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# Application of burnt clay shale as pozzolan addition to lime mortar

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## ABSTRACT

Burnt Czech clay shale of different grain fineness is applied as a new pozzolan addition to lime mortar. Experimental results show that the new lime–pozzolan mortars have significantly better mechanical properties and frost resistance than the reference lime mortar. The fineness of burnt Czech clay shale is a very important parameter affecting the properties of lime–pozzolan mortars; the best results are achieved with an average particle size of 4 μm. In a comparison with a lime–metakaolin mortar of the same composition, the frost resistance of the new lime–pozzolan mortars is significantly better, the mechanical, fracture-mechanical, hygric and thermal properties are either comparable or slightly better. Therefore, it can be concluded that the burnt Czech clay shale has a good potential to be used in lime–pozzolan mortars for renovation of historical buildings.

## 1. Introduction

Rendering mortars composed of quicklime and pozzolan additions were used since the ancient times. The reaction of pozzolan with lime formed hydrated calcium silicates which imparted higher durability to the renders. Due to the higher resistance of these materials to the environment, some original plasters or plaster fragments were conserved up to now. Volcanic materials such as volcanic ash, tuff and crushed volcanic rock acting as natural pozzolans were the first pozzolanic materials used in a wide extent, either in the form of coarse aggregates or powders, which was due to their wide availability within the territory of ancient Rome [1–5]. Lime plasters containing volcanic materials were found also in the Maya lowlands [6,7]. However, there are still questions regarding the locations of volcanic deposits exploited, the periods in which reactive volcanic materials were used in Maya plasters, and the specific hydraulic compounds that are found in ancient Maya plasters [8]. Artificial pozzolans, such as crushed bricks or brick dust, were used by Romans whenever natural pozzolanic materials were not available and a mortar insoluble in water was needed. The use of ceramic powder or fragments for the improvement of hydraulic properties of lime mortars within the territory of ancient Rome was reported by many investigators [9–14].

In the medieval times, the quality of mortars was often lower compared to Roman times as pointed out by Miriello et al. [14] who studied Roman, proto-Byzantine and medieval mortars and found the most friable sample to be a mixture of clay, lime and volcanic sand belonging to the Middle Ages. In some cases, certain impure limestones from specific quarries were used to produce limes, which had to be slaked on use because they hardened fast and set under water [15]. The renaissance mortars were often mixed according to Vitruvius guidelines for the choice and preparation of raw materials. The architects distinguished between the use of white lime obtained from the calcination of river pebbles and dark lime (hydraulic lime) obtained from the calcination of grey and dark limestones as substitutions of the pozzolans [15].

During the 19th century Portland cement gradually displaced other hydraulic materials in construction; as a component of plasters it was used since the 1920s. However, due to the limited physico-chemical, mechanical, and esthetic compatibility of cement mortars with the old masonry and architectural surfaces [11] the use of cement in renovation of historical buildings began to subside, in particular during the last several decades. In many European countries, the requirements of supervisory authorities taking care of historical monuments were becoming stricter as for the compatibility of wall materials and conservation mortars with the original masonry. Therefore, new solutions were sought to prevent damage to the architectural heritage. Cortina et al. [16] presented a technological solution to obtain lime-based hydraulic mortars with the addition of chamotte or burnt clay powder obtained from the ceramic industry's waste. By doing this, hydraulic properties have been incorporated and mortars with great improvements in mechanical properties were produced. Maravelaki-Kalaitzaki et al. [12] designed, characterized and then

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monitored the performance of repair mortars and plasters composed of natural hydraulic lime with pozzolanic additions as the binding material and aggregates of siliceous sand and crushed brick. Zawawi and Banfill [17] proposed an artificial hydraulic lime for repair and conservation of historic masonry which was produced using limestone and siliceous waste materials such as pulverized fuel ash, glass cullet, silica sand, crushed rock and spent oil shale. Černý et al. [18] analyzed three lime–pozzolan plasters containing metakaolin, ground brick and ground enamel glass and found them suitable for application in the reconstruction of historical buildings. Cultrone et al. [5] proposed several combinations of brick and calcarenite with lime- and lime–pozzolan mortars. Snellings et al. [19] and de la Villa et al. [20] showed a potential of natural zeolites for production of lime–pozzolan mortars.

Interesting solutions for lime–pozzolan mortars potentially applicable in renovation of historical buildings also appeared in other countries. Yang et al. [21] presented a systematic study of sticky rice–lime mortar technology aimed at the determination of the proper courses of action in restoring ancient buildings in China. Martirena et al. [22,23] performed studies of different wastes of the sugar industry, mainly sugar cane bagasse ash and sugar cane straw ash, and have shown that such byproducts are likely to be pozzolanic and their use in lime–pozzolan binders could become an interesting alternative for developing countries. Nair et al. [24] investigated the properties of rice husk ash pozzolans in a mixture with lime for an alternative use in rural housing.

In the Czech Republic, the current procedures in renovation of historical buildings are very rigorous. The materials for repair or innovation of renders are supposed to have the most similar composition to the historical materials and they have to be applicable by the original methods. This concerns especially the number and the structure of coated layers, the manner of plaster surface treatment by striking, indentation or smoothing [25,26]. Also, it is considered unacceptable to use lime–cement renders in Romanesque, Gothic, Renaissance and Baroque buildings. Taking into account the high purity of currently produced lime hydrates and the general unavailability of hydraulic lime, adding pozzolans to lime seems to be the most prospective option. As no natural pozzolans can be found within the Czech territory, a logical option is to employ artificial pozzolans. Brick dust and metakaolin can be considered feasible solutions in that respect [18]; clays from the kaolinite, illite or montmorillonite groups were available and widely used in high amounts also in historic times. In this paper, we present another idea and introduce a specific type of clay shale (“lupek” in the Czech language). As there is no exact translation of this rock to English (the exact equivalents exist only in German – “Letten” and Polish – “lupek osadowy”, apparently due to the availability of this rock only within the territory of Central Europe), we will denote it “Czech clay shale” in what follows.

The Czech clay shale is extracted from several mines which are mostly located close to the pitcoal mines. At present, in natural form it is used in production of refractory ceramics, in burnt form as grog in the ceramic industry. After burning at temperatures similar to the burning of kaolinite in metakaolin production the Czech clay shale exhibits pozzolanic properties. Therefore, it has potential for use in lime–pozzolan mortars and renders.

This paper presents a systematic research on lime mortars containing burnt Czech clay shale of different particle size distribution as pozzolan addition. Basic material characteristics, mechanical and fracture-mechanical properties, durability characteristics, hydric and thermal properties are analyzed. The obtained results are compared with the parameters of lime mortar without any additives, a lime–metakaolin mortar and a commercial renovation mortar.

## 2. Materials and samples

A CL-90 lime hydrate (Kotouč Štramberk) complying with the European standard EN 459-1 was used for the preparation of lime–pozzolan mortars. Its composition is given in Table 1. The applied burnt Czech clay shale with the composition given in Table 2 was produced by České lupkové závody Nové Strašecí in three different variants, denoted as L10, L05, and L03. Their particle size distributions are presented in Fig. 1. All three distribution curves were rather broad; the smallest particles present in all types of burnt Czech clay shale were of the same size 0.5 μm; the largest particles were observed in L10. The average particle size (median of cumulative passing curve) of L03 was 4 μm, for L05 it was 9 μm, and for L10 10 μm.

The composition of the three studied lime–pozzolan mortars, LCS10, LCS05, and LCS03, containing the burnt Czech clay shale is shown in Table 3 where w/ds is the water to dry solids ratio by mass. The amount of burnt Czech clay shale in the lime–pozzolan binder was chosen as 20% of the mass of lime hydrate. According to the study presented in [33] for metakaolin with a similar composition this dosage makes it possible to achieve significantly better strengths than for pure lime mortars but the water vapor transport properties are not negatively influenced by such a pozzolan addition.

Three other mortars were investigated as well, in order to compare their properties with the new lime–pozzolan mortars (Table

**Table 1**
Chemical composition of lime.

| Component | Mass (%) |
|---|---|
| CaO | 95.7 |
| MgO | 1.1 |
| $SO_3$ | 0.1 |
| $CO_2$ | 0.9 |

**Table 2**
Chemical composition of pozzolans by mass (%).

| Component | Metakaolin | Burnt Czech clay shale |
|---|---|---|
| $Al_2O_3$ | 38.50 | 41.90 |
| $SiO_2$ | 58.70 | 52.90 |
| $K_2O$ | 0.85 | 0.77 |
| $Fe_2O_3$ | 0.72 | 1.08 |
| $TiO_2$ | 0.50 | 1.80 |
| MgO | 0.38 | 0.18 |
| CaO | 0.20 | 0.13 |
| Loss on ignition | 1.67 | 1.40 |

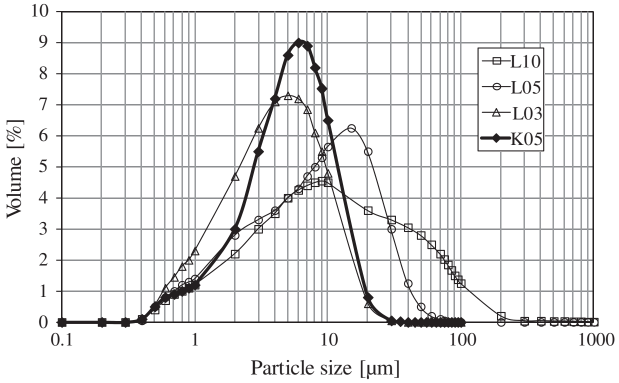

**Fig. 1.** Particle size distributions of pozzolan additions.

**Table 3**
The mass composition of studied mortars.

| Mortar | Type of pozzolan | Pozzolan (kg) | Lime (kg) | Natural quartz and basalt sand, 0–4 mm (kg) | w/ds (–) |
|---|---|---|---|---|---|
| LR | – | – | 2.5 | 7.5 | 0.29 |
| LCS10 | L10 | 0.42 | 2.08 | 7.5 | 0.25 |
| LCS05 | L05 | 0.42 | 2.08 | 7.5 | 0.23 |
| LCS03 | L03 | 0.42 | 2.08 | 7.5 | 0.24 |
| LM | K05 | 0.42 | 2.08 | 7.5 | 0.258 |
| CV2 | 3.33 kg of dry binder mix and 6.66 kg of 0–4 mm aggregates | | | | 0.375 |

3). The reference lime mortar LR was prepared without any pozzolanic additions. The lime–metakaolin mortar LM contained metakaolin Mefisto K05 (produced by the same company as the burnt Czech clay shale; the composition is given in Table 2) in the same amount as L10, L05 and L03 in LCS10, LCS05 and LCS03. The commercial renovation mortar CV2 was on the lime basis. In the preparation of this mortar the manufacturer's instructions were followed, including the higher w/ds ratio as compared to the other mortars. The exact composition of CV2 was not known.

The measurement of material parameters was done (unless stated otherwise) after 28 days of standard curing in a conditioned laboratory at the temperature of 22 ± 1 °C and 25–30% relative humidity. The following specimens were used in the experiments: bulk density, matrix density and open porosity – six specimens of 50 × 50 × 25 mm, bending strength – six specimens of 40 × 40 × 160 mm, compressive strength – the halves of the specimens left over after the bending tests, fracture-mechanical properties – three specimens of 40 × 40 × 160 mm, freeze/thaw resistance – three sets of three 40 × 40 × 160 mm specimens, water transport properties – five specimens of 50 × 50 × 20 mm, water vapor transport properties – two sets of three cylindrical samples with the diameter of 100 mm and height of 20 mm, thermal properties – three specimens of 70 × 70 × 70 mm.

## 3. Experimental methods

The bulk density, open porosity, and matrix density were determined using the water vacuum saturation method [27]. The particle size distribution was measured by a laser particle size analyzer Mastersizer 2000 (Malvern), the pore size distribution by Mercury Intrusion Porosimetry (MIP) using the porosimeters Pascal 140 and 440 (Thermo).

The measurement of compressive and bending strength was done using the testing devices WPM 100 kN and WPM 50 kN, respectively. A three-point bending test of a specimen having a central edge notch length of about 1/3 of the depth of the specimen was used in the measurement of fracture-mechanical parameters. The effective fracture toughness and effective toughness were determined using the Effective Crack Model [28]; the fracture energy was obtained by the RILEM method [29].

The frost resistance test was performed according to ČSN 72 2452 [30]. Each freeze/thaw period consisted of 15 cycles. The frost resistance coefficient $K$ was determined as the ratio of bending or compressive strength of specimens subjected to the specified number of freezing and thawing cycles to the strength of reference specimens which did not undergo the frost resistance test. A material was considered frost resistant for $K > 0.75$.

The water absorption coefficient was determined in a water-sorptivity experiment with automatic data acquisition [31]. The apparent moisture diffusivity was calculated using the data for water absorption coefficient and vacuum saturation moisture content, according to the basic formula given in [32]. The wet-cup method and dry-cup method were employed in the measurements of the water vapor diffusion coefficient $D$ and water vapor diffusion resistance factor $\mu$ ($\mu = D_a/D$, where $D_a$ is the diffusion coefficient of water vapor in air) [27]. The thermal conductivity and specific heat capacity were determined using an Isomet 2104 (Applied Precision) working on an impulse principle.

## 4. Results and discussion

The lowest open porosity was achieved by the lime–pozzolan mortars LCS05 and LCS03 with the finest pozzolan particles (Table 4). The mortar with coarser particles of burnt Czech clay shale, LCS10, had almost the same porosity as the lime–metakaolin mortar LM, about 5% higher than LCS05 and LCS03. The porosity of the reference lime mortar without pozzolan admixture, LR, was in between. The pore size distribution of all lime–pozzolan mortars was also similar to the reference lime mortar (Fig. 2), with a main peak at 0.6–0.7 μm. Accordingly, the bulk- and matrix densities were also rather close, within a 3% margin (Table 4). This was a first indication of a successful mix design as the lime–pozzolan mortars should have similar basic physical properties to the lime mortars if they are supposed to be used in the renovation of historical buildings. The commercial renovation mortar CV2 had about 20% higher open porosity than the other mortars but its matrix density was similar to lime–pozzolan mortars (Table 4), as well as its pore size distribution determined by MIP (Fig. 2). This implied that CV2 could be based either on a lime–pozzolan- or a lime–cement binder. Its higher porosity was certainly at least partially related to its higher w/ds ratio as compared with the other lime–pozzolan mortars, possibly also some foaming admixtures were used. The excess pores were thus mainly bigger pores (>100 μm) of technological origin which were not detectable by MIP.

The highest compressive strength within the studied time period of 7–90 days was exhibited by the lime–pozzolan mortar LCS03 (Table 5). This was apparently related to the finest particles of burnt Czech clay shale in this material (Fig. 1), so that the silicate

**Table 4**
Basic physical properties of mortars.

| Mortar | Bulk density (kg m$^{-3}$) | Matrix density (kg m$^{-3}$) | Open porosity (%m$^3$ m$^{-3}$) |
|---|---|---|---|
| LR | 1726 | 2648 | 34.6 |
| LCS10 | 1660 | 2573 | 35.5 |
| LCS05 | 1689 | 2533 | 33.3 |
| LCS03 | 1689 | 2543 | 33.6 |
| LM | 1716 | 2669 | 35.7 |
| CV2 | 1479 | 2539 | 41.8 |

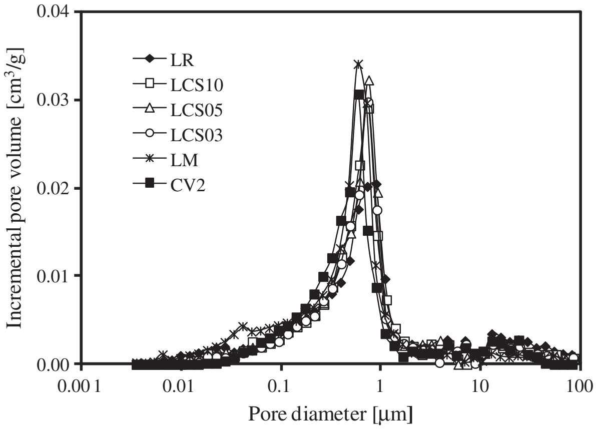

**Fig. 2.** Pore size distributions of studied mortars.

**Table 5**
Compressive strength of mortars (MPa).

| Time period (days) | Mortar | | | | | |
|---|---|---|---|---|---|---|
| | LR | LCS10 | LCS05 | LCS03 | LM | CV2 |
| 7 | 0.6 | 2.1 | 2.1 | 3.5 | 2.03 | 2.5 |
| 28 | 0.9 | 2.9 | 2.8 | 4.7 | 4.74 | 3.5 |
| 56 | – | 3.2 | 3.3 | 5 | 4.74 | 4.4 |
| 90 | 0.9 | 3.4 | 4.1 | 6.3 | 5.83 | 4.3 |

**Table 6**
Bending strength of mortars (MPa).

| Time period (days) | Mortar | | | | | |
|---|---|---|---|---|---|---|
| | LR | LCS10 | LCS05 | LCS03 | LM | CV2 |
| 7 | 0.1 | 0.6 | 0.6 | 0.8 | 0.6 | 0.6 |
| 28 | 0.2 | 0.8 | 0.8 | 1.4 | 1.4 | 0.8 |
| 56 | – | 0.8 | 0.9 | 1.4 | 1.5 | 0.9 |
| 90 | 0.5 | 0.8 | 0.8 | 1.3 | 1.29 | 1.1 |

and aluminate ions were able to react very quickly with $Ca^{2+}$ ions, forming CSH gels, $C_4AH_{13}$, $C_3AH_6$ and $C_2ASH_8$ in the lime–pozzolan mortar [34]. Also, the presence of smaller and more numerous particles led to smaller interparticle spaces, with a corresponding increase in strength. The second highest compressive strength was presented by the lime–metakaolin mortar LM, but its initial strength growth was slower, apparently due to the slightly coarser particles of metakaolin (Fig. 1). LCS10 and LCS05 had up to 50% lower compressive strength than LCS03, giving a clear evidence of the importance of fine grinding of the burnt Czech clay shale. The compressive strength of the commercial renovation mortar CV2 was at first slightly higher than LM, then up to 25% lower. This may indicate the presence of either fine grained metakaolin or a small amount of cement in CV2. The reference lime mortar LR had up to seven times lower compressive strength as compared with the lime–pozzolan mortars which underlined the importance of pozzolan additions to the lime binder.

A comparison of results obtained in this paper with the measurements presented by other investigators could not be done directly as the burnt Czech clay shale is a local pozzolan which is not available outside the territory of Central Europe. However, as was shown in Table 2, its composition is relatively similar to metakaolin. Therefore, lime–metakaolin mortars are the closest materials for comparison to our lime–pozzolan mortars with burnt Czech clay shale. The compressive strength $R_c$ of lime–metakaolin mortars was measured mostly for mixes with lower lime:pozzolan (L:P) ratios than in this paper. Billong et al. [35] achieved $R_c = 10.2$ MPa for L:P = 0.3:0.7 after 28 days as the best result. Sepulcre-Aguilar and Hernández-Olivares [36] obtained after 21 days $R_c = 12–15$ MPa for L:P = 1:1 mixes cured under 60 °C warm water. Fortes-Revilla et al. [37] measured $R_c = 10–14$ MPa for L:P = 1:1 after 25 and 75 days. Veiga et al. [38] for a mix with higher L:P, 1:0.5 obtained after 90 days only a $R_c = 1.3$ MPa. In a comparison with these results, our mix design with the L:P ratio of 5:1 can be considered very successful from both the technical and economical points of view; $R_c = 6.3$ MPa for LCS03 after 90 days achieved with only a fraction of pozzolan addition as compared with [35–37] is a good outcome.

The investigations presented in [35–38] revealed that – on a general level – it was difficult to determine an optimum L:P ratio because too many different factors were in play at the same time. Fortes-Revilla et al. [37] presented an analysis of the mutual effects of binder:sand (B:S) ratio, L:P ratio, and use of superplasticizer on the strength and porosity. They found B:S ratio the most important factor affecting the compressive strength, while L:P had only a moderate effect. Qualitatively similar results were obtained in less detailed studies presented in [35,36,38]. However, it should be noted that the range of studied L:P ratios was in all cases relatively narrow and other parameters than strength and porosity were not taken into account.

The bending strengths (Table 6) followed a similar course as the compressive strengths. LCS03 showed once again the fastest increase of bending strength $R_f$ with time up to 7 days but in later times its $R_f$ values were almost the same as LM. CV2 achieved up to 40% lower $R_f$, together with LCS10 and LCS05. The bending strength of the reference lime mortar LR was up to seven times lower than for lime–pozzolan mortars but the difference decreased with time, apparently due to carbonation.

In the measurement of bending strength of lime–metakaolin mortars, Fortes-Revilla et al. [37] obtained $R_f = 2.5–3.5$ MPa for L:P = 1:1 after 25 and 75 days, while Veiga et al. [38] for a mix with L:P = 1:0.5 measured only $R_f = 0.4$ MPa. Also in this case our LCS03 mortar (L:P = 5:1) with $R_f = 1.4$ MPa after 28 days performed very well by comparison.

The lime–pozzolan mortar LCS03 with the finest pozzolan particles exhibited by far the highest fracture-mechanical parameters (Table 7); the second best, CV2, being only about one half to one third of the LCS03 values. The remaining lime–pozzolan mortars LCS10, LCS05 and LM were on about the same level in the effective fracture toughness and effective toughness but the fracture energy of the lime–metakaolin mortar LM was only about one half of the values measured for LCS10 and LCS05. The fracture-mechanical parameters of the reference lime plaster LR could not be determined because their values were lower than the sensitivity limit of the applied measuring device.

If compressive strength was taken as the main criterion of frost resistance, all lime–pozzolan mortars with the burnt Czech clay shale could be classified as frost resistant; they achieved $K > 0.75$ in both testing periods (Table 8). The commercial renovation mortar CV2 performed similarly. The lime–metakaolin mortar LM showed the worst performance among the lime–pozzolan mortars, with $K$ values of only about 0.5–0.6. The reference lime plaster was disintegrated already after the third freeze/thaw cycle. The frost resistance coefficient $K$ calculated as the ratio of bending strengths was much lower than in the case of the ratio of compressive strengths (Table 8); no studied material achieved $K > 0.75$ in both

**Table 7**
Fracture-mechanical properties of mortars.

| Parameter | Mortar | | | | | |
|---|---|---|---|---|---|---|
| | LR | LCS10 | LCS05 | LCS03 | LM | CV2 |
| Effective fracture toughness ($MPa\ m^{1/2}$) | – | 0.086 | 0.092 | 0.204 | 0.082 | 0.123 |
| Effective toughness ($N\ m^{-1}$) | – | 1.38 | 1.42 | 7.35 | 1.2 | 3.73 |
| Fracture energy ($J\ m^{-2}$) | – | 11.6 | 11.5 | 53.9 | 6.0 | 19.6 |

**Table 8**
Frost resistance coefficient of mortars.

| Mortar | Frost resistance coefficient $K$ as the ratio of compressive strengths (–) | | Frost resistance coefficient $K$ as the ratio of bending strengths (–) | |
|---|---|---|---|---|
| | 1st Period | 2nd Period | 1st Period | 2nd Period |
| LR | – | – | – | – |
| LCS10 | 1.03 | 1.03 | 0.500 | 0.500 |
| LCS05 | 1.18 | 1.04 | 0.625 | 0.375 |
| LCS03 | 0.96 | 0.85 | 0.571 | 0.571 |
| LM | 0.621 | 0.536 | 0.627 | 0.218 |
| CV2 | 1.17 | 1.11 | 0.625 | 0.375 |

the first and second testing period. The best performance was exhibited by LCS03, the worst was LM with $K \approx 0.2$ after the second period. The commercial renovation mortar CV2 was on the same frost resistance level as LCS05, while LCS10 was slightly better.

The lowest water absorption coefficient $A$ was measured for the lime–pozzolan mortars LCS03 and LCS05 (Table 9) which was in accordance with their low porosities (Table 4). The $A$-value of the lime–metakaolin mortar was about 10% higher, of the lime–pozzolan mortar LCS10 with the coarsest particles of burnt Czech clay shale 30% higher and of the reference lime mortar LR 50% higher. The commercial renovation mortar CV2 exhibited a similar $A$ value as LCS03 and LCS05 despite its much higher porosity. This could be caused either by the vertical orientation of the water absorption experiment – the big pores of technological origin which were not detected by MIP (Fig. 1) but appeared in the total open porosity determined by vacuum water saturation method (Table 4) might not be able to transport water against the gravity force – or by using a hydrophobic admixture.

In the investigations of lime–metakaolin mortars, Veiga et al. [38] obtained for a mix with L:P = 1:0.5 a water absorption coefficient $A = 0.209\ \mathrm{kg\ m^{-2}\ s^{-1/2}}$, which was about 50% higher than for our lime–pozzolan mortars LCS03 and LCS05. On the other hand, the mix with L:P = 1:1 studied in [18] had only $A = 0.108\ \mathrm{kg\ m^{-2}\ s^{-1/2}}$. Taking into account the differences in mortar composition, the performance of our mixes with L:P = 5:1 should be considered satisfactory.

The highest water vapor diffusion coefficient $D$ in both dry-cup and wet-cup arrangements was exhibited by the reference lime plaster (Table 10). The $D$-values of lime–pozzolan mortars were about 40–50% lower which still could be considered acceptable from the point of view of the required open character of renovation mortars. The lime–metakaolin mortar LM had the water vapor diffusion coefficient in between these two limits. The commercial renovation mortar CV2 evaluated in the dry-cup arrangement achieved a $D$-value similar to that of the lime–pozzolan mortar LCS03 despite its higher porosity, but for the wet-cup arrangement, its water vapor diffusion coefficient was the second highest after LR which indicated the importance of capillary condensed water in the water vapor transport. This was in accordance with the pore distribution curve (Fig. 1) which showed an increased amount of pores in the range of 0.1–0.5 μm.

**Table 9**
Water transport properties of mortars.

| Mortar | Water absorption coefficient ($\mathrm{kg\ m^{-2}\ s^{-1/2}}$) | Apparent moisture diffusivity ($\mathrm{m^2\ s^{-1}}$) |
|---|---|---|
| LR | 0.215 | 5.17E−07 |
| LCS10 | 0.197 | 3.13E−07 |
| LCS05 | 0.14 | 1.78E−07 |
| LCS03 | 0.145 | 1.86E−07 |
| LM | 0.159 | 2.02E−07 |
| CV2 | 0.145 | 1.18E−07 |

**Table 10**
Water vapor transport properties of mortars.

| Mortar | 5/50% | | 97/50% | |
|---|---|---|---|---|
| | Water vapor diffusion coefficient ($\mathrm{m^2\ s^{-1}}$) | Water vapor diffusion resistance factor (–) | Water vapor diffusion coefficient ($\mathrm{m^2\ s^{-1}}$) | Water vapor diffusion resistance factor (–) |
| LR | 1.64E−06 | 14.05 | 4.52E−06 | 5.24 |
| LCS10 | 1.16E−06 | 19.83 | 3.02E−06 | 7.69 |
| LCS05 | 1.11E−06 | 20.83 | 3.24E−06 | 7.15 |
| LCS03 | 1.02E−06 | 22.71 | 2.66E−06 | 8.7 |
| LM | 1.43E−06 | 16.1 | 3.00E−06 | 7.7 |
| CV2 | 9.93E−07 | 23.32 | 3.50E−06 | 6.67 |

The lowest thermal conductivity $\lambda$ in the dry state (Table 11) was measured for the commercial renovation mortar CV2. This was in accordance with its highest porosity (Table 4). The three lime–pozzolan mortars with burnt Czech clay shale had almost the same $\lambda$ values, about 5% higher than the lime–metakaolin mortar LM and 60% higher than CV2. The reference lime mortar had the highest thermal conductivity, about 10% higher than the lime–pozzolan mortars. This could be explained by its different microstructure which did not include the silicate and aluminate components found in the mortars with pozzolans. The specific heat capacity $c$ of the lime–pozzolan mortars was similar to that of the lime–metakaolin mortar (Table 11). For the reference lime mortar, $c$ was 5–10% lower but these differences were on the edge of the error range of the measuring method. The commercial mortar CV2 had a $c$ value about 5–10% higher than the lime–pozzolan mortars. Although this difference itself may not be convincing, it could reflect the presence of additives in CV2 (foaming agents, hydrophobes).

The increase of thermal conductivity of all investigated mortars with increasing moisture content was very substantial (Fig. 3); up to three times higher $\lambda$ values were observed for a water saturated state as compared with the dry state. This may have significant consequences for the thermal performance of such mortars in building envelopes. The commercial mortar CV2 had the lowest thermal conductivity in the whole range of moisture content. While in the dry state this was expected, as pointed out before, the low values of thermal conductivity at high moisture contents were probably caused by a hydrophobe which was already indicated by the low value of water absorption coefficient of CV2 (Table 9). It could prevent water from an active contact with the pore walls, forcing it to form discontinuous drops which then decreased its effect on heat transfer.

The specific heat capacity of all mortars significantly increased with increasing moisture content (Fig. 4) which was caused by the high specific heat capacity of water relative to the other

**Table 11**
Thermal properties of mortars in dry state.

| Mortar | Thermal conductivity ($\mathrm{W\ m^{-1}K^{-1}}$) | Specific heat capacity ($\mathrm{J\ kg^{-1}K^{-1}}$) |
|---|---|---|
| LR | 0.836 | 867 |
| LCS10 | 0.747 | 962 |
| LCS05 | 0.751 | 904 |
| LCS03 | 0.749 | 937 |
| LM | 0.706 | 921 |
| CV2 | 0.464 | 994 |

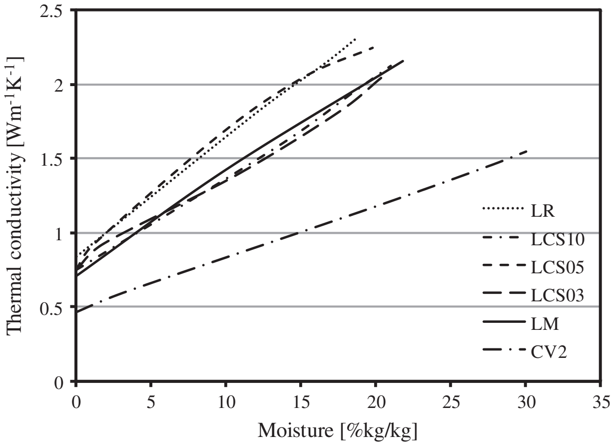

**Fig. 3.** Thermal conductivity as a function of moisture content.

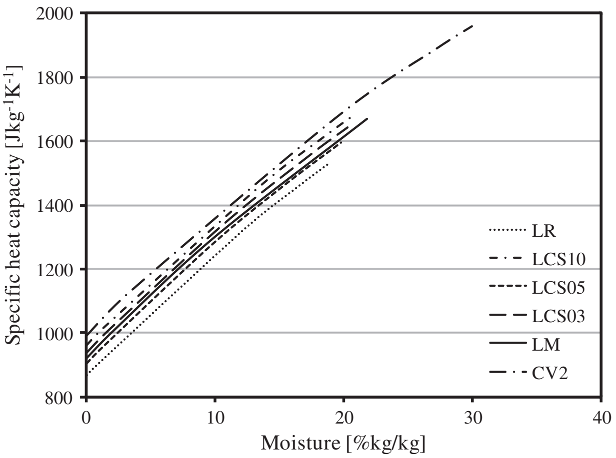

**Fig. 4.** Specific heat capacity as a function of moisture content.

components of the mortar. The measured data were compared with the theoretical relation

$$c_{\mathrm{wet}}(u) = \frac{c_{\mathrm{dry}} + c_{\mathrm{w}}u}{1 + u} \qquad (1)$$

($u$ is the moisture content by mass in kg/kg, $c_{\mathrm{wet}}$, $c_{\mathrm{dry}}$ and $c_{\mathrm{w}}$ are the specific heat capacities of the wet material, the dry material and water, respectively), which was derived in [39] under the assumption that the specific heat capacity as a heat storage parameter can be considered an additive quantity in the sense of the linear theory of mixtures. A comparison of experimental results presented in Fig. 4 with the theoretical calculations using Eq. (1) showed that the experimental values were systematically higher than the calculated data but the differences were lower than 10%, which was within the uncertainty range of the measurement of specific heat capacity.

## 5. Conclusions

Three lime-based mortars containing burnt Czech clay shale of different grain fineness as a new pozzolan addition were studied in the paper. Experimental results showed that the burnt Czech clay shale has a good potential to be used in lime–pozzolan mortars for renovation of historical buildings as a local alternative to metakaolin. The main findings can be summarized as follows:

- All three mortars with burnt Czech clay shale had significantly better mechanical properties than the reference lime mortar; up to seven times higher strength values were observed. They also exhibited up to 30% lower water absorption and water vapor diffusion coefficients.
- The frost resistance of the new lime–pozzolan mortars was far better as compared with the reference lime mortar. After 30 freeze/thaw cycles they retained more than 80% of their compressive strength and more than one half of their bending strength, while the reference lime mortar was disintegrated already after the third freeze/thaw cycle.
- The fineness of burnt Czech clay shale was a very important parameter affecting the properties of lime–pozzolan mortars; the best results were achieved with the average particle size of 4 μm. Apparently, in the finest burnt Czech clay shale particles, the reactions of silicates and aluminates with $Ca^{2+}$ ions are faster, resulting in a more effective formation of the complex system of lime–pozzolan hydration products.
- In a comparison with the lime–metakaolin mortar of the same composition, the mechanical and fracture-mechanical properties of all three lime–pozzolan mortars containing burnt Czech clay shale were either comparable or better, the frost resistance significantly better, the water absorption coefficient and water vapor diffusion coefficient slightly lower, and the thermal properties comparable.
- The commercial renovation mortar analyzed for the sake of comparison of the new lime–pozzolan mortars with the products available on the current market exhibited similar mechanical, water and water vapor transport properties as the lime–pozzolan plaster with the finest burnt Czech clay shale particles although its open porosity was about 20% higher. As its exact composition was not known, we can only speculate about the possible reasons. A logical explanation could be the use of foaming agents, together with a small amount of cement and a hydrophobic admixture. Adding a hydrophobe to the LCS03 mortar would be a useful topic for future research.

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## References

[1] Degryse P, Elsen J, Waelkens M. Study of ancient mortars from Sagalassos (Turkey) in view of their conservation. Cem Concr Res 2002;32:1457–63.
[2] Bruno P, Calabrese D, Di Pierro M, Genga A, Laganara C, Manigrassi DAP, et al. Chemical–physical and mineralogical investigation on ancient mortars from the archaeological site of Monte Sannace (Bari—Southern Italy). Thermochim Acta 2004;418:131–41.
[3] Sanchez-Moral S, Luque L, Canaveras J-C, Soler V, Garcia-Guinea J, Aparicio A. Lime pozzolan mortars in Roman catacombs: composition, structures and restoration. Cem Concr Res 2005;35:1555–65.
[4] Cultrone G, Sebastian E, Ortega Huertas M. Forced and natural carbonation of lime-based mortars with and without additives: mineralogical and textural changes. Cem Concr Res 2005;35:2278–89.
[5] Cultrone G, Sebastian E, Ortega Huertas M. Durability of masonry systems: a laboratory study. Constr Build Mater 2007;21:40–51.
[6] Hansen E, Rodrıguez-Navarro C, Hansen RD. Incipient Maya burnt lime technology: characterization and chronological variations in preclassic plaster, stucco and mortar at Nakbe, Guatemala. Mater Res Soc Symp Proc 2007;462:207–16.
[7] Barba LA, Blancas J, Manzanilla L, Ortiz A, Barca D, Crisci GM, et al. Provenance of the limestone used in Teotihuacan (Mexico): a methodological approach. Archaeometry 2008;51:525–45.
[8] Villasenor I, Graham E. The use of volcanic materials for the manufacture of pozzolanic plasters in the Maya lowlands: a preliminary report. J Archaeol Sci 2010;37:1339–47.
[9] Baronio G, Binda L, Lombardini N. The role of brick pebbles and dust in conglomerates based on hydrated lime and crushed bricks. Constr Build Mater 1997;11:33–40.
[10] Bakolas A, Biscontin G, Moropoulou A, Zendri E. Characterization of structural byzantine mortars by thermogravimetric analysis. Thermochim Acta 1998;321:151–60.
[11] Maravelaki-Kalaitzaki P, Bakolas A, Moropoulou A. Physico-chemical study of Cretan ancient mortars. Cem Concr Res 2003;33:651–61.
[12] Maravelaki-Kalaitzaki P, Bakolas A, Karatasios I, Kilikoglou V. Hydraulic lime mortars for the restoration of historic masonry in Crete. Cem Concr Res 2005;35:1577–86.
[13] Robador MD, Perez-Rodriguez JL, Duran A. Hydraulic structures of the Roman Mithraeum house in Augusta emerita, Spain. J Archaeol Sci 2010;37:2426–32.
[14] Miriello D, Bloise A, Crisci GM, Apollaro C, La Marca A. Characterisation of archaeological mortars and plasters from Kyme (Turkey). J Archaeol Sci 2011;38:794–804.
[15] Moropoulou A, Bakolas A, Anagnostopoulou S. Composite materials in ancient structures. Cem Concr Compos 2005;27:295–300.
[16] Cortina MG, Dominguez LD, de Madrid EUAT, de Madrid ETSA. Aired-lime and chamotte hydraulic mortars. Mater Constr 2002;52:65–76.
[17] Zawawi R, Banfill PFG. Effect of burning conditions on properties of artificial hydraulic lime mortar obtained from limestone and siliceous waste materials. Adv Appl Ceram 2006;105:175–8.
[18] Černý R, Kunca A, Tydlitát V, Drchalová J, Rovnaníková P. Effect of pozzolanic admixtures on mechanical, thermal and hygric properties of lime plasters. Constr Build Mater 2006;20:849–57.

[19] Snellings R, Mertens G, Hertsens S, Elsen J. The zeolite–lime pozzolanic reaction: reaction kinetics and products by in situ synchrotron X-ray powder diffraction. Micropor Mesopor Mater 2009;126:40–9.
[20] de la Villa RV, Fernandez R, Garcaa R, Villar-Cocina E, Frias M. Pozzolanic activity and alkaline reactivity of a mordenite-rich tuff. Micropor Mesopor Mater 2009;126:125–32.
[21] Yang FW, Zhang BJ, Ma QL. Study of sticky rice–lime mortar technology for the restoration of historical masonry construction. Acc Chem Res 2010;43:936–44.
[22] Martirena Hernandez JF, Middendorf B, Gehrke M, Budelmann H. Use of wastes of the sugar industry as pozzolan in lime–pozzolan binders: study of the reaction. Cem Concr Res 1998;28:1525–36.
[23] Martirena F, Middendorf B, Day RL, Gehrke M, Roque P, Martinez L, et al. Rudimentary, low tech incinerators as a means to produce reactive pozzolan out of sugar cane straw. Cem Concr Res 2006;36:1056–61.
[24] Nair DG, Jagadish KS, Fraaij A. Reactive pozzolans from rice husk ash: an alternative to cement for rural housing. Cem Concr Res 2006;36:1062–71.
[25] Michoinová D. Questions about renovation plasters. Zprávy památkové péče 2005;65:313–6 [in Czech].
[26] Michoinová D. Preparation of lime plasters in the care of historical monuments. Prague: ČKAIT; 2006 [in Czech].
[27] Roels S, Carmeliet J, Hens H, Adan O, Brocken H, Černý R, et al. Interlaboratory comparison of hygric properties of porous building materials. J Therm Envelope Build Sci 2004;27:307–25.
[28] Karihaloo BL. Fracture mechanics of concrete. New York: Longman Scientific & Technical; 1995.
[29] RILEM Committee 50-FMC (Recommendation). Determination of the fracture energy of mortar and concrete by means of three-point bend test on notched beams. Mater Struct 1985;18:258–290.
[30] ČSN 72 2452. Testing of frost resistance of mortar. Prague: Czechoslovak Standardization Institute; 1968.
[31] Vejmelková E, Pavlíková M, Jerman M, Černý R. Free water intake as means of material characterization. J Build Phys 2009;33:29–44.
[32] Kumaran MK. Moisture diffusivity of building materials from water absorption measurements. J Therm Envelope Build Sci 1999;22:349–55.
[33] Vejmelková E, Pernicová R, Sovják R, Černý R. Properties of innovative renders on lime basis for the renovation of historical buildings. In: Brebbia C, editor. Structural studies, repairs and maintenance of heritage architecture, vol. XI. Southampton: WIT Press; 2009. p. 221–9.
[34] Baronio G, Binda L. Study of the pozzolanicity of some bricks and clays. Constr Build Mater 1997;11:41–6.
[35] Billong N, Melo UC, Njopwouo D, Louvet F, Bonnet JP. Effect of mixture constituents on properties of slaked lime–metakaolin–sand mortars containing sodium hydroxide. Cem Concr Compos 2009;31:658–62.
[36] Sepulcre-Aguilar A, Hernández-Olivares F. Assessment of phase formation in lime-based mortars with added metakaolin, Portland cement and sepiolite, for grouting of historic masonry. Cem Concr Res 2010;40:66–76.
[37] Fortes-Revilla C, Martinez-Ramirez S, Blanco-Varela MT. Modelling of slaked lime–metakaolin mortar engineering characteristics in terms of process variables. Cem Concr Compos 2006;28:458–67.
[38] Veiga MR, Velosa A, Magalhaes A. Experimental applications of mortars with pozzolanic additions: characterization and performance evaluation. Constr Build Mater 2009;23:318–27.
[39] Jerman M, Keppert M, Výborný J, Černý R. Moisture and heat transport and storage characteristics of two commercial autoclaved aerated concretes. Cement Wapno Beton 2011;16(/78):18–29.