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PHYSICO-CHEMICAL AND THERMAL CHARACTERISTICS OF LIME-SILICA FUME PASTES

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Abstract

Five lime-silica fume pastes were investigated using initial CaO/SiO_2 molar ratios of 0.80, 1.0, 1.30, 1.70 and 2.0. The kinetics and mechanism of hydration interaction between lime and silica fume were studied on the basis of the phase composition and the physical state of the formed hydration products. The developed strength could be related to the lime content of the lime-silica mixture and the formed hydrates.

Keywords: lime-silica fume pastes, thermal and physicho-mechanical properties

Introduction

Condensed silica fume is a by-product during the manufacture of silicon and ferro-silicon. It is mainly composed of silica particles, and different impurities present in the glassy phase. Its specific surface area is about 20 $m^2\ g^{-1}$.

It is known that the lime-silica hydration reaction depends on many factors such as the type of silica, CaO/SiO_2 molar ratio, curing conditions, surface area of materials, amount of water and type of lime. The CaO/SiO_2 molar ratio of tobermorite is 0.83 as recommended by Brunauer and Greenberg [1], but in the artificially prepared tobermorite, the ratio ranges up to 1.75 and possibly higher. Taylor differentiated between low-lime calcium silicate hydrates {C–S–H(I)} with a C/S molar ratio <1.5 and high-lime calcium silicate hydrates {C–S–H(II)} with a C/S molar ratio >1.5 [2]. The results of X-ray diffraction analysis carried out by Burkes showed that the reaction product formed in $Ca(OH)_2$ – silica fume mixtures at ordinary temperatures consists mainly of {C–S–H(I)} [3]. Other investigators reported that the C–S–H product formed at various curing periods had a C/S ratio in the range 1.1–1.26 [4]. Further studies indicated the formation of different hydrates. These are xonotlite and C–S–H(I) at 190–200°C [5], jennite at 80°C [6] as

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well as C–S–H(I) and/or C–S–H(II) at 25°C [7] depending on the initial C/S ratio of the solid mixture.

The objective of the present investigation is to study the physicochemical and thermal characteristics of lime-silica fume pastes at room temperature with respect to the kinetics and mechanism of hydration as well as phase composition of the formed hydrates.

Experimental

The oxide composition of silica fume was found to be: SiO_2, 95.75%, Al_2O_3, 1.56%, Fe_2O_3, 0.34% and ignition loss, 1.45%.

Five lime-silica fume mixtures were made using different CaO/SiO_2 molar ratios of 0.80, 1.0, 1.30, 1.70 and 2.0. The pastes were prepared by the mixing of each dry mixture with distilled water up to standard consistency; mixing was carried out continuously for 4 min. Each paste was hydrated for various time intervals of 0.5, 2, 6 and 24 h and 3, 7, 28 and 90 days. Curing was first done at 100% relative humidity for 24 h, then all pastes were cured under water for the successive hydration periods.

At each curing age, the hydration reaction was stopped, and then free lime [8], free silica [9] and chemically combined water contents were determined using dried samples according to the methods reported earlier [7]. The phase composition of the formed hydrates was studied using differential thermal analysis (DTA) and X-ray diffraction (XRD). Compressive strength tests were carried out on one inch cubic specimens.

Results and discussion

Kinetics and mechanism of hydration

The kinetics of hydration of lime-silica fume mixtures was studied by determining the contents of free lime, free silica and chemically combined water at various ages of hydration. The results are represented in Figs 1–3, respectively.

The results in Fig. 1 indicate that the free lime content decreases with increasing time of hydration. An initial sharp decrease was noticed during the first 0.5 h of

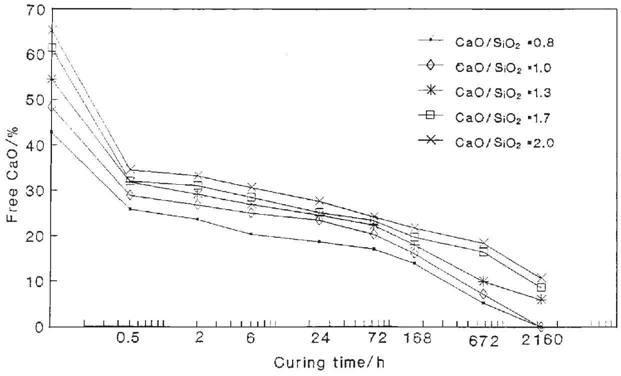

Fig. 1 Free lime contents of hydrated silica fume-lime pastes as a function of curing time

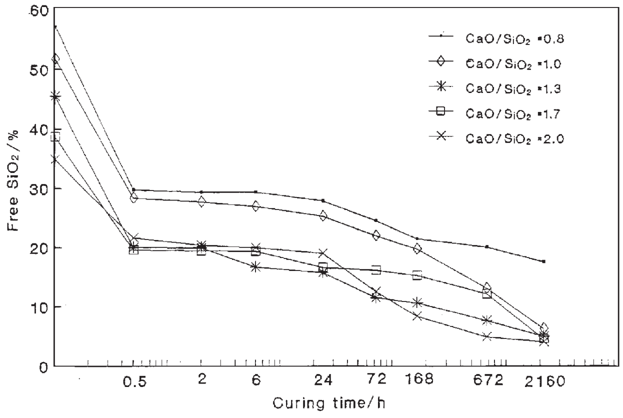

Fig. 2 Free silica contents of hydrated silica fume-lime pastes as a function of curing time

hydration, this was followed by a slight decrease from 0.5 to 24 h and finally a continuous decrease was observed up to 90 days of hydration.

In all mixes, about 45% of the total lime is consumed after 0.5 h indicating the occurrence of a very fast stage in the hydration reaction during the first 30 min of hydration (pre-dormant period). The free lime is completely consumed after 90 days of hydration for mixes made with CaO/SiO_2 molar ratios of 0.80 and 1.0, while the free lime is still detected for the mixes made with CaO/SiO_2 ratios of 1.3, 1.7 and 2.0 after 90 days of hydration.

The free silica contents shown in Fig. 2 indicate that the silica fume-lime hydration reaction is very fast in the very early stages of hydration (30 min); a marked decrease in free silica content was observed in all mixes at 0.5 h of hydration where about 40–50% of

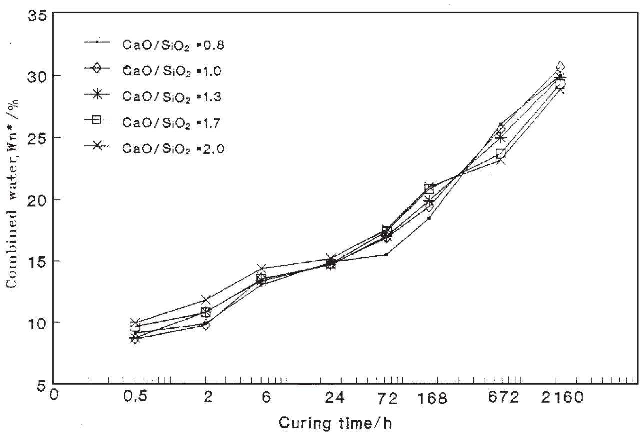

Fig. 3 Combined water contents of hydrated silica fume-lime pastes as a function of curing time

the silica reacted. The mode of variation of the free silica content with the time of hydration shown in Fig. 2 is similar to the variations of the free lime content (Fig. 1).

The chemically combined water contents shown in Fig. 3, for all mixes investigated indicate relatively high values of combined water content during the first 30 min, followed by a gradual increase up to 6 h, a slight increase between 6 and 24 h and finally a noticeable increase from 24 h up to 90 days of hydration.

From the results in Figs 1–3, a mechanism for the hydration of silica fume-lime mixtures could be derived which can be summarized as follows:

1. Due to the amorphous character and the very large surface area of silica fume, it possesses a very high pozzolanic activity and acts as sites for the rapid hydration reaction with calcium hydroxide to form a hydrated layer of calcium silicate hydrate (C–S–H) on the silica surface as lime-rich C–S–H. This is mainly associated with the sharp decrease in both of free lime and free silica during the first 30 min of hydration; during this very early stage, the combined water content is high. During this stage, the initially formed high-lime C–S–H is highly amorphous in character. This is the ‘pre-dormant period’ as suggested by several investigators [10–15].

2. During the period 0.5–6 h, the hydration interaction between the silica fume grains and the initial lime-rich C–S–H coatings lead to a decrease in the lime content of the initially formed C–S–H product [12, 14]. This results in a slight decrease in both of the free lime and free silica contents with a gradual increase in the chemically combined water content. From 6–24 h, the hydration reaction is retarded due to the impervious coatings of the amorphous C–S–H around the silica fume grains; this is the ‘dormant period’ as reported in earlier publications [12–14]. The ill-crystallized character of the formed C–S–H around the active silica fume might hinder the hydration interaction between lime and silica fume with a preferential hydration reaction between the hydrated C–S–H layers and active silica up to one day of hydration. There appeared a very slight decrease in both of the free lime and free silica contents and a very slight increase in the combined water content between 6 h and one day of hydration (Figs 1–3).

3. An ‘acceleration stage’ was observed during the hydration period from 24 h up to 90 days for the pastes made with CaO/SiO_2 molar ratios of 0.80, 1.0 and 1.30; the results in Figs 1–3 reflect the increase in the rate of hydration as indicated by the decrease of free silica at 24 h for most samples and around 72 h for the free lime, while the combined water content increases. For the pastes made with CaO/SiO_2 molar ratios of 1.70 and 2.0, there appeared a ‘second dormant’ period between 7 and 28 days; i.e. the hydration period 1–90 days is divided into 3 stages, namely: a ‘first acceleration’ period between 1 and 7 days , a ‘second dormant’ period between 7 and 28 days and a ‘second acceleration’ period between 28 and 90 days (Fig. 3). The relatively low values of combined water contents observed at the later stages of hydration (28–90 days) for mixes made with CaO/SiO_2 molar ratios of 1.70 and 2.0 are mainly due to the presence of large amounts of free lime which act as coating layers on the silica fume grains leading to a sort of retardation of the hydration reaction [15–17].

Phase composition of the formed hydrates

From the free lime and free silica contents, the CaO/SiO_2 molar ratios of the formed C–S–H, obtained as a result of hydration of the different lime-silica fume mixtures, could be calculated. The derived CaO/SiO_2 molar ratios of the hydrated calcium silicate phases are (1.078–1.154), (1.135–1.168), (1.250–1.255), (1.81–1.75) and (1.79–1.89) at the hydration ages 28–90 days for the mixes made with initial CaO/SiO_2 molar ratios of 0.80, 1.0, 1.30, 1.70 and 2.0, respectively. Therefore, C–S–H(I) represents the main hydration product of the mixes made with the lower initial CaO/SiO_2 ratios (0.80, 1.0 and 1.30), while C–S–H(II) represents the main hydrate formed as a result of hydration of lime-rich mixes (CaO/SiO_2 molar ratios of 1.70 and 2.0).

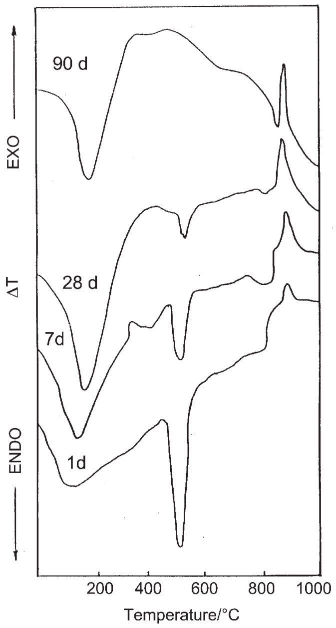

Fig. 4 DTA curves of the pastes having a CaO/SiO_2 ratio of 0.8 with curing time

The results of differential thermal analysis (DTA) of the hydrated lime-silica fume samples at different curing ages are shown in Figs (4–6) for the mixes made with CaO/SiO_2 molar ratios of 0.80, 1.0 and 1.70, respectively. The DTA curves indicate endothermic effects at 100–150, 160–200, 350–400, 500–550 and 700–800°C as well as an exotherm at 800–900°C. The endothermic effects located below 400°C are attributed to the release of interlayer water of calcium silicate hydrates (C–S–H) having various compositions and degrees of crystallinity. The endothermic peak at 500–550°C is due to the decomposition of free $Ca(OH)_2$, whereas the endotherm in the range 700–800°C is due to the decomposition of $CaCO_3$. The exotherm located at 800–900°C is mainly characteristic of the calcium silicate hydrate; this exotherm is

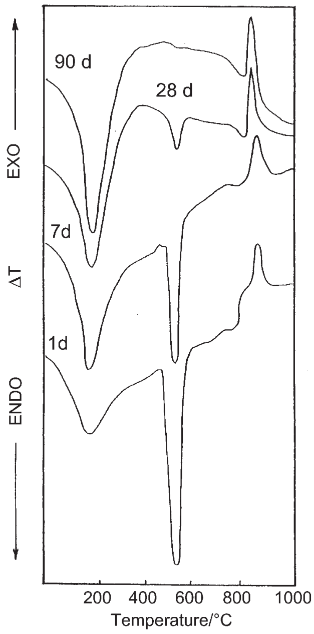

Fig. 5 DTA curves of the pastes having a CaO/SiO_2 ratio of 1.0 with curing time

developed during the process of crystallization of monocalcium silicate as a result of the decomposition of CSH(I) [18].

With increasing age of hydration, the intensity of the peak characterizing $Ca(OH)_2$ decreases, it disappears completely at 90 days of hydration for mixes made with low lime contents (initial CaO/SiO_2 molar ratios of 0.80 and 1.0), whereas for lime-rich mixes (e.g. CaO/SiO_2 molar ratios of 1.70 and 2.0) this peak is still existing over all ages of hydration. In addition, the endotherm at 160–200°C characteristic of a more crystalline C–S–H only appeared at the later ages of hydration (28–90 days). The increased degree of crystallinity of C–S–H with increasing age of hydration is actually reflected by the increased intensity of the exotherm located at 800–900°C which is due to C–S–H(I) [19].

The DTA curves obtained for the hydrated samples made from lime-silica mix with CaO/SiO_2 molar ratio of 1.70 exhibit the lowest endotherms of C–S–H up to 400°C, the lowest exotherms of C–S–H(I) and highest endotherms of $Ca(OH)_2$ until the age of 90 days of hydration (Fig. 6) as compared with those of the other two mixes (Figs 4 and 5). Therefore, an increase in the initial CaO/SiO_2 molar ratio of lime-silica fume mix results in a decrease in the amount of C–S–H(I) which is confirmed by the exotherm at 800–900°C and the appearance of C–S–H(II) with a higher CaO/SiO_2 molar ratio. The indication of the appearance of CSH(II) in the DTA curves is the appearance of the exotherm at 800–900°C [16].

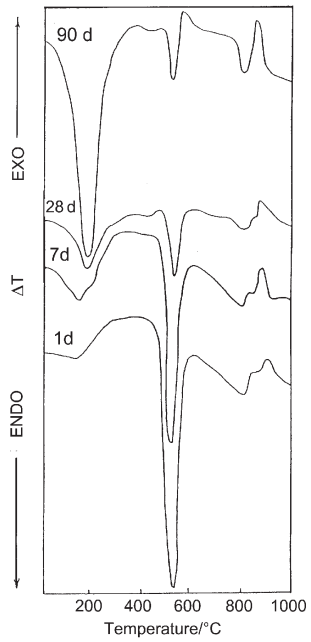

Fig. 6 DTA curves of the pastes having a CaO/SiO$_2$ ratio of 1.7 with curing time

Compressive strength

Compressive strength values of the hydrated lime-silica fume pastes are plotted as a function of curing time in Fig. 7. Obviously, the strength of each paste increases with increasing time of hydration for all the mixes investigated. As hydration proceeds, more hydrated calcium silicates, C–S–H(I) and/or C–S–H(II), are formed and deposited in the open pore system of the hardened paste leading to a continuous increase in compressive strength of the hardened paste. With the exception of the low-lime mix

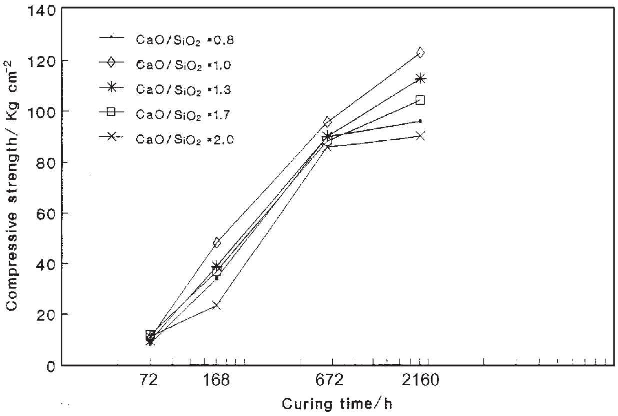

Fig. 7 Compressive strength of hydrated silica fume-lime specimens with curing time

made with an initial CaO/SiO_2 molar ratio of 0.80, the strength values decrease with increasing initial CaO/SiO_2 molar ratio of the lime-silica fume mixture. This result is mainly due to the presence of larger amounts of C–S–H(II) as well as appreciable quantities of free lime which possess weaker binding forces; lime-rich C–S–H(II) has poorer strength characteristics as compared with low-lime C–S–H(I) [20]. In addition, the strength of lime-rich mixes (1.70 and 2.0 CaO/SiO_2 molar ratios) is slightly increased at the later ages of hydration due to the process of carbonation of free lime which retards the continuous formation of C–S–H as representing the main binding centres of the hardened paste. However, the relatively low later strength values of the 0.80 CaO/SiO_2 molar ratio mix is mainly attributed to the presence of insufficient amounts of lime for the continuous formation of C–S–H. These findings account with the results obtained in recent publications [21–24].

References

1 S. Brunauer and S. A. Greenberg, Proc. 4th Inter. Symp. Chem. Cement, Washington I 1960, p. 135.
2 H. F. W. Taylor, J. Chem. Soc., (1950) 3682.
3 A. D. Duck and J. P. Burkes, 3rd Int. Conf. Cement Microscopy, Houston 1981, p. 279.
4 Z. Wu and J. F. Young, J. Mater. Sci., 19 (1984) 3477.
5 N. Hara and N. Inoue, Cem. Concr. Res., 10 (1980) 677.
6 B. Curbs, F. Bukula and K. R. Gorbroves, Cem. Concr. Res., 15 (1985) 134.
7 N. M. Guindy, S. A. Abo-El-Enien, F. I. El-Hosiny and S. M. A. Gamal, J. Therm. Anal., Eng., 40 (1993) 151.
8 F. M. Lea, 'The Chemistry of Cement and Concrete', Ed., Edward Arnold Ltd., London (1970).
9 R. Kondo, S. A. Abo-El-Enein and M. Daimon, Proc. 3rd Inter. Symp., 'Aut. Calcium Silicate Build. Prods'. Netherlands, p. 25; Bull. Chem. Soc., Japan, 48 (1975) 222.
10 C.-Y. Huang and R. F. Feldman, Cem. Concr. Res., 15 (1985) 585.
11 S. A. Greenberg, J. Phys. Chem., 65 (1961) 12.
12 S. A. Abo-El-Enein, M. Daimon. S. Ohsawa and R. Kondo, Cem. Concr. Res., 4 (1974) 299.
13 S. A. Abo-El-Enein, M. A. Shater and M. Nowar, Il-Cemento, 78 (1981) 137.
14 S. A. Abo-El-Enein, E. E. Hekal, M. Abdel-Khalik and F. I. El-Hosiny, ibid., 87 (1990) 147.
15 P. K. Mehta, J. Am. Ceram. Soc., 56 (1973) 315.
16 A. Khalil and H. El-Didamony, Thermochim. Acta, 40 (1980) 337.
17 A. M. Sharara, H. El-Didamony, E. Ebied and S. Abd-El-Aleem, Cem. Concr. Res., 24 (1994) 966.
18 V. S. Ramachandran, Chem. Publ. Co. Inc., New York (1969).
19 M. J. J. Purton, Appl. Chem., 20 (1970) 293.
20 C.-Y. Huang and R. F. Feldman, 'Characteristic of the Pore Structure of Blend Cement Pastes, Blended with Silica Fume', Guisuanayan Xeebao, 13 (1985) 301.
21 C. Shi, Cem. Concr. Res., 26 (1996) 1351.
22 M. Saad, S. A. Abo-El-Enein, G. B. Hanna and M. F. Kotkata, Cem. Concr. Res., 26 (1996) 1479.
23 D. R. G. Mitchell, I. Hinczak and R. A. Day, Cem. Concr. Res., 28 (1998) 157.
24 L. Lam, Y. L. Wong and C. S. Poon, Cem. Concr. Res., 28 (1998) 271.