METAKAOLIN–LIME HYDRATION PRODUCTS

M.A. SERRY, A.S. TAHA, S.A.S. EL-HEMALY and H. EL-DIDAMONY

*National Research Centre, Dokki, Cairo and Faculty of Science, Zagazig University, Zagazig
(Egypt)*

(Received 21 March 1984)

ABSTRACT

Four mixtures were prepared of weight ratios 80:20, 70:30, 60:40 and 50:50 of china kaolin/pure $Ca(OH)_2$. Each mix was activated for 2 h at 800°C and then paste hydrated at room temperature and 100% RH for up to 28 days. The hydration products were studied by XRD as well as DTA and TG techniques. The chemically-combined water and $Ca(OH)_2$ contents were quantitatively determined from the TG curves. The results illustrate the formation of gehlenite hydrate (C_2ASH_8) as the main hydration product; its amount increases with the curing time. Hydrogarnet is also formed at the early stages of hydration in the mixes of lower lime content (e.g., mix 80:20) and increases on prolonged hydration; this is probably due to the lower pH of the reaction medium. CSH gel could not be easily detected by XRD because of its low degree of crystallinity. However, this phase was identified by DTA and gives the characteristic losses on the TG curves. $Ca(OH)_2$ is consumed gradually as the hydration proceeds and disappears nearly completely after long periods (after 28 days).

INTRODUCTION

Calcium silicate hydrate is the most significant phase in portland cement hydration. The physico-mechanical properties of hardened cement pastes depend on the type of hydration products. It is well known that CSH gel, C_4AH_{13}, gehlenite hydrate (C_2ASH_8) and hydrogarnet are the hydration products normally formed during the hydration of slag glasses in the system $CaO-Al_2O_3-SiO_2$ [1]. The formation of gehlenite hydrate in the calcined-kaolin/lime mixtures has been established [2,3] and hydrogarnet has been also recorded [4]. Hydrates of calcium aluminate-and-silicate have been characterized as the products of certain lime–bentonite reactions [5,6]. In another study, the reaction products of the hydrated lime–kaolinite and quartz have been studied [7].

Calcium silicate hydrate and calcium aluminate hydrate were reported to be the hydration products of the kaolinite–lime mixtures, whereas calcium silicate hydrates were only the main products for quartz–lime mixtures. Room temperature preparations tend to produce hydrates with a low degree of crystallinity. Turriziani [4] mentioned that gehlenite hydrate (C_2ASH_8)

changes into hydrogarnet in the presence of $Ca(OH)_2$ and that at $50\,^{\circ}C$ it is unstable relative to hydrogarnet in the series $C_3AH_6-C_3AS_3H_n$. It has been assumed that in clay–lime reactions separate C–A–H phases are not developed to the extent expected on stoichiometric grounds, where Al replaces Si in the C–S–H phase [8].

The present work deals with the hydration characteristics of metakaolin in the presence of varying amounts of lime within the system $CaO-Al_2O_3-SiO_2-H_2O$. The hydration products were investigated using XRD as well as DTA techniques, whereas the kinetics of hydration was followed by TG analysis.

EXPERIMENTAL

A washed china clay (Bolus Alba Kaolin) produced by VEB Laborchemie Apolda, E. Germany, was used in the present work. According to the analysis data provided to this kaolin, it contains more than 52% of particles finer than 2 μm in size and comprises mainly kaolinite clay (75%) in addition to 9% other clay minerals and 16% quartz. Its chemical analysis is: combined SiO_2, 38.78; free SiO_2, 16.0; Al_2O_3, 32.22; Fe_2O_3, 0.45; TiO_2, 0.30; $Na_2O +$ K_2O, 0.38; CaO, 0.15; MgO, 0.28; and ignition loss, 11.73%. The kaolin was dry-mixed with BDH analytical grade $Ca(OH)_2$ in the mass ratios 80 : 20, 70 : 30, 60 : 40 and 50 : 50 kaolin/lime. Each mix was mechanically mixed in a porcelain ball mill for 0.5 h then calcined in a platinum dish using a muffle furnace at $800\,^{\circ}C$ for 2 h. On cooling, hydration was carried out by the addition of distilled water at a water/solid ratio of 1.0 by weight. The preparation of the pastes was carried out according to a previously described method [9]. Hydration was conducted in an atmosphere of 100% RH and the samples were covered with moistened cotton to minimize the effect of carbonation on the hydrated pastes. The samples were cured from one to 28 days.

After the predetermined curing time, the hydration was stopped using a previously described technique [10–12]. The phase constitution of the paste was determined using XRD and DTA analyses. Moreover, the mechanism of hydration was also followed using TG analysis by determining the chemically-combined water and free $Ca(OH)_2$ contents. The combined water was considered to be equal to the total loss minus the loss at $480-520\,^{\circ}C$ due to the decomposition of $Ca(OH)_2$ on the TG curves. DTA and TG runs were carried out at a heating rate of $10\,^{\circ}C$ min^{-1}; a nitrogen atmosphere was applied during the TG analysis.

RESULTS AND DISCUSSION

Figure 1 illustrates the X-ray diffraction patterns of metakaolin–lime mixtures, of varying proportions, hydrated for 28 days. These mixtures
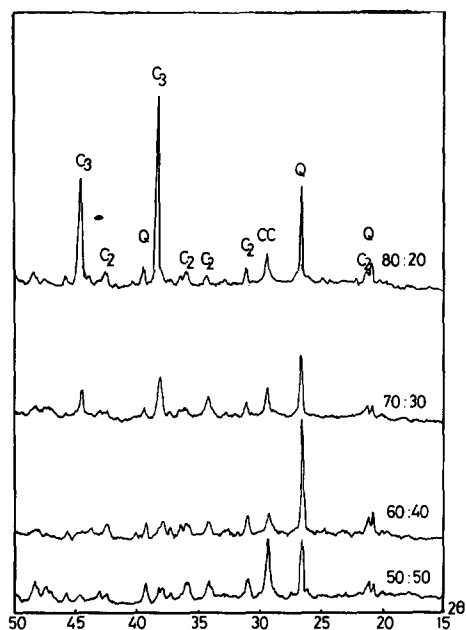
Fig. 1. XRD pattern of metakaolin/lime pastes cured for 28 days. Q, quartz; CC, $CaCO_3$; C_2, C_2ASH_8; C_3, C_3AH_6.

contain 50, 40, 30 and 20% of $Ca(OH)_2$. It is clear that the $Ca(OH)_2$ is almost completely consumed during the hydration of all the mixtures. The gehlenite hydrate (C_2ASH_8) appears as the predominant phase. The content of this phase increases with the lime content, i.e., mix 50 : 50 metakaolin/lime shows more gehlenite hydrate than that of mix 80 : 20. Calcium carbonate is also detected, the amount of which increases with the $Ca(OH)_2$ content. Mix 80 : 20 shows the C_3AH_6 lines as the predominant phase, decreasing with increasing $Ca(OH)_2$. This compound does not appear in the mixtures rich in lime, e.g., 60 : 40 and 50 : 50 mixtures. These findings are in agreement with the previous work of Wall and De Wet [13]. C_2AH_6 changes to hydrogarnet in the presence of excess $Ca(OH)_2$. The X-ray pattern also shows residual free quartz in all mixes.

Figure 2 demonstrates the X-ray diffraction pattern of hydrated metakaolin–lime mix 80 : 20 for one and 28 days. The sample hydrated for one day illustrates the presence of unreacted quartz as the main characteristic phase. $C_3A\ H_6$ is detected after one day, whereas the pattern of gehlenite hydrate C_2ASH_8 indicates its low degree of crystallinity. As hydration proceeds the amount of C_3AH_6, as well as that of gehlenite hydrate, increases and that of $Ca(OH)_2$, accordingly, decreases.

Figure 3 illustrates the DTA thermograms of the hydrated metakaolin–lime mix 50 : 50 in relation to curing time. The results show four characteristic endothermic effects at 100–150, 150–220, 220–300 and
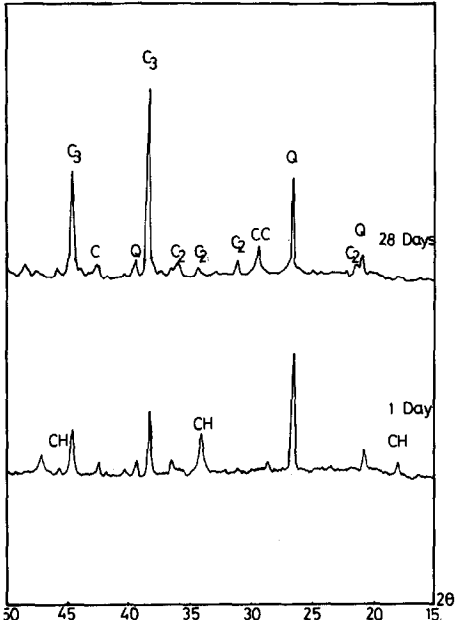
Fig. 2. XRD pattern of 80:20 kaolin/lime pastes. Q, quartz; CC, $CaCO_3$; C_2, C_2ASH_8; C_3, C_3AH_6; CH, calcium hydroxide.

420–520°C. The low endothermic effect mainly indicates the presence of calcium silicate hydrate, while the second endotherm is attributed to the gehlenite hydrate. The third peak (220–300°C) is due to the presence of the hydrogarnet series [14], and the fourth endotherm is related to the decomposition of $Ca(OH)_2$. The sample hydrated for one day shows the three characteristic endothermic effects of calcium silicate hydrate, gehlenite hy-
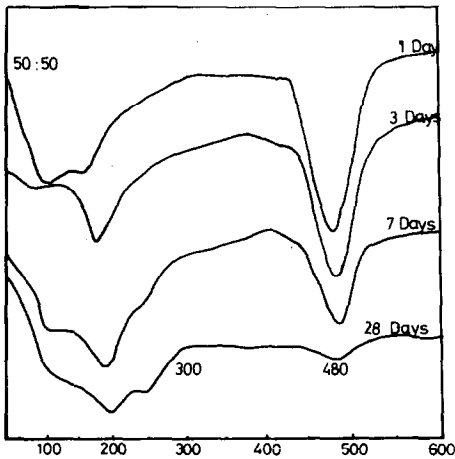

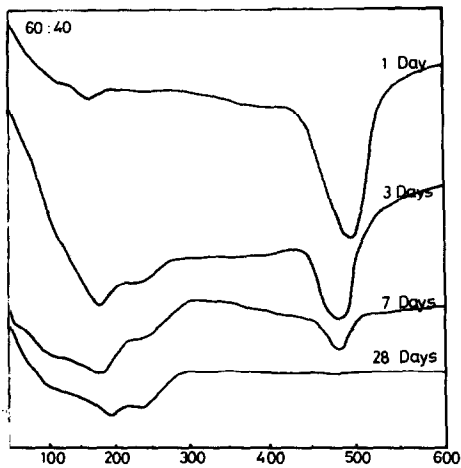Fig. 3. DTA thermograms of mix 50:50 kaolin/lime hydration products.

Fig. 4. DTA thermograms of mix 60 : 40 kaolin/lime hydration products.

drate and calcium hydroxide. On prolonged hydration (three days) the amount of gehlenite hydrate increases while that of calcium hydroxide decreases. After seven days, the third endothermic peak (220–300 °C) appears, which confirms the existence of the hydrogarnet. In the sample hydrated for 28 days the amount of hydrogarnet increases further and the lime is still present in a small proportion only.

The DTA thermogram of the hydrated 60 : 40 mix as a function of curing time is shown in Fig. 4. It is clear that the endothermic peak of gehlenite hydrate (150–220 °C) appears after one day of hydration. The sample hydrated for three days shows the endothermic effect of hydrogarnet at 200–300 °C, whereas the content of $Ca(OH)_2$ decreases. As hydration proceeds, the amounts of silicate hydrate, gehlenite hydrate and hydrogarnet are increased further. The sample hydrated for 28 days shows only the peaks of the hydrated phases with no detection of $Ca(OH)_2$.

Figure 5 shows the DTA thermograms of hydrated 70 : 30 metakaolin–lime mix. The $Ca(OH)_2$ is completely consumed after three days of hydration. The endothermic effects of this series are almost identical to those of the preceding group (60 : 40). Figure 6 illustrates the DTA thermograms of mix 80 : 20. The curves show the disappearance of $Ca(OH)_2$ during the first three days of hydration and an increase of the amount of hydrogarnet (C_3AH_6) with time. The main hydration products are gehlenite hydrate and hydrogarnet.

At the beginning of the metakaolin–lime–water reaction within the quaternary system $CaO-Al_2O_3-SiO_2-H_2O$, Ca^{2+} ions enter solution and the pH increases as the reaction proceeds. The Al^{3+} ions have the tendency to dissolve at lower pH values compared with that required for SiO_4^{4-} ions. The Al^{3+} ions start to combine with the readily available Ca^{2+} ions via meta-
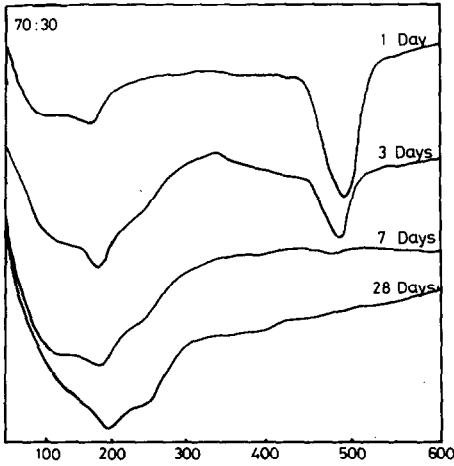
108

Fig. 5. DTA thermograms of mix 70:30 kaolin/lime hydration products.

stable phases forming C_3AH_6 as shown in the XRD pattern after one day of hydration in the low-lime content mix (80:20). On prolonged hydration, the Ca^{2+} ions are nearly totally consumed with the increase in C_3AH_6.

When the lime content increases more Ca^{2+} ions are available, the pH value rises and the SiO_4^{4-} ions enter into solution more readily. The latter react with the C_3AH_6 initially formed, forming gehlenite hydrate C_2ASH_8 as shown by the DTA as well as XRD patterns. The DTA thermograms indicate the formation of gehlenite hydrate after one day and its amount increases with time. The X-ray pattern, however, does not show the presence of this phase after one day, probably due to its low degree of crystallinity. The results of the X-ray analysis are in a good agreement with those of the DTA.
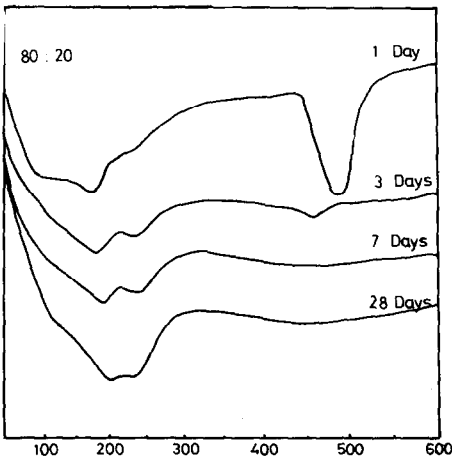

Fig. 6. DTA thermograms of mix 80:20 kaolin/lime hydration products.

HYDRATION KINETICS OF METAKAOLIN–LIME

The chemically-combined water and free $Ca(OH)_2$ contents of the hydrated metakaolin–lime pastes were taken as a measure of the degree of hydration. Figure 7 represents the hydration kinetics of the various mixes under investigation as a function of curing time. Mix 80 : 20 shows a very slight increase of chemically-combined water content after one day which is followed by a sharp increase up to seven days, and a significant change is hardly seen from seven to 28 days. The increase in lime content (mix 60 : 40) results in a pronounced increase in the chemically-combined water content after one day of hydration. This value is sharply increased after three days, followed by a slow increase up to 28 days. The mix 50 : 50 shows an increase in the chemically-combined water, compared to the previous mix, in the early stages of hydration (one day), then it progressively increases, though at a slower rate, up to 28 days.

The pronounced increase in the chemically-combined water for mixtures rich in lime after one day of hydration is related to the presence of more hydrated phases. The comparatively slow rate of hydration after the first day could be attributed, at least partly, to the presence of relatively excess amounts of $Ca(OH)_2$ which act as a retardant for the further formation of hydrates [15,16]. As hydration proceeds the $Ca(OH)_2$ films, precipitated on the hydrated grains, become unstable, because the formation of more hydrates consumes these films on reaction with alumino-silicates.

The results indicate that the free $Ca(OH)_2$ is diminished with increasing hydration time. The consumption of free lime is very rapid during the early stages of hydration; this is followed by a gradual decrease in the free lime content. The consumption of lime occurs after shorter periods in lime-poor mixes rather than those rich in lime. The free lime content in the hydrated
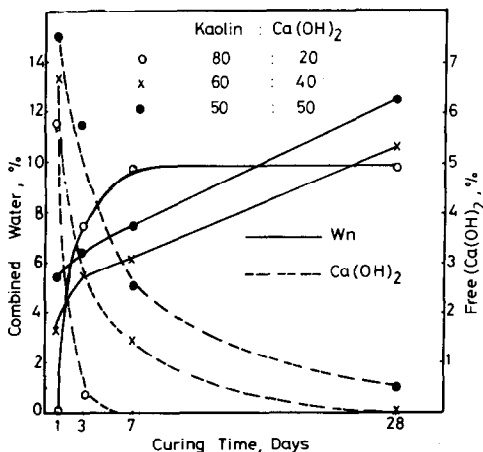
Fig. 7. Hydration kinetics of metakaolin–lime pastes.

pastes were consumed after three, seven and 28 days for mixes 80 : 20, 60 : 40 and 50 : 50, respectively.

REFERENCES

1 A. Dasgupta, Indian J. Technol., 13 (1975) 355.
2 W. Sträetling, Reaction Between Calcined Kaolin and Lime in Aqueous Solutions, Zement-Verlag, Berlin, 1938.
3 J. Jamlov, Mag. Concr. Res., 15 (1963) 132.
4 R. Turriziani, in H.F.W. Taylor (Ed.), Chemistry of Cement, Vol. 1, Academic Press, London and New York, 1964, p. 233.
5 J.L. Eades, F.P. Nicols and R.E. Grim, Highw. Res. Board, Bull., 335 (1962) 32.
6 G.R. Glenn and R.L. Handy, Highw. Res. Board, Bull., 29 (1963) 70.
7 Z.-Chieh Moh, 44th Ann. Meet. Highw. Res. Board, Washington, DC, Jan. 1965.
8 S. Diamond and E.B. Kinter, Highw. Res. Rec., 92 (1965) 83.
9 F.H. Mosalamy, M.A. Shater and H. El-Didamony, Thermochim. Acta, 74 (1984) 113.
10 H. El-Didamony, M.Y. Haggag and S.A. Abo-El-Enein, Cem. Concr. Res., 8 (1978) 351.
11 H. El-Didamony, Thermochim. Acta, 35 (1980) 201.
12 H. El-Didamony and A.A. Khalil, Zem.-Kalk-Gips, 34 (1981) 660.
13 J.W. Wall and J.D. De Wet, J. Am. Ceram. Soc., 55 (1972) 432.
14 C. Samanta and M.K. Chaterjee, Indian J. Technol., 15 (1977) 490.
15 P.K. Mehta, J. Am. Ceram. Soc., 56 (1973) 315.
16 A.A. Khalil and H. El-Didamony, Thermochim. Acta, 40 (1980) 337.