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EFFECT OF DIFFERENT CALCIUM ALUMINATE HYDRATES ON ETTRINGITE FORMATION AND EXPANSION OF HIGH ALUMINA CEMENT-BASED EXPANSIVE CEMENT PASTES

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ABSTRACT

Different hydrated high alumina cement (H-HAC) mixtures containing mainly CAH_{10}, C_2AH_8 or C_3AH_6 obtained at different temperatures were studied with respect to their performance as the Al-bearing component in HAC-based expansive additives. Free expansion and ettringite formation potentials of expansive cement using the different H-HAC preparations were reported. It was shown that H-HAC containing predominantly CAH_{10} and C_2AH_8 reacted more rapidly to form ettringite in HAC-based expansive cement systems than anhydrous HAC or H-HAC containing C_3AH_6. The expansion of the expansive cement containing CAH_{10} and C_2AH_8 developed mostly during the first day hydration. The presence of C_3AH_6 in the expansive cement appeared to delay the expansion and decrease the ultimate expansion value significantly.

Introduction

The use of high alumina cement (HAC) as an alumina-bearing component in expansive additives or cements has been reported by researchers since the 1920's [1–3]. An HAC-based expansive additive is generally a dry mixture comprising different types of particulates including high alumina cement, calcium sulphate hemihydrate or gypsum and lime or hydrated lime. It can be simply obtained by mixing commercially available materials. Its application is however limited due to the problems of quick setting and unstable expansion. The use of hydrated high alumina cement (H-HAC) instead of high alumina cement in the composition of expansive cement was reported to be a potential solution to the quick-setting problem [4]. The expansion characteristics of expansive cement containing pre-hydrated high alumina cement have been reported [5–7]. Pre-hydrated high alumina cement was prepared and dried at room temperature on a relatively small laboratory scale. It was found that the expansion characteristics of such pre-hydrated HAC-based expansive cement products are greatly affected by the production parameters of the pre-hydrated HAC for example the preparation temperature. This is due to different expansion potentials of various calcium aluminate hydrates in the expansive additive.

A newly developed compounded-expansive additive has been reported [8]. The compounded-expansive additive comprises mainly calcium aluminates, calcium sulphate and calcium hydroxide. The mixture containing expansive components is chemically compounded. The primary difference between the H-HAC system and the compounded-expansive additive system is that the latter contains all the expansive components in the compounded material. Particulate products are formed during the process of compounding. The expansion behaviour of HAC-based expansive cement is determined by the existence of different calcium aluminates in the expansive additive.

The objective of this study is to demonstrate the effect of different calcium aluminate hydrates, e.g. CAH_{10}, C_2AH_8, and C_3AH_6, on ettringite formation and expansion of expansive cement pastes.

Experimental

Materials.

Type I Portland cement (OPC): Supplied by Lafarge Inc.;
High Alumina Cement (HAC): Ciment Fondu, supplied by Lafarge Inc.;
Quick setting plaster: Calcium sulphate hemihydrate $CaSO_4 \cdot 0.5H_2O$;
Hydrated finishing lime: Calcium hydroxide, $Ca(OH)_2$.

The oxide compositions of OPC and HAC are listed in following table:

	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	$Na_2O + K_2O$
OPC	19.8	61.2	4.2	3.2	4.1	1.27
HAC	4.5	39.8	41.2	11.3	0.6	0.1

Sample Preparation. Mixtures containing different calcium aluminate hydrates, e.g. CAH_{10}, C_2AH_8 and C_3AH_6, were prepared by hydrating HAC at different temperatures. A mixture comprising 86% HAC and 14% $Ca(OH)_2$ was also used (designated H-HAC/CH, see Table 1). The HAC slurries were made with an initial w/c greater than 3.

Cylinders containing the HAC slurries were placed on rollers during the first 24 hours to avoid hardening. The slurries were filtered after 2 months hydration under CO_2-free environ-

TABLE 1

Preparation Conditions of Calcium Aluminate Hydrate Mixtures

Name of Mixtures	Curing Temperature (°C)	Main Mineral Component	Moisture State
M_{CAH10}	0	CAH_{10}	Paste
M_{C2AH8}	23	C_2AH_8	Paste
$^*M_{C3AH6}$	38	C_3AH_6	Dry powder
H-HAC/CH	23	C_3AH_6	Paste

**-cured at 38°C for 2 months followed by 24 hours drying at 85°C.*

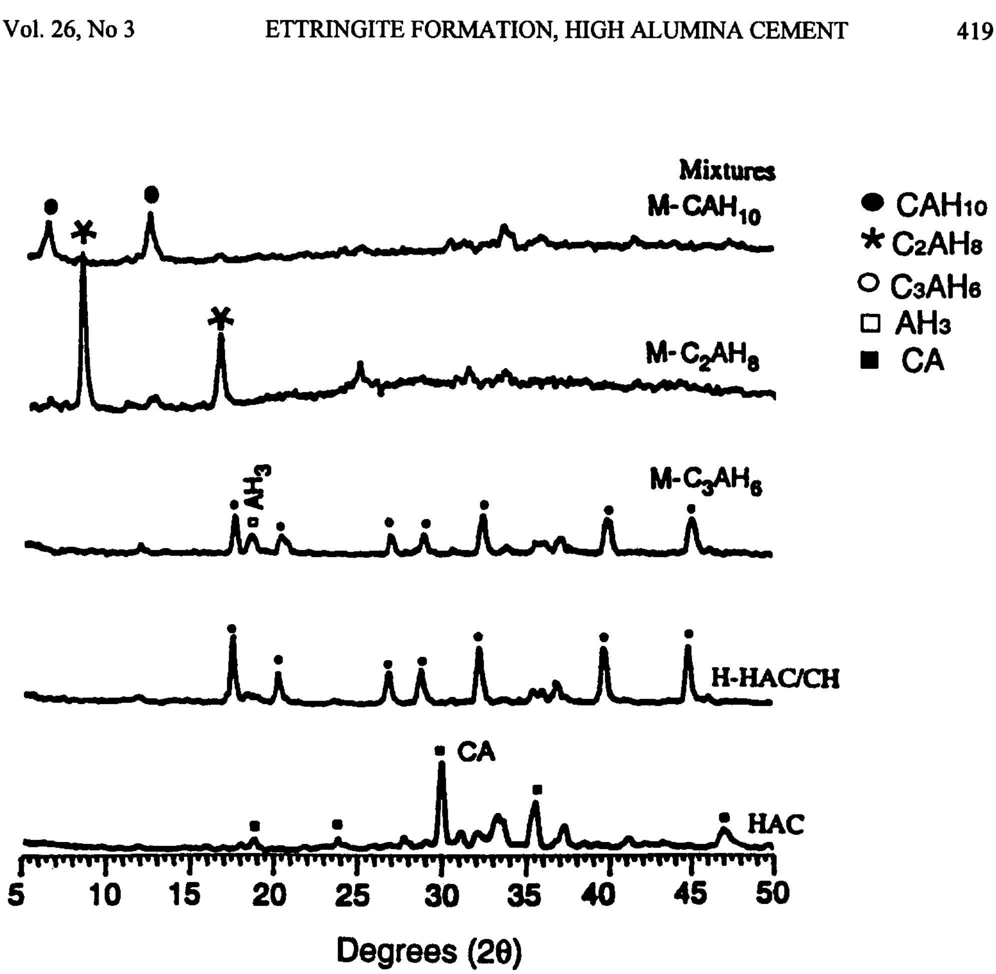

FIG. 1.
XRD spectra of different H-HAC mixtures containing different calcium aluminate hydrates.

ment. Paste samples were obtained for the mixtures containing significant amounts of CAH_{10}, C_2AH_8 and H-HAC/CH. Since CAH_{10} and C_2AH_8 are unstable at ambient temperature, CAH_{10} will readily convert to C_2AH_8 and finally to C_3AH_6. Wet CAH_{10} and C_2AH_8 mixtures stored at low temperature (5°C) were used as Al-bearing materials in expansive additives. Dry powder from the mixture containing primarily C_3AH_6 was also prepared. Dry powder was utilized because C_3AH_6 is the most stable form of the calcium aluminate hydrates so that the drying process used does not affect its crystallinity.

The water content (including combined water) of the paste mixtures was determined in two steps: (1) weight loss due to drying the sample in an oven at 85°C; (2) weight loss from 85 to 1000°C (using a Dupont 955 Thermogravimetric Analyzer). Different types of calcium aluminates, as major phase in each mixture, were identified using a Rigaku X-ray Diffractometer System Geigerflex D/Max-B. The comparison is based on significant difference of Al-bearing materials as shown in Fig. 1.

The expansive cement pastes were prepared by mixing Portland cement and different expansive additives in amounts of 30% (solid) by mass of Portland cement. The water/solid (Portland cement and expansive additive) ratio used was 0.45. Expansive additives contained an Al-bearing component (60 mass%), calcium sulphate hemihydrate (30 mass%) and hydrated finishing lime (10 mass%). The Al-bearing components were either anhydrous HAC, or mixtures containing CAH_{10}, C_2AH_8, C_3AH_6 or H-HAC/CH. The amount of the Al-bearing component used in the additives was based on a determination of the dehydrated solid content. Therefore, the calcium aluminate content expressed in terms of equivalent amounts of monocalcium aluminate (CA) is assumed to be the same in each expansive additive.

A uniformly mixed cement paste was cast in steel prism moulds for fabrication of 25 × 25 × 150 mm specimens. The gauge length for expansion measurements was 125 mm. Studs at the specimen ends were used as reference points. The specimens were cured initially in a fog room before demolding at a relative humidity of 100% and 23 °C. Specimens were demoulded after setting. The initial length of the specimens was measured after demoulding. The specimens were moist-cured (100% r.h.) for the first 24 hours and then water-cured at 23 °C. The expansion measurements and XRD analyses were taken at designated ages until either the specimens cracked or the length of the specimens approached a constant value.

Since drying will cause the deposition of ettringite phase, wet sample was used in the XRD study. The wet cement paste sample was carefully mounted on the sample slide using identical process. The peak height was calculated using Rigaku Standard Data Processing software. The relative error of peak height (ettringite at d-0.973 nm) from four different tests was less than 7%. Intentions to use an internal standard failed in XRD test when using wet cement paste samples, resulting in unacceptable error, due to (1) water evaporation and (2) non-uniformly mixing.

Results and Discussion

Either CAH_{10}, C_2AH_8 or C_3AH_6 is the major component for each different mixture as indicated in Fig. 1. The major component of the H-HAC/CH mixture also appeared to be C_3AH_6. The mixtures might contain some other hydrates derived from the HAC hydration, e.g. alumina gel AH_3. It is believed on the basis of XRD analyses that some minor components were present in small amounts relative to the major component in each mixture. The comparison is based on significant differences between the mixtures. Little or no free CH existed in the H-HAC/CH mixture, indicating a high capacity for adsorption of CH in HAC products. Addition of CH to HAC appeared to promote C_3AH_6 formation. The use of calcium aluminate mixtures prepared from HAC hydration rather than pure synthetic calcium aluminates in this research is more relevant to the application of HAC-based expansive cement.

The effect of different calcium aluminate hydrates on free expansion is shown in Fig. 2. The test was repeated twice. The relative error was ??. It was apparent that the expansion of expansive cement pastes containing CAH_{10} or C_2AH_8 mixture started at very early ages (about 1 hour), and developed mainly in the first 3 hours. Their 3-hour expansion and ultimate expansion were 0.58 and 0.65% respectively. The expansion of specimens containing additives based on anhydrous HAC and H-HAC/CH mixture developed after 3 hours. The former had the largest ultimate expansion (around 0.8%) at about 10 days, the latter a much lower expansion than the cement pastes containing expansive additives based on CAH_{10} or C_2AH_8 mixtures. Its ultimate expansion was about 0.45%. The cement paste containing the expansive additive based on the C_3AH_6 mixture showed very delayed and lower expansion compared to the other samples. The expansion of this sample started slowly after 1 day, and approached 0.25% gradually at 100 days.

The effect of different calcium aluminate hydrates on ettringite formation is shown in Figs. 3 to 7. The ettringite peak was detected at 4 hours and its intensity increased at one day. Little change of the ettringite peak intensity occurred from 1 day to 5 days. No gypsum peak was

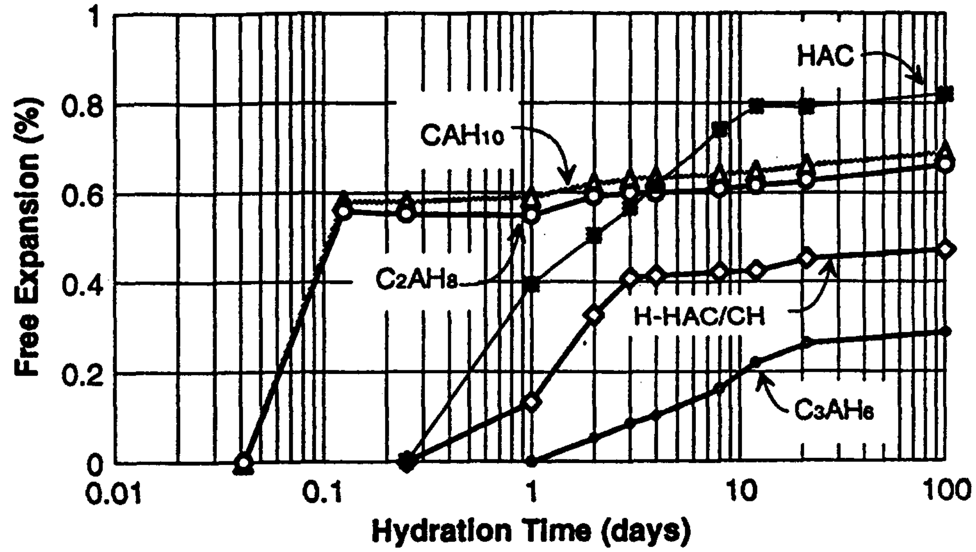

FIG. 2.
Effect of expansive additives based on different calcium aluminate hydrates or HAC on free expansion of cement paste.

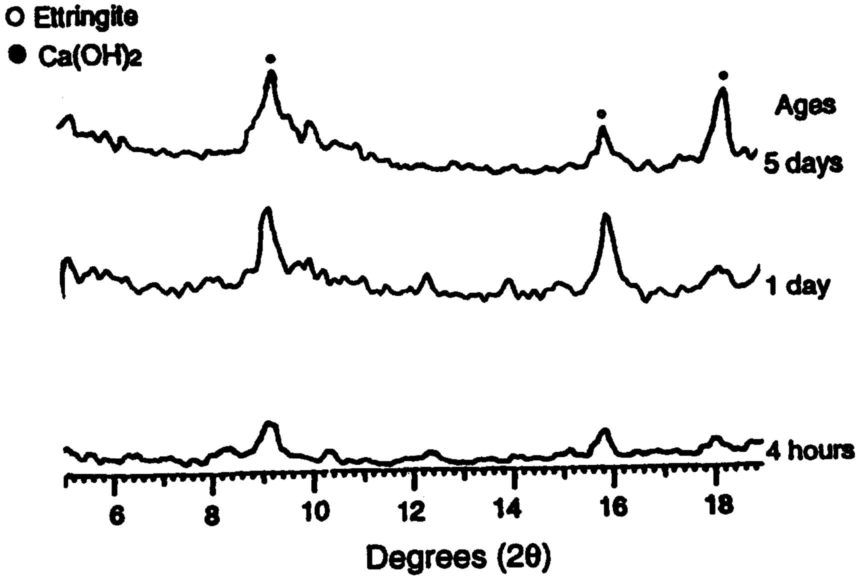

FIG. 3.
XRD spectra of expansive cement containing an expansive additive based on a CAH_{10} mixture at different ages.

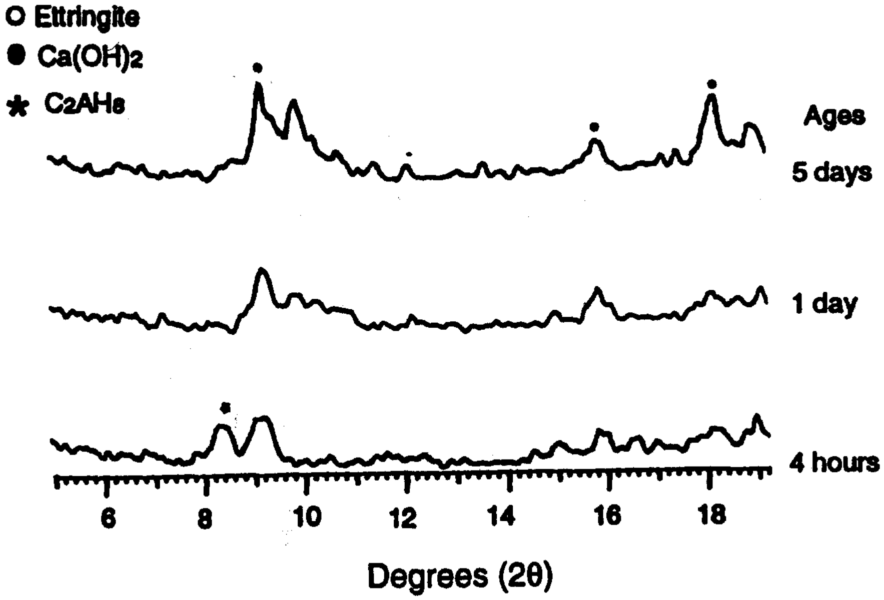

FIG. 4.
XRD spectra of expansive cement containing an expansive additive based on a C_2AH_8 mixture at different ages.

found even at very early ages. This indicated that reactions in this system were very fast. Hemihydrate ($CaSO_4 \cdot 0.5H_2O$) dissolved and reacted with CAH_{10} and C_2AH_8 to form ettringite directly. Calcium hydroxide (CH, d = 0.49 nm) could be detected at the beginning. A significant increase occurred between 1 and 5 days. Increase of the CH phase was attributed to the later hydration of Portland cement. Rapid formation of ettringite at early ages required a large amount of CH, resulting in the disappearance of free CH in the system. Ettringite crystallization results from reactions between aluminates and dissolved calcium and sulphate ions.

The C_2AH_8 phase existed in the cement paste containing the expansive additive based on the C_2AH_8 mixture at 4 hours and disappeared at one day (Fig 4). Ettringite formed during the first 4 hours. Its peak intensity increased slightly with age. Gypsum was absent. A high peak intensity for CH was observed at 5 days.

Ettringite formation in the expansive cement paste containing the C_3AH_6 based expansive additive was delayed (Fig. 5). No ettringite was detected in the first four hours. Ettringite was found after one day hydration. The peak size was smaller than those in the samples containing CAH_{10} or C_2AH_8 based additive (Figs. 3 and 4, having the same ordinate scale). The peak intensity increased slightly with hydration time. A gypsum peak (d = 0.756 nm) could be found until one day. It disappeared at 5 days. The C_3AH_6 phase could be detected at all ages. A large CH peak occurred from the first day. More free gypsum and CH existed in the system corresponding to the slow formation of ettringite.

The behavior of ettringite formation in the cement paste containing the H-HAC/CH based expansive additives was, in general, similar to that for the C_3AH_6 based additive sample (Fig. 6). The ettringite peak intensity at 5 days was apparently higher than for the C_3AH_6 sample (Fig. 5, having the same ordinate scale). A high peak for gypsum was found at 1 hour. It then de-

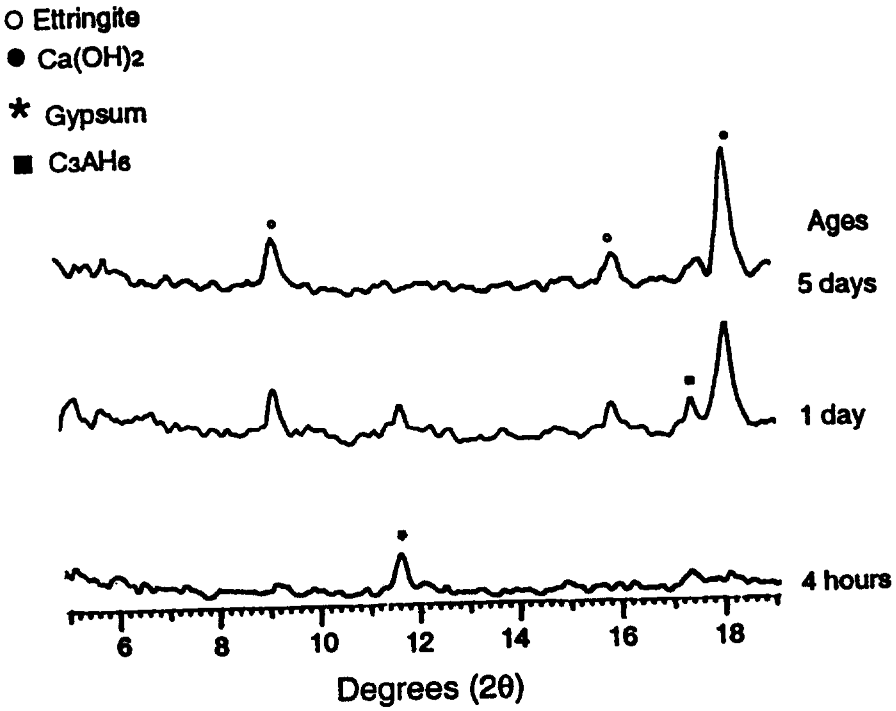

FIG. 5. XRD spectra of expansive cement containing an expansive additive based on a C_3AH_6 mixture at different ages.

creased at four hours and disappeared after 1 day. C_3AH_6 existed at all ages. A high peak intensity for the CH phase also occurred after 1 day. The H-HAC/CH and C_3AH_6 based additives both contained mainly C_3AH_6; alumina gel (AH_3) also existed in both mixtures. The differences between them are: the H-HAC/CH mixture was synthesized at 23°C; the C_3AH_6 mixture was prepared at 38°C followed by 24 hours drying at 85°C. The former contained wet alumina gel which may also contribute to ettringite formation and hence expansion. The latter contained aged gibbsite (also in the form of AH_3); it may only have a small contribution to early expansion.

Ettringite formation in the expansive cement paste containing anhydrous HAC was relatively faster than in the samples containing the C_3AH_6 or H-HAC/CH mixtures, but slower than in the samples containing the CAH_{10} or C_2AH_8 mixtures (Fig. 7). Ettringite could be detected after 1 hour. The increase of ettringite peak intensity with hydration time was slow. Gypsum was detected at 1 hour. Its peak intensity decreased at 4 hours and disappeared at 1 day. The CH phase could be found after 1 day hydration and increased greatly at 5 days. No other HAC related hydrates, i.e. CAH_{10}, C_2AH_8 and C_3AH_6, were detected.

Different calcium aluminate hydrates exhibited very different behavior in ettringite formation and expansion. The reaction rate of CAH_{10} and C_2AH_8 to form ettringite appeared much faster than the other forms of calcium aluminates studied. The use of CAH_{10} or C_2AH_8 alone as the Al-bearing component in the formulation of expansive cement may result in little expansion in concrete members. This is due to the timing effect postulated by Aroni, et al. [9] The magnitude of expansion is relatively small when the ettringite crystals grow too quickly in the early stage,

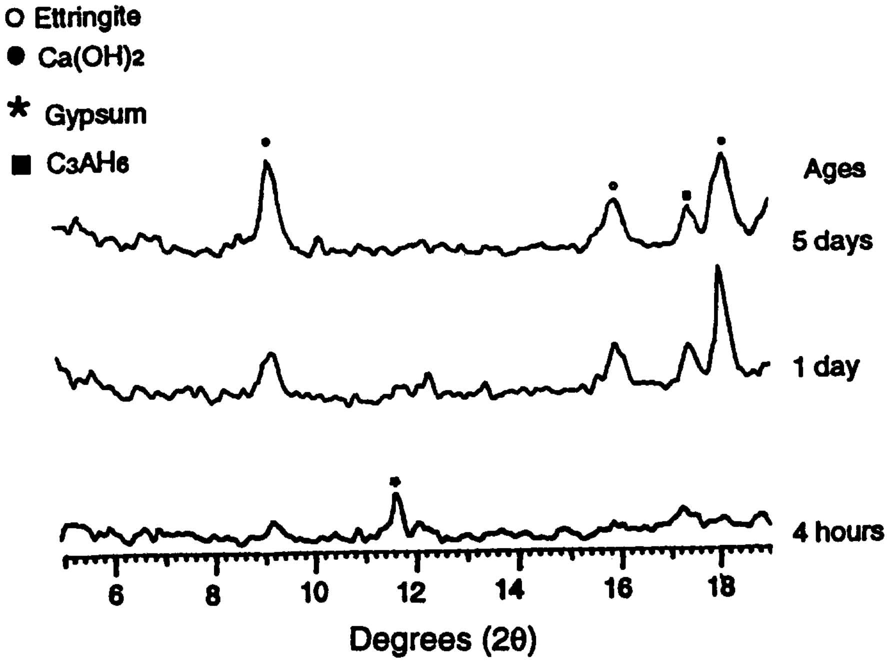

FIG. 6.
XRD spectra of expansive cement containing an expansive additive based on an H-HAC/CH mixture at different ages.

as the structure of cement paste is not well formed. Ettringite just fills in voids and produce little expansion when the strength of expansive cement paste is very low before 1 day. Ettringite formation from the reaction of C_3AH_6 was apparently delayed and reduced. This makes the Al-bearing material inefficient. Delayed ettringite formation also causes stability problems. The expansion period of such expansive cement can last up to 28 days. It is not desirable for the application of shrinkage compensating cement concrete. A good HAC-based expansive additive may be in the form of an optimum composition comprising anhydrous HAC, CAH_{10} and/or C_2AH_8 present in the surface layer of HAC particles. This surface layer prevents quick setting. It will react with sulphate to form ettringite and adjust the hydration rate of the inner anhydrous HAC. This optimized structure of expansive additive particles provides expansive cement with controllable expansion characteristics. A newly developed compounded-expansive additive appears to be an example of this material-design philosophy [8].

Conclusions

1. The expansion of portland cement containing expansive additives based on CAH_{10} and C_2AH_8 mixtures develops rapidly during the first day of hydration.
2. The expansion of portland cement containing an expansive additive based on a C_3AH_6 mixture is apparently delayed and reduced.

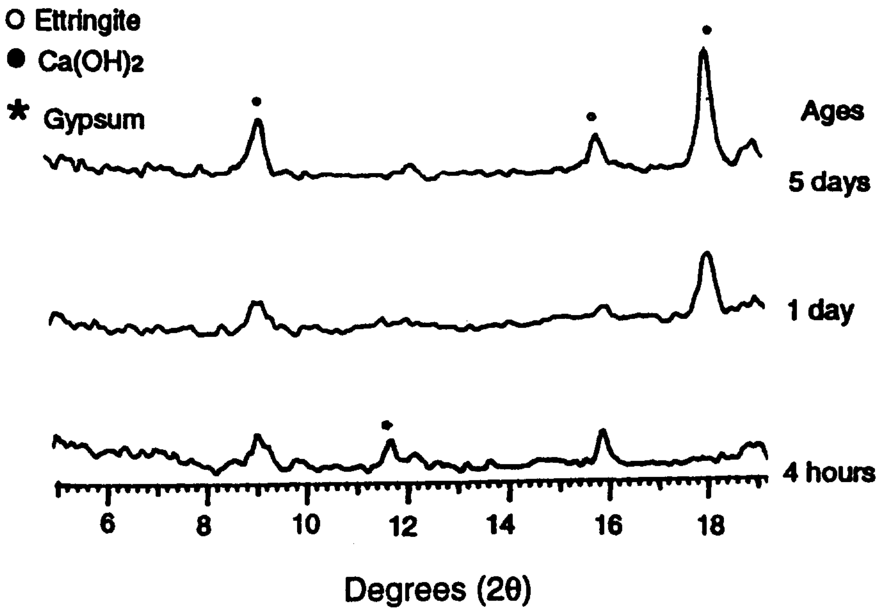

FIG. 7.
XRD spectra of cement containing an expansive additive based on anhydrous HAC at different ages.

3. Expansive cement additives CAH_{10} and C_2AH_8 react much faster to form ettringite than anhydrous HAC in portland cement systems.
4. An expansive cement additive based on C_3AH_6 delays ettringite formation in portland cement systems. The amount is also decreased.
5. Pre-hydrated HAC/CH mixtures prepared at 23 °C comprises mainly C_3AH_6; the expansion and ettringite formation potentials of portland cement containing H-HAC/CH expansive additives is higher than that containing C_3AH_6 prepared at 38 °C.

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