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Role of delayed release of sulphates from clinker in DEF

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Abstract

Two clinkers rich in sulphate burned in the pilot plant rotary kiln and cements prepared from them were investigated. Clinker richer in sulphate ($SO_3 = 3.6\%$) contained independent anhydrite grains as well as inclusions of anhydrite in belite. The mortar from it expanded after heat treatment at 90 °C and the addition of Na_2SO_4 or NaOH accelerated and increased this expansion. The expansion occurred irrespective of the fact that the clinker contained only 3% of C_3A, although the C_4AF content was 13%. The second clinker with 2.6% SO_3 contained mainly calcium langbeinite and expanded only when 2% of Na_2SO_4 was added. The SEM examination of the mortars revealed the presence of numerous bands of massive ettringite around sand grains. Agglomerates of cracked ettringite in cement gel were also present. In addition, microcracks were seen inside the darker C–S–H gel. The conclusion is that anhydrite forming inclusions in belite gives an expanding mortar after heat treatment at 90 °C independently of the tricalcium aluminate content. Such clinkers are not typical of industrial conditions. The expansion is caused by the bands of massive ettringite as well as its agglomerates present in the cement gel and nanometric ettringite in the C–S–H phase. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ettringite; Anhydrite; Ca_2SiO_4; Sulphate; $Ca_3Al_2O_6$

1. Introduction

Many papers have been devoted to the problem of delayed ettringite formation (DEF). However, the mechanism of expansion is not yet fully understood [1–12]. Day [13] and Thomas [14] presented very interesting reviews of this literature.

One of the hypothesis of DEF and concrete expansion concerns the presence of anhydrite in clinker or, generally speaking, the delayed release of sulphates from clinker compounds [15–17]. However, Klemm and Miller [18] demonstrated that, in industrial clinkers rich in sulphates and with high $[SO_3]/[Na_2O_e]$ ratio, only soluble anhydrite and calcium langbeinite were present. Miller and Tang [19] found that, in clinkers with high sulphate content, some sulphate was detected in silicate phases and the level was in the range of 0.07–0.83% SO_3.

Sulphate solubility studies were also undertaken by Michaud and Suderman [20] who found that "dead-burned" anhydrite showed reduced solubility. However, most of it dissolved after 2 days and all of it after 4 days. Michaud and Suderman [21] prepared also laboratory clinker with an extremely high level of sulphate and found that 2.1% SO_3 was present as calcium langbeinite, 0.7% was in the silicate and 0.65% was present as anhydrite. Most of this anhydrite was dissolved quickly within a few hours and nearly all of it was gone after a few days. Herfort [22] found that the

Table 1
Chemical and mineralogical (Bogue) composition of clinkers

Clinker	1	2
SiO_2	22.43	23.57
Al_2O_3	3.74	3.81
Fe_2O_3	4.28	1.62
CaO	63.28	66.26
MgO	0.70	0.58
SO_3	3.62	2.48
K_2O	0.35	0.34
Na_2O	0.08	0.08
Na_2O_e	0.32	0.30
$[SO_3]/[Na_2O_e]$	9.05	6.46
C_3S	42	51
C_2S	33	29
C_3A	3	7
C_4AF	13	5
$CaSO_4$	6	4

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Table 2
Clinker phase composition as determined by XRD

Clinker	1	2
C_3S	39	55
C_2S	42	36
C_3A	3	5
C_4AF	14	4
$CaSO_4$	1	0

sulphate in silicate phases correlates well with the total SO_3 and $[SO_3]/[Na_2O_e]$ ratio and was relatively very high, amounting to 1.45% SO_3. This high SO_3 content in silicates increased also the Al_2O_3 content and the ratio $[Al_2O_3]/[SO_3]$ was greater than 1. Herfort [22] expressed an opinion that they are released at the same rate thus favouring the formation of monosulphate rather than ettringite. The dissolution of anhydrite from the clinker was rather quick and a substantial part of it was dissolved after 10 min of hydration and the XRD peak of anhydrite disappeared after 7 h.

Kelham [7,23] followed the expansion of heat-cured mortars using cements prepared from clinkers of various sulphate content up to 2.6% SO_3. The expansion was observed for most cements when mortars were heat-cured at 90 °C, except the cements produced from sulphate-resisting cement clinker. Kelham [23] is of the opinion that the source of sulphate, including clinker sulphate, has little impact on the behaviour of mortars.

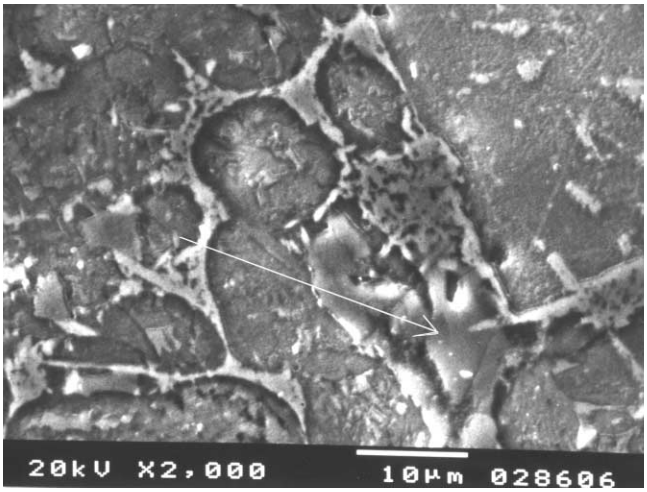

Fig. 1. Anhydrite in clinker 1.

The literature in general and the papers especially of Kelham [18], Michaud [20,21] and Herfort [22] do not contain any hypothesis on clinker sulphate causing DEF. Hence, the question is still open.

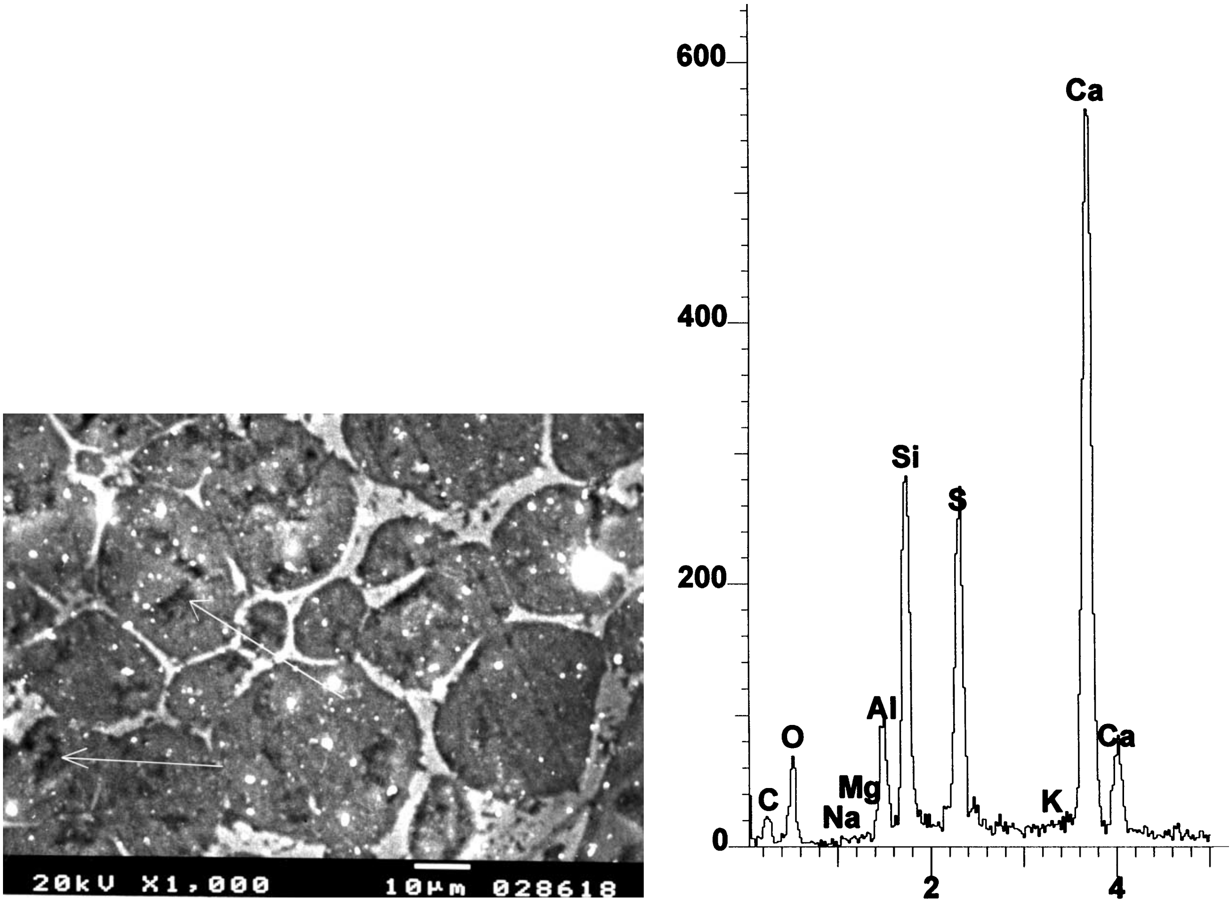

Fig. 2. Anhydrite inclusions in belite in clinker 1 (left) and its EDS (right).

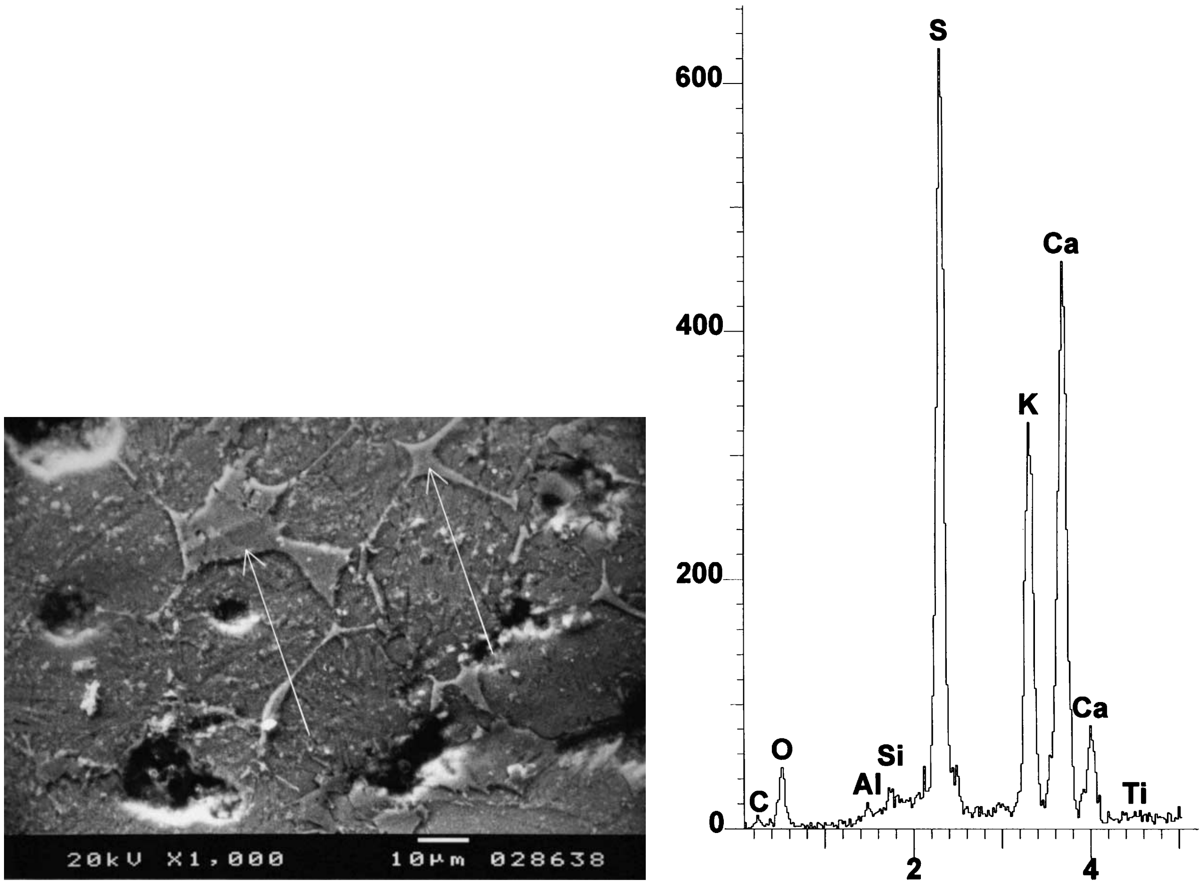

Fig. 3. Calcium langbeinite in clinker 2 (left) and its EDS (right).

This paper presents the results of examination of two clinkers, rich in sulphate produced in a laboratory scale rotary kiln.

2. Materials

In the laboratory scale rotary kiln, two clinkers were produced, rich in sulphate and with very low Na_2O_e content (Table 1). These clinkers are certainly not characteristic of industrially produced ones but they were synthesized with high amounts of sulphate in order to study the behaviour of the anhydrite content in cement paste after heat treatment.

The phase composition of these clinkers was also followed by XRD using Rieteveld [24] program. The results are shown in Table 2.

The comparison with calculated mineral composition (Table 1) shows that the correlation is relatively good. The only exception is anhydrite. To verify this difference, we dissolved the silicates phases using maleic acid and repeated XRD for the remaining sample. The results were as follows:

Clinker	1	2
$CaSO_4$	2%	0.3%
$Ca_2K_2(SO_4)_3$	trace	0.4%

In SEM examination of the polished section of clinker 1, the presence of anhydrite was detected (Fig. 1). The anhydrite phase was also seen to form frequent inclusions in belite crystals (Fig. 2).

The possible mechanism, which could explain this behaviour, is that anhydrite can be the product of decomposition of sulphate spurrite, which is stable only up to about 1200 °C. Simultaneously, the belite phase was rich in sulphate and its content was near 1.5% SO_3, which is close to Herfort [22] data. Assuming that this content represents average value, it gives us about 0.6% of SO_3 in clinker. The content of K_2O in the belite phase was also high and close to 1%. It means that practically all potassium was incorporated

Table 3
Na_2O_e and SO_3 content in cements and ratios SO_3/Na_2O_e and SO_3/Al_2O_3

	Na_2O_e		SO_3		SO_3/ Na_2O_e	SO_3/ Al_2O_3 C_3A	SO_3/ Al_2O_3 total
Cement	Clinker	Total	Clinker	Total	mol	mol	mol
1	0.31	0.31	3.62	3.62	9.05	4.7	1.24
1NS	0.31	1.18	3.62	4.75	3.11	6.16	1.63
1N	0.31	1.18	3.62	3.62	2.4	4.7	1.2
2	0.30	0.30	2.48	2.48	6.41	1.15	0.84
2NS	0.30	1.17	2.48	3.61	2.38	1.67	1.21

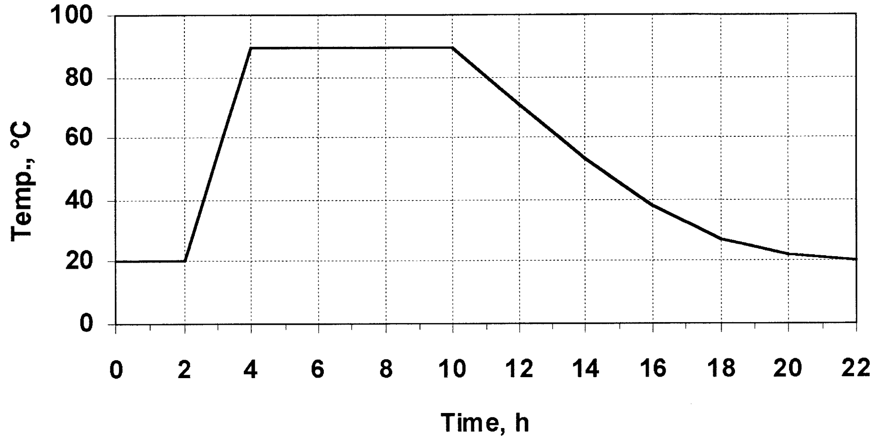

Fig. 4. Program of heat treatment.

in belite. Taking this into account, we can evaluate the content of anhydrite as being approximately 5%.

Another situation is in clinker 2. The SEM observation of this clinker revealed only frequent appearance of calcium langbeinite (Fig. 3). No anhydrite crystals were found.

Taking into account that K_2O content in clinker 2 was 0.34% and assuming that the majority of it forms calcium langbeinite we have 1.6% of this phase. As in the previous case of clinker 1, we have high content of sulphate in belite. Taking the same value, we have 0.4% of SO_3 and in calcium langbeinite about 1% than the remaining SO_3 is about 1%. It should be in the form of anhydrite, which was confirmed by XRD of a sample after dissolution of silicate phases in maleic acid.

From clinkers 1 and 2, five cements were obtained, each ground to the specific surface of about 400 m^2/kg. The compositions of these cements were as follows:

1 — clinker 1 without additions,
1-NS — clinker 1 + 2% Na_2SO_4,
1-N — clinker 1 + 0.87% of Na_2O as NaOH,
2 — clinker 2 without additions,
2-NS — clinker 2 + 2% Na_2SO_4

The sodium equivalent of these cements as well as SO_3 content and ratios of SO_3 to Na_2O_e and to Al_2O_3 were calculated (Table 3).

From these cements, the mortars were prepared according to the European Standard EN-196-1. The mortars were cast in the form of standard bars of the dimension 4 × 4 × 16 cm. These mortars bars were cured for 2 h in humid conditions (100% RH) and then subjected to heat treatment at 90 °C. The heat treatment program is shown in Fig. 4. After heat treatment, all samples were cured in water at 20 °C.

3. Methods

The change of linear dimension of mortar bars were measured according to Graf-Kaufmann method.

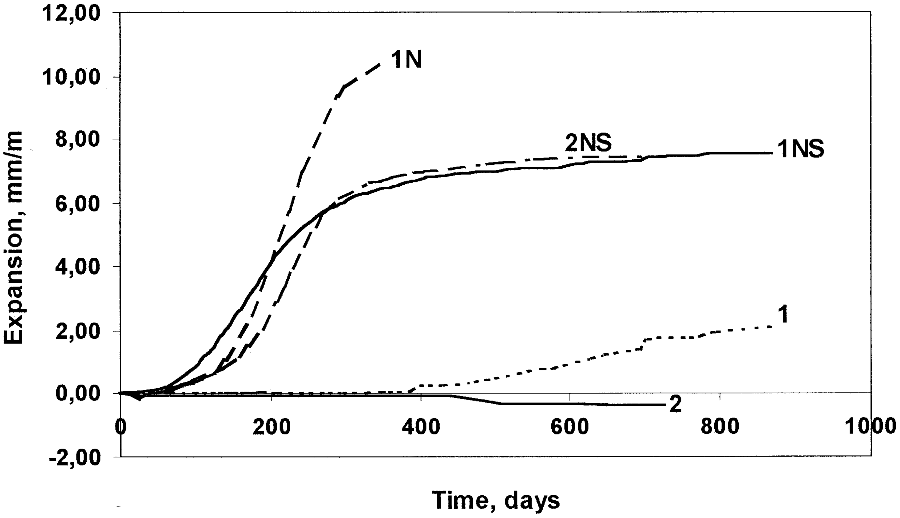

Fig. 5. Expansion curves of the mortars.

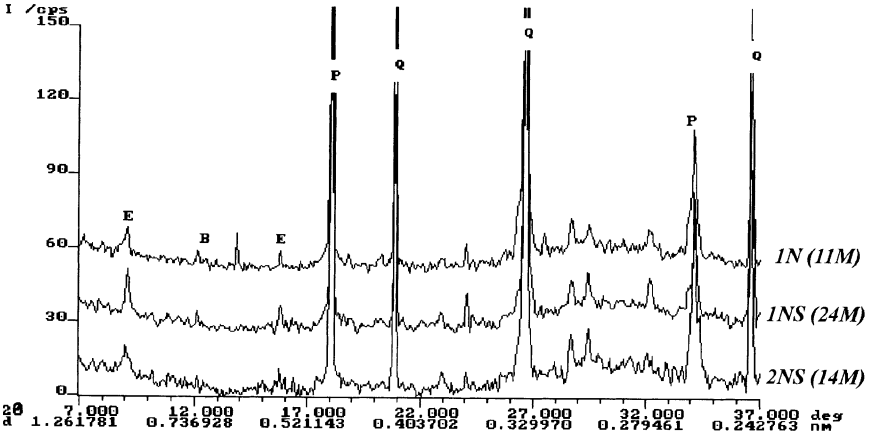

Fig. 6. XRD patterns of the mortars, M = months.

SEM was applied for the examination of the polished section of the mortars.

Finally, XRD was used for mortars examination. The samples were prepared by grinding in an agate mortar and sieving of the sand fraction larger than 40 μm.

4. Results and discussion

As it is shown in Fig. 5, four mortars presented expansion. Only the mortar of cement 2 did not undergo expansion after 700 days of curing in water. The largest expansion — about 10 mm/m — was shown by the mortar of cement 1 N. This expansion started already after about 50 days of water curing. The expansion in case of the mortar of cement 1 NS is smaller, amounting to about 7 mm/m and the steep increase of expansion tampered off after about 250 days. The expansion of mortar 1 started only after about 400 days but the increase in length of the bars was very slow and after 900 days reached only about 2 mm/m.

In all expanding mortars, the presence of ettringite was confirmed by XRD method (Fig. 6).

The examination of the polished section of the mortar 1 NS under SEM revealed a few rims of massive ettringite around the sand grains. However, numerous conglomerates of big ettringite crystals were found in cement gel (Fig. 7). One may also see some microcracks inside the C–S–H dark gel, very similar to the ones described by Yang [25] (Fig. 8).

It is evident that very small ettringite crystals must have been formed in the C–S–H matrix during water curing. It seems that the Scrivener [4] hypothesis is much more probable because this C–S–H phase is formed in the space occupied previously by silicates and not in the volume previously filled with water. Contrary to Scrivener [4], the hypothesis by Famy [9] claims that the small ettringite crystals are formed in outer C–S–H phase in the space occupied previously by water. But from our observation of mortar 1 NS it is evident that it is not the case.

In mortar of cement 2 NS the situation is different. There are numerous bands of massive ettringite around the sand

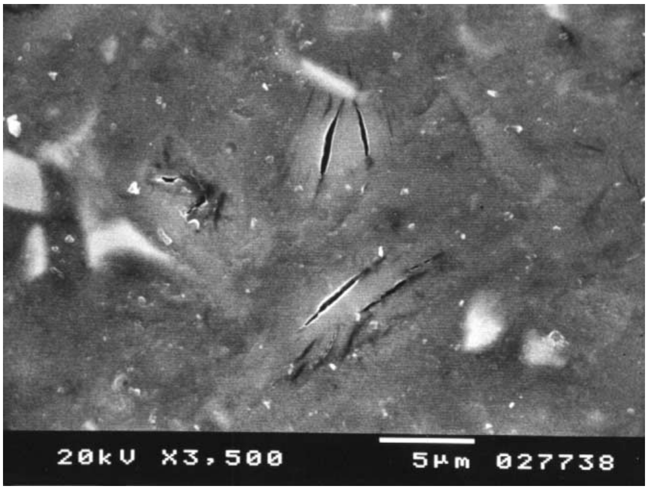

Fig. 7. Big ettringite crystals in cement gel of mortar 1 NS.

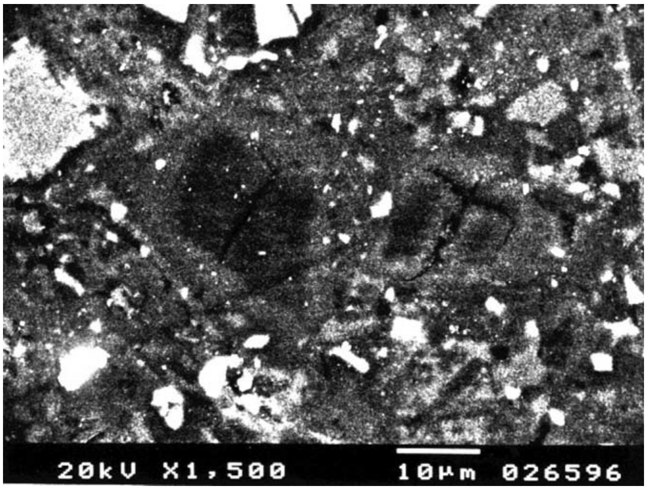

Fig. 8. Dark cracked C–S–H phase in mortar 1 NS.

grains (Fig. 9). The microcracks are going from these bands in the direction of cement gel (Fig. 10).

This situation seems to prove that the massive ettringite must, at least partially, contributes to the expansion. A similar view has been expressed by Yang and co-authors [25,26].

From the examination of the mortars, some further conclusions can be drawn. Firstly, the expansion of mortars obtained from cement of series 1 shows that the tricalcium aluminate content cannot play the decisive role in expansion. Cement 1 contained only 3% of C_3A and relatively high content of brownmillerite, namely 14% (Table 2). It appears that brownmillerite can also participate in DEF. These results are in disagreement with Kelham [7] who claims that sulphate resisting cement does not give expansion.

In case of cements of series 1, the main reason of DEF is anhydrite probably present as inclusions in belite crystals. In this case, the expansion takes place independently of the Na_2O_e value, which is very low for cement 1. However, the expansion takes place late and is very small. The examination of this mortar is continued. The increase of Na_2O_e content (cement 1 N) drastically accelerates the start of expansion and increases its value. It is probable that addition of sodium accelerates the hydration of belite thus participating in the quicker sulphate release during water curing of mortars. The increase of SO_3 (cement 1 NS) does not change very much the situation and the expansion is smaller. Finally, it is evident that the anhydrite expansion occurs in a different manner than that caused by gypsum. The expansion of mortar 1 takes place independently of a very high SO_3/Na_2O_e molar ratio (Table 3), which, according to Glasser's [27] calculations, should give the stability of ettringite during heat treatment.

In clinker 2, no anhydrite inclusions in belite were found, presenting no expansion till 560 days of water curing. However, the addition of 2% of Na_2SO_4, which caused the increase of Na_2O_e to about 1.2% resulted in quick expansion, very similar to the mortar of cement 1 NS.

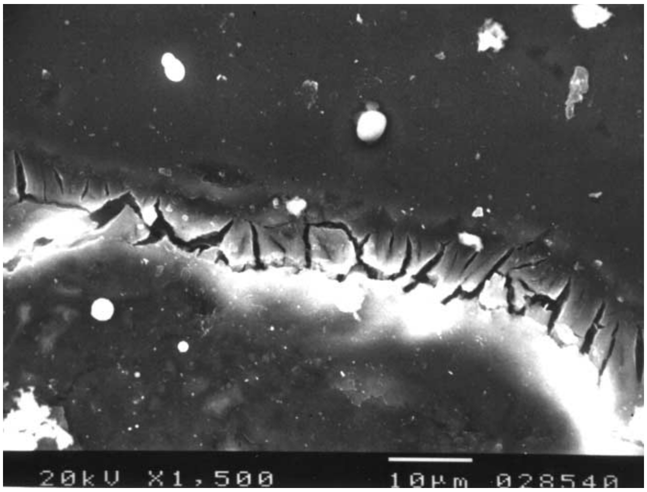

Fig. 9. Bands of massive ettringite around sand grains in mortar 2NS.

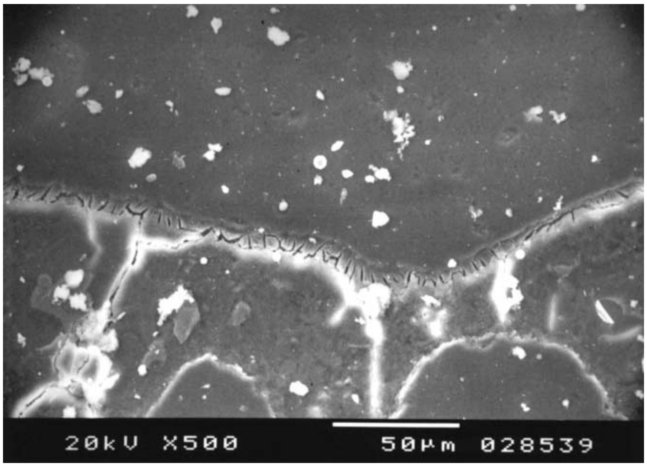

Fig. 10. Microcracks in mortar 2 NS.

The absence of expansion of mortar 2 can be linked with relatively low SO_3/Al_2O_3 molar ratio which is close to 1 (Table 3).

Based on the observations made by the SEM examination of the polished section of the mortar, one may conclude that there are at least two mechanisms to cause the expansion. Firstly, formation of massive ettringite around sand grains and in cement gel matrix. In the last case, one cannot exclude the fact that they are probably formed in the space previously occupied by anhydrite. Secondly, small ettringite crystals are formed inside the darker C–S–H phase, developed during water curing of the mortar. This mechanism seems to be in agreement with Scrivener's [4] hypothesis.

5. Conclusions

From the presented experiments, the following conclusions can be drawn.

1. Anhydrite, when present in belite-rich (33% belite) and high-sulphate clinkers (SO_3/Na_2O_e molar ratio = 9) can form inclusions in belite. Such anhydrite can be the source of DEF expansion after heat treatment of the mortar at 90 °C, although such a composition is not very typical of the industrially produced clinkers.
2. DEF caused by anhydrite can occur in cements poor in alkalis ($Na_2O_e = 0.31$).
3. Higher alkali content accelerates and increases the expansion in cement from anhydrite containing clinkers.
4. DEF can occur in cements poor in C_3A but rich in C_4AF.

Acknowledgments

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