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EFFECTS OF CEMENT COMPOSITION AND TEMPERATURE OF CURING ON AAR AND DEF EXPANSION IN STEAM-CURED CONCRETE

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ABSTRACT

Steam-curing of concrete at high temperatures has been reported to have induced deterioration of field concrete structures due to delayed ettringite formation (DEF). However, other researches have found that the deterioration could, at least partly, be attributed to other expansive mechanisms, such as AAR. This issue has remained highly controversial and investigators often differ on the main mechanism of deterioration. Large scale and expensive litigation following the emergence of cases of deterioration, have not helped the controversy, and the opposing parties have been taking sides to blame their legal opponents, rather than genuinely attempting to find a scientific answer to the problem. This paper reports on a study which attempts to address this issue by investigating the effects of many parameters such as sulfate, aluminate, alkali content and curing temperature on the expansion of concrete. This study has shown that most cases of deleterious expansion have been associated with AAR expansion arising from the presence of high alkali content and reactive aggregate in the concrete, regardless of the curing temperature. However, on rare occasions when all the parameters, high aluminate, high sulfate, high alkali and high temperature of curing are concurrently present then DEF expansion may occur in the absence of reactive aggregate. Incorporation of appropriate amounts of supplementary cementitious materials in concrete removes the risk of both AAR and DEF.

Keywords: Aggregate, Cement, Concrete, AAR, DEF, Ettringite, Expansion, Steam-Curing

1 INTRODUCTION

The deterioration of some heat-cured, precast concrete products such as deck slabs, beams and concrete railway sleepers, has variously been attributed to delayed ettringite formation (DEF) resulting from excessive temperatures, alkali-aggregate reaction (AAR), or often a combination of these two factors. The DEF refers to the effects of heat curing at high temperature, under which condition, the primary ettringite (that normally forms in concrete at very early stages to control its setting) is destabilised, but forms later after the concrete has hardened, allegedly causing expansion. Despite considerable research efforts in the past two decades, a good deal of confusion still exists on the main causes of deterioration of precast products. This paper does not intend to review the vast literature on these issues, but to present some examples to highlight the conflicting views expressed on these issues. This confusion has not been helped by commercial interest and large litigation cases in which the parties involved inevitably try to blame the other party for the problem. The cement supplier is blamed for high alkali and sulfate contents, the aggregate supplier for the reactivity of the aggregate, and the manufacturer for excessive heat-curing of the product and/or for combining materials which are incompatible with respect to concrete durability. Consequently, each party presents a different mechanism for the deterioration, suiting the commercial interest of their own side. Although not explicitly, the bias has been reflected in some published papers. Of course, genuine efforts have also been made to resolve the issues, but perhaps due to the limited number of factors investigated, the conclusions have not been comprehensive. This paper provides some background information on the deterioration of some heat-cured elements, and present data on a range of parameters influencing the deterioration.

2 BACKGROUND

After the initial report of Heinz and Ludwig (1986) and Heinz, Ludwig and Rüdiger (1989) which attributed the deterioration of heat-cured concrete to subsequent or delayed ettringite formation, a number of publications reported DEF as the cause of deterioration of heat-cured concrete elements or excessive expansion of heat-cured laboratory specimens. In the case of field structures, this conclusion appears to have been reached largely based on the observation of ettringite in cracks and pores in the cement paste and around some aggregate particles, often without consideration of other possible expansive processes. For example, Tepponen and Eriksson (1987) attributed the deterioration of Finnish concrete sleepers to DEF. Shayan and Quick (1992), who reported AAR as the cause of cracking of Australian concrete sleepers, doubted the conclusion regarding the Finnish sleepers, and subsequently examined a sample of the deteriorated Finnish concrete sleeper (Shayan and Quick, 1994), and clearly demonstrated that AAR was present in the concrete, in which the cement alkali level was 1.15% Na_2O equivalent.

Later production of Finnish sleepers used a cement alkali level of 0.76% Na_2O equiv. and no steam curing, and these had not cracked at the age of 5 years. If they still have not cracked, then this could not merely be attributed to the fact that they were not steam-cured, but more likely to the lower level of alkali content and suppression of AAR.

Oberholster et al. (1992) also found AAR to be the main cause of cracking of South African concrete sleepers, and that only those sleepers containing reactive quartzite or granite had cracked, whereas those containing a non-reactive dolerite had not. Visual manifestations of DEF were also present only in those sleepers which had exhibited AAR, and not in those containing the non-reactive dolerite.

Shayan and Quick (1992) had stated that AAR was the main cause of cracking of the Australian concrete sleepers, and that DEF precipitation in the cracks had occurred as a consequence of AAR microcracking and space being made available for ettringite precipitation. Shayan (1993) demonstrated that the granitic aggregate used in the Australian concrete sleepers caused significant expansion and cracking in concrete blocks of the same cross section as the concrete sleepers (300 mm cubes) without the steam-curing process. This further validated the AAR mechanism as the cause of cracking. Shayan and Ivanusec (1996) showed that in laboratory specimens which had the potential for either AAR or DEF, only those with AAR potential developed deleterious expansion, and no evidence of DEF expansion was noted. However, when specimens had the potential for both AAR and DEF they developed additional expansions, compared to those with AAR alone under steam-curing conditions (75°C) which was attributed to contribution from DEF.

Diamond (1994) suggested that growth of ettringite in pre-existing microcracks could cause expansion, whereas Johansen et al. (1994), Scrivener and Taylor (1993), and Glasser et al. (1995) suggested that it did not. However, Deng and Tang (1994), and Xie and Beaudoin (1992) state that if micro-cracks are filled with a solution which is supersaturated with respect to ettringite, then crystallisation of ettringite could cause expansive forces through hydrostatic pressure in the confined areas. This supports the experimental observations made by Diamond (1994), and Shayan and Ivanusec (1996) of additional expansion in AAR-affected specimens, which they suggest was due to ettringite formation in microcracks. This would not exclude any contribution that could have been made to the expansion by the reaction of sulfate ions with aluminate phases in the cement to form additional ettringite. The AAR-induced microcracks in these specimens would be expected to be saturated with water under the storage conditions of 100% RH used for AAR expansion measurements. Nevertheless, the mere observation of recrystallised ettringite in voids and microcracks in concrete does not necessary indicate that an expansive process has taken place.

Of course, some cements high in SO_3 and aluminates are prone to expansion caused by ettringite formation, resulting from the reaction of sulfate with the aluminate phases in the cement. Kelham (1997) found that high temperature of heat curing (90°C) had a major effect on expansion of mortar prisms and that 4% SO_3 gave the maximum expansion, whereas at 20°C increasing SO_3 contents produced progressively increasing expansion. Also increasing the fineness of cement reduced the expansion at 20°C, but increased it at 90°C curing temperature. Results of Lawrence (1999) also pointed to the importance of high temperature on expansion, and showed that concrete expanded less than mortar and the onset of expansion was also later. He found that expansion was larger in mortars with water/cement ratio of 0.45 than 0.375, and that the nature of the aggregate had a large effect on the expansion; inert quartz giving much larger expansion than flint and limestone.

Lawrence (1999) also showed that higher alkali content of cement gave larger mortar bar expansion, but could not explain this observation. This is very likely due to the increased concentration of sulfate ions in the pore solution of concrete in the presence of elevated alkali hydroxide (Diamond 1994; Shayan, 1995), which enhances the possibility of DEF taking place. This is in addition to the effect of high temperature, which increases the sulfate concentration in the pore solution of concrete. Kelhem (1999) found that high alkali lowers the temperature at which DEF expansion occurs, i.e., low alkali cements caused expansion only at (or above)

90°C, and not at 80°C, whereas high alkali cement caused DEF expansion at 80°C and above.

Results of Scrivener and Taylor (1993), Scrivener and Lewis (1997), Famy et al. (2002) indicate that the sulfate content of the CSH phase increases at high curing temperatures, which could later be released under moist conditions to enhance DEF. Johansen et al. (1994), and Johansen and Thaulow (1999) proposed that a homogenous paste expansion takes place as a result of the reaction of the released sulfate with the aluminate phases in the hardened paste, and this causes gaps around the aggregate particles at the paste-aggregate interfacial zones, which later gets filled with ettringite, the latter not contributing to the expansion.

The tendency of various cements to cause DEF as a result of heat curing has been related to its composition, with SO_3, aluminate and alkali contents being the major factors (e.g. Kelhem, 1996, 1997, 1999; Hobbs, 1999, Lawrence 1999). Some publications relate the tendency for DEF expansion not only to the high alkali and high sulfate contents, but also to the presence of a slowly soluble anhydrons $CaSO_4$ in the clinker, which is alleged to release sulfate at later ages, causing DEF expansion (Marusin, 1995; Hime and Marusin, 1999). Kurdowski (2002) has also concluded that anhydrons $CaSO_4$ formed in belite crystals was the cause of expansivity resulting from heat-curing. However, Hertfort et al. (2003) strongly refuted Kurdowski's conclusions, claiming they were erroneous, which would also apply to similar statements made by Marusin (1995) and Hime and Marusin (1999). Moreover, Kelham, 1999; Michaud and Suderman, 1999; and Klemm and Miller, 1999 found that anhydrous $CaSO_4$ in clinker dissolved rapidly and did not cause DEF expansion, whereas added alkali sulfates did, which also invalidates Kurdowski's conclusions and Marusin's and Hime's assertions.

The conclusions some workers have reached based on laboratory test results have been extended by others to interpret observed field deterioration problems. For instance, if boiling of some specimens in the laboratory caused DEF expansion, then expansion and cracking of steam-cured field concrete was also attributed to DEF. Unfortunately, some of the interpretations have been either misguided or biased. An example of inadequate investigation was given earlier (Tepponen and Eriksson, 1987) regarding concrete sleepers from Finland, which resulted in the erroneous/incomplete conclusion that DEF was responsible for the problem. A similar claim was made by Marusin (1995) regarding concrete sleepers in the north east of USA, despite ample evidence of AAR in the concrete, documented by other researchers. The first author of the present paper has examined specimens of the U.S. concrete sleepers (unpublished work), and with more than 20 years of experience in examination of concrete, he is confident of a very strong case of AAR in the concrete, although in those sleepers which exhibited AAR symptoms, evidence of DEF was also noted in microcracks. This is not surprising as data of Shayan et al. (1993) and Michaud et al. (1997) show that formation of AAR products encourages ettringite formation.

Marusin (1995) and later Hime and Marusin (1999) did not elaborate on the relevance of AAR to the deterioration of the concrete sleepers at all, and only advanced DEF as the cause of the problem. These authors, unashamedly, accused other researchers of misinterpreting ettringite for ASR gel, whereas in the view of the present author such a mistake is very improbable, particularly when advanced techniques such as scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) are used to examine freshly exposed fracture surfaces of concrete; the technique commonly used by experienced researchers. In fact, the reverse has happened on the part of some inexperienced researchers who have examined sawn surfaces of concrete and failed to recognise AAR because sawing removes the easily visible AAR products and their morphological features. These are best seen on fracture surfaces of concrete, and their composition can be confirmed by EDX. It is strange that these authors are intent on not revealing the evidence of AAR in the concrete sleepers, and other elements which appear to have undergone AAR.

Other examples of similar cases in Texas are presented by Lawrence et al. (1999). They document studies of deterioration of cast-in-place and precast concrete elements, in which completely insufficient attention has been paid to the possibility of AAR being involved, but instead DEF has been claimed to have been the cause of significant cracking. This is despite the fact that indications for AAR were present and needed to be further evaluated. However, in one of the cases, the cement supplier had evidently commissioned a separate study which reached the opposite conclusion, stating that AAR was the main cause of the cracking, but DEF could have contributed to it. It appears that Marusin and Hime were co-investigators who attributed the deterioration to DEF at least in one of the cases. The present author believes that these cases need re-examination to provide a more complete basis for drawing conclusions regarding the cause(s) of the observed deterioration.

The main source of complication of these studies is that both AAR and DEF products are present, sometimes in close association. Shayan (2003) listed a number of Australian structures with cast-in-situ and precast elements which he had previously shown to contain evidence of both AAR and DEF. These structures exhibited very strong cases of AAR, and the presence of DEF was largely due to the fact that AAR had provided space in the form of microcracks for ettringite precipitation. This may have contributed to further expansion under the condition of water saturation in the microcracks. Symptoms of DEF in the Australian cast-in-situ concrete elements listed by Shayan (2003) have occurred only in large elements, e.g. mass concrete or columns of about 1 m in diameter, in which hydration temperature must have reached 80°C, or higher, to cause destabilisation of primary ettringite followed by ettringite deposition in the AAR-induced microcracks.

Results of Shayan and Quick (1991/1992) show that symptoms similar to DEF (ettringite mats lining cracks) were present in laboratory specimens containing reactive aggregates, which had been cured at 40°C and expanded significantly due to AAR. They noted more DEF in specimens cured at 80°C which had exhibited more extensive AAR products. In both cases AAR was the cause of expansion, but specimens with larger expansion and more microcracking had more ettringite in the microcracks. It is astonishing that Collepardi (1997) attributed the cause of severe cracking of concrete pedestals of an electric power distribution line in Italy (which had previously been diagnosed to have suffered AAR) to DEF, just because ettringite was found in the cracks. Shayan et al. (1993) provided mineralogical and electron optical evidence that chemical changes in the pore solution, induced by AAR in steam cured concrete, favoured the formation of ettringite at the AAR sites because of the consumption of alkali hydroxide in the vicinity of such sites, and the consequent reduction in the pH. Moreover, Michaud et al. (1997) showed that ettringite and other sulfoaluminates were unstable in alkali-silica solutions, similar to those generated by alkali-silica reactions, forming amorphous or poorly crystalline sulfoaluminate phases. They noted that reduction in Si concentration (e.g. by precipitation of AAR gel) promoted formation of crystalline sulfoaluminate (ettringite). This could also have been influenced by the reduction in pH resulting from AAR gel formation.

It should be noted that the mere observation of ettringite in cracks is not sufficient to conclude that an expansive DEF process has taken place in the concrete. Scrivener and Lewis (1997) have shown that formation of XRD-detectable ettringite was unrelated to the expansion of the element concerned. Both expansive and non-expansive heat-cured mortars contained XRD-detectable ettringite, and even for those that expanded, increasing amounts of ettringite were detected after expansion had ceased. They related the observed expansion to ettringite formation within the CSH gel (i.e. paste expansion), and not in cracks. Stark and Seyfarth (1999) also found that the extent of damage to heat-cured concrete was unrelated to the amount of ettringite detected in the element, being about 3% in the cases they examined.

Formation of ettringite has also been blamed for the deterioration of cast-in-situ concrete pavement (Stark and Bollmann, 1997). However, in this case the expansion observed over different stages was partly due to filling of cracks developed in the matrix (i.e. the same as the case reported by Shayan, 1985 for calcium hydroxide filling cracks caused by sequential drying shrinkage) and partly due to the filling of air voids with ettringite, that reduced the resistance of concrete to freezing and thawing damage (cracking). These observations indicate that the mechanism of "simultaneous AAR and ettringite formation", suggested by Shayan and Ivanusec (1996), may be operating.

To explain the various observations made regarding AAR and DEF, Collepardi (1997) suggested the so-called holistic approach, stating that pre-existing microcracking, moisture and potential for late sulfate release were the three essential factors for DEF distress to occur. This author appears to present a confused picture of DEF distress. If DEF causes any distress, then this would initially be brought about by the reactions that cause paste expansion, as indicated by the results of Scrivener and Lewis (1997), which may finally lead to microcracking of the paste and gap formation at the paste-aggregate boundaries. In contrast, Collepardi (1997) suggested that the microcracking is needed to generate DEF distress, which may or may not be relevant, depending on the conditions.

This seems to have been confused with the fact that microcracks largely facilitate the visualisation of DEF in the form of ettringite bands, because ettringite tends to precipitate in open spaces, be it microcracks or other voids in the concrete. As stated before, the filling of the microcracks with ettringite may or may not cause further expansion, depending on the conditions. Diamond (1996) favoured the mechanism of ettringite crystallisation pressure at crack tips causing expansion. However, the origin of the microcracks, in which ettringite is to precipitate, has not been explained, unless this is assumed to have been caused by other processes such as AAR. Sahu, Clark and Lee (1998) did not support the mechanism of uniform paste expansion, neither did they entirely support the "crystal growth pressure" hypothesis, but concluded that localised (non-uniform) paste expansion could lead to gaps being generated in concrete, and crystallisation of ettringite could further enhance expansion.

Whether or not initial paste expansion and microcracking takes place, ettringite crystallisation in microcracks may cause additional expansion under certain conditions, as stated earlier. In some cases repeated deposition of calcium hydroxide in microcracks, caused by drying shrinkage of concrete, has been shown to cause expansion and warping of concrete panels (Shayan, 1985; Shayan and Quick, 1994).

It appears that this misunderstanding led Collepardi (1997) to attribute a case of AAR damage of in-situ-cast concrete pedestals to distress caused by DEF, just because ettringite was found in cracks.

The cement apparently contained 4.4% SO_3, and it appears that the large amount of ettringite that would form from 4.4% SO_3 must have got redistributed and accumulated in the crack spaces caused by AAR. This case merits re-examination. In fact, Petrov and Tagnit-Hamou (2003) have shown that pre-existing microcracks decrease DEF expansion by providing space for ettringite deposition outside of the solid paste.

Clarification of the type of confusion mentioned above would enable better understanding of the processes involved in the deterioration. Unfortunately, inaccurate or incomplete statements regarding these processes could cause further confusion. For instance, Mehta (2000) stated that "*the fundamental mechanism underlying DEF or internal sulfate attack are not different from those of external sulfate attack. Irrespective of the source of sulfate ions, the presence of interconnected microcracks and water are necessary components of any sulfate-related distress in concrete*", again requiring the presence of microcracking as a pre-requisite for the development of DEF distress. As explained above, other researchers have provided evidence to the effect that, when other expansive processes such as AAR are absent, then microcracking is the result of DEF distress, not the initial cause of it.

Moreover, Mehta (2000) quoted another researcher, presumably to reinforce the view that the majority of AAR cases are harmless. This is a vague statement which could potentially mislead some asset owners. Certainly, many major structures have suffered significant deterioration due to AAR, requiring considerable maintenance cost. AAR is an ongoing expansive process, and although the cracking induced by AAR may not cause immediate failure of a structure, it would continue to diminish structural strength and significantly enhance other deterioration processes, depending on the exposure conditions. AAR can cause expensive maintenance problems and should not be encouraged to be viewed as harmless.

The aim of this paper is to attempt to clarify the influence of some major factors involved in both DEF and AAR expansion.

3 EXPERIMENTAL WORK

The experimental work involved manufacturing mortar and concrete specimens, using various aggregates and cements of different C_3A, SO_3 and alkali contents, treating them under different temperature regimes, and measuring their expansion properties. Details of these are given below.

Aggregates: For the manufacture of mortar bars the non-reactive Excel sand was used as the non-reactive material and 5% of the sand was replaced by Opal to make a reactive sand. For testing concrete a basalt was used as non-reactive aggregate and a known metagreywacke as the reactive aggregate. Excel sand was used as non-reactive sand in both concretes.

Cements: Australian and Canadian cements and their mixtures were used to provide various levels of C_3A, sulfate and alkali contents. Gypsum and/or alkali were added to some cements (Table 1) to provide the desired levels of the ingredients. Their chemical compositions are given in Table 2.

3.1 Procedures

Mortar and concrete specimens were prepared using the different cements listed in Table 1. Mortar cubes and bars were cast according to ASTM C109 using a sand/cement ratio of 2.75 and water/cement ratio of 0.485. These are different from the ratios in ASTM C227 for alkali-reactivity test, but were adopted to enable the strength and expansion to be measured on the same mix. After preparation of each mortar mix its flow was measured using a flow table as described in ASTM C109 (see later).

The mortar and concrete specimens were cured at curing temperatures of 23°C, 65°C and 85°C. The 65°C and 85°C regimes involved a pre-curing period of 2.5—3 hours, a ramp up rate of 18°C per hour, a soak time of 8 hours, followed by cooling which occurred at about 20°C per hour. Demoulding of specimens took place when they had reached ambient temperature of around 20°C.

After the appropriate temperature curing, mortar cubes (50 mm) were stored at 23°C (100% RH) and at the age of 28 days tested for strength. Mortar bars 25 × 25 × 285 mm were stored for expansion measurements. Initially, all the various mortar bars were stored at 23°C in a fog room for 3 weeks protected from dripping water. Those that had not been heat treated remained in the fog room, but the heat-treated ones were then stored at 38°C, 100% RH for expansion measurement. After a few months it appeared that expansion was slow in the fog room and the specimens stored there were also transferred to 38°C, 100% RH.

Table 1: Various cement combinations used

BC	Blue Circle HES cement
BC 3.5	Blue Circle HES cement with gypsum to obtain $SO_3 = 3.5\%$
BC 4.5	Blue Circle HES cement with gypsum to obtain $SO_3 = 4.5\%$
C3	0.6 T10 Canadian + 0.4 Blue Circles HES to obtain cement for alkalis effect
C3-Na*	C3 cement + NaOH to obtain cement with 1.25% Na_2O equiv.
C3-K*	C3 cement + KOH to obtain cement with 1.25% Na_2O equiv.
T30	Canadian HES cement
T10 per SSA	Canadian T10 per cement + gypsum to obtain 4.5 SO_3 for SSA specific surface area parameter
T10 PER	Canadian T10 per cement Normal cement with light colour
T10	Canadian T10 per cement Normal cement
C4	T10 Canadian + T10 PER to obtain cement with $C_3A = 5\%$
BCL	Blue circle low C_3A cement

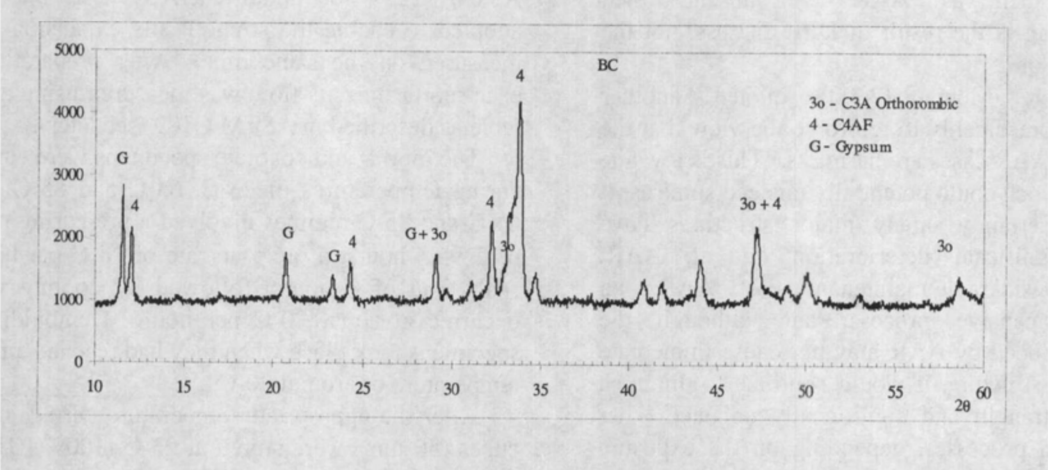

Fig. 1 - X-Ray diffractogram of cement BC after salicylic treatment

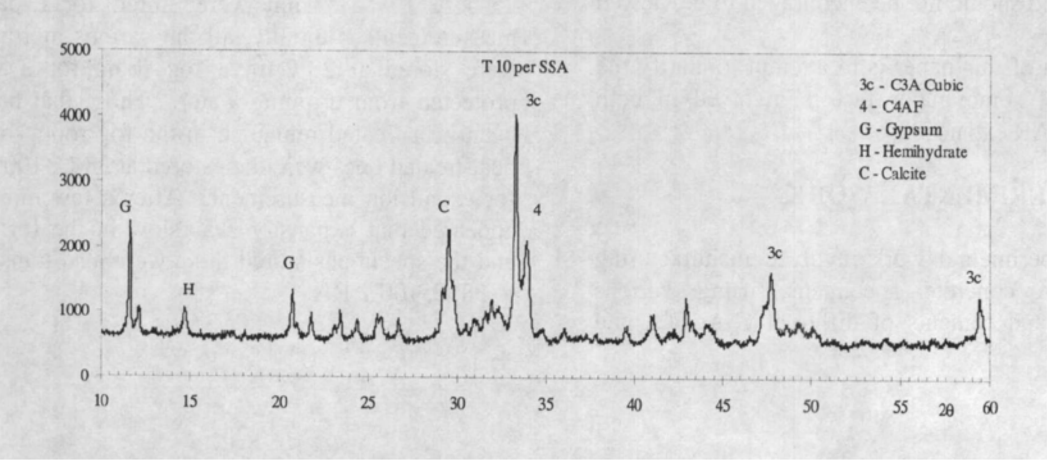

Fig. 2 - X-Ray diffractogram of cement T10perSSA after salicylic treatment

Table 2: Chemical Composition and Bogue Potential Phase Composition of Cements

	BC	**BC 3.5**	**BC 4.5**	**C3**	**C3-Na***	**C3-K***	**T30**	**T10 per SSA**	**T10 PER**	**T10**	**C4**	**BCL**
SiO_2	20.13	19.73	19.37	19	19.41	19.418	19.8	20	19.9	19	19	19.73
Al_2O_3	4.73	4.63	4.56	4.9	4.93	4.93	5.4	4.9	5	5	4.65	4.27
Fe_2O_3	4.57	4.49	4.33	3.8	3.8	3.8	2.2	2.4	2.3	3.2	4.05	5.53
CaO	64.82	64.18	63.09	62	62.29	62.29	61.3	61	61.4	60.2	61	63.59
MgO	0.89	0.85	0.95	1.9	1.94	1.94	2.8	2.4	2.4	2.6	2.08	1.37
SO_3	2.6	3.42	4.41	3.5	3.49	3.49	4.5	4.4	3.9	4	4.06	2.53
K_2O	0.56	0.53	0.57	0.08	0.84	1.62	1.15	1	1.08	1.03	0.76	0.32
Na_2O	0.00	0.00	0.00	0.1	0.70	0.18	0.27	0.2	0.24	0.31	0.26	0.35
Na_2O.eq	0.37	0.35	0.38	0.67	1.25	1.25	1.03	0.89	0.95	0.99	0.76	0.56
CaOf		0.00	0.00				1		0.07	0.07		
LOI	1.4	1.77	2.30	2.6	2.63	2.63	1.1	3	2.5	3.2	3.50	2.67
SSA (m^2/kg)	461	451	459	413	413	413	587	409	394	391	408	417
Ins. Residue SO_3/Al_2O_3	0.55	0.74	0.97	0.71	0.71	0.71	0.83	0.90	0.78	0.80	0.87	0.59
(%) SO_3/Al_2O_3 (Molar)	0.71	0.94	1.23	0.90	0.90	0.90	1.06	1.15	0.99	1.02	1.11	0.76
C_3S	65	64	60	58	58	58	47	50	51	51	56	65
C_2S	9	8	10	12	12	12	21	19	19	16	12	7
C_3A	5	4	5	7	7	7	11	9	9	8	5	2
C_4AF	14	14	13	12	12	12	7	7	7	10	12	17

Table 3: Details of concrete mixes

Cement	Aggregate	Na_2O (%)	SO_3 (%)	Temp. °C	28-day strength (MPa)
BC	HK	1.4	2.6	85	46.1
		1.4		23	58.2
		0.37		85	68.2
	NSW	1.4	2.6	85	45.2
		1.4		23	49.8
BC/fly ash	NSW	1.4	2.6	85	42.1
BC-54.5	HK	1.4	4.5	65	64.1
				85	60.4
	HK	0.37	4.5	85	77.9
	NSW	1.4	4.5	65	50.7
				85	49.2
BC/T30 mixture	HK	1.4	3.5	23	63
				85	57.5
	NSW	1.4	3.5	23	56.0
				85	46.7
BC/T30-55	HK	0.7	5	85	79.7
		1.4	5	23	74.3
				65	66.3
				85	63.5
	NSW	0.7	5	85	62.4
		1.4	5	23	66.3
				65	51.4
				85	55.6
BC/T30-S5/fly ash	NSW	1.4	5	85	52.3

3.2 Concrete mixes

For the purpose of testing concrete specimens a mix design was used containing cement, aggregate, sand and water of 410, 1327, 689 and 140 kg/m^3, respectively. Cement BC was used as the reference cement. In one variation, the SO_3 content of this cement was increased to 4.5% (C_3A = 5%). In another variation a 50/50 mix of BC and T30 was made yielding SO_3 content of 3.5% (C_3A = 8%), and in a third variation the SO3 content of the mixture was increased to 5% (C_3A = 8%). Two types of aggregate designated as HK (non-reactive), NSW (reactive), and the non-reactive Excel sand were used as concrete ingredients.

Two levels of alkali were used, a high alkali level in which the alkali content of the cement was raised to 1.4% Na_2O equivalent and a low alkali level which was 0.37% Na_2O equivalent for BC cement and 0.70% for the BC/T30 mixtures.

For both BC and BC/T30 mixes containing high alkali and reactive aggregate, a parallel mix was made containing a fine fly ash at 25% replacement for cement, to assess its potential for suppressing AAR expansion in steam-cured concrete. Table 3 provides a summary of concrete mixes used and their 28 day compressive strength.

Results in Table 3 showed that, generally, alkali addition and high temperature of steam-curing reduced the strength, whereas addition of gypsum (higher SO_3 levels) increased it

4 RESULTS

4.1 Cements

The mineralogical composition of the main cements were determined after salicylate treatments and two examples are presented in Figures 1 and 2, which show the aluminate and sulfate phases for cements BC and T10 per SSA. The difference in gypsum content was evident in the XRD patterns for the cements with added gypsum. The Tetracalcium ferroaluminate (C_4AF) phase is dominant in cement BC, with much less tricalcium aluminate (C_3A), whereas in the Canadian cement T10 per SSA the C_3A phase is greater than the C_4AF phase, and it contains limestone (calcite). Other cements were intermediate between these.

Cements used for assessing alkali effect (C3): Cement C3, which is the mixture of 60% T10 cement and 40% BC cement, was used to assess the effects of alkali content on expansion. The alkali content was increased by adding NaOH or KOH in the mix water to the mortar mixture. The XRD analysis of this cement showed that C_4AF content was larger than C_3A. The C_3A is a mixture of cubic and orthorhombic forms but mainly in cubic form. Alkali sulphates were in K_2SO_4 form (arcanite).

Cements used for fineness effect (T30 and T10 per SSA): The T30 cement is rich in C_3A (11%) and its fineness is very high (587 m^2/kg). The alkali content is also high (Na_2O equiv – 1.03%). The T10 per SSA

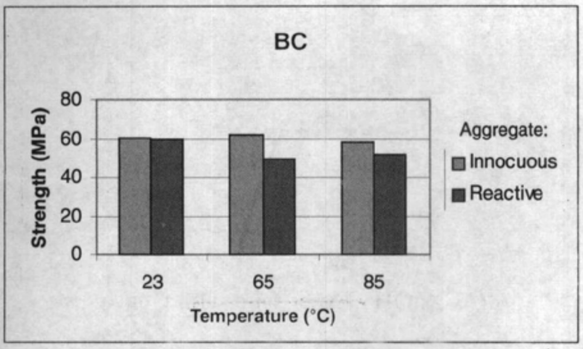

Fig. 3 - Compressive strength data for mortar specimens made with BC cement and the two aggregates indicated, and subjected to the three curing temperatures.

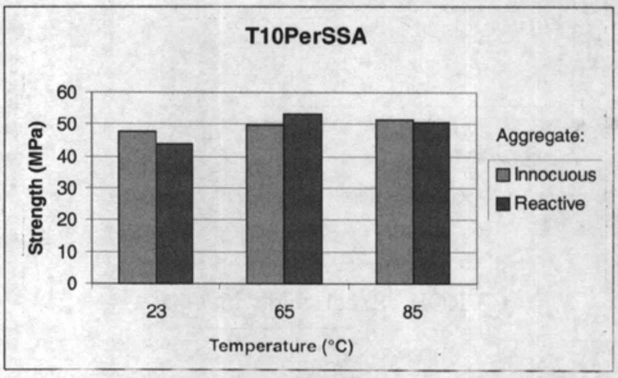

Fig. 4 - Compressive strength data for mortar specimens made with T10 per SSA cement and the two aggregates indicated and subjected to the three curing temperatures.

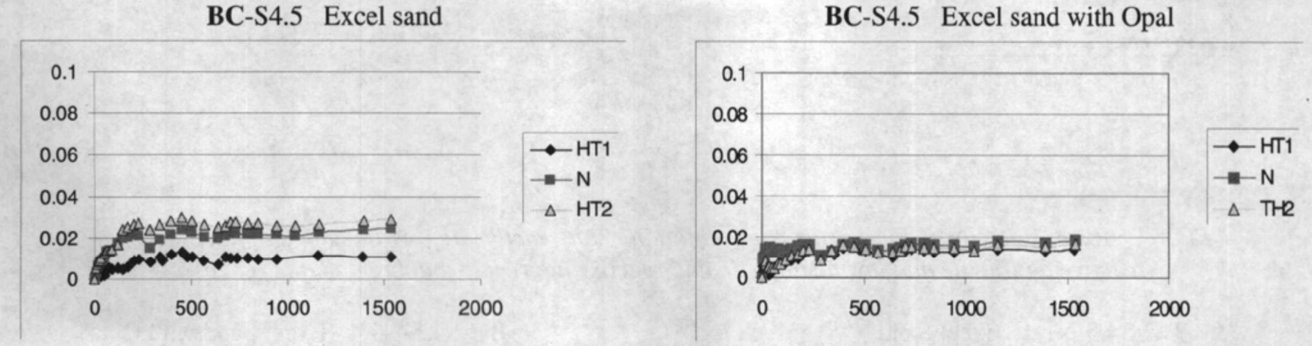

Fig. 5a

Fig. 5b

Fig. 5 - Expansion curves for mortar bars containing BC cement at 4.5% SO_3 and 0.37% alkali contents, without (5a) and with (5b) reactive aggregates.

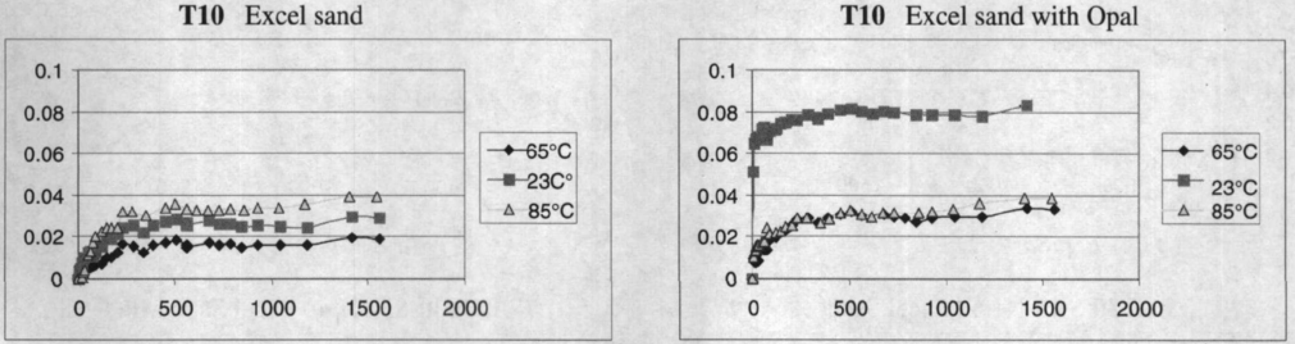

Fig. 6a

Fig. 6b

Fig. 6 - Expansion of mortar bars containing T10 cement (8% C_3A) at 4% SO_3 without (6a) and with (6b) reactive aggregate. Alkali content of cement was 0.99%.

C3-KOH Excel sand

C3 Excel sand with Opal

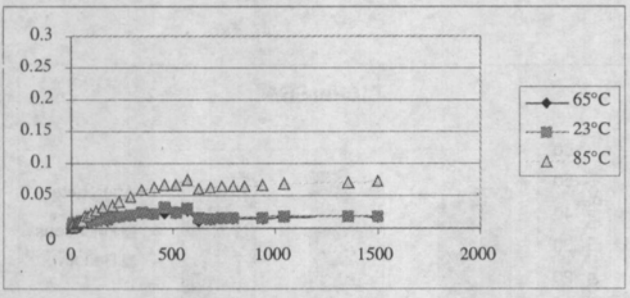

Fig. 7a

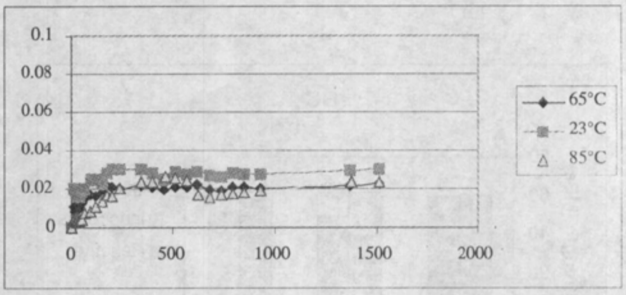

Fig. 7b

C3-KOH Excel sand with Opal

C3-NaOH Excel sand with Opal

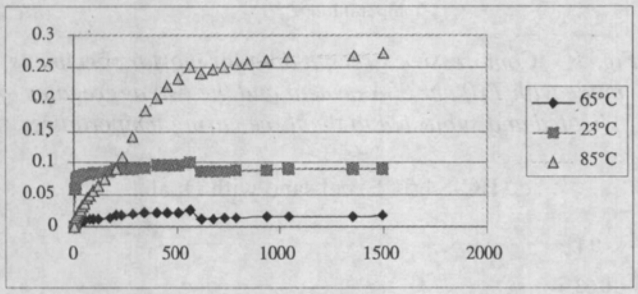

Fig. 7c

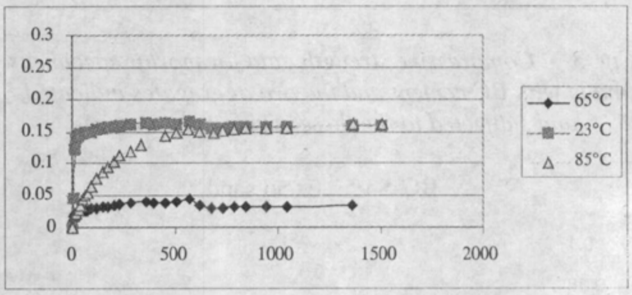

Fig. 7d

Fig. 7 - Expansion curves for mortar bars containing non-reactive aggregate and high alkali (7a), reactive aggregate and low alkali (7b), and reactive aggregate and high alkali (7c, 7d).

BC-S4.5-N1.4 Excel Sand

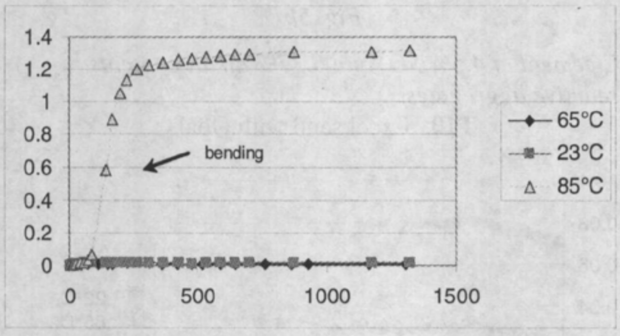

Fig. 8a

BC-S4.5-N1.4 Excel Sand with Opal

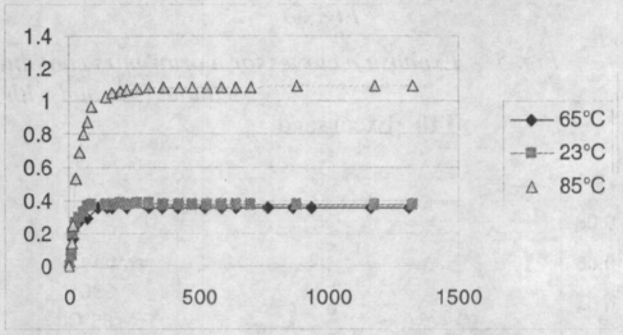

Fig. 8b

BCT30-S4.5-N1.4 Excel Sand

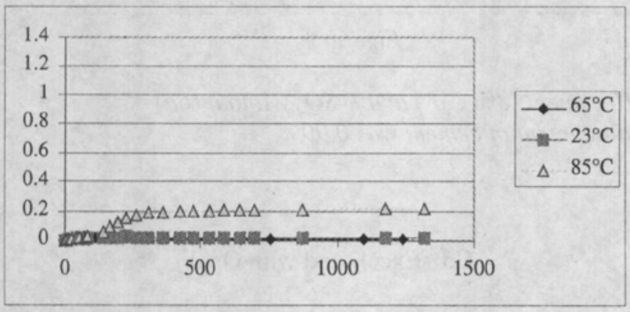

Fig. 8c

BCT30-S5-N1.4 Excel Sand with Opal

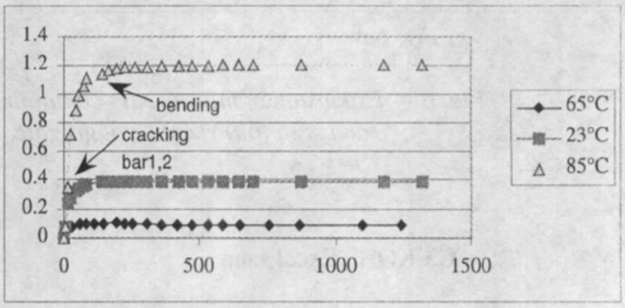

Fig. 8c

Fig. 8 - Effects of elevated SO3, alkali and aluminate contents on expansion of mortar bars with and without reactive aggregate at the three temperatures indicated.

BC-S4.5-N1.4 Excel Sand

BC-S4.5-N1.4 Excel Sand with Opal

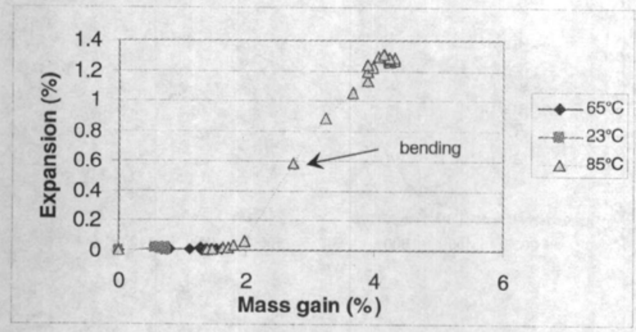

Fig. 9a

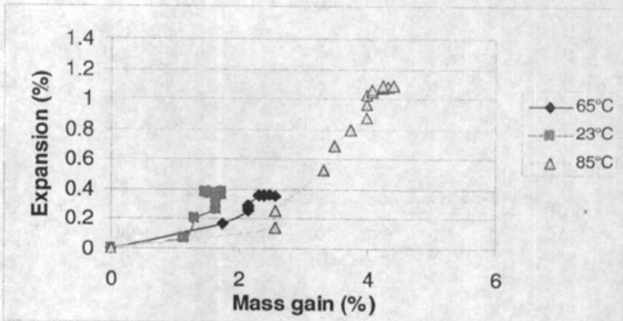

Fig. 9b

BCT30-S5-N1.4 Excel Sand

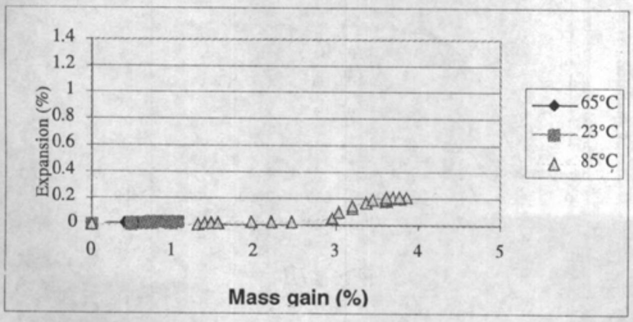

Fig. 9c

BCT30-S5-N1.4 Excel Sand with Opal

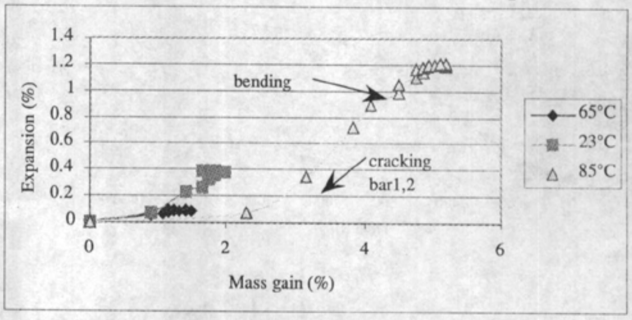

Fig. 9d

Fig. 9 - Relationship between expansion and mass increase (%) for the mortar bars containing high SO_3 and high alkali contents.

BC Cement-HK aggregate

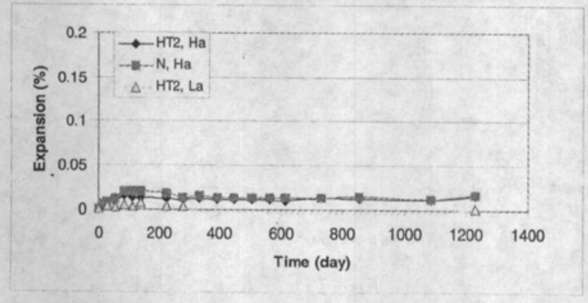

Fig. 10a

BC Cement, 4.5% SO_3-HK aggregate

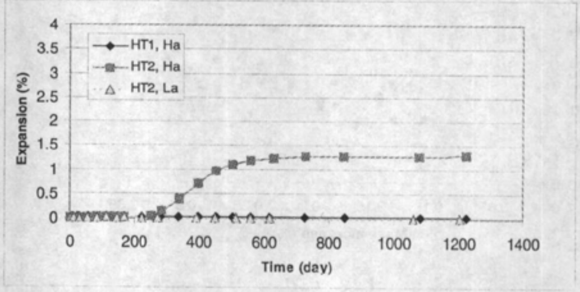

Fig. 10b

BC Cement-NSW aggregate

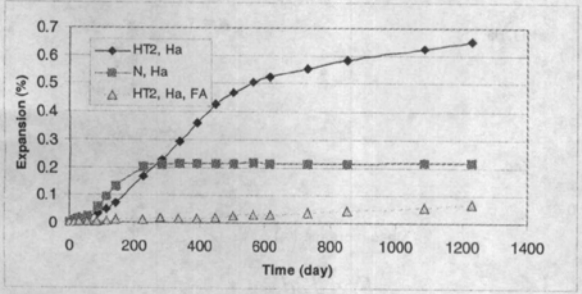

Fig. 10c

BC Cement, 4.5% SO_3-NSW aggregate

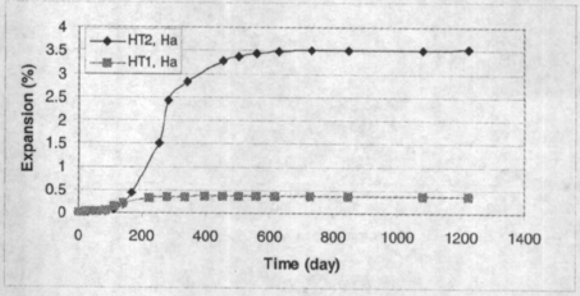

Fig. 10d

Fig. 10 - Expansion curves for concrete prisms made with cement BC at high alkali (Ha) and low alkali (La) and cured at different temperatures (N = 23 °C, HT1 = 65 °C, HT2 = 85 °C). FA refers to mixes that contained 25% of fly ash.

BCT30 Cement-HK aggregate

BCT30 Cement, 5% SO_3-HK aggregate

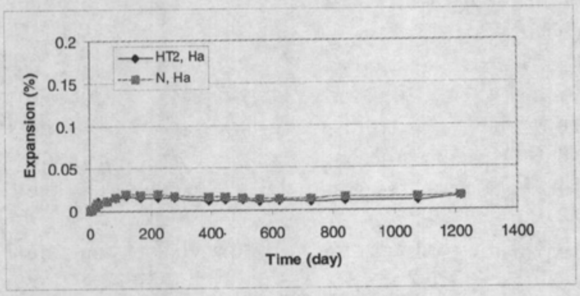

Fig. 11a

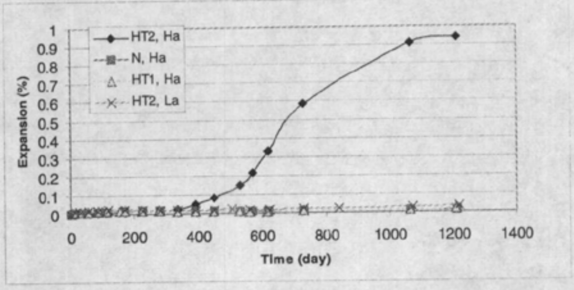

Fig. 11b

BCT30 Cement-NSW aggregate

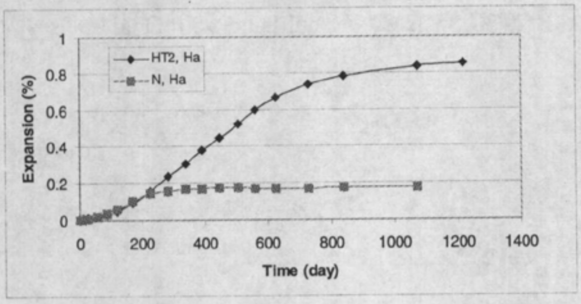

Fig. 11c

BCT30 Cement, 5% SO$_3$-NSW aggregate

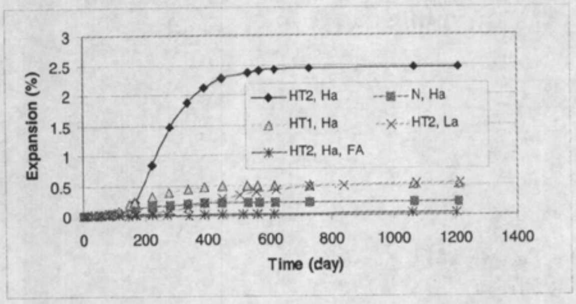

Fig. 11d

Fig. 11 - Expansion curves for concrete prisms made with cement BCT30 at high alkali (Ha) and low alkali (La) and cured at different temperatures (N = 23^o C, HT1 = 65^o C, HT2 = 85^o C). FA refers to mixes that contained 25% of fly ash.

BC Cement-HK aggregate

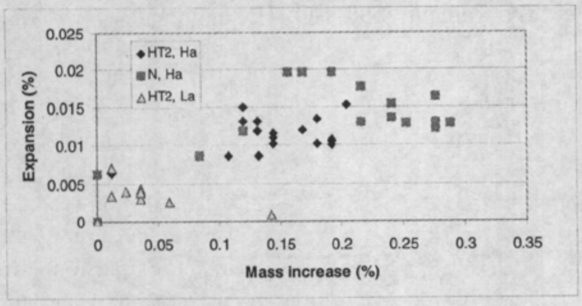

Fig. 12a

BC Cement, 4.5% SO$_3$-HK aggregate

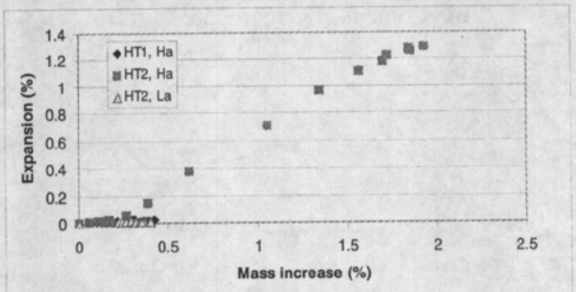

Fig. 12b

BC Cement-NSW aggregate

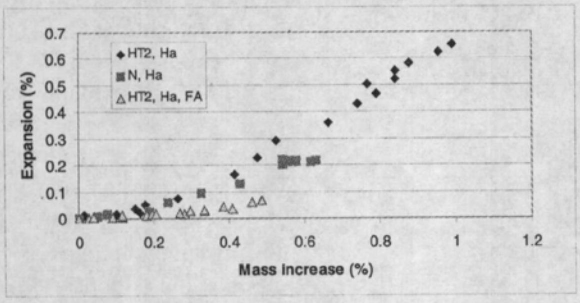

Fig. 12c

BC Cement, 4.5% SO$_3$-NSW aggregate

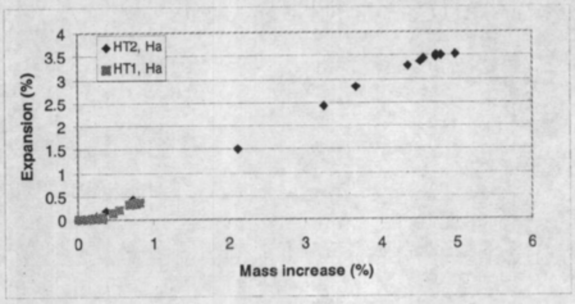

Fig. 12d

Fig. 12 - Relationship between expansion and mass increase (%) for concrete prisms made with BC cement.

cement is a mixture of T10 per cement and gypsum. The gypsum was added in order to increase the SO_3 content to that of T30 cement. As shown in Table 2 the SO_3 content is 4.5 and 4.4% for cement T30 and T10 per SSA. The final fineness of the latter cement after gypsum addition was 409^2/kg. Its XRD analysis showed that it had a higher amount of C_3A than C_4AF. The C_3A is in cubic form. Alkali sulphates were present as arcanite (K_2SO_4). The calcium sulphate in this cement was present as mixture of gypsum ($CaSO_4$, $2H_2O$) and Hemihydrate ($CaSO_4$, $^1/_2H_2O$).

Cements used for C_3A effect (T10 PER, T10 and C4): The C_3A contents of these 3 cements are 9, 8 and 5% for cements T10 PER, T10 and C4, respectively. Their fineness is almost the same and around 400 m^2/kg. The alkali contents are respectively 0.95, 0.99 and 0.76% as Na_2O equiv. Cement T10 per SSA which is the mixture of T10 and T10 PER and gypsum contained both gypsum and hemihydrate. The alkali sulphate in these 3 cements was in arcanite form, and C_3A in cubic form.

Temperature of curing: Three temperatures were used 23°C, 65°C and 85°C. The latter were achieved by steam curing. The samples were cured 3 hours after casting at a temperature rise of 18°C/hr and soak time of 8 hours at the maximum temperature. Cooling was at a rate of 20°C/hr until ambient temperature was reached.

4.2 Flow and compressive strength of mortar mixes

Mortar mixes were tested for flow on a flow table (ASTM C109) and the average diameter of the moulded 100 mm wide mortar cone was measured after giving it 25 drops in 15 seconds. The flow was satisfactory and varied in the range of 170-200 mm, and depended on the type of cement, being lowest for T30 cement (~170) and 180-200 mm for all other cements. Examples of strength data are graphically illustrated in Figures 3 and 4. Within each type of cement the variation in strength was probably largely due to random variations and no definite trend of the effect of temperature was evident. The variation between cements is due to their different chemical properties and finenesses, and increasing the sulfate content marginally increased the strength.

4.3 Expansion of mortar bars

Expansion curves for mortar bars containing the BC cement (native SO_3 content = 2.6%, C_3A = 5%, and Na_2O equiv. = 0.37%), as well as BC cement at raised levels of SO_3 content, showed that regardless of the type of aggregate and temperature of steam-curing, no expansion occurred over a period of 1600 days. Examples of the expansion curves are shown in Figures 5a and 5b for the reactive and non-reactive aggregates, respectively. This indicates that at the level of variables used (up to 4.5% SO_3, 5% C_3A and 0.37% Na_2O equivalent) the steam-curing even at high temperature does not cause expansion due to delayed ettringite formation (DEF). The level of alkali was not adequate to cause expansion due to alkali-aggregate reaction (AAR) with the reactive aggregate containing opal. The low level of alkali must also have suppressed DEF (by reducing the decomposition tendency of primary ettringite), because the sulfate content of 4.5% is close to that needed for maximum DEF expansion (Kelham, 1997).

Expansion curves for mortar bars containing cements C4, T10 and T10 PER, all of which had about 4.0% SO_3, but C_3A contents of 5, 8 and 9%, showed small and limited expansions in some mortar bars containing the reactive aggregate. Expansion curves for the mortar bars made with T10 cement, which showed the largest expansion, are represented in Figures 6a and 6b. The lack of expansion above 0.08% was probably due to insufficient alkali contents (less than 1.0% Na_2O equivalent). The increase in C_3A per se did not cause further expansion at 4% SO_3 content.

It is noted that expansion at 85°C for the reactive mortar bars is lower than that at ambient temperature. This effect was also noted in an earlier study (Shayan and Ivanusec, 1996) where it was suggested that the reaction of opal and alkali during the steam-curing period was responsible for the lower expansion measured after the steam-curing. Because the initial length of the specimens is measured after some reaction has taken place, the expansion caused by this amount of reaction is missed, and the expansion magnitude is, consequently, underestimated.

Figure 7 shows the effect of increasing the alkali content in mortar bars containing the C3 cement (native alkali = 0.67% Na_2O equiv; SO_3 = 3.5%; C_3A = 7%). In C3-KOH and C3-NaOH, the level of Na_2O equivalent of cement was raised to 1.25%, with the other parameters remaining unchanged. For the case of non-reactive excel sand no expansion was observed regardless of the level of alkali (Fig. 7a). Significant expansion was caused only when the aggregate was reactive and the level of alkali was sufficient (Figures 7c and 7d). No significant expansion occurred in the presence of reactive aggregate when the alkali level was 0.67% (Fig. 7b). Here, it is significant that steam-curing at 85°C has caused continued expansion. The expansion curves for the C3-KOH mortar bars with opal can be explained as follows.

Under ambient 23°C curing temperature, followed by storage at 38°C, 100% RH, a certain level of expansion was achieved, which is attributed to AAR. With steam-curing at 85°C, the subsequent expansion is underestimated, as described earlier, but it appears that another process (most likely DEF) was contributing to the later rapid expansion. However, this was virtually absent when no AAR was present (Fig. 7a), although in both cases the specimens contained 3.5% SO_3 and 7% C_3A. For the 65°C (HT1) the AAR expansion was again underestimated, and there was no additional expansive process like DEF, so the expansion curve remained flat. In the presence of NaOH the initial expansion at 23°C was larger, but the rapid phase of expansion for the 85°C cured specimens did not exceed the expansion at 23°C. However, in the presence of KOH, expansion at high temperature (85°C) increased significantly beyond that of the ambient temperature, or that in the presence of NaOH. It appears that K has a larger effect on expansion.

In addition to the above, two other cement compositions were examined in which the possibility of both AAR and DEF were enhanced. In all cases the SO_3 and alkali contents of BC cement in the mortar bars were increased to 4.5% and 1.4%, respectively. The C_3A content remained at about 5% with C_4AF at 14%. In the other case, 50% of each of the cements BC and T30 were thoroughly mixed to yield C_3A and C_4AF contents of 8% and 10.5% respectively, and the SO_3 and alkali contents were adjusted to 5% and 1.4%, respectively. Figure 8 shows the expansion results for the combination of these cements with reactive and non-reactive aggregates, and for the different curing temperatures. In these cases large expansions occurred in the presence of reactive aggregate, and it appears that 85°C steam-curing has caused additional expansion most likely as a result of DEF. These results are in agreement with those of Shayan and Ivanusec (1996).

More significantly, it is seen that the mortar bars containing the combination of these cements (high sulfate, high alkali) with the non-reactive aggregate also developed very large expansions at the curing temperature of 85°C. It is very likely that the expansion of these mortar bars was caused by DEF. The difference in the behaviour of the two cements in the presence of the non-reactive aggregate may be related to their C_3A and C_4AF contents. Another difference between the two cements was in their native alkali content, and the fact that more soluble alkali was added to cement BC (alkali content = 0.37% Na_2O equiv) than to the BCT30 mixture (alkali content = 0.70% Na_2O equiv) to raise their alkali levels to 1.4% Na_2O equiv. The addition of alkali used for BC cement may have caused larger ettringite formation. Figure 9 presents graphs corresponding to those in Figure 8 which show that the observed expansion was accompanied by significant mass increases which are probably due to the formation of the hydrated AAR products and ettringite.

The expansion curves for the mortar bars discussed above indicate that deleterious AAR was the main mechanism of deleterious expansion in the mixes containing reactive aggregate and adequate alkali contents, and that DEF could occur in them only at the 85°C (or higher) curing temperature, and when the sulfate and aluminate contents were sufficiently high. However, the combination of high alkali, high SO_3, high aluminate and high temperature (85°C) could also cause significant deleterious expansions in the presence of non-reactive aggregate, which is attributed to the DEF mechanism. This occurrence was less frequent than the cases of expansion caused by AAR.

4.4 Expansion of concrete prisms

Figures 10 and 11 show expansion curves for concrete prisms made using the various concrete compositions and curing temperatures. In these figures also N, HT1 and HT2 refer to 23°C, 65°C and 85°C temperatures of curing, and Ha and La refer to high and low alkali as mentioned earlier. FA refers to mixes that contained fly ash. For concrete prisms expansion values above 0.04% are considered deleterious.

Figure 10 indicates that in the absence of reactive aggregate, concrete expansion would be very low (Fig. 10a) unless the mix contained high alkali and high sulfate and was cured at 85°C (Fig. 10b). All these factors need to be present concurrently, as very little expansion took place at 65°C (HT1), although the sulfate and alkali levels were high. These observations are the same as those for mortar bars, indicating that the larger size of aggregate in the concrete did not affect the result, but only delayed the expansion.

Significant expansion occurred in the presence of the reactive NSW aggregate and high alkali (Fig. 10c, 10d). This aggregate was not used in combination with low alkali levels, as it would have behaved similarly to the non-reactive aggregate HK. The 85°C curing caused considerable additional expansion compared to 23°C and 65°C expansion levels, which is attributed to DEF. It is clear that the DEF is much enhanced in the presence of reactive aggregate, as compared to the non-reactive aggregate. The reason for this was explained by Shayan et al. (1993) to be related to the consumption of alkali hydroxide and reduction in the pH, under which conditions ettringite is more stable. It is also clear that the addition of SO_3 to BC cement enhanced the DEF and increased the expansion. This is in agreement with the literature cited earlier in this paper. Figure 10c shows that the addition of fly ash as a supplementary cementitious material has dramatically reduced both DEF and AAR expansion. This is also in accord with similar findings of Shayan et al. (1993) for the effects of silica fume.

Very similar results were obtained for the case of cement BC-T30, as shown in Figure 11. Here, it is also shown that the presence of a class F fly ash has completely suppressed the expansion resulting from both AAR and DEF. Therefore, in steam-cured concrete, class F fly ash and probably other suitable pozzolanic materials could be used as cement replacement materials to counter the adverse effects of both AAR and DEF. Figure 12 shows the relationship between expansion and mass increase for concrete prisms, which have the same trend as the mortar bars. The mass increase was very small when no AAR or DEF occurred (Fig. 12a), and larger when DEF alone was present (Fig. 12b), but much larger in the presence of reactive aggregate where both AAR and DEF occurred Figures 12c and 12d).

These results again indicate that AAR can be considered the main cause of expansion of the specimen. Only under the conditions where all of the factors of high alkali, high sulfate, high aluminate and high temperature are concurrently present, can DEF alone cause deleterious expansion as a separate mechanism, whereas deleterious AAR may occur under a wider range of conditions.

5 CONCLUSIONS

Expansion curves obtained on the various mortar bars and concrete prisms indicate that the main cause of expansion in most cases is AAR and that DEF may contribute to the AAR expansion when adequate sulfate and aluminate components are present and the curing temperatures is around 85°C or higher. In the absence of reactive aggregate DEF may occur only when all the factors including high alkali, high sulfate, high aluminate and high temperature of curing (around 85°C) are present concurrently. Incorporation of good quality class F fly ash in the concrete was able to completely suppress expansion caused by both AAR and DEF.

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