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CHARACTERIZATION OF THE SUBSTRATES FROM TWO CULTURAL-HERITAGE SITES AND A PREPARATION OF MODEL SUBSTRATES

KARAKTERIZACIJA GRADBENIH MATERIALOV IZ DVEH OBJEKTOV KULTURNE DEDIŠČINE IN PRIPRAVA MODELNIH MATERIALOV

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In this study the microstructural characteristics of the materials selected from two cultural-heritage sites (the Dornava Manor, Slovenia, and the Bač Fortress, Serbia) and of the model samples – the control and aged ones – were investigated. The samples were characterized by means of mercury intrusion porosimetry (MIP) and total-specific-area analysis (BET). A good agreement was achieved between the samples of the brick and mortar from the Bač Fortress, or the samples of the natural stone and render from the Dornava Manor, and the corresponding model samples.

Keywords: cultural heritage, microstructure, brick, natural stone, mortar, frost resistance

Prispevek obravnava mikrostrukturne lastnosti izbranih materialov iz dveh objektov kulturne dediščine (dvorec Dornava v Sloveniji in trdnjava Bač v Srbiji) ter modelnih materialov – kontrolnih in staranih. Vzorce smo preiskali z živosrebrno porozimetrijo in plinsko sorpcijo. Med vzorci iz objektov kulturne dediščine in modelnimi vzorci smo dosegli dobro ujemanje, tako v primeru opeke in malte s trdnjave Bač kot naravnega kamna in ometa z dvorca Dornava.

Ključne besede: kulturna dediščina, mikrostruktura, opeka, naravni kamen, malta, zmrzlinska obstojnost

1 INTRODUCTION

Within the scope of the 7th FP HEROMAT project (*Protection of cultural heritage objects with multifunctional advanced materials* ENV-NMP.2011.3.2.1-1 NMP) the main goals is to develop the consolidants and multifunctional photocatalytic coatings for cultural-heritage sites in order to conserve degraded materials and to prevent their further degradation. To meet the set goals and develop the basis for further applications, the following steps were implemented: (i) an analysis of the microstructure of the substrates from the two studied facilities (the Dornava Manor, Slovenia, and the Bač Fortress, Serbia); (ii) the preparation of a model substrate, simulating the substrates from such sites for the preliminary testing of the newly developed products; (iii) an analysis of the microstructure of the model substrate before and after the ageing procedure, and a comparison of this substrate with the substrates from the two selected sites.

The Dornava Manor Complex, with its accompanying park, is one of the most important monuments of the late Baroque period in Slovenia. Because of a long exposure to a strong degradation and inappropriate restoration procedures, the stone elements of the exterior, i.e., the statues and ornaments of the garden, the balustrades and the main building, show only a faint picture of the past. The Bač Fortress, Serbia (currently included in the UNESCO Tentative List) is the best preserved brick-built medieval fortress in Vojvodina. This, first a Hungarian and later on an Ottoman stronghold, has been in ruins for centuries as a result of various physical, chemical and biological degradation processes. Its physical integrity has been substantially lost, but the preserved elements indicate the sophisticated architecture of the fortification school of the high Gothic style, with the elements of the early Italian Renaissance.

Among the most active causes for the weathering of the historical monuments exposed to the outdoor environment is frost. A common degradation phenomenon of the porous materials such as mortars, stone and brick is a loss of cohesion of the binder-aggregate/grain system. This process is usually followed by a deposition and formation of new products, a loss of mechanical strength, a loss of the material from the surface, and chromatic alterations.[1] The cohesion recovery between these particles, released by the binder loss, can be achieved through an application of consolidants.[2]

Porosity and pore-size distribution can have a major effect on the durability of porous materials, influencing the effectiveness of a consolidation, the depth of a consolidant, etc.[3,4] No consolidation action can be reasonably justified without having access (directly or by deduction) to the information on all these aspects.[5]

Taking into consideration the fact that porosity is the most important factor with regard to the absorption and fluid transport in porous materials, the present study focuses on the characterization of the porosity and pore-size distribution as well as determining the specific surface area. In this study the microstructural characteristics of the selected materials from the Dornava Manor and the Bač Fortress are determined. In order to assess the changes that occur in the microstructure after a freeze/thaw cycles, model substrates were prepared. The samples were characterized with mercury intrusion porosimetry (MIP) and total-specific-area analysis (BET).

2 EXPERIMENTAL WORK

2.1 Materials and sample preparation

Four substrates were selected among various materials from the two historical sites: (i) sandstone (designated as Stone Dornava) and (ii) a render sample from the Dornava Manor (designated as Render Dornava); (iii) lime mortar with a carbonate aggregate (designated as Mortar Bač) and (iv) a brick from the Bač Fortress (designated as Brick Bač).

Based on the mineralogical and petrographic analyses, a quartzitic-micaceous sandstone from the Dornava Manor was recognised as the Vunduški sandstone outcropping in the eastern part of Slovenia. As a model stone, a bulk sample of the Vundušek sandstone (from the Middle-Miocene geological period) was taken from the Jelovice quarry, located near the town of Majšperk, in the eastern part of Slovenia. Samples were cut having a dimension of 5 cm × 5 cm × 1 cm and designated as Model Stone or Model Stone F, where F means that the sample was exposed to freezing and thawing.

The model render was prepared on the basis of a petrographic analysis of render sample DOR 137 from the Dornava Manor. A silicate gravel fraction of 0–4 mm was obtained from the Hoče quarry (Slovenia) and sieved in order to get a grading curve for the aggregate similar to that of the analyzed render. In order to weaken the mechanical properties of the cement part of the model samples, a Portland cement (CEM I 42.4, Lafarge) mixed with tuff (Ecotrass, Saning, d. o. o.) was used. The traditionally prepared slaked lime from the local producers was also used. The substrates were prepared by combining together coarse and fine renders in order to achieve the appropriate thickness. On an approximately 3.5 cm thick coarse layer, a 3–4 mm thick layer of fine render was applied. Steel moulds with the dimensions of 16 cm × 4 cm × 4 cm and 15 cm × 15 cm × 4 cm were used for the preparation of the models that were then cut out to the dimensions required for the testing. The samples were cured at 100 % relative humidity at room temperature for a minimum of 14 d before the cutting was performed.

The model bricks were prepared by hand in the traditional way, using an old crushed brick and the clay from a pit situated near the Bač Fortress. Based on the mineralogy and chemical composition of the examined historical-brick samples, the optimum formulation for the raw-material mixture and firing temperature was determined. The clay material was based mainly on quartz and carbonates such as dolomite and calcite. The raw material was hand-moulded in the laboratory. The moulds were filled and then air-dried for a period of two weeks. When an adequate strength was obtained, the model bricks were fired in a laboratory kiln (T max of 980 °C). The prepared model-brick samples were then exposed to a laboratory degradation, followed by a characterization procedure. Samples with the dimensions of 5 cm × 5 cm × 1 cm were prepared.

For the preparation of the model mortar, the following components were used: lime putty, micronized quicklime, sand and water (the hot-lime-mix method). The selected components provided a mineralogical and chemical composition that was as close as possible to the characterized historical mortars. All the mortars were prepared in the traditional way, in a wooden dish. The prepared mortars were moulded in specially designed moulds. The interior surfaces of the moulds were coated with TFE-fluorcarbon (Teflon) that did not affect the setting of the mortar, also preventing any damage to the mortar surfaces. During the first weeks, carbonation was achieved in a moist room and after that all the samples (5 cm × 5 cm × 1 cm) were placed in a chamber with a constant flow of CO_2 (accelerated carbonation).

2.2 Methods

The freeze/thaw cycling was performed according to standard EN 12371:2010. All the samples were exposed to 50 cycles of freezing and thawing, where one cycle consists of (1) a sample being in water for 5.5 h and at 15 °C, (2) sucking the water from the chamber so that the temperature reaches –4 °C within 2 h, (3) cooling down over the next 4 h to –10 °C, and (4) pouring the water again into the chamber.

The porosity and pore-size distribution of the investigated samples were determined by means of mercury intrusion porosimetry (MIP). Small blocks, approximately 1 cm^3 in size, were dried in an oven for 24 h at 105 °C, and then analysed using a Micromeritics Autopore IV 9500 Series pore-size analyzer. The samples were analysed in the range of 0–414 MPa, using solid penetrometers.

On the basis of the BET (Brunauer-Emmet-Teller) method, the total specific area of a sample surface was determined with nitrogen adsorption at 77 K within a relative pressure range of 0.05 to 0.3 using a Micromeritics ASAP-2020 analyzer. Prior to the performance of these measurements, the samples (2 to 3 small blocks

Table 1: Comparison of the porosity and specific surface (the average of 2 measurements) of the samples from Dornava Manor and Bač Fortress with the corresponding values for the model substrates before and after the ageing (F – exposure to freezing/thawing)
Tabela 1: Primerjava poroznosti in specifične površine (povprečje 2 meritev) vzorcev iz dvorca Dornava in vzorcev iz trdnjave Bač z ustreznimi vrednostmi modelnih podlag pred staranjem in po njem (F – izpostavitev zmrzovanju in odtajanju)

	Brick Bač	Model brick	Model brick F	Mortar Bač	Model mortar	Model mortar F
Porosity (%)	42.0 ± 4.4	45.6 ± 0.4	43.5 ± 0.8	40.3 ± 0.8	32.2 ± 4.1	29.6 ± 0.6
BET (m^2/g)	5.4 ± 0.9	2.03 ± 0.7	5.0 ± 1.4	2.8 ± 0.3	2.3 ± 0.2	1.8 ± 0.2
	Stone Dornava	Model stone	Model stone F	Render Dornava	Model render	Model render F
Porosity (%)	9.8 ± 0.2	13.4 ± 1.2	17.1 ± 2.8	26.7 ± 1.6	38.6 ± 1.0	27.8 ± 0.2
BET (m^2/g)	1.9 ± 0.3	2.3 ± 0.5	3.5 ± 0.1	10.3 ± 0.5	4.8 ± 0.4	9.3 ± 0.3

with a weight of approximately 1 g) were being degassed for at least 3 h.

3 RESULTS AND DISCUSSION

The results of the porosity and BET specific-surface tests are presented, for the all prepared samples, in **Table 1**, from which it can be seen that there is a very good agreement between the samples from the historical sites and the model samples obtained, in the case of the brick and mortars, from the Bač Fortress, and a fairly good agreement with the stone and render from the Dornava Manor. For example, the overall porosity of the Brick Bač sample was 42.0 %, whereas it was 45.6 % for the model-brick sample. In the case of the Mortar Bač sample it was 40.3 % compared to 32.2 % for the model-mortar sample. The porosity of the Stone Dornava sample was found to amount to 9.8 % compared to 13.4 % for the model-stone sample, whereas the porosity of the original render from Dornava reached 26.7 % and that of the model-render sample was 38.6 %.

After an exposure to the freeze/thaw cycling, only a slight increase in the porosity of the model-stone sample was observed. On the other hand, the sample's average pore diameter increased significantly, shifting from 0.04 μm to 0.26 μm (**Figure 1**). The pore-size distribution was unimodal, with an intrusion peak at 2 μm. The BET surface-area values also increased. The pressure caused by freezing range from 14 MPa to 138 MPa, with a decrease in the temperature of between –1.1 °C and –12.5 °C.[6] During the ageing test performed within the scope of this study, the temperature fell by up to –10 °C. The temperature range considered critical for a deterioration of natural stone is from about –4 °C to –15 °C.[6] A stone with a higher quantity of smaller pores is more prone to frost deterioration as well as salt crystallisation, although stone damage is more specifically influenced by nanopores in the case of salt crystallisation, and by micropores in the case of frost damage.[7]

The porosity of the model-render sample reduced significantly after the freeze/thaw cycling, whereas the change in the average pore size was not significant (0.04 μm and 0.06 μm). The main intrusion peak after the freeze/thaw cycling shifted from 1 μm to 0.15 μm (**Figure 2**). A significant increase in the BET surface area of the render was observed after the freeze/thaw cycling. Both of these phenomena can be ascribed to the dissolution/precipitation processes that occur due to the water exposure in the freezing/thawing test.

The overall porosity of the model-brick sample decreased slightly after the freeze/thaw cycling tests, which can be attributed to the natural re-carbonation of the calcium hydroxide inside the porous media, thus also contributing to an improvement in the durability.[8] Additionally, the average pore diameter also decreased (from 0.57 μm to 0.21 μm). However, a certain increase was observed in the case of bigger pores – there are three peaks above 10 μm, representing either pores or cracks. This could mean that the brick might be susceptible to

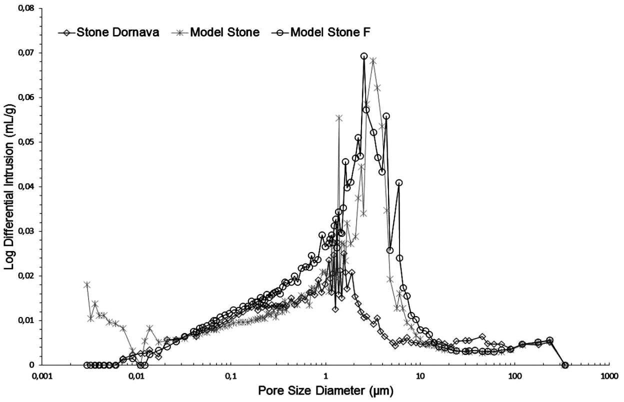

Figure 1: Pore-size distributions for the samples of natural stone
Slika 1: Porazdelitev velikosti por v vzorcih naravnega kamna

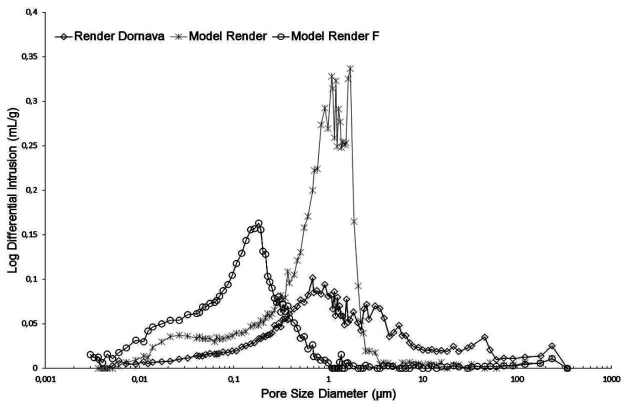

Figure 2: Pore-size distributions for the samples of render
Slika 2: Porazdelitev velikosti por v vzorcih ometa

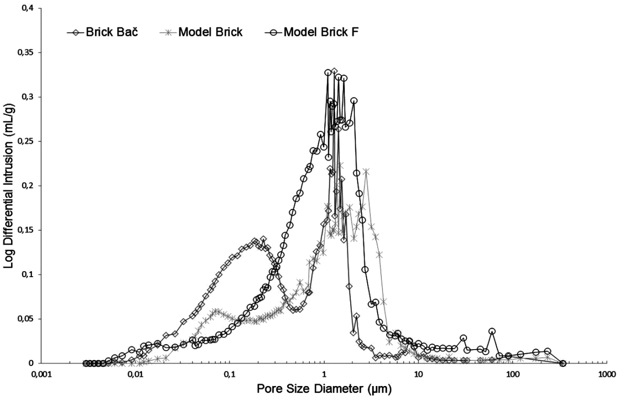

Figure 3: Pore-size distributions for the samples of brick
Slika 3: Porazdelitev velikosti por v vzorcih opeke

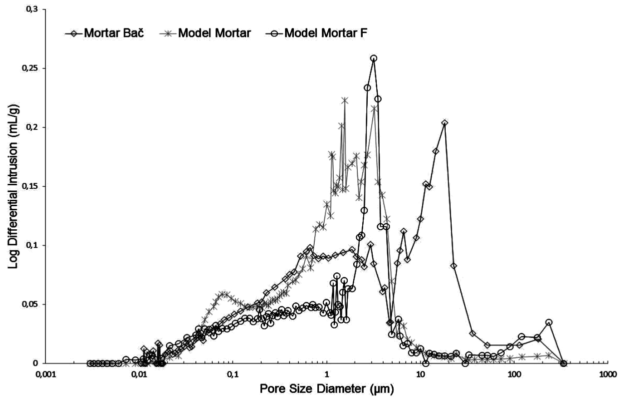

Figure 4: Pore-size distributions for the samples of mortar
Slika 4: Porazdelitev velikosti por v vzorcih malt

freezing. The values of the BET surface area increased significantly after the ageing. The pore-size distribution of Brick Bač and model-brick samples was bimodal, but after the freeze/thaw cycling it became unimodal (**Figure 3**).

The values of the porosity and the average pore diameter for the model-mortar sample decreased after the freeze/thaw cycling, most probably due to the dissolution/reprecipitation processes inside the pores. The pore-size distribution of the control sample was bimodal – this distribution was observed for a significant number of historical mortars[9], becoming unimodal after the ageing[10] (**Figure 4**). The values of the BET surface area increased significantly after the freeze/thaw cycling, indicating a deleterious effect of freezing on the mortar.

4 CONCLUSIONS

Samples of the selected substrates from the two monuments and model substrates – the control and aged ones, were investigated by means of mercury intrusion porosimetry (the total porosity, the average pore diameter, the pore-size distribution) and gas sorption (the BET surface area). A good agreement between the samples from the historical sites and the model samples was obtained for the brick and mortars from the Bač Fortress as well as for the natural stone and render from the Dornava Manor.

On the basis of these results, the selected model substrates will be used with newly developed materials in order to test and otherwise scrutinize them before applying them to the valuable substrates belonging to cultural-heritage sites.

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