

## **INTERNAL HYDROPHOBIZATION BY MEANS OF ORGANOSILICON COMPOUNDS**

**K. Grabowska (1), A. Wieczorek (1), M. Koniorczyk (1)**

(1) Department of Building Physics and Building Materials, Lodz University of Technology, Poland

### **Abstract**

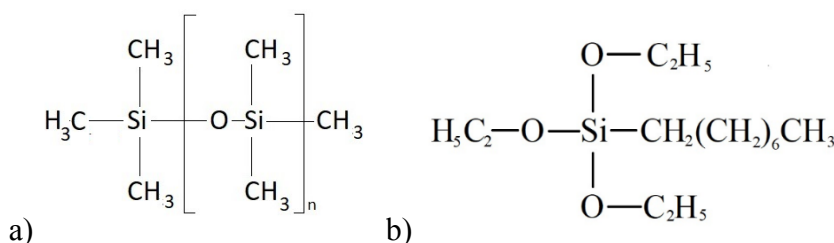
The porous structure of building materials significantly affects their properties including their durability. Freezing water, salt crystallization, mold and fungi growths and general deterioration in thermal conditions caused by moisture in building materials lead to shorter life and the sustainability of the material. Internal hydrophobization by means of organosilicon compounds, such as silanes and siloxanes, can significantly improve their durability by increase water resistance and thus extend the application areas. In our paper we investigated the influence of silanes and siloxanes on the aeration, strength characteristics and water absorption of cement mortar. The possible changes in the microstructure of examined mortar was analyzed by mercury intrusion porosimetry (MIP). The heat of cement hydration of cement paste with organosilicon admixtures was studied by using isothermal calorimetry. Internal hydrophobization might be an alternative method to surface treatment. The obtained results showed that it is possible to use organosilicon compounds as admixtures to improve the water resistance, however, it is associated with changes in material properties.

### **1. INTRODUCTION**

In the building industry the used materials are mostly porous especially cementitious one. Their porous structure significantly affects their properties, durability and lifespan. Water and salts dissolved in it might be easily transported by a network of connected capillaries. Water in the material may freeze and salts may crystallize, leading to the destruction of the material and deterioration of its properties. As first, soaps and waxes (e.g., stearates and oleates) were used as hydrophobic agents to protect against water and moisture [1,2]. Since the 50's of the 20th century organosilicon compounds (popularly called "silicones") were used as water-repellents for surface protection of the materials against detrimental effects of water in the industry and construction sectors [3,4]. The most popular hydrophobic agents based on silicon are represented by alkyl siliconates and silanes, siloxanes, polysiloxanes and silicone resins [1,5]. Due to chemical structure and physico-chemical characteristics of the organosilicon compounds and similarity to carbon-based materials organosilicon compounds are considered as very good agents to hydrophobic protection of inorganic, porous building materials (both surface and

volume (internal) hydrophobization). As a result of a chemical reaction, due to the chemical bonds are formed, of organosilicon compounds with cement matrix the permanent connection with the material is formed. Hence, the surface of the pores in cementitious material becomes hydrophobic, and the penetration of liquid water or moisture into the material structure is hinder, but with keeping vapor-permeable properties. The main structure of organosilicon compound is long polysiloxane chain containing oxygen and silicon atoms bonding each other alternately ( $-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-$ ). In addition, their structure includes an organic, alkyl substituent attached to the silicon atoms. Therefore, these compounds are called amphiphilic one. This means that they combine the properties of inorganic silicon-oxygen chain and organic non-polar alkyl groups. These alkyl substituents make interactions with the other organic compounds easier. The main function of alkyl groups, due to their non-polar character, is to give hydrophobic properties. Theoretically it is assumed that longer and higher branching of the alkyl group improves hydrophobic effects. The function of inorganic part of organosilicon compounds (meaning siloxane chain) provide interaction with inorganic substrates (meaning cement phases) [1,5]. In our study we investigated the influence of three commercial admixtures based on poly(dimethylsiloxane) (PDMS) (Fig. 1a) and triethoxyoctylsilane (Fig. 1b). Poly(dimethylsiloxane) is macromolecular, polymeric compound with two methyl groups. Triethoxyoctylsilane, contrary to poly(dimethylsiloxane), is a single monomer with three ethoxy ( $-\text{O}-\text{C}_2\text{H}_5$ ) groups and one octyl group ( $-\text{C}_8\text{H}_{17}$ ). During chemical reactions the ethoxy groups enables hydrolysis the silanes molecules to the silanols. Subsequently polycondensation reactions occur which lead to forming of siloxane chains. Long octyl group is responsible for hydrophobic effects.

The purpose of this preliminary studies is to investigate the functionality of commercially available water-repellents based on organosilicon compounds to internal hydrophobization of porous, cementitious building materials and their impact on the properties of the material, both negative and positive.



**Figure 1: Schematic structure of a) poly(dimethylsiloxane) b) triethoxyoctylsilane**

## 2. MATERIALS

The paper shows results of internal hydrophobized cement mortar. Four types of cement mortars were prepared. Reference mortar, which contains only three basic ingredients: cement, water and sand, and three type of cement mortar with organosilicon, hydrophobic admixture. Three different commercially available organosilicon admixture were used. Two of them are based on triethoxyoctylsilane and the third one on poly(dimethylsiloxane). The dosage of the first admixture named OTES A was 0.3%, the second named OTES B was 0.8% and the third one named PDMS was 3%. The amounts of used admixtures were in line with the manufacturers' recommendations and they were dosed per cement mass. All three silicon-based

admixtures are recommended for internal hydrophobization of cement-based materials. OTES B and PDMS types admixtures were added to the batch water before cement. The OTES A type was added just after mixing all basic ingredients. The specific cement mortar compositions are presented in Table 1 and represent amounts of ingredients required for one batch of mortar. Each type of mortar was prepared according to EN 196-1 [6]. The Portland Cement CEM I 42.5 R was used and the water to cement ratio (w/c) was equal to 0.5.

**Table 1: Cement mortar composition**

	Water repellent agent		
	OTES A	OTES B	PDMS
	0.3%	0.8%	3%
W/C	0.5		
Cement [g]	450		
Water [g]	1350		
Sand [g]	225		
Admixture [g]	1.35	3.60	13.50

### 3. METHODS

The air content in fresh mortar was determined by the pressure air measurement method according to EN 1015-7 [7] standard. A specially intended for aeration test air entrainment meter was used. A fresh mortar was placed in cylindrical container and compacted in four layers. Mechanical tests of compressive strength have been carried out on the prismatic samples with dimensions 40x40x80 mm (left after flexural strength test) after 28 days of curing according to EN 1015-11 [8] standard. The capillary water absorption test was carried out on six prismatic mortar samples (40x40x80 mm). After 28 days of curing, mortar beams were dried after constant mass were obtained. After removing from the dryer and reaching room temperature, the side walls of all the mortar beams were covered with sealant. After next 24 hours samples were vertically immersed in water to a depth of 1 cm. The weight of samples was examined after 10 min, 30 min, 60 min, 90 min, 2h, 3h, 4h and 24h. The capillary water absorption test was carried out according to the EN 1015-18 [9] standard. By mercury intrusion porosimetry (MIP) we investigated the pore structure of cement mortar. The MIP measurements were carried out with Micromeritics AutoPore IV9500 instrument. Cylindrical samples (6x6 mm) were cut out of the cement mortar. Then they were kept in isopropanol to until the constant mass was achieved and next, they were dried at 30°C in a vacuum dryer. The heat of cement hydration with organosilicon admixtures was measured by isothermal calorimeter TAM Air. The test was carried out on cement pastes with water to cement ratio equal 0.5 and the Portland cement 42.5R was used. The dosage of hydrophobic admixture was the same as in cement mortar. The heat released during cement hydration was measured by 7 days, at temperature  $T=20^{\circ}\text{C}$ . For each type of cement paste two samples were prepared.

## 4. RESULTS AND DISCUSSION

### 4.1 Air content

The measurement of air content in the fresh mortar showed significant differences between tested organosilicon admixture. The hydrophobic admixtures based on triethoxyoctylsilane do

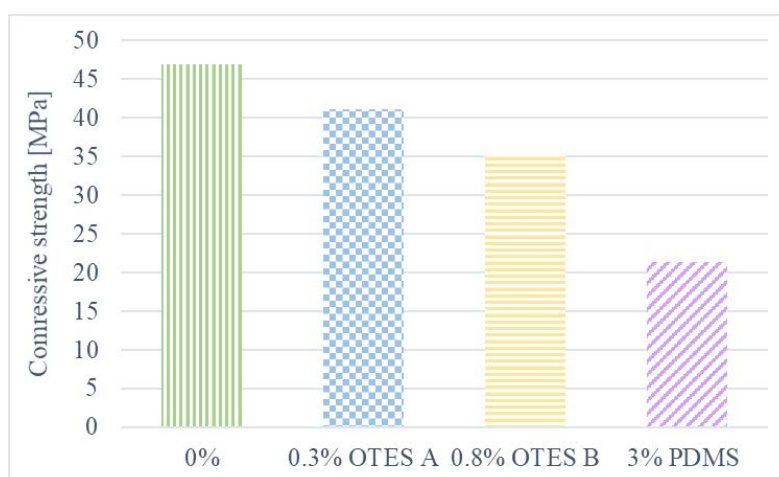
not caused excessive air entrainment of cement mortar in contrast to poly(dimethylsiloxane), which causes a 2.5-fold increase in aeration of fresh cement mortar (Table 2). It can be safely assumed that this will affect the properties of the hardened mortar. We suppose that excessive air entrainment is caused by methyl groups detaching from the poly(dimethylsiloxane) during admixture – cement interactions and after attaching hydrogen atoms, as gaseous products, caused the increase in aeration.

**Table 2: Aeration of fresh mortar**

Type of mortar	Aeration
Reference sample	9.5 %
0.3% OTES A	10.5 %
0.8% OTES B	11.5 %
3% PDMS	25.0 %

#### 4.2 Compressive strength

Fig. 2 shows the result of compressive strength test of cement mortar carried out after 28 days of curing. All three hydrophobic admixtures caused a noticeable decrease in mechanical strength. As we assumed the admixture based on PDMS caused the most significant decreased in compressive strength (over 50% according to reference mortar). The admixtures based on triethoxyoctylsilane: OTES A and OTES B decreased the compressive strength by 13% and 25% respectively. In case of PDMS it is probably the result of excessive air entrainment and the structure of poly(dimethylsiloxane) itself. PDMS is a macromolecular, polymeric, most likely spaces, branched structure, which can also hinder and delay cement hydration and thus affect the properties of the cement mortar. As it shown at Fig. 2 triethoxyoctylsilane also decreased compressive strength, but less than PDMS. In case of OTES based admixtures, we assume that the presence of long alkyl groups, such as octyl groups –  $C_8H_{17}$ , hinder the cement hydration. The method of adding the hydrophobic admixture into the mortar (with batch water or after mixing all components) might be also important. The obtained results indicate that the addition of admixture later to the fresh mortar mix might soften the influence of admixture on mechanical properties of cementitious materials.



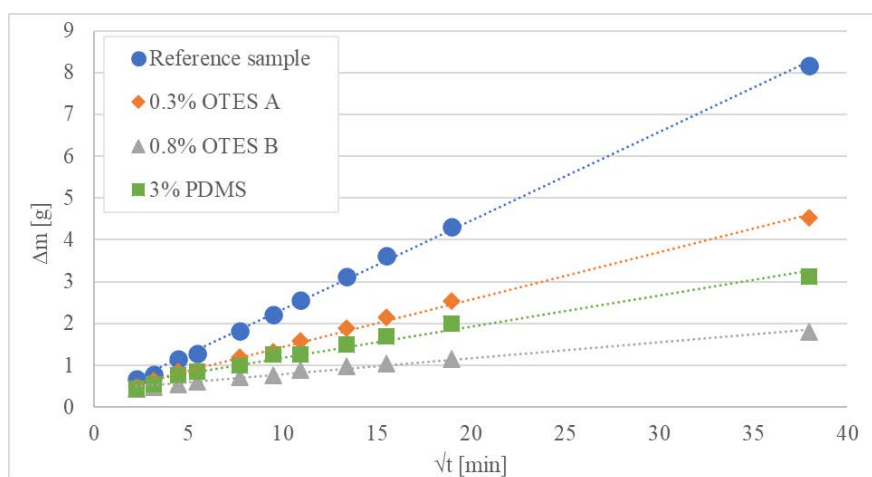
**Figure 2: Compressive strength of cement mortar after 28 days of curing**

### 4.3 Capillary water absorption

The capillary water absorption test is a good tool for confirmation of internal hydrophobization by means of organosilicon admixtures. Table 3 and Fig.3 demonstrate the results of capillary water absorption test of cement mortar. Results shown below represent the average value taken over six samples. The results of capillary water coefficient proved that each used in our research silicon-based admixture decreases capillary absorption of cement mortar. The results indicate that the better hydrophobic effect can be achieved by OTES based admixtures. The addition of 3% of PDMS based admixture provided similar capillary water coefficient as OTES A, but the coefficient was bigger and the amount of used admixture was 10 times more. The best hydrophobic effect provided OTES B admixture. The amount of 0.8% of admixture per cement mass caused the decrease of capillary water coefficient by 81% to reference sample. The obtained results clearly indicate that hydrophobic admixture based on silanes, when the reactions of polycondensation occurs during cement hydration, gives better hydrophobic effects. The type of alkyl sidechains is also important in internal hydrophobization. In case of triethoxyoctylsilane the presence of non-polar groups as octyl groups –  $C_8H_{17}$  results in better hydrophobization than the presence of methyl groups –  $CH_3$  in poly(dimethylsiloxane). The differences between OTES A and OTES B result primarily from the method of entering the admixture to the fresh mix. The addition of OTES B admixture with batch water provides better integration into the structure of the hydrating cement.

**Table 3: Capillary water coefficient**

Type of mortar	Capillary water coefficient
Reference sample	0.143
0.3% OTES A	0.068
0.8% OTES B	0.027
3% PDMS	0.072



**Figure 3: Mass changes of cement mortar during capillary water absorption test.**

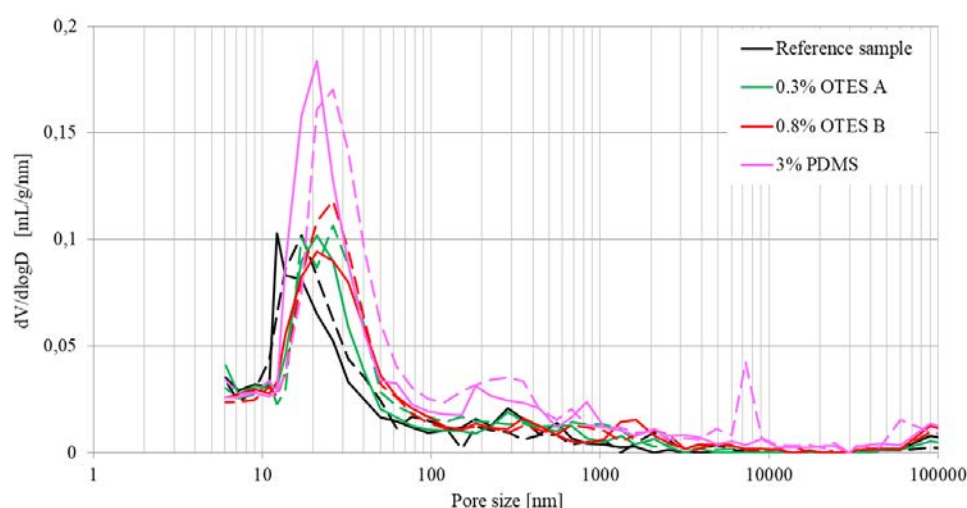
### 4.4 Mercury Intrusion Porosimetry

The mercury intrusion porosimetry is a good technique to show the differences in microstructure of cement mortar. Two samples of each type of cement mortar (with three

different organosilicon admixture and reference one) were used to determine the differences in mortar microstructure. The PDMS admixture affects the most on the microstructure of hardened cement mortar (Table 4, Fig. 4). At the Fig. 4 the significant increase in differential pore volume distribution for PDMS samples is noticeable. The highest increase in average pore volume, porosity and total pore area is also prominent for PDMS samples (Table 4). The increase in average pore diameter and porosity and neglectable decrease in total pore area is also visible for OTES based admixtures, but without increase in differential pore volume distribution (Fig. 4). We suspect that such significant changes in the microstructure in cement mortar with poly(dimethylsiloxane) is caused by the macromolecular, polymeric structure of the PDMS which leads to increase in pore diameter and porosity and thus leads to changes in mechanical properties of hardened mortar.

**Table 4: Microstructure of cement mortar**

Type of mortar	Average pore diameter [nm]	Porosity [%]	Total pore area [m <sup>2</sup> /g]
Reference sample	22.1	14.8	12.6
0.3% OTES A	24.4	15.6	12.3
0.8% OTES B	28.8	17.8	12.1
3% PDMS	30.5	23.6	16.3



**Figure 4: Pore size distribution in cement mortar**

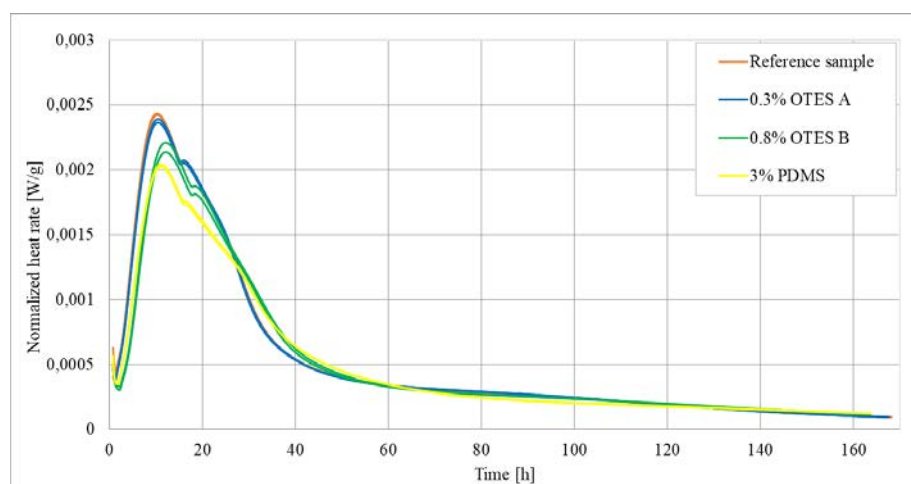
#### 4.5 Heat of hydration

By isothermal calorimetry we were able to examine the impact of silicon-based admixtures on Portland cement hydration. As you can see in Table 5 and at Fig. 5 OTES B and PDMS admixtures decreased the heat of cement hydration. Only OTES A admixture did not affect significantly on the amount of released heat during Portland cement hydration. The lowest value of released heat is observed for PDMS admixture which is the most probably associated with the structure of poly(dimethylsiloxane), polymer one. It might hinder the interaction of water with cement phases and thus delay or even stop the cement hydration and thus decrease in mechanical properties of hardened cement mortar. Compared two admixtures based on the same

main compound: triethoxyoctylsilane, it can be concluded that long, non-polar alkyl group such the octyl group, may slow down the hydration if the hydrophobic admixture will be added with batch water.

**Table 5: Heat of hydration after 41h**

Type of mortar	Average heat of hydration after 41 h [J/g]
Reference sample	206.7
0.3% OTES A	203.9
0.8% OTES B	192.1
3% PDMS	185.1



**Figure 5: Normalized heat rate during cement hydration.**

## 5. CONCLUSIONS

- The organosilicon admixtures provide effective internal hydrophobization of porous cementitious based materials such as cement mortar.
- The effectiveness of internal hydrophobization is influenced by the type of compound (silane or macromolecular polymer), the type of non-polar, alkyl substituent (octyl or methyl group) and the dosing method (with batch water or after mixing all components).
- Better hydrophobic effects, with less impact on the other properties, provide OTES admixtures. It suggests that if the reaction of polycondensation occurs during cement hydration it provides better internal hydrophobization.
- Due to the fact that the commercially available admixtures were tested it should be undertaken in recognition that the rest of admixture components could also have impact on the material properties.
- The internal hydrophobization by means of silicon-based compounds is a very good alternative to surface hydrophobization. It guarantees decrease in capillary water absorption in porous cement-based materials which lead to improving their durability, but it still has a few drawbacks to keep in mind.

## REFERENCES

- [1] Barnat-Hunek, D. 'Surface Free Energy as a Factor Affecting Hydrophobisation Effectiveness in Protection of Building Construction' (in Polish), Publishing House Lublin University of Technology, Lublin, Poland, 2016, 39-59.
- [2] Ignierowicz, A. and Oleksik, M. 'Hydrophobic admixtures in the production of vibro-pressed products' (in Polish), *BTA*, 4(2012), 74-76.
- [3] Wendler, E., and von Plehwe-Leisen, E. 'Water Repellent Treatment of Porous Materials. A New Edition of the WTA Leaflet'. 5th International Conference on Water Repellent Treatment of Building Materials, Hydrophobe V, Freiburg: Aedificatio Publishers, 2008, 155-168.
- [4] Roos, M., König, F., Stadtmüller, S. and Weyershausen B. 'Evolution of Silicone Based Water Repellents for Modern Building Protection'. 5th International Conference on Water Repellent Treatment of Building Materials, Hydrophobe V, Freiburg: Aedificatio Publishers, 2008, 3-16.
- [5] Charola, A.E. 'Water Repellents and Other "Protective" Treatments: A Critical Review'. 3th International Conference on Water Repellent Treatment of Building Materials, Hydrophobe III, Aedificatio Publishers, 2001, 3-20.
- [6] European Committee for Standardization. EN 196-1:2005 Methods of testing cement – Part 1: Determination of strength. CEN: Brussels, Belgium, 2005.
- [7] European Committee for Standardization. EN 1015-7:1998 Methods of test for mortar for masonry – Part 7 : Determination of air content of fresh mortar. CEN: Brussels, Belgium, 1998.
- [8] European Committee for Standardization. EN 1015-11:1999 Methods of test for mortar for masonry – Part 11: Determination of flexural and compressive strength of hardened mortar. CEN: Brussels, Belgium, 1999.
- [9] European Committee for Standardization. EN 1015-18:2002 Methods of test for mortar for masonry – Part 18: Determination of water absorption coefficient due to capillary action of hardened mortar. CEN: Brussels, Belgium, 2002.