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

V.S. RAMACHANDRAN

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LA CINETIQUE DE L'HYDRATATION DU SILICATE TRICALCIQUE EN PRESENCE DU CHLORURE DE CALCIUM ETUDIEE PAR ANALYSE THERMIQUE

SOMMAIRE

Des analyses thermiques ont servi à étudier l'influence du chlorure de calcium sur l'hydratation du silicate tricalcique pour des périodes allant de quelques minutes à un mois. Les deux méthodes d'analyse thermique différentielle et thermogravimétrique ont indiqué une bonne concordance dans l'évaluation de la quantité de Ca(OH)_2 à différents stades de l'hydratation. En présence de CaCl_2 la période inactive a été réduite de sorte qu'avec 5% elle est passée de 4 heures à 2 heures. Le montant d'hydratation au bout de 6 heures exprimé en fonction de la quantité estimée de Ca(OH)_2 était de l'ordre de $\text{C}_3\text{S} + 4\% \text{CaCl}_2 > \text{C}_3\text{S} + 1\% \text{CaCl}_2 > \text{C}_3\text{S} + 0\% \text{CaCl}_2$, et à 30 jours, $\text{C}_3\text{S} + 1\% \text{CaCl}_2 > \text{C}_3\text{S} + 0\% \text{CaCl}_2 > \text{C}_3\text{S} + 4\% \text{CaCl}_2$. Cependant, exprimé en fonction d'une diminution de C_3S le montant d'hydratation à 6 heures ou à 30 jours était de l'ordre de $\text{C}_3\text{S} + 4\% \text{CaCl}_2 > \text{C}_3\text{S} + 1\% \text{CaCl}_2 > \text{C}_3\text{S} + 0\% \text{CaCl}_2$. Ces résultats indiquent qu'en présence de pourcentages plus élevés de CaCl_2 , le C_3S devient hydraté pour former C-S-H avec un rapport CaO/SiO_2 plus élevé. Les courbes thermiques indiquent certains points d'inflections qui représentent probablement la formation de surfaces complexes au cours des périodes inactive et accélérée.

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

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ABSTRACT

Thermal methods were applied to investigate the influence of 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 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 C_3S , 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 CaCl_2 , C_3S hydrates to form C-S-H* with a higher CaO/SiO_2 ratio.

Thermal curves showed an endothermic effect at 550 to 590°C during the dormant period in samples hydrated with CaCl_2 . This could be attributed to the formation of a surface complex of chloride on the C_3S 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 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^{1,2} 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 = CaO , S = SiO_2 , A = Al_2O_3 , and H = H_2O .

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 CaCl_2 on cements³. Candlot in 1886 described in a publication that the use of CaCl_2 solutions up to 50 g/l increased the strength of cement⁴. Since then, extensive data have been published about the effect of CaCl_2 on the properties of cement and concrete. Vollmer⁵ prepared an annotated bibliography of the publications pertaining to the effect of 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 CaCl_2 .

According to earlier concepts, CaCl_2 facilitates strength development in cement by forming a complex compound with the tricalcium aluminate phase, which implies thereby that CaCl_2 does not have any influence on the hydration of C_3S 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 CaCl_2 .

Sloane *et al.* found some evidence that the hardening of pure calcium silicates is accelerated⁶ by CaCl_2 . This important observation has been confirmed recently by others⁷⁻²⁶. 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^{27,28}. These techniques have not yet been applied systematically to follow the hydration of C_3S in presence of CaCl_2 . The object of the present investigation is to examine the influence of different amounts of CaCl_2 on the progress of hydration of C_3S 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; SiO_2 , 26.17; Al_2O_3 , 0.08; free CaO (ASTM), 0.18; free CaO (Franke), 0.46. *Mineralogical:* C_3S , 99.33; C_2S , 0.00; C_3A , 0.21; CaO (Franke), 0.46. *Fineness:* Blaine 3310 cm^2/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% 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 C_3S 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 CO_2 .

A similar method was followed for the hydration experiments in presence of different concentrations of CaCl_2 . The solution/silicate (vol./wt.) ratio was kept at 0.5. This could be achieved with 1, 4 or 5% CaCl_2 (with respect to C_3S) by adding 10 ml each of 2, 8 or 10% CaCl_2 solution, respectively, to 20 g of C_3S .

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°C with crushed ice. In experiments, especially those involving samples with higher 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 H_2O 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°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 C_3S 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°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°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°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°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 endothermal 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 endothermal 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 endothermal valley between 340 and 480°C is also much more pronounced than that for C_3S hydrated without $CaCl_2$. The intensity of this endothermal valley decreases with the progress of hydration. This series shows that up until 2 h, there is an additional endothermal peak at about 550°C, not detected in corresponding samples in Fig. 1. The small endothermal 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 endothermal 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°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°C following the exothermal effect. After 1 day it is absent.

In Fig. 3, thermograms of C_3S hydrated in the presence of 4% 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°C) which is less pronounced except in a few samples. The endothermic peak at 570°C , which corresponds to the

Fig. 3. Rate of hydration of $3\text{CaO}\cdot\text{SiO}_2$ in presence of 4% CaCl_2 by DTA.

550°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°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% 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% CaCl_2 has the least intensity. In samples hydrated with 4% 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 endothermal 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 C_3S , and also electrical conductivity, heats of hydration, or strength, have been adopted to follow the hydration of C_3S . In this work the quantity of $\text{Ca}(\text{OH})_2$ was estimated at different stages of hydration of C_3S , with or without CaCl_2 , by DTA and TGA techniques. These methods served as a reasonable basis for investigating the accelerating influence of 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 C_3S .

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 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 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 Ca(OH)_2 determined by TGA at various stages of hydration. A comparison of the TGA and DTA methods of estimation of Ca(OH)_2 indicates a linear relationship (Fig. 6).

Thermograms of pure C_3S , as well as of C_3S cured at earlier times, indicate three endothermal peaks at about 680, 930, and 970–980°C, the one at 930°C being of highest intensity (Fig. 1). The transitions in the C_3S , *viz.* $\alpha \rightarrow \beta$ in the triclinic form, triclinic $\rightarrow$ monoclinic, and monoclinic $\rightarrow$ trigonal forms, may respectively explain these effects²⁹. The intensity of these peaks diminishes with the progress of hydration.

The two low-temperature endothermal 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 endothermal valley between 340 and 480°C, which is more evident in some samples than others, may represent the dehydration effect of Ca(OH)_2 when it is present in a non-crystalline form, and also the evolution of firmly-bound H_2O from C–S–H³⁰. 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 endothermal 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 Ca(OH)_2 . Small amounts of Ca(OH)_2 are present initially due to hydration of C_3S 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 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 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 Ca(OH)_2 produced up to 30 days is formed. After 8 h 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–H³¹ and decarbonation of very small amounts of CaCO_3 that might have formed in those samples.

Hydration of $3\text{CaO} \cdot \text{SiO}_2$ in presence of 1% CaCl_2

The comparative rates of hydration of C_3S with or without 1% CaCl_2 may be studied from Figs. 1, 2, 4, and 5. In presence of 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) endothermal effects exhibited by some samples in the hydrated C_3S (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 CaCl_2 (Fig. 1) indicates that more hydration takes place in samples hydrated in presence of 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% CaCl_2 show an additional endotherm at 550°C up to 2 h that is not observed in those hydrated in the absence of CaCl_2 (Figs. 1 and 2). This endotherm is not evident at later periods; in C_3S samples hydrated with 4% CaCl_2 , it is accentuated (Fig. 3). This peak is ascribed to the presence of a complex of CaCl_2 on the surface of the hydrating C_3S 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°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% CaCl_2 , the dormant period is about the same as that without CaCl_2 , but the reaction is accelerated much more from the end of this period. For example, at 4 h C_3S hydrated in 1% CaCl_2 has about double the amount of $\text{Ca}(\text{OH})_2$ that is present in C_3S hydrated without 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 C_3S hydrated in presence of 1% CaCl_2 than that without 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°C . Whenever present in a sample, this exothermal effect is always followed by a large endothermal dip at about 800 to 840°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 CaCl_2 , C_3S does not exhibit the high temperature endothermic effects at 930 and 980°C in most of the samples, and that an exothermal effect is registered in some samples in the range from 950 to 1000°C . It seems that the high temperature crystalline transitions of C_3S are modified in the presence of 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°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% CaCl_2 . It is known that CSH(I), a low CaO/SiO_2 ratio hydrate, gives a large exothermic peak around 800°C . Collepardi *et al.*²⁰ have reported that C_3S hydrated in low concentrations of 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% 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% CaCl_2 (Figs. 3, 4, and 5). The endothermal effects caused by a surface complex of chloride on hydrating C_3S , occur as a higher intensity endotherm, and persist until 8 h in the range from 570 to 590°C . Its presence at later periods cannot be confirmed due to the masking effect of the exotherm. The low temperature endothermal curve below about 400°C continues right up to the temperature of onset of dehydration of Ca(OH)_2 . The resultant endotherm seems to be larger than the corresponding effect for hydrated C_3S in presence of 0 or 1% CaCl_2 solution, showing thereby that more water is held in these products.

No Ca(OH)_2 peak is observed till 45 min; at 1 h the endothermal effect suddenly emerges. At 2 h, the peak due to Ca(OH)_2 decreases slightly, possibly because the excess of Ca(OH)_2 was being incorporated in the C-S-H product, with some combining with CaCl_2 at the surface. It is likely that the degree of hydration, in terms of C_3S consumed, is greater at 2 than at 1 h. The doublet at 1 h may represent the formation of some non-crystalline Ca(OH)_2 . A sudden increase in the rate of formation of 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°C . Interestingly enough, of the total lime estimated at 30 days, about 50% of the Ca(OH)_2 is formed within the first 6 h of hydration.

In terms of the amount of Ca(OH)_2 formed, C_3S with 4% CaCl_2 hydrates to the greatest extent in the first 12–16 h, after which time it is exceeded by C_3S with 1% CaCl_2 , and is exceeded in about 22–24 days by the C_3S hydrated with 0% CaCl_2 . The hydration reaction of C_3S in presence of 4% CaCl_2 seems to be almost completed within about 15 days, judging by the estimated amount of Ca(OH)_2 (Figs. 4 and 5). At 30 days, in terms of Ca(OH)_2 formed, the extent of hydration with C_3S plus 1% CaCl_2 is greater than C_3S plus 0% CaCl_2 , which is greater than C_3S plus 4% CaCl_2 .

The larger endothermal effect at 810 to 850°C , following the exothermal effect, is present along with the exothermal effect from 3 h to 30 days. The endothermal effects representing C_3S transitions beyond 900°C are absent.

In presence of 5% 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_2 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_2 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_2O system increases with $CaCl_2$ concentration¹⁷.

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 CaCl_2 was increased. With higher percentages of CaCl_2 , the C-S-H product seemed to have a higher CaO/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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