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DETERIORATION OF HEAT-CURED MORTARS DUE TO THE COMBINED EFFECT OF DELAYED ETTRINGITE FORMATION AND FREEZE/THAW CYCLES

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ABSTRACT

The interaction between freeze/thaw (F/T) exposure and delayed ettringite formation (DEF) and their combined effect on the performance of heat-cured mortar specimens are reported. The results show that heat-cured mortar, not subject to F/T, starts to expand gradually after a long induction period ([approx]150 days). This period is shortened and the extent of the expansion is increased as a result of F/T exposure. The longer the period of water storage at 20°C before F/T exposure, the greater the rate and extent of expansion immediately after F/T exposure and during the water storage period. The expansion observed in heat-cured mortars seems to be associated with delayed ettringite band formation. Mortar specimens that exhibit marked expansion show a corresponding decrease in strength and increase in oxygen gas permeability. © *1997 Elsevier Science Ltd*

Introduction

It is generally accepted that ettringite formed in mortar or concrete can be partly or completely destroyed when exposed to temperatures over 70°C and reformed when subsequently stored in water or moist air at room temperature (1–7). In parallel with this reformation of ettringite, a general expansion of the mortar or concrete is often observed. This phenomenon is referred to as delayed ettringite formation (DEF).

In recent years, deterioration of some precast concrete elements cured at elevated temperatures and subsequently exposed to moist environments has been observed (8–11). Internal examination of the damaged concretes showed a heavily cracked paste matrix with ettringite deposited in cracks and pores and in uniform rims around aggregate particles. Some alkali silica gel infilling the cracks was also often found. The cause of this deterioration has long been discussed in the literature. Lawrence and Ludwig (6,12) attribute the deterioration to DEF. Shayan and Johansen (13,14) attribute the deterioration to both alkali-silica gel and ettringite, but in many cases alkali-silica reaction appears as the first cause of deterioration.

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Taylor (4) proposed that microcracks in the paste are a necessary condition for expansion to occur. Expansion is increased if the material is weak and perhaps more specifically if the paste-aggregate interfacial bond is weak. It is suggested (13) that any other factor that is capable of producing microcracks, particularly in heat-cured mortar or concrete, may cause the formation of delayed ettringite in the resulting cracks, which then induces the expansion.

The exposure of mature mortar or concrete to alternating F/T cycles cannot be avoided in many parts of the world. F/T exposure can give rise to microcracks or flaws, which, in addition to the general weakening of the structure of mortar or concrete that these cracks can cause, can also provide nucleation sites for DEF and paths for ionic diffusion and moisture ingress. Overall, this could induce or accelerate the DEF-associated deterioration of heat-cured mortar or concrete. This paper summarises findings of an experimental programme devised to investigate the effect of F/T cycles on the development and progress of DEF and also to highlight the combined effect of F/T exposure and DEF on the performance of heat-cured and nonheat-cured mortar specimens.

Experimental Programme

The experimental programme consisted of assessing the performance of heat-cured and nonheat-cured (control) mortar specimens after exposure to F/T cycles, ranging from 0–80 cycles. Two mortar prisms were tested for each condition. Each set of two specimens was subjected to a specific number of F/T cycles, after which the specimens were stored in a water bath kept at 20°C and monitored to an age of 400 days after casting. Hence, each set of specimens was subjected only once to F/T cycling, and this was performed at 1, 28, or 150 days after casting. The following list shows the different conditions investigated:

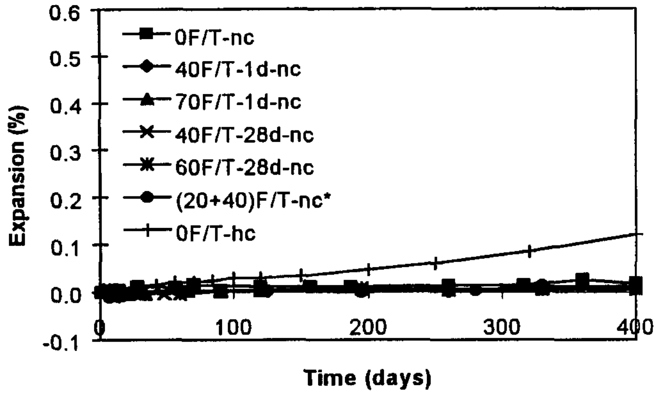
1) No heat curing and no F/T exposure (control), [specimens: 0F/T-nc];
2) No heat curing with F/T exposure (control), [specimens: 40–70F/T-nc in Figure 1];
3) Heat curing with no F/T exposure (control), [specimens: 0F/T-hc in Figure 2];
4) Heat curing with F/T exposure (at 1, 28, or 150 days after casting), [specimens: 10–80F/T in Figures 3–7].

Materials

It was found from literature that the expansion associated with DEF can take a number of years to develop, depending on a number of parameters, one of which is the type of cement used. Therefore, a pilot study was conducted (15) on nine commercially available UK cements, and the one which exhibited an expansion potential within a reasonably short time (at 90°C) was used in this investigation.

The chemical composition of the cement used was as follows: SiO_2 20.73%, Al_2O_3 4.89%, Fe_2O_3 2.77%, CaO 63.91%, MgO 2.2%, SO_3 3.18%, Na_2 0.10%, K_2O 0.71%. The specific surface area was approximately 488 m^2/kg.

German Normensand (a European standard quartzite sand) was used in order to eliminate the development of alkali-silica reaction. No other materials or admixtures were added to the mortar.



***(20+40)F/T-nc: Prisms exposed to 20 cycles immediately after curing and submitted to 40 cycles after 280-day water storage**

FIG. 1.
Expansion measurements for nonheat-cured control specimens and heat-cured control (0F/T-hc) specimens.

Specimen Preparation

The mix proportions, by weight, for all mortar specimens were cement:sand:water = 1:3:0.5. Mortar prisms (40 × 40 × 160 mm) and cubes (50 × 50 × 50 mm) were cast following the procedure laid down in BS 4551: 1980.

All specimens, after casting, were covered with a polythene sheet and kept standing at 20°C for 2 h before either storing in a mist room at 20°C (nonheat-cured control specimens (nc)), or placing in a water bath for heat curing. The heat curing cycle consisted of raising the temperature of the water to 90°C at a rate of 18°C/h. The specimens were kept at peak temperature for 8 h before they were allowed to cool down gradually to 20°C over a 10-h period. The specimens were then de-moulded and were either exposed to F/T immediately (~1 day after casting) or stored in water at 20°C awaiting subsequent F/T exposure (i.e., at 28 or 150 days after casting). Control

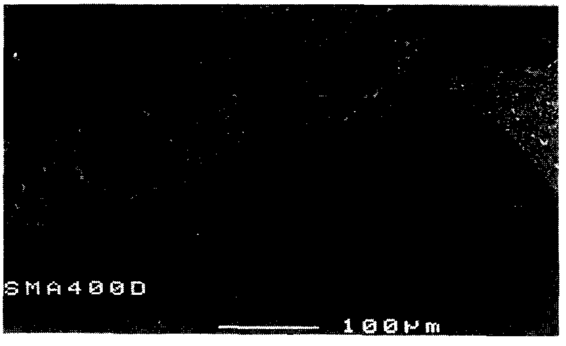


FIG. 2.
SEM micrograph of non-F/T heat-cured mortar at the age of 400 days.

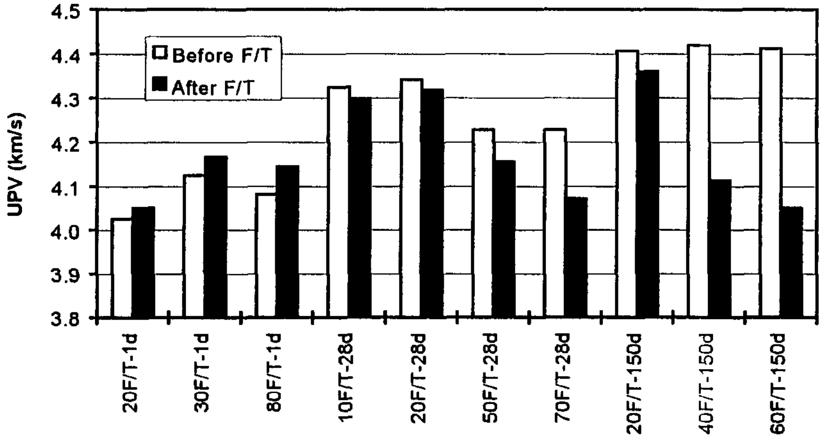


FIG. 3.
Changes in UPV values for heat-cured mortar prisms before and after F/T exposure.

nonheat-cured specimens were also de-moulded 24 h after casting and then exposed to F/T cycling in a similar manner.

Freeze/Thaw Cycle

The F/T cycle was based on the procedure outlined in BS 5075: Part 2: 1982. The cycle consisted of 6 h for freezing and 6 h for thawing; two cycles per day. The temperature range covered in each cycle was from −17.8°C to 20°C. The specimens were both frozen and thawed in water. The F/T exposure was carried out in an automated environmental chamber.

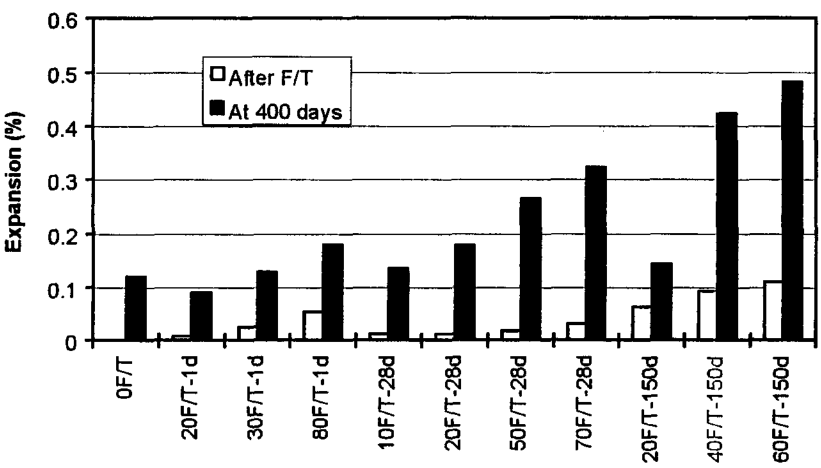


FIG. 4.
Expansion of heat-cured mortar prisms measured immediately after F/T and at the age of 400 days.

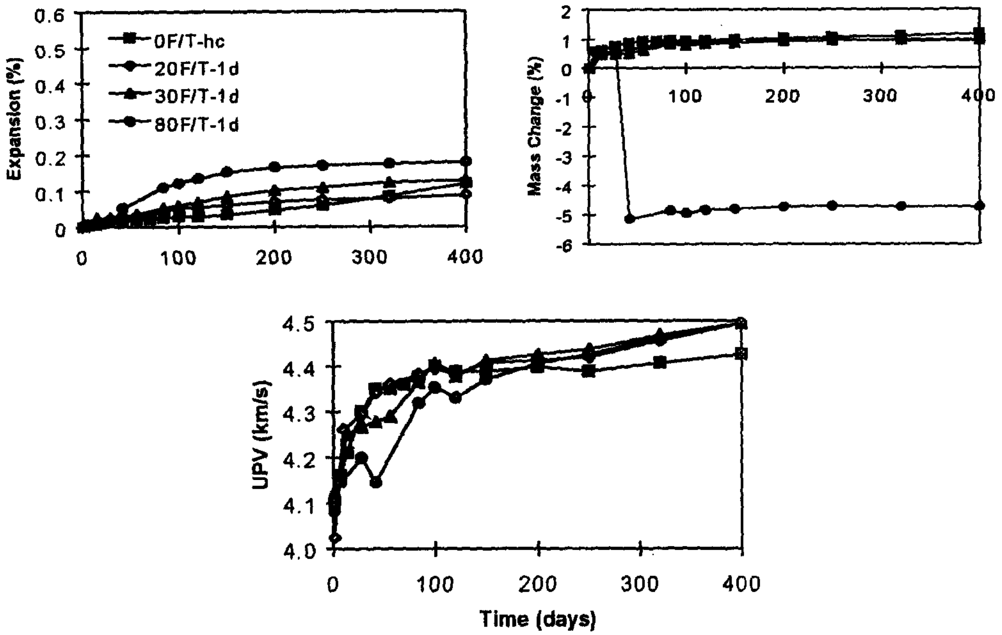


FIG. 5.
Changes in length, mass, and UPV values for heat-cured mortar prisms exposed to F/T at the age of 1 day.

Test Procedures

In order to assess the extent of deterioration of the specimens, as a result of F/T exposure and/or storage time, changes in length, mass, and ultrasonic pulse velocity (UPV) of mortar prisms were monitored at regular intervals. The compressive strength and oxygen gas permeability were also measured at different ages before and after F/T exposure. The initial values of length, mass, and UPV of the prisms were measured immediately after de-moulding. SEM measurements were conducted on polished surfaces of selected mortars using backscattered electron imaging.

Change in length was determined using a standard apparatus (British Standard BS 1881: Part 5: 1983) equipped with a dial gauge accurate to 0.001 mm. Stainless steel inserts were embedded into each end of the mortar prisms during casting to facilitate length measurements. A *PUNDIT* apparatus was used to test the UPV of mortar prisms. The compressive strength of 50 × 50 × 50 mm mortar cubes was determined using a hydraulic testing machine according to BS 4551:1980. The permeability of 25 mm (diameter) × 40 mm (height) cylindrical specimens was measured using an oxygen gas permeameter (16). The results presented for the various tests represent average values of two measurements.

Results and Discussion

The nonheat-cured control specimens (identified with "nc" in Fig. 1), irrespective of whether they were exposed to F/T or not, did not exhibit any expansion or show any signs of deterioration during the time frame of the investigation.

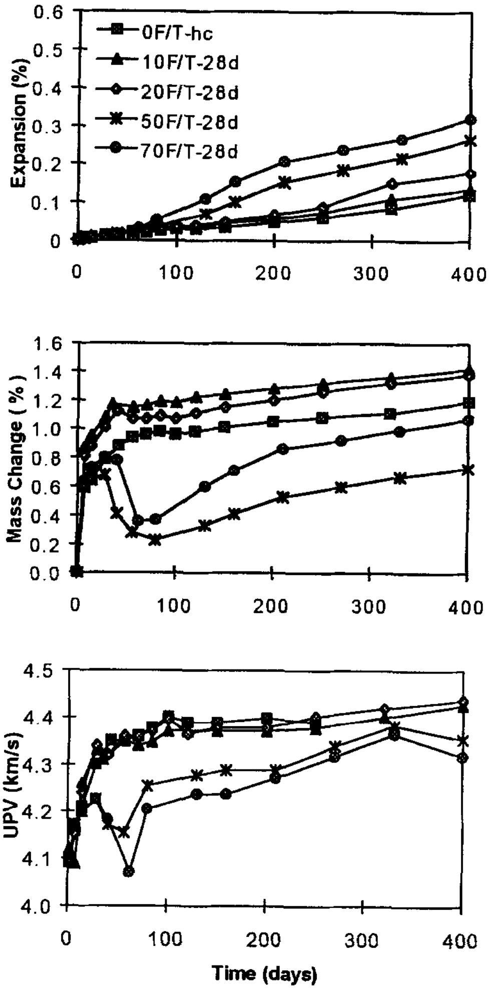


FIG. 6.
Changes in length, mass, and UPV for heat-cured mortar prisms exposed to F/T at 28 days.

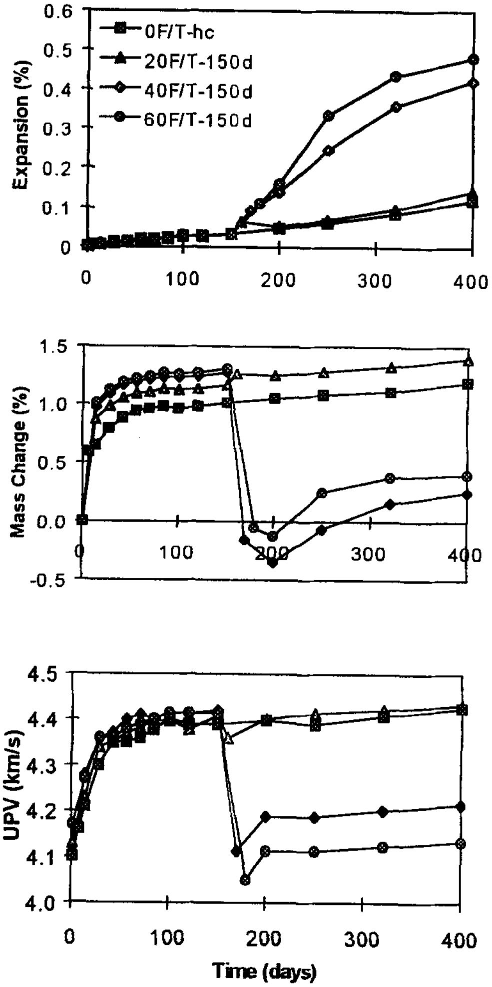


FIG. 7.
Changes in length, mass, and UPV for heat-cured mortar prisms exposed to F/T at 150 days.

The heat-cured mortar prisms, however, exhibited expansion and other deterioration signs, and the features of these were influenced by the exposure to F/T cycles, the number of cycles employed, and the age of the specimen at which the F/T exposure was carried out, as discussed below:

Heat-Cured Specimens With No F/T Exposure

These specimens (represented by curve 0F/T-hc in Fig. 1) exhibited expansion, and the expansion started at around 150 days of water storage after casting and reached 0.12% at the age of 400 days. The upward slope of the expansion curve vs. time suggests that the expansion is ongoing and has not been exhausted at 400 days. Backscattered electron microscopy (Fig. 2) of heat cured mortar (not exposed to F/T cycles) stored in water at 20°C for 400 days after casting revealed the formation of bands of ettringite around aggregate particles and also within the matrix. This suggests that the expansion is probably associated with the formation of these bands, as discussed elsewhere (17).

Heat-Cured Specimens With F/T Exposure

The performance of these specimens was determined in two ways: 1) immediately after exposure to F/T cycles at 1, 28, or 150 days after casting, in order to determine the extent of damage caused by the F/T exposure alone; and 2) regular monitoring during the subsequent water storage period, in order to determine if any further damage is caused by another mechanism (e.g., DEF) and whether this has been exacerbated by the F/T exposure.

Measurements Immediately After F/T Exposure. The UPV results (Fig. 3), and the expansion measurements (Fig. 4), suggest that damage is taking place as a result of F/T exposure, and this is particularly evident when F/T exposure is carried out at later ages (i.e., 150 days), where microcracks are visible on the surface of the prisms. The damage (i.e., reduction in UPV values, Fig. 3) is also related to the number of cycles imposed; the more cycles, the greater the damage. It can also be seen that a lower number of cycles was required (~40 cycles) to cause a marked reduction in UPV for the 150-day-old concrete in comparison to that required (~70 cycles) in the case of 28-day-old mortar. It seems, from these results, that the frost resistance of heat-cured mortars reduces with increasing time delay before the application of F/T cycling.

The reduction in the frost resistance with age is possibly due to 1) the effect of the heat-curing cycle and the associated flaws and microcracking that take place around aggregate particles due to the mismatch in the coefficient of thermal expansion between the matrix and aggregate (with prolonged storage in water, these flaws fill up with water, causing greater damage during F/T exposure); and 2) the growth of delayed ettringite, within the matrix and at the aggregates-paste interface, developing additional internal stresses aiding this overall progressive deterioration during F/T cycling. It is also possible that ettringite bands create weak planes within the microstructure along which slippage can take place.

In an accompanying investigation (17), running in parallel to this one and using the same materials and mix design, it was found that DEF starts to manifest itself in the form of expansion at around 150 days after casting. This gives support to the observations shown here, suggesting that the reduction in the F/T resistance of heat-cured mortar is related to the deposition of delayed ettringite within the microstructure. A similar study on the effect of DEF on the frost resistance of air-entrained mortar is under way, and the results will be reported in a future paper.

Changes During Water Storage After F/T Exposure. The changes observed during water storage also depended on the age of mortar at which F/T exposure was carried out.

F/T Exposure at 1 Day. Compared to specimens not exposed to F/T cycling, these specimens exhibited similar magnitude of expansion after 400 days when exposed up to 30 F/T cycles, and slightly higher expansion when exposed to 80 F/T cycles (Fig. 5). The onset of expansion for the F/T-exposed specimens is earlier than that for the non-F/T-exposed specimens. Moreover, it is interesting to note that the expansion curves for these specimens reach a plateau at around 200 days, unlike the non-F/T-exposed specimens, where the expansion curve has a rising slope. This is also different from the expansion curves of specimens subjected to F/T exposure at 28 or 150 days after casting (Figs. 6 and 7), where the expansion seems to be in progress at 400 days. This suggests that exposure to F/T cycling immediately after heat curing has a stabilising effect with respect to long-term DEF-associated expansion.

The damage caused by 80 F/T cycles is reflected in the drop in UPV values (Fig. 5). A significant reduction in mass was noted for these prisms, which was due to surface "popouts" as a result of F/T exposure. The drop in UPV for these specimens was completely recovered during subsequent storage in water at 20°C. This is possibly due to the infilling of the microcracks with normal hydration products (i.e., autogenous healing) in these young-age specimens, together with other reaction products such as delayed ettringite.

F/T Exposure at 28 Days. The expansion potential for these specimens is much greater than for those exposed to F/T cycling at 1 day. The expansion curves for these specimens (Fig. 6) indicate that the expansion is increasing with the period of water storage with no signs of abating at 400 days.

For specimens submitted to greater than 20 F/T cycles, the expansion is greater than that for non-F/T-exposed specimens. The onset of expansion for the F/T-exposed specimens is also earlier than that for non-F/T exposed specimens.

Specimens exposed to 50 and 70 F/T cycles exhibited marked drops in mass and UPV values (Fig. 6), but these recovered to a large extent during subsequent storage in water. For the specimens that exhibited large expansions (i.e., those subjected to greater than 20 F/T cycles), a high rate of mass gain was noticed immediately after F/T exposure, probably reflecting the rapid uptake of water in the newly developed cracks as a result of F/T cycling.

F/T Exposure at 150 Days. A small number of cycles (i.e., 20 cycles) seems not to have affected the expansion trend or extent as seen for the non-F/T-exposed specimens (Fig. 7). However, the most significant expansion occurred when the specimens were exposed to greater than 40 F/T cycles at the age of 150 days and were subsequently stored in water at 20°C. Expansion for these specimens rose quickly between 150 and 300 days, beyond which the rate of increase appeared to be slowing down. The drop in mass and UPV due to F/T for these specimens was also significant. Corresponding to the high expansions exhibited (specimens subjected to 40 and 60 F/T cycles), a high rate of mass gain was observed during subsequent storage in water shortly after the F/T exposure, as a result of water uptake in newly developed cracks. However, the overall loss in mass is greater for these specimens, compared to those exposed to F/T after 28 days, as a result of surface scaling, signifying the greater degree of damage caused in the 150-day-exposed specimens

The recovery of loss in UPV values was limited, unlike that seen in the series exposed to F/T immediately after heat curing, or after 28 days of water storage, and was no longer able to raise the values close to those of non-F/T-exposed specimens. This is possibly because 1) there is less subsequent infilling of the cracks with cement hydration products in these matured specimens; and 2) delayed ettringite is being deposited inhomogeneously (i.e., in concentrated areas) creating or extending wide cracks that are difficult to bridge. An SEM micrograph (Fig. 8) in one of these specimens shows localised DEF, where the cracks around

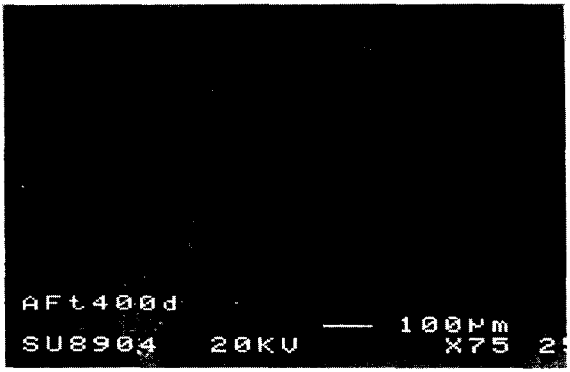


FIG. 8.
SEM micrograph of heat-cured mortar at the age of 400 days.

aggregate particles are being filled with ettringite bands, and the bands can also be seen to extend into the paste matrix. The bands are wider than those noted in the non-F/T mortar (Fig. 2).

Compressive Strength. The data shown in Table 1 indicate that the significant 400-day expansion exhibited by specimens subjected to 40 F/T cycles at 150 days is associated with a 36% reduction in compressive strength, in comparisons with non-F/T-exposed specimens. Specimens subjected to 20 F/T cycles at 150 days and stored to 400 days in water at 20°C show no appreciable reduction in compressive strength (in comparison with the non-F/T-exposed specimens). This follows the same pattern found for the expansion measurements for these specimens (Fig. 7)

Oxygen Permeability. Oxygen permeability results (Table 1) indicate that permeability increased nearly sevenfold immediately after 40 F/T cycles, for specimens subjected to F/T exposure at 150 days after casting, with a further 2.5-fold increase during storage to 400 days. Oxygen permeability, a property that is sensitive to changes in microstructure (16), appears

TABLE 1
Strength, oxygen permeability, and corresponding expansion values of heat-cured mortars subjected to F/T cycling at 150 days

Mortar No.	Expansion (at 400 days) (%)	Comp. Strength (at 400 days) (MPa)	K* (after F/T) ($\times 10^{-17}$, m^2)	K (at 400 days) ($\times 10^{-17}$, m^2)
0F/T-hc control	0.120	66.00	2.63**	2.18
20F/T-150d	0.143	63.25	5.09	2.52
40F/T-150d	0.424	42.35	17.90	42.35

* Intrinsic oxygen permeability.
** Measured at 150 days after casting.

to be more sensitive than compressive strength in differentiating between non-F/T-exposed and F/T-exposed specimens

The results also suggest that for mortar exhibiting a small amount of expansion after 150 days (i.e., exposed to less than 20 F/T cycles), the oxygen permeability values reduce with continuous water immersion to 400 days, possibly as a result of the self-healing and the deposition of delayed ettringite.

Conclusions

The following conclusions can be drawn from the above results:

1) It is confirmed that expansion occurs in heat-cured mortar during subsequent storage in water. This expansion, which starts at around 150 days after casting, is associated with delayed ettringite formation. SEM images show that the delayed ettringite bands prefer to form at the transition zone between paste and aggregate and extend into the cement paste matrix.
2) For heat-cured mortar, the onset of the expansion can be significantly accelerated, and the extent of the expansion can be considerably increased by exposure to F/T cycling, but this is dependent on the age at which F/T exposure is conducted, suggesting an interaction between the development of DEF and the performance of mortar in F/T cyclic exposure.
3) The expansion due to the combined effect of DEF and F/T exposure consists of two parts; a small amount of expansion exhibited after F/T cycling and a much larger expansion taking place during subsequent storage in water at 20°C. The first part reflects the F/T resistance of the mortar and the second shows the induced expansion due to DEF. This indicates that the overall expansion exhibited is largely related to DEF.
4) The frost resistance (i.e., deterioration immediately after F/T exposure) of heat-cured mortar decreases with increasing length of water storage period between heat curing and exposure to F/T cycles. The worse the frost resistance of the mortar, the greater the damage caused immediately after F/T, which, in turn, induced greater expansion during subsequent water storage. The development of ettringite within the structure is believed to be an important contributor to these effects, as discussed above.
5) The results seem to suggest that early exposure of heat-cured specimens to F/T cycling ([approx]1 day after casting) has a stabilising and limiting effect on the long-term expansion associated with DEF.
6) The probable sequence of events leading to expansion in heat-cured mortars seems to be that defects (internal microcracks or flaws) are first developed by a variety of preliminary mechanisms (including heat curing and F/T cycles), possibly involving a limited overall expansion, and then additional and substantial expansion is generated by the crystallisation of ettringite within these flaws.
7) The compressive strength of the mortar is decreased and its oxygen gas permeability increased with an increase in expansion. This indicates that the combination of DEF and F/T exposure has a cumulative detrimental effect on the mechanical properties and durability of mortar.

Acknowledgments

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References

1. H.M. Sylla, Beton 38, 449–454 (1988).
2. U. Ludwig, International Building Material and Silicate Convention, Weimar FGR, 6–10, May, 1991.
3. K.L. Scrivener and H.F.W. Taylor, Adv. Cem. Res. 5, 139–146 (1993).
4. H.F.W. Taylor, Am. Ceram. Soc., Pacific Rim Meeting, Hawaii, Nov. 1993.
5. P.W. Brown and J.V. Bothe, Jr., Adv. Cem. Res. 5, 47–63 (1993).
6. C.D. Lawrence, BCA, C/16, May (1993).
7. R. Yang, C.D. Lawrence, and J.H. Sharp, Cem. Concr. Res. 26, 1649–1659 (1996).
8. P. Tepponon and B.E. Erickson, Nordic Concr. Res. 6, 199–209 (1987).
9. A. Shayan and G.W. Quick, ACI Mater. J. 89, 348–361 (1992).
10. R.E. Oberholster, N. Maree, and J.H.B. Brand, 9th Int. Conf. on Alkali-Aggregate Reaction, London, 2, 739–749 (1992).
11. W.G. Hime and S. Marusin, BIBM 93, Nat. Precast Concr. Assoc., pp 282–286, Washington, 1993.
12. D. Heinz, U. Ludwig, and I. Rudiger, Concr. Precasting Plant and Technol. 11, 56–61 (1989).
13. A. Shayan and G.W. Quick, Adv. Cem. Res. 16, 149–157 (1992).
14. V. Johansen, N. Thaulow, and J. Skalny, Adv. Cem. Res. 5, 23–29 (1993).
15. Y. Shao, C.J. Lynsdale, J.H. Sharp, and C.D. Lawrence, Institute of Materials Meeting, Sheffield, UK, July, 1996.
16. J.G. Cabrera and C.J. Lynsdale, Mag. Concr. Res. 40, 177–182 (1988).
17. R. Yang, C.D. Lawrence, C.J. Lynsdale, and J.H. Sharp, Submitted to Cem. Concr. Res.