BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. 69(1), 2021, Article number: e136042
DOI: 10.24425/bpasts.2021.136042

Microscopic methods for analysis of mortars from historical masonry structures

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Abstract. The process of historical building conservation includes the repair of mortars eroded due to material and environmental factors. Identification of old mortar constituents is necessary to enable duplicating the material. Information on the binder and aggregate types and contents can be obtained from microscopic observation used in combination with instrumental methods. This paper presents the results of microstructure and mineral composition tests of mortars collected from the walls of thirteenth century buildings. A combination of techniques was used, which included X-ray diffraction, transmitted light optical microscopy and scanning electron microscopy with micro-area elemental composition analysis. The test results revealed porous lime and sand mortars with a binder-aggregate ratio often beyond the commonly adopted values. The mortars contained sand grains of up to 0.5 mm and larger pieces of limestone, flint, feldspar and brick. Transmitted light optical microscopy and scanning microscopy were found to be essential techniques for mortar characterization in existing buildings and structures.

Key words: historical buildings; mortar; microscopic methods.

1. Introduction

Mortars in historical buildings served both functional and visual purposes, serving to bond bricks and stones together or provide plaster and render coatings, flooring foundations or ornamental finishing [1]. About two centuries ago, clay, gypsum and lime were the most common binders. They were later replaced by Roman cement and subsequently by Portland cement, now the dominant type of binder used in construction. The compositional complexity of historical mortars reflects regional and temporal variations [2]. In Poland, lime was the predominantly used binder in historical mortars, often with an addition of clay or organic fibers.

One of the elements in the process of historical building conservation is the repair of mortars eroded due to material and environmental factors. Identification of old mortar constituents is necessary to produce a matching material for original masonry. In the engineering of building materials, there is also a tendency to control the properties at an even lower, i.e. subtler, level of microstructure [3]. Information on the type and content of the binder and aggregate can be obtained from microstructure tests performed with the use of microscopic techniques and mortar phase composition methods. These include X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), thermal methods and infrared spectroscopy. Mineralogical identification and quantification outcomes should be confirmed via several methods [4, 5].

In order to ensure that suitable materials are obtained in sufficient quantity, the spatial and temporal distribution of mortars in building components is taken into account even before sampling starts. The purpose of the test (maintenance, repair, scientific or archaeological research) and the formulation of damage mechanism hypotheses determine the choice of analytical method. The method requires a specific type of samples in relevant quantity. Before samples are taken, the location of the object should also be described, photographic documentation should be made, the condition of the mortar should be recorded and sampling methods should be described. When extracting samples from historical buildings, destruction and damage should be minimized. In the case of historical buildings, statistically sufficient, limited quantities of samples are accepted due to the culturally valuable nature of the materials. In the case of mortars, they can stand at about 100 g [6].

The samples should be representative and collected by experienced researchers, thus avoiding later problems with testing and interpretation of results. Proper sampling and test sample preparation is critical; care must be taken to cause minimum or no physical damage to the historical structure.

The objective of this paper was to characterize the microstructure of mortars collected from the walls of thirteenth century buildings. The testing was conducted using transmitted light optical microscopy and scanning microscopy combined with micro-area elemental composition analysis.

2. Testing materials and methods

2.1. Materials. The samples were collected from the mortar joints in the walls of thirteenth century sacral buildings currently under conservation. The designation of the samples and types of structures from which the mortars were collected are summarized in Table 1. Immediately after sampling, mortar samples, 150 g each, were placed in sealed containers and fur-

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Manuscript submitted 2020-09-25, revised 2020-11-06, initially accepted for publication 2020-11-17, published in February 2021

Table 1
Designation of samples and collection sites

Sample designation	Type of structure	Construction period
Z1	belfry of the Dominican monastery	late 13th century
Z2	cellar of the Dominican monastery (Sandomierz)	late 13th century
Z3	post-Cistercian chapter house (Koprzywnica)	13th century

ther tests were carried out under laboratory conditions. Photographs of the historical buildings are shown in Figs. 1–3.

The photograph in Fig. 1a shows a belfry of the Dominican monastery in Sandomierz, added to the western wall of the Romanesque church in the 2nd half of the thirteenth century. The brick structure with a stone plinth has remained unchanged since its erection. Despite its artistic and historic value, it has never undergone any professional conservation. As a result, serious damage has been done to the original bricks and mortar joints. The mortar test samples were collected from the southern external wall at the height of 2.5 m above ground level (Fig. 1b).

Fig. 1. a) Dominican monastery belfry, Sandomierz, 1b) sampling point

The photograph in Fig. 2a shows the Romanesque cellar of the Dominican monastery in Sandomierz. The rectangular brick structure with a cross vault supported with a central octagonal column is located in the southern part of the monastic foundation. The main structure was erected in the 2nd half of the thirteenth century. Today it is a valuable source of knowledge, providing information of significant importance for the studies of Romanesque architecture.

The mortar samples were collected from the western internal wall, 1 m above the foundation level (Fig. 2b).

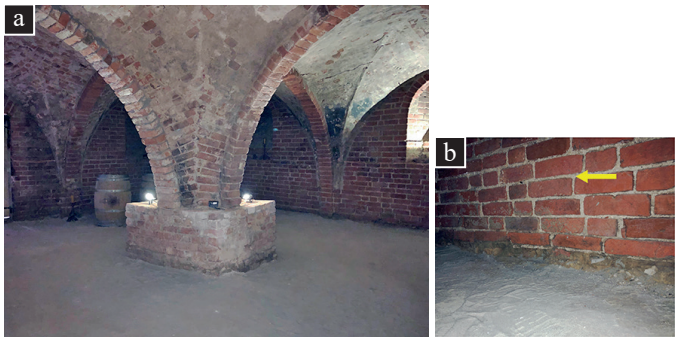

Fig. 2. a) Romanesque cellar in the Dominican monastery in Sandomierz, b) sampling point

The photograph in Fig. 3a shows the post-Cistercian capitulary, a part of the thirteen-century monastery complex in Koprzywnica. The structure is situated in the eastern wing of the former monastery, approximately one meter below the present ground level. The architecture of the interior with a rib vault supported on two columns, has maintained its original Romanesque character.

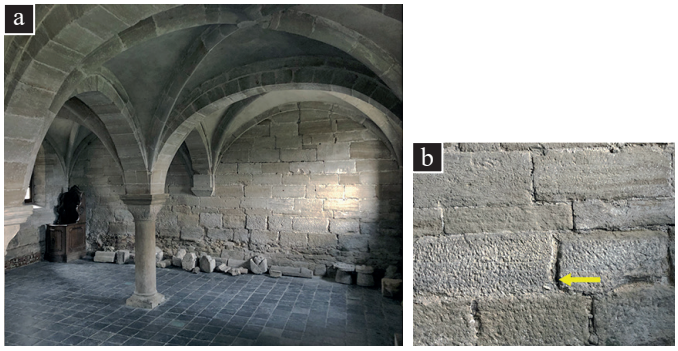

Fig. 3. a) Post-Cistercian chapter house in Koprzywnica, 3b) sampling point

The chapter house currently hosts a lapidarium, where remnants of the stone architectural elements from the church and monastery are stored. The beginnings of the Cistercian monastery in Koprzywnica date back to 1180s. The founder of the entire complex was Mikołaj Bogoria, a dignitary who, having obtained a permission from the Krakow-based prince Casimir II the Just, brought the first monks from the Burgundian monastery in Morimond in 1185. The samples were collected from the southern internal wall at the height of 0.5 m above ground level (Fig. 3b).

2.2. Testing methodology.

2.2.1. Petrographic analysis. One of the basic methods of mortar testing is optical microscopy with transmitted and reflected light. Thin sections are observed using a petrographic microscope in transmitted light to determine the mineralogy of the constituents and the texture of the mortar. The method allows identification of aggregates, binder (including anhydrous clin-

ker), organic and non-organic additives (including pozzolans) porosity, cracks and secondary minerals formation. Reflected light microscopy is used to identify hydraulic binders, anhydrous clinker and opaque mineral types by viewing polished sections. As magnification of the light microscope is limited to a resolution of approximately 1 micrometer and the test surfaces can be several square centimeters in size, the choice of representative samples is important, especially in the case of large aggregate and mortar particles that have undergone macroscopic changes.

The thin sections of the mortar fragments selected based on macroscopic observations were subjected to petrographic examinations in transmitted light, using an OLYMPUS BX51 petrographic microscope with a DP12 digital camera. Microscopic analyses were conducted to determine mineral components, particle size distribution and pore content. Quantitative analysis of petrographic composition was performed using an ELTINOR integrating point counter device.

2.2.2. SEM-EDS analysis. A large depth of field distinguishes scanning microscopy among other methods and enables direct observation of fracture surfaces of solid mortar samples. The microscope has a resolution of a few nanometers. Scanning electron analysis is used for the evaluation of the shape and size of particles, morphology and interrelationships between mortar constituents, the presence of inclusions, cracks, void filling, and the shape of pores. Relatively simple preparation of samples is the advantage of this method. In some techniques (backscattered electrons), observations are conducted on polished sections. An energy-dispersive (X-ray) spectrometer (EDS) coupled with a scanning electron microscope allows for quick analysis of elemental composition. The sample representativeness is of key importance for the interpretation of the microstructure observed in a very small scale.

Selected mortar pieces were cut into cubes having each side of the area of 20 mm^2. One face of each cube was impregnated with resin and polished. The microstructure of the mortar was determined using the polished sections under a QUANTA FEG 205 scanning electron microscope (FEI Company) equipped with an EDS detector. The SEM-EDAX test was conducted at low vacuum and accelerating voltages of 20 kV, beam current of 36 mA, vacuum pressure (in column) of 8.3×10^{-8} mbar, sample pressure of 4.5×10^{-6} mbar, EDS counting time of 400 s and beam size of 1 μm.

3. Test results

3.1. Analysis of mineral components. Selected based on macroscopic observations, the mortar fragments from the belfry of the Dominican monastery were subjected to petrographic analysis. The mineral composition of the samples was determined on thin sections using a transmitted light optical microscope. Petrographic evaluation revealed that the samples consisted of porous lime and sand mortar. The cumulative empty pore volume in the sample was approximately 3%, while the size of usually rounded pores did not exceed 0.5 mm. Hardened lime paste was a dominant component in the mortar (approx. 67% by volume), while the proportion of sand aggregate was relatively low (33% by volume). The dominant mineral in the aggregates was quartz (76% by volume), mostly in the form of well-rounded monocrystalline grains. Polycrystalline grains were also observed, consisting of many small domains characterized by wavy extinction. The quartz grain size ranged from 0.05 to approximately 0.5 mm, whereas in terms of volume, the prevailing size was 0.2 to 0.5 mm.

The composition of the aggregate was complemented by flint particles and pieces of sandstone and feldspar, with slightly fewer grains of limestone. Flint particles (about 9% by volume) consisted of microcrystalline phases of silica: chalcedony and microquartz. They were usually slightly less rounded than the quartz grains and their size ranged from 0.2 to 0.5 mm. Feldspar in the aggregate (6% by volume) was represented by alkaline varieties and plagioclases in the form of angular grains of up to 0.5 mm in size. Fine-grained quartz sandstones with a regenerative binder were as common as feldspar (5% vol.). Another component – pieces of limestone – was present in the aggregates at 4 vol%. Grains of limestone were represented by organodetritic varieties and those of sparite and micrite. Limestone fragments often reached much larger sizes than other aggregate components, up to a maximum of 3 mm. In addition to the components described, the aggregate contained few small (up to 2 mm) fragments of bricks (Fig. 4) and single plates of muscovite.

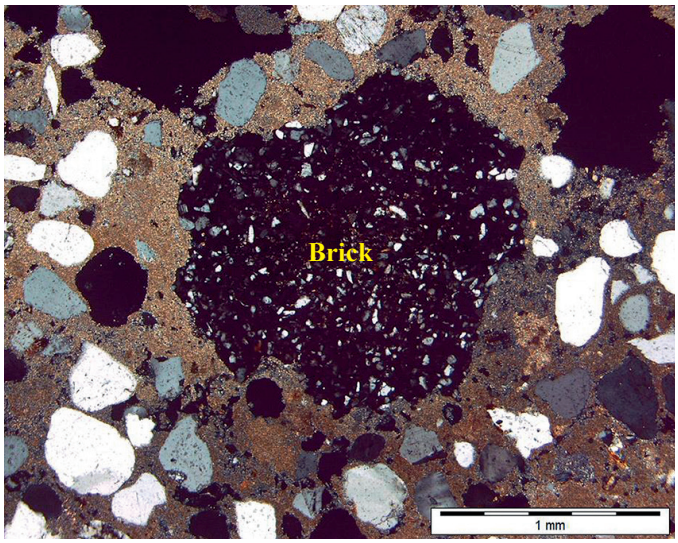

Fig. 4. Photomicrograph of hardened lime paste, showing a large brick fragment surrounded by sand grains; cross-polarized light

Visible between the aggregate grains was the lime paste, occupying about 2/3 of the volume of the mortar, comprising microcrystalline components, predominantly calcite mudstone. The size of the crystals amounted to about 1 μm. Quartz-free zones of up to several millimeters were observed (Fig. 5). The calcite content in the paste varied and increased substantially in the vicinity of limestone grains.

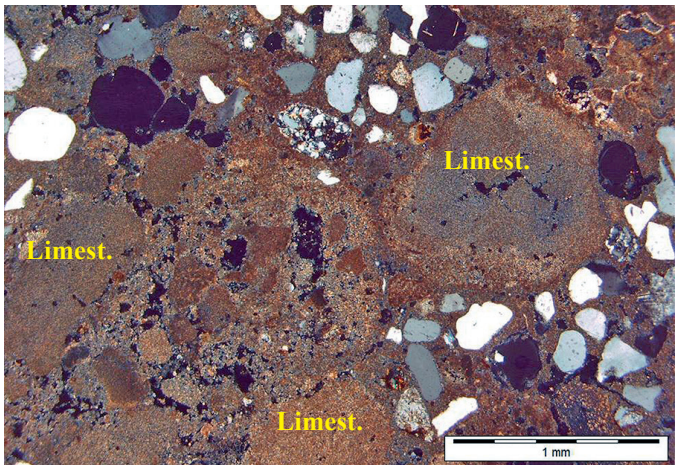

Fig. 5. Photomicrograph of the fragment with numerous limestone grains; cross-polarized light

Observations under the scanning microscope were conducted on polished surfaces impregnated with epoxy resin. Figure 6 shows the microstructure of the mortar from the belfry of the Dominican monastery in Sandomierz.

The SEM observations confirmed the presence of fully carbonated lime binder. The aggregate consisted mainly of quartz sand less than 0.5 mm in size (Fig. 6a) and feldspar grains (Fig. 6c, point 1). Algae thallus was surrounded by microcrystalline carbonated lime binder (Fig. 6b, point 1). The binder was composed of fully carbonated slaked lime in the form of a microcrystalline mass at the calcium hydroxide locations (Fig. 6c, point 3). Well-developed calcite crystals (Fig. 6c, point 2) filled the voids. Some pores contained shreds of fungi (Fig. 6c, point 4).

Figure 7 shows the microstructure of the mortar sampled from the cellar in the Dominican monastery.

The sample was porous lime and sand mortar. The size of the usually rounded pores was up to 0.5 mm and constituted about 5% of the volume of the sample. The mortar consisted of sand aggregate (approximately 58% by volume) and hardened lime paste (approximately 42% by volume). Quartz was the dominant mineral in the aggregate composition (approximately 87% by volume), having very well rounded monocrystalline grains. Polycrystalline grains occurred distinctly less frequently. The quartz particle size ranged from 0.05 to about 1 mm, whereas in terms of volume, grains from 0.4 to 0.8 mm predominated (Fig. 7). Flint grains as well as limestone, sandstone and feldspar fragments were also present in the aggregate composition. The flint grains (approx. 5% by volume) consisted of chalcedony and microquartz, 0.3 to 1.0 mm in size and less rounded relative to the grains of quartz (Figs. 7 and 8).

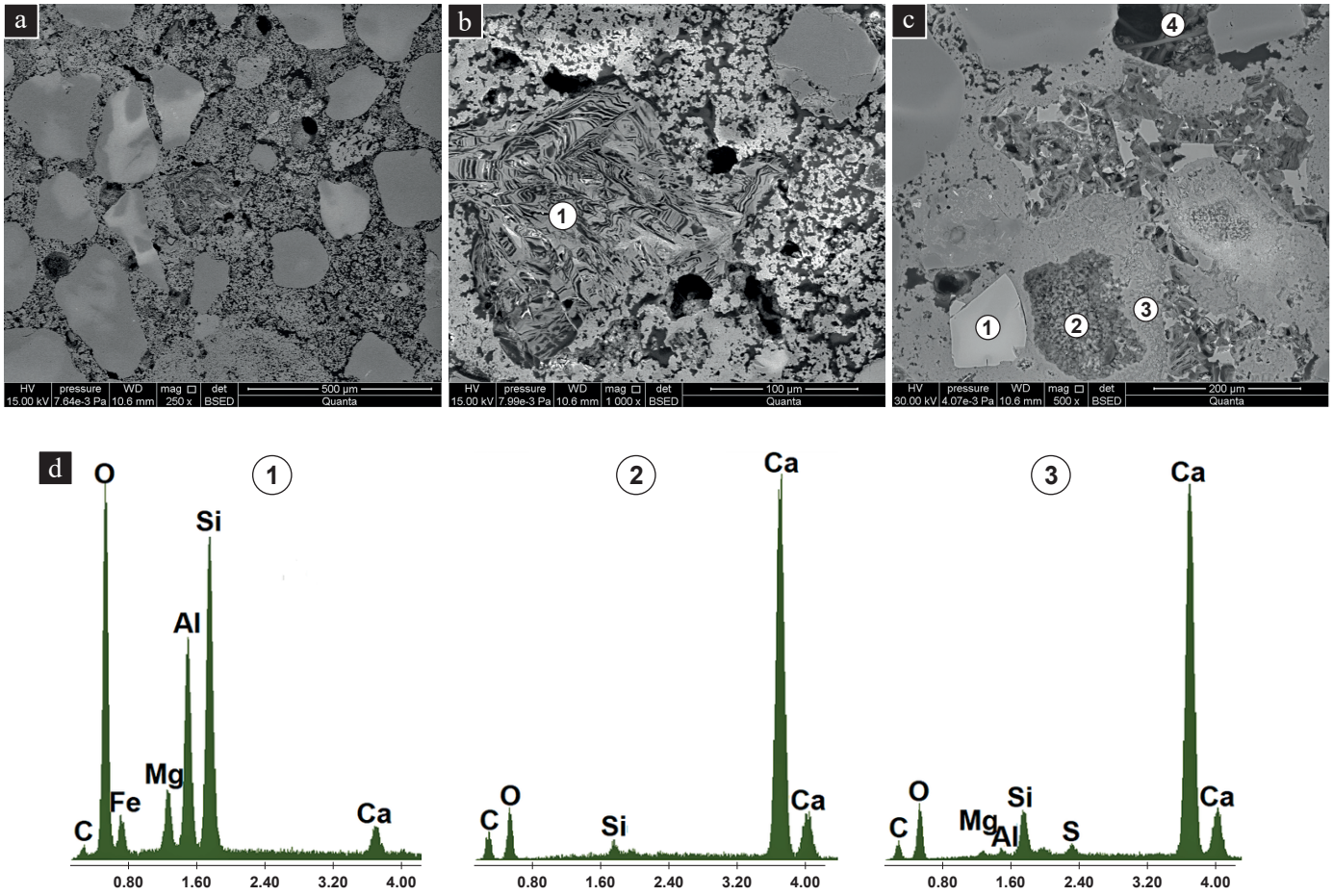

Fig. 6. Microstructure of the mortar from the Dominican monastery belfry in Sandomierz

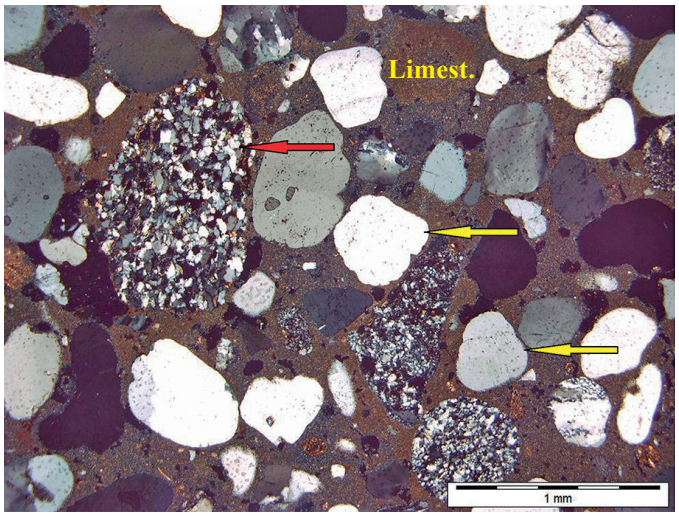

Fig. 7. Photomicrograph of hardened lime paste with rounded quartz and flint grains (yellow arrows), fine-grained quartz sandstone fragments (red arrow) and micritic limestone fragments; cross-polarized light

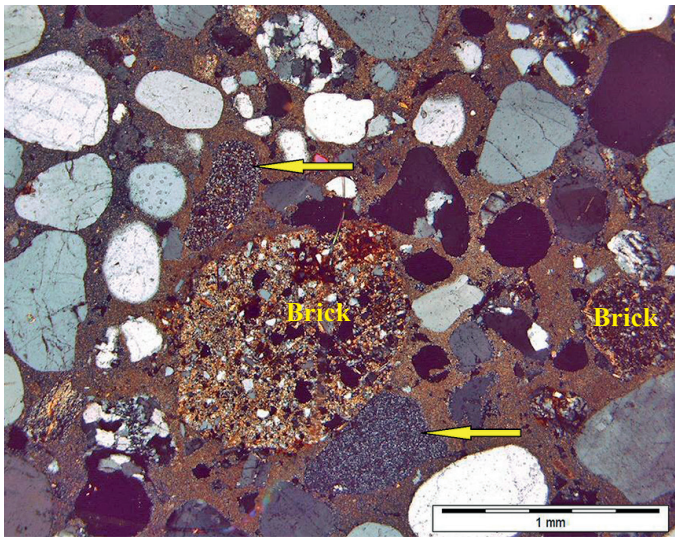

Fig. 8. Photomicrograph of hardened lime paste with brick fragments and flint grains (arrows) and quartz; cross-polarized light

The least pronounced component (approximately 2% by volume) was feldspar in the form of sharp-edged grains with the size of 0.5 mm, represented both by alkaline varieties and plagioclases. The aggregate also included a minor number of small (up to 2 mm) brick fragments and single muscovite plates.

The grains of the mortar aggregate were cemented by hardened lime paste, consisting of microcrystalline components, mostly of micritic calcite with crystal size of approximately 1 μm. The calcite content in the paste varied and increased substantially in the vicinity of limestone grains.

The SEM observations of the mortar polished sections revealed aggregates composed mainly of quartz sand less than 0.5 mm in size (Fig. 9a) and feldspar grains. Some pores showed shreds of fungi (Fig. 9b). The binder was fully car-

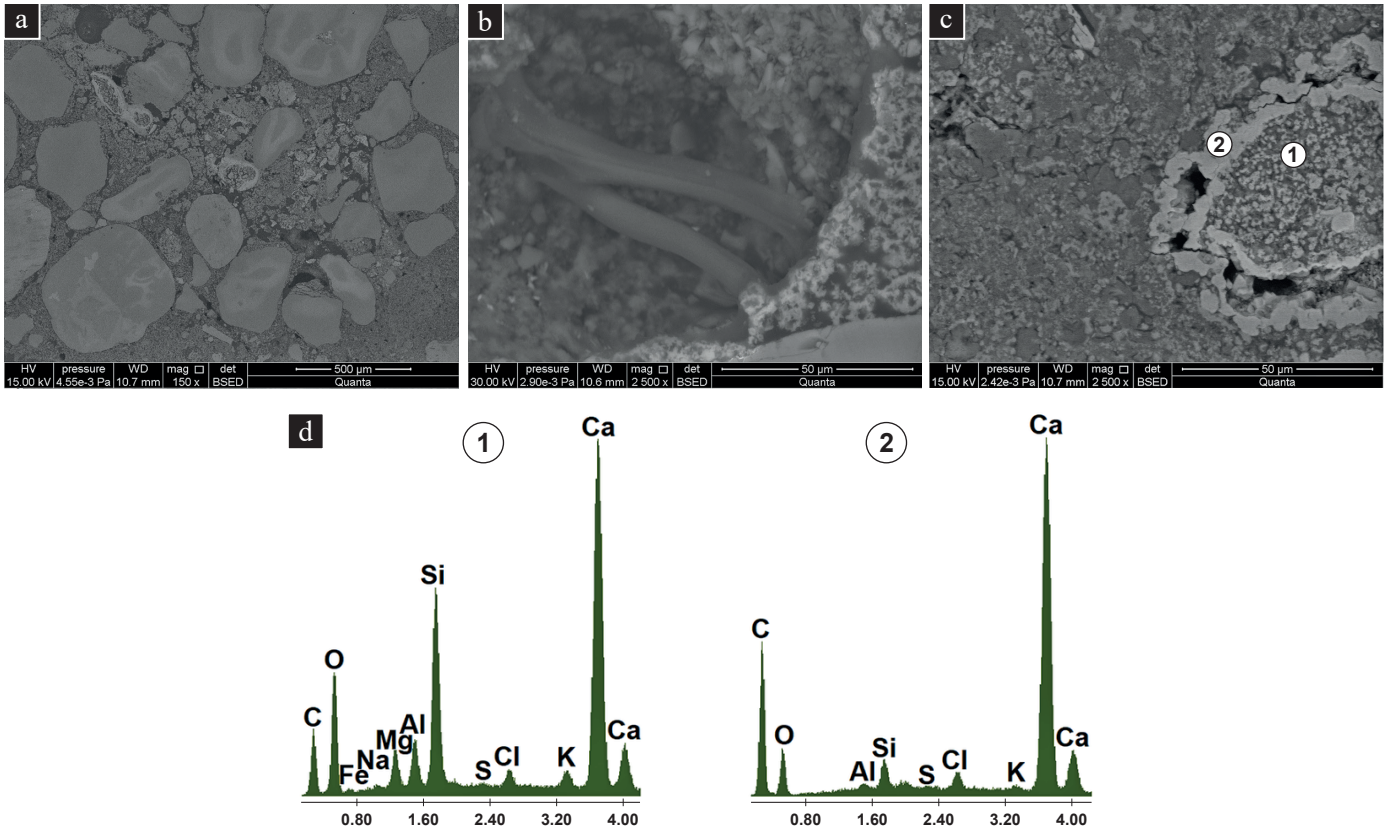

Fig. 9. Microstructure of the mortar sampled from the cellar of the Dominican monastery

bonated slaked lime in the form of a microcrystalline mass at calcium hydroxide locations (Fig. 9c, point 2). Sulfur, chlorine and alkalis were likely to have originated from the groundwater surrounding the foundation (Fig. 9c, point 1).

Figure 10 shows the microstructure of the mortar collected from the walls of the post-Cistercian chapter house in Koprzywnica. The sample consisted of porous lime and sand mortar. The size of usually rounded pores was up to 0.5 mm. The pore volume in the sample was about 5%. The quartz sand in the mortar occupied 56% of its volume, and the hardened lime paste occupied about 44% of the volume of the mortar. Quartz (approx. 89% of the aggregate volume) in the form of mostly well rounded monocrystalline particles was the dominant mineral. Fewer polycrystalline grains were found. The quartz grain size ranged from 0.1 to about 1 mm, whereas in terms of volume, particles of 0.2 to 0.6 mm prevailed. The aggregate also included limestone fragments, flint, sandstone and feldspar grains. The limestone fragments amounted to about 5% by volume of the aggregate and were represented by varieties of sparite and micrite (Fig. 10). The fragments showed various degrees of roundness and their sizes were close to 1 mm, rarely reaching 5 mm. Another component of the aggregate was feldspar (approx. 2% by volume), represented by alkali varieties and plagioclases in the form of very angular grains, 0.5 mm in size (Fig. 10).

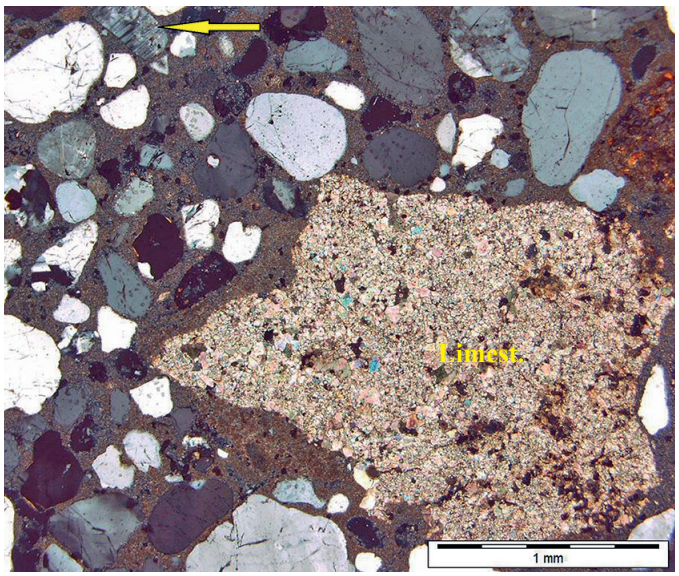

Fig. 10. Photomicrograph of the mortar with an irregular, large grain of limestone; a plagioclase grain (arrow) is visible in the upper part of the image; cross-polarized light

The flint grains (approximately 2% of the aggregate volume) consisted of microcrystalline silica in the form of chalcedony and micro-quartz. The rounding of the grains, ranging in size from 0.3 to 1.0 mm, was not as good as that of quartz grains. Well rounded, fine-grained quartz sandstones (2% by volume) with quartz-type regenerative cement and ferruginous (Fig. 11) or carbonate cements were also found.

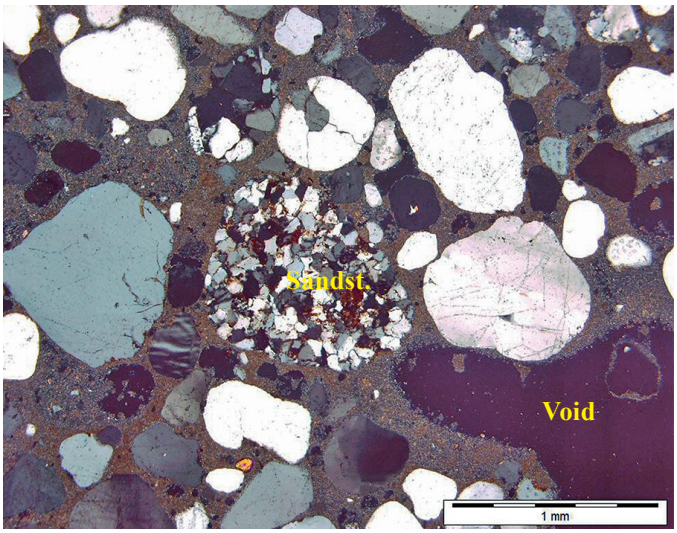

Fig. 11. Photomicrograph of the mortar with a rounded grain of microcrystalline sandstone in ferruginous cement, and an oval void (P); cross-polarized light

The aggregate consisted mainly of quartz sand of different grading, with grain size of less than 0.5 mm (Fig. 12a). The binder was composed of fully carbonated slaked lime in the form of a microcrystalline mass at calcium hydroxide locations (Fig. 12b). Larger calcium hydroxide crystals filled the voids (Fig. 12c). The chlorine and alkalis were likely to have originated from the groundwater surrounding the foundation (Fig. 12d).

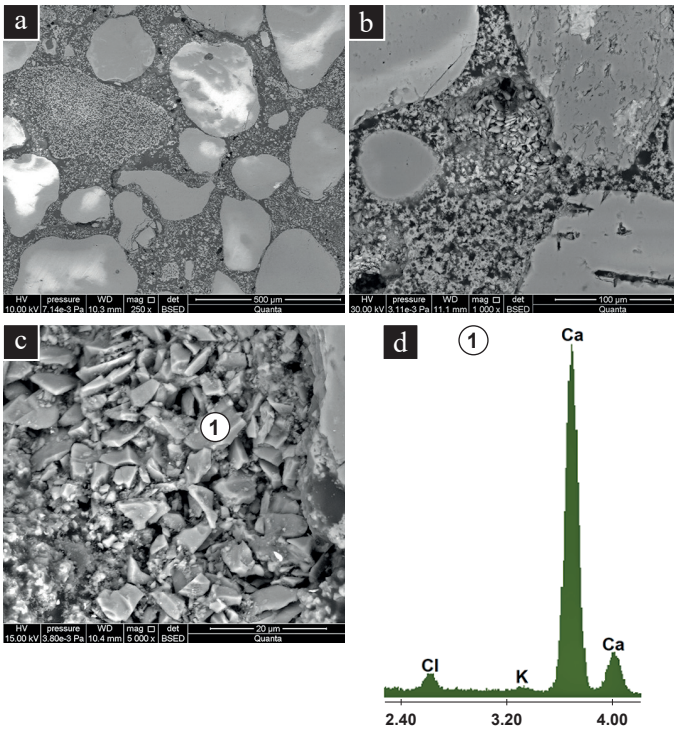

Fig. 12. Microstructure of the mortar from the post-Cistercian chapter house in Koprzywnica

Table 2
Binder and aggregate contents in mortars

Designation of samples	Aggregate content, vol%	Binder content, vol%	Binder pores, vol%	Aggregate grains, vol%				
				quartz	flint	limestone	sandstone	feldspar
Z1	58	42	3	87	5	3	3	2
Z2	33	67	5	76	9	4	5	6
Z3	56	44	5	89	2	5	2	2

4. Discussion and conclusions

The results of the microstructure testing of the mortars collected from the walls of thirteenth century historical buildings indicate that the type of non-organic aggregates varies, but the dominant mineral in all mortars is quartz sand, along with sandstone and feldspar fragments, and grains of flint and limestone. The mineralogy of the aggregates identified using standard petrographic methods applied in geological sciences reflects their geological origin and provides valuable information. The mortars also contain few fragments of bricks and do not include organic components such as charcoal (as residue from lime-burning) or organic fibers (animal fur, straw, etc.) encountered in historical building plasters. The fibers traditionally served to improve tensile strength of the material.

Table 2 shows the composition of the mortar samples determined using optical microscopy.

The binder type was determined using optical and scanning microscopy. The type used in all the mortars examined was lime binder. The matrix of binders in historical lime mortars, as observed microscopically, in most cases is composed of very finely crystalline calcite derived from the carbonation of slaked lime. The size as well as texture of the calcite crystals can be associated with the environmental conditions of carbonation. The phenomena of dissolution and precipitation in historical mortars can conceal their original characteristics and lead to substantial secondary porosity of the binder, which can affect the determination of the binder-aggregate ratio. Several researchers have mentioned the presence of binder-related grains in historical lime mortars, referred to as “lime lumps” [7, 8].

They originate from the binder but act as forms of aggregate, which makes their identification difficult. Optical microscopy is the only method currently available that allows calculating the correct binder-aggregate ratio through the quantification of lime lumps. Other types of binder-related particles, underburnt or overburnt fragments, provide information about the nature and origin of the raw materials and historical technologies used for lime and mortar manufacture.

Approximately 5% of the volume of mortars under analysis consists of coarse pores more than 100 μm in diameter, formed by trapped or entrained air. The pores formed during mixing have an irregular shape and distribution, while the pores formed by introducing admixtures, which probably in historical mortars are organic materials, including proteins [9], are spherical pores distributed in the mortar matrix. Several authors have undertaken the task of characterizing pores in historical mortars [10].

The use of transmitted light optical microscopy on thin sections is of primary importance for the characterization of mortars from historical buildings, both due to the complex composition of these composite materials and the fact that the mortars are exposed to long-term environmental impacts. This method is most suitable as the first step in identification of non-organic and organic materials.

By applying the quantitative methods of optical microscopy, it is possible to determine the contents of aggregate and binder grains as well as the pore structure, which in the case of historical mortars is a very useful method due to the limited sample quantity. Historical mortars interact with the environment during hardening and carbonization, and the calcite dissolution and precipitation processes on the pore walls and in fractures contribute to the development of secondary porosity [7].

The findings from this study reveal a substantially larger binder-aggregate ratio than that often attributed to renovation mortars, i.e. 1:3. These greater binder-aggregate proportions probably derive from the presence of lime lumps which must be considered as a separate phase for the quantitative characterization of historical mortars [9].

Optical microscopy is a suitable method for diagnosing historical mortar degradation and studying the interphase zone along with potential products of the reaction between the binder and aggregates, bricks or building stones. Quantitative analyses with the use of optical microscopy are difficult due to the complex nature of the historical mortar composite material. Automated image analysis techniques allow determining the proportions of the components used as well as binder-aggregate ratios.

5. Summary

This study revealed that porous lime and sand mortars with an increased binder-aggregate ratio were applied for binding the masonry units in the thirteenth century historical buildings in question. The mortars are made up of fragments of limestone, flint, feldspar and bricks with the size larger than that of sand grains. The binder is a fully carbonated calcium hydroxide with no pozzolanic additives. The results of the microstructure and phase composition tests can serve as a reference material while selecting components of renovation and repair mortars for historical buildings. The microstructure tests will be supplemented with determinations of mortar porosity and physical properties.

The most effective method of characterizing a mortar is to use several techniques, because each of them alone ensures only

partial characterization. Research objectives and experience of researchers determine the selection of appropriate test method combinations.

The identification of components required to duplicate the mortar, the determination of the type and content of the binder and classification of aggregates were based on microscopic observation of samples combined with micro-area elemental composition analysis.

Acknowledgements. The paper was prepared under "Technology and methods of improving the properties and durability of building composites" SUBB.BKTO.20.002.

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