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MICROCRACKING AS A PRECURSOR TO DELAYED ETTRINGITE FORMATION IN CEMENT SYSTEMS

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ABSTRACT

Concretes, made with ASTM Type I, III and V cements were subjected to different microcrack-inducing treatments, i.e. drying/re-wetting, freezng/thawing and loading/unloading. Expansion of the concretes due to delayed ettringite formation (DEF) was measured. Crack surface composition was studied using x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA). The results confirmed that microcracking in concrete and mortar made with ASTM Type III Portland cement can lead to increased deterioration resulting from DEF subsequent to high temperature curing followed by severe thermal-drying.

Introduction

The deterioration of concrete due to delayed ettringite formation (DEF) in high temperature cured cement products has been reported extensively[1-5]. Damage of concrete due to DEF (as distinct from secondary ettringite formation (SEF) which does not necessarily require initial high temperature curing) has been investigated primarily in concrete members subjected to high temperature curing followed by open-air weathering and hence drying/re-wetting cycles, e.g. precast front panels and railway sleepers[6]. Cases have been observed in Germany, Finland, Australia, South Africa and USA. These concretes were mostly made with high early strength portland cement and accelerated steam curing was employed. The products underwent drying/wetting, freezing/thawing and fatigue cycles year around. Heat-drying is possibly experienced during summer.

Studies on the effect of cement type and composition on DEF have been well documented[1-5]. It is known that ASTM Type III cement is more susceptible to DEF. Cements used in this work were ASTM Type I, III and V. The objective of this paper is to investigate the relative importance of microcrack formation following high temperature curing on subsequent deterioration of concrete due to DEF.

Experimental

Concrete. Typical ASTM Type I, III and V portland cements were used in this study. The fineness and oxide composition of the cements are shown in Table 1. Minus 25 mm crushed

TABLE 1
Fineness and Oxide Composition of the Cements

	Fineness	Oxide Composition (%)							
Cement	(cm²/g)	SiO_2	CaO	Fe_2O_3	Al_2O_3	MgO	SO_3	Na_2O	K_2O
Type I	2560	20.56	63.10	3.59	6.28	0.82	2.59	0.27	0.58
Type III	4370	20.21	63.00	2.67	6.07	0.46	3.80	0.12	0.94
Type V	2630	23.18	56.77	4.12	5.19	3.64	2.76	1.08	0.52

limestone was used as the coarse aggregate, and the fine aggregate was natural river sand. Aggregates were washed using tap-water and dried at room temperature. The specific gravities of the coarse and fine aggregates were 2.56 and 2.65 respectively. The aggregate was in the saturated-surface-dry state.

Concrete having a water/cement ratio 0.43 and a cement:sand:stone ratio of 1.00:1.14:2.32 by mass was prepared. The fresh concrete containing Type I, III or V portland cement was mixed for 5 minutes and then cast in PVC molds, 200 mm long by 100 mm in diameter. The concrete cylinders were kept at room temperature for one hour. They were then put in a sealed curing-box at 100% relative humidity and placed in an oven. The temperature of the specimens reached 85 °C after one hour heating. The concrete specimens were moist-cured at 85 °C for 12 hours and then cooled naturally to room temperature. Different treatments to create microcracks were applied after 24 hours (Table 2):

The specimens were placed in lime-water after the microcrack-inducing treatments. The specimens were cured for at least 14 days to allow the length recovery to a stable value. Studs were installed at the ends of the specimen to facilitate measurement of the longitudinal expansion. The initial length of the cylinders was measured on the concretes after the 14 days in lime-water. The expansion of the concrete specimens was recorded at designated times following the initial measurement.

Mortar. Preliminary attempts to develop a test method to evaluate the DEF potential of given cements were carried out on an ASTM Type III cement mortar specimen. The prism specimen had dimensions of 77 × 77 × 298 mm (3 × 3 × 11¾ in). Natural river sand was used. The sand to cement mass ratio was 2.75 and the water to cement ratio was 0.48. The fresh mortar was mixed for 3 minutes and then cast into steel molds. The curing procedures of the mortar specimens were the same as those of concrete specimens. The temperature of the specimens reached 95 °C after one hour heating. After cooling, hardened mortar specimens were dried at 85 °C for 24 hours and then placed in lime-water at 23 °C. Control

TABLE 2
Microcrack-Inducing Treatments Applied to the Concrete

Treatment	Description
Control	Continuously cured in lime-water at 23 °C.
85 °C drying/re-wetting	85 °C drying in the oven for 24 hours and then cooling to ambient temperature; re-wetting at 23 °C.
23 °C drying/re-wetting	Drying at 23 °C and 50% R.H. for 14 days; re-wetting at 23 °C.
Loading/unloading	10 loading/unloading cycles followed by drying under ambient condition for 14 days. Loading to 90% of compressive strength was applied; each increment of load was held for 3 minutes.
Freezing/thawing	14 freezing and thawing cycles. A cycle consisted of 12 hours freezing at -24 °C and 8 hours thawing in water at ambient temperature.

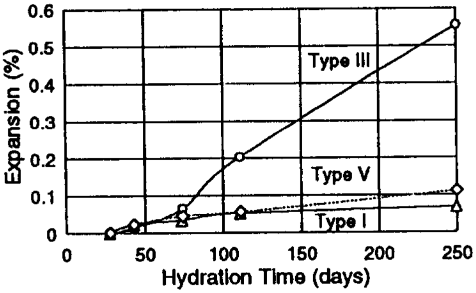

FIG.1.
Expansion of the concretes subjected to thermal-drying treatment (see Table 2).

specimens with the same composition but moist-cured at 23 °C were also prepared. The initial length of the cooled specimens was measured immediately after the initial curing (e.g. high-temperature curing). Expansion was recorded every week. Photographs of the crack patterns were taken. The samples were then intentionally fractured along the crack and beyond. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were performed on the cracked surfaces. X-ray diffraction (XRD) analysis was carried out on cement paste. Cement paste was prepared by carefully grinding and sieving the mortar sample. A Cambridge Stereoscan S250 SEM/EDXA instrument and a Rigaku X-ray Diffractometer System D/Max -B with copper Ka radiation were used.

Results

Concrete. The results indicated that only the high temperature cured Type III cement concrete followed by severe heat-drying suffered large expansion due to delayed ettringite formation (DEF) (Fig.1). The other treatments, such as loading/unloading cycles, freezing/thawing cycles and room temperature drying, did not show DEF-induced expansion. The expansion of heat-dried Type III cement concrete increased to about 0.2% after 110 days curing and reached about 0.5% at 250 days.

Mortar. The effect of curing conditions and subsequent treatment on Type III portland cement mortar is shown in Fig.2. The control mortar, moist-cured at room temperature, did

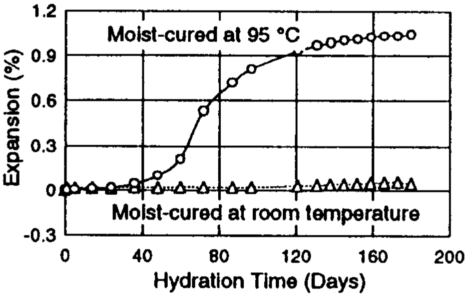

FIG.2.
Expansion of ASTM Type III cement mortars.

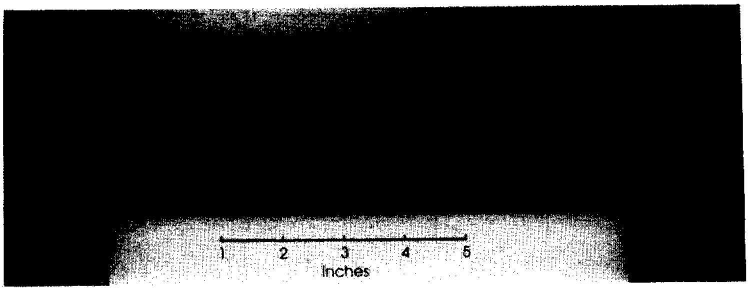

FIG. 3.
Cracking of ASTM Type III cement mortar (initially moist cured at 95 °C followed by 85 °C drying), after 180-days curing in lime-water at 23 °C.

not show expansion; the specimens, moist-cured at high temperature, followed by thermal-drying, started to expand at about 40 days. The expansion accelerated at 60 days and reached a maximum at about 160 days. The ultimate expansion value was about 1.0%. The expansion of cement mortar was apparently larger than that of the concrete. This may be due to (1) the higher initial curing temperature (95 °C) for the mortar than the concrete specimen (85 °C); (2) more ASTM Type III cement contained in a unit volume of mortar specimen than in the concrete.

Visible cracks were found on the surface of the expanded specimen at about 90 days. The cracks extended with time. A photograph of the crack pattern was taken at 180 days (Fig.3). The crack density on the surface of the specimen was 36.2 m/m^2. The XRD analysis was carried out on cement pastes taken from the mortars (Fig.4). An intense peak of ettringite at d-spacing=0.97 nm (9.2°, 2θ) was recorded for the expanded mortar. It was not detected in the mortar sample cured only at room temperature. The investigation on the cracked surfaces was performed using SEM/EDXA analysis (Fig.5). The entire area of the crack surfaces was covered with ettringite crystals. The size of the ettringite crystals was typically about 1-2 mm long and 0.3 mm in diameter. The EDXA spectrum showed that the crystals contained mainly calcium, sulfur and aluminum. The sulfur peak was much higher than that usually found in normal Portland cement paste, indicating that sulfate ions had migrated from the cement matrix into the cracks to satisfy the supersaturation condition for ettringite crystallization.

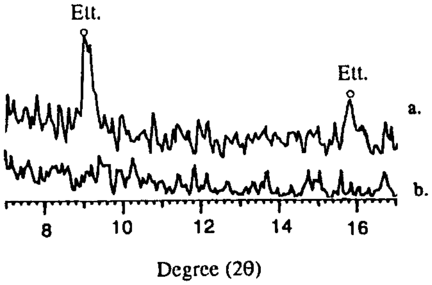

FIG. 4.
XRD spectra of ASTM Type III cement pastes (extracted from mortar). (a) moist-cured at 95 °C followed by 85 °C drying; (b) moist-cured at 23 °C.

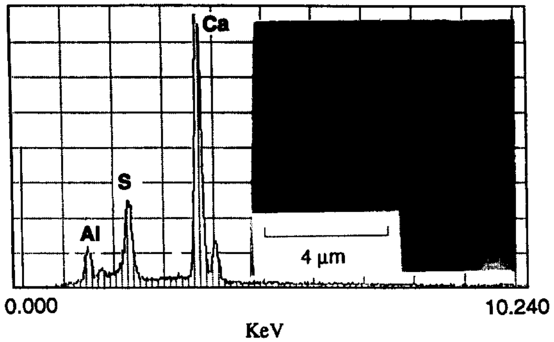

FIG. 5.
SEM/EDXA analysis on a crack surface of ASTM Type III cement mortar (initially cured at 95 °C followed by 85 °C drying) after 180-days curing in lime-water 23 °C.

Discussion

This study confirms the work of others that expansion behavior of cement systems due to DEF is influenced by: cement type (e.g. Type III cement); high temperature moist-curing; severe thermal-drying [1-5]. It is well-known that Type III Portland cement may contain more C_3A and SO_3 in the form of calcium sulfate than Type I cements. Gypsum is normally used in portland cement to regulate its setting behavior. The Type III portland cement contains more C_3A in order to promote high early strength. The Type III cement can contain up to 4.5% SO_3. The maximum SO_3 content in the Type I or V cement is, however, generally less than 3.5%. The fineness of the Type III cement can be up to 7000 cm^2/g, i.e. about three times that of the other cements. Type III cement with fineness of 4000-5000 cm^2/g is normally produced. High temperature curing makes it possible for Type III cement to hydrate and form more C-S-H gel quickly during the critical heat-curing period.

Previous studies[7,8] indicate that C-S-H gel can adsorb sulfate rapidly at temperatures higher than 65 °C. These sulfate ions are released more slowly at later ages. This is the so-called internal sulfate source that is a precursor to DEF as distinct from SEF. Therefore, high curing temperature and quick formation of C-S-H gel from finely-ground cement are the major factors controlling the internal sulfate source. A high SO_3 content in the cement increases the amount of sulfate stored in the internal sulfate source available for DEF. Rapid formation of C-S-H gel from Type III cement also increases the density of the microcracks formed at early ages due to drying shrinkage. Thermal-drying enhances the creation of microcracks. Drying of a C-S-H rich concrete at 85 °C may be more severe (more conducive to microcrack formation) than the other treatments, e.g. 10 loading/unloading cycles, 14 freezing/thawing cycles or room temperature drying. These microcracks exist in the cement matrix and especially in the transition zone between aggregates and cement paste. The cracks in the concrete subjected to loading and unloading or freezing and thawing cycles usually occur in certain weak areas. Therefore the crack density appears to be less than that in thermal-dried Type III cement concrete. Expansion is a direct result of crack opening processes. Ettringite is believed to preferentially nucleate and grow in pre-existing cracks. The sulfate ions released from the internal source, i.e. C-S-H complex or "phase X"[9], will likely migrate to the nearest crack. Nucleation of ettringite crystals occurs, if the concentration of aluminate in the crack is sufficient to create supersaturation conditions necessary for forming ettringite.

Calcium aluminate is present primarily in the solid state. The solubility of the aluminate hydrates is relatively low, and thus aluminate ions do not migrate as readily as sulfate ions. Therefore, mobilization of sulfate in the concrete determines the rate of DEF and hence the expansion. Ettringite formation in large voids may not cause the deterioration of the concrete. Growth in cracks will easily extend the cracks and requires much less energy than creating a new crack in the concrete[10].

Conclusions

The results confirm that concrete made with ASTM Type III Portland cement appears more vulnerable to the deterioration due to delayed ettringite formation (DEF) under the condition of high temperature curing followed by severe thermal-drying. No deleterious expansion occurs in the concrete made with ASTM Type I or V cement exposed to the same curing cycles. Further evidence is provided underlying the relevant importance of pre-existing microcracks in cement systems as a precursor for DEF formation. Cracking occurs in mortar, made with ASTM Type III Portland cement and subjected to high temperature curing followed by severe thermal-drying, at about 90 days. The crack surfaces are covered with ettringite crystals.

Acknowledgement

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