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Occurrence of thaumasite in gypsum lime mortars for restoration

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Abstract

For restoration purposes, it is essential to have compatible mortars for historic masonry built originally with gypsum mortars. For that reason, gypsum lime mortars with high weathering resistance were developed. Due to the added hydraulic components and carbonate components of the used limes of these mortars, the occurrence of thaumasite can take place. Different mortar mixtures with variable binder contents, using lime with differing amounts of hydraulic components, were prepared and stored under two contrasting curing conditions. Over 90 days of curing, these mortars were investigated using physical–mechanical and chemical–mineralogical techniques. The results have shown that the potential for the growth of thaumasite depends on the composition of the raw materials, especially of the lime. In gypsum lime mortars which were used for restoration purposes, small amounts of thaumasite were also detected, but these small amounts of thaumasite do not reduce mechanical properties. This assumption was confirmed by investigations of gypsum lime mortars, which were exposed outdoors for 13 years.

Keywords: Thaumasite; Mortar; Gypsum; Lime; Restoration; Durability

1. Introduction

Increasing cases of deteriorations of concrete and historic building materials caused by the formation of thaumasite have drawn the attention of experts [1,2,13]. Thaumasite as well as ettringite were detected in some damaged concretes. Thaumasite was also particularly found in gypsum lime mortars and plasters in masonry of historic buildings. Deterioration was detected mostly as spalling of the masonry and as a reduction of strength. Nowadays, it is proved that the formation of thaumasite causes this reduction of strength without necessarily leading to an expansive reaction [14].

Thaumasite is a calcium–silicate–carbonate–sulphate–hydrate with prismatic crystals and a similar crystal structure to ettringite and it is difficult to distinguish between thaumasite and ettringite by using X-ray diffraction (XRD). Low temperature in combination with high humidity fosters a formation of thaumasite in building materials containing hydraulic components. Therefore, the growing of thaumasite in masonry built with gypsum lime mortars seems to be possible.

The conference “Thaumasite in Cementitious Materials” in Watford, UK in 2002 [1] demonstrated that scientists and civil engineers are often confronted with the problem of occurrence of thaumasite in building materials. Lipus and Puntke [11] published a paper about sulphate resistance of different concretes which were composed by using different Portland limestone cements according to EN 197 [7]. As a result, it was shown that concretes containing a high content of limestone powder have a higher potential for thaumasite growth than concretes with ordinary Portland cements. In [4], it is mentioned that in Portland limestone cements the potential for the occurrence of thaumasite does not restrict their use for preparing concretes. Because gypsum lime mortars with a high content of hydraulic components and limestone powder as an admixture are currently used for restoration of historic masonry which were originally built with calcium sulphate based mortars, the potential of thaumasite production is of major interest [12]. For that reason, an experimental program was designed to investigate the formation of thaumasite potential in gypsum lime mortars.

Looking at the chemical formula of thaumasite, it can be seen that for the formation of thaumasite, sulphate, silicate and carbonate as well as calcium and water are necessary. The formation of thaumasite takes place at a pH-value <10.5 and is

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favoured by low temperatures (0–15 °C) combined with a high moisture content [10]. Thaumasite has a hundred times lower solubility at 5 °C than at 20 °C. Thaumasite is mainly found in deeper parts of masonry where the humidity is in general, higher than on the surface.

There are two ways that thaumasite is formed [2,13]. On the one hand, it can be formed by the reaction of carbonate, sulphate and silicate in combination with calcium and water which is shown in (1):

$$\begin{aligned}&\mathrm{CSH + gypsum + calcite + water}\\&\quad\rightarrow \mathrm{thaumasite + portlandite}\\&Ca_3Si_2O_7\cdot 3H_2O + 2CaSO_4\cdot 2H_2O + 2CaCO_3 + 24H_2O\rightarrow\\&Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2\cdot 24H_2O + Ca(OH)_2\end{aligned}\tag{1}$$

On the other hand, it can be formed from ettringite. After the formation of ettringite, the alumina content will be substituted by carbonate and silicate ions and the solid solution called Woodfordite is the result:

Ettringite $Ca_6Al_2[(OH)_4SO_4]_3\cdot 26H_2O$

Thaumasite $Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2\cdot 24H_2O$

Summarizing, it can be said that thaumasite is a complex reaction product of a sulphate attack at lower temperature. Thaumasite results in a decrease of strength in mortar or concrete and the reaction product is a white-grey mass without cohesion.

2. Experimental programme

2.1. Materials

For the development of compatible gypsum lime mortars for restoration purposes, with high water and sulphate resistance, commercial available raw materials were used. Due to quality control, this approach ensures constant and reliable product quality. Commercial calcium sulphate α-hemihydrate, β-hemihydrate, calcium sulphate anhydrite and slaked lime (CL 70, acc. EN 459) were used, combined with calcitic and quartzitic aggregates.

Table 2
Mortar mixtures of long-term exposed gypsum lime mortars

	Sample	S20	S24	S32
Binder	α-Hemihydrate (wt.%)	20	20	20
	β-Hemihydrate [wt.%]	50	50	50
	CL 70 (wt.%)	30	30	30
Aggregate	Limestone powder (wt.%)	20	0	25
	Quartz sand (wt.%)	0	20	25

For the classification of the hydraulic components of the slaked lime that was used, the Boynton equation was applied [3]. In this classification (2), the cementation index CI is defined as:

$$\mathrm{CI} = \frac{2.8{*}SiO_2 + 1.1{*}Al_2O_3 + 0.7{*}Fe_2O_3}{CaO + 1.4MgO}\tag{2}$$

The cementation index of the slaked lime CL 70 (acc. EN 459 [8]) was CI = 0.68. This high value shows a high potential for formation of thaumasite. The CI of CL 70 can be compared with those of other slaked limes acc. EN 459 of different producers as follows:

$$\mathrm{CL\ 80,\ CI = 0.012\ to\ 0.44}$$

$$\mathrm{CL\ 90,\ CI = 0.008\ to\ 0.04}$$

To check the thaumasite formation potential, the hydraulic component of experimental mortars were increased by the addition of ordinary Portland cement (OPC) CEM I 52.5R acc. EN 197-1 [7]. The aggregate components were limestone and quartz sand with grain sizes of 0.063–5 mm as well as fine grained limestone powder. To optimise the workability of the calcium sulphate hemihydrate samples, tartaric acid was used as retardant. K_2SO_4 was used as activator for the calcium sulphate

Table 1
Mortar mixtures

	Sample	253	135	135 K	802	505	505 K	A82	A55	A55K	C253	C135K
	Binder/aggregate ratio	1:4	1:4	1:4	1:3,5	1:3,5	1:3,5	1.2	1.2	1.2	1:4	1:4
Binder	α-Hemihydrate (wt.%)	20.00	14.30	14.30	80.00	50.00	50.00				20.00	14.30
	β-Hemihydrate (wt.%)	50.00	35.70	35.70							50.00	35.70
	$CaSO_4$-Anhydrite (wt.%)							80.00	50.00	50.00		
	CL 70 (wt.%)	30.00	50.00	50.00	20.00	50.00	50.00	20.00	50.00	50.00		
	CEM I 52.5R (wt.%)										30.00	30.00
Aggregate	Limestone powder (wt.%)	3.75	3.75	15.00	3.75	3.75	15.00	3.75	3.75	15.00	3.75	15.00
	Limestone sand (wt.%)	75.50	75.50	66.68	75.50	75.50	66.68	75.50	75.50	66.68	75.50	66.68
	Quartz sand (wt.%)	20.75	20.75	18.32	20.75	20.75	18.30	20.75	20.75	18.32	20.75	18.32
Additives	Tartaric acid [a]	x	x	x	x	x	x				x	x
	K_4SO_4 [b]							x	x	x		
	Water/binder ratio	0.93	1.00	1.05	0.63	0.81	0.90	0.51	0.66	0.71	0.88	0.93

[a] 0.1% by weight tartaric acid based on hemihydrate.
[b] 0.75% by weight K_2SO_4 based on anhydrite.

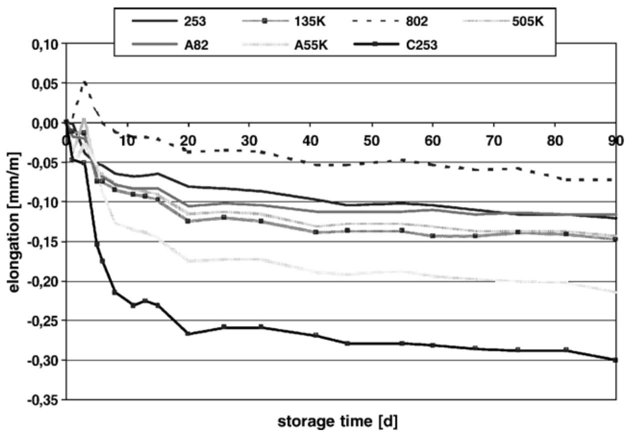

Fig. 1. Expansion and shrinkage curves of different laboratory prepared gypsum lime mortars; storage condition 20/65.

anhydrite samples. The mortar mixtures prepared are listed in Table 1.

2.2. Mortar production

For this research work, different types of mortars were prepared, which are partially listed in Table 1. There the binder/aggregate ratio, the water/binder ratio, the amounts of binder and aggregate as well as the used chemical additives are shown for the prepared mortar mixtures (samples).

In a first mixture, the binders α- and β-hemihydrate were mixed with the slaked lime CL 70 in a ratio by weight of 20% α-hemihydrate, 50% β-hemihydrate and 30% lime. Limestone powder, limestone gravel sand and quartz sand were used as aggregate. The binder aggregate value was 1/4 and tartaric acid as retarder was used. To increase the thaumasite potential, the ratio of the hemihydrates to lime was changed in further mixtures, which can be seen in Table 1. Furthermore, mixtures with an increased limestone powder content (sample 135 K) were prepared as well as mixtures with pure α-hemihydrate or anhydrite binder contents. For comparison, and to make sure that the experimental investigations were correctly performed, mixtures with 30% and 50% by weight OPC respectively were also prepared. These mixtures are also listed in Table 1 and are

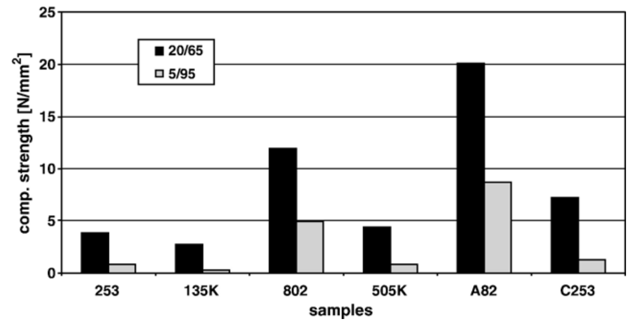

Fig. 3. Compressive strength of laboratory gypsum lime mortars at different storage conditions.

marked as samples with a C (C253, C135K). For the investigation program, 11 different mortar mixtures were designed.

2.3. Preparation and storage conditions

The mortars were laboratory prepared as prisms (160 mm × 40 mm × 40 mm) according with DIN 1164-7 [9] and were stored in two different climatic conditions. One set of samples were stored in a climatic chamber at 20 °C and 65% relative humidity (20/65); another set of samples were stored in a climate of 5 °C and 95% relative humidity (5/95).

3. Tests of the laboratory prepared mortars

During the complete storage time expansion and shrinkage of the prisms by measuring the change of elongation was controlled according to DIN 52450 [6] for both storage conditions (20/65 and 5/95). The compressive and tensile strengths as well as the dynamic modulus of elasticity (acc. EN 196-1 [5]) were measured after 7, 28 and 90 days. To characterise the microstructure and to detect reaction products, scanning electron microscopy (SEM: Philips, XL30i with integrated EDX), mercury intrusion porosimetry (MIP: Micromeritics, Autopore II 9220) and X-ray powder diffraction (XRD: Philips, PW 1710) were used. For the SEM and MIP investigations, the samples were dried at 40 °C and were

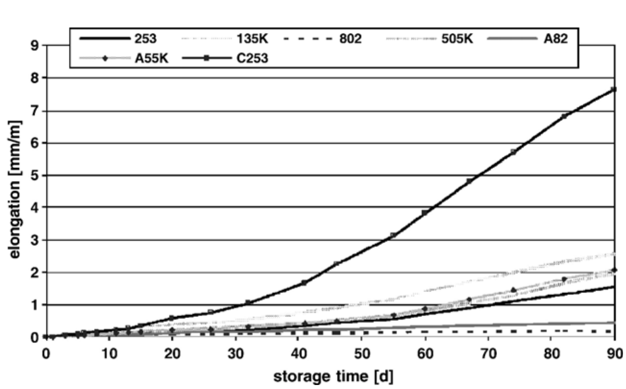

Fig. 2. Expansion curves of different laboratory prepared gypsum lime mortars; storage condition 5/95.

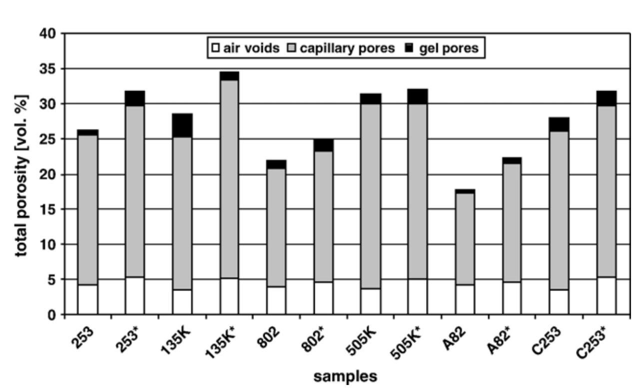

Fig. 4. Porosity of laboratory gypsum lime mortars at different storage conditions (*5/95).

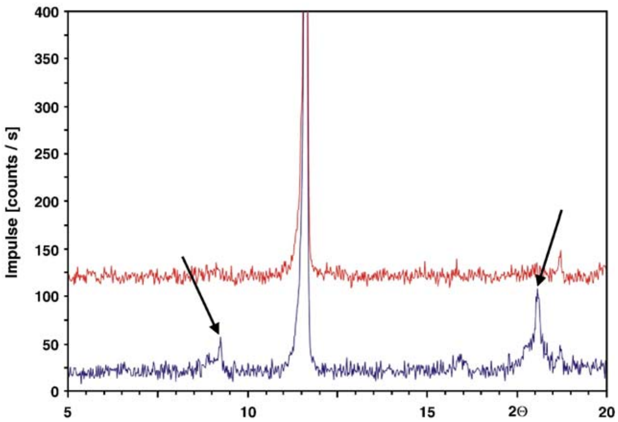

Fig. 5. XRD diagrams of sample 253 stored at 20/65 (top) and 5/95 (down), arrows mark thaumasite or ettringite peaks.

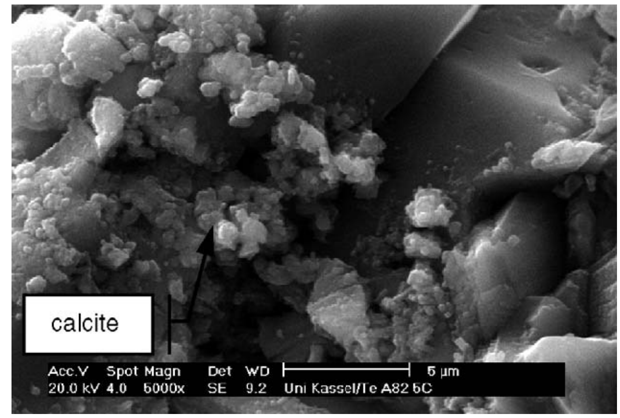

Fig. 7. SEM pictures of mortar sample A82 stored at 5/95.

carefully prepared by using pincers to get sizes from 2 to 4 mm. The XRD measurements were done on powder with a grain size smaller than 40 µm. For all SEM, MIP and XRD investigations, the samples were stored at least 90 days in the above mentioned controlled climatic conditions (20/65, 5/95).

4. Tests of outdoor exposed mortars

Gypsum lime mortars subjected to long-term exposure were also investigated. The samples were taken from test panels of the brick masonry of the St. Wilhadi Church in Stade which is located in the northern part of Germany. The mortars analysed (Table 2) were exposed for 13 years in atmospheric conditions.

These samples were also investigated by using SEM including EDX, MIP and XRD. The results were compared to the laboratory prepared mortar results.

5. Results and discussion

As seen in Fig. 1, the laboratory prepared samples which were stored in 20/65 do not shown any long-term expansion. However, it can be easily seen that the samples have shown a slight shrinkage. The OPC containing sample C253 shows the highest shrinkage; the mortars prepared with hemihydrate as binder show the lowest shrinkage. These results were expected.

Fig. 2 shows the expansion results of the different mortar mixtures which were stored at 5/95. It is obvious that mixtures with high contents of hydraulic components (hydraulic lime, OPC) show a high expansion. Nevertheless, it can also be seen that the mixtures with low contents of hydraulic components (samples 253, A82 and 802) show a small amount of expansion. These results show that there is a close correlation between the amount of hydraulic components and expansion of the mortars.

In Fig. 3, the measured compressive strength after 90 days of mortar samples which were stored under different climatic conditions are shown. It is obvious that the samples which were stored at 20/65 have a much higher compressive strength than the samples which were stored at 5/95. These results did not necessarily show that the decrease in strength at lower temperature is a result of formation of thaumasite, because it is well known [14] that the strength of gypsum based building materials decrease when the moisture content increases.

Fig. 4 shows the results of the mercury intrusion porosity measurements of the different samples. From these results, it

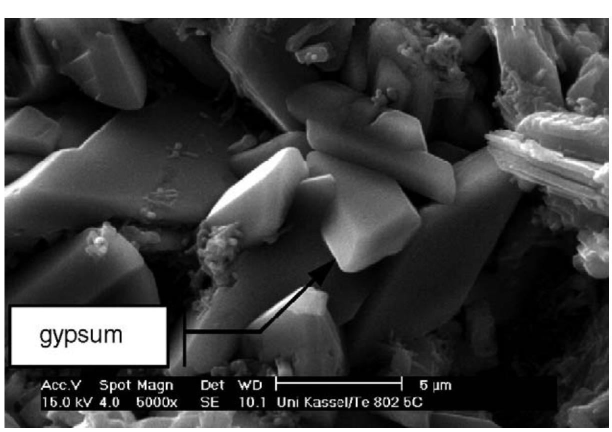

Fig. 6. SEM pictures of mortar sample 802 stored at 5/95.

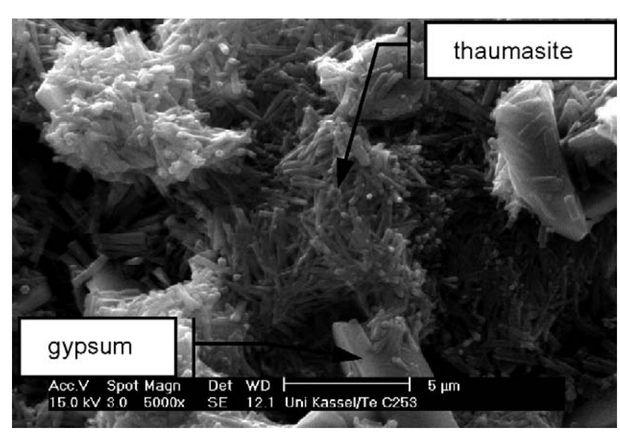

Fig. 8. SEM pictures of mortar sample C253 stored at 5/95.

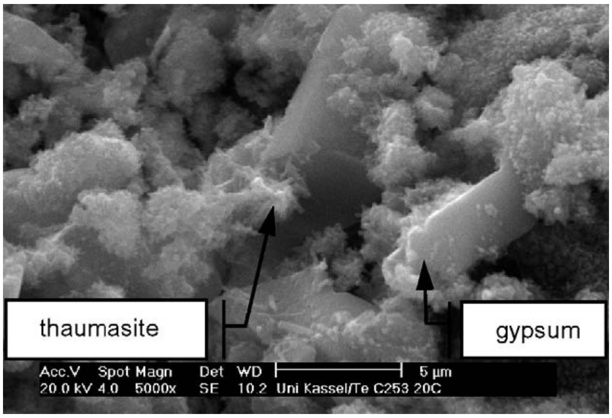

Fig. 9. SEM pictures of mortar sample C253 stored at 20/65.

can be seen that, in general, the samples stored at 5/95 have a higher porosity than the samples stored at 20/65, which possibly suggests thaumasite or ettringite formation. Looking at the X-ray diffraction results, it is obvious that the mortar samples which were stored at 20/65 do not show any peak of thaumasite or ettringite. In identical samples stored at 5/95, small amounts of the phases ettringite and/or thaumasite can be detected (Fig. 5).

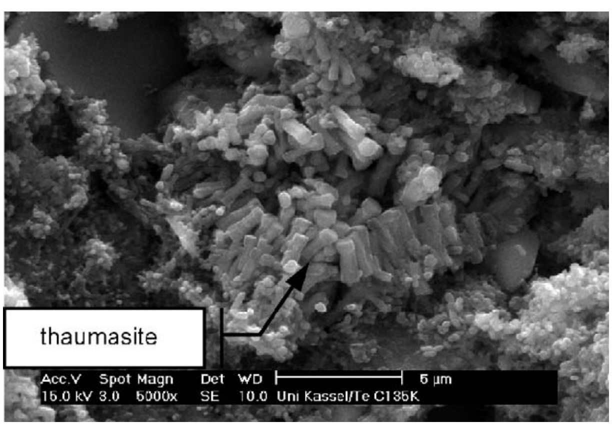

Fig. 10. SEM pictures of mortar sample C135K stored at 5/95.

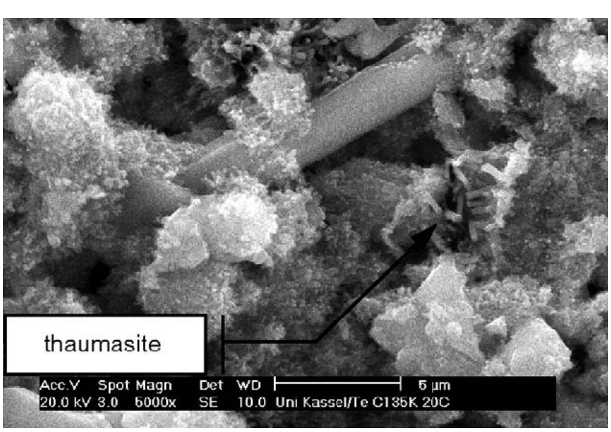

Fig. 11. SEM pictures of mortar sample C135K stored at 20/65.

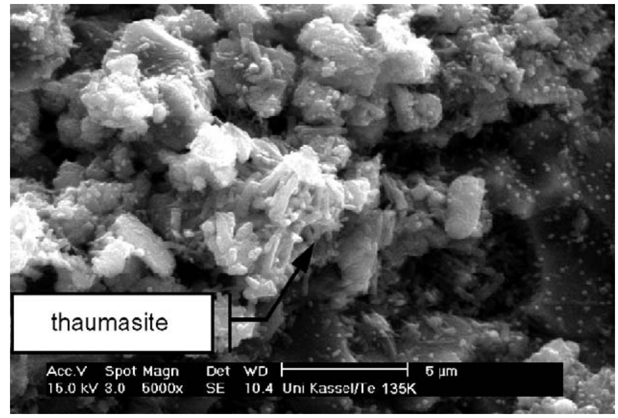

Fig. 12. SEM pictures of mortar sample 135 K stored at 5/95.

The results of XRD measurements as well as the SEM investigations show that in the gypsum lime mortars which are actually used as restoration materials (samples 253, 802 and A82) at low temperature (5/95) only small amounts of ettringite and thaumasite are detectable. Based on the results of the expansion measurements (Fig. 2) as well as on the results of light microscopy investigations, it can be said that this small amount does not cause any damage of the microstructure.

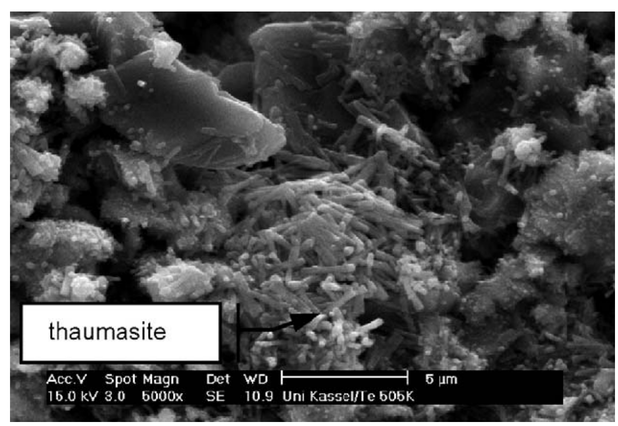

Fig. 13. SEM pictures of mortar sample 505 K stored at 5/95.

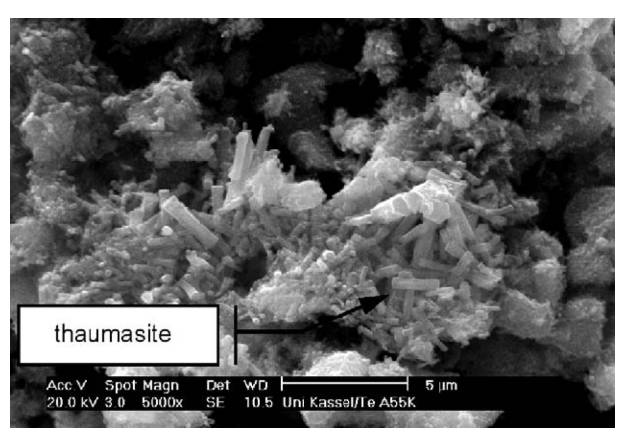

Fig. 14. SEM pictures of mortar sample A55K stored at 5/95.

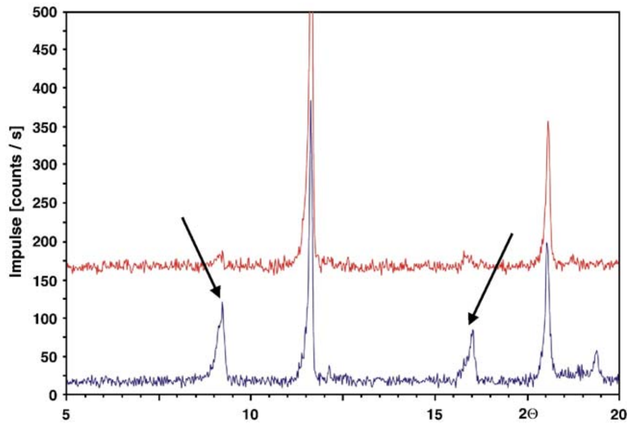

Fig. 15. XRD diagrams of sample C253 stored at 20/65 (top) and 5/95 (down), arrows mark thaumasite or ettringite peaks.

Furthermore, the results of mortar samples with higher amounts of hydraulic components show that there is a high potential of thaumasite formation at low temperature. Looking to the results of the OPC containing mortar sample C253 or to sample 135 K with the high amount of CL 70, it can be seen that both samples show high expansion and a decrease in compressive strength, which can be indicative of thaumasite formation. In mortar samples with a small amount of hydraulic phases, thaumasite cannot be detected by SEM/EDX (Figs. 6 and 7). On the contrary, in samples with high amounts of hydraulic components, thaumasite is easily detectable by using SEM/EDX as shown in Figs. 8–14, as well as by XRD (Fig. 15).

From these results, it can be deduced that small amounts of hydraulic components in gypsum lime mixtures will not result in a decrease in mechanical properties. However, if the amount of hydraulic components exceed a limiting value (e.g. $CI \geq 0.4$, acc. Eq. (2)) the physical–mechanical properties decrease dramatically due to ettringite and thaumasite formation. In that case, long-term sustainability cannot be guaranteed.

In 1992, prototypes of gypsum lime mortars were applied in a test field at the masonry of St. Wilhadi Church in Stade, northern Germany. These mortars are comparable with the lab

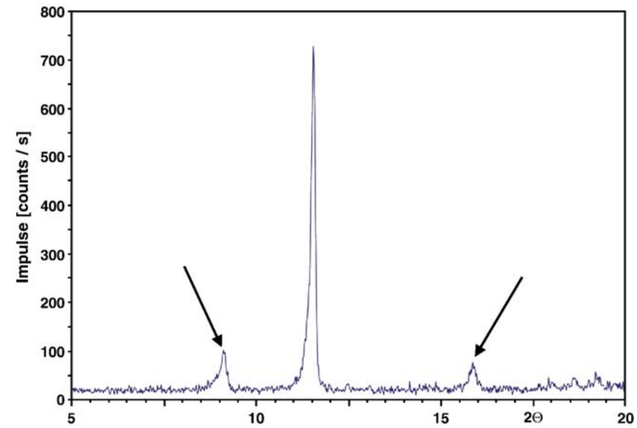

Fig. 17. XRD diagram of sample S24, arrows mark thaumasite or ettringite peaks.

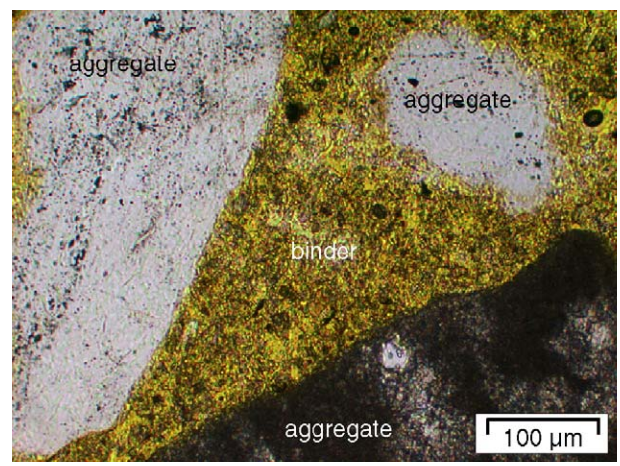

Fig. 18. Microstructure of hardened gypsum lime mortar after 13 years exposure, thin section.

prepared sample 253. After 13 years of exposure, no damage was obviously detectable on the masonry (Fig. 16). These long-term exposed samples were taken and analysed using XRD and SEM/EDX. By using XRD, small amounts of thaumasite and

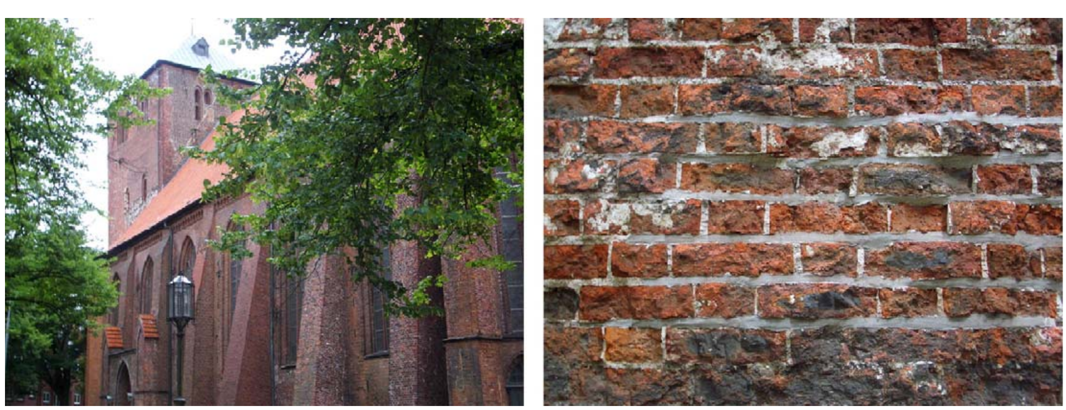

Fig. 16. St. Wilhadi Church in Stade (left), test field (right).

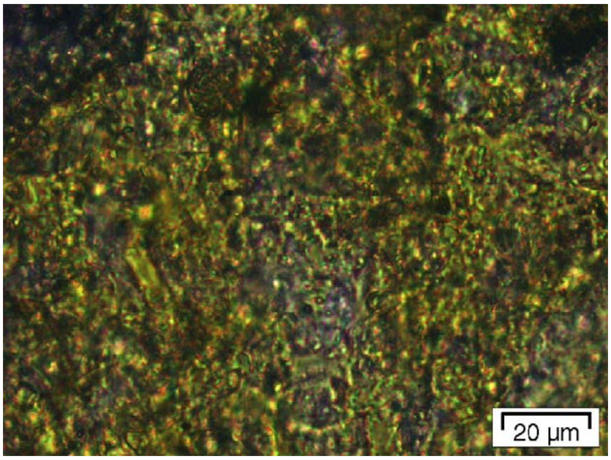

Fig. 19. Detailed view to binder; see Fig. 18.

ettringite could be detected (Fig. 17). Furthermore, some thaumasite crystals could be identified using SEM/EDX. Nevertheless, no microstructural damage could be detected by using different microscopic techniques (Figs. 18 and 19).

6. Conclusions

There are a number of approaches to increase the water resistance of calcium sulphate based mortars for restoration purposes. One approach is the inherent surface passivation due to the use of complex gypsum lime mortars, which provokes dissolution and precipitation of gypsum, causing a denser microstructure and finally a lower porosity [12]. However, chemical–mineralogical investigations have shown that ettringite or thaumasite can be formed at low temperatures in gypsum lime mortars prepared with hydraulic lime and carbonates aggregates. On the one hand, the results have shown that these formations in the binder system of gypsum lime depend mainly on the content of hydraulic components of the lime that is used. By decreasing the cementation index CI of the lime used, the amount of generated thaumasite can be controlled. To guarantee that the gypsum lime mortars are durable, the cementation index of the lime used should be lower than 0.3 and the amount of lime in the binder mix should be not more than 30 wt.%.

On the other hand, it can be stated that small amounts of ettringite and/or thaumasite in gypsum lime mortars do not decrease the physical–mechanical properties and the long-term resistance. In 13-year-old gypsum lime mortars which were exposed in atmospheric conditions small amounts of thaumasite could be detected which did not result any kind of apparent microstructural damage.

These results provide useful information on the development of water-resistant calcium sulphate based mortars for restoration purposes.

Summarizing, it can be said that small amounts of thaumasite and ettringite are still part of the microstructure of the analysed samples but do not cause an evident decrease in durability.

Acknowledgements

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References

[1] Proceedings of the First International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, Garston, Watford, England, UK, 2002.

[2] Bellmann, F., Stark, J. Ein Beitrag zum Chemismus der Thaumasitbildung. Tagungsband der 15 IBAUSIL des FIB der Bauhaus-Universität Weimar, 2-0659ff.

[3] R.S. Boynton, Chemistry and Technology of Lime and Limestone, John Wiley & Sons Inc NY, USA0470093900, 1980, 532 pp.

[4] Deutscher Ausschuss für Stahlbeton (DAfStB), Sulfatangriff auf Beton-Stellungnahme des DAfStB, Berlin, 2003.

[5] EN 196-1 (1995): Methods of testing cement—determination of strength.

[6] DIN 52450 (1985): Testing of inorganic non-metallic building materials; determination of shrinkage and expansion on small specimens.

[7] EN 197-1 (2004): Cement: Part 1. Composition, specifications and conformity criteria for common cements, German version EN 197-1:2000 +A1:2004.

[8] EN 459-1 (2002): Building lime: Part 1. Definitions, specifications and conformity criteria, German version EN 459-1:2001.

[9] DIN 1164-7 (1978): Portland-, Eisenportland-, Hochofen-und Traßzement; Bestimmung der Festigkeit.

[10] H. Kollmann, G. Strübel, Mineralsynthetische Untersuchungen zu Treibursachen durch Ca-Al-Sulfat-Hydrat und Ca-Si-Carbonat-Sulfat-Hydrat, Tonindustriezeitung 3 (1977) 63–70.

[11] K. Lipus, S. Puntke, Sulfatwiderstand unterschiedlich zusammengesetzter Betone, Teil 1 und 2, Beton 2, S. 97, Beton 3, S. 153, 2003.

[12] B. Middendorf, Physico-mechanical and microstructural characteristics of historic and restoration mortars based on gypsum: current knowledge and perspective, Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies. Special Publication, Geological Society, London, ISBN: 1-86239-123-8, 2003, pp. 165–176.

[13] Mulenga, M. (2002): Zum Sulfatangriff auf Beton und Mörtel einschließlich der Thaumasitbildung. Dissertation zur Erlangung des akademischen Grades Doktor-Ingenieur, Weimar.

[14] J.J. Russel, Einfluss des Feuchtigkeitsgehaltes auf die Druckfestigkeit kleiner Gipswürfel, Zement-Kalk-Gips 8 (1960) 345–351.