EFFECT OF LINSEED OIL ON THE MECHANICAL PROPERTIES OF LIME MORTARS

C.P. Nunes*, Z. Slížková**, D. Křivánková***, D. Frankeová****

Abstract: Linseed oil was commonly used in former times as an additive for mortars to improve hydrophobicity. However, linseed oil has also an important role on the mechanical behaviour of mortars that is strongly dependent on the type of binder. The effect of linseed oil addition in 1.5% by the weight of the binder was studied in two different mortar mixtures: air lime mortar and air lime-metakaolin mortar. The degree and the order of carbonation and hydration reactions were studied by thermogravimetric analysis and flexural and compressive strength were evaluated along curing time: 14, 28, 60 and 90 days. The results point out that carbonation process was slightly improved by the addition of linseed oil whereas the hydraulic effect of the pozzolan metakaolin was reduced. However, it is the lower capillarity coefficient, which involves a water intake reduction that may be reported as the main factor improving the mechanical behaviour of lime with linseed oil mortar exposed to freeze-thaw cycles and hence, its durability in wet and freezing conditions.

Keywords: Linseed oil, lime, metakaolin, mechanical strength, hydrophobic effect.

1. Introduction

The scientific interest of mortars based in traditional formulations is that they show great compatibility with ancient building materials and hence fulfil the recommendations of ICCROM for use in repairs (Lanas & Alvarez, 2003). Furthermore, they have been widely used in modern work with decorative and protective purposes. Both uses require the mortars to be durable, which is also an important economic issue.

However, today’s lime mortars with compositions similar to ancient mortars, and thus more suitable to ensure the aesthetical and functional compatibility with pre-existing materials, have presented durability problems mainly when exposed to weathering agents like water and freeze-thaw cycles (Veiga, 2003).

Nowadays air lime mortars are very porous and their mechanical strength and durability are low when exposed to water and frost even though if only occasionally. One way to improve the strength and durability of air lime mortars is to partially replace air lime by other materials such as pozzolanas. The promising pozzolanic material in this regard that has also been used in the past is metakaolin (Aggelakopoulou et al., 2011). The air lime-metakaolin mortar properly designed may be promising as repair mortar because it can achieve much higher mechanical strength than pure air lime mortar but it is not strong enough to generate stress that might lead to failure in the original system to be repaired (Fortes-Revilla et al., 2006; Slížková, 2009; Válek et al., 2010).

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The territory of Central Europe always lacked the natural pozzolanas, thus the artificial pozzolanas were supposed to be used. A possibility to obtain artificial pozzolanas presents calcination of some rocks, in particular consolidated sediments, such as clay shales. In the Czech Republic, there is a specific type of clay shale that is extracted from several mines. After burning at temperatures similar to the burning of kaolinite in metakaolin production, the Czech clay shale exhibits pozzolanic properties. Therefore, it has a potential for use in lime-pozzolana binders. (Vejmelková et al., 2011)

The hereby designated metakaolin corresponds to the burnt Czech clay shale. Besides being a national material, burnt Czech clay shale was selected taking into account the previous studies of lime-metakaolin mortars in the Czech Republic (Vejmelková et al., 2011; Slížková, 2009; Válek, 2007).

Lime mortars blended with pozzolanas and other additives seek to recover ancient techniques and improve lime mortars behaviour. However, there is much to learn about which additives to use, how to use them and in what suitable application fields (Veiga, 2003).

Since liquid transport is one of the key factors influencing durability (Roels, 2000) additives which grant hydrophobic properties to mortars have become of great interest to the scientific community (Blachnik, 2001; Stolz, 2007; Izaguirre et al., 2010).

The design of lime mortars with linseed oil additive has the main goal of ensuring a degree of internal hydrophobicity and, consequently, lessen the damage from salt and frost. However, data from literature show that addition of oils to lime mortars reduces their mechanical strength by partially inhibiting carbonation reactions (Oliveira & Santiago, 1992; Sá, 2002; Veiga, 2003; Čechová, 2009). Other studies indicate significant compressive strength increment (Rovnaníková, 2002; Sá 2005; Ventolá et al., 2011).

The main goal for using oil as an additive for mortars relies in its hydrophobic properties. Hence, it may be a very efficient additive to improve durability by restraining water penetration. Linseed oil was one of the main lipid additives used for mortars formulation in former times according to ancient treatises, e.g. Vitruvius (Maciel, 2009), Pliny (Bostock, 1857), Palladio (Tavernor & Schofield, 1997). However, there is lack of information about the formulation technique.

Čechová’s (2009) recent study about the effect of linseed oil in lime based mortars gave a new insight on the potential of this ancient and widely used additive in the improvement of mortars properties for restoration purposes. The addition of 1%-w of linseed oil (by weight of binder) has proved to have a positive effect on the properties of different lime based mortars. It limits water absorption into mortar without significantly affecting the total open porosity or decreasing the degree of carbonation. On the other hand, lime mortars and lime with pozzolana mortars with 3 months of age with 1% and 3% oil showed significant strength reduction, particularly in the case of 3% oil addition.

Owing to the proved influence of oils on the mechanical properties and durability of mortars the aim of this paper is to study mechanical behaviour of hardened lime-based mortars (lime and lime-metakaolin) enriched with 1.5%-w linseed oil (to the weight of binder) and to relate it with its resistance to freeze-thaw cycles.

2. Experimental study

2.1. Materials

The materials used for the mortars preparation were all from local suppliers. Table 1 presents the materials and respective provider company.

All the mortars were prepared in laboratory conditions with a binder: aggregate proportion of 1:3 (by weight), using a siliceous sand as aggregate. Designations and proportions of the mortars are presented in Table 1. The percentage weight of linseed oil added in respect to the weight of binder was 1.5%. This proportion was chosen on the basis of the results achieved by Rovnaníková (2002) and Čechová (2009) that used proportions of 1%, 5% and 10% of boiled linseed oil (oil varnish) and 1% and 3% of raw linseed oil respectively.

The commercial hydrated air lime powder (class CL 90) was supplied by Vápenka Čertovy Schody a.s. Čerták® and the aggregate by Provodínské písky a.s. The hereby designated metakaolin
corresponds to burnt Czech clay shale Mefisto L05 and was supplied by České Lupkové Závody a.s. The raw linseed oil was supplied by GRAC s.r.o.

**Tab. 1: Mortar designation and constitution (by weight).**

<table>
<thead>
<tr>
<th>Mortar code</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>Lime : Sand (1:3-w)</td>
</tr>
<tr>
<td>LO</td>
<td>Lime : Sand (1:3-w) + linseed oil</td>
</tr>
<tr>
<td>LM</td>
<td>Lime : Metakaolin : Sand (0.75:0.25:3-w)</td>
</tr>
<tr>
<td>LMO</td>
<td>Lime : Metakaolin : Sand (0.75:0.25:3-w) + linseed oil</td>
</tr>
</tbody>
</table>

**2.2. Sample preparation and curing conditions**

Binder and aggregate were mechanically mixed for 6 min using an automatic mortar mixer MATEST-E093 at low speed. Regarding mortars with linseed oil addition, binder and aggregate were mixed for 3 min and a bit of dry mixture (approximately 50g) was blended with oil in a plastic cup and mixed manually for 3 min. The oiled mixture was then added to the dry mixture and blended for plus 3 min in the automatic mixer. Water was then added and the mixtures were blended for plus 3 min in the automatic mixer. The amounts of water were designed so that each mortar could get comparable consistencies using the flow table test (170 ±5 mm).

Mortars were mechanically compacted in prismatic 20×20×100mm and 40×40×160mm casts with ten falls in each one of the two layers which completes the casts. A plastic foil was put on the bottom of the casts to facilitate de-moulding.

In order to analyse the characteristics of the different mortars along time, twenty 20×20×100mm and five 40×40×160mm specimens were prepared with each of the mortars. The samples were kept for one day inside the casts and then demoulded. During the first day inside the casts and for six days further the samples were stored at 90±5% of relative humidity. The mortar beams were further stored until testing days under controlled ambience at a temperature of 20±5°C and 60±10% on grid-lined shelves to ensure the contact of all the sides with air and homogeneous progress of the carbonation reaction. Table 2 summarizes results of water/binder ratio, consistency and air content obtained for the fresh mortars.

**Tab. 2: Fresh mortars properties. The values correspond to the average of 3 values ± standard deviation and were determined through the preparation of 2kg of dry mortar.**

<table>
<thead>
<tr>
<th>Mortar Code</th>
<th>Water/binder ratio</th>
<th>Consistency [cm]</th>
<th>Air content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1.04</td>
<td>16.8 ± 0.1</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>LO</td>
<td>1.08</td>
<td>16.6 ± 0.1</td>
<td>5.4 ± 0.2</td>
</tr>
<tr>
<td>LM</td>
<td>0.96</td>
<td>17.1 ± 0.3</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>LMO</td>
<td>1.02</td>
<td>16.5 ± 0.1</td>
<td>4.0 ± 0.1</td>
</tr>
</tbody>
</table>

**2.3. Testing program and results**

Samples to be mechanically tested were taken from the room with controlled ambience conditions and tested within half an hour later.

Five specimens 20×20×100mm of each mortar were tested after 14, 28, 60 and 90 days, so that the evolution of their characteristics could be analysed. For the characterization of 90 days of age mortars, five specimens 40×40×160mm of each mortar were also used. All the specimens of each mortar were used for flexural and compressive strength tests. Half of each specimen 20×20×100mm (five half parts) were used for compressive strength and half were used for carbonation rate determination by thermogravimetric analysis.
Half of each specimen 40×40×160mm 90 days of age were also used for bulk density, open porosity, pore size distribution and water absorption by capillarity determinations after being dried to constant mass at 60°C.

2.3.1. Flexural and compressive strength

Flexural and compressive strength were determined based on the Czech standard ČSN EN 1015-11, in a universal traction machine, following the classic method of performing the compressive test with half samples obtained from the flexural test. Following the time intervals for strength testing of lime based mortars proposed by Lawrence et al., 2006, so far the specimens were tested at the ages of 14, 28, 60 and 90 days. In Table 3 flexural and compressive strength development of the mortars cured up to 90 days is given. Fig. 1 plots the graphics of mechanical strength results for specimens 40×40×160mm 90 days of age and Fig. 2 shows the mechanical strength development of 20×20×100mm samples along time.

A correlation between 20×20×100mm and 40×40×160mm values for all mortars with the age of 90 days cannot be established, particularly in the case of mortar L. The differences are assigned to the size effect influencing both the attained strength values (Drdácky et al., 2011) and the degree of reactions generating the strength gain, particularly carbonation reaction.

Tab. 3: Flexural and compressive strength (average values ± standard deviation) of mortars cured up to 14, 28, 60 and 90 days (* specimens 40×40×160mm).

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Flexural strength [Mpa]</th>
<th>Compressive strength [Mpa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 d</td>
<td>28 d</td>
</tr>
<tr>
<td>L</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>±0.03</td>
<td>±0.07</td>
</tr>
<tr>
<td>LO</td>
<td>0.41</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>±0.03</td>
<td>±0.07</td>
</tr>
<tr>
<td>LM</td>
<td>1.86</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>±0.55</td>
<td>±0.60</td>
</tr>
<tr>
<td>LMO</td>
<td>1.17</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>±0.13</td>
<td>±0.15</td>
</tr>
</tbody>
</table>

Fig. 1: Graphics of flexural and compressive strength of 90 days of age mortar specimens 40×40×160mm.
2.3.2. Bulk density and open porosity

These tests were performed based on the Czech standard ČSN EN 1936 by total saturation with water under vacuum and hydrostatic weighing. Results of each mortar with 90 days are given on Table 4 in terms of average values and standard deviation.

Tab. 4: Bulk density and open porosity (average values ± standard deviation) of mortars 90 days of age.

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Bulk density [kg·m⁻³]</th>
<th>Open porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1767,82 ±0,18</td>
<td>32,01 ±0,19</td>
</tr>
<tr>
<td>LO</td>
<td>1645,33 ±9,99</td>
<td>34,44 ±0,58</td>
</tr>
<tr>
<td>LM</td>
<td>1688,80 ±0,95</td>
<td>34,35 ±0,13</td>
</tr>
<tr>
<td>LMO</td>
<td>1611,06 ±7,84</td>
<td>32,41 ±0,50</td>
</tr>
</tbody>
</table>

2.3.3. Mercury porosimetry

Pore size distribution was performed with a mercury porosimeter Quantachrome Poremaster® PM-60-13 with a specimen from each mortar with 90 days of age.

Two equivalent penetrometers were used with a 5cm³ bulb and a total intrusion capacity of 0,500cm³. Low pressure testing ranged from 6894,7Pa (1Psi) to 344737Pa (50Psi) and high pressure analysis from 275790,3 (40Psi) to 172368925Pa (30000Psi). Equilibration times were 15s for low pressure and 30s for high pressure. As mercury parameters, the following were used: advancing and receding contact angle = 140º; surface tension = 0,485 N/m; and density = 13,5487g/ cm³.

Pore size distribution curves are plotted in Fig. 3 and represent the calculated pore size diameter of each mortar for the stated measurement conditions.
2.3.4. Capillary water absorption

The test was performed based on the testing procedures of the Czech standards ČSN EN 1015-18 and ČSN EN 15801. Lateral surfaces of samples were sealed with epoxy resin. Half of each sample 40x40x160mm was immersed in 5mm of water (over absorbent textile) inside a covered box to maintain constant hygrothermal conditions and to limit the water evaporation from the samples. The weight of the absorbed water per unit of the exposed surface immersed, function of the square root of time (in hours), was registered. The tests were carried out until the absorption reached an asymptotic value. The capillary water absorption coefficient was determined by the angular coefficient of the curve. The results are presented in Table 5 and in Fig. 4.

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Capillary coefficient [kg·m⁻²·h⁻¹/₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>2.77 ±0.03</td>
</tr>
<tr>
<td>LO</td>
<td>0.51 ±0.02</td>
</tr>
<tr>
<td>LM</td>
<td>0.97 ±0.03</td>
</tr>
<tr>
<td>LMO</td>
<td>0.42 ±0.02</td>
</tr>
</tbody>
</table>

Fig. 4: Capillary water absorption test curves of mortars 90 days of age.

2.3.5. Thermogravimetric analysis - TGA

TGA was used in order to follow the progress of the hardening reactions of carbonation and hydration in the course of time. The analysis was carried out using a TA instrument, model SDT Q600-
TGA/DSC in static nitrogen atmosphere at a temperature range between 20-1000°C and at a controlled heating rate of 20°C/min. The first derivative of thermogravimetry was used in order to identify the hydrated and the carbonated phases at their characteristic decomposition temperatures, and to follow up their formation in time qualitatively.

For this analysis 20×20×100mm half of samples that remained from the mechanical tests were used. Table 6 reports the portlandite (Ca(OH)₂) content in the mortars along time and Fig. 5 shows the ratio between hydration and carbonation reactions in time. While products of hydration reaction are visible at the temperature range 100-370°C, the carbonation manifests as an increasing peak reaching maximum value between 700°C and 800°C.

Tab. 6: Portlandite content development determined by thermogravimetric analysis in mortars up to 90 days of age.

<table>
<thead>
<tr>
<th>Test day</th>
<th>Portlandite [Ca(OH)₂] (%)</th>
<th>L</th>
<th>LO</th>
<th>LM</th>
<th>LMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td></td>
<td>17,64</td>
<td>15,07</td>
<td>7,69</td>
<td>8,23</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td>14,68</td>
<td>11,42</td>
<td>6,34</td>
<td>6,17</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>8,40</td>
<td>5,90</td>
<td>4,76</td>
<td>3,50</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>4,93</td>
<td>5,51</td>
<td>2,81</td>
<td>2,38</td>
</tr>
</tbody>
</table>

Fig. 5: DTG graphics of analysed mortars at 14, 28, 60 and 90 days of age.
2.3.6. Freeze-thaw testing program

Samples 40×40×160mm of lime and lime with linseed oil with 90 days of age were dried to constant mass at 60°C before being tested. The freezing tests were performed based on the Czech standard ČSN 72 2452. Samples were immersed in water at ambience temperature (20±5°C) until achieving constant mass. After saturation in water samples were subjected to -20°C (±5°C) in a freezer during four hours and then thawed in water at ambience temperature (20±5°C) for at least two hours before performing another cycle. Three samples were subjected to the freezing cycles and three samples were maintained immersed in water throughout the test (reference samples).

Lime mortar samples crumbled after one freezing cycle (Fig. 6.a). Under the binocular microscope microfissuration around the sand grains and powdering of binder could be observed on the fresh broken pieces (Fig. 6.b).

Lime with linseed oil mortar was subjected to ten cycles after which the samples showed moderate degradation by binder powdering and, consequently, sand disintegration, particularly on the edges (Fig. 7.a). Under the binocular microscope micro-fissuration on the surfaces could be observed (Fig. 7.b). Hence, after 10 cycles it was decided to perform flexural and compressive strength tests. Prior to the mechanical tests, samples were dried to constant mass at 60°C. The results of mechanical strength after freezing tests are given in Table 7 and Fig. 8.

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**Fig. 6: Aspect of L mortar 90 days of age after one freezing cycle: a) General view; b) Detailed view (millimeter scale).**

**Fig. 7: Aspect of LO mortar 90 days of age after 10 freezing cycles: a) General view of a reference and aged sample; b) Detailed view of a sample after 10 freezing cycles (millimeter scale).**
Table 7: Flexural and compressive strength (average values ± standard deviation) of mortars 90 days of age after the freezing test.

<table>
<thead>
<tr>
<th>Mortar</th>
<th>Flexural strength [MPa]</th>
<th>Compressive strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO – Not Aged</td>
<td>1.34 ±0.07</td>
<td>1.01 ±0.03</td>
</tr>
<tr>
<td>LO – Age Reference</td>
<td>0.32 ±0.04</td>
<td>0.69 ±0.12</td>
</tr>
<tr>
<td>LO – 10 Cycles</td>
<td>0.30 ±0.03</td>
<td>0.55 ±0.06</td>
</tr>
</tbody>
</table>

Fig. 8: Flexural and compressive strength for LMO mortar 90 days of age after freezing test.

3. Analysis and discussion of results

3.1. Mechanical strength

L and LO mortars indicate similar flexural strength development until 90 days of age. LO mortar has slightly higher values but significant regarding the compressive strength (Fig. 2). LO compressive strength increases till 60 days after when slightly drops to the same value of L mortar and TGA shows the same evolution for the carbonation rate (Fig. 5). However, 40×40×160mm specimens 90 days of age results indicate remarkably higher flexural and compressive strength values (148% and 127% strength increment, respectively) for LO mortar compared to L mortar (Fig. 1). Hence, it can be assumed that linseed oil is improving mechanical strength on air lime mortar.

Lime-metakaolin mortars, LM and LMO, show different strength development behaviour. Contrary to the pure air lime mortars the flexural and compressive strength of LMO is significantly lower than that of LM, particularly at early ages (14 and 28 days) after which the values become practically equal (Fig. 2). Regarding these results, it must be taken into account that strengths determined at early ages (up to 28 days) are not conclusive because they are strongly influenced by the water content of the mortar. Values of 4×4×16cm samples 90 days of age show a marked difference between LM and LMO strengths (Fig. 1): oil addition promoted a reduction of 23% on flexural strength and 40% on compressive strength.

In lime-metakaolin mortars, hardening reactions are hydration and carbonation while calcium hydroxide mortars harden only due to carbonation reaction. Obviously, because of binder hardening, the mechanical strengths of lime mortars increase with curing time. In lime-metakaolin mortars, a combined reaction of hydration and carbonation takes place. Hydration reactions initiate first resulting in the formation of hydrated phases such as calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) phases. This provides an initial set to the mortars. Subsequently carbonation of free lime takes place, which is mostly after 14 days (Cizer, 2009).

In lime-metakaolin mortars, a combined reaction of hydration and carbonation takes place in lime-metakaolin mortar. Hydration reaction is the first reaction and carbonation of lime is the complementary reaction in the strength gain (Cizer, 2009). Under curing conditions used in the experiment (20°C and 60%) the
hydration (pozzolanic) reaction prevailed within 28 days while the carbonation reaction prevailed afterwards. Carbonation dominance in hydration/carbonation completion causes the strength reduction in lime-metakaolin mortar during the monitored time period 28-90 days. Regarding LMO results, the addition of oil to lime-metakaolin mortar might inhibit CSH and/or CAH formation that are the main phase responsible for imparting strength to the mortar at early ages.

A possible explanation that can account for the strength improvement in lime mortar and strength reduction in lime-metakaolin mortar is that when oil is added into mortar, triacylglycerols undergo hydration resulting in formation of insoluble calcium salts of fatty acids (Rovnaníková, 2002). Due to their interaction with calcium they are well bounded in the mortar structure and the hydrophobic alkyl chain will cause mortar repulsion (Rovnaníková, 2002) and maybe strength improvement in the case of lime mortars. Regarding lime-metakaolin mortar, the formation of insoluble calcium salts may prevent the formation of CSH and/or CAH phases by depleting calcium hydroxide.

### 3.2. Porosity and capillarity

Concerning density and open porosities although the air content values of fresh mortars with linseed oil addition are much higher than the reference mortars (Table 2), values of porosity of hardened mortars are very similar (Table 3). Hence, a relationship between mechanical properties and porosity cannot be established as it is usually possible (Pandley & Sharma, 2000; Lanas et al., 2003; 2006).

Rovnaníková (2002) achieved similar results on lime mortar enriched with 1% boiled linseed oil, i.e., air content of fresh mortar with linseed oil was significantly higher than that of the reference but hardened mortars had similar open porosity values. Čehová (2009) also obtained similar open porosity results for lime mortar and lime with natural pozzolan a mortar three months of age with 1% linseed oil.

The mechanical strength differences cannot be explained regarding the porosity characteristics of hardened mortars nor the water/binder ratio that is also very similar in all mortars. However, the significantly higher air content values of mortars with linseed oil may actually play an important role on the higher rate of carbonation at young ages. In the case of the LO mortar, the high air content may account for the improvement of the carbonation rate by allowing better carbon dioxide diffusion within the mortar matrix.

Although the difference in the air content is very high, no significant changes were detected between curing evaporation curves of reference and modified mortars. However, difference in moisture content between LM and LMO mortars after 90 days was significant: mortar with oil addition has approximately less 3%-w moisture than the reference mortar. Table 8 presents the moisture content determined for 90 days of age mortar specimens by means of their drying at 60°C to constant mass.

The differences in moisture content of reference and modified mortars may be explained by the pore size distribution curves (Fig. 3). The addition of oil to lime-metakaolin mortar strongly influences the porometry by shifting the size of the pores towards higher values hence promoting higher water evaporation which may account for the lowering of the mechanical strength of LMO mortar. Contrarily, oil addition to lime mortar shifts the pore size towards lower values but the influence is not so significant and the moisture content is not altered.

**Tab. 8: Moisture content (average values ± standard deviation) of mortars 90 days of age.**

<table>
<thead>
<tr>
<th>Mortar code</th>
<th>Moisture content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>LO</td>
<td>0.49 ± 0.08</td>
</tr>
<tr>
<td>LM</td>
<td>5.67 ± 2.41</td>
</tr>
<tr>
<td>LMO</td>
<td>2.77 ± 0.23</td>
</tr>
</tbody>
</table>

Porosity results are very similar between reference mortars and mortars with oil but the capillary coefficients are relevantly different. Capillary coefficient reduction promoted by the addition of oil on
L mortar is approximately 82% and on LM mortar 57% and these features cannot be explained on the basis of the porometry results (Fig. 3). Particularly in the case of lime-metakaolin mortars porometry, LMO pore sizes were shifted towards bigger pores: the peaks related to 0.14 μm and 0.32 μm pores in LM mortar were merged into a narrower unimodal distribution with a stronger peak centered on 0.59μm. The percentage of total intrusion volume remained similar: 32% for LM and 35% for LMO. It could be expected that such a modification of pore size generated by the oil addition would influence the water absorption coefficient taking into account that pores situated around 1μm have the highest effect on capillarity (Barsottelli et al., 2001). However, Wendler & Charola (2008) suggest that water will move by capillary transport only in pore sizes ranging from 10μm to 1mm so, according to these authors, the pore size distribution determined for both mortars will have no influence on water absorption by capillarity.

Nevertheless, the extremely slow capillary water absorption rate of mortars with linseed oil compared to the reference may be rather assigned to the hydrophobic effect of the oil that grants higher contact angle of water on the hydrophobic mortars surface and inhibits water penetration into the voids.

Porometry modification promoted by the addition of linseed oil may however contribute to the reduction of the mechanical strength of lime-metakaolin mortar.

3.3. Thermogravimetric analysis

Lime with linseed oil shows slightly faster carbonation rate up to 60 days of age as it is illustrated by the stronger peaks assigned to calcite formation (~750-800 °C) and less pronounced peaks assigned to portlandite dehydroxilation (~400-475°C) in DTG curves (Fig. 5). It can be assumed that the values of calcium hydroxide content are well correlated with mortars compressive strength development.

As abovementioned, in lime-metakaolin mortars, hydration reactions initiate first resulting in the formation of hydrated phases such as CSH and CAH phases. Subsequently carbonation of free lime takes place, which prevails mostly until 28 days of age.

It can be noticed that LM mortar peak concerning the presence of CAH phase (~230°C) is slightly more pronounced than that of LMO throughout the curing time. CSH peak (~150°C) is very strong at young ages in LM curve whereas in LMO is less strong but its decomposition is less affected during time. On the other hand, carbonation rate is slightly improved in LMO mortar after 28 days of curing.

Nevertheless, the differences in DTG curves of reference mortars and mortars with oil may be found to influence the mechanical strength negligibly.

3.3. Freeze-thaw resistance

Improved durability of lime mortar with linseed oil addition has been confirmed by testing their freeze-thaw resistance: lime mortar was destroyed after one cycle whereas lime with linseed oil endured ten cycles after which showed visual moderate degradation but mechanical strength significantly decreased. After ageing LO flexural strength value is close to that of lime mortar not aged while compressive strength is two times lower.

Unexpected is that reference samples, which have been kept immersed in water throughout the test, have similar mechanical strength compared to the specimens subjected to the freezing cycles. This behaviour outlines that the freezing test is not affecting significantly the mortar strength but it is rather the prolonged action of water that is probably promoting dissolution of the not-carbonated binder fraction.

Mechanical strength can be related to durability of the mortar: specimens with higher strength (LO) show higher resistance as it is usually reported (Lanas et al., 2006; Botas, 2009; Čechová, 2009). But in the present case this fact is mainly influenced by the hydrophobicity of the mortar that prevents water from penetrating the sample. Capillarity coefficients of the mortars confirm this assumption: the lower the amount of absorbed water, the better the mechanical performance and durability.

The same damage resistance behaviour is expected for lime-metakaolin mortar with linseed oil although its mechanical strength is lower compared to the reference.
4. Conclusions

Mechanical strength and porosity are important indirect parameters to assess mortar durability. In the case of linseed oil addition to lime based mortars the results indicate that the modification of the chemical composition of the mortar can have greater significance for the mortar durability by hindering water intake, thus lessening related problems.

The lower capillarity coefficient, which implies a water intake reduction, may be pointed as the main factor improving the performance of lime mortar with linseed oil exposed to freeze-thaw cycles and hence, its durability. The extremely slow capillary water absorption rate of mortars with linseed oil compared to the reference may be assigned to the hydrophobic effect of the oil that grants higher surface tension to the mortars thus inhibiting water penetration into the voids.

Although previous research studies outlined that oil addition to lime mortars decreases mechanical strength by restraining carbonation, the results obtained in the present study show the contrary. This is possibly due to a combination of different factors, particularly the chemical composition of the oil, the type of binder and the amount of oil added.

Regarding the results of the study by Čechová (2009) showing that linseed oil addition in 1%-w/w and 3%-w/w promotes a marked reduction of mechanical strength (particularly with 3%) it can be assumed that slight modifications on the amount of oil added to the mortar mixture can have great influence on the mechanical behaviour.

In the present study it was highlighted that porosity and carbonation rate has low influence on the mechanical behaviour of mortars with oil 90 days of age. The strength modification may be rather assigned to formation of insoluble calcium salts of fatty acids that are well bounded in the mortar structure improving strength in lime mortar and decreasing it in lime-metakaolin mortar. Furthermore, the new compounds formed by the oil addition seem to promote higher surface tension and prevent water absorption. However, one must take into account that the combination of the small variations determined for each parameter may play a significant role for the obtained modifications on mortar strength. Hence, air content and porometry may be outlined as the most important indirect contributing factors due to their influence in the moisture content during the curing process.

Further research developments focused on the chemistry of the processes will certainly contribute to clarify the questions on mortar strength and durability raised by the results reported.

Acknowledgement

The present study was supported by the Czech national project MK ČR NAKI DF11P01OVV0080 entitled “High Valuable and Compatible Lime Mortars for Application in the Restoration, Repair and Preventive Maintenance of the Architectural Heritage”.

References


ČSN EN 1936 Zkušební metody přírodního kamene - Stanovení měrné a objemové hmotnosti a celkové a otevřené povrchnosti.

ČSN EN 1015-18 Zkušební metody malt pro zdivo - Část 18: Stanovení koeficientu kapilární absorpce vody v zatvrdlé maltě.

ČSN EN 15801 Ochrana kulturního dědictví – Metody zkoušení – Stanovení nasákovosti vody kapilárním vzlínáním.

ČSN 72 2452 Zkouška mrazuvzdornosti malty.