WATERPROOF IMPREGNATION OF CERAMIC BRICK WITH EMULSIONS OF LOW VOC CONTENT

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Summary:
The aim of the research presented in the paper was to evaluate the feasibility of using hydrophobizing preparations based on organosilicon compounds for impregnation of ceramic bricks. The process of surface hydrophobization 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 hydrophobization is concerned.
The following laboratory tests were performed: the analysis of physical properties of the tested materials, water drop absorption test, water absorption by weight of the hydrophobized samples, water vapour diffusion, frost resistance, the analysis of silica gel properties in electron microscopy.
Based on the results of the above mentioned, the analysis of effectiveness and desirability of hydrophobization using emulsion with a low VOC content was carried out.

Keywords: hydrophobization, organosilicon compounds, absorbability, frost-resistance

Introduction

The use of hydrophobizing 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 hydrophobization in building engineering, particularly in relation to historic buildings, but also a large number of new hydrophobizing products appearing on the market. An important advantage of hydrophobization is the fact that preparations used for this purpose form a thin, colorless coating showing good adhesion properties and resistance to aging (Łukaszewicz J., 2002). The hydrophobic coating should be impermeable to water and aqueous solutions, while ensuring evaporation of water contained in the material (Płuska I., 2005).

Nowadays organosilicone compounds are used for hydrophobization. Silicones belong to the most effective and safe agents for hydrophobization. As silicone hydrophobizing agents are used alkyl-potassium silicates, alkoxysilanes, 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) (Barnat-Hunek D i in., 2013). Other compounds are soluble only in organic solvents.

A controversial component of hydrophobizing 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 (Directive 2004) 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. For the purpose of renovation and maintenance of the buildings, Member States may grant individual licenses for sale and use of specific quantities of products which do not meet the VOC limits set out in the Directive.

Solvent impregnating agents play an important role in a range of hydrophobizing 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 volatile organic solvents (Osterholtz F. D., Pohl E. R., 1992, Kaesler K. H., 2006, Barnat-Hunek D, 2010). 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.

The most suitable hydrophobizing preparations with good properties of penetration into the stone (Łukaszewicz, J., 2002, Krzywobłocka - Laurów R., 2001, Sasse R., 2001, Płuska I., 2005, Bai Y, i in., 2003) and those which do caused sealing the surface. 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 (Borgia G. C. i in., 2001).

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 (Łukaszewicz J. 2002).

Experimental investigations

Scope of studies

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 alkiloalkoksysiloxane 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 hydrophobized 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 hydrophobization, some additional tests would have to be performed. The P1 preparation was diluted according to the instructions in proportion of 1:6 respectively, other hydrophobizing agents are not subject to dilution.

In order to perform the test, samples of cubic bricks were prepared with dimensions of 4 x 4 x 4 cm. All samples, before being subjected to hydrophobization treatment, had undergone seasoning for 30 days in the laboratory at room temperature of 20 ± 2°C and relative humidity of 60 ± 5%. Six samples were taken for each test.

The analysis of physical characteristics of bricks prior to impregnation was performed. A direct water drop absorption test and water absorbability test were conducted. In addition, water vapor diffusion outflow test was carried out in order to check whether hydrophobization does not cause sealing the pores of the materials tested and whether it does not interfere with the diffusion of gases and liquids. Based on the analysis results, the effectiveness of brick hydrophobization was performed.

Physical characteristics of the materials

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 = 1,75 g/cm³, density ρ_r = 2,61 g/cm³, open porosity ρ_o = 18,31 %, total porosity P = 27,37 %.

Water drop absorption ratio WA

Water drop absorption test was carried out according to ZUAT 15/VI.11-2/2001 ITB (Krzywobłocka – Laurów R., 2001). Adsorption time through the hydrophobized surfaces is calculated based on the formula (2.1),

$$WA=\left(1-\frac{t_x-t_n}{t_x}\right)\cdot 100 \tag{2.1}$$

where:

WA – water drop adsorption ratio, (%)
$\mathbf{t_x}$ – adsorption time into the hydrophobized surface, (s or min.)
$\mathbf{t_n}$ – adsorption time into the into the sample taken for a model one, (s or min.).

During the test, one could have observed spherical droplets which showed no adhesion to the base tested. Extreme angle of a waterdrop on the surface of the brick samples impregnated with the chemical agents based on silicones did not change significantly until the time when water has evaporated. However, the water-based P2 preparation has got a small wetting angle. Droplets applied into such coating are characterized by flat surface. The minimum adsorption time for the hydrophobic surface was 133 minutes for P2 preparation. Other chemicals have reached the time t = 193 minutes, which proves a decreased porosity of the brick.

ZUAT requirements regarding the value of WA have been met by the tested preparations with respect to all the bricks involved in the tests (WA ≤ 5%, WR ≥ 95%). The highest WA ratio (0,53%) for the brick was obtained at the surface hydrophobization using the P2 preparation. The lowest WA ratios were achieved at hydrophobization by the use of other preparations (0,3%). The duration of water drop absorption in the non-hydrophobized brick which was less than one minute.

The preliminary test of the effectiveness of hydrophobization showed that all hydrophobized samples were fully water-resistant.

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 (Krzywobłocka – Laurów R., 2001). In order to check the effectiveness of hydrophobization 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:

$$W_n = 100 - \frac{n_h}{n_b} \cdot 100 \tag{2.2}$$

in which:

W_n – hydrophobization effectiveness, (%)
n_h – wettability of the hydrophobized sample by weight, (%)
n_b – wettability of the non-hydrophobized sample by weight, (%).

Test results are shown in Tab. 1.

Tab. 1. Hydrophobization effectiveness for ceramic brick, [%]

	P1	**P2**	**P3**	**P4**
30 min	97,47	95,49	99,85	99,87
6 h	97,03	89,12	97,69	98,62
24h	92,56	82,44	98,78	97,05
48 h	83,23	77,49	98,06	96,87
7 days	78,57	64,35	89,73	94,55
14 days	64,79	56,27	82,14	93,19

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 hydrophobization 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 hydrophobization after the period of 14 days ranges 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.

Capability to diffusion of water vapor of impregnated samples of ceramic bricks

In order to verify whether hydrophobization does not disturb the diffusion of vapor and gas, vapor 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 brick prior to and after hydrophobization after the period of 14 days of drying the samples (Table 2).

Tab. 2. Percent decrease in moisture after 14 days of drying the samples, [%]

PERCENT DECREASE IN MOISTURE				
PREPARATION	**P1**	**P2**	**P3**	**P4**
MOISTURE DECREASE [%]	90,52	85,45	51,45	69,18

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 51,45%.

The P1 water-based preparation achieved the biggest decrease in humidity – 90,52% at water absorbability by weight n_w equal to 1,36%.

Hydrophobizing 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 ceramic materials.

Frost-resistance by means of a direct method

Frost-resistance of bricks was determined based on the PN-EN 12012:2007 and EN 13581:2004. The brick was subjected to 50 cycles of freeze-thaw. 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.

The smallest weight loss was observed for ceramic brick in the case of P4 preparation, which amounted to 0,10%, while the P2 samples were characterized by the biggest weight loss of 0,60% among the hydrophobizing preparations. The weight loss of reference samples was 0,67%.

This means that hydrophobization by means of oligomers (P4) had a considerable impact on the frost-resistant properties of the brick. However, impregnation by the use of macromolecular siliconates does not protect the brick against damage caused by frost to a sufficient degree.

Silicone resin distribution in the microstructure of ceramic brick

The analysis of hydrophobic coating distribution in the pores of ceramic bricks using scanning electron microscopy SEM was performed. The resin texture at the brick fracture has been shown in Figure 1 and 2.

Macromolecular methylosilicone resins and alkyl alkoxysilane oligomers produced a coating evenly distributed in the microstructure of the brick. Polysiloxane coating (Fig. 1a, b), compared to the reference brick (Figure 2b) does not cause sealing the pores, and thus it should not interfere with the diffusion of gases and vapors.

a) b)

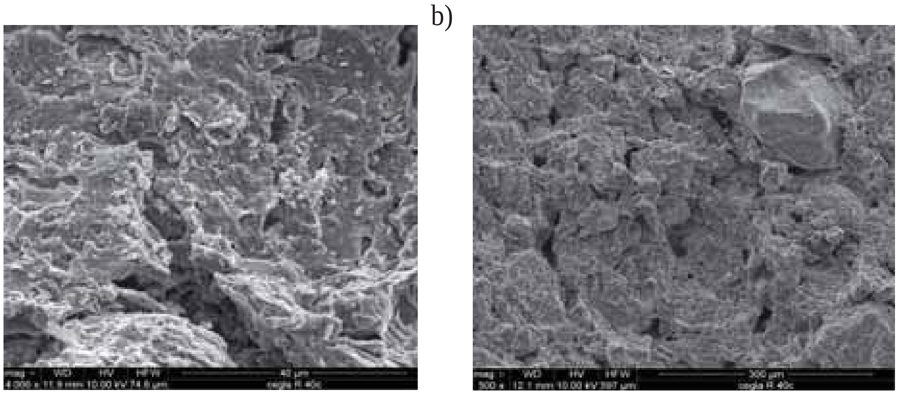

Fig. 1. Water-soluble preparations in the structure of ceramic bricks: a) P4 preparation in the structure of ceramic bricks: a) magnified by 4000x, b) magnified by 500x.

Water-dilutable macromolecular P2 siliconates formed a thick coating of silicone that covers the microstructure of ceramics and shows cracks in many places (Fig. 2a). This did not disturb normal diffusion of water vapor from the ceramic material, however it did not protect against water and frost action effectively, as proved by previous studies.

a) b)

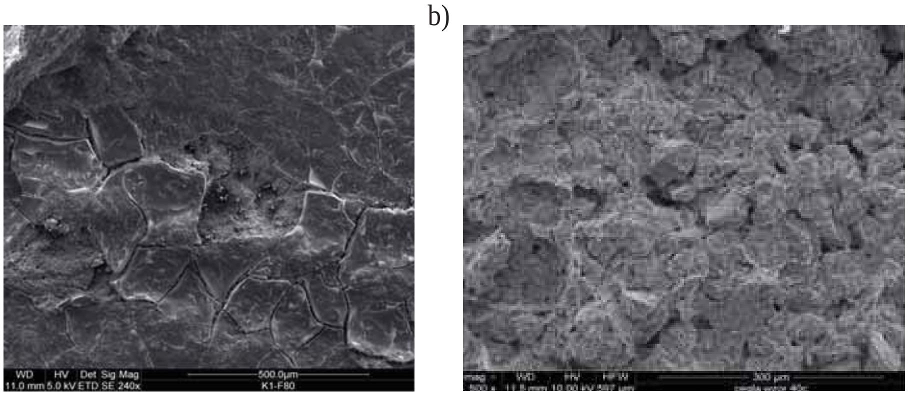

Fig. 2. Microstructure of the tested ceramic brick: a) P2 preparation (240x), b) reference brick (500x).

Conclusions

The following conclusions are drawn based on the studies performed on brick hydrophobization: The best effect in protecting solid ceramic 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 hydrophobization effectiveness of the brick after 14 days showed a decrease in absorbability by weight from 56% to 93%. Organic solvent based hydrophobizing 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 hydrophobization treatment by means of hydrocarbon solvents based preparations. Despite sealing the rock structure, these preparations have the best hydrophobizing properties (Łukaszewicz J., 2002, Sobkowiak D., Zapałowski G., 2000, Sobkowiak D., Zapałowski G., 1997, Meinhardt – Degen J., 2004) and they do not make clay minerals swell. The amount of vaporized 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 ceramic brick is provided by small molecular oligomers. Application of these preparations resulted in a decrease in weight equal to 0.10% after 50 cycles of freeze-thaw actions.

Organic solvent based hydrophobizing preparations, such as methylosilicone resins in white spirit or oligomers cause the most effective hydrophobization. Despite the fact that, in practice, these preparations often cause sealing surface which hinders diffusion of water vapor from materials, water vapor permeability tests showed a decrease of moisture from 51,45-69,18% after 14 days.

A Guarantee of good hydrophobic effect are: low density, viscosity, low concentration of the active substance and large quotient of surface tension to the viscosity of the solution. This is confirmed by the presented studies and the research of other scientific centers (Domasłowski W., 1993, J. Lukaszewicz, 2002).

The effectiveness of hydrophobization 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 silicon film provides effective hydrophobization.

The resin obtained from macromolecular siliconate (P2) cannot guarantee a satisfactory hydrophobic effect. The preparation does not "rise" in 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 (Domasłowski W., 1993, J. Łukaszewicz 2002 Geih H., 2004). Then, hydrophobization does not significantly alter vapor permeability of the material, and smooth two-way movement of gases and vapors is not disturbed.

In practice, prior to taking decision regarding hydrophobization, it is necessary to carry out a preliminary analysis of the effectiveness of material hydrophobization to determine whether the anticipated effect will be proportional to the costs incurred.

For the purpose of a more precise analysis of the impact of organosilicon compounds on building ceramics, one should conduct additional studies on, among others concentration of the preparation, the number of layers of hydrophobizing agents applied, the effect of coating aging on the effect of hydrophobic effect, qualitative and quantitative analysis of ions and anions present in ceramics after hydrophobization (Barnat-Hunek D., Klimek B, 2012).

When deciding on hydrophobization 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 alkyloalkoxysiloxane 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.

References:

1. Łukaszewicz J. W., 2002: Badania i zastosowanie związków krzemoorganicznych w konserwacji zabytków kamiennych. UMK Toruń.
2. Płuska I., 2005: Konserwacja kamienia w architekturze i sztuce. Renowacje i Zabytki 1 (13)/2005
3. Barnat-Hunek D., Góra J., Brzyski P. 2013: Ocena skuteczności hydrofobizacji powierzchniowej betonu. Izolacje 6/2013.
4. DYREKTYWA 2004/42/WE PARLAMENTU EUROPEJSKIEGO I RADY z dnia 21 kwietnia 2004 r. w sprawie ograniczeń emisji lotnych związków organicznych w wyniku stosowania rozpuszczalników organicznych w niektórych farbach i lakierach oraz produktach do odnawiania pojazdów, a także zmieniająca dyrektywę 1999/13/WE.
5. Osterholtz F. D., Pohl E. R., 1992: Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes: a review, Journal of Adhesion Science Technology 6/1992.
6. Kaesler K. H., 2006: Powłoki silanowe i siloksanowe. Skuteczna ochrona przed wodą i zabrudzeniami. Rynek chemii budowlanej 5/2006.
7. Barnat-Hunek D. 2010: Hydrofobizacja opoki wapnistej w obiektach zabytkowych Kazimierza Dolnego. Monografia Wydziału Budownictwa i Architektury. Wydawnictwo Politechniki Lubelskiej, Lublin 2010.
8. Krzywobłocka – Laurów R., 2001: ZUAT -15/VI.11-2/01 wyd. I. Preparaty do powierzchniowej hydrofobizacji wyrobów budowlanych. Część 2. Wyroby ceramiczne. ITB, Warszawa.
9. Sasse R., 2001: Inżynierskie problemy ochrony budowli zabytkowych. Materiały Budowlane 8/2001.

10. Bai Y., Thompson G. E., Martinez – Ramirez S., Brüeggerhoff S., 2003: Mineralogical study of salt crusts formed a historic building stones. The Science of the Total Environment 302.
11. Borgia G. C., Bortolotti V., Camaiti M., Cerri F., Fantazzini P., Piacenti F., 2001: Performance evolution of hydrophobic treatments for stone conservation investigated by MRI. Elsevier Science Inc. Magnetic Resonance Imaging 19/2001.
12. PN-EN 1936:2010 Metody badań kamienia naturalnego. Oznaczanie gęstości i gęstości objętościowej oraz całkowitej i otwartej porowatości.
13. PN-EN 12012:2007 Metody badań elementów murowych – Określanie odporności na zamrażanie-odmrażanie elementów murowych ceramicznych.
14. PN-EN 13581:2004 Wyroby i systemy do ochrony i napraw konstrukcji betonowych – Metody badań – Oznaczanie ubytku masy betonu hydrofobizowanego przez impregnację po działaniu zamrażania – rozmrażania w obecności soli.
15. Sobkowiak D., Zapałowski G., 2000: Badania środka Sarsil W produkcji Instytutu Chemii Przemysłowej, Zakładu Doświadczalnego Silikonów w Nowej Sarzynie do wzmacniania i hydrofobizacji materiałów budowlanych w obiektach zabytkowych. Pracownie Konserwacji Zabytków, Laboratorium Naukowo – Badawcze w Toruniu.
16. Sobkowiak D., Zapałowski G., 1997: Badania środków Ahydrosil K, Ahydrosil KT/K, Sarsil H-14/R, Sarsil H-15, Sarsil ME-25 – produkcji Instytutu Chemii Przemysłowej, Zakładu Doświadczalnego Silikonów – do impregnacji wodoodpornej materiałów budowlanych. Pracownie Konserwacji Zabytków, Laboratorium Naukowo – Badawcze w Toruniu.
17. Meinhardt – Degen J., 2004: Durability of hydrophobic treatment of sandstone facades – investigations of the necessity and effects of re – treatment. 10th International Congress on Deterioration and Conservation of Stone. Stockholm June 27 – July 2 2004.
18. Domasłowki W., 1993: Profilaktyczna konserwacja kamiennych obiektów zabytkowych. UMK skrypty i teksty pomocnicze.
19. Geih H., 2004: Recent developments in protecting facades with silicones. 10th International Congress on Deterioration and Conservation of Stone. Stockholm June 27 – July 2. 2004.
20. Barnat-Hunek D., Klimek B.2012: Hydrofobizacja cegły ręcznie formowanej. Materiały Budowlane 3/2012, str. 19-20.
21. Krzywobłocka – Laurów R., Rościszewski P., Zielecka M.: Badania trwałości zabezpieczeń hydrofobowych środkami krzemoorganicznymi obiektów zabytkowych. Instytut Techniki Budowlanej.