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Effect of Internal Hydrophobization on the Properties of Porous, Cementitious Materials

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Abstract. *Water is one of the main factors affecting the durability of porous materials and it is one of the most common causes of their degradation. Physical phenomena such as freezing or salt crystallization, as well as the development of fungi and moulds, are caused by the presence of moisture. In wet material thermal conductivity coefficient increases and the heat loss begins to rise. Hydrophobization is one of the protecting methods of porous materials against water. Two different type of water-repellent agents were used for the internal hydrophobization. The first of them is an aqueous emulsion of silane: triethoxy(octyl)silane (OTES) and the second one is also an aqueous emulsion but the matrix is poly(dimethylsiloxane) (PDMS). The paper focuses on the use of organosilicon water repellents. The main purpose of this paper is to determinate the possibility of use organosilicon agents as admixtures to internal hydrophobization. We compared results obtained for two different silicon-based admixtures. We investigated influence of both water-repellents on basic characteristics such as: absorbability, capillary water absorption and mechanical properties of cement mortar as well as heat of hydration of cement paste.*

Keywords: *Internal Hydrophobization, Cement Mortar, Silane, Siloxane.*

1 Introduction

In 2018, in Poland, cement sales amounted to 18 million tons (Polish Central Statistical Office, 2019). And it is growing every year. Cement-based building materials are one of the most commonly used one. But, as all we know, they are porous, which means that their resistance to water is insufficient. Water is one of the main factors affecting the durability of porous materials and it is one of the most common causes of their degradation. Physical phenomena such as freezing or salt crystallization, as well as the development of fungi and moulds, are caused by the presence of moisture. In wet material thermal conductivity coefficient increases and the heat loss begins to rise. Not to mention aesthetic features (*e.g.* stains) and deterioration of the microclimate. The appropriate design and composition of building material may already be a part of protection against water. The hydrophobization process might complement to these actions. Hydrophobization can be carried out in two ways from the technological point of view. The material may become hydrophobic by applying water-repellent coatings on the surface or by using suitable admixtures as one of the components. Internal hydrophobization carried out with the hydrophobic admixtures causes, contrary to surface treatment, the hydrophobization of the surface and internal surface (Barnat-Hunek, 2016).

There are very limited number of regular studies or they are insufficient in determining the effectiveness of internal hydrophobization of cement-based building materials with organosilicon compounds. In this paper we investigate the influence of two different silicon-based admixtures on fundamental properties of cement mortar/paste. The addition of hydrophobic admixtures to the batch water was intended to create a hydrophobic material in its whole volume.

2 Hydrophobizing Agents

Considering the chemical nature of porous building materials, it can be seen, that silicon compounds (silicon dioxide, silicates, aluminosilicates etc.) are part of natural and manufactured building materials. Therefore, organosilicon compounds have found practical use in the hydrophobization of building objects. They are mainly based on and silicon-oxygen (Si-O) and silicon-carbon (Si-C) bonds. The basic structure of organosilicon compounds is a polysiloxane chain (O-Si-O-Si-O) and the type of substituents affects the diversity of spatial arrangements that can be created from the basic chains (Barnat-Hunek, 2016).

Science the 1950's silicon-based compounds have been used in industrial applications. Hydrophobic agents based on organosilicon compounds are the youngest, and the most promising, group of hydrophobic agents for internal treatment. The main groups of these compounds are alkylsilanes, arylsilanes, halosilanes, silanols, siloxanes, silylamines and silyl esters. Among all different kind of hydrophobic products developed for the building industry, silicone resins, silanes, oligomeric and polymeric siloxanes have proved to perform best in surface hydrophobization. Until recently stearates and oleates were used as waterproofing admixtures. Effective surface hydrophobization with organosilicon agents caused attempts to use them as admixtures. It turned out that organosilicon compounds used as water-repellent admixtures are the most efficient in protecting from water penetration (Barnat-Hunek, 2016; Grabowska *et al.*, 2019; Roos *et al.*, 2008).

2.1 Triethoxy(octyl)silane

Silanes are monomeric molecules (have one atom of silicon) with low molecular weight of 178. They are a silicon analogue of methane. Silane derivatives of the general formula: R_nSiX_{4-n} have the most important practical significance (R can be a hydrogen atom, an alkyl or aryl group, X can be a halogen atom or an alkoxy group). Longer alkyl chain-length provides desired water resistance of the modified material and steric protection to the silicon-oxygen bond. Initially silanes undergo hydrolysis and polycondensation reactions. Subsequently they cross-link under elimination of alcohol and as a result of which polymers, with polysiloxane chain, are formed. (Ciabach, 2001; Roos *et al.*, 2008). Triethoxy(octyl)silane is an alkyl alkoxy silane with three ethoxy groups and one octyl group in its structure (Fig 1).

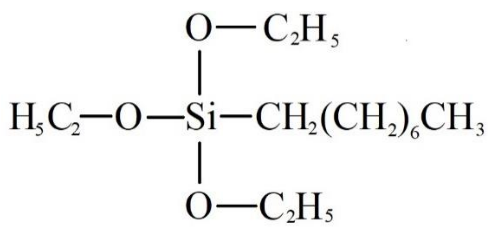

Figure 1. Structure of triethoxy(octyl)silane.

2.2 Poly(dimethylsiloxane)

Siloxanes are oligomeric molecules with a molecular weight about 400-600. The basic structure of siloxanes is a polysiloxane chain (O-Si-O-Si-O). Polysiloxanes are versatile materials. They have an excellent chemical, physical, and electrical properties. Poly(dimethylsiloxane) (PDMS) is an important example and the most common polysiloxane of this class of polymers. The chains of polysiloxanes consist alternately connected silicon and oxygen atoms. Inorganic chain and the presence of strong bonds (Si-O and Si-C) provide significant thermal and oxidative resistance as well as resistance to UV radiation of polysiloxanes. Despite of the polar character of siloxane bonds (Si-O bonds have ionic character in 50%) organosilicon compounds show similarity to paraffins in terms of low critical surface tension. Siloxanes have very low surface energy and exceptional hydrophobicity. PDMS chains are arranged in helixes and present of the methyl groups ($-CH_3$) give hydrophobic character of modified materials. Weak intermolecular interactions, characterizing PDMS, provide a significant gas diffusion coefficient. Organosilicon compounds, compared to other polymers, are characterized by very high oxygen, nitrogen and water vapor permeability (Chruściel *et al.*, 2008, Cypryk *et al.*,2007; Grabowska *et al.*, 2019;).

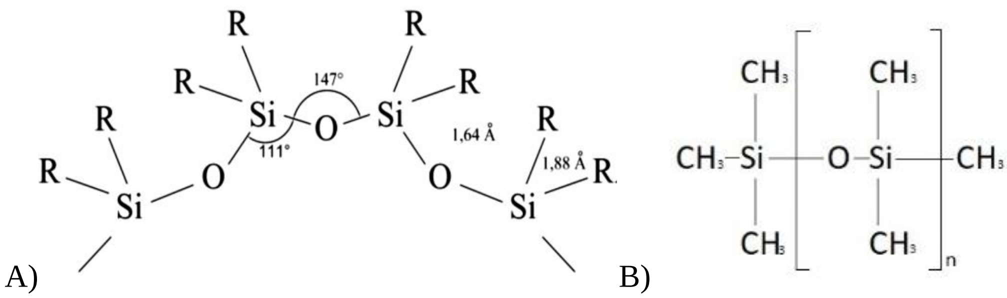

Figure 2. A) Polysiloxane chain (Cypryk *et al.*,2007), B) Structure of PDMS.

3 Materials

The Ordinary Portland Cement 42.5 R was used. Table 1 shows composition of investigated cement mortars. They were prepared according to Polish standard PN-EN 196-1 with a water-cement ratio (w/c) equal to 0.5. Prismatic samples of mortar, with dimensions160x40x40 mm, were prepared for mechanical, absorbability and capillary water absorption tests. Isothermal calorimeter was used to determine the influence of organosilicon admixtures on the heat of hydration of cement paste.

Two different type of water-repellent agents were used for the internal hydrophobization. The first of them is an aqueous emulsion of silane: triethoxy(octyl)silane (OTES). The second admixture is also an aqueous emulsion but the matrix is poly(dimethylsiloxane) (PDMS). The amount of the hydrophobic admixture in cement mortar or paste was 0%, 1%, 2% or 3% (refer to cement mass). They were added to the batched water. Both admixtures are recommended for volume hydrophobization.

Table 1. Composition of cement mortar.

	Water repellent agent		
	OTES/ PDMS		
	1%	***2%***	***3%***
W/C	0.5		
Cement [g]	450		
Sand [g]	1350		
Water [g]	225		
Admixture [g]	4.5	9.0	13.5

4 Results

4.1 Mechanical Test

Table 2 shows the results of mechanical test received after 1, 2, 7 and 28 days of curing for hydrophobized cement mortars. Results shown in Table 2 represent the average value taken over six samples. The compressive strength test was carried out on halved, prismatic samples left after flexural strength test. Results of each test of cement mortar admixed PDMS show substantial decrease in mechanical strength. After 28 days of ageing addition of poly(dimethylsiloxane) (PDMS) based admixture decreases the mechanical properties by almost a factor of two. The addition of 1% silane admixture does not decreases significantly compressive strength after 1, 2, or 7 days of curing. Noticeable loss of the strength is observed for 2% and 3% addition of silane after 1, 2, 7 and 28 days and for 1% of OTES after 28 days.

Table 2. Compressive strengths after 1, 2, 7 and 28 days of curing.

Water repellent agent	**Amount**	**Compressive strength [MPa]**			
		1 day	2 days	7 days	28 days
Reference	0%	14.40	23.04	31.16	45.25
OTES	1%	13.17	22.34	32.71	38.35
	2%	8.27	18.22	28.72	38.19
	3%	7.05	17.18	27.59	36.36
PDMS	1%	5.03	8.76	10.47	25.84
	2%	3.83	8.31	9.02	23.53
	3%	3.65	9.07	11.91	22.16

4.2 Absorbability

Absorbability of hydrophobized cement mortar is shown in Table 3. The test was carried out on three specimens for each composition. After 28 days of curing prismatic samples were dried and, after that, progressively flooded with water. Subsequently mortar samples were weighed every 24 hours until constant weight was received. The addition of silane admixture and 2% of PDMS admixture decrease significantly absorbability. Lower values was observed for silane.

Table 3. Results of absorbabilty test of hydrophobized cement mortar.

Water repellent agent	Amount	Absorbability
Reference	0%	7.6%
OTES	1%	3.9%
	2%	2.3%
	3%	2.2%
PDMS	1%	6.3%
	2%	3.7%
	3%	6.5%

4.3 Capillary Water Absorption Test

One of the most common tests to show hydrophobic effect is capillary water absorption test. Table 4 presents the results taken over three halved, prismatic samples (six in total). Test was carried out according to PN-EN 1015-18. After 28 days of curing mortar samples were dried at $80^{o}C$. Thereafter sealing material was applied on the side surfaces of mortar specimens (40 x 80 mm). Mortar prisms were vertically immersed in water to a depth of 1 cm and weighed after 10 min, 30 min, 60 min, 90 min, 2h, 3h, 4h and 24h. Both used admixtures decrease capillary water absorption coefficient. Lower values were observed for silane.

Table 4. Results of capillary water absorption test of hydrophobized cement mortar.

Water repellent agent	Amount	Capillary water absorption coefficient, $\frac{kg}{m^2 * min^{0,5}}$
Reference	0%	0.206
OTES	1%	0.042
	2%	0.023
	3%	0.020
PDMS	1%	0.115
	2%	0.106
	3%	0.098

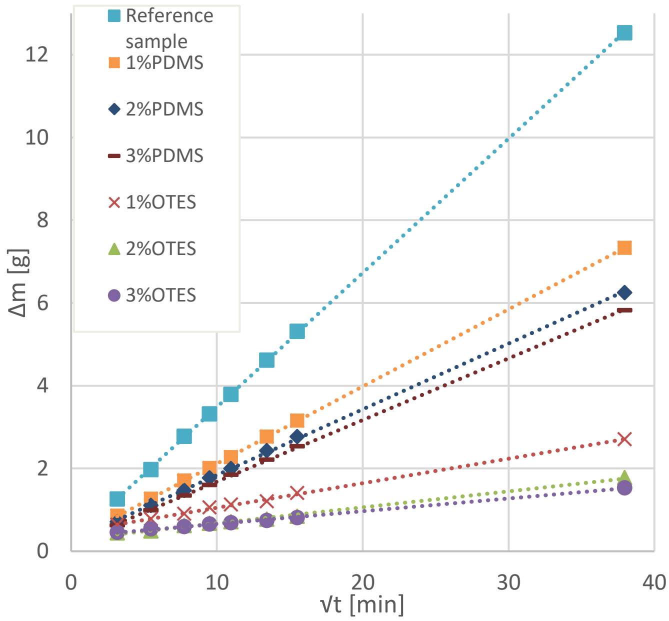

Figure 3. Mass changes of cement mortar samples during capillary water absorption test.

4.4 Heat of Hydration

The heat of hydration of cement paste with organosilicon admixtures was measured. The w/c ratio was 0.5 and the Portland Cement 42.5 R was used. Test was carried out in an isothermal calorimeter TAM Air, at temperature T=20°C. The heat was measured during 7 days for each sample. Two samples were analyzed for each composition of cement paste. 1%, 2% or 3% of organosilicon admixture was added per cement mass. The heat of hydration after 41 hours is shown in Table 5.

Table 5. Influence of organosilicon admixtures on heat of hydration.

Water repellent agent	Amount of admixture	Average hydration heat after 41 h [J/g]
Reference	0%	217.25
OTES	1%	180.00
	2%	157.78
	3%	149.12
PDMS	1%	187.10
	2%	199.70
	3%	182.05

5 Discussion

The presented test results unequivocally demonstrate the interaction between used admixtures and the cement matrix. Both admixtures gave a visible hydrophobic effect. The addition of admixture based on PDMS successfully reduces capillary water absorption. For reference sample capillary water absorption coefficient was 0.21 kg/(m^2*$min^{0.5}$) and 0.098 kg/(m^2*$min^{0.5}$) for cement mortar containing 3% of PDMS admixture. Absorbability of hydrophobized cement mortar decrease to 3.7% from 7.6%. As it was shown in Table 5 poly(dimethylsiloxane) also interacts with Portland cement. The heat of hydration of Portland cement decrease from 217,25 J/g to 182,05 J/g. Even better hydrophobic results in reducing capillary water absorption and absorbability were obtained for the second admixture based on triethoxy(octyl)silane. This water-repellent agent decreases capillary water absorption by almost 90% (from 0.21 kg/(m^2*$min^{0.5}$) to 0.02 kg/(m^2*$min^{0.5}$)) and reduce absorbability by 70% (from 7.6% to 2.2%) at the maximum amount of admixture. Also, in case of silane admixtures heat of hydration was reduced. The lowest value was obtained for 3% of OTES (149.12 J/g). Unfortunately, both admixtures decrease compressive strength of cement mortar. The largest decreases in compressive strength were observed for the content of 3% of silicon-based admixtures. PDMS admixture reduce mechanical strength of cement mortar by an average of 50% and OTES one only by 15%.

The present of non-polar such as methyl groups ($-CH_3$) and octyl groups ($-C_8H_{17}$) attached to the silicon atom provide desirable effect of internal hydrophobization of cement mortar. For the same reason the compressive strength of cement mortar might have been decreased. Changes in the heat release, during hydration process**,** indicate that the admixtures can bind to the cement phases (alite, belite or tricalcium aluminate) making water-cement reaction more difficult. This may cause incomplete hydration of the cement and thus a subsequent decrease in strength.

6 Conclusions

From the obtained results obtained the following conclusions can be drawn:

- Internal hydrophobization by using organosilicon admixtures is possible, but it has its own limitations. The hydrophobic effect depends on type of used organosilicon compound.
- Both admixtures were recommended for internal hydrophobization of cementitious materials by the producers. But treatment with triethoxy(octyl)silane gives better hydrophobic effect than poly(dimethylsiloxane) by reducing the capillary water coefficient by 90%.
- Both admixtures decrease in compressive strength, but OTES based admixture reduce it by 15% and PDMS one by up to 50%.

As a conclusion, it can be said that triethoxy(octyl)silane is an efficient water-repellent agent for cementitious materials. However, the first results are very promising, but this issue still requires more studies. Especially when it comes to mechanical properties.

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