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DEVELOPMENT AND APPLICATION OF NEW METHODS FOR THE CONSERVATION OF CERAMICS

Summary of Doctoral Dissertation

Physical sciences, Chemistry (03 P)

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FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

TOMAS PETRĖNAS

ŠIUOLAIKINIŲ KERAMIKOS KONSERVAVIMO METODŲ KŪRIMAS IR PRITAIKOMUMO TYRIMAS

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1. INTRODUCTION

During the preservation or restoration of ceramic historical cultural heritage finds and buildings it is highly important not to damage the surface of an object of study and not to change its inner structure and chemical composition. Thus, the conservation procedure must preserve an object for the future rather than cause even more damage. As a result, the search for and development of new and advanced materials and technologies for the conservation of cultural goods are among the most significant and relevant goals of our times posed for conservators and restorers. The protective coatings of ceramics have to protect its surface effectively against the harmful impact of external environment.

During the past several decades, the preservation of architectural heritage has united not only biologists, chemists, physicists, but also architects, engineers and archaeologists. Restoration and conservation are the main processes enabling the preservation of utilized cultural goods. The construction of the majority of historical buildings had lasted for several decades, therefore the restoration and conservation of such cultural heritage causes the greatest problems. A wide variety of structural materials is one of them. When a historical brick wall is being restored, it is necessary to use such bricks or other structural materials that would remain in aesthetic as well as chemical balance with authentic parts of a building. As it has already been mentioned, the selection of conservation substances is one of the main things in order to properly preserve cultural goods. The conservation substances have to ensure the most effective and economical protection, possess hydrophobic features and, simultaneously, be water vapour-permeable, be chemically and photochemically stable, demonstrate good optical characteristics in order to maintain the original colour of material and conform to the environmental requirements.

In this doctoral dissertation, various conservation methods have been applied for the first time for the conservation of contemporary and historical structural ceramics with the help of both ordinary and new ceramics conservation substances. The efficiency of conservation technologies while protecting the ceramics from the harmful impact of exterior environment was assessed by means of modern research methods. The impact of exterior environment was modelled in such a way so as to imitate the consequences of long-term acid rains or the effect of various ground waters. A highly sensitive inductively coupled plasma mass spectrometry (ICP-MS) was used to detect the quantity of migrated cations from coated ceramics. The most important aspects of the originality and novelty of the dissertation are the following: the use of ordinary and new conservation substances for the conservation of different chemical and physical composition ceramics, the study of their efficiency by means of the most modern research methods and the modelling of real environment impacts.

The aim of the doctoral dissertation is to develop effective technologies for the conservation of ceramic materials. The following objectives have been set to achieve the aim of the dissertation:

1. To study the efficiency of the polymeric coating used for the conservation of contemporary ceramics by detecting the cation migration from preserved and non-preserved ceramics.
2. To study the chemical and physical composition as well as surface morphological features of the samples of historical structural ceramics from the Monastery of St. Philip (San Filippo di Fragalà, Sicily).
3. To develop new conservation technology for the historical structural ceramics of the Monastery of St. Philip (Sicily).
4. To restore the 14th-16th century Lithuanian ceramics.
5. To verify a new conservation method of ceramic materials using the restored samples of the 14th-16th century Lithuanian ceramics.

2. EXPERIMENTAL PART

2.1. The reagents, Materials and Solutions

The following analytical grade materials and reagents were used: nitric acid (HNO_3; Merck, Germany), ammonium acetate (CH_3COONH_4, Merck, Germany), ammonia (NH_4OH, Merck, Germany), polyvinyl alcohol (PVA $[-CH_2CHOH-]_n$, Fluka, Germany); standard solution (ICP multi-elemental IV, Merck, Germany), white spirit (Neste Oil, Finland), acetone (VWR International GmbH, Austria), ethanol (AB Stumbras, Lithuania), toluene (VWR International GmbH, Austria), Plexisol P550-40 (40% poly (butyl methacrylate) solution in white spirit, Kremer Pigmente, Germany), Silres BS 16 (55% aqueous solution of potassium methylsiliconate, Wacker, Germany), Paraloid B-82 (copolymer of 50 % ethylacrylate (EA) and 50 % methyl methacrylate (MMA), Rohm and Haas Deutschland GmbH, Germany), Plextol B 500 (50% aqueous emulsion of a copolymer, a copolymer composition of 66% ethyl acrylate and 34% methyl methacrylate, Rohm and Haas Deutschland GmbH, Germany), distilled and deionised water.

Contemporary ceramic samples from the enterprise Palemonas (Kaunas, Lithuania) were selected for the investigation of cation migration from preserved and non-preserved ceramics. The samples were produced by using the clay from the pit in Kertupiai. The same size (2cm x 2.5cm x 0.5cm) ceramic specimens were prepared for this investigation. The historical ancient ceramics from the Monastery of St. Philip (Sicily, Italy) were used in this study. Ancient brick samples were taken from different places of the monastery: sample I (near the gate, bottom and side yard) and sample II (different fragments from the ruins of monastery courtyard). Also, the samples of restored historic Lithuanian ceramics were used for studies of cation migration. The samples were prepared with the help of the 14^{th}-16^{th} century brick production technology, using the clay from the pit in Ukmergė Region.

2.2. The Experiment Methods

To study the cation migration from conserved ceramics, ceramic plates of the same size were soaked in 2% polyvinyl alcohol (PVA) solution for 15 min and left to dry at room temperature for two days. The plates were soaked in 50 ml of 10 mM ammonium acetate solutions (pH values: 3, 5, 7, 9, 11). The migrations lasted for 3, 6 and 12 h in a 25 °C temperature thermostatic water bath. The samples were mineralized by means of dry mineralization before taking the measurements. Thus, 10 ml of a sample was taken and evaporated to dry residues in quartz crucibles and then heated at 800 °C for 3 h. After the heating, dry residues were dissolved in 10 ml of 2% HNO_3.

The St. Philip structural ceramic samples were prepared from ceramic bricks. Pieces of ancient bricks were crushed in an agate mortar and sieved through a 45 μm sieve. 250 mg of crushed ceramics was pressed into tablets under the pressure of 110-120 bar. Ceramics conservation was performed by soaking the tablets in conservation substance solutions for 2 min, after which the tablets were taken out and dried in desiccators. The study on the cation migration from conserved ceramics was carried out in the following way: the tablets were soaked in 25 ml of 10 mM ammonium acetate solutions (pH values: 3, 5, 7, 8, 11). The migration lasted for 3, 6 and 12 h at 40°C in thermostatic water bath. Analogous dry mineralization of the sample was performed before taking the measurements.

During the investigation of the restored Lithuanian structural ceramics, two clay plates of the same size were prepared. They were heated in an electric furnace in the mode corresponding to Lithuanian brick burning temperatures of the 14^{th}-16^{th} centuries. Two conservation solutions had been prepared before the conservation. The first solution was Silres BS-16 (an aqueous solution containing 5% of potassium methyl siliconate), and the second was Silres BS-16 (an aqueous solution containing 5% of the ceramics that had been crushed in an agate mortar and sieved through a 45 μm sieve). The conservation process was performed by brushing the solutions onto the clay plates with a paintbrush, after which the plates were dried in room temperature until a constant weight was achieved. The study on the cation migration from conserved ceramics was carried out in the following way: the plates were soaked in 10 mM ammonium acetate solutions (pH values: 3, 5, 7, 8, 11). The solution volume differed for each conserved or non-conserved ceramic plate but the ratio was constant, i.e. five millilitres of solution (where the migration study was carried out) for one gram of a clay plate. The migration lasted for 3, 6, 12 and 24 h at 40°C in thermostatic water bath. Analogous dry mineralization of the sample was performed before taking the measurements.

2.3. The Characterization Techniques

The migration was carried out in a thermostatic water bath with a shaker (Memmert GmbH, Germany). The quartz crucibles were used for heating and an ultrasonic bath with a heater (Banderlin, Germany) was employed to improve the reconstruction of dry residues. The solution was filtered through Teflon filters Albeta (Spain) (PTFE; pore size 0.45μm). The pH-meter WTW inoLab Weilheim (Germany) was used for the measurement of pH.

Scanning electron microscopes CAM SCAN S4 or Helios NanoLab 650 (FEI, the Netherlands), or EVO 50 EP (Carl Zeiss SMT GmbH, Germany) with energy-dispersive X-ray spectroscopy were used to characterize the surface morphology and determine elemental composition. Also, the optical microscope Leitz Wetzlar (Germany) was used for the characterization of surface morphology. The determination of metal concentration was performed with the help of the Perkin Elmer ELAN DRC-e ICP-MS with „–AS-93 plus“ autosampler. Elemental composition of ceramics was also measured with the Perkin Elmer ELAN 9000 LA ICP mass spectrometer. The thermogravimetric analysis (TG) was performed using the STA6000 Pyris 1 Perkin-Elmer thermobalance system. The contact angle measurements were performed using the KSV Instruments LTD (MODEL CAM 200). The X-ray diffraction analysis (XRD) was performed with the MiniFlex II Rigaku powder diffractometer working in Bragg-Brentano (θ/2θ) geometry and using CuKα1 radiation.

3. RESULTS AND DISCUSSIONS

3.1. The Study of the Migration of Cations from Preserved and Non-Preserved Contemporary Ceramics

The main goal of this study was to determine the suitability of the conservation technology developed in our laboratory for the conservation of contemporary ceramics.

3.1.1. The Preservation of Contemporary Ceramics with the Polymeric PVA Coating

The surface of the PVA coating was initially analysed with an optical microscope. It was observed that a high quality colourless PVA polymer coating was laid on a ceramic surface. Polymeric PVA coatings were analysed with the SEM as well. Fig. 1 shows the SEM micrograph of a contemporary ceramic sample before conservation. The surface of the ceramic from Palemonas is quite rough and porous (the size of pores is ~2 µm) and is composed of different size crystallites. Fig. 2 shows the SEM image of a contemporary ceramic surface coated with a PVA coating. As seen, the surface is smooth and without porosity, i. e. the PVA coating was covered effectively.

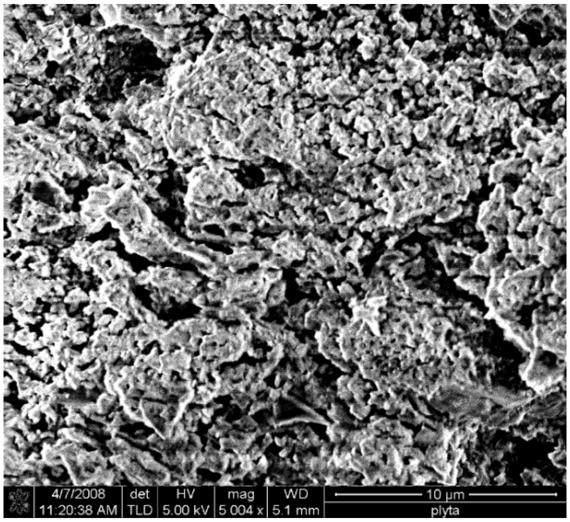


Fig. 1. The SEM micrograph of contemporary pottery before conservation.

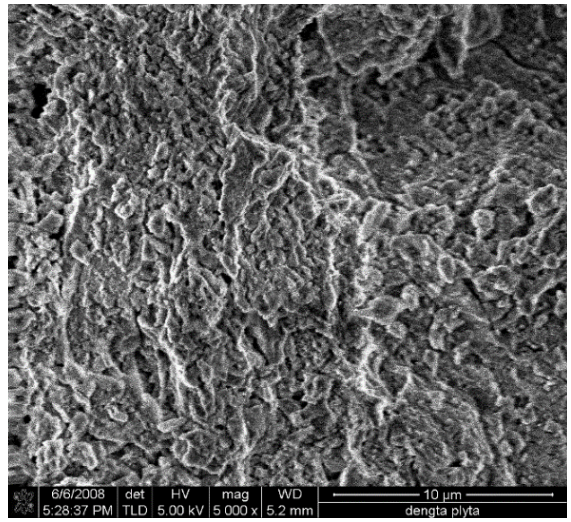


Fig. 2. The SEM micrograph of contemporary pottery after conservation.

The elemental composition of the surface and the cross-section of contemporary ceramics were determined with the help of the EDX analysis. The results of the EDX analysis of ceramics coated with PVA and uncoated are presented in Table 1.

Table 1. The results of the EDX analysis for contemporary ceramics.

Elements	Weight percentage, %		
	Ceramic surface	Ceramic cross-section	Ceramic surface covered with PVA
C	2.2	1.19	9.04
O	33.72	25.16	42.06
Na	0.75	0.83	1.02
Mg	1.76	2.34	2.42
Al	7.77	13.18	9.34
Si	40.87	30.37	23.77
K	3.79	6.2	3.03
Ca	3.79	9.63	5.00
Fe	5.34	11.1	4.32

As seen, the elemental composition is very uneven in the surface and cross-section of ceramic samples. The EDX analysis results show that the ceramic is very inhomogeneous. It is only logical to conclude that this determined significantly higher O (by ~2 times) and C (by ~4 times) concentrations in the PVA coated surface of ceramic compared with uncoated ceramic.

3.1.2. The Investigation of Cation Migration from Ceramics

The dependencies of cation migration from PVA coated and uncoated ceramic samples on the solution pH and the duration of the exposition to the solution were investigated. The amount of cations that migrated to the solution was determined quantitatively with the help of the ICP – MS method. It was discovered that with increasing pH the concentration of Al in the solution decreased steadily. This can be explained by the formation of aluminium hydroxide in alkaline medium. The highest efficiency of the coating for the Al ions was observed in acid medium. The migration of Ca and Mg ions is protected in a similar way. Also, the migration of cations increased with increased exposure time. To summarise, the polymer coating slightly reduces the migration throughout the investigated pH range.

The obtained data reveals that the polymeric PVA coating or pH of the solution has no effect on the migration of Na ions from ceramics to the solution. The results are scattered and non-recurring. The reason for this could be high non-homogeneity of the sample, the rugged and porous surface of the investigated ceramics and unevenness of the polymer coating. The protective coating is not suitable for stopping the sodium ion leaching from ceramic to solution. The results of the investigation of Cr, Li, Sr and Zn ions migration from ceramics are scattered and non-recurring. Also, it was noted that a longer soaking did not cause greater concentration of elements in the solution. Most probably this is due to a very small amount of these ions in the ceramics.

The polymer PVA coating prevents the migration of iron from contemporary ceramic plates to the aqueous solution quite effectively. To summarize the results of the ion migration from contemporary ceramics, it can be stated that the migration of cations to the solution reduced significantly in alkaline medium. Besides, it was noted that longer soaking (up to 12 h) caused greater concentration of elements in the solution.

3.2. The Development of New Methods for the Conservation of Historical Ceramics

3.2.1. The Study of the Composition of the Ceramics from the Monastery of St. Philip

The XRD patterns of the investigated archaeological ceramic samples from the Monastery of St. Philip (Sicily, Italy) are shown in Figs. 3 and 4.

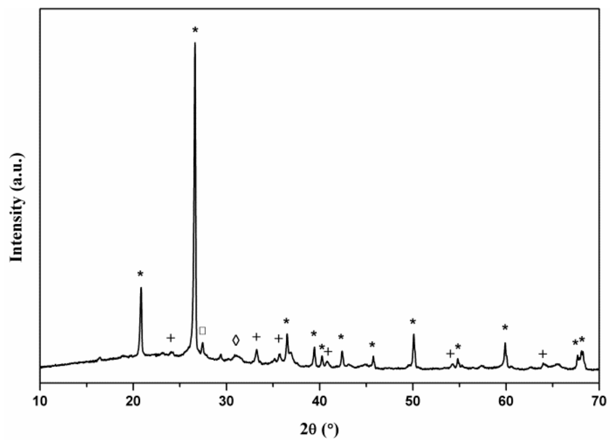


Fig. 3. The XRD pattern of the archaeological ceramic sample I. The crystalline phases are marked: * – quartz, SiO_2 (PDF [46-1045]), + – hematite, Fe_2O_3 (PDF [89-599]), □ - sodium aluminium trisilicate $NaAl_3Si_3O_{11}$ (PDF [46-740]), ◊ – kilchoanite, $Ca_6(SiO_4)(Si_3O_{10})$ (PDF [29-370]).

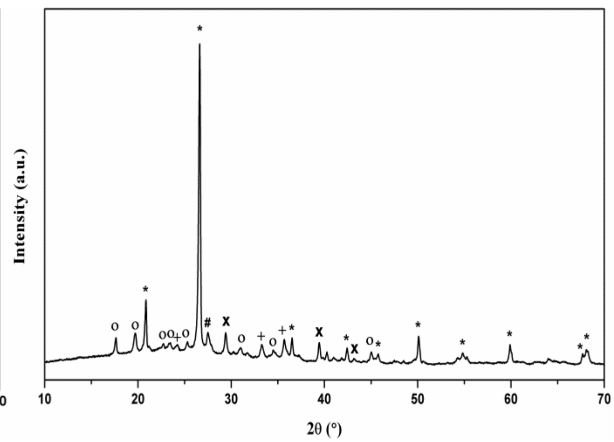


Fig. 4. The XRD pattern of the archaeological ceramic sample II. The crystalline phases are marked: * – quartz, SiO_2 (PDF [46-1045]), + – hematite, Fe_2O_3 (PDF [89-599]), x – calcite, $CaCO_3$ (PDF [5-586]), o – potassium aluminium trisilicate, $KAl_3Si_3O_{11}$ (PDF [46-741]), # – microcline, $KAlSi_3O_8$ (PDF [19-926]).

As seen, quartz (SiO_2) is present in both samples as the main phase. It is obvious that the second main crystalline component in the ceramic sample II is calcite ($CaCO_3$). The calcite phase is very important for the selection of an appropriate method of conservation. Such phases as sodium aluminium trisilicate ($NaAl_3Si_3O_{11}$) and kilchoanite, $Ca_6(SiO_4)(Si_3O_{10})$ were identified in the sample I. Meanwhile, trisilicate ($KAl_3Si_3O_{11}$), microcline ($KAlSi_3O_8$) and calcite ($CaCO_3$) phases were identified in the sample II. Moreover, a negligible amount of hematite (Fe_2O_3) phase was also determined in both samples.

3.2.2. The Study of Surface Morphology and Elemental Composition of Coated and Uncoated Ancient Building Ceramics

The suitability of materials for preserving outdoor ceramic surfaces of ancient buildings was assessed by the SEM characterization. As seen from Fig. 5, the surface morphology of both samples is very different. Sample I consists of plate-like grains with different-size crystallites (3-5 µm). The SEM image of sample II shows flat surface containing more agglomerated particles.

a) b)

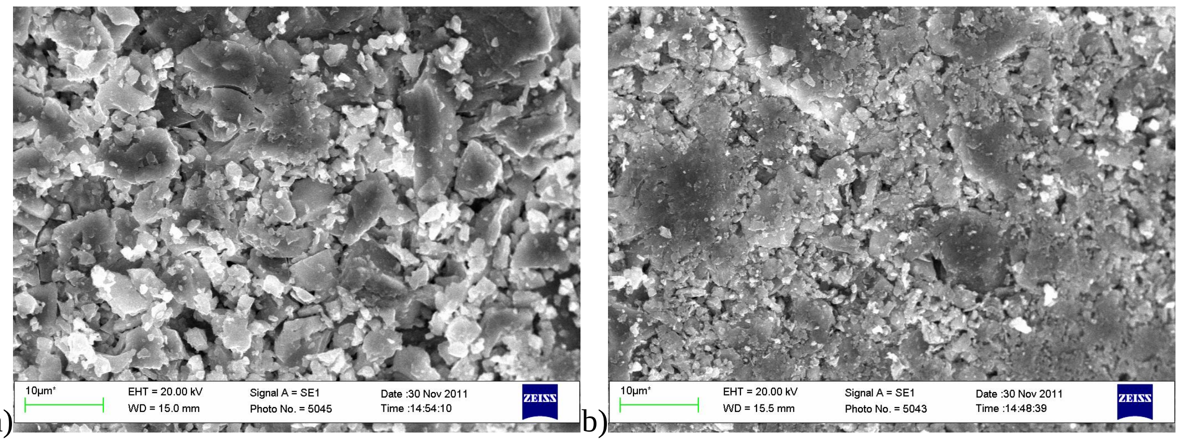


Fig. 5. The SEM micrographs of the archaeological ceramic samples from the Monastery of St. Philip: sample I (a) and sample II (b).

The SEM images of the ceramic samples coated with Plexisol P550-40, Silres BS – 16, Plextol B 500 and Paraloid B-82 are shown in Fig. 6. All SEM images reveal that the surfaces of both samples were successfully coated with polymers; however, the surface of sample II was covered more effectively with Silres BS-16 and Paraloid B-82 coatings.

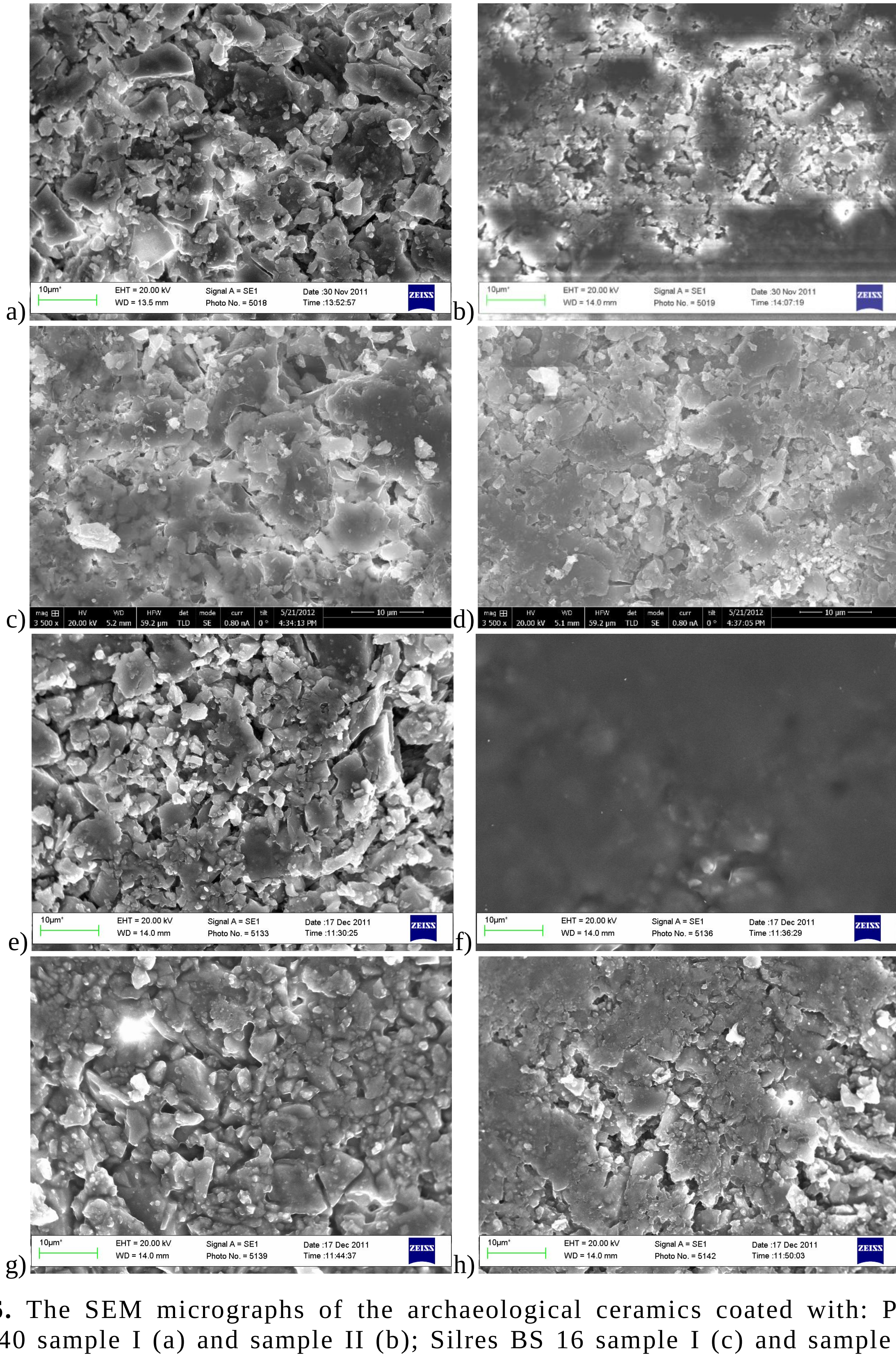


Fig. 6. The SEM micrographs of the archaeological ceramics coated with: Plexisol P550-40 sample I (a) and sample II (b); Silres BS 16 sample I (c) and sample II (d); Plextol B 500 sample I (e) and sample II (f); Paraloid B-82 sample I (g) and sample II (h).

The elemental composition of the historical ancient ceramics from the Monastery of St. Philip was determined with the help of the EDX analysis. The results showed that the elemental compositions of preserved and non-preserved samples were different. The amount of carbon was much higher in the coated ceramic samples in comparison with uncoated ones. These EDX results once more demonstrate that the surfaces of ceramic samples were saturated with polymeric compounds. Other determined elements were distributed evenly in the specimens.

3.2.3. The Characterization of Coated and Uncoated Historical Ceramics with the Help of the Thermogravimetric Analysis

In this part, the historical ancient ceramics was investigated with the help of the TG method. The loss of mass of the ceramic samples during the TG analysis is related to the evaporation of moisture and water of crystallization, the pyrolysis of organic constituents and decomposition of carbonates.

3.2.4. The Characterization of Coated and Uncoated Historical Ceramics with the Help of the Contact Angle Method

The suitability of materials for preserving historical ancient ceramics from the Monastery of St. Philip was assessed by the measurements of the contact angle. As seen, the surfaces coated with Plexisol P550-40 and Silres BS-16 were hydrophobic. (Figs. 7 and 8).

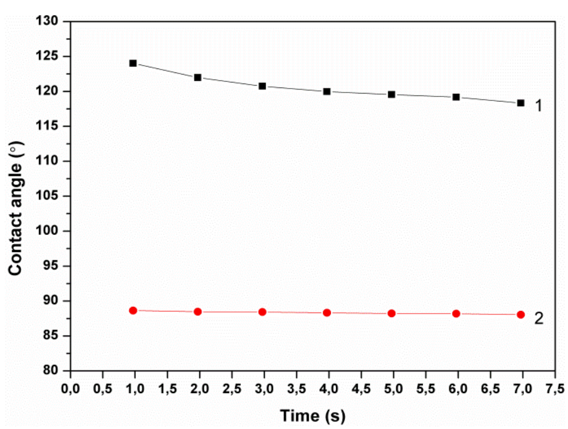


Fig. 7. The changes of the contact angle on the surface of the archaeological ceramic samples I and II coated with Plexisol P550-40. (n=3).

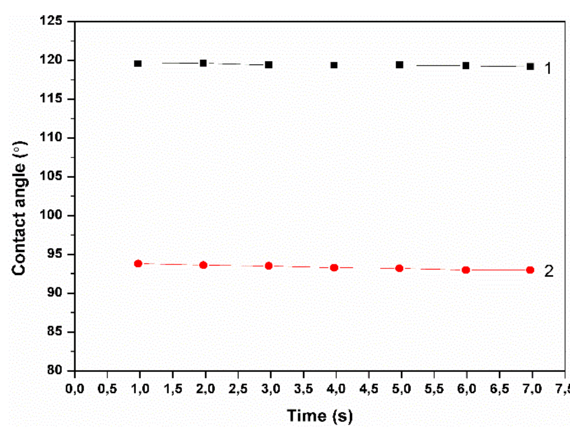


Fig. 8. The changes of the contact angle on the surface of the archaeological ceramic samples I and II coated with Silres BS-16. (n=3).

The contact angle of sample I decreased from 125 ^{o} to 120 ^{o} in 7 seconds. Thus, the following values of the contact angle confirmed that the surface of sample I was hydrophobic. The contact angle of sample II remained stable at around 90^{o}C during 7 seconds. The established dependencies showed the suitability of conservation materials for preserving and protection of the outdoor ceramics from moisture.

3.2.5. The Study on the Migration of Metal Ions from Coated and Uncoated Historical Ceramics

The migration of Mg, Ca, Sr and Ba ions from the ceramics coated with Silres BS-16 was suppressed efficiently, especially in acidic and neutral range of pH. Fig. 9 shows the dependence of the migration of Ca and Mg ions on pH from non-preserved ceramics as well as the ceramics coated with Silres BS-16. The migration of Al, Fe and Mn ions from the ceramics coated with Silres BS-16 was stopped effectively in acid medium. The efficiency of Al ions migration prevention was over 90% in an acid medium (Fig. 10). The remaining three polymeric coatings were effective only in the case of ceramic sample II. It is difficult to assess the results at pH 5 as the value of migrated Al ions from preserved and non-preserved ceramics was on the limit of quantification. The received data showed that the release of aluminium from conservated ceramics was protected in the remaining pH range. It was noted that the more alkaline the environment, the more effective prevention of the Al ion migration. However, neither of the polymeric coatings preserved from the migration of B, Zn and Cu ions in the entire pH range.

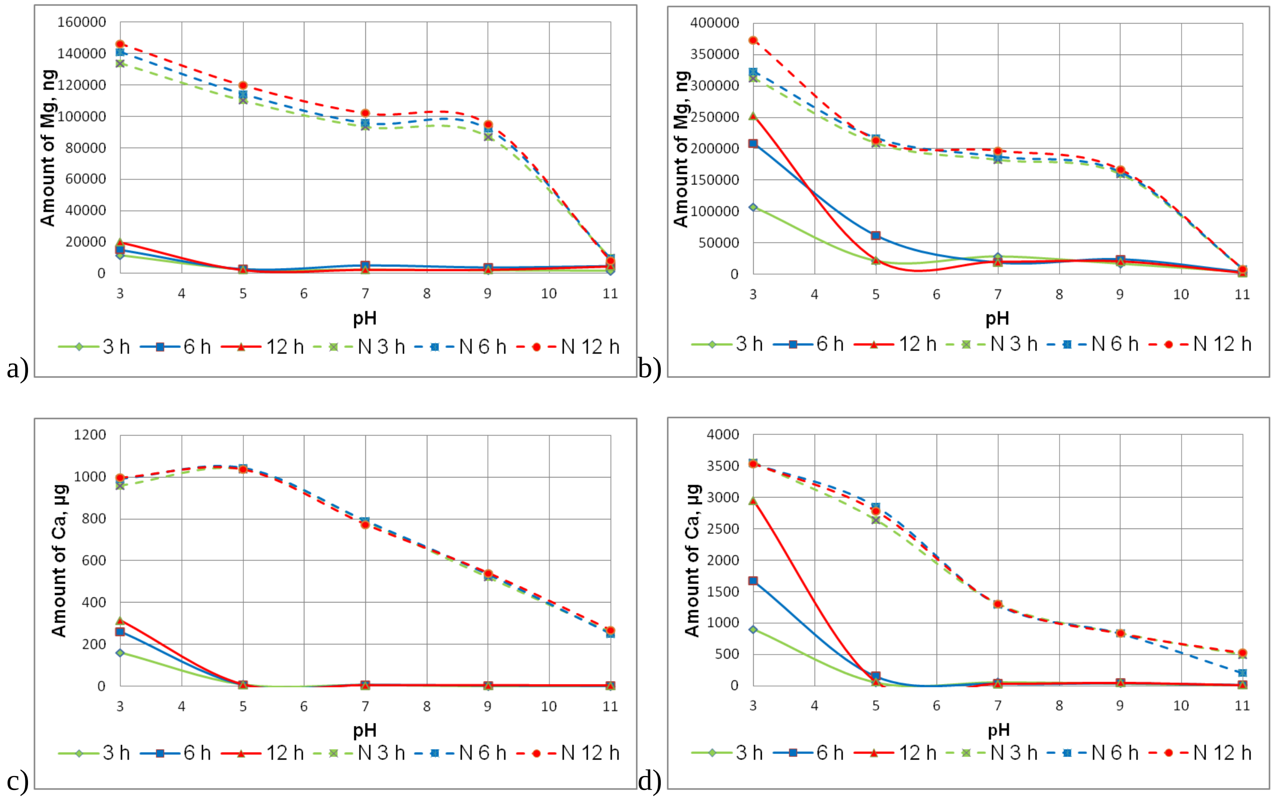


Fig. 9. The results of the migration of Mg ions ((a) sample I and (b) sample II, and K ions ((c) sample I and (d) sample II from the historical ancient ceramics coated with Silres BS-16. The dashed lines indicate non-preserved samples.

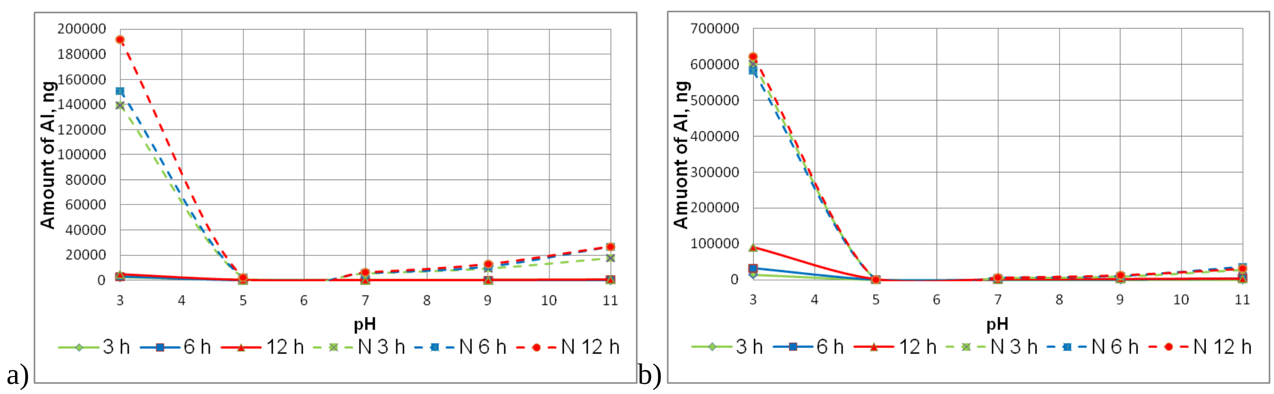


Fig. 10. The results of the migration of Al ions from the historical ancient ceramics coated with Silres BS-16: a) sample I and b) sample II. The dashed lines indicate non-preserved samples.

It was determined that the Silres BS-16 coating protected from the migration of Fe ions. The Plexisol P550-40 and Plextol B 500 coatings released the leaching of iron ions in acidic and neutral media. The protective coating Paraloid B-82 lost its feature to prevent the migration of Fe ions especially in the case of the ceramic sample I. Nevertheless, the migration of iron from the ceramic sample II was suspended in the same way as with other polymer coatings (Fig. 11).

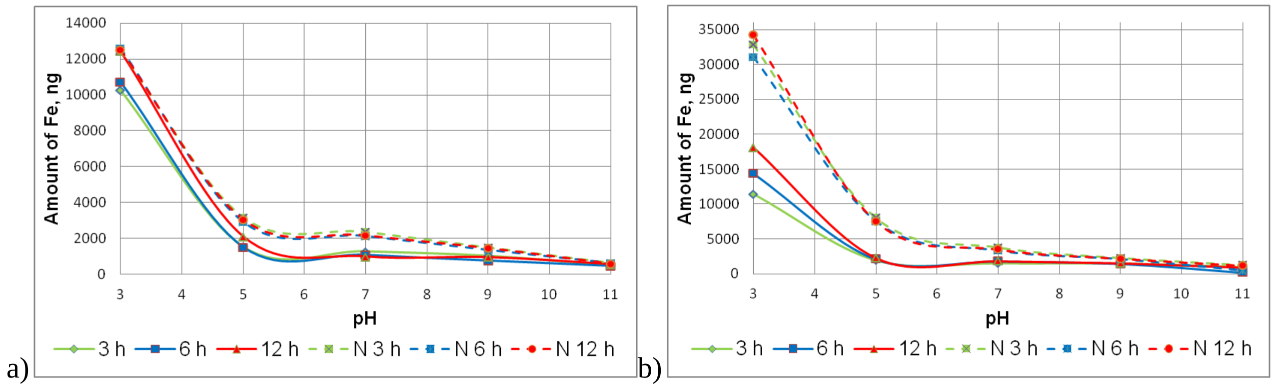


Fig. 11. The results of the migration of Fe ions from the historical ancient ceramics coated with Paraloid B-82: a) sample I and b) sample II. The dashed lines indicate non-preserved samples.

Protective features of Plextol B 500, Paraloid B-82 and Plexisol P550-40 coatings can only be observed with magnesium. The results of the migration of Mg ions from the ceramic sample I are more scattered than the results from the ceramic sample II. Therefore, it is difficult to determine the trends. The coatings prevent effectively the migration of Mg from sample II at pH = 5, 7 and 9. Fig. 12 illustrates the magnesium migration dependency on pH from uncoated ceramics and the ceramics coated with Paraloid B-82.

As it has already been mentioned, the Silres BS 16 coating stops effectively the migration of calcium and barium ions from ceramics throughout the entire pH range. The other three polymeric coating stop effectively the migration of calcium and barium ions but not in the entire pH range. These coatings prevent efficiently the migration at pH = 5, 7, 9; however, they do not prevent the migration of calcium in acid and alkaline medium. Completely opposite trends were observed with Ba. The barium migration from the ceramic sample II was prevented effectively in acid medium; however, the coatings lost their protective features in neutral and alkaline mediums.

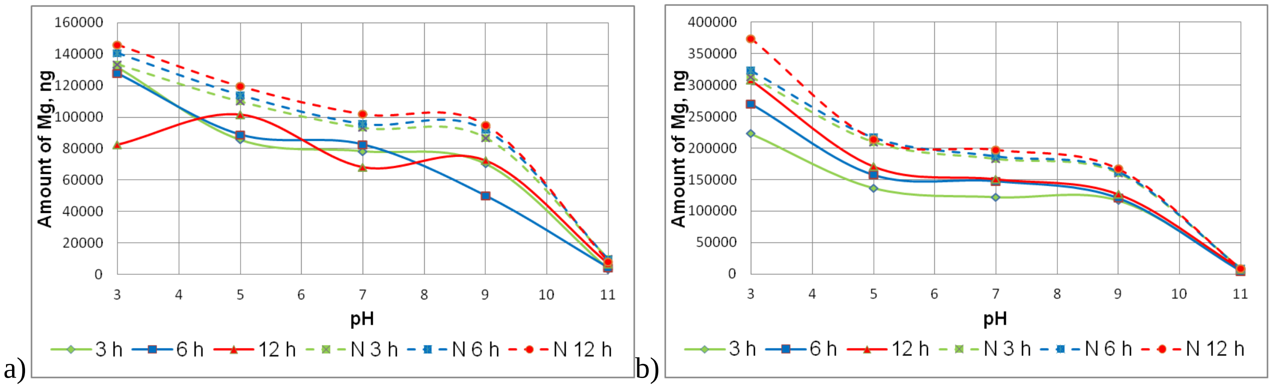


Fig. 12. The results of the migration of Mg ions from the historical ancient ceramics coated with Paraloid B-82: a) sample I and b) sample II. The dashed lines indicate non-preserved samples.

The Silres BS 16 coating stops effectively the migration of Na ions from ceramics throughout the entire pH range (Fig. 13).

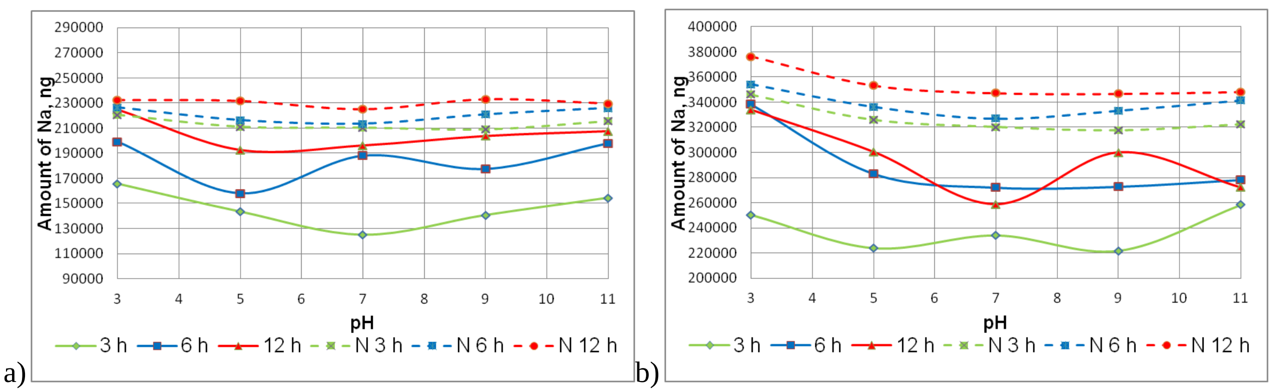


Fig. 13. The results of the migration of Na ions from the historical ancient ceramics coated with Silres BS-16: a) sample I and b) sample II. The dashed lines indicate non-preserved samples.

All other polymeric coatings also protect from the migration of Na ions but it is difficult to interpret the results as they are scattered and have no tendentious dependencies. Highly ambiguous results were obtained from the migration of potassium. For example, the polymer Paraloid B-82 failed completely to protect the release of K from sample I; however, it turned out to be efficient enough in the case of sample II. A similar protective effect was observed with the polymer Plextol B 500. The polymer Plexisol P550-40 protected from the release of K from both samples. However, similarly to the K ions, the migration suspension throughout the pH range was not constant, if we compared the results obtained at different intervals of expositions. The most probable reason to explain this could be uneven properties of the protective coating, which determined the migration of these alkali metal ions.

To generalize, the conclusion was drawn that no universal conservation reagent for this ancient structural ceramics was discovered to protect the ceramics efficiently from the negative environmental impact. Nevertheless, one of the most effective preservatives was Silres BS-16.

3.3. The Conservation and Investigation of the Restored Historical 14th-16th Century Lithuanian Ceramics

The samples of restored historical Lithuanian structural ceramics were prepared according to the 14th-16th century brick production technology, using the clay from the pit in Ukmergė Region.

3.3.1. The Restoration of Historical Lithuanian Ceramics

It is highly important to prepare the raw material properly and correctly in order to produce a high-quality structural brick from clay which must be matured appropriately. During the maturation the clay particles decompose at their weakest bonds. This helps to prevent cracking while heating. Dug out clay contains a high percentage of small stones and other additions. Therefore, the clay was diluted with water to a milky state to remove such impurities by filtration through 300 μm sieves. Fig. 14 illustrates how water was expressed from milky clay.

Fig. 14. The expression of water from milky clay (on the left) and the formation of clay bricks with the help of wooden frames (on the right).

Raw clay was left for final maturation, i.e. for one more winter season. In spring fully matured clay was put into wooden frames to shape a structural brick (Fig. 14). Outside air-dried bricks were placed into wood furnace for the burning at the same temperatures as in the 14th-16th century Lithuania. Identical clay plates (1.5x2.5x0.8 cm) were made from matured raw clay for the experiments. Dry plates were burnt in an electric furnace at the temperatures indicated in Table 2.

Table 2. The mode of heating temperatures for structural ceramics

Step No.	Temperature, °C	Duration of step, h
1	50	1
2	400	7
3	900	5
4	1,100	12
5	25	At 1,100°C the program ends and cools down

3.3.2. The Description of Coated and Uncoated Ceramics

In the previous part of thesis it was determined that one of the most efficient preservatives for the ancient structural ceramics was Silres BS 16. Therefore, the same substance was chosen for the preservation of historical Lithuanian 14th-16th century ceramics. The XRD pattern of the restored ancient structural Lithuanian ceramics is provided in Fig. 15.

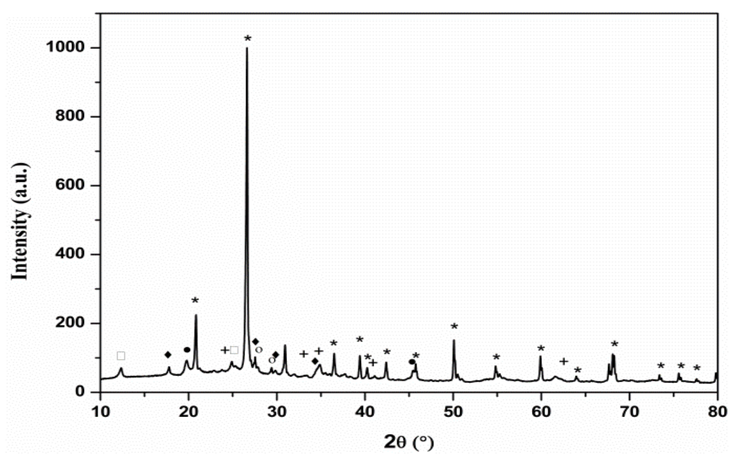
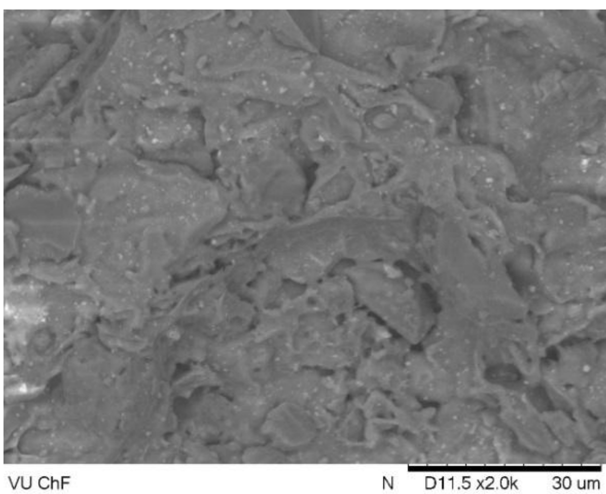


Fig. 15. The XRD pattern of the Lithuanian ceramic brick restored in laboratory conditions. The crystalline phases are marked: * - SiO_2 [00-046-1045]; + - Fe_2O_3 [00-033-0664]; o - $CaTiO(SiO_4)$ [00-025-0177]; ♦ - $(Ca,Na)(Si,Al)_4O_8$ [00-041-1481]; ● - $(K,Na)(Al,Mg,Fe)_2(Si_{3,1}Al_{0,9})$ $O_{10}(OH)_2$ [00-007-0042], □ - $Al_4(OH)_8(Si_4O_{10})$ [00-078-2109].

The main crystalline phase in an industrially manufactured brick sample is quartz. Small amounts of hematite, titanite, albite as well as potassium aluminium silicate hydroxide were also determined. The same crystal substances were discovered in the clay plates made from matured clay for the experiments of this dissertation (Fig. 15). The sample of the brick made according to the instructions used in the Grand Duchy of Lithuania (GDL) additionally contained the phase of kaolinite ($Al_4(OH)_8(Si_4O_{10})$).

The restored historical Lithuanian 14th-16th century ceramics was preserved with the Silres BS 16 polymer. All the samples of restored ceramics were studied by means of the XRD and thermal analyses. The TG and DSC curves of an uncoated sample showed that the sample lost ~0.4% of its weight when heated up to 950 ^{o}C. The TG and DSC curves of the sample coated with Silres BS 16 indicated that the mass loss was twice as high. These results prove that the surface of the ceramics was saturated with the polymer.

The SEM micrographs of the surface of an industrially manufactured brick and restored in the laboratory are given in Fig. 16.

a) 

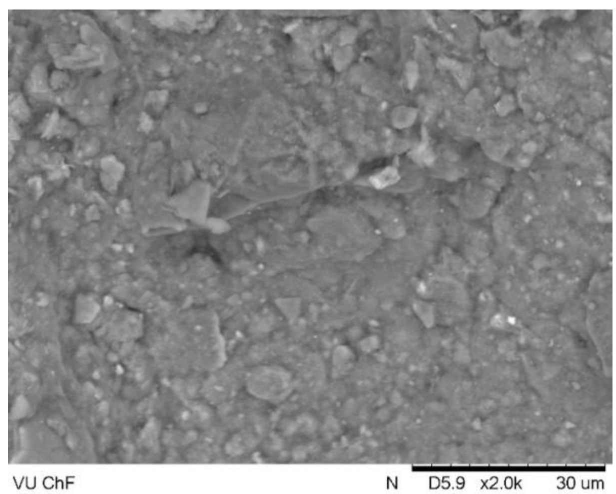
b) 

Fig. 16. The SEM micrographs of Lithuanian ceramic bricks: a) industrially manufactured brick sample, b) the brick restored in the laboratory.

The surface of the industrially manufactured ceramics is comprised of various-sized planar particles (from 3 to 20 μm). The surface is porous, without delocalized cracks. Such surface morphology is usually characteristic of the ceramics burnt at high temperatures. The surface morphology of the restored Lithuanian ceramics is slightly different from that of industrially manufactured. The spherical and planar particles (3-5 μm in size) form agglomerates and thus comprise the entire microstructure of a ceramic product. The SEM morphological study of the restored ceramics sample coated with the Silres BS 16 solution indicated that the surface was coated evenly with the polymer. Moreover, the EDX results showed the presence of carbon (around 44.5%) on the sample surface. These results allowed the drawing of preliminary conclusions that an efficient ceramics conservation method was developed.

The values of the contact angles were measured for the restored and preserved ceramics as well as preserved ceramics samples containing 5% of crushed ceramics. The dependence of the contact angle on time is presented in Figs. 17 and 18.

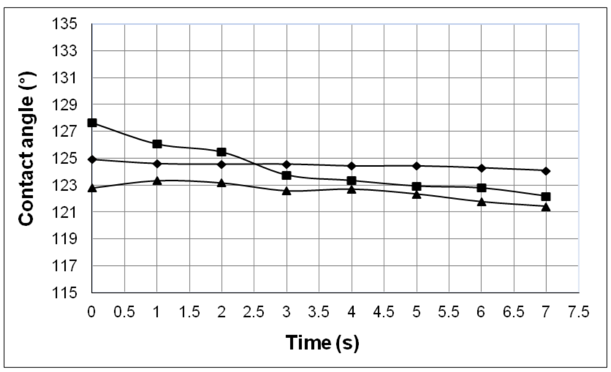


Fig. 17. The changes of the contact angle on the surface of restored historical Lithuanian ceramics coated with Silres BS-16.

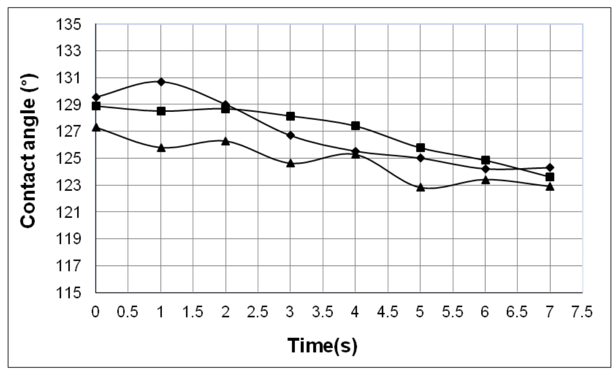


Fig. 18. The changes of the contact angle on the surface of restored historical Lithuanian ceramics coated with Silres BS-16 containing 5% of crushed ceramics.

The dependence revealed in Fig. 17 illustrates clearly that the surface of the restored Lithuanian ceramics was preserved with the Silres BS 16 solution. The contact angle changed from approximately 127.5-125 degrees to 120-122 degrees in 7 s. Fig. 18 shows the contact angle measurement results for the ceramics preserved with 5% Silres BS 16 solution containing 5% of crushed ceramics. The contact angle changed from approximately 129.5-127 degrees to 125-123.5 degrees in 7 s. Thus, it is possible to state that the polymer coating Silres BS 16 and the polymer coating with 5% crushed ceramics Silres BS 16 are suitable for the protection of ceramics from moisture and a negative environmental impact.

3.3.3. The Study on the Migration of Metal Ions from Preserved and Non-preserved Ceramics

Fig. 19 illustrates the calcium migration dependency on time in various pH value solutions.

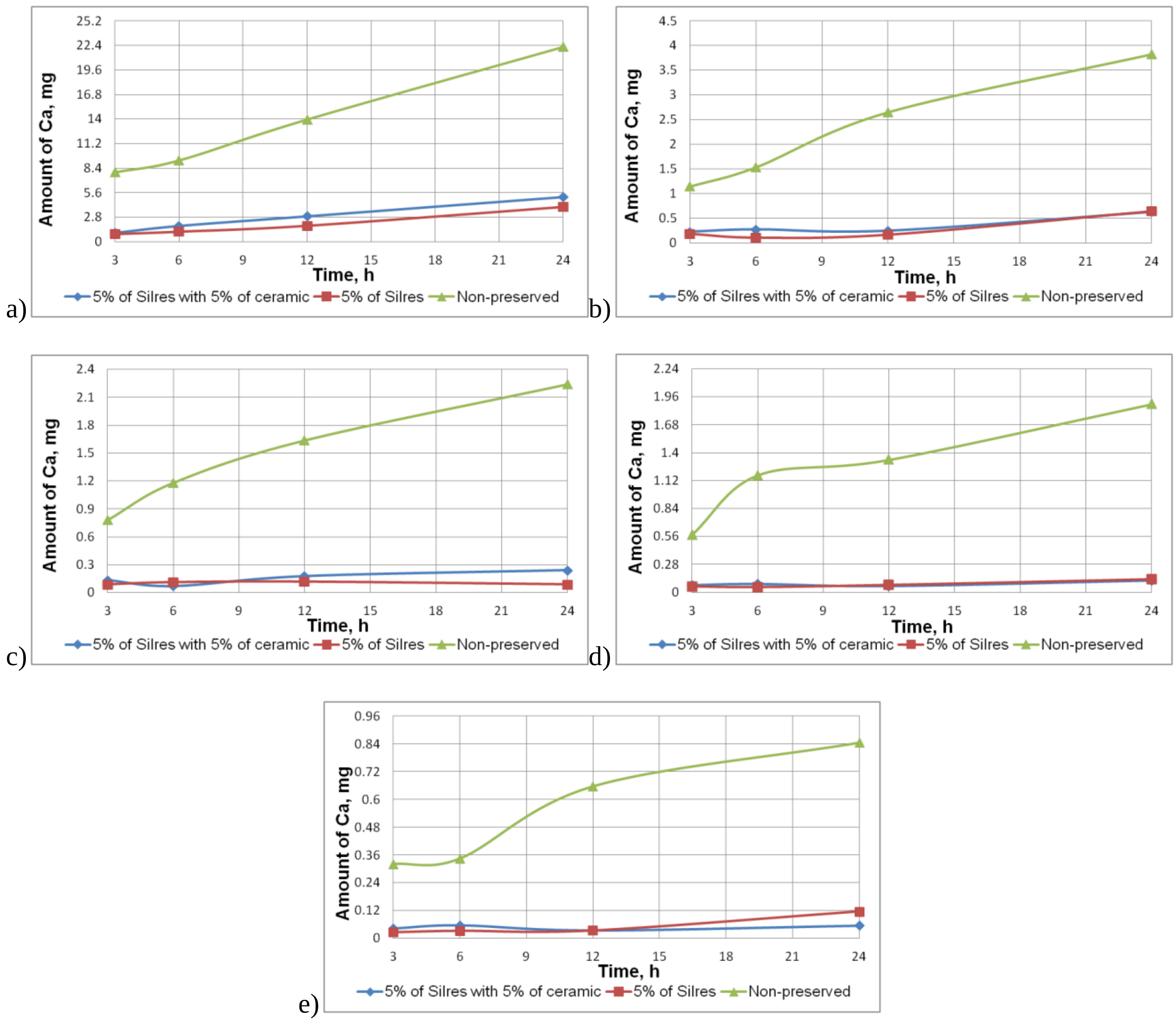


Fig. 19. The dependency on the soaking time of the calcium migration from preserved and non-preserved ceramics: a) pH=3; b) pH=5; c) pH=7; d) pH=9 and e) pH=11.

The received data reveals the tendency that the release of calcium from preserved ceramics is protected effectively by the polymer coating in the pH range from 3 to 11. The migration of Ca ions from preserved historical ceramics does not take place in neutral and alkaline medium for as long as 24 h. However, after soaking in acid medium the small amount of Ca were detected in the solution. The protective impact of the coating on strontium and magnesium is almost identical to that on Ca. Protective features of the coating can be observed throughout the entire pH range. The protective coating loses its feature to prevent the migration of magnesium ions only in alkaline medium. This can be related to the formation of insoluble magnesium hydroxide in alkaline medium.

The polymer coating Silres BS 16 prevents partly the migration of Al ions from the restored Lithuanian ceramics (Fig. 20).

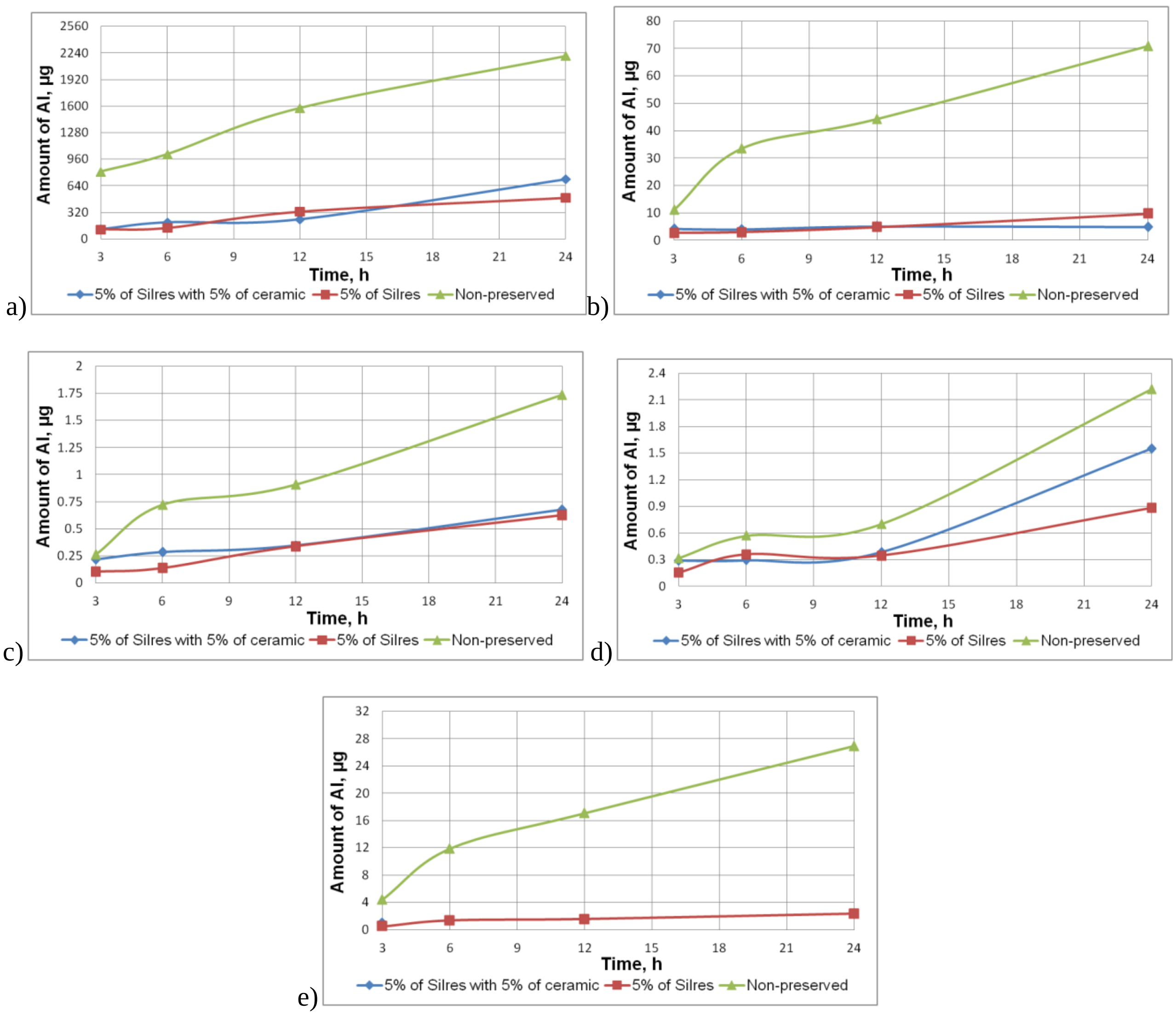


Fig. 20. The dependency on soaking time of the aluminium migration from preserved and non-preserved ceramics: a) pH=3; b) pH=5; c) pH=7; d) pH=9 and e) pH=11.

The provided dependencies reveal that Al is eluted both from non-preserved ceramics and preserved ceramics; however, the amount is significantly lower in the latter case. The migration of Mn and Cu ions is protected in a similar way, yet this polymer preservative prevents the elution of Fe ions only in acid medium (pH=3).

To summarize the results, it can be stated that the coating Silres BS 16 protects efficiently from the cation migration. It should also be noted that when the exposition time is longer, the efficiency of the protective coating increases, which only proves the suitability of this coating for the protection of ceramics from harmful environmental impacts. No big differences between the coating containing 5% of crushed ceramics and the one without it have been observed.

CONCLUSIONS

1. A protective polyvinyl alcohol (PVA) polymer coating was formed on the surface of contemporary ceramics from the enterprise Palemonas. It was determined by means of the scanning electron microscopy (SEM) that rough and porous ceramic surface was covered efficiently with an even polymer PVA coating. Energy-dispersive X-ray spectroscopy (EDS) showed that ceramics was inhomogeneous.
2. Inductively coupled plasma mass spectrometry (ICP-MS) revealed that the polymer coating slightly decreased the migration of Al, Ca, Mg and Fe ions; however, it had no effect on the migration of Li, Na, K, Sr, Cr and Zn ions from ceramics to the solution. The results received allowed the drawing of the conclusion that the polymeric coatings used for the conservation of ceramics indicated in literature do not protect from the elution of cations from ceramics throughout the investigated pH range (from 3 to 11).
3. It was determined that the dominant crystalline phases in the ancient structural ceramics from the Monastery of St. Philip (Sicily, Italy) were quartz (SiO_2) and calcite ($CaCO_3$) along with kilchoanite ($Ca_6(SiO_4)(Si_3O_{10})$), microcline ($KAlSi_3O_8$), hematite (Fe_2O_3) and sodium aluminium trisilicate ($NaAl_3Si_3O_{11}$). It was suggested that ancient structural ceramic samples could be grouped according to the quantity of CaO and MgO.
4. The following preservatives were employed for the conservation of ancient structural ceramics: 5% Plexisol P550-40, 5% Silres BS 16 and 5% Paraloid B-82. The SEM and TG results showed that the ceramic surfaces coated with these substances were more solid and more even compared with uncoated ceramics and were saturated with conservation substances.
5. While performing the contact angle measurements, it was determined that the surface of ancient structural ceramics was preserved sufficiently with currently used 5% Plexisol P550-40 and newly offered 5% Silres BS 16. The surfaces were hydrophobic as the contact angle values exceeded 90 degrees.
6. To summarize the findings of the study on the migration of cations (B, Na, K, Ca, Mg, Al, Sr, Mn, Cu, Zn, Fe, Ba) from ancient ceramics, the conclusion was drawn that no

universal conservation reagent for this ancient structural ceramics was discovered to efficiently protect the ceramics from the negative environmental impact. Nevertheless, one of the most effective preservatives was Silres BS 16.

7. The Silres BS 16 coating stopped effectively the migration of magnesium, calcium, strontium and barium ions from ceramics throughout the entire pH range and efficiently prevented the migration of aluminium, iron and manganese ions in acidic and neutral medium. However, the Silres BS 16 protective coating did not prevent the migration of boron, zinc and copper ions from the samples of ancient ceramics throughout the entire pH range.
8. Historical Lithuanian structural ceramics was restored from the clay obtained in Ukmergė Region using the 14^{th}-16^{th} century brick production technology. It was determined that the main crystalline phases in the heated sample were quartz (SiO_2) along with hematite (Fe_2O_3), titanite ($CaTiO(SiO_4)$), albite ($(Ca,Na)(Si,Al)_4O_8$), kaolinite ($Al_4(OH)_8(Si_4O_{10})$) and small amounts of other aluminium silicates.
9. The restored historical Lithuanian 14^{th}-16^{th} century ceramics was preserved with the most efficient preservative Silres BS 16. The results of the TG, DSC and SEM confirmed proper saturation of the surface of the ceramic samples with the polymer. The contact angle of preserved hydrophobic ceramic samples changed from approximately 129.5-127 to 125-123.5 degrees in 7 s.
10. It was determined that a new Silres BS 16 coating prevented effectively the migration of magnesium, calcium and strontium ions from ceramics throughout the entire pH range from 3 to 11. Aluminium, manganese and copper ions were eluted from preserved ceramics at a slower pace. However, this polymer preservative did not prevent the elution of iron ions from the restored ceramics. The polymer coating was rather efficient in protecting ceramics from the migration of iron ions only in acid medium (pH = 3). Also, when the exposition time is longer, the efficiency of the protective coating increases.

THE LIST OF ORIGINAL PUBLICATIONS BY THE AUTHOR

Articles in Journals

1. T. Petrėnas, O. Opuchovič, J. Senvaitiene, A. Beganskiene and A. Kareiva. A Novel Polymeric Conservation Method of Historical Outdoor Ceramics. *Materials Science (Medžiagotyra),* **21** (2015) 293-297.
2. T. Petrenas, J. Kiuberis, O. Opuchovic, S. Tautkus and A. Kareiva. A Closer Look at the Ancient Bricks of Historical Monuments: Essential Step for the Conservation of Pottery. *Chemija,* **23** (2012) 194–202.

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3. T. Petrenas, O. Opuchovic, A. Beganskienė and A. Kareiva. Possible Conservation Routes to the Historical Outdoor Ceramics. *REHAB 2014: Proceedings of the International Conference on Preservation, Maintenance and Rehabilitation of Historical Buildings and Structures, Tomar, Portugal 19-21 March / Edited by Rogério Am.* (2014) 1099-1105.
4. T. Petrenas, A. Zalga, A. Beganskiene and A. Kareiva. Investigation of Cation Migration from Non-Conserved and Conserved Ceramic Surfaces. *Proceedings of 2nd Int. Conf. "Corrosion and Material Protection,"* Ed. SVUOM Ltd. (2010) Praha, 1-6.

Published Contributions to Academic Conferences

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2. T. Petrenas, A. Zalga, A. Beganskiene and A. Kareiva. Investigation of Cation Migration from Non-Conserved and Conserved Ceramic Surfaces. 2nd Int. Conf. "Corrosion and Material Protection." Prague, the Czech Republic, April 19-22, (2010) 003.
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Proceedings of Ukrainian Conference with International Participation, 15-17 May, 2013, Kyiv, Ukraine.

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ŠIUOLAIKINIŲ KERAMIKOS KONSERVAVIMO METODŲ KŪRIMAS IR PRITAIKOMUMO TYRIMAS

SANTRAUKA

Šiuolaikinės keramikos tyrimams buvo panaudoti Palemono keramikos gamykloje pagamintos statybinės plytos. Šiuolaikinės keramikos paviršius padengtas apsaugine poliviniloalkoholio (PVA) polimerine danga buvo tirtas SEM metodu. Buvo nustatyta, kad grublėtas ir akytas keramikos paviršius buvo efektyviai padengtas lygia polimerine PVA danga. Atlikus EDX analizę buvo nustatyta, kad keramika yra labai nehomogeniška, nes kiekybinis elementų pasiskirstymas įvairiose keramikos vietose, tiek paviršiaus, tiek skersmens plote yra labai skirtingas. Metalo jonų jonų koncentracija tirpaluose, po migracijos tyrimo, buvo tirta ICP-MS metodu. Buvo nustatyta, kad polimerinė danga nežymiai sumažina Al, Ca, Mg ir Fe jonų migraciją, tačiau visiškai neturi įtakos Li, Na, K, Sr, Cr ir Zn jonų perėjimui iš keramikos į tirpalą. Pastebėta, kad ilgėjant mirkymo laikui iki

12 h elementų koncentracija tirpale didėja. Gauti rezultatai leido padaryti išvadą, kad literatūroje pasiūlytas polimerinis keramikos konservavimo metodas neapsaugo nuo katijonų išplovimo iš keramikos visame tirtame pH intervale (nuo 3 iki 11).

Istorinės keramikos tyrimams buvo panaudoti du statybinės keramikos pavyzdžiai iš Šv. Pilypo vienuolyno (Sicilija, Italija). Abiejuose mėginiuose vyraujanti kristalinė fazė buvo kvarcas (SiO2). Antrame mėginyje buvo nustatyta kalcito (CaCO3) kristalinė fazė. Istorinės statybinės keramikos konservavimui panaudoti šie konservantai: Plexisol P550-40, Silres BS-16, Plextol B500 ir Paraloid B-82. SEM tyrimai parodė, jog šiomis medžiagomis konservuotos keramikos paviršius buvo vientisesnis ir tolygesnis lyginant su nekonservuota keramika. TG analizės metodu papildomai įrodyta, kad Šv. Pilypo vienuolyno keramika buvo įsotinta konservavimo medžiagomis, o bandinio sudėtyje yra kalcito. Atliekant kontaktinio kampo matavimus nustatyta, kad geriausiomis hidrofobinėmis savybėmis - kontaktinio kampo reikšmės buvo didesnės nei 90 laipsnių, pasižymėjo keramikos paviršiai dengti šiuo metu naudojama Plexisol P550-40 danga bei naujai pasiūlyta Silres BS-16 danga.

Apibendrinant katijonų (B, Na, K, Ca, Mg, Al, Sr, Mn, Cu, Zn, Fe, Ba) migracijos iš istorinės keramikos tyrimų rezultatus, buvo padaryta išvada, kad nerasta universalaus šios senovinės statybinės keramikos konservavimo reagento, kuris galėtų labai efektyviai apsaugoti keramiką nuo neigiamo aplinkos poveikio. Tačiau vienas efektyviausių konservantų buvo Silres BS 16. Ši danga labai efektyviai sustabdė magnio, kalcio, stroncio, bario jonų migraciją iš keramikos visame pH intervale, o rūgščioje ir neutralioje terpėje efektyviai sustabdo aliuminio, geležies ir mangano jonų migraciją. Tačiau boro, cinko ir vario jonų migracijos iš istorinės keramikos pavyzdžių, Silres BS 16 apsaugine danga neapsaugojo visame tirtame pH verčių interval.

Taip pat, šio darbo tikslas buvo atkurti istorinės lietuviškos statybinės keramikos pavyzdžius ir įvertinus gautos keramikos sudėties ir paviršiaus ypatumus, verifikuoti naują keraminių medžiagų konservavimo metodą. Lietuviška statybinė keramika atkurta pagal XIV-XVI a. Lietuvos plytų gaminimo technologiją, naudojant molį iš Ukmergės rajono karjero. Nustatyta, kad pagrindinė kristalinė fazė iškaitintame mėginyje yra kvarcas (SiO2).

Taip pat keramikoje buvo aptikta hematito (Fe2O3), titanito (CaTiO(SiO4)), albito ((Ca,Na)(Si,Al)4O8), kaolinito (Al4(OH)8(Si4O10) ir nedideli kiekiai kitų aliumosilikatų.

Atkurta istorinė lietuviška XIV-XVI a. keramika buvo konservuota efektyviausiu konservantu Silres BS 16. Keraminių pavyzdžių paviršiaus tinkamą įsotinimą polimeru patvirtino TG/DSC ir SEM analizių rezultatai. Konservuotų hidrofobinių keramikos pavyzdžių kontaktinis kampas per 7 s pakito nuo maždaug 129,5-127 iki 125-123,5 laipsnių.

Apibendrinant jonų migracijos rezultatus, galima teigti, jog nauja Silres BS 16 danga efektyviausiai sustabdo magnio, kalcio ir stroncio jonų migraciją iš keramikos pH intervale nuo 3 iki 11. Aliuminio, mangano ir vario jonų išplovimas iš konservuotos pakankamai efektyviai stabdomas rūgštinėje ir smarkiai šarminėje terpėje. Tačiau šis polimerinis konservantas nesustabdo geležies jonų išplovimo iš atkurtos keramikos. Tik rūgštinėje terpėje (pH = 3) polimerinė danga gana efektyviai apsaugo keramiką nuo geležies jonų migracijos. Taip pat pastebėta bendra visiems jonams būdinga savybė, kad ilgėjant ekspozicijos laikui, migracijos stabdymo efektyvumas taip pat didėja.