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A Physico-chemical Study of Lime-based Mortars from Different Historical Periods

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Abstract

Nowadays, strengthening interventions and protective treatments on heritage masonry structures require compatibility of the new material for improving effectiveness and avoiding future damage. Knowledge of the physical, chemical, and mineralogical properties of the mortars represents an invaluable tool for deepening this aspect. This study focuses on three types of samples of lime-based mortars that come from different historical periods: a medieval lime mortar (14th century), a lime mortar from the turn of the 18th/19th century, and, for comparison, a modern cement-lime mortar of M7 class. Samples of historical mortars have been collected from historic buildings located in southern Poland. These materials have been characterized experimentally using destructive and non-destructive techniques, such as X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and petrographic microscopy in order to obtain mineralogical and chemical information on the samples. These analyses also provide information on the physical properties in the reference periods analyzed. Our results evidenced differences in the use of feldspars among the different historic periods but similar composition of quartz and calcite. Furthermore, evaluation of the internal structure of the samples using X-ray micro-computed tomography (micro-CT) and double punch compressive tests on historic mortar joints and mortar plates of the materials have been performed, highlighting the influence of the micro-scale properties on the compressive strength.

Keywords

Lime-based mortars, Historical periods, Mineralogical characterization

Introduction

The physical, chemical, and mineralogical characterization of mortars is crucial for a comprehensive study of masonry heritage sites, from the choice of raw materials to the final completion of the structure, through the different construction phases [1]. The necessity of these investigations is also aimed to prepare appropriate materials with compatible physico-mechanical behavior, for effective retrofitting intervention on existing buildings [2]. In the second half of the 18th century, hydraulic lime began to replace common lime mortars and its use declined further with the development of Portland cement in the second half of the 19th century. Only in the last 30 years has there been a rebirth of the application of lime mortar for the repair of historic buildings, due to the recognition of the unfavourable properties of Portland cement mortars, including brittleness, high strength and a coefficient of thermal expansion that can be double than that of lime mortars and most types of bricks and stones [3]. The growing interest in lime mortars for the repair of historic structures has led to numerous research projects [4, 5]. A lack of correct information on the exact methodology of ancient building materials led to the improper use of modern materials in restoration work, such as the addition of cement in lime mortars to help the mixture harden and accelerate restoration procedures. The processing parameters of ancient mortars and the compatibility between mortar and previously used bricks have rarely been taken into consideration. Because of the size, shape and restrictions related to the sampling of lime-based specimens from historical structures, the execution of the standard engineering tests is non-trivial and chemical analyses are most common in this field [6]. In order to overcome the difficulties arising during mechanical characterization, Magalhães and Veiga [7] adapted the shape of mortar samples to the shape of the standard specimens, according to EN 1015-11 [8] with a confinement cement mortar. Almesfer et al. [9] applied the compressive test method ASTM C 109-08 [10] on 19th century cubic samples and subsequently converted the values obtained using two shape factors, accounting for the slenderness and the footprint of the samples. The dependence of compressive strength on the slenderness of specimens has been also studied by Drdácký et al. [11] with differences in test results due not only to the shape of the specimens but also to different mortar types and their quality. More recently, double punch tests have been used as a substitute to standard procedures, allowing to directly test the mortar joint for obtaining information on the compressive strength or as a supportive tool for further *in situ* investigations [12, 13].

In this work, mortars from different historical periods have been characterized using destructive and non-destructive techniques. In addition, standard compressive EN 1015-11 [8] and double punch tests of new mortars were performed and compared with double punch test results of historical mortar joints. An analysis of the relation between compressive strength and porosity is proposed, considering the chemical and mineralogical properties, with the future objective of a multiscale assessment of masonry material [14].

Materials and Method

Samples studied are from different historical periods: a medieval lime mortar (14th century), a lime mortar from the turn of the 18th/19th century, and, for comparison, a modern cement-lime mortar of class M7. Samples of historical mortars have been collected from the castle Schloss Neudeck, located in the city of Świerklaniec, in southern Poland. In figure 1 is given the historical mortar joints sampling location. Mortars of the 14th century were obtained from the underground brickworks of the original body of the building, while mortars from the turn of the 18th/19th century come from the remains of the ruins of the northern wing of the castle, built in this period. Lime-based mortars are nanoscale materials.

An analytical protocol for the study of these mortars was developed and tested on the above samples. It consists of a combination of petrographic-mineralogical techniques for phase identification such as XRD analysis, FTIR spectroscopy and a survey method by means of micro-CT for the analysis of the spatial distribution and quantification of pores and secondary phases, using high-resolution contrast images.

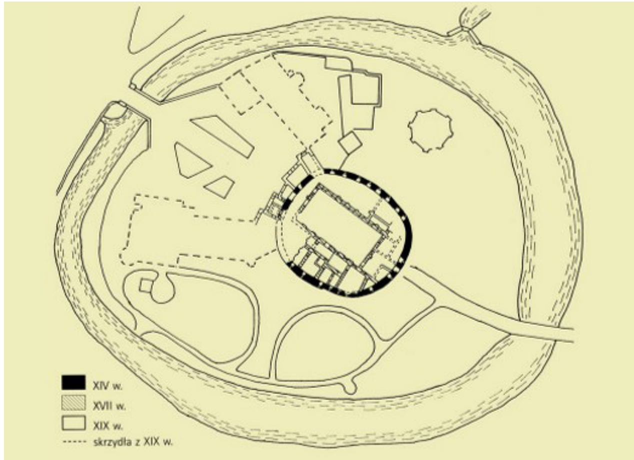

Figure 1: Historical mortar joints sampling location.

The first phase consists of the mineralogical characterization of the crystalline phases present in the powder mortars. XRD analyses were performed using a PANalytical X'Pert Pro X-ray diffractometer. The following conditions were applied: Cu Kα radiation, λ = 1.5405 Å, 3° - 70° 2θ explored range, scanning rate of 0.11° 2θ/s. XRD patterns were interpreted using the High Score Plus software package to obtain semi-quantitative data, using the reference intensity ratio method. FTIR analysis was performed using a ATRproONE-FTIR, Jasco Model 6600 with a frequency range from 400 cm^{-1} to 4000 cm^{-1} and a resolution of 2 cm^{-1} and 100 accumulations. Petrographic thin sections were studied by means of optical microscopy using reflected light to study the mineralogy and texture of the mortars and the Feret diameter of pores and quartz grains were analysed with Fiji software. Subsequently, further characterization of the texture of the mortars was performed by micro-CT of cylindrical sections of 0.7 cm in diameter and 1.2 cm in height, using a Xradia 510 (VERSA ZEISS) equipment. This allows obtaining information on the 3D spatial distribution, structure, and quantification of empty spaces (pores) using high-resolution contrast images. Scans were performed at 40 kV and 5 μA. Data were acquired with a 4x magnification CCD objective for a total scan time of 15 h including the collection of reference images. The voxel size achieved under these conditions was 3 μm.

Finally, the compressive strength of the samples was determined by means of double punch and standard compressive tests according to EN 1015-11 [8]. In particular, the standard procedure was adopted for new mortar specimens while double punch tests were used for historical mortar joints and plates of contemporary mortars. The latter investigation consists in increasing the compressive load of mortar plates coming from the joints in load-control till the achievement of the peak strength with circular steel punches having diameter of 20 mm According to the specific German standardization of this test [15], the specimens should be plates with width and length of 50 mm, but due to difficulties in extracting and cutting samples from masonry, 40 x 40 mm specimens were used only in the case of contemporary mortars. An overview of the number of samples and shape is given in table 1. This combined analytical approach allows a complete characterization of the materials. and enables obtaining information on the strength and durability of the analysed material.

Results

Mineralogical characterization

The results of the XRD analysis are presented in figure 2. The MR1 sample shows up to 2 wt.% calcium silicate, the highest content among all the mortar specimens analysed. Calcium feldspar was not found in this sample. The MR2 sample has the simplest composition, containing only quartz (86%) and calcite (14%). The MR3 sample has a lower amount of calcite (6 wt.%) but includes feldspars (anorthite and microcline) in concentrations of 9 and 11 wt.%, respectively. This modern mortar is the one that contains the lowest percentage of quartz and calcite.

The FTIR results are shown in figure 3. The bands around 1420 cm^{-1} and 874 cm^{-1} could be assigned to the presence of calcite from carbonated lime or undecomposed limestone, which is the raw material for lime production. The bands in the vicinity of 774 cm^{-1} and 1040 cm^{-1} associated with Si-O stretching vibration can be assigned to quartz, which is the aggregate in the mortars. FTIR spectroscopy confirmed the mineral composition previously determined by XRD analysis, providing additional valuable information on the crystallinity of the material, ruling out the presence of amorphous phases which could not be seen in XRD, but they are not detected by FTIR either.

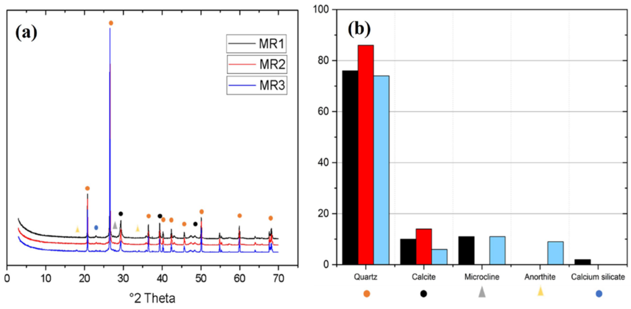

Figure 2: XRD analysis on the three studied mortars. **(a)** XRD patterns and **(b)** phase content determined from semi-quantitative phase analysis using the RIR method. The reference codes for the presented phases are as follows: Quartz (98-009-6453), Calcite (98-002-1944), Microcline (98-001-7293), Anorthite (98-001-2602), and Calcium Silicate (98-009-9693).

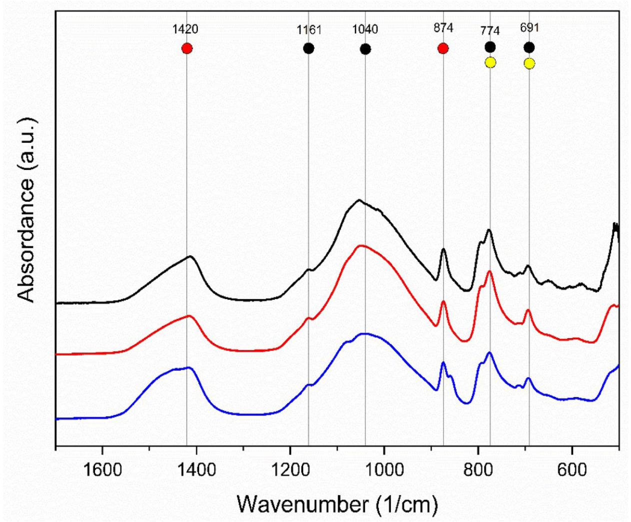

Figure 3: FTIR spectra on the three mortars studied. The bands corresponding to quartz, calcite and feldspar are indicated (black, red, and yellow points, respectively).

Morphological and physical properties

A petrographic analysis of the thin sections of the samples (Figure 4d, 4e, and 4f) was performed to obtain insights into the microstructure and mineralogical composition of the mortars. This analysis was complemented by the study of the 3D microstructure and porosity of the mortars using micro-CT. In the petrographic sections, we can see the same mineralogical phases evidenced by XRD and FTIR analyses. Both optical and X-ray tomography images show that in the older sample (Figure 4a and 4d) the aggregate shows rounded morphologies, and the porosity is of small to medium size (Feret diameter ~ 560 µm). Analyses of the modern sample (Figure 4b and 4e), on the other hand, show more angular clasts. Regarding porosity, in the MR2 sample pores are on average smaller in size (Feret diameter ~ 480 µm) and are present not only at the interface between matrix and aggregate but also in the matrix. The modern sample shows larger quartz grains (Feret diameter ~ 860 µm). The porosity in this sample has approximately the same Feret diameter as the quartz grains but the number of pores in the thin section is significantly smaller than in the older samples.

Mechanical properties (compressive strength)

The knowledge of the compressive strength of a mortar, along with that of bricks, is essential for estimating the value of the compressive strength of masonry, according to the actual codes [16], even though there is also a clear relation between masonry compressive strength and the mortar-brick bond [17]. While the mechanical characterization of mortar

Table 1: Characteristics of the specimens tested in compression.

Specimens	Shape	Number of samples	Thickness (CoV) [mm]	Remarks
MR1-IR	Irregular Plate - IP	10	14.02 (0.04)	Plate cut from brickwork (XIV c.)
MR2-IR	Irregular Plate - IP	7	13.92 (0.04)	Plate cut from brickwork (XVIII c.)
MR3-ST	Prismatic 40 x 40 x 80 mm	6	80.0 (0.01)	Modern standard specimen (XXI c.) according to EN 1015-11 [8]
MR3-R	Regular Plate - RP	6	11.60 (0.04)	Plates cut from modern standard specimen (XXI c.)

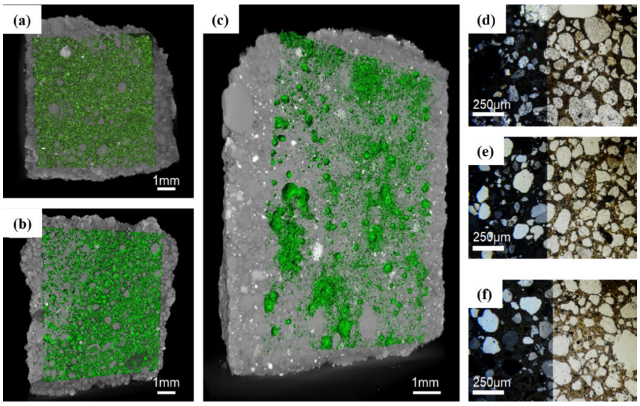

Figure 4: Micro-CT **(a, b, c)** and petrographic thin section images **(d, e, f)** of the mortars studied with a 10x magnification. Images correspond to sample **(a, d)** MR1, **(b, e)** MR2, and **(c, f)** MR3. Green areas in the Micro-CT images show voids (i.e., pores) and the right part of the petrographic thin section is obtained with plane light and the left part it is obtained with crossed nicols.

for new construction is straightforward, the assessment of the mechanical properties of a mortar coming from the joints of existing structures is challenging. Several authors have for example studied the influence of the specimen shape by means of laboratory tests and finite element models [18]. Furthermore, the presence of weak lime mortars, as it is common for historic buildings, in masonry subjected to vertical loads, results in a triaxial state of stress for the bed joints [19] which is even more complicate to reproduce than a uniaxial state of stress. In the case of contemporary mortars, the mean value of the flexural strength of 2.23 ± 0.24 MPa was determined according to EN 1015-11 [8]. The 6 half beams resulting from the 3-point bending test were used for the determination of the compressive strength of standard specimens (Figure 5a). An additional specimen of the same material was used for obtaining plates MR3-R (Table 1) tested in a double punch test. The difference between plates and standard specimens' compressive strength is given in figure 4a, while figure 5b shows the differences between the compressive strength obtained using the punch tests for all the three materials.

Compressive strengths of 3.01 MPa, 26.84 MPa and 7.08 MPa were reached for mortars MR1, MR2 and MR3, respectively, determined using irregular mortar plates. As expected, the compressive strength of medieval specimens is the lowest compared to the rest of the mortars.

Discussion

According to Jedrzejewska et al. [20], ancient mortars produced in Poland can be divided into 6 different types. Based on the results of our compositional analysis, lime mortars MR1 and MR2 can be classified as category 6 with a gray exterior and different state of preservation. Compositionally, the presence of 10% and 14% of carbonates for MR1 and MR2 samples, respectively, is partially responsible for the differences in strength due to the carbonation process together with the quantity and volume of the aggregates (sand, 76% for MR1 and 86% for MR2). In particular, the higher amount of quartz in MR2 could be responsible for the higher mechanical strength compared to the MR1 mortar, while presenting comparable values of total porosity. The difference in porosity could be explained by the presence of feldspars (both alkali feldspars and plagioclase) in the modern samples. Feldspars are incorporated into lime-based mortars and cements as a typical enhancement in the construction process of modern mortars to improve thermal and optical properties, whiteness, and hardness [21]. In tomography, the microstructural properties of the mortar change as they contain a large number of voids, but with smaller volumes than those found in older mortar samples.

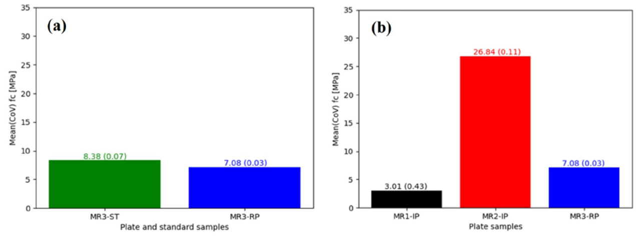

Figure 5: (a) Compressive strength of contemporary mortar determined by means of the standard procedure (MR3-ST) and double punch test on plates cut from the standard specimens (MR3-RP). **(b)** Double punch compressive strength of the three material types.

From a mechanical point of view, the highest value of the compressive strength was found for the 18th century mortar, which was unexpected considering that this mortar showed the highest value of porosity (Figure 6). This seems in contrast with the result of the compressive strength of the contemporary mortar with the lowest level of porosity. Evidently, there is a difference between new and old mortars given the *in situ* conditioning of the old mortars inside the joints and the laboratory conditions prescribed for the compressive test EN 1015-11 [8] of new ones. This diversity has been already noted by Sassoni et al. [22] showing that the double punch compressive strength of mortars extracted from masonry walls can be more than 3 times higher than both the double punch compressive strength of plates cut from standard specimens and the standard compressive strength of the same mortar. In their case [22], apart from the differences related to the confinement, shape, and size of samples in standard and double punch test, variation of the microstructure of the specimens

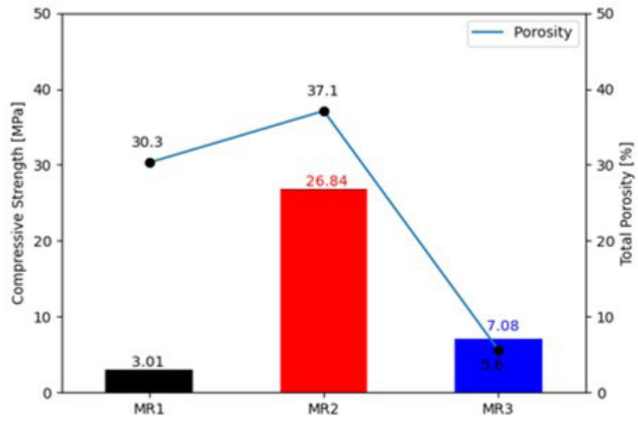

Figure 6: Relation between porosity and compressive double punch strength of analysed mortars.

were also crucial with standard prisms showing open porosity about 50% higher than samples coming from the masonry joints. In this case, considering the relation of Drdácký et al. [11] that adequately predicted the standard compressive strength of the lime cement mortar mix class M5 of Sassoni et al. [22], it is possible to obtain ranges of compressive strength values of 0.99 - 0.64 MPa for MR1 and 8.72 - 5.66 MPa for MR2 considering the irregularity of old mortar joints with a variation of the maximum base edge length of the samples of 40 - 60 mm. Based on these assumptions, the strength of 18th century and modern mortars is comparable and the compressive strength of medieval samples reaches the literature values typical of historic, pure lime mortars. Furthermore, a reduction in the porosity of the new mortar, already characterized by the lowest level of porosity among the tested samples, is expected for its use inside masonry joints.

Conclusion

An experimental programme is undertaken to determine the mineralogical, physical, and mechanical properties of historical mortar joints and commercial mortars for evidencing their different behaviour. The following conclusions can be drawn based on the experimental characterization. The mineralogical characterization of the mortars from different periods is crucial for giving insight into the fundamental changes in the properties of the raw products. Quantity and dimensions of pores can be greater when carbonates are present (MR2 samples) instead of feldspars (MR3 samples). Micro-CT and optical images of petrographic thin sections provide information regarding the microstructural properties of the samples in terms of porosity and shape of the voids and help to understand the differences found in the results of the compressive tests. The porosity and compressive strength differences between contemporary mortar in double punch and standard compressive tests and old mortars (14th and 18th centuries) joints in double punch tests are affected by the diversity of the mix formulations and curing conditions. Based on experimental relationships available in literature, the compressive strength of the 14th century mortar is the lowest of the samples studied, while the 18th century and contemporary mortars have comparable strengths. A reduced level of porosity should be expected for application of new mortars in masonry building construction. Future studies will deal with the characterization and modelling of masonry wallets made of different historical materials, allowing their comparative multiscale assessment.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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