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CHARACTERISTICS OF LIME-SILICA FUME MIXTURES

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Abstract

The hydration of two calcium hydroxide-silica fume mixtures was studied at 25°C. The mixtures were prepared at lime/silica molar ratios of 1.0 and 1.7. The free lime, free silica and chemically combined water contents were determined after various periods of hydration (0.5 h - 90 days). Thus, the molar ratios CaO/SiO_2 and H_2O/SiO_2 molar in the calcium silicate hydrates (C–S–H) formed could be derived. The hydrates formed were identified by using differential thermal analysis. The mechanism of the hydration-gardening thermal analysis. The mechanism of the hydration-hardening reaction between lime and silica fumes was suggested. The changes in the molar ratios CaO/SiO_2 and H_2O/SiO_2 in the C-S-H formed with the time of hydration were found to follow the same trends as observed during the hydration course for the suggested mechanism.

Keywords: calcium hydroxide-silica fume mixtures

Introduction

Several studies have been reported on lime-silica, including silica fumes, lime-cement, lime-pozzolana and cement-silica mixtures [1–10]. In these studies, the effects of the lime/silica ratio and the addition of alkalies and some metal oxides were examined.

Earlier work on the lime-silica–water system, especially at ordinary temperature, showed that it is difficult to assign a simple chemical formula to any phase, and in some cases widely differing compositions concerning water content and the ratio CaO/SiO_2 occur within the phase. On the other hand, products with the same composition are often represented by several phases and occur in a very fine crystalline state, usually called gels.

The present study is concerned with the formation and molar composition of calcium silicate hydrates (C–S–H) produced in the hydration reaction between lime and silica fumes.

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Experimental

Two solid mixtures were prepared, at molar ratios CaO/SiO_2 of 1 and 1.7. These are designated Mix I and Mix II, respectively.

Each mixture was immersed in ethanol for 2 h to obtain a homogeneous mixture and was then evaporated at 100°C. The dry mixtures were ground in a ball mill for 3 h to ensure complete homogeneity. Each dry mixture was mixed with water at a water/solid weight ratio of 0.8, then stirred for 3 min, moulded in cylindrical specimens and cured at 100% relative humidity for 24 h. Subsequently, they were demoulded and cured under water for 1, 3, 7, 28 or 90 days at room temperature. At the end of each hydration time interval, a certain amount of the resulting paste was ground and stirred for 30 min in 100 ml of a 1:1 methanol-acetone mixture (by volume) in order to remove free water. The residue was washed 3 times with ether, dried at 80°C for 3 h and kept in a desiccator.

The hydration and the mechanism of formation of the C–S–H products were studied by determining the combined water, free lime and free silica contents after various times of hydration [11, 12]. The combined water contents ($Wn\%$) were corrected for the C–S–H formed, and are designated $Wn^*\%$. The Wn^* values were calculated from the Wn values by subtracting the amount of water corresponding to the free lime present in each specimen, provided that each mole of free CaO is accompanied by 1 mole of non-evaporable water. The variation in the molar ratio CaO/SiO_2 in the C–S–H formed as a function of the hydration time was calculated.

The C–S–H formed were identified by differential thermal analysis, using a Shimadzu DT3OH apparatus, in the presence of Al_2O_3 as reference material, with a Pt–Pt/Rh thermocouple.

Results and discussion

Hydration mechanism

A. Mix I

The estimated non-evaporable (chemically-combined) water, free lime and free silica contents of Mix I (molar ratio $C/S=1.0$) are represented graphically in Fig. 1. This shows an initial marked increase in the combined water content ($Wn^*\%$) in the C–S–H formed during the first 30 min of hydration. This is attributed to the sudden conversion of silica fume particles into a 'sol' or a 'gel', which then agglomerates [13] and reacts with the calcium hydroxide to form a lime-rich C–S–H. Figure 1 also reveals a sharp consumption of the free lime content during the first 30 min of hydration, whereas the free silica content is consumed gradually. The initial formation of a high-lime C–S–H was also re-

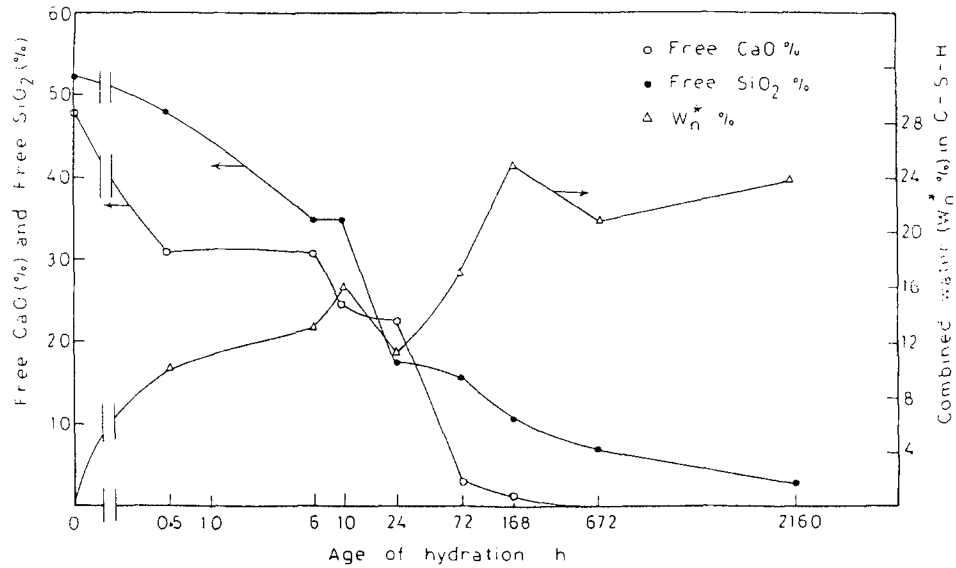

Fig. 1 Hydration characteristics of lime-silica fume specimens (Mix I)

ported earlier [14–17]. The formation of a lime-rich C–S–H is always accompanied by an increase in the chemically combined water content in the hydrate [18, 19]. The gradual increase in the non-evaporable water content between 30 min and 6 h of hydration is mainly attributed to the interaction between the silica fume grains and the initial lime-rich C–S–H coating, leading to a further decrease in the lime content of the initially formed C–S–H. Between 6 and 10 h of hydration, the noticeable increase in the *Wn** content is due to the interaction between the relatively low-lime C–S–H and free lime, leading to an increase in the lime content of the C–S–H formed. During this stage, the free lime content in the lime-silica fume paste decreases while the free silica content remains unchanged. Between 10 and 24 h of hydration, the decrease in the *Wn** content is attributed to some transformation of the relatively-lime C–S–H having a high water content into another C–S–H with a low water content. The C–S–H is thus produced as a result of a hydration interaction between the initially formed hydrates and the unhydrated parts of silica fume grains. The small particles of silica fume act as nucleation sites for the final C–S–H products. In this period of hydration, there is a slight decrease in free lime content, and a sharp decrease in free silica content. This is attributed to the interaction between active silica fume and the initially formed hydrates with a small free lime content, to form hydrates with a lower lime content. The further increase in the *Wn** content up to 7 days of hydration reflects an increase in the rate of hydration between lime and active silica fumes, leading to a large consumption of the free lime content up to 3 days of hydration and a slight decrease in the free silica content. On the other hand, the slight decrease in *Wn** content with hydration time up to 28 days is mainly attributed to a second stage of interaction between the coated layers of the C–S–H products formed and the remaining unhydrated parts of the active silica fume, leading to the formation of other hydrates with lower lime content; these low-lime hydrates always have a low combined water content [20]. During this time of hydration, all the free lime is consumed, while a gradual decrease is observed in the free silica content up to 90 days.

B. Mix II

The estimated results concerning the non-evaporable (chemically-combined) water content in the C–S–H formed, *Wn**% indicate a high rate of hydration interaction between lime and silica fume during the first 0.5 h of hydration; this represents the 'pre-dormant' period reported earlier in this investigation (Fig. 2). There is then an insignificant increase in the combined water content during the period from 0.5 to 6 h, which is mainly attributed to the coverage of the unhydrated grains by the initially formed C–S–H, as well as by large amounts of free lime in the lime-silica mixture (Mix II). The period 0.5–6 h represents a 'dormant period' in the mechanism of hydration. During this period, some sort of stabilization via crystallization of the initial lime-rich C–S–H product takes place [21]. After 6 h of hydration, the combined water content shows a marked increase up to 1 day. This increase in *Wn** content reflects an increase in the rate of the hydration reaction between lime and active silica fume; this stage represents the 'acceleration period' in the hydration mechanism. A decrease in the *Wn** content is then observed after 1 day of hydration, which is

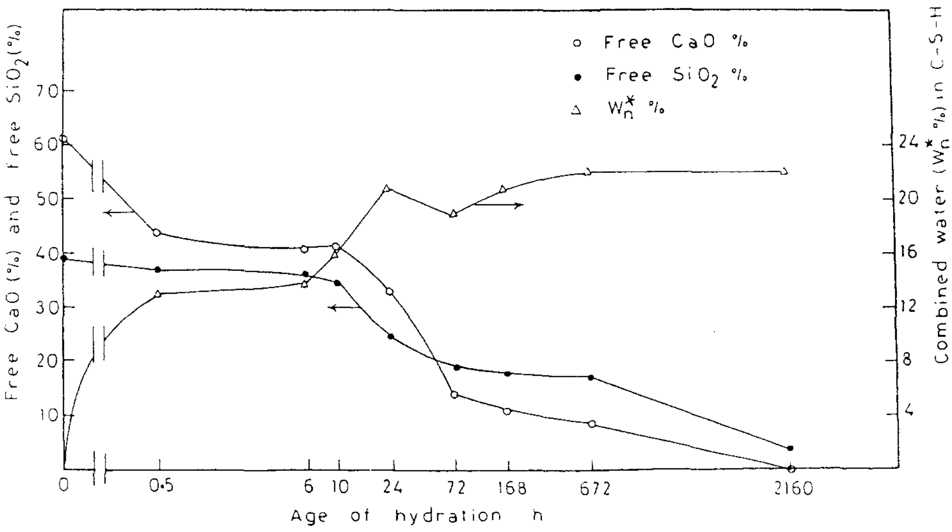

Fig. 2 Hydration characteristics of lime-silica fume specimens (Mix II)

mainly attributed to the formation of C–S–H containing a low combined water content. In the period 3–28 days, the water content exhibits a slight increase, indicating a 'diffusion period' in the mechanism of hydration between lime and silica fume; this stage is associated with the formation of the final hydration products. Later, the $Wn^*\%$ values assume a constant magnitude up to the final stage of the hydration reaction (90 days). This represents the stabilization of the hydrates formed, mainly C–S–H(I) and C–S–H(II).

The free lime contents in Fig. 2 indicate a continuous decrease in the free lime with increasing time of hydration, and all the lime is consumed after 90 days of hydration. Five stages of hydration can be distinguished, as shown in Fig. 2: (i) an initial sharp decrease in the free lime up to 30 min of hydration; this stage represents the initial formation of high-lime C–S–H, (ii) a very slight decrease in the free lime content between 0.5 and 10 h; during this stage, a stabilization of the initial hydrate takes place (dormant period), (iii) a marked decrease in the free lime content between 10 h and 3 days of hydration; this represents the 'acceleration period', (iv) a slight decrease in the free lime content up to 28 days of hydration (a second dormant period) and (v) a noticeable decrease in the lime content up to 90 days of the hydration interaction between lime and the remaining unhydrated parts of the silica grains. The free lime is consumed after 90 days of hydration. Therefore, two fast steps were detected in the hydration reaction, during the periods 0–30 min and 10 h - 3 days; a third, noticeable accelerated stage in also distinguished between 28 and 90 days of hydration.

The free silica contents shown in Fig. 2 indicate four stages in the suggested mechanism: (i) a slight decrease in the free silica content up to 10 h of hydration, (ii) a marked decrease in the free silica content between 10 h and 3 days, (iii) again a slight decrease in the free silica content between 3 and 28 days, and (iv) a second noticeable decrease in the free silica up to the final stage of hydration (90 days).

The results in Fig. 2 reveal that the mode of decrease in both free lime and free silica with hydration time up to 10 h reflects the formation and later stabilization of the initial high-lime C–S–H product. The high consumption of both free lime and free silica contents between 10 h and 3 days is mainly due to the interaction between active silica fume, lime and the initially formed high-lime hydrates to give C–S–H with a lower lime content [C–S–H(I) and C–S–H(II) phases]; later, these hydrates are stabilized, via crystallization, up to 90 days of hydration.

Molar composition

The molar ratio CaO/SiO_2 for the C–S–H formed was calculated from the combined lime, combined silica and combined water contents. The molar ratios CaO/SiO_2 and H_2O/SiO_2 of the C–S–H formed for Mixes I and II are presented in Tables 1 and 2, respectively.

Table 1 illustrates the mode of irregular variation of the ratios CaO/SiO_2 and H_2O/SiO_2 for the formal C–S–H in Mix I with curing time; these are nearly parallel during all the stages of hydration, which reflects that the main hydration product is tobermorite-like C–S–H during the stages between 6 h and 90 days. Obviously, the changes in the ratios CaO/SiO_2 and H_2O/SiO_2 of the formed C–S–H with the duration of hydration follow the same trends during the 6 stages of hydration reported earlier in the suggested mechanism. Table 1 also illustrates that the increase in lime content (CaO/SiO_2) of the C–S–H product is always accompanied by an increase in the water content (H_2O/SiO_2).

Table 1 Variations of H/S and C/S molar ratios for C–S–H formed of different ages of hydration of Mix I

Age of hydration	H/S molar ratio	C/S molar ratio
0.5 h	7.339	4.516
6 h	2.822	1.130
10 h	3.135	1.274
1 day	1.093	0.717
3 days	1.752	1.342
7 days	2.006	1.240
28 days	1.539	1.149
90 days	1.671	1.064

Table 2 reveals that the ratios CaO/SiO_2 and H_2O/SiO_2 for Mix II first decrease considerably between 0.5 and 6 h of hydration and then decrease sharply from 6 to 24 h. These stages represent the initial formation and subsequent stabilization of high-lime C–S–H with a high water content. These hydrates are then transformed into a low-lime C–S–H with a lower water content up to 24 h. After 3 days of hydration, the molar ratios H_2O/SiO_2 and CaO/SiO_2 exhibit al-

Table 2 Variation of H/S and C/S molar ratios for C–S–H formed of different ages of hydration of Mix II

Age of hydration	H/S molar ratio	C/S molar ratio
0.5 h	25.521	11.181
6 h	19.971	9.413
10 h	14.906	6.215
1 day	5.042	2.215
3 days	3.165	2.559
7 days	3.487	2.578
28 days	3.448	2.619
90 days	2.125	1.878

most parallel changes up to the final stage of the hydration process. This indicates the variations in lime content of the formed hydrates, associated with similar variations in the chemically combined water contents of these hydrates.

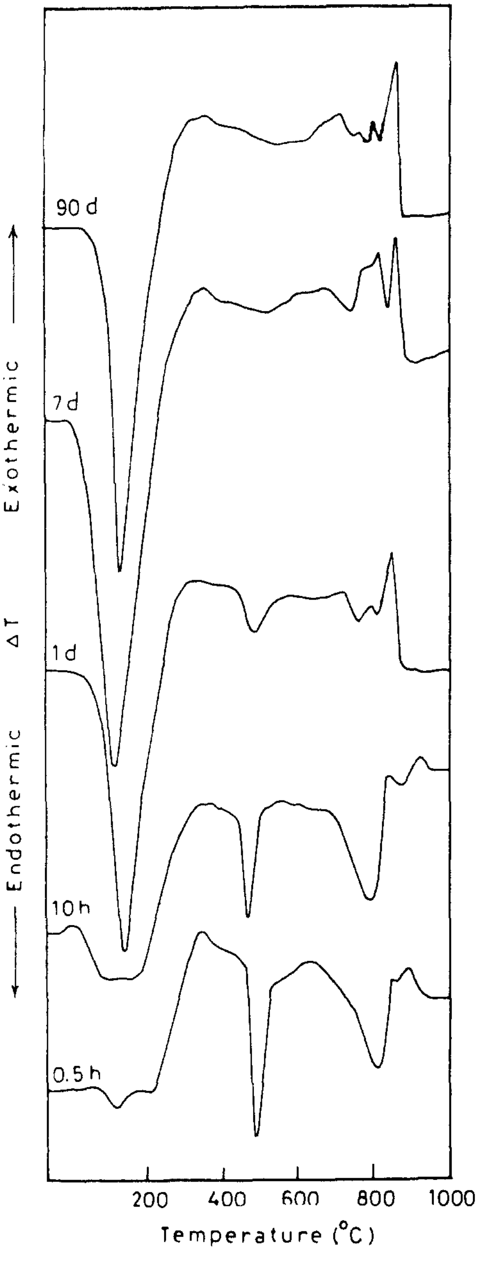

Fig. 3 Differential thermal analysis curves of lime-silica fume specimens (Mix I)

Fig. 4 Differential thermal analysis curves of lime-silica fume specimens (Mix II)

Differential thermal analysis (DTA)

Figure 3 shows DTA curves of hydrated Mix I. They indicate a strong endothermic peak at 510°C, due to the dehydration of calcium hydroxide subjected to a 30-min hydration, and a weak endothermic peak in the temperature range 115–230°C, due to dehydration of poorly-crystallized C–S–H(I) and tobermorite gel [22, 23]. The endothermic peak at 800°C is attributed to the decomposition of $CaCO_3$, and the small exothermic peak at 900°C to the transition of the decomposed C–S–H(I) to wollastonite. On increase of the duration of hydration, up to 10 h, 1, 7 and 90 days, the intensity of the endothermic peak at 120°C increased, indicating that C–S–H(I) is the predominant species, while $Ca(OH)_2$ gradually disappeared and was consumed after 7 days. Additionally, the intensity of the exothermic peak at 900°C increased with increasing time of hydration, due to the dehydration of C–S–H(I) with a resulting increase in stability.

Figure 4 shows the DTA curves of hydrated Mix II. They indicate that after 30 min of hydration the endothermic peaks at 110, 510 and 800°C characterize the decomposition of C–S–H(I) and/or C–S–H(II), $Ca(OH)_2$ and $CaCO_3$, respectively. The formation of C–S–H(II) is distinguished by its low-temperature decomposition peak at 100–110°C as it is less stable than C–S–H(I). With increasing duration of hydration, the intensity of the endothermic peak at 110°C (C–S–H) increased, while the intensity of the endothermic peak at 510°C, characterizing $Ca(OH)_2$, decreased. The appearance of an exothermic peak characterizing the transition of C–S–H(I) to wollastonite at 900°C indicates that the main hydration product is C–S–H(II).

Conclusions

The hydration reaction between lime and active silica fumes takes place in 6 steps. Increasing lime content in Mix II leads to the formation and stabilization of C–S–H at earlier stages of hydration, and to the formation of C–S–H(II) as well as C–S–H(I).

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