

1 Article

2 Lime mortar - sustainable construction material. Frost re- 3 sistance study.

4 Dana Janotová ¹, Zuzana Slížková ^{2,*} and Dita Frankeová ²

5 ¹ National Museum of Agriculture, Kostelní 1300/44, 170 00 Prague, Czech Republic; Dana.Janotova@nzm.cz

6 ² Institute of Theoretical and Applied Mechanics of the Czech Academy of Sciences, Prosecká 809/76, 190 00
7 Prague, Czech Republic; slizkova@itam.cas.cz

8 * Correspondence: slizkova@itam.cas.cz

9 **Abstract:** The study focused on lime mortar, that represent sustainable and environmentally
10 friendly construction material widely used all over the world on architectural surfaces since the
11 classical times. Repair mortars in relation to expected freeze-thaw loading should be designed and
12 applied within the conservation interventions. The frost attack effects on microstructure and me-
13 chanical characteristics of lime mortars with different binder composition were studied for this pur-
14 pose. The mortar with pure air lime binder showed a lowest mechanical strength and low durability
15 when the mortar was subjected to freeze-thaw cycles. Lime-pozzolanic mortar based on metakaolin
16 improved mechanical strength and frost resistance and did not produce shrinkage cracks. Regard-
17 ing hydraulic lime mortars, the compressive strength of all frost-aged specimens increased after 10
18 freeze cycles, indicating a beneficial effect of the water on the hydration of unreacted hydraulic
19 binder. On the other hand, the flexural strength of the frost-aged hydraulic mortars specimens de-
20 creased significantly after 10 freeze cycles. The reduction of mixing water would contribute to better
21 frost resistance of all types of tested lime based mortars. As lime mortars are characterized by slow
22 hardening process, testing procedures should be adapted to this fact by using smaller specimens
23 than 4x4x16 cm, e.g. 2x2x10 cm.

24 **Keywords:** lime binder; lime mortar; air lime; hydraulic lime; metakaolin; testing; durability; freeze-
25 thaw resistance; historic buildings repair

27 1. Introduction

28 Recently, lime has become one of the main materials used to protect and restore his-
29 toric buildings. It is probably the most versatile structural binder available that can be
30 adapted to suit a variety of uses and exposures. The lime plasters, renders or masonry
31 mortars are commonly utilized for the repair of cultural build heritage, because of their
32 compatibility with traditional historic masonry fabrics [1]. Lime-based mortars offer nu-
33 merous eco-benefits and they can be used not only in retrofitting, but also in new con-
34 structions. Low energy consuming production of lime in comparison with Portland ce-
35 ment makes lime be sustainable and environmentally friendly construction material. Lime
36 binder is also sequestering CO₂ from the atmosphere during its hardening process. The
37 research of high-performance lime-based mortars contribute to the urgently needed CO₂
38 abatement by rethinking traditional approaches to maintaining continuity where neces-
sary, as in the building conservation sector, while providing modern solutions for con-
temporary architecture.

The lime binder quality affects fundamentally a performance and durability of lime
mortars manufactured from them, particularly in case when the building construction
containing lime mortar is exposed to frequent water penetration and freezing-thawing
events.

28 **Citation:** To be added by editorial
29 staff during production.

30 Academic Editor: Firstname Last-
31 name

32 Received: date

33 Revised: date

34 Accepted: date

35 Published: date



36 **Copyright:** © 2023 by the author

37 Submitted for possible open access

38 publication under the terms and

conditions of the Creative Common

40 Attribution (CC BY) licens

41 (https://creativecommons.org/licenses/by/4.0/).

42

45 Generally, the air (non-hydraulic) lime and the hydraulic lime binders (depending
46 on the chemical composition of the limestone from which the lime was burned) have been
47 used for historic lime mortars produce, in history and also today. From the studied litera-
48 ture follows that hardened air lime mortars are porous and their mechanical strength and
49 durability is low when exposed to frost in wet condition even if frost occurs only occa-
50 sionally [2]. Analyzed samples of historical air lime mortars show high porosity (ranging
51 from 30-40%) and well interconnected pore structure with a predominant pore size of
52 around 1 μm in diameter. It is also evident that the original mortar mixture was often very
53 rich in lime, about 1: 1.5 binder to the aggregate, or even larger [3]. However, lime mortars
54 based only on the air lime binder take a long time to harden and they are very vulnerable
55 to frost particularly during this hardening period. To achieve the intended mortar perfor-
56 mance, the air lime binder in mortars have been modified by admixtures or additives for
57 various reasons in building practice very often.

58 One way to avoid the shortcomings of air lime mortar applied in cold and humid re-
59 gions is to blend the air lime binder with pozzolans [4]. The addition of pozzolanic mate-
60 rials to air lime generally shortens the binder setting time and improves the mortar
61 strength. Various natural and artificial materials exhibit pozzolanic properties (e.g. re-ac-
62 tivity with slaked air lime) thanks to their silica or alumino-siliceous chemical compo-
63 sition and the amorphous character of these components. Both the natural pozzolans and
64 the artificial pozzolanic materials can be used in modifications of air lime binders. His-
65 torically, mainly soils or crushed rocks of volcanic origin were used (including Italian poz-
66 zolan quarried near Napoli); recently also industrially burned clays, crushed bricks or
67 brick dust, silica fume, and fly ashes have been studied and used for the same purpose.
68 Especially metakaolin (produced by burning kaolin or clay shale at temperatures around
69 750 $^{\circ}\text{C}$) has been researched [5], [6], [7] and used in many conservation projects.

70 Increasingly, naturally hydraulic limes (NHLs) are also used to conserve and restore
71 historic buildings, when a mortar with a high resistance to moisture and freeze-thaw
72 events is required. Naturally hydraulic limes (NHLs) were traditionally used as binders
73 for preparing mortars [7] and are nowadays often used in commercial mixes because of
74 their rapid setting compared to the air lime, and good mechanical performance [8]. NHLs
75 based mortars are generally known to have a lower porosity than air lime mortars; for the
76 mix ratio 1:2.5 of the binder NHL3.5 and the aggregate, the hardened mortar have the po-
77 rosity of 25%. The denser microstructure is characteristic for NHL mortars when com-
78 pared to air lime mortar [9]. The 10-200 nm pore fraction is characteristic of hydraulic
79 phases [10].

80 Some craftsmen used to add Portland cement as the hydraulic admixture to air lime
81 in situations when the resistance of lime mortars to frost was necessary and (NHLs) bind-
82 ers were not available. Now, the risk of damage of historic porous building materials con-
83 sequently to the Portland cement presence in repair mortars is known and must be taken
84 into account in case of conservation of valuable historic structures [11]. Generally, objec-
85 tions to the use of Portland cement for rendering and plastering of historic masonry are
86 based on its high strength, its rather impermeable character and the risk of transferring
87 soluble salts, especially sodium salts, to vulnerable masonry materials [12]. Therefore, the
88 amount of Portland cement in mortars applied on historic masonries must be well
89 founded and always precisely defined.

90 Most cultural heritage structures are subjected to a range of environmental risks such
91 as critical climatic events but also salt damage, biological attack and air pollution. Frost
92 damage is a further important physical cause of decay of building materials [13]. The in-
93 tensity, rate and duration of freezing, the cyclic action, as well as interstitial moisture de-
94 termine the severity of the effect [14]. Noticeable frost damage effects mainly take place
95 on porous materials (i.e. porosity > 5%) saturated in water. Shaffer in his pioneering book
96 [15] mentions a Hirschwald saturation coefficient of around 0.85 as a limit beyond which
97 materials are prone to be damage by frost.

Frost resistance is naturally limited if the binder in the mortar has a relatively low strength. High strength binders, such as hydraulic lime or Portland cement, are able to withstand higher stress induced by freeze/thaw cycles (F/T). However, in order to protect traditional masonry, it is necessary to make a compromise: to increase the strength of the mortar to withstand F/T and not to lose the real function of the mortar, such as drying the walls and maintaining the masonry unit [11]. The repair mortar composition and mortar durability should be designed considering both the exposure conditions of the construction and function of the mortar to be applied.

The experiment presented in this article focuses on the frost and wet resistance of lime mortars prepared from various lime binders. The aim of the experiment was to determine the effect of the binder quality on mortar performance when it is exposed to freezing-thawing cycles or immersed in water for some period. In order to demonstrate the effect of the binder, various experimental mortars were prepared containing different type of the binder. As the binder, air lime or natural hydraulic lime was used. The variant of the air lime was studied without or with pozzolanic or hydraulic admixture (metakaolin or Portland cement). The binder components for the experiment were chosen considering raw materials available for the repair mortar to be designed today. The amount and nature of the aggregate, and also the binder: aggregate ratio in studied mortars were invariable. The framework of the study was described in Janotova [16]. The selection of studied building materials based also on the published knowledge of composition of historical lime mortars and their properties.

2. Materials and Methods

2.1. Mortar mixtures

Six different mortar mixtures were prepared. A hydrated air lime powder CL 90 (Čerfák®, Vápenka Čertovy schody, a.s.), a metakaolin admixture (Mefisto L05, České lupkové závody, a.s.), two types of natural hydraulic limes, NHL3.5 (Calcidur®, Zement- und Kalkwerke Otterbein) and NHL5 (Hydradur®, Zement- und Kalkwerke Otterbein) and a white Portland cement (HET, CEM I 52.5 R, Aalborg Portland A/S, Denmark) were used as the binders. A pure silica sand with controlled particle size distribution 0 - 4 mm supplied by Provodín Sands a.s. was used as the aggregate. Table 1 shows the weight ratios of binder to aggregate and water to dry-solids used in the preparation of the mortar specimens.

Table 1. Mortars composition and the water to dry solid ratio.

Mortar	L	LM	NHL3.5	NHL5	CL1	CL2
Composition ¹ weight parts	CL90:agg 1:3	CL90:M:agg (0.75:0.25):3	NHL3.5:agg 1:3	NHL5:agg 1:3	CL90:wPC:agg (0.9:1):15	CL90:wPC:agg (0.5:1):10
w/ds ¹	0.26	data ¹	0.17	0.17	0.14	0.13

¹ CL90 = hydrated lime powder; M = metakaolin; NHL = natural hydraulic lime; wPC = white Portland cement, agg = aggregate; w/ds = water to dry solids weight ratio.

Mortar mixtures were prepared using the desirable amount of kneading water to obtain good workability and comparable consistency in all the mortars, 170±5 mm, measured using the flow table test [17]. The binder and dry aggregate were mixed for three minutes at low speed using a laboratory mixer MATEST-E093. Water was then added and the mixtures were blended for another 1.5 min. The fresh mortars were mechanically compacted into prismatic casts of dimensions 40×40×160 mm. The specimens were left inside the moulds for one day and were then stored for a further six days at 90±5 % relative humidity at room temperature 20±5 °C. The mortar prisms were then stored for 360 days under controlled conditions at a temperature of 20±5 °C at 60±10 % relative humidity, and placed

143 on grid-lined shelves to provide air flow. The 60% RH value was chosen with respect to
144 the average relative air humidity in Prague during the construction season [18].
145

146 2.2. Methods of Testing Hardened Mortar Samples

147 The open porosity of the mortar specimens was determined by means of hydrostatic
148 weighing under low pressure after total immersion in water for 24h according to the pro-
149 cedure described in [19].

150 Pore size distribution was analyzed using mercury intrusion porosimetry (Poremas-
151 ter PM 60-13, Quantachrome). The pressure applied in the measurement (0.0055 to 200
152 MPa) corresponds to pore sizes with a diameter of 258 μm to 6 nm. Two specimens of each
153 mortar type were analyzed.

154 The morphologies of the mortar specimens after the freezing test were observed by
155 optical microscopy (Olympus BX53M). One thin section from each hardened mortar cate-
156 gory (40 \times 40 mm) was prepared.

157 Flexural strength was determined based on the three-point flexural test, and the com-
158 pressive test was done with half of the remaining samples obtained from the flexural test,
159 according to [20].

160 Dynamic modulus of elasticity was obtained based on determination of longitudinal
161 resonance frequency using the ultrasonic device USG 40 (Krompholz Geotron Elektronik,
162 FRG, 250 kHz, USG-T transmitter and USE-T receiver).

163 Water absorption coefficient ($\text{kg}\cdot\text{m}^2\cdot\text{hod}^{-1/2}$) was measured in a free-water intake ex-
164 periment [21]. The three halves of the 4 \times 4 \times 16 cm samples that remained after the me-
165 chanical tests were immersed in 1 mm of water (using glass rods) inside a covered box to
166 maintain constant hygrothermal conditions and to limit water evaporation from the sam-
167 ples.
168

169 2.3. Frost aging test

170 The frost resistance test was performed according to the Czech standard procedure
171 [22]. Three specimens of standard dimensions 40 \times 40 \times 160 mm and an age of 360 days
172 were initially dried to a constant mass at 60 $^\circ\text{C}$. The specimens were then immersed in
173 water at an ambient temperature of 20 ± 5 $^\circ\text{C}$ for 24 h and then exposed to freezing at -20 ± 5
174 $^\circ\text{C}$ in a freezing box for a period of four hours (Figure 1). The specimens were then thawed
175 in water at an ambient temperature of 20 ± 5 $^\circ\text{C}$ for at least two hours before performing
176 another cycle. This group of the frost exposed specimens was labelled "F".

177 During the freeze-thaw procedure the water absorption was monitored by weighing
178 the thawed specimens on hydrostatic scales to follow changes in water uptake (in w.%).
179 The total loss of mass of the material remaining in the vessels used for thawing the sam-
180 ples was also recorded. Morphological changes by photographic recording, weight varia-
181 tions of the specimens and ultrasonic wave velocity propagation were measured during
182 the ageing tests.

183 The frost resistance test was terminated when the samples (F) showed moderate to
184 severe degradation patterns. The samples were then dried at 60 $^\circ\text{C}$ to constant weight and
185 subjected to the dynamic modulus of elasticity, the flexural and the compressive strength
186 characterizations. The halves of the specimens remaining after the mechanical tests were
187 used to determine changes in the water transport properties of mortars that could indicate
188 their porosity modification due to frost loading: capillary absorption coefficient [21], and
189 water uptake at saturation by immersion under reduced pressure [19].
190

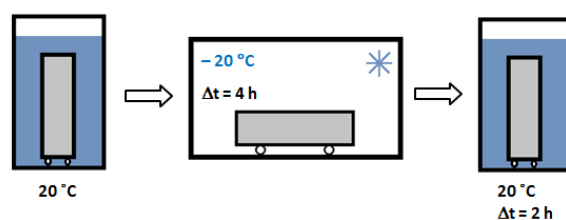


Figure 1. Scheme represents the steps for performing one cycle of the frost ageing test.

3. Results and Discussion

3.1. Fresh mortar properties

The mixing water amounts needed to prepare fresh mortar of consistency 170 mm (flow table) are summarised in Table 1 for all types of tested mortar. The largest amount was needed to the lime mortar L due to the large specific surface area of the hydrated lime powder particles. The rapid drying of the mixing water caused the formation of shrinking cracks in the hardened L mortar which displayed in the pore size distribution within the pore size range from 7 to 217 μm (Figure 2). The substitution of 25-w% of lime hydrate by metakaolin decreased the water consumption in the lime-metakaolin mortar LM by less than 8 % compared to the L mortar. Similar water consumption in the mortar with the same type of metakaolin was also reported in [6]. The reason for the lower water consumption is probably the fact that the specific surface area of the metakaolin (SBET Mefisto L05 = 15.41 $\text{m}^2\cdot\text{g}^{-1}$) is slightly smaller compared to the specific surface area of lime hydrate (SBET CL90 = 16.84 $\text{m}^2\cdot\text{g}^{-1}$). In the case of the NHL3.5 and NHL5 mortars, the kneading water consumption was 36 % resp. 33 % lower in comparison with air lime mortar L. This can also be explained by the lower specific surface area of the hydraulic lime particles [23]. The low shrinkage of that mortar can be attributed to the consumption of some water during hydration instead of evaporation. The low w/ds ratios of the CL1 a CL2 lime-cement mortars are assigned to the amount of cement used [24]. Since the aerial lime proportion is larger in the CL1 mortar, also the largest water demand was observed.

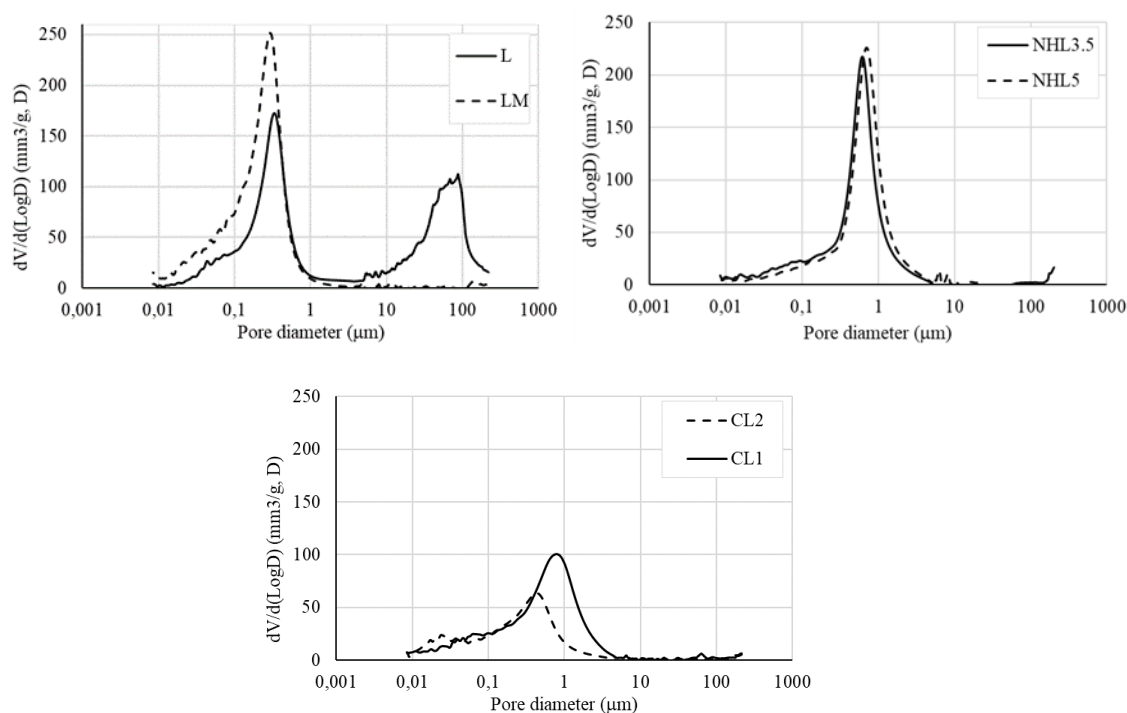
3.2. Hardened mortar properties

Table 2 summarizes the mortars properties in 360 days of age (these values represent the average of at least three measurements). The water accessible porosity was 32 % for the lime mortar L and its pore size distribution curve showed the presence of two peaks (Figure 2). The first peak in the range 0.1-1 μm was assigned to the binder porosity while the second in 10-100 μm range to shrinkage cracks. Slightly higher open porosity, of 34 %, was for the lime-pozzolan LM mortar (Table 2), which can be explained by the porous character of the pozzolanic reaction products, mainly the C-S-H gels [25], [26]. The gel pores, smaller than 0.1 μm , are shown in the distribution curve of this mortar (Figure 2). LM mortar did not develop shrinkage cracks like L mortar which is probably related to the improvement of the mechanical properties granted by the rapid pozzolanic reaction [27]. Hydraulic limes mortars had porosity approximately 28 % and the pore size distribution of these mortars was unimodal. The wide peak of pores in the range 0.5-1 μm is attributable to portlandite reaction while the 0.01-0.2 μm porosity fraction to hydraulic phases [28]. The addition of the white portland cement to the lime in CL1 and CL2 mortars visibly shifts the pores sizes into a lower range and macropores occurring in the pure air lime mortar L have completely disappeared. This tendency is more noticeable in CL2 with higher Portland cement amount.

233

Table 2. Properties of the hardened mortar with 360 days of age.

Mortar	Open porosity [%-v]	Water absorption coefficient [$\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$]	Flexural strength [MPa]	Compressive strength [MPa]
L	31.4 (± 0.3)	32.2 (± 1.4)	0.6 (± 0.1)	1.8 (± 0.2)
LM	34.1 (± 0.2)	8.6 (± 1.4)	1.9 (± 0.4)	5.9 (± 0.4)
NHL3.5	25.9 (± 0.4)	16.4 (± 0.8)	1.0 (± 0.17)	6.8 (± 0.3)
NHL5	26.8 (± 0.2)	18.9 (± 0.3)	0.8 (± 0.3)	6.1 (± 0.7)
CL1	23.3 (± 0.5)	10.9 (± 1.1)	2.7 (± 0.3)	7.9 (± 0.7)
CL2	20.5 (± 0.3)	4.6 (± 0.4)	4.8 (± 0.4)	19.6 (± 1.9)



234

235

236

237

Figure 2. Mercury intrusion curves show the relative pore size distribution of the mortar after 360 days of curing.

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

253

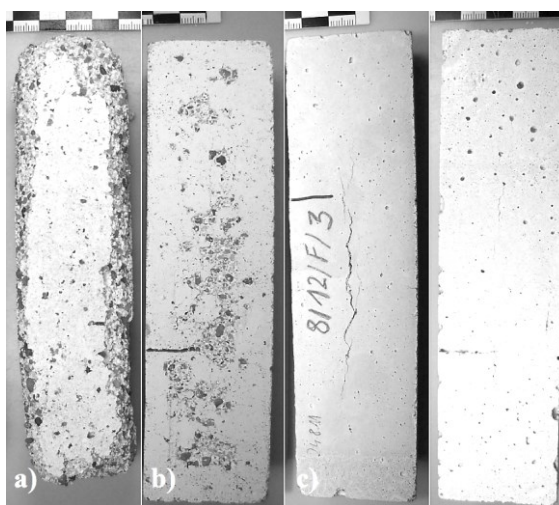
The capillary water uptake behaviour of the studied mortars strongly relates to the pore size values determined by mercury intrusion porosimetry (Figure 2). The highest water absorption coefficient, of $32 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$, was measured for the air lime mortar L (Table 2). This value correlates well with the presence of pores between 10 and $100 \mu\text{m}$. Conversely, the LM mortar had the capillary absorption coefficient nearly 4 times lower in comparison with L. This is in accordance with the observed pores size distribution curve with the main peak shifted towards smaller pore diameters which are not capillary active. Similar capillary absorption rate was also recorded on similar composition lime-metakaolin mortar [25]. The main reason for the slow liquid water transport in lime-metakaolin mortar is probably the effect of CSH gels that can bond by van der Waals forces more water molecules in the pore walls than calcium carbonate [25]. [23] reported reduction of the capillary absorption coefficient of lime-pozzolana mortars with the increasing amount of metakaolin. The mortars with hydraulic lime NHL3.5 and NHL5 also showed low capillary absorption coefficient (16.4 and $18.9 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$) corresponding to the presence of hydration products in the microstructure [29]. The slowest capillary transport was determined for lime-cement mortars CL1 and CL2 (10.9 and $4.6 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1/2}$). Hydrated

254 phases affect the capillary pores with a decrease in the total porosity and a shift to finer
255 pores [30].

256 Table 2 shows the flexural and compressive strength of the samples with 360 days of
257 age. The lowest values of flexural and compressive strength obtained for the lime mortar
258 L can be attributed to the shrinkage cracks. Relatively low measured strengths of the nat-
259 ural hydraulic lime mortars NHL3.5 and NHL5 was probably caused by a combination of
260 two factors which negatively influenced the strengthening: 1) insufficient amount of
261 kneading water used for the fresh mortar preparation and 2) not enough wet curing con-
262 ditions. [30] state that the optimum value of the mortar flow rate of lime NHL3.5 and
263 NHL5 should approach 185 mm. [31] admits that the strength of hydraulic mortars may
264 not always correspond to the classification according to EN 459-1. The values of both com-
265 pressive and bending strength of the lime-pozzolana plaster LM containing metakaolin
266 can be clearly attributed to the formation of C-S-H and hydrated calcium aluminate struc-
267 tures that have higher strength than calcium carbonate [25]. The highest values of
268 strengths showed the lime-cement mortar CL2 (with a higher amount of white Portland
269 cement), followed by the lime-cement mortar CL1. However, it must be considered that
270 the strength of the repair mortar containing Portland cement may be too high compared
271 to mechanical characteristics of used historic building materials and compatibility with
272 historic construction properties should be assessed.

273 3.3. Resistance to frost aging

274 Some visible aspects of mortars damage exhibited in the form of surface spalling or
275 micro-crack formation (Figure 3). Lime mortar proved to be highly susceptible to the
276 freezing and thawing action after it broke down after the 4th cycle. Hydraulic lime mortars
277 showed several longitudinal cracks already after the 5th cycle although the specimens
278 maintained their cohesion up to the 10th cycle. Degradation was faster for NHL5 mortar.
279 After the 3rd cycle, LM/F mortar also showed significant degradation signs as a dense
280 network of fine surface cracks on the specimen's surface. Immediately after the freezing
281 step very fine ice crystals were observed growing from these cracks. The cracks developed
282 only along with the 40×160 mm side faces of the mortar prisms, i.e. parallel to the
283 compaction plane, the top surface showing no signs of visually detectable crack
284 development. After completion of the test and final drying, the specimens emitted a
285 hollow sound when tapped. Cement-lime mortars CL1 and CL2 exhibited fine hairline
286 fissures in several areas after the 8th and 15th cycle, respectively.



287
288 **Figure 3.** Degradation pattern of specimens after frost aging: a) progressive granular disintegration
289 of L/F specimens after 3rd cycle; b) surface fissuration of LM/F after 10 cycles; c) deep fissures of
290 NHL5 after 10 cycles; d) hairline cracks of CL2 after 20 cycles. Scale next to the specimens shows
291 1mm intervals.

Table 3 shows changes of mortars properties after 10 resp. 20 cycles of freeze-thaw aging, except data for L mortar that was destroyed after four cycles. The compressive strength of all frozen specimens with the hydraulic binder increased, indicating a beneficial effect of the water on the hydration previously unreacted hydraulic binders. On the other hand, the flexural strength of the Frost-aged specimens decreased significantly after 10 and 20 freeze cycles, respectively, indicating the drastic character of the test performed. (E.g. The flexural strength of the 360-day-old LM mortar decreased by 74 % compared to the strengths of the same old non-freezing set. The flexural strength of frozen mortar specimens NHL3.5, NHL5 and CL1 decreased almost by 40, 63 and 56 % after 10 cy freezing, while the flexural strength of CL2 decreased by 69 % after 20 freeze cycles. Based on a comparison of the resulting strength values, the most frost resistant/durable mortar appear to be NHL3.5, NHL5, CL1 and CL2. he text continues here.

Table 3. Change of mortars properties after freeze-thaw aging. (The down / up arrow symbol clearly indicates the trend of decrease / increase of the characteristic after the end of the freezing test.)

Mortar (Nr. of cycles)	Capillary absorption coefficient [kg·m ⁻² ·h ^{-1/2}]	Open porosity [%]	Flexural strength [MPa]	Compressive strength [MPa]	Dynamic modulus of elasticity Edyn [MPa]
L (4 cy)	-	-	-	-	-
LM (10 cy)	3.5 % ↓	1.5 % ↑	74 % ↓	3.4 % ↓	55.9 % ↓
NHL3.5 (10 cy)	2.5 % ↓	0.4 % ↑	40 % ↓	35.3 % ↑	48.6 % ↓
NHL5 (10 cy)	11 % ↓	3.7 % ↑	62.5 % ↓	1.6 % ↑	21.9 % ↓
CL1 (10 cy)	16.5 % ↓	0.4 % ↑	55.6 % ↓	20.3 % ↑	55.6 % ↓
CL2 (20 cy)	46 % ↓	4 % ↓	68.7 % ↓	25.5 % ↑	31.9 % ↓

The lowest dynamic modulus loss was determined for LM and CL1 samples after ten cycles (reduction of 45 %), followed by NHL3.5 (loss of 51 %) and NHL5 (loss of 78 %). CL2 mortar exhibited the dynamic modulus loss of 68 % after 20 cycles. The lower reduction of dynamic modulus of elasticity obtained for LM and CL1 indicates a better mechanical durability of these mixtures against the freeze-thaw cycles. Cracks formed in frozen specimens work similarly to capillary active pores and are able to absorb additional amount of water [32]. However, in our case there was only a slight increase in open porosity (maximum NHL5 3.7 %). In this case, the effect of storing samples in water prevailed, which had a favorable effect on the additional hydration of previously unreacted hydraulic binders as a result of which the capillary absorption coefficient significantly decreased. The additional hydration of the binder created smaller pores in the mortars which transport water more slowly. The largest capillary absorption coefficient increase is evident in CL1 and CL2 mortars with a Portland cement.

The phenolphthalein staining test (1 % vol. Phenolphthalein solution) revealed a surprising conclusion. Deep purple color indicates that the central portion of the Frost-aged specimens was not completely cured even after 360 days. Photographs of cross-sections of the Frost-aged specimens test in Figure 4 indicate that 10-30 % of the volume of the test specimens contained unreacted binder.

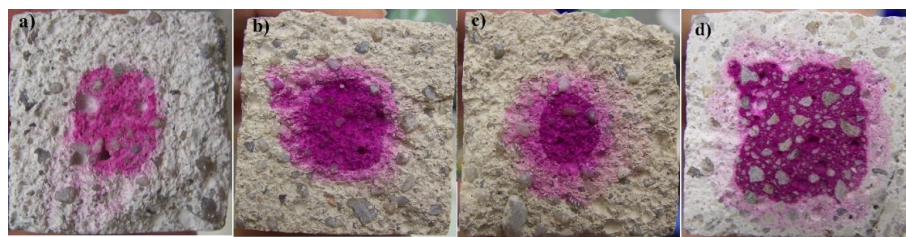


Figure 4. Cross-sections of the Frost-aged specimens. The purple color marks the part of the specimen area (4×4 cm) that contains the unreacted binder: a) LM, 10 cy; b) NHL3.5, 10 cy; c) NHL5, 10 cy; d) CL2, 20 cy.

4. Conclusions

Most cultural heritage structures are subjected to a range of environmental risks including frost damage. Repair mortars with appropriate microstructure and durability in relation to expected freeze-thaw loading should be designed and applied within the conservation interventions. The frost attack effects on microstructure and mechanical characteristics of lime mortars was studied for this purpose. In the same time, the used testing procedure based on saturation of the test specimens with water was assessed with respect to the observed lime mortars characteristics and behaviour.

Although samples of lime mortars (in the form of standard test samples $4 \times 4 \times 16$ cm) were stored in regulated laboratory conditions recommended by the standard and subsequently in laboratory regulated conditions corresponding to real external conditions, the binder was not homogeneously matured even after one year (360 days), as is evident from the phenolphthalein test. The least cured is air lime mortar, however, lime-cement mortars also have immature centers of beams. It follows that lime mortars are tested in a different hardened state, which affects (distorts) the test result. The frost resistance test should be adapted for lime mortars, e.g. using smaller specimens.

The mortar with pure air lime binder showed significant shrinkage apparently due to the large amount of mixing water which resulted in a low mechanical strength (mainly bending strength) and low durability when the mortar was subjected to freeze-thaw cycles. It has been confirmed that the preparation of mortar with an air lime binder requires great care. The appropriate consistency should be achieved by kneading fresh mortar with a minimum amount of water. Subsequently, the lime mortar must be protected against rapid drying and the hardening mortar must be repeatedly moistened by gentle spraying with water. In order to create a microstructure of the mortar without cracks, and thus more resistant to frost.

Lime-pozzolan mortar based on metakaolin admixture to pure air lime improved mechanical strength and did not produce shrinkage cracks. Due to the pozzolanic reaction of the binder and the formation of C-S-H gels, the pores in the porous structure predominate in the range of $0.01\text{--}1\ \mu\text{m}$, which limit capillary suction rate (the water absorption coefficient dropped to a quarter of that observed for pure air lime mortar). The compressive strength of the mortar increased, but the flexural strength decreased significantly after 10 freezing cycles. After the 3rd cycle, mortar showed significant degradation signs as a dense network of fine surface cracks on the specimen's surface. Even in this case, we can assume that the amount of mixing water required with respect to the required consistency of 170 mm was too high and that the reduction of mixing water would contribute to better frost resistance.

Hydraulic limes mortars possessed also lower porosity and lower water absorption coefficient compared to the air lime mortar. Contrary to expectations, low flexural strengths have been established for these mortars which has had a negative impact on frost resistance. Hydration of hydraulic binders has probably been negatively influenced either by the low relative humidity setting for a curing ($90\pm 5\%$ for 1 week then $60\pm 5\%$ RH) or too much mixing water played a role. Hydraulic lime mortars showed several

longitudinal cracks already after the 5th cycle although the specimens maintained their cohesion up to the 10th cycle.

Lime-cement mortars CL1 and CL2 achieved the highest compressive and flexural strengths. However, even after 360 days, the standard beams of lime-cement mortars were not cured until the middle of the beam. The porosity accessible to water is the lowest of the mortars compared. The porous structure is dominated by pores smaller than 0.1 μm , which do not transport liquid water, but can retain it on the surface of the pores through hydrogen bonds. There is also a significant slowing down of water transport through capillary pores in comparison with other studied mortars.

The compressive strength of all Frost-aged specimens with the hydraulic binder component increased, indicating a beneficial effect of the water on the hydration previously unreacted hydraulic binders. On the other hand, the flexural strength of the Frost-aged specimens decreased significantly after 10 and 20 freeze cycles, respectively, indicating the drastic nature of the test performed.

Author Contributions: Conceptualization: Z.S.; D.J.; Methodology: Z.S.; D.J.; D.F.; Investigation: D.J.; Resources: D.J.; Data Curation: D.J.; Writing – original draft preparation: D.J.; Z.S.; Writing – review and editing: Z.S.; D.F.; Project administration: D.F.; Funding acquisition: D.F.; Z.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministry of Culture of the Czech Republic, grant number DH23P03OVV024, program NAKI III, project title: “Technologies and practices for the preservation of historic masonry bridges from the 19th and early 20th centuries”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Cristiana Lara Nunes Paulos for consultations, Ondřej Vála for performing the strength tests and Milan Svoboda for analyzing the porometric data of mortars.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pavia, S.; Fitzgerald, B.; Treacy, E. An assessment of lime mortars for masonry repair. In *Concrete Research in Ireland Colloquium*, Ciaran McNally Ed., University College Dublin, 2005; p. 101-108.
2. Veiga, R. As Argamassas na Conservação, Actas das Primeiras Jornadas de Engenharia Civil da Universidade de Aveiro, COM 103, p. 1–2. Lisbon: LNEC. Veiga, M. R. As argamassas na conservação. 1^{as} Jornadas de Engenharia Civil da Universidade de Aveiro. Avaliação e Reabilitação das Construções existentes. Aveiro, 26 de Novembro de 2003. Coleção Comunicações, COM 103, LNEC, Lisboa 2003.
3. Wiggins, D. Hot-mixed Lime Mortars: Microstructure and Functional Performance. Technical Paper 27, Technical, Advice & Guidance, Technical Paper 27, Historic Environment Scotland 2018.
4. Křivánková, D.; Nunes, C.L.; Slížková, Z.; Frankeová, D.; Niedoba, K. High-Performance Repair Mortars for Application in Severe Weathering Environments: Frost Resistance Assessment Historic Mortars, 2018, p. 155–168, *Advances in Research and Practical Conservation* Editors: John J. Hughes, Jan Válek, Caspar J. W. P. Groot. 10.1007/978-3-319-91606-4_12
5. Vejmelková, E., Keppert, M., Rovnaníková, P., Kešner, Z., Černý, R. Properties of lime composites containing a new type of pozzolana for the improvement of strength and durability, *Composites Part B: Engineering*, 2012, vol. 43, p. 3534-3540. 10.1016/j.compositesb.2011.11.053
6. Slížková, Z. Charakteristiky malt modifikovaných metakaolinem aplikovaných na historických objektech. Characteristics of mortars modified with metakaolin applied to historical objects. Proc. Seminář Metakaolin 2009, Brno, Faculty of Civil Engineering VUT in Brno p. 146-155.
7. Válek, J., Slížková, Z. and Zeman, A. Mechanické a fyzikální zkoušky vápenných malt přidavkem metakaolinu a jejich vhodnost pro opravy památkově chráněných objektů. Mechanical and physical tests of lime mortars with the addition of metakaolin and their suitability for repairs of heritage-protected buildings. Proc. Seminář Metakaolin 2007, Brno, Faculty of Civil Engineering VUT in Brno, p. 121-129.

8. Gulotta, D., Goidanich, S., Tedeschi, C., Nijland, T. G., Toniolo, L. Commercial NHL-containing mortars for the preservation of historical architecture. Part 1: Compositional and mechanical characterisation. *Construction and Building Materials*, 2013, vol. 38, p. 31–42. [10.1016/j.conbuildmat.2012.08.029](https://doi.org/10.1016/j.conbuildmat.2012.08.029)
9. Grilo, J., Faria, P., Veiga, R., Santos Silva, A., Silva, V., Velosa, A., New natural hydraulic lime mortars – Physical and microstructural properties in different curing conditions. *Construction and Building Materials*, Volume 54, 15 March 2014, Pages 378–384. <https://doi.org/10.1016/j.conbuildmat.2013.12.078>
10. Arizzi, A., Viles, H., Cultrone, G., Experimental testing of the durability of lime-based mortars used for rendering historic buildings. *Construction and Building Materials*, 2012, vol. 28, 807–818. [10.1016/j.conbuildmat.2011.10.059](https://doi.org/10.1016/j.conbuildmat.2011.10.059)
11. Allen, G.C., Allen, J., Elton, N.J., Farey, M., Holmes, S.D., Livesey, P., Radonjic, M. *Hydraulic Lime Mortar for Stone, Brick and Block Masonry* Donhead Publishing Ltd. 2003, Taylor & Francis Ltd
12. Silva, B.A., Ferreira Pinto, A.P., Gomes, A., Natural hydraulic lime versus cement for blended lime mortars for restoration works. *Construction and Building Materials*, 2015, vol. 94, p. 346–360. [10.1016/j.conbuildmat.2015.06.058](https://doi.org/10.1016/j.conbuildmat.2015.06.058)
13. Brimblecombe, P., Grossi C.M., Damage to Buildings from Future Climate and Pollution. *APT Bulletin: The Journal of Preservation Technology*, 2007, vol. 38, no. 2/3, p. 13–18. JSTOR, <http://www.jstor.org/stable/40004714>.
14. Grossi C.M., Brimblecombe P., Harris I., Predicting long term freeze–thaw risks on Europe built heritage and archaeological sites in a changing climate. *Science of The Total Environment*, 2007, vol. 377, p. 273–281. <https://doi.org/10.1016/j.scitotenv.2007.02.014>
15. Shaffer R.J. *The Weathering of Natural Building Stones* (1932), Donhead, 2004 Edition, 149 p.
16. Janotova, D., & Slizkova, Z. (2021, November). Lime-based mortars with various binder composition: characterization and freeze-thaw resistance assessment. In *IOP Conference Series: Materials Science and Engineering* (Vol. 1205, No. 1, p. 012009). IOP Publishing.
17. EN 1015-3; 1999. Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table).
18. Average relative humidity data in Prague during the period from April to September 2011 reported on the website of the Czech Hydrometeorologic Institute (retrieved on June 2021). <http://portal.chmi.cz/historicka-data/pocasi/mesicni-data>.
19. EN 1936; 2007. Natural stone test methods. Determination of real density and apparent density, and of total and open porosity.
20. EN 1015-11; 1999. Methods of test for mortar for masonry: Determination of flexural and compressive strength of hardened mortar.
21. EN 1925; 1999. Natural stone test methods. Determination of water absorption coefficient by capillarity.
22. ČSN 72 2452; 1968. Testing of frost resistance of mortar.
23. Silva, B. A., Ferreira, Pinto. A.P., Gomes, A. Influence of natural hydraulic lime content on the properties of aerial lime-based mortars. *Construction and Building Materials*, 2014, vol. 15, p. 208–218. <https://doi.org/10.1016/j.conbuildmat.2014.09.010>
24. Zhang, D., Zhao, J., Wang, D., Xu, Ch., Zhai, M., Ma, X. Comparative study on the properties of three hydraulic lime mortar systems: Natural hydraulic lime mortar, cement-aerial lime-based mortar and slag-aerial lime-based mortar. *Construction and Building Materials*, 2018, vol. 186, 20. p. 42–52. <https://doi.org/10.1016/j.conbuildmat.2018.07.053>
25. Černý, R., Kunca, A., Tydlitát, V., Drchalova, J., Rovnanikova. P. Effect of pozzolanic admixtures on mechanical, thermal and hygric properties of lime plasters. *Construction and Building Materials*, 2006, vol. 20, p. 49–57. <https://doi.org/10.1016/j.conbuildmat.2005.07.002>
26. Vejmelková, E., Keppert, M., Keršner, Z., Rovnaníková, P., Černý, R. Mechanical, fracture-mechanical, hydric, thermal, and durability properties of lime–metakaolin plaster for renovation of historic buildings. *Construction and Building Materials*, 2012, vol. 31, p. 22–28. <https://doi.org/10.1016/j.conbuildmat.2011.12.084>
27. Gameiro, A., Santos, Silva. A., Veiga, R., Velosa, A. Hydration products of lime–metakaolin pastes at ambient temperature with ageing. *Thermochimica Acta*, 2012, vol. 535, p. 36–41. <https://doi.org/10.1016/j.tca.2012.02.013>
28. Arizzi, A.; Viles, H.; Cultrone, G. Experimental testing of the durability of lime-based mortars used for rendering historic buildings. *Construction and Building Materials*, 2012, vol. 28, p. 807–818. <https://doi.org/10.1016/j.conbuildmat.2011.10.059>
29. Arandigoyen, M.; Alvarez, J.I. Pore structure and mechanical properties of cement-lime mortars, *Cement and Concrete Research*, 2007, vol. 37, p. 767–775. [10.1016/j.cemconres.2007.02.023](https://doi.org/10.1016/j.cemconres.2007.02.023)
30. Hanley, R.; Pavia, S. A study of the workability of natural hydraulic lime mortars and its influence on strength. *Materials and Structures*, 2008, vol. 41, p. 373–381. [10.1617/s11527-007-9250-0](https://doi.org/10.1617/s11527-007-9250-0)
31. Figueiredo, C., Lawrence, M., Ball, R. Chemical and physical characterisation of three NHL 2 binders and the relationship with the mortar properties. in *REHABEND 2016 Euro-American Congress: Construction Pathology, Rehabilitation Technology And Heritage Management* (6th REHABEND Congress), L Villegas, I Lombillo, H Blanco & Y Boffill (eds), 2016, C2.2.17, Santander, Spain.
32. Michoinová, D. Příprava vápenných malt ve stavební památkové péči. Preparation of lime mortars in built cultural heritage. Informační centrum ČKAIT Praha, 2006, ISBN 80-86769-81-X.

480 **Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual au-
481 thor(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to
482 people or property resulting from any ideas, methods, instructions or products referred to in the content.