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# Relationship between delayed ettringite formation and delayed expansion in massive shrinkage-compensating concrete

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## Abstract

The possibility of delayed expansion induced by delayed ettringite formation in massive shrinkage-compensating concrete was investigated. Mortars were prepared using ordinary Portland cement and a sulfoaluminate-based expansive agent. They were cured in three different moist conditions at elevated temperature in a temperature match conditioning process to simulate the temperature development in the interior of massive concrete, and then at ambient temperature. Changes in quantity and morphology of ettringite were examined using semi-quantitative X-ray diffraction and scanning electron microscopy. The time-dependent length change of restrained mortars was also measured. The results show that, in addition to the quantity of ettringite, the structure of mortar, morphology of ettringite and curing conditions also influenced expansion of mortars induced by delayed ettringite formation. The expansion mechanism of delayed ettringite formation and the relationship between curing conditions and length change, delayed expansion and damage to concrete structure are discussed.

*Keywords:* Delayed ettringite formation; Massive shrinkage-compensating concrete; Curing condition; Expansion

## 1. Introduction

Nowadays, sulfoaluminate-based expansive agents are widely used in China to construct shrinkage-compensating concrete with large section size for the foundations of high-rise buildings and for huge infrastructure. The designed strength class and dimension of these concrete structures increase continuously with the increase of the height and volume of the buildings. For example, the concrete foundation of Shanghai Jinmao Building, which is the tallest building in China, was placed in the strength class of C50 at a thickness of 4 m [1]. The concrete foundation of Beijing Orient Plaza was placed in the strength class of C30–C40 at a thickness of 5.1 m [2]. A large amount of concrete placed in a short period of time results in an obvious rise of temperature in the interior of the massive concrete, due to the release of hydration heat of cement. A peak temperature of 97 °C was recorded in 40 h after placing the concrete foundation of Shanghai Jinmao Building [1].

It is known that the main hydration product of sulfoaluminate-based expansive agents is ettringite. Its formation leads to a volume expansion which compensates the cooling and drying shrinkage of concrete. Ettringite formed in the early hydration period decomposes when it is subjected to temperatures above 70 °C. This phenomenon was first recognised by Ludwig and his coworker [3] as “delayed ettringite formation (DEF)” and has been confirmed as a destructive phenomenon occurring in many concrete structures [4]. Taylor et al. [5] defined DEF as the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete, that involves none of the sulfate originates from an external source. We have most recently demonstrated that DEF can also occur in massive shrinkage-compensating concrete [6].

Research work on DEF has largely been focused on heat-cured, precast concrete elements, for example railway sleepers in which cracking appears mainly on the top surfaces where there is little restraint on the concrete [7–10]. Unconfined mortar or concrete samples were often prepared, cured under saturate atmosphere in the temperature range of 80–100 °C for a few days, then kept humid at ambient temperature. The dimension

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variation of samples and ettringite's characteristics were investigated to verify whether DEF occurs [11–13]. Yang et al. [14] emphasized that the late formation or regrowth of ettringite in mortars cured at ambient temperature may not result in expansive damage. The condition in the massive concrete is, however, very different from that in small concrete elements. There is strong restriction and it is difficult for the migration of water in the massive reinforced concrete foundation. So the critical question is whether or not DEF can induce a delayed expansion, or even cracking, under these conditions. In this paper, the relationship of DEF and delayed expansion of restricted mortar is investigated under conditions simulating a massive reinforced concrete foundation.

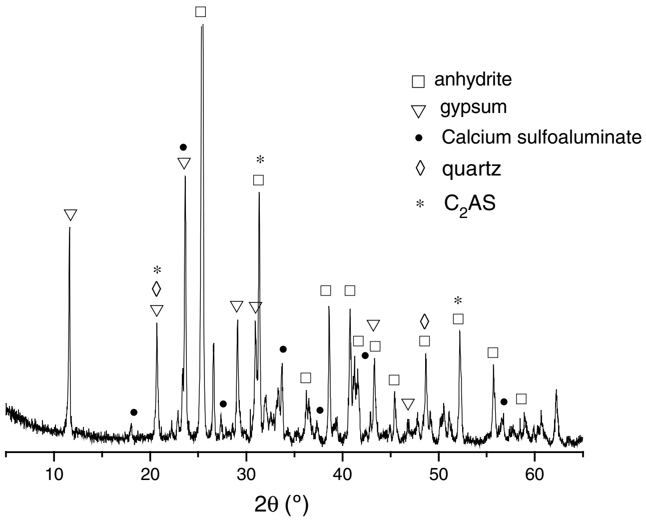


Fig. 1. XRD pattern of expansive agent.

## 2. Experiment

The materials used in this study included PO-525 ordinary Portland cement, complying with Chinese National Standard GB 175-92, and an expansive agent (commercially named UEA), complying with Chinese National Standard JC476-1998. Their chemical compositions are shown in Table 1. The Bogue calculation of the Portland cement gives 53% $C_3S$, 23% $C_2S$, 6% $C_3A$ and 12% $C_4AF$. The X-ray diffraction (XRD) pattern (Fig. 1) of the expansive agent shows that it is composed of calcium sulfoaluminate, anhydrite, gypsum, quartz and $C_2AS$.

The binder used consisted of 92% Portland cement and 8% UEA. The water binder ratio of prepared mortars was 0.45, and the sand binder ratio 2. The mixed mortars were cast into $40 \times 40 \times 140$ mm moulds, with the restraining frame consisting of a 4 mm diameter steel bar and two 4 mm thick steel plates welded on both ends of the bar (Fig. 2) and kept in humid air at $20 \pm 2$ °C for 18 h. Pastes having the same composition and water binder ratio were also prepared. After demoulding, the initial length of the restrained mortar prisms was measured. Then, the samples were cured at the different conditions as listed in Table 2.

A temperature match conditioning (TMC) system was developed to simulate the temperature development in the interior of fresh massive concrete [6]. The temperature in the curing bath, associated with the TMC system, rose from ambient temperature to 70 °C in 48 h and was kept at over 70 °C for 72 h. The highest temperature reached was 85 °C. After cooling down to 60 °C in the subsequent 48 h, the temperature was no longer controlled and fell to ambient temperature within 3 h. Samples were divided into three groups according to the humidity in the TMC process. Group 1 comprises Samples 0, 1 and 2, which were sealed during the TMC curing. Therefore, there was no exchange in humidity between mortars and the environment. Group 2 comprises Samples 3, 4 and 5, which were cured in saturated steam. Group 3 comprises Samples 6, 7 and 8, which were cured under water. After the TMC curing, the samples were stored at ambient temperature but at different moistures as listed in Table 2. A control sample (No. t) was cured continuously in the standard condition (ambient temperature and humid air).

The length of the mortar specimens was measured at scheduled ages. Pastes for XRD examination were ground, washed with acetone and filtered to stop hydration at the scheduled ages. Semi-quantitative assessment of ettringite (AFt) and mono-sulfoaluminate hydrate (AFm) in pastes was done by means of step scanning X-ray diffraction using Cu $K_\alpha$ radiation in the $2\theta$ range of 8.5–10°. The scanning step was 0.05°, signal collection time was 20 s per step (i.e. 0.15°$2\theta$/min). The intensities of the diffraction peak (1 0 0) of AFt ($d = 0.973$ nm) and peak (0 0 3) of AFm ($d = 0.89$ nm) were measured. The area between each peak and the baseline was integrated to indicate the relative quanti-

Table 1
Chemical composition of Portland cement and expansive agent

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $SO_3$ | Loss |
|---|---|---|---|---|---|---|---|---|---|
| Portland cement | 22.17 | 5.43 | 3.16 | 60.87 | 1.67 | 1.10 | 0.07 | 2.30 | 4.18 |
| Expansive agent | 10.45 | 11.70 | 2.00 | 35.80 | 3.28 | | 0.11 | 28.44 | 0.52 |

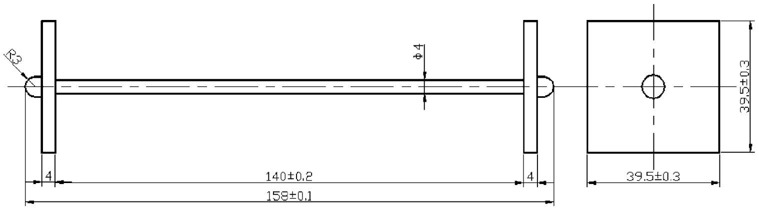


Fig. 2. The restraining frame for the preparation of restrained mortar prism.

Table 2
Curing condition of the mortars and pastes

| No. | Temperature scheme during first 1–7 days | Humidity condition during first 1–7 days | Storage temperature after 7 days | Humidity condition after 7 days |
|---|---|---|---|---|
| 0 | TMC 85 °C | Sealed | Ambient temperature | Sealed |
| 1 | | | | RH > 90% |
| 2 | | | | under water |
| 3 | TMC 85 °C | Steam | Ambient temperature | Sealed |
| 4 | | | | RH > 90% |
| 5 | | | | under water |
| 6 | TMC 85 °C | Under water | Ambient temperature | Sealed |
| 7 | | | | RH > 90% |
| 8 | | | | under water |
| *t* | Ambient temperature | RH > 90% | Ambient temperature | RH > 90% |

tative change of the AFt and AFm. Fractured surface of pastes was coated with an evaporated carbon film at scheduled ages for morphological investigation using scanning electron microscopy (SEM).

## 3. Result and discussions

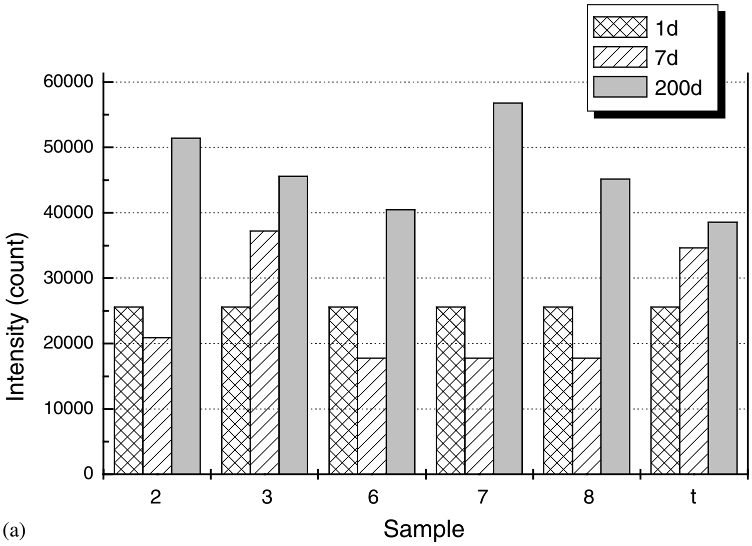
### 3.1. The time-dependent change of AFt and AFm relative quantity

The time-dependent variation of AFt and AFm relative quantity in the cement paste samples cured under different conditions is shown in Fig. 3. Some of ettringite were formed during the first hydration day in pastes prepared with Portland cement and expansive agent. There was a considerable increase in the AFm quantity and a gentle decrease in the AFt quantity, with only one exception, after 7 days of curing at the end of the TMC curing process. Heat curing enhances the hydration rate of the binder and hence increases the total quantity of sulfoaluminate hydrates. AFt is unstable under high temperature, but it is only partially decomposed and transformed into AFm during the TMC process. There may be a kinetic barrier to AFt decomposition. AFt can be restored slowly from AFm during a long period of storage at ambient temperature. Therefore, AFt quantity increased moderately and AFm quantity decreased significantly during 200 days of storage at ambient temperature. AFt quantity increased moderately and AFm quantity almost kept constant during long term storage in the control sample no. *t*. This indicates that DEF occurred in the samples initially cured under the TMC regime.

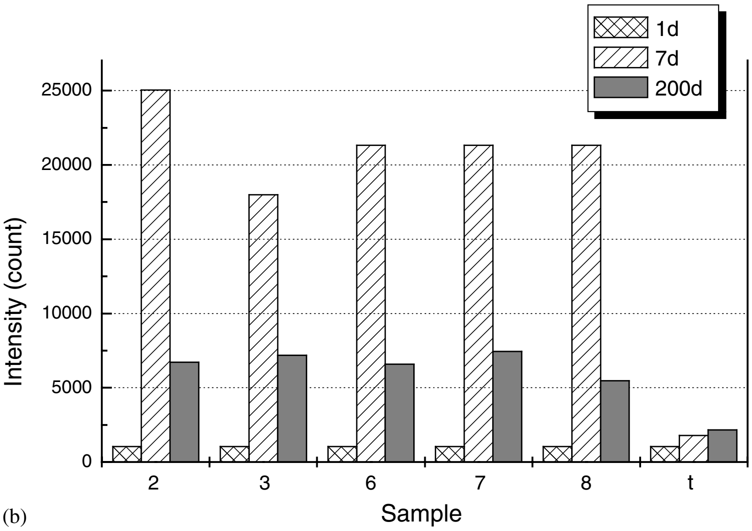
### 3.2. The time-dependent length change of restrained mortars

The time-dependent length change of the three groups of restrained mortars and the control sample are shown in Figs. 4–6.

The extent of initial expansion in restrained mortars was proportional to the humidity of the TMC process. The mortars which were sealed during the TMC process showed no expansion after 7 days at the end of the TMC process (Fig. 4). The mortars which were cured in saturated steam in the TMC process showed gentle expansion on the seventh day (Fig. 5). The mortars which were cured under water in the TMC process showed the largest expansion on the seventh day (Fig. 6) although they had the lowest ettringite content at that moment (Fig. 3). No extra moisture could have migrated into the sealed mortar. The degree of cement hydration in sealed mortar was not as high as those cured under moist conditions. As a result, the structure of sealed mortar no. 1 is more porous (Fig. 7) than that of mortar no. 6 cured under wet conditions (Fig. 8). Some large stick-like ettringite crystals were sparsely scattered in the sealed mortars, whereas there were mainly amorphous hydration products in the wet cured mortars, consisting



(a)



(b)

Fig. 3. The time-dependent variance of AFt (a) and AFm (b) in the cement paste samples cured in different conditions: (no. 2) sample was sealed in the TMC process and wet cured after the TMC process; (no. 3) sample was wet cured in the TMC process and sealed after the TMC process; (no. 6) sample was cured under water in the TMC process and sealed after the TMC process; (no. 7) sample was cured under water in the TMC process and wet cured after the TMC process; (no. 8) sample was cured under water in the TMC process and after the TMC process; (no. *t*) sample was cured continuously under the standard condition.

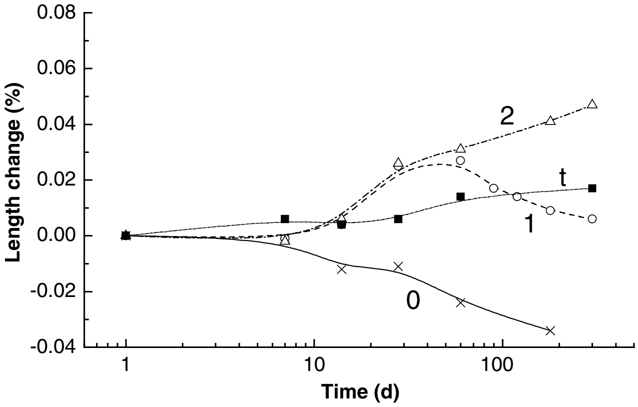


Fig. 4. The time-dependent length change of group 1 of restrained mortars and the control sample.

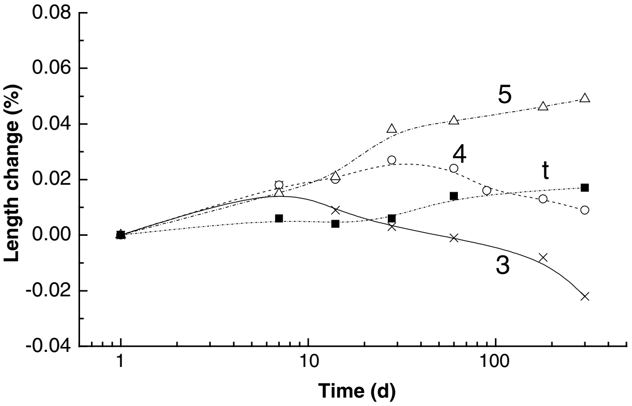


Fig. 5. The time-dependent length change of group 2 of restrained mortars and the control sample.

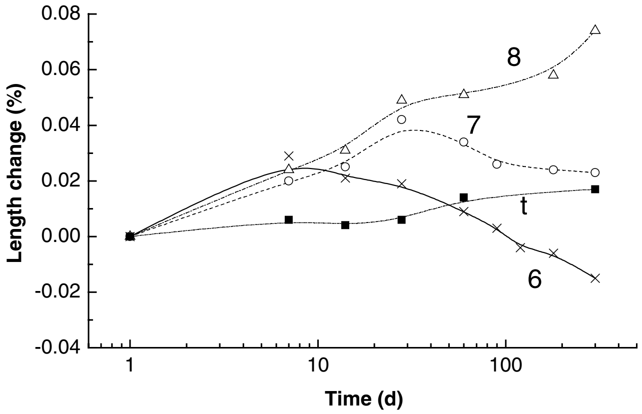


Fig. 6. The time-dependent length change of group 3 of restrained mortars and the control sample.

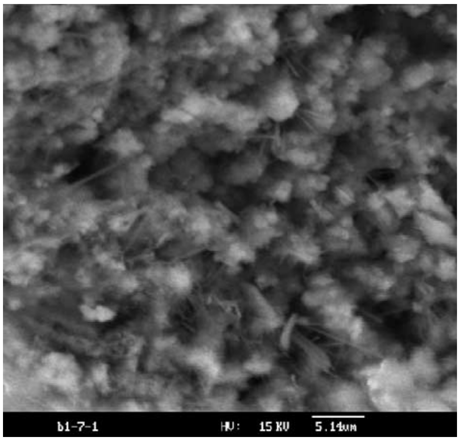


Fig. 7. Morphology of mortar no. 1 on the seventh day, i.e., the end of the TMC process.

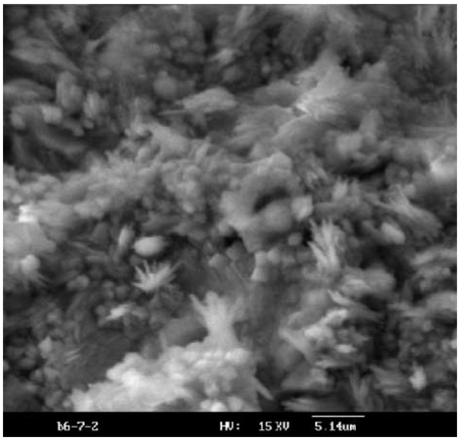


Fig. 8. Morphology of mortar no. 6 on the seventh day, i.e., the end of the TMC process.

of intermixed colloidal ettringite and C–S–H gel. Negro and Bachiorrini [15] concluded that mortar expansion is related to colloidal ettringite formation. The expansive efficiency of large ettringite crystals in porous mortars is lower than that of colloidal ettringite in dense mortars, even though there are similar quantities of ettringite in both the mortars. Therefore it becomes clear that the quantity of ettringite is not the exclusive factor determining the expansion of mortars; the mortar structure, morphology of ettringite, and extent of humidity in the curing process also contribute.

The control sample that was not subjected to the heat-curing procedure expanded slightly in the initial hydration period, then its longitudinal expansion increased gently but continuously with simultaneous strength increases. The expansive power was small and the expansion was suppressed by restraint from the steel frame in the initial hydration period. Strength and expansive power increase simultaneously along with the increase of ettringite quantity in mortar and density of the mortar structure. Harmonious increase of strength and longitudinal expansion in a confined mortar results in a prestress that compensates the drying shrinkage developed in later periods. Its expansion tends to become stable after 100 days.

The tendencies of length change of these mortars in the same group are different during the period after TMC process because the mortars were stored in different moisture environment. Sealed mortars begin to shrink after the TMC process while they cannot get more water for further hydration of the binder. There is an obvious fall in the expansion, due to drying shrinkage of the sealed mortars. Volume shrinkage of massive concrete structure cannot be compensated by addition of sulfoaluminate expansive agent in the relatively dry condition. The wet cured mortars expanded until about a month, and then began to shrink. Following a subtle reduction in the rate of expansion, the volume change tended to stabilise after 3 months for the wet cured mortars. No expansion for the mortar no. 1 that was sealed in the TMC process, and 0.02% for the mortar no. 7 that was cured under water in the TMC process remained after 300 days storage. It seems that volume shrinkage of massive concrete structure can be compensated when it is stored in humid conditions at later periods. Mortars cured under water expand continuously and do not show a decreasing tendency. There was an obvious delayed expansion for the mortars stored under water in later periods regardless of the moisture condition in the TMC process.

### *3.3. Mechanism of delayed expansion in restrained shrinkage-compensating mortar*

There are two different hypotheses to explain the expansion due to DEF. One focuses on the homogeneous expansion of paste due to swelling of colloidal ettringite [16], while the other considers local expansion due to growth pressure arising from crystallization of ettringite in existing gaps or at the interfaces between cement paste and aggregate [17]. The present study seemed to favour the former stand-point.

The length change of restrained shrinkage-compensating mortars stored in different humidity, after the same TMC process, showed obviously different tendencies (Figs. 4–6) even though they had similar quantities of AFt and AFm (Fig. 3). Samples cured under water during the TMC process showed similar dense microstructure after 200 days of storage in different conditions (Figs. 9 and 10). Both sealed and wet cured mortars had amorphous hydration products. The colloidal ettringite could not grow up into large crystal in the limited space of the restrained samples. Therefore, the large stick-like ettringite crystals formed due to precipitation from solution in existing gaps were rarely observed in mortars. The colloidal ettringite swelled considerably when it adsorbs more water in moist condition, as for sample no. 8. The colloidal ettringite could not swell with only limited moisture supply in a dry condition, as for sample no. 6. The mortars were unable to swell and showed shrinkage.

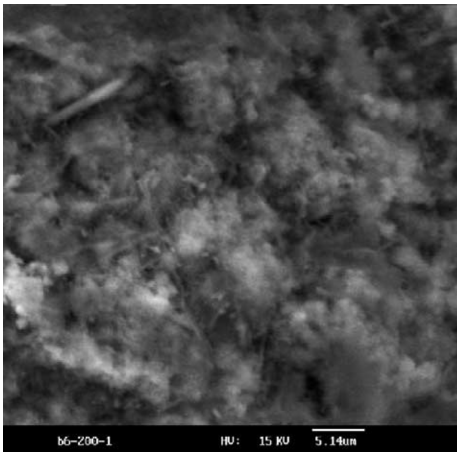


Fig. 9. Morphology of mortar no. 6 on the 200th day.

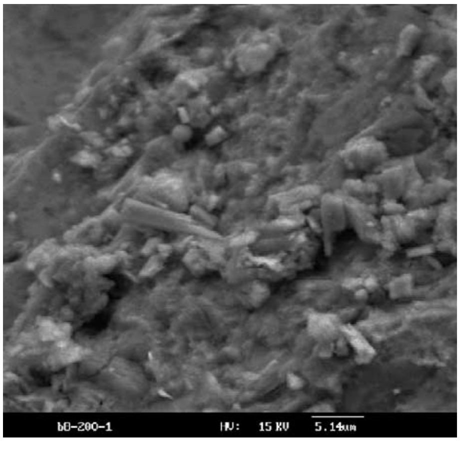


Fig. 10. Morphology of mortar no. 8 on the 200th day.

Local stress concentration occurs if there is local expansion because of the growth of ettringite crystals in gaps. It may result in cracking in hardened mortar that is brittle and cannot bear large tensile stresses. No cracking was observed by microscope on the surface of hardened mortars cured under water in the period after the TMC process, despite expansion strains much larger than 400 microstrains, which is usually considered to be the critical level of strain leading to concrete cracking. In the current case, uniform expansion took place in the restrained shrinkage-compensating mortars. A uniform delayed expansion does not always cause destruction of restrained concrete. Restrained shrinkage-compensating concrete may even be strengthened by a moderate uniform delayed expansion.

## 4. Conclusion

DEF occurs in shrinkage-compensating concrete subjected to temperatures higher than 70 °C. The restrained shrinkage-compensating mortars have similar quantity of ettringite but show different tendencies of time-dependent length change when they are cured under different moisture conditions. The quantity of ettringite is a very critical factor in determining the expansion of mortars, but mortar structure, morphology of ettringite and curing humidity are also relevant. The expansion induced by DEF is caused by colloidal ettringite. It does not, however, always result in the destruction of a concrete structure.

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