Pergamon

Cement and Concrete Research, Vol. 26, No. 11, pp. 1649-1659, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00161-5

DELAYED ETTRINGITE FORMATION IN 4-YEAR OLD CEMENT PASTES

R. Yang, C.D. Lawrence and J.H. Sharp
Department of Engineering Materials and Centre for Cement and Concrete
The University of Sheffield
Mappin Street, Sheffield, S1 3JD, UK

(Refereed)
(Received April 23, 1996; in final form September 11, 1996)

ABSTRACT

Cement paste prisms (40 × 40 × 160 mm) made from portland cement have been cured at 100°C for 3 hours, followed by extended water storage at room temperature. Large expansions have been observed after 2½ years for prisms made with a certain portland cement. Backscattered electron imaging (bse) in a scanning electron microscope (SEM), combined with x-ray microanalysis and quantitative x-ray diffraction analysis, was employed to examine the microstructure, the distribution and the quantity of ettringite formed. Bands of ettringite could be readily observed in a heat cured prism near one of its long surfaces, but not in the central region of the prism. X-ray microanalysis demonstrated that S and Al species, initially dispersed in the outer and the inner hydration products around cement grains during heat curing, diffused from these hydration products during the period of 2½ to 3½ years water storage at room temperature to form the ettringite bands. Trends between the occurrence of ettringite bands and paste expansion suggest that a causal relationship may exist between these factors. *Copyright © 1996 Elsevier Science Ltd*

Introduction

Comprehensive laboratory studies have indicated that ettringite in hydrated portland cement products can be fully or partly destroyed when the materials are cured at a temperature above 70°C for a few hours [1, 2]. Furthermore, ettringite can reform after a few weeks when the hardened products are subsequently stored at room temperature under water, or in a moist atmosphere. Eventually, in certain cases, expansion and disruption may occur after further delays of months or years; the term Delayed Ettringite Formation (DEF) is used to describe this form of disruption. The internal deterioration of heat-cured precast portland cement concretes has been reported in several countries [3-13], and many laboratory observations [2, 4, 14-17] have demonstrated that expansions can occur in heat-cured mortars and concretes made from portland cements produced in many different countries. Bands of ettringite form around the aggregate grains and can be seen by optical or electron microscopy, both in deteriorated steam cured concretes from site and in heat-cured mortars and concretes from laboratory investigations [18-22]. Ettringite crystal growth pressure and ettringite band formation have sometimes been regarded as important factors in accounting for the DEF expansion of mortars and concretes [11, 14].

There have been relatively few reports concerning the behaviour of cement pastes, but it is agreed that portland cement pastes, heat-cured at elevated temperature and subsequently stored at room temperature, take much longer (more than one year) before the onset of expansion than do mortars and concretes [2,23,24]. Odler and Chen [25] observed the variations of ettringite contents in the heat cured cement pastes (w/c = 0.4 and 0.5, heated at 50°C and 90°C) during the period of DEF expansion. They found that the extent of DEF expansion and the amount of ettringite formed increased with the amount of water supplied to the cement pastes from outside. Scrivener and Taylor [26] described the microstructures of heat-cured portland cement pastes (w/c = 0.5, heated at 80°C) during the period of subsequent water storage at room temperature, but before DEF expansion occurred.

Several cement pastes have shown expansion after heat cure after very long storage in our laboratory. Expansion after curing at 100°C is significantly more advanced than those cured at 80°C. For the present report, the same portland cement (cement 3982 from ref. 23) as used by Scrivener and Taylor [26] was employed. The microstructures of the cement paste prisms which had been heat cured at 100°C for 3 hours, and eventually showed a large DEF expansion, were examined at an age of 4 years by using backscattered electron imaging (bse) of SEM, combined with quantitative x-ray microanalysis (EDS). The contents of ettringite were determined by quantitative X-ray diffraction analysis (QXDA). The results are relevant to an understanding of the mechanism of DEF expansion.

Experimental Material and Procedures

Cement. ASTM Type III portland cement was used. Its chemical composition and its mineral composition are shown in Table 1.

Casting. Cement was mixed with distilled water at a water:cement ratio = 0.45 and cast into 40 × 40 × 160 mm prisms, using standard steel moulds. The moulds allowed small stainless steel inserts to be cast into the ends of the prisms to allow for more precise measurements of length change to be made during subsequent monitoring.

Heat Curing Regime. The cement pastes were precured at room temperature for 2 hours, then placed in a water bath while still in their steel moulds and heated to 100°C at a rate of 20-25°C per hour, held at 100°C for 3 hours, and finally cooled slowly to room temperature over a period of about 16 hours, while still under water.

Curing at Room Temperature. After heat treatment, the prisms were demolded and marked, then stored under water at 20°C ± 3°C. The cement paste prisms without heat treatment were demolded after 24 hours in the mist room, and subsequently stored under water in the same conditions.

Microstructural Examination. Camscan scanning electron microscope, Series 2 fitted with a Link System energy dispersive X-ray analyser (EDS) was used to examine the microstructure and phase distribution of polished sections of the cement pastes. X-ray microanalysis was performed at an accelerating voltage of 20 kV by using ZAF procedure for matrix cor-

TABLE 1
Chemical and Mineralogical Composition of ASTM Type III Portland Cement

Oxides	%weight	Minerals	%weight (*QXDA*)	%weight (*Bogue*)	%weight (*m-Bogue*)
SiO_2	20.9	Alite	64.0	51.2	71.1
Fe_2O_3	2.8	Belite	14.5	21.3	7.9
Al_2O_3	4.3	$\alpha'-C_2S$	2.0		
CaO	62.8	C_3A	3.5	6.7	5.2
MgO	2.1	Ferrite	9.5	8.5	8.8
SO_3	4.2	Gypsum	0.5		
K_2O	1.0	Hemihydr.	1.5		
Na_2O	0.3	Anhydrite	0.0		
LOI	0.9	Total	95.5	87.7	93.0
Total	99.3				

Bogue: determined by Bogue calculation;
m-Bogue: determined by modified Bogue calculation [27].

rections. For quantitative microanalysis, the EDS system was calibrated using pure cobalt and other pure compounds, including Al_2O_3, $CaSiO_3$ and $CaSO_4$. A Philips x-ray diffractometer was used to examine the ettringite content in the cement pastes quantitatively. A sample of pure ettringite used as the standard for QXDA was provided by Mr. W.A. Gutteridge of the British Cement Association.

Results

Expansion Measurements and Observation of Macro-Cracking. Expansions were measured by means of a hand operated length change comparator, utilising a standard invar length to calibrate the instrument at each time of reading. Readings were taken at about monthly intervals. The cement paste prisms cured at 100°C for 3 h started to expand after approximately 2½ years water storage at room temperature and large expansions (over 1%) have been observed in the further storage period of more than 1½ years that has elapsed up to the present time (Fig. 1).

Macro-cracks were observed in the expanding cement paste prisms during the later periods of water storage at room temperature, mainly in regions along one surface of the prisms. Some of the prisms eventually showed non-uniform expansion and were bent. Larger expansion was observed where macro-cracking had occurred.

Examinations by XRD. Quantitative analyses by x-ray diffraction for the amount of ettringite found in various cement pastes are given in Table 2. The absolute values must be treated with caution, but the relative values are meaningful. Although no large differences were observed between the amount of ettringite in the 4-year old cement pastes with and

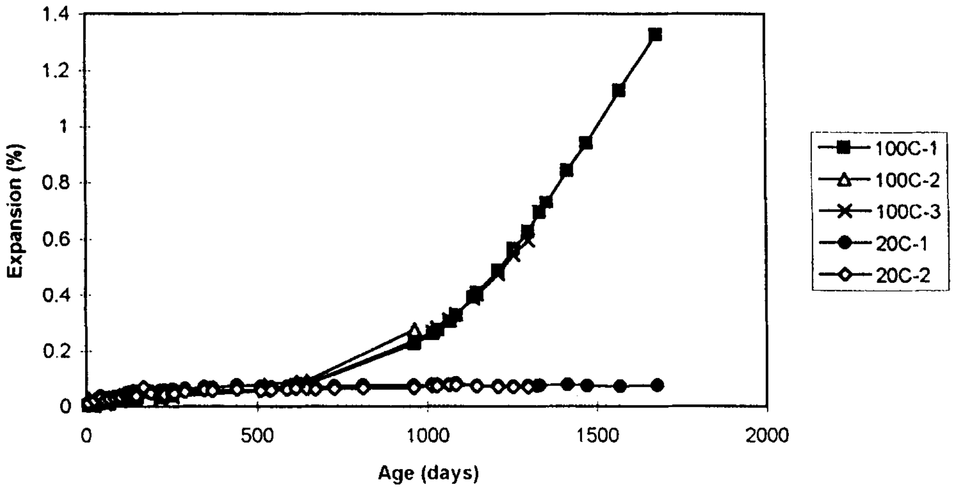

FIG. 1.
Expansions of the cement pastes cured at 100°C for 3 hours and subsequently stored under water at 20°C, compared with that cured at 20°C.

without heat treatment, more ettringite was detected in the paste cured continuously at 20°C than in that pre-cured at 100°C for 3 hours. Furthermore, ettringite was unevenly distributed in the prisms exhibiting large expansions; it was found in somewhat larger amounts near the surface of the prisms, where many cracks were observed, than in the central region where few cracks were observed.

Microstructural Features. Examination of the backscattered electron images by SEM of portland cement pastes, which had been cured at 100°C for 3 hours, revealed the appearance of ettringite bands in the region of the prisms with macro-cracks as shown at low magnification in Figure 2a. The microstructural features of this area at higher magnification are illustrated in Figure 2b, 2c and 2d.

The profile of the prisms from the edge to the centre exhibited a gradual reduction in the amount of ettringite bands observed, with few appearing in the central region (compare Fig. 2a with Fig. 3a), thus supporting the evidence from x-ray diffraction. Ettringite bands could be clearly seen in the outer areas of the prisms (Fig. 2b, 2c and 2d). Many micro and macro cracks pass along one side of these ettringite bands, but some ettringite bands are in intimate contact with the paste (Fig. 2d). Some cracks near the ettringite bands are empty. Commonly, the bands containing ettringite were markedly wider than the empty cracks. In contrast, only empty cracks could be observed in the paste cured at 20°C (Fig. 5a). The wider cracks in the paste cured at 20°C had roughly similar widths to those of many of the empty cracks in the expansive paste cured at 100°C. Clearly some of the cracks were not related to the expansive process, for example drying shrinkage might have taken place during sample

TABLE 2
The Percentages of Ettringite in 4-Year Old Cement Pastes

Phase	Paste 20	Paste 100 M	Paste 100 C
Ettringite	10.7	8.0	7.1

Paste 20 = the cement paste cured at 20°C
Paste 100 M = the cement paste in the region of the prism with macro-cracking after curing at 100°C;
Paste 100 C = the cement paste in the central region of the prism after curing at 100°C.

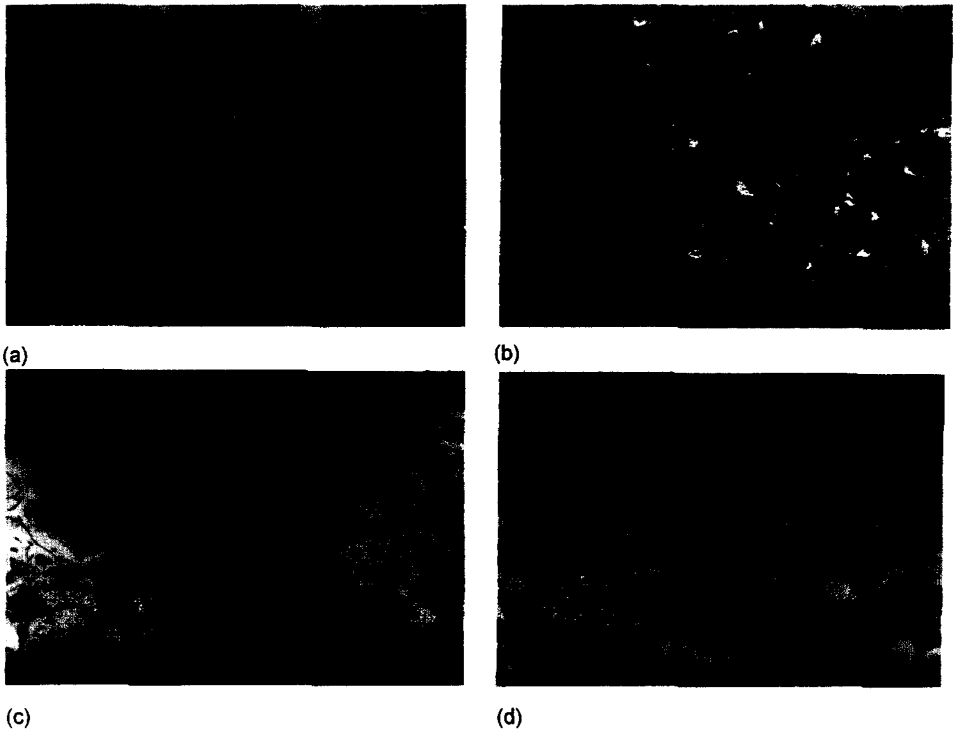

FIG. 2.
Microstructures of the heat-cured cement paste in the outer regions of the macrocracked prism.

preparation. Many more regions were observed to be occupied by ettringite in the heat cured paste than in the paste without heat curing.

Most of the alite grains were completely hydrated in both heat cured and room temperature cured 4-year old cement pastes. There were obvious differences in the microstructural features between the inner products in the cement pastes cured at 100°C and that cured at 20°C. Two zones within the inner products in the heat cured paste have been reported by

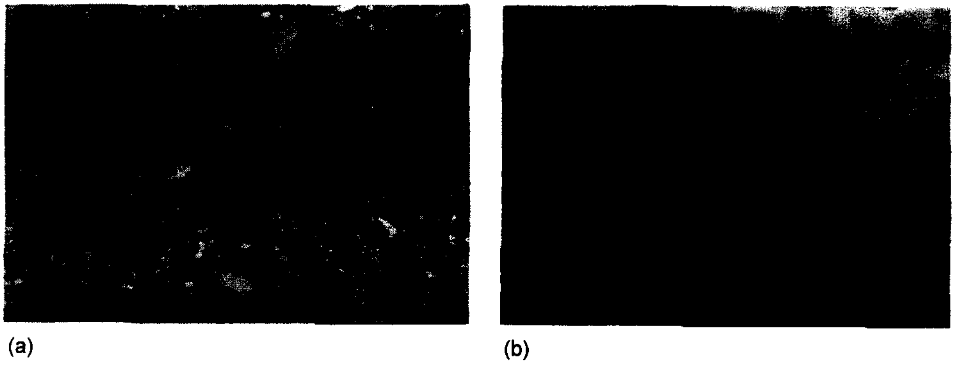

FIG. 3.
Microstructures of the heat-cured cement paste in the central area of the prism.

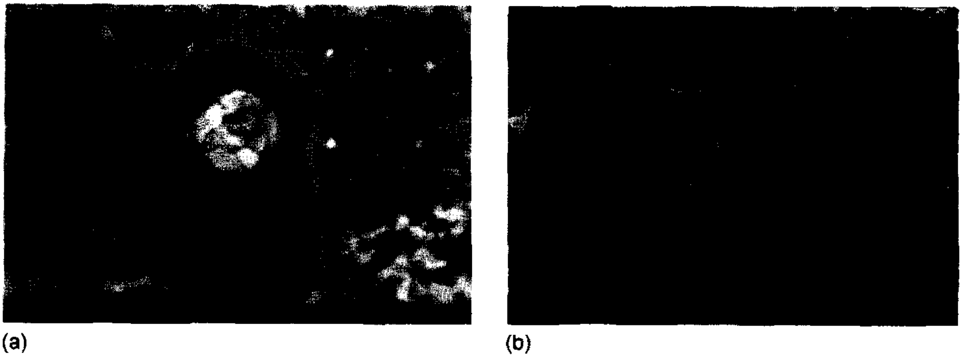

FIG. 4.
Ettringite crystallization (a) and cracking (b) in the inner and darker zone of the inner products in the heat-cured cement paste.

other researchers [26,28], and these were also observed in the present investigation. The outer and brighter zone, visible in Fig. 3b, is believed to have formed during the hydration in the period of the heat curing, whereas the inner and darker zone is believed to have formed during the hydration at room temperature following the heat cure. In the 4-year old heat treated cement pastes, it was noted that ettringite formation (Fig. 4a) and cracks (Fig. 4b) sometimes appeared in the inner and darker zones of the inner products, whereas nothing similar occurred in the inner products of the cement paste which had not been heat treated (Fig. 5b). The cracks that developed in the inner and darker zones mostly appeared in the region near the surface where overall surface macro-cracking occurred, rather than in the central area of the prism.

X-ray Microanalysis. Areas occupied by unhydrated cement clinker, calcium hydroxide and other hydrates can be identified by the contrast in the bse image, while the inner products and the outer products of alite hydration, and areas rich in the sulphoaluminate hydrates can be identified by the morphology of the phases in the bse image, as shown in Fig. 3b, 5b and 2b, respectively. Quantitative x-ray microanalysis was performed independently on the inner products and the outer products in the cement pastes by avoiding the calcium hydroxide-rich, the sulphoaluminate hydrate-rich areas and the unhydrated clinker grains. The atomic ratio

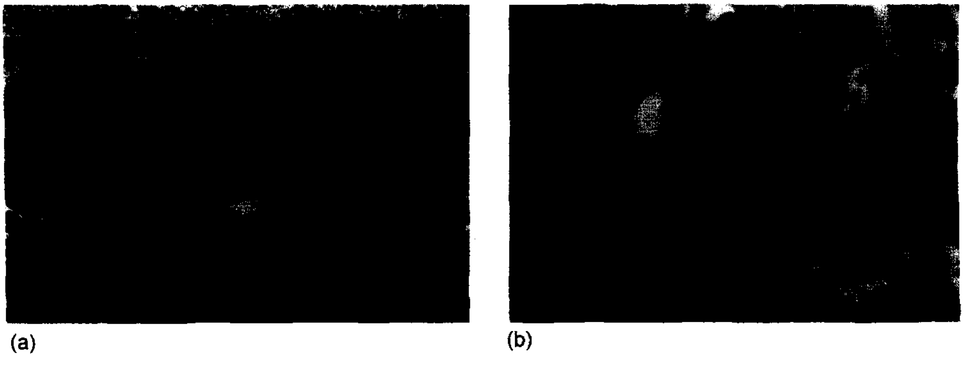

FIG. 5.
Microstructures of the cement paste cured at room temperature.

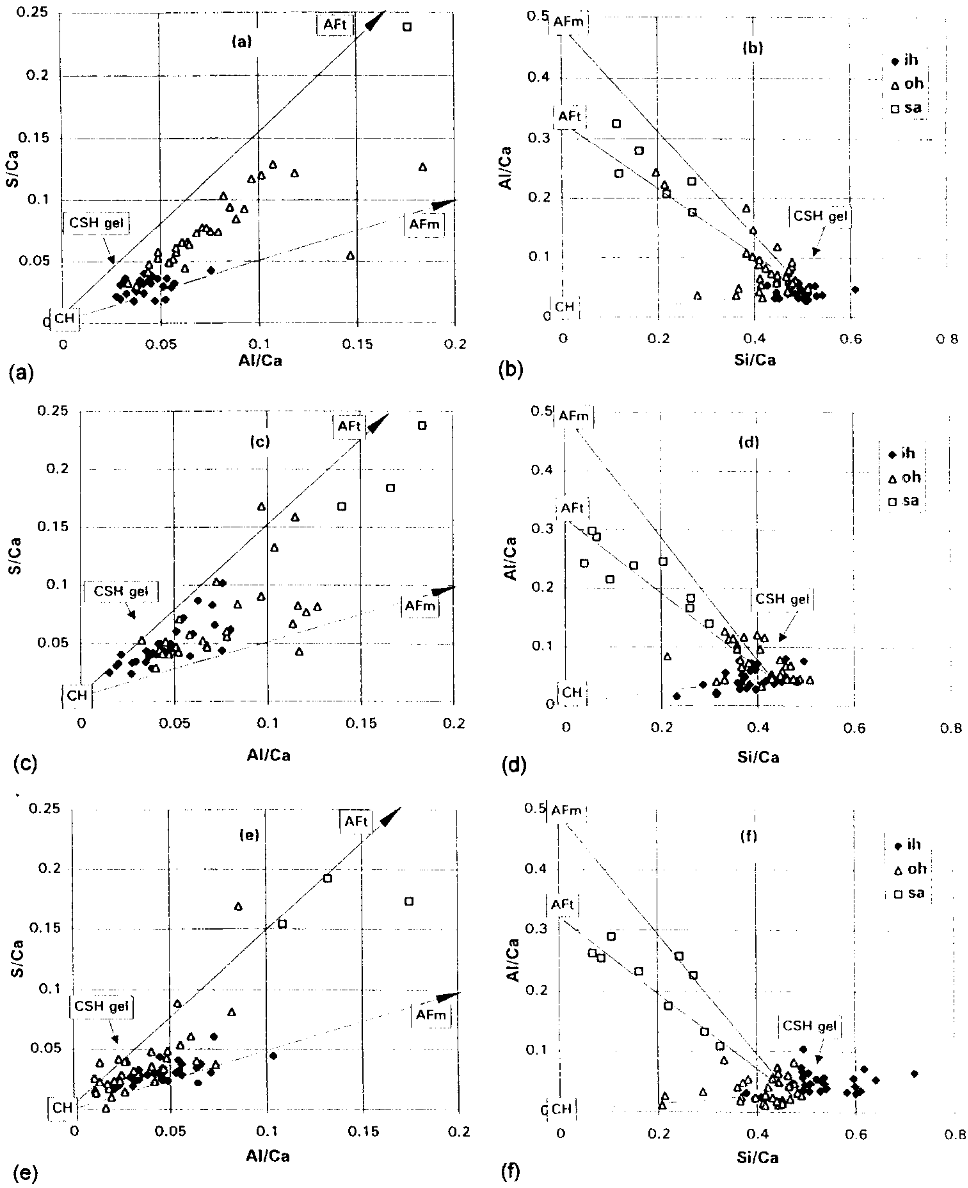

FIG. 6.

Atomic ratio plots for the cement paste cured at 20°C (a, b), and for the heat-cured cement pastes in the central regions (c, d) and in the outer regions (e, f) of the prism.

plots of S/Ca vs. Al/Ca and Al/Ca vs. Si/Ca for the 4-year old cement pastes, based on quantitative X-ray microanalysis, are shown in Fig. 6.

X-ray microanalysis on the inner products showed that the analyses in the cement paste cured at 20°C were concentrated in a relatively small region on the plots of S/Ca vs. Al/Ca, and Al/Ca vs. Si/Ca (Fig. 6a and 6b), whereas the results for the inner and darker zones in the central areas of the heat cured paste were scattered towards the directions of high contents of sulphoaluminate hydrates (AFt, AFm, etc.) or CH (Fig. 6c and 6d). In the outer section of the heat cured prism with macro-cracks, the analyses in the inner and darker zones shifted down on plots of S/Ca vs. Al/Ca, compared with those in the inner section of the heat cured prism (Fig. 6e and 6c) and approached the S/Ca and Al/Ca ratios of the analyses of the inner products in the paste cured at 20°C. The inner and darker zone of the former was, however, much more Si-rich, with the Si/Ca ratio ranging between 0.55 and 0.8 (Fig. 6f).

The analyses of the outer products in the 20°C cured paste were basically separated from those of the inner products and were distributed between those of the inner products, sulphoaluminate hydrates (concentrated areas of ettringite or monosulphate) and calcium hydroxide. In contrast, the composition of the outer products partly overlapped that of the inner products for the heat treated paste in the central areas (Fig. 6c and 6d). In the outer region of the heat treated paste where macro-cracking and ettringite bands developed, the S/Ca and Al/Ca ratios of the analyses of the outer products were markedly reduced in comparison with those in the cement paste cured at 20°C and in the central region of the heat cured prism. Most of the analyses of the outer products coincide with the analyses of the inner hydrates in the atomic ratio plot of S/Ca vs. Al/Ca (Fig. 6e).

X-ray microanalysis demonstrated that the composition of the inner products in the outer and lighter zones in the heat treated paste was basically consistent with the average composition of the inner products in the inner and darker zones, but the analyses in the outer and lighter zones grouped together rather than scattered (Fig. 7).

Discussion

The observed expansions of the cement paste prisms cured at elevated temperature under a heating regime typically employed for laboratory investigations of DEF [2], and then stored at room temperature, prove that DEF expansions do not necessarily depend on the presence of aggregate particles, in agreement with the conclusion by Odler and Chen [25]. Furthermore, these expansions do not depend upon the presence of extraneous cracking caused by factors such as ASR, inadequate pre-curing prior to heat treatment, freeze-thaw cycles, etc., although these factors can surely much reduce the induction period for the expansion. 3:1 siliceous sand:cement mortars using the present cement (cement 3982) have been shown to be readily expansive after heat curing [23], with significant expansions starting after less than 100 days water storage.

Ettringite bands form directly in the heat cured cement pastes after long term water storage at room temperature. Based on the results of x-ray microanalysis and the observations of microstructures of the cement pastes, it can be taken that a considerable amount of S and Al is available for formation of ettringite bands in both the outer and the inner products of the heat treated cement paste. Dissolution of ettringite originally present probably also makes some contribution to ettringite band formation.

In the room temperature cured cement paste, ettringite is probably very finely intermixed with C-S-H gel in the outer products, because distinctly fewer concentrated areas of ettringite can be observed by bse image of the 20°C cured paste than those in the heat cured paste, although the ettringite contents as determined by QXDA are higher than those of the heat cured paste. This kind of fine intermixing between ettringite and C-S-H gel has previously been reported by Scrivener and Taylor [26] and appears to be relatively stable.

In the heat treated cement paste, however, the lower total ettringite contents but greater areas of well crystallized ettringite, compared with the case of room temperature cured paste, imply that its outer and inner calcium silicate hydration products contain a higher proportion

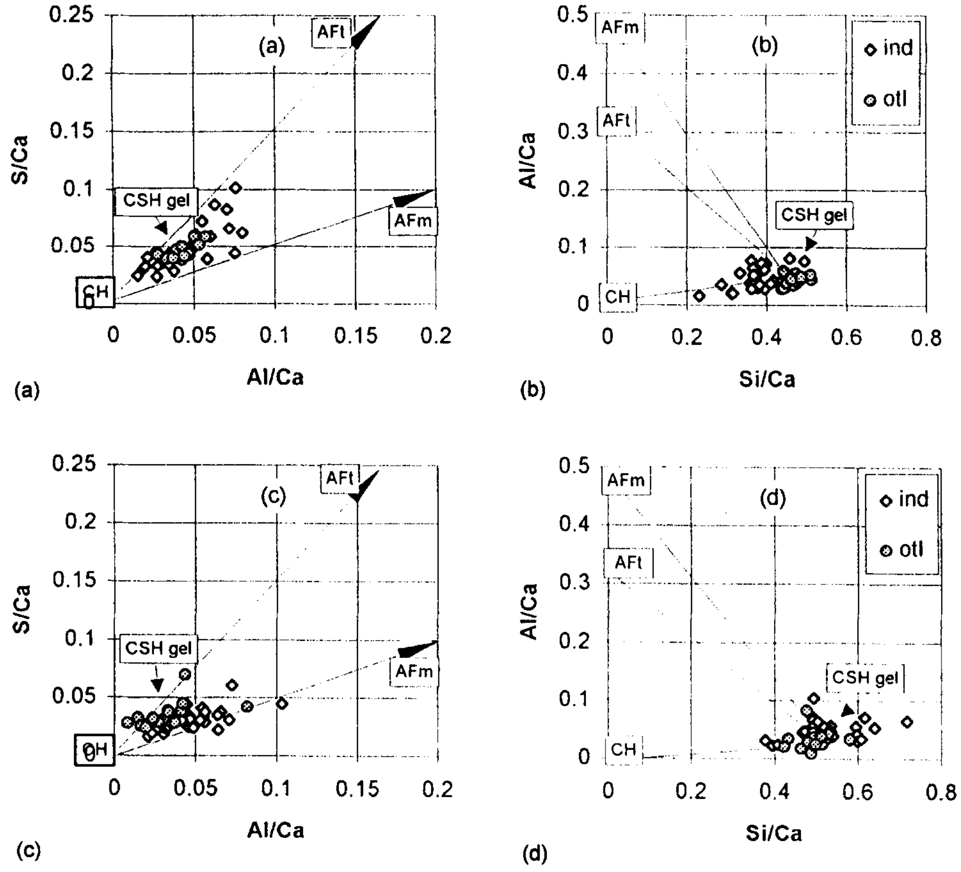

FIG. 7.

Atomic ratio plots for the inner products in the central areas (a, b) and in the outer region with macro-cracking and ettringite bands (c, d) of the heat-cured cement prism.

of S and Al, which are not present in the form of finely dispersed ettringite or monosulphate. Possibly S and Al species are sorbed initially onto C-S-H gel, as suggested by Scrivener and Taylor [26], during the period of heat cure.

These S and Al species sorbed onto C-S-H gel become unstable when the heat cured paste is stored at room temperature under water, and tend to be expelled from the C-S-H gel to form initially micro-crystalline ettringite and eventually crystalline ettringite. The ettringite crystallizing in the heat cured paste during water storage at room temperature presumably cannot intermix with the outer product C-S-H gel as easily as in the case of the room temperature cured paste, because of the dense structure of the outer products that has been established during the heat cure. Thus, ettringite forming in the heat cured paste is forced either to occupy voids and the inner and darker zones as shown in Fig. 4a, or to form crystalline ettringite bands (Fig. 2).

The current observations that the ettringite bands concentrate in the region in which larger overall expansions occur and are generally wider than empty cracks are not inconsistent with the statement that ettringite band formation causes the expansion of the cement paste. Nevertheless, they are not conclusive and further evidence is required to prove this hypothesis. It seems unlikely that expansion results directly from cracks formed in the inner and darker zones in the inner products in the heat treated paste, because most of these cracks are not connected with ettringite bands or cracks outside the inner products. It is possible that such cracking, together with ettringite crystallization, in the inner and darker zones may weaken the structure of the paste and so indirectly contribute to the overall expansion.

Conclusions

1. Heat-cured portland cement pastes can suffer expansions associated with DEF, but only after much longer induction periods than mortars and concretes made using the same cement.
2. It follows that the presence of aggregate particles or cracks caused by other factors are not essential to the observation of expansions associated with DEF, although expansions are greatly accelerated when aggregate particles are present.

3 No more (and possibly less) ettringite is found in heat-cured cement pastes than in those cured at 20°C, but it is more concentrated within narrow bands in the heat cured paste.

4. Ettringite concentrations appear within the inner and darker zone of the calcium silicate hydration products of heat-cured pastes, but it is considered unlikely that these features directly contribute to the overall expansion.
5. The observations reported here are not inconsistent with the hypothesis that delayed ettringite band formation causes expansion of the cement paste, but further evidence is required to prove this statement.

Acknowledgements

We should like to thank Mr. W.A. Gutteridge for helpful discussions. We are grateful to the British Cement Association for providing the Fellowship to Dr C.D. Lawrence and to the Cement and Concrete Centre of the University of Sheffield for providing the scholarship to Mr R. Yang during the period of this study.

References

1. Day, R.L., Civil Engineering Report CE92-2, Department of Engineering, University of Calgary, PCA Project 92-05, 113 (May 1992).
2. Lawrence C.D., Materials Science of Concrete, American Ceramic Society, Edited by J Skalny and S Mindess, IV, 113 (1994).
3. Tepponen P., Eriksson B-E, Nordic Concrete Research, No 6, 199 (1987).
4. Lawrence C.D., Dalziel J.A., Hobbs D.W., British Cement Association, Crowthorne, Berkshire, U.K., Interim Technical Note 12, May (1990).
5. Eriksson Bo-Erik, Tepponen P., Betonintuote, 2 (1985).
6. Hempel G., Bohmer A.; Otte M., Betonwerk+Fertigteil-Technik, 5, 75 (1992)
7. Shayan A., Quick G.W., ACI Materials Journal, 348, July/August (1992).
8. Oberholster R.E.; Maree, N., Brand J.H.B., 9th International Conference on Alkali-Aggregate Reaction, London. the Concrete Society, 2, 739 (1992).
9. Hime W.G., Marusin S., BIBM 93, National Precast Concrete Association, Extended Abstracts, 282-286, Washington U.S.A., 12, September (1993).
10. Johansen V., Thaulow N., Jakobsen U.H., Palbol L., 3rd Beijing International Symposium on Cement and Concrete, Beijing, 3, 144 (1993).
11. Heinz D., Ludwig U., Rudiger I., Concrete Precasting Plant and Technology, No11, 56 (1989).

12. Jones T.N., Poole A.B., 7th Int. Symp. on Concrete Alkali-Aggregate Reactions, edited by Grattan-Bellow, 446 (1987).
13. Jones T.N., Chemistry and Industry, No2, 18 Jan. 40 (1988).
14. Ghorab H.Y., Heinz D., Ludwig U., Meskendahl T., Wolter A., 7th International Conference Chemistry of Cement, Paris, IV, 493 (1980).
15. Heinz D., Ludwig, U., 8th Int. Cong. Chemistry of Cement, Rio de Janeiro, V, 189 (1986).
16. Heinz D., Ludwig U., ACI SP100, 2, 2058 (1987).
17. Sylla H-M, Belton, 38, 449 (1988).
18. Diamond S., Ong S., American Ceramic Society, Pacific Rim Meeting, Hawaii, 11, November (1993).
19. Ludwig U., International Building Materials and Silicate Convention, Weimar FGR, 6, May (1991).
20. Shayan A., Quick G.W., Proceedings of 14th International Conference on Cement Microscopy, Edited by Gouda, Nisperos and Bayles. 11 (1992).
21. Shayan A., Quick G.W., Proc. 6th Int. Cong. on Cement Microscopy, Virginia, 69 (1994).
22. Crumbie A.K., Taylor H.F.W., Pratt P.L., 9th Int. Cong. on Chemistry of Cement, New Delhi, IV, 131 (1992).
23. Lawrence C.D., Cem. Concr. Res. 25, No.4, 903 (1995).
24. Gabrowski E., Czarnecki B., Gillott J.E., Duggan C.R., Scott J.F., ACI Materials Journal, 89, 469 (1992).
25. Odler I., Chen Y., Cem. Concr. Res. 25, No.4, 853 (1995).
26. Scrivener K.L., Taylor H.F.W., Advances in Cement Research, 5, No.20, 139 (1993).
27. Taylor H.F.W., Adv. Cem. Res., 2, No.6, 73 (1989).
28, Scrivener K.L., Cem. Concr. Res., 22, No.6, 1224 (1992).