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The semiquantitative determination and morphology of ettringite in pastes containing expansive agent cured in elevated temperature

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Abstract

The semiquantitative determination and morphological investigation of ettringite in the paste containing 10% expansive agent was done with XRD and SEM-EDS under the temperature match conditioning (TMC), simulating the hydrating condition in shrinkage-compensating massive concrete. Elevated curing temperature over 70°C impedes the formation of ettringite or even induces its destruction. The relative humidity in the TMC process and later curing period with ambient temperature is a crucial factor determining the quantity, morphology and, as a result, the expansive potential of delayedly formed ettringite. Besides its amount, the morphology of ettringite is also an important factor to influence its expansive effect. The great expansion takes place only with the later formation of microcrystalline ettringite abundantly in the dense paste cured under water-saturated condition. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ettringite; Semiquantitative determination; Morphology; Temperature match conditioning

1. Introduction

Delayed ettringite formation (DEF) in the heat-cured concrete product has become of increasing concern [1–3]. It may cause the deterioration of the products during the later using time. Besides precast concrete products, some field cases of damage in concrete associated with DEF were reported [4–6]. The sulfoaluminate type expansive agent is widely used in China to prepare shrinkage-compensating massive concrete for the construction of the base of high-rising buildings. About 8–12% of binder are substituted by expansive agent. The SO_3 content in the binder is over 5%. The temperature in core of massive concrete may rise to over 80°C due to the hydration exothermicity of binder. Therefore, there is a potential possibility of DEF in shrinkage-compensating massive concrete [7].

Expansion, cracking and then destruction of concrete are associated with DEF. Collepardi [8] determined the preconditions of DEF based on a holistic viewpoint. They are microcrack, release of sulfate in later period and full supply of water. It cannot result in the damage due to DEF in absence of any one factor. There are two different expansion mechanisms of DEF: the uniformly expansion of paste and the crystalline pressure of ettringite [9,10]. The focus of argument is that there are preexisting microcracks in concrete before ettringite forms and the expansive mechanism of ettringite [11]. For example, Shayan and Ivanusec [12] considered cracking of alkali-aggregate reaction as the precursor of DEF, whereas Yang et al. [13] pointed out that the microcracks are induced by DEF.

In this work, the semiquantitative determination and morphological investigation of ettringite was done with XRD and SEM-EDS in the paste containing expansive agent under the temperature match conditioning (TMC), simulating the hydrating condition in shrinkage-compensating massive concrete. The expansion mechanism induced by DEF was discussed based on the experiment results.

2. Experiment

The used materials in the studies included PO-525 ordinary Portland cement complying with Chinese National Standard GB 175-92 and an expansive agent (the commer-

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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	TiO_2	P_2O_5	Loss
Portland cement	22.17	5.43	3.16	60.87	1.67	1.10	0.07	2.30	0.25	0.11	4.18
UEA	23.93	12.55	1.65	19.59	2.40	0.73	0.11	31.75	0.49	0.19	6.15

Table 2
Composition and curing condition of the pastes

Group no.	Sample no.	UEA (%)	W/B	Curing temperature during the first 1–7 days	Curing RH during the first 1–7 days	Curing RH after 7 days
1	1	0	0.44	TMC	Steam-curing	> 90%
	2	10		Ambient temperature	>90%	
	3	10		TMC	Steam-curing	
2	4	0	0.33	TMC	Under water	Under water
	5	10		Ambient temperature	Under water	
	6	10		TMC	Under water	
3	7	0	0.38	TMC	Sealed	80%
	8	10		Ambient temperature	80%	
	9	10		TMC	Sealed	

cial name is UEA) composed of sulfoaluminate clinker, gypsum and alunite complying with Chinese National Standard JC476-1998. Their chemical compositions are shown in Table 1. The Bogue calculation of used Portland cement gives 53% C_3S, 23% C_2S, 6% C_3A and 12% C_4AF.

The designations, water/binder ratios, substituting ratio of expansive agent and curing conditions of pastes are listed in Table 2. The nine samples can be subdivided into three groups according to water/binder ratios and the curing relative humidity. The pastes were mixed by machine for 3 min and cast into 20 × 20 × 20 mm moulds. The samples were kept in humid air at 20 ± 2°C for 18 h. After demoulding, the samples were cured under different conditions listed in Table 2.

A TMC system was developed to simulate the temperature development in the core of fresh massive concrete [7]. The temperature in the curing container slowly rose from ambient temperature to 70°C in 48 h and was kept over 70°C for 72 h. The highest temperature was 80°C. The curing temperature was not controlled and fell down to ambient temperature in 3 h after 7 days of TMC curing. Then, samples were cured in ambient temperature but different relative humidity. Parts of samples were cured without TMC, only in ambient temperature but different relative humidity.

Pastes for XRD test were ground, washed and filtered with acetone and then dried above silica gel in a desiccator to stop hydration at the scheduled ages. The semiquantitative assessment of ettringite (AFt) and monosulfoaluminate hydrate (AFm) in pastes was done by the means of the step scanning of X-ray diffraction with Cu K_α target in the two θ range of 8.5–10°. The scanning step was 0.02°, and signal collection time was 20 s per step. The intensities of peak (100) of AFt ($d = 9.73$ angstrom) and peak (003) of AFm ($d = 8.90$ angstrom) were measured. The area between the peak and the baseline is integrated after a correction of adsorption to indicate the relative semiquantitative change of the AFt and AFm. The freshly crushed fracture of pastes

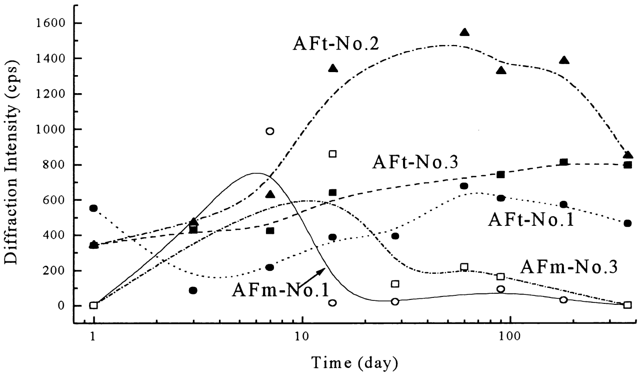

Fig. 1. The relative quantitative alternation of AFt and AFm in Group 1 pastes at the different time.

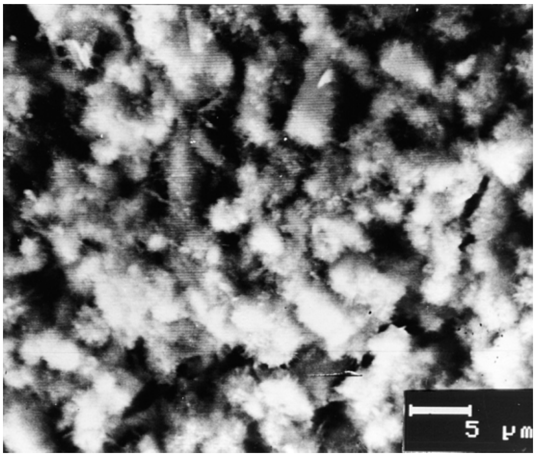

Fig. 2. Small acicular ettringite crystal in porous paste on the first hydrating day.

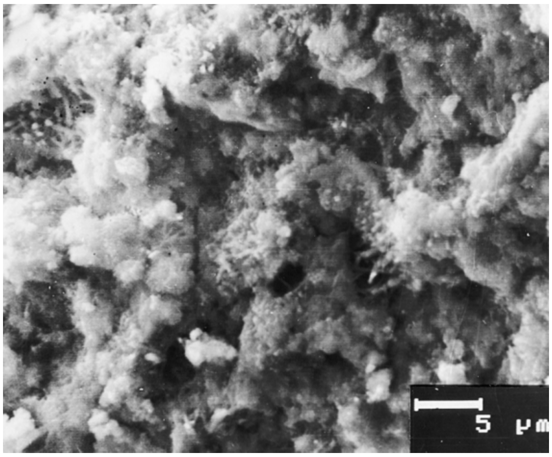

Fig. 3. Ettringite is seldom found in the dense paste no. 3 on the seventh day after TMC process.

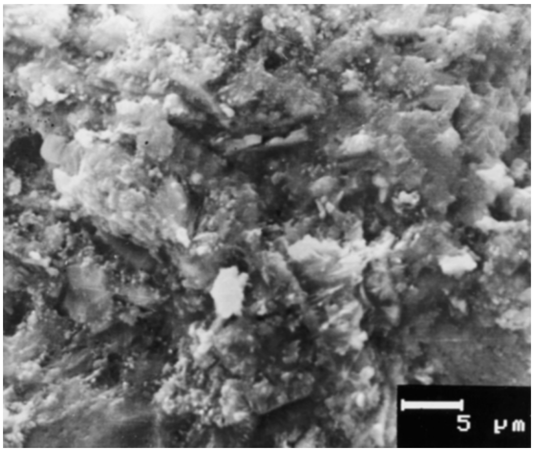

Fig. 5. Ettringite crystal cannot be found in paste no. 3 after 1 year.

was sprayed with a carbon film for morphological investigation and element microanalysis with SEM-DES at the scheduled ages.

3. Results and discussion

3.1. The semiquantitative assessment and morphology of ettringite in the first group of samples

The first group of samples was cured with relative humidity higher than 90%. Therefore, there was rather full supply of water during the hydration of binder. Fig. 1 shows the relative quantitative alternation of AFt and AFm in the different time determined with semiquantitative XRD. The amount of AFt is similar and AFm is ignored in all three pastes when they are cured in ambient temperature for 1 day. SEM investigation shows that some of small acicular ettringite crystal has been formed in the porous paste on the first hydrating day (Fig. 2). The amount of AFt in paste no. 2 that contains 10% UEA expansive agent and is cured in ambient temperature increases gradually during the first 28 days of hydration and changes little after then. AFm is little in the whole investigating period. This performance makes concrete prepared in same condition expand properly to compensate its shrinkage in early hydration period [7].

There is an obvious decrease of AFt amount in paste no. 2 after half year. According to the chemical composition of Portland cement and expansive agent, there are 6.14% of Al_2O_3 and 5.25% of SO_3 in the paste. If all of Al_2O_3 is used to form ettringite ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$), it needs 14.45% of SO_3 simultaneously. The great amount of ettringite formed in early period may be decomposed in later period due to the absence of SO_3, which results in the decrease of AFt amount. However, AFm is not detected by semiquantitative XRD at same time. The reason for this phenomenon is not clear yet and needs more research.

On the seventh day after the end of TMC process, paste no. 3 is dense and ettringite is found seldom (Fig. 3), as contrasted with paste no. 2 that is still porous and small

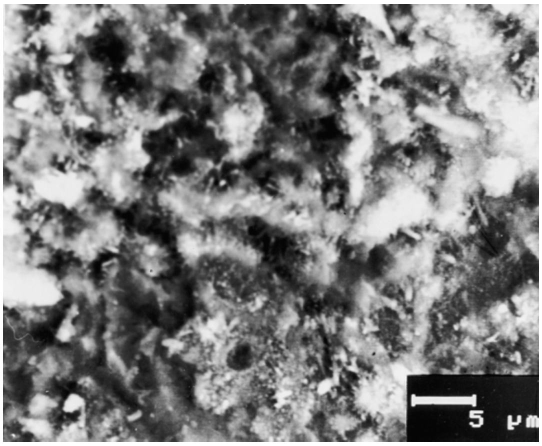

Fig. 4. Small acicular ettringite scatters in porous paste no. 2 on the seventh day.

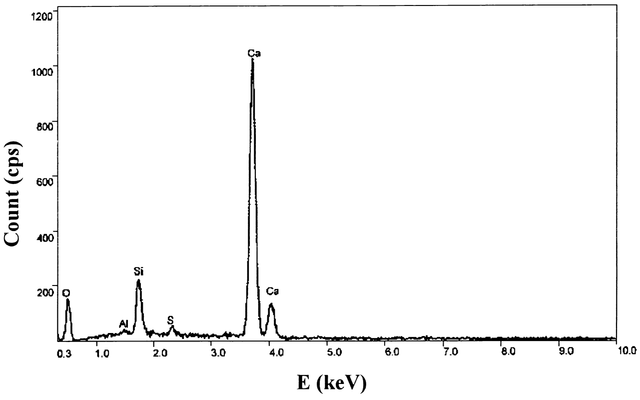

Fig. 6. The EDS microanalysis shows the existing Al and S in the uniform part of paste no. 3.

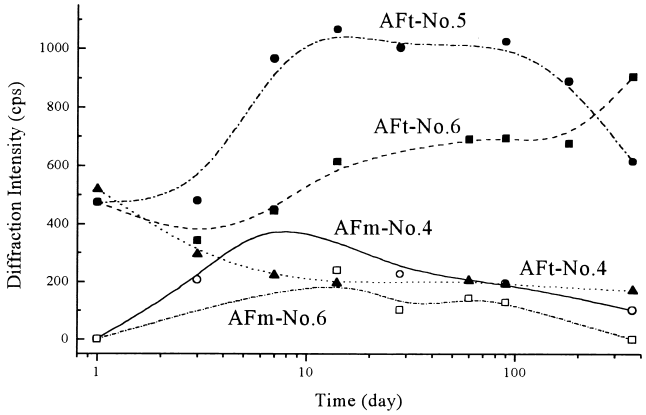

Fig. 7. The relative quantitative alternation of AFt and AFm in Group 2 pastes at the different time.

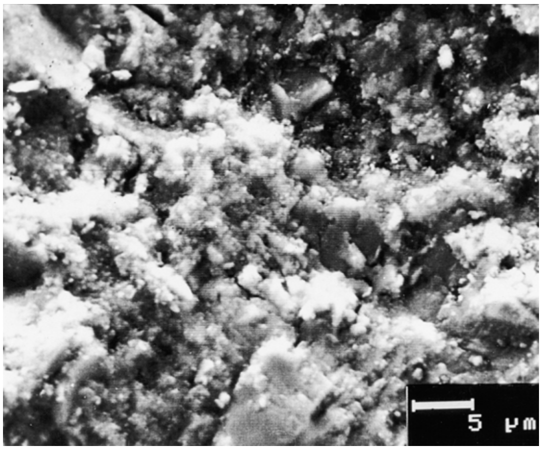

Fig. 9. Ettringite is seldom found in dense paste no. 6 on the seventh day after TMC process.

acicular ettringite scatters in it at same time (Fig. 4). The amount of AFt in paste no. 3 is less than that in paste no. 2 on the seventh curing day, the end of TMC process and in later period. The amount difference of AFt between paste nos. 2 and 3 enlarges with prolongation of hydration time. AFm forms in paste no. 3, reaches the peak value in 14 days and then decreases slowly. Therefore, the formation of AFt in paste no. 3 is impeded during the TMC process and increases a little after the paste cools to ambient temperature. Paste no. 1 that contains no UEA expansive agent but is cured with TMC regime shows a decrease of AFt amount. Its AFm peak value is higher and comes earlier than paste no. 3 because it contains less SO_3. There is a time delay between the lowest value of AFt and the peak value of AFm. Thus, there may not be a direct transformation of AFt into AFm but a complex multistep change.

After 1 year, paste no. 3 is dense and ettringite crystal cannot be found obviously in the paste (Fig. 5) although XRD measure shows its presence (Fig. 1). The microanalysis by EDS indicates that the uniform parts of paste contain S and Al element (Fig. 6). Therefore, ettringite whose formation was impeded during the TMC process has been formed lingeringly in the long curing period and is intermixed with C-S-H gel. It means that there is possibility of DEF in the pastes cured with TMC. Scrivener et al. [14] indicated that the microcrystalline ettringite formed in later period in the dense C-S-H gel exhibits large expansive tendency and is the cause of expansion. However, a restricted amount of ettringite in more porous paste introduced of higher water/binder ratio than other two groups of samples can result only in less expansion [7].

3.2. The semiquantitative assessment and morphology of ettringite in the second group of samples

The second group of samples was cured under water. Fig. 7 shows the relative quantitative alternation of AFt and AFm in the different time determined with semiquantitative XRD. Ettringite forms after 1 hydrating day. There is a decrease of AFt amount and an appearance of AFm in paste nos. 4 and 6 after TMC processing. It shows the destruction of original ettringite during the TMC process. Then, there

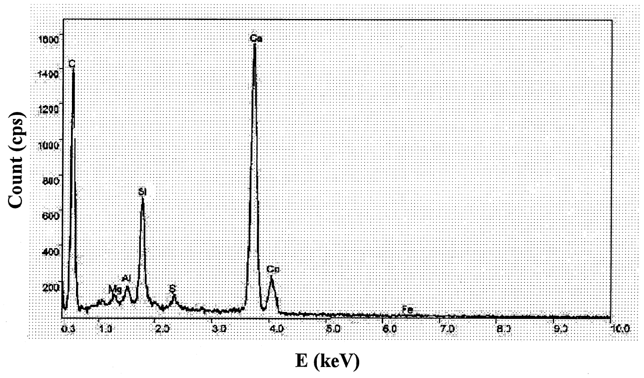

Fig. 8. The EDS microanalysis shows the existing Al and S in dense paste no. 6.

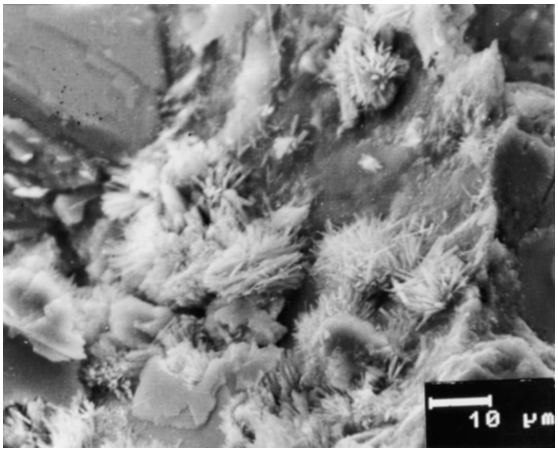

Fig. 10. Ettringite clusters scatter in dense paste no. 6 after 1 year.

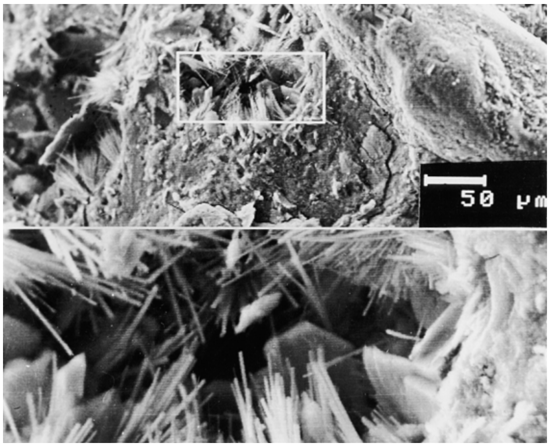

Fig. 11. Big ettringite crystals gather only in cavities in paste no. 5 after 1 year.

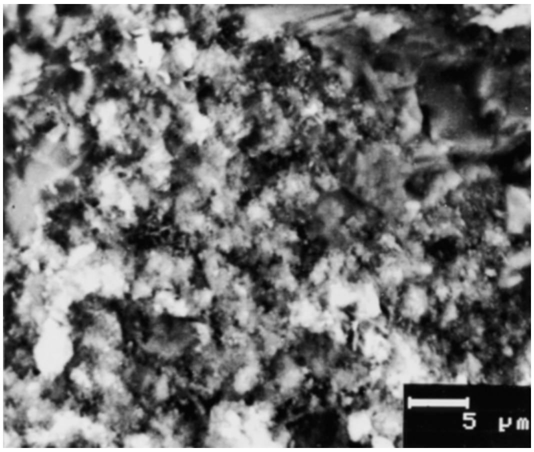

Fig. 13. The morphology of porous paste no. 9 after 1 year.

are two obvious increases on the amount alternation curve of ettringite in paste no. 6. One appears in the period soon after the finish of TMC process due to the quick reformation of ettringite in the environment of saturated humidity. EDS analysis indicates that there is some of S and Al element in the dense paste no. 6 (Fig. 8), but ettringite crystal can be detected seldom by SEM (Fig. 9). These crystalline ettringites are too small to be detected by SEM because the ettringite formed lately in hardened paste and enwrapped by C-S-H gel has no enough space to grow up. Another increase of AFt amount appears after 180 days when the initial cracking may take place in the paste due to gradual transfer and gather of microcrystalline ettringite in it. This phenomenon was described recently by Scrivener et al. [14]. A great amount of ettringite clusters scatters in the fracture of dense paste (Fig. 10), by contrast to that big ettringite crystals gather only in cavities in paste no. 5 cured all the time in ambient temperature (Fig. 11). The amount of ettringite in paste no. 6 is less than that in paste no. 5 during the first half year (Fig. 7), but the confined expansion of paste no. 6 is the largest in all the samples in this period [7]. It reaches 0.1% after 1 year, which can results in cracking in concrete. Therefore, besides the amount of ettringite, its morphological characteristics also affect greatly the expansive properties of samples. There is also an obvious decrease of AFt amount in paste no. 5 after half year. The reason can be considered as same as that in paste no. 2.

3.3. *The semiquantitative assessment and morphology of ettringite in the third group of samples*

The third group of samples was sealed during the TMC process and then cured in a hygrostat with relative humidity of 80%. Fig. 12 shows the relative quantitative alternation of AFt and AFm in the different time determined with semiquantitative XRD. There is also a decrease of AFt amount in paste nos. 7 and 9, which experience TMC process, but AFm forms only in paste no. 7. Absence of AFm in paste no. 9 means that initially formed ettringite

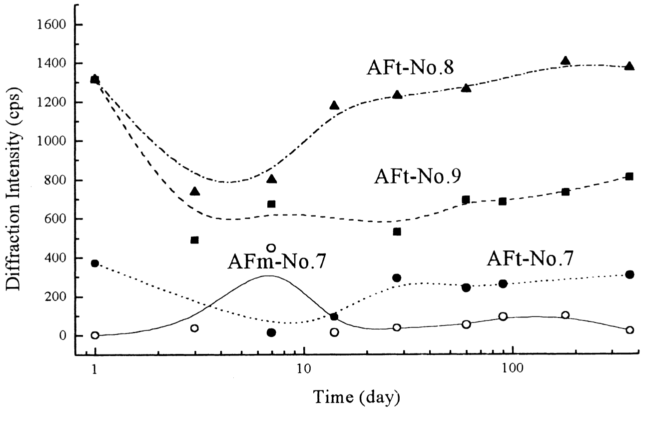

Fig. 12. The relative quantitative alternation of AFt and AFm in Group 3 pastes at the different time.

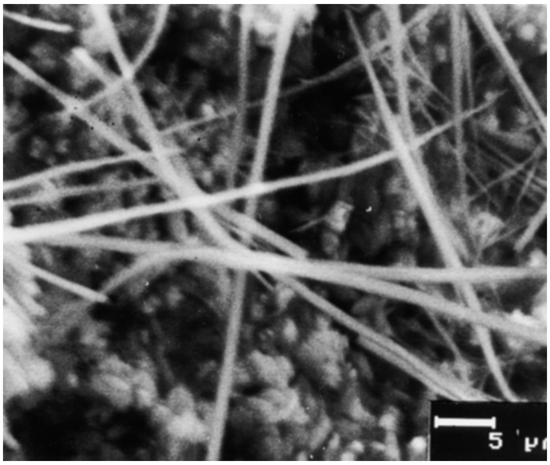

Fig. 14. Big dendritic ettringite crystals in paste no. 9.

does not transform into AFm but decomposes directly into SO_4^{2-} and Al^{3+}, which are adsorbed by C-S-H gel when the curing environment is dry. The hydration in the third group of samples is inhibited from the short of water supply. The amount of AFt in paste no. 9 does not increase much along the prolongation of curing time. Thus, the paste is not so dense as that in other two groups of samples (Fig. 13). There is more space allowing original or reformed ettringite to grow. This kind of big dendritic ettringite crystal growing in empty space (Fig. 14) has too little expansive effect to compensate the shrinkage of prisms. The third group of samples shrinks notably in later age [7].

4. Conclusions

Elevated curing temperature over 70°C impedes the formation of ettringite or even induces its destruction in the paste containing expansive agent, which results in the formation of monosulfoaluminate hydrate or the adsorption of SO_4^{2-} and Al^{3+} by C-S-H gel. The relative humidity in the TMC and later curing period with ambient temperature is a crucial factor that determines the amount, morphology and, as a result, the expansive potential of delayedly formed ettringite in the paste. Besides its amount, the morphology of ettringite and hardened paste is also an important factor to influence ettringite's expansive effect. The great expansion takes place only with the later formation of microcrystalline ettringite abundantly in the dense paste cured under water-saturated condition.

Acknowledgments

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