DEF-Related Expansion of Concrete as a Function of Sulfate Content in the Clinker Phase or Cement and Curing Temperature

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Synopsis*:* Delayed ettringite formation (*DEF*) occurs at *late* ages and the related *heterogeneous* expansion in a hardened concrete can produce cracking and spalling. There are two different types of *DEF* depending on the sulphate source: *DEF* caused by external sulphate attack (*ESA*) or internal sulphate attack (*ISA*). In the present paper only *ISA*-related *DEF* is studied with reference to the following three parameters:a) the sulfate content in the clinker phase or the cement; b)the curing temperature; c) the presence of preliminary cracks in concrete specimens.

Concretes manufactured at room temperature (20°C) do not show any form of DEF-related expansion independently of the SO_3 content of the clinker (1-2%) or the portland cement (2-4%). On the other hand, concretes steam-cured at 90°C and then kept under water show significant expansion related to DEF provided that the SO_3 content of the portland cement is relatively high (> 4%). The higher SO_3 content in the clinker phases (> 2%) or the presence of pre-existing cracks exacerbate the DEF-related expansion. Deposition of ettringite fiber crystals occurs in the preexisting cracks or within the new microcracks. Curing at temperatures lower than 80°C, preferably lower than 70°C, is strongly recommended to avoid *DEF*-related risk. Blended cements with a lower SO_3 content should be used in case this limit in curing temperature cannot be safely ensured.

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INTRODUCTION

Ettringite formation is associated with expansion and many hypotheses of ettringite related expansion have been advanced [1-4]. However, not necessarily any ettringite-related expansion produces damaging disruption of concrete structures.

Early Ettringite Formation: When ettringite ($C_3A \cdot 3C\bar{S} \cdot H_{32}$) occurs *homogeneously* and *immediately* (within hours), it does not cause any significant localized disruptive action (*early ettringite formation*, **EEF**). This type of harmless ettringite formation happens, for instance, when gypsum ($CaSO_4 \cdot 2H_2O$) reacts with anhydrous calcium aluminate (C_3A) in a through-solution reaction and acts as a set retarder in Portland cement mixtures:

$$C_3A + 3(CaSO_4 \cdot 2H_2O) + 26\,H_2O \longrightarrow C_3A \cdot 3C\bar{S} \cdot H_{32} \qquad (1)$$

The retardation has been attributed to the early formation of an ettringite layer which acts as a coating over the surfaces of the cement grains soon after mixing [3]. This type of ettringite may also be called "**primary**" ettringite as opposite to "secondary" ettringite which will be defined later [1]. The formation of "primary" ettringite occurs in the plastic stage of the cement mixture and does not produce any significant harmful stress. Another example of harmless and useful **EEF** occurs when, under proper restraint, a calcium aluminate sulphate ($C_4A_3\bar{S}$) hydrates within few days producing ettringite uniformly distributed and then homogeneous expansion throughout the hardened concrete (expansive cements):

$$C_4A_3\bar{S} + 6Ca(OH)_2 + 8(CaSO_4 \cdot 2H_2O) + 74\,H_2O \longrightarrow 3(C_3A \cdot 3C\bar{S} \cdot H_{32}) \qquad (2)$$

In such a case, the restrained expansion is advantageously transformed into a rather useful compressive stress (0.2 - 0.7 Mpa) in shrinkage-compensated concrete, or in a larger stress of 3 to 8 MPa in self-stressed reinforced concrete provided that a certain strength level and a corresponding modulus of elasticity are reached within few days.

Delayed Ettringite Formation: When ettringite forms *later* (after several months or years) - *DEF* - the related *heterogeneous* expansion in a very rigid hardened concrete can produce cracking and spalling. The disruptive effect is due to the non-uniform expansion localized only in the area of the concrete structure where ettringite forms. Therefore *DEF*, and not *EEF*, is associated with a damaging sulphate attack. There are two different types of *DEF*-

related damage depending on the sulphate source, as shown in Table 1: external or internal sulphate attack. External sulphate attack (*ESA*) occurs when environmental sulphate (from water or soil) penetrates concrete structures. Internal sulphate attack (*ISA*) occurs in a sulphate-free environment when the sulphate source is inside the concrete and comes from either cement with high sulphate content or gypsum-contaminated aggregate.

According to the terminology currently used, "*DEF*" or "secondary ettringite" [5, 6] is related only to the *ISA*, particularly in heat-cured concrete structures where "primary" ettringite, responsible for setting regulation, is thermally decomposed and then forms again in an atmosphere that is saturated intermittently or continuously. However, correctly speaking the term *delayed* ettringite formation only means that ettringite forms *later* and therefore it should include both *ESA* and *ISA* as shown in Table 1. The following terms are used in the present paper: "*ESA*" or "*ISA*" to indicate *DEF* related to *external* or *internal* sulphate attack, respectively.

PURPOSE OF THE WORK

According to some previous studies of field concretes [7-10] delayed ettringite formation (*DEF*) could cause damage even in structures not experienced at high temperature. This was ascribed to the presence of excessive SO_3 in the clinker phases from which it would be only slowly released. From these field inquiries the exposure to moisture appeared to be very important in accelerating the *DEF*-related damage. Moreover, the *DEF* appeared to be exacerbated by the presence of pre-existing cracks caused by the manufacturing process.

On the other hand, many other papers [11-17] indicated that both over-heating of concrete and high SO_3 content are needed to promote *DEF*-related expansion [6, 10-17].

The purpose of this work was to study the role played by the following parameters on the *DEF*-related concrete deterioration caused by *ISA*:

- sulfate content in the clinker phase and cement;
- curing temperature (20°C vs 80°C);
- pre-existing cracks.

EXPERIMENTAL

In the following paragraphs the raw materials and the proportions of concrete mixtures, as well as the curing process ad length change measurement, will be examined.

Clinker and cements: Two clinkers were used with approximately the same mineralogical composition in terms of XRD patterns(Fig. 1). The main difference being the sulpate content: 1.05% in clinker 1 and 2.15% in clinker 2 (Table 2), both percentages in terms of SO_3.

Four different Portland cements (Table 3) were manufactured by grinding clinker 1 and 2 and different amounts of gypsum in order to obtain regular setting times (Table 4). Cement code *C12* means that there is about 1% SO_3 in the clinker phase and about 2% as total SO_3 (really this is 2.70% as shown in Table 3).

On the basis of preliminary tests of steam-curing, it was found that for the cements shown in Table 3, the critical temperature causing the thermal decomposition of ettringite and its transformation into monosulfate ($C_3A \cdot 3C\overline{S} \cdot H_{12}$) was 80°C [11]. Figure 2 shows the XRD patterns of the four anhydrous cements and of the corresponding hydrated products at 1 day

with a curing at room temperature (20°C) or a steam-curing at a maximum temperature of 80°C.

Curing of concrete specimens and expansion measurements: On the basis of the above results on cement pastes, concrete mixtures were cured at room temperature (20°C) or steam-cured at T_{max} of 80°C, so that ettringite was respectively stable or transformed into monosulfate ($C_3AC\overline{S}H_{13}$), at the end of the curing process (Fig. 2). For each concrete mixture (Table 5) two different types of specimens (80 x 80 x 280 mm) were prepared: sound specimens and cracked specimens obtained by localized compressive stress on the specimens under steel cutters. Table 6 shows the identification of the concrete specimens. For instance, *C14S* indicates sound (*S*) concrete manufactured with the cement *C14*, that is containing about 1% of SO_3 in the clinker phase and 4% in the cement. On the other hand, *C14C* indicates the same concrete in form of cracked (*C*) specimens. Both sound and cracked specimens with crack-opening width in the range of 0.2-1 mm, were cured at 20°C with R.H. of 95% for three weeks. Then they were permanently exposed under water and the length change was measured, as a function of the time under water at 20°C, for about 2 years.

Steam-cured concrete speciments (preliminary curing at 20°C for 3 hr; heating from 20°C to 80°C in 7 hr; curing regime at 80°C for 4 hr; cooling from 80°C to 20°C in 6 hr), were submerged in water after an additional curing at 20°C with R.H. of 95% for two weeks. Then the length change, as a function of time under water at 20°C, was measured for about 2 years.

Other steam curing process at 90°C or high-pressure steam curing at 170°C were also adopted.

RESULTS AND DISCUSSION

Figures 3-8 show the length change results of the concrete specimens kept under water at 20°C. Similar results were also obtained in concrete specimens cured at 90°C or autoclaved at high-pressure steam curing at 170°C, ant then only the results obtained on the 80°C-cured specimens will be discussed in the present paper.

There is no significant expansion in concrete specimens cured at 20°C (Fig. 3) independently of the pre-existing cracks or the SO_3 content in portland cement (2.60-4.20%) and in the clinker phase (1.02-2.15%); the expansion of about $200\text{-}300 \cdot (10^{-6})$ after some months of permanent immersion under water is normal and can be related to the swelling effect of the cement paste under water [18].

On the other hand, when concretes are steam-cured at temperature as high as 80°C (Fig. 4) there is a significant expansion ($\approx 1500 \cdot 10^{-6}$ in less than 1 year) for the sound specimens *C24S* immersed under water.

The expansion is higher and quick in the concrete specimens with pre-existing cracks, *C24C* and *C14C* than in the corresponding crack-free specimens, *C24S* and *C14S*, (Fig. 5 and 6).

No significant length change was recorded for both sound and cracked steam-cured specimens when a relatively low sulfate content ($< 2.70\%$) was adopted in the cement (Fig. 7 and 8).

Moreover, the expansion is exacerbated by the higher sulphate content in the clinker phase (*C24C > C14C*; *C24S > C14S*). All these results could be related to the disappearance of ettringite caused by the steam-curing process at relatively high temperatures ($> 80°C$) as shown by the cement paste experiments (Fig. 2) and on its subsequent reformation at *later ages* (*DEF*) when kept under water.

In order to confirm this hypothesis concrete specimens were observed by optical microscope in order to assess the width change of the pre-existing cracks (Fig. 9) or the appearance of new microcracks on the surface of the originally sound specimens. The white material filling the pre-existing cracks (Fig. 10) or depositing within microcracks of the originally sound specimens (Fig. 11) was analyzed by X-Ray Diffraction (XRD) analysis. The XRD patterns (Fig. 12) indicate that ettringite (E), beside calcium hydroxide (CH), are the main products filling the pre-existing cracks or within the new microcracks of the originally sound specimens.

The SEM/EDS results of the material filling the pre-existing cracks or the new microcracks are shown in Fig. 13. The main difference in the morphology is in the better growth of the ettringite fibers filling the pre-existing cracks of the *C24C* specimen, with respect to the stubby ettringite crystals mixed with some C-S-H filling the new microcracks formed in the originally sound specimen (*C24S*).

CONCLUSIONS

1. Expansion related to *DEF* occurred only in some concrete specimens steam-cured at 80°C ot at higher temperatures due to the thermal decomposition of the ettringite formed during the early stage of the portland cement hydration.

2. *DEF*-related expansion of concrete specimens steam-cured at 80°C occurred only when portland cements with about 4% of SO_3 were used independently of the SO_3 content (1 or 2%) in the clinker phases. These results agree with those obtained by Zhang et al. [16, 17]. However, the *DEF*-related expansion of steam-cured concrete specimens, at the same total SO_3 content of 4% in the cements, was quicker and higher when clinkers richer in the SO_3 content (2% vs 1%) were used. No *DEF*-related expansion occurred when cement with a total content of about 2% SO_3 were used independently of the curing temperature and SO_3 content in the clinker phases.

3. *DEF*-related expansion of concrete specimens manufactured with about 4% SO_3 content in Portland cement and steam-cured at 80°C is quicker in the presence of pre-existing cracks. However, it can occurs even in sound specimens although at much lower rate.

4. SEM and EDS studies combined with XRD analysis indicated the formation of well crystallized ettringite fibers (20 μm long and 0.5 μm thick) deposited into the pre-existing cracks or the new micro-cracks formed during the exposure to moist environment.

5. These results seem to agree with the expansion mechanism suggested by H.F.W. Taylor, C. Famy and K. Scrivener [14, 15] based on the growth of sub-micrometre ettringite crystals from monosulfate incorporated in the *C-S-H* gel.

6. These laboratory experiences under controlled conditions did not confirm studies of field concretes and the corresponding conclusions that *DEF* could also occur in structures not experienced at high temperature.

7. From a practical point of view, with a curing at temperature lower than 80°C there is no thermal decomposition of ettringite and then no risk of *DEF*-related damage in concrete structures independently of the SO_3 content in the clinker phases (up to 2.7%) or portland cement (up to 4.2%). However if, for some reasons, a curing temperature higher than 80°C, preferably 70°C, cannot be excluded, then it would be better to limit the amount of SO_3 in the cement at percentage lower than 4% by using, for instance, blended cements, as suggested by Lawrence [5].

REFERENCES

[1] Collepardi, M., *"A state-of-the-art review an delayed ettringite attack on concrete"*, Cement & Concrete Composites, 25, 401-407, 2003.

[2] Mehta, P.K., "*Sulfate Attack on Concrete - A Critical Review*", *Materials Science of Concrete III*, The American Ceramic Society, 1993 pp. 105-130.

[3] Taylor, H.F.W., "*Cement Chemistry*", 2nd Edition, Thomas Telford Publishing, London, 1997, pp. 459.

[4] Lawrence, C.D., "Physiochemical and Mechanical Properties of Portland Cements", *Lea's Chemistry of Cement and Concrete*, 4rth Editions, Arnold Publisher, Edited by P.C. Hewlett, 1998, pp. 343-419.

[5] Lawrence, C.D., *"Laboratory Studies of Concrete Expansion Arising from Delayed Ettringite Formation"*, BCA Publication C/16, British Cement Association, Crowthorne, Berres, U.K., 1993, 147 pp.

[6] Heinz, D. and Ludwig, U., *"Mechanism of secondary ettringite formation in mortars and concretes subjected to heat treatment"*, Concrete Durability – Katharine and Bryant Mather International Symposium, SP-100, ACI, Fargmington Hills, Mich., 1987, pp 2059-2071.

[7] Mielenz, R.C., Marusin, S.L., Hime, W.G., and Jugovic, Z.T., "Investigation of Prestressed Concrete Railway Tie Distress", *Concrete International*, V. 17, No.12, December 1995, pp. 62-68.

[8] Collepardi, M., "Damage by Delayed Ettringite Formation - A Holistic Approach and New Hypothesis", *Concrete International*, Vol. 21, No. 1, January 1999, pp. 69-74.

[9] Marusin, S.L., "Deterioration of Railroad Ties in the USA", *CANMET/ACI International Workshop on Alkali-Aggregate Reactions in Concrete*, Nova Scotia, 1995, pp. 243-256.

[10] Hime, W.G., "Clinker Sulfate: A Cause for Distress and a Need for Specification", *Concrete in the Service of Mankind"*, E.& F.N. Spoon, 1996, pp. 387-395.

[11] Collepardi, M., Ogoumah Olagot, J.J., *"The influence of sulfate content and curing temperature on DEF-related expansion of concrete"*, Proceedings of the Internationa Workshop on Internal Sulfate Attack and Ettringite Formation, pp. 1-17, RILEM 2003.

[12] Klemm, W.A. and Miller, F.M., "Plausibility of Delayed Ettringite Formation as a Distress Mechanism - Consideration at Ambient and Elevated Temperatures", Proceedings, *10th International Congress on the Chemistry of Cement*, Gothenburg, Sweeden, 4i 59, 1997, pp. 10.

[13] Kelham, S., "Effects of Cement Composition and Hydration Temperature on Volume Stability of Mortar", Proceedings, *10th International Congress on the Chemistry of Cement*, Gothenburg, Sweeden, 4iv60, 1997, pp. 8.

[14] Taylor, H.F.W., Famy, C., and Scrivener, K., *"Ettringite in Hydration of Portland Cement Concrete and its Occurrence in Mature Concretes"*, ACI Material Journal, 2001, pp. 350-356.

[15] Taylor, H.F.W., Famy, C., and Scrivener, K., *"Delayed Ettringite Formation"*, Cement and Concrete Research, 2001, pp. 683-693.

[16] Zhang, Z., Olek, J. and Diamond, S., "*Studies on Delayed Formation in Early-Age, Heat-Cured Mortars. I. Expansion measurements, change in dynamic emodulus of elasticity, and weight grains*", Cement and Concrete Research, 32, pp. 1729-1736, 2002

[17] Zhang, Z., Olek, J. and Diamond, S., "*Studies on Delayed Formation in Early-Age, Heat-Cured Mortars. II. Characteristics of cement that may be susceptible to DEF*", Cement and Concrete Research, 32, pp. 1737-1742, 2002

[18] Neville, A.M., "*Properties of Concrete*" 4th Edition, Longman Group Limited

Table 1 - Delayed ettringite formation by external and internal sulphate attack.

FORMATION
DELAYED ETTRINGITE

EXTERNAL SULPHATE ATTACK

- It occurs when environmental sulphate (from water or soil) penetrates concrete structures in service.

- It occurs in a permeable concrete.

- It occurs in a moist environment favouring diffusion of SO_4 through the aqueous phase of the capillary pores

INTERNAL SULPHATE ATTACK

- It occurs in a sulphate-free environment for the late sulphate release from gypsum-contaminated aggregates or thermal decomposition of ettringite.

- It is favoured by prliminary microcracks where deposition of ettringite crystals can occur.

- It occurs in a moist environment favouring diffusion of SO_4 and other reacting ions (Ca++ and aluminate through water-saturated capillary pores.

Table 2 – Chemical Analysis of Clinkers

Component	Clinker 1	Clinker 2
SiO_2	21.42	21.37
Al_2O_3	6.18	5.81
Fe_2O_3	2.36	2.07
CaO	65.07	64.99
MgO	1.04	1.43
K_2O	1.15	1.20
Na_2O	0.10	0.09
SO_3	1.02	2.15

**Table 3 – The SO$_3$ content in the clinker and the total SO$_3$
in the cement after gypsum addition.**

Cement Code	SO$_3$ (%) in the clinker phase	SO$_3$ (%) as gypsum additon	Total SO$_3$ (%)
12	1.02	1.68	2.70
22	2.15	0.45	2.60
14	1.02	2.98	4.00
24	2.15	2.05	4.20

Table 4 – Setting time for the four Portland cements.

Cement Code	Setting times (hr:min)	
	initial	**final**
12	1:40	2:05
22	1:55	2:40
14	1:48	2:30
24	2:05	2:55

Table 5 – Composition of concrete mixtures at a w/c=0.50 and slump fo 250 mm..

Cement Code	Composition (kg/m^3)			
	Cement	Sand 0-4 mm	Gravel 4-25 mm	Water
C12	450	870	869	225
C22	452	868	868	220
C14	448	871	871	224
C24	450	870	870	225

Table 6 – Identification of concrete specimens.

Code Symbol	Approximate SO$_3$ (%) in:		Type of concrete specimen
	clinker	cement	
C12S	1	2	SOUND
C22S	2	2	SOUND
C14S	1	4	SOUND
C24S	2	4	SOUND
C12C	1	2	PRE-CRACKED
C22C	2	2	PRE-CRACKED
C14C	1	4	PRE-CRACKED
C24C	2	4	PRE-CRACKED
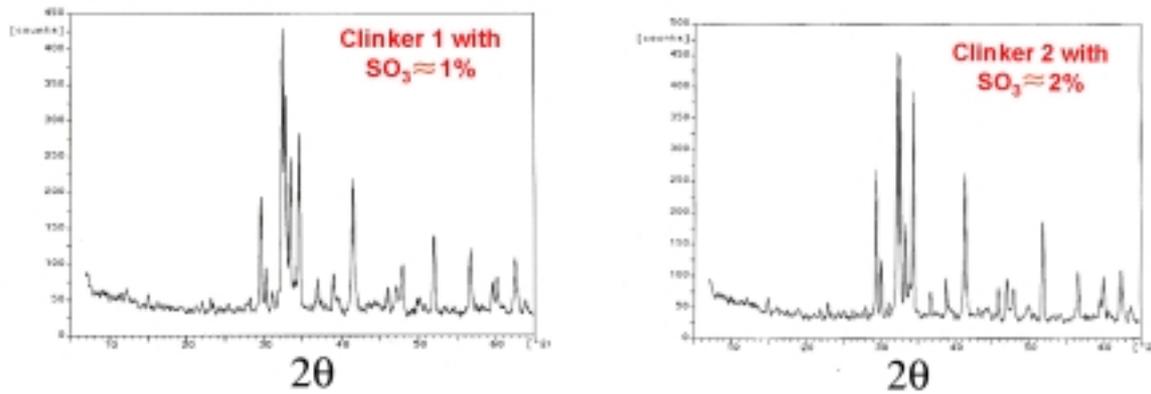
Fig. 1 – XRD patterns of the two clinker with the SO₃ content of about 1% and 2%.
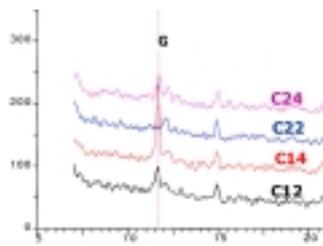
Anhydrous cements
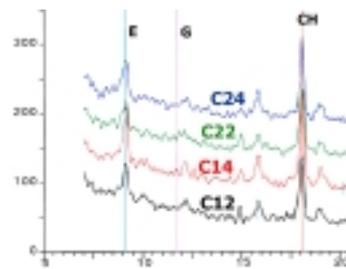
$T_{max}=20°C$ – Time = 24 hrs
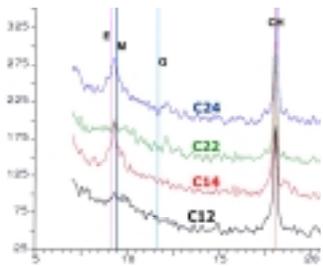
$T_{max}=80°C$ – Time = 24 hrs

Fig. 2 – XRD patterns of anhydrous or hydrated cements at 24 hrs cured at 20°C or steam-cured at 80°C: G=gypsum; CH=Calcium hydroxide; E=Ettringite; M=Monosulfate.
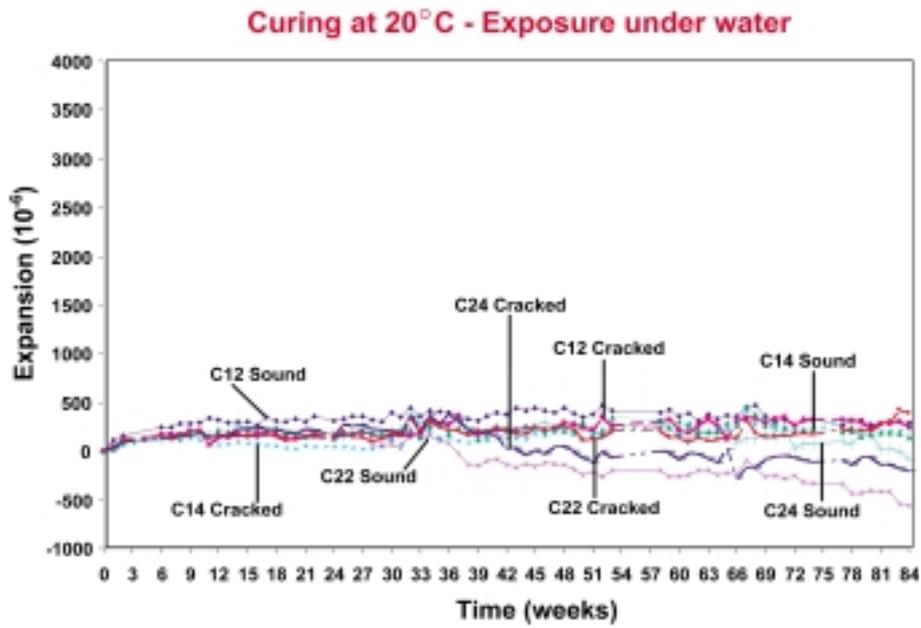
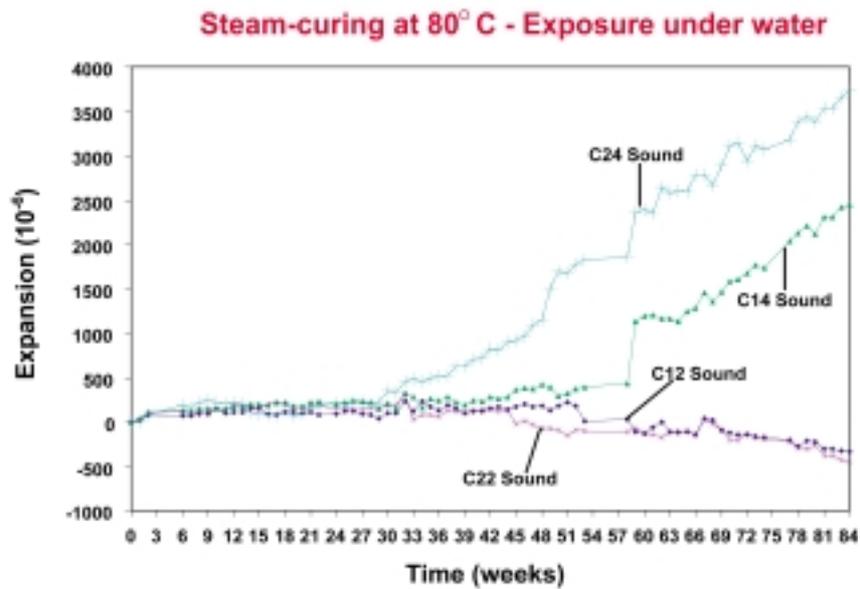**Fig. 3 – Change length of concrete specimens cured at 20°C and then permanently submerged under water.**

Fig. 4 - Change length of sound concrete specimens cured at 80°C and then permanently submerged under water.
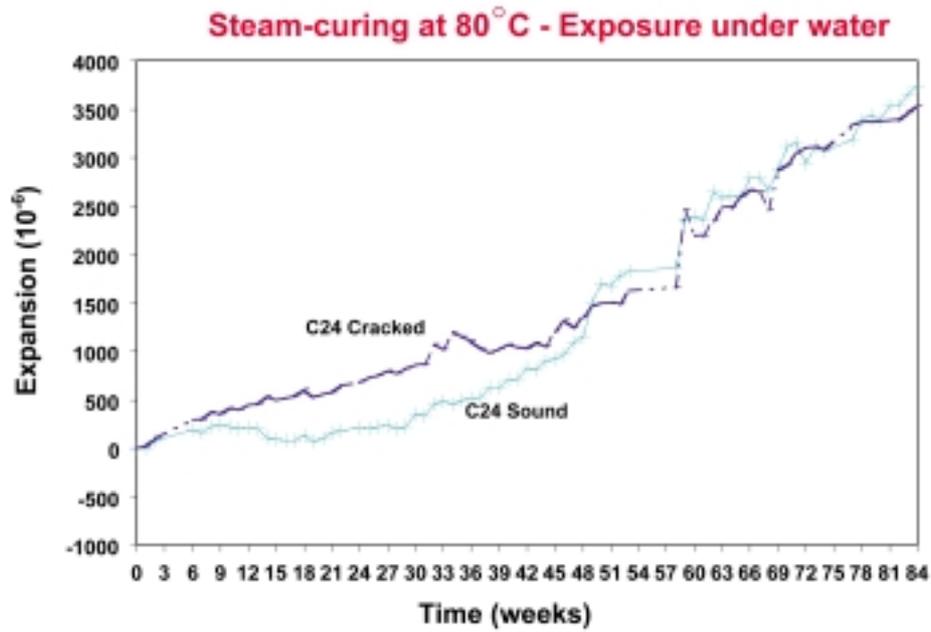
Fig. 5 - Change length of cracked and sound specimen cured at 80°C and then permanently submerged under water.
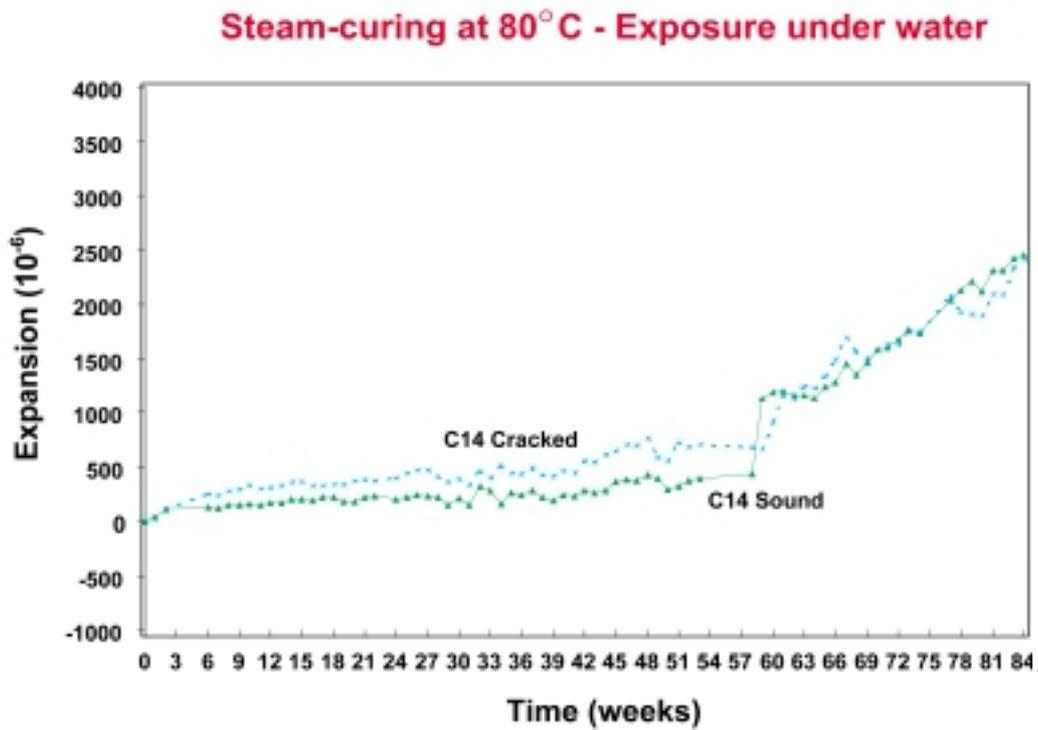
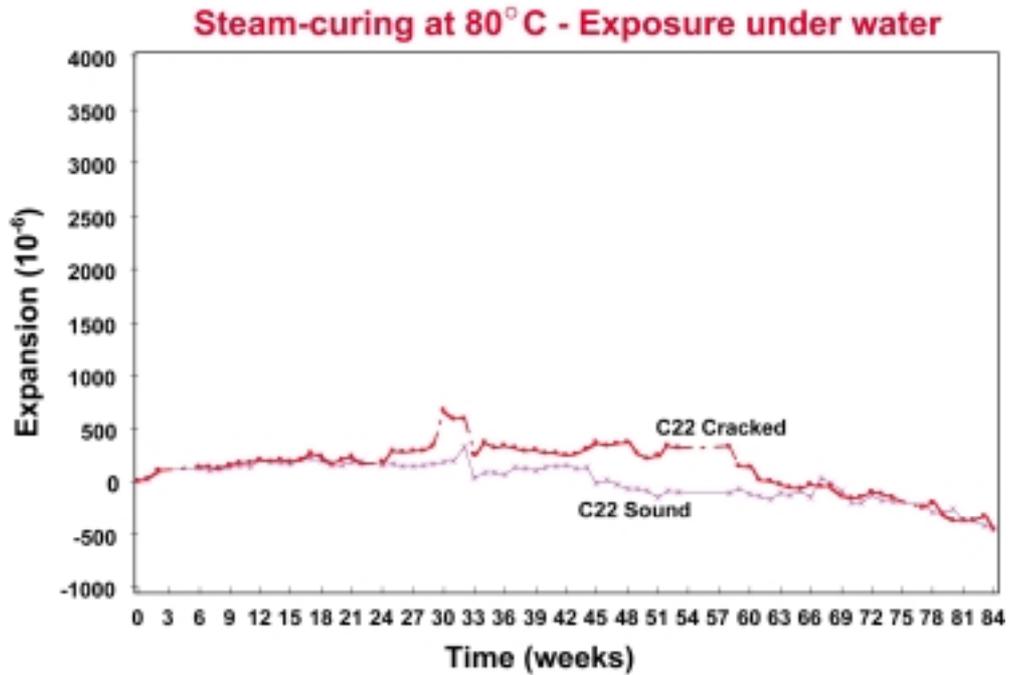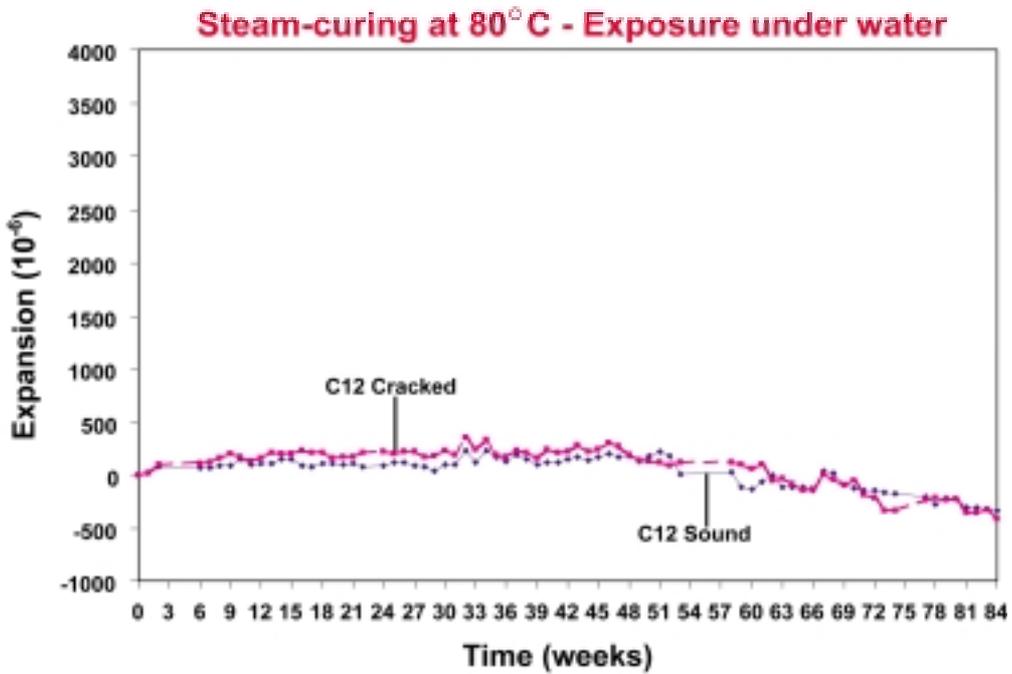**Fig. 6 - Change length of cracked and sound specimen cured at 80°C and then permanently submerged under water.**

Fig. 7 - Change length of cracked and sound specimen cured at 80°C and permanently submerged under water.

Fig. 8 - Change length of cracked and sound specimen cured at 80°C and permanently submerged under water.

Fig. 9 – Observation of the width-crack by optical microscope.

Fig. 10 – White material filling the pre-existing cracks.

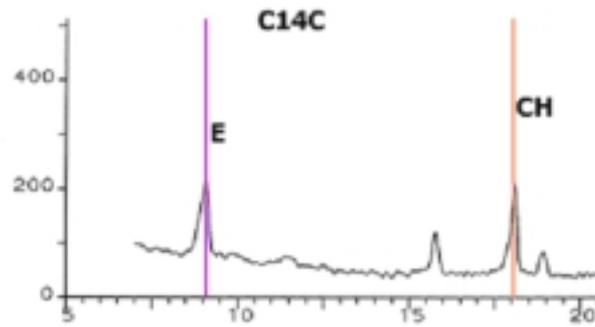**Fig. 11 – White material filling the microcracks of the orginally
sound concrete specimens.**

Fig. 11 – Typical XRD pattern of the white material filling the pre-existing cracks of the C14C concrete specimens.
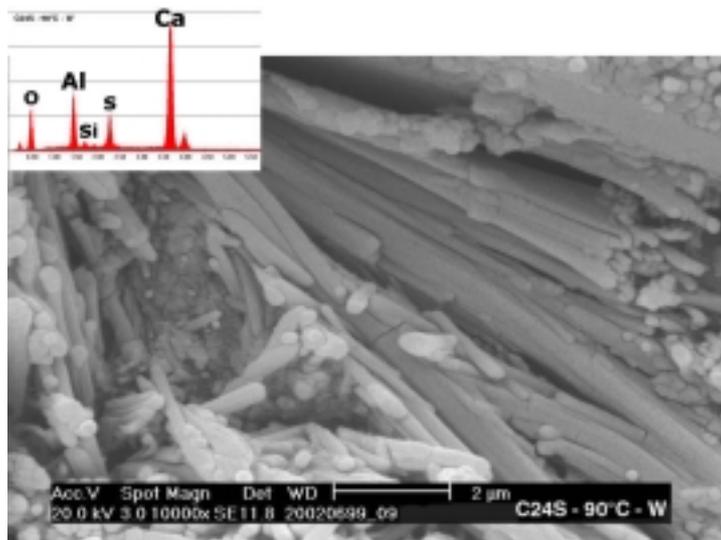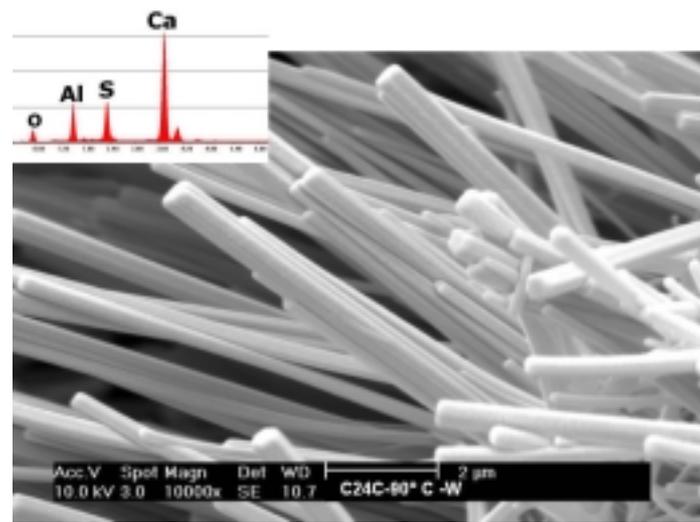

Fig. 14 – SEM/SED of ettringite deposited into the pre-existing cracks (above) and within the new microcracks (below).