PREPARATION OF MORTARS FOR RESTORATION OF ARCHITECTURAL MONUMENTS

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Mortar mixtures were prepared considering the microscopic observation, granulometric analysis, mercury porosimetry, XRD analysis, thermogravimetric and differential thermal analysis of the original plaster. Two series of lime mortar samples containing identical mixture of aggregates and admixtures but varying in the kind of a lime binder were prepared. In addition, the sample series varied in the ratio between mixing aggregate and binder. Prepared test bodies were subjected to accelerated carbonation process. Carbonated samples were characterized by the measurement of compressive strength, open porosity, water absorption and resistance to salt crystallization. The samples were also again compared with the original plaster by optical microscopy and XRD analysis. Based on the results of analyses of the original plasters and prepared samples of repair mortar the sample containing lime slurry with the mixture of aggregates in the mixing ratio of 1 : 2 was recommended for the restoration procedure.

INTRODUCTION

Historical mortars are complex systems, containing aerial or hydraulic binders or their blend, aggregates (not always crystalline) and admixtures that interact with the given binder. Additional materials may be added to modify properties or appearance of mortars. Mortars are also dynamic materials; they continue to interact with their environment after hardening and carbonation processes. [1]

Today, when restoring plaster of historical buildings, we have to decide whether to comply with the original formula preserved in written documents or derived from analytical results or whether to use new standardized materials (present materials) that usually display more favourable properties [2]. Current conservation of monuments prefers the maximal effort aiming at preservation of historical materials [3], so, for the reconstruction of the St. Giles church in Uhlířské Janovice, traditional techniques and materials were used.

Inadequate intervention in historical buildings and the use of inappropriate mortars when restoring historical renderings can cause more damage than benefit because of negative interactions between a new mortar and the original materials [4].

The damage caused is due to the fact that, if compared to historical mortars, new repair mortars: can be less permeable, retain excess water which can generate alteration phenomena, are less able to accommodate the masonry structure movements (thermal and humidity effects) due to its higher hardness and rigidity, lack of required little shrinkage of repair mortar [5].

Therefore, firstly, a historical-scientific study of the original materials needs to be carried out before any intervention in historical buildings is performed, and, secondly, the data obtained must be used either to produce a similar material or to formulate a restoration mortar from modern materials without significant negative interactions with the original materials.

Analyses of historical mortars in the conservation and restoration field aim at specific information about a historical mortar to formulate compositions for compatible repair mortars [6,7], to understand possible reasons for degradation of old mortars and to distinguish different building phases throughout the history. The requirements for building conservation regarding formulations for repair mortars are mainly: hydraulicity of a binder, mixture proportions (aggregate/binder ratio) and aggregate grading in order to identify the necessary components to produce a compatible mortar [8].

The use of techniques for technological research of materials allows for the determination of the composition and of some characteristics of the mortars.

Until 1970-1980 the characterization of historical mortars was mostly based on traditional wet chemical analyses. [9, 10] The interpretation of these results

however is difficult and often impossible without good knowledge of the nature of different mortar components [11]. The majority of later mortar characterization and/or identification schemes propose optical microscopy and X-ray diffraction techniques (XRD) as a first step in the qualitative identification of different mortar components. These procedures describe several chemical and other analytical techniques for further qualitative and quantitative analyses like scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), microprobe, differential scanning calorimetry (DSC), thermogravimetric and differential thermal analysis (DTA, TGA), Fourier transform infrared spectroscopy (FTIR), etc. [12–14] The choice of the appropriate analytical technique depends mainly on the questions that have to be answered and on the amount of material available.

As the main basis for the selection of suitable materials for the preparation of the repair mortar for the reconstruction of the St. Giles church in Uhlířské Janovice there were applied results of microscopic observation, granulometric analysis, mercury porosimetry, XRD, DTA and TGA of samples of the original Gothic plaster.

Based on the research results of the historical plaster [15] it was decided that the newly proposed repair mortar would be based on the composition of the original Gothic plaster from the late 14th century (sample V4). This gothic plaster, which carries murals, is preserved in the greatest extent in the higher parts of the walls of the presbytery. The new mortar should also be designed so that its physical and mechanical properties as well as durability and appearance are close to the original mortar.

Repair mortars should be durable, practical in application, and should not have a negative effect on the durability of the existing masonry (mortar should be considered expendable; it is easier to repair mortar joints than replace masonry units). [16]

Durability is not only dependent on the mortar mix but also on how it is installed and cured, on the compatibility between the masonry unit and the mortar, and on the severity of the environmental exposure, which in turn depends on weather, design details, construction practice, operation, and maintenance. Other requirements for repair mortar are: resistance to frost action and salts where needed, thermal and moisture expansion properties compatible with the existing masonry, texture and color of the mortar are important if they are to blend with an existing mortar, or if required for historical authenticity. Mortars should be practical in application to support good workmanship, too. [5]

EXPERIMENTAL

Requirements for repair mortar resulting from performed analyses

As aggregates of the repair mortar there should ideally be used dredged sand angular grains with uneven distribution of particles within the range 0–2 mm. From the mineralogical point of view it should include quartz, feldspar, mica, a small proportion of clay minerals and organic impurities in the form of fibres and crushed bricks. The binder should be of a lime type, or it may be partially hydraulic with respect to the current state of the object (especially moistening) to achieve the mechanical properties required. The mixing ratio of the binder to aggregates should be based on the corresponding ratio of the Gothic plaster sample. Greater quality of present materials allows us to slightly lower the proportion of the binder (when compared to the original Gothic plaster). Porosity of the newly prepared plaster should be in the range from 20 to 35 %.

Specifications of used materials

Binders (Table 1):

- Lime slurry (Contractor: AQUA restoration of buildings, Ltd.), activated and stored long term.
- Mixed lime binder VAPO (Contractor: AQUA restoration of buildings, Ltd.), formulated lime according

Table 1. Selected properties of used binders.

Properties of binders	Lime slurry	Mixed lime binder VAPO
Hydraulicity according to [17]	air – white lime (CL)	hydraulic – formulated lime (FL)
Colour	white	light ochre
Density [kg/l]	1.45	0.65 (bulk)
pH	13	12.50
Water content in the binding [wt. %] (Determined by drying to constant weight)	49.60	0
Determination of normal consistency, respectively amount of added water [ml] to obtain specified workability according to [18]	0	42.50 ml of water per 100 g of binder
Water/binder ratio (w)	0.98	0.43

to the standard ČSN EN 459-1 [17]. Chemical composition: hydrated lime finely ground (particle size 90 μm), metakaolin, marble powder, organic additive (< 0.2 vol. %).

Aggregates:

- Clay plaster Picas Econom gross (Contractor: Rigi) mixed with sand, fraction of grains 0 - 4.0 mm.
- Clay plaster Picas Econom fine (Contractor: Rigi) mixed with sand, fraction of grains 0 - 1.0 mm and finely ground hemp fibres (7 vol. %).
- Ground quartz SKP 14.21.12. (Contractor: Sklopísek Střeleč, Inc.), fraction of grains < 0.063 mm.
- Potassium Feldspar Ž75K13 (Contractor: LB Minerals Ltd.), fraction of grains 0 - 0.5 mm, feldspar content from 75 to 85 % max. content of Fe_2O_3 0.13 %.
- Sodium-Calcium Feldspar Ž80NaCa40 (Contractor: LB Minerals Ltd.), fraction of grains 0.25 - 1 mm, feldspar content 80 %, max. content of Fe_2O_3 0.31 %.
- Ground mica (Contractor: AQUA restoration of buildings, Ltd.), fraction of grains 0.5 - 0.063 mm.
- Clay CS 1 - Standard (Contractor: Civas, Ltd.), size of grains 0.5 - 0.25 mm.

Mixing water:

- Drinking water.

Preparation of mortars or test bodies

Preparation of mortar mixture

Initially, an appropriate mixture of aggregates, the same for all newly proposed samples, was prepared due to the results of analyses of the original Gothic plaster. [15] As binders there were used ripened lime slurry for one half of the samples and a mixed lime binder VAPO for the other half. Mixing ratios of binders to aggregates were again selected with regard to the binder content determined in the sample of the original Gothic plaster (sample V4), i.e. 1 : 1.5 and 1 : 2 for both series and 1 : 2.5 only for the group using lime slurry as a binder (Figure 1). The optimum amount of mixing water to obtain specified workability of mortars, i.e. normal consistency of binders, was determined according to the standard ČSN EN 1015-4 [18].

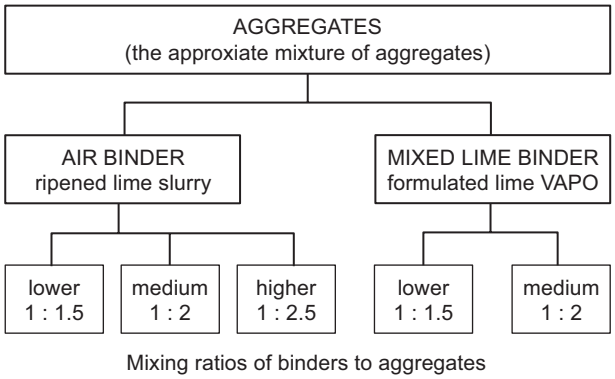


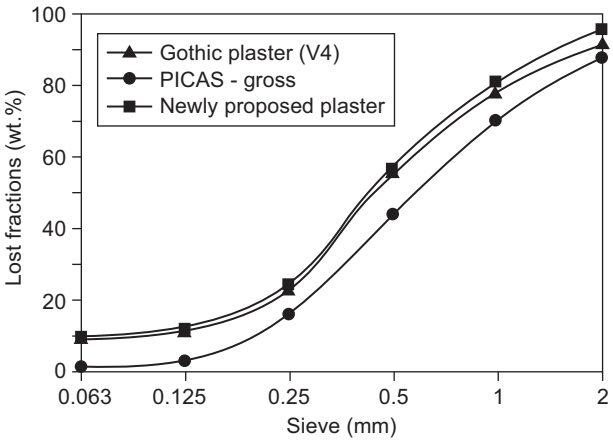
Figure 1. Scheme of mortar mixture preparation.

Aggregates

Primary aggregates were selected representing individual fractions and mineralogical composition similar to the sample V4 (Tables 2, 3) - clay plaster PICAS gross was adjusted to the required composition of the aggregate mixture with almost identical size distribution as the original plaster through numerous corrections including additional (missing) fractions of the required composition (Graph I). There was also achieved a very similar mineralogical composition (including crushed bricks), colour and characteristic as the sample V4.

Table 2. Weights and percentages of captured and lost fractions of original sample of Gothic plaster (V4). The base (100 %) is the total weight of sieved aggregates (m_{aggreg} = 9.6606 g).

Sieve (mm)	Captured fractions		Lost fractions	
	m (g)	(wt. %)	m (g)	(wt. %)
2	0.8183	8.47	8.8425	91.53
1	1.2955	13.41	7.5469	78.12
0.5	2.1553	22.41	5.3916	55.81
0.25	3.1938	33.06	2.1978	22.75
0.125	1.0975	11.36	1.1003	11.39
0.063	0.2261	2.34	0.8743	9.05
< 0.063	0.4028	4.17	–	–
Losses	0.5130	5.31	–	–



Graph I. Granulometric curves of Gothic plaster, of the strain of newly proposed plaster – i.e. clay plaster PICAS gross, and curve of the newly proposed plaster.

Correction of the particle size distribution of the original Gothic plaster was performed by completing the basic strain, i.e. the clay plaster PICAS gross, with a clay plaster PICAS fine containing 7 vol. % of hemp fibres, sodium-calcium feldspar (size of grains 0.25 – 1 mm),

potassium feldspar (size of grains 0 – 0.25 mm), ground quartz SKP 14.21.12. (size of grains up to 0.063 mm), ground mica (size of grains 0.063 – 0.5 mm) and clay CS1- standard (fraction 0.25 – 0.5 mm) - Table 4. All the components are commercially available.

The selected mixture of aggregates for repair mortar contains all kinds of grains from the finest to the grossest, up to the particle size of less than 4 mm. This allows good filling of the space between grains, which improves properties of the mortar, such as permeability, strength, dimensional stability and durability. [3] The presence of clay (identified in the original plaster) affects not only the physical and chemical properties of the mortar after hardening, but also affects its final colour. Feldspar, mica and natural pozzolana were added to the mixture to reach the mineralogical composition of the original Gothic plaster and to adjust the structure of the newly proposed mortar with sharp-edged grains. Quartz, being the mineral represented in the original Gothic plaster in the greatest amounts, was used in the ground form to complement fine fractions of the newly proposed aggregates.

In the original Gothic plaster there were identified crushed bricks, which are represented by clay CS1 in our designed repair mortar. In the presence of lime the crushed bricks act as a pozzolanic additive and they are able to contribute to the formation of hydraulic hardening products, which also increases the resistance of mortars against aggressive substances present in the environment. [19]

Other common admixtures are plant fibres that can be proved with instrumental analysis during the analysis of historical mortars. However, in many cases it is not possible to determine their species due to their low quantities in mortars. [20]. Plant fibres in newly prepared mortars were represented in the form of hemp fibres. The presence of fibrous admixtures affects the properties of mortars by performing a general role of scattered reinforcement. For this function the stability of organic admixtures in alkaline lime mortar is another necessary property, which hemp fibres comply with. Previously though, the presence of organic fibres in mortar was rather haphazard (e.g. plant fibres as dirt of dredged sand).

Binders

It is desirable that the new supplements of lime mortars were also connected with lime, in terms of material compatibility of supplements with the original.

Table 3. Results of semi-quantitative XRD analysis - relative abundance of different phase composition of the original Gothic plaster sample (V4).

Sample	Quartz SiO_2	Feldspar		Mica	Clay minerals
		Albite, Plagioclases $(Na,Ca)Al(Si,Al)_3O_8$	Microcline $KAlSi_3O_8$	Muscovite $KAl_2(Si,Al)_4O_{10}(OH)_2$	Kaolinite $Al_2Si_2O_5(OH)_4$
Gothic plaster (V4)	strongly	moderately	moderately	moderately	slightly

Table 4. Composition of resulting mixture of aggregates for the newly proposed plaster (with slight correction for practical use).

Type of aggregates	Fractions on the sieve	Weight (g)	Percentage (%)	Bulk density (kg/l)
Clay plaster PICAS econom gross	from all sieves, excluding the share fraction on the sieve with the mesh size of 4 mm	1000	67.34	1.79
Clay plaster PICAS econom fine + hemp fibres	from all sieves	165	11.11	1.89
NaCa feldspar	1.0 mm	20	1.35	1.44
	0.5 mm	40	2.70	1.31
	0.25 mm	35	2.36	1.55
K feldspar	0.25 mm	35	2.36	1.55
	0.125 mm	10	0.67	1.28
	0.063 mm	20	1.35	1.44
	from the bottom of sieve separator	35	2.36	1.51
Ground quartz SKP 14.21.12.	from the bottom of sieve separator	80	5.40	1.30
Ground mica	0.5 – 0.063 mm	15	1.01	0.30
Clay CS 1 - Standard	0.5 – 0.25 mm	30	2.02	1.10
Resulting mixture	from all sieves	Total: 1485	Total: 100 %	1.94

Therefore, after considering the age of the object, the required parameters of resistance and physical properties declared by the manufacturer, lime has been chosen as a binder for the preparation of test samples. For the first series of mortar samples there was used air lime in the form of ripened lime slurry and for the second series of samples there was used a formulated lime VAPO.

For preparation of the repair mortar the ripened lime slurry was applied without addition of more water. Using the maturing lime slurry improves volume stability, strength and frost resistance of mortars prepared from it. For a good quality of the lime mortar its correct processing, use and subsequent treatment are required. [19] Mixed lime binder VAPO was selected due to its composition, which really tries to get close to the lime types frequently used in the past. Historical lime almost always contained certain percentage of hydraulic components, which among other things increase the resistance of walls against the moistening which we meet in the presbytery of the church.

Water

Amount of mixing water during preparation of mortar was restricted as much as possible. Shrinkage after hardening, which is reflected in the limitations of occurrence and spreading of shrinkage cracks, significantly decreases with the reduction of the water contents in the mortar. The less mixing water is in the mortar the lower is the porosity, but the higher its strength and resistance to frost.

Water content to achieve a normal consistency of mortar, when the binder was used in the form of the lime slurry, was 49.6 ml per 100 g of the dry binder - this amount has already been included in the lime slurry, so more water was not added. Water content to achieve a normal consistency of the mortar, when the binder was used in the form of the mixed lime binder VAPO, was 42.5 ml per 100 g of the dry binder. The water ratio of VAPO is then about a half lower than in the lime slurry.

Mixing ratios of binder to aggregates

The proposed mixing ratios of the binder to the aggregates in samples of newly prepared mortars are based on the mixing ratio corresponding to the sample of the original Gothic plaster V4 (1 : 1.5). The first series of samples have the same mixing ratio as the sample V4, i.e. 1 : 1.5. It was possible to slightly lower the share of the binder (when compared to the original plaster) because of the higher quality of current materials. So, mixing ratios for the other two series of the samples were chosen to be 1 : 2 and for the group using lime slurry as a binder also 1 : 2.5. (Mixing ratio 1 : 2.5 was not chosen for mortar with VAPO, because it is really outlying mixing ratio than the manufacturer´s recommended, i.e. from 1 : 1 to 1 : 1.5.)

Mixing and preparation of samples

Mortars were mixed with an electric mixer for 10 minutes, followed by a 10-minute delay and another 5-minute interval of stirring. Firstly, dry ingredients were mixed, then the binder was added, and finally, if it was needed, water was poured in gradually during mixing. This process of mixing with a minimal amount of added water enabled to obtain homogeneous appearance and a plastic characteristic of the resulting mortar which is typical with its good workability, which is a prerequisite for its optimum hardness.

Then the samples with dimensions of 4×4×4 cm were prepared from these mortars by adequate compacting in the moulds. Filled moulds and the samples extracted subsequently (demold was made after 48 hours) were stored in the laboratory at an average temperature of 22°C and relative humidity of 45 %.

Conditions of setting and hardening

Demolding of mortar specimens can be carried out after 48 hours. Hardening was carried out with both normal and then accelerated carbonation processes. Samples of mortar were exposed to the normal process of carbonation in air for 28 days with repeated regular intervals of four-day wetting made by fine spraying with water. Samples of mortar were then subjected to further processes of accelerated carbonation (4 cycles) in order to determine the properties and behaviour of fully hardened mortars, which corresponds to the 100 % level of carbonation. It consisted in repetitive 2 - 3 hr dives of samples (always after about 5 days) into the fresh 10 % solution of ammonium bicarbonate (NH_4HCO_3) and subsequent free drying at room temperature.

During repetitive dives there could be observed a lower resistance of samples with the mixed lime binder VAPO against the 10 % NH_4HCO_3 solution, because there occurred partial disintegration. Controlled carbonation of these samples was also slightly faster than in the samples with the lime slurry. Accelerated hardening in the presence of hydrocarbonate could theoretically convert into carbonate even that part of calcium ions, which would bind under "normal" carbonation conditions to the metakaolin that carries the strength of formulated lime VAPO. Therefore, there may be expected better, subsequently measured, mechanical properties for naturally carbonated mortars with the hydraulic binder VAPO.

RESULTS AND DISCUSSION

Properties of mortars during processing

The following properties were determined in mortars during processing (Table 5): Bulk density of fresh mortar according to the standard ČSN EN 1015-6 [21];

beginning of setting time and time of workability of mortar according to the standard ČSN EN 1015-9 [22]; test of mortar volume stability was performed according to the standard ČSN EN 196-3 [23].

Bulk density of fresh mortar is generally slightly lower for mortars with the lime slurry than for mortars using VAPO. In both groups of samples the bulk density increases with a decreasing amount of the used binder, i.e. with a higher mixing ratio of the binder to aggregates. The average bulk density of all samples of prepared mortars is about 2.0×10^{-3} kg/m^3.

Workability time of mortars prepared from the lime slurry is twice the time of workability of mortars with VAPO, approximately 300 min. For mortars with VAPO time of workability is about 140 - 150 min. The time of workability is generally always the longest for the highest binder content and with its decreasing amount these times decrease in both groups of samples.

Volume stability of mortars is better for the samples prepared from the lime slurry – i.e. their shrinkage is lower than in the case of mortars with the mixed lime binder VAPO. Volume stability for samples with the lime slurry decreases with increasing amounts of the binder in mortars. The highest volume stability for samples with the binder VAPO is in the group of mortars with the mixing ratio of the binder to the filler of 1 : 1.5 (i.e. the manufacturer's recommended mixing ratio). Volume stability of the samples with VAPO is even similar to the samples of mortars prepared from the lime slurry in the mixing ratio of 1 : 1.5.

Properties of hardened mortars

For hardened mortars there were determined the following properties (Table 6): compressive strength using the universal tensile machine Heckert FPZ 100/1 (VEB Rauenstein TIW) according to the standard ČSN EN 1015 – 11 [24]; porosity by mercury porosimetry (Graph II, III) using the unit PoreSizer 9320 (Micromeritics), water absorption, open porosity and bulk density of hardened mortar prepared according to the standard ČSN EN 13755 [25] and ČSN EN 1936 [26]; resistance to salt crystallization (Figure 2) according to the standard ČSN EN 12370 [27] and the literature [28]. X-ray diffraction analysis (XRD) was also carried out using θ-θ powder diffractometer X'Pert PRO in Bragg-Brentan parafocusing geometry. Data were scanned with a detector and evaluated using X'Celerator HighScore Plus program. Polished sections of mortar samples were microscopically observed and compared with the microstructure of the sample V4 using a polarizing microscope Olympus BX60 in the mode of impact light and photographs of polished sections of mortars were taken with an Olympus E-520 with appropriate magnification (Figure 3, 4).

Determination of compressive strength after 28 days

The measurement results of the compressive strength of mortar samples with the lime slurry are somewhat unexpected – they are higher than the results of the mortars with the slightly hydraulic binder VAPO. (The compressive strength and flexural strength should be increased with the increasing amount of metakaolin or other pozzolanic admixtures. [29] The prerequisite for this is of course sufficient time for natural carbonation of formulated lime mortars, which in this case was not completely fulfilled.) The highest compressive strength

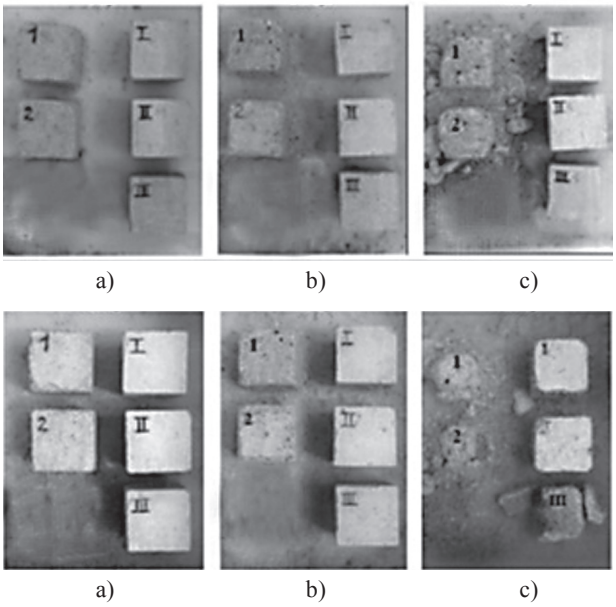


Figure 2. Condition of samples after 5 and 10 cycles in the solutions of salts; a) solution of 3 % KNO_3, b) solution of 3 % NaCl, c) solution of 10 % Na_2SO_4. Marking of samples: 1 – VAPO (1 : 2), 2 – VAPO (1 : 1.5), I – lime slurry (1 : 2), II – lime slurry (1 : 1.5), III – lime slurry (1 : 2.5).

Table 5. Properties of mortars during processing.

Properties	Type of mortar (according to the mixing ratio)/ Lime slurry			Mixed lime binder VAPO	
	1 : 1.5	1 : 2	1 : 2.5	1 : 1.5	1 : 2
Bulk density of fresh mortar $\rho_m \times 10^{-3}$ [kg/m^3]	1.86	1.98	2.07	1.93	2,01
Time of workability [min]	320	300	285	150	140
Volume stability ε_s [‰]	-6.04	-2.76	-1.25	-5.56	-7.35

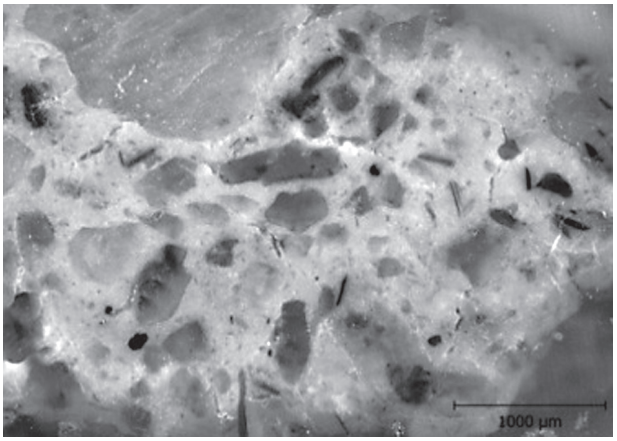
in the group of mortars with the lime slurry is shown by a sample with the highest proportion of the binder, i.e. with the mixing ratio of 1 : 1.5. With decreasing content of the binder the compressive strength of mortars should also decrease, but the results of measurements with respect to the standard deviation show that the strength of mortars with the lime slurry with the mixing ratio of 1 : 2 and 1 : 2.5 differ little and the expected decrease in strength does not occur. In case of VAPO the highest compressive strength is observed in the samples with the manufacturer's recommended mixing ratio of 1 : 1.5. This strength value is a little higher than in the case of mortars with the lime slurry with the mixing ratio of 1 : 2 and 1 : 2.5. The difference in favour of higher compressive strength for formulated lime mortars would be expected to be more distinct. Even the assumption that a higher

Table 6. Properties of hardened mortars.

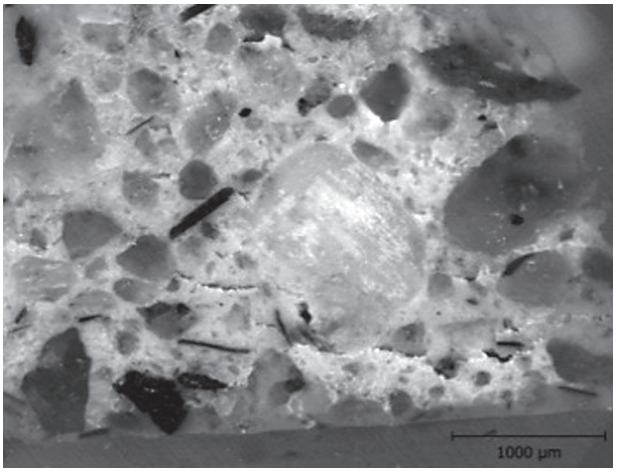
Properties	Type of mortar (according to the mixing ratio)/ Lime slurry 1 : 1.5	Lime slurry 1 : 2	Lime slurry 1 : 2.5	Mixed lime binder VAPO 1 : 1.5	Mixed lime binder VAPO 1 : 2
Determination of compressive strength after 28 days					
Average value of R [MPa]	4.07	3.53	3.71	3.82	3.27
Standard deviation σ_R [MPa]	0.18	0.13	0.09	0.12	0.14
Mercury porosimetry – measured values and deducted values from graphs					
Median PCB × 10^{-2} [μm]	1.06	2.92	0.59	0.49	2.43
Porosity [%]	28.46	25.91	25.70	35.69	29.74
Radius of the most represented pores r [μm] 1st maximum	0.25	0.25	0.21	0.36	5.00
Distributions of pore size others widely represented pores [μm]	0.01 – 0.05 8 – 1.5	2 – 6.5	2 – 12.5	---	---
Determination of water absorption, open porosity and bulk density of hardened mortar					
Water absorption (A) [%] after 48 hrs. under atmospheric pressure	17.16	14.83	12.72	18.93	17.41
Open porosity (e^{Ψ}) [%] after 48 hrs. under atmospheric pressure	29.61	26.53	23.45	32.43	30.63
Bulk density (OH) × 10^{-3} [kg/m^3] after 48 hrs. under atmospheric pressure	1.73	1.79	1.84	1.71	1.76
Open porosity (e^{Ψ}) [%] after 8-hr evacuation	33.17	32.09	29.64	33.98	33.07
Bulk density (OH) × 10^{-3} [kg/m^3] after 8-hr evacuation	1.02	1.04	1.07	1.03	1.06
Determination of resistance to salt crystallisation – weight changes					
Solution of 3 % KNO_3 after 5 cycles Δm_5	+ 1.10	+ 1.80	+ 1.91	- 0.98	- 1.50
after 10 cycles Δm_{10}	+ 1.15	+ 1.85	+ 1.98	- 1.36	- 2.05
Solution of 3 % NaCl after 5 cycles Δm_5	+ 1.82	+ 2.36	+ 2.99	- 2.83	- 4.31
after 10 cycles Δm_{10}	- 0.21	- 0.85	- 2.12	- 4.79	- 6.52
Solution of 10 % Na_2SO_4 after 5 cycles Δm_5	+ 2.16	+ 4.82	+ 6.03	- 45.34	- 38.28
after 10 cycles Δm_{10}	- 6.27	- 6,38	disintegrated after 10 cycles	disintegrated after 9 cycles	disintegrated after 7 cycles
Results of semiquantitative XRD analysis - relative abundance of individual phases					
Aggregates*	60	70	76	53	65
Lime binder Calcite $CaCO_3$	36	28	24	37	28
Aragonite $CaCO_3$	0	0	0	10	7
Portlandit $Ca(OH)_2$	4	2	0	0	0

** Aggregates have known mineralogical composition: Quartz - SiO_2, Feldspar - albite, plagioclases $(Na,Ca)Al(Si,Al)_3O_8$ or microcline $KAlSi_3O_8$, Mica - muscovite $KAl_2(Si\,Al)_4O_{10}(OH)_2$, Clay minerals - illite $K(Al_4Si_2O_9(OH)_3)$.*

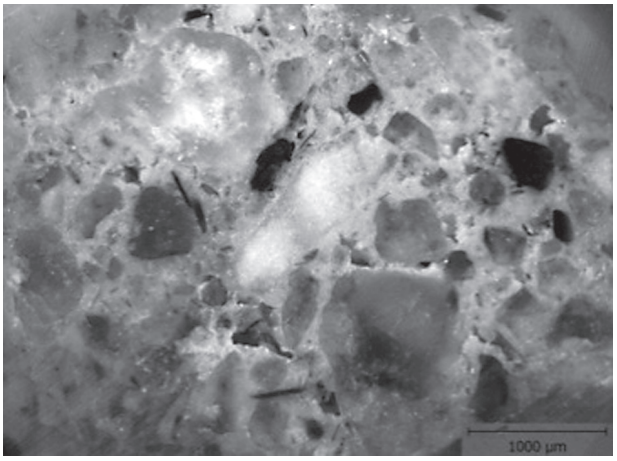
content of a binder is a prerequisite for higher strength does not apply in case of mortars with VAPO. This is undoubtedly related to their partial disintegration during the process of accelerated carbonation and the lack of development of pozzolanic reaction products, which are responsible for strength and firmness.



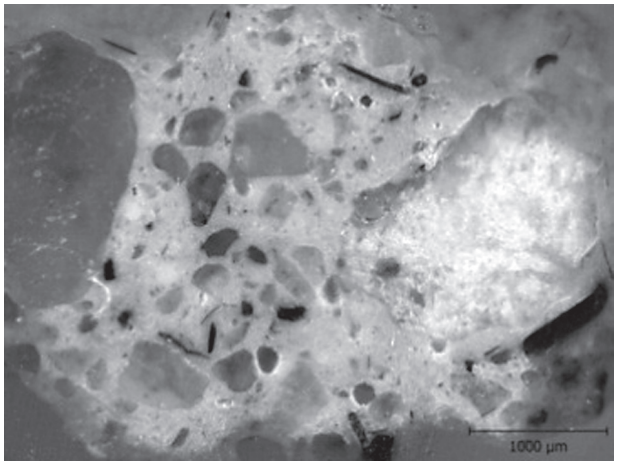
a) Lime slurry (1 : 1.5)



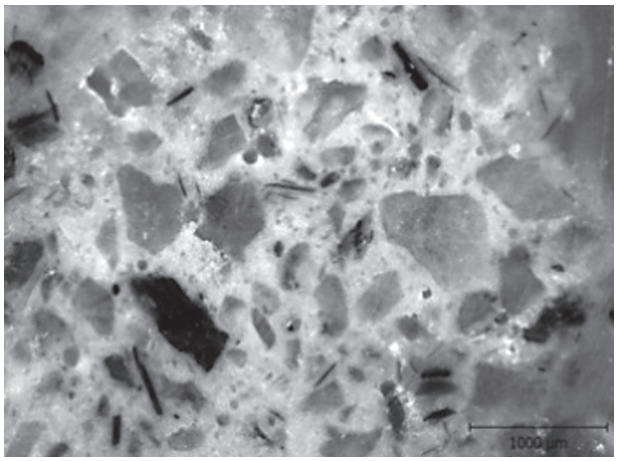
b) Lime slurry (1 : 2)



c) Lime slurry (1 : 2.5)



d) VAPO (1 : 1.5)



e) VAPO (1 : 2)

Figure 3. Polished cross sections of newly mortar samples (zoom 40×).

Determination of porosity
by mercury porosimetry

The aim was to prepare repair mortar samples with porosity corresponding to the Gothic plaster, i.e. within the range 25 – 35 %, because the system original plaster – repair mortar displays better quality due to similar proportion of the pores in the new repair mortar, when compare to the original mortar. [30] This requirement was achieved primarily by appropriate mixing of mortar and addition of mixing water.

All samples of newly prepared plasters meet the required range of porosity. For mortars with VAPO the porosity of the samples is slightly larger in comparison with the samples of mortars with the lime slurry and grows with the amount of binder contents and metakaolin in mortars. [3] The growing trend of porosity with increasing content of a binder can also be observed for mortars with the lime slurry. Distributions of pore size of mortars with different content of the lime slurry are very similar according to the graph II. The most frequent pores found in these mortars have a radius from 0.20

to 0.25 μm and there is also a smaller amount of pores with a radius of 2 to 10 μm. Distributions of pore size of mortars with the mixed lime binder VAPO, which differ in the mixing ratio, are quite different according to the graph III, even though the same procedures for mixing and addition of mixing water were still followed.

The sample with a mixing ratio of 1 : 1.5 from the group of mortars with the formulated lime VAPO is closest to the radius of the pore size distribution of mortars with the lime slurry. The position of its maximum of the most representative pore radius corresponds to the value of 0.36 μm. Frequency curve characterizing the porosity of mortars with the binder VAPO with the mixing ratio of 1 : 2 has almost the same course as the frequency curve of the above mentioned mortar with the binder VAPO in the recommended mixing ratio of 1 : 1.5, but the position of the maximum of the most representative pore radius is moved towards higher values (about 5 μm). The position of this peak also corresponds to the distribution of size of pore radius more widely represented in mortars with the lime slurry.

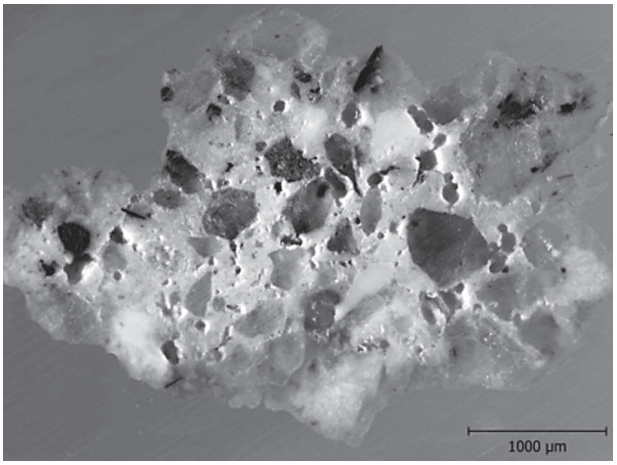
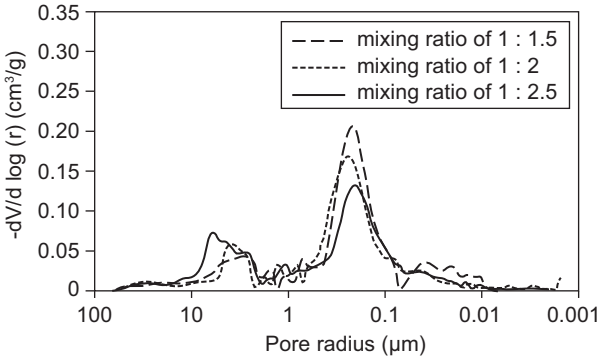


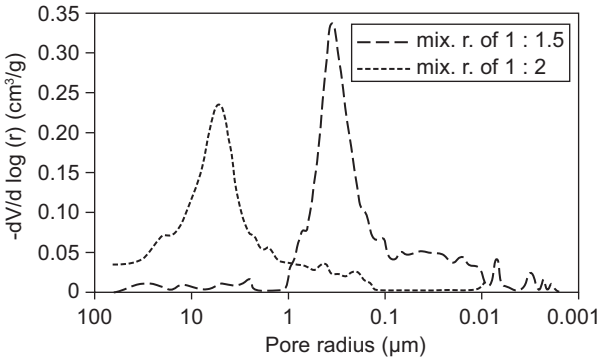
Figure 4. Polished cross -section of original Gothic plaster V4 for comparison with the microstructures of new mortar samples (zoom 40×).

Determination of water absorption, open porosity and bulk density of hardened mortar

The value of open porosity of mortar samples measured after 48 hours is for all samples nearly the same as the value of porosity, which was determined by mercury porosimetry and its value is around 25 - 30 %. Mortars with formulated lime exhibited slightly higher open porosity than mortars with the lime slurry. Porosity in both groups of the samples increases with the increasing content of a binder in mortars. Bulk density of mortars has the opposite trend – it decreases with the higher amount of a binder and higher content of pores. Water absorption of samples of mortars measured after 48 hours always increases proportionally with the increasing number of pores and its value for all samples is between 12 – 19 %.



Graph II. Frequency curves of samples of mortars with lime slurry.



Graph III. Frequency curves of samples of mortars with VAPO

The open porosity of samples of mortars measured after 8-hour evacuation is several units higher than the values measured after 48 hours under atmospheric pressure in water. Under atmospheric pressure during immersion the water fills mainly pores of larger radius, during immersion under lower pressure even smaller radius pores are expected to be filled. It can be concluded that the difference in open porosity under lower pressure and atmospheric pressure indicates the number of small pores present in mortar. Representation of smaller pores in mortars with the lime slurry is larger (range 3.5 - 6.2 %) than in mortars with formulated lime VAPO (range 1.5 - 2.5 %).

Determination of resistance to salt crystallisation

Results of determination of resistance to salts show that all samples of mortars with the lime slurry as a binder are not damaged in the nitrate and chloride solutions even after 10 cycles, not even if they contain salt crystals in their structure (observed during microscopic

examination). As for the samples that were soaked in a solution of nitrate, the salts began to crystallize on their surface after 5 cycles. Partial damage of samples wetted in the solution of sulfate occurred after 5 cycles and the sample with a mixing ratio of 1 : 2.5 disintegrated after 10 cycles. In these samples there might be formed gypsum and ettringite with large molar volume, resulting in the formation of cracks on the surface and inside the samples.

As for the samples of mortars with formulated lime VAPO as a binder, there was a visible crystallization of salts (sulfates and nitrates) on the surface of samples, but their collapse was caused by rather low cohesion in aqueous environment due to the previous soaking of the samples in a solution of 10 % NH_4HCO_3 to accelerate the carbonation process. Due to the presence of an aluminate phase and metakaolin that are contained in this mixed lime binder, the reaction with sulfates occurred probably more easily than in the case of mortars with the lime slurry. [28]

It is obvious that the resistance of prepared mortars in solutions of salts decreases with lowering contents of a binder in mortars. The most aggressive environment of the investigated solutions of salts is displayed by the solution of 10 % Na_2SO_4 and the highest resistance is exhibited by mortars against the solution of 3 % KNO_3.

Microscopic examination

Observation and comparison of polished cross sections of samples of repair mortars (Figure 2) brought very satisfactory results. It achieved a similar structure as that of the original Gothic plaster for all the samples prepared from the lime slurry and from the mixed lime binder VAPO (Figure 3). It is obvious that the highest similarity with the original structure of the Gothic mortar (sample V4) is shown by the mortars with the mixing ratio of 1 : 1.5, which was chosen exactly according to the calculated mixing ratio of the binder to the filler in the Gothic plaster in its current state.

X-ray diffraction analysis (XRD)

XRD analysis determined the relative amount of aggregates and a binder in samples of prepared mortars only approximately. Mixing ratios of the binder to the filler in newly prepared mortars roughly correspond to this semi-quantitative determination. In this case, measurements were primarily concentrated on the binder, i.e. in what form the present lime occurs. The most represented mineral in all hardened mortars was $CaCO_3$ in the form of calcite. With the growing amount of a binder the content of calcite also increases. The presence of $CaCO_3$ in the form of aragonite was identified in all samples of mortars with the formulated lime VAPO, but not in the samples of mortars with the lime slurry. The content of aragonite also increased with the higher amount of a binder in mortars. In the samples the relative amount of aragonite to the calcite is approximately 1 : 3.7 – 4. Formation of aragonite only in mortars with the mixed lime binder VAPO can be explained on the basis of different mechanisms of carbonation of mortars with the air and formulated lime.

The presence of very low content of portlandit - $Ca(OH)_2$ (non-carbonated share) in samples of mortars with the lime slurry shows that carbonation of the lime slurry is slower than it is in the case of the mixed lime binder VAPO, where the content of portlandit is almost zero. The amount of portlandit increases with the content of the binder in samples, but it is so small that it can be neglected for other purposes and the binder can be considered as fully hardened.

CONCLUSION

On the basis of results of the chemical-technological research using instrumental analysis of the original Gothic plaster (sample V4) it has been possible to formulate the request for ingredients for the repair mortar. The formulation has been prepared with regard to the commercial availability of all the used materials, which opens a possibility of practical use of this mortar.

The above determination of properties during processing of mortars and properties of hardened mortars showed that almost all of the requirements for the composition, physico-mechanical and aesthetic characteristics and resistance to aggressive environment are best fulfilled by mortars using lime slurry as a binder.

Aggregates of this mortar are: dredged sand with angular grains of uneven distribution of particles in the range 0–2 mm containing quartz, feldspar, mica, a small proportion of clay minerals, organic impurities in the form of plant fibres and crushed bricks. The mixing ratio of the binder to the aggregates is 1 : 2 in this mortar. The time of workability is 300 minutes. The volume stability of the mortar is constant - shrinkage during total carbonation was only 2.76 ‰. From the hardened mortar properties there should be mentioned mainly its optimal compressive strength 3.53 MPa and porosity 25.91 %, which is very close to the porosity of the original Gothic plaster. The most represented pore sizes in the mortar are 0.25 μm and 2–6.5 μm. Water absorption under atmospheric pressure is 14.83 %, open porosity accessible to water under atmospheric pressure is 26.53 % and open porosity measured under reduced pressure is 32.09 %. The mortar exhibited very good resistance to solutions of nitrates and chlorides, in which the mortar samples were soaked for 10 cycles without damage. The mortar had a bit lower resistance to the solution of sodium sulfate - first cracks appeared on the samples during the eighth soaking cycle. Microscopic examination confirmed that a structure similar to the original Gothic plaster was achieved during the mortar preparation.

Therefore, this mortar can be recommended as a suitable one for restoration of plaster in the presbytery of St. Giles church in Uhlířské Janovice.

The aim of further work will be to apply the mortar in the form of samples on the real surface, specifically masonry, in the presbytery of the church, and to verify practically its adhesion to the surface and its properties in the real environment.

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