Construction and Building Materials 189 (2018) 787–796

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

# Influence of linseed oil on the microstructure and composition of lime and lime-metakaolin pastes after a long curing time

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## HIGHLIGHTS

- Linseed oil imparted similar hydrophobic properties to lime and lime-metakaolin pastes.
- Linseed oil delayed carbonation and promoted the development of amorphous phases.
- Linseed oil can have a beneficial effect on the pozzolanic reaction of lime-metakaolin.

## ARTICLE INFO

*Article history:*
Received 18 June 2018
Received in revised form 10 August 2018
Accepted 8 September 2018

*Keywords:*
Linseed oil
Lime
Metakaolin
Carbonation
Hydration
Hydrophobicity
Amorphous calcium carbonate

## ABSTRACT

This study investigates the effect of linseed oil on the microstructure of lime and lime-metakaolin pastes after 68 months of curing under controlled conditions. The hydrophobicity imparted by linseed oil to the pastes' bulk was confirmed by measuring water drops' contact angle. The results of thermal analysis, X-ray powder diffraction, and Fourier transform infrared spectroscopy showed that linseed oil significantly hindered the carbonation reaction in both lime and lime-metakaolin pastes and promoted the development of amorphous phases. The obtained results also indicated that linseed oil could foster the pozzolanic reaction in the lime-metakaolin system by stabilizing and/or promoting the development of hydration products resulting in reduced shrinkage in comparison with the reference.


## 1. Introduction

Aerial lime mortars and finishing coatings (paints) are known as one of the most compatible types of materials for the restoration of the historical heritage in which masonry and coatings were based on those materials [1]. Plastering and painting are amongst the most frequent maintenance activities in architectural restoration interventions. The significantly high number of publications dealing with the design of lime-based repair mortars for historical constructions reflects the need for more durable, while compatible, materials. One way to improve the durability of lime mortars and coatings is through the addition of additives, which are selected according to the functional requirements of the restoration material, e.g. [2–4]. Cases in point are water-repellents that aim at ameliorating the durability of mortars by hampering water ingress into the structures on which they are applied, e.g. [5–7]. Current research trends drive towards durability, compatibility, and sustainability in new construction and restoration sectors. In this context, natural additives are of growing interest to the scientific community, e.g. [8–12].

Natural oils and fats were one of the most common types of water-repellent additives used in mortars and coatings in the antiquity, and linseed oil is frequently mentioned in the European literature (e.g., *De architectura* by Vitruvius [13]). It is a highly chemically reactive oil because it contains a high amount of linolenic (48–60 wt%) and linoleic (14–19 wt%) acids with three and two double bonds, respectively. It is mostly used as a varnish thanks to its fast polymerization, e.g. [14]. The unsaturated triglycerides present in linseed oil polymerize by oxidation when exposed to atmospheric oxygen and also by photo-oxidation when exposed to light, forming macromolecular solid products [15]. When added to lime-based slurries, the glycerides present in the oil hydrolize when reacting with the alkaline binders. Subsequently, the carboxyl

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https://doi.org/10.1016/j.conbuildmat.2018.09.054
0950-0618/

groups coordinate with calcium to form insoluble calcium salts of fatty acids; their non-polar units are directed to the mortar-air interface, resulting in a water-repellent material [10].

Fatty acids are known to affect the crystallization process and the morphology of calcium carbonate from solutions [15,16], during carbonation reaction of lime slurry [17] and hydration products [18], which will consequently affect the porosity and PSD of a system. Other studies on the effect of vegetable oils on the properties of lime-based mortars have also shown alterations on the porosity and PSD between the reference and the mortars with additives, e.g. [3,19,20]. Regarding the effect of linseed oil on mortars, Čechová [21] has reported that an amount of 1 wt% of oil caused a slight reduction of porosity and pore size diameter (water and MIP) of aerial lime, natural hydraulic lime, lime-pozzolan, lime-brick dust and lime-cement mortars with three months and one year of age whereas an amount of 3 wt% of oil increased the porosity and the main pore radius. The mechanical strength generally improved with 1 wt% of oil addition, but 3 wt% reduced the strength substantially. Rovnaníková [22] studied the effect of stand oil in different concentrations (1, 5, and 10 wt%) in aerial lime mortars and observed a decrease in porosity (water) with increasing amount of oil. The compressive strength significantly increased with oil addition, but the flexural strength was reduced. In another work [23], both linseed and stand oil added in 1.5 wt% to aerial lime and lime-metakaolin mortars (using the same materials as in this study) resulted in a similar increment in porosity (water and MIP) and increment of the main pore radius after six months of curing. In general, the mechanical strength was reduced with both types of oil. Justnes et al. [10] reported negligible changes in the porosity (water) of Portland cement mortars with varying oil amounts (0.5–1 wt%) at 28 days of age, but a relevant decrease in the mechanical strength. Based on the reported literature, we can infer that some physical changes induced by vegetable oils in mortars are highly dependent on the type of oil (reactivity and amount), type of binder, mixing procedure, and mortar age, resulting in very different properties of the hardened material, namely regarding the porosity and mechanical strength. Thus, it is difficult to compare the results of different studies, namely when different types of oils and binders are used.

Linseed oil can be considered an eco-friendly alternative to synthetic (e.g., metal soaps and silanes) as a water-repellent additive for mortars and coatings since it gives comparable results [23]. The investigation of the effect of vegetable oils on the properties of aerial lime and lime-pozzolan materials is a recent field of research which has been mainly focused on the physical characterization and durability of mortars, e.g. [3,19,24,21,25]. This work aims at gaining further insights into the influence of linseed oil on the microstructural and compositional features of aerial lime and lime-pozzolan pastes. Paste specimens were used to focus the study on the interaction with the binder, responsible for the setting and hardening of mortars. As noted by Vejmelková et al. [26], Central Europe lacks natural pozzolans, and a possibility to obtain artificial pozzolans in the Czech Republic is the calcination of clay shales. The so-called 'burnt Czech clay shale' [26], henceforth designated as metakaolin, was selected as the pozzolanic material for this study. Regarding the composition of the specimens with oil addition, one of the objectives of this study was also to try to detect calcium salts of fatty acids, which are theoretically formed when oil reacts with the alkaline environment of the paste, as described previously. To our knowledge, calcium salts of fatty acids have been only detected in ancient samples of lime and tung oil pastes which were fully carbonated [12]. Therefore, we expected to have better chances of identifying the calcium salts having the samples matured after a long curing period. This is also the reason why we added a significantly higher amount of linseed oil (9 wt% in respect to the weight of binder) than that which has been found to be sufficient (1 to 3 wt%) to impart water-repellency to lime-based systems and achieve higher durability in comparison with the references [21,24,27]. We believe that this research is the first attempt to characterize the effect of linseed oil on the microstructure of lime and lime-metakaolin pastes.

## 2. Experimental

### 2.1. Materials and specimen preparation

The specimens were prepared in the lab with an industrially produced hydrated lime powder class CL90 (Čerták), metakaolin (Mefisto L05), and raw linseed oil (GRAC s.r.o.). According to the analysis performed by Nežerka et al., 2014 [28] on the same binders used in this study (same producer), the lime used is of high purity (98.98 wt% CaO + MgO) and the metakaolin is mainly composed of $SiO_2$ (52.1 wt%) and $Al_2O_3$ (43.4 wt%). The grading analysis showed that the predominant particle diameter in lime is 15 μm; 50% of the cumulative volume corresponds to a particle diameter of 13 μm and 90% to 38 μm; the specific surface area is 16.5 $m^2/g$. In the case of metakaolin, 50% of the cumulative volume corresponds to 4 μm and 90% to 11 μm; the specific surface area of metakaolin is 12.7 $m^2/g$ [28]. Dry lime hydrate was preferred to lime putty to have more precision in the weight measurements because the water content in lime putty can vary substantially. The composition of the specimens is given in Table 1. The oil was added in the mass ratio of 1:0.1 (lime:oil); this ratio corresponds to 9 wt% of oil with respect to the binder weight. A water/binder ratio of 1.06 was used to prepare all pastes. The consistency of the fresh paste determined with the modified Vicat apparatus according to ASTM C110 [29] in triplicate is also given in Table 1.

In the case of the lime-metakaolin specimens, the dry components were first hand-mixed for 3 min with a spoon. Linseed oil was mixed with the dry components as follows: i) weighing the oil in a cup, adding a small portion of the dry component (ca. 5 g), and hand-mixing with a spoon for 2 min to obtain a homogeneous paste; ii) adding a small portion of dry component as in the first step and mixing for 2 min; iii) adding the double of the previous amount of dry component and mixing for 2 min; iv) sieving the resulting mixture with a mesh of 500 μm and mixing the retained clusters with a similar amount of dry component used in the first step in a mortar and pestle and repeating this procedure until no more clusters remain in the sieve; v) gently stir the oil-powder mix with the remaining dry portion for 3 min. The dry mixes were then hand-blended for ca. 3 min with a pre-determined amount of water necessary to achieve suitable workability for preparing paste specimens while keeping the water/binder ratio as low as possible to avoid cracking due to shrinkage during curing. The consistency of the pastes was reduced with linseed oil addition because oil reduces the adsorption of water to the binder particles. Nevertheless, the workability of the pastes with linseed oil, when worked out with a baker's knife while preparing the specimens, was better, probably because of bubble development during mixing, as described in Section 3.2, and possibly increased viscosity.

The fresh pastes were molded in rings with an inner diameter of 70 mm and a thickness of 10 mm. The geometry of the specimens was chosen based on previous experience with standard prismatic specimens used for mortar preparation in which more than 50% of the prismatic specimens fractured during curing. On the other hand, cylindrical flat specimens, identical to those used in the water vapour permeability test for mortars [30], did not fracture, probably because the cylindrical shape and lower thickness reduces corner effects and stress development during water evaporation in the early stage of curing. Moreover, the hardening reactions are also supposed to progress more homogeneously in cylindrical specimens in comparison to prismatic ones. Hence, we decided to prepare cylindrical samples instead of the prisms usually used for most of the standard evaluation tests for mortars.

During the first seven days, the pastes were kept inside the molds at 90 ± 5% relative humidity (RH) inside closed boxes at room temperature. This was mainly done with the purpose of facilitating de-moulding the specimens because after this period the paste is slightly more consistent as a consequence of some limited evaporation. After this period, the pastes were de-molded and left to cure over grid-lined shelves in a room with 60 ± 10% RH, 20 ± 5 °C, and 500 ± 50 ppm of atmospheric $CO_2$. The selection of the curing conditions was based on the average RH of the ambient air in the Czech Republic during the construction/repair activity period (April-September) which is between 60 and 70% [31]. Therefore, 60% RH was chosen as being representative of the on-site conditions from the beginning of the curing

**Table 1**
Composition by mass and resulting consistency of the fresh paste.

| Specimen | Materials | Ratio | Consistency (mm) |
|---|---|---|---|
| L | Lime | – | 20 ± 2 |
| LO | Lime:Oil | 1:0.1 | 16 ± 3 |
| LM | Lime:Metakaolin | 0.75:0.25 | 21 ± 3 |
| LMO | Lime:Metakaolin:Oil | 0.75:0.25:0.1 | 18 ± 4 |