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Dependence of Fineness of Calcium Carbonate on the Hydration Behaviour of Tricalcium Silicate

by V.S. Ramachandran and Zhang Chun-Mei

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RÉSUMÉ

On a hydraté du silicate tricalcique (C_3S) dans des rapports eau/solide de 0,7 et 2,0 en présence de 0, 5, 10, 15 et 50 % de $CaCO_3$. Des particules de carbonate de calcium de dimensions moyennes diverses (3,2, 4,4, 10,7, 14,5, 21,0 et 77,0 μm) ont été ajoutées au C_3S , et on a observé le rythme d'hydratation en déterminant la teneur du C_3S en $Ca(OH)_2$ et en eau non évaporable, ainsi que son degré d'hydratation. L'addition de $CaCO_3$ a accéléré l'hydratation, l'effet augmentant avec la quantité de produit ajouté et sa finesse. Le rapport CaO/SiO_2 a augmenté légèrement en présence du $CaCO_3$. Il appert que 25 % du $CaCO_3$ ajouté ont été incorporés à la phase C-S-H lorsque le C_3S a été hydraté avec 5 % de $CaCO_3$ pendant trois jours. L'examen au microscope électronique à balayage a révélé que les produits d'hydratation croissaient sur les particules de C_3S et sur celles de $CaCO_3$.

DEPENDENCE OF FINENESS OF CALCIUM CARBONATE ON THE HYDRATION BEHAVIOUR OF TRICALCIUM SILICATE

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ABSTRACT

Ramachandran, V.S. and Zhang Chun-mei, 1986. Dependence of fineness of calcium carbonate on the hydration behaviour of tricalcium silicate. *Durability of Building Materials*, 4: 45–66.

Tricalcium silicate (C_3S) was hydrated at water/solid ratios of 0.7 and 2.0 in the presence of 0, 5, 10, 15 and 50% $CaCO_3$. Calcium carbonate of various mean particle sizes (3.2, 4.4, 10.7, 14.5, 21.0 and 77.0 μm) was added to C_3S and the rate of hydration followed by determining $Ca(OH)_2$ and non-evaporable water contents as well as degree of hydration of C_3S . Addition of $CaCO_3$ accelerated hydration, the effect increasing with the amount and fineness of $CaCO_3$. The CaO/SiO_2 ratio increased slightly in the presence of $CaCO_3$. There is evidence that as much as 25% of the added $CaCO_3$ was incorporated into the C—S—H phase when C_3S was hydrated with 5% $CaCO_3$ for three days. Scanning electron microscope (SEM) examination revealed that hydration products grow on both C_3S and $CaCO_3$ particles.

1 INTRODUCTION

Limestone (Ls) is used for various purposes in concrete technology, as raw material for clinker production, partial replacement of gypsum, and as coarse or fine aggregate. Limestone dust, produced in quarrying operations, poses disposal and environmental problems and has been suggested for use as an additive to Portland cement. Some standards allow its use as an addi-

tive in cement provided the properties of the concrete made with such a cement are not adversely affected.

Studies of the effect of calcium carbonate on hydrating cement show that physical and mechanical characteristics are influenced to different extents. These differences, particularly at early ages, are attributed to interactions between calcium carbonate and the tricalcium aluminate phase (Bensted, 1980, 1983; Berthonneau and Marseault, 1981-82; Longuet, 1983; Lyubimova et al., 1972; Mortureux et al., 1982; Spohn and Lieber, 1965; Timashev and Kolbasov, 1981). It is implied that the hydration kinetics of the C_3S phase remains unaffected. Some workers have indicated that higher strengths in Portland cements containing $CaCO_3$ may be related to an overall increase in the rate of cement hydration (Soroka and Setter, 1977; Soroka and Stern, 1976). Recent work shows that finely divided $CaCO_3$ accelerates the hydration of C_3S and influences other properties (Ramachandran and Zhang, to be published).

In practice, crushed limestone contains particles of various sizes, and each fraction may have its own effect on the hydration of C_3S . It was the objective of the study to show how the hydration characteristics of C_3S are influenced by $CaCO_3$ of differing particle size fractions, since this may have implications in terms of the durability of concrete containing $CaCO_3$ as an aggregate.

2 EXPERIMENTAL

2.1 Materials

Tricalcium silicate (triclinic) was supplied by the Portland Cement Association, U.S.A., with a Blaine surface area of $3600 \text{ cm}^2/\text{g}$. Calcium carbonate powder was supplied by the Anachemia Chemical Company. Its N_2 surface

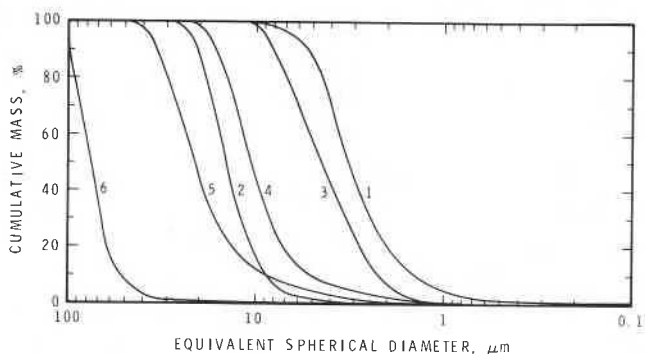


Fig. 1. Particle size distribution of different types of $CaCO_3$: (1) Anachemia (Ac) $CaCO_3$; (2) Fisher (Fr) $CaCO_3$; (3) Limestone (Ls) $< 10 \mu\text{m}$; (4) Limestone (Ls) $10-20 \mu\text{m}$; (5) Limestone (Ls) $20-45 \mu\text{m}$; (6) Limestone (Ls) $74-149 \mu\text{m}$.

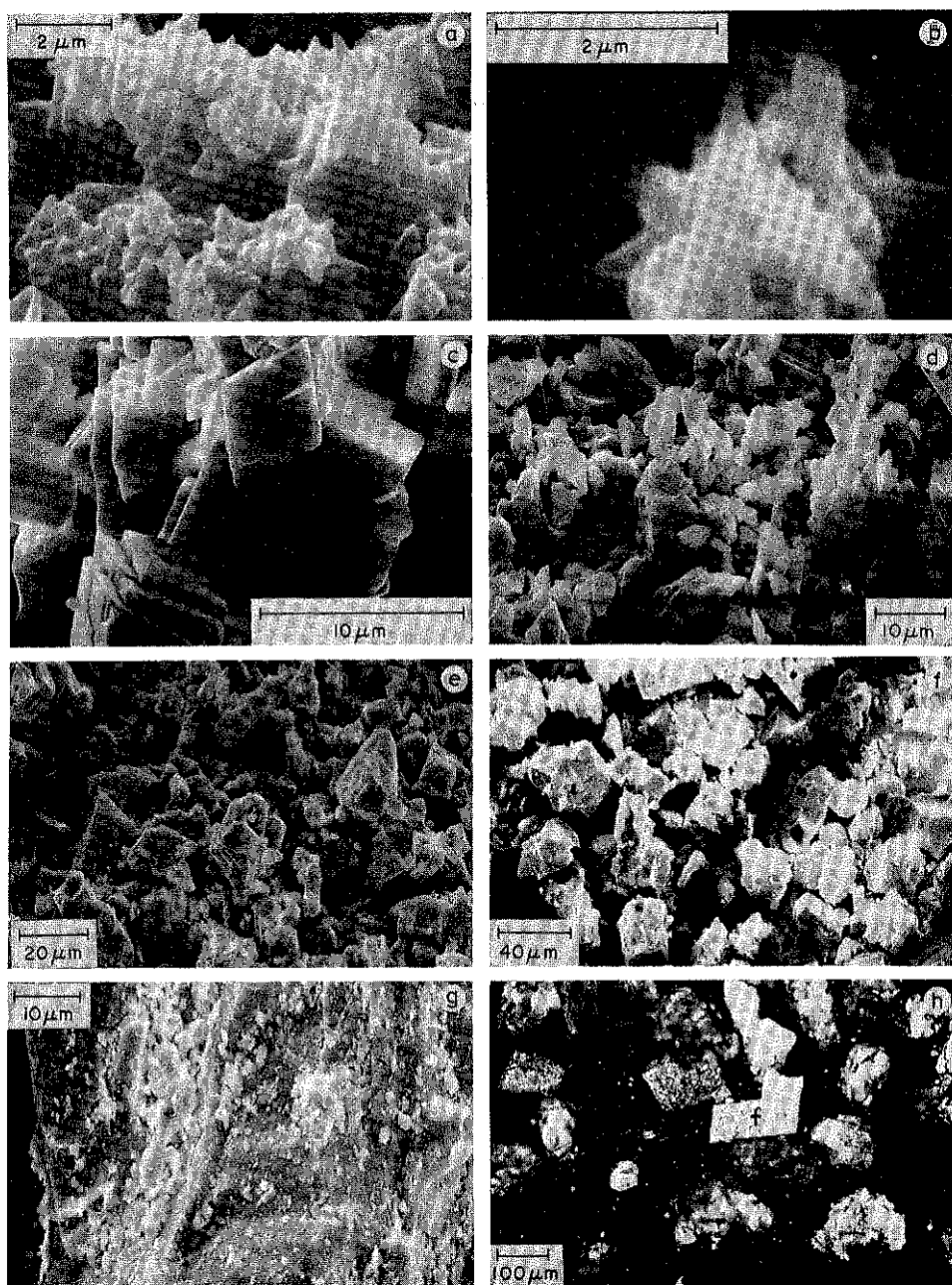


Fig. 2. Morphological features of CaCO_3 : (a) Ac CaCO_3 ; (b) Ac CaCO_3 (high magnification); (c) Fr CaCO_3 ; (d) Ls $< 10 \mu\text{m}$; (e) Ls $10\text{--}20 \mu\text{m}$; (f) Ls $20\text{--}45 \mu\text{m}$; (g) Ls $74\text{--}149 \mu\text{m}$; (h) Ls $74\text{--}149 \mu\text{m}$ (low magnification).

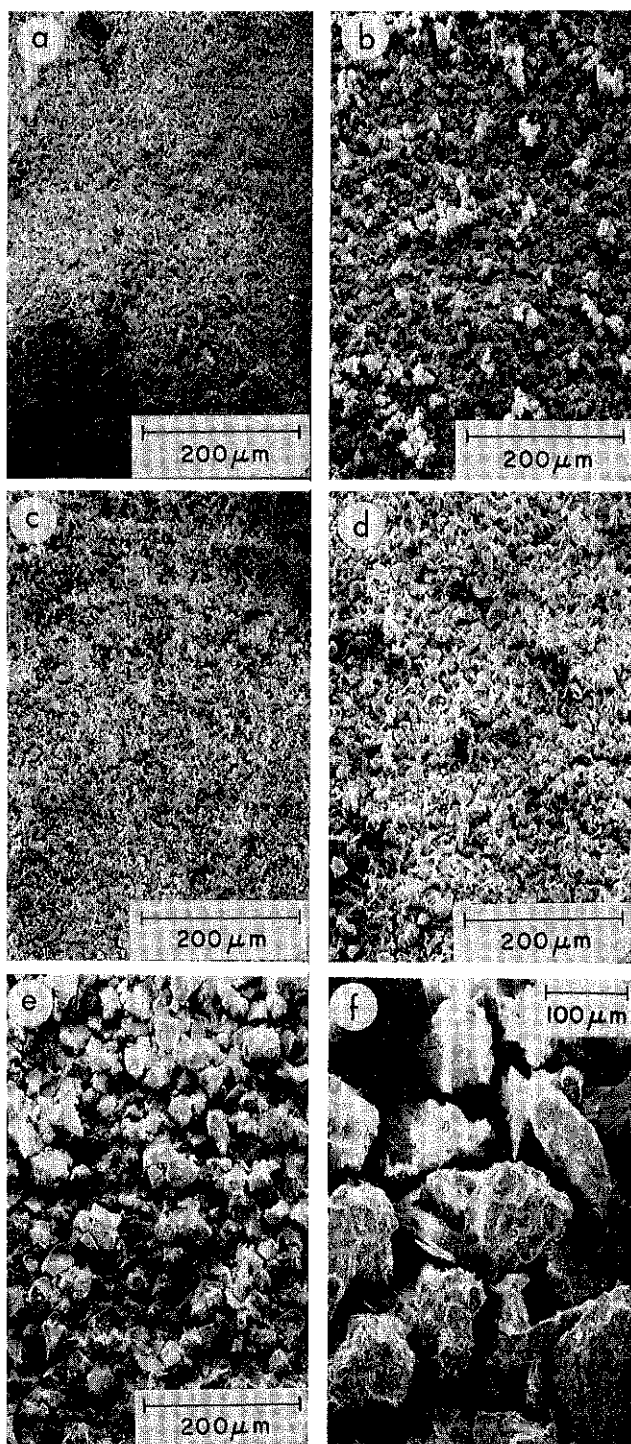


Fig. 3. Examination of CaCO_3 particles by SEM, all at same magnification: (a) Ac CaCO_3 ; (b) Fr CaCO_3 ; (c) Ls $< 10 \mu\text{m}$; (d) Ls $10\text{--}20 \mu\text{m}$; (e) Ls $20\text{--}45 \mu\text{m}$; (f) Ls $74\text{--}149 \mu\text{m}$.

TABLE 1

Physical characteristics of calcium carbonate samples

Sample no.	Material	Designation	Particle size range (μm)	Mean particle size (μm)	N ₂ surface area (m^2/g)
1	Anachemia CaCO ₃	Ac	<10	3.2	6.5
2	Fisher CaCO ₃	Fr	<25	14.5	0.4
3	Limestone	Ls	<10	4.4	1.5
4	Limestone	Ls	10—20	10.7	0.7
5	Limestone	Ls	20—45	21.0	0.4
6	Limestone	Ls	74—149	77.0	0.2

area was $6.5 \text{ m}^2/\text{g}$ and the mean particle diameter about $3 \mu\text{m}$. Another sample, reagent CaCO₃ with a surface area of $0.4 \text{ m}^2/\text{g}$, was supplied by Fisher Scientific Company. Limestone containing 98.23% CaCO₃ was ground to different particle sizes varying from $143 \mu\text{m}$ to less than $10 \mu\text{m}$ and divided into four fractions. Details are given in Fig. 1 and Table 1. The CaCO₃ used in this work was also examined by SEM and by optical microscope.

The Anachemia CaCO₃ (Ac CaCO₃) has an elongated shape with well-developed scalenohedral faces. The mean crystal size is about $1 \mu\text{m}$ in the long axis and $0.4 \mu\text{m}$ in width (Fig. 2a,b). The Fisher CaCO₃ (Fr CaCO₃) has a variable grain size and is much coarser than Ac CaCO₃ (Fig. 2c). The individual crystals of rhombohedra vary in size from about 4 to $15 \mu\text{m}$.

The morphology of the crushed limestone is shown in Figs. 2g,h and 3f. Most of the fraction is below $150 \mu\text{m}$ in size and consists of irregularly shaped particles, some exhibiting rhombohedral cleavage planes. Optical examination (Fig. 2h) showed some cleavage fragments. The grain size changed with the degree of grinding and sieving. In the $10\text{-}\mu\text{m}$ material the particle size varied from 2 to $10 \mu\text{m}$ (Fig. 2d); in the fraction of size $74\text{--}149 \mu\text{m}$ the mean particle size was about $100 \mu\text{m}$. Sedimentation analysis showed a value of $77 \mu\text{m}$ (Fig. 1).

Figure 3 comprises micrographs of samples of CaCO₃, all with the same magnification. They clearly show that particle size has a significant influence on texture. The Anachemia CaCO₃ and limestone ($\leq 10 \mu\text{m}$) appear to be similar.

2.2 Sample preparation

Series I

Tricalcium silicate was mixed with different amounts of CaCO₃ (0, 5 and 15% with respect to the total weight of C₃S + CaCO₃) and transferred to a 10-ml polyethylene vial. Glass spheres 5 mm in diameter were added to

the dry mix and vibrated on a Spex high-speed mixer for 2 minutes. Carbon dioxide-free distilled water was added at a water/solid (w/s) ratio of 0.4, then the mixture was capped and vibrated for 20 s. The polyethylene vials were placed in a plexiglas tube that was put on rollers and rotated for up to one day. After this, the sealed samples were left to hydrate for varying intervals of time. Before examination they were dried by continuous vacuum pumping for a day. Care was taken throughout to prevent contamination with CO_2 . Individual samples were prepared for any required period of hydration, viz. 1, 3, 7 and 28 days.

Series II

A second series of C_3S pastes was similarly prepared using 0, 15 and 50% CaCO_3 at a water/solid ratio of 2.0. These samples were hydrated for different periods and examined by SEM before the solution phase was analysed for Ca^{2+} determination.

2.3 Method

Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a 1090 DuPont thermal analyser containing a 951 TGA accessory. In each experiment a 30-mg sample was heated at $20^\circ\text{C}/\text{min}$ in a continuous flow of nitrogen gas. The TGA equipment gave both thermogravimetric and differential thermogravimetric curves. The DTA cell could be used up to 1200°C . These methods were used to estimate C_3S , $\text{Ca}(\text{OH})_2$, CaCO_3 and non-evaporable water.

Conduction calorimetry

The rate and amount of heat development by C_3S with and without CaCO_3 , for w/s ratios of 0.7 and 2.0, and for a temperature of 25°C , were measured using a conduction calorimeter supplied by the Institute of Applied Physics, Delft, in the Netherlands (Ramachandran, 1973). For data acquisition and processing, the calorimeter was interfaced with an Apple IIe computer using a Taurus One 12-bit analogue-to-digital converter and an Apple super serial interface card.

Estimation of Ca^{2+} in the solution phase

Two grams of C_3S with 0, 15 or 50% CaCO_3 were mixed continuously by hand at a w/s ratio of 2.0 for 30 s. At specified intervals the mixture was subjected to high-speed centrifuge at 12,000 rpm. The supernatant solution (1 ml) was taken, diluted, and analysed for Ca^{2+} with a Perkin-Elmer 403 atomic absorption spectrophotometer.

Particle-size distribution

Particle-size distribution (100–0.1 μm range) was determined by a Micro-

meritics, Sedigraph 500E particle-size analyser. Sedisperse A-12 solution (density 0.810 g/ml and viscosity 4.542×10^{-3} Pa·s at 24°C) was used as a dispersant for particle-size measurement of CaCO_3 .

Specific surface area

Surface area was obtained with N_2 as adsorbate, using a Quantasorb Model QS-7 sorption system.

Scanning electron microscope (SEM)

Microstructural examination was conducted on fractured pieces of specimen using a Cambridge Stereoscan, Mark 2A. These were given a conductive coating of carbon and gold.

RESULTS AND DISCUSSION

3.1 Hydration kinetics

The rate of hydration of C_3S may be followed by estimating the amount of $\text{Ca}(\text{OH})_2$ or the non-evaporable water formed at different times of hydration, or by following the rate of disappearance of C_3S .

The $\text{Ca}(\text{OH})_2$ formed during hydration may be estimated by chemical extraction, using thermoanalytical or QXRD methods. The chemical extraction method yields higher values. In the present work the thermogravimetric method was used. Calcium hydroxide exhibits a peak at about 460–475°C. The area of this endothermal effect was used to determine the amount of $\text{Ca}(\text{OH})_2$.

Figures 4 and 5 show, respectively, the effect of 5 and 15% CaCO_3 on the formation of $\text{Ca}(\text{OH})_2$ at different times. The TGA curves indicate that the amplitude of the peak at 460–475°C increases as hydration period increases. In quantitative terms, the amount of lime formed at 0% CaCO_3 (C_3S basis) increases from 8.1% at 1 day to 22.3% at 28 days. A literature survey (Celani et al., 1966; Collepari and Massidda, 1971a; Kantro et al., 1966; Kurczyk and Schwiete, 1960; Locher, 1966; Ramachandran and Feldman, 1984; Rio et al., 1970; Valenti and Sabatelli, 1974) indicates that the amount of $\text{Ca}(\text{OH})_2$ formed at 28 days varies from 20 to 40%. This large variation results from the different techniques adopted, the differences in the physical and chemical properties of the C_3S material, and the preparation method. Addition of CaCO_3 increases the amount of $\text{Ca}(\text{OH})_2$ at all times of hydration. Rate of hydration is greater with larger amounts of CaCO_3 , indicating that CaCO_3 increases the rate of hydration of C_3S . The rate also depends on the particle size of CaCO_3 , larger sizes leading to lower accelerating effects. For example, at 28 days the amounts of $\text{Ca}(\text{OH})_2$ formed with 15% CaCO_3 , Ls (74–149 μm) and Ac CaCO_3 , are 24.3 and 25.5%, respectively.

The degree of hydration of cements and cement components was also

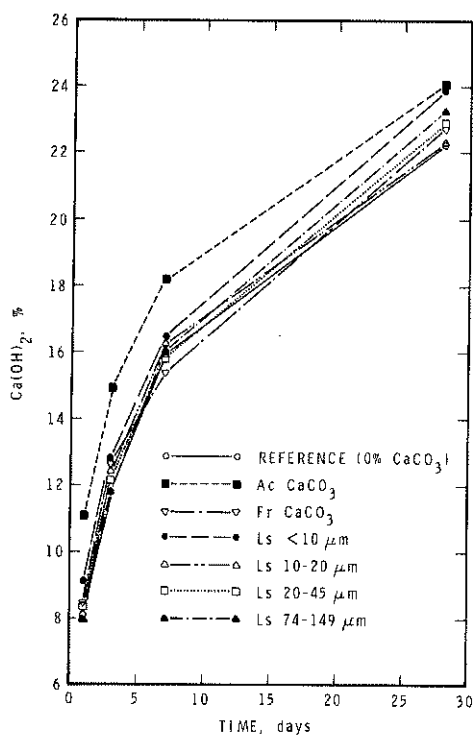


Fig. 4. Formation of Ca(OH)_2 at different hydration times of C_3S , 5% CaCO_3 .

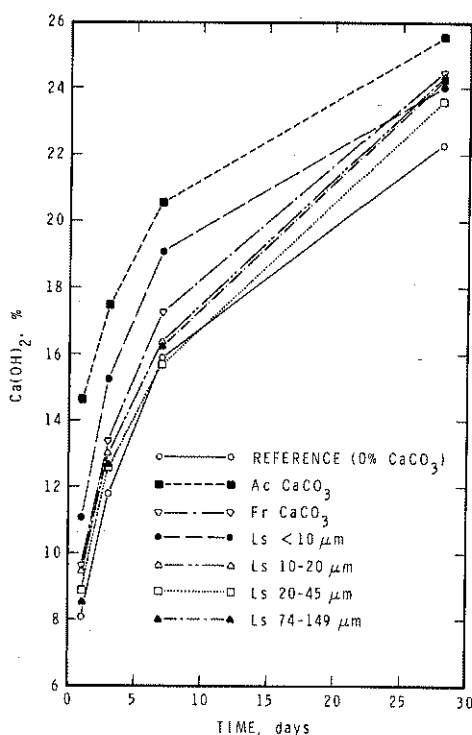


Fig. 5. Formation of Ca(OH)_2 at different hydration times of C_3S , 15% CaCO_3 .

estimated using percent non-evaporable-water content. This required determination of chemically-held water by CH and C-S-H phases. Weight loss was based on the loss between 100 and 1000°C in the TGA apparatus. The results (based on C_3S) for the samples containing 5 and 15% CaCO_3 are shown in Figs. 6 and 7, respectively.

The values for non-evaporable-water content are higher as the period of hydration increases. At a particular period of hydration they decrease as follows: C_3S -15% $\text{CaCO}_3 > \text{C}_3\text{S}$ -5% $\text{CaCO}_3 > \text{C}_3\text{S}$ -0% CaCO_3 . For samples containing no CaCO_3 , the value at 1 day is 4.9%, increasing to 16.1% at 28 days; values in the literature vary between 13% and 17% for C_3S hydrated for 28 days (Locher, 1966; Odler and Skalny, 1973; Valenti and Sabatelli, 1974). The non-evaporable water contents are highest for C_3S containing 15% Ac CaCO_3 . At 1 day, the addition of 15% Ac CaCO_3 to C_3S increases the non-evaporable water content by 120%, the corresponding value at 28 days being 30%. This indicates that acceleration of hydration is particularly high at early periods of hydration. As the particle size of CaCO_3 increases, the effect on acceleration decreases, the coarsest sample,

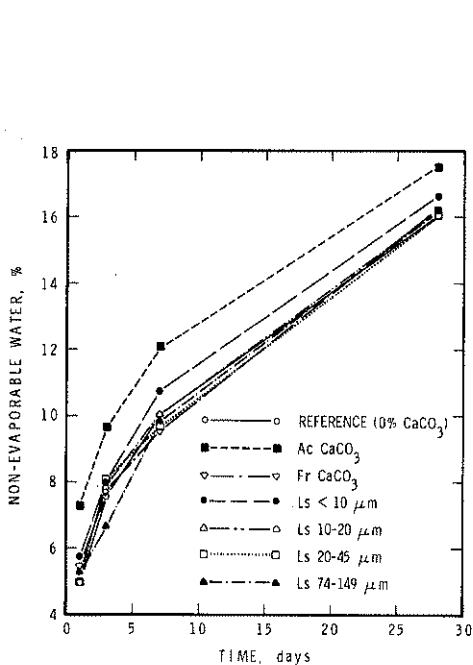


Fig. 6. Non-evaporable water content as a function of hydration time of C_3S , 5% $CaCO_3$.

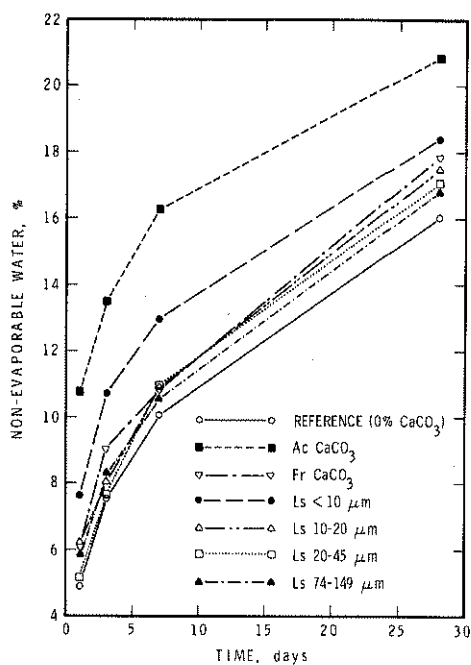


Fig. 7. Non-evaporable water content as a function of hydration time of C_3S , 15% $CaCO_3$.

size 74–149 μm , showing a 19% increase at 1 day and 5% at 28 days with respect to the reference sample (Fig. 7).

The hydration rate may also be monitored by determining the amount of C_3S remaining unhydrated at different times. Generally, the QXRD method is adopted for this purpose. Ramachandran (1971a) has shown that C_3S can be estimated by determining the area of the endothermal peak occurring at about 915°C (Triclinic \rightleftharpoons Monoclinic Transition, heat of transformation, 1 cal/g) in DTA.

Figure 8 shows the amount of C_3S hydrated at different times in mixtures with 0 and 5% $CaCO_3$. The results indicate that at all times more hydration has occurred in pastes containing higher-surface-area $CaCO_3$. These trends are similar to those based on determinations of $Ca(OH)_2$ and non-evaporable water content.

C_3S containing no $CaCO_3$ shows a degree of hydration of 21.5 and 63.0% at 1 and 28 days, respectively (Figs. 8–10). According to published values, the degree of hydration of pure C_3S may vary between 55 and 90% at 28 days, depending on surface area, estimation method, and curing conditions (Bentur and Berger, 1979; Berger et al., 1979; Bürge, 1983; Celani et al., 1966; Collepardi and Massidda, 1971b; Kantro et al., 1966; Kurczyk and Schwiete, 1960; Lawrence and Young, 1973; Locher, 1966;

Milestone, 1979; Mukherjee and Ludwig, 1973; Odler and Skalny, 1973; Ramachandran and Feldman, 1984; Rio et al., 1970; Valenti and Sabatelli, 1974; Young et al., 1973). Almost all CaCO_3 additions show an accelerating effect. In samples containing 15% CaCO_3 it is more significant, especially

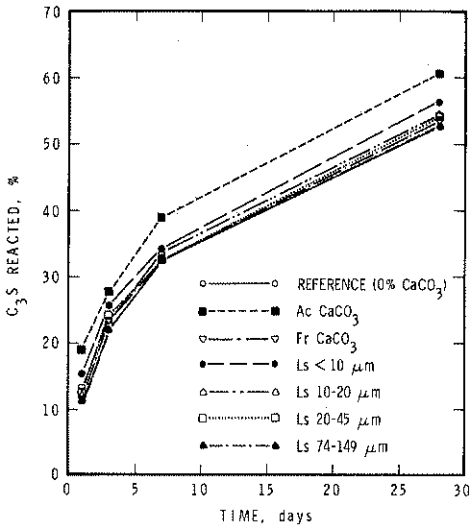


Fig. 8. Amount of C_3S hydrated as a function of hydration time, 5% CaCO_3 (C_3S basis).

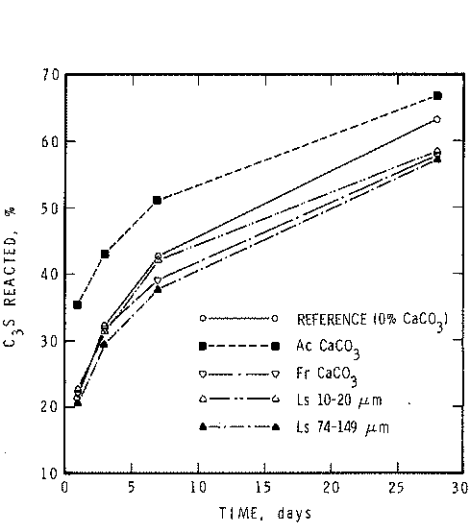


Fig. 9. Amount of C_3S hydrated as a function of hydration time, 15% CaCO_3 ($\text{C}_3\text{S} + \text{CaCO}_3$ basis).

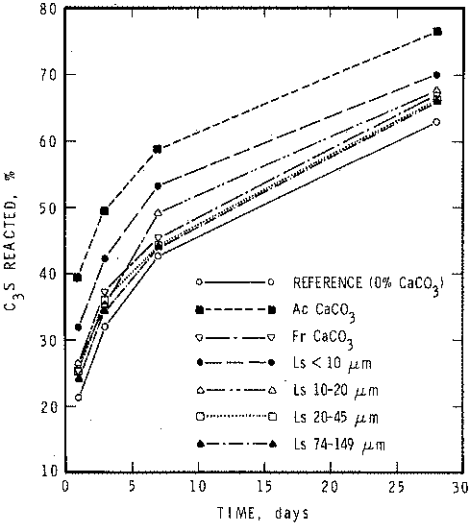


Fig. 10. Amount of C_3S hydrated as a function of hydration time, 15% CaCO_3 (C_3S basis).

when determined on the basis of C_3S (Figs. 9, 10). At 28 days $Ac\ CaCO_3$, $Ls (<10\mu m)$ and $Ls (74-149\ \mu m)$ show increases in hydration (with respect to the reference) equal to 21.6, 11.0 and 5.8%, respectively. Thus, the substantial accelerating effect of $CaCO_3$ is evident at 15% addition (Fig. 10).

Some correlation is also evident in the plot of percentage C_3S reacted versus percentage $Ca(OH)_2$ (Fig. 11). In the presence of $CaCO_3$, therefore, the C/S ratio of the C-S-H product may not be significantly affected, especially after hydration has proceeded beyond about 20%.

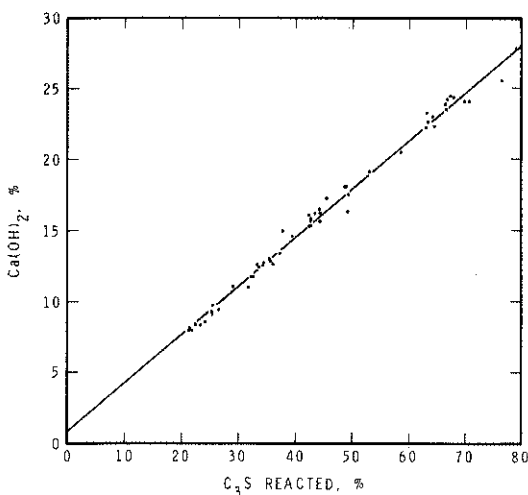


Fig. 11. Percentage C_3S hydration versus $Ca(OH)_2$ content in C_3S pastes, 0, 5 and 15% $CaCO_3$.

3.2 Rate of heat development

Conduction calorimetric curves giving the rate of heat development of C_3S during hydration up to 24 h, in the presence of 0, 5, 10, 15 and 50% $CaCO_3$, are shown in Figs. 12–16. Figures 12 and 13 refer to the effect of $Ac\ CaCO_3$. The onset of the accelerating period representing hydration of C_3S with 0% $CaCO_3$ occurs at about 1 h. In the presence of $CaCO_3$ it may occur about 30 min to 1 h earlier (Fig. 12). The larger the amount of added $CaCO_3$, the sooner acceleration starts. The amplitude of the peak is affected, the intensity (on C_3S basis) increasing as the amount of $CaCO_3$ increases. Comparison with the total amount of heat developed shows that at 24 h the total heat development decreases in the following manner: $C_3S-15\% CaCO_3 > C_3S-10\% CaCO_3 > C_3S-50\% CaCO_3 > C_3S-5\% CaCO_3 > C_3S-0\% CaCO_3$ (based on $C_3S + CaCO_3$ total weight). It may be concluded that $CaCO_3$ accelerates the hydration of C_3S . To eliminate the dilution effect of $CaCO_3$, the heat effect was re-calculated on the basis

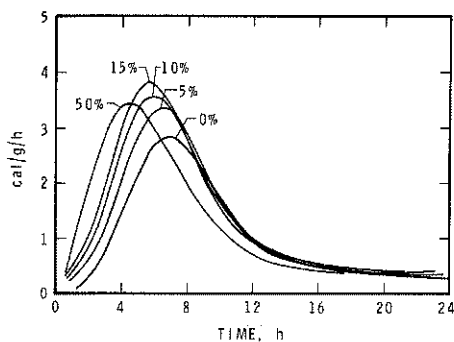


Fig. 12. Conduction calorimetric curves of C_3S hydrated with different amounts of Ac $CaCO_3$ ($C_3S + CaCO_3$ basis), $w/s = 0.7$.

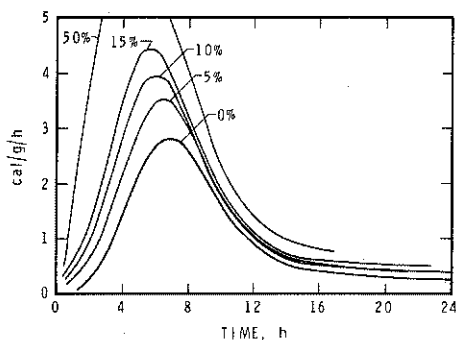


Fig. 13. Conduction calorimetric curves of C_3S hydrated with different amounts of Ac $CaCO_3$ (C_3S basis), $w/s = 0.7$.

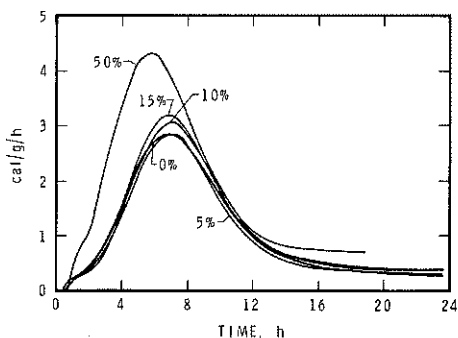


Fig. 14. Conduction calorimetric curves of C_3S hydrated with different amounts of Fr $CaCO_3$ (C_3S basis), $w/s = 0.7$.

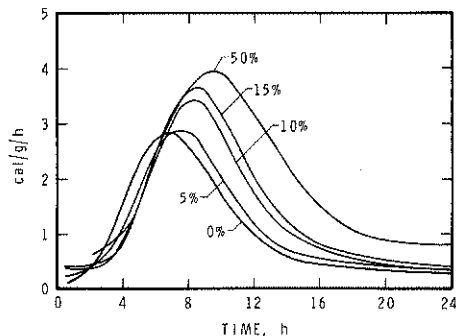


Fig. 15. Conduction calorimetric curves of C_3S hydrated with different amounts of powdered limestone, $L_s < 10 \mu m$ (C_3S basis), $w/s = 0.7$.

of C_3S (Fig. 13). The accelerating effect decreased as follows: $C_3S-50\% CaCO_3 > C_3S-15\% CaCO_3 > C_3S-10\% CaCO_3 > C_3S-5\% CaCO_3 > C_3S-0\% CaCO_3$.

Figure 14 refers to the effect of Fr $CaCO_3$ (coarser than Ac $CaCO_3$) on heat development. The effect is marginal during the induction period and the amplitude of the peaks is increased, although not to the same extent as shown in Fig. 13. Figure 15 shows the effect of fine particles of limestone ($< 10 \mu m$). The induction period is practically unaffected, and the peak is shifted towards longer times (with respect to the sample with 0% $CaCO_3$). The amplitude of the peaks, especially at 10, 15 and 50%, is higher, however. The slow rate of heat developed in the earlier period (in these mixes)

may be due to a coating formed on the particles during grinding. This coating matter may have originated with impurities present in the limestone or with the steel discs in the grinder. Water did not wet these particles as easily as it did the coarser ones.

The influence of CaCO_3 on the rate of hydration depended on the time interval chosen. At 10–15% CaCO_3 it is slightly retarding at 3–4 h, but accelerating at 1 day. Addition of admixtures such as triethanolamine induces such behaviour in C_3S (Ramachandran, 1972). As can be expected from other results, the coarser particles of CaCO_3 have a significantly lower accelerating effect on C_3S than fine particles (Fig. 16). The heat development at 1 day with 5% fine CaCO_3 (Fig. 13) is more than that developed in the presence of 50% coarse CaCO_3 (74–149 μm).

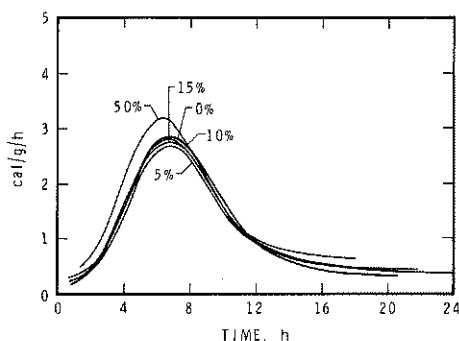


Fig. 16. Conduction calorimetric curves of C_3S hydrated with different amounts of powdered limestone, Ls 74–149 μm (C_3S basis), $w/s = 0.7$.

3.3 CaO/SiO_2 ratio

In the presence of certain admixtures such as CaCl_2 the C/S ratio of the C-S-H product changes, so that the degree of hydration based on either $\text{Ca}(\text{OH})_2$ or non-evaporable-water content may not show a good correlation with the rate of hydration of C_3S (Ramachandran, 1971b). The CaO/SiO_2 ratio of the C-S-H phase in C_3S pastes was calculated at different hydration times as follows.

By using a known amount of vacuum-dried paste and carrying out TGA, the percentage of ignited weight (m_2) and percentage $\text{Ca}(\text{OH})_2$ (m_3) were determined. Applying DTA, the percentage of unhydrated C_3S remaining in the paste was determined (m_4). The CaO/SiO_2 molar ratio can be computed (Ramachandran and Zhang, to be published) to be:

$$\frac{M_{\text{CaO}} \left(\frac{3(m_2 - m_4)}{M_{\text{C}_3\text{S}}} - \frac{m_3}{M_{\text{CH}}} \right)}{(m_2 - m_4) \frac{M_{\text{SiO}_2}}{M_{\text{C}_3\text{S}}}} \bigg/ M_{\text{SiO}_2}$$

where M_{CaO} , $M_{\text{C}_3\text{S}}$, M_{CH} and M_{SiO_2} are the molecular weights of CaO, C_3S , $\text{Ca}(\text{OH})_2$ and SiO_2 , respectively.

This can be simplified to

$$\text{CaO/SiO}_2 = 3 - 3.081 \frac{m_3}{m_2 - m_4}$$

A small amount of carbonation in some of the pastes has been taken into account for calculation, but it is not included in the equation. Similar calculations were also carried out for mixtures with added CaCO_3 . TGA was used to estimate CaCO_3 .

The C/S ratios of the C—S—H product are shown as a function of time in Fig. 17. The ratio increases more significantly between 1 and 3 days than at later periods. There is evidence that the paste containing CaCO_3 has a slightly higher CaO/SiO_2 ratio than that without CaCO_3 . As the particle size of CaCO_3 increases (not shown in the figure) the C/S ratio approaches the values for C—S—H formed in C_3S paste with 0% CaCO_3 .

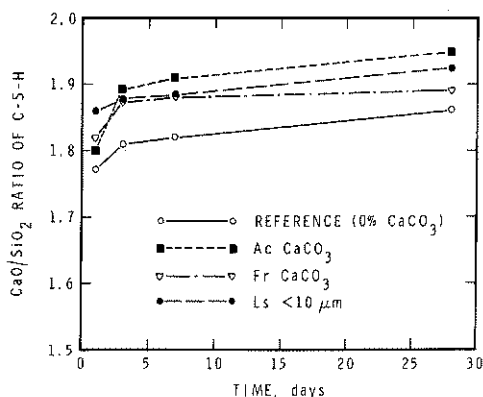


Fig. 17. CaO/SiO_2 ratios of C—S—H formed during hydration of C_3S , 15% CaCO_3 .

A part of the explanation for higher C/S ratios is that some CaCO_3 is incorporated into the C—S—H phase. At 28 days, the C/S ratio of the C—S—H phase for C_3S paste with 0% CaCO_3 is 1.86, compared with 1.95 for paste containing 15% Ac CaCO_3 . The C/S ratios quoted in the literature for C_3S paste hydrated for 28 days vary between 1.4 and 2.0 (Dent Glasser et al., 1978; Kondo and Daimon, 1969; Le Sueur et al., 1984; Taylor and Roy, 1980). The values depend on the w/s ratio and the method of determination. Use of lower w/s ratios tends to give higher C/S ratios. The chemical-extraction method yields lower values than thermal methods. For pastes prepared at a w/s ratio of 0.45, Locher (1966) obtained a C/S ratio of 1.5–1.6 using the chemical-extraction method, and a value of about 2.0 using the thermogravimetric method. It is possible that the chemical method may extract some of the bound CH from the C—S—H phase.

3.4 State of CaCO_3

It has been shown that, in the hydration of C_3A , calcium carbonate reacts with it to form a carboaluminate complex. Similarly, CaCl_2 forms a chloroaluminate complex with C_3A . Although it is assumed that CaCl_2 is inert with respect to hydrating C_3S , both Ramachandran (1971c) and Richartz (1969) found evidence that it is bound strongly as a complex with the C_3S paste. Experiments were therefore carried out to investigate whether CaCO_3 is also bound to the C_3S paste as a complex.

Thermogravimetric analysis of the $\text{C}_3\text{S} + \text{CaCO}_3 + \text{H}_2\text{O}$ system indicates that as hydration proceeds the peak due to CaCO_3 diminishes. This suggests that some CaCO_3 is consumed during the hydration reaction. Figure 18 shows the amount of free CaCO_3 remaining at different hydration times. In the $\text{C}_3\text{S}-\text{CaCO}_3$ mixture containing 15% Ac CaCO_3 and 5% Ac CaCO_3 , 14.5 and 25.0% of the added CaCO_3 reacted with the hydrating C_3S at three days. Consumption of CaCO_3 decreased as particle size increased, indicating that the reaction is influenced predominantly by the exposed surface. After three days of hydration there was little consumption of CaCO_3 in most samples.

Earlier work, in which the paste was heated to different temperatures, showed that the part of CaCO_3 that is combined with the C-S-H phase is released at or before 525°C (Ramachandran and Zhang, to be published). This has implications in terms of the accelerating effect of CaCO_3 on C_3S ,

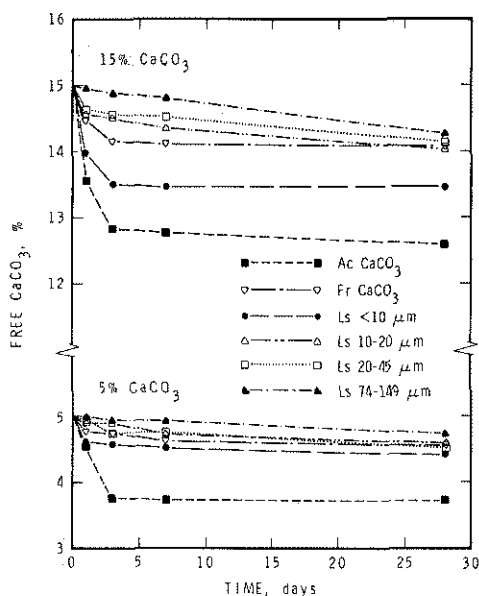


Fig. 18. Free CaCO_3 remaining in C_3S pastes at different times of hydration (based on $\text{C}_3\text{S} + \text{CaCO}_3$).

the determination of the optimum amount of CaCO_3 needed to replace gypsum (wholly or partly) in cement, and the durability of concrete containing CaCO_3 as a coarse or fine aggregate.

3.5 Accelerating mechanism

Some understanding of the hydration mechanism may be obtained by following the Ca^{2+} concentration in the solution. This is facilitated by using a higher w/s ratio than 0.7. Experiments were therefore conducted at a w/s ratio of 2.0, using 0, 15 and 50% Ac CaCO_3 . The conduction calorimeter curves are shown in Figs. 19 and 20.

Concentrations of Ca^{2+} in solutions of pastes containing 0, 15 and 50% Ac CaCO_3 are shown in Fig. 21. In pastes with 0% CaCO_3 , the Ca^{2+} concentration exceeded the saturation level at 15 min, continued to increase

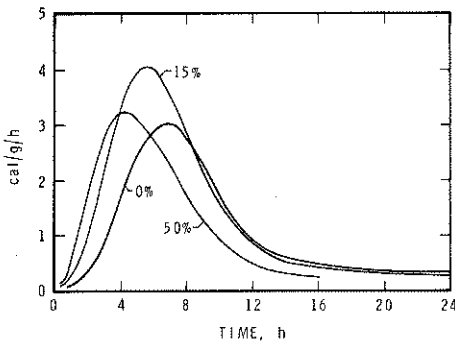


Fig. 19. Conduction calorimetric curves of C_3S hydrated with different amounts of Ac CaCO_3 ($\text{C}_3\text{S} + \text{CaCO}_3$ basis), w/s = 2.0.

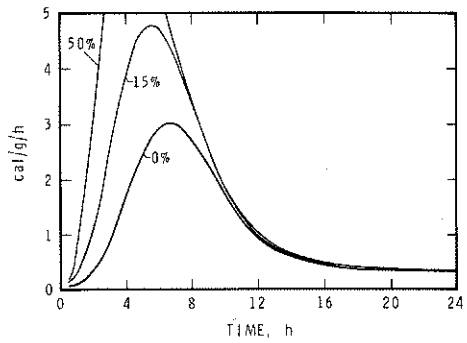


Fig. 20. Conduction calorimetric curves of C_3S hydrated with different amounts of Ac CaCO_3 (C_3S basis), w/s = 2.0.

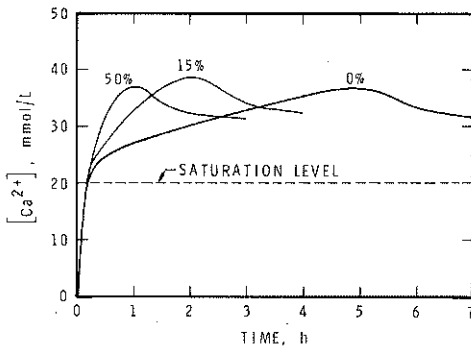


Fig. 21. Influence of CaCO_3 on concentration of Ca^{2+} in the solution phase during C_3S hydration.

to a peak at about 5 h, then decreased. Several investigators have observed that the peak of the Ca^{2+} concentration curve coincides with the termination of the induction period (Skalny and Young, 1980; Young et al., 1977). In the present work, the peak occurred several hours after the induction period had terminated (Figs. 19 and 20). In other words, at 5 h a substantial amount of C_3S had already hydrated. That the maximum Ca^{2+} concentration does not correspond to the end of the induction period has already been reported (Fierens and Verhaegen, 1976; Kurdowski and Nocun-Wezelik, 1983; Menetrier et al., 1980; Odler and Dörr, 1979; Skalny and Young, 1980; Slegers and Rouxhet, 1977; Taylor et al., 1984). This may imply

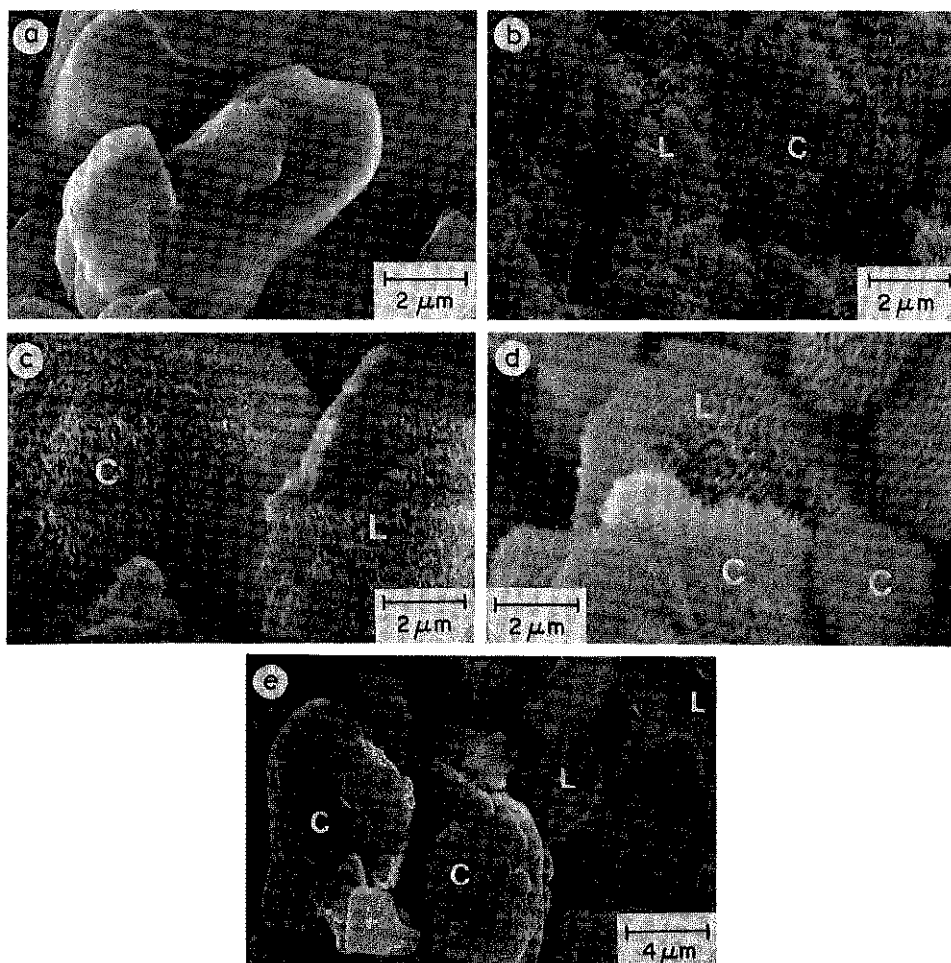
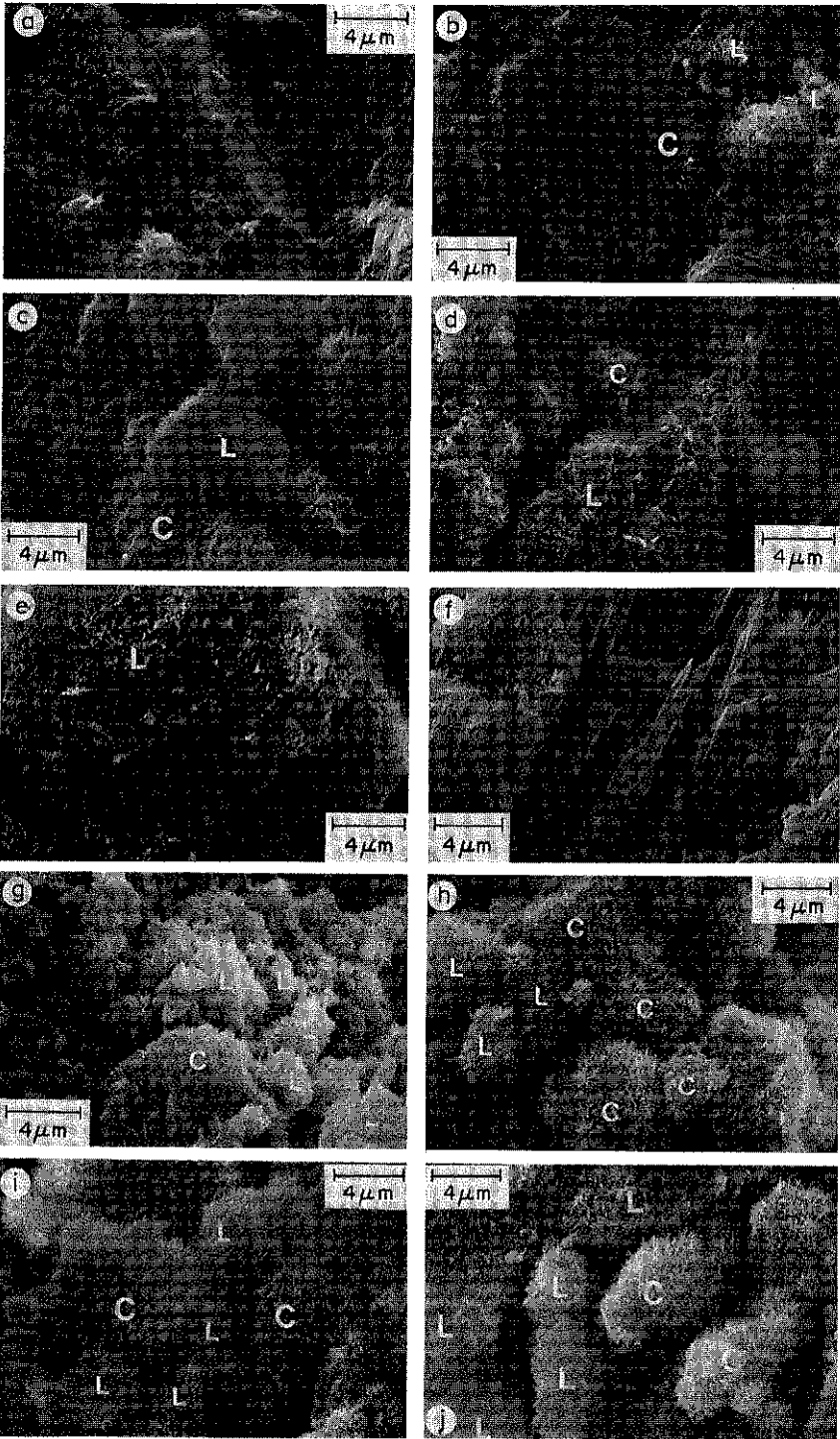


Fig. 22. Micrographs of C_3S pastes containing 0 or 50% CaCO_3 , hydrated for 1 day ($w/s = 0.7$) (C: Growth on C_3S ; L: Growth on calcium carbonate). (a) 0% CaCO_3 ; (b) 50% Ac CaCO_3 ; (c) 50% Fr CaCO_3 ; (d) 50% Ls $< 10 \mu\text{m}$; (e) 50% Ls $74\text{--}149 \mu\text{m}$.



that the nucleation of $\text{Ca}(\text{OH})_2$ crystals does not control the induction period. A possibility exists that crystalline $\text{Ca}(\text{OH})_2$ forming near the grain surfaces may act as nuclei. Localised $\text{Ca}(\text{OH})_2$ concentrations at or near the C_3S particles may be high (Berger and McGregor, 1973; Skalny and Young, 1980).

Conduction calorimetric curves for C_3S hydrated with 15 and 50% Ac CaCO_3 at $w/s = 2.0$ indicate that the rate of heat development in these mixes was higher than that with 0% CaCO_3 (Figs. 19 and 20). SEM studies show that very little hydration had taken place in any of the samples in the first 2 h. At 3 h only a small amount of hydration had occurred with 0% CaCO_3 , but a larger amount had formed with 50% CaCO_3 . At 6 h more hydrated products were formed in samples with 0% and 50% CaCO_3 . The microstructural results are in agreement with heat-development curves in Fig. 19. Total heat development was also higher in the presence of CaCO_3 . It is clear, therefore, that the addition of Ac CaCO_3 accelerates C_3S hydration.

The Ca^{2+} ion concentration of the solution increased sharply in the presence of Ac CaCO_3 , that with 50% showing a peak at about 1 h and that with 15% having a peak at 2 h (Fig. 21). In both samples the peak of the Ca^{2+} ion concentration occurred close to the acceleration peak effect. SEM studies (of C_3S hydrated at $w/s = 0.4$ and 0.7) show that the hydration product grows in the form of fibres on both C_3S and CaCO_3 (Figs. 22 and 23). SEM microanalysis of the surface indicated the existence of Si and Ca in these fibrous particles. The paste hydrated with 0% CaCO_3 showed columns of $\text{Ca}(\text{OH})_2$ dispersed in the matrix (Fig. 23a,f), but that with CaCO_3 only occasionally showed columns or plates (Fig. 23b-e, g-j).

The fibrous growth of the hydrated products on CaCO_3 may indicate that calcium carbonate particles are acting as nuclei. Growth of CH and C-S-H would decrease the concentration of ions in the solution phase and accelerate their transfer from the C_3S surface to the solution phase. C-S-H formed on the CaCO_3 surface may incorporate some CaCO_3 .

The preferential formation of large crystals of $\text{Ca}(\text{OH})_2$ in paste without CaCO_3 may be explained as follows: in normal hydration of C_3S , $\text{Ca}(\text{OH})_2$ grows into large crystals in the pore spaces. In the presence of high-surface-area CaCO_3 , $\text{Ca}(\text{OH})_2$ grows preferentially on the innumerable sites available and this would prevent local growth in a particular area.

Figure 18 shows that in the early period of hydration some CaCO_3 is incorporated into the C-S-H phase. If this were to occur in the C-S-H

Fig. 23. Micrographs of C_3S pastes containing CaCO_3 of different particle sizes, hydrated for 28 days. (C: Growth on C_3S ; L: Growth on calcium carbonate). (a) 0% CaCO_3 , $w/s = 0.4$; (b) 15% Ac CaCO_3 , $w/s = 0.4$; (c) 15% Fr CaCO_3 , $w/s = 0.4$; (d) 15% Ls < 10 μm , $w/s = 0.4$; (e) 15% Ls < 74–149 μm , $w/s = 0.4$; (f) 0% CaCO_3 , $w/s = 0.7$; (g) 50% Ac CaCO_3 , $w/s = 0.7$; (h) 50% Fr CaCO_3 , $w/s = 0.7$; (i) 50% Ls < 10 μm , $w/s = 0.7$; (j) 50% Ls < 74–149 μm , $w/s = 0.7$.

formed at the surface of C_3S it could result in the formation of a higher permeable C—S—H membrane, or this phase might itself be a nucleating agent for the hydrated products. Either possibility could result in accelerated C_3S hydration.

Fibrous growth occurred over all the particles of C_3S and $CaCO_3$ (Fig. 23) and C/S ratio (by microanalysis) varied between 1.9 and 17, indicating that C—S—H formed on both C_3S and $CaCO_3$. Generally, the C/S ratios of the hydrated C_3S particles varied between 1.9 and 2.4; those on the $CaCO_3$ particles varied in the range 5–17. The higher values on $CaCO_3$ can be attributed to (1) background excitation from $CaCO_3$, because the hydrated products on the $CaCO_3$ surface are thin, and (2) the incorporated $CaCO_3$ in the C—S—H phase. Generally, it is known that C—S—H forms as an "inner" and an "outer" product close to the original unhydrated C_3S (Fig. 23b), whereas CH formation is not confined to this boundary (Dent Glasser et al., 1978; Pommersheim and Clifton, 1982; Skalny and Young, 1980). In the presence of $CaCO_3$ it appears that silicate ions can migrate farther from the confines of the C_3S phase and grow as C—S—H on the $CaCO_3$ particles.

As already shown, the rate of hydration is increased as the amount and surface area of $CaCO_3$ are increased. This is reflected in the growth of hydration products (Fig. 22). It is expected that both factors also enhance nucleation and surface interaction effects on the hydrating C_3S surface.

CONCLUSIONS

Addition of $CaCO_3$ increases the rate of hydration of C_3S and this accelerating effect increases as the particles sizes become finer and the amount of $CaCO_3$ is increased. The C/S ratio of C—S—H is modified slightly. There is evidence of partial incorporation of $CaCO_3$ into the C—S—H phase. The hydrate products form on both $CaCO_3$ and C_3S particles. Acceleration may result from a nucleating effect of $CaCO_3$ and modification of the C—S—H membrane forming over the hydrating C_3S surface. In addition to existing as "inner" and "outer" products, the C—S—H phase may also grow outside the confines of these zones.

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