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Effect of SO_3 content and fineness on the rate of delayed ettringite formation in heat cured Portland cement mortars

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Abstract

This paper presents the findings of a long-term study on the expansion rate and microstructure of heat cured cement mortars. For this purpose, cements with different fineness and SO_3 contents were produced by using the same clinker. Different mortar specimens were prepared and subjected to heat curing. Length changes of specimens were measured within a period of 540 days. The microstructures of young (2 day after heat curing) and old (1.5 years after heat curing) specimens were also investigated by SEM and EDS analysis. The expansion rates and microstructures observed were compared with the control specimens.

Results showed that, at the initial stages of testing (2–3 months), expansion rates of heat cured mortars prepared with finer cements were less than those prepared with coarser cements. However, in the long term, the rate of expansion of mortars prepared with finer cements exceeded the coarser ones' expansion values. This result may be attributed to the different hydration characteristics and pore structure of heat cured mortars including cements of different fineness.

Keywords: Delayed ettringite formation; Blaine fineness; SO_3 content; Expansion; Early strength

1. Introduction

It is generally accepted that ettringite formation in fresh mortar or concrete can be partly or completely destroyed when exposed to temperatures over 70 °C. Subsequently, ettringite may reform in the hardened state within a humid environment. In parallel with this reformation, a general expansion of the mortar or concrete is often observed. This phenomenon is referred to as "delayed ettringite formation" (DEF) [1]. This destructive reaction occurs months or years after placement in an environment where the concrete is frequently or continually exposed to moisture. It should be noted that, researchers disagree on whether DEF necessarily involves heat curing, that is, when concrete is steam cured or cast in hot weather [2].

Investigators evaluated numerous factors believed to influence the occurrence of DEF [2]. The evaluations included examining Portland cement specimens that have been produced with cements of different chemical composition [3–9] and have been subjected to various curing regimes (time, temperature, and moisture conditions) [10–12], have been designed with different aggregate types [13–16], mineral additives [11,17] or have been treated with different chemicals [7,10,18].

Application of heat curing is beneficial for fabrication of precast products due to the accelerated strength development of concrete. It should be noted that, to achieve high early strengths, cement composition and physical characteristics may also be manipulated. However, the cement characteristics that promote the early strength, in particular high fineness, usually increases the DEF susceptibility of heat cured mortars in case of high curing temperatures and the presence of sufficient amounts of SO_3 and Al_2O_3 [19]. For example, DEF susceptibility of high early strength

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(ASTM Type III) cements can be attributed to their high fineness [20].

In this study, cements with various fineness and SO_3 contents were prepared from the same clinker and the effects of these parameters on time dependent expansion, and microstructural characteristics of heat cured and standard cured samples were investigated. In this respect, the other important parameters related with DEF, such as C_3A, eq. alkali and C_3S contents were kept almost constant by using the same clinker.

2. Experimental

2.1. Materials

Nine cement samples with different fineness and SO_3 contents were prepared by using the same clinker. Clinker and gypsum were grounded to desired fineness values by using a Bond mill. Gypsum was added so as to produce cements with 2.5% (L), 3.5% (M) and 4.5% (H) of SO_3 content. The grinding times were arranged to obtain Blaine fineness values of 300, 400 and 500 m^2/kg, respectively. The chemical analysis, physical properties and compound compositions of cements are presented in Tables 1 and 2. Crushed limestone sand which was in conformity with EN 12620 [21] standard was used. De-ionised water was used in all mixes.

2.2. Mortar preparation and curing procedures

Mortars were prepared at a constant water/cement ratio of 0.44 and sand/cement ratio of 2.5. Fresh mortars were tested by using a flow table conforming ASTM C230 [22] standard. The flow diameters of mortars were within the range of 128–135 mm. Mortars were cast in 25 × 25 × 285 mm molds with stainless steel studs in their end faces. Four prisms were prepared for each mortar mix. Half of the specimens were standard cured in water at 20 °C. In order to investigate the DEF potential, the other half of the specimens were subjected to heat curing regime described by Grabowski et al. [23]. After a pre-curing period of 2 h at 20 °C, the temperature was increased at a rate of 25 °C/h up to the required maximum temperature (85 °C) which was maintained for 4 h. Cooling rate was also 20 °C/h. All prisms were demolded after 24 h. The method of Grabowski et al. [23] describes series of wetting and drying periods after heat curing. After 3 days of waiting period in de-ionised water, specimens were subjected to three cycles of drying and wetting. Any procedure that weakens the material will lower its ability to resist expansion. Repeated heating and cooling may form microcracks due to thermal stresses. This will favour DEF since water will penetrate in more easily and it will also weaken the paste-aggregate bonds [7]. The heat cycle described by Grabowski et al. [23] has a primary role in initiating and

Table 1
The basic oxide compounds of cements (%)

Label	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	Free lime	Loss on ignition	Insoluble residue
L/300	63.76	20.22	5.25	2.72	2.40	0.40	1.07	2.45	1.04	1.23	0.21
M/300	63.40	19.88	5.03	2.70	2.35	0.40	1.06	3.52	0.92	1.64	0.15
H/300	62.42	19.54	5.15	2.70	2.35	0.40	1.04	4.45	1.07	1.92	0.27
L/400	63.58	20.25	5.26	2.75	2.39	0.40	1.07	2.43	0.94	1.36	0.19
M/400	62.78	19.76	5.28	2.70	2.40	0.40	1.05	3.53	1.04	1.72	0.32
H/400	62.45	19.34	4.80	2.66	2.23	0.40	1.03	4.45	1.01	2.19	0.12
L/500	63.81	20.24	5.17	2.75	2.34	0.40	1.08	2.53	1.27	1.40	0.16
M/500	63.05	19.86	5.21	2.72	2.37	0.40	1.06	3.43	1.04	1.67	0.11
H/500	62.09	19.32	5.19	2.66	2.36	0.40	1.02	4.51	1.25	2.03	0.10

Table 2
The Bogue major compounds and other properties

Label	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	SM[a]	AM[b]	LSF[c]	Blaine SSA (m^2/kg)
L/300	58.5	10.2	9.3	8.3	2.54	1.93	98.7	304
M/300	58.1	9.6	8.8	8.2	2.57	1.86	100.1	304
H/300	53.3	12.3	9.1	8.2	2.49	1.91	99.8	307
L/400	57.5	11.0	9.3	8.4	2.53	1.91	98.3	402
M/400	54.8	11.7	9.4	8.2	2.48	1.96	99.2	402
H/400	57.4	8.7	8.2	8.1	2.59	1.80	101.5	405
L/500	58.9	10.0	9.1	8.4	2.56	1.88	98.8	501
M/500	55.9	11.2	9.2	8.3	2.50	1.92	99.3	508
H/500	53.2	11.8	9.3	8.1	2.46	1.95	100.2	535

[a] Silicate modulus: $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$.

[b] Alumina modulus: $\frac{Al_2O_3}{Fe_2O_3}$.

[c] Lime saturation factor: $\frac{CaO}{2.80SiO_2+1.18Al_2O_3+0.65Fe_2O_3} \times 100$.

accelerating the resulting expansion [10]. Finally, the specimens were stored in water at 20 °C. Lengths of specimens were measured for a period of 1.5 years. The results were recorded as an average of two mortar bar specimens. In addition to the mortar bar specimens, 50 mm mortar cube specimens were prepared from each mix. After the first day, mortar cubes were demolded and cured in water until the day of testing. The 2, 7 and 28 days compressive strengths were determined.

3. Results and discussion

3.1. Expansion rate–time relationship

In discussing the expansion results, it is obvious that a consistent and easily recalled nomenclature is needed to facilitate the comparisons. Accordingly, each mortar series has been described by a three-component code designation: the letter reflecting the curing history, as heat cured (H) or standard cured (S), followed by the letter L, M, or H reflecting SO_3 contents 2.5% low, 3.5% medium and 4.5% high, and, finally, a third component of numbers designating the fineness of cements in m^2/kg. For example, a mortar bar prepared with a SO_3 content of 3.5% and SSA of 500 m^2/kg subjected to heat curing is coded as: HM/500.

Figs. 1 and 2 provide the expansion vs. time data for the standard cured and heat cured specimens. As can be expected, mortars cured at 20 °C gave no significant expansion while the 85 °C cured mortars expanded at different rates as a function of time. Also, the expansion values after 540 days for heat cured specimens with low SO_3 content and low fineness were lower than those with higher SO_3 content and greater fineness. On the other hand, the highest expansions were derived from the mortar bars prepared with the highest SO_3 ratio (4.5%) in the order of HH/500, HH/400 and HH/300, respectively. However, when

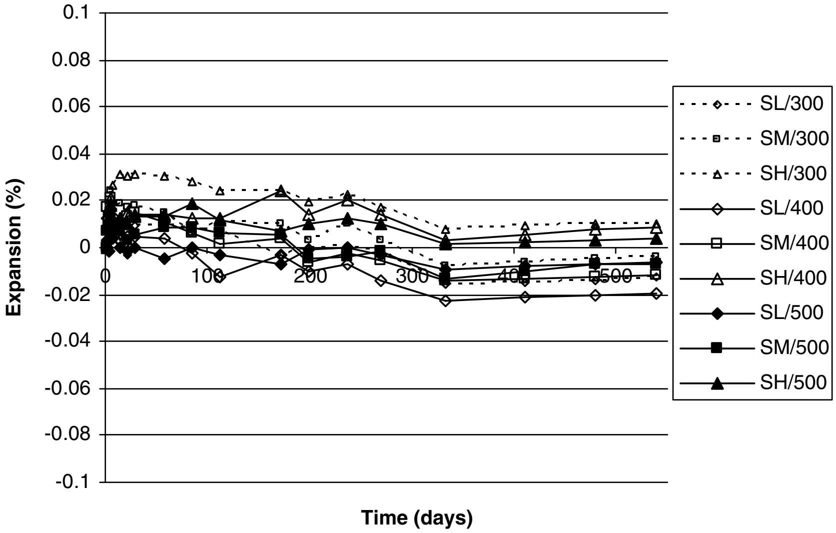

Fig. 1. The expansion vs. time data for the standard cured specimens.

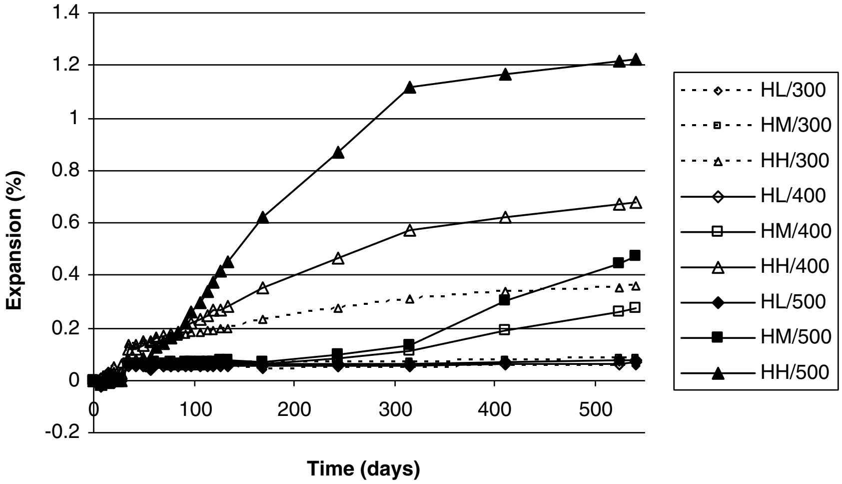

Fig. 2. The expansion vs. time data for the heat cured specimens.

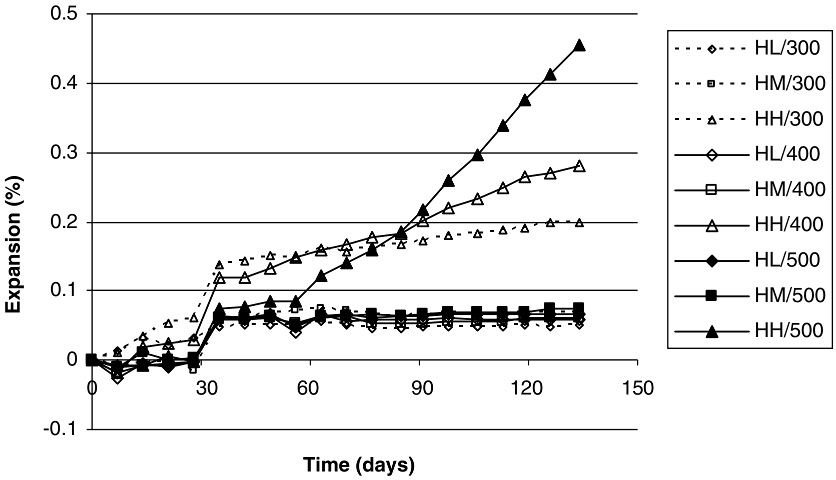

Fig. 3. The expansion vs. time data for the heat cured specimens at 150 days.

expansion rates for the first two months are examined (Fig. 3), it may be observed that the highest expansions were measured in the reverse order of HH/300, HH/400 and HH/500, respectively. After the initial rapid expansion, continued water storage gave further slow expansion rate for the mortar bars prepared with coarser cements. It is suggested that; for early ages, the coarser cement propagated the expansion due to the rapid formation of ettringite on the surface of unhydrated cement particles (the high permeability of mortar at this stage supplies the water needed for ettringite formation) and at later ages, the rate of formation of ettringite tends to slow down due to the difficulties of penetration of water into the deeper regions of unhydrated cement. Inner regions of coarse unhydrated cement slowly react with water and the initial pore structures of mortars prepared with coarser cement are more porous which relieves most of the expansion.

In case of higher fineness, initial transport of moisture was very low due to the relatively dense paste structure, low porosity and fine-pored microstructure. However, the slow penetration of water into the matrix phase in a long period of time began to propagate the ettringite formation when the conditions are ready (supersaturation of pore water and matrix phase with water, SO_3 and Al_2O_3 and alkalis). This delayed reaction results in a quick and deleterious expansion. Both the expansion measurements and SEM investigations (to be discussed in the subsequent section) confirmed these results.

3.2. Expansion rate–fineness–SO_3 content relationship

Both the chemical composition and fineness are important factors affecting the DEF related expansion. Lawrence [5] studied the expansion behavior of 55 Portland cements of different chemical composition and SSA subjected to heat curing. The correlation coefficients between expansion and SSA were quite low due to the difference between chemical compositions.

Figs. 4 and 5 show the dependence of the early age expansion (90 days) and ultimate expansion (540 days) of mortars cured at 85 °C on the SO_3 content and the specific surface area of cement prepared. Note that, standard cured mortars (Fig. 1) with the same cements showed no expansion at 540 days. From Fig. 5, it can be seen that for all SO_3

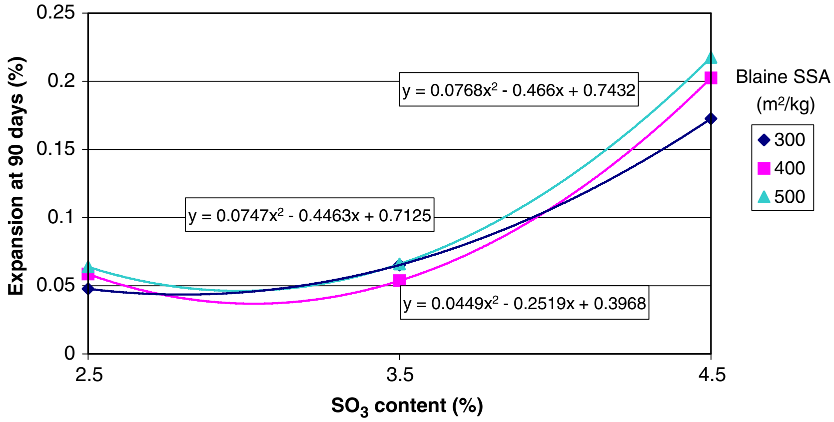

Fig. 4. Relationship of early age expansion values (90 days) of mortars cured at 85 °C on the SO_3 content and the specific surface area of cement.

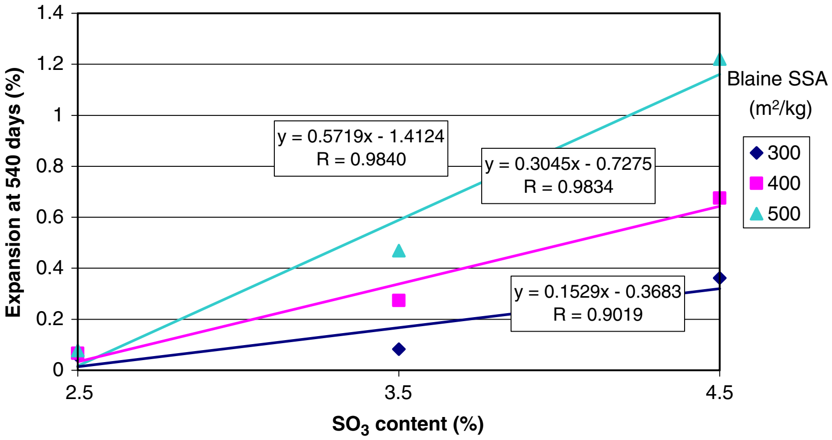

Fig. 5. Relationship of the ultimate expansion values (540 days) of mortars cured at 85 °C on the SO_3 content and the specific surface area of cement.

ratios, where ultimate expansion takes place, an increase in the specific surface area gives an increase in ultimate expansion (Fig. 5). However, in the short term, the effect of specific surface area is not significant (Fig. 4).

High SO_3 and C_3A content in cement and the increase of the molar ratio of SO_3 to Al_2O_3 have been considered to be the important compositional factors in DEF susceptibility of cements [8,19,24–28]. However, later research carried out by different researchers under different experimental conditions did not find this increasing tendency to progressively higher expansions with increased SO_3/Al_2O_3 molar ratios. They found that expansion values were highest for specimens made from cements in which this ratio was close to a pessimum value. Cements with molar ratios higher than this showed reduced expansion levels [23,7]. The presence of pessima depends on the formation mechanism of ettringite. If ettringite forms in such a way as to cause expansion, there are various pessima. If there is too much SO_3, ettringite and not monosulfate will be present at the end of the heat treatment. If there is no Al_2O_3, there can again be no ettringite, and if there is too much, monosulfate and not ettringite will be present after storage. The pessimum SO_3 is likely to increase with the content of Al_2O_3, which produces a pessimum in the SO_3/Al_2O_3 ratio. Some researchers were also reported that there may be a pessimum but it cannot be generalized to all cements or curing cycles [7].

While SO_3/Al_2O_3 molar ratio is indeed an important compositional factor in predicting the extent of DEF-induced expansion, other compositional factors may intervene and limit or prevent expansion even if the SO_3/Al_2O_3 molar ratio is in the expansive range [24]. Thus, they concluded that, such compositional factors may include the actual SO_3 content, the C_3A content (a separate consideration from the Al_2O_3 content since in different cements, varying proportions of the Al_2O_3 are tied up as C_4AF) and especially the cement alkali content. They finally proposed a "DEF index," which is a joint function of the SO_3/Al_2O_3 molar ratio and two other components that relate to expansive potential. One of these is the combined content of SO_3 and C_3A in the cement. Clearly, even if the ratio of SO_3 to Al_2O_3 is in the right range, if little SO_3 is in fact present, or if much of the Al_2O_3 is tied up as C_4AF, only little ettringite is likely to be formed. Zhang et al. [24] also noted that, although the fineness of the cement also played an important role, the effect of fineness was specifically excluded in their study. The DEF index proposed is defined by the following equation:

$$\text{DEF index} = (SO_3/Al_2O_3)_m \times [(SO_3 + C_3A)_w/10] \times \sqrt{Na_2O_{eq}} \qquad (1)$$

where $(SO_3/Al_2O_3)_m$ is the molar ratio of SO_3 to Al_2O_3 of the cement; $(SO_3 + C_3A)_w$ is the combined weight percentage of SO_3 and Bogue-calculated C_3A in the cement; and $\sqrt{Na_2O_{eq}}$ is the square root of the weight percentage of Na_2O_{eq} in the cement.

Zhang et al. [24] showed that, the heat cured mortars made from two of the six "oversulfated" cements failed to expand. Of these, one had an extremely low alkali content, the other an extremely low C_3A content. Presumably, high alkali contents and appreciable C_3A contents are also required for the development of DEF. A more comprehensive study on predicting the possible expansion from the chemical composition and fineness was carried out by Kelham [19]. The expansion at 90 °C is defined by the following equation:

$$\begin{aligned}\text{Expansion at } 90\,^\circ\text{C} = {} & 0.00474 \times \text{SSA} + 0.0768 \\ & \times MgO + 0.217 \times C_3A \\ & + 0.0942 \times C_3S \\ & + 1.267 Na_2O_{eq} - 0.737 \\ & \times \text{abs}(SO_3 - 3.7 - 1.02 \\ & \times Na_2O_{eq}) - 10.1 \qquad (2)\end{aligned}$$

The SO_3/Al_2O_3 and $(SO_3)^2/Al_2O_3$ ratios of the cements produced in this study and the 540 days of expansion of mortars prepared with these cements are listed in Table 3. The Al_2O_3 ratios of all cements were approximately

Table 3
The SO_3/Al_2O_3 and $(SO_3)^2/Al_2O_3$ ratios of cements employed and 540 days expansions of heat cured mortars prepared in this study

Sample number	Expansions at 540 days (%)	SO_3/Al_2O_3	$(SO_3)^2/Al_2O_3$
HL/300	0.056	0.47	1.14
HM/300	0.082	0.70	2.46
HH/300	0.362	0.86	3.85
HL/400	0.066	0.46	1.12
HM/400	0.273	0.67	2.36
HH/400	0.675	0.93	4.13
HL/500	0.077	0.49	1.24
HM/500	0.470	0.66	2.26
HH/500	1.220	0.87	3.92

constant and the SO_3/Al_2O_3 and $(SO_3)^2/Al_2O_3$ ratios increase with SO_3 content. In the literature, molar ratios of SO_3/Al_2O_3 between 0.85 and 1.4 fall into expansive range [24], while the critical value was found as 2 for the expression of $(SO_3)^2/Al_2O_3$ [19]. The 540 days expansion values confirmed that both the SO_3/Al_2O_3 and $(SO_3)^2/Al_2O_3$ ratios are not sufficient to advocate an independent relationship between these ratios and expansion. For example, while the SO_3/Al_2O_3 and $(SO_3)^2/Al_2O_3$ ratios were approximately the same for HH/300, HH/400 and HH/500 series, the expansion values measured were quite different. The HH/500 samples expanded three times more than HH/300 mortars.

DEF indices according to Zhang et al.'s [24] equation and expansion at 90 °C (in this study very similar – 85 °C) according to Kelham's equation [19] were calculated with the cements used in this study. The measured expansions were plotted in Fig. 6(a) and (b), respectively. It was realized that due to the absence of fineness factor in DEF index proposed by Zhang, the correlation coefficient of the relationship with the measured expansions were lower when compared with correlation between Kelham expansion. Kelham expansions measured were usually negative which indicates shrinkage. However, all measured values indicate expansion.

It should be noted that, the temperature of heat cure is also critical. Yang and Sharp [27,28] in their comprehensive study found that ettringite present in mortars immediately after a short term cure at 60 °C, subsequently convert to monosulfate at 85 °C and hydrogarnet at above 85 °C. If hydrogarnet is formed, it is stable to subsequent sulfate attack, but increases the SO_3/Al_2O_3 ratio in the pore water to favour DEF.

All the above mentioned comparison efforts have revealed that, it is possible to predict the expansion rate and amount for a given heat curing temperature of a mortar prepared with a cement having specific chemical composition and fineness. However, the relation cannot be generalized for other cements. Only expansion potential can be predicted. It can be concluded that, if the predicted expansions according to Kelham's [19] equation are positive, mortars prepared with these cements may be regarded as potentially expansive.

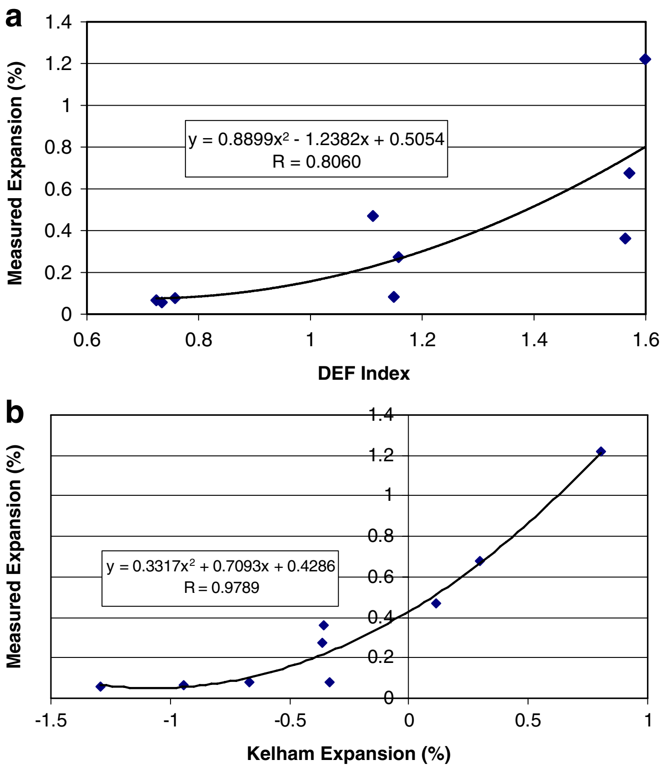

Fig. 6. The 540 days measured expansions vs. (a) DEF index [24], (b) Kelham [19] expansion (%) of heat cured mortars.

3.3. Relationship between expansion and early strength

Increasing the fineness significantly increased the early strengths as expected. The main factors which have been identified as increasing expansions [SSA, alkali, SO_3 (up to optimum value) and C_3A] are also recognized as factors which increase early strengths [12,19]. Figs. 7 and 8 show the early age (90 days) and long term (540 days) expansion data of heat cured mortars at 85 °C plotted against 2 days mortar strength cured at 20 °C. From the figures it can be said that, increasing the fineness of cement or decreasing the content of SO_3 tended to increase early strength. The former is valid. In general, increase in SO_3 content,

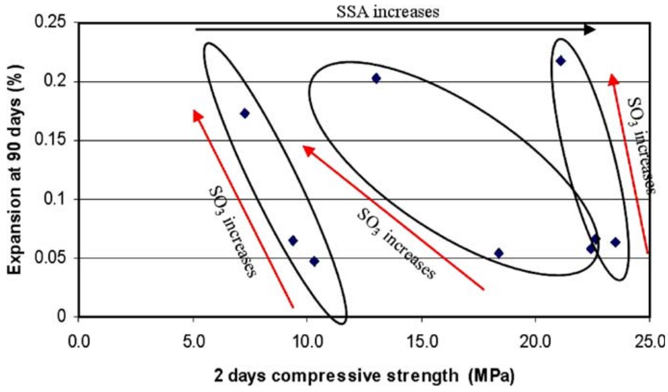

Fig. 7. The effect of fineness and SO_3 content on the relationship between early age strength and expansion at 90 days.

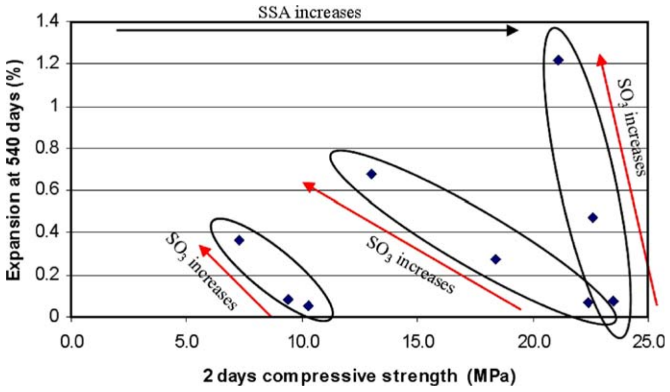

Fig. 8. The effect of fineness and SO_3 content on the relationship between early age strength and expansion at 540 days.

increases the early age strength up to an optimum value. However, in this study, increase in SO_3 content decreased the 2 days compressive strengths. This unexpected result can be attributed to the lower optimum SO_3 content of the cements prepared. On the contrary, the 28 days compressive strengths were higher for mortars prepared with cements of high SO_3 content at the same fineness (Fig. 9).

The mechanism of relationship between early strength and expansion can be explained as follows: during the early hydration of cement at ordinary temperatures substantial amounts of ettringite can be formed. Due to the plastic nature of fresh paste, the hazardous effect of expansion is eliminated. However, in case of DEF, the material has hardened before the ettringite formation begins. Expansion also depends on the characteristics of the pore space. At initial period of DEF, ettringite deposited in freely available space and does not contribute expansion. For this reason, the amount of ettringite formed may not indicate any expansion at this period. The length of this period depends on the pore structure and permeability of mortar. A given amount of ettringite will produce more expansion if the pores in which it is deposited are small and poorly connected then if they are large and more highly connected. In other words, lower permeability may increase the long term susceptibility of heat cured mortars to DEF. So, one would expect the expansion from DEF to increase with the degree of hydration at the end of the heat treatment, since this decreases the volume, size, and connectivity of the capillary pores. The degree of hydration also correlates with the compressive strengths. One would therefore expect that increasing fineness both increase the early strength and ultimate expansion from DEF.

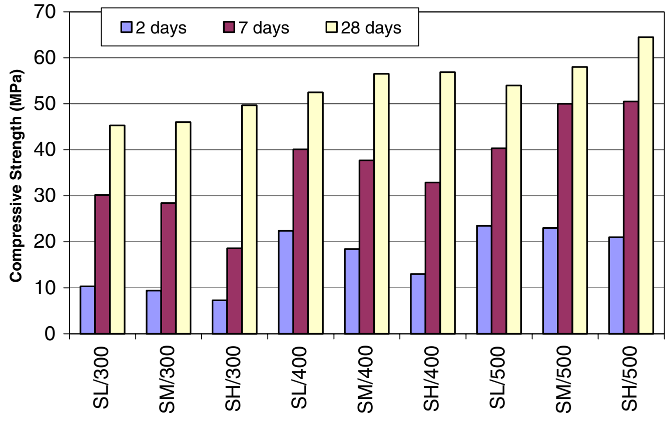

Fig. 9. Compressive strength development of standard cured mortars.

4. Microstructural investigations

4.1. Sample preparation

For all cement types, prismatic specimens of 50 × 50 × 25 mm were prepared and the same curing process was applied. SEM specimens were prepared by fracturing the specimens. The fractured surfaces are perfect for showing crystals of DEF in paste, voids or aggregate paste interfaces [29]. Fractured surfaces will also expose the weakest sections, the most affected areas from any kind of deterioration. Specimens were dried in an oven at 50 °C for 1 day before vacuuming and gold coating. In order to investigate the morphology of fractured surfaces in three dimensions, the electron micrographs were obtained by using low-energy secondary electrons (SE). A beam of electrons with an accelerating voltage of 20 kV was applied. Additionally, the EDS spectrums of specific points notated on the micrographs were analyzed (Figs. 10–12).

4.2. SEM analysis of heat cured and standard cured mortars

For SEM investigations, specimens were selected from the heat cured mortars of highest fineness with highest SO_3 content (HH/500: 1.22% at 540 days) and the lowest fineness with highest SO_3 content (HH/300: 0.36% at 540 days). Additionally, for comparison purpose, standard cured mortars of the same cements were also investigated (SH/500 and SH/300, respectively). All mortars were studied at early age (2 days) and at 540 days of hydration. The notation was an addition of Y (young) for early age and O (old) for later age investigations.

4.2.1. SEM studies of HH/500-Y mortar

Heat curing has an important influence on the stability of ettringite during hydration at high temperatures. The rapid formation of C–S–H due to heat curing reduces ettringite stability by acting as a sink for aluminate (through substitution of silicate) and for sulfate (through adsorption) [7,19]. On the other hand, due to higher stability of monosulfate at higher temperatures ettringite decomposes and monosulfate begins to form. Microstructural investigations of HH/500-Y mortar have shown that, normal finely divided ettringite within the paste microstructure was largely destroyed during heat cure. High amounts of monosulfate formation were observed on the matrix phase of cracked surface of mortar (Fig. 10). The EDS analysis of

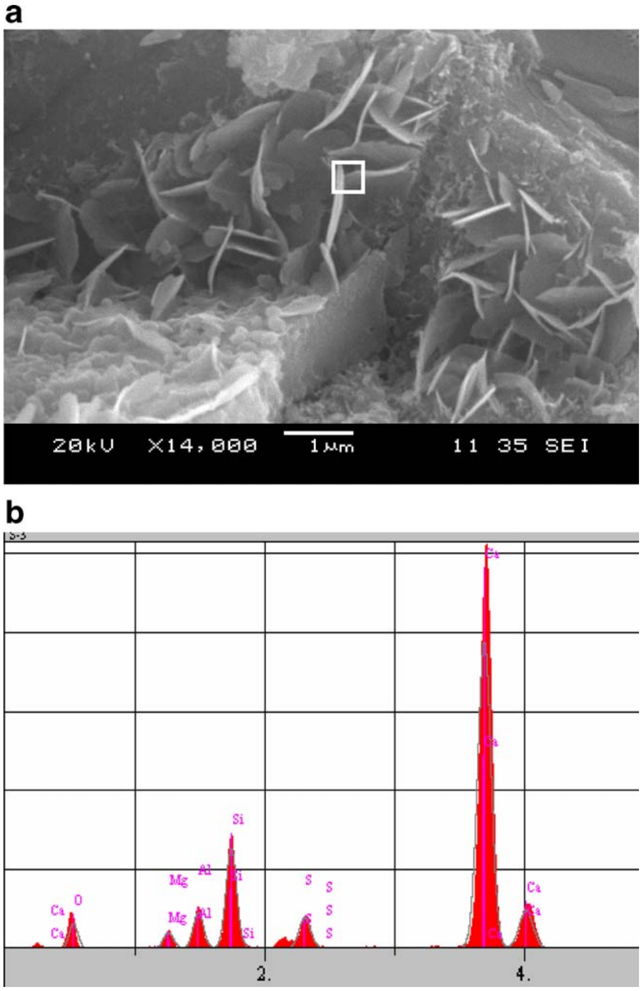

Fig. 10. (a) Micrograph of monosulfate formation in young HH/500 mortar 2 days after heat curing, (b) EDS spectrum of the notated rectangular in (a).

notated rectangular on Fig. 10 confirmed that these formations were either monosulfate or monosulfate-like materials with Si peak in their EDS spectra. Note that, some Si may form in EDS spectra. This may be due to the fact that monosulfate crystals form perpendicular to the cracked surface and the secondary electrons collected may be reflected from the bottom which includes some Si element. The selection of EDS was due to the hardness of detection of monosulfate in XRD pattern [30–33]. Due to the amorphous, poorly-crystalline structure of monosulfate the XRD data do not exhibit very strong diffraction peaks [31]. Dehydration or relative humidity during powder preparation also create many problems with identification of monosulfate peaks (confusion with ettringite) [32].

4.2.2. SEM studies of HH/500-O mortar

Severe cracking and prominent delayed ettringite formation (DEF)-induced expansions were observed in HH/500-O mortar bars. As expected, when compared with HH/500-Y (the same mortar at 2 days) no monosulfate was detected. Due to the instability of monosulfate at room temperature, decomposition takes place and the delayed formation of ettringite in aged concrete typically was detected both in pores and matrix phase. Additionally, large amounts of sulfate and aluminate may slowly release

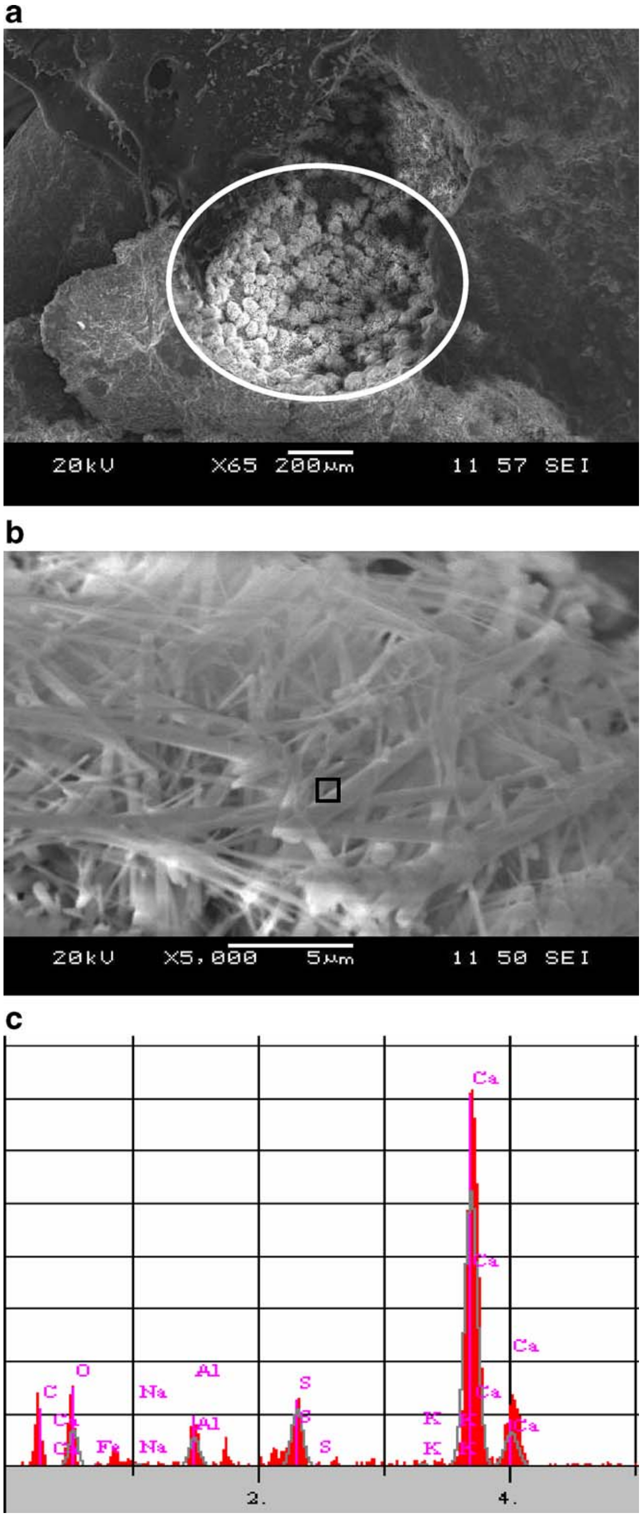

Fig. 11. Micrographs of HH/500-O mortar. (a) The ball type ettringite formation in large pores of HH/500-O mortar, (b) a close look to the rounded ettringite clusters generating ball ettringite, (c) EDS spectrum of the ball ettringite (notated rectangular in (b)).

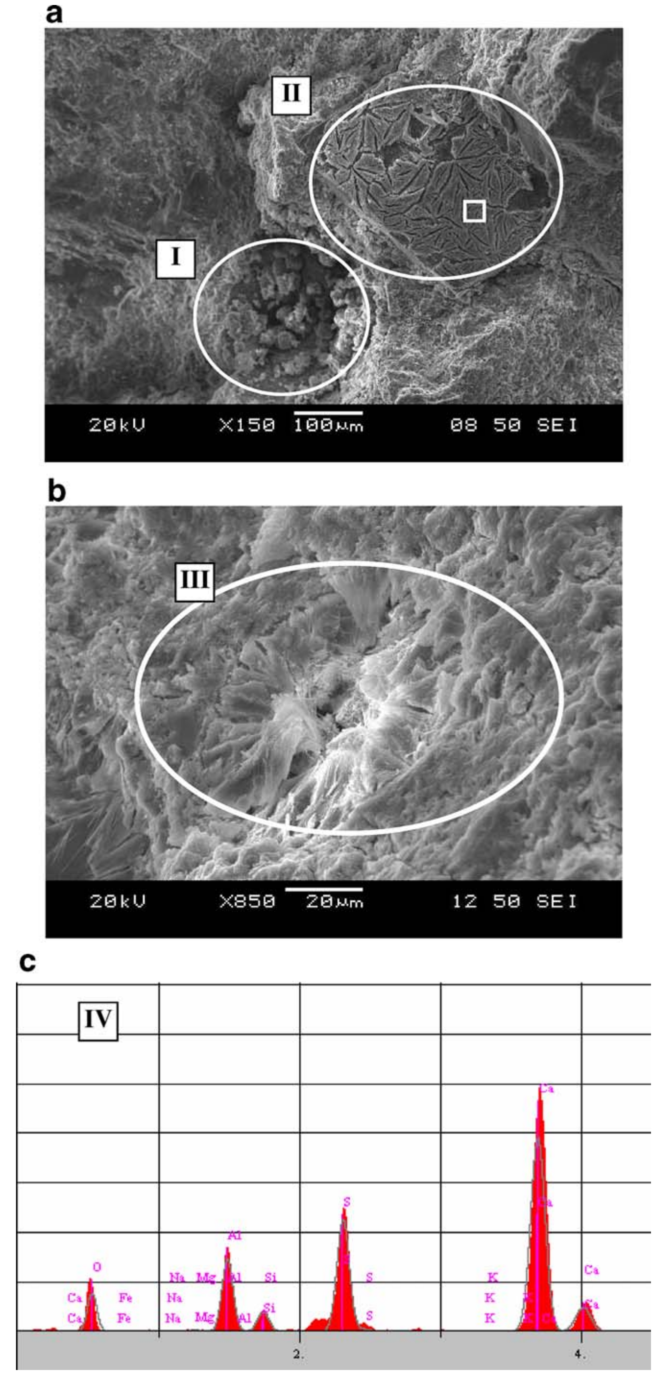

Fig. 12. Micrographs of HH/500-O mortar. (I) shows an air void containing balls of ettringite, which look as if they are composed of a jumble of fine needles, (II) shows a sand grain surrounded with an massive ettringite deposit, (III) massive deposits of ettringite can also be seen in very small air voids, (IV) EDS spectra of massive ettringite taken from (I) (region notated with rectangular).

from C–S–H; which is the result of significant increase of ettringite content [3,12]. In particular most of the large pores were completely or partially filled with rounded clusters of ettringite (Fig. 11(a) and (b)). The EDS spectrum of ball type ettringite is given in Fig. 11(c).

The expansion associated with the formation of a given amount of ettringite is influenced by the microstructure of the material. Ettringite in aged concrete typically forms in air and water voids, cracks and aggregate-paste interfaces. Ettringite morphology is directly dependent to the microstructure of paste phase. There are two types of ettringites with different morphologies identified in SEM analysis of HH/500-O mortar: ball type and massive ettringite. According to the place of formation, identified ettringites can be divided into three groups:

1. The occurrence of air voids containing "balls" of ettringite, which look as if they are composed of a jumble of fine needles (Fig. 12(I)). It is suggested that this ettringite was formed by a through-solution mechanism in which critical components are first made soluble and then reprecipitated [2]. It should be noted that the size of these pores is an important factor determining the ettringite formation mechanism. SEM observations revealed that in particular air voids whose diameter is greater than 100 μm usually contain ettringites of ball type morphology. Interestingly, Yan et al. [30] observed ettringite clusters on the fractured surface of dense paste.
2. Ettringite also can occur in fairly massive deposits on aggregates, such as sand grains or on matrix phase [34]. SEM micrographs showed individual sand grains containing "deposits" of massive ettringite needles (Fig. 12(II)). This type of occurrence seems to indicate that the ettringite was formed by a topochemical or solid-state reaction (that is, the ettringite formed in place on the sand grains) [2]. Collepardi [35] defines the massive ettringite as a gel-like mass in the cracks of the damaged structures.
3. Massive deposits of ettringite can also be seen in very small air voids, <100 μm (Fig. 12(III)).

Ettringite with "massive" morphology seems to form in narrow spaces, such as aggregate-paste interfaces, matrix phase or small pores; on the other hand "ball" type ettringite can form in large air voids.

Fig. 12(IV) shows the EDS spectra of massive ettringite taken from Fig. 12(II) (region notated with a rectangle). There was a difference between the EDS spectra of massive ettringite and ball ettringite from the view point of S content. The sulfur content of massive ettringite was much higher than that of ball ettringite. This may be due to the different ages of these ettringite formations. The older one seems to be massive ettringite and it captures more sulfur into its structure.

As previously mentioned by Yang and Sharp [27], ettringite crystals of identical composition and similar morphology may sometimes cause expansion and sometimes not, depending on the microstructure into which they are deposited [27,28].

From the microstructural point of view, two main hypotheses tries to explain the mechanism of expansion. One view is that; expansion is caused by the growth of the relatively large crystals that form at aggregate interfaces and elsewhere. The other is that is caused, or at least begins, with the growth of the much smaller crystals formed within the paste [7]. Both assumptions are valid, however, the magnitude of expansion depends on the ettringite saturation of the related regions which is a time dependent phenomena. In particular, matrix phase related expansion seems to start first due to the insufficient available space to fill. On the other hand, air void (in particular the coarser ones) related expansion seems to cause delayed expansion. This confirms the expansion reducing effect of pores as a safe field of ettringite formation without causing expansion. In this respect, cement fineness plays an important role both in reducing the pore size and increasing the reaction rate of DEF related cement compounds.

4.2.3. SEM studies of HH/300-Y mortar

Microstructural investigations of HH/300-Y mortar revealed that, monosulfate formation was rarely detected on the matrix phase of cracked surface. An example of monosulfate formation is given in micrograph in Fig. 13. When compared with HH/500-Y, significantly lower amounts of monosulfate formed which may be attributed to the fineness of H/300 cement. The entrapped C_3A in the unhydrated core of coarse cement seems to delay the reaction between SO_3 and reduce the amount of calcium sulfo aluminate phases present.

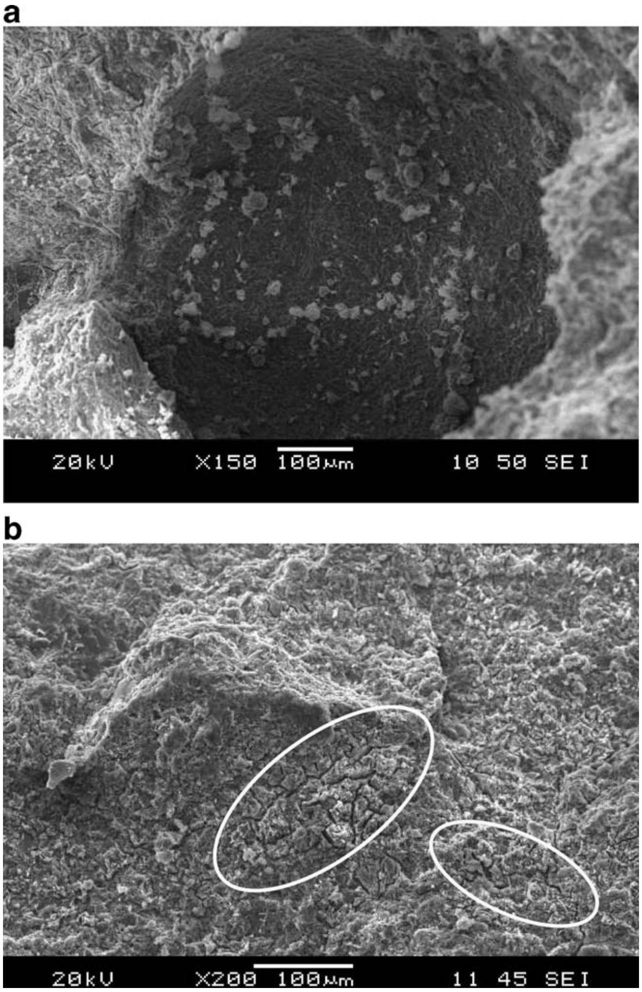

Fig. 14. Micrographs of HH/300-O mortar (pores–matrix phase).

4.2.4. SEM studies of HH/300-O mortar

The 540 days expansion value of HH/300 mortar bar was 0.36%. The representative micrographs of HH/300-O mortar are given in Fig. 14. The pores were occasionally filled with materials like ball ettringite (Fig. 14(a)), however the EDS analysis confirmed that these formations were not ettringite. They were identified as CH particles. On the other hand, some evidence of massive ettringite formation was detected in the matrix phase (Fig. 14(b)). When compared with HH/500-O, the amount of massive ettringite was lower. The ettringite formation responsible for expansion seems to be related with matrix phase massive ettringite rather than ball ettringite in pores. Investigations have revealed that, due to the reduction in fineness, the formation of ettringite in pores was slowed, most of the ettringite forms in matrix phase. The coarse nature of cement tends to reduce the leaching and penetration of sulfate to the available space (air voids, matrix, aggregate-paste interface).

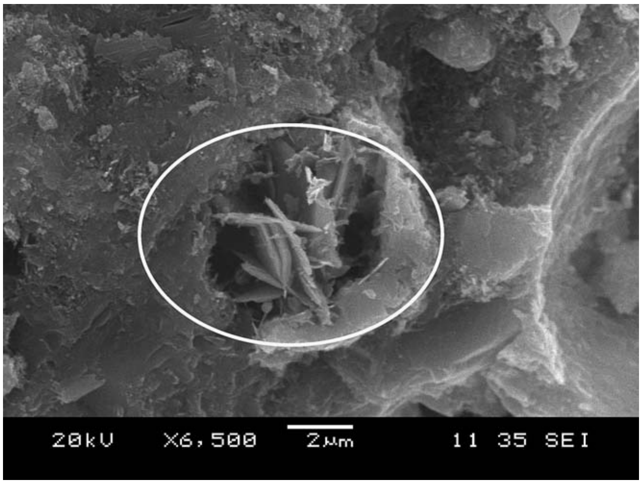

Fig. 13. Micrograph of HH/300-Y mortar (monosulfate formation at early age).

In order to study the influence of fineness on the size of ettringite crystals, comparative investigations were conducted on HH/500-O and HH/300-O samples. However, no significant difference was observed between the sizes of ettringite crystals as a function of fineness.

4.2.5. SEM analyses of standard cured mortars

As previously mentioned, no significant expansion was derived from standard cured mortars. For comparison purpose SH/300 and SH/500 mortars were investigated. The 540 days expansion of SL/300 and SH/500 mortar bars were 0.0105% and 0.0040%, respectively. Despite their high SO_3 contents, no expansion or other visible indication of distress was observed for any of the continuously stan-

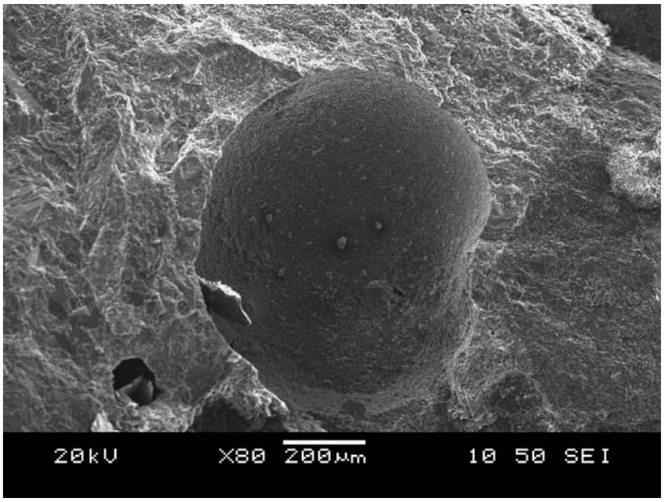

Fig. 15. An empty pore of fractured specimens of SH/500-O. (After standard curing of 540 days.)

dard-cured mortars. From SEM investigations, it can be said that specimens were sound and no detectable ettringite formation of cracking was observed both in cement–aggregate interface or matrix phase. Pores were empty or small amounts of $Ca(OH)_2$ crystals present (Fig. 15).

5. Conclusions

1. Fineness of cement significantly affects the expansion rate of heat cured mortars that are susceptible to DEF. For early ages, lower fineness of cement propagated the expansion due to the rapid formation of ettringite on the surface of unhydrated cement particles with high permeability. At later ages, the rate of formation of ettringite tends to slow down due to the difficulties of penetration of water into the deeper regions of unhydrated cement. Inner regions of coarse unhydrated cement will slowly react with water and the initial pore structure of mortars prepared with coarser cement will be more porous which relieves most of the expansion. In case of higher fineness, initial transport of moisture was very low due to the dense paste structure, low porosity and fine-pored microstructure. However, the slow penetration of water into matrix phase in a long period of time began to propagate the ettringite formation when the conditions are available (supersaturation of pore water and matrix phase with water, SO_3 and Al_2O_3 and alkalis). This delayed reaction results in a quick and deleterious expansion. Both the expansion measurements and SEM investigations confirmed these results.
2. It is possible to predict the expansion rate and amount for a given heat curing temperature of a mortar prepared with a cement of specific chemical composition and fineness. However, the relation may not be generalized for other cements. Only expansion potential for a given curing regime can be predicted.
3. The SO_3 content and SSA of cement should be limited in order to reduce the expansion risk of DEF related damage for heat treated concrete production.
4. There are two types of ettringites with different morphologies identified in SEM analysis of HH/500-O mortar: ball type and massive ettringite. The main difference between the ball type and massive ettringite was the sulfur content derived from EDS analysis, which was significantly higher for massive ones.
5. Relationships between expansion and DEF related chemical and physical parameters are more valid for long term expansions. This may be due to the pore structure of specimens. It seems that, in the long term, pores saturate with ettringite and the relations of ettringite formation and expansion becomes more valid. However, it should be noted that, this is valid for only saturated mortars still have a potential to produce ettringite (in particular the cements with highest SO_3 and fineness).
6. No expansions or other symptoms of damage were developed in mortars that were kept in standard curing conditions even prepared with fine cements at high SO_3 ratios.

Acknowledgements

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References

[1] Shao Y, Lynsdale CJ, Lawrence CD, Sharp JH. Deterioration of heat-cured mortars due to the combined effect of delayed ettringite formation and freeze/thaw cycles. Cem Concr Res 1997;27(11): 1761–71.
[2] Ormsby C, Liu R. A look at transportation forensics. J Public Roads, US Department of Transportation, Federal Highway Administration 2005;68(6).
[3] Zhang Z. Delayed ettringite formation in heat cured cementitious systems. PhD thesis, Purdue University, 1999.
[4] Fu Y. Delayed ettringite formation in Portland cement products. PhD thesis, University of Ottawa, 1996.
[5] Lawrence CD. Mortar expansions due to delayed ettringite formation. Effects of curing period and temperature. Cem Concr Res 1995;25(4):903–14.
[6] McDonald D. Technical note: delayed ettringite formation and heat curing—implications of the work of Kelham. Cem Concr Res 1998;28(12):1827–30.
[7] Taylor HFW, Famy C, Scrivener KL. Review: delayed ettringite formation. Cem Concr Res 2001;31(5):683–93.
[8] Zhang Z, Olek J, Diamond S. Studies on delayed ettringite formation in early-age, heat-cured mortars: I. Expansion measurements, changes in dynamic modulus of elasticity, and weight gains. Cem Concr Res 2002;32(11):1729–36.
[9] Collepardi M. A state-of-the-art review on delayed ettringite attack on concrete. Cem Concr Comp 2003;25(4–5):401–7.

[10] Ramadan EO. Experimental and theoretical study of delayed ettringite damage in concrete. PhD thesis, University of Maryland College Park, 2000.

[11] Ceesay J. The influence of exposure conditions on delayed ettringite formation in mortar specimens. MSc thesis, University of Maryland College Park, 2004.

[12] Scrivener KL, Damidot D, Famy C. Possible mechanism of expansion of concrete exposed to elevated temperatures during curing (also known as DEF) and implications for avoidance of field problems. Cem Concr Aggr 1999;21(1):93–101.

[13] Boyd SR. The effect of lightweight fine aggregate on alkali-silica reaction and delayed ettringite formation. MSc thesis, The University of New Brunswick, Canada, 1998.

[14] Azzam AE. Delayed ettringite formation, the influence of aggregate types, curing conditions, exposure conditions, alkali content, fly ash, and mix water conditioner (MWC). PhD thesis, University of Maryland College Park, 2002.

[15] Grattan-Bellew PE, Beaudoin JJ, Vallée V-G. Effect of aggregate particle size and composition on expansion of mortar bars due to delayed ettringite formation. Cem Concr Res 1998;28(8):1147–56.

[16] Yang R, Lawrence CD, Sharp JH. Effect of type of aggregate on delayed ettringite formation. Adv Cem Res 1999;11(3):119–32.

[17] Zacarias PS. The suppression of expansion in heat-cured mortars by fly ash and other additives. MSc thesis, Unıversıty of Toronto, Canada, 2002.

[18] Ekolu SO. Role of heat curing in concrete durability: effects of lithium salts and chloride ingress on delayed ettringite formation. PhD thesis, University of Toronto, Canada, 2004.

[19] Kelham S. The effect of cement composition and fineness on expansion associated with delayed ettringite formation. Cem Concr Comp 1996;18(3):171–9.

[20] Fu Y, Beaudoin JJ. Microcracking as a precursor to delayed ettringite formation in cement systems. Cem Concr Res 1996;26(10):1493–8.

[21] EN 12620 aggregates for concrete. CEN European Committee for Standardization, 2004, Brussels.

[22] ASTM C 230-98. Standard specification for flow table for use in tests of hydraulic cement, Annual Book of ASTM Standards, 2002.

[23] Grabowski E, Czarnecki B, Gillott JE, Duggan CR, Scott JF. Rapid test of concrete expansivity due to internal sulfate attack. ACI Mater J 1992;89(5):469–80.

[24] Zhang Z, Olek J, Diamond S. Studies on delayed ettringite formation in heat-cured mortars: II. Characteristics of cement that may be susceptible to DEF. Cem Concr Res 2002;32(11):1737–42.

[25] Heinz D, Ludwig U. Mechanism of secondary ettringite formation in mortars and concretes subject to heat treatment. Concrete durability. Proceedings of Katharine and Bryant Mather international conference, vol. 2, ACI SP-100. Detroit: American Concrete Institute; 1987. p. 2059–71.

[26] Odler L, Chen Y. On the delayed expansion of heat cured portland cement pastes and concretes. Cem Concr Comp 1996; 18(3):181–5.

[27] Yang R, Sharp JH. Hydration characteristics of portland cement after heat curing: I. Degree of hydration of the anhydrous cement phases. J Am Ceram Soc 2001;84(3):608–14.

[28] Yang R, Sharp JH. Hydration characteristics of portland cement after heat curing: II. Evaluation of crystalline aluminate-bearing hydrates. J Am Ceram Soc 2001;84(5):1113–9.

[29] Marusin SL. Sample preparation – the key to SEM studies of failed concrete. Cem Concr Comp 1995;17(4):311–8.

[30] Yan P, Qin X, Yang W, Peng J. The semiquantitative determination and morphology of ettringite in pastes containing expansive agent cured in elevated temperature. Cem Concr Res 2001;31(10): 1285–1290.

[31] Stutzman PE. Deterioration of Iowa highway concrete pavements: a petrographic study. Building and Fire Research Laboratory, NISTIR 6399, 1999, 72p.

[32] Csizmadia J, Balazs G, Tamas FD. Chloride ion binding capacity of tetracalcium aluminoferrite. Periodica Polytechn Ser Civ Eng 2000;44(2):135–50.

[33] Lee H, Cody RD, Cody AM, Spry PG. The formation and role of ettringite in Iowa highway concrete deterioration. Cem Concr Res. 2005;35(14):332–43.

[34] Batica OR, Milanesia CA, Maizab PJ, Marfil SA. Secondary ettringite formation in concrete subjected to different curing conditions. Cem Concr Res 2000;30(9):1407–12.

[35] Collepardi M. Damage by delayed ettringite formation. Concr Int 1999;1(1):69–74.

[36] Tosun K. The effects of different types of cements on delayed ettringite formation. PhD thesis, Dokuz Eylul University, İzmir, 2006.