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New Approaches to Increase Water Resistance of Gypsum Based Building Materials

ABSTRACT

Gypsum is a major binder in a variety of dry mortar formulations such as gypsum lime plasters, finish plasters, gypsum board jointing compounds or anhydride screeds.

Gypsum offers a number of advantages for the use as a building material. It is largely available in most countries. Application and workability properties are excellent. Gypsum based materials have nearly no shrinkage problems and provide high fire resistance. In addition, carbon footprint of gypsum is significant lower compared to cement.

The main disadvantage of gypsum, especially versus cement, is the poor water resistance. There are only limited possibilities to increase water resistance of gypsum building products, because the common hydrophobizing agents which are used for cementitious systems are not working in gypsum based materials.

The present paper discusses existing and new approaches to increase water resistance of gypsum based dry mortars.

Key words: gypsum based dry mortars, increased water resistance, hydrophobizing powder additives

1. INTRODUCTION

Gypsum is a naturally occurring mineral. In chemical terms, gypsum is calcium sulfate dihydrate ($\text{CaSO}_4 \times 2 \text{H}_2\text{O}$). When calcium sulfate dihydrate is heated sufficiently crystal water is driven off. Depending on the temperature, either calcium sulfate hemihydrate ($\text{CaSO}_4 \times 1/2 \text{H}_2\text{O}$ at about 140°C) or calcium sulfate anhydrite (CaSO_4 at about 600°C) is formed. This process is called calcination of gypsum. When mixed with water calcined gypsum reverts to the original calcium sulphate dihydrate – the set and hardened gypsum product. The process of hydration and de-hydration and its natural occurrence makes gypsum to a sustainable resource, which in principle can be infinitely recycled.

Gypsum and anhydrite deposits are found in many countries. The best known deposits of natural gypsum are those of the Paris Basin and the areas around the Mediterranean. Beside natural occurring gypsum, this material is also produced as a by-product in industrial processes. So-called flue-gas gypsum (FGD gypsum) is obtained from the desulfurization of combustion gases of fossil fuels such as oil or bituminous coal. Gypsum, in particular in the dehydrated form of calcium sulfate α - and β -hemihydrate is a very common building raw material.

Both, natural gypsum and flue-gas gypsum are used to produce hemihydrate. The relatively low calcination temperature of about 140°C and the fact that gypsum releases no crystalline CO_2 results in a significantly lower carbon footprint compared to cement. The lower weight compared to cement, a high fire resistance and low shrinkage are further advan-

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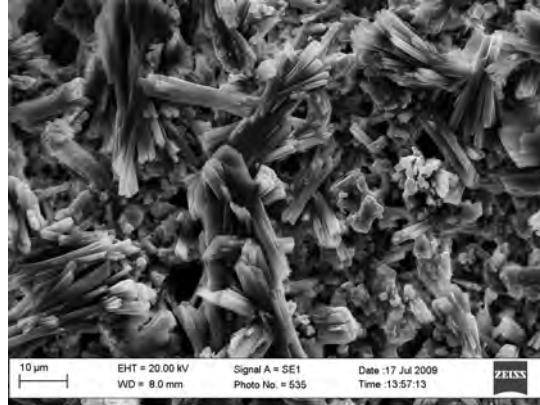


Figure 1: Scanning electron microscopy (SEM) image of a gypsum based joint filler. Relatively large aggregates of gypsum crystals and pores in between dominate the structure.

tages of gypsum based products. Calcium sulfates are used in a variety of building formulations such as gypsum lime plasters, finish plasters, gypsum board jointing compounds or anhydride screeds. The high water sensitivity of gypsum based products, however, limits their use to dry indoor applications. For interior applications, where a certain level of water resistance is required, such as in bathrooms, kitchens, staircases, storage rooms, cellars, garages, warehouses or seashore areas, the gypsum formulations have to be hydrophobized in order to achieve sufficient water resistance.

Cured gypsum mortar consists of 50-60 vol% pores, most of them having a pore size between 0.3 – 1.0 µm. This means that pores in a gypsum matrix have diameters, where capillary suction forces are active (Jakobsmeier, 2000). The high content of these macropores, the water solubility of gypsum and the relative large gypsum crystals are factors, which highly contribute to the water sensitivity of such building materials. When exposed to water or high humidity gypsum based building materials can be severely damaged. Figure 2 shows a plaster wall damaged by the influence of water.

Lots of efforts have been made in order to increase the water resistance of gypsum. Nevertheless, there are still only a few hydrophobizing additives on the market which are suited to increase the water resistance of gypsum based building materials. Many of those additives are in liquid form and therefore excluded for the production of dry mortars.

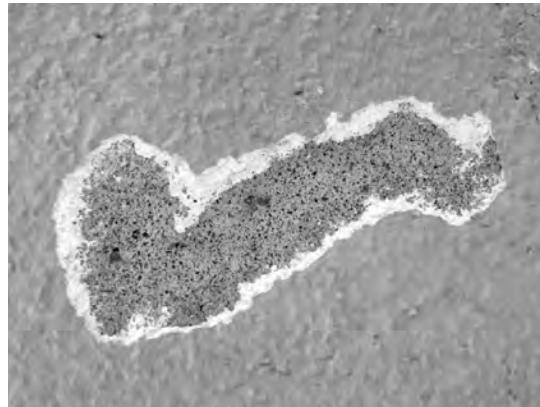


Figure 2: Water damaged plaster wall.

Thus, there is still a need for hydrophobizing powder additives enabling the formulation of gypsum based dry mortars. The present paper discusses the most common used hydrophobizing additives for gypsum based dry mortar formulations and presents latest developments in this field of research.

2. METHODS AND MATERIALS

2.1 Following methods were used to evaluate water resistance in this study:

2.1.1 Determination of the water absorption of gypsum mortars on gypsum plaster-boards, following EN 520 – water uptake after 2 hours.

The dry gypsum formulation is added to the required amount of mixing water while stirring slowly. This mixture is further stirred for one minute with a propeller stirrer with a speed of 950 rpm. After a maturing time of 3 minutes the mortar is stirred again by hand for 15 seconds and then applied with 1.5 mm thickness onto a 12 mm thick gypsum plaster board and stored at 23°C/50% relative humidity for 7 days. After 6 days polypropylene rings with an inner diameter of 100 mm and a height of 100 mm are fixed on top of the mortar surface with the aid of silicone paste. The next day the board is weighed, and subsequently being filled with 250 g of water and left for 2 hours. After removal of the remaining water the wet surface is wiped off and weighed

again. The water absorption is being calculated by the difference in the weight values measured before and after the water treatment, which is indicated in kg/m².

2.1.2 Determination of the surface hydrophobicity – water drop test

The gypsum formulation is applied the same way as for the water absorption test onto the gypsum plaster-boards and stored at 23°C/50% relative humidity for 7 days. 5 drops (circa 0.2 ml) of water are applied onto the mortar surface and the time for complete absorption is measured.

2.2 Materials

2.2.1 Gypsum based dry mortar formulations

A gypsum plaster formulation and a jointing compound for plasterboards were tested according to their water resistance. The compositions of the investigated dry mortar formulations are given in Table 1.



Figure 3: Setup to measure water uptake (Cobb-test).

Table 1: Composition of the tested gypsum formulations.

Component	Interior gypsum plaster Hand or machine applied [weight %]	Jointing compound for plasterboards [weight %]
α - and or β -Hemihydrate	20 - 40	40 - 60
Hydrated Lime**	0.5 - 3	0 - 3
Calcium Carbonate	55 - 75	30 - 40
China Clay	0	5 - 6
Mica Filler	0	8 - 10
Light weight Filler	0 - 3	0
Air entraining Agent	0.01 - 0.03	0
Set Retarder	0.05 - 0.07	0.05 - 0.15
Cellulose Ether	0.1 - 0.3	0.2 - 0.4
Starch Ether	0.02 - 0.04	0.01 - 0.03
Redispersible Polymer Powder	0	2 - 3
Mixing Water *	40 - 45	40 - 45

* Based on total dry mix formulation

** A small portion of hydrated lime is present in both formulations in order to enable fast hydrolysis of silanes (one class of the tested hydrophobizing additives). At neutral pH, silanes are not effective

2.2.2 Hydrophobizing additives

The following hydrophobizing additives were included in this study

- Fatty acids and their salts (liquid and powder form)
- Wax emulsions (liquid state)
- Additives based on silane or siloxane technology
 - Standard alkyl oxy silanes as used for cementitious systems (powder form)
 - H-terminated silanes and H-terminated polysiloxanes (liquid state)
 - Alkyl silicon resins (powder form)
 - New development additives based on special alkyl oxy silane chemistry, e.g. Elotex BN Seal 712 (powder form)

3. RESULTS

The effect of hydrophobizing additives which belong to the above mentioned chemical classes was measured for a gypsum plaster and for an gypsum based jointing compound. Resulting water uptake according to the Cobb test and surface hydrophobicity (water drop test) are shown in Figures 4 – 7. Beside the resulting water resistance, also fresh mortar properties were evaluated. The results are summarized in Table 2.

3.1 Effect of hydrophobizing additives in gypsum based jointing compound

Fig. 4 and Fig. 5 show the water uptake of a gypsum based jointing compound without and with hydrophobizing additives.

Significant reduced water uptake of the jointing compound is achieved with hydrophobizing additives based on H-terminated silane, alkylsilicon resin on inorganic carrier and the newly developed dry powder additive based on a new encapsulated silane technology.

Fatty acid based additives, paraffin / montan wax emulsions and standard alkyl alkoxy silane used for cementitious systems (e.g. Elotex Seal 80) cannot decrease water uptake of the tested jointing compound, even when used at relatively high dosages.

Very good surface hydrophobicity (water drop remains > 300 minutes on surface) is achieved with H-terminated silanes, alkyl silicon resins and with the dry powder additive based on a new encapsulated silane technology.

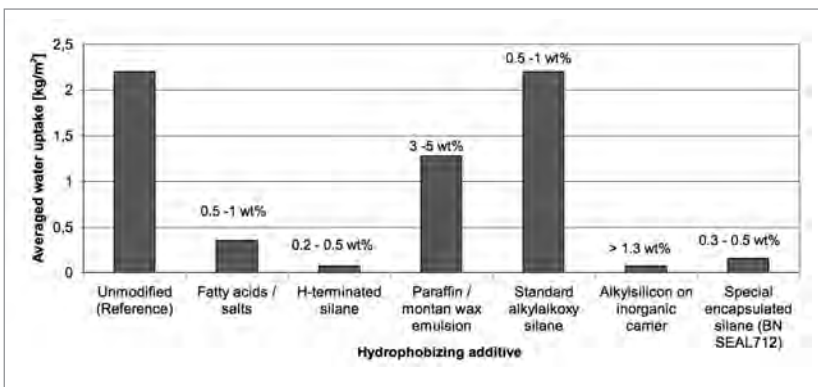


Figure 4: Averaged water uptake reduction of gypsum based jointing compound with different hydrophobizing additives at the given typical concentration in comparison to the non hydrophobized gypsum based jointing compound according to formulation given in Table 1. Typical concentration range of hydrophobizing additive is given in weight percent on total dry mix

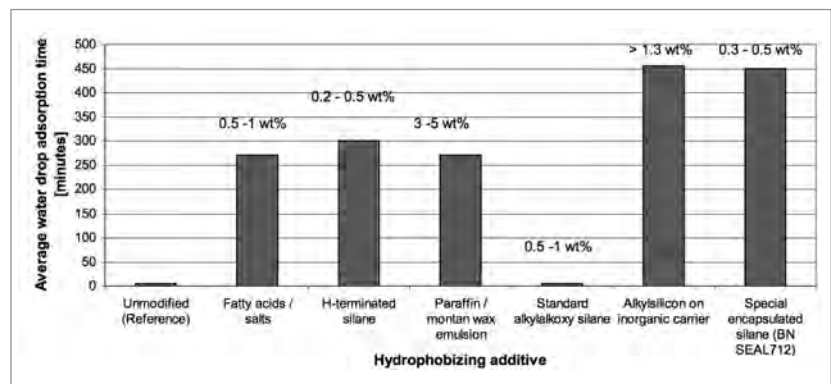


Figure 5: Averaged surface hydrophobicity (water drop test) of gypsum based jointing compound with different hydrophobizing additives at the given typical concentration in comparison to the non hydrophobized gypsum based jointing compound according to formulation given in Table 1. Typical concentration range of hydrophobizing additive is given in weight percent on total dry mix.

3.2 Effect of hydrophobizing additives in indoor gypsum plaster

Fig. 6 and Fig. 7 show the water uptake of a indoor gypsum plaster without and with hydrophobizing additives.

As for the jointing compounds, significant reduced water uptake is achieved with additives based on H-terminated silane, alkylsilicon resin on inorganic carrier and the newly developed dry powder additive based on a new encapsulated silane technology.

In addition, also additives based on fatty acids can decrease water uptake of the tested gypsum plaster formulation. Powder based on standard alkyl oxy silane technology (as used for cementitious systems) cannot reduce water uptake of the gypsum plaster.

A very good surface hydrophobicity, marked by an adsorption time of a water drop on the surface larger than 450 minutes is achieved with alkyl silicon resins and with the dry powder additive based on a new encapsulated silane technology.

Acceptable surface hydrophobicity, marked by an adsorption time of water drop on the surface no longer than 300 minutes is reached with additives based on fatty acid chemistry, H-terminated silanes and paraffin / montan wax emulsions.

3.3 Fresh Mortar Properties

Beside increased water resistance of the cured gypsum material, also fresh mortar properties, such as wetting, mixing and workability, are of great importance. Table 2 summarizes fresh mortar properties and resulting water resistance of the investigated hydrophobizing additives in dependence of their composition, appearance and concentration.

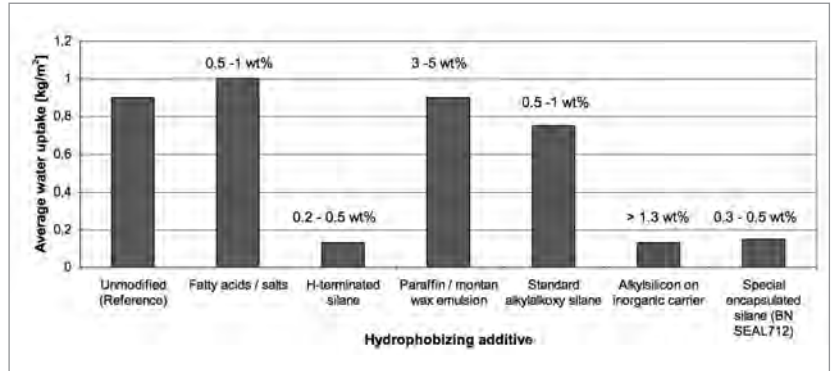


Figure 6: Averaged water uptake of indoor gypsum plaster with different hydrophobizing additives at the given typical concentration in comparison to the non hydrophobized gypsum plaster according to formulation given in Table 1. Typical concentration range of hydrophobizing additive is given in weight percent on total dry mix.

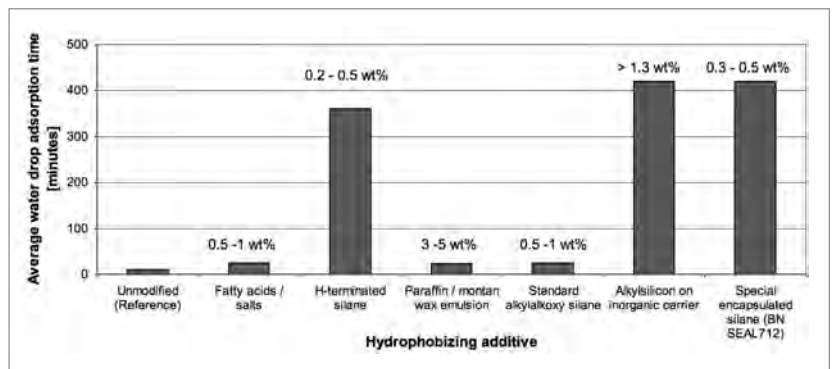


Figure 7: Averaged surface hydrophobicity (water drop test) of indoor gypsum plaster with different hydrophobizing additives at the given typical concentration in comparison to the non hydrophobized gypsum plaster according to formulation given in Table 1. Typical concentration range of hydrophobizing additive is given in weight on total dry mix.

Table 2

Hydrophobizing additive – chemical basis	Dosage [wt % on dry formulation]	Appearance	Fresh mortar properties			Cured mortar
			Wetting	Mixing	Workability	Water resistance
Blank	-	-	+	++	++	-
H-terminated silanes	0.1 – 0.5	Liquid form	-	-	-	++
Alkyl silicon resin on inorganic carrier	0.5 – 2	Powder form	-	-	+	++
Wax emulsion	2 – 5	Liquid form	-	-	0	-
Fatty acids or salts thereof	0.5 - 1	Liquid / Powder form	-	-	+	- / + **
Elotex Seal 80	0.3 – 0.5	Powder form	+	++	++	-
Elotex BN Seal 712	0.2 – 0.5	Powder form	+	++	++	++

Scale: Poor (-), neutral (0), good (+), very good (++)

** Water resistance fatty acids: poor results in jointing compound; acceptable results in plaster.

Table 2: Overview of the resulting fresh mortar properties and water resistance of cured gypsum mortars using the investigated hydrophobizing additives in comparison to Elotex Seal 80. This is an hydrophobizing additive for cement based products based on an encapsulated standard alkyl oxy silane.

4. DISCUSSION

Hydrophobizing powder additives for cement based dry mortars are well known. Many of them are based on fatty acids or alkyl oxy silane types (e.g. Elotex Seal 80).

To increase water resistance of gypsum based dry mortars, however, remains still challenging.

Detailed discussion of the tested additives

– Fatty acids and their salts

Fatty acids and their salts are common additives to hydrophobise cementitious systems. In our gypsum test formulations, however, we could measure no (in case of jointing compound), respectively limited increase of water resistance (in case of gypsum plaster). In order to obtain a significant increase in water resistance, relatively high dosages are required, which results in poor fresh mortar properties.

– Wax emulsions

Wax emulsions, such as paraffin or montan wax emulsions are also used to increase water resistance of gypsum. Such additives are used and known for the plasterboard production (US patent, US005437722A). In gypsum based dry mortars, such as joint fillers or renders we could measure nearly no effect with this type of additives even when used in dosages up to 5 wt% based on the dry formulation.

– Silane or siloxane technology

Various technologies are described in literature and patents which use silane or siloxane based compounds as hydrophobizing components for gypsum based products (e.g. US2002/0040666 A1 or WO 9950200).

Common to all these type of additives is the requirement of a catalyst to enable fast hydrolysis of the silane. In most cases, a high pH acts as the catalyst. For cementitious systems this is automatically given, whereas to the gypsum formulations a small portion of e.g. lime has to be added (see Table 1).

Silane and siloxane technology can be divided into different sub-classes.

a.) Standard alkyl alkoxy silanes

For cementitious dry mortars modern hydrophobicity additives are available (such as Elotex Seal 80 with no delay in wetting upon mixing).

However, this type of silane cannot increase water resistance of gypsum based systems. In best case, a slight improve in surface hydrophobicity can be observed.

b.) H-terminated silanes and polysiloxanes

So called H-terminated silanes or H-terminated polysiloxanes are commonly used to increase water resistance of gypsum based building products, especially of plasterboards. An alkaline pH is required in order to have a sufficiently rapid hydrolysis and condensation reaction taking place during the casting and drying steps of plasterboard manufacturing process. The hydrolysis reaction releases hydrogen. Upon use in gypsum based dry mortars, this induces a poor surface quality (e.g. surface blow up) as well as a poor workability, already noticeable at dosages as low as 0.1 wt%. This severely limits the use of H-terminated silanes and H-terminated polysiloxanes in dry mortars.

On the other hand, the achieved increase in water resistance of this type of silanes is excellent.

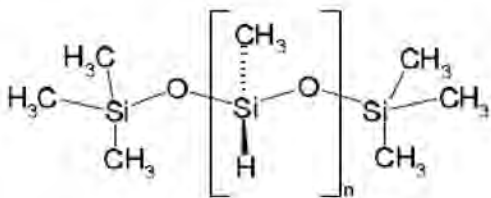


Figure 8: Chemical structure of H-terminated silane. n = 1-4: oligomeric H-terminated siloxane; n > 4: polymeric H-terminated siloxane

c.) Alkyl silicon resins

Alkyl silicon resins with alkoxy functionalities are also used to increase water resistance of gypsum based building products. In alkaline environment these silicon resins can hydrolyse and further condensate forming a 3-dimensional network which permanently bonds to the gypsum crystals.

In order to make them available in powder form, silicon resins can be adsorbed on an inorganic carrier. Main disadvantages of such powders are their hydrophobic surface which results in strong delayed wetting and their poor long-term storage stability, which often results in a loss of performance over extended period of time.

d.) New developments based on special encapsulated alkyl oxy silane

The state-of-the-art hydrophobizing additives which allow to decrease the water resistance of gypsum based materials are either only available in liquid form or cause delayed wetting. Furthermore, the storage stability of the dry mix is often reduced, meaning that the hydrophobic effect decreases when the dry mix is stored for a few months.

Therefore, there is still a need for dry powder additives, which deliver excellent hydrophobicity of gypsum based materials. Furthermore, the additive itself, as well as the dry mortar containing the additive must have a sufficient storage stability and provide a good wettability upon mixing with water.

A new developed hydrophobizing additive in powder form based on a special, encapsulated alkoxy-silane technology, Elotex BN Seal 712 fulfils these requirements. Despite the high reactivity of the silane molecules, the shelf life of the dry powder as well as of the dry mortar containing the additive is excellent.

Figure 9: Water uptake of gypsum based joint filler versus dosage of Elotex BN Seal 712

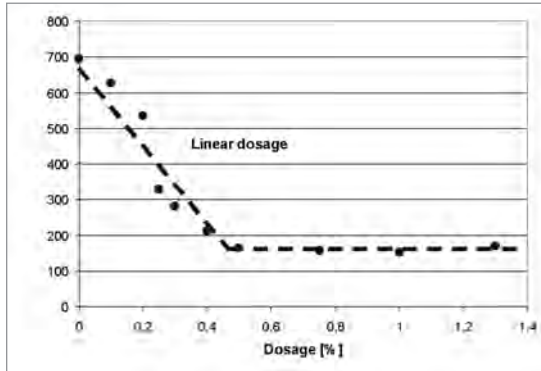


Figure 9 shows a linear dependence of the water uptake with the Elotex BN Seal 712 dosage until a plateau is achieved at around 160 g/m² (Cobb test), a value well below the limit of 180 g/m² set by the European standard EN 520. Hence, the required level of water resistance can easily be adjusted via the dosage of Elotex BN Seal 712.

Figure 10 shows the gypsum plaster formulation as given in Table 1 with and without the modification of Elotex BN Seal 712. Clear improvements of water resistance with this product can be seen on the untreated surface, as well as on the scratched/sanded surface.

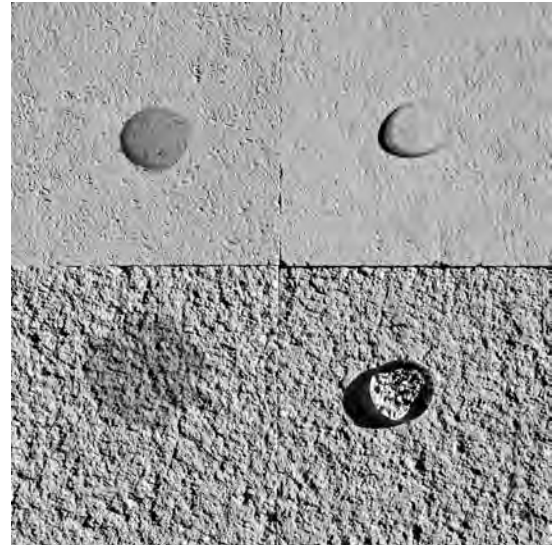
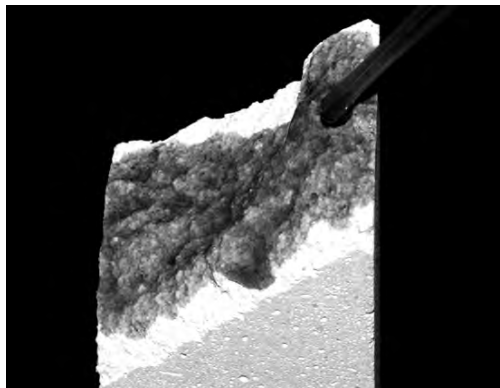
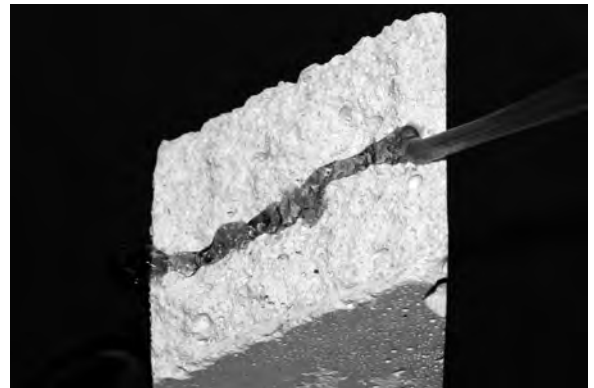


Figure 10: Improvement of the water resistance of the gypsum-lime plaster formulation by addition of 0.5wt% Elotex BN Seal 712 (right) in comparison to the non modified gypsum-lime plaster formulation (left) by water drop test. Comparison of untreated surface (upper pictures) and scratched/sanded surface (lower pictures).

The capability of Elotex BN Seal 712 to protect beside the surface also the bulk of gypsum based building mortars and products against water penetration is demonstrated in Figure 11.



a.) Colored water added on fractured surface of a commercial interior gypsum-lime plaster formulation without hydrophobizing additive (reference).



b.) Colored water added on fractured surface of a commercial interior gypsum-lime plaster formulation with 0.5wt% Elotex BN Seal 712 hydrophobizing additive.

Water is adsorbed immediately on the fractured surface of a commercial interior gypsum-lime plaster formulation without hydrophobizing additive (reference). When modified with 0.5wt% Elotex BN Seal 712 the fracture surface shows a strong pearling effect. Water does not penetrate into the gypsum matrix, hence protecting the gypsum-lime plaster against the detrimental effects of frequent water exposure.

5. CONCLUSION AND OUTLOOK

Main disadvantage of gypsum based building materials is their poor water resistance. When modified with hydrophobizing additives, the water resistance and durability of gypsum based building products is greatly improved. This opens the possibility to widen the use of gypsum mortars in wet humid indoor areas, such as kitchen, bathroom, staircase, storage rooms, cellars, garages, warehouse or seashore areas as alternative solution to today's cementitious products. Furthermore, hydrophobic modified gypsum based dry mortars open the possibility to be used as final coatings with decorative function without being over-painted (all-in-one building system).

Based on our study, most suited hydrophobizing additives for dry gypsum mortars are based on silane or siloxane technology. The new developed hydrophobizing additive in powder form, Elotex BN Seal 712, results at low dosage in very low water uptake and eliminates the drawbacks of today's gypsum hydrophobizing additives, such as their poor workability, poor mixing properties or loss of performance upon ageing.

In order to have sufficient water resistance a catalyst is required to speed up the hydrolysis reaction of silane-based hydrophobizing additives. A certain amount of lime present in the dry gypsum formulation or the addition of aliquot of cement can act as such a catalyst. Consequently, dry gypsum based mortar formulations when mixed with water are highly alkaline. The high pH is not always acceptable. Therefore additional efforts will be necessary to

develop an hydrophobizing additive which also works at neutral pH. First promising lab results based on a complete new technology show that it is also possible to achieve very low water uptake of gypsum based building materials at neutral pH with a dry powder hydrophobizing additive.



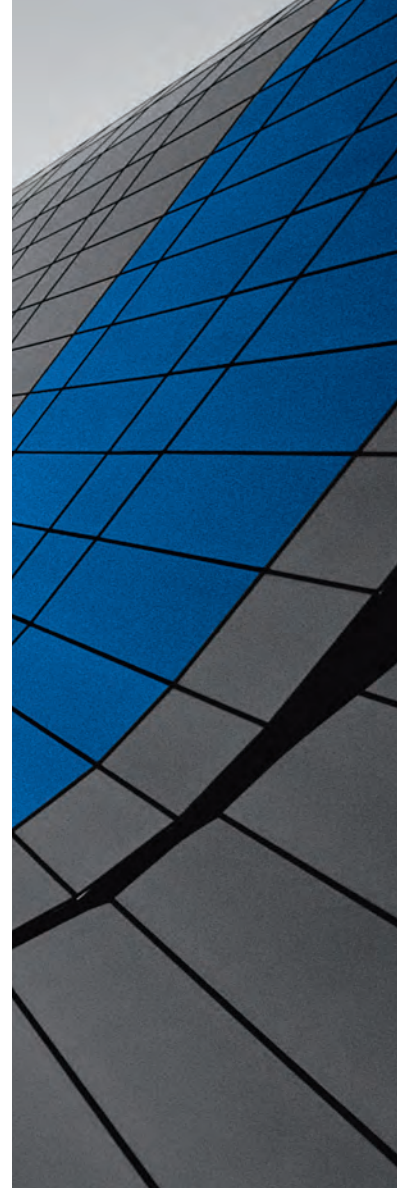
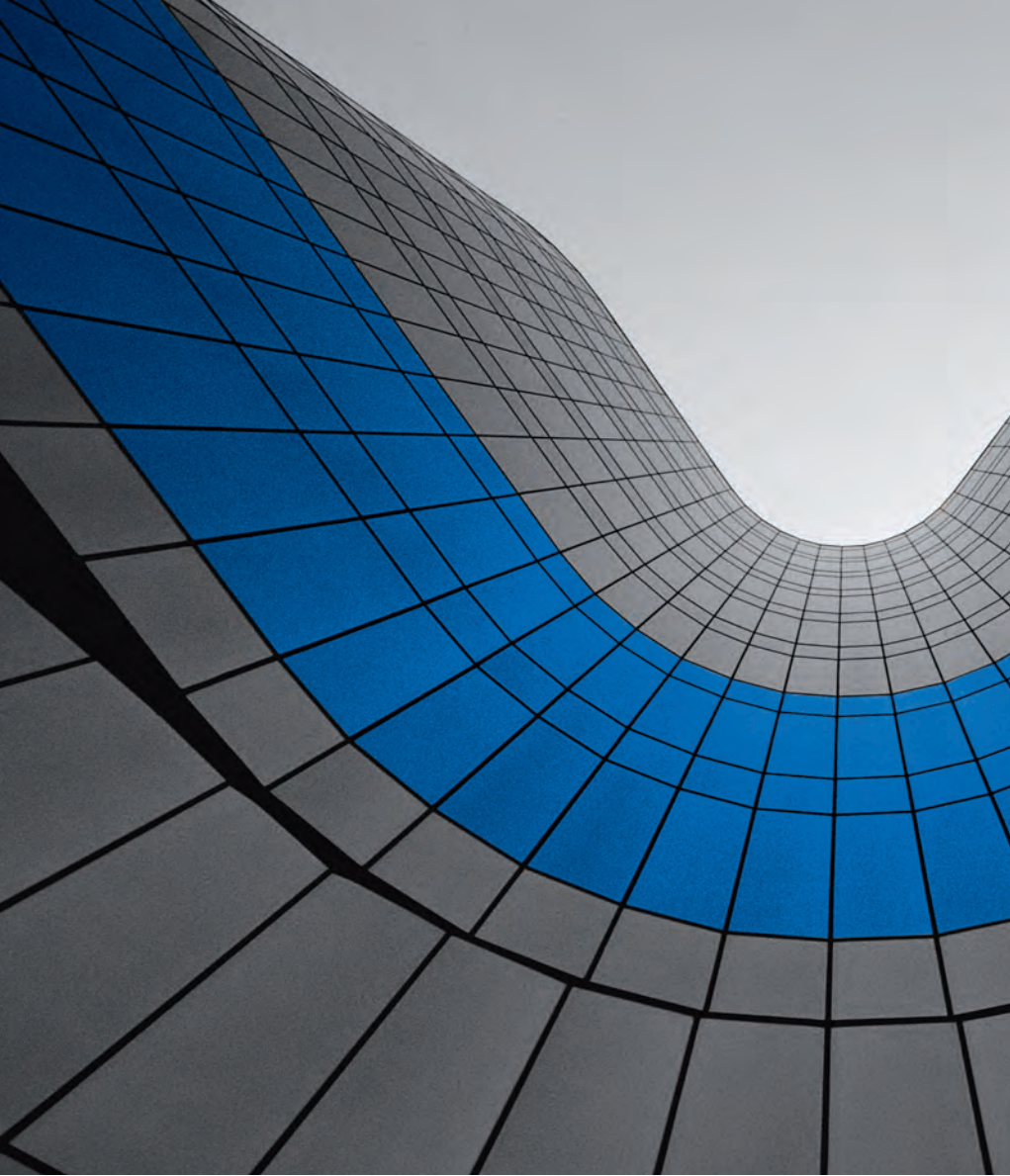
Figure 12: Water drop on surface of gypsum based joint filler modified with Elotex experimental hydrophobizing additive for neutral pH.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Roger Zurbriggen, Mr. Adrian Keller and Mr. Joerg Lang for their inputs and help. Special thanks to Mr. Joerg Lang for providing the various pictures used in this study.

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