INTERNATIONAL JOURNAL
OF
CONSERVATION SCIENCE

ISSN: 2067-533X Volume 9, Issue 4, October-December 2018: 641-652 www.ijcs.uaic.ro

EVALUATION OF THE ORGANOSILICON MATERIALS FOR ANCIENT GREY BRICKS PRESERVATION

Yue YUAN[1], Jie MI[1], Xiaozhen WANG[1], Zhengrong FU[2], Chenglei MENG[2], Hui ZHANG[1,*]

[1] Department of Cultural Heritage and Museology, Zhejiang University, Hangzhou, China
[2] Zhejiang Provincial Institute of Cultural Relics and Archaeology, Hangzhou, China

Abstract

Grey bricks were produced manually and used as the major traditional building materials in ancient China. However, the characteristics of grey bricks make them vulnerable to water, salt and other environmental factors. Organosilicon materials have been tested as the effective protective agents for silicate based stones. In this study, we evaluated the effectiveness of different organosilicon materials on grey bricks by total and half immersions. The penetration depths, appearance alterations, water adsorptions, hydrophobic properties, porosities and compressive strengths were measured after the treatments. The samples were also experienced the salt solution immersion, freeze-thaw and UV aging tests to evaluate the durability of different preservation treatments. It is found that different characteristics of the organosilicon materials lead to different preservation performances, but it remains difficult to determine an appropriate material for the preservation of ancient architectures built with grey bricks, considering the consolidation performance, water resistance property and durability.

***Keywords**: Grey bricks; Organosilicon; Preservation; Deterioration and degradation cycles*

Introduction

Grey bricks constitute an important part of the construction materials of historic buildings in China, especially during the Ming and Qing dynasties (AD 1368 - 1911) [1]. Grey bricks were produced manually and fired in the reducing atmosphere at low temperature. However, the high porosity and fragile nature of grey bricks make them vulnerable to water, salt and other environmental factors. The preservation and restoration of ancient brick masonry has been an emergency for heritage preservation in many countries since bricks were such widely used materials in historic architectures.

Many efforts have been performed to preserve and reinforce the brick structures, such as testing properties of ancient bricks [2-6], the disease analysis [7-9], the seismic performance evaluation[10], reinforcement of ancient masonry and mortars[11, 12], test of material performance of bricks under freeze-thaw cycles [13, 14] and modern non-destructive testing technology in the application of preservation [15]. Some synthesized materials, both inorganic and organic, have also been studied to test their performances in preservation of ancient bricks, such as TEOS [16], silane/siloxane macroemulsions [17, 18] and fluoropolymer [19]. But for the protection of ancient grey bricks, the comparison of the preservation performance has not

* Corresponding author: huizhang@zju.edu.cn

been fully investigated, especially the durability of bricks treated with different materials when experiencing the deterioration factors.

In this work, aiming at the preservation of ancient grey bricks by preservation materials, four protecting organosilicon reagents were selected to evaluate the effectiveness of different materials on grey bricks by different treating methods. Based on the requirements for preservation treatment, the penetration depths, the appearance alterations, water adsorptions, hydrophobic properties, porosities and compressive strengths were evaluated. The deterioration cycle experiments were also performed on the bricks treated with different materials to test their durability under environmental attacking factors.

Data from laboratory tests will help us analyze the influence of different organosilicon materials on grey bricks. This study aims to determine which one is suitable for the protection of ancient architectures composed of grey bricks. The results thus can serve also as an instrumental and methodological example applicable for conservation monitoring of other masonry structures.

Materials and methods

Commercial grey brick samples ($5\times5\times3cm^3$) were prepared by wet cutting and dried for further tests and deterioration cycles. The manufacturing of grey bricks in China has been quite mature and stable for hundreds of years, so that modern commercial grey bricks can be selected as the test objects. The brick samples were dipped in water for 24h and then dried in oven until constant weights.

Four commercial organosilicon materials were selected in this study: Tegovakon V100 (an ethyl silicate based material, by Evonik Industries AG), Wacker BS 4004 (an organosiloxane based material, by Wacker-Chemie), Wacker BS Crème C (a silane-based creamy product) and HZSI-1 (a silicone resin based material). HZSI-1 was provided by Hangzhou Institute of Chemical Engineering in China, where the organosilicon material was developed and applied in a few conservation projects of stone and earthen relics in the past few years. These materials were used as received except Wacker BS 4004 which was diluted with deionized water with the weight ratio of 1:5 according to the manufacturer's instruction.

There were different procedures of applying the materials on brick samples: full immersion, half immersion and brushing. In the full immersion, the brick samples were totally dipped in the materials solution while keeping the solution level 3mm above the brick surface. In the half immersion, the material solution level was kept 1.5cm above the bottom, which was just half of the brick sample height. One exception is the treatment with Crème C, which was brushed onto the sample surface directly until no more agent could penetrate the sample. The immersion time was 30min and the excess of the material on sample surface was removed after the treatments. Then the samples were cured at room condition for one month. The fully immersed samples treated with Tegovakon V100, Wacker BS 4004, Wacker BS Crème C and HZSI-1 were marked as 'T', 'W', 'BS' and 'S' respectively, and the half-immersed ones were marked as 'T_h', 'W_h', and 'S_h' respectively. While the blank samples without any treatments were marked as 'B' so that the brick samples treated with materials can be compared with the untreated ones.

The ideal protective materials should make little change of grey bricks' appearances with good permeability and waterproof performance, and improve their compressive resistance. Therefore, the following properties were mainly tested in the lab: the penetration depths of the materials, the alteration of appearance presented by the color and glossiness difference, waterproof property which was mainly measured by water adsorption and contact angle of the brick surface, the effectiveness of consolidation which was characterized by the compressive strength of the brick.

*L*a*b** parameter is a perceptibly uniform 3D color space, where color vectors can be represented and determined by the coordinates *a** and *b**, while *L** represents the lightness [20-23]. The CIE *L*a*b** color parameters were obtained by a colorimeter (Konica Minolta CR-10) and, by comparing the untreated and treated samples, the color changes were expressed as total color difference (ΔE*), obtained by $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$. The glossiness was measured by a gloss meter (WG-68, Shenzhen Wave Optoelectronics Technology Co.).

The contact angle of the brick surface was measured using a surface tension meter (JC200A, Shanghai Zhongchen Instrument). The water adsorption coefficient of the sample was measured using the following method: the sample was initially stored in oven under 105 °C until constant weight, which was recorded as m_0 (g). The sample was then immersed in deionized water for 24h. After that, the sample was taken out and its weight was recorded as m_1 (g) after the removal of water on the surface. The water adsorption coefficient Δm_a (%) was calculated using the equation: $\Delta m_a = 100 \cdot (m_1 - m_0)/m_o$ (%).

The compressive strength of the brick samples was measured by a universal testing machine (SANS-CMT5205, MTS China) according to National Standard GB/T 2542-2012 (The Test Methods for Wall Bricks). The porosities of the samples were measured by Mercury Intrusion Porosimetry, MIP (AutoPore IV-9510). The reinforcement situations of three organosilicon materials were observed in scanning electron microscope (SEM, FEI SIRION-100) images with both 2000 and 5000 magnification.

In addition, to investigate the long-term protection effects of materials, durability tests composed of 50 deterioration cycles were conducted for fully immersed samples. Given the actual risks which the bricks always faced, salt solution immersion, freeze-thaw cycles and UV aging tests were arranged as the deterioration cycles to simulate a vastly degraded ambient condition. In each cycle, the brick samples were fully immersed in saturated sodium sulfate solution for 12h, then the samples were taken out and kept under -20℃ for 4h in a freezer, after that, the samples were stored under 65℃ in an oven for 6h, finally they experienced an UV aging test for 30min in an UV ageing oven (Common Wealth Industrial Corporation). The wavelength of the UV light was 365nm, with the power of 0.5kW and lighting area of 30cm×30cm. The degree of damage in each cycle was measured as the weight loss of the brick sample using the equation: $\Delta m = 100 \cdot m_f/m_i$ (%).

Where m_f was the final weight of the brick sample after each cycle and m_i was the initial weight before the cycle. During the deterioration cycles, all the measurements were taken for 3 samples. Thirty deterioration cycles were conducted on half treated bricks because it was found that half treated samples were more vulnerable to deterioration cycles. Data from experiment on half treated ones could enable us to have further understanding of what to do in the process of the actual strengthening protection.

Results and discussion

Basic physical properties after treated with preservation materials

Appearance alterations

Quantified differences of appearance can be seen in chroma value and glossiness, listed in Table 1. The surfaces of samples treated with HZSI-1 appeared obviously darker than the untreated ones with high glossiness. For the other three materials, the appearance of the sample surface didn't change much and their color differences were all below 5, which is acceptable for the conservation practice.

Hydrophobic performance

Hydrophobic performance of bricks treated with the organosilicon materials characterized by contact angle data presented considerable difference. Wacker BS 4004 improved the hydrophobic property of bricks most with the contact angle value of 134.3°, while silicone resin with the value of 100.4°, Crème C with the value of 93.8°, and Tegovakon V100 with the value of 71.5°. The untreated brick was hydrophilic because water can easily penetrate the brick.

Table 1. Appearance Alteration and Water Adsorption Property of Samples

Sample	Glossiness before treatment (85°)	Glossiness after treatment (85°)	L^*a^*b data of the treated and untreated brick samples L^*	a^*	b^*	Capillary water absorption
S	0.61	4.26	49.8	0.2	0.6	1.34%
W	0.50	0.86	55.7	0.1	1.8	4.66%
T	0.49	0.54	55.1	0.4	3.8	12.86%
BS	0.50	0.72	54.3	0.6	4.1	1.15%
B	—	—	57.7	0.1	3.2	20.76%

Penetration depth

The penetration depth is a key factor for the assessment of the treatment efficiency. If the preservation substance does not penetrate at a sufficient depth, there is the risk of further accelerated degradation resulting in the loss of the valuable historic material. The penetration depth was measured by the following simple procedure: the treated brick was cut and water was dropped onto the cross-section of the brick and the wetting phenomena were observed. It was found that grey bricks can basically be fully penetrated after fully immersed in the organosilicon materials for half an hour. But for the half-immersed ones, the materials could not fully penetrate the bricks. It is noted that Crème C can fully penetrate the brick samples even by brushing method because of its low molecular weight.

Water adsorption

After treated with organosilicon materials, hydraulic permeability of bricks was greatly reduced as shown in Table 1. Water absorption of brick samples were greatly reduced, especially the bricks treated with silicone resin HZSI-1, Wacker BS 4004 and Crème C. V100 showed much less hydrophobic than the other materials perhaps because that the hydrolysis of ethyl silicate will form the precipitated amorphous silica gel, which is totally an inorganic product. This result agreed with the contact angle measurement indicating that V100 has the weakest water resistance among the four materials.

Compressive strength

Compared with the blank ones, the compressive strength values of the samples fully immersed in HZSI-1 and V100 increased 37 and 73% respectively, as shown in Fig. 1 While Wacker BS 4004 and Crème C showed no improvement in mechanical property.

Therefore, BS 4004 and Crème C might be more appropriate for the surface coating due to its great hydrophobicity shown above. Remarkably, for the half-immersed samples, their compressive strengths were not improved as much as the fully immersed ones. This implies that only the penetrated part of the brick samples shows obvious reinforcement effect and in the practical preservation work, if the materials could not penetrate deep enough into the brick surface, the improvement of brick's mechanical property could not be considerable.

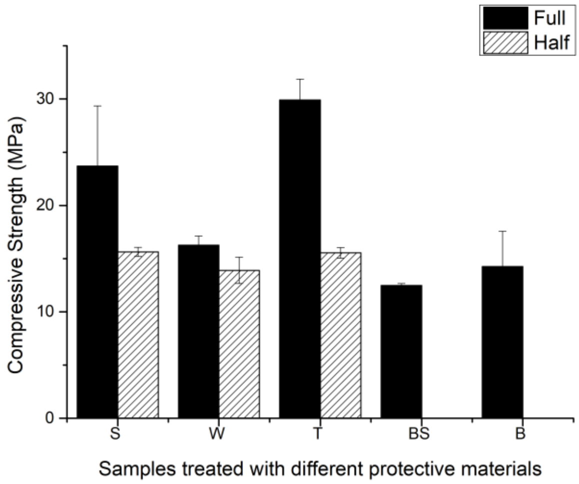

Fig. 1. Comparison of the compressive strength between the full, half treated and untreated grey brick samples.

SEM and MIP test

From scanning electron microscopy (SEM) pictures with 2000x magnification as shown in Fig. 2, the organosilicon materials showed different ways of reinforcement in the heterogeneous porous system, which could be also observed from the mercury intrusion porosity test as shown in Fig. 3. The pore size ranged from 100nm to 1000nm, which belonged to capillary pores. BS 4004 and Crème C didn't alter the porosity and pore diameter of the brick samples much, while V100 and HZSI-1 reduced them significantly. After treated with HZSI-1, the small pores in the brick samples increased possibly because the larger pores were filled with the material and converted into small pores. This was consistent with the compressive strength test that after the application of preservation materials, the compressive strength of the samples was improved more with the lower porosity. However, after capillary pores remained the highest occupation of total apparent porosity, it could be supposed that good water and air permeability of the bricks would still be kept.

Table 2. Porosity results and average pore diameters of the samples

Sample	Porosity (%)	Average Pore Diameter (nm)
Blank	38.4957	630.9
S	29.6121	67.2
W	36.8868	426.3
T	27.5085	107.4
BS	36.2396	782.2

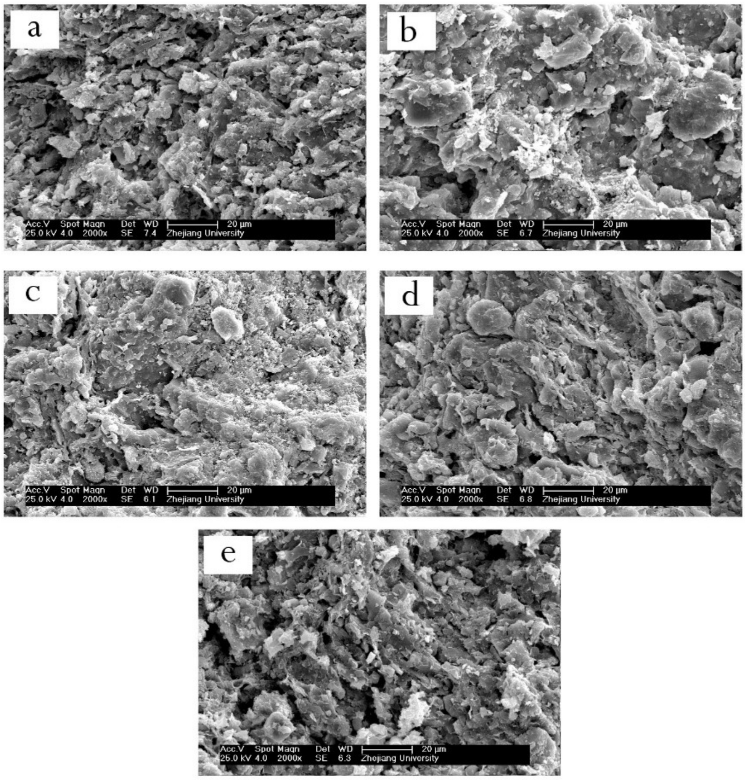

Fig. 2. Scanning electron microscopy (SEM) images of bricks treated with silicone resin (a), Wacker BS 4004 (b), Tegovakon V100 (c), Wacker BS Crème C (d) and blank one (e) with 2000x magnification.

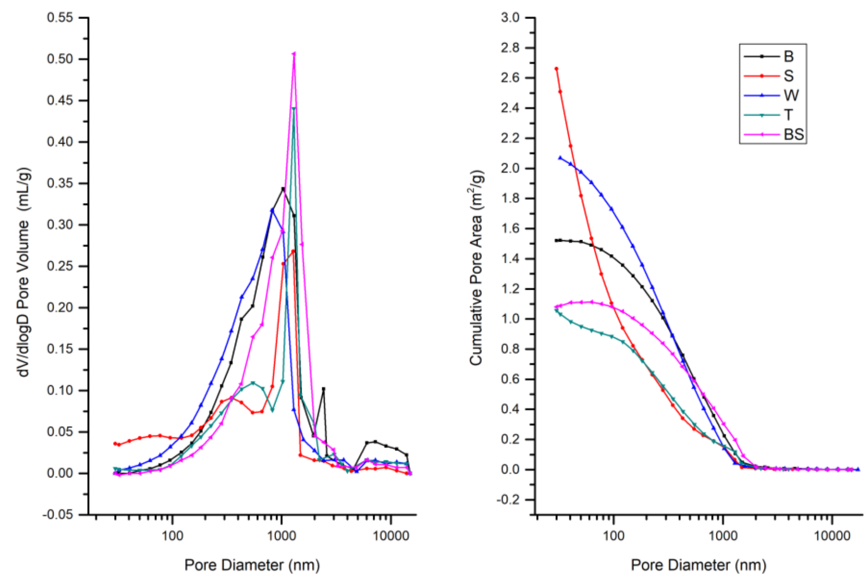

Fig. 3. Pore size distribution (left) and cumulative pore area distribution (right) of the samples treated with different preservation materials.

Durability tests

Tests of fully-immersed bricks

Alteration of appearance - After the deterioration cycles, brick samples fully immersed with HZSI-1 showed nearly intact in appearance, as shown in Fig 4. Bricks fully immersed with V100 showed peeling layers clearly and Wacker BS 4004 ones seemed to have chunks of spalling while the blank ones suffered the biggest damage. The samples treated with Crème C, however, didn't show much damage during the deterioration cycles.

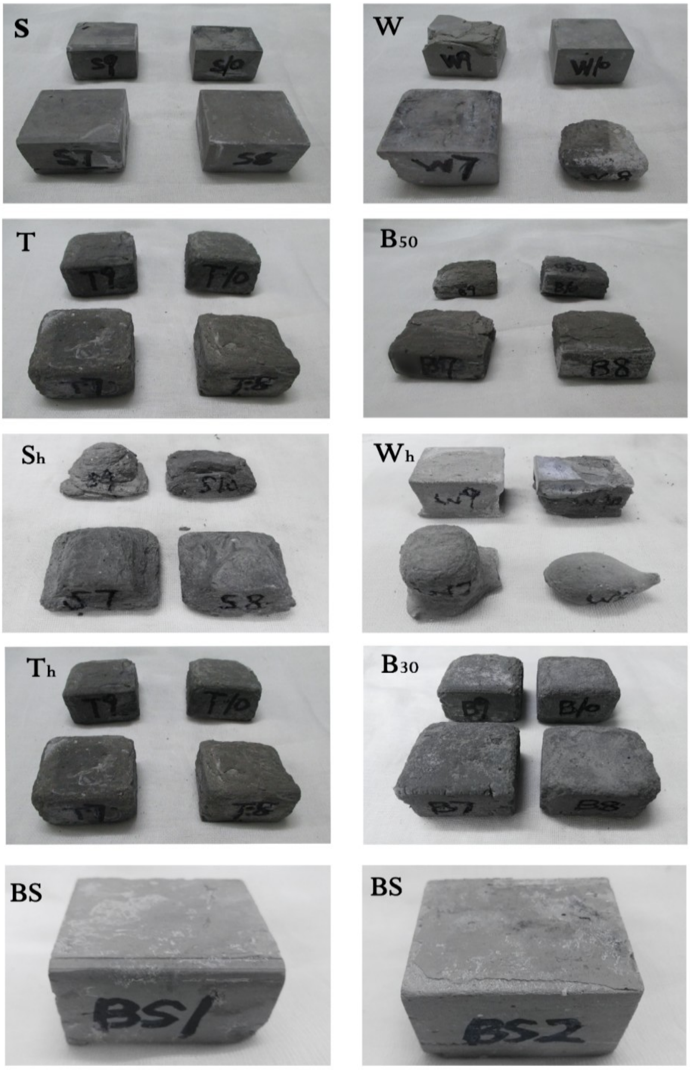

Fig. 4. Appearance of samples with full and half immersion after 50 and 30 deterioration cycles respectively. B_{50}: Blank sample after 50 deterioration cycles; $B_{30:}$ Blank sample after 30 deterioration cycles.

White crystals obviously appeared on the surface of bricks treated with V100. XRD analysis showed that the crystals were mainly quartz and sodium sulfate. Quartz could come from the hydrolysis of TEOS, and the presence of sodium sulfate on the brick surface indicated that soluble salts could easily migrate with water in the TEOS treated samples, which might be more vulnerable to the salt damage.

Weight changes – Fig. 5 shows that the weights of bricks fully immersed in HZSI-1 and treated with Crème C were relatively stable, while samples fully immersed in V100 and Wacker BS 4004 showed significant weight losses, which is consistent with the observations in sample appearance. The untreated samples were the most vulnerable compared with the treated ones. HZSI-1 seems to perform the best in terms of durability if the material can penetrate entirely into the bricks.

Hydrophobic performance - The hydrophobic performance of grey bricks is determined by contact angle. Untreated grey bricks are hydrophilic, shown as the line of zero in Fig. 6. After several deterioration cycles, contact angles of samples treated with V100 can hardly be measured. Samples treated with BS 4004 and Crème C remained high contact angles, while samples treated with HZSI-1 had relatively stable contact angle data, remaining around 80°. As a result, Wacker BS 4004, Crème C and HZSI-1 are effective water-repelling materials, but V100 lost its hydrophobicity fast in the deterioration cycles.

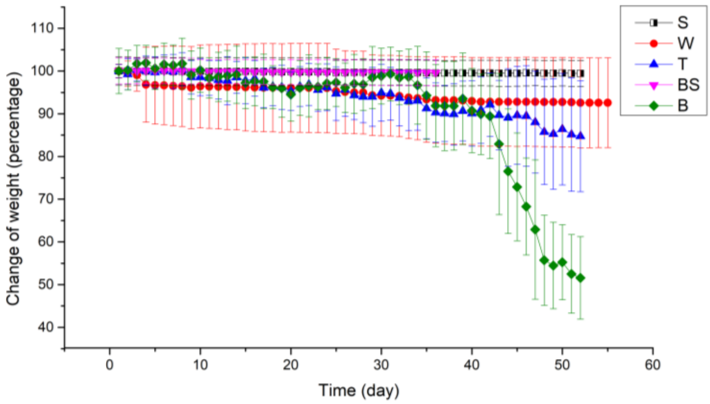

Fig. 5. The fully-treated samples' weight changes during the deterioration cycles.

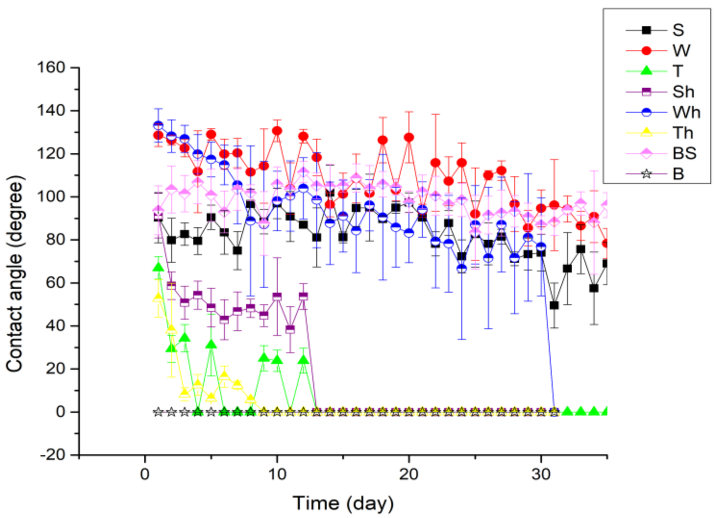

Fig. 6. Tendency of samples' waterproof properties characterized by contact angles.

Test of half immersed bricks

Considering the protection methods and effects in conservation practice, a half immersion test is needed for simulating the real situation. Bricks were carefully treated with the same organosilicon materials.

Change of appearance - There was a big difference of appearance changes between half and fully immersed bricks. Clear signs of detachment between the penetrated and non-penetrated parts in the bricks were observed in all the treated samples. Bricks treated with HZSI-1 and Wacker BS 4004 were almost broken after only several cycles, completely different from fully immersed ones. Flakes appeared on bricks half immersed in V100 (as shown in Fig. 4). The treated parts got detached probably because of soluble salt gathered at the interface between the penetrated and non-penetrated parts, as salt crystals were observed right on the interface where the breakage occurred, which is quite similar to what we have observed in the consolidation treatment in stone samples [24].

Weight Changes - As shown in Fig. 7, the weight of S_h sharply decreased after only 10 cycles, like the ones half treated with Wacker BS 4004.

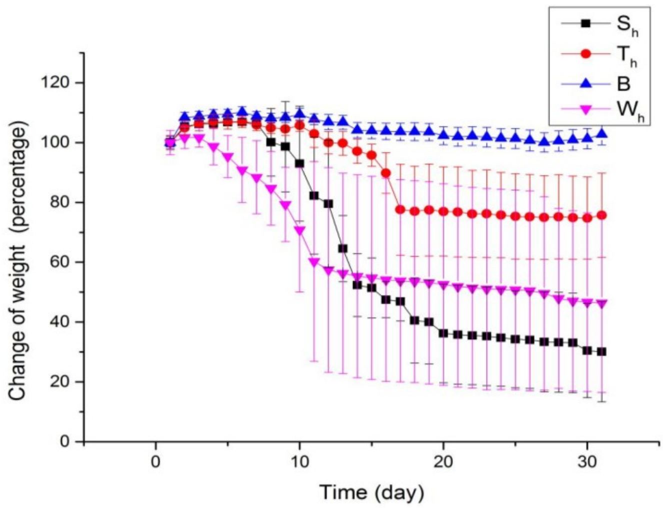

Fig. 7. The half-treated samples' weight changes during the deterioration cycles.

By contrast, T_h samples were damaged more slowly and slightly than S_h and W_h. It is interesting to find that the blank ones, which were not treated with any materials, experienced only a little weight loss during the 30 deterioration cycles. Compared with Fig. 5, the significant weight loss occurred after 40 cycles for the blank samples. The organosilicon materials could be protective if they can penetrate the entire brick, otherwise they can cause more severe damage to the bricks. It is because that the two parts with and without organosilicon materials show quite different physical properties, such as thermal and moisture expansion, water adsorption and hydrophobicity. The stress between the two parts become significant during the freeze-thaw, wet-dry and salt ingress cycles, finally the bricks will be damaged. Since it is almost impossible to make the protective materials penetrate the whole brick structures in the field work, the application of these organosilicon materials must be cautious.

Hydrophobic performance - As shown in Fig. 6, bricks half treated with Wacker BS 4004 maintained good hydrophobic property over the deterioration cycles, while the samples half treated with HZSI-1 lost the hydrophobicity quickly, also quite different from the fully treated ones. The quick loss of hydrophobicity may be due to the quick loss of weight for samples S_h, while the samples were almost entirely broken after about 13 cycles. Similar to samples fully treated with V100, T_h samples lost their hydrophobicity quickly.

Conclusions

It is found that all the protective materials have good penetration property and can reduce the water adsorption drastically under the condition of full immersion. V100 and HZSI-1 increased the compressive strength a lot while BS 4004 and Crème C showed little improvement in mechanical property. After the deterioration cycles, bricks fully treated with HZSI-1 showed nearly intact in appearance, weight and hydrophobicity, while samples fully treated with V100 and 4004 showed significant weight losses. The hydrophobic nature of samples treated with V100 was lost in just a few cycles and white salt crystallization appeared on the brick surface.

However, in the real preservation work, the reinforcement with full penetration of preservation materials is almost impossible. In that case, silicone resin may not be the best choice for large brick structures. Among the four protective materials, only Crème C could be appropriate for the surface coating as water repellant, considering its good hydrophobic property and durability. On the other hand, it is necessary to take the binders for brick architectures, usually mortars, into consideration when investigating the performance of protective materials, which will be studied in the future.

Acknowledgements

This work was financially supported by the Fundamental Research Funds for the Central Universities and Conservation Science and Technology Project of Zhejiang Provincial Administration of Cultural Heritage. The authors are also grateful for Mr. Wenlin Zhou at Hangzhou Institute of Chemical Engineering for providing the silicone resin.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

[1] Z. Jinfeng, *Discussion of regulations for the maintenance of masonry monuments*, **Sciences of Conservation and Archaeology, 22**(2), 2010, pp. 79-86.

[2] E.U. Sagin, H. Boke, *Characteristics of bricks used in the domes of some historic bath buildings*, **Journal of Cultural Heritage, 14**(3), 2013, pp. E73-E76.

[3] J. Wang, A. Heath, P. Walker, *Experimental investigation of brickwork behaviour under shear, compression and flexure,* **Construction and Building Materials, 48**, 2013, pp. 448-456.

[4] L. Yonghui, X. Huarong, W. Jianguo, L. Xinjian, W. Jingxiu, E*xperimental research on isothermal sorption properties of early modern and modern gray bricks in Wujiang, Suzhou, China,* **Journal of Southeast University (Natural Science Edition), 44**(2), 2014, pp. 441-444.

[5] C. Giannattasio, S.M. Grillo, S. Murru, *The Sardinian coastal towers in the Mediterranean (16th–17th century): An archaeometrical approach for the study of masonry,* **Journal of Cultural Heritage, 22**, 2016, pp. 1072-1078.
[6] R. Scalenghe, F. Barello, F. Saiano, E. Ferrara, C. Fontaine, L. Caner, E. Olivetti, I. Boni, S. Petit, *Material sources of the Roman brick-making industry in the I and II century A.D. from Regio IX, Regio XI and Alpes Cottiae*, **Quaternary International, 357**, 2015, pp. 189-206.
[7] P. Foraboschi, A. Vanin, *Experimental investigation on bricks from historical Venetian buildings subjected to moisture and salt crystallization*, **Engineering Failure Analysis, 45**, 2014, pp. 185-203.
[8] C. Rodriguez-Navarro, E. Doehne, E. Sebastian, *How does sodium sulfate crystallize? Implications for the decay and testing of building materials*, **Cement and Concrete Research, 30** (10), 2000, pp. 1527-1534.
[9] F. Sandrolini, E. Franzoni, G. Cuppini, L. Caggiati, *Materials decay and environmental attack in the Pio Palace at Carpi: A holistic approach for historical architectural surfaces conservation,* **Building and Environment, 42**(5), 2007, pp. 1966-1974.
[10] H. Bingkan, Z. Liqin, L. Chunxian, *Disaster analysis and control countermeasures of brick-wood structure type protective buildings*, **Journal of Natural Disasters, 13**(6), 2004, pp. 105-111.
[11] V. Fassina, M. Favaro, A. Naccari, M. Pigo, *Evaluation of compatibility and durability of a hydraulic lime-based plaster applied on brick wall masonry of historical buildings affected by rising damp phenomena*, **Journal of Cultural Heritage, 3**(1), 2002, pp. 45-51.
[12] F. Matero, *Mud Brick Metaphysics and the Preservation of Earthen Ruins,* **Conservation and Management of Archaeological Sites, 17**(3), 2015, pp. 209-223.
[13] B. Perrin, N.A. Vu, S. Multon, T. Voland, C. Ducroquetz, *Mechanical behaviour of fired clay materials subjected to freeze-thaw cycles*, **Construction and Building Materials, 25**(2), 2011, pp. 1056-1064.
[14] M. Uranjek, V. Bokan-Bosiljkov, *Influence of freeze-thaw cycles on mechanical properties of historical brick masonry,* **Construction and Building Materials, 84**, 2015, pp. 416-428.
[15] W. Jianglong, *Research Situation of Historical Masonry Structure*, **Earthquake Resistant Engineering and Retrofitting, 33**(4), 2011, pp. 116-119.
[16] E. Franzoni, B. Pigino, A. Leemann, P. Lura, *Use of TEOS for fired-clay bricks consolidation,* **Materials and Structures, 47**(7), 2014, pp. 1175-1184.
[17] J. MacMullen, J. Radulovic, Z. Zhang, H.N. Dhakal, L. Daniels, J. Elford, M.A. Leost, N. Bennett, *Masonry remediation and protection by aqueous silane/siloxane macroemulsions incorporating colloidal titanium dioxide and zinc oxide nanoparticulates: Mechanisms, performance and benefits*, **Construction and Building Materials, 49**, 2013, pp. 93-100.
[18] K. Matziaris, M. Stefanidou, G. *Karagiannis, Impregnation and superhydrophobicity of coated porous low-fired clay building materials*, **Progress in Organic Coatings, 72**(1-2), 2011, pp. 181-192.
[19] H. Ling, Z. Gang, Z.W. qiang, *The deterioration and consolidation of Dayan Pagoda and Famen Temple*, **Sciences of Conservation and Archaeology, 16**(3), 2004, pp. 33-39.
[20] Y.N. Vodyanitskii, N.P. Kirillova, *Application of the CIE-L*a*b* system to characterize soil color*, **Eurasian Soil Science, 49**(11), 2016, pp. 1259-1268.
[21] V. Pelin, I. Sandu, S. Gurlui, M. Branzila, V. Vasilache, E. Bors, I.G. Sandu, *Preliminary investigation of various old geomaterials treated with hydrophobic pellicle,* **Color Research and Application, 41**(3), 2016, pp. 317-320 Special Issue: SI, DOI: 10.1002/col.22043

[22] S. Pruteanu, I. Sandu, M.C. Timar, M. Munteanu, V. Vasilache, I.C.A. Sandu, *Ecological Systems Applied for Cleaning Gilding in Old Icons,* **Rev.Chim.(Bucharest), 65**(12), 2014, pp. 1467-1472.
[23] A.M. Saviuc-Paval, A.V. Sandu, I.M. Popa, I.C.A. Sandu, A.P. Bertea, I. Sandu, *Colorimetric and microscopic study of the thermal behavior of new ceramic pigments,* **Microscopy Research and Technique, 76**(6), 2013, pp. 564-571. DOI: 10.1002/jemt.22201
[24] H. Zhang, Q. Liu, T. Liu, B. Zhang, *The preservation damage of hydrophobic polymer coating materials in conservation of stone relics*, **Progress in Organic Coatings, 76**(7-8), 2013, pp. 1127-1134.

Received: January 10, 2018
Accepted: November 08, 2018