8 months
- (2) 1 treated with 5% CaCl_2
- (3) 2 extracted with alcohol
- (4) 2 extracted with water
- (5) 1 treated with 1% CaCl_2
- (6) C_3S hydrated for 6 hours + 1% CaCl_2
- (7) C_3S hydrated for 6 hours.

probable that some CaCl_2 in the free state may be inaccessible to $\text{C}_2\text{H}_5\text{OH}$. Considerable quantities, however, are chemisorbed on the C-S-H surface. For example, specific surface areas of hydrated portland cement calculated from H_2O , N_2 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and C_6H_{12} adsorption (using molecular areas of 11.4, 16.2, 18.1, 27.7 and 39 $\text{\AA}^2$, respectively) are 194.6, 97.3, 88.5, 49.0 and 48.0 m^2/g , respectively [38]. The molecular area of $\text{C}_2\text{H}_5\text{OH}$ is more than that for CH_3OH but less than that for C_6H_{12} ; it is reasonable to expect about 30 to 40 per cent of the surface to be accessible to $\text{C}_2\text{H}_5\text{OH}$, but hydrated C_3S cured for 7 days showed that $\text{C}_2\text{H}_5\text{OH}$ removes very little chloride. This should confirm that most of the chloride ions are chemisorbed on the hydrated C_3S (or in a state not freely removable with $\text{C}_2\text{H}_5\text{OH}$). The above argument is based on the premise that the surface area, with H_2O , represents the correct figure. There is strong evidence, however, that the surface area by N_2 adsorption is in fact the true figure. If so, there is stronger evidence that Cl^- may be chemisorbed.

There is every possibility that the influence of CaCl_2 on hydrating C_3S creates conditions under which chloride ions may also exist in the interlayer space of the C-S-H product. These chloride ions may be unaffected by $\text{C}_2\text{H}_5\text{OH}$, whereas H_2O , being smaller in diameter and with higher dipole moment is capable of extracting them from the interlayer even though the samples are dried prior to leaching. Feldman and Sereda [39, 40] have demonstrated, by means of scanning isotherms, and Feldman, by recent investigation of helium diffusion into cement paste, that water enters the interlayer spaces even at low humidities.

The intense exothermic peak obtained in hydrating C_3S in the presence of CaCl_2 can also be reproduced by treating completely hydrated C_3S with a

weak solution of CaCl_2 . Figure 8 gives the DTA curves of C_3S hydrated for 8 months before and after treatment with 1 per cent or 5 per cent CaCl_2 (fig. 8, curves 1, 2 and 5). Exothermic peaks are evident in both samples, followed by typical endothermal dips. Washing with alcohol has no effect on the exothermic peak, whereas washing with water removes it (fig. 8, curves 3 and 4). Even a 30 min contact of the CaCl_2 solution with completely hydrated C_3S is sufficient to produce this exothermic peak. In such a short period and with low concentrations of CaCl_2 no drastic structural changes in the C-S-H phase could be expected. The exothermic peak can also be generated at any stage of hydration of C_3S . An example is given for C_3S hydrated for 6 hr and treated with 1 per cent CaCl_2 (fig. 8, curves 6 and 7). The exothermal peaks occur at higher temperatures with 1 per cent CaCl_2 and this is also observed in hydrating C_3S containing 1 per cent CaCl_2 . As stated before, chemisorption of chloride on the C-S-H surface plus its presence in the interlayer spaces and subsequent interaction during heating may be responsible for this peak.

That the exothermic peak is not just a solid-solid interaction between CaCl_2 and C-S-H was checked by carrying out DTA on a mixture of powdered CaCl_2 and C_3S prehydrated for 8 months. No exothermic peak resulted, indicating that addition of water in the $\text{C}_3\text{S} + \text{CaCl}_2$ system is essential for the production of the exothermic peak.

It was of interest to investigate whether the exothermic peak was a result of oxidation effects in the system. Samples of C_3S hydrated in 4 per cent CaCl_2 for 4 or 14 days were subjected to continuous-vacuum DTA. The results show that the exothermic peak is eliminated (fig. 9). One might conclude that oxidation was involved in the evolution of this exothermic peak, but when the samples were subject-

ed to DTA in an N_2 atmosphere the exotherms persisted. Elimination of the exothermic peak in continuous vacuum was in fact not real and seems to have been a masking action of the endothermal effect. Continuous vacuum may decrease the temperature of high-temperature endothermal effect by more than $150^\circ C$ [41]. This observation has an important implication in vacuum DTA studies so far reported.

Fig. 9. — Thermal behaviour of $3CaO.SiO_2$ hydrated in presence of $CaCl_2$: effect of vacuum or nitrogen.

The C_3S samples hydrated in 1 per cent $CaCl_2$ are different from those hydrated with higher $CaCl_2$ contents in that they exhibit two exothermal peaks. One is attributed to the chemisorbed interlayer chloride on the C-S-H produce, and the other to the crystallization of the dehydrated C-S-H. A completely hydrated C_3S treated with 1 per cent $CaCl_2$ fails to show more than one exothermic effect. Samples hydrated for 6 or 8 hr and washed with alcohol do not influence either of these exothermal peaks, whereas water removes only a single exotherm in the samples cured for 8 hr (fig. 10). The second exothermic peak seems to be retained but now occurs beyond $800^\circ C$ owing to the crystallization effect.

In hydrating C_3S containing $CaCl_2$ the endothermal dip following the exothermal effect always coexists with the latter. Both are removed by washing with water, but they are resistant to washing with alcohol. Together these effects may represent reactions involving combination and decomposition.

Incorporated Cl^- in the Lattice of C-S-H

In samples hydrated for longer periods significant amounts of chloride ions are not removed by leaching with water. There is every possibility that these chloride ions are intimately associated in the C-S-H lattice, but the exact position and nature of the forces involved should await more detailed analysis. The C-S-H is known to incorporate SO_3^{--} and to modify the morphology. Similar effects are possible in the chloride treated C-S-H products. In a recent paper Richartz [42] found that prolonged treatment of C_3S with $CaCl_2$ at $80^\circ C$ under autoclave conditions indicated some entry of chloride ions into the lattice of C-S-H.

Fig. 10. — Effect of leaching on the exothermal characteristics of $3CaO.SiO_2$ hydrated in presence of $CaCl_2$.

- (1) $C_3S + 1\% CaCl_2$ hydrated 6 hours
- (2) $C_3S + 1\% CaCl_2$ 8 hours (alcohol leached)
- (3) 1 leached with water
- (4) 2 leached with water

Role of $CaCl_2$ in the Hydration of $3 CaO.SiO_2$.

Search for a possible chloride complex in the $C_3S-CaCl_2-H_2O$ system has so far proved to be of no avail. Present data show that calcium chloride may exist in four or five forms, including complexes, during the hydration of C_3S , the relative amounts depending on how far the hydration has progressed and on the concentration of $CaCl_2$. Especially during the induction period, it is present mainly as free calcium chloride. As soon as the $CaCl_2$ solution comes into contact with the C_3S surface, some of it is avidly adsorbed. In the acceleratory stage and later it is bound as a chemisorbed layer on the C-S-H surface and may exist in the interlayer. At later periods the chloride also is firmly incorporated in the C-S-H phase, but the exact forces and position are not yet clear.

There is general agreement that as soon as C_3S comes into contact with water the first product formed during the dormant period is a coating with a CaO/SiO_2 ratio of nearly 3 [43 to 47]. In the acceleratory period the CaO/SiO_2 ratio of the C-S-H product is much lower than 3. At this stage the increased rate of reaction may be due to one or more of the following effects: autocatalytic effect, splitting off the layer, nucleating effect or formation of reaction centres, increase in the permeability of the layer, etc.

It is possible that the rate of formation of the initial layer of high CaO/SiO_2 ratio, its conversion to a hydrate with lower CaO/SiO_2 ratio and ultimate conversion to hydrate, possibly with a slightly higher CaO/SiO_2 ratio than the second, are reflected as changes in induction period, setting time, surface area, rate of hydration, microstructure, shrinkage and strength (table I). The type and rate of inter-

conversion may be dictated to a large extent by the nature of the surface of the silicate phase at various stages of hydration, and this in turn may depend on environmental conditions.

TABLE I
RELATIVE PROPERTIES OF C_3S HYDRATED IN H_2O OR $CaCl_2$ SOLUTIONS

Properties	$C_3S + 0\% CaCl_2$	$C_3S + 1\% CaCl_2$	$C_3S + 4\% CaCl_2$
1. Setting time $1C_3S:1C_2S$ mixture (8)	790 min	525 min	105 min (2 % $CaCl_2$)
2. pH at 4 hr	12.40	11.95	11.55
3. Induction period by $Ca(OH)_2$ estimation.	3-4 hr	3-4 hr	about 3 hr; bout 2 hr (5 % $CaCl_2$)
4. a. Period required to attain max rate of heat evolution ($w/s = 1.0$)	about 14 hr	about 9 hr	about 6 hr
b. Heat evolved at the above period, approx. (14)	1.5×10^{-3} Cal $Sec^{-1}g^{-1}$	3×10^{-3} Cal $Sec^{-1}g^{-1}$	5.7×10^{-3} Cal $Sec^{-1}g^{-1}$
5. Degree of hydration by $Ca(OH)_2$ estimation* 6 hr	α_3	α_2	α_1
30 days	α_2	α_1	α_3
6. Degree of hydration in terms of C_3S reacted* 6 hr	α_3	α_2	α_1
30 days	α_3	α_2	α_1
7. Compressive strength at 28 days Kg/cm^2 (3).	190	310	250 (3 % $CaCl_2$)
8. Surface area of C-S-H product hydrated for 30 days (N_2).	24.8	32.7	69.92
9. CaO/SiO_2 ratio of C-S-H at 28 days (3).	~ 2.0	~ 1.97	~ 2.16
10. Morphology of C-S-H at 30 days.	Needle-like	Platy and crinkled foils	Platy

* Degree of hydration is qualitatively represented by $\alpha_1, \alpha_2, \alpha_3$, where $\alpha_1 > \alpha_2 > \alpha_3$.

It is evident that on immediate contact of the C_3S surface with $CaCl_2$ solution there should be an interference and even alteration of the type of the surface layer formed otherwise. The importance of surface in the hydration of C_3S in the presence of retarding admixtures has been recognized.

In the first few hours, adsorption of chloride ions modifies the ratio of CaO/SiO_2 of the hydrate to a lower value, compared with that formed without $CaCl_2$ [15]. The adsorption of chloride may also modify one or more factors, viz., permeability, dispersibility, adhesive force of the initial layer to the C_3S surface, and the nucleating or reaction centre. For example, $CaCl_2$ on silica gel has been reported to decrease the permeability of the surface [48]. Reduction of the induction period at higher concentrations of $CaCl_2$ and early setting depend on these factors. In the acceleratory period it is also possible that $Ca(OH)_2$ which envelops the C_3S surface is removed by interaction with $CaCl_2$. At the same time, chloride ions are continuously adsorbed on the C-S-H phase, and subsequently in the interlayers, and these in turn influence the rate of conversion and number and type of layers of C-S-H formed, and subsequently, their morphology and specific surface. Ultimate strength is not dependent solely on the degree of hydration, but on the type of C-S-H formed and the amount of $CaCl_2$ intimately associated with C-S-H. For example, a higher CaO/SiO_2 product formed in the presence of 4 or 5 per cent $CaCl_2$ has more incorporated chloride ions, and this may be a factor in making the resultant product weak compared with C_3S hydrated with lower $CaCl_2$ concentration (table I).

Higher compressive strengths in the C_3S - $CaCl_2$ - H_2O system need not be due to the C-S-H products

being of higher area, as has been assumed by Celani et al [10]. Surface area results using N_2 as adsorbate gives values for C-S-H product at 30 days equivalent to 24.8, 32.7 and 69.92 m^2/g for $C_3S + 0$ per cent $CaCl_2$, $C_3S + 2$ per cent $CaCl_2$ and $C_3S + 4$ per cent $CaCl_2$, respectively. Although C_3S with 4 per cent $CaCl_2$ shows highest surface area, this sample shows lowest mechanical strength, indicating that the nature of the C-S-H product and CaO/SiO_2 ratio have to be taken into account in establishing a relation between strength and other properties and surface areas. The higher strengths with 1 or 2 per cent $CaCl_2$ should mean that, under these conditions, C-S-H produced has a lower CaO/SiO_2 ratio product than that with 4 per cent $CaCl_2$ and also a high surface area. In addition, the microstructure may play an important role in the development of strength. A comparison of the electromicrographs of C_3S hydrated for 30 days with 0, 1 or 4 per cent $CaCl_2$ and dispersed in alcohol shows the presence of small needles in C_3S hydrated with water, whereas that hydrated with $CaCl_2$ showed platy or crumpled foil-like structure predominating (fig. 11). Collepardi [49] also has observed that $CaCl_2$ stabilizes the platy structure. The chemisorption of chloride on the C-S-H surface may be responsible for the changes in morphology.

The chloride ions incorporated into C-S-H are not expected to be mobile enough in water solution to cause corrosion in reinforced systems. In essence the reaction of C_3S with water in the presence of $CaCl_2$ is very complex. It is to be recognized that adsorption, substitution, and solubility may all play significant roles to different degrees, depending on the reactants, experimental conditions, and duration of hydration. These, in turn, influence the physical, chemical and mechanical properties of the products.

(a) $C_3S + 0\% \text{ CaCl}_2$

(b) $C_3S + 1\% \text{ CaCl}_2$

(c) $C_3S + 4\% \text{ CaCl}_2$

Fig. 11. — Electron micrographs of tricalcium silicate hydrated for one month (mag: $\times 12,000$).

CONCLUSIONS

Calcium chloride may exist in different forms in hydrating tricalcium silicate, depending on the initial mix proportions and duration of hydration. These are (i) free calcium chloride, (ii) a complex on the surface of C_3S during the dormant period, (iii) a chemisorbed layer on the hydrated calcium silicate, (iv) interlayer chloride, and (v) chloride intimately bound in the lattice.

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RÉSUMÉ

Etats possibles du chlorure au cours de l'hydratation du silicate tricalcique en présence de chlorure de calcium. — L'hydratation du silicate tricalcique en présence de chlorure de calcium s'accompagne de réactions endo et exothermiques qu'on n'observe pas dans d'autres circonstances. La réaction endothermique, qui se produit entre 550 et 590 °C est attribuée à la formation d'une couche de chlorure à la surface du silicate lors de l'avant-prise.

Une intense réaction exothermique, apparaissant entre 640 et 690 °C coïncide avec une période d'hydratation accélérée et est attribuée à la sorption-combinaison de chlorure sur le silicate et à la présence de chlorure dans les couches de structure. On peut obtenir cette réaction exothermique en faisant agir CaCl_2 sur le silicate tricalcique à tout moment de l'hydratation. L'analyse thermique différentielle continue sous vide permet d'éliminer le pic exothermique, excepté lorsque l'expérience se fait dans un courant d'azote. L'endotherme obtenu durant l'avant-prise et le pic exothermique formé lors de la période d'accélération peuvent être éliminés par lavage à l'eau des éprouvettes. On peut

extraire à l'alcool environ 13 % du chlorure ajouté durant quatre heures d'hydratation, mais après sept jours, le chlorure n'est pratiquement plus extrait. Les valeurs correspondantes pour l'extraction à l'eau sont de 86 et de 78 %.

Il est supposé que le chlorure de calcium existe sous quatre ou cinq formes différentes, même complexes, lors de l'hydratation du silicate tricalcique, selon sa proportion et la durée de l'hydratation. Il y a présence de CaCl_2 libre dans les premiers temps de l'hydratation. Durant l'avant-prise, le chlorure est adsorbé aussi à la surface du silicate tricalcique. Au cours de la période d'accélération, et après le chlorure est adsorbé sur les silicates hydratés produits, et en partie sur les couches de structure. Ultérieurement une quantité importante de chlorure s'incorpore intimement aux formations de silicates hydratés et ne peut être extraite à l'eau. En fonction de la durée d'hydratation et des formes diverses de chlorure, il est possible qu'une action s'exerce sur : l'avant-prise, le temps de prise, l'accélération, la surface développée, le retrait, le rapport $\frac{\text{CaO}}{\text{SiO}_2}$ du silicate hydraté produit, la morphologie et la résistance.

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