Pergamon

Cement and Concrete Research, Vol. 25, No. 6, pp. 1295–1304, 1995

0008-8846/95 $9.50 + .00

0008-8846(95)00122-0

EXPANSION CHARACTERISTICS OF A COMPOUNDED-EXPANSIVE ADDITIVE AND PRE-HYDRATED HIGH ALUMINA CEMENT BASED EXPANSIVE ADDITIVE

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(Refereed)
(Received November 30, 1994; in final form January 6, 1995)

ABSTRACT

The expansion characteristics of a newly developed compounded-expansive additive (CEA) and a pre-hydrated high alumina cement based particulate expansive additive are reported. Effect of temperature during pre-hydration and drying of high alumina cement is studied. The quick setting mechanism and volume stability of expansive cements containing different types of expansive additives are also discussed. It is apparent that high temperature treatment, an integral step in the production of pre-hydrated high alumina cement, will significantly reduce the expansion value and delayed expansion development. The compounded-expansive additive has desirable expansion characteristics with potential industrial application.

INTRODUCTION

Developments related to high alumina cement (HAC) - based expansive cements or additives, referred to as Type M expansive cements, have been reported by researchers since the 1920's [1-3]. 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. Quick setting and unstable expansion are usually the major problems associated with use of this material. There are generally two reasons for quick-setting phenomenon. One is rapid ettringite formation. The other is the effect of calcium hydroxide quickly formed on the surface of HAC particles [4, 5]. 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 [6]. The expansion characteristics of expansive cement containing pre-hydrated high alumina cement have been reported [7-9]. Pre-hydrated high alumina cement was prepared and dried at room temperature on a relatively small laboratory scale. It was found that the use of such pre-hydrated HAC as an expansive additive would slightly reduce and delay the expansion. Industrial production of an H-HAC based expansive additive requires pre-hydration of large amounts of HAC followed by thermal drying and grinding procedures. It augments cost and increases energy consumption.

A newly developed compounded-expansive additive (designated as Type CEA expansive additive) is reported. The compound-expansive additive comprises mainly calcium aluminates, calcium sulphate and calcium hydroxide with a composition similar to the previously reported HAC-based expansive additive [6-9]. The mixture containing expansive components is chemically compounded. The primary difference between the H-HAC system and the CEA system is that the latter contains all the expansive components in the compounded material. Particulate products are formed during the process of compounding. Process details are provided elsewhere [10] This production technique is more cost effective. The relative expansion characteristics of the compounded-expansive additive and a pre-hydrated high alumina cement based expansive additive are presented in this paper.

EXPERIMENTAL

Materials

Type 10 Portland cement:	chemical composition (% by mass): SiO_2=19.83; CaO=61.21; Fe_2O_3=3.20; Al_2O_3=4.18; MgO=4.09; SO_3=3.93; Na_2O=0.45 and K_2O=0.82;
Quick setting plaster:	calcium sulphate hemihydrate in the form of $CaSO_4 \cdot 1/2H_2O$;
High Alumina Cement:	supplied by Lafarge Inc.;
Hydrated finishing lime:	calcium hydroxide;

Expansive additives

Type HAC expansive additive: High alumina cement (60 mass%), calcium sulphate hemihydrate (30 mass%) and hydrated finishing lime (10 mass%) were mixed in a conventional mixer.

Type H-HAC expansive additive: High alumina cement paste having water/cement ratio 0.5 was cast in plastic cylinders (100 mm in diameter). The cylinders were cured at 0 and 23 °C for 24 hours. Hardened HAC pastes were crushed and then dried in an open tray exposed to ambient air at different temperatures and for different times. The stack height of crushed HAC pastes during drying was about 100 mm. HAC pre-hydrated at 0 °C was dried at 0 °C for 7 days; HAC pre-hydrated at room temperature was dried at 23 °C for 3 days; and HAC pre-hydrated at room temperature was dried at 85 °C for 12 hours. Dried H-HAC was ground into cement-like powders. Hydrated high alumina cement (60 mass%), calcium sulphate hemihydrate (30 mass%) and hydrated finishing lime (10 mass%) were then simply mixed to form a uniform particulate mixture of the individual phases. Heat drying may be required in pre-hydrated HAC production for industrial application. Pre-hydrated HAC dried at 85 °C was used in the Type H-HAC expansive additive formulation unless otherwise indicated.

Type CEA expansive additive: A compounded-expansive additive (CEA), comprising calcium aluminates, calcium sulphate and calcium hydroxide, was made primarily from high alumina cement, gypsum and lime with a composition similar to HAC type expansive additive. Energy consuming processes involved in the production of type H-HAC expansive additive, such as pre-hydration, drying and grinding, are not required when type CEA expansive additive is used. The distinction is that the mixture containing type CEA expansive components is chemically compounded. A particulate additive is formed during the process of compounding; the production process requires relatively little energy consumption.

Tests

The expansive cement pastes were prepared by mixing Portland cement and different expansive additives in amounts of 20, 30, 40, 50, 60, and 70% by mass of Portland cement. The water/solid (Portland cement and expansive additive) ratio used was 0.35. A uniformly mixed cement paste was cast in steel prism moulds for fabrication of 25x25x150 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 at a relative humidity of 100% and temperature of 23 °C. Specimens were demoulded after 24 hours. The initial length of the specimens was measured after demoulding. The specimens were then water-cured at 23 °C. The expansions measurements were taken once a day until either the specimens cracked or the length of the specimens approached a constant value.

Expansive cement pastes containing different types of expansive additives (50% by mass of cement) were prepared for setting time measurements. These tests were conducted according to ASTM C 806 - 89. Expansive cement mortars containing 30 and 50% (by mass of cement) Type CEA or Type H-HAC expansive additive were tested to determine the flow loss according to ASTM C 230 - 90.

One-day and 28-day compressive strengths were also determined on expansive cement mortars containing different types of expansive additive (10% and 40% by mass of cement). Water/solid (OPC and expansive additive) ratio was 0.45 and sand/solid ratio was 2.75. The mortar specimens (50x50x50 mm) were moist-cured at 23 °C.

RESULTS

The setting time and unconfined compressive strength of expansive cement pastes or mortars containing different types of expansive additive are listed in Table 1. Pre-hydrated HAC dried at 85 °C was used in Type H-HAC expansive additive formulations as previously indicated to meet industrial requirements. The expansive cement mortars containing 10% expansive additive had high values of unconfined compressive strength (> 50 MPa) at 28 days.

The dependence of flow loss on hydration time for Type H-HAC or Type CEA expansive cement mortars is shown in Fig. 1. The flow loss of expansive cement mortar containing 30% Type CEA expansive additive was similar to that of expansive mortar

Table 1. Setting Time and Compressive Strength

Name	Setting Time (Minutes)		Compressive Strength (MPa)		
			10% expansive additive by mass of OPC		40% expansive additive by mass of OPC
	Initial	Final	1 day	28 days	1 day
Type HAC	10	15	21.5	51.2	11.9
Type H-HAC	120	160	24.1	50.3	13.2
Type CEA	110	160	23.3	52.2	12.3

containing an equal amount of Type H-HAC expansive additive. The initial flow value of expansive cement mortar containing 50% Type H-HAC expansive additive dropped to only half of that of expansive cement mortars containing equal amount of Type CEA expansive additive. The flow value decreased to about 30-40% for all the expansive cement mortars.

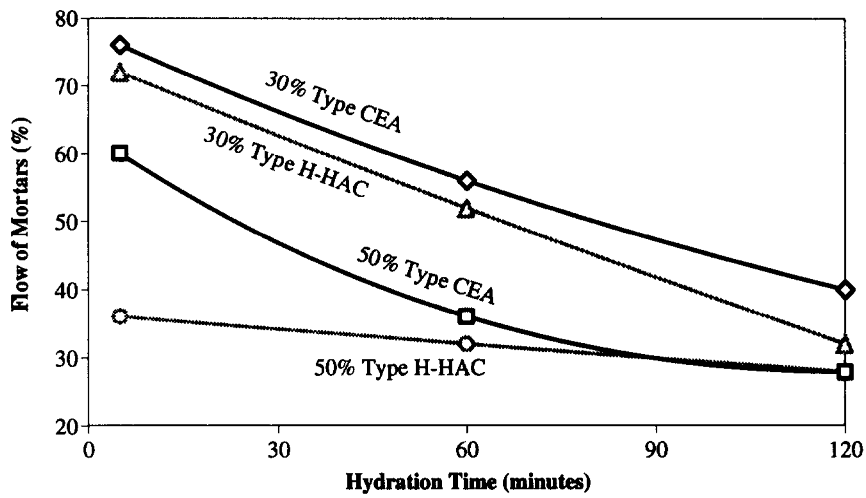

Figure 1. Flow loss of expansive cement mortar containing Type CEA or Type H-HAC expansive additive.

The free expansion values of expansive cement pastes containing different types and amounts of expansive additive are shown in Fig. 2. The expansion of expansive cement paste containing Type CEA expansive additive was generally much larger than that of the expansive cement pastes containing the other types of expansive additive. The paste containing 20% Type CEA expansive additive had an ultimate free expansion of about 1%. The pastes containing 20% Type HAC or Type H-HAC expansive additive had only one-third of the expansion developed by the Type CEA expansive cement paste. The ultimate expansion increased to nearly 6% for Type CEA expansive cement paste as the addition of expansive additive increased to 30%. At this content, the expansion of Type HAC expansive cement paste was still one-third of that of Type CEA expansive cement paste, while that of Type H-HAC was only about one-tenth of the expansion. The expansion of Type CEA expansive cement paste increased significantly to 16% as 40% expansive additive was added. The expansion of Type HAC expansive cement paste was about the half of that of Type CEA. The increase of expansion with expansive additive addition for Type H-HAC expansive cement paste was relatively small. The difference in ultimate free expansion between Type CEA or Type HAC and Type H-HAC is apparently enhanced, and that between Type CEA and Type HAC diminished, with increase in amount of expansive additive. The expansion of both Type CEA and Type HAC expansive cement pastes at the 50% addition level developed quickly. At about 8 days the specimens broke as the expansion was close to 18%. The expansion rate of Type CEA expansive cement paste was slightly higher than that of Type HAC expansive cement paste. The expansion of Type H-HAC expansive cement paste was very small compared to those of Type CEA and Type HAC. A 30% addition of Type CEA expansive additive was equivalent to about 50% Type H-HAC additive in terms of ultimate expansion.

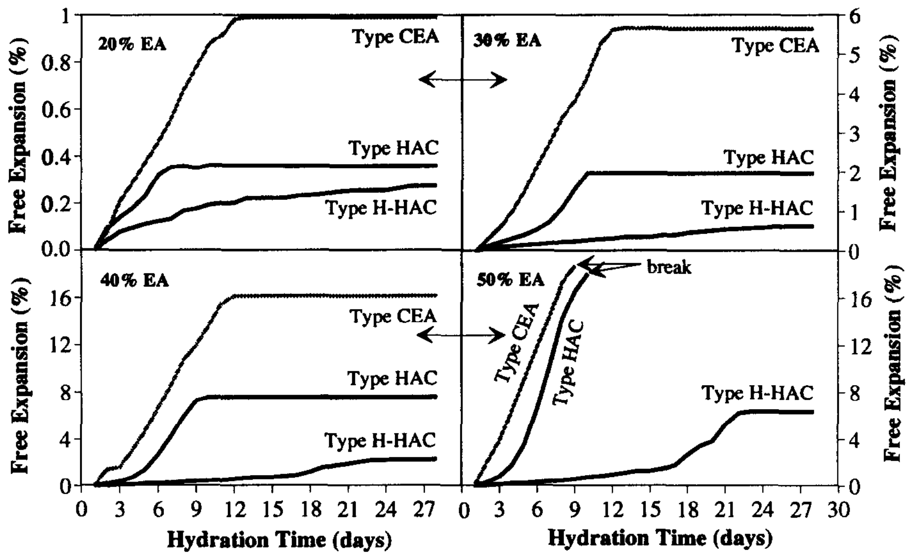

Figure 2. Free expansion of expansive cement paste containing different types and amounts of expansive additives.

The relationships between expansive additive content and free expansion for the different types of expansive cement pastes are presented in Fig. 3. It was confirmed that the free expansion increased exponentially with addition of expansive additive. Regression analysis gave excellent correlation coefficients, i.e. all were above 0.99. A rapid increase of expansion was obtained for Type CEA and Type HAC expansive cement pastes at contents of expansive additive greater than 20-30%. The increase of expansion with expansive additive addition in Type H-HAC expansive cement paste was relatively slow. Type CEA expansive additive was more effective than HAC-based expansive additives. For example, 20% Type CEA expansive additive was equivalent to 27% Type HAC and 34% Type H-HAC for a similar level of expansion useful in shrinkage compensation applications; 40% Type CEA was equivalent to 48% Type HAC and 65% Type H-HAC for large expansion values of use in drilled shafts.

The period after which the expansive cement paste reaches a dimensionally stable state for the pastes containing different types of expansive additive is shown in Fig. 4. It

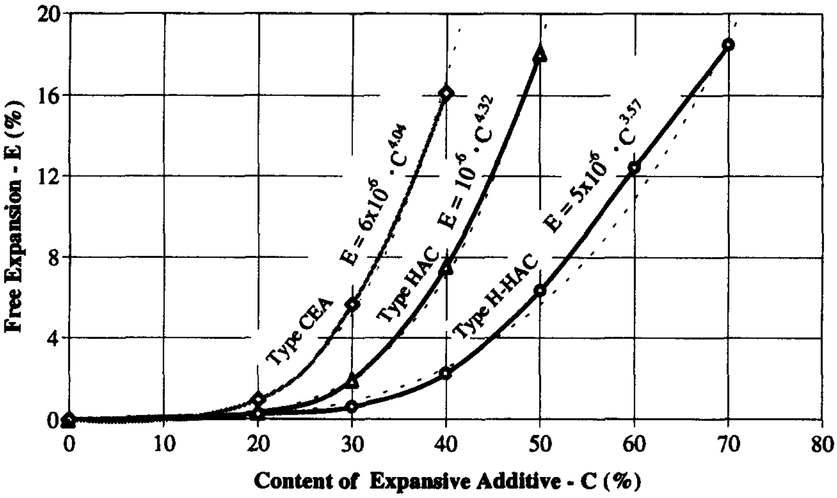

Figure 3. Relationships between free expansion and expansive additive content.

is clear that the expansion for Type CEA and Type HAC expansive pastes developed within 14 days. The stabilization period for Type CEA paste was slightly longer than that of Type HAC paste. It was prolonged to about 25 days for Type H-HAC paste. The content of expansive additive in expansive cement pastes appeared to have little effect on the expansion stabilization period.

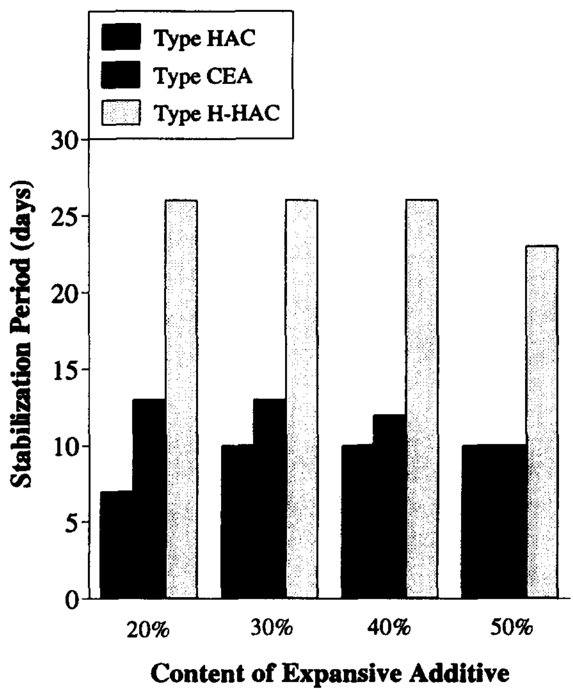

Figure 4. Stabilization period for expansion of cement pastes containing different types and amounts of expansive additive.

Since drying is an integral process in the preparation of pre-hydrated high alumina cement, drying temperature is an important parameter affecting both the economy and expansion characteristics of the material. The effect of drying temperature on the expansion of expansive cement paste containing Type H-HAC expansive additive is shown in Fig. 5. It is apparent that free expansion is significantly reduced and delayed by an increase of drying temperature of pre-hydrated HAC. The expansion of expansive cement paste containing pre-hydrated HAC dried at 0°C developed faster than that of

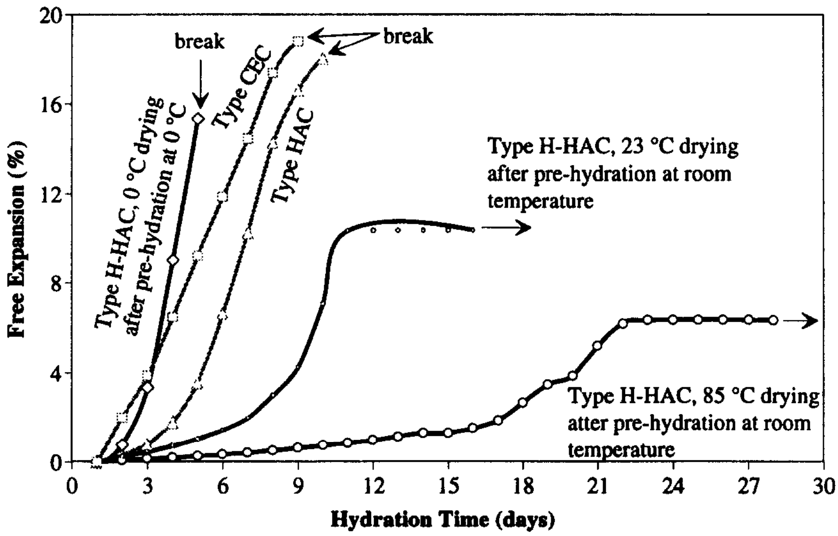

Figure 5. Effect of temperature during pre-hydration and drying of HAC on expansion of Type H-HAC expansive cement pastes.

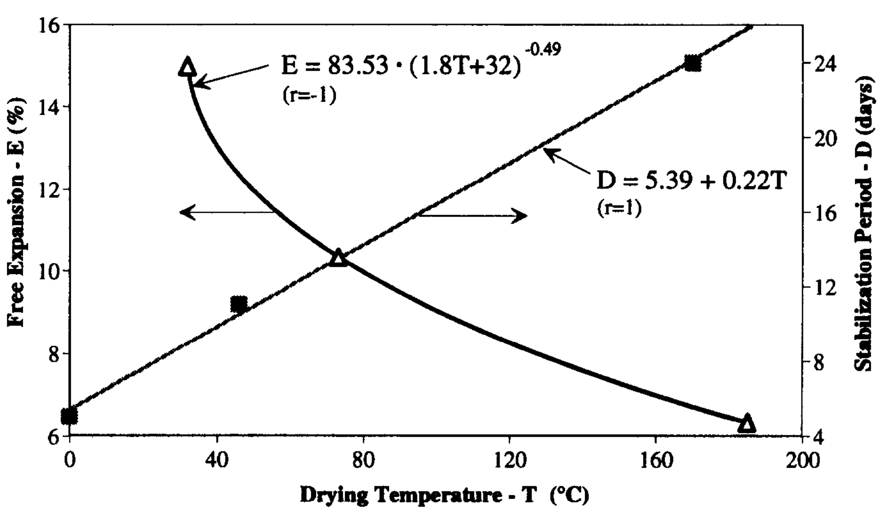

Figure 6. Effect of temperature during pre-hydration and drying of HAC on ultimate free expansion and stabilization period for Type H-HAC expansive cement pastes

Type CEA and Type HAC. It reached 15% at 5 days and then broke. The ultimate expansion of expansive cement paste containing pre-hydrated HAC dried at room temperature was only half of that for Type CEA and Type HAC expansive cement pastes, and the development of expansion was delayed for about 9 days. The further reduction of expansion by the increase of drying temperature was demonstrated on the expansive cement paste containing pre-hydrated HAC dried at 85 °C. The expansion of this specimen was greatly delayed for about 18 days.

The relationships between drying temperature of pre-hydrated HAC and free expansion and expansion stabilization period are presented in Fig. 6. The ultimate expansion decreased exponentially with increase of drying temperature of pre-hydrated HAC used in Type H-HAC expansive cement pastes. The expansion was reduced from 15% to 6% when the drying temperature of pre-hydrated HAC increased from 0 to 85 °C. The expansion stabilization period increased linearly with drying temperature of pre-hydrated HAC. The period was prolonged from 7 to 24 days as drying temperature increased from 0 to 85°C.

DISCUSSION

Control of Setting Time

Uncontrollable fast setting has been recognized as one of the major problems in the application of HAC-based expansive cement. The hydration characteristics of the OPC - HAC - H_2O system during the setting period have been reported [11, 12]. Both OPC and HAC in this system appear to be responsible for the quick set. It is believed that flash set of OPC occurs due to rapid hydration of C_3A in absence of gypsum. In the HAC-based expansive cement system (HAC - OPC - sulphate - CH - H_2O), the gypsum phase could exist for at least 3 days [8]. Therefore, OPC hydration may not contribute to quick setting behavior. Flash setting of HAC concrete due to the addition of calcium hydroxide and/or calcium sulphate from Portland cement has been reported [11]. This can be attributed to two possible reactions: (1) quick formation of calcium aluminates on the surface of HAC particles; (2) quick formation of ettringite when sulphate exists. It is therefore believed that the quick-setting behavior of HAC-based expansive cement is highly related to the hydration of HAC. This is confirmed by the use of pre-hydrated HAC instead of unhydrated HAC in the expansive cement and the resulting normal setting behavior. The use of chemical admixtures has been excluded as the solution for quick setting problem in HAC-based expansive cement, as retarder or superplasticizer addition to HAC may delay the setting time of the expansive cement and significantly reduce the expansion [6, 13].

Effect of HAC Pre-hydration on Expansion Characteristics

Pre-hydration of HAC not only significantly changes the setting behavior, but also affects the expansion characteristics of the expansive cement. The hydration products of HAC vary with age and environmental conditions such as temperature and relative humidity. HAC hydrates to CAH_{10} at low temperature and early ages. It then converts to C_2AH_8 at room temperature and later ages. Both CAH_{10} and C_2AH_8 are hexagonal, crystalline and thermodynamically unstable at high temperature, e.g. above 25 °C. They will finally convert to the stable cubic crystalline C_3AH_6. Pre-hydration and drying temperature of HAC can greatly affect the expansion value and expansion stabilization period of Type H-HAC expansive cement. The expansion potential of expansive cements based on Type H-HAC decreases in the following order in terms of the temperature for pre-hydration and drying of HAC:

$$0\ °C > \text{unhydrated HAC} > 23\ °C > 85\ °C$$

High temperature treatment in the production of pre-hydrated HAC is inevitable because (1) temperatures above 100 °C can be reached in HAC paste during hydration due to its high heat of hydration [14]; (2) heat drying will satisfy industrial requirements. Low expansion and delayed expansion development is derived from production processes involving drying of pre-hydrated HAC.

Stability of CEA, HAC and H-HAC - based Expansive Cements

The expansion of expansive components in a compounded state, e.g. Type CEA, is apparently faster than those existing as separate particulates, e.g. Type HAC and H-HAC. The expansion characteristics of Type CEA expansive cement appear to be more comparable to Type K cement than those of Type HAC and H-HAC. Compound particles in Type CEA expansive additive comprise components including Al-, SO_3- and Ca-bearing materials favorable to ettringite formation. Since sulphate ions are concentrated around the aluminate phase, ettringite can form directly upon hydration. Expansion is thus quickly developed in Type CEA expansive cement paste.

Unstable expansion may arise in a system comprised of separate particulates, e.g. HAC-based expansive components. Since the expansive components in Type HAC or Type H-HAC expansive cements, comprise mixed particles from high alumina cement, hemihydrate or gypsum and hydrated lime, individually and uniformly separated in a Portland cement matrix, the requirements for monosulfate formation around high alumina cement particles can be easily fulfilled as a high concentration of aluminate ions exists there at early ages. Once formed the monosulfate transforms to ettringite relatively slowly. Delayed ettringite formation results in microcracks created in some location. Delayed ettringite nucleation and crystallization can preferentially occur in pre-existing microcracks [15]. This oriented crystal growth in certain cracks leads to nonuniform expansion of expansive cement products. Type H-HAC expansive additive containing high temperature treated H-HAC may still be a desirable material for use in highly confined drilled shafts. Delayed expansion can allow expansion of all the drilled shafts to develop uniformly and simultaneously after construction is completed. Type H-HAC expansive additive having delayed expansion, however, may not be of use in shrinkage compensating or self-stressing expansive cements because of potential nonuniform expansion.

CONCLUSIONS

Expansive cement containing a compounded-expansive additive (CEA) has greater expansion potential than other HAC-based expansive cements containing unhydrated or pre-hydrated HAC. Addition of type CEA expansive additive results in normal setting behavior, accelerated expansion development and uniform volume deformation. Increase of pre-hydration and drying temperature of HAC, the Al-bearing agent in Type H-HAC expansive additive will greatly reduce and delay the expansion of the expansive cement.

Acknowledgment

Financial support from NSERC and the Network of Centers of Excellence on High Performance Concrete is gratefully acknowledged.

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