

## **HYDRATION CHARACTERISTIC OF LIME – SILICA FUME PASTES**

*Nabila M. Guindy, S. A. Abou El Enien, F. I. El Hosiny and S. M. A. El Gamal*

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, AIN SHAMS UNIVERSITY, ABBASSIA, CAIRO, EGYPT

The hydration of two calcium hydroxide – silica fume mixtures was studied at 25°C, these are Mix I and Mix II with molar lime/silica ratios of 1 and 1.7, respectively. The free lime, free silica and chemically combined water contents were determined at various time of hydration from which the molar CaO/SiO<sub>2</sub> ratios of the formed calcium silicate hydrate, C–S–H, were calculated. The results indicated that hydration takes place in six steps where C–S–H (I) is formed at early stages of hydration, for Mix I, while for Mix II formation of C–S–H (I) and C–S–H (II) were detected by X-ray diffraction analysis and differential thermal analysis.

**Keywords:** lime, silica fume

### **Introduction**

Several investigations have been reported on lime – silica systems, including silica fumes, lime – cement, lime – pozzolana and cement – silica mixtures [1–5]; these have covered the effect of lime-silica ratio, addition of alkalies, and metal oxides. Results show that products with the same chemical composition are represented by several phases and occur in very fine crystalline state called gels. The present study is concerned with the formation and molar composition of calcium – silicate hydrates produced by the hydration of lime – silica fume mixtures for various times up to 90 days.

### **Experimental**

Two solid mixtures were prepared using two different CaO/SiO<sub>2</sub> molar ratios of 1 and 1.7. These are referred to as Mix I and Mix II, respectively. Each dry

mixture was mixed in ethanol for two hours then evaporated at 100°C. The dry mixture was mixed in a ball mill for 3 hours to obtain complete homogeneity, mixed with water at a water/solid weight ratio 0.8, then stirred for 3 minutes, and finally molded in cylindrical containers and cured at 100% relative humidity for 24 hours. After demoulding the specimens were cured under water for 0.5, 6, 10 hours, 1, 3, 7, 28 and 90 days at room temperature. Preparation details and methods of study are reported elsewhere [6, 7].

Phase compositions of the cured specimens were determined by X-ray diffraction and differential thermal analysis.

## Results and discussion

### Hydration mechanism

Mix I (C/S = 1.0 molar ratio) showed a marked increase in chemically combined water ( $W_n^*$ ) during the first 30 minutes of hydration (Fig. 1). This is attributed to a rapid conversion of the silica fume particles into a 'sol' or a 'gel', which then reacts with calcium hydroxide to form a lime-rich calcium silicate hydrate (C-S-H). This represents the initially formed hydration product.

Figure 1 also shows that the free lime is rapidly consumed during the first 30 minutes of hydration, whereas the free silica reacts only gradually. The initial formation of a light lime C-S-H has also been reported earlier [6-8]. Formation of a lime-rich calcium silicate hydrate is always accompanied by an increase in chemically combined water [9, 10]. The gradual increase in combined water between 30 minutes and 6 hours hydration (Fig. 1) is attributed mainly to the interaction between the silica fume grains and the initial lime-rich C-S-H coatings, leading to a decrease in the lime content of the product. Between 6-10 hours

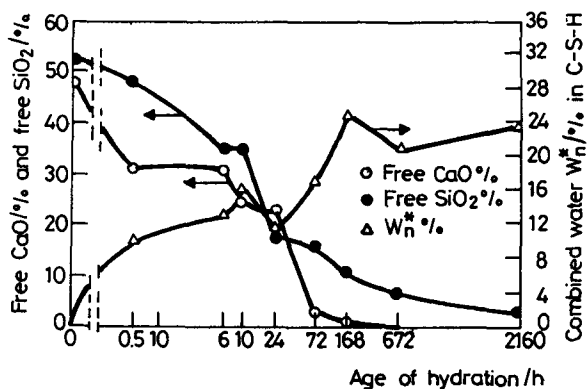


Fig. 1 Hydration characteristics of lime-silica fume specimens (Mix I)

hydration, the marked increase in  $Wn^*$  is due to interaction between the relatively low-lime C-S-H and the free lime, leading to an increase in the lime content of the formed calcium silicate hydrate; the free lime content of the lime – silica fume paste decreases while the free silica content remains almost constant. The subsequent decrease in  $Wn^*$  after one day of hydration is mainly attributed to transformation of higher water content C-S-H phase into another with lower water content; this could have been due to interaction of initially formed hydrates with unhydrated parts of silica fume grains. During the initial stage of hydration reaction (up to 10 hours) formation of poorly crystallized calcium silicate hydrates around active silica could have hindered the hydration interaction between lime and silica. The further increase in  $Wn^*$  up to 7 days of hydration reflects an increase in the rate of hydration between lime and active silica fume with a large consumption of the free lime content. Again the slight decrease in combined water with hydration time up to 28 days is mainly attributed to a second stage of interaction between coating layers of the formed C-S-H products and the remaining unhydrated parts of the active silica fume, leading to the formation of other hydrates with a lower lime content; these low lime hydrates always have low combined water contents. The slight increase in combined water up to 90 days of hydration indicates a third stage in the hydration reaction between formed C-S-H hydrates and the remaining active silica, with formation of the final C-S-H products. These changes in  $Wn^*$  are reflected by changes in free-lime and free-silica contents. The free lime results plotted in Fig. 1 indicate a variable decrease with increasing time of hydration and that all the lime was consumed after 28 days' curing under water. Five stages can be distinguished from Fig. 1:

- (i) an initial sharp decrease in free lime up to 0.5 hour of hydration
- (ii) the free lime content remains constant from 0.5 to 6 hours hydration
- (iii) a noticeable decrease in free lime content between 6 hours and one day of hydration
- (iv) a second, sharp decrease in free lime up to 3 days of hydration
- (v) a final gradual decrease in the free lime content up to 7 days curing, where all the free lime was consumed after 28 days of the hydration process.

Changes in free silica contents are also shown in Fig. 1, which indicates that the hydration reaction between lime and active silica takes place in six steps:

- (i) a pre-dormant stage taking place up to 0.5 hour of hydration, where the silica fume spheres agglomerate and interact with  $\text{Ca}(\text{OH})_2$
- (ii) a sharp decrease in free silica with no consumption of free lime during 0.5–6 hours, which is attributed to interaction between initially formed lime-rich C-S-H, as representing the initial coating film around the silica fume particles, and the unhydrated active silica grains engulfed by the high-lime C-S-H film, to form C-S-H of a lower lime content

(iii) the free silica content remains unchanged from 6 to 10 hours of hydration whilst, the free lime decreases

(iv) a second sharp decrease in free silica between 10 hours and one day of hydration which is attributed mainly to interaction between active silica fume and initially formed hydrates with a small amount of free lime to form hydrates with a lower lime content

(v) a slight decrease in free silica between one and three days of hydration, where a sharp consumption of free lime takes place leading to a further increase in the lime content of the C-S-H product

(vi) a gradual decrease in the free silica content during the period of 3–90 days indicating marked consumption of silica, even after the complete consumption of free  $\text{Ca}(\text{OH})_2$  where the remaining unhydrated parts of silica grains interact with the calcium silicate hydrates to form other hydrates having a lower lime content (low-time C-S-H).

### Molar composition

$\text{CaO}/\text{SiO}_2$  ratios of the C-S-H products were calculated from the combined lime, combined silica and combined water contents. Figure 2 shows that the  $\text{CaO}/\text{SiO}_2$  and  $\text{H}_2\text{O}/\text{SiO}_2$  ratios of the formed (C-S-H) in Mix I vary in a similar fashion during all stages of hydration, which reflects the fact that the main hydration product is a tobermorite-like C-S-H phase.

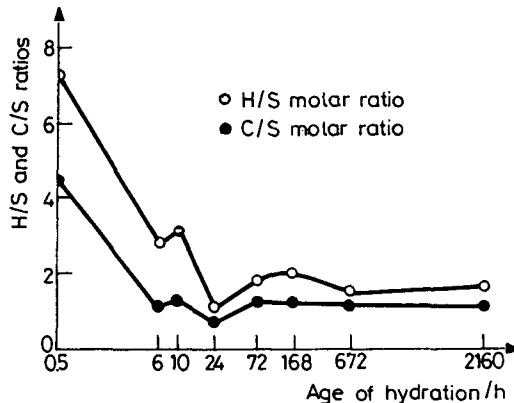


Fig. 2 Molar  $\text{CaO}/\text{SiO}_2$  and  $\text{H}_2\text{O}/\text{SiO}_2$  ratios as a function of curing time for the hydrates of lime-silica fume specimens (Mix I)

### XRD analysis

XRD analysis of Mix I showed formation of C-S-H (I) after 7 days, while peaks of  $\text{Ca}(\text{OH})_2$  disappeared completely. For Mix (II), XRD analysis indicated formation of a poorly crystallized C-S-H phase characterized by a peak at  $3.06 \text{ \AA}$  after 30 min. With increase in hydration C-S-H peak intensities increased; the phase present after 90 days was mainly C-S-H (I) with some C-S-H (II).

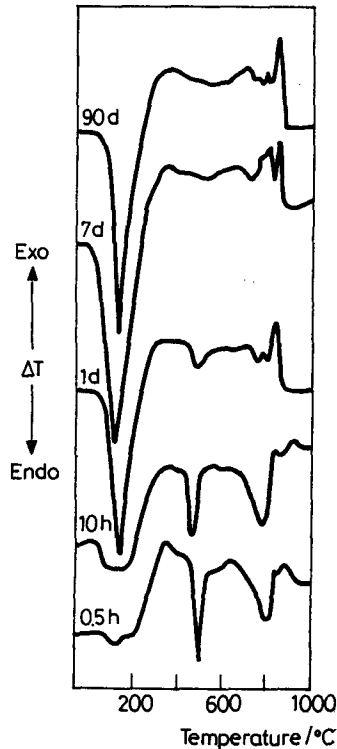


Fig. 3 DTA curves of lime-silica fume specimens (Mix I)

### DTA

Figure 3 shows the DTA curves of hydrated Mix I. These show a strong endothermic peak at  $510^\circ\text{C}$  due to the dehydration of calcium hydroxide and a weak endothermic peak between  $115\text{--}230^\circ\text{C}$  due to dehydration of poorly crystallized calcium silicate hydrate (C-S-H (I)) and tobermorite gel [11, 12]. The endother-

mic peak at 800°C is attributed to decomposition of  $\text{CaCO}_3$  while the small exothermic peak at 900°C is due to the transformation of decomposed C-S-H (I) to wollastonite. With increasing time of hydration (over 10 hours) the intensity of the endothermic peak at 120°C increased, indicating that C-S-H (I) is the predominant species, while  $\text{Ca(OH)}_2$  disappeared gradually, being consumed after 7 days. In addition, the intensity of the exothermic peak at 900°C increased with increasing time of hydration due to the dehydration of C-S-H (I).

Figure 4 shows that after 30 minutes hydration endothermic peaks at 110°, 510° and 800°C characterize decomposition of C-S-H (I) and/or C-S-H (II),  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$ , 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 time of hydration the intensity of the endothermic peak at 110°C of C-S-H increased, while the intensity of the endothermic peak at 510°C due to  $\text{Ca(OH)}_2$  decreased. The appearance of an exothermic peak

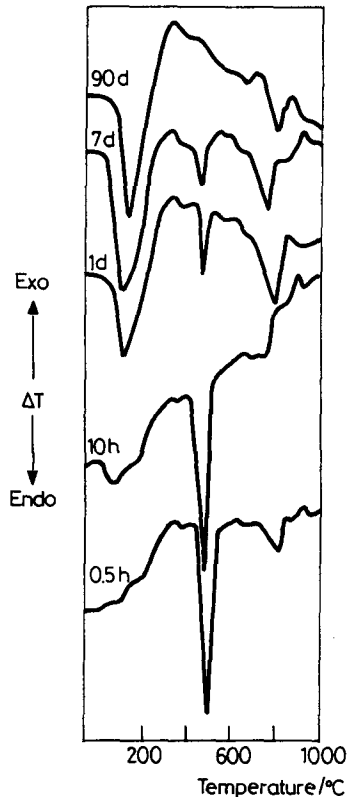


Fig. 4 DTA curves of lime-silica fume specimens (Mix II)

due to the transformation of C-S-H (I) to wollastonite at 900°C indicates that the main hydration product C-S-H (I).

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**Zusammenfassung** — Bei 25°C wurde die Hydratation von zwei Calciumhydroxid-Siliziumdioxid-Aschegemischen untersucht. Dieses sind die Gemische Mix I und Mix II mit einem molaren Kalk/Kieselerde-Verhältnis von 1 und 1.7. Zu verschiedenen Hydratationszeiten wurde der Gehalt an freiem Kalk, freier Kieselerde und chemisch gebundenem Wasser bestimmt, woraus das molare CaO/SiO<sub>2</sub> Verhältnis des gebildeten Calciumsilikathydrates C-S-H berechnet wurde. Die Hydratation verläuft in sechs Teilschritten, wobei im Falle von Mix I das C-S-H (I) in den Anfangsschritten gebildet wird, während Röntgendiffraktion und DTA bei Mix II die Bildung von C-S-H (I) und C-S-H (II) zeigen.