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About thaumasite formation in Portland-limestone cement pastes and mortars—effect of heat treatment at 95 °C and storage at 5 °C

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Abstract

Owing to the presence of finely divided calcite, mortars and concretes made with Portland-limestone cements are particularly susceptible to damaging thaumasite formation during sulfate attack at lower temperatures. This work reports the results of investigations on mortars made according to DIN/EN 196 and pastes (*w*/*c* ratio of 0.5) with CEM I 42,5 R, as well as with mixtures of cement with limestone filler. Some of the samples were heat-treated at 95 °C. The length changes and resonant frequencies of the samples were measured during long-term water-storage at 20 and 5 °C. There was no evidence from X-ray diffraction data of thaumasite formation in the samples. Only for pastes containing 30 wt.% limestone filler were small areas found by SEM and X-ray microanalysis whose chemical analysis matched thaumasite or a thaumasite–ettringite solid solution.

Keywords: Thaumasite; Limestone cement; Heat-treatment; Soundness

1. Introduction

The risk of destruction of mortar and concrete made with Portland-limestone cement in particular is increased by the presence of fine calcite particles due to the formation of thaumasite during sulfate attack at low temperatures [1]. It is supposed that thaumasite only forms when all the tricalcium aluminate contained in the cement has reacted with calcium sulfate to form ettringite [2]. Sylla [3] tested the effects of changed sulfate binding caused by early heat treatment which led to the formation of new phases and particularly thaumasite. Solid solutions of ettringite and thaumasite with a high proportion of thaumasite were identified in suspensions of heat-treated cement samples after a storage period of 3 months at 5 °C with CO_2 addition. It was shown that, in this case, no excess of sulfate supplied through sulfate attack was essential for the formation of thaumasite.

In addition to sulfate, Portland-limestone cement contains calcite, which is a reaction partner of tricalcium aluminate from the beginning of the cement hydration-process. This could influence the reaction processes during the hydration of cement. In this respect interest is focussed on the formation of sulfate-containing phases during the hydration of heat-treated Portland-limestone cement, whereby CSH phases are a further source of sulfate.

The aim of this research was to find out about the hydration and in particular the (potential) formation of thaumasite in mortars and pastes made with Portland-limestone cement and stored at 5 °C.

2. Materials and methods of testing

In the experiments a cement, type CEM I 42,5 R and its mixes with 15 and 30 wt.% limestone from Jurassic limestone (Jurakalk) was used. The limestone was milled to a degree of fineness similar to that of limestone in Portland-limestone cement (94% <63 μm). The particle size of the original materials was characterised using air jet screening. The density was determined with a helium pycnometer, the specific area was measured according to the Blaine method. The results are shown in Table 1.

The chemical analyses of the original materials was determined by X-ray fluorescence analysis after the samples had been ignited at 1000 °C. The Na_2O, K_2O, SO_3 and Cl contents were determined according to DIN/EN 196, part 2 and part 21. The content of CO_2 was measured volumetrically. For the calculation of clinker-phases according to Bogue, it was supposed that all of

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Table 1
Particle size distribution (air-jet screening), density and specific surface of cement and limestone

Particle size (mm)	Cement CEM I 42,5 R (wt.%)		Limestone (wt.%)	
	F	R	F	R
>0.09	–	–	0.6	0.6
0.09–0.063	–	–	5.2	5.8
0.063–0.04	–	–	4.4	10.2
0.04–0.032	1.2	1.2	9.7	19.9
0.032–0.025	7.2	8.4	6.2	26.1
0.025–0	91.6	100.0	73.9	100.0
Density (g/cm^3)	3.14		2.77	
Spec. surface acc. Blaine (cm^2/g)	4900		9000	

F: part of fraction; R: coarse of the screen.

the SO_3 content was bound as $CaSO_4$ and all of the CO_2 content was bound as $CaCO_3$. The results are shown in Table 2. Powder XRD analysis showed the presence of the anhydrous phases in the cement: C_3S, β-C_2S, C_3A, periclase (MgO), anhydrite ($CaSO_4$), calcite ($CaCO_3$) and brownmillerite ($C_2(A,F)$). In addition to calcite, small amounts of dolomite, quartz, mica and illite were identified in the limestone.

The mortars were prepared according to DIN/EN 196 part 1. The pastes were prepared in accordance to DIN/EN 196, part 3 with a water/cement ratio of 0.5. For the investigations flat prisms ($1\times4\times16$ cm^3) with gauge studs were cast using pure cement and mixes with 15% and 30% of limestone. Part of these samples were stored for 2 h and then treated in water at 95 °C for 4 h. The rest of the samples were first stored for up to 24 h in an environment of 20 °C and 95% relative humidity. The ensuing storage was in water at 5 and 20 °C.

Table 2
Chemical composition of cement and limestone

Components	Cement CEM I 42,5 R	Limestone
SiO_2	20.80	7.59
Al_2O_3	4.90	2.76
Fe_2O_3	2.24	1.01
CaO	62.60	86.57
MgO	2.80	1.44
K_2O	1.41	0.18
Na_2O	0.11	0.03
TiO_2	0.31	0.16
ZnO	0.07	0.03
Mn_2O_3	0.44	0.06
P_2O_5	0.06	0.03
SO_3	3.85	0.03
Total	99.59	99.89
LI 1000 °C	3.05	41.18
CaO_{free}	0.60	–
CO_2	2.19	39.05
Na_2O_{eq}	1.04	0.15
C_3S	43.8	–
C_2S	26.6	–
C_3A	8.5	–
C_4AF	8.2	–

3. Results and discussion

3.1. Length change and resonance frequency of the samples

The length change and resonance frequency of the heat-treated samples were measured after different periods of hydration (Figs. 1–4). Mortar samples without heat-treatment after 720 days showed a low expansion of ca. 0.20 mm/m at 20 °C storage temperature and even lower shrinkage at 5 °C. The expansion decreased with increasing limestone content. After increasing during the

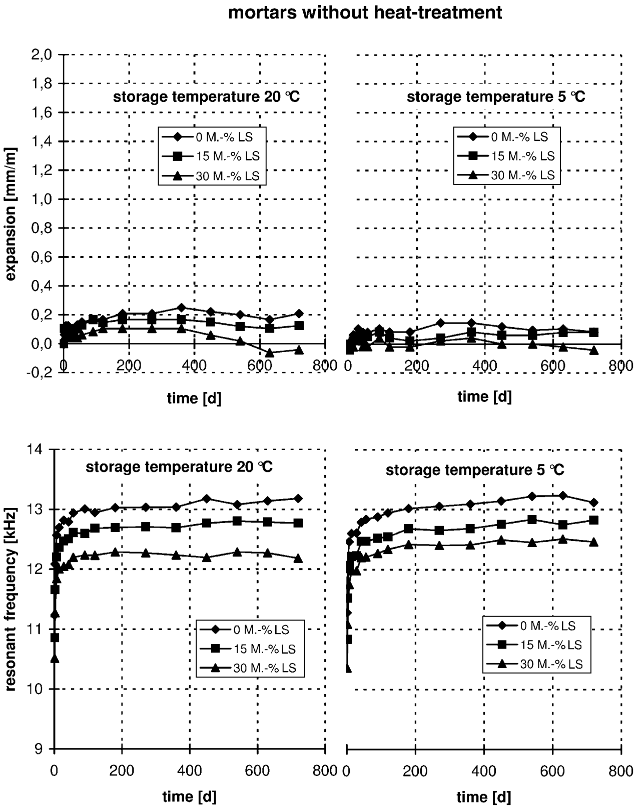


Fig. 1. Length change and resonant frequency of mortars without heat-treatment (LS = limestone).

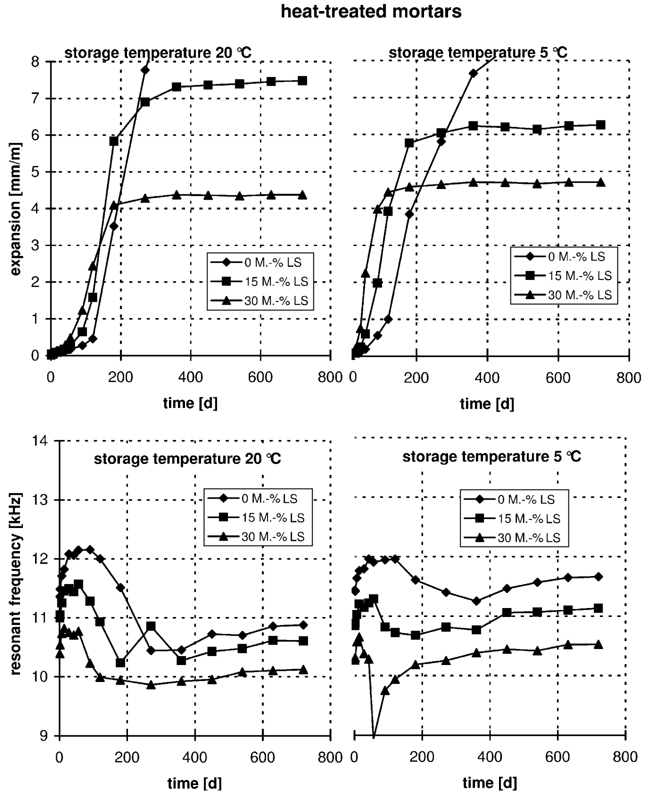


Fig. 2. Length change and resonant frequency of mortars with heat-treatment (LS = limestone).

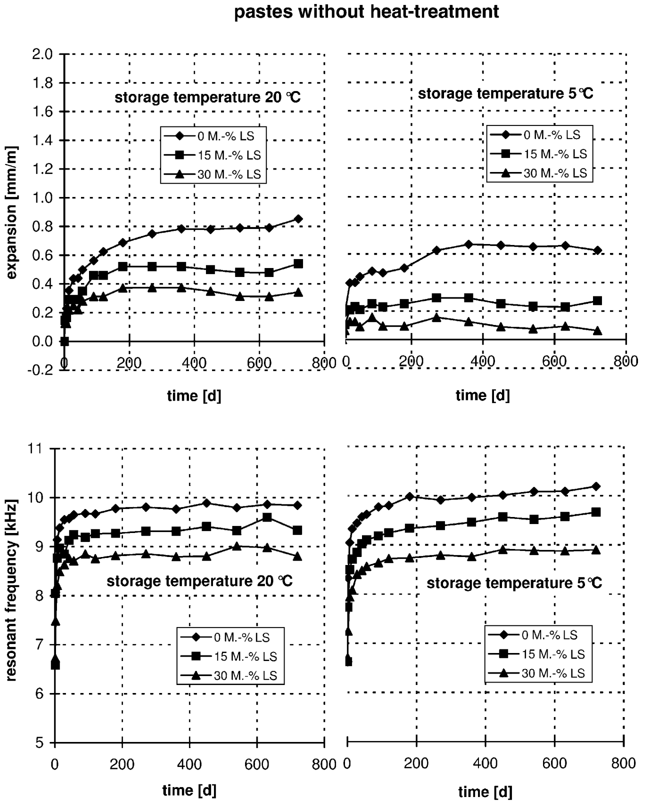


Fig. 3. Length change and resonant frequency of pastes without heat-treatment (LS = limestone).

first 6 months, the resonant frequency remained almost constant for the following 18 months. The resonant frequency decreased as the limestone content increased.

Heat-treated mortar samples, on the otherhand, showed high expansions of up to 11.3 mm/m during the time of examination (Fig. 2). The evolution of expansion depends on the amount of limestone and on the storage conditions. An earlier beginning of the expansion was observed with an increasing amount of limestone and/or a decrease of storage temperature. The addition of limestone led to earlier termination of the main expansion phases and to lower expansion after 720 days. The resonant frequency decreased during the expansion period. Afterwards the resonance frequency stayed constant or increased slightly. Cracks occurred in all the samples stored for longer than 6 months at 20 °C. For up to 720 days storage, paste samples without heat treatment showed higher rates of expansion than the mortar samples (Fig. 3). Similar to the mortar prisms, the expansion increased at lower limestone contents or higher temperature of storage. The resonance frequency increased for the first 180 days and then stayed almost constant.

It was observed that after one year, in contrast to samples not subjected to heat-treatment, the heat-treated samples exhibited higher expansion rates with an increasing amount of limestone (Fig. 4). For example, samples with 30% of limestone extended by 1.17 mm/m at 20 °C and 0.90 mm/m at 5 °C after one year. In the second year of storage at 20 °C, the samples with limestone showed distinct expansion. At 5 °C the expansion remained at a low level. The resonant frequencies showed no significant decrease during that period.

3.2. Mineralogical analyses

The hydrates formed in the aged samples were examined by X-ray diffraction analysis (XRD), scanning electron microscope (SEM) and X-ray microanalysis. The content of ettringite in the hydrated samples was determined using the method of internal standards. Calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$) was used as the internal standard. For XRD and X-ray microanalysis, fragments of the mortar and paste samples were sputtered with carbon. The results of the analyses are presented in the Figs. 5–8 and in the Tables 3 and 4. Ettringite and monocarboaluminate hydrate were identified in the mortar samples after 360 days storage at 5 and 20 °C. The concentration of monocarboaluminate was found to increase with the amount of calcium carbonate in the cement. No thaumasite was identified for mortar samples stored at either 5 or 20 °C.

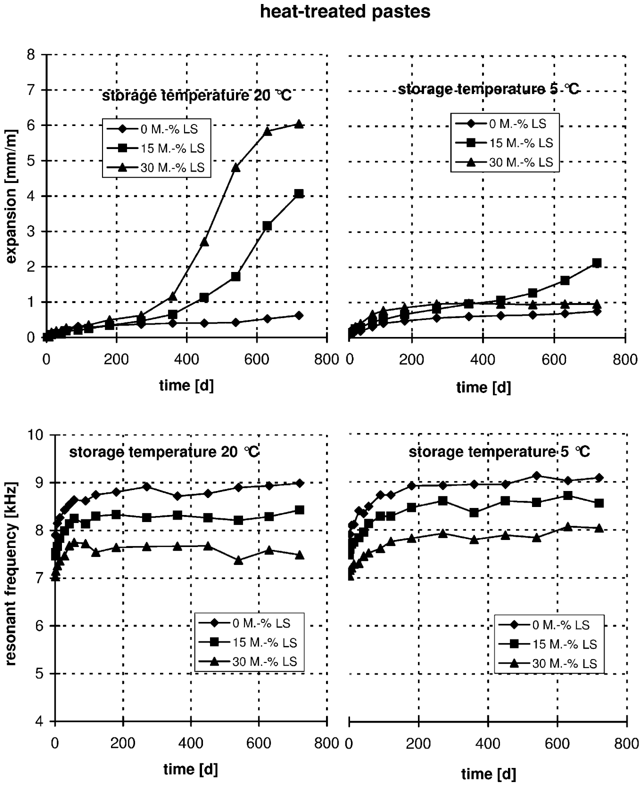


Fig. 4. Length change and resonant frequency of pastes with heat-treatment (LS = limestone).

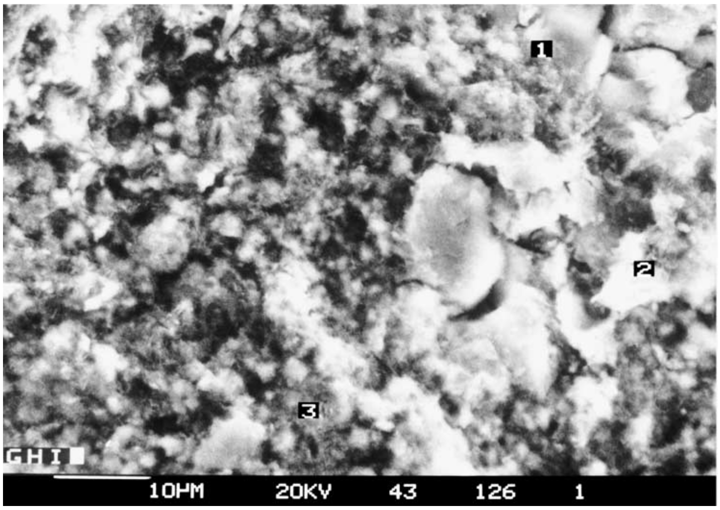
Compared to the heat-treated samples, a lower amount of ettringite and higher amount of monocarboaluminate was found in the samples without heat treatment after 360 days. In the heat-treated mortar samples no thaumasite was identified by XRD. As in the mortar samples, ettringite and monocarboaluminate hydrate were also identified in paste samples stored at 5 and 20 °C after 360 or 720 days hydration. The amount of ettringite was found to increase slightly with decreasing limestone content and storage temperature.

Monosulphoaluminate hydrate and a small amount of ettringite were identified in heat treated pastes containing no limestone and stored at 5 and 20 °C. The same hydrates were found in the pastes prepared with 15% limestone stored at 20 °C. A higher amount of ettringite was identified in the paste prepared with 15% limestone and stored at 5 °C. The same was found for the paste prepared with 30% limestone and stored at 5 and 20 °C. The amount of monocarboaluminate hydrate observed by XRD increased with increasing $CaCO_3$ content in the samples.

To give proof of the existence of thaumasite–ettringite solid solution the d-spacings of the ettringite peak at about 9.1° were measured exactly. The existence of the solid solutions shifts the peak to a lower value. The d-spacings listed in Table 4 which deviate only slightly from that of ettringite, give no indication for the formation of ettringite–thaumasite solid solutions.

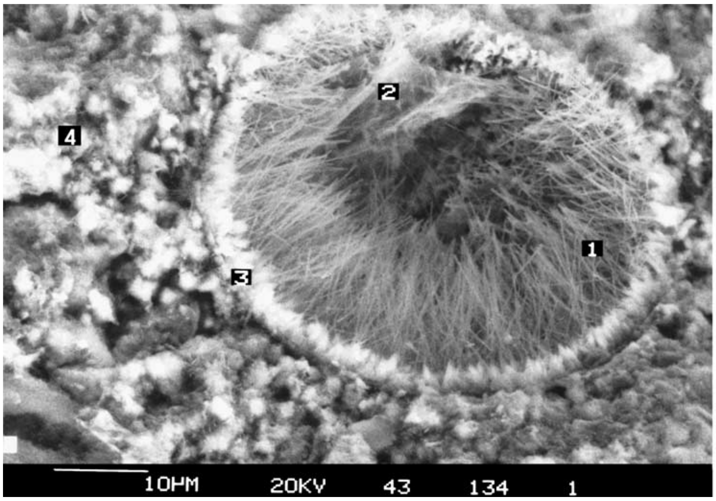
The results of SEM- and X-ray microanalysis of samples of mortars and pastes containing 30% of limestone, stored at 5 °C after 360 days are presented in the Figs. 5–8. Although particles with chemical composition high in sulfate were identified, no needle-like crystals of ettringite were found in the non-heat-treated mortar samples. The irregular shaped particles found with extended part a high content of sulfate are an ettringite-like phase, mixed with calcium silicate hydrate, as indicated by the chemical composition (Fig. 5). According to the low Al_2O_3 and Fe_2O_3 content, the high sulfate content of the area marked “1” (Fig. 5) cannot only be attributed to the presence of calcium sulpho-aluminate or ferrite phases. This might be a mixture of calcium silicate hydrate and a thaumasite-like phase.

In the mortar samples treated at 95 °C, needle-like crystals of ettringite could be identified (no Figure). The



	1	2	3
	[wt.-%]		
MgO	-	5.3	5.21
Al_2O_3	1.7	10.3	8.5
SiO_2	21.2	8.6	8.7
SO_3	8.5	13.3	20.3
CaO	66.5	52.5	54.0
Fe_2O_3	2.0	10.0	3.2

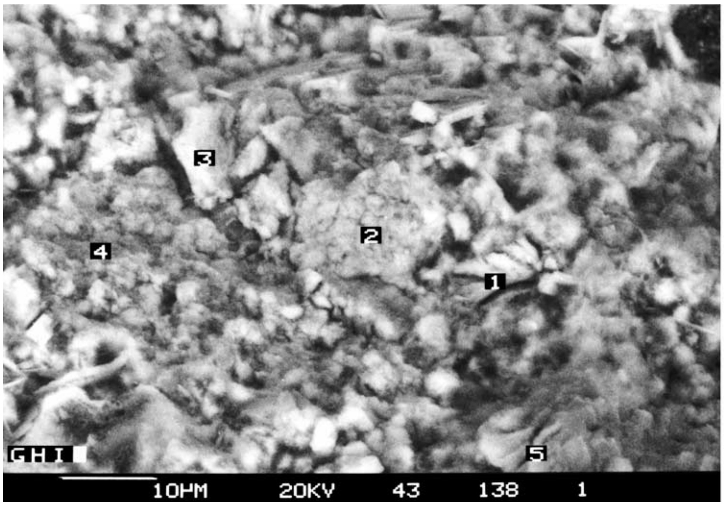
Fig. 5. SEM and X-ray microanalysis of mortar with 30% limestone in cement after 360 d storage at 5 °C.



	1	2
	[wt.-%]	
MgO	-	-
Al_2O_3	8.1	2.6
SiO_2	1.1	13.1
SO_3	14.0	5.8
CaO	76.8	78.5
Fe_2O_3	-	-

	3	4
	[wt.-%]	
MgO	-	4.6
Al_2O_3	4.3	5.3
SiO_2	18.2	24.8
SO_3	8.8	7.9
CaO	68.7	55.5
Fe_2O_3	-	1.8

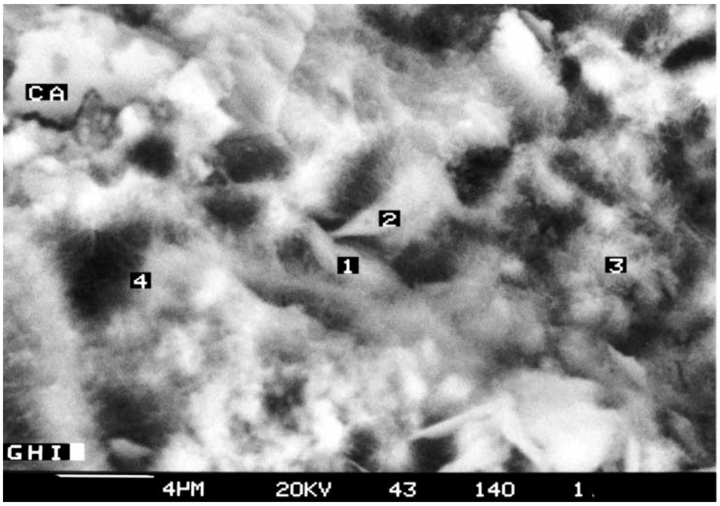
Fig. 6. SEM and X-ray microanalysis of cement paste with 30% limestone in cement after 360 d storage at 5 °C.



	1	2	3
	[wt.-%]		
MgO	-	-	-
Al_2O_3	9.9	6.3	7.1
SiO_2	6.2	14.9	9.1
SO_3	29.0	-	13.6
CaO	55.0	77.8	70.2
Fe_2O_3	-	-	-
K_2O	-	1.0	-

	4	5
	[wt.-%]	
MgO	1.6	6.9
Al_2O_3	12.8	4.3
SiO_2	-	35.9
SO_3	85.7	3.8
CaO	-	47.7
Fe_2O_3	-	1.4

Fig. 7. SEM and X-ray microanalysis of heat-treated cement paste with 30% limestone in cement after 360 d storage at 5 °C.



	1	2
	[wt.-%]	
MgO	-	-
Al_2O_3	4.7	4.8
SiO_2	8.1	11.5
SO_3	15.6	10.8
CaO	71.6	70.0
Fe_2O_3	-	3.0

	3	4
	[wt.-%]	
MgO	-	2.5
Al_2O_3	3.9	2.6
SiO_2	25.4	24.2
SO_3	4.0	2.7
CaO	66.7	66.0
Fe_2O_3	-	2.1

Fig. 8. SEM and X-ray microanalysis of heat-treated cement paste with 30% limestone in cement after 360 d storage at 5 °C.

Table 3
Amount of ettringite in the mortars and pastes (XRD determination)

Addition of limestone (M%)	Storage temperature (°C)	Amount of ettringite (wt.%)			
		2 h	1 d	28 d	360 d
Heat-treated mortar					
0	20	n.d.	n.m.	n.m.	3.1
0	5	–	–	0.60	3.3
15	20	n.d.	n.m.	0.90	3.3
15	5	–	–	0.90	2.6
30	20	n.d.	n.m.	0.90	2.9
30	5	–	–	1.10	2.4
Pastes without heat-treatment					
0	20	2.5	5.5	6.6	7.3
0	5	–	–	6.4	8.0
15	20	2.2	6.0	6.6	6.7
15	5	–	–	6.6	7.4
30	20	1.8	4.6	5.4	4.9
30	5	–	–	5.6	5.4
Heat-treated pastes					
0	20	–	n.m.	2.2	2.9
0	5	–	–	2.0	3.6
15	20	–	n.m.	2.5	2.6
15	5	–	–	2.3	5.3
30	20	–	n.m.	2.9	6.4
30	5	–	–	3.6	5.4

n.d.: no determinate; n.m.: not measurable.

Table 4
d-Spacings from ettringite interference at 9.1° 2θ in cement pastes and mortars after 360 d (720 d) storage at the different conditions

Admixture of limestone (wt.%)	Storage temperature (°C)	Ettringite d-spacings at 2θ about 9.1° Å			
		Mortar		Paste	
		Without HT[a]	With HT	Without HT	With HT
0	20	9.72	9.73	9.69	9.70
0	5	9.70	9.69	9.71	9.71
15	20	9.71	9.70	9.71	9.69
15	5	9.71	9.68	9.71	9.71
30	20	9.70	9.71	9.69	9.72
30	5	9.70	9.68 (9.68)	9.70	9.71 (9.70)

$d_{ettringite} = 9.72$ Å (JCPDS-card Nr. 37-1476). $d_{thaumasite} = 9.56$ Å (JCPDS-card Nr. 25-128).

[a] HT: heat-treatment.

chemical composition of these crystals showed only slight deviation from the theoretical composition. Based on the present results it cannot be stated whether the presence of SiO_2 and excess of CaO are due to traces of calcium silicate hydrate, calcite or portlandite or a matter of accommodation of SiO_2 in the crystal structure of ettringite. In the same sample only one composition with SiO_2 and a higher molar SO_3/Al_2O_3 ratio (of 3.6) than expected for ettringite was found (no Figure). The identified irregularly formed particle which is rich in sulfate is a mixture of ettringite, CSH-phases and possibly calcite or portlandite.

There are also irregularly formed particles in the non-heat-treated paste samples. They are rich in sulfate and besides the components typical for AFT-phases (CaO, Al_2O_3 and Fe_2O_3), they contain MgO and SiO_2. In the pores needle-like ettringite crystals are apparent. The SO_3/Al_2O_3 ratio was found to be lower than the theoretical value typical for ettringite. Furthermore, SiO_2 was detected (Fig. 6). In heat-treated paste samples, no needle-like ettringite crystals appeared. It was shown by X-ray microanalysis that areas rich in sulfate are mainly mixes of different phases (Figs. 7 and 8). The chemical composition at mark 1 (Fig. 8) shows a much higher SO_3/Al_2O_3-molar ratio (of 4.22) than for ettringite and might indicate the presence of thaumasite or an ettringite–thaumasite solid solution.

4. Discussion and conclusions

During the storage of cured samples made with Portland-limestone cement, the following reactions (presented in simplified form) may compete with one another:

$$C_3A \cdot CaSO_4 \cdot 12H_2O + 2CaSO_4 \text{ (from CSH)} + 20H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad (1)$$

$$C_3AH_6 + 3CaSO_4 \text{ (from CSH)} + 26H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad (2)$$

$$C_4AH_{19} + 3CaSO_4 \text{ (from CSH)} + 13H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad (3)$$

$$C_3AH_6 + CaCO_3 + 5H_2O \rightarrow C_3A \cdot CaCO_3 \cdot 11H_2O \qquad (4)$$

$$C\text{–}S\text{–}H + CaCO_3 + CaSO_4 + xH_2O \rightarrow CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O \qquad (5)$$

During the storage of cured samples reactions 1 and 2 are normally expected. Generally delayed ettringite formation is accelerated by lower temperature of storage and $CaCO_3$ addition. Although $CaCO_3$ and sulfate compete to react with tricalcium aluminate hydrate, the amount of ettringite formed is higher than expected. More investigations are needed to identify and explain the latter reaction path.

The formation of thaumasite in mortars and concretes usually depends on a surplus of sulfate ions, the existence of $CaCO_3$ and humid storage conditions at low temperature. If mortars are heat treated at 95 °C, some of the sulfate ions are incorporated in the CSH phase. The delayed formation of ettringite, and consequently the damage to mortars is often observed during further storage of heat treated mortars ([5,6]). The presence of $CaCO_3$ in combination with low temperature storage should lead theoretically to formation of thaumasite. This occurs especially in micro-areas where CSH phases rich in sulfate have close contact with $CaCO_3$ or it is due to carbonation of the CSH-phase. According to Bensted [4], the latter mechanism of thaumasite formation is called the "direct CSH route" (reaction 5).

The investigation showed that crystal-mixes appeared in micro-areas of pastes with 30% (wt.) of limestone filler which were heat treated and stored at 5 °C. The amount of thaumasite or ettringite–thaumasite mixed crystals present was too small to be identified by XRD. Sulfate from the CSH phases and $CaCO_3$ which are both part of the cement in the first place react with calcium aluminate hydrate and form monocarbonate-aluminate hydrate ($C_3A \cdot CaCO_3 \cdot 11H_2O$) and ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$).

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