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STUDY OF THE HYDRATION PRODUCTS OF THE SYSTEM $CaO—Al_2O_3—SO_3—SiO_2$ WITH VARYING CaO MOLE RATIO

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ABSTRACT

The hydrated phases of the system $CaO—Al_2O_3—SO_3—SiO_2$ were studied, and the effect of the presence of varying amounts of CaO on the hydrated phases was also investigated. These phases were assessed by the aid of differential thermal analysis (DTA) and X-ray diffractometry. The hydration kinetics of the pastes under study were followed by the determination of the chemically combined water.

Results revealed that 1 mole of CaO in excess reacts with the available SiO_2 and initiates the formation of sulphoaluminate hydrates. As the CaO is increased, the amount of such hydraulic phases is increased and, accordingly, the rate of hydration enhanced. The addition of 2 moles of CaO results in the formation of appreciable amounts of ettringite among the sulphoaluminate hydrates, but some anhydrous forms still exist. On the other hand, 4 moles give better formation of the hydraulic phases and some excess $Ca(OH)_2$ is also detected.

INTRODUCTION

The products formed during the hydration of slags with different activators, such as $CaSO_4$, CaO or portland cement clinker, are very important in studying the hydration reactions of slag, supersulphated and pozzolanic cements. These cements are usually prepared from granulated slag, gypsum, pozzolana and lime or portland cement [1]. The hydraulic properties of such cements are said to be due to the formation of certain products such as Ca sulphoaluminate hydrates and Ca silicate hydrates [2]. Gehlenite hydrate (C_2ASH_8) * is formed by the reaction of lime, released from C_3S or β-C_2S during hydration, with Ca aluminate ($C_{12}A_7$, CA_2) or Ca sulphoaluminate $C_4A_3\overline{S}$ [3]. It was found that solutions rich in lime and gypsum decompose the gehlenite hydrate and produce ettringite when the $C/\overline{S}$ ratio of the hydrate is decreased. Solutions rich in CaO and poor in SO_3, however, favour the gehlenite hydrate formation.

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* Normal cement notation has been used in this work, viz. C = CaO, S = SiO_2, A = Al_2O_3, $\overline{S}$ = SO_3, and H = H_2O.

Forsen [4], Mori [5], and Copeland and Kantro [6] pointed out that $Ca(OH)_2$, either added or liberated during the hydration of alite, controls the reactions leading to the formation of ettringite, even in the early stages of C_3A hydration with gypsum. Mehta [7] concluded that the presence of lime somewhat retarded the hydration of $C_4A_3\bar{S}$ during the first 6-h period; thereafter the hydration proceeded uniformly until no anhydrous $C_4A_3\bar{S}$ was detected after 7 days. Lime, accordingly, initially slightly reduced the rate of ettringite formation. Collepardi et al. [8] also reported that the hydration rate of $C_4A_3\bar{S}$ was reduced when $Ca(OH)_2$ and gypsum were added simultaneously to the system.

The activating action of $Ca(OH)_2$ upon the hardening process of calcium silicates in C_2S, C_3S_2, and CS slags is certainly ascertained. Thus, while a group of researchers [9,10] consider that the role of $Ca(OH)_2$ is to provide a certain basicity to the medium, thus permitting a relatively high-speed formation of hydrosilicates, others [11] consider that, in the process of hydration the silicate slag binds the resulting calcium hydroxide.

In a previous work, the authors studied the hydration of the system CaO—Al_2O_3—SO_3 with varying amounts of silica [12]. They found that 1 mole of SiO_2 added to the stoichiometric composition of trisulphate (3 CaO · Al_2O_3 · 3 $CaSO_4$) favours the formation of ettringite on hydration. When the silica was increased, the hydration products showed no hydraulic properties and calcium sulphoaluminate hydrates were not formed. The authors suggested that silica added in excess (2 and 4 moles) tries to interact with the available CaO, giving calcium aluminosilicates (C_2AS, CAS_2), which delays the formation of $C_4A_3\bar{S}$, and consequently retards the formation of any of the calcium sulphoaluminate hydrates on hydration.

The present work deals with the influence of varying amounts of CaO on the hydration products of the system CaO—Al_2O_3—SO_3—SiO_2 after 3 h, 1, 3, 7 and 28 days. The formed phases were identified by DTA and X-ray analyses. In addition, the chemically combined water was measured to follow the hydration kinetics of the system under investigation.

EXPERIMENTAL

The following anhydrous mixes were prepared using analytical grade reagents [13].

Mix 1: 3 CaO—Al_2O_3—3 $CaSO_4$—2 SiO_2;
Mix 2: 4 CaO—Al_2O_3—3 $CaSO_4$—2 SiO_2;
Mix 3: 5 CaO—Al_2O_3—3 $CaSO_4$—2 SiO_2;
Mix 4: 7 CaO—Al_2O_3—3 $CaSO_4$—2 SiO_2.

The ignited samples were hydrated with distilled water, using a water/cement ratio of 10.0. Samples were weighed into polyethylene bottles with the appropriate volume of water and sealed during the hydration period. After the pre-determined curing time, the hydration of the sample was stopped using the technique described previously [14,15]. The phase constitution of each paste after 3 h, 1, 3, 7 and 28 days was followed using DTA and X-ray analysis. Moreover, the chemically combined water, W_n, was also determined by heating the samples to constant weight at 1000° C, to trace the hydration kinetics of the hardened pastes. In all these studies, samples of the same weight were taken for the sake of comparison.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the samples of mix 1. This mix has 2 moles of silica over the stoichiometric composition of the trisulphate ($3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4$). The phase composition of the anhydrous sample (fired at 1250° C) reveals the presence of extensive amounts of $CaSO_4$, gehlenite (C_2AS) and small amounts of the Ca sulphoaluminate ($C_4A_3\bar{S}$). Hydration of this sample for 3 h shows insignificant change in its phase composition. Moreover, using X-ray diffractometry, no other hydrated products were ever seen when the curing time was increased to 28 days. Calcium silicate hydrate, on the other hand, is expected to be formed

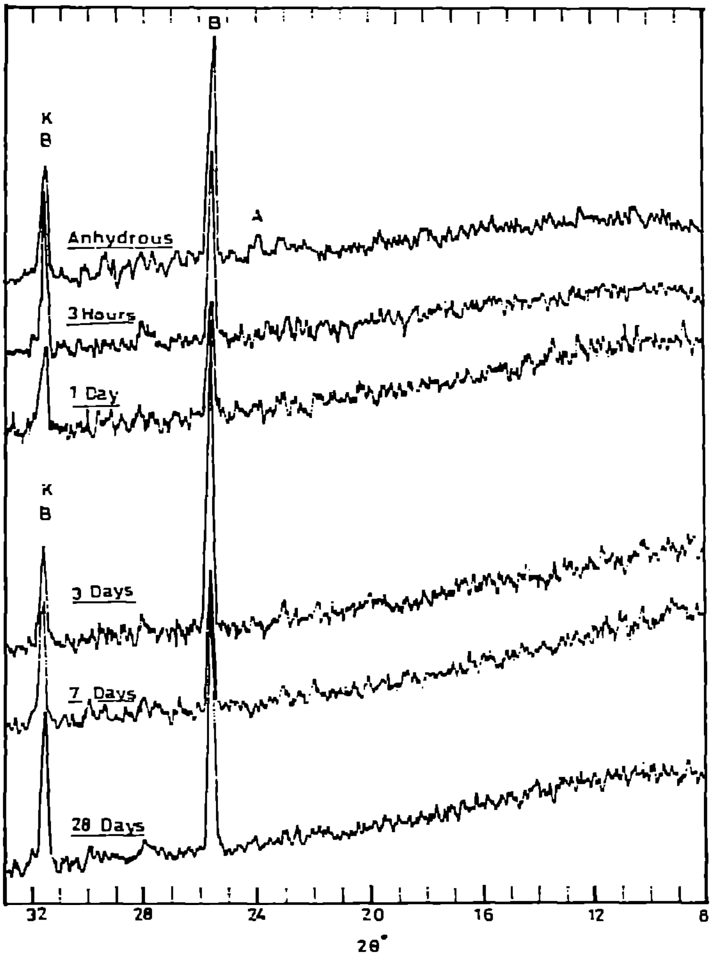


Fig. 1. X-Ray diffraction patterns of mix 1 samples after different curing periods. A, $3\ CaO \cdot 3\ Al_2O_3 \cdot CaSO_4$; B, $CaSO_4$; and K, gehlenite (C_2AS).

in such pastes but it is hardly detected because it is a poorly crystalline phase and is traced with difficulty by X-ray.

Differential thermograms of these samples are shown in Fig. 2, which shows the appearance of two endothermic effects. Their peak temperatures are at about 150 and 280°C and are related to the dissociation of calcium silicate hydrate, Ca sulphoaluminate or aluminate hydrates. Since the X-ray study of this mix has indicated the absence of Ca sulphoaluminate in the hydrated pastes, these endotherms are mainly due to the presence of the silicate or aluminate hydrates. Prolonged curing of these samples shows insignificant changes and no other thermal effects were seen when the time was increased from 3 h to 28 days. It could be concluded that the presence of increased amounts of silica favours the dissociation of $C_4A_3\bar{S}$ in the anhydrous sample, with the subsequent formation of gehlenite. The latter has no hydraulic properties, except in the presence of CaO where gehlenite hydrate may form on hydration [3].

X-Ray diffraction patterns of mix 2 samples are illustrated in Fig. 3. These samples contain 1 mole of CaO more than the previous mix, i.e. this mix contains 2 moles of SiO_2 and 1 mole of CaO more than the stoichiometric composition of the trisulphate. The anhydrous sample consists of $CaSO_4$ as the main component, with some gehlenite (C_2AS) and small amounts of $C_4A_3\bar{S}$. However, minute amounts of $2(C_2S) \cdot C\bar{S}$ were found to co-exist. Three hours of hydration of these samples reveal insignificant changes. Curing for 1 day, however, sees the disappearance of $C_4A_3\bar{S}$, while the other phases still exist. Three days of hydration result in the formation of some ettringite along with the co-existing phases $CaSO_4$ and gehlenite. The ettringite formation was found to diminish after hydration for 7 and 28 days; it

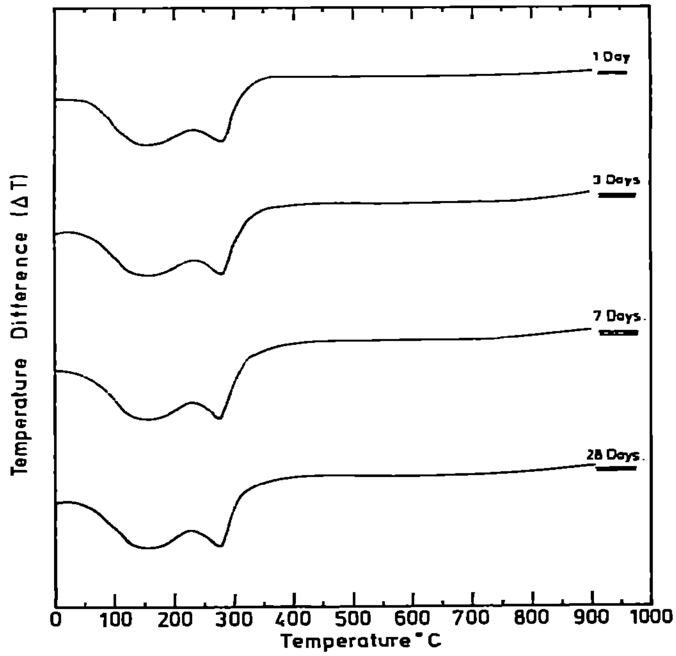


Fig. 2. Differential thermograms of mix 1 samples after different curing periods.

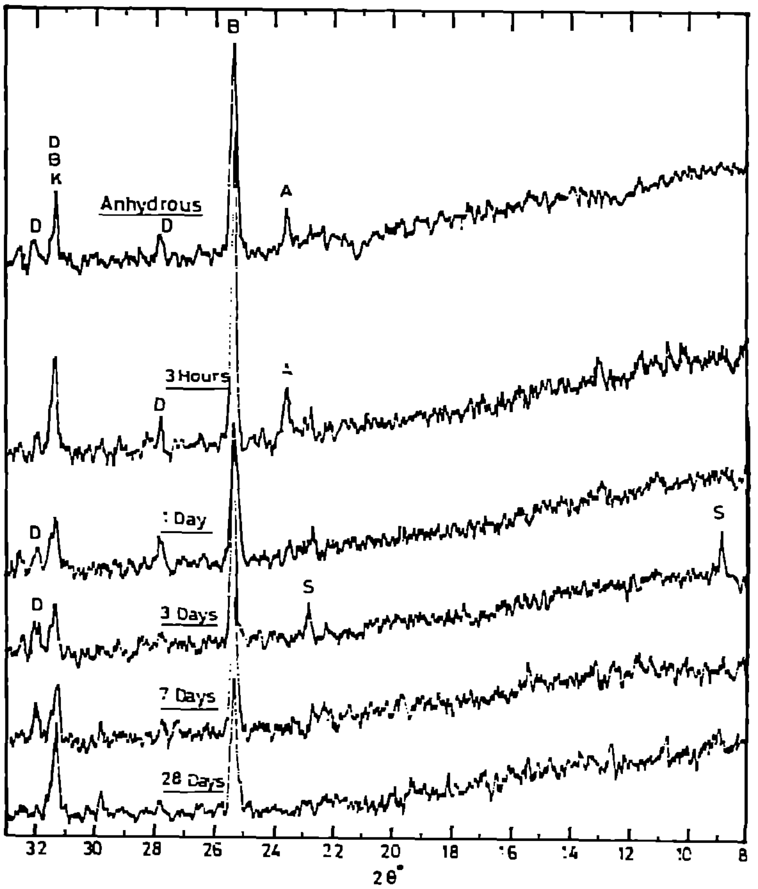


Fig. 3. X-Ray diffraction patterns of mix 2 samples after different curing periods. A, 3 CaO · 3 Al_2O_3 · $CaSO_4$; B, $CaSO_4$; D, $2(C_2S) \cdot C\bar{S}$; K, gehlenite; and S, ettringite.

may be transformed into the solid solution of the two sulphoaluminate hydrates. The presence of ettringite in the early ages of hydration of this mix is related to the presence of more CaO than in mix 1. Such CaO content is not sufficient to react with all the $CaSO_4$ and $C_4A_3\bar{S}$ to give the maximum formation of ettringite; accordingly, the partial formation of the latter was evident.

DTA of mix 2 samples are shown in Fig. 4. The examined samples show three endothermal peaks at about 150, 280 and 510°C. Thermal effects at 150 and 280°C are due to the presence of Ca silicate hydrates and sulphoaluminate hydrates, respectively. The peak at 510°C, on the other hand, characterises the presence of $Ca(OH)_2$. However, it should be noted that the intensity of the first two peaks was enlarged when the curing time reached 3 days, after which there was insignificant change until 28 days. Moreover, the $Ca(OH)_2$ characteristic peak was absent after 7 and 28 days. This means that the rate of hydration increases from 1 to 3 days and all the liberated CaO was consumed in the reaction, forming the ettringite and/or the solid solution of the sulphoaluminates. Thus, there is no possibility of $Ca(OH)_2$ being formed.

Figure 5 demonstrates the X-rays of mix 3 samples. This mix contains 2

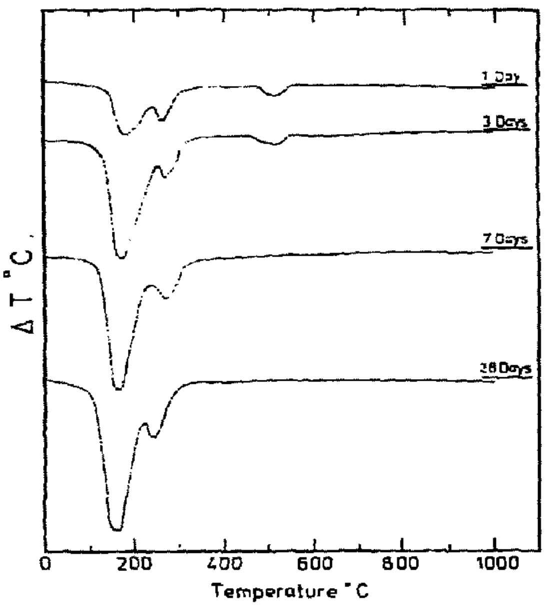


Fig. 4. Differential thermograms of mix 2 samples after different curing periods.

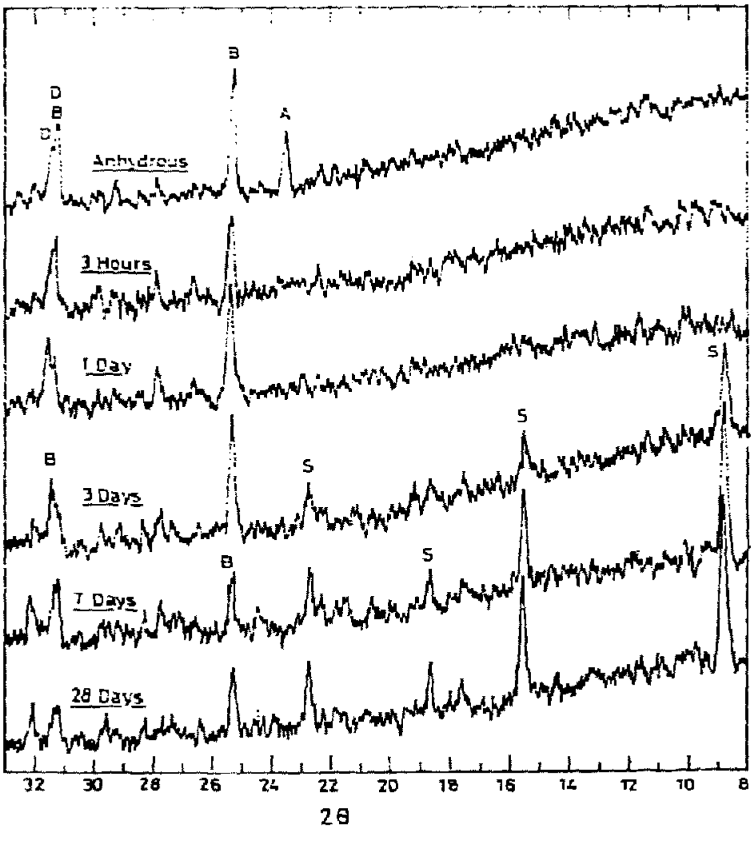


Fig. 5. X-Ray diffraction patterns of mix 3 samples after different curing periods. A, 3 CaO · 3 Al_2O_3 · $CaSO_4$; B, $CaSO_4$; D, $2(C_2S) \cdot C\overline{S}$; and S, ettringite.

moles of CaO more than mix 1 and 1 mole more than mix 2. From Fig. 5, it is clear that the anhydrous sample consists of $CaSO_4$, anhydrous $C_4A_3\bar{S}$ and $2(C_2S)\cdot C\bar{S}$. The intensities of the peaks reveal the predominance of $CaSO_4$ and the presence of Ca sulphoaluminate and $2(C_2S)\cdot C\bar{S}$ in appreciable amounts. On hydration for 3 h and 1 day, the only phases identified were $CaSO_4$ and $2(C_2S)\cdot C\bar{S}$. Hydration for 3 days, on the other hand, causes the formation of appreciable amounts of ettringite along with some residual unreacted $CaSO_4$ and $2(C_2S)\cdot C\bar{S}$. The intensities of ettringite peaks increased with the increased hydration period. Longer curing times show the presence of ettringite as the main component, with some unreacted $CaSO_4$. These findings confirm the previously postulated criterion seen in mix 2 where more CaO in mix 3 gives better formation of ettringite. It could be observed that the ettringite formation in the hydrated samples of mix 3 is much greater than the corresponding ones of mix 2 because mix 3 contains more CaO than mix 2. Meanwhile, the presence of unreacted $CaSO_4$ in mix 3 is related to the presence of CaO in lower amounts than required for completion of the reaction (ettringite formation). The deficiency of CaO allows the $CaSO_4$ to co-exist unreacted.

The differential thermograms of mix 3 samples are shown in Fig. 6, from which it is clear that most of the tested samples show four endothermal effects, with their peaks at 160, 280, 490 and 780° C. The first peak is related to the presence of ettringite and Ca silicate hydrate, while the second may be attributed to the solid solution of the two sulphoaluminate hydrates. Endothermic peaks at 490 and 780° C are related to the presence of $Ca(OH)_2$ and

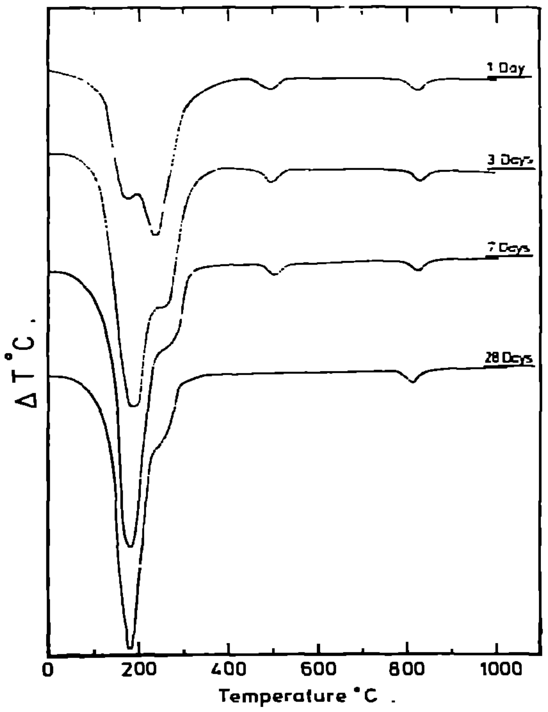


Fig. 6. Differential thermograms of mix 3 samples after different curing periods.

$CaCO_3$, respectively. The intensities of the first two endotherms at 160 and 280°C indicate that small amounts of ettringite are formed after 1 day but this increases as the hydration proceeds from 1 to 28 days. Such an increase in the ettringite formation was found to be at the expense of the monosulphate which decreased on ageing. Higher ageing times, however, reveal the presence of monosulphate hydrate in small amounts. It should be noted that $Ca(OH)_2$ disappeared after 28 days; this is related to its total consumption in the formation of sulphoaluminate hydrates. These findings are in agreement with the results deduced from X-ray diffractometry of this mix.

Figure 7 shows the X-ray diffraction of mix 4 samples which represent the presence of 4 moles of CaO more than mix 1. The anhydrous sample consists of C_4A_3S, $CaSO_4$, CaO and $2(C_2S) \cdot CS$. There is an insignificant change in such phase composition after hydration for 3 h but after 1 day, $Ca(OH)_2$ appears with the subsequent decrease of $C_4A_3\bar{S}$ and $CaSO_4$. Moreover, ettringite starts to appear in comparatively small amounts at such early ages of hydration. The intensities of the ettringite peaks demonstrate its increase as the time was increased to 3 days. Meanwhile, $CaSO_4$ seems to diminish, the amount of anhydrous $C_4A_3\bar{S}$ decreases and $Ca(OH)_2$ remains constant. In addition to this, small amounts of $2(C2S) \cdot C\bar{S}$ are evidenced after 3 days. As

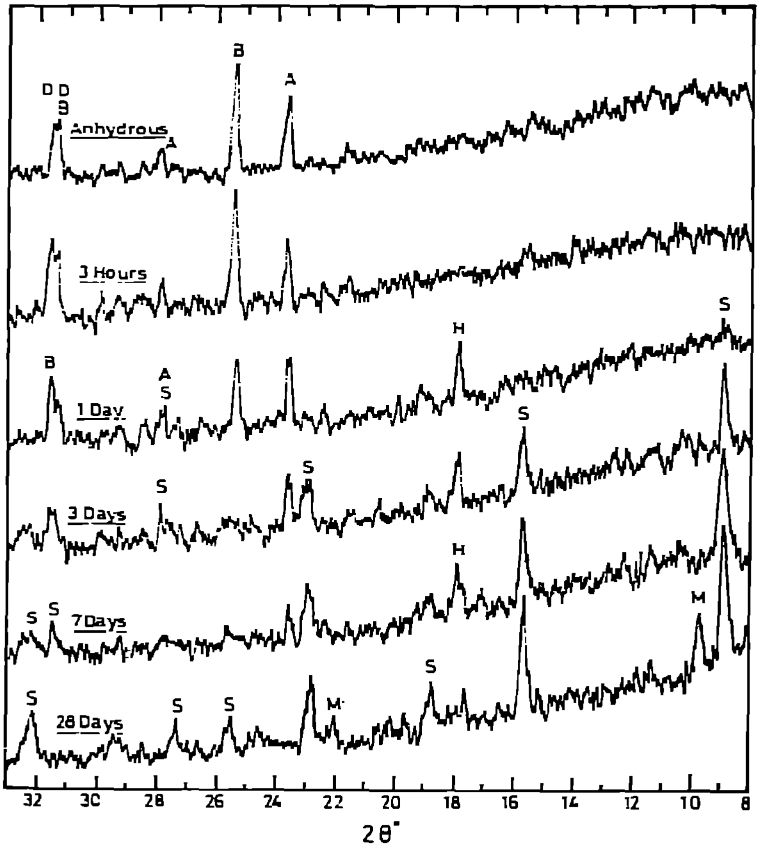
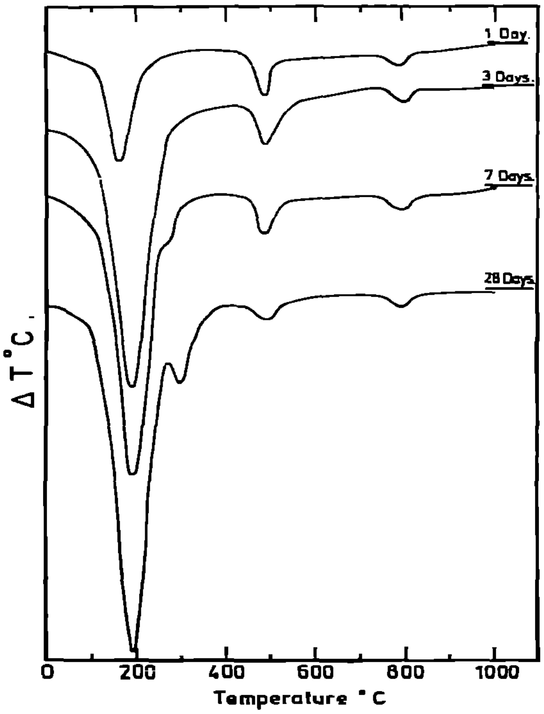


Fig. 7. X-Ray diffraction patterns of mix 4 samples after different curing periods. A, $3 CaO \cdot 3 Al_2O_3 \cdot CaSO_4$; B, $CaSO_4$; D, $2(C_2S) \cdot C\bar{S}$; H, $Ca(OH)_2$; M, monosulphate and S, ettringite.

the time proceeds to 7 and 28 days, the ettringite formation predominates with the presence of appreciable amounts of $Ca(OH)_2$ and residual anhydrous $C_4A_3\bar{S}$. The latter diminishes after 28 days, leaving the well-defined ettringite, $Ca(OH)_2$ and the monosulphate as the only phases identified at this ageing time. It could be postulated that the formation of monosulphate is due to the presence of CaO in amounts higher than required by the stoichiometric composition of the ettringite. This deduction is confirmed by the presence of $Ca(OH)_2$ even after 28 days and the earlier disappearance of $CaSO_4$. It could be concluded that the presence of 4 moles of CaO in excess in mix 4 favours the consumption of all the anhydrous forms; $CaSO_4$ and $C_4A_3\bar{S}$ resulting in the complete formation of ettringite. CaO in this mix is, on the other hand, more than that required for the ettringite formation in the above-mentioned way. Excess CaO acts to form the monosulphate or exists as a separate hydrated phase [$Ca(OH)_2$].

DTA of group 4 samples are shown in Fig. 8, from which it is clear that the hydrated samples, after different curing periods, exhibit three endothermic effects at 190, 490 and 780°C. These peaks characterise the presence of ettringite and/or Ca silicate hydrate, $Ca(OH)_2$ and $CaCO_3$, respectively. It should be noted, however, that although the endotherms for the hydroxide and carbonate are nearly constant, that of the ettringite varies according to the curing time. The latter observation means the progressive increase in the ettringite formation as the hydration proceeds. An additional point of interest is the appearance of the high-temperature endotherm, denoting the



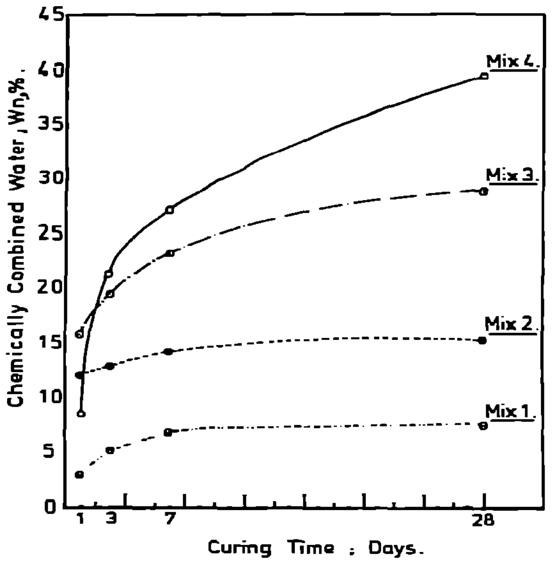


Fig. 8. Differential thermograms of mix 4 samples after different curing periods.

Fig. 9. Hydration kinetics of the mixes used.

presence of $CaCO_3$. despite its absence in the X-ray diffractometry of these samples. This may be due to its presence in relatively small amounts (below the X-ray limits of accuracy of $<5\%$). An additional low-temperature endotherm at about 280°C was observed after 7 days and became very pronounced after 28 days of hydration. This peak characterises the presence of the monosulphate hydrate or the solid solution of the two sulphoaluminates. Meanwhile, it was observed that the marked increase of this endotherm from 7 to 28 days was accompanied by the subsequent decrease of the $Ca(OH)_2$ endotherm under the same conditions. These results are in agreement with the X-ray findings and confirm the previously postulated presence of the monosulphate after 28 days of hydration.

Figure 9 shows the hydration kinetics of the various mixes as a function of the curing time. As mentioned previously, the chemically combined water, W_n, was taken as a measure of the degree of hydration of the hardened samples. Mix 1 shows a slight increase in hydration as the time increases from 1 to 7 days but only an insignificant change could be seen from 7 to 28 days. The addition of 1 mole of CaO results in a pronounced increase in the hydration kinetics of mix 2. A slight change in the hydrated samples followed on ageing. The marked increase in the degree of hydration in mix 2, as compared with mix 1, is readily observed and can be related to the pronounced decrease in non-hydraulic constituents, e.g. gehlenite and the subsequent formation of the sulphoaluminate hydrates.

When the sample has 2 moles of CaO in excess (mix 3), a slight increase in the early stages of hydration is evident in comparison with mix 2. The increase in the hydration rate becomes vigorous and intensive after 1 day and follows almost the same rate from 7 to 28 days of curing. The pronounced increase in the hydration kinetics is again related to the presence of more hydraulic components with the gradual decrease of the non-hydraulic phases. The comparatively slow rate of increase in this mix after 1 day could be partly related to the presence of a relative excess of $Ca(OH)_2$ which acts as a retarder for the formation of calcium sulphoaluminate hydrates [7]. After 3 days, the formed film becomes unstable, because the progressive formation of ettringite requires the consumption of this film in the reaction with $CaSO_4$ and $C_4A_3\bar{S}$; accordingly, a pronounced increased rate of hydration follows. In the case of mix 4 which contains 4 moles of CaO in excess, the above-mentioned phenomenon is exaggerated. There is a pronounced decrease in the hydration kinetics of this mix after 1 day, whereas longer ageing reveal a marked increase. The decrease in the hydration after 1 day is discussed in the light of the presence of more excess CaO than in all the previous mixes, where it forms a thick coat retarding the hydration at such low ageing times. As the hydration proceeds, such a film is removed and reacts with the other anhydrous forms, forming the Ca sulphoaluminate hydrates. It should be noted, however, that as this coat re-dissolves, the amounts of the hydraulic constituents are increased and this explains the marked increase in the hydration kinetics of this mix after 3, 7 and 28 days.

CONCLUSIONS

The following conclusions may be drawn from the above findings.

(1) Addition of 2 moles of SiO_2 to the stoichiometric composition of the trisulphate favours the dissociation of $C_4A_3\bar{S}$ and forms gehlenite. On hydration, it gives the non-hydraulic phases $CaSO_4$, gehlenite and some Ca-silicate hydrates.

(2) 1 mole of CaO added to the previous mixes reacts with the excess SiO_2 present and the hydraulic compounds begin to form.

(3) 2 moles of CaO accelerate the formation of the sulphoaluminate hydrates. Some residual unreacted anhydrous phases are still present ($CaSO_4$ is predominant).

(4) When the CaO content reaches 4 moles, better formation of the hydraulic compounds (mainly ettringite and Ca sulphoaluminate hydrates) occurs. Excess CaO is still present in such a mix which on hydration forms $Ca(OH)_2$. This delays the hydration in the early stages and results in a pronounced increase afterwards. Some of the excess $Ca(OH)_2$ reacts with the atmospheric CO_2 to form $CaCO_3$.

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