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Effect of ettringite morphology on DEF-related expansion

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ABSTRACT

In this study, time dependent ettringite formation in heat-cured mortars has been investigated. In order to clarify the effect of formation place and morphology of ettringite on expansion, secondary electron images of cracked surfaces of mortars at three ages were analysed by SEM–EDS. Also, the X-ray microtomography analysis has been performed to observe the crack formation. The expansive role of delayed formed ettringite was related with its time dependent morphology as a function of formation place. From these observations, mechanism of ettringite reformation after heat curing has been proposed. Alumina rich species were the primary sources of ettringite formation as the starting nuclei. At later ages, if S and Al sources are readily available, the mentioned alumina rich nuclei will grow up and build ball ettringite. At long term, ball type ettringites (non-expansive) converted to massive type (expansive). These conversions can only take places if the form of available space is narrow (preformed micro-cracks). Massive ettringites exert pressure in these narrow spaces and cause expansion of mortar. If the form of the available space is spherical (entrapped air voids) ball ettringites preserve their initial form and do not cause any expansion.

1. Introduction

In the late 1980s, Heinz and Ludwig published a series of papers on expansion of laboratory and field mortars and concretes that were exposed to elevated temperatures and subsequently cured at room temperature under moist conditions [1]. Since then, hundreds of papers were published based on both laboratory studies to elucidate the mechanisms involved and on damaged concrete structures to correlate the experimental findings with the field [2–7]. From these literature, sensitivity of concrete to steam curing seems to be related to these phenomena: (a) decomposition or non-formation of ettringite due to high-temperature; (b) adsorption of the released sulfate by C–S–H or formation of monosulfoaluminate; (c) possible formation of initial micro-cracks due to thermal expansion; (d) release of sulfate from C–S–H upon cooling and subsequent ambient temperature (moist curing); (e) subsequent formation of micro-cracks as a result of drying shrinkage; (f) formation of ettringite nuclei in the pre-existing cracks or tiny micropores, and (g) growth of the nuclei resulting in expansion of paste.

There are two different hypotheses about expansion mechanisms of delayed ettringite formation (DEF): the uniform expansion of paste and the crystalline pressure of ettringite [4,8,9]. However, the crystal growth pressure hypothesis appears to be rather less convincing than the paste expansion hypothesis [7]. Furthermore, the paste expansion hypothesis is most strongly supported by the fact that neat cement paste also suffers from DEF-related expansion, which clearly demonstrates that the presence of aggregate particles is not a necessary condition for the expansion to occur. Odler and Chen [10,11] observed considerable expansion in neat Portland cement pastes approximately one year after high-temperature curing. Similarly, Yang et al. [12] reported that a neat cement paste expanded after 2.5 years, while the same cement mixed with siliceous sand started to expand in less than 100 days.

The above mentioned literature reviews repeatedly cited the significance of microstructure formation in the expansion mechanism. The microstructure and pore structure govern various physical properties, such as strength, permeability, connectivity, and diffusivity, and thus control pore solution transport in the system. There have been indications that these transport properties are important factors in the DEF-related expansion, however, these are not well established. Thus, the majority of studies focused only on the chemical aspects of DEF. In contrast, very little has been reported on the influences of physical properties of the system, and their relationships to the chemical reactions. Thus, there is a lack of information on the physical parameters that has left many uncertainties in understanding the DEF mechanism [7].

Most of the available microscopic information in literature has been obtained using light optical microscopy and scanning electron microscopy (SEM) in back-scattered electron (BSE) mode including microanalytical studies [13]. Reported microscopic observations of concrete damage include [1]:

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1. Expansion of the cement paste as revealed by formation of partial or complete rims (gaps, bands, circumferential cracks), up to about 25–30 micrometers wide, around the aggregate particles (e.g. Johansen et al. [14]);
2. partial or complete filling of these gaps by secondary ettringite formation;
3. formation of "nests" of ettringite in the cement paste (e.g. Marusin [15]);
4. formation of two-tone C–S–H features with values chemical compositions also known as inner and outer C–S–H (e.g. Scrivener [13]);
5. microcracking of the paste;
6. microanalytical studies on the composition of hydration products, (e.g. Scrivener and Taylor [16]; Famy [17]).

Microstructural observations were seldom related with the morphology of ettringite structure as a function of time and place of formation [8,18]. According to Famy et al. [19], expansion is attributed to the formation of microcrystals of ettringite in tiny places containing monosulfoaluminates, when sulfate is released from C–S–H. Besides its amount, the morphology of ettringite is also an important factor to influence its expansive effect. Secondary electron images of cracked surfaces were rarely employed. However, the secondary electron images can be valuable tools in qualitative determination of time dependent development of crystal structures on weak sections of mortars (pores and cracked surfaces).

The aim of this study is to investigate the microstructure of heat cured cement mortars (potentially susceptible to DEF by composition) and to find a relationship between expansion and ettringite morphology as a function of time and place of ettringite formation. The physical characterization of morphology of delayed formed ettringite has become possible by employment of secondary electron images.

2. Experimental

2.1. Materials

Cement characteristics that promote the early strength, in particular high fineness and high SO_3 content usually increases the DEF susceptibility of heat-cured mortars [20]. For this reason, special DEF susceptible cement with 4.5% of SO_3 has been prepared in the laboratory. A Blaine value of 535 m^2/kg has been achieved by extra grinding. Compressive strengths of standard mortar samples prepared with this cement were 21.1, 50.2 and 64.8 MPa at 2, 7 and 28 days, respectively. The Bogue compound composition of the cement was C_3S: 53.24%, C_2S: 11.75%, C_3A: 9.25% and C_4AF: 8.09%. This cement can be classified as high strength cement which is usually preferred by precast concrete producers.

Standard graded siliceous sand was used. Previous studies have revealed that natural siliceous sand is the most DEF susceptible sand due to its high thermal coefficient of expansion and low strength of interface with poor mechanical interlocking behaviour compared to crushed limestone sand [21,22]. SEM images demonstrating the improved interlocking mechanism of crushed limestone sand (Fig. 1a) compared to siliceous sand (Fig. 1b) are presented comparatively in Fig. 1.

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 [23] standard. The flow diameters of mortars were within the range of 128–135 mm. Mortars were cast in 25 × 25 × 285 mm prismatic moulds with stainless steel studs in their end faces. In order to investigate the DEF potential, half of the specimens were subjected to heat curing regime described by Grabowski et al. [24]. After a pre-curing period of 2 h at 20 °C, the temperature has been increased at a rate of 25 °C/h up to the required maximum temperature (85 °C) which has been kept constant for 4 h. Cooling rate was also 20 °C/h. All prisms were demoulded after 24 h. Duggan method describes series of wetting and drying periods after heat curing. After three days of waiting period in de-ionised water, specimens were subjected to three cycles of 1 day drying in an oven at 85 °C and 1 day wetting at 20 °C. The purpose of this additional process is to speed up the DEF. Any procedure that weakens the material will also lower its ability to resist expansion. Repeated heating and cooling may form microcracks due to thermal stresses. This will accelerate DEF, since water will penetrate in more easily and it will also weaken the paste-aggregate bonds [6,25]. Finally, the specimens were stored in water at 20 °C. The other half of the specimens were standard cured in water at 20 °C. Lengths of specimens were measured for a period of more than 2 years. The results recorded as the average of two mortar bar specimens.

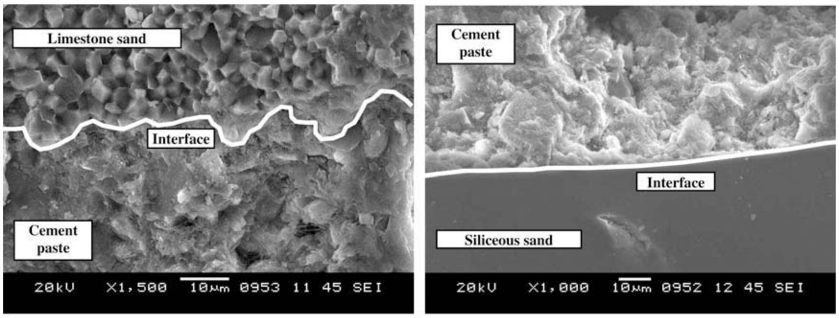
2.3. Length change measurements

The length change of mortar prisms at a period of 800 days is presented in Fig. 2. As can be expected, there is a considerable difference between the expansion characteristics of heat cured and control mortars. All mortar prisms stored in water at 20 °C. The expansion of heat-cured mortars started immediately after heat curing (Fig. 2a). On the other hand, control mortars preserved their initial length and no considerable expansion was observed. In case of heat-cured mortars, the rate of acceleration increased before 90 days (Fig. 2b). After 90 days rate of acceleration started to decrease and expansions slow down between 90 days and 500 days. Beyond 500 days, length of specimens did not change. From these observations, the expansion history of mortar prisms can be divided into four critical time intervals: Initial or migration period (0–I: just after steam curing, up to 2 days-old), seeding and acceleration period (I–II: 2–90 days), deceleration period (II–III: 90–500 days), saturation period (III–∞: after 500 days). In order to investigate the influence of microstructural changes on expansion, samples were taken at three critical ages (at the beginning of acceleration period, in the middle of the acceleration period and from the end of the deceleration period). The possible reasons for the change of expansion rate at different time intervals will be discussed in the next section.

2.4. Microstructural investigations

2.4.1. Methodology

Cracked surfaces have been selected for investigations since during hydration of steam cured mortars most of the ettringite form in voids of varying size and shapes besides the micro-cracks in paste phase. A new product can only be formed in voids and/or cracks and they are the weakest link of a section which can appear after fracture. Fracturing of the specimen by hammer introduces additional cracks. Due to this fact, the fractured surfaces can not be used to study the crack patterns in the cement matrix or the cracking of the aggregate. In order to examine the crack pattern, X-ray microtomography (XMT) method has been used. Since, XMT is a non-destructive and versatile characterization technique for microstructural investigation of cement mortar and concrete, there is no need to make any sample preparation as in the case of polished surface investigations [26–28]. However, fractured surfaces are excellent for exhibiting ettringite crystalline structure in cracks, voids or at aggregate interface [29]. On the other hand, due



(a) (b)

Fig. 1. Cracked surface view of cement paste: (a) crushed limestone sand, (b) siliceous sand interfaces.

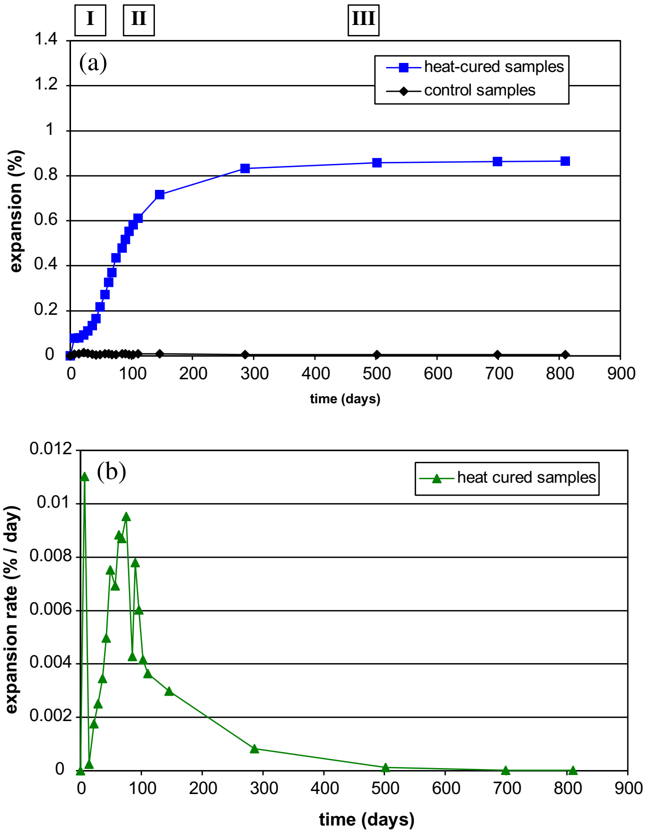


Fig. 2. Length change and expansion rate relationship of heat cured and control mortar prisms.

to the loss of their structure by grinding and polishing, it is not possible to investigate the morphological structure of ettringite crystals if polished surfaces are used.

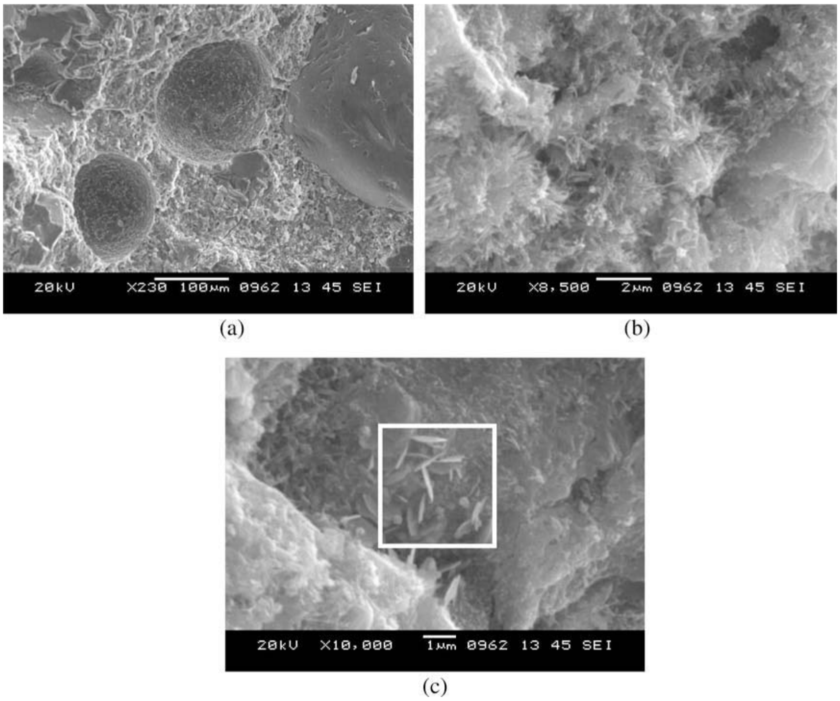
The microstructural changes in steam cured mortars of 2 days (initial), 2 months (middle age) and 1.5 years (long term) old fractured surfaces were investigated. A JEOL JJM 6060 scanning electron microscope (SEM) with EDS equipment was used. Samples were vacuum dried and gold coated before investigation. This drying process was mandatory and possibly caused loss of water molecules from ettringite structure. However, crystal morphology still preserves its structure. The pores, aggregate surfaces, aggregate-paste interfaces (in the zones where aggregates detached), and cracked paste surfaces (the fractured region which can be the weakest section including micro-cracks, capillary pores and weakest interfaces at highest proportion) were investigated at each age.

2.4.2. Stages of analysis

2.4.2.1. Initial stage: just after steam curing. Two days old heat cured samples were used in the initial period analysis. The pores on fractured surfaces were empty and small $Ca(OH)_2$ crystals were rarely visible (Fig. 3a). Sand particles were usually detached and their surfaces were also clear. Sample surface was detected to a limit of 10,000× magnification and there was no sign of any ettringite formation. Higher magnifications were not possible due to loss of image quality. In case of standard curing conditions, ettringite formation is a normal and anticipated process of Portland cement hydration [21]. Elevated curing temperature over 70 °C impedes the formation of ettringite or even induces its destruction in the paste, which results in the formation of monosulfoaluminate hydrate or the adsorption of SO_4^{2-} and Al^{3+} by C–S–H gel [7,8,17]. Simultaneously a light grey coloured inner C–S–H formation has been observed during this period under high curing temperatures. Cement paste surface was covered with newly formed C–S–H with freshly formed coral-sponge like structure (Fig. 3b). The inner C–S–H absorbs the sulfate ions produced from the ettringite decomposition, and also incorporates aluminium ions into the C–S–H structure. According to Scrivener and co-workers [6,16], the amount of sulfate and aluminate in the inner product C–S–H increases with temperature, and the sulfur–aluminium atomic ratio, taken immediately after the heat treatment, is indicative of the potential for future expansion. In Fig. 3b, the S/Ca and Al/Ca ratios of C–S–H was measured at 10 randomly selected points by using EDS. The average values of S/Ca and Al/Ca were 0.086 and 0.087, respectively. On the other hand, the C–S–H structure of control specimens (without heat curing) was also examined. The average of S/Ca and Al/Ca ratios of ten randomly selected points were 0.007 and 0.012, respectively. These results confirmed that some of S and Al have been initially absorbed by C–S–H in case of heat treatment. It should be noted that, at very high magnifications 10,000× (Fig. 3c) monosulfoaluminate (AFm) crystals can also be observed in deep regions of heat cured cement pastes. The difficulty in detecting monosulfoaluminate is due to the extremely small size of these crystals. Glasser [30] showed that, the presence of host AFm phase providing a rich source of calcium and aluminium ions is necessary for the nucleation of newly formed ettringite crystals, which then grows as sulfate ions become available through diffusion. The ettringite that forms within the AFm phase occluded in dense inner C–S–H gives rise to expansive pressure.

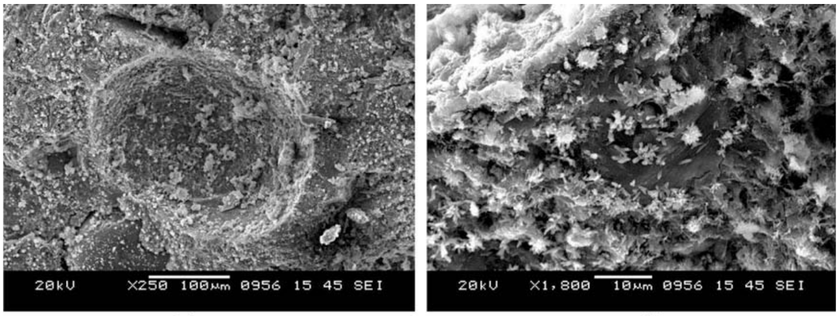
In summary, two indications responsible for the DEF susceptibility of heat-cured mortars were observed at 2 days old fractured surface of heat-cured mortars: (1) Absorption of S and Al by outer C–S–H; (2) Formation of monosulfoaluminate embedded in deeper regions of inner C–S–H.

2.4.2.2. Mid-term stage: two months after steam curing. The general view of 2 months old fractured surface of heat cured sample is



(a) (b) (c)

Fig. 3. (a) Empty or rarely CH filled pores just after steam curing, (b) cement paste with newly formed micro-crystalline C–S–H structure, (c) monosulfoaluminate formations at deeper sections of cement paste, visible only at high magnifications.



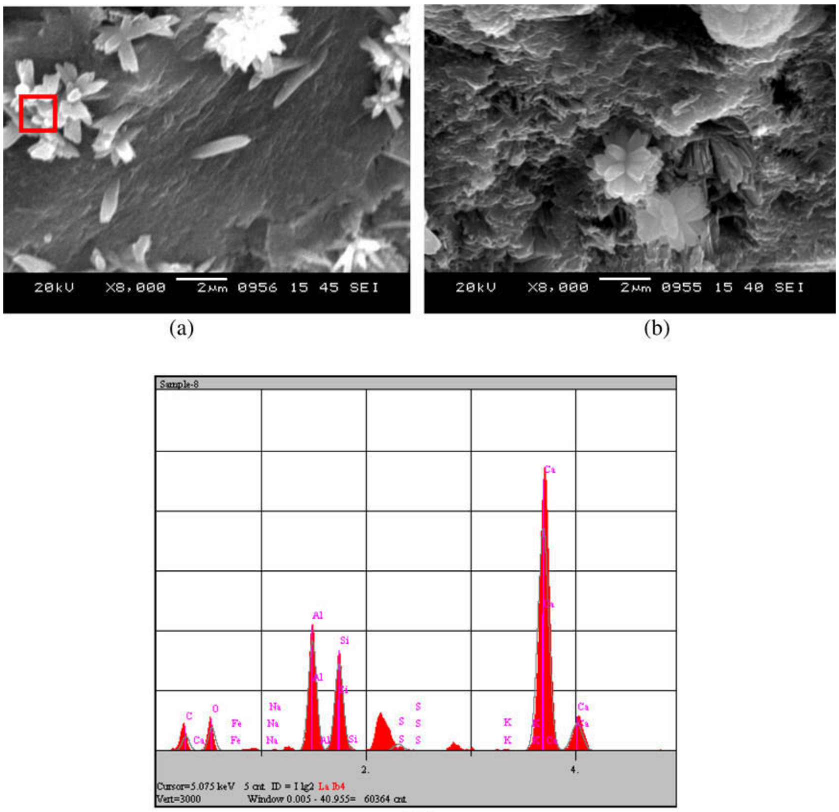
(a) (b)

Fig. 4. (a) Pore rarely filled with ball type ettringite. Some Al-rich species seeding the whole cement paste surface, (b) overview of Al-rich species at different maturity.

presented in Fig. 4a. Cracked surface of the paste was covered with newly formed very small pieces of hydration products which seem to be the nuclei of ball ettringite (Fig. 4b). EDS analysis proved that, they are very rich of alumina. Figs. 5 and 6 represent the different forms of these Al-rich species. As can be seen from the images they have different morphological forms. According to our view, they might be the nuclei of ball ettringite and will convert to mature ball ettringite at later stages of hydration.

Following high-temperature curing, the mortar samples were placed in water at ambient temperature, leading to alkali leaching. As the temperature and alkalinity of the system decrease, the solubility of ettringite also decreases and ettringite begins to form. According to technical literature, this promotes ettringite crystalline formation of sub-micrometer size from monosulfoaluminate. Also C–S–H and the pore solution within the fine pores in outer C–S–H, generates expansive pressure [31]. According to our study, the idea of direct formation of sub-micrometer ettringite is partially true. The exact starting mechanism of ettringite formation follows a step by step process: The evaluation of ettringite nuclei is shown in Figs. 5 and 6. Note that, the EDS analysis revealed that smaller needle like formations were rich of Al and poor in S (Figs. 5c and 6c). When they were transformed to nuclei ball type, the content of S has been increased (EDS Fig. 6c). As the popcorn like structure began to form, the content of S has also been increased. It seems that, these Al-rich species served as seeds of ball ettringite both in pores and narrow spaces in cement paste. Some of them were more quickly formed than others in available spaces. It may be due to the difference of pore solution concentration in terms of S and Al contents. The rate of ettringite formation in different cementitious systems may vary greatly depending on the phase serving as the source of Al^{3+}. There are indications that in most instances the rate of dissolution of the Al-bearing phase is the factor that controls the overall rate of reaction [32]. It was observed that, the ball ettringites formed in pores were relatively more developed than the ones in cement paste. It should also be noted that, the diameter of largest and matured ball ettringite was approximately 5–10 µm. Aggregate surfaces were clear and monosulfoaluminate of sub-micrometer size embedded in cement paste was detectable at high magnification rates (10,000×).

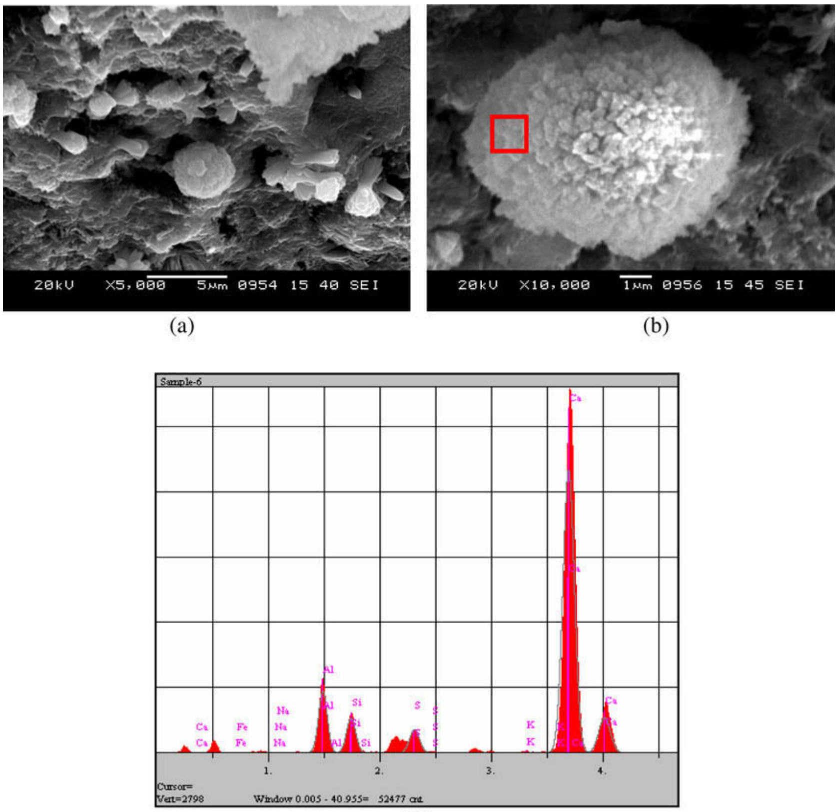
In a series of articles, Fu et al. [33,34] and Fu and Beaudoin [35] have suggested that heat-induced expansion may be preconditioned by prior formation of ettringite nuclei in the paste



(a) (b)

(c)

Fig. 5. (a,b) SEM images of premature Al-rich species, (c) EDS spectra of Al-rich particle (selected with rectangle in Fig. 5a).



(a) (b)

(c)

Fig. 6. (a) Cores of ball ettringite, (b) close view of core of ball ettringite, (c) EDS spectra of popcorn type Al-rich particles possibly covered with sulfur.

micro-cracks, specifically at the crack tips. In their interpretation, excessive curing temperature and, possibly, the accompanying or subsequent high-temperature drying, lead to rapid adsorption of sulfate by C–S–H, followed by its slow release upon cooling and subsequent moist curing into the liquid phase. Once supersaturation of the liquid phase with respect to ettringite formation is reached, nuclei of ettringite forms by a through-solution mechanism, preferably in pre-existing cracks. The size of these cracks may be critical; larger pre-existing cracks will lead to greater expansion. The growth of the ettringite nuclei in limited space, results in crystallization pressure and subsequent extension of the cracks.

2.4.2.3. Long-term stage: 1.5 years after steam curing. The pores of 1.5 years old samples were partially filled with ettringite balls and some pores were nearly saturated (Fig. 7). It is important to note that the diameter of these aged ball ettringites were approximately 15–20 μm. Crystal growth can be pronounced in this respect. Clusters of ettringites like ball type were also observed by Ceesay [25]. Additionally the term of "ball ettringite" has been used by Dubberke [36]. Ball ettringite crystals appear to completely fill voids. However, ettringite, found in these pores should not be interpreted as the cause of the expansion leading to deterioration of mortar, since they exert no pressure until they fully saturate the pore. The cracked surface of cement paste was partially covered with massive ettringite structure. These massive ettringites were also visible on some parts of sand surfaces (Fig. 8). Previously formed microcrystals in tiny pores or narrow cracks converted to massive ettringites which were found to be the primary source of expansion in heat-cured mortars. They can be identified as the aged ball ettringites previously formed at narrow spaces.

From EDS analysis, it was observed that, there is a considerable difference between the S/Ca ratio of ball type and massive type ettringites. The sulfur content and S/Ca ratio of massive ettringite was always much higher than that of ball ettringite. This compositional difference may be originated from their formation places and ages. 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. The aged one seems to be massive ettringite and it captures more sulfur into its structure (Figs. 8 and 9). Captured sulfur may expand the ettringites structure and cause expansion.

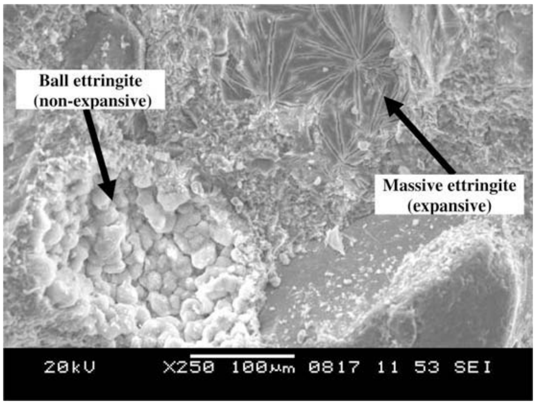


Fig. 8. Massive ettringite on aggregate surface and ball ettringite in pores.

Another explanation for expansive character of massive ettringite can be attributed to the additional massive ettringite formation at the bottom layers (Fig. 9). Ettringite was still forming at the bottom and pushing the previously formed ettringite fibres upwards [36]. Torn surface observed in Fig. 9 may be a proof of this possible mechanism.

Interestingly, the growth of massive ettringite on aggregate surface is somewhat different than its growth in cracked surface of cement paste. A growth at a very thin section was observed and mostly parallel to aggregate surface. Note that Fig. 10 on the right very thin needles start to form and grow up parallel to the surface. This kind of growth seems less expansive and slower than massive ettringites found in micro-cracks of cement paste. These findings are logical, since the distance of sulfate source is far away from the aggregate surface compared to the massive ettringites on the cracked surface that are closer to the cement paste. Although this is an indication of ettringite formation in cement aggregate interface, previous studies confirmed that the primary formation of ettringite did not took place at the interface. Later precipitation of ettringite to the transition zone can be pronounced.

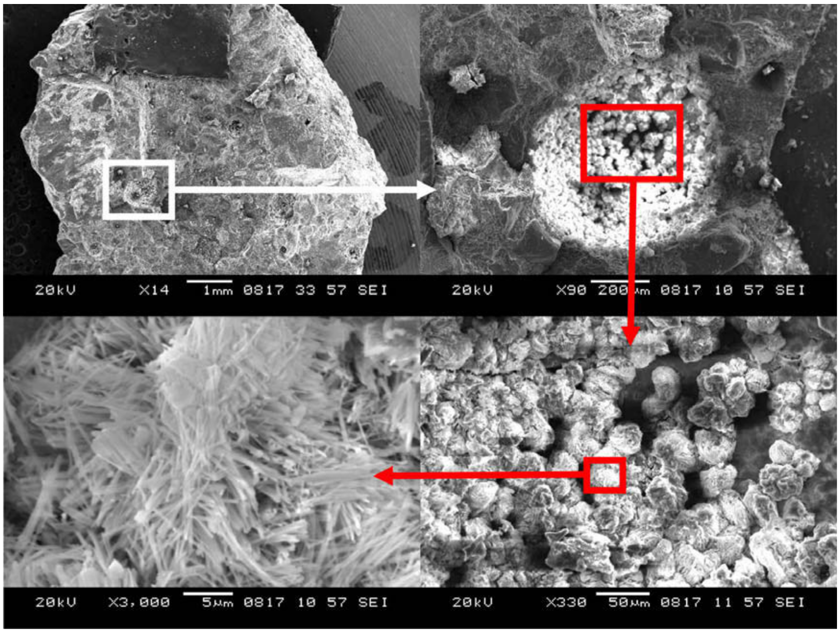


Fig. 7. Pores partially saturated with ball ettringite.

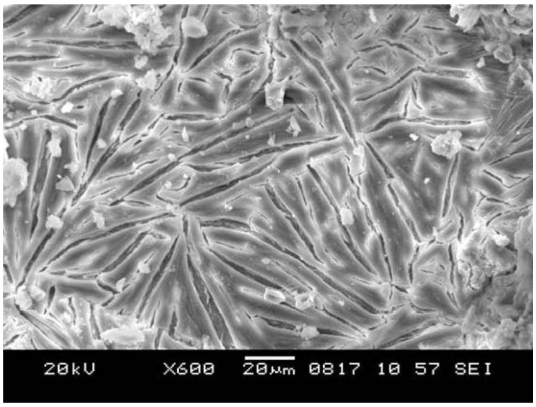


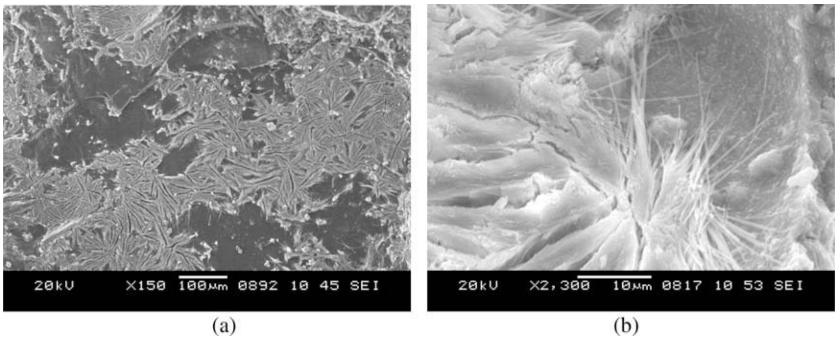
Fig. 9. SEM image of massive ettringite-covered matrix surface.

2.4.3. X-ray microtomography analysis

Tomography based micro investigation techniques present a wide variety of advantages and application possibilities in the area of non-destructive microstructure research. The crack formation of heat-cured mortar was studied using synchrotron X-ray microtomography on the 8.3.2 beamline at the Advanced Light Source without artifacts of specimen preparation. In synchrotron XMT, a wide parallel X-ray beam passes through the sample, and the transmitted fraction is detected as an image by a charge couple device (CCD) area detector. The sample is mounted on a stage with four degrees of freedom: *x*, *y*, and *z* transition for positioning and centering of the sample, and rotation for data acquisition. The rotary stage allows for many X-ray transmission images of the sample to be recorded for a series of orientations. At the ALS superbend beamline 8.3.2, the transmitted beam is detected by a scintillator that converts X-rays to visible light, which is imaged by magnifying lenses onto a CCD. The available optics allow for spatial resolutions between 0.44 μm/pixel and 11.5 μm/pixel. The monochromator is tunable to X-ray energies between 5 keV and 35 keV by means of a double multilayer mirror arrangement. The monochromator optics can also be removed from the beam, allowing a white light mode of operation that is broadly polychromatic in the 30–70 keV range by means of metal filters. The more detailed information about the principles of XMT has been presented in the study of Monteiro et al. [26].

Depending on the sample age and dimension, "whitelight mode" was selected. 1800 projections with an angle step of 0.1° and an exposure time of 10 ms each were acquired on a Nikon CCD camera equipped with a 1× magnification optical objective. The pixel resolution under these conditions was 8.675 μm. The images were processed by using Octopus program and obtained 485 "reconstructed images" from 1800 sinograms. Then, reconstructed slices were processed using the Avizo Program at the Advanced Light Source Beamline 8.3.2.

Ettringite in aged concrete typically forms in pores, cracks and aggregate-paste interfaces. The crack formation around the aggregates and matrix phase and also many of the pores partially or fully filled with ettringite can be seen in Figs. 11 and 12. It can be observed that big pores were not fully saturated. It should be noted that the size of these pores is an important factor determining the ettringite formation mechanism. Fig. 12 shows, the cracking propagated not only in matrix but also in aggregate-paste interface.



(a) (b)

Fig. 10. (a) Massive ettringites formed on aggregate surface, (b) close view of new formation of massive ettringites parallel to aggregate surface.

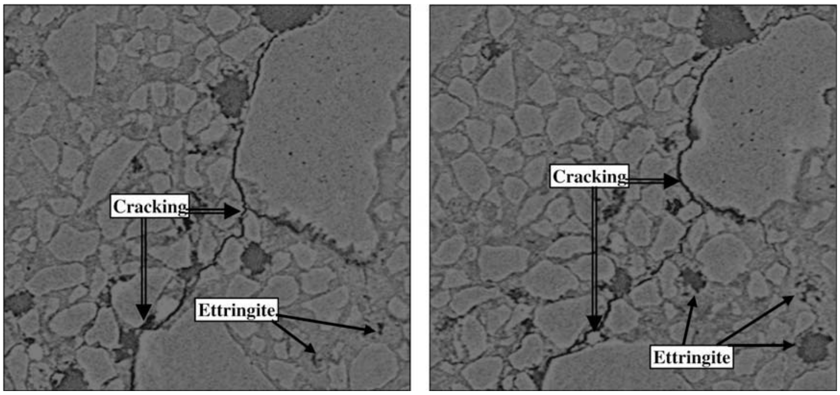


Fig. 11. Reconstructed 2D microtomography images of DEF-damaged sample at long-term stage.

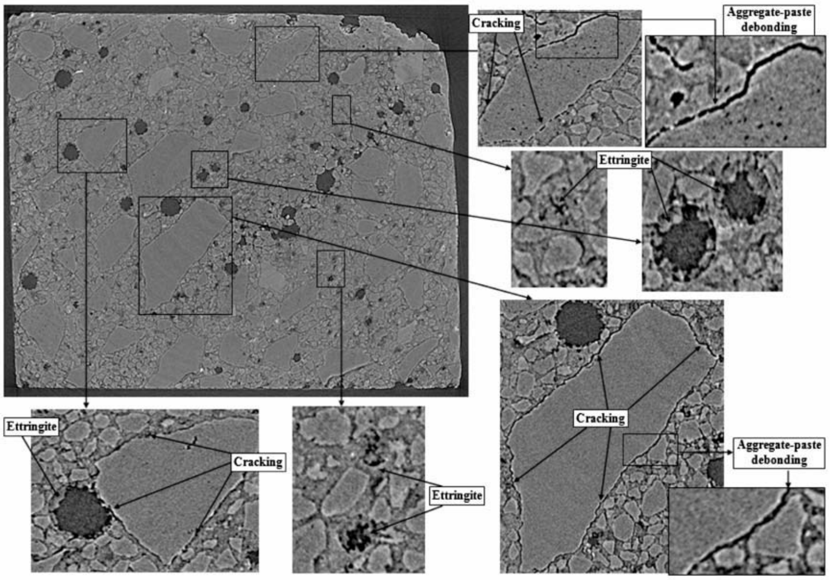


Fig. 12. Crack and ettringite formation and aggregate-paste debonding of DEF-damaged sample.

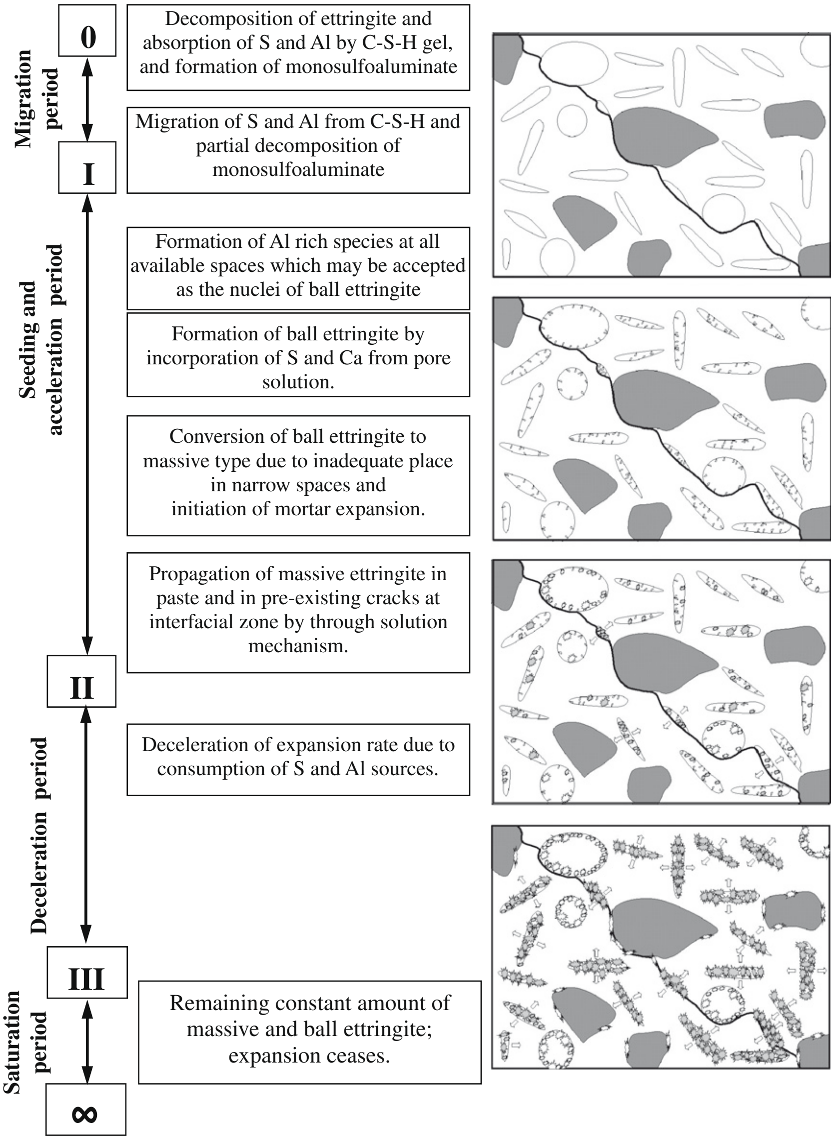


Fig. 13. The proposed mechanism for expansion history of heat-cured mortars.

3. Discussion of proposed mechanism

Two mechanisms are usually mentioned about the DEF-related expansion of heat-cured mortars. Some researchers claim that the concrete expansion is caused by delayed formation of ettringite in the paste and its subsequent expansion and cracking [14]. Others claim the secondary ettringite deposition or reprecipitation within the cracks, air voids and gaps, to be expansive, or attribute the damage to the effect of nucleation of ettringite in the crack tip zone [33–35], or to the hydraulic pressure originating in osmosis [37]. The crystallization pressure may originate from the stress generated by crystals growing within cracks, particularly at the crack tips, rather than within the cement paste. In fact, some investigators strongly supported this view that ettringite growth in micro-cracks is fully or partly responsible for the expansion. Fu et al. [34] discussed the relationship between the free energy of critical nuclei formation and the surface tension at different interfaces. They concluded that, nuclei preferentially form in crack tips rather than on plane solid surfaces. These cracks are then extended, resulting in the expansion of cement paste. It was also suggested that, larger cracks which require less expansive pressure to be extended, are responsible for severe expansion when fully saturated. In order to confirm this view, pre-existing cracks were purposely introduced in cement paste specimens in their experiments. These specimens exhibited significant expansion following high-temperature curing in comparison to those without cracks or cured at lower temperatures [7]. Fu and Beaudoin [35] examined the influence of microcracks by subjecting steam cured concrete specimens to drying/rewetting, freezing/thawing, and loading/unloading cycles. Expansion was observed only after the thermal drying cycle. The expansion was attributed to the severe microcracking observed in cement paste and at paste-aggregate interfaces, in which ettringite recrystallized, while the other treatments led to the crack formation only in certain weak areas. They concluded that, the expansion is a direct result of crack opening by ettringite formation, and that the pre-existing cracks in cement systems are the precursor of DEF-related expansion. The expansion observed here, however, may simply be the result of additional exposure to heat in the drying process, which promotes further decomposition of primary ettringite and intensifies subsequent secondary ettringite formation, rather than the effect of severity or location of the microcracking. They also demonstrated the diffusion of the reactant ions through the pore solution, which is an essential mechanism for the preferred ettringite nucleation in cracks [35].

In this study, it was observed that both mechanisms took place however, the exact cause of expansion is the through-solution mechanism in narrow micro-cracks and capillary pores by the formation of massive ettringites. As can be seen in Figs. 11 and 13, the essential role of cracks and other structural defects appears to be in facilitation of DEF-related expansion, rather than being the precursor of expansion. For the nucleation and growth of a crystal to overcome a mechanical constraint-meaning to cause expansion – the solution from which the crystal precipitates must be supersaturated [9]. Pore solution extractions are not necessarily representative of the solution existing within the paste. However, studies by Wieker et al. [38] indicated that levels of SO_4^{2-} in solution at 24 h, although higher than in room-temperature-cured pastes, decreased to normal levels over a few days, long before expansions were observed. Regardless of the degree of supersaturation it will always be more favourable for a crystal to precipitate in a pre-existing pore or void than to overcome the constraint of its surroundings and cause expansion. But when there is no way to migrate to another pore, the growing pressure may exert expansion [9].

Fig. 13 demonstrates the mechanism of DEF-related expansion behaviour of cement mortars based on the results of this study. Schematic figures simulate typical crack surfaces of mortars. Narrow micro-cracks on the surface can easily be detected when the mortar is fractured since cracking exposes the weak parts (narrow micro-cracks in paste). The evaluation of expansion was studied at intervals divided by four critical stages: Migration (Initial) period (0–I), seeding period followed by acceleration of rate of expansion (I–II), deceleration (of rate of expansion) period (II–III) and finally saturation period (III–∞).

At the initial period (0–I), decomposition of ettringite and absorption of S and Al by C–S–H gel, and monosulfoaluminate formation took place. If conditions are available ettringite reformation starts with the formation of Al-rich species as a topochemical reaction in these spaces. This period may be accepted as seeding period and responsible for the approximately 20% of ultimate expansion (see Fig. 2a, expansion at 2 months). At narrow spaces as a result of through-solution mechanism S and Ca ions precipitate onto these small ettringite nuclei and captured by ettringite's structure [39]. When these balls start to enlarge in narrow micro-cracks, due to the inadequate space, they change their form and convert to massive etrringites which exert pressure in these narrow cracks (I–II). In other words, massive ettringites were previously formed as small ball etrringites. Formation of these massive ettringites may cause detrimental expansion due its narrow place between C–S–H. Acceleration of rate of expansion (I–II) was observed in this period and this period is responsible for nearly 80% of total expansion. On the other hand, ball ettringites formed in big entrapped pores also enlarge and fill the space. However, due to the availability of the space, they did not cause any pressure until full saturation of the pore space. Full saturation was rarely observed even, at later periods (III–∞). For this reason ball ettringite is not the main cause of expansion. However, they are the starting elements of the formation of massive ettringite on the paste surface where narrow micro-cracks exist. These findings proved the importance of location of formation of ettringite, rather than its content on expansion of mortars. After this acceleration period, rate of expansion decreases but expansion slightly increases (II–III). Beyond saturation point (III), no considerable expansion has been observed. This may be due to the consumption of possible S and Al sources at later periods of hydration.

4. Conclusions

Morphology of ettringite determines its expansive character which is related with age and location of formation. Time dependent SEM–EDS studies have revealed that, from the point of view of expansion, location of formation of delayed ettringite is a crucial factor that governs the long term stability of heat-cured mortars. Initially, formation of delayed ettringite starts with the formation of ball ettringite independent of the place of formation. A topochemical reaction with Al-rich nuclei species is responsible for the initial expansion. Ettringite structure expands by later precipitation of S and Ca ions over these small ettringite nuclei as a result of through-solution mechanism. Ball ettringites keep their stability when formed in large entrapped air pores and do not cause any expansion until they saturate the pore space. On the other hand, later conversion of ball ettringite to massive type has been observed at narrow spaces (especially shrinkage induced micro-cracks) due to lack of available places. The formation of massive ettringites has been found responsible for the deleterious expansion that took place in heat-cured mortars.

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