The effect of silanes as integral hydrophobic admixture on the physical properties of cement based materials

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Abstract. The paper explores the possibility of using organosilicon compounds (e.g., poly(dimethylsiloxane) and triethoxyoctylsilane) in commercial admixtures as internal hydrophobization agents for porous cement-based materials. The study involved the cement mortar with five different hydrophobic admixtures. Four of them is based on triethoxyoctylsilane, but with various concentration of the main ingredient, and one of them on poly(dimethylsiloxane). Mechanical properties, capillary water absorption, as well as microstructure were investigated. The organosilicon admixtures efficiently decrease the capillary water absorption even by 81% decreasing mechanical strength of cement mortar at the same time even by 55%. Only one admixture, based on poly(dimethylsiloxane) caused significant changes in microstructure of cement mortar.

1. Introduction
The building constructions are extremely exposed to many harmful factors. Water and moisture and thus freezing water, salt crystallization and moulds growth as considered as the most dangerous. The development of the engineering, construction industry and many related disciplines such as chemical admixtures' industry provide improvement in durability of porous, cementitious building materials. One of the protection methods against water might by hydrophobization. The term "hydrophobization" is a word of Greek origin, and it means water (hydro) and fear (phóbos). The process of hydrophobization provides to materials surfaces or entire internal structures hydrophobic properties. To explain it with images the hydrophobic structure or surface repel the molecules of water away from itself thus preventing the surface from wetting and the penetration of water into the material. There are generally two types of the hydrophobization. The surface hydrophobization is meaning as the application of a hydrophobic layer to the surface or the penetration of the hydrophobic agent into the near-surface layers of the impregnated material. The second one, a volumetric or internal hydrophobization, is understood as giving the hydrophobic properties to the materials in their entire structure by using hydrophobic agents during the production process. Both approaches have advantages and disadvantages. However, the internal treatment seems to be simpler and more effective. The hydrophobization carried out in mass (volume) of the material do not require such precise and careful surface preparation, scrupulous selection of the hydrophobic agent (due to the type and the condition of the substrate as well as penetration properties of the water-repellent gent) or large amount of work and technical knowledge. But, the fact that any scratch or deterioration of the hydrophobized surface might undermine or damage the hydrophobic protection seems to be the biggest disadvantage of the surface treatment [1-3].

Exploring the chemical nature of inorganic, porous cement-based building materials, it was noted that silicon compounds, i.e., silicon dioxide, silicates, aluminum silicates enter the composition of many building materials. The group of compounds which are based on silicon and oxygen are organosilicon
compounds. The use of organosilicon compounds for hydrophobization has proved to be particularly effective. Organosilicon compounds are the youngest group of compounds, and at the same time the most popular one used in both surface and internal hydrophobization of building materials [1,4]. In our preliminary research we examined the influence of five commercially available admixtures. One of them is based on poly(dimethylsiloxane) (PDMS) (Figure 1a) and four of them is based on triethoxysilane (OTES) (Figure 1b). Poly(dimethylsiloxane) is macromolecular, polymeric compound with a molecular weight of 400-600 and with two methyl groups attached to the one silicon atom. The main structure of PDMS is a siloxane chain (─Si─O─Si─O─Si─). Triethoxysilane (OTES) is a monomer with a molecular weight of 178. OTES has three ethoxy (─O─C₂H₅) groups and one octyl group (─C₈H₁₇) attached to one silicon atom. In the presence of water, the ethoxy groups hydrolysis reactions take place and the silanes transform to the silanols. Subsequently, polycondensation reactions (combining silanols with the release of alcohol molecules (─EtOH)) occur and the siloxane chains are formed. Long, non-polar, organic octyl group (─C₈H₁₇) provides hydrophobic effects in case of OTES [1,2,4].

![Figure 1. Schematic structure of a) poly(dimethylsiloxane) PDMS b) triethoxysilane OTES.](image)

The purpose of the research presented in this paper was to investigate the impact of two different organosilicon compounds (OTES and PDMS) used in commercial admixtures on the properties of cement mortar. One of our aims is to confirm the effectiveness of water-repellent admixtures based on different organosilicon compounds, recognition and elimination of the weaknesses of the internal hydrophobization approach to improve the internal treatment.

2. Materials

Five types of internal hydrophobized cement mortars were prepared. As a reference samples, a cement mortar without any admixture was also composed. Five different commercially available organosilicon admixture were used. Four of them (OTES_4.4, OTES_1, OTES_0.8 and OTES_0.3) are based on triethoxysilane (OTES) and the fifth one (PDMS_3) on poly(dimethylsiloxane) (PDMS). The dosage of each admixture is the number after the abbreviation of the name of organosilicon compound. The amounts of used admixture are also given in Table 1. The amounts of used admixtures were in line with the manufacturers’ recommendations and they were dosed per cement mass. All used silicon-based admixtures are recommended for internal hydrophobization of cement-based materials. All admixtures, except OTES_0.3, were added to the batch water before cement. The OTES_0.3 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 [5]. After casting, the specimens were covered by adhesive plastic foil at 20°C for 1 day, then demolded and cured for 28 days in water bath until the moment of test. 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_4.4 | OTES_1 | OTES_0.8 | OTES_0.3 | PDMS |
|-----------------------|----------|--------|----------|----------|------|
| W/C                   | 4.4%     | 1%     | 0.8%     | 0.3%     | 3%   |
| Cement [g]            |          |        |          |          | 450  |
| Water [g]             |          |        |          |          | 225  |
| Sand [g]              |          |        |          |          | 1350 |
| Admixture [g]         | 19.8     | 4.5    | 3.6      | 1.35     | 13.5 |

3. Methods
The preliminary studies such as compressive strength test, capillary water absorption test and mercury intrusion porosimetry (MIP) was carried out. After 28 days of curing five prismatic specimens (40x40x80 mm) of each type of cement mortar were used for mechanical test according to EN 1015-11 [6] standard. The capillary water absorption test was carried out on six prismatic mortar samples (40x40x80 mm) of each type of cement mortar. After being demoulded, mortar beams were stored at water for 27 days (28 days of curing in total) and after that dried in 60°C until constant mass were obtained. Before the capillary water absorption test the side walls of all the mortar samples were covered with sealant. Subsequently samples were vertically immersed in and weight 5 min, 10 min, 20 min, 30 min, 60 min, 90 min, 2h, 3h, 4h, 6h and 24h. The capillary water absorption test was carried out according to the EN 1015-18 [7] standard. The impact of organosilicon admixture on the microstructure of cement mortar samples was investigated by mercury intrusion porosimetry (MIP). MIP measurements were carried out with Micromeritics AutoPore IV9500 instrument. Cylindrical samples (6x6 mm) were cut out of the central part of mortar beam. Subsequently the cylindrical specimens were kept in isopropanol and next, they were dried at 30°C in a vacuum dryer until the constant mass was obtained.

4. Results and discussion
4.1. Mechanical test
Figure 2 shows the result of compressive strength test of cement mortar carried out after 28 days of curing. As Figure 2 show, all organosilicon hydrophobic admixtures decrease in mechanical strength. The admixture based on poly(dimethylsiloxane) caused the most significant decreased in compressive strength (almost 55% according to reference mortar). The hydrophobic admixtures based on triethoxyoctylsilane: OTES_4.4, OTES_1, OTES_0.8 and OTES_0.3 decreased the compressive strength by 9%, 18%, 20% and 12% respectively. It is highly probable that the drop in mechanical strength is caused by the chemical structures of silane and polysiloxane as the main component of used admixtures. In case of PDMS we are dealing with a macromolecular, polymeric, most likely spaces, branched structure It may be stated with a high degree of probability that structure of poly(dimethylsiloxane) hinder and delay cement hydration and thus affect the properties of the cement mortar. A similar situation occurs in case of triethoxyoctylsilane based admixtures. Although the chemical structure of silane is a little different from polysiloxane the silane hydrolysis reaction and polycondensation of the siloxane chain runs parallel to the hydration process. So, it cannot be ruled out that the ongoing silane reactions do not hinder cement hydration, thus affecting the final properties of the mortar. As it shown at Figure 2 triethoxyoctylsilane also decreased compressive strength, but less than PDMS. In case of OTES based admixtures, we also assume that, except ongoing hydrolysis and polycondensation reactions, the presence of long alkyl groups, such as octyl groups – C₈H₁₇, might also hinder the cement hydration. In addition, the impact of the other components of admixtures should not
be ignored. The method of adding the hydrophobic admixture into the mortar (with batch water or after mixing all components) might be also important.

![Figure 2](image)

Figure 2. Compressive strength of cement mortar after 28 days of curing.

The number after the abbreviation of the name of organosilicon compound is denoted as a concentration of used admixture by weight of cement. The first four of them (OTES_4.4, OTES_1, OTES_0.8 and OTES_0.3) are based on triethoxyoctylsilane (OTES) and the fifth one (PDMS_3) on poly(dimethylsiloxane).

### 4.2. Capillary water absorption test

The results of capillary water absorption test shown an effect of internal hydrophobization by means of organosilicon admixtures and they are shown in Table 2 and at Figure 3 The obtained results of capillary water coefficient proved that each used in our research silicon-based admixture decreases water absorption of cement mortar caused by capillary suction. It cannot be unequivocally said which organosilicon compound is better. According to the latest scientific knowledge the silane-based admixtures should decrease capillary water absorption more strongly than poly(dimethylsiloxane). It is related with occurring reactions of polycondensation of silane and the type of alkyl sidechain. In case of triethoxyoctylsilane the presence of non-polar groups as octyl groups – C₈H₁₇ should provide better hydrophobic effects than the presence of methyl groups – CH₃ in poly(dimethylsiloxane). But the results of PDMS_3, OTES_4.4 and OTES_0.3 are quite similar (Table 2). We assume that in case of OTES 0.3 the time of admixture addition and small dosage of admixture is responsible. The addition of hydrophobic admixture with batch water provides better integration into the structure of the hydrating cement. In case of OTES_4.4 the smallest hydrophobic effect was achieved which was caused by the smallest concentration of active organosilicon ingredient in the admixture. The best hydrophobic effect provided OTES_1 and OTES_0.8 admixtures. The amount of 1% of hydrophobic admixture per cement mass caused the decrease of capillary water coefficient by 73% and the addition of 0.8% by 81% to reference sample.

### Table 2. Capillary water coefficient.

| Type of mortar | Capillary water coefficient $k_g \text{ m}^{-2} \cdot \text{min}^{0.5}$ |
|----------------|---------------------------------|
| Reference sample | 0.143 |
| OTES_4.4 | 0.072 |
| OTES_1 | 0.038 |
4.3. Mercury intrusion porosimetry

The impact of organosilicon admixtures on the microstructure of cement mortar was investigated by mercury intrusion porosimetry. Two cylindrical samples of each type of cement mortar (with five 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 (Figure 4). Results shown at the Fig. that the OTES based admixtures, contrary to PDMS one, do not the significant increase in differential pore volume distribution. For PDMS samples the parameter is almost twice. MIP results for poly(dimethylsiloxane) are consistent with mechanical results. 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.

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

| Admixture | Mass change |
|-----------|-------------|
| OTES_0.8  | 0.027       |
| OTES_0.3  | 0.068       |
| PDMS_3    | 0.072       |
5. Conclusions

- The organosilicon compounds such as silanes and siloxanes used as main component of admixtures might provide an effective internal hydrophobization of porous cement-based materials such as cement mortar.
- The type of used silicon-based agent (silane monomer or polymeric siloxane), the type of non-polar, organic sidechains (octyl or methyl group), the adding method and the amount of used admixture have the crucial influence on the effectiveness of internal hydrophobization of cementitious materials. It might be assumed that silanes with octyl substituents provide better internal hydrophobization by means of decrease in water absorption of cement mortar.
- The studies carried out showed that organosilicon admixtures more or less affect the mechanical properties of the cement mortar. Poly(dimethylsiloxane) caused 55% decrease in compressive strength of cement mortar when the maximum drop in compressive strength for OTES admixtures was 20%.
- In case of OTES_0.8 and OTES_1 the capillary water absorption was definitely lower than in case of PDMS_3, which indicate for better internal hydrophobization. It suggests that if the reactions of silane such as hydrolysis and polycondensation occurs during cement hydration the siloxane chains might embed into hydrating cement phases and thus provides better internal hydrophobization.
- The internal hydrophobization of porous, cementitious buildings materials by means of organosilicon compounds is a beneficial and convenient alternative to surface hydrophobization. Internal hydrophobization provides a decrease in capillary water absorption.
which lead to improving their durability and protection against harmful influence of the environments. However, it needs to be remembered that for now the method still has a few limitations which need to be eliminated.

References
[1] Barnat-Hunek D 2016 *Surface Free Energy as a Factor Affecting Hydrophobisation Effectiveness in Protection of Building Construction (in Polish)* Publishing House Lublin University of Technology: Lublin, Poland
[2] Grabowska K and Koniorczyk M 2019 *Cem. Lime Concr* 4 320
[3] Charola A E 2001 *Proc. Int. Conf. on Surface Technology with Water Repellent Agents* (Aedificatio Publishers) p 3
[4] Roos M, König F, Stadtmüller S and Weyershausen B 2008 *Proc. Int. Conf. on Surface Technology with Water Repellent Agents* (Aedificatio Publishers) p 3
[5] European Committee for Standardization 2005 EN 196-1:2005 *Methods of testing cement – Part 1: Determination of strength* CEN: Brussels Belgium
[6] European Committee for Standardization 1999 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
[7] European Committee for Standardization 2002 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