Miličić, Ljiljana, Delić-Nikolić, Ivana, Nikolić, Emilija, Jovičić, Mladen, Vučetić, Snežana. “Following the Ancients - Conservation Mortars for the Danube Limes in Serbia”. In: Proceedings pro136: Workshop “Lime-based materials for repairing historic structures”, Eds. Ioanna Papayianni, Jan Válek, Champs-sur-Marne: RILEM Publications S.A.R.L., 2024, pp. 308-319; ISBN 978-2-35158-240-4, e-ISBN: 978-2-35158-237-4

Following the Ancients – Conservation Mortars for the Danube Limes in Serbia

Ljiljana Miličić[1], Emilija Nikolić[2], Snežana Vučetić[3], Ivana Delić-Nikolić[1], and Mladen Jovičić[2]

[1] Institute for Testing of Materials, Serbia, ljiljana.milicic@institutims.rs

[2] Institute of Archaeology, Serbia

[3] Faculty of Technology, Novi Sad, University of Novi Sad, Serbia

Abstract. Sustainable preservation of historic buildings is a long-term process that begins with the analysis of all data related to their creation and further duration and ends with the proposal of measures to preserve their current condition and prevent future damage. In accordance with this, the most important goal of the project *Mortar Design for Conservation - Danube Roman Frontier 2000 Years after - MoDeCo2000*, was set. Data obtained from the archaeological, architectural, and geological context research with the thorough laboratory testing of sampled Roman mortars along the river Danube in Serbia was used to create valuable proposals for the design of compatible mortar mixtures that could be used for the conservation of the structures in the investigated area.

1 Introduction

The topic of this paper is a review of the procedures carried out within the *MoDeCo2000* project, in order to form proposals for the design of mortars that could be recommended for the conservation of monuments along part of the former Danube Limes in present-day Serbia [1]. The investigated buildings are dated to the period from the 1st to the 6th century AD and are currently on the preliminary list for the UNESCO World Heritage List, under the name *Frontiers of the Roman Empire – The Danube Limes (Serbia)* [2].

To create the proposals, laboratory research of a large number of mortar samples originating from 40 built structures from many archaeological sites was performed. In the laboratories, while respecting the principle of compatibility, which means that the new mortar in no way endangers the old material or the structure built from it [3], mortar recipes based on local raw materials were prepared. The technology of making new mortars was based on traditional techniques, whose traces of use throughout history can often be identified through the analysis of old mortars.

2 Process Methodology

Work on the design of conservation mortars during the *MoDeCo2000* project includes the following actions:

- Multidisciplinary research on the spatial context and the choice of structures
- A sampling of the historical mortars from the chosen structures
- Laboratory research of sampled mortars
- Interpretation of the research results
- Search for raw materials
- Design, creation, ageing, and examination of conservation mortars
- Application of conservation mortars in the laboratories and on-site
- Monitoring and examination of applied conservation mortars
- Conclusions with recommendations for the future use of the mortars
- Publication of the project results

After conducting the first four steps, it was concluded that the project *MoDeCo2000* should offer an overall picture of the technology involved in the preparation of Roman mortars and of the use of raw materials, along the large area of 588 km of the Danube flow through the Republic of Serbia. It should also provide recommendations for the preparation of conservation mortars, with numerous possible recipes of compatible mortars. These should then be modified in future, based on further trials and in situ applications at a particular structure within a site. The interpretation of the results of mineralogical, chemical, and analyses of physical and mechanical properties of historic mortars provided necessary data for the creation of the composition and component ratios of new mortars, with the overall aim of fulfilling different criteria as part of mechanical, chemical, and aesthetical compatibility [3].

Fig. 1 Raw materials used during the design of conservation mortars (Photo-documentation of the MoDeCo2000 project)

Following this, the search for raw materials recognised in the historic mortars was conducted. The archaeological site of *Viminacium* [4] is one of the best researched along the Danube Limes in Serbia and it offered us many samples of historic mortars, having various roles in structures (bedding, rubble core, rendering, plastering, and floor mortars), that were used in the buildings of different functions. Since several sites of ancient and modern exploitation of raw materials are situated in its surroundings - the deposits of the schist from the nearby village of Ram, the clay used for the today's local manufacture of bricks, and the layers of rock and soil naturally burnt by the combustion of the lower coal layers and solidified into the natural brick [5], they were all visited and various different raw materials were sampled for further research.

The preparation of the laboratory models of mortars included the use of quicklime, slaked lime (lime putty) and river aggregate of different grain sizes, but also crushed and ground brick, and crushed stone and clays of different origins, which were added to mortar mixtures to improve the properties of their basic mass and give them performance close to that of historical mortars (Fig.1).

After research into the characteristics of the Danube sand and gravel exploited at different sites along the river, it was concluded that they vary minimally and, thus, their exact local origin was not considered important for the choice of aggregate that would be used in the new mortar mixtures. Considering the binder, it was very important to have a good quality lime for the laboratory models. Since the origin of limestone used for the mortars along the Danube Limes was not precisely determined, we have endeavoured to find the one that satisfies the essential need – the reactivity, and that could be produced using traditional firing technologies in lime kilns. Our choice was the lime from the central part of Serbia. However, being limited by the project duration, we used lime whose age ranged from 3 to 6 months. Since the concept of the project relies on the use of local raw materials, and in the territory of Serbia, the production of hydraulic lime was not developed, all models were created with non-hydraulic lime. The DSC/TG/MS analyses of sampled historic mortars gave a direction for the research on the use of hydraulic lime for their preparation. However, based on current knowledge, it cannot be presumed that Romans used hydraulic lime along the Danube Limes in Serbia on purpose, and the presence of impure limestone in the Roman lime kiln could often have been a coincidence [6]. The future research of the found lime lumps will hopefully give us more information.

3 Design of Conservation Mortars

During the design of conservation mortars, the characterisation of their component materials was carried out. The slaked lime-putty contained 26% of free water, so it was not necessary to add additional water to the mortars prepared with it. The content of inextinguishable particles in it is 0.56%, which classifies it as lime of good quality. Quicklime was highly reactive, and by measuring the slaking speed we obtained a value of about 16°C/min. Inextinguishable particles were present in the amount of 0.12%, and the yield was 3.8 dm^3/kg, which also confirmed its good quality [7].

The sand and gravel originating from the Danube were used in fractions of 0-2mm, 0-4mm, and 2-4 mm, in different percentages. The presence of brick was determined in a large number of historic mortar samples, so several series of mortars with a different participation of crushed and ground bricks scattered in fractions of 0-1 mm, 1-2 mm, 2-4mm, and 4-8 mm were prepared. The bricks were Roman, originating from *Viminacium*, but also modern bricks made by crafstmen in Serbia using local raw materials (firing temperature is around 900°C), since it cannot be expected that in future conservation processes ancient bricks will always be available for use in mortars. The amount and fraction of added bricks were also varied in order to obtain a colour that is close to that of the original mortars. In addition to the aforementioned clay from the Viminacium area that was ground in the laboratory, kaolin clay, whose mineral kaolinite was confirmed by XRD as present in some sampled historic mortars of very high compression strength, was also used. However, since the origin (or the occurrence) of the found kaolinite is still unknown, and the thermally activated kaolin clay (metakaolin) is not produced in Serbia [8], kaolin clay from Central Serbia was used and activated by grinding (to get micron particles) [9], to better react with lime. The use of kaolin clay was conducted only in the mixture with slaked lime, since large evaporation during the slaking of quicklime (the temperatures are over 100°C) would leave the clay with insufficient water for the reaction with lime, and the further addition of water would decrease the mechanical properties of the mortar mixture. The process of creating a mortar mixture with satisfactory characteristics would be feasible in laboratory conditions, but this would not be the case on site. The zeolite mineral clinoptilolite was also confirmed in particular historic mortars. It was found independently, but also in combination with kaolinite. This combination was found in the mortar having the highest compression strength of all examined samples – 15.7 MPa. Only a few studies have been done in Serbia related to the potential use of zeolite in conservation mortars [10,11]. Thus, various conservation models with the addition of these natural materials with pozzolanic properties were created and are currently being cured in laboratory conditions. The models with "natural brick" (whose pozzolanic features were investigated [5]) will also be made in the future.

The ratios between the raw materials were determined with the aim of achieving their optimal mutual relationship and the highest possible level of compatibility of the new model with the historical sample. For each ratio of binders and aggregates of historical mortars, two or three mixtures were made, and their ratio varied by a small percentage. For example, for the binder-aggregate ratio 40:60 (volume ratio), models were prepared with the final result of the binder-aggregate ratio in the range from 35:65 to 45:55. In this way, a wider range of ratios is covered, since mortars sampled from the same building sometimes had almost the same compositions and a slightly different ratio of binder to aggregate.

Slaked lime mortar mixtures were prepared using hand tools and mixing a measured amount of aggregates and additives without adding water, while in the quicklime process water was slowly added with constant stirring until a mortar of a consistency suitable for pouring into moulds was obtained. During the preparation of the mortar with quicklime, it was slaked, the exoteric reaction led to the intense release of heat, and the temperature of the mortar rose. The mixtures were installed in moulds measuring 50 x 50 x 50 mm, and cured for 7 days in standard laboratory conditions, after which the samples were removed from the moulds and air-cured for another 28 days, without exposure to increased humidity or water, in standard laboratory conditions, on grid supports, and open on all sides. To test the compatibility, other samples were prepared, in which a piece of old mortar was pressed into the newly prepared fresh mortar. The contact formed between the new and old mortar was monitored, and some samples are still being tested (compression strength tests at 28/90 days after mould removal). In all models, the appearance of cracks and flakes, visual appearance and colour were monitored. After 35 days, the physical and mechanical properties, i.e. compression strength (Toni Technik, model 2020), bulk density, visual appearance, and colour were tested. Their smooth surface was always lighter in colour due to the smoothing of the mortar during the moulding, which draws a larger amount of binder to the surface, which usually has lighter shades than the aggregates and additions. Thus, the visual appearance was observed, and the colour was measured on the obtained fractures with a portable spectrophotometer (ColorLite sph870) (Fig. 2).

Fig. 2 Conservation mortar models - measuring components, manual mixing of mortar, moulding (top); mortar components, testing compression strength, and colour measuring (bottom) (Photo-documentation of the MoDeCo2000 project)

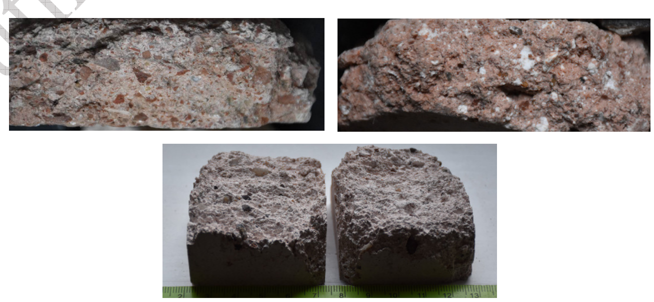

Fig. 3 Work on the conservation mortar model for a floor mortar (Photo-documentation of the MoDeCo2000 project)

After the design and testing of the dozens of conservation models, the most suitable were selected and they were applied, in open-air conditions in the *Viminacium* Archaeological Park, to experimental masonry structures (using different types of stone and brick), and to authentic walls of a tomb near Belgrade (in the village of Brestovik), dated to the period from the 3rd - 4th century CE [12]. The mortars were prepared on site by craftsmen using hand tools, as were the ingredients (crushing of brick and stone, and the comminution of local clay). The condition of the applied mortars is currently being monitored.

As an example, a sample of a floor mortar is shown here (Fig. 3) - original sample (top left), conservation mortar sampled from the trial application in open-air conditions, where it was created by the manual mixing and use of quicklime (top right), and its laboratory model after the compression strength test was completed (bottom). Lime lumps are clearly visible in the conservation mortar, being larger than in the original sample. The compression strength of the conservation mortar prepared and applied by craftsmen, and cured in open-air conditions, was lower than the strength of the more compact model formulated in the laboratory by equipment and cured in a closed and controlled atmosphere for the same period. Work on the optimisation of the model will continue.

4 Discussion of the Laboratory Results

Following the activities on the preparation of conservation mortar mixtures in the laboratories (Table 1), certain conclusions were gained.

All samples made with quicklime had higher values of compression strength, except one, the one with the highest mass (g) of the brick addition (the percentage of the brick addition was 1.6 times higher than the sand aggregate). The lowest values of compressive strength were obtained in models with slaked lime, in which part of the aggregate was replaced with crushed schist grains - up to 0.74 MPa. The values gained in models with quicklime were up to 2.13 MPa, so the samples with the addition of schist showed the greatest difference between the values of compression strength gained with the use of slaked and quicklime. These models will be researched further.

Mortars based on aggregates and lime without additions reached a strength of up to 1.12 MPa in mixtures made with slaked lime, while mixtures with quicklime obtained compressive strengths up to 1.92 MPa. This difference can be attributed to the accelerated hardening reaction in quicklime due to the initial high temperature obtained by releasing energy during hydration, which raises the temperature of the mortar, causing the excess water to evaporate. Considering that the period of 35 days is short for reaching the final strength of lime mortar [13], it is expected that the previously mentioned values will be closer to each other over time.

Table 1. Selected laboratory models for conservation mortars sorted by the increase of the compression strength – with slaked lime (table left); with quicklime (table right) (Documentation of the *MoDeCo2000* project)

sample	aproximate ratio (vol.) binder/aggregate	compression strength (MPa)
11G	60/40	0.49
10G	60/40	0.72
9G	60/40	0.74
4G	50/50	0.82
6G	50/50	0.88
8G	30/70	0.94
5G	50/50	0.98
7G	30/70	1.01
1G	40/60	1.06
2G	40/60	1.08
3G	40/60	1.12
14G	50/50	1.64
13G	40/60	1.97
16G	50/50	3.54
15G	40/60	5.23

sample	aproximate ratio (vol.) binder/aggregate	compression strength (MPa)
13Ž	40/60	1.15
1Ž	40/60	1.50
11Ž	60/40	1.74
2Ž	40/60	1.84
10Ž	60/40	1.87
7Ž	30/70	1.88
3Ž	40/60	1.92
6Ž	50/50	1.99
14Ž	50/50	2.05
5Ž	50/50	2.08
9Ž	60/40	2.13
4Ž	50/50	2.31
12Ž	50/50	2.56
13ŽP	40/60	2.63
16Ž	50/50	2.73

no additions
modern brick
ancient brick

schist
clay
kaolin clay

The already known facts that smaller fractions of bricks (brick dust) contribute to a higher strength of mortar and that bricks baked at lower temperatures, i.e. fragments of bricks taken from archaeological sites, show much better results in terms of pozzolanic features than modern bricks fired at higher temperatures [14,15], were confirmed by making conservation models with different brick fractions of both ancient and modern products. At lower brick firing temperatures (up to 900°C) there is no complete formation of the ceramic structure, so in such bricks minerals are retained that have only lost their crystal structure, and whose pozzolanic properties have, thus, been expressed. The mixtures with ancient bricks that had the largest percentage of the smallest fractions showed the highest compression strength of all mortar models made with quicklime (2.73 MPa), while those with the slaked lime were second best (3.54 MPa).

The strengths of clay mortar mixtures range from a maximum of 2.63 MPa in mixtures with quicklime and ground local clay, to a maximum of 5.23 MPa in mixtures with slaked lime and activated kaolin clay. The last value also represents the highest strength of all models made so far. It is expected that mortars with the addition of more, different, natural materials with pozzolanic features detected in particular samples will gain even higher compression strengths. Interestingly, the models with quicklime and local clay showed the lowest and almost highest values, depending on the amount of water, where the higher amount produced much weaker mortars, which is in accordance with the previously discussed reason for not using quicklime with thermally treated kaolin clay.

5 Conclusions

As has already been mentioned, the conservation mortar models of the *MoDeCo2000* project were made in accordance with the overall data interpretation gained after the research of all sampled historic mortars. It was concluded that for the production of lime mortars in the Roman period, used for the building of the Danube Limes, the same raw materials were used – Danube river aggregate, lime, and brick, while local stones were sometimes used as part of the aggregate. However, a few samples were very characteristic, having natural additions with pozzolanic features in their composition and, thus, possessing great mechanical characteristics. They were researched independently and the conservation mortars based on these samples are currently being created as separate case studies. The results are expected to give directions for the improvement of the mortar models already created.

Although many mortar mixtures were created and examined through the project, its intention was not to provide final mortar recipes for all sampled buildings. Detection of historic raw materials and technologies used in the ancient period, as well as the laboratory and open-air (on-site) trials of many mixtures made with different natural materials available in Serbia, have created a solid base for future conservation works on any Roman site along the former Danube Limes in today's Serbia. When the time for the restoration or repair of a particular building comes, the responsible team of conservators can securely lean on the project conclusions, but would also need to build upon them with further data and research. The choice of conservation mortar depends on the characteristics and conditions of the original mortar, but also the position and exposure of the structure, the function of the conservation works, and aesthetics [13]. Particular conservation mortars should be designed based on the level of presentation, the need for structure repair or maintenance, and the decision as to whether the building will be covered by the protective construction and protected from the violent exterior conditions, or completely exposed to them. In the end, each historic structure is unique in its own particular way, and all conservation works should be carefully planned and preceded by scientific and professional research.

6 References

1. Korać M, Golubović S, Mrđić N, Jeremić G, Pop-Lazić S (2014) Roman Limes in Serbia/ Rimski limes u Srbiji. Institute of Archaeology, Belgrade
2. UNESCO (2015) Frontiers of the Roman Empire – The Danube Limes in Serbia. https://whc.unesco.org/en/tentativelists/6475/. Accessed 28 February 2022
3. Schueremans L, Cizer Ö, Janssens E, Serre G, Van Balen K (2011) Characterization of Repair Mortars for the Assessment of their Compatibility in Restoration Projects: Research and Practice. Constr Build Mater. 25/12: 4338-4350
4. Korać M (2019) Viminacium. Urbs et castra legionis. Research, Protection, Presentation and Valorisation. Institute of Archaeology, Belgrade
5. Nikolić E, Tapavički-Ilić M, Delić-Nikolić I (2022) Viminacium Landscape (Trans)formation. In: D'Amico S, Venuti, V (eds) Handbook of Cultural Heritage Analysis. Springer Nature Switzerland

6. Nikolić E, Rogić D (2018) Short Observations on the Possible Hydraulicity of Viminacium Lime Mortars Based on the Results of the Laboratory Research. Archaeology and Science 14/2018:39-50
7. BS EN 459-1:2015 (2015). Building Lime - Part 1: Definitions, Specifications and Conformity Criteria
8. Ilić B, Mitrović A, Miličić Lj, Zdujić M (2018) Compressive Strength and Microstructure of Ordinary Cured and Autoclaved Cement-based Composites with Mechanically Activated Kaolins. Constr Build Mater. 178: 92-101
9. Ilić B, Mitrović A, Miličić Lj (2019) Mechanically Activated Kaolin as Supplementary Cementitious Material. In: Proceedings of the 15th International Congress on the Chemistry of Cement (ICCC 2019) Prague, Czech Republic
10. Николић Е (2014) Примена кречног малтера приликом рестаурације римског амфитеатра Виминацијума током 2013. године. In: Младеновић Д, Васић-Петровић, Е (eds). Грађевински материјали и конзерваторско-рестаураторски поступци – малтери. Београд, Друштво конзерватора Србије
11. Aškrabić M, Zakić D, Savić A, Miličić Lj (2019) Effects of natural zeolite addition to lime based render layers for restoration of historical buildings. In: Ignacio Álvarez J, María Fernández J, Navarro Í, Durán A, Sirera R (eds). 5th Historic Mortars Conference, Pamplona, Spain, Proceedings PRO 130. Paris, RILEM Publications
12. Vučetić S, Nikolić E, Jovičič M, Delić-Nikolić I, Miličić Lj, Ranogajec J, Hiršenberger H (2022) Design of Compatible Mortars for a Late Roman Tomb in Serbia. In: The proceedings of Heri-Tech - The Future of Heritage Science And Technologies Conference (in print)
13. Henry A, Stewart J (2011) English Heritage Practical Building Conservation. Mortars, Renders & Plasters. Ashgate Publishing Limited, Farnham
14. Teutonico JM, McCaig I, Burns C, Ashurst J (1993) The Smeaton Project: Factors Affecting the Properties of Lime-Based Mortars. APT Bulletin: The Journal of Preservation Technology 25/3-4:32-49
15. Nikolić E. Rogić D, Milovanović B (2015) The Role of Brick in Hydraulicity of Viminacium Mortars: Decorative Mortars from the Thermae. Archaeology and Science 10/2014

Funding: This research was supported by the Science Fund of the Republic of Serbia, PROMIS, #6067004, MoDeCo2000. **Author Contributions:** Sampling of raw materials, I.D.N., M.J., E.N, and Lj.M..; laboratory work, Lj.M., S.V., I.D.N., and E.N.; on-site work, E.N, M.J., S.V., Lj.M., and I.D.N.; writing - original draft preparation, Lj.M., and E.N.; writing - review and editing, E.N., Lj.M., I.D.N., S.V., and M.J.; and supervision, E.N. All authors have read and agreed to the published version of the manuscript. **Conflicts of Interest:** The authors declare no conflict of interest regarding this manuscript. **Acknowledgments:** The authors are grateful to prof. Jonjaua Ranogajec from the Faculty of Technology Novi Sad, for the participation in the research activities, as well as to Nevenka Mijatović, from the Institute for Testing of Materials, for conducting XRF analyses.