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Mineralogical characteristics of Ettringites synthesized from solutions and suspensions

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Abstract

Due to the wide technical importance of Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) in hydrated cement based systems, four different synthesis methods were applied to get a better overview on how and under what favoring conditions Ettringite can be formed. In the first step different precipitation methods resulting in Ettringite were established. For all methods Al^{3+} was supplied by aqueous CO_2-free solution of $Al_2(SO_4)_3 \cdot 18H_2O$. As a source of CaO-supply a clear solution and otherwise a $Ca(OH)_2$-suspension was utilized. Four synthesis routes with and without sucrose were employed.

Variation of reaction parameter like temperature, time of reaction, pH-value of synthesis solution and influence of additional Gypsum were investigated. The qualitative phase analysis was performed by X-ray diffraction method (XRD). Morphological aspects of some synthesis products were studied by scanning electron microscopy (SEM). Finally lattice and structural parameter of the Ettringites were determined by refinement of XRD-pattern using the Rietveld-Method.

Keywords: Ettringite; Characterization; SEM; X-ray diffraction

1. Introduction

Ettringite-type compounds are naturally occurring minerals, which also may be present in hydrated Portland Cements and Calcium Aluminate Cements. Ettringite was labeled "cement bacillus" by Ref. [1], because it was observed in damaged concrete. The appearance of this mineral always was associated with poor concrete performance. Nowadays Ettringite can always be found in concrete, which does not reduce concrete to an insufficient product. Primary Ettringite is not hazardous. In contrast it is also known that controlled Ettringite formation can result in unique hydraulic properties used for building chemistry purposes: very high early strength, superior sulfate resistance and lower drying shrinkage [2].

For this purpose the formation of Ettringite as main hydration product can be obtained by mixing calcium aluminate oxides (CA, CA_2, $C_{12}A_7$, C_3A) with sulfate (anhydrite, hemihydrate, gypsum) and water. CA, CA_2 and $C_{12}A_7$ are phases occurring in CAC clinkers whereas C_3A is a less abundant phase in OPC clinkers compared to C_3S. In the wide range of formulations for building chemistry applications both CAC and OPC are used in mixtures together with sulfate because of their very rapid early strength.

Fig. 1 shows composition of some phases projected on a ternary $CaO–Al_2O_3–SO_3$-grid. The arrow points to the projected anhydrous "$C_6A_{\bar{S}3}$" composition of Ettringite. In the plotted system $C_{\bar{S}}$ represents anhydrous composition of $CaSO_4$ (anhydrite), $CaSO_4 \cdot 0.5H_2O$ (hemihydrate) and $CaSO_4 \cdot 2H_2O$ (gypsum). The only true ternary phase in the system is calcium sulfoaluminate $C_4A_3\bar{S}$, a compound with sodalite structure. The CA_6 is the only calcium aluminate without hydraulic properties.

The presented investigation is targeted on mineralogical characterization of reaction products from various Ettringite synthesis methods with and without sucrose. Emphasis is

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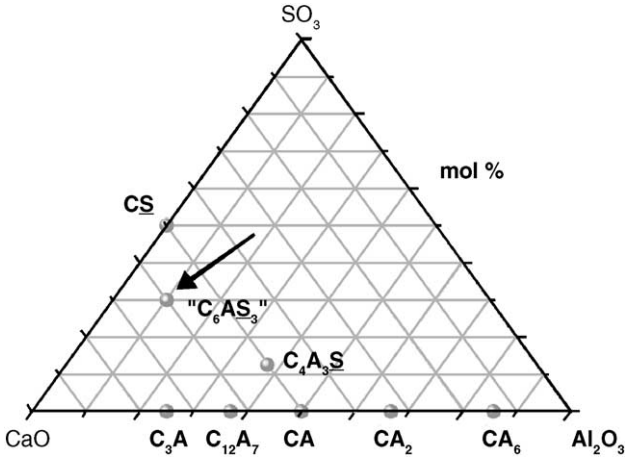

Fig. 1. Composition of some phases projected on a ternary $CaO–Al_2O_3–SO_3$-grid. The projected composition of Ettringite is "$C_6A\bar{S}_3$".

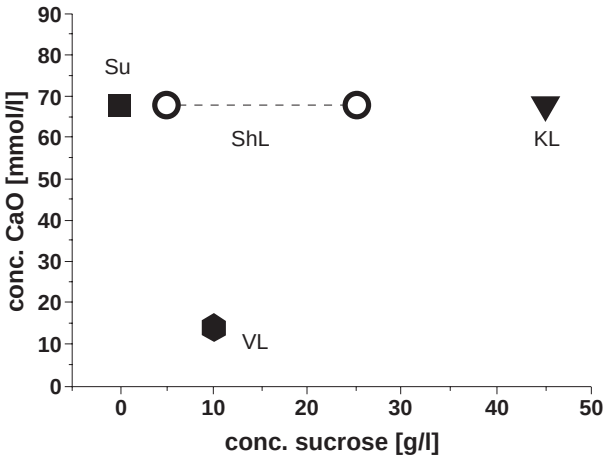

Fig. 2. CaO and sucrose concentrations of the Ettringite synthesis methods.

put on morphological and XRD investigation of Ettringite. Rietveld refinement of the XRD data was employed for crystallographic characterization of the Ettringites by using the structure proposed by Ref. [3].

2. Experimental

2.1. Synthesis

For all methods Al^{3+} was supplied by aqueous CO_2-free solution of $Al_2(SO_4)_3 \cdot 18H_2O$. Molar ratio of CaO to Al_2O_3 in the reaction solution resp. suspension was 6:1 for any synthesis. Only absolute concentrations of CaO plus Al_2O_3 in the solutions or suspensions were different (Fig. 2).

(A)	In order to permit high concentration of CaO while inhibiting precipitation of $CaCO_3$ the CaO was dissolved in aqueous solutions of sucrose [4].
VL	Precipitation from clear diluted solution of Ca^{2+} in H_2O (c_{CaO}=14 mmol/l and c_{Suc}=10 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=2.3 mmol/l)
KL	Precipitation from clear concentrated solution of Ca^{2+} in H_2O (c_{CaO}=68 mmol/l and c_{Suc}=45 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l)
ShL	Precipitation from sucrose/CaO-suspension (c_{CaO}=68 mmol/l and c_{Suc}=5–25 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l)
(B)	For comparison Ettringites from sucrose-free suspension were precipitated:
Su	Crystallization from aqueous $Ca(OH)_2$-suspension (c_{CaO}=68 mmol/l without sucrose) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l)

2.2. Microscopic examination

Selected Ettringite samples were sputtered with gold and investigated by SEM (LEO 1530). Although it is known that Ettringite dehydrates in vacuum, SEM micrographs are of excellent use to determine morphological differences of Ettringites. We could not observe any visible decomposition effects from our samples. SEM micrographs were used for determination of length and diameter of Ettringites by point counting method.

2.3. Thermal analysis

Thermal analysis was performed with a SDT 2960 Simultaneous DTA-TGA (TA Instruments) in air and in nitrogen atmosphere. For the investigation of the Ettringite samples a heating rate of 10°C/min and a gas flow of 100 ml/min were set.

2.4. X-ray diffraction analysis

X-ray investigations were carried out with a Siemens D5000 diffractometer using the following adjustments (Table 1):

Additionally XRD-pattern of the wet compounds at higher relative humidity could be recorded by using a SIEMENS X-ray powder diffractometer equipped with a reaction chamber. This device was used in step scan mode with fixed slits at 35 kV and 20 mA. With Rietveld method all XRD patterns of Ettringites were fitted in order to refine

Table 1
Instrument parameter for X-ray diffraction analysis

Generator: 30 mA, 40 kV	Detector slit: 0.2 mm
Tube: fine focus	Detector: scintillation
X-ray: CuK_α	Step/time: 0.02°/2s
Slits: fixed=0.5°	Range: 7–60° 2θ

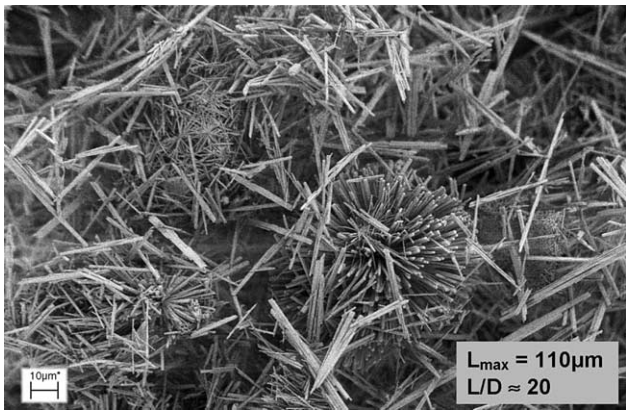

Fig. 3. SEM micrograph of precipitation product from synthesis method VL at pH 9.5: precipitation from clear diluted solution of Ca^{2+} in H_2O (c_{CaO}=14 mmol/l and c_{Suc}=10 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=2.3 mmol/l).

lattice parameters. For correction of preferred orientation the March–Dollase–Function [5] was applied:

$$I_{corr} = I_{calc} G_{hkl}(\text{March} - \text{Dollase})$$

with $G_{hkl}=[G_1^2 \cdot \cos^2(\alpha)+G_1^{-1} \cdot \sin^2(\alpha)]^{-3/2}$, G_1=refineable parameter, which gives information about relative orientation of crystals in the diffractogram (no orientation=>G_{hkl}=1,0), α=angle between Bragg angle and the perpendicular to the oriented plane (hkl).

3. Results

3.1. Morphological differences of synthetic Ettringites

Transmitted light microscopy was used to estimate the crystal sizes of Ettringites from different synthesis methods and to check for Calcite contamination in the dried synthesis products. Morphological information was exclusively obtained from SEM investigation. The values for determination of L/D (length/diameter) of the precipitated crystals

Fig. 4. SEM micrograph of Ettringite from synthesis method VL at pH 12.5: precipitation from clear diluted solution of Ca^{2+} in H_2O (c_{CaO}=14 mmol/l and c_{Suc}=10 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=2.3 mmol/l).

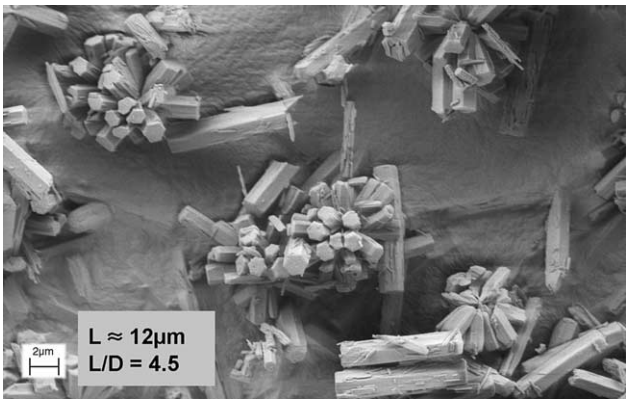

Fig. 5. SEM micrograph of Ettringite from synthesis method (VL) at pH 12.5. Rosettes of hexagonal prisms with longitudinal striation.

are the result from 40 to 90 single measurements on SEM micrographs.

3.1.1. Ettringite from diluted solution (VL)

Variation of reaction temperature from 8 to 30 °C and synthesis time from 2–62 days did not affect the crystal morphology of the Ettringites from clear diluted solution of Ca^{2+}in H_2O (c_{CaO}=14 mmol/l and c_{Suc}=10 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=2.3 mmol/l). Depending on pH, two extreme crystal morphologies of Ettringite could be determined. At pH of 9.5 in solution the precipitated Ettringite crystals can be assigned to two different populations. First groups of Ettringites exhibit a very thin extremely acicular shape and are grown together in the direction of *c*-axis. The hexagonal prisms are up to 110 µm in length and their *L*/*D* value is about 20. They form fibrous, radial crystal aggregates (Fig. 3). Between the large other aggregates of small acicular non-idiomorphic crystals can be observed.

Whereas, change of pH to 12.5, by addition of sodium hydroxide, led to more prismatic hexagonal crystals which can achieve length up to 20 µm in direction of *c*-axis (Fig. 4). But more noticeable are the aggregates of smaller

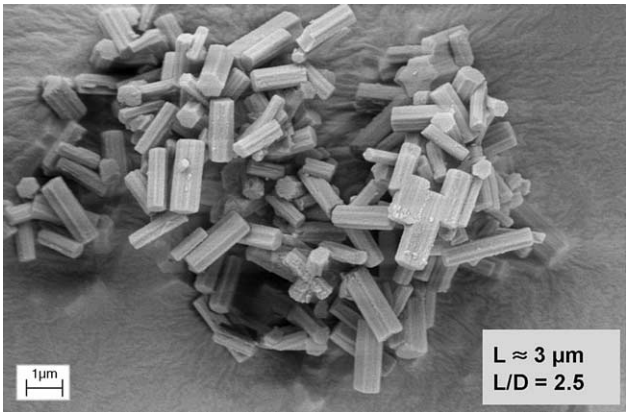

Fig. 6. SEM micrograph of Ettringite from method KL at pH 12.5. Precipitation from clear concentrated solution of Ca^{2+} in H_2O (c_{CaO}=68 mmol/l and c_{Suc}=45 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l).

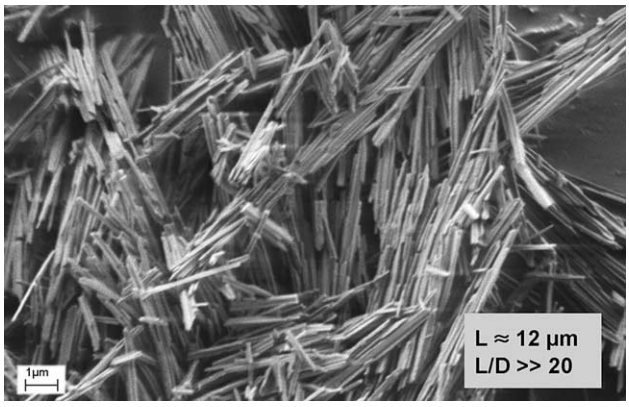

Fig. 7. SEM micrograph of Ettringite from method Su at pH 12.5: crystallization from aqueous $Ca(OH)_2$-suspension (c_{CaO}=68 mmol/l without sucrose) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l).

crystals of about 12 µm in length (L/D value=4.5). The crystals show clearly the {100} prism faces. Sometimes longitudinal striation is visible, which can be an evidence of a growing together of smaller crystals in the direction of c-axis (Fig. 5).

3.1.2. Ettringite from concentrated solution (KL)

Very small crystals are formed from concentrated solution. SEM micrographs of Ettringite from synthesis method KL clearly show small and short prismatic (barrel-shaped) crystals with 3 µm length and L/D value of 2.5 (Fig. 6). The prism faces exhibit polysynthetic twinning. Almost none of the particles are covered by epitaxial growth.

3.1.3. Ettringite from concentrated solution and variable sucrose concentration (ShL)

Ettringites after synthesis time of less than 10 days are very similar to those from concentrated solution. The precipitates after more than 20 days of reaction time show again a second generation of smaller elongated lath-shaped Ettringite crystals.

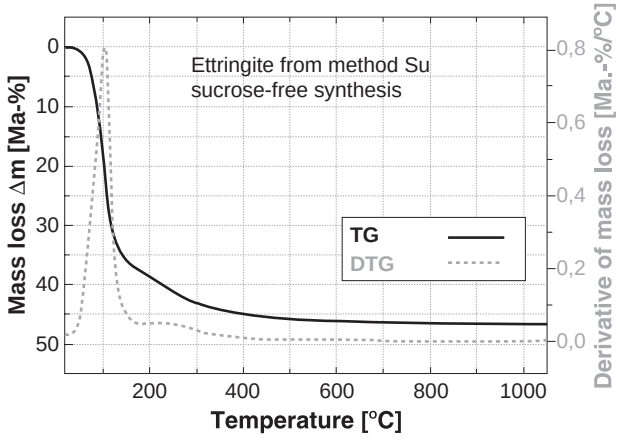

Fig. 8. Thermal analysis of Ettringite from method Su at pH 12.5: crystallization from aqueous $Ca(OH)_2$-suspension (c_{CaO}=68 mmol/l, sucrose free) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=11.4 mmol/l).

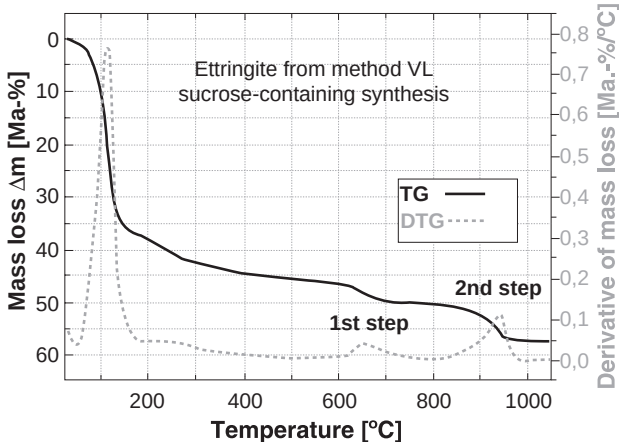

Fig. 9. Thermal analysis of Ettringite from synthesis method VL at pH 12.5: precipitation from clear diluted solution of Ca^{2+} in H_2O (c_{CaO}=14 mmol/l and c_{Suc}=10 g/l) and solution of $Al_2(SO_4)_3$ nH_2O ($c_{Al2(SO4)3}$=2.3 mmol/l).

3.1.4. Ettringite from sucrose-free suspension (Su)

Ettringite crystals synthesized from sucrose-free suspension (Su) exhibit a very distinct acicular shape in the direction of c-axis. They form fibrous, polycrystalline aggregates of Ettringite crystals with individuals of 12 µm length and L/D about 20. No other minor phases could be detected (Fig. 7).

3.1.5. Comparison of morphological appearances

The micrographs from method VL at pH of 9.5 and 12.5 indicate a clear correlation of morphology and pH in synthesis solution. At high pH the short prismatic shape of Ettringite crystals with L/D=2.3 is very distinct.

The morphology of Ettringite crystals from suspension method (Su) is despite of pH 12.5 lath-shaped elongated with L/D values above 20.

3.2. Dehydration of Ettringite

The results of thermal analysis under N_2-atmosphere show clearly the difference between synthesis products from solutions or suspensions of sucrose/CaO and from sucrose free synthesis methods. Analysis of Ettringite from method Su (sucrose free) confirms the expected thermal behavior: two endothermic dehydration reactions can be observed at 80 to 90 °C and at 200 °C. A water content of 32.4±1.3 H_2O per formula unit was determined by LOI of 10 samples (Figs. 8 and 9).

In contrast to sucrose-free method Su the dehydration of Ettringites from sucrose containing synthesis solution (VL, KL, ShL) always show two additional thermal events at about 630 °C and 850 °C. This effect is very intensive under

Table 2
Refined lattice parameter of all synthesized Ettringites

Synthesis	VL	KL	ShL	Su
a_0 [Å]	11.233 (6)	11.226 (6)	11.227 (8)	11.237 (5)
c_0 [Å]	21.474 (7)	21.472 (14)	21.470 (8)	21.474 (11)

N_2-atmosphere. We assume that this is due to a reduction–oxidation reaction of SO_4^{2-}in the presence of little contamination of organic carbon, resulting from dehydration of sucrose at about 200 °C:

1st step: SO_4^{2-} to SO_3^{2-}(reduction by organic carbon)
2nd step: SO_3^{2-} to $SO_2\uparrow$ (decomposition)

A clear thermal event could not be observed, which would be characteristic for decomposition of crystalline sucrose, because only little sucrose is necessary for the reduction effect.

3.3. Refinement of lattice parameter by Rietveld analysis

With Rietveld method all XRD patterns of Ettringites from the 4 synthesis methods lattice parameter were refined. The determined mean values of *a*- and *c*-parameters from every 10 synthesized Ettringites are not significantly different (Table 2).

Additional information, which can be deduced from Rietveld refinement of XRD-data, is represented by the values for preferred orientation of Ettringite crystals perpendicular to (100)-plane. In accordance to morphological investigations we could determine a very strong orientation of Ettringite powder samples from method Su with G=0.6; the orientation of Ettringite from all synthesis methods with sucrose (VL, KL, ShL) always showed G values of about 0.9, which indicates much less orientation in the powder sample (Fig. 10).

Information about crystallite sizes of Ettringite from different synthesis method could not be collected from Rietveld refinement. The structural model for Ettringite proposed by [3] is not adequate enough for refinement of structural parameter like occupancy factors and atomic positions. The structure misses all 128 positions for H in the model.

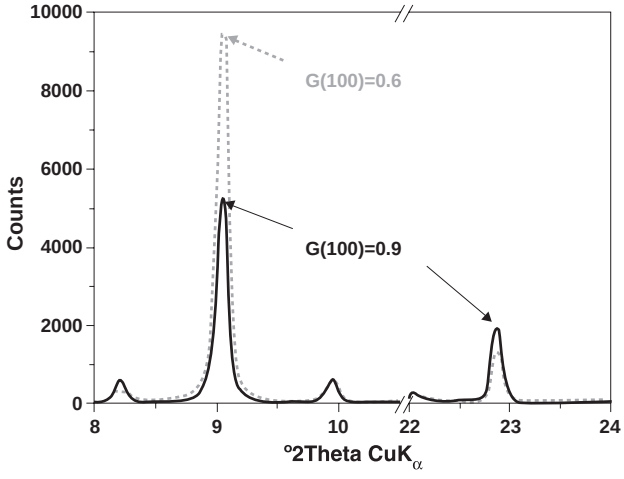

Fig. 10. Typical XRD-pattern of Ettringites from method Su (G=0.9) and KL (G=0.6).

Nevertheless, the position that the reaction parameters, like concentration of CaO and $Al_2(SO_4)_3$ nH_2O, sucrose concentration, pH, temperature, and reaction time, influence lattice parameter could be not confirmed. No significant differences except for preferred orientation could be determined.

4. Conclusion

From our investigations we can conclude that *L*/*D* values of Ettringite crystals are higher at pH 9.5 than at pH 12.5 (=>VL). At constant pH of 12.5 *L*/*D* values decrease with sucrose concentration in the synthesis solution.

Synthesis methods with sucrose (VL, KL, ShL) led to less oriented particles in the powder sample.

Investigations of dehydration of Ettringites from sucrose method by thermal analysis show additional thermal effects (reduction–oxidation) due to molecular sucrose.

Synthesis method has no influence on lattice parameter of Ettringite and on chemical composition of Ettringite (except organic carbon). The ratio of CaO/Al_2O_3 is very good and reproducible for any synthesis method. This led us to the conclusion that sucrose may only be adsorbed at the crystal surfaces of the Ettringite structure.

5. Discussion

As consequence from our investigation we cannot recommend synthesis of Ettringite by methods employing sucrose. The possible incorporation of sucrose into the precipitated Ettringites very much depends on the chosen synthesis route and therefore from concentration in synthesis solution.

All operations during synthesis, filtration, and storage of Ettringites synthesized by sucrose methods are very sensitive to calcite formation.

For quantitative analysis of concrete further investigation on Ettringite structure is needed. In the first published Ettringite structure, proposed by Moore and Taylor [3], all 128 positions for H are missing in the unit cell, which results in reduced scattering power by use of this model for quantification purposes. For precise quantification of Ettringite in mixtures with anhydrous phases the scattering contribution of all atoms inclusive the H-positions is indispensable and has to be included. We have worked out a revised structure model of Ettringite, which includes the H-positions with the appropriate thermal parameter and which will be published in the near future.

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