PII: S0958-9465(95)00013-3

Cement & Concrete Composites **18** (1996) 171–179
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0958-9465/96/$15.00

The Effect of Cement Composition and Fineness on Expansion Associated with Delayed Ettringite Formation

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Abstract

A large number of laboratory ground cements were prepared from five production clinkers. Grind variables included cement SO_3*, source of added* SO_3 *and specific surface area. Mortar prisms were cast as described in EN 196-1 except that the prisms were 16 × 16 × 160 mm with stainless steel pins cast in their end faces. Sets of prisms were cured for 12 h at 70°, 80° and 90°C in addition to the standard storage at 20°C. After demoulding at 24 h the prisms were stored in water at 20°C and lengths and weights monitored for periods up to ~1800 days. Expansions typical of DEF were normally only observed in prisms cured at 90°C. The magnitude of the expansion increased with fineness and passed through a maximum at a cement* SO_3 *content of ~4%. No expansions were obtained with a low* C_3A *sulfate resisting clinker but there was little difference in the behaviour of the other clinkers. Natural gypsum, natural anhydrite and desulfurisation gypsum gave similar expansions. Adding KOH or* K_2SO_4 *dissolved in the mixing water accelerated and increased expansions greatly. Some mortars containing added alkali expanded after curing at 80°C. © 1996 Elsevier Science Limited.*

INTRODUCTION

The expansion of heat treated mortars and concretes during subsequent moist storage has been studied widely in recent years.[1–14] The expansion is associated with delayed (or secondary) ettringite formation (DEF). The ettringite is found filling voids and cracks, particularly around aggregate particles. The paste/aggregate interface appears to be important, since the nature of the aggregate affects expansions, but expansions have also been reported in paste samples.[11] A full explanation of the expansion process is not yet available.

The published data indicate a critical temperature of ~70°C below which no expansions are observed. Higher temperatures may lead to subsequent expansion but some cements do not expand even after prolonged curing at 100°C.[11] The present study is an attempt to clarify the influence of cement composition and fineness on expansions associated with DEF. A set of laboratory prepared cements has been used to allow controlled variations of the factors believed to be important. Knowledge of the factors which determine the relative susceptibility of cements will assist in the development of models of the expansion process.

MATERIALS

Clinkers

Five UK works clinkers were used to produce the cements tested. The chemical analyses of the clinkers are given in Table 1 together with phase compositions from Bogue calculations. Clinker A is high in C_3A, clinker B high in K_2O, clinker C high in MgO and low in Na_2O eq. and clinker D low in SO_3. Clinker E is low in C_3A and suitable for producing sulfate resisting cement to BS 4027 or ASTM C 150 Type V.

Sulfates

Three sources of SO_3 were used: a natural gypsum, a natural anhydrite and a flue gas desulfurisation (FGD) gypsum. The natural

Table 1. Clinker analyses (% w/w)

Clinker	*A*	*B*	*C*	*D*	*E*
SiO_2	20·7	21·6	19·8	22·4	21·4
Al_2O_3	6·0	5·2	5·2	5·1	3·5
Fe_2O_3	2·4	3·2	3·0	2·4	5·1
CaO	66·8	66·3	66·2	67·5	66·0
MgO	0·7	1·0	2·5	0·6	2·0
SO_3	1·5	1·0	1·6	0·3	0·4
Ignition loss	0·4	0·2	0·2	0·3	0·3
K_2O	0·59	0·83	0·48	0·48	0·51
Na_2O	0·22	0·17	0·06	0·26	0·14
Na_2O eq.	0·61	0·72	0·38	0·58	0·48
Free lime	1·5	0·4	1·8	0·4	2·0
C_3S	64·8	64·6	72·5	65·2	67·1
C_2S	10·5	13·2	2·1	15	10·8
C_3A	11·8	8·4	8·7	9·5	0·6
C_4AF	7·3	9·7	9·1	7·3	15·5

anhydrite was used blended with a small proportion of the natural gypsum, giving 20% of the SO_3 present as the dihydrate. Chemical analyses are given in Table 2.

Limestone

Table 2 includes data on the limestone used in some grinds. The limestone meets the requirements in BS 7583 and ENV 197-1 for the production of Portland Limestone Cements.

Grinds

The cements were ground in a 450 mm diameter laboratory mill. The grinding was carried out cold and the cements then heat treated at 105°C for 4 h to produce a similar degree of gypsum dehydration to that found in production cements. The grinds carried out are summarised in Table 3. For most combinations of clinker and sulfate, cements with targets of 350 and 450 m^2/kg SSA and 4% and 5% SO_3 were ground. The limestone was used in grinds with clinker A and the natural gypsum. Although the target SSAs are given as 350 and 450 m^2/kg these grinds were actually designed to give a similar clinker fineness to that in the equivalent grind without limestone, as indicated by the 45 μm residue. The actual SSAs were therefore higher, particularly for the 15% limestone grinds.

METHODS

Mortars (3:1:0·5 sand:cement:water) were prepared as described in EN 196-1. The standard silica sand used was German 'Normensand' supplied in pre-weighed bags. 16 × 16 × 160 mm prisms were cast with stainless steel studs in their end faces. Up to four moulds, each containing three prisms, were used for each mortar mix. The prisms were cast in a single layer and compacted with 60 jolts. After striking off excess mortar a top-plate in each prism compartment provided essentially sealed curing conditions. Each mould was further sealed in a

Table 2. Sulfate and limestone analyses (% w/w)

	Natural gypsum	*Natural anhydrite*	*Anhydrite blend*	*FGD gypsum*	*Limestone*
SiO_2	0·6	1·4		0·7	2·4
Al_2O_3	0·5	0·3		0·0	0·1
Fe_2O_3	0·0	0·2		0·0	0·0
CaO	33·9	40·0		32·7	54·2
SO_3	44·9	54·6	53·5	44·4	0·1
$CaSO_4$	1	84	73	0	
$CaSO_4 \cdot 2H_2O$	96	11	22	95	
CO_2					42·7
Total organic carbon					0·06
Methylene blue absorption					0·2

Table 3. Grinds prepared and tests performed

Sulfate	*SSA* *(m^2/kg)*	*SO_3* *(%)*	*Clinker*						
			A	*B*	*C*	*D*	*E*	*A+5% limestone*	*A+15% limestone*
Gypsum	250	4	○	—	—	—	—	—	—
		5	○	—	—	—	—	—	—
	350	4	○	○	○	●	●	○	○
		5	○	○	○	●	●	○	○
	450	4	●	●	●	●	●	●	●
		5	○	○	○	●	●	○	●
Anhydrite	250	4	●	—	—	—	—	—	—
		5	○	—	—	—	—	—	—
	350	4	●	○	○	●	●	—	—
		5	○	○	○	●*	●	—	—
	450	3	●	●	●	●	—	—	—
		4	●K	●K	●KH	●	●	—	—
		5	●H	●	●H	●*	●	—	—
FGD	350	4	●	●	—	—	—	—	—
		5	●	●	—	—	—	—	—
	450	4	●	●	—	—	—	—	—
		5	●	●	—	—	—	—	—

*Clinker D, anhydrite, grinds were 4·6% and 5·6% in place of 5%.
— No cement ground.
○ Tested at 20°, 70°, 80°C.
● Tested at 20°, 70°, 80°, 90°C.K
Also tested with added K_2SO_4.
H Also tested with added KOH.

polyethylene bag together with a water soaked cloth to ensure 100% RH during curing. Samples were either maintained at 20°C or subjected to a heat treatment regime. 70° and 80°C cures were carried out in environmental cabinets. After a 20°C pre-cure for 4 h the temperature was increased by 20°C/h up to the required maximum temperature, which was maintained for 12 h. Cooling was also at 20°C/h. 90°C curing was carried out in an accelerated curing tank. The moulds were held ~50 mm above the surface of the water. After the 4 h pre-cure at 20°C the water was heated to 95°C in 1 h and maintained at this temperature for 12 h. Calibration with sand filled moulds showed that this gave a sample temperature of 90°C. Unforced cooling to 20°C took ~6 h.

All prisms were demoulded at 24 h and subsequently stored in water at 20°C. Lengths and weights were measured at regular intervals. Data for up to 5 years of water storage are available. All cements were tested with 20°, 70° and 80°C curing. Those also tested at 90°C are indicated in Table 3. Some additional mortars were prepared with K_2SO_4 or KOH dissolved in the mixing water to raise the SO_3 and/or Na_2O eq. levels. The cements used are also indicated in Table 3.

RESULTS

Typical expansion data

Figure 1 shows typical expansion results. The mortars cured at 20°, 70° and 80°C gave no significant expansion while the 90°C cured mortars expanded by ~1% between 56 and 200 days. The data plotted are means at each age for three replicate prisms. Agreement between replicates was always very good, ±~0·01% for prisms showing no expansion and ±~0·02%

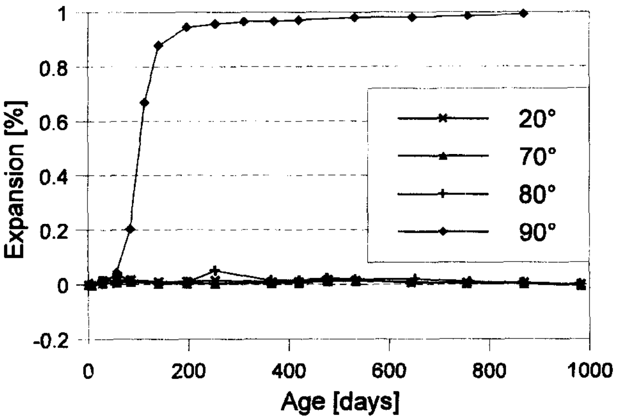

Fig. 1. Typical expansion data. (Clinker A, anhydrite, 4·3% SO_3, 456 m^2/kg.)

for prisms giving ~1% expansion. Data are available for storage periods up to ~1800 days. The only mortars to expand after curing at 80°C were those containing added K_2SO_4 or KOH.

No expansions were observed with cements containing the sulfate resisting clinker (E). After the initial rapid expansion, continued water storage gave further slow expansion but, in order to analyse the effect of various parameters on the expansion, plots such as Fig. 1 have been used to estimate a value for the ultimate long term expansion for each set of prisms. Expansions were associated with increases in weight, 1% expansion corresponding to ~1·5% weight increase.

Effect of fineness

Figure 2 shows the dependence of the ultimate expansion on the cement surface area for mortars cured at 90°C. The lines connect data for cements with the same combination of clinker, sulfate type and sulfate content, thus differing only in their finenesses. It can be seen that in all cases where expansion takes place an increase in surface area gives an increase in expansion. The results for cements based on clinker E are not included. The cements with low expansions at ~450 m^2/kg are based on clinkers B and D and have SO_3 contents > 5%.

Effect of cement SO_3

In Fig. 3 the lines connect points for cements with different SO_3 contents but constant values for other variables. The expansions pass through a maximum at sulfate contents near 4%. Only clinker C gives expansion at 3% SO_3.

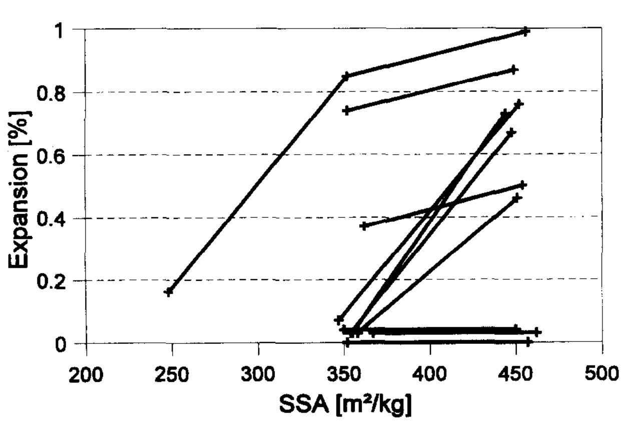

Fig. 2. Effect of cement fineness on expansion after curing at 90°C.

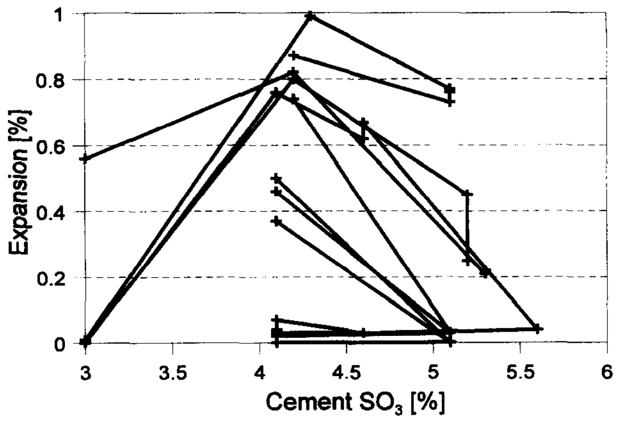

Fig. 3. Effect of cement SO_3 content on expansion after curing at 90°C.

The results for cements based on clinker E are not included. The cements giving low expansions at ~4% SO_3 are ~350 m^2/kg grinds based on clinker D. The vertical lines on the plot indicate results from repeated tests and show good reproducibility.

Effect of clinker and SO_3 sources

The most obvious dependence of expansion on clinker type is the absence of any expansion in all the cements containing clinker E, the sulfate resisting clinker. Of the other clinkers, A and C tend to give higher expansions than B and D. The small differences between the grinds with different sulfate sources are not considered significant. They can be related to differences in the actual SO_3 contents and finenesses. Figure 4 shows the variations in expansion for a single set of grind parameters.

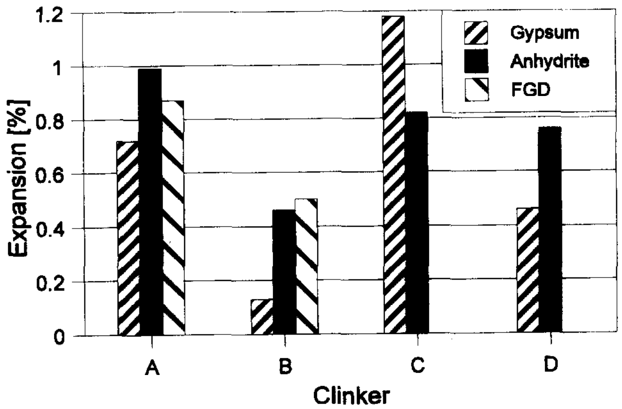

Fig. 4. Effects of clinker and sulfate source on expansion after curing at 90°C. (Grinds ~4% SO_3, ~450 m^2/kg.)

Effect of interground limestone

The grinds containing limestone gave similar ultimate expansions to the equivalent grind without limestone, although the expansion occurred earlier.

Effect of added K_2SO_4 or KOH

Adding K_2SO_4 gave large, rapid expansions. Figure 5 includes sets of data for clinkers A, B and C, all of which show similar behaviour. The 4% SO_3 grinds gave expansions of ~1%. Adding sulfate as $CaSO_4$ caused a significant reduction in expansion while adding the same amount of sulfate in the form of K_2SO_4 led to a large increase in expansion, to ~2%.

The influence of increasing the alkali content was investigated by adding KOH dissolved in the mixing water. Table 4 gives the details of the sulfate and alkali contents of the mortars containing added KOH, together with those of the related mixes containing added K_2SO_4. The expansions of the mortars are plotted against Na_2O eq. in Fig. 6. The line 'A5·1' shows the large increase in expansion associated with increasing the alkali content from 0·58 to 1·23% by the addition of KOH to the cement based on clinker A with a sulfate content of 5·1%. The point 'A4·3S' is the result for the cement based on clinker A with a sulfate content of 4·3% with K_2SO_4 added, which raises the sulfate content to 5·1% and the alkali content to 1·2% (see Table 4). The overall chemistry is thus very similar for the high alkali point on line 'A5·1' and the point 'A4·3S' and the expansions are almost identical. The line 'C5·3' and the point 'C4·2S' are the equivalent data for clinker C cements. The agreement in expansions is not so close in this case but it is clear that alkali added either as KOH or as K_2SO_4 gives similar expansions for the same total sulfate content. The increase in expansion for a given increase in alkali content is similar for the two clinkers studied. The line 'C4·2' shows the effect of increasing alkali content by adding KOH to a cement with a lower sulfate content. The rate of increase of expansion with alkali content is lower than for the higher sulfate cements. At ~0·4% Na_2O eq. the cement with 4·2% SO_3 has a significantly higher expansion than the cement with 5·3% SO_3 but at ~1·2% Na_2O eq. the expansions are similar.

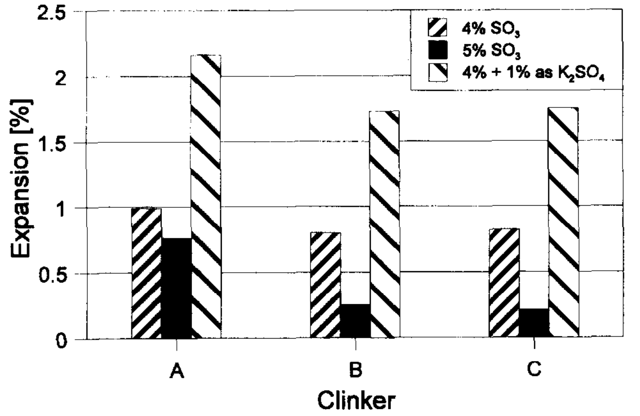

Fig. 5. Effect of adding K_2SO_4 on expansion after curing at 90°C. (Grinds anhydrite, ~450 m^2/kg.)

DISCUSSION

Previous investigations

The early work on expansion of heat treated mortars by Ghorab *et al.*[1] suggested that cement type had a large effect of on the behaviour. A low C_3A sulfate resisting cement gave no expan-

Table 4. Chemistries of mortars with added KOH or K_2SO_4 (% w/w cement)

Code	*Clinker*	*SO_3*				*Na_2O eq.*				*Expansion*
		Clinker	*$CaSO_4$*	*K_2SO_4*	*Total*	*Clinker*	*$CaSO_4$*	*K_2SO_4*	*Total*	
A5·1	A	1·5	3·6		5·1	0·58			0·58	0·77
A5·1	A	1·5	3·6		5·1	0·58		0·65	1·23	2·10
A4·3S	A	1·5	2·8	0·8	5·1	0·58	0·62		1·20	2·16
C4·2	C	1·6	2·6		4·2	0·38			0·38	0·82
C4·2	C	1·6	2·6		4·2	0·38		0·2	0·56	0·95
C4·2	C	1·6	2·6		4·2	0·38		0·4	0·78	1·51
C4·2	C	1·6	2·6		4·2	0·38		0·8	1·18	1·40
C5·3	C	1·6	3·7		5·3	0·38			0·38	0·21
C5·3	C	1·6	3·7		5·3	0·38		0·8	1·18	1·30
C4·2S	C	1·6	2·6	1·1	5·3	0·38	0·85		1·23	1·75

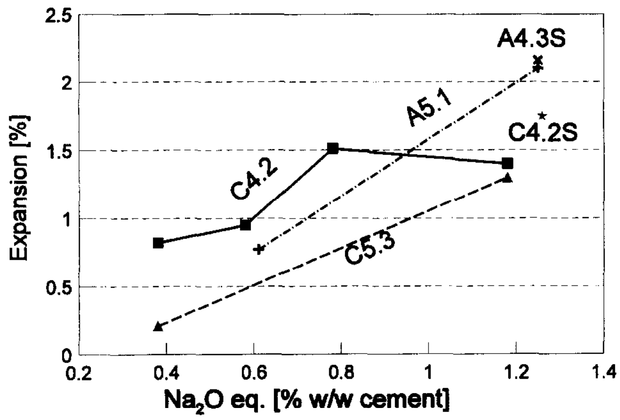

Fig. 6. Effect of adding alkali on expansion after curing at 90°C. (Grinds anhydrite, $\sim$450 m^2/kg.)

sion while a high early strength PZ 55 cement gave expansions of $\sim$1% with the same heat treatment. No details of the PZ 55 cement are given except for the high (4%) SO_3 content, but it would be expected to have had a high surface area, and possibly high C_3A and/or Na_2O eq. contents. Heinz and Ludwig[2] systematically varied the SO_3 content of a PZ 55 (12% C_3A) cement and obtained a maximum expansion at 3·8% SO_3. It was suggested that the important parameter was the SO_3/Al_2O_3 ratio, with no expansion for values < $\sim$0·7. The alkali content of the cement was not given. Heinz *et al.*[3] analysed expansion data from a wider range of cements and found a critical value of 2 for the expression $(SO_3)^2/Al_2O_3$(active), where active Al_2O_3 is that in C_3A. In agreement with the present study they found that the inclusion of 8% ground limestone had no effect on expansion. Müller *et al.*[4] varied the SO_3 and alkali contents of high and low C_3A cements by adding ground gypsum and potassium carbonate. However, the expansion data reported for a storage period of one year do not show any significant expansion associated with the heat treatment (6 h at 90°C). By blending two clinkers, Hempel *et al.*[5] produced cements with a wide range of C_3A and SO_3 contents. These were cured at various temperatures up to 100°C. Both paste and concrete prisms were tested. Expansions in the pastes were $\sim$0·1% at 600 days and were associated with high values of C_3A and SO_3. The concrete expansions were generally small, except for a single sample in which the alkali content had been increased to 1·5% Na_2O eq., which gave an expansion of $\sim$0·33%.

Day[6] reviewed the literature and based on Heinz *et al.*'s expression concluded that there was a risk of damaging expansions when using some North American cements, particularly high early strength cements (Type III or Type 30). Subsequently[7] he has suggested limiting cement SO_3 and C_3A contents and specific surface areas (SSA) in order to reduce the risks for heat treated concretes. The reference to SSA is apparently based on the correlation between high SSA and high SO_3 in high early strength cements. Lawrence[8] reported expansion data for a large number of cements and carried out linear regression analyses. Correlations were noted with cement SO_3, MgO, CaO and combined (i.e. not rapidly soluble in water) Na_2O contents. Taylor[9] analysed Lawrence's data and proposed critical values for SO_3, MgO and either Na_2O or Na_2O eq. Almost all cements for which two or more of the limits were exceeded expanded under the test conditions used, while cements which did not exceed any of the limits did not expand. Odler and Chen[10] studied pastes containing cements with C_3A contents of 7% or 10% and SO_3 contents of 3·4% or 5%. Only the high C_3A, high SO_3 combination gave significant expansion. They concluded that the SO_3/Al_2O_3 ratio was not important but the individual values of SO_3 and Al_2O_3 were. Lawrence[11] updated his analyses, including expansion data up to ages of 1200 days, and obtained similar results to those in Ref. 8. However, the difficulties in carrying out linear regressions on a relatively small data set were noted, with apparently significant correlations being found between, e.g. (CaO and MgO), (CaO and Na_2O eq.) and (C_3A and MgO).

Effects of fineness and sulfate content

The present results support many of the proposed correlations with cement composition and fineness. It has generally been noted that the risk of expansion is high with high early strength cements, which will generally be more finely ground. The data in Fig. 2 demonstrate that there is a dependence on fineness independent of chemistry. The effect of cement SO_3 content shown in Fig. 3 is similar to that obtained by Heinz and Ludwig[2] and compatible with the results from other investigations. Portland cement SO_3 contents are normally in the range 2–4% and data for these cements will give increasing expansion with increasing SO_3. The position of the maximum does not seem to be related to the C_3A content. Expansion is clearly influenced by cement alkali content, as indicated in Lawrence's work.[8,11] The present results also indicate a link between the SO_3 and alkali contents, with the pessimum value of SO_3 increasing with the alkali content. Wieker and Herr,[12] Damidot and Glasser[13] and Brown and Bothe[14] have shown that alkali content has a large effect on ettringite stability at high temperatures.

Glasser *et al.*[15] considered the stable phases at different temperatures and calculated changes in solid volumes. The volume change on cooling from 85°C to 25°C was found to increase sharply at a cement SO_3 content of 4% and decrease at high SO_3 ($\sim$9%) with an alkali content of 0·8% Na_2O eq. and an Al_2O_3 content of 4%. An expansion potential diagram is only given for these values but it would appear that the SO_3 content for maximum expansion potential increases slowly with increasing alkali content and is approximately proportional to the Al_2O_3 content. This would seem to support the use of SO_3/Al_2O_3 as a key parameter but the potential increase in solid volume is only one factor in determining actual expansion.

Expansion and early strength

The main factors which have been identified as increasing expansions — SSA, alkali, SO_3 (up to $\sim$4%) and C_3A — will be recognised as factors which increase early strengths. Figure 7 shows the expansion data plotted against 2 day mortar strength (EN 196-1, 20°C). While there is a clear correlation, there is no clear boundary between expansive and non-expansive cements. Increasing early strengths is, of course, the reason for using high temperature curing in precast production. It is not clear whether obtaining a target strength with a high early strength cement cured at a given temperature is safer or not than using a standard cement cured at a higher temperature. High early strength cements will also give higher temperature rises in large pours, increasing the risk of damage.

Prediction of expansions

Figures 2 and 6 suggest that expansion increases linearly with SSA and Na_2O eq. and the shape of Fig. 3 can he modelled with an expression using the 'absolute value' function for the difference between the cement SO_3 and a constant ($\sim$4). Using this as a basis an expression has been derived to predict the ultimate expansion following curing at 90°C for 12 h from the composition and fineness of the cement. In order to obtain a good fit with the present data and data for a range of other cements tested in the same manner, terms involving C_3A, C_3S and MgO, had to be included, giving the expression

$$\begin{aligned}\mathrm{Exp}(90°\mathrm{C}) = {} & 0{\cdot}00474{*}\mathrm{SSA}+0{\cdot}0768{*}\mathrm{MgO}\\ & +0{\cdot}217{*}\mathrm{C_3A}+0{\cdot}0942{*}\mathrm{C_3S}\\ & +1{\cdot}267{*}\mathrm{Na_2Oeq.}\\ & -0{\cdot}737{*}\mathrm{ABS}[\mathrm{SO_3}-3{\cdot}7\\ & -1{\cdot}02{*}\mathrm{Na_2Oeq.}]-10{\cdot}1 \qquad (1)\end{aligned}$$

Figure 8 compares predicted and measured expansions. Obviously, negative predicted

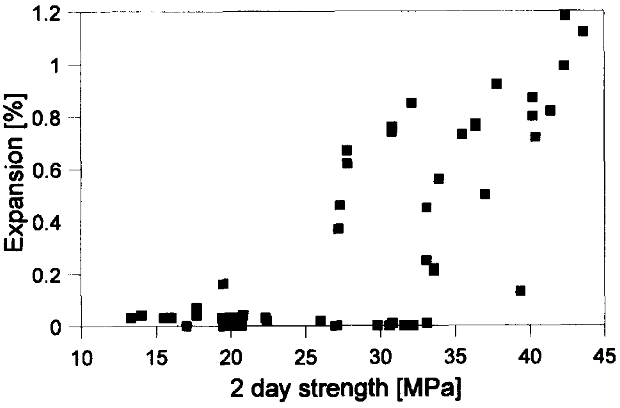

Fig. 7. Expansion after curing at 90°C plotted against EN 196-1 mortar strength at 2 days.

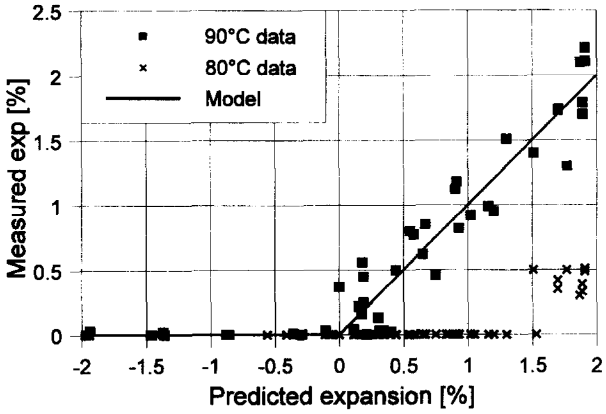

Fig. 8. Comparison of predicted and measured expansions.

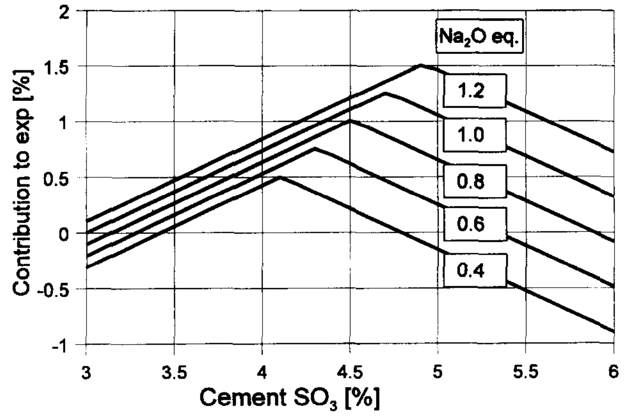

Fig. 9. Contributions of SO_3 and Na_2O eq. to predicted expansion.

expansions map to zero measured expansion. No expansions were observed in cements predicted to give no expansion and no cement with a predicted expansion > 0·4% did not expand by a significant amount. The factors in eqn (1) for SSA, SO_3 and Na_2O eq. are consistent with the data in Figs 2, 3 and 6.

Figure 9 is a plot of the contribution from the terms involving SO_3 and Na_2O eq. in the above expression. It shows an increase in the pessimum SO_3 with Na_2O eq. The low dependence on Na_2O eq. at low SO_3 and high dependence at high SO_3 is consistent with Fig. 6.

Influence of C_3A, C_3S and MgO

The inclusion of C_3A in the expansion model is obviously supported by the association between expansion and ettringite formation, since C_3A is the main source of alumina from which ettringite can be formed. C_3S has been shown by Brown and Bothe[14] to have an important influence on the stability of ettringite during hydration at high temperatures. The rapid formation of C–S–H reduces ettringite stability by acting as a 'sink' for aluminate (through substitution of silicate) and for sulfate (through adsorption).

Lawrence[11] obtained negative correlations with C_3S (Bogue) and C_3A (QXRD) but the large differences between the correlation coefficients for the Bogue and QXRD phase contents raises doubts over the significance. A much higher positive correlation was found with MgO, in agreement with the model presented here. MgO could influence the high temperature hydration through the formation of hydrotalcite phases or could be involved in initiating cracks through periclase hydration.

Effect of curing temperature

Included in Fig. 8 are data for expansions measured after curing at 80°C. Only mortars containing added KOH or K_2SO_4 gave expansion with this cure, between 1% and 1·5% less than the expansion after curing at 90°C. This suggests that the above expression may provide a general indication of the susceptibility of cements to expansion after high temperature curing. However, further work on production cements has been less encouraging. In particular, two cements gave significant expansions after curing at 80°C when both the measured and predicted expansions at 90°C were less than 1%. It would therefore appear that the factors in the prediction equation are dependant on the details of the conditions. It may be noteworthy that the two cements which gave unexpectedly large expansions after curing at 80°C were both high in alkali (~1% Na_2O eq.) and MgO (~2·5%). Both the peak temperature and the timescale of the high temperature period need to be considered. Most of the curing regimes used in laboratory studies have been based on cycles used in curing precast elements, typically involving periods of 12 h or less at the peak temperature. High temperatures in large pours of high cement content concrete will only be reached after ~2 days and the temperature may remain high for many days. Further work is required to determine the effect of such temperature cycles.

CONCLUSIONS

The dominant factor in determining expansions is the curing temperature. Curing at 70°C would seem to be safe for current UK cements but the effect of curing time needs more study. For the curing regimes used in this study, expansions increase with

Cement fineness (SSA)
Alkali (Na_2O eq.) content
C_3A (Bogue) content
C_3S (Bogue) content
MgO content.

There is a pessimum cement SO_3 of ~4%, increasing with cement alkali content. Many of the factors are also linked with high early strength.

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