Pergamon

Cement and Concrete Research, Vol. 25, No. 6, pp. 1311-1319, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00124-7

STRÄTLINGITE FORMATION IN HIGH ALUMINA CEMENT - SILICA FUME SYSTEMS: SIGNIFICANCE OF SODIUM IONS

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(Refereed)
(Received November 30, 1994; in final form February 24, 1995)

ABSTRACT

The effect of sodium sulphate on strätlingite formation in the high alumina cement - silica fume -water system is described. The reaction mechanisms associated with strätlingite and hydrogarnet formation are discussed. The effect of silica fume addition on the microstructure of HAC paste is also reported. Sodium ions have a significant influence on strätlingite formation in these systems. A mechanism for strätlingite formation is postulated. It involves reactions between CAH_{10} or C_2AH_8 and dissolved silica. Presence of sodium ions accelerates dissolution of silica required for strätlingite formation.

INTRODUCTION

High early strength, good chemical resistance and high temperature resistance of high alumina cement (HAC) products have encouraged the use of high alumina cement concrete in certain construction engineering applications. However, conversion of hexagonal phases, CAH_{10} or C_2AH_8, to C_3AH_6 and AH_3 in hydrated HAC concrete under certain temperature conditions has been a major problem limiting its use. The conversion process can result in significant reduction of strength during the service life of the concrete. The presence of a minor amount of C_2ASH_8 (strätlingite) in HAC at later ages, was reported by Midgley [1, 2]. It was suggested that strätlingite formation might be responsible for the strength recovery after conversion as it has relatively high strength. Microsilica has been reported to favour the formation of strätlingite [3]. Granulated blast-furnace slag can also react with high alumina cement phases resulting in the formation of strätlingite [4-9]. It was suggested that the reduction of strength in HAC due to conversion might be preventable. This was attributed to strätlingite formation in preference to C_3AH_6. Bentsen et al [3] reported that strätlingite could crystallize as a stable phase in the temperature range, 20 to 70 °C. Fentiman et al [10] suggested that in a HAC-based system the optimum curing temperature for strätlingite formation was about 40 °C, above which more C_3AH_6 would form. A synthetic strätlingite has been observed in the form of thin hexagonal plate crystals [11]. The use of silica fume in HAC paste was described by Majumdar and Singh [8]. The compressive strength of HAC/silica fume paste (HAC/silica fume mass ratio = 60/40) was significantly lower than that of plain HAC paste when water-cured at 40 °C up to one year, although strength reduction due to conversion was avoided. Strätlingite was detected in the paste at 28 days hydration. Hydrogarnet (C_3AH_6) phase converted from hexagonal hydrates (C_2AH_8) was still present. The use of silica fume in combination with sodium tripolyphosphate as a defloculating agent in HAC mortars was reported by Marcdargent et al [12]. The sodium tripolyphosphate addition improved workability and reduced strength reduction of the HAC/silica fume mortar prepared at w/c=0.3 and water-cured at 38 °C. The action of sodium tripolyphosphate in preventing strength reduction in the HAC/silica fume mortar was not fully understood. Recently the significant role of alkali ions on strätlingite formation in the HAC-microsilica system has been elucidated [13-16]. Silica reacts to form silicates in a high pH environment. This reaction is accelerated in presence of an increased amount of alkali ions. The alkali ions may act as a catalyst activating microsilica surfaces. Silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite.

The objective of this paper is to demonstrate the significance of sodium ions in strätlingite formation and hydrogarnet prevention in the HAC/silica fume system.

EXPERIMENTAL

Materials included Ciment Fondu, a high alumina cement (HAC), produced by Lafarge Calcium Aluminates, Virginia, USA; Silica Fume supplied by the SKW Co., Montreal, Canada; reagent grade sodium sulphate. The oxide compositions of HAC and silica fume are listed in Table 1.

Table 1. Oxide Compositions of HAC and Silica Fume

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	SO_3
HAC	4.5	41.2	39.8	11.3	0.60	0.10	-
Silica Fume	95.17	0.21	0.23	0.13	0.15	0.37	0.12

HAC paste mixes prepared for X-ray diffraction analysis are listed in Table 2:

Table 2. Mix Components of Cement Pastes prepared for XRD Analysis (grams)

Name	HAC	Silica Fume	Sodium Sulphate	Calcium Hydroxide	Water
MS-164	100	-	-	-	60
MS-71	100	30	-	-	78
MS-163	100	-	4.7	-	60
MS-72	100	30	4.7	-	78
MS-200	100	-	-	-	60
MS-202	100	-	-	1	60

Cement paste samples having a high water/solid ratio (0.60) were used for XRD analysis. The major peaks associated with the strätlingite C_2ASH_8 phase (d=1.258 nm) and the hydrogarnet C_3AH_6 phase (d=2.04 nm) were monitored for all the samples. The test was designed for comparison of parallel samples. The comparison is based on significant differences between parallel samples. The cement pastes were cast in plastic bottles (25 mm in diameter) and rotated on rollers for 24 hours. The hardened cement paste samples after demoulding were cured in water. Some pastes (MS- 71, 72, 163 and 164) were cured at 38 °C and the others (MS- 200 and 202) were cured at 23 °C. The sample cut from the cylinders was ground in acetone and then scanned by XRD (degrees 2θ from 3 to 60°) at designated ages. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used. Copper Kα radiation was employed. The peak height was calculated using Rigaku Standard Data Processing software. SEM micrographs were obtained using a Cambridge Stereoscan S250.

The HAC mortars containing 2% sodium sulphate by weight of HAC were prepared for determination of compressive strength. The mixes are listed in Table 3:

Table 3. Mix Components of Cement Mortar for Compressive Strength Test (arbitrary mass units)

name	HAC	silica fume	sodium sulphate	SMF*	sand	water	water/solid** ratio
MS-1	1	-	-	-	2.75	0.4	0.40
MS-133	1	0.2	0.02	-	2.75	0.48	0.40
MS-105	1	0.3	0.02	-	2.75	0.60	0.46
MS-129	1	0.3	0.02	0.006	2.75	0.52	0.40

*SMF - superplasticizer, sodium sulfonated melamine formaldehyde; ** solid - HAC + silica fume.

The compressive strength test was carried out on cube specimens (50x50x50 mm). The specimens were moist-cured at 23 °C for 24 hours and then water-cured at 38 °C after demoulding.

RESULTS AND DISCUSSION

Although microsilica is believed to promote strätlingite formation in HAC paste, it is still not able to prevent hydrogarnet formation [8]. A significant change in the hydration of the HAC - silica fume system could be observed as sodium sulphate was added (Fig. 1). The HAC pastes (water-solids ratio = 0.6) were water-cured at 38 °C for 120 days.

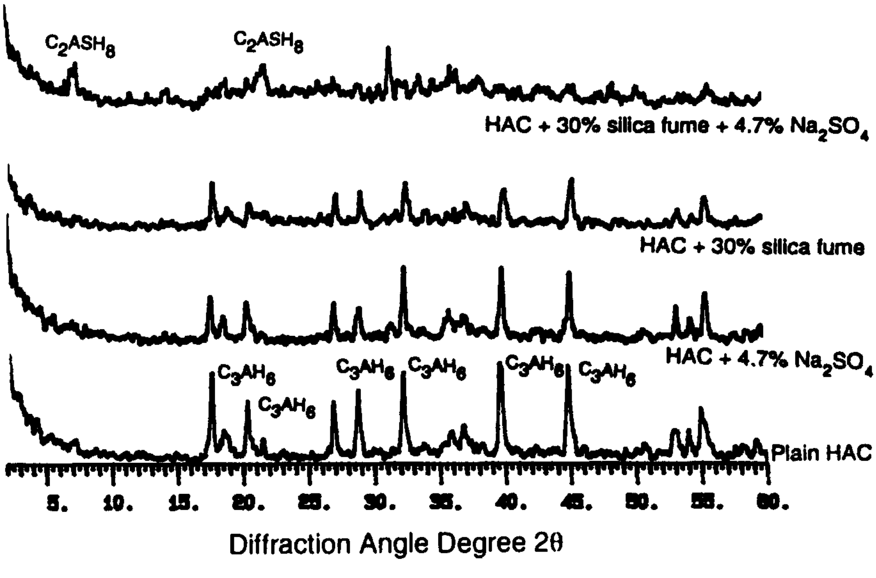
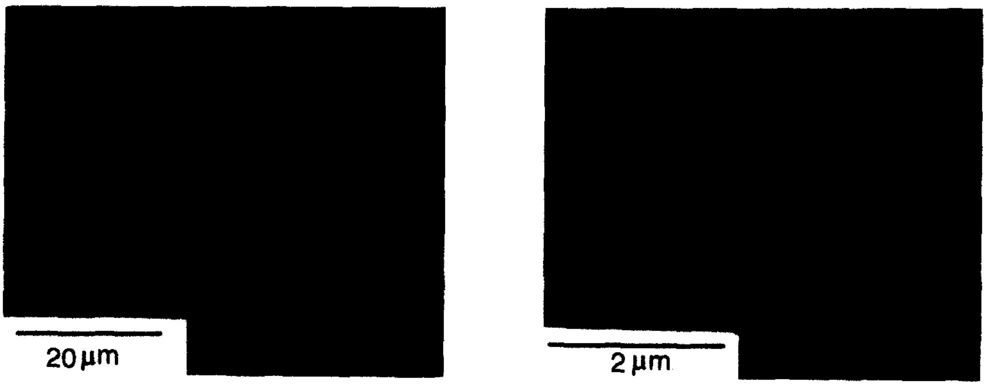


Figure 1. XRD patterns for HAC/silica fume paste with or without sodium sulphate at 120 days age.

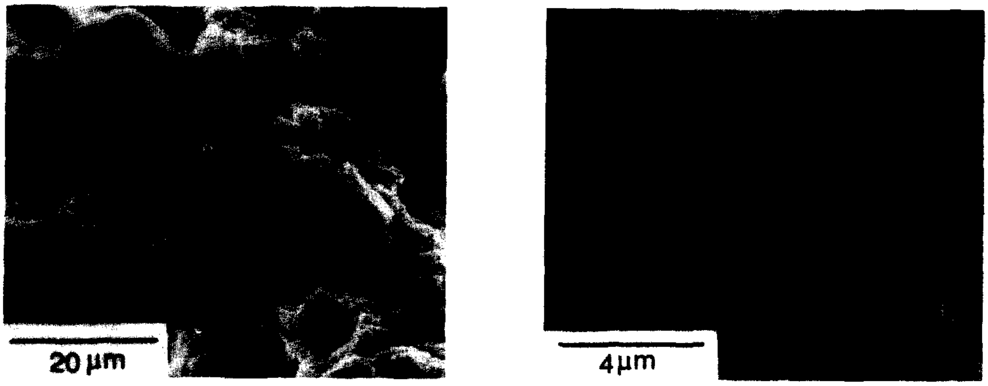
Very high intensity hydrogarnet peaks were recorded by XRD analysis on the plain HAC paste. Addition of sodium sulphate alone in HAC paste slightly reduces the peak intensities of the C_3AH_6 phase. Silica fume appeared to be more effective in reducing C_3AH_6 formation in HAC paste. It, however, does not eliminate the conversion. Hydrogarnet was still the major phase in the HAC/silica fume paste. Very little strätlingite phase was detected in these samples. The hydration process in HAC paste was essentially different as silica fume was added in combination with sodium sulphate. The hydrogarnet phase almost disappeared and strätlingite became the dominant phase in HAC/silica fume paste containing 4.7% sodium sulphate. Hydrogarnet, a stable product from the traditional conversion, was replaced by strätlingite.

The microstructure of HAC/silica fume pastes was examined by SEM analysis (Fig. 2). A large number of silica fume particles still remained in HAC/silica fume paste



a. HAC/silica fume paste.
(w/s = 0.6, 120 days)

b. Silica fume on the surfaces of hydration products in HAC/silica fume paste.
(w/s = 0.6, 120 days)



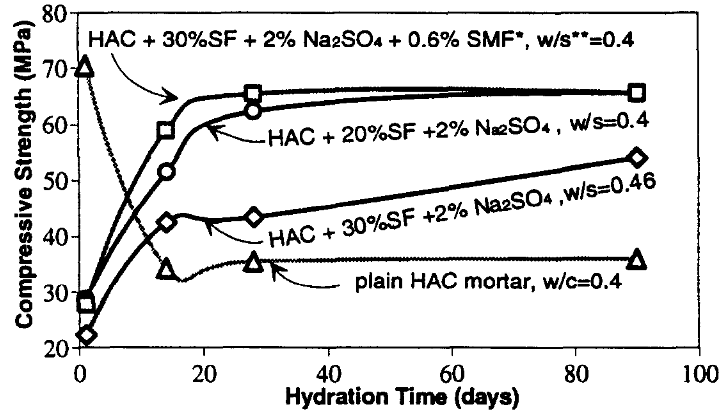
c. HAC/silica fume paste containing 4.7% sodium sulphate.
(w/s = 0.6, 120 days)

d. Strätlingite plates in HAC/silica fume paste containing 4.7% sodium sulphate.
(w/s = 0.6, 120 days)

Figure 2. SEM analysis for HAC/silica fume paste with or without sodium sulphate water cured at 38 °C for 120 days.

water-cured at 38 °C for 120 days (Fig. 2, a). It was found that these non-reacted silica fume particles resided on the surface of hydration products or were present in space between the hydration products (Fig. 2, b). This apparently weak structure may be responsible for the low strength of HAC/silica fume paste. The amount of unhydrated silica fume particles appears to be relatively less in HAC/silica fume paste containing 4.7% sodium sulphate (Fig. 2, c). Strätlingite plates were commonly found (Fig. 2, d). Addition of sodium sulphate apparently increased the reactivity of silica fume and promoted strätlingite formation.

The significance of sodium salts in preventing strength reduction due to conversion is shown in Fig. 3. The compressive strength of plain HAC mortar was about 70 MPa at one-day. It, however, dropped to about 32 MPa at 14 days hydration. Little recovery of the strength then developed with the hydration. The HAC mortar containing 20% silica fume and 2% sodium sulphate had relatively low compressive strength (about 28 MPa) at the first day. The strength then quickly increased to above 50 and 60 MPa at 14 and 28 days, respectively. The strength development after 28 days was minimal. The increase of silica fume content to 30% in HAC mortar significantly decreases the 28-day strength. The reasons for this might be: (1) the corresponding increase of water/solid ratio requirement from 0.4 to 0.46 to satisfy workability as the silica fume content was increased from 20% to 30%; (2) the retarding effect of microsilica as reported by the authors [12]; and (3) weak structure characterized by a large amount of unhydrated silica fume particles. Sodium sulfonated melamine formaldehyde, a superplasticizer, was used to reduce the water/solid ratio of HAC mortar containing 30% silica fume and 2% sodium sulphate. The HAC/silica fume mortars containing 20% or 30% silica fume and with the same water/solid ratio 0.4 had very similar strength development. This indicated that the addition of 20% silica fume and 2% sodium sulphate in HAC paste was sufficient to prevent significant strength reduction related to conversion. It is therefore relevant that addition of a small amount of sodium sulphate can effectively reduce the amount of silica fume in HAC required to achieve the same objective.



SMF= superplasticizer, sodium sulfonated melamine formaldehyde;
*** s= solid including HAC and silica fume (SF)*

Figure 3. Effect of sodium sulphate on strength of HAC/silica fume mortars (moist-cured at 23 °C in the first 24 hours and then water-cured at 38 °C).

The effect of silica fume and sodium sulphate on hydrogarnet formation in HAC paste with hydration time is shown in Fig. 4. The peak intensity was calculated using Rigaku Standard Data Processing software. Small peak intensities (e.g. less than 50 Cps units) can be detected by the computer program; they may not be clearly visible in the spectra (see Fig. 1). Hydrogarnet in plain HAC paste cured at 38 °C mostly formed during the first day of hydration. Little change in hydrogarnet peak intensities in plain HAC paste was found at later ages. Silica fume and sodium sulphate delay hydrogarnet formation for about 3 days, respectively. Sodium sulphate can react with the calcium ions liberated from HAC during hydration. A high pH environment accelerates the hydrogarnet formation [17]. The effect of calcium hydroxide addition on hydrogarnet formation in HAC paste is shown in Fig. 5. It is evident that the addition of calcium hydroxide to HAC promotes the conversion process even at low temperature (23 °C). Wu et al. reported that relatively higher CaO concentrations in HAC stabilized crystalline hydrogarnet [18].

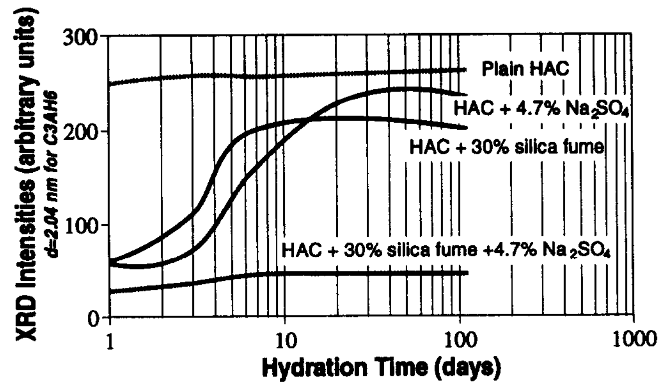


Figure 4. Effect of silica fume and sodium sulphate on hydrogarnet formation in HAC paste water-cured at 38 °C for 120 days.

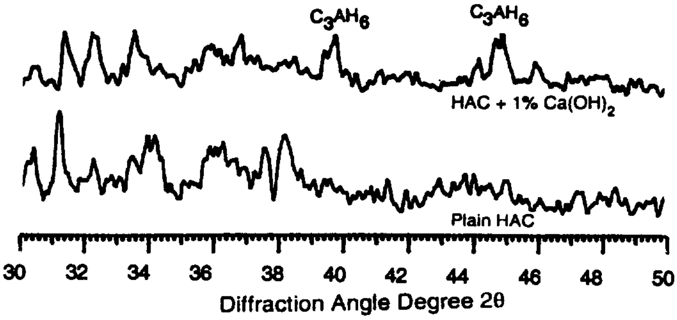


Figure 5. Effect of calcium hydroxide on hydrogarnet formation in HAC paste moist-cured at 23 °C for 4 days.

The effect of silica fume and sodium sulphate on strätlingite formation in HAC paste with hydration time is shown in Fig. 6. A small peak at d=1.258 nm was detected in plain HAC paste water-cured at 38 °C for 3 days. This might be attributed to the presence of strätlingite. The peak intensity increased slightly up to 10 days hydration and then remained approximately constant. Silica fume slightly accelerates strätlingite formation at early ages. A small increase in intensity of strätlingite peaks was found in HAC paste containing silica fume compared to plain HAC paste. Sodium sulphate greatly accelerated strätlingite formation during the first day hydration. Since there were no additional silicate sources, the strätlingite peak intensities in HAC paste containing 4.7% sodium sulphate were finally the same as that in plain HAC paste. Addition of silica fume in combination with sodium sulphate significantly increased strätlingite formation. The first day peak intensities of strätlingite in the HAC paste containing 30% silica fume and 4.7% sodium sulphate were about 50% greater than the ultimate peak intensities of strätlingite in the other samples. A large increase in strätlingite formation was found from 3 to 10 days. It has been postulated that sodium ions might play an important role in increasing dissolution of silicate in the HAC system containing silica fume[13]. This reaction mechanism may be operative in the period of accelerated strätlingite formation. The equilibrium X-ray peak intensity of the strätlingite phase in such paste was about 3 times that of in the other samples.

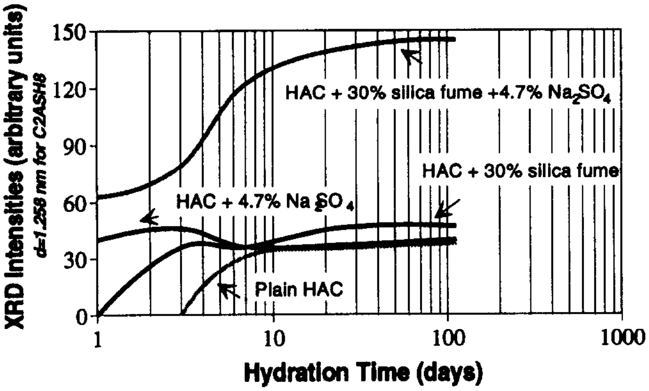


Figure 6. Effect of silica fume and sodium sulphate addition on strätlingite formation in HAC paste water-cured at 38 °C for 120 days.

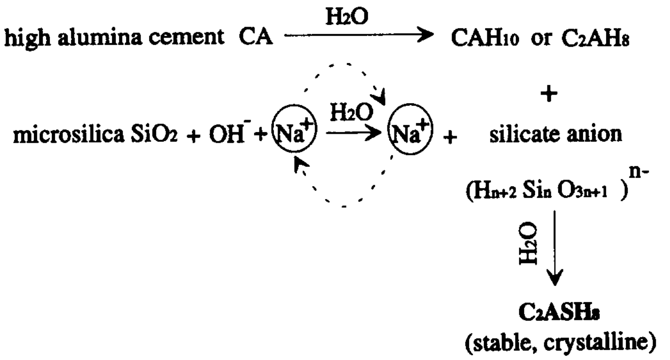
Since hexagonal calcium aluminate hydrates in traditional HAC products are thermodynamically unstable, they generally convert to stable cubic hydrogarnet. In the absence of additional measures strength reduction of HAC products after conversion is likely to occur. The addition of silica fume in combination with sodium salt in the HAC system alters the conventional conversion process. Metastable hydrates react with dissolved silica to form strätlingite rather than convert to different aluminates. Dissolved silica from microsilica promotes strätlingite formation in the HAC-microsilica system. Sodium ions play an important role in activating silica fume to form dissolved silica. The reaction mechanisms referred to above are briefly described as follows:

- **Classical conversion reaction in an HAC system:**

$$CA \xrightarrow{H_2O} CAH_{10} \text{ or } C_2AH_8 \xrightarrow{H_2O} C_3AH_6$$

(stable, crystalline)

- **Modified conversion reaction in an HAC - microsilica - sodium salt system:**



CONCLUSIONS

Sodium ions appear to play a significant role in strätlingite formation in HAC - silica fume systems. It is postulated that crystallization of strätlingite results from the reaction between CAH_{10} or C_2AH_8 and dissolved silica. Sodium ions promote increased dissolution of silica required for strätlingite formation. Hydration of silica fume in HAC paste without addition of sodium salt is very slow. Large amounts of unhydrated silica fume on HAC hydrate surfaces may result in low strength of HAC paste.

ACKNOWLEDGMENTS

Financial support from NSERC and the Network of Centers of Excellence on High Performance Concrete is gratefully acknowledged. Thanks are extended to Mr. E. G. Quinn for the preparation of SEM micrographs.

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