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STUDY OF HYDRATION MECHANISMS IN THE HIGH ALUMINA CEMENT - SODIUM SILICATE SYSTEM

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ABSTRACT

The retarding effect of sodium silicate on high alumina cement (HAC) hydration is demonstrated. The effect of sodium silicate addition on phase formation in HAC paste during hydration is studied. A reaction mechanism involving strätlingite formation in the HAC-sodium silicate system is postulated. Test results indicate that presence of silicate can strongly retard the hydration of high alumina cement. It promotes the formation of strätlingite.

Introduction

Hexagonal calcium aluminate hydrates (CAH_{10} or C_2AH_8) will convert to cubic hydrogarnet (C_3AH_6) in hydrated HAC concrete under certain environmental conditions (e.g. elevated temperature and high relative humidity) [1]. An HAC-based blended cement containing about equal amounts of granulated blast-furnace slag by mass was reported by Majumdar et al [2-6]. Inhibition of the conversion reaction was attributed to strätlingite formation in preference to the hydrogarnet. Microsilica has also been reported to favour the formation of strätlingite in HAC [7]. The early strength of such material containing silica fume or granulated blast-furnace slag is significantly reduced compared to that of plain HAC [5]. The strength then slowly increases to a value approaching the one-day strength of HAC concrete at 1-2 years when water-cured at 20 °C. Hydrogarnet was still formed in the HAC paste containing silica fume water-cured at both 20 and 40 °C. The retarding effect of microsilica on HAC was reported by Bentsen et al [7]. They argued that there is a connection between the retardation phenomenon and the reduction of pH value and amount of calcium interacting with the microsilica.

The objective of this study is to demonstrate the effect of sodium silicate addition on the HAC hydration, setting time and strätlingite formation.

Experimental

The materials used in the current study included Ciment Fondu, a high alumina cement (HAC), produced by Lafarge Calcium Aluminates, Virginia, USA; reagent grade sodium silicate supplied by Silicates National Ltd, Toronto, Canada. Mixes for X-ray diffraction analysis of HAC pastes are listed in the following table:

Mix Quantities for XRD Analysis of Cement Pastes (grams)

name	HAC	sodium silicate
MS-200	100	-
MS-170	100	0.25
MS-169	100	0.5
MS-171	100	0.75
MS-194	100	1
MS-195	100	1.5

Cement paste samples having a water/solid ratio (0.60) were used for XRD analysis. The high water/solid ratio allows the rapid completion of hydration. The test was conducted at 23 °C. The major peaks associated with the strätlingite (C_2ASH_8) phase (d=1.26 nm), the C_2AH_8 phase (d=1.07 nm), unhydrated CA (d=0.298 nm) and the hydrogarnet (C_3AH_6) phase (d=0.204 nm) were selected and monitored for all the samples. The test was designed for the comparison of parallel samples prepared by an identical process. The comparison is based on significant differences between parallel samples. Some samples were repeated three times. The relative error of peak height (e.g. C_2ASH_8 at d=1.07 nm) was 10%. The cement pastes were cast in plastic bottles (25 mm in diameter) and rotated on rollers for 24 hours at 25 °C. The hardened cement paste samples after demoulding were water-cured at 23 °C. The sample cut from the cylinders was ground in acetone and then scanned by XRD 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.

A separate series of HAC pastes, with water/cement = 0.25 and sodium silicate contents, 0, 0.25, 0.5, 0.75, 1.0, 1.5% by mass of HAC, were prepared for determination of setting time and compressive strength. The lower water/cement ratio is consistent with the provisions of ASTM C 807-89. Setting was determined according to ASTM C 807-89. The compressive strength test was carried out on prism specimens (25x25x40 mm). The hardened paste specimens were water-cured at 23 °C.

Results and Discussion

The effect of sodium silicate on the setting time of HAC paste is shown in Fig. 1. The setting time can be retarded by 3 hours for the HAC paste containing 1% sodium silicate. Since addition of sodium hydroxide to HAC paste is known to cause quick setting [8,9], it appears that (1) sodium ions may not contribute to the retarding mechanism; (2) silicate can strongly retard the hydration of HAC.

The retarding effect of sodium silicate on HAC hydration was also reflected in the strength development curve (Fig. 2). The compressive strength of HAC paste at 1 day decreased dramatically with the addition of sodium silicate up to 0.5% by mass of HAC. Little difference in strength was found when the addition of sodium silicate was higher than 0.5%. Little effect of sodium silicate on 21-day compressive strength values was found.

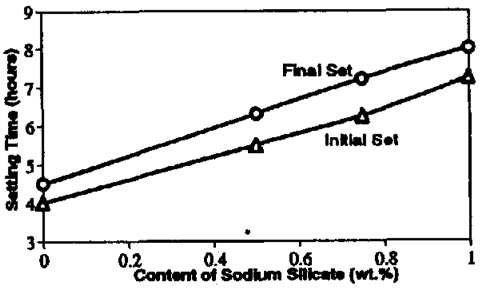

FIG. 1.
Effect of sodium silicate on setting time of HAC paste.

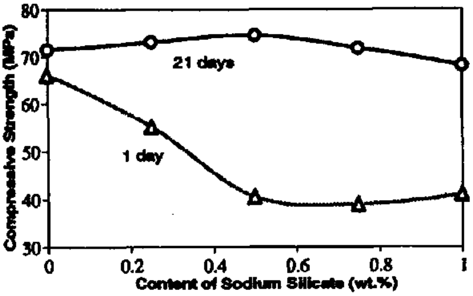

FIG. 2.
Effect of sodium silicate on strength development of HAC paste.

The effect of sodium silicate on CA depletion and C_2AH_8 formation in HAC paste at 1-day is shown in Fig. 3. The tests were carried out at 23 °C. More CA remained and correspondingly less C_2AH_8 formed in HAC paste as sodium silicate addition increased from zero to 1.5%. No C_2AH_8 phase was detected in the HAC paste containing 1.5% sodium silicate at 1-day. CA depletion with hydration time is illustrated in Fig.4. CA was nearly all hydrated in the first day in plain HAC paste. The residual CA was eventually constant after 2 days. CA hydration was obviously delayed as sodium silicate was added. CA depletion in the HAC pastes containing sodium silicate reached an equilibrium state after 5-days' hydration. An increase of sodium silicate clearly increases the retarding effect on CA hydration.

The effect of sodium silicate on the phase formation in HAC paste during hydration is shown in Fig.5 and 6. CA depletion and hydrate formation in plain HAC paste appears to be nearly complete after the first day. C_2AH_8 was the major hydration product. Small peaks of C_2ASH_8 and C_3AH_6 were detected after 3 days. The C_2ASH_8 formation in plain HAC paste resulted from the hydration of some minor silica-bearing constituents in high alumina cement such as C_2AS

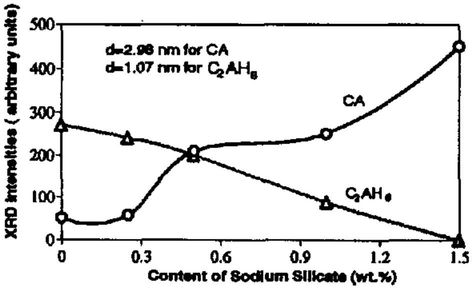

FIG. 3.
Effect of sodium silicate (SS) on CA depletion and C_2AH_8 formation in HAC paste at 23 °C and 1-day.

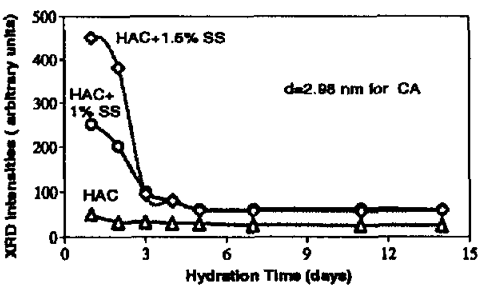

FIG. 4.
Effect of sodium silicate (SS) content on CA depletion with hydration time in HAC Paste.

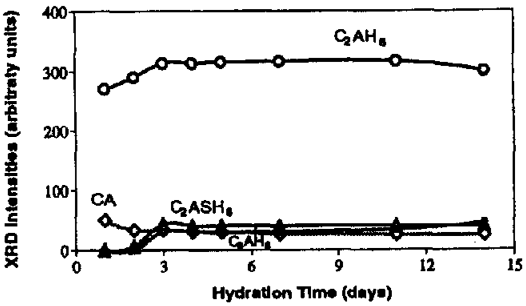

FIG. 5.
Phase formation in plain HAC paste.

and β-C_2S [7, 9]. CA depletion and C_2AH_8 formation in HAC containing 1% sodium silicate occurred gradually in first 5 days. The C_2AH_8 peak intensity then decreased with hydration time. The peaks for C_2ASH_8 and C_3AH_6 phases increased throughout the hydration period investigated. The XRD peak intensities of C_2ASH_8 and C_3AH_6 phases in HAC paste containing sodium silicate were higher than those in plain HAC paste.

The effect of sodium silicate content on the formation of C_2AH_8 and C_3AH_6 in HAC paste is shown in Fig. 7 and 8, respectively. It is apparent that C_2AH_8 formation in plain HAC paste occurs mainly in the first day of hydration. Hydrogarnet phase (C_3AH_6) also was detected in plain HAC paste after 3 days hydration. No obvious change in C_3AH_6 peak intensity was found in the paste during 14 days hydration. The C_2AH_8 formation rate in the HAC paste containing 1% sodium silicate was greatly retarded. The C_2AH_8 peak intensity gradually increased during the first five days hydration and then decreased. The C_3AH_6 peak intensity increased continuously with hydration time. As the C_3AH_6 formation in the sample containing 1.5% sodium silicate was slower than that in the sample containing 1% sodium silicate, little decrease of the C_2AH_8 peak intensity with hydration time was recorded from 5 to 9 days. A small amount of silicate addition appeared to lead to greater C_3AH_6 formation in the HAC paste

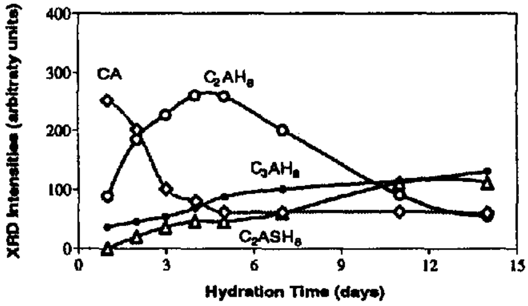

FIG. 6.
Phase formation in HAC paste containing 1% sodium silicate.

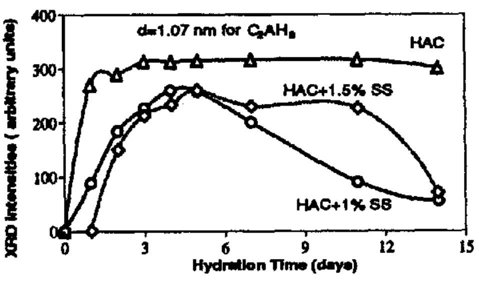

FIG. 7.

Effect of sodium silicate (SS) content on C_2AH_8 formation in HAC paste during hydration.

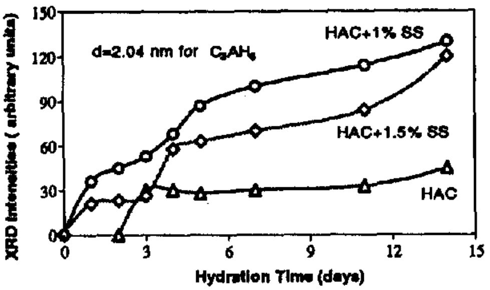

FIG. 8.

Effect of sodium silicate (SS) content on C_3AH_6 formation in HAC paste during hydration.

even at normal temperature (e.g. 23 °C). This may be attributed to the effect of high pH of the HAC paste by addition of sodium silicate [9]. A larger amount of sodium silicate results in the formation of other hydration products, e.g. strätlingite, which might temporarily prevent the formation of C_3AH_6. More C_3AH_6 formed after the silicate had been consumed to form C_2ASH_8. Since the amount of CA in the paste has reached an equilibrium state after 3 days hydration (Figure 6), the newly formed C_3AH_6 after 5 days hydration would appear to be converted from the C_2AH_8 phase.

The effect of sodium silicate content on formation of strätlingite is shown in Fig.9. The strätlingite phase could be detected in HAC pastes after 1-day hydration. Its peak intensity in plain HAC paste reached a maximum value at 3 days and then remained nearly constant. The strätlingite peak intensities in the HAC pastes containing sodium silicate greatly increased after 5 days hydration. The intensity reached maximum value at about 10 days age. Increase of sodium silicate content in HAC paste increases the formation of strätlingite.

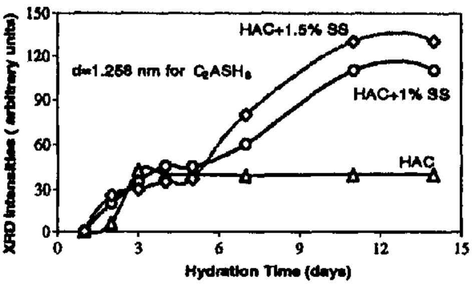

FIG. 9.

Effect of sodium silicate (SS) on formation of strätlingite in HAC paste during hydration.

Conclusions

1. Sodium silicate strongly retards the hydration of high alumina cement (HAC).
2. Sodium silicate addition promotes formation of strätlingite in HAC paste.
3. A small addition of sodium silicate to HAC can delay hydrogarnet formation, It is not sufficient to prevent the conversion reactions.

Acknowledgment

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