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MORTAR EXPANSIONS DUE TO DELAYED ETTRINGITE FORMATION. EFFECTS OF CURING PERIOD AND TEMPERATURE.

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ABSTRACT

The expansion behavior of 55 portland cements, utilizing mortar prisms (40x40x160 mm), is reported for a range of initial elevated temperature cures followed by storage under water at 20°C. The relationship between expansion and curing condition is complex: increasing expansiveness accompanies higher curing temperatures and a minimum curing temperature for expansion is found to lie between 65°C and 70°C; greatly extended periods of elevated temperature curing result in much reduced expansions, suggesting that a progressive neutralization of the chemical components critical for expansion may be taking place during periods at elevated temperatures. The chemical composition of a cement is an important factor determining expansion behavior. Linear correlation coefficients between expansions after curing at 100°C for 3 hours and chemical compositions show a number of chemical parameters to be significant, including %MgO and %SO_3.

Introduction

A durability problem is documented in the literature for certain mortars and concretes that have experienced elevated temperatures during initial cure (1-16). The expansions responsible are reported to take many months to develop and are associated with the delayed formation of substantial deposits of well-crystallized ettringite (DEF) as bands around certain of the sand and aggregate particles in the hardened mix. The mechanism by which expansion occurs is not well-understood at the present time, and the significance of these bands is disputed (11-14). Microscopic studies of some damaged heat-cured concrete products have reported that certain cracks contained needle-shaped crystals (ettringite) that had grown perpendicular to the crack walls; other cracks were empty or contained crystals of $Ca(OH)_2$. This evidence was regarded as proof that cracking had occurred before deposition of the ettringite, from some cause possibly unconnected with ettringite formation, although an increase in the crack width due to ettringite crystal growth pressure was not ruled out (7).

Microstructural investigations of cementitious pastes and mortars have shown the normal finely divided ettringite within the paste microstructure to be largely destroyed during heat cure, only re-forming on cooling after a few weeks delay (2,3,12). Quantitative analyses for ettringite, using QXRD, indicated that the percentage of ettringite was gradually reduced with increasing curing temperature and increasing curing time, but an extended pre-cure period at room temperature allowed some of the ettringite that had developed to be retained throughout the heat curing period (7).

TABLE 1
Analyses of Cements Examined/by mass of cement as received

Cement	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	Na_2O %	K_2O %	Na_2O Equivalent %	Specific surface m^2kg^{-1}.
3970	21.0	4.96	2.76	64.6	1.10	3.80	0.21	0.75	0.705	430
3971	20.6	4.80	3.15	64.8	1.01	3.46	0.21	0.50	0.540	468
3973	22.2	3.94	2.44	65.4	0.89	2.72	0.14	0.71	0.609	339
3974	20.8	4.12	3.76	64.1	2.28	2.84	0.25	0.64	0.672	400
3975	20.5	4.9	3.15	63.3	2.48	3.17	0.32	0.84	0.874	374
4023	20.2	4.95	3.05	63.1	2.17	3.77	0.32	0.85	0.881	540
4024	20.5	4.91	2.94	63.7	2.83	3.09	0.30	0.82	0.841	490
4025	21.7	5.16	1.76	64.5	1.07	3.56	0.15	0.81	0.68	505
4026	20.4	5.0	1.61	65.0	1.02	3.17	0.13	0.75	0.625	355
3982	20.9	4.32	2.80	62.8	2.14	4.19	0.32	1.02	0.99	552
3984	21.3	4.36	2.82	63.3	2.15	3.30	0.31	0.99	0.96	537
4037	20.0	4.82	2.19	62.7	2.61	4.14	0.41	0.83	0.95	583
3986	21.4	4.09	2.91	63.0	2.64	3.02	0.41	0.78	0.92	521
3988	21.0	4.01	2.85	62.4	2.60	3.93	0.42	0.77	0.93	543
3990	20.8	3.97	2.82	62.1	2.58	4.55	0.40	0.77	0.91	547
3992	20.3	5.08	2.28	63.3	2.70	3.23	0.44	0.86	1.00	529
3994	20.0	4.99	2.24	62.8	2.66	4.12	0.37	0.85	0.93	547
3996	19.8	4.93	2.22	62.5	2.63	4.80	0.38	0.85	0.94	552
4031	19.9	5.91	2.15	65.0	1.22	3.41	0.28	0.95	0.91	410
4036	20.9	5.08	2.04	64.4	1.76	2.98	0.20	1.12	0.94	384
4044	20.3	4.88	3.02	63.4	2.13	3.21	0.40	0.86	0.90	511
D58	21.6	4.89	2.69	64.2	1.18	2.88	0.06	0.75	0.56	405
3572	20.6	4.56	3.09	64.1	2.6	3.29	0.33	0.85	0.89	460
3579	21.9	3.55	1.44	65.5	1.07	2.97	0.12	0.47	0.43	545
3580	19.8	5.88	2.29	64.0	1.3	3.24	0.23	0.94	0.85	484
3577	21.3	4.94	1.99	65.6	0.94	3.01	0.17	0.78	0.68	418
3578	20.6	5.02	2.51	64.3	1.21	2.90	0.13	0.67	0.57	529
3596	20.4	4.73	3.27	64.4	1.2	2.97	0.14	0.91	0.74	528
3595	19.9	4.41	3.13	63.7	1.2	3.92	0.14	0.91	0.74	494
3594	20.2	4.69	3.01	63.9	1.2	3.31	0.13	0.83	0.68	478
3597	20.9	4.83	3.30	65.1	1.2	2.06	0.14	0.91	0.74	526
3730	20.2	5.01	3.30	63.7	2.68	2.86	0.04	0.60	0.44	399
3747	20.2	5.55	2.62	64.3	1.16	3.15	0.17	0.58	0.55	515
3748	19.5	5.48	2.27	65.0	1.0	3.52	0.30	0.41	0.57	558
3749	19.6	4.63	3.26	63.9	2.47	3.11	0.05	0.44	0.34	449
3750	20.3	5.64	2.23	65.0	0.98	3.07	0.22	0.63	0.64	767
3751	21.1	4.63	0.16	68.0	0.4	2.84	0.16	0.14	0.25	1050
3752	19.9	3.97	5.34	64.5	2.0	2.59	0.18	0.35	0.41	642
3740	20.0	5.84	2.21	65.0	1.25	3.31	0.22	0.92	0.83	434
3753	20.5	4.82	3.2	62.3	2.62	2.82	0.44	1.16	1.21	354
3576	21.1	4.90	1.97	64.7	0.93	3.55	0.14	0.75	0.64	422
3721	20.5	4.71	3.05	64.6	1.19	2.8	0.12	0.58	0.50	442
3722	21.7	3.6	1.45	66.1	1.02	3.27	0.11	0.31	0.31	510
3723	19.5	6.14	2.21	64.3	1.31	3.39	0.21	0.92	0.82	414
3724	19.6	5.8	2.23	65.3	0.99	3.21	0.09	0.80	0.62	481
3725	20.1	5.59	2.72	64.3	1.06	3.22	0.11	1.05	0.80	462
3999	20.7	4.45	2.04	64.4	1.85	3.47	0.27	0.80	0.80	580
4000	19.4	6.10	2.63	63.9	1.19	3.38	0.21	1.05	0.90	557
4144	20.0	5.47	2.44	62.3	2.66	3.83	0.28	0.81	0.81	536
4019	22.1	3.78	2.6	65.8	0.75	2.70	0.15	0.71	0.62	335
4077	20.6	5.18	3.29	63.9	2.46	2.80	0.30	0.56	0.670	450
4078	20.9	3.64	4.06	64.7	2.22	2.55	0.19	0.58	0.573	460
4167	21.1	4.35	2.83	63.0	2.15	3.25	0.25	1.00	0.91	571
4174	21.5	5.37	2.72	63.5	1.56	2.50	0.17	0.76	0.67	318
4811	21.8	4.1	2.3	65.3	1.4	2.84	-	-	0.34	542

One view of the expansion mechanism for mortars and concretes considers that a greatly delayed ettringite recrystallization is nucleated at interfaces between the cement paste fraction and the aggregate particles (or at other defects within the microstructure), and results in the development of crystal growth pressures and expansion (2,3,9). The main evidence for this mechanism is the obvious ettringite crystal growth taking place at these interfaces when expansion occurs.

TABLE 2
Effect of Curing Temperature on Subsequent Mortar Prism Expansion in Water

Cement	Elevated Temperature Curing Conditions									
	60°C 16 h	65°C 16 h	70°C 16 h	75°C 16 h	80°C 5 h	85°C 16 h	100°C 3 h	100°C 16-24 h	98°C 2-3 d	98°C 7-10 d
3970		O					X			
3971		O					X			
3973		O					X			
3974		O		O			X			
3975		O		X			X			
4023		O					X			
4024		O					X			
4025		O					(X)			
4026		O					O			
3982	O	O	O	X	X		X	X	X	O
3984							X			
4037					O		X			
3986							X			
3988							X			
3990							X			
3992	O	O	X	X			X			
3994							X			
3996							X			
4031	O	O	O	X			X			
4036							X			
4044							X			
D58							O	X		(X)
3572		O				X	X	X		
3579							O	X		
3580							X			
3577							O	O	X	O
3578							O	X		
3596							O	X		
3595		O				X	X			
3594		O				X	X	X		
3597							O	O		
3730							O	X		
3747							O			
3748		O				X	X			
3749		O				X	X			
3750		O				X	X			
3751							O	O		
3752							X			
3740							X	X		
3753	O	O	O	X		X	X	X		
3576							O	X		
3721							O			
3722							O			
3723							O			
3724							O			
3725							O			
3999							X			
4000							X			
4144							X			
4019		O					O			
4077		O					X			
4078		O					X			
4167							X			
4174							O			
4811							X			

O: No significant expansion. X: Expansion. (X): Possible expansion beginning.

An apparent lack of expansion shown by un-damaged heat treated neat cement paste prisms, and the large influence of the nature of the aggregate/cement paste interfaces, were initially considered to offer clear support for an ettringite recrystallization mechanism of expansion (15). Recent evidence from long-term expansion measurements (storage for over 2 years) has relegated the influence of aggregate type to that of modifying the rate of expansion rather than determining the occurrence of expansion (17), and has shown that certain undamaged cement pastes do expand after heat cure, albeit very much less readily than the corresponding mortars (Figure 1, cement paste expansions, water:cement ratio = 0.45). Cement paste expansions have been reported by other investigators, but somewhat smaller than those of the corresponding mortars and concretes (5,21); certain investigations have found that only pre-cracked pastes expanded, undamaged pastes remaining stable (7,10). Emphasis has been placed on the role of cracks in a cement paste (water:cement ratio = 0.5) as precursors for the occurrence of expansion by ettringite crystal growth pressures (10): steam cure, 95°C/6 hours, followed by various treatments including drying at 85°C or controlled crack initiation, utilizing a saw cut filled with expansive cement, showed pre-cracking to be the determining factor for subsequent expansion.

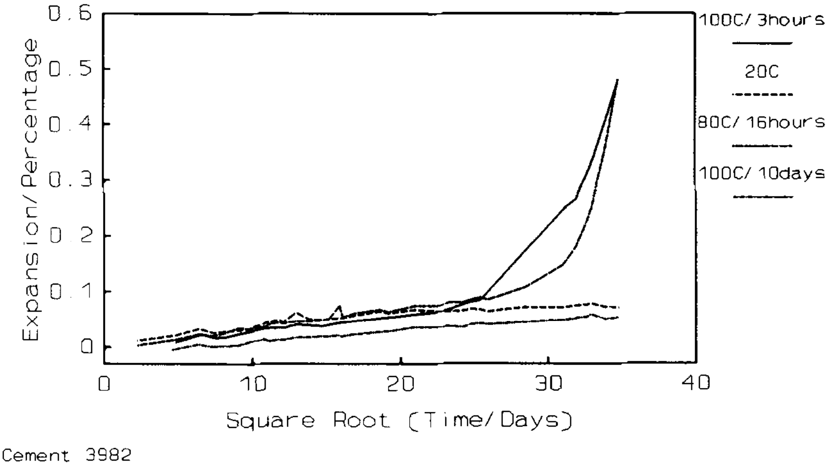


FIG 1
Cement paste prism expansions after curing at different temperatures

Objections have been raised to the ettringite crystal growth mechanism for expansion (11-14): firstly, on the grounds that high and sustained degrees of supersaturation (that are considered unlikely to occur) are assumed to be necessary to produce the large and sustained expansions observed; secondly, on the grounds that ettringite crystal growth is a normal feature of a wide range of concrete microstructures, and is not usually accompanied by expansion. As an alternative, it has been suggested that expansion of the cement paste fraction is the prime cause of overall expansion (ettringite deposits at the cement paste/aggregate interface being the consequence of the expansion rather than the cause), although the paste expansion mechanism involved has not been described. The main evidence for this mechanism is the apparent direct relationship between the width of the ettringite filled gap (or band) at the aggregate/paste interface and the size of the aggregate particle, suggesting that the cement paste fraction has expanded away from the aggregate particles for field concretes (13,14).

One difficulty with this approach is that it does not readily explain the influence of aggregate type on rate of overall expansion (9,15), nor the fact that a mixed aggregate type within a mortar results in certain aggregate particles being surrounded by ettringite bands while other aggregate particle types are free from these ettringite deposits (17).

Alkali silica gel has often been observed in close proximity to well-crystallized ettringite (19-25), and Hobbs (26) has observed that cases of cracking and expansion of concrete resulting from DEF have wrongly been attributed to expansion due to ASR. Several authors have concluded that the primary cause of distress was expansion induced by alkali-silica gel formation. The amount of gel required to cause disruption has been reported to be very small where certain polymineralic aggregates, which include reactive siliceous particles, are present. The view appears to be that a lack of obvious gel formation does not rule out an expansive mechanism based on ASR. Taylor (27) has presented a detailed review of this durability problem and has proposed a mechanism which involves both ASR and DEF: DEF expansion is considered to generate a relatively weak disruptive force which requires flaws to be present, or another expansive mechanism to be active, before expansion due to ettringite growth can begin; ASR frequently plays the role of this preliminary expansive process in practice.

Diamond (20-22) has conducted experiments where DEF and ASR can take place simultaneously: the expansion of mortar prisms made from a Type I portland cement (equivalent % Na_2O = 1.14, % SO_3 = 2.8) were reported over a period of 9 months after a 95°C/10 hours cure following a 6 hour pre-cure period at room temperature. Subsequent storage was at 20°C under 100% relative humidity in order to minimize leaching of alkalis from the specimens. The sand was a dolomite-free calcitic limestone, with particle size as specified in ASTM C227.

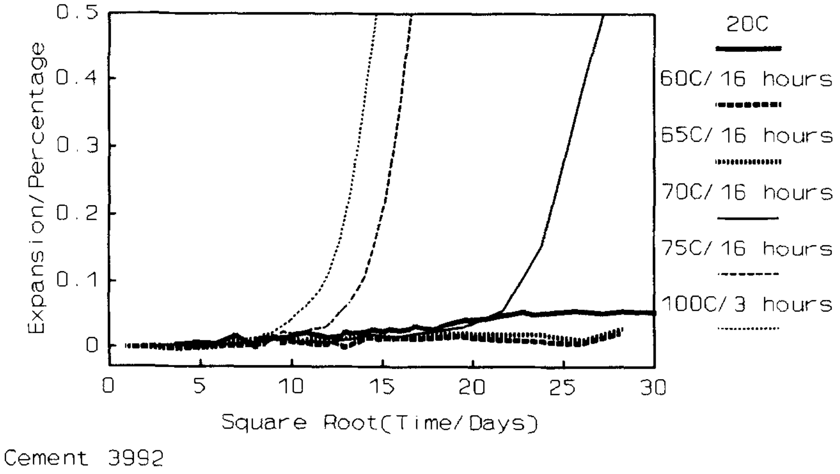


FIG 2
Mortar prism expansions after heat curing at different temperatures

Some of the mortars had 4.5% of the limestone replaced by Beltane opal while some had 30% replaced by Blue Circle calcined flint (cristobalite). The pure limestone mortars did not expand; in contrast, the mortars containing reactive aggregates showed rapid and continuing expansion, amounting to between 0.5% and 0.9% after a period of 9 months, compared to expansions between 0.2% and 0.4% for room temperature cured specimens. It is commented that the heat cure greatly accelerated the ASR expansion, but that DEF may have exacerbated the expansion.

It is clear that at least two opposing views on the mechanism of DEF expansion can be supported from published expansion evidence, but there is little doubt that DEF expansion does exist and is distinct from ASR expansion. The clearest evidence for this statement is the expansion reported for cement paste specimens after heat curing, where there is obviously no possibility of ASR induced expansion. The present report has been written with the primary objective of publishing a summary of experimental expansion data for a wide range of portland cement mortars after curing at elevated temperatures between 60°C and 100°C, together with linear correlations of expansions against cement composition. Relatively long term expansion data are becoming available and the dangers of drawing premature conclusions from data after shorter storage periods of 1 or 2 years have now become apparent. The work is a continuation of a programme that has already been reported in the literature (1,15), but the opportunity is taken of amplifying and correcting the conclusions previously drawn.

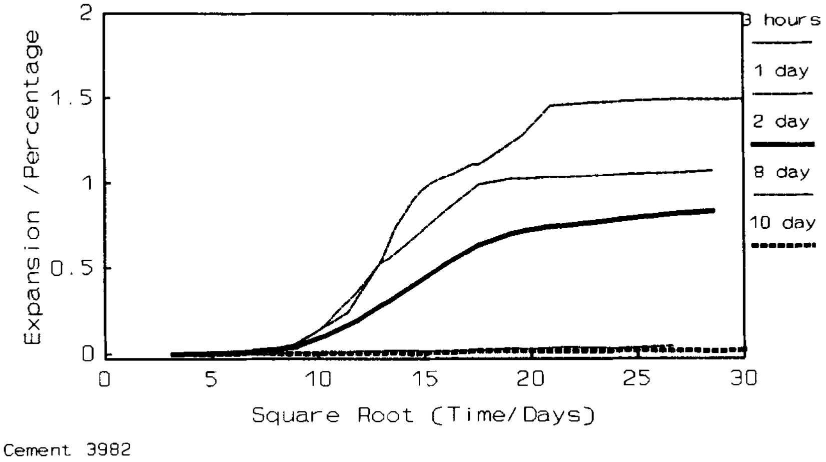


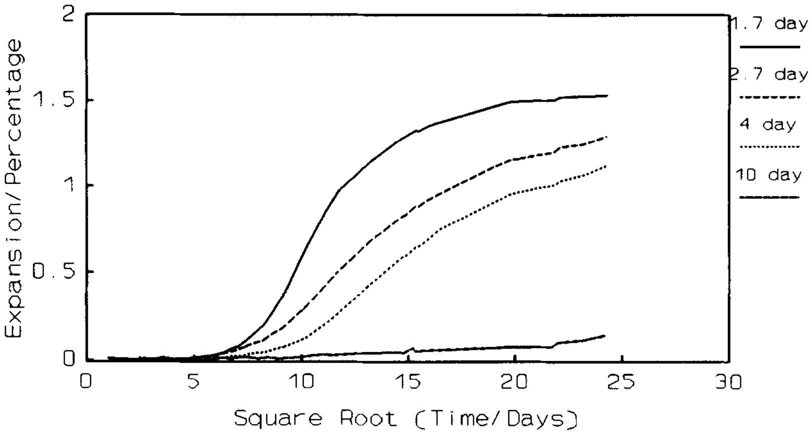
FIG 3
Mortar prism expansions after extended heat cure periods at 95° to 100°C

Experimental

Mortar prisms (40x40x160 mm) containing stainless steel end inserts, were cast using European standard procedures (water:cement ratio = 0.5, sand:cement = 3.0). A hardening period at room temperature of 2 hours was generally allowed before a heat cure at elevated temperature was applied to the specimens submerged under water (still in their steel molds). A slow cool back to room temperature took place, also while the specimens were submerged (1), the whole temperature cycle usually occupying approximately 24 hours. Only limited protection against leaching was provided by the presence of the steel mold. Subsequently, the mortar specimens were stored under water at 20°C and again leaching of soluble components from the mortars may have occurred. Siliceous sands, composed largely of quartz, were employed, about half the specimens being made with German standard sand and half with UK standard sand.

Results

Chemical analyses for the major components of the portland cements examined are shown in Table 1. Expansion data (average of 3 prisms) showed that somewhat larger expansions occurred when UK rather than German standard siliceous sand was used. The influence of curing temperature and the period of cure is presented in Table 2. At temperatures of 60°C or 65°C, none of the mortars exhibited significant expansion (i.e. expansions greater than 0.2%); at 70°C only one cement mortar has shown expansion; at 75°C, 5 out of the 6 cements have shown



Cement 3577

FIG 4
Mortar prism expansions after extended heat cure periods at 95° to 100°C

TABLE 3
Correlation Coefficients between Mortar Prism Expansions (after heat cure at 100°C for 3 hours) and Composition Parameters of the Cements

Storage/days	100	200	400	800	1200
%SiO_2	**-0.3461**	-0.3056	-0.2747	-0.3198	-0.3102
%Al_2O_3	0.2717	0.0302	-0.0755	-0.0741	-0.0838
%Fe_2O_3	-0.0771	-0.0340	0.0550	0.1114	0.1143
%CaO	-0.2635	**-0.5152**	**-0.6169**	**-0.6942**	**-0.6946**
%MgO	0.1317	**0.4653**	**0.6023**	**0.6669**	**0.6790**
%SO_3	**0.5465**	**0.6958**	**0.6243**	**0.5954**	**0.5926**
%Na_2O	**0.6185**	**0.4363**	**0.3483**	0.2927	0.2768
%K_2O	0.2693	**0.3356**	0.3095	0.2930	0.2797
%Na_2O equivalent	**0.6207**	**0.4803**	**0.3750**	**0.3530**	**0.3348**
Specific surface	0.0759	0.1981	0.2692	0.2634	0.2565
%Na_2O combined	0.1869	**0.4955**	**0.6276**	**0.6639**	**0.6866**
%K_2O combined	0.0811	0.1203	0.0324	-0.0030	-0.0130
%Na_2O soluble	**0.5798**	0.3083	0.1819	0.1151	0.0926
%K_2O soluble	0.2730	0.3254	**0.3605**	**0.3671**	**0.3582**
Equ. %Na_2O combined	0.1748	**0.4045**	**0.4377**	**0.4398**	**0.4487**
Equ. %Na_2O soluble	**0.6208**	**0.3862**	0.2803	0.2206	0.1971
%SO_3 soluble	**0.5703**	0.3144	0.1872	0.1245	0.1026
%Free CaO	-0.1563	-0.2722	-0.3269	**-0.3624**	**-0.3890**
%BaO	-0.1399	-0.3180	**-0.3530**	**-0.3769**	**-0.3907**
%SrO	0.0838	**0.4857**	**0.6406**	**0.6849**	**0.7016**
%TiO_2	0.0490	0.0050	-0.0496	-0.0608	-0.0680
%Mn_2O_3	-0.0617	-0.2560	**-0.3432**	**-0.3527**	**-0.3612**
%P_2O_5	0.2137	0.2739	0.2747	0.2888	0.2975
%Cr_2O_3	0.2888	0.3304	0.3284	0.3116	0.3140
Bogue %C_3S	-0.2882	**-0.4128**	**-0.4382**	**-0.4617**	**-0.4630**
Bogue %C_2S	0.1070	0.2340	0.2695	0.2751	0.2803
Bogue %C_3A	0.2411	0.0400	-0.0841	-0.1121	-0.1208
Bogue %C_4AF	-0.0771	-0.0340	0.0550	0.1114	0.1143
QXRD %Alite	0.1418	0.0143	-0.0404	-0.0630	-0.0723
QXRD %Belite	-0.1056	-0.1250	-0.1010	-0.0872	-0.0824
QXRD %C_3A	0.0099	-0.2535	**-0.3737**	**-0.4010**	**-0.4067**
QXRD %C_3A (ortho)	-0.2097	-0.1960	-0.1966	-0.1741	-0.1708
QXRD %Ferrite	-0.0958	-0.0138	0.0898	0.1435	0.1486

Underlined values are considered to show **significant correlations**

expansion; curing at 100°C for 3 hours resulted in 37 out of 55 cements showing expansion. The number of cements showing expansions after heat curing at 100°C for 16 to 24 hours rose to 11 out of the 14 cements tested; it was clear that cements were more likely to be expansive when curing at 100°C for 16 to 24 hours than for only 3 hours. Details of the effect of curing temperatures between 60°C and 100°C on the expansions of mortar prisms are illustrated in Figure 2 for one cement. It is apparent that the critical temperature for expansion for this group of 55 cements is between 65°C and 70°C.

Increasing the period of the cure at about 100°C to 7 or 10 days has been investigated for three cements, D58, 3982 and 3577 and has resulted in reduced expansion (Figures 3 to 5) in each case. For cement 3982, the pre-cure period at 20°C was increased to 5 hours before curing at 100°C for 3 hours. Four cement mortars made with cements D58 and 3577 were initially cured for 3 hours at 100°C and monitored for over 1500 days under water at 20°C without showing significant expansion; these specimens were then re-heated at 100°C for increasing periods up to 7 or 10 days and then re-immersed in water at 20°C for continued monitoring (Figures 4 and 5). Although specimens heat cured for 7-10 days have shown little or no expansion at the present time, past experience dictates that expansions may yet begin.

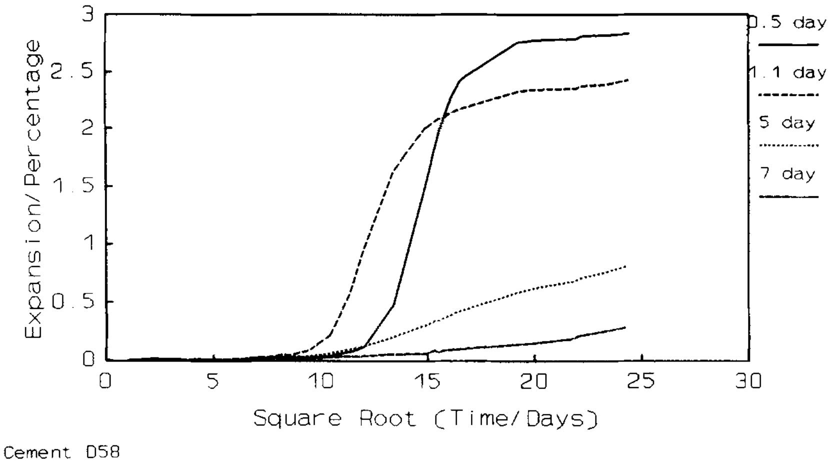


FIG 5
Mortar prism expansions after extended heat cure periods at 95° to 100°C

Discussion

It has been established that the lower temperature limit below which expansion does not occur is in the range of 65°C to 70°C. If a direct relationship between ettringite formation and the development of expansion is accepted, the behavior of mortars under increasing temperature and periods of cure requires evidence for a gradual enhancement of the possibilities of ettringite formation as the curing temperature is increased. In contrast, as the period of elevated temperature curing is increased at a given temperature, expansion behaviour requires that a gradual enhancement of the possibilities of ettringite formation should be followed by an attenuation of these possibilities as period of cure becomes very extended. One interpretation is that combination of silicate and aluminate hydrates is slowly occurring at elevated temperatures, so free aluminate is gradually absorbed and causes the free aluminate:sulfate ratio to fall and pass through the optimum ratio (formula ratio) for ettringite formation at some intermediate heating condition.

It is relevant to point out that extended curing of cement pastes (water:cement ratio of 0.4) at 80°C and at 110°C (for 3 to 28 days) has been reported to result in an absence of ettringite after 3 months subsequent water storage at 25°C, while elevated temperature curing for only 1 day resulted in ettringite formation at this time (18). This observation appears to mirror the expansions reported here for extended elevated temperature cures, assuming the appearance of ettringite can be taken to indicate the possibility of subsequent expansion, while non-appearance indicates no significant expansion is possible.

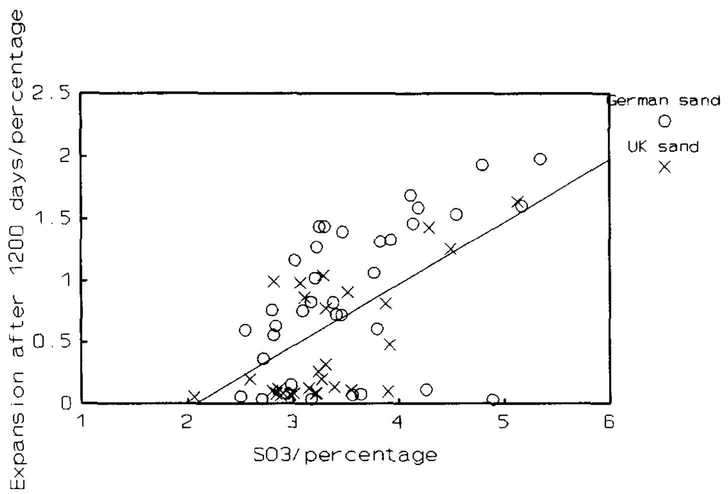


FIG 6
Correlation of expansions after heat curing with percentage SO_3 contents of cements

Linear correlation coefficients between cement composition and mortar prism expansion after different periods of water storage up to 1200 days are presented in Table 3 (highly significant correlations are underlined). The data were treated either as a single combined population or as separate populations of German and UK sand mortars: the results from the three analyses of the data were somewhat different in details but similar in essentials. All methods of treating the data resulted in highly significant correlations between expansion and a wide range of different chemical parameters including %SO_3, %MgO, %combined Na_2O, %SrO and %CaO contents of the cements. Combined alkalis are defined as those remaining in the cement after shaking with water, at room temperature, at

TABLE 4
Correlation Coefficients between Chemical Parameters for the Group of Portland Cements Examined

	CaO	MgO	SO_3	BaO	SrO	Eq.Na_2O	Na_2O comb.	QXRD C_3A
CaO	1	-.81	-.35	+.43	-.63	-.72	-.59	+.41
MgO	-.81	1	+.18	-.48	+.64	+.10	+.61	-.65
SO_3	-.35	+.18	1	-.13	+.39	+.37	+.46	+.11
BaO	+.43	-.48	-.13	1	-.39	-.13	+.44	+.30
SrO	-.63	+.64	+.39	-.39	1	-.03	+.65	-.40
Eq. Na_2O	-.72	+.10	+.37	-.13	-.03	1	+.70	-.10
Na_2O comb.	-.59	+.61	+.46	+.44	+.65	+.70	1	-.20
QXRD C_3A	+.41	-.65	+.11	+.30	-.40	-.10	-.20	1

water:cement ratio = 1.0 for 1 hour. Negative correlations were observed between mortar prism expansion and %CaO, %free lime, %BaO, calculated %C_3S and QXRD %C_3A contents. Linear correlations between three chemical factors and expansion after 1200 days water storage are illustrated in Figures 6 to 8.

The significance of the high correlations between expansion and %CaO and %MgO can only be speculated upon at the present time. By chance, there are close correlations between %MgO, %CaO, %Equivalent Na_2O, %combined Na_2O and %SrO for the group of cements chosen for this study (Table 4), so some of the relationships between expansions and chemical compositions (Table 3) are probably fortuitous.

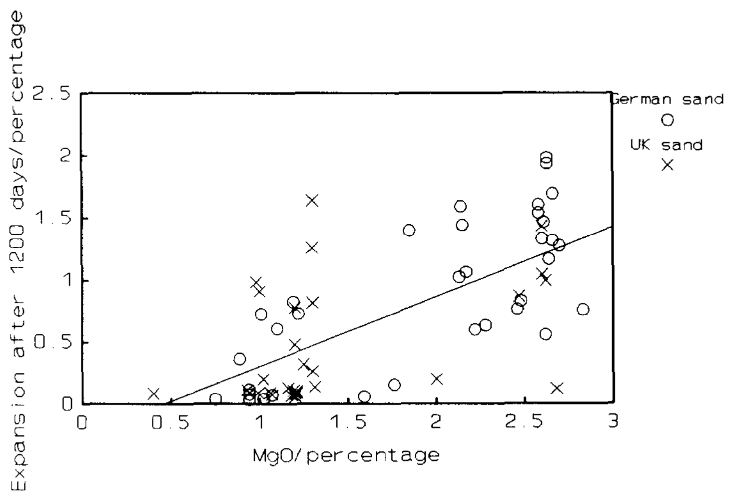


FIG 7
Correlation of expansions after heat curing with percentage MgO contents of cements

Possibly only one of these factors is important in controlling DEF expansions: multiple correlation analyses, which include %SO_3 level on the grounds that the

TABLE 5
Multiple Correlation Coefficients between Chemical Parameters and Mortar Prism Expansions after 800 days Water Storage

Chemical parameters	Multiple Correlation Coefficient	Significance Level			
		%SO_3	%MgO	Sp. Surf.	%CaO
SO_3, MgO	0.8268	0.00%	0.00%		
SO_3, MgO, Sp. Surf.	0.8552	0.00%	0.00%	0.26%	
SO_3, MgO, Sp. Surf., CaO	0.8672	0.00%	0.20%	0.07%	3.70%
		%SO_3	%CaO	Sp. Surf.	MgO
SO_3, CaO	0.7930	0.01%	0.00%		
SO_3, CaO, Sp. Surf. (400 day exp)	0.8288	0.00%	0.00%	0.02%	
SO_3, CaO, Sp. Surf., MgO	0.8672	0.00%	3.70%	0.07%	0.20%
		SO_3	Na_2O comb.	MgO	Sp. Surf.
SO_3, Na_2O comb.	0.7793	0.01%	0.00%		
SO_3, Na_2O comb., MgO	0.8521	0.00%	0.47%	0.00%	
SO_3, Na_2O comb., MgO, Sp.Surf	0.8672	0.00%	3.69%	0.00%	1.98%

quantity of ettringite (which contains sulfate) is a likely factor determining expansion (Table 5), seem to indicate that MgO content is a more significant factor than %CaO, in spite of the linear correlation between CaO and expansion being apparently more important (Table 3). The $\%SO_3$ does not correlate closely with other chemical parameters.

An obvious possibility is that hydration of MgO is occurring during the elevated temperature hydration or during room temperature water storage, and resulting in limited expansion, which possibly acts as an initiator for subsequent ettringite recrystallization pressure generation and expansion. The presence of aggregate particles possibly independently generates other defects and the ease of crystal growth of ettringite is related to a summation of these effects, leading to expansion as already suggested in certain references (10,27).

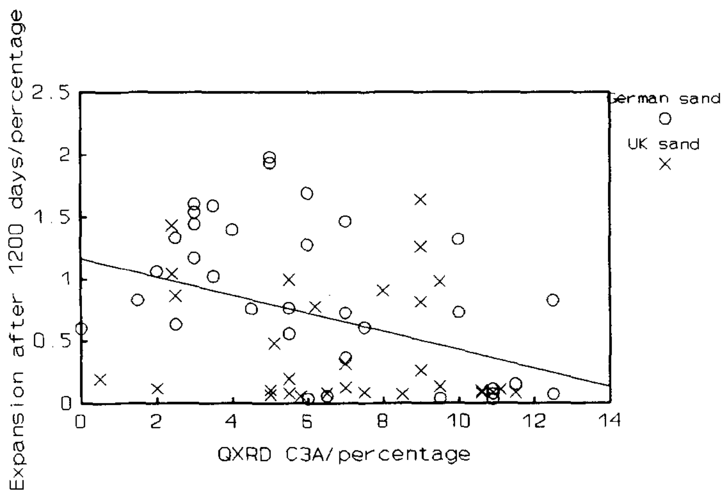


FIG 8
Correlation of expansions after heat curing with percentage QXRD C_3A contents of cements

Accepting that prior defects or additional expansive processes have a large influence on subsequent expansion due to ettringite crystal growth, it follows that field concretes, having undergone unknown and possibly multiple degradation processes, are likely to be unsuitable for studies on the basic mechanisms of expansion involving ettringite crystal growth.

Conclusions

Expansion measurements on mortar prisms after elevated temperature curing show a complex pattern which is influenced by the composition of the cement and the detailed curing conditions imposed. The correlation between expansion and sulfate content of the cement points to the importance of ettringite in the expansion mechanism. The correlation of expansion and MgO content of the cement suggests that expansive hydration of MgO may increase the sensitivity of cements to heat cure. Extended periods of elevated temperature curing lead to much reduced expansions, mirroring reported chemical changes involving the possibility of ettringite formation after heat cure. In view of the expansions shown by cement pastes, the involvement of alkali-silica reaction in these expansions is not an essential feature, and the existence of a distinct expansion mechanism is indicated for certain portland cement products subject to heat cure.

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