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Roughness and Surface Free Energy of Silicate Brick Hydrophobised with Emulsions of Low VOC Content

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Abstract. The aim of the research presented in the paper was to evaluate the feasibility of using hydrophobising agents based on organosilicon compounds for impregnation of silicate bricks. The process of surface hydrophobisation both using solvents and water substances was analyzed. The effectiveness of four preparations which differed in terms of hydrolytic polycondensation degree, viscosity and concentration, as these are the factors that are decisive as far as the end result of hydrophobisation is concerned. The following laboratory tests were performed: the analysis of physical properties of the tested materials, water absorption coefficient of the hydrophobised samples, water vapour diffusion, frost resistance, contact angle, surface free energy, roughness and the analysis of silica gel properties in electron microscopy. Based on the results of the above mentioned, the analysis of effectiveness and desirability of hydrophobisation using emulsion with a low VOC content was carried out.

1. Introduction

The use of hydrophobising preparations for impregnating the building materials has been increasing over the last few years. This has been proved by not only an increase in the use of preparations for hydrophobisation in building engineering, particularly in relation to historic buildings, but also a large number of new hydrophobising products appearing on the market. An important advantage of hydrophobisation is the fact that preparations used for this purpose form a thin, colorless coating showing good adhesion properties and resistance to aging [1,2]. The hydrophobic coating should be impermeable to water and aqueous solutions, while ensuring evaporation of water contained in the material [2]. Nowadays organosilicone compounds are used for hydrophobisation. Silicones belong to the most effective and safe agents for hydrophobisation. As silicone hydrophobising agents are used alkyl-potassium silicates, alkox-ysilanes, siloxanes and hydrated siloxanes and siloxanes in the form of hydroxide. Alkyl-potassium silicates as the only ones are available on the market in the form of a strongly alkaline aqueous solution, (pH=14) [2]. Other compounds are soluble only in organic solvents. A controversial component of hydrophobising preparations are organic solvents. The volatiles contained in hydrocarbon preparations, can be toxic, carcinogenic or mutagenic. The most important legislation act regulating the VOC emission in the EU is Council Directive 2004/42/EC [3] on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes. It limits the VOC content in products for decorative painting and renovation. Solvent impregnating agents play an important role in a range of hydrophobising substances, and due to the high efficiency, their use is mostly preferred in comparison to water-based preparations. Nowadays, manufacturers of building chemicals need to face necessity to protect natural environment which is related to amendments to regulations requiring the limitation of emissions of VOC [4]. The most important ways to decrease the VOC emissions from the impregnating agents are: the use of water-based instead of solvent-based preparations, decreasing the solvent content, decreasing the VOC content in water-based preparations. The law regulations made the chemical concerns develop and manufacture water-based impregnating emulsions. Water-based emulsions of silanes are suspensions composed of two insoluble liquids. Silane is mixed with water and an emulsifier. Water-based preparations may sometimes cause swelling of clay minerals contained in building materials which, by narrowing the capillary lumen are limiting penetration of the solution into the structure of the material [1]. The most suitable hydrophobising preparations with good properties of penetration into the materials show in papers [1, 2, 5-7].

Waterproof impregnation is only effective when the critical depth of penetration has been reached, and the surface has taken an appropriate amount of impregnating agents. Penetration depends on such factors as: the duration of contact between the silane and the surface of the material, the chemical reactivity of the silanes used, the type of solvent, the viscosity of the solution and roughness [8]. To the best of our knowledge, silicate bricks have not been tested in terms of roughness and its influence on wettability, surface free energy (SFE) and frost corrosion. Therefore, determining the relation between interphase roughness of silicate bricks as well as wettability and SFE seems necessary, because the roughness of material has a great impact on the type of damage. The physical condition of thin siloxane film in capillaries of porous materials was investigated and analysed on the basis of silicate bricks.

2. Experimental investigations

2.1. Materials and methods

The paper analyzes the effectiveness of four organosilicone agents recommended for ceramic building materials.

The following preparations have been selected to laboratory tests:
P1 – water-based solution of methylosilicone resin in the potassium hydroxide
P2 – water-dilutable siloxane
P3 – organic solvent based methylosilicone resin
P4 – organic solvent based alkilo-alkoksy-siloxane oligomer.

Preparations of well-known manufacturers which differed in the type of solvent and physical characteristics were adopted to tests. The concentration of the product and the amount of layers applied were not subjected to the analysis due to the fact that the samples had been hydrophobised according to the manufacturers' instructions by using a brush. In order to perform a thorough analysis of the impact of concentration of the active substance on the effectiveness of brick hydrophobisation, some additional tests would have to be performed. The P1 preparation was diluted according to the instructions in proportion of 1:6 respectively, other hydrophobising agents are not subject to dilution. Samples marked as P0 are reference samples without a hydrophobic coating.

The samples were dried to constant weight, weighed, and hydrophobised (by applying the preparation twice using a brush) with the preparations. Before other investigations were carried out, the samples were seasoned for 7 days under laboratory conditions in order to enable the hydrolytic polycondensation to occur, yielding polysiloxane gel in the subsurface zone of mortars. Density, as well as volumetric and apparent densities, and open porosity of mortars was carried out in line with PN-EN 1936:2010 standard [9]. The research involved 6 samples with the dimensions of 40×40×160 mm. Absorptivity of bricks was indicated in accordance with BS 1881-122:2011 standard [10]. The samples were studied in 30 min., 6 h, 24 h, 48 h, 7 and 14-day intervals in order to determine the impact of moisture on the hydrophobised bricks. The resistance to freezing-thawing cycles was determined on the basis of PN-EN 12012:2007 standard [11]. 50 cycles were conducted instead of the required 25 to prove the increased frost resistance of the examined bricks. Determination of surface roughness and 3D topography was conducted in a T8000 RC120-400 device by T8000 RC120-140. The contact angle characterizing the liquid drop was measured on a research stand, comprising a goniometer. Neumann model, which constitutes one of the most common methods of calculating SFE, was used in order to determine this parameter [1, 2, 12]. Based on the analysis results, the effectiveness of brick hydrophobisation was performed.

2.2. Basic physical characteristics of the silicate brick

According to the PN-EN 1936:2010 determination of bulk density, density, open and total porosity was performed.

The results were as follows: bulk density ρ_b = 1.85 g/cm³, density ρ = 2.61 g/cm³, open porosity P_o = 18.87 %, total porosity P = 29.11 %.

2.3. Water absorption coefficient

Measurement of water absorbability of bricks by weight for the four periods: after 0.5 h, 6 h, 24 h, 48 h. In order to check the effectiveness of hydrophobisation in conditions of dampness which lasts for a long period of time, two additional times of water absorbability test were introduced: after 7 and 14 days. Long-lasting dampness may occur in horizontal parts of the walls (cornices, stains due to faulty flashing) and in the period of continuous rain.

A measure of the effectiveness of surface impregnation is wettability of the protected base, expressed by the following formula:

$$W_n = 100 - \frac{n_h}{n_b} \cdot 100 \tag{1}$$

in which:

$\boldsymbol{W_n}$ –hydrophobisation effectiveness, (%)

$\boldsymbol{n_h}$ – wettability of the hydrophobised sample by weight, (%)

$\boldsymbol{n_b}$ – wettability of the non-hydrophobised sample by weight, (%).

Test results are shown in table 1. After 48 hours from actually having applied the coating, a decrease in brick resistance to water action has been observed. The P4 sample which was subjected to hydrophobisation by means of oligomers is an exception thereto. The difference in the effectiveness of impregnating the brick after the period of 14 days from protecting the material is clearly visible. The effectiveness of hydrophobisation after the period of 14 days ranging from 56.27% to 93.19%, depending on the impregnating agent used.

Preparations based on organic solvents are found to be more effective. The longer the contact of the preparation with water, the weaker the effectiveness of impregnation becomes.

2.4. Capability to diffusion of water vapour

In order to verify whether hydrophobisation does not disturb the diffusion of vapour and gas, vapour permeability test of the brick were carried out. After having completed the wettability test, the samples were dried, and then left in laboratory conditions at 20 ± 5°C and relative humidity of 60 ± 5% to get dry. At this time, the rate of drying the samples was determined by measuring the weight loss of the samples, which indicated the amount of evaporated water. Percent decrease in moisture content was determined as the humidity indicator of the silicate brick prior to and after hydrophobisation after the period of 14 days of drying the samples (Table 2).

Table 1. Hydrophobisation effectiveness for silicate brick, (%)

Period of test	P1	P2	P3	P4
30min	97.47	95.49	99.85	99.87
6h	97.03	89.12	97.69	98.62
24h	92.56	82.44	98.78	97.05
48h	83.23	77.49	98.06	96.87
7days	78.57	64.35	89.73	94.55
14 days	64.79	56.27	82.14	93.19

Table 2. Diffusion of water vapour, frost resistance (%)

Parameters	P0	P1	P2	P3	P4
Moisture decrease (%)	97.2	88.5	85.5	57.4	69.8
Frost resistance - mass loss after test (%)	0.6	0.4	1.5	0.08	0.05

Water has evaporated the fastest from the non-impregnated material. After 14 days of drying, P3 samples achieved the lowest average humidity decrease equal to 57.4%.

The P1 water-based preparation achieved the biggest decrease in humidity – 88.5% at water absorbability by weight n_w equal to 1.6%. Hydrophobising preparations based on organic solvents (P3, P4) cause the biggest sealing of the surface of the tested material, which makes it slightly difficult to evaporate moisture from silicate materials.

2.5. Frost-resistance

After 50 cycles thereof, the samples were dried again until they have reached a constant weight and then the percentage weight loss of the sample was determined (table 2). The smallest weight loss was observed for silicate brick in the case of P4 preparation, which amounted to 0.05%, while the P2 samples were characterized by the biggest weight loss of 1.5% among the hydrophobising preparations. This is 2.5 times more than the reference brick, which indicates the negative effect of this preparation on the brick. The weight loss of reference samples was 0.6%. This means that hydrophobisation by means of oligomers (P4) had a considerable impact on the frost-resistant properties of the silicate brick. However, impregnation by the use of macromolecular siliconates does not protect the brick against damage caused by frost to a sufficient degree.

2.6. Roughness

Microroughness, as well as the representative profilograms showing the surface of P0 before and P1 after surface modification with polysiloxanes – were presented in Figure 1. a,b.

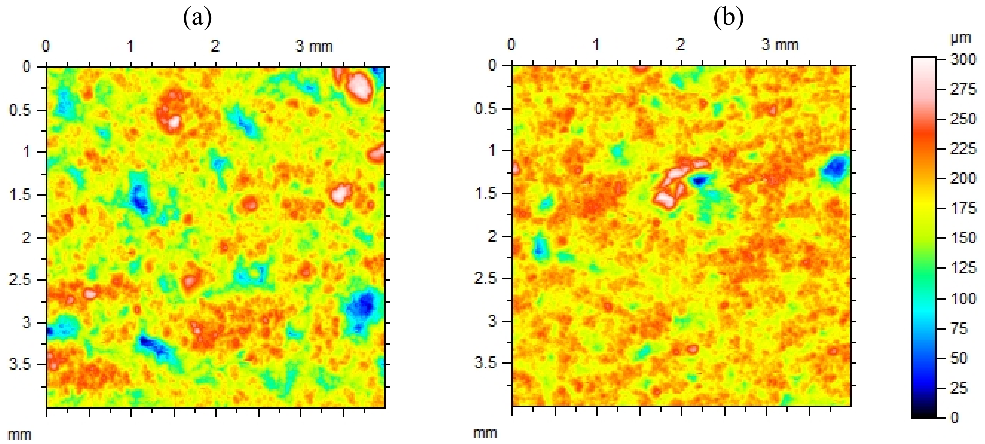


Figure 1. Microroughness and representative profilograms showing the surface of silicate bricks: (a) unmodified P0; (b) P1 with polysiloxane coating.

The roughness parameters have been defined on the basis of the EN15178N standard [13]:
S_p – Maximum Peak Height as the maximum height of peak within evaluation length;
S_v – Maximum Valley Depth as the maximum depth observed within the evaluation length;
S_t – Maximum Peak-to-Valley Height understood as total height $S_t = S_v + S_p$.

The characteristics of roughness obtained for the tested bricks are presented in Table 3.

Table 3. Roughness characteristics of silicate bricks

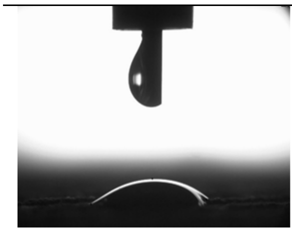
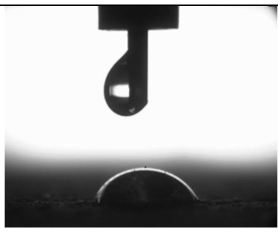
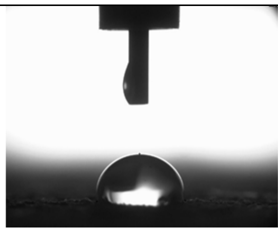
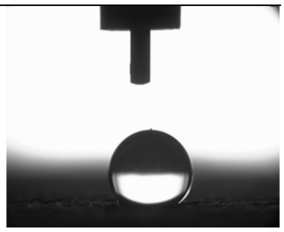
Parameters (µm)	P0	P1	P2	P3	P4
S_a	30.1	25.0	19.0	24.4	25.7
S_p	130	114	98	102	115
S_v	202	188	101	130	158
S_t	332	302	199	232	273

The presented study on surface roughness enables to indicate differentiation in the geometrical structure of the surface of both hydrophobised as well as reference bricks. The analysed roughness parameters indicate that the hydrophobisation caused an decrease in the average roughness S_a, especially a P2 preparation with large particles. Polysiloxane coating utilized in P2 bricks decreased the average roughness S_a by up to 37% for the standard bricks. Alkilo-alkoksy-siloxane oligomer is characterized by a fine molecular structure and reduced the average roughness only by 14.6%. The smallest S_p can also be seen in the case of P2 bricks. The standard bricks are characterized by the greatest roughness, which is 40% higher than S_t of bricks P2 and 9% than of bricks P1. A border layer weakening adhesion is formed when bubbles of air become trapped under the thin film of hydrophobising agent [1, 14], what happened in the P2 coating. Water-dilutable siloxane filled the pores and surface irregularities without creating a thin hydrophobic film, but a thick coating, as demonstrated by SEM images analysis. The representative surface profilograms (figure 1) of silicate bricks present visible differences in microroughness of bricks before and after the application of polysiloxane film. Large polysiloxane gel molecules partly fill the pores of rough surface of bricks, which was clearly presented in SEM images (figure 3).

2.7. Contact angle, surface free energy

Table 4 presents the CA of water measured on P0, P1, P2 and P4 bricks and SFE calculated on its basis.

Table 4. Contact angle of a water drop in silicate bricks

(a) P0	(b) P1	(c) P2	(d) P4
			
CA = 32.1° SFE = 63.5 mJ·m^{-2}	CA = 52.7 ° SFE = 52.2 mJ·m^{-2}	CA = 120.4 ° SFE = 11.4 mJ·m^{-2}	CA = 130.1 ° SFE = 6.8 mJ·m^{-2}

The obtained results indicate that the type of hydrophobising preparations governs the values of contact angle (CA). The CA measurements showed that the contact angles of hydrophobised bricks are significantly higher than in standard mortars (by up to 76% for P4). The lowest contact angle value was obtained in P1 bricks with water-based solution of methylosilicone resin in the potassium hydroxide. Hydrophobisation reduced CA by 39% for P1. In our study, low SFE values were obtained for polysiloxane films, ranging from 6.8 to 52.2 mJ·m^{-2} depending on the hydrophobising preparation. The lowest SFE values and the highest efficiency of hydrophobisation were obtained for the P4 preparation with the smallest molecule. The Cappalletti G. et al. [7] examined different types of hydrophobic films, based on silanes, chlorosilanes, siloxanes, and others. In majority of cases, the obtained SFE values did not exceed 42 mJ·m^{-2}; for octadecyltrichlorosilane were lower than 23.5 mJ·m^{-2}. CA over 120° can be obtained through chemical modification of surface with siloxanes. Our other studies of hydrophobic coatings showed similar low SFE values [1, 2, 5, 6].

2.8. Microstructure of silicate brick

The analysis of hydrophobic coating distribution in the pores of bricks using scanning electron microscopy SEM was performed. The resin texture at the brick fracture has been shown in figures 2 and 3.

Macromolecular methylosilicone resins and alkyl-alkoxy-siloxane oligomers produced a coating evenly distributed in the microstructure of the brick. Alkyl-alkoxy-siloxane coating (Figure 1), compared to the reference silicate brick (figure 1b) does not cause sealing the pores, and thus it should not interfere with the diffusion of gases and vapours. A similar situation was observed by the authors in their other studies on ceramic bricks [14]. Water-dilutable macromolecular P2 siliconates formed a thick coating of silicone that covers the microstructure of bricks and shows cracks in many places (Figure 2a). This did not disturb normal diffusion of water vapour from the material, however it did not protect against water and frost action effectively, as proved by previous studies.

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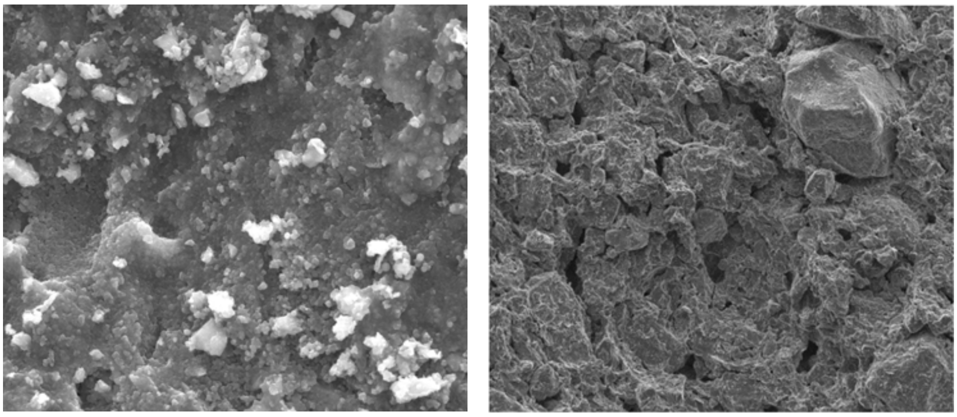
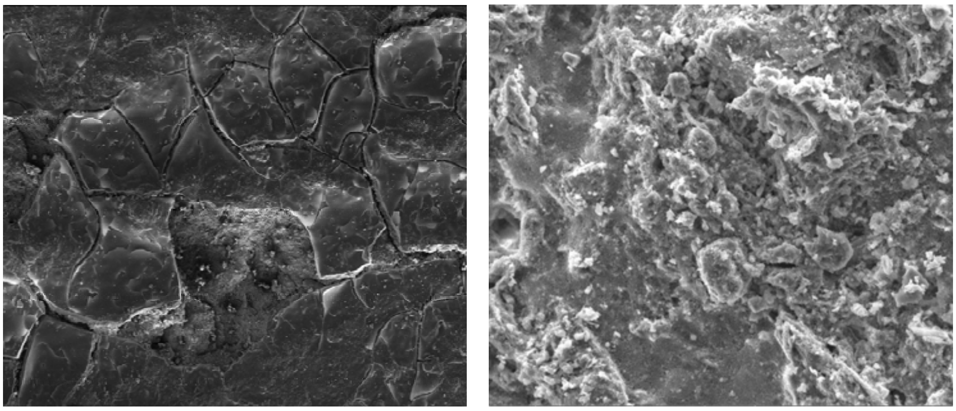


(a) (b)

Figure 2. Microstructure of silicate brick: a) P4 preparation in the structure of silicate bricks magnified by 8000x, b) reference brick (500x)



(a) (b)

Figure 3. Microstructure of polisiloxane gel in the tested silicate brick: a) P2 preparation (300x), b) P1 preparation (2000x)

3. Conclusions

The following conclusions are drawn based on the studies performed on silicate brick hydrophobisation:

The best effect in protecting solid silicate brick against penetration of water was obtained using P4 preparation based on small molecule oligomers. This preparation makes hydrophobic properties of the brick increase by 99%.

The weakest protection against water absorption for bricks are water-based preparations such as P1, P2. The use of these preparations increased hydrophobicity of the brick by 95%. Test results of hydrophobisation effectiveness of the brick after 14 days showed a decrease in absorbability by weight from 56% to 93%. Organic solvent based hydrophobising preparations cause the biggest sealing of the surface, which makes evaporation of moisture difficult. In the context of the afore said observations one should not disregard hydrophobisation treatment by means of hydrocarbon solvents based preparations. The amount of evaporated water as well, what is very important, absorbed water in the same moisture conditions will be relatively low as compared with water-diluted coatings.

The best protection against frost for silicate brick is provided by small molecular oligomers. Application of these preparations resulted in a decrease in weight equal to 0.05% after 50 cycles of freeze-thaw actions.

Organic solvent based hydrophobising preparations, such as methylosilicone resins in white spirit or oligomers cause the most effective hydrophobisation. Despite the fact that, in practice, these preparations often cause sealing surface which hinders diffusion of water vapour from materials, water vapour permeability tests showed a decrease of moisture from 57.4-69.8% after 14 days.

The effectiveness of hydrophobisation is affected by: the nature of silica gel, its distribution in the pores, aggregates, the effect of "spilling" as well as cracking net of the coating. These features are found in electron microscopy SEM. Resins are composed of fine particles, which are evenly distributed in the brick microstructure. A thin polysiloxane film provides effective hydrophobisation.

The resin obtained from macromolecular siliconate (P2) cannot guarantee a satisfactory hydrophobic effect. The preparation does not “rise” in silicate brick, but seals, clogs surface pores. Siliconate does not form a thin hydrophobic film, but a thick cracked layer. A thin hydrophobic coating should slightly cover the capillary walls, and not to fill the entire volume of the pores. Then, hydrophobisation does not significantly alter vapour permeability of the material, and smooth two-way movement of gases and vapours is not disturbed.

When deciding on hydrophobisation treatment not only technical, but also ecological and economical aspects play an important role. The selection of impregnating agents cannot be accidental, one should not rely solely on recommendations of the technical advisors, but it should be considered in the context of the impact on the environment. This is only feasible through the use of water-based or solvent-based impregnating agents which have a reduced content of organic solvents.

The research conducted so far have shown that low molecule alkylo-alkoxy-siloxane oligomers penetrate the most deeply into the structure of porous materials, the weakest penetration are those of water-diluted polymer preparations.

However, in many cases, modern emulsions with a low VOC content are as effective as the products containing organic solvents.

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