

# Supersulfated Cement in Optimized Restoration Mortars and their Application at the Restoration of the Holstentor in Lübeck, Germany

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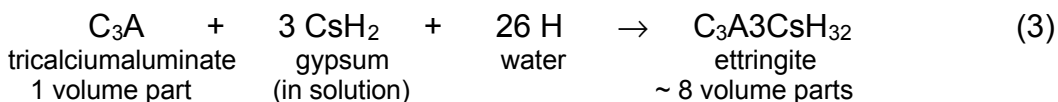
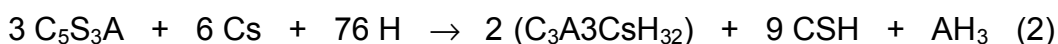
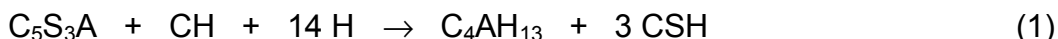
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## 1 INTRODUCTION

Supersulfated Cement based on blast furnace slag, gypsum (or optimized system of sulphate carrier) and Portland Cement (SGP) was investigated. This work was based on former investigations described in [1, 2, 3, 4]. The binder system was optimized for industrial production in the dry mortar section concerning the thermodynamic and kinetic properties of slag cements [5] with regard to the requirements of the market and various applications. Thus the developed product systems for mortar and plaster work fulfill the requirements of the European DIN EN 1015 and the "Merkblatt Sanierputzsysteme E 2-9-04/D" and "Opferputze E-2-10-06/D" of the Wissenschaftlich-Technische Arbeitsgemeinschaft (WTA e.V.). This offers a very broad field of possible applications.

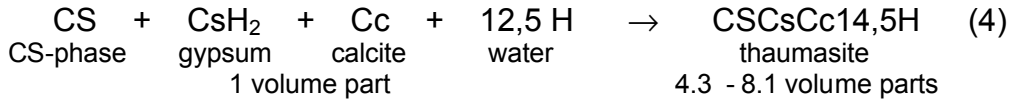
In former R&D-projects product systems for the restoration were developed, which guarantee a high durability and compatibility and also withstand against salt attack [3, 4]. Some Products for special applications contain a component for shrinkage compensation (SC, 1 : 1 mixture CAC and gypsum) to allow the filling of big volumes in one step avoiding cracking of the splice interfaces (mortar/brick) and hydraulic fracturing [2].

The hardening of a SGP-system is mainly based on ettringite formation (especially when a SC-component is used, Eq. 3) and the formation of crystalline  $C_xA_yH_z$  and amorphous CSH phases (Eq. 1). Due to the special compensation of the developed binder system the reaction equations are different from the ordinary well known supersulfated cement hydration. The main reaction is the hydration of amorphous blast furnace slag activated by increased pH-value (pH ~ 10.6, Eq. 1) and sulphate (Eq. 2):



In a secondary reaction phase (within a few weeks and increasing carbonatisation of the ettringite) thaumasite formation (Eq. 4) can be observed resulting in loss of strength and increasing inner stress, but no damage of the mortar matrix. This process depends on the degree of

carbonatisation, especially carboettringite formation or decomposition of ettringite (followed by recrystallisation of  $C_3H_2$  in the matrix, [6]) and the content of soluble  $SiO_2$ -phases in the mortar.

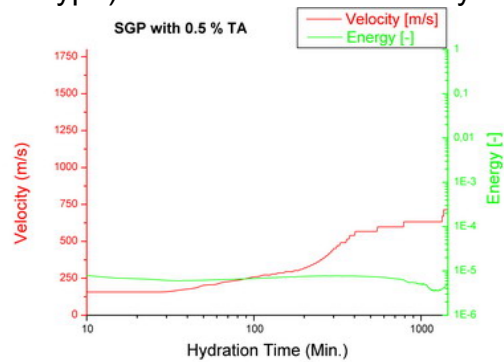


We observed under conditions of 23/50 only carboettringite formation for our systems. The presence of significant phase modifications or secondary phase formations were investigated in carbonated and also non carbonated systems (inner carbonate through natural gypsum) in the presence of soluble silica under wet conditions in low temperature regimes. QXRD investigations have shown only in one case, in the interface between the SGP-system and a lime-cement based wall mortar, thaumasite formation within 28 days with an final water content of 10 % at 9/50.

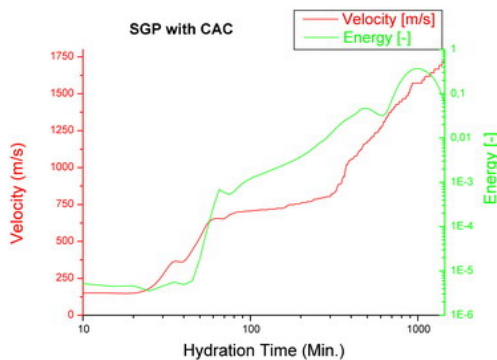
## 2 METHODS AND RESULTS

### 2.1 Ultrasonic measurements

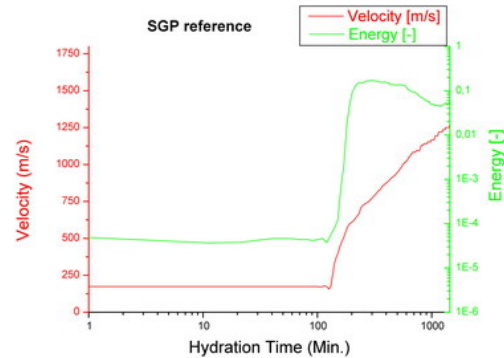
Ultrasonic measurements were performed parallel to in situ XRD measurements to investigate the phase and structural changes during the hydration. A function generator HM 8131-2 (Hameg), a amplifier WBHV 350 (Develogic), a measuring cell (prototype) and the software Analysis graph 2.1 were used to obtain and analyse the data. Graph 2.1 shows compared to the reference (graph 2.4) a significant hydration disturbance through complexation of  $Ca^{2+}$ -Ions of the  $\beta$ -HH by tartaric acid (TA, with high amounts (retarding effect) no gypsum formation within 24 hours). If the SGP binder is used with amounts



Graph 2.1: SGP with 0.25 % tartaric acid



Graph 2.2: SGP with CAC



Graph 2.3: SGP reference

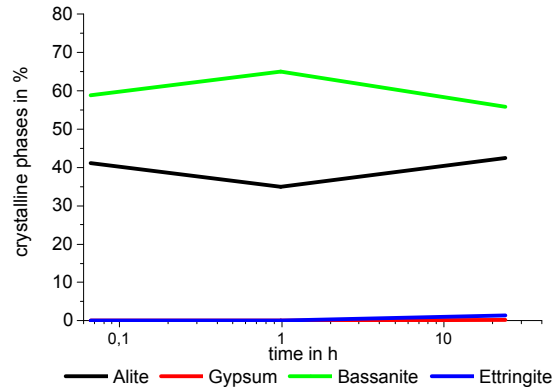
of up to 10 % CAC and gypsum one can observe a primary ettringite formation (graph 2.2) that can be used to determine together with TA (as accelerator or retarded) the setting time. Graph 2.3 shows a perfect setting of the SGP system with sufficient structure development (see energy curve).

## 2.2 In situ QXRD

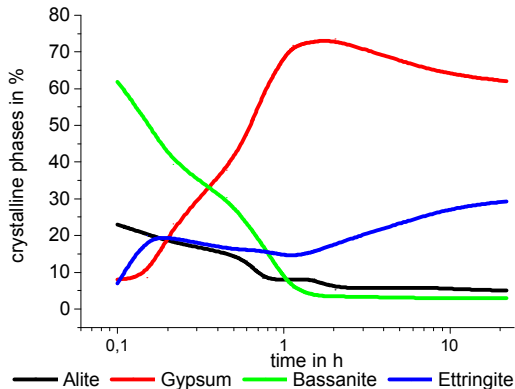
The in situ QXRD measurements were performed with a X'Pert Pro (PANalytical) set up with a PMT detector under use of a in situ measuring cell with a foil cover to guarantee 100 % rel. humidity during measurement [7]. According to the ultrasonic measurements the increase in the ultrasonic velocity can primary be traced back to the ettringite formation in the system. Especially CAC modified SGP systems (graph 2.7) allow the development of products with technical properties comparable to lime-gypsum/cement/trass products. The CAC modified systems have also a good machine runability and by using tartaric acid it was possible to develop pumpable product systems with good initial hardness. Graph 2.5 shows the reason for the retarding effect of higher amounts of TA. There was no gypsum formation observed within 24 h by using 0.5 % TA. In mortar systems with a binder to aggregate ration of 1:5 this amount acts as a accelerator due to a dilution effect.

## 2.3 Influence of carbonate and lime filler on the stability of ettringite

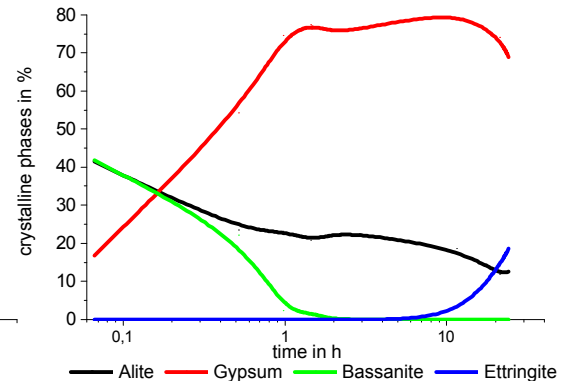
We investigated the influence of Cc and CH<sub>2</sub> on the ettringite structure as well as the type of structure modifications of ettringite in our SGP systems. In all Cc and CH<sub>2</sub> systems we



Graph 2.4: SGP with 0.25 % tartaric acid



Graph 2.5: SGP with CAC



Graph 2.6: SGP reference

found independent from the temperature after 28 d a sulphate ettringite structure under 100 % rel. humidity. Only during the primary ettringite formation we observed a carbonate-sulphate exchange [8]. The samples for the XRD measurements were prepared in Aceton and measured with a grading of smaller than 40  $\mu\text{m}$ .

	Cc in %	CH in %	C <sub>3</sub> S in %	CsH <sub>1/2</sub> in %	Amorph. in %		
M1	0.1	0.0	6.1	9.9	83.9		
M2	0.0	3.2	6.5	9.7	80.6		
M3	2.4	0.0	6.3	9.7	81.7		
	Cc in %	C <sub>3</sub> S in %	Ettr. in %	CsH <sub>2</sub> in %	Amorph. in %	Ettr. a in Å	Ettr. c in Å
<i>7 d</i>							
M1, 5/100	22.3	17.9	56.6	3.1	n. d.	11.22	21.37
M2, 5/100	23.6	20.1	50.5	5.8	n. d.	11.21	21.35
M3, 5/100	19.0	25.7	51.9	3.4	n. d.	11.22	21.36
M1, 23/100	34.3	14.4	49.7	1.7	n. d.	11.22	21.41
M2, 23/100	24.4	9.3	64.8	1.5	n. d.	11.23	21.39
M3, 23/100	21.8	14.9	61.4	1.9	n. d.	11.23	21.41
M1, 40/100	38.9	9.9	47.2	4.0	n. d.	11.23	21.44
M2, 40/100	25.2	8.9	64.3	1.5	n. d.	11.23	21.44
M3, 40/100	24.5	12.0	59.9	3.6	n. d.	11.23	21.44
<i>28 d</i>							
M1, 5/100	5.5	< 1	10.0	< 0.5	74.4	11.21	21.36
M2, 5/100	2.7	< 1	11.2	< 0.5	76.3	11.20	21.34
M3, 5/100	4.0	< 1	9.4	< 0.5	77.7	11.20	21.36
M1, 23/100	5.8	< 1	8.3	< 0.5	77.2	11.22	21.41
M2, 23/100	2.8	< 1	8.0	< 0.5	79.3	11.22	21.38
M3, 23/100	2.5	< 1	7.9	< 0.5	79.9	11.22	21.41
M1, 40/100	6.1	< 1	7.5	< 0.5	77.4	11.22	21.44
M2, 40/100	3.2	< 1	8.2	< 0.5	78.9	11.23	21.43
M3, 40/100	3.1	< 1	7.8	< 0.5	80.5	11.23	21.43

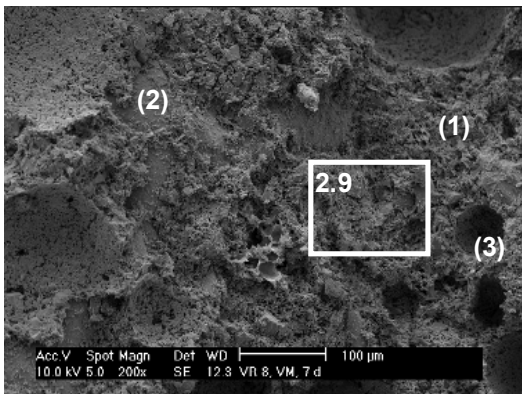
**Table 2.1:** QXRD results for the Cc- and CH<sub>2</sub>-SGP systems

## 2.4 SEM and AFM measurements of the micro- and nanostructure

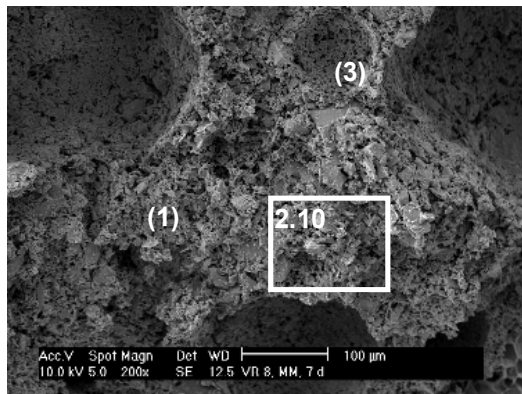
The micro- and nanostructures were investigated in order to characterize reaction products with an energy dispersive x-ray detector (EDX) and to characterize the topochemical reaction behavior of the aggregates and filler in order to optimize the mortar systems. Figure 2.7 and 2.8 give an overview over the microstructure of a mortar used for the restoration of the Holstentor. We investigated different water to dry mortar ratios in order to satisfy the different conditions of applications.

Figure 2.9 shows the typical ettringite-slag matrix. Figure 2.10 gives an overview of the morphology of gypsum (left side) in a CAC/TA modified system. On the right side one can see the typical slag grains. This gives an impression of the slow reaction rate of TA/CAC-modified SGP. Under real conditions we observed in former work [2, 3] sanding of mortars after several months to two years in case of weathering on facades with carbonatisation. This effect was not observed in polymer modified systems. Here the interface between quartz aggregate and the slag matrix is additionally improved through the adhesion of the polymer.

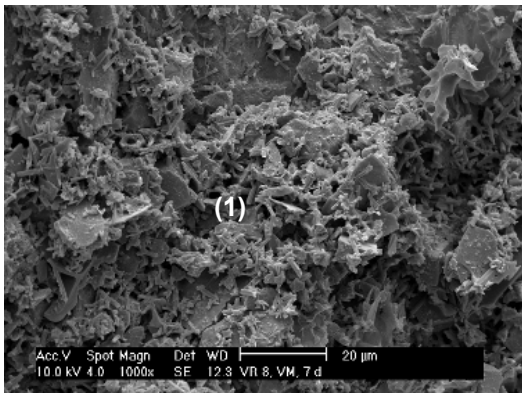
In dry mortars redispersion powders of polystyrene-butadiene copolymer with polyvinylalcohol as protective colloid were used. Their film formation and time dependent influence of the microstructure and the technical parameters was investigated. For the investigations with Pulsed Force Mode AFM (Alpha-SNOM, WITec) we breached the specimens, scanned with a Confocal Laser Scanning Microscope (Alpha-SNOM, WITec) the surface and put the AFM tip on topographically adequate positions. Under different experimental conditions this method gives an insight in the changes of the morphology related to the polymer superstructure.



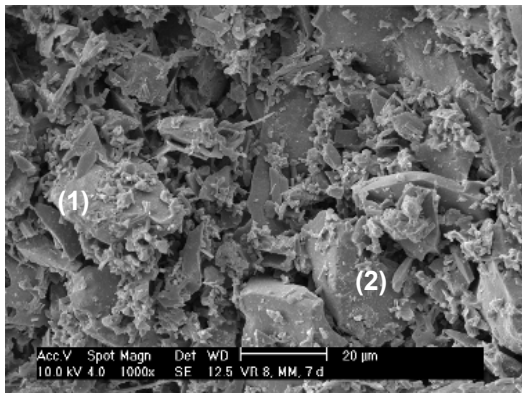
**Figure 2.7:** SGP matrix (1), 15 % water, 7 d, 20/90, quartz grain (2), micro pores (3)



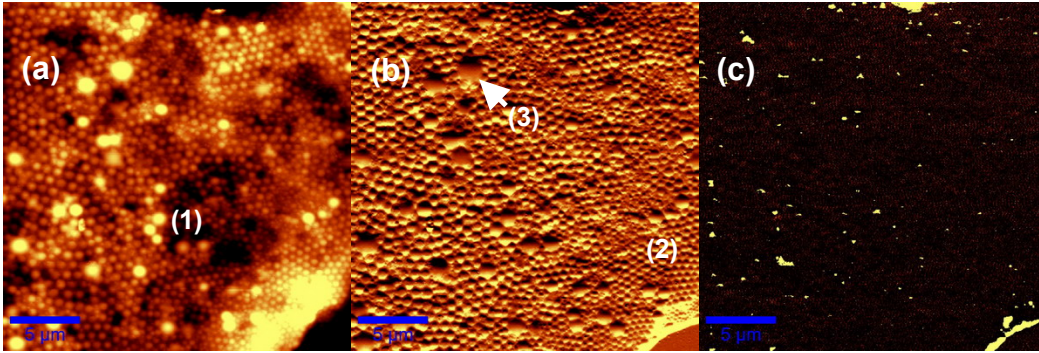
**Figure 2.8:** SGP matrix (1), 20 % water, 7d, 20/90, micro pores (3)



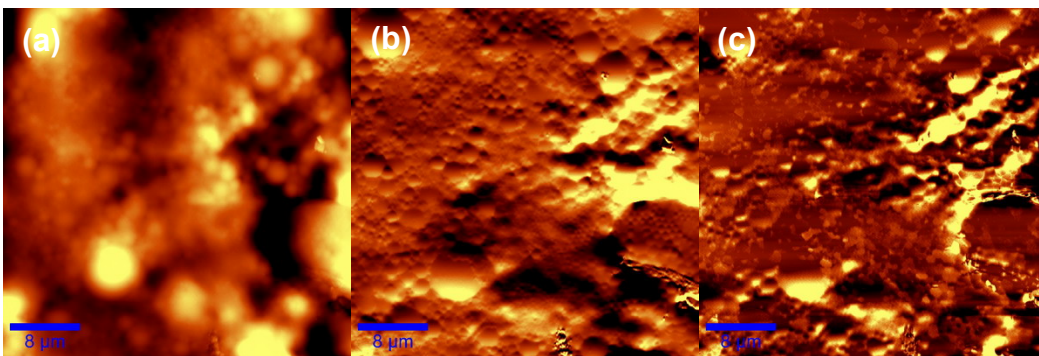
**Figure 2.9:** mortar, 15 % water, 7 d, 20/90, ettringite on slag grains (1)



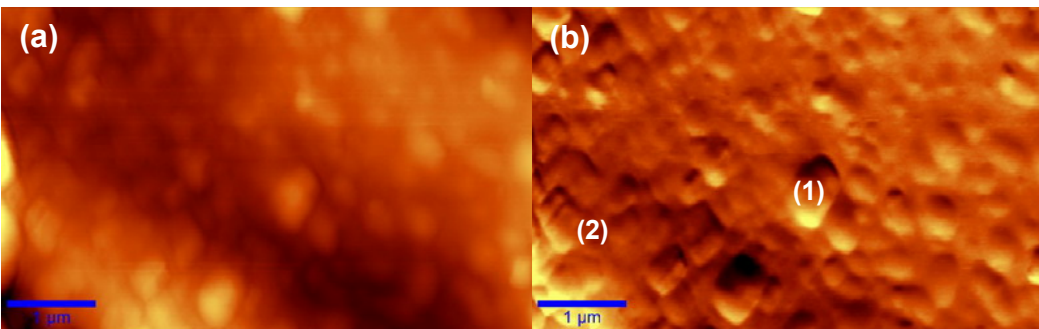
**Figure 2.10:** mortar, 20 % water, 7 d, 20/90, gypsum grain (1), slag grain (2)



**Figure 2.11:** polymer film of polystyrol-butadien-copolymer in mortar after 1 h at 23/50  
 Holes (1), single dispersion particles (2), water (3)  
 (a) topography (b) stiffness (c) adhesion



**Figure 2.12:** polymer film of polystyrol-butadien-copolymer in mortar after 7 d at 23/50  
 (a) topography (b) stiffness (c) adhesion



**Figure 2.13:** polymer film of polystyrol-butadien-copolymer in mortar after 360 d at 23/50  
 Calcium carbonate particle (1), crystal steps of gypsum (2)  
 (a) topography (b) stiffness

The film formation at early age was observed and characterized on different crystal surfaces in the specimens. Figure 2.11 shows the beginning film formation at early age on a quartz surface. Seven days after the begin of the film formation one can not distinguish between the single dispersion particles (figure 2.12). In older specimens we found the films preferably in micro-, nanocracks and air voids of the binder. The films were in most cases irregular formed and contained small crystals of calcium carbonate and gypsum in/on their interfaces (figure 2.13, here:

polymer film on a gypsum crystal). But one has to note that not all polymer films can be investigated with this method. In most cases SEM investigations have shown that polymer films also occur in zones where a topographical scan of an AFM can not reach them.

### **3 PRODUCT DEVELOPMENT**

In order to avoid secondary ettringite formation in the SGP mortar systems it was necessary to optimize the sulphate content of the mortar mixtures with regard to a complete reaction without formation of calcium aluminate hydrate phases after 28 d. As basic requirements for mortar for restoration and repairing applications we had to fulfill the DIN EN 1015, Merkblatt Sanierputzsysteme E 2-9-04/D (WTA) and for restoration applications additionally the key parameters given in [10].

The restoration mortar for the Holstentor had to be developed within some months. Therefore we had to consider the technical parameters of old bricks and terracotta. Additionally we had to guarantee a compatibility of the SGP mortar with lime, gypsum and cement based mortars of earlier age with soluble salt contents (Alkali-/earth alkali sulphates, nitrates, chlorides) of up to 5 % [13]. This was done by testing SGP-mortar specimens prepared with 15 % aggregate of 28 d old hydrated CAC, CEM and Gypsum over 90 d at 5 °C and 20 °C, with and without water, respectively. After this period SEM-EDX measurements were performed. The maximum expansion found was 2 mm/m (gypsum aggregate at 5 °C). The SEM investigations lead to the result that no damaging reaction in the matrix or the aggregate-matrix interface happened.

#### **3.1 SGP binder**

A system according to [1, 2, 3, 4] with Thyssen blast furnace slag with a grinding fineness of 5000 Blaine and an aluminate content < 13 % was used. As sulphate carrier a combination of a technical  $\beta$ -HH, a natural anhydrite and a dihydrate was used to gain the requirements for the technical handling and an optimized setting. As cement we used a CEM I HS-NA.

#### **3.2 Shrinkage Compensation**

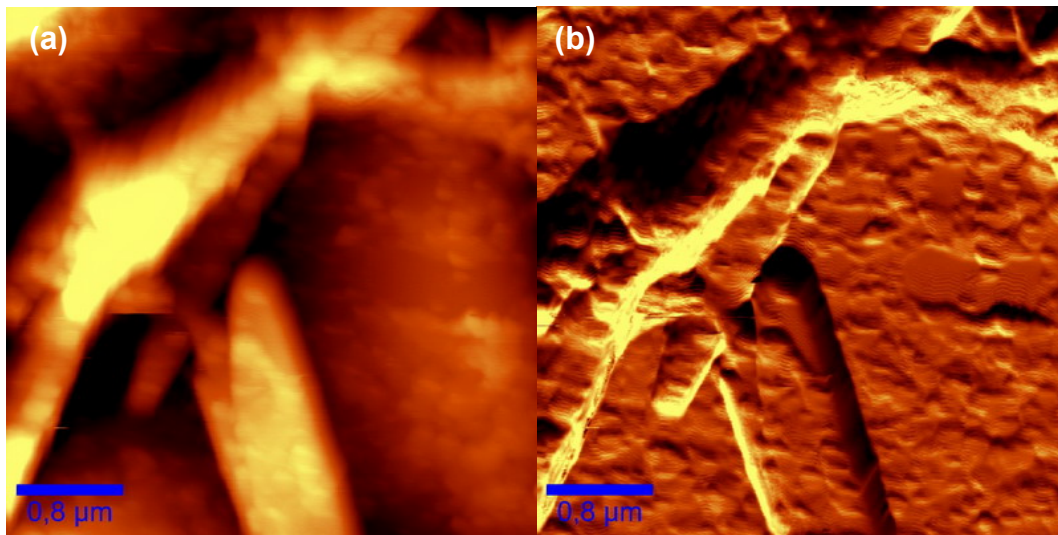
A 1:1 mixture of CAC with gypsum (or HH/A) was used to gain a complete shrinkage compensation under application technical conditions (pore size distribution and the required amount of water). The expansion value was 0.04 mm/m and the shrinkage value 0.01 mm/m after 28 days. This system can be seen as an optimized expansion cement [11, 12].

### 3.3 Aggregate

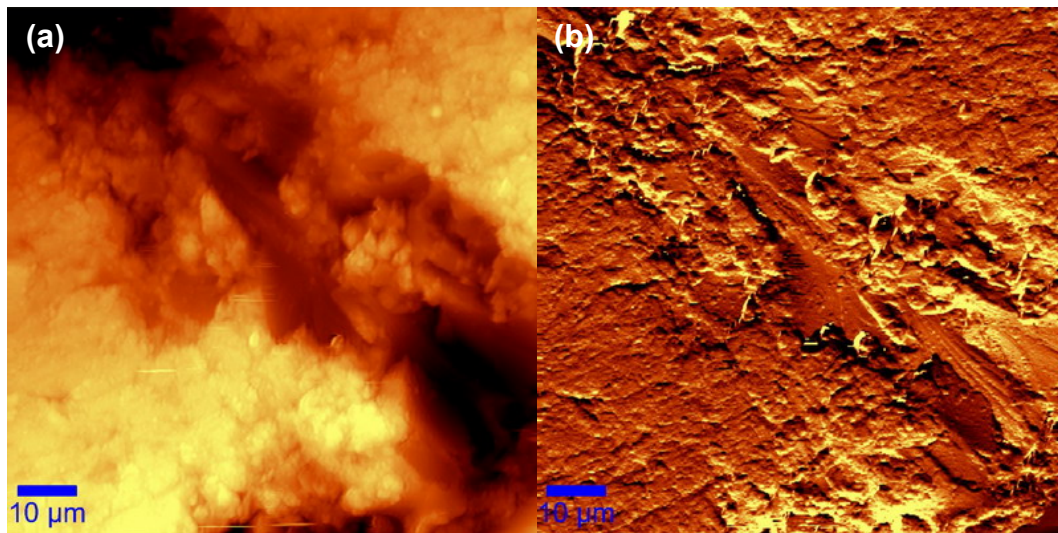
We investigated several aggregates like quartz and calcite sands, perlite, cellular glasses from different industrial sides and expansive clay. A combination of this aggregates delivered the best results for the restoration mortar for the Holstentor in Lübeck. In red pigmented joint mortar of the Holstentor the expansive glass and clay fulfilled the technical and optical requirements according to the preservation order.

### 3.4 Additives

Further we had to optimize several additives as accelerators, retarders, polymer dispersions/redispersions, air entraining agents and stabilizers. This was done in order to optimize the pore size distribution, the sanding effect and especially enable best workability. We also investigated their



**Figure 3.1:** technical cellulose ether on gypsum crystals after 60 minutes hydration  
(a) topography (b) stiffness



**Figure 3.2:** interface between mortar and brick (a) topography (b) stiffness



influence on different crystalline phases. It was also possible to relate different types of cellulose ether with the morphology of their films as shown in figure 3.1 (small crystals of gypsum on a surface of a bigger gypsum crystal with a film of cellulose ether, see also [9]).

### **3.5 Technical Parameters of the restoration mortar**

The mortar for the Holstentor had to be optimized with regard to good behavior in leveling out the terracotta friezes as well as for attaching new terracotta and filling the joints (table 4.1). In the joints the mortar has additionally to fulfill high static bending strengths. Especially for the winter applications we gained the requirement of a fast hardening in the first 7 days. Additionally the resistance to efflorescence over 6 weeks with overall 12 wet-dry cycles after [10] was tested. In the used dry mortar mixtures no efflorescence could be observed.

### **3.6 Characterization of the SGP-mortar-building-materials interface**

For testing the SGP-mortar-brick interface the adhesive strength of the mortar was tested after [10]. As brick Egersunder Ziegel ® was used. Here we got with the Holstentor mortar adhesive strengths of over 1 N/mm<sup>2</sup>. Figure 3.2 shows a interface between mortar and brick. In the upper right and lower left two sand grains of the brick and mortar can be seen. Additionally the interfaces between SGP-mortar and gypsum as well as Portland Cement mortars was investigated. Here we also found adhesive strengths between 0.5 and 1.0 N/mm<sup>2</sup>. SEM investigations delivered the information that the microstructure of the SGP binders has a very toothing behavior with a high amount of capillary pores in all three possible structures. The improved water retention capacity allows also good hydration behavior in structures with high porous bricks.

## **4 APPLICATIONS**

For the commercial more interesting field of restoration applications it was necessary to fulfill normative requirements as described in section 3. Therefore we developed a complete product system with a basecoat, spatterdash repair mortar, restoration plaster, a smoothing compound and a filling mortar. Exemplary shown is a restoration mortar system (table 4.1, M1 spatterdash repair mortar, M2 basement mortar, M3 restoration mortar, M4 basecoat ) for restoration measures in the field of high salt containing grounds. The application of this system was tested on up to 10 percent sulfate, nitrate and chloride salts containing grounds. The withstand against salt attack and compatibility of this system overcomes the most European restoration plaster systems.

Mortar/plaster type	Holstentor		System for plaster work			
	H 1, 25 °C	H 2, 5 °C	M 1	M 2	M 3	M 4
Workability in h:	5-6	5-6	0.75	0.75	0.75	0.75
Green density (fresh mortar) in g/cm <sup>3</sup> :	~ 1.6	~ 1.6	~ 1.5	~ 1.4	~ 1.4	~ 1.4
Decrease of slump after 1 h in cm:	~ 0.6	~ 0.5	~ 3.0	~ 3.0	~ 3.0	~ 3.0
Compressive strength 7 d in N/mm <sup>2</sup> :	4.0-8.0	3.0-4.5	3.4	3.9	1.6	3.6
Compressive strength 28 d in N/mm <sup>2</sup> :	7.5-11.0	4.5-7.5	5.8	5.4	3.5	5.1
Compressive strength 90 d in N/mm <sup>2</sup> :	7.0-11.5	7.0-11.5	-	-	-	-
Compressive strength in the joint 28 d in N/mm <sup>2</sup> :	8.5	8.0	-	-	-	-
Bending tensile strength 7 d in N/mm <sup>2</sup> :	1.5-3.0	1.4-2.4	0.9	0.8	0.5	1.0
Bending tensile strength 28 d in N/mm <sup>2</sup> :	3.0-3.5	2.8-4.5	1.0	2.0	1.4	1.8
Bending tensile strength 90 d in N/mm <sup>2</sup> :	4.0-5.5	4.1-6.3	-	-	-	-
E-Modulus 7 d in kN/mm <sup>2</sup> :	7.5	7.5	5.3	3.5	2.2	4.2
E-Modulus 28 d in kN/mm <sup>2</sup> :	10.0	10.3	6.4	5.5	2.7	5.5
E-Modulus 90 d in kN/mm <sup>2</sup> :	10.0	10.3	-	-	-	-
Bulk density 7 d in g/cm <sup>3</sup> :	1.7-1.8	1.7-1.8	1.6	1.4	1.3	1.4
Bulk density 28 d in g/cm <sup>3</sup> :	1.5-1.7	1.5-1.7	1.6	1.5	1.3	1.4
Bulk density 90 d in g/cm <sup>3</sup> :	1.5-1.6	1.5-1.6	-	-	-	-
Adhesive tensile strength 28 d in N/mm <sup>2</sup> :	> 0.5	> 0.5	0.3	0.6	0.3	0.3
Adhesive tensile strength 90 d in N/mm <sup>2</sup> :	> 1.0	> 1.0	-	-	-	-
Carbonatisation depth prism 28 d in mm:	14-20	11-16	-	-	-	-
Coefficient of resistance to water vapor diffusion ( $\mu$ ) 28 d:	10-15	7-26	14	17	11	17
Equivalent air layer thickness $s_d$ 28 d:	0.22-0.30	0.14-0.54	0.27	0.34	0.22	0.35
water absorption coefficient C in kg/(m <sup>2</sup> min <sup>0.5</sup> ):	0.34-0.59	0.06-0.71	1.71	0.96	0.78	1.03
degree of water absorption $w_{24h}$ in %:	9.3-11.6	4.6-13.9	-	-	-	-
Water absorption $A_b$ in %:	18.1-24.3	13.9-14.8	-	-	-	-
Water emission coefficient $C_{ab}$ in kg/(m <sup>2</sup> min):	0.0012-0.0017	0.0025-0.029	-	-	-	-
Degree of water emission $w_{ab24h}$ in %:	3.6-4.8	5.6-9.4	-	-	-	-

**Table 4.1:** overview over technical properties of the restoration mortar for the Holstentor in Germany (for winter and summer applications, H1/2) and a restoration mortar system (M1 to M4) for facade restoration.

## 5 CONCLUSION

The systematic optimization of SGP binders developed in the early 90's of the last century made it possible to design dry mortars for industrial applications that fulfill various requirements. Big advantages of the SGP-mortars are the great withstand against salt attack and easy reaction control by varying the CAC and TA contents. Change in the grinding fineness of the slag or changes in the glass content or chemistry of the slag were not considered due to uneconomical reasons at the moment. The investigations of described binder system have also shown that the results of laboratory investigations are not complete comparable with mortars under building site conditions. Only combined technical, empirical and scientific studies allow steps forward to high end applications.

The analytical investigations of the micro- and nanostructure will be brought forward to other cement systems in order to optimize additives like redispersions powders and cellulose ethers to gain optimal properties for every different system.

It is obvious that products with higher requirements and different technical properties based on alternative binder systems will be developed in the next years in order to gain lower emission rates, to optimize recycling cycles and deliver products with a higher sustainability to satisfy the increasing demands of the market.

## 6 LITERATURE

[1] K. G. Böttger, D. Knöfel, SGP – a binder with high sulphate resistance for mortars and concrete, in: Proceedings of the 6<sup>th</sup> Canmet/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, 1998, Bangkok, Supplementary Papers, 307-322

[2] K. G. Böttger, D. Knöfel, Restoration with mortars based on optimized supersulphated cement (SGP) – examples on historical buildings in Germany, in: Proceedings of the 11<sup>th</sup> International Congress on the Chemistry of Cement, Durban, 2003, 1707-1718

[3] F. Winnefeld, PhD-Thesis: Mauer- und Putzmörtel zur Restaurierung historischer Ziegelbauten, Universität-Gesamthochschule Siegen, 1998

[4] D. Knöfel, M. Dengenkolb, F. Winnefeld, Modifizierung von Mörteln auf Basis sulfatisch aktivierter Hüttensand-Bindemittel, in: Advances in Building Materials Science, Festschrift Wittmann, Hrsg. A. Gerdes, Aedificatio Publishers, Freiburg, Unterengstringen, 1996, 229-242

- [5] M. Daimon, Mechanism and kinetics of slag cement hydration, in: Proceedings of the 7<sup>th</sup> International Congress on the Chemistry of Cement, Paris, 1980, Vol. I, III-2/1-2/9
- [6] T. Nishikawa, K. Suzuki, S. Ito, Decomposition of synthesized ettringite by carbonatisation, Cem Concr Res 22 (1992) 6-14
- [7] H. Pöllmann, Methoden und Charakterisierung von Phasen bei der Hydratation zementärer Systeme, in: Tagungsbericht 16. Internationale Baustofftagung, FIB Weimar, 2006, Band 1, pp. 331-346
- [8] J. Neubauer, F. Götz-Neunhoeffler, D. Schmitt, M. Degenkolb, U. Holland, In-situ Untersuchung der frühen PZ-Hydratation, in: Tagungsbericht 16. Internationale Baustofftagung, FIB Weimar, 2006, Band 1, pp. 375-382
- [9] F. Liebert, T. J. Heinze, Exploitation of Reactivity and Selectivity in Cellulose Functionalization Using Unconventional Media for the Design of Products Showing New Superstructures, Biomacromolecules 2 (2001) 1124-1132
- [10] D. Knöfel, P. Schubert, Mörtel und Steinerfüllstoffe in der Denkmalpflege, 1993
- [11] I. Chartschenko, J. Stark, Theoretische Grundlagen zur Anwendung von Quellzementen in der Baupraxis, Internationales Symposium "75 Jahre Quellzement", 11.-13. Dezember 1995, Weimar, 31-46
- [12] J. Stark, I. Chartschenko, Entwicklung der Quellzemente für die Baupraxis, Internationales Symposium "75 Jahre Quellzement", 11.-13. Dezember 1995, Weimar, 5-30
- [13] S. Freyburg: Holstentor Lübeck – Zustandsanalyse Terrakotta, FIB der Bauhaus-Universität Weimar, 1998