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HYDRATION CHARACTERISTICS OF METAKAOLIN–LIME–GYPSUM

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ABSTRACT

The hydration characteristics of some metakaolin–lime–gypsum mixtures were studied by the determination of their hydration products using XRD as well as DTA techniques. The effect of the phase constituents on the compressive strength of the hardened pastes was also investigated. The results revealed that at all ages of hydration the compressive strength increases with the increase in gypsum content up to 10% and then decreases. Generally, the compressive strength of these pastes increases with curing time. Pastes with 15 and 20% gypsum show an increase in strength for seven days and then deteriorate. The gehlenite hydrate is formed in pastes with small amounts of gypsum (5–10%), whereas the presence of enough gypsum (15–20%) prevents the formation of gehlenite with an increase in the ettringite phase.

INTRODUCTION

The physicomechanical properties of hardened cement pastes depend on the type of hydration products. It is well known that calcium silicate hydrate (CSH), calcium aluminate hydrate (C_4AH_{13}), gehlenite hydrate (C_2ASH_8) and hydrogarnet (C_3ASH_6) are the main hydration products formed during the hydration of clay–lime mixtures [1–5].

Supersulphated cements are usually prepared from mixtures of granulated slag, anhydrite and lime or portland cement [6]. The hydraulic properties that develop in such cements are due to the hydration products of calcium sulphoaluminates and calcium silicates. Therefore, pozzolanas, which, chemically, are aluminosilicates, when activated by lime–gypsum would produce such supersulphated pozzolanic cements on hydration because of the formation of calcium sulphoaluminate hydrates, e.g., ettringite and calcium silicate hydrates.

In a previous work [7] an attempt was made to study the possibility of producing supersulphated pozzolanic cement from burnt clay pozzolanas by lime–gypsum mixed activation. The hydration products were mainly ettringite and calcium silicate hydrate.

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The aim of the present work is to find out the effect of gypsum content on the hydration products as well as on the mechanical properties of metakaolin–lime mixtures in relation to curing time. The hydration products were identified using XRD and DTA techniques. The influence of mix composition and hydration products on the mechanical properties of the hardened pastes was also studied.

EXPERIMENTAL

A China clay (Bolus Alba Kaolin) produced by VEB Laborchemie Apolda, E. Germany, and analytical grade $Ca(OH)_2$ and gypsum obtained from BDH, England were used in this work. The China clay contains more than 52% particles finer than 2 μm in size and is composed mainly of kaolinite (75%), in addition to 9% other clay minerals and 16% quartz. On the basis of a previous investigation on metakaolin–lime, a 60:40 (w/w) mixture of kaolin–lime was selected as a suitable mixture for the present study [5]. Different ratios of gypsum were added to the above mixture from zero up to 20 wt.% with an interval of 5%. Each mix was mechanically dry mixed in a porcelain ball mill for 0.5 h, calcined in a platinum dish at 800°C for 2 h and then suddenly cooled in air. Hydration was carried out using a water/solid ratio of 1.0 by weight. The preparation of the paste was as described previously [8]. The paste was moulded into 1-in. cubes and cured in a humidity chamber (100% RH) at room temperature for 24 h. The specimens were demoulded, covered with moistened cotton to minimize their carbonation and continously cured in the same cabinet. The hardened cubes were tested after 1, 3, 7 and 28 days. After the predetermined curing time, the compressive strength was tested and hydration was stopped [9,10]. The phase constituents were identified using XRD and DTA techniques.

RESULTS AND DISCUSSION

Figure 1 shows the DTA thermograms of the hydrated metakaolin–lime mix (60:40), without any gypsum, as a function of curing time. The results illustrate four characteristic endothermic effects at 100–150, 150–220, 220–300 and 420–520°C. The lowest endothermic effect mainly indicates the presence of calcium silicate hydrate, while the second endotherm is attributed to gehlenite hydrate. The third peak (220–300°C) is due to the presence of hydrogarnet series [5,7], and the fourth to the decomposition of $Ca(OH)_2$. The sample hydrated for one day shows the three characteristic effects of calcium silicate hydrate, gehlenite hydrate and calcium hydroxide. On prolonged hydration, the amount of gehlenite hydrate increases while that of $Ca(OH)_2$ decreases, and the peak of the hydrogarnet appears. After

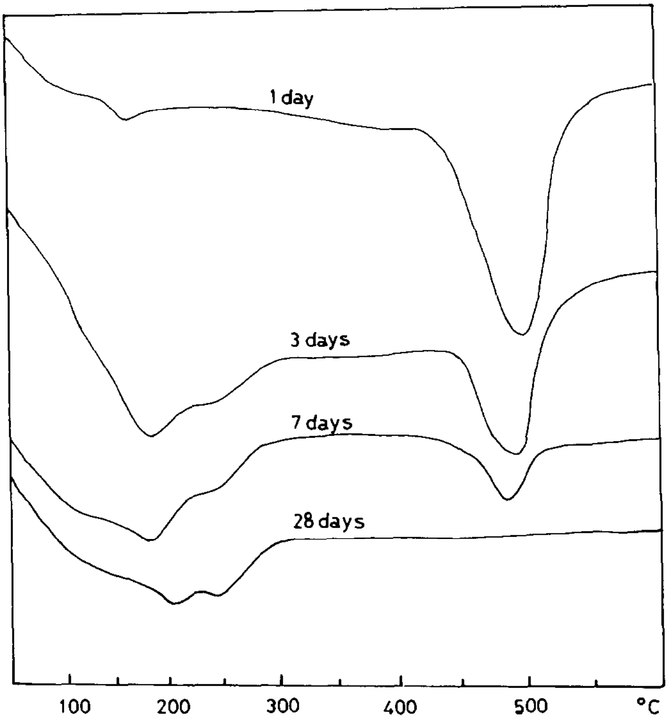

Fig. 1. DTA curves of metakaolin–lime (60 : 40%).

seven days, the amounts of calcium silicate hydrate, gehlenite hydrate and hydrogarnet are also increased, whereas the lime content decreases. The sample hydrated for 28 days shows only the three peaks of the hydrated phases without any detection of $Ca(OH)_2$.

Figure 2 shows the XRD patterns of the hydrated samples containing 5% gypsum in relation to curing time. The sample hydrated for one day indicates the presence of calcium sulphoaluminate hydrates (ettringite, monosulphate hydrate or solid solution) with the detection of $Ca(OH)_2$ and quartz. The ill-crystalline calcium silicate hydrate is also present. After three days, the gehlenite hydrate appears together with hydrated calcium sulphoaluminates and calcium silicates, and a decrease in $Ca(OH)_2$. As the hydration proceeds, the sulphoaluminate hydrates become constant with an increase in calcium silicate and gehlenite hydrate, whereas the lines of $Ca(OH)_2$ completely disappear. After 28 days, further crystallization of calcium silicate hydrate occurs in comparison with that at seven days, while the sulphoaluminate and gehlenite hydrates are more or less constant. It is clear that the sulphoaluminate hydrates are formed at early ages of hydration and remain constant, whereas the amount of calcium silicate hydrate increases with curing time. Some lines of calcium carbonate are found in the sample hydrated for 28 days.

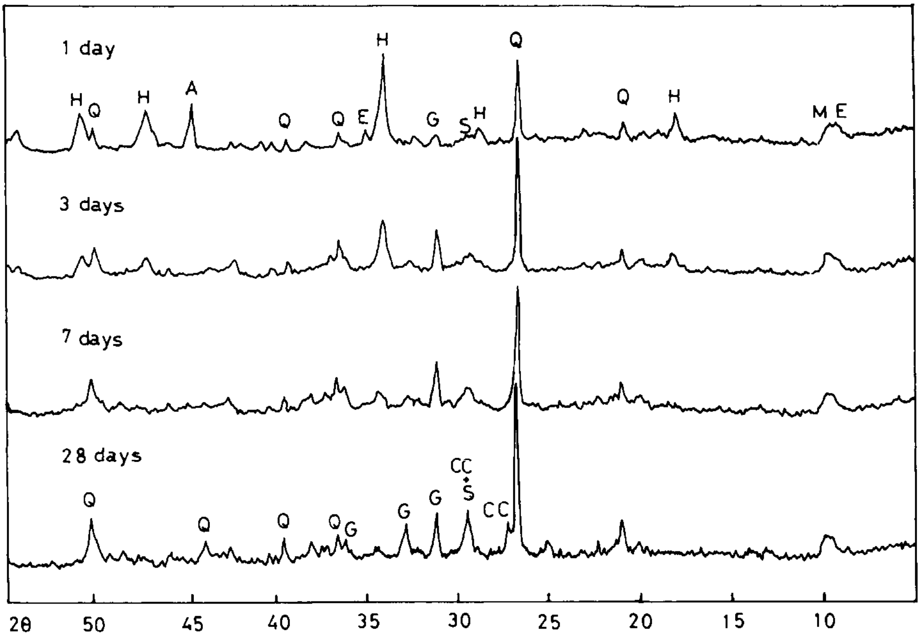

Fig. 2. XRD patterns of metakaolin–lime with 5% gypsum. E = Ettringite; M = calcium monosulphate hydrate; S = calcium silicate hydrate; A = calcium aluminate hydrate; G = C_2ASH_8; H = $Ca(OH)_2$; CC = calcium carbonate; Q = quartz; $\overline{CS}$ = $CaSO_4$.

The DTA thermograms of the hydrated metakaolin–lime with 5% gypsum as a function of curing time are shown in Fig. 3. The sample hydrated for one day shows an endothermic peak at 150°C followed by a slight peak at 220–300°C and an intense one at 480°C. The first two endothermic peaks are mainly due to ettringite and monosulphate hydrate, respectively. The third endothermic effect is due to the decomposition of $Ca(OH)_2$. After three days, the endothermic peak of the hydrated calcium silicate appears at 110°C overlapped by the endotherm of ettringite at 150°C. The endothermic peak of monosulphate hydrate increases and that of $Ca(OH)_2$ diminishes. The endothermic effect of gehlenite hydrate is overlapped by that of monosulphate hydrate at 220–300°C [11]. As the hydration progresses from seven to 28 days, the peak of $Ca(OH)_2$ disappears and the hydrated phases detected are calcium silicate, calcium sulphoaluminates and gehlenite.

Figure 4 illustrates the XRD patterns of the hydrated system with 10% gypsum in relation to curing time. The sample hydrated for one day shows the formation of the hydrates of calcium sulphoaluminate (ettringite and monosulphate hydrate), calcium silicate, gehlenite and calcium aluminate [5]. In addition to the above phases, free $Ca(OH)_2$ and some unreacted $CaSO_4$ are detected. On prolonged hydration from 3 to 28 days, free $Ca(OH)_2$ and $CaSO_4$ disappear, whereas the crystallization of the hydrated calcium silicate, calcium sulphoaluminate and gehlenite is increased.

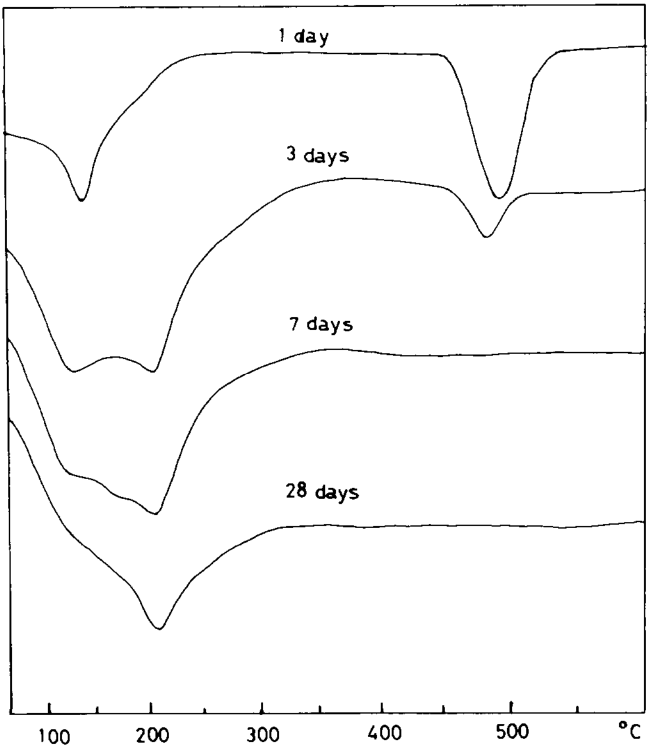

Fig. 3. DTA curves of metakaolin–lime with 5% gypsum.

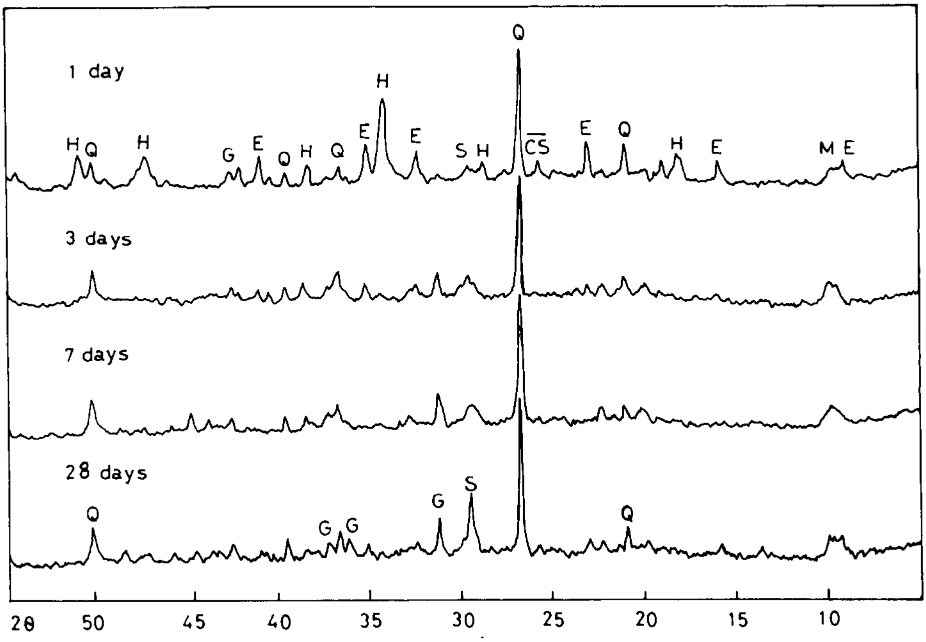

Fig. 4. XRD patterns of metakaolin–lime with 10% gypsum (see Fig. 2 for meanings of symbols).

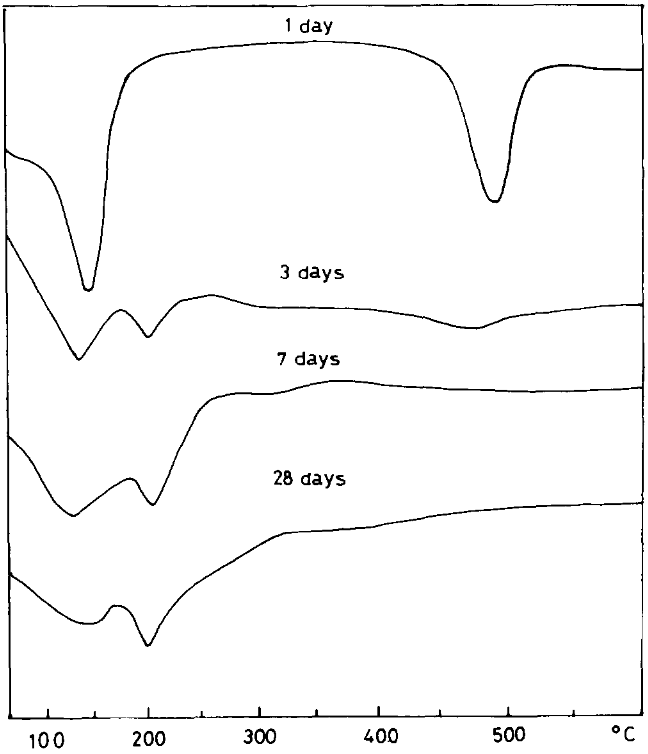

Fig. 5. DTA curves of metakaolin–lime with 10% gypsum.

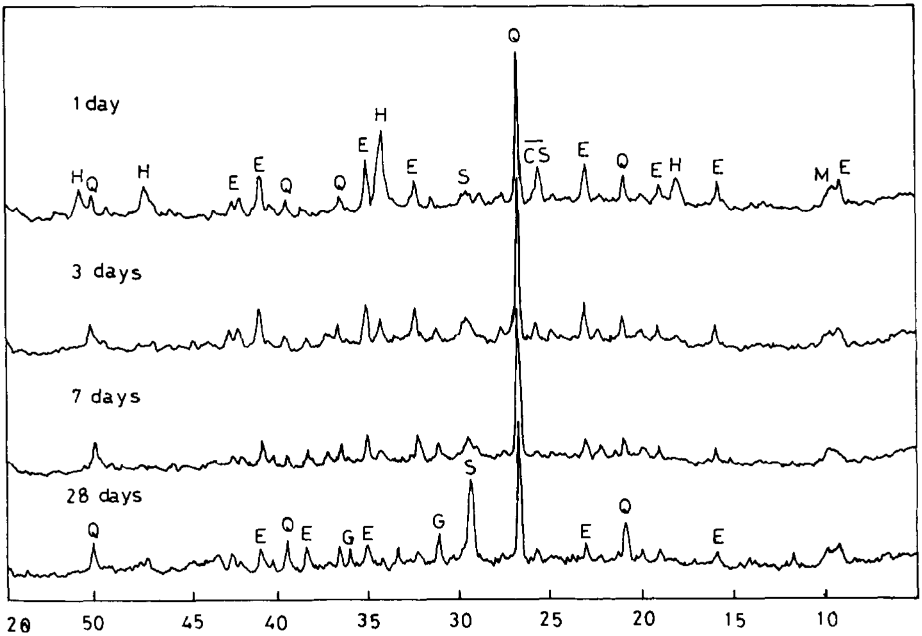

Fig. 6. XRD patterns of metakaolin–lime with 15% gypsum (see Fig. 2 for meanings of symbols).

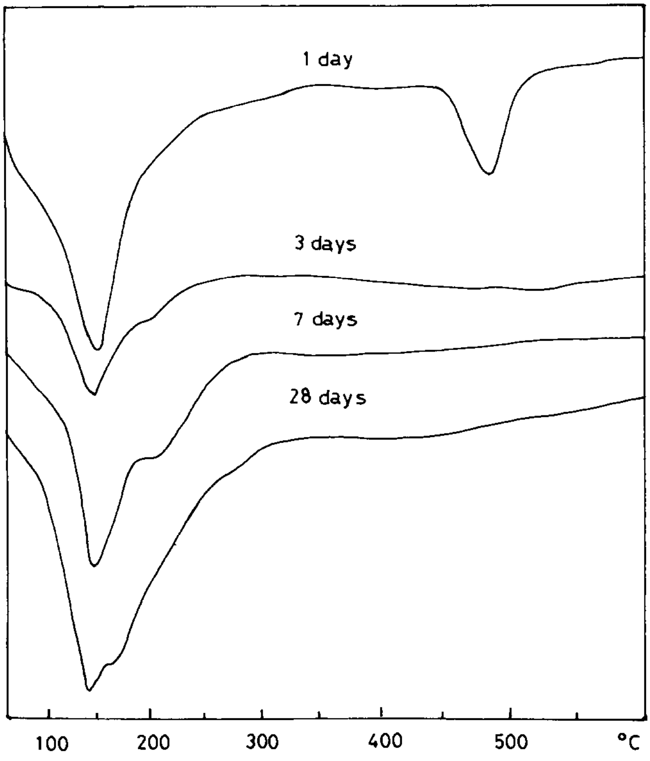

Fig. 7. DTA curves of metakaolin–lime with 15% gypsum.

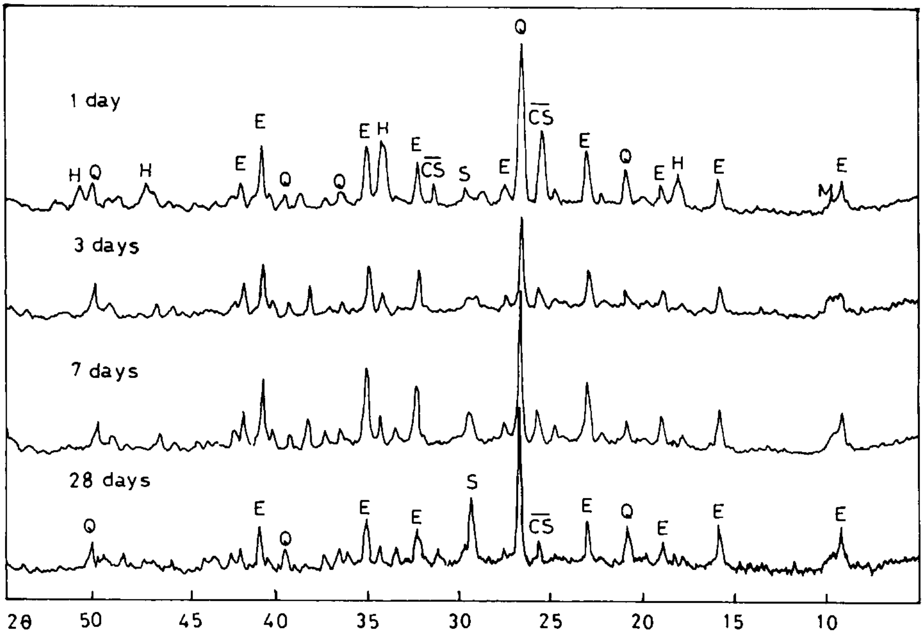

Fig. 8. XRD patterns of metakaolin–lime with 20% gypsum (see Fig. 2 for meanings of symbols).

Figure 5 exhibits the DTA thermograms of the hydrated system with 10% gypsum. After one day, the thermogram illustrates the presence of ettringite and calcium silicate hydrate as indicated by the sharp endothermic effect at 150°C, and also $Ca(OH)_2$ with an endothermic peak at 480°C. After three days, an endothermic peak at 200°C appears which is attributed to the monosulphate hydrate and/or gehlenite hydrate. As the hydration proceeds, the above hydrated phases increase and the free $Ca(OH)_2$ disappears.

The XRD patterns and DTA curves of the system with 15% gypsum are exihibited in Figs. 6 and 7, respectively. It is evident that $Ca(OH)_2$ disappears after only three days and the gehlenite hydrate is not formed. The presence of sufficient $CaSO_4$ in this mix prevents the formation of gehlenite hydrate and hydrogarnet because the Ca^{2+} ions react with the available Al^{3+} ions in the presence of $CaSO_4$ forming hydrated calcium sulphoaluminates. The free $CaSO_4$ is completely consumed after seven days in the formation of

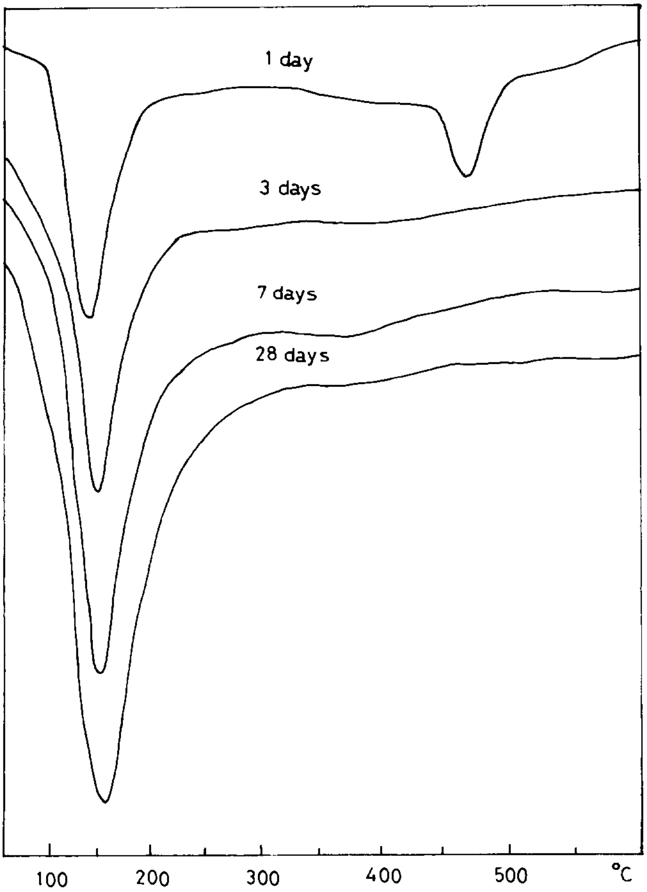

Fig. 9. DTA curves of metakaolin–lime with 20% gypsum.

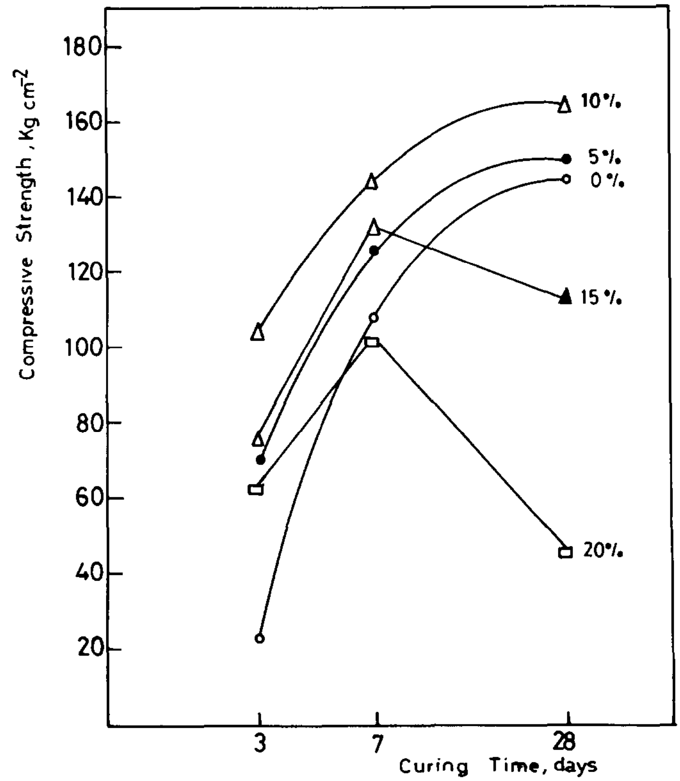

Fig. 10. Compressive strength of hydrated metakaolin–lime with varying proportions of gypsum.

calcium sulphoaluminate hydrate. The amounts of the hydrated calcium silicate and calcium sulphoaluminate increase with curing time.

Figures 8 and 9 illustrate the XRD patterns and DTA curves of the hydrated samples with 20% gypsum. It is evident that the hydrated phases formed in this mix are ettringite and calcium silicate hydrate and their amounts increase with curing time. $Ca(OH)_2$ also disappears after three days. The presence of a relatively high content of $CaSO_4$ in this mix leads to the formation of ettringite without any evidence of the formation of monosulphate hydrate.

The compressive strength values of the hydrates samples with varying $CaSO_4 \cdot 2H_2O$ contents in relation to curing time are shown in Fig. 10. The compressive strength increases with increasing gypsum content up to 10% at all ages of hydration as well as with curing time. On increasing the amount of gypsum to 15 and 20%, the corresponding compressive strength increases for seven days and then deteriorates at later ages. The hydrated samples containing 10% gypsum give the optimum compressive strength at all ages of hydration. The higher strength at early ages of hydration (1–7 days) is mainly due to the formation of a suitable amount of ettringite. At later ages of hydration (7–28 days) the increase in strength is mainly due to the formation and later accumulation of calcium silicate hydrates. The behaviour of the strength of the hydrated samples having 15 and 20% gypsum can be attributed to the formation of excess amounts of ettringite on hydration up to 28 days. The formation of greater amounts of ettringite is accompanied by a volume increase, which results in internal stresses inside the hydrated samples and, thus, their compressive strength deteriorates.

CONCLUSION

The following conclusions may be deduced from the above findings. The type of hydration products affects the physicomechanical properties of the hardened pastes. Samples with lower than 10% gypsum give gehlenite hydrate whereas the other samples with 15 and 20% gypsum give sufficient amounts of ettringite. Therefore, the pastes containing either gehlenite hydrate or enough ettringite show low compressive strength values. The hydration products of metakaolin–lime are gehlenite hydrate with calcium silicate hydrate, whereas the presence of excess gypsum delays the formation of gehlenite hydrate and the ettringite is formed with calcium silicate hydrate.

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