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**THE EFFECT OF LINSEED OIL ON THE
PROPERTIES OF LIME-BASED RESTORATION
MORTARS**

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Abstract

THE EFFECT OF LINSEED OIL ON THE PROPERTIES OF LIME-BASED RESTORATION MORTARS

The traditional lime mortar is composed of hydrated lime, sand and water. Besides these constituents it may also contain additives aiming to modify fresh mortar's properties and/or to improve hardened mortar's strength and durability. Already in the first civilizations various additives were used to enhance mortar's quality, among the organic additives, linseed oil was one of the most common. From literature we know that it was used already in Roman period to reduce water permeability of a mortar, but the mechanism and the technology, e.g. effects of different dosages, are not clearly explained. There are only few works studying the effect of oil experimentally. Knowing the function of oil in historical mortars is important for designing a new compatible repair mortar. Moreover, linseed oil addition could increase the sometimes insufficient durability of lime-based mortars used for reparation and it could be a natural alternative to synthetic additives.

In the present study, the effect of linseed oil on the properties of six various lime-based mortars has been studied. Mortars' compositions have been selected with respect to composition of historical mortars, but also mortars used in a modern restoration practise have been tested. Oil was added in two different concentrations – 1% and 3% by the weight of binder.

The addition of 1% of linseed oil has proved to have positive effect on mortars' properties. It improves mechanical characteristics and limits water absorption into mortar without affecting significantly the total open porosity or decreasing the degree of carbonation. On the other hand, the 3% addition of linseed oil is making mortar to be almost hydrophobic, but it markedly decreases mortars' strength. However, all types of tested lime-based mortars with the oil addition showed significantly decreased water and salt solution absorption by capillary rise. Addition of oil into mortars is also decreasing the proportion of pores which are easily accessible to water. Furthermore, mortars with linseed oil showed significantly improved resistance to salt crystallization and freeze-thaw cycles.

On the base of the obtained results, the addition of 1% of linseed oil can be taken into consideration in the design of mortars meant to repair or replace historic mortars.

List of symbols and abbreviations

A	[mm ²]	area on which the load is applied (compressive strength testing)
ASTM		American Standard Testing Method
b	[mm]	width of specimen
c	[MPa]	compressive strength
C	[kg/(m ² .min ^{0.5})]	coefficient of water (salt solution) absorption
C_2S		Dicalcium silicate 2CaO. SiO ₂
C_3A		Tricalcium aluminate 3CaO. Al ₂ O ₃
C_3S		silicate 3CaO. SiO ₂
C_4AF		Tetracalcium aluminoferrite 4CaO. SiO ₂ . Al ₂ O ₃ . Fe ₂ O ₃
C_a		coefficient of pores accessibility to water
C_v	[g.h ⁻¹ .m ⁻²]	water vapour permeability coefficient
C-S-H		Calcium silicate hydrate
d	[mm]	depth of specimen
E_{dyn}	[GPa]	dynamic modulus of elasticity
e.g.		exempli gratia (= for example)
EN		European Standard
f	[MPa]	flexural strength
F_f	[N]	maximum load applied to the specimen (flexural strength test)
F_c	[N]	maximum load applied to the specimen (compressive strength test)
φ		angle with vertical direction

g	[$m.s^{-2}$]	gravity acceleration, $g = 9.81 m.s^{-2}$
h	[m]	distance reached by water in the capillary
h_0	[m]	height of water above entrance pore
$\Delta h/\Delta t$	[$m.s^{-1}$]	capillary absorption rate
i.e.		id est (= that is)
l	[mm]	distance between the axes of the support rollers
L	[m]	length of the specimen
m_0	[kg]	mass of the empty vassel
m_0	[kg]	mass of the dry specimen
m_1	[kg]	mass of the empty container
m_2	[kg]	mass of the container and test specimen
m_{10}	[kg]	mass after 10 minutes
m_{90}	[kg]	mass after 90 minutes
m_A	[kg]	mass of the empty pycnometer
m_B	[kg]	mass of the pycnometer filled with distilled water
m_C	[kg]	mass of the pycnometer filled with ethanol
m_D	[kg]	mass of the specimen
m_E	[kg]	mass of the pycnometer filled with ethanol and the specimen
m_{fm}	[kg]	mass of vassel with fresh mortar
m_{h1}	[kg]	mass of the saturated specimen after 48 hours weighed hydrostatically
m_{h2}	[kg]	mass of the saturated surface dry specimen after vacuum evacuation weighed hydrostatically
m_{SSD1}	[kg]	mass of the saturated surface dry specimen after 48 hours

m_{SSD2}	[kg]	mass of the saturated surface dry specimen after vacuum evacuation
n	[Hz]	fundamental frequency in longitudinal mode of vibration of the specimen
v	[m.s ⁻¹]	ultrasonic pulse velocity
η	[Ns.m ⁻²]	water viscosity
OPC		Ordinary Portland Cement
p_{48}	[%]	porosity after 48 hours, i.e. porosity easily accessible to water
P_{H_2O}	[%]	porosity accessible to water, i.e. open porosity
r	[m]	capillary radius
RH	[%]	relative humidity
ρ	[kg.m ⁻³]	density of the material (dynamic modulus of elasticity testing)
ρ_a	[kg.m ⁻³]	apparent density
ρ_b	[kg.m ⁻³]	bulk density of fresh mortar
ρ_{H_2O}	[kg.m ⁻³]	distilled water density at 20 °C, $\rho_{H_2O} = 998,2 \text{ kg.m}^{-3}$
ρ_c	[kg.m ⁻³]	density of ethanol at 20 °C
ρ_l	[kg.m ⁻³]	loose bulk density
ρ_p	[kg.m ⁻³]	particle density determined
σ	[N.m ⁻¹]	surface tension of the water
T	[s]	pulse transit time
τ	[h]	time between two successive measurements (water vapour permeability test)
θ		contact angle between water and the solid surface

V	$[m^3]$	capacity of the container
V_{fm}	$[m^3]$	volume of fresh mortar
wt		weight (percentage per weight)
WA	[%]	water absorption after vacuum evacuation
WA_{48}	[%]	water absorption after 48 hours

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1 Introduction

The traditional lime mortar is composed of hydrated lime, sand and water. Besides these constituents it may also contain additives aiming to improve fresh mortar's workability and/or to improve hardened mortars' strength and durability.

The idea of improving mortar's properties by using various additives is not new, but something which has been known already by the first civilizations^(1; 2). Lime-based mortars used in ancient times were sometimes of poor quality; therefore masons were employing various additives to reach desired properties. There are records that egg whites, bullock's blood, fruit juices, keratin and casein were used in Ancient Egypt^(3; 4). Bitumen as an oldest known natural organic additive was used already in Mesopotamia some 4000 years ago^(5; 6; 7). Romans were known to use pozzolanic materials, which were giving hydraulic properties to mortar, but these were not always available and cost was also a large factor⁽⁸⁾. Consequently locally available materials increased in use. Variety of substances of different origin were used, such as local agroproducts (cereals, juices from trees, fruits and vegetables), oils and fats, milk, eggs, but also blood, dung, urine or other materials like animal hair. Although it looks that almost everything available went into mixes, there seemed to be a method behind their madness⁽³⁾. Unfortunately there is not much information in literature about the technology of mortars preparation. This being their livelihood, masons were scared to write about the things they knew and often the knowledge and experience were buried with them⁽⁶⁾. On the other side we have legends of excellent durability of some historic mortars, which has been accredited just to the use of natural polymeric additives.

Nowadays it is quite complicated to analyze organic additives in historical mortars since they were probably added in very small amounts which may be under the detection limit of some analytical methods. Thus it is probable that most of the information of using natural polymeric additives is based on the study of historical sources rather than on the exact material analysis of preserved monuments⁽⁹⁾. Among organic materials, linseed oil is one of the most commonly used additive in past. It was used already in Roman period^(1; 2) to

reduce water permeability of a mortar. It was used especially in mortars for pavement to increase their durability.

The motivations justifying the renewed interest in the use of natural polymeric additives can be summarized as follows:

- The only information we inherited from ancient treatises is that linseed oil was added to decrease mortar's water permeability. There are only few works studying the effect of oil experimentally. The mechanism and the technology, e.g. effects of different dosages, are not clearly explained.
- Knowing the function of oil and purpose of its addition can help us to explain some particular characteristics of historic mortars, which is important for designing a new compatible repair mortar⁽¹⁰⁾.
- Lime-based mortars by itself are sometimes not meeting the requirements of certain types of restoration interventions due to their little durability. On the other hand, more durable cement mortars are not suitable for historical monuments restoration because of their excessively high strength and sulphate content. The use of additives seems to be a way to improve properties of lime-based mortars. Since the trends in the restoration of historic monuments are to prefer the use of natural materials, linseed oil can be a valid alternative to the synthetic additives. Furthermore, the replacement of synthetic additives by natural ones can be an actual topic even out of restoration field, using of linseed oil as a so called bio-admixture is in accordance with the recent policy of sustainable development.

In this research linseed oil is has been added in different percentages, i.e. 1% and 3% by the weight of binder, in order to study its influence on mortar's properties systematically.

The research objectives of this thesis are:

- To study linseed oil's effect on the properties of lime-based mortars;
- To experimentally verify the assumption that the addition of linseed oil is increasing mortar's resistance to deterioration;
- To interpret and describe the mechanism of linseed oil's action in mortars;
- To develop a mortar with improved durability suitable for restoration.

2 Theory

2.1 DEFINITION OF MORTAR

A mortar can be defined as a mixture of one or more inorganic or organic binders, mostly fine aggregates, water and sometimes additives and/or admixtures in the proportions necessary to give to the mixture proper workability in the fresh state and adequate physical and mechanical properties, outward aspect, durability etc, in the hardened state ⁽¹¹⁾.

Mortar can be divided according to its use as either:

- bedding and jointing mortar – to bond masonry units (brick and/or stones) together;
- plastering mortar – for external coating of masonry;
- rendering mortar – for internal application on masonry; or
- stucco – decoration mortar.

Ad Cowper ⁽¹²⁾ uses the term “mortar” for bedding and jointing mortar only:

“Mortar is defined as any material used in a plastic state which can be troweled, and becomes hard in place, and which is utilized for bedding and jointing. The word “mortar” is thus used without regard to the composition of the material, but simply defining its use as a bonding material, and to distinguish it from “stuccos” and “plasters”. ⁽¹²⁾

However standard EN 459-1/2001 ⁽¹³⁾ uses term “mortar” as a general term for all the types of mortar mentioned above.

The primary functions of hardened bedding and jointing mortar in a construction are ⁽¹⁴⁾:

- To provide an even bed so that the load on the wall is distributed evenly over the whole bearing area of the masonry units;
- To bond the units together and help them resist lateral forces, and
- To seal joints against the penetration of rain.

The main function of plastering and rendering mortar is to level walls surface asperity and to protect the masonry against weathering. According to EN 459-1:2001⁽¹³⁾ rendering and plastering mortars can be further divided

- according to the concept as either:
 - *Designed mortars* - mortar whose composition and manufacturing method is chosen by the producer in order to achieve specified properties (performance concept); or
 - *Prescribed mortars* - mortar made in pre-determined proportions, the properties of which are assumed from the stated proportion of the constituents (recipe concept).
- according to the mode of manufacture as either:
 - *Factory-made mortars* - mortar batched and mixed in a factory. It may be 'dry mortar' which is ready mixed only requiring the addition of water, or 'wet mortar' which is supplied ready for use;
 - *Semi-finished factory mortars* which can be either
 - prebatched rendering/plastering mortar - mortar whose constituents are wholly batched in a factory, supplied to the building site and mixed there according to the manufacturer's specification and conditions;
 - premixed lime-sand rendering/plastering mortar - mortar whose constituents are wholly batched and mixed in a plant, supplied to the building site where further constituents specified or provided by the factory are added (e.g. cement)); or
 - *Site-made mortars* - mortar composed of individual constituents batched and mixed on the building site.
- according to the properties and/or use, as either:
 - *General purpose rendering/plastering mortar* - rendering/plastering mortar without special characteristics. It can be prescribed or designed;
 - *Lightweight rendering/plastering mortar* - designed rendering/plastering mortar with a dry hardened density below a prescribed figure;

- *Coloured rendering mortar* (designed rendering/plastering mortar specially coloured, the colour is achieved e.g. with pigments or coloured aggregates);
- *One-coat rendering mortar for external use* (designed rendering mortar applied in one coat which fulfils all the functions of a multicoat system used externally and which is usually specifically coloured. One coat mortars for external use may be manufactured using normal and/or lightweight aggregates);
- *Renovation rendering/plastering mortar* (designed rendering/plastering mortar used on moist masonry walls containing water soluble salts. These mortars have a high porosity and vapour permeability and reduced capillary action);
- *Thermal rendering/plastering insulating mortar* (designed mortar with specific insulating properties).

According to binder (or the combination of binders) used mortars can be divided as either:

- Clay (adobe) mortar;
- Gypsum mortar;
- Lime mortar;
- Pozzolanic mortar;
- Hydraulic lime mortar;
- Portland cement mortar;
- Mixed mortars (lime-clay, lime-gypsum, lime-cement...); or
- Special mortars (water-proofing, desalination, WTA, thermo-isolating mortars...).

2.2 MORTAR COMPOSITION

Mortar is composed of a binder, aggregate, water and additives. Each component will be described more in detail in the following chapters.

2.2.1 BINDERS

In general, the purpose of the binder is to hold the sand particles together and to fill the voids in between the grains of sand ⁽¹⁴⁾.

Binders' characteristics and hardening processes will be particularly described in section 2.3.

2.2.1.1 TERMINOLOGY ON LIME

According to the standard EN 459-1 ⁽¹³⁾ on building lime following terms and definitions apply:

Lime - material comprising any physical and chemical forms under which calcium and/or magnesium oxide (CaO and MgO) and/or hydroxide (Ca(OH)₂ and Mg(OH)₂) can appear.

Building limes - limes used in building construction and civil engineering. They are either air limes or hydraulic limes.

- **Air limes** - limes mainly consisting of calcium oxide or hydroxide, which slowly harden in air by reacting with atmospheric carbon dioxide. Generally, they do not harden under water as they have no hydraulic properties. They may be either quicklimes or hydrated limes.
 - **Quicklimes (Q)** - air limes mainly consisting of calcium oxide and magnesium oxide produced by calcination of limestone and/or dolomite rock. They have an exothermic reaction when in contact with water. They are offered in varying sizes ranging from lumps to ground powder materials. They include calcium limes and dolomitic limes.
 - **Hydrated limes (S)** - calcium limes or dolomitic limes, resulting from the controlled slaking of quicklimes. They are produced in the form of a dry powder or putty or as a slurry (milk of lime).
 - **Calcium limes (CL)** - limes mainly consisting of calcium oxide or calcium hydroxide without any additions of hydraulic or pozzolanic materials.

- **Dolomitic limes (DL)** - limes mainly consisting of calcium oxide and magnesium oxide or calcium hydroxide and magnesium hydroxide without any additions of hydraulic or pozzolanic materials.
 - **Semi-hydrated dolomitic limes** - hydrated dolomitic limes mainly consisting of calcium hydroxide and magnesium oxide.
 - **Completely hydrated dolomitic limes** - hydrated dolomitic limes mainly consisting of calcium hydroxide and magnesium hydroxide.
- **Hydraulic limes (HL)** limes mainly consisting of calcium hydroxide, calcium silicates and calcium aluminates produced by mixing of suitable materials. They have the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process.
 - **Natural hydraulic limes (NHL)** - limes produced by burning of more or less argillaceous or siliceous limestones with reduction to powder by slaking with or without grinding. All NHL have the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process.
 - **Natural hydraulic limes with additional material (Z)** - special products may contain added suitable pozzolanic or hydraulic materials, up to 20 % by mass, are additionally designated by "Z".

2.2.2 AGGREGATE

Aggregate forms the main mass of mortar, it is responsible for the mortar structure, which plays a key role in the development of strength and permeability.

Sand is the most common aggregate in mortars. It can be either mined (river sand, marine sand) or pit sand. Mined sand has rounded grains, usually poorly-graded and it contains only little proportion of very fine particles. Mined sand is quite clean with little clay impurities. Pit sand contains both spherical and angular grains and has wider grain size distribution. Usually it contains some clay proportion⁽¹⁵⁾. Soft sands with fine spherical grains make weak mortars. Sharp sands with angular particles including some 3-4 mm grit produce the strongest mortars⁽¹⁴⁾.

An alternative to sand could be a grounded natural stone, which may be advantageous for repair mortars in terms of compatibility to original stone.

The key characteristic of aggregate is the particle size distribution, i.e. proportion of grains of different sizes. In order to prepare strong mortar it is essential to make enough connection points between individual aggregate grains. The smaller are the grains, the higher will be the binder consumption. If all the grains are of the same size, part of binder is consumed to fill in the voids without increasing the final strength proportionally. Consequently it is beneficial to fill the voids among big grains by smaller grains, thus the binder consumption will be decreased, and so will be the porosity and water absorption of the resulting mortar. ⁽¹⁵⁾

2.2.3 WATER

The quality of water can affect the setting and strength of the mortar. Water should not contain suspended solids, which add to the salt content, nor dissolved solids, which might cause staining of the hardened mortar. Dissolved salts can be detrimental to the durability of mortar and organic impurities can affect hardening and durability. Therefore the potable water should be used in appropriate amount. ⁽¹⁴⁾ Mortar with too little water will have bad workability; on the other hand too much water will decrease the mortar strength by holding the grains apart thus leaving an open structure when dry ^(14; 16). This effect can be dramatic. ⁽¹⁴⁾

2.2.4 ADDITIVES AND ADMIXTURES

Additives and admixtures are added to a mortar to improve the plastic properties of fresh mortar and/or to enhance the hardened mortar's properties. They can be either inorganic (e.g. pozzolanic materials) or organic, and either natural (e.g. linseed oil) or synthetic, such as polymer dispersions, redispersible polymer powders, polymers soluble in water, liquid resins or monomers. Inorganic materials added to mortar are mostly called additives, they are added usually in concentration higher than 5% by the weight of binder, while organic additions are usually called admixtures (less than 5% by the weight of binder) ⁽⁴⁾. According to Lea's chemistry of cement and concrete: "*Admixtures should be distinguished from additives and additions in that these materials are usually solids and are*

added o the cement during its manufacture”⁽¹⁷⁾. However, when speaking about natural polymers added to historical mortars, the term “additive” is usually used, and so will be for the purposes of this thesis.

Due to the topic of the thesis, only natural polymeric additives will be described in detail, in the section 2.5.

2.3 TYPES OF MORTAR

2.3.1 LIME MORTAR

2.3.1.1 BINDER PROPERTIES

Lime is one of the oldest binding materials. In literature there are mentions that lime was used in constructions dated back to 7000 B.C. (e.g. some buildings in today’s Syria)⁽¹⁸⁾. Based on identification analysis, use of lime is possible to date to the period of Ancient Egypt where it was used together with gypsum for building the pyramids⁽⁴⁾. Knowledge of lime manufacture and use spread from Egypt to Mesopotamia and then to Greece, China and Rome⁽⁴⁾. First known treatises on lime are coming from this period; such is Vitruvius’ Ten books on Architecture⁽¹⁾.

The basic raw material for lime manufacture is limestone. Limestone is a rock containing mostly calcite, which is chemically calcium carbonate (CaCO_3). Pure calcite is used for calcium limes preparation. In nature, pure calcites are however rare, usually they contain impurities such is clay minerals or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$); these calcites are used for preparation of dolomitic lime.^(12; 18; 15; 4)

Raw grounded limestone is burnt in lime-kilns. Chemical process involved consists essentially in the dissociation by heat (around 900°C at normal pressure 101,3 kPa) of calcium and magnesium carbonates according the equation:



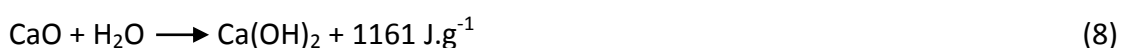
Or alternatively,



The speed of the reaction depends primarily on the reaction temperature and also on thermal conductivity of the material and the removal of carbon dioxide. Obtained product is

called burned lime or quicklime. The temperature of burning defines lime microstructure, which affects its activity, rate of slaking, efficiency and plasticity. Limes burned at lower temperatures (up to 1050°C) have higher porosity and higher specific surface. Thus hydration of this lime is fast and efficient in a short time. Limes burned at temperatures higher than 1050°C have higher bulk density, lower porosity and thus smaller specific surface. Their hydration is slower as it is determined by the rate of diffusion of water to not hydrated lime. These limes are more likely to form lumps if not slaked well.

Lime slaking is in principle a hydration of calcium oxide:



There are two ways of lime slaking differing in the amount of water added. By the first way an excess amount of water is added to calcium oxide. Slaked lime prepared this way need to be stored before its actual use to allow additional slaking of clustered grains of calcium oxide and formation of hydro-gel of calcium hydroxide. Well tempered lime has excellent plasticity and bonding properties⁽¹²⁾. Already Vitruvius pointed out that the slaked lime had to be stored for three years before its use to get lime of good quality⁽¹⁾. This way of preparation when excess of water is used is called “wet way” and the product is lime-putty. Another way of slaking of lime is a “dry way” when the amount of water only slightly higher than the stoichiometric amount is used. This way of preparation gives rise to coarse particles of calcium hydroxide and hence the final product does not have as good rheological properties as the lime prepared with the excess of water. However it does meet the requirements of building industry satisfactorily⁽⁴⁾.

2.3.1.2 HARDENING PROCESS

The process of hydrated lime hardening is composed of two phases, a physical process and a slow chemical process called carbonation.

When fresh mortar is applied on masonry, firstly the excess water is absorbed by substrate. Then starts the process of setting, which is in fact a colloidal shrinkage of fresh mortar. In the process of mortar preparation, after blending lime and aggregate together with water, particles of lime integrate with the particles of aggregate forming colloidal gel. Important characteristic of this system is thixotropy⁽¹⁹⁾, i.e. property of some non-newtonian pseudoplastic fluids to show a time-dependent change in viscosity; the longer the fluid

undergoes shear stress, the lower its viscosity ⁽²⁰⁾. Setting gives mortar the initial strength, which enables mortar to hold together and prevents it to stream down. ⁽¹⁹⁾

Second phase of lime mortar hardening is the actual carbonation, during which insoluble calcium carbonate (solubility of CaCO_3 is 1,3mg in 100g of water at 20°C) crystallizes from supersaturated solution of calcium hydroxide. Crystallization starts on coarse particles of aggregates, which serve as nuclei for formation of colloidal aggregations (spheruliths). The ongoing chemical reaction can be expressed by following equation:



The rate of reaction is affecting the size of calcium carbonate crystals. The slower is the reaction rate, the bigger will be the crystals precipitating, and consequently the bond between binder and the grains of aggregate will be influenced. For lime mortar is characteristic that it contracts considerably when drying due to the its colloidal character. It is desirable that the colloidal shrinkage takes place soon after mortar application to limit formation of micro-cracks in mortar structure ⁽¹⁹⁾.

The process of mortar carbonation is slow; the rate is dependent on the concentration of carbon dioxide in the air and on the rate of evaporation of the reaction water, hence on the relative humidity (RH) and temperature. If is $\text{RH} < 50\%$ or $\text{RH} > 95\%$, the reaction will takes place very slowly. At high relative humidity capillary condensation will take place and pores will get filled by water, in consequence the diffusion of carbon dioxide will be lowered approximately ten times. On the other hand, if RH is too low, carbon dioxide cannot be transported into mortar, and the carbonation reaction will not take place either.

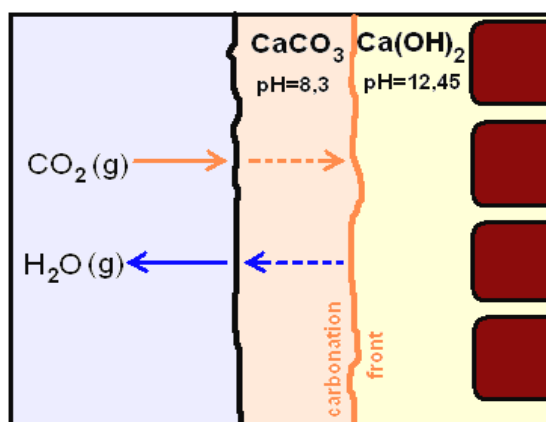


Figure 1: Scheme of lime mortar carbonation ⁽⁴⁾

As seen in **Figure 1** on the previous page, carbonation progresses from mortar's surface into the structure, thus the deeper is the mortar from the surface the longer it stays fresh – uncarbonated, depending on the rate of diffusion of carbon dioxide through the porous system of mortar. Macerate of mortar after 78 days of curing has been found to have pH= 11,3, while the pH of the water macerate of fully carbonated mortar was 8,3⁽⁴⁾. After two years of carbonation hydrated lime mortar contained 14% of uncarbonated calcium hydroxide⁽⁴⁾..

Change of pH and strength development in mortar layer is showed in **Figure 2**.

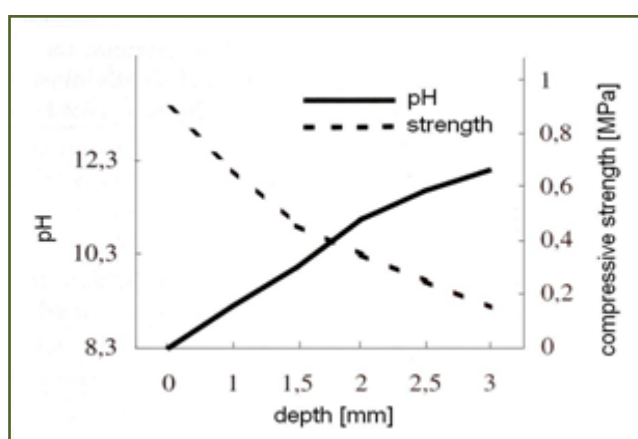


Figure 2: Compressive strength and pH development in mortar layer after 7 days of carbonation⁽⁴⁾

2.3.2 HYDRAULIC MORTARS

The term “hydraulic” refers to two related properties: the ability to harden also under water and the property of hardening when water is added to the dry binder. In order to obtain hydraulic mortars, materials of different origin have been added to lime since the ancient times. As early as the 10th century B.C., the Phoenicians and the Israelites were familiar with the techniques of producing hydraulic mortars to protect all hydraulic works (e.g. aqueducts, ports, tanks) where washing used to cause the rapid decay of ordinary lime mortars⁽²¹⁾. The drinking-water reservoirs that King Solomon ordered to be built in Jerusalem were protected by hydraulic mortar obtained by mixing lime and crushed ceramics (cocciopesto)⁽²¹⁾. The Greeks employed pozzolanic sand obtained by adding volcanic ash from the island of Santorini^(22; 21). However it was Romans who fully understood the importance of pozzolan and they utilized it regularly to prepare mortar more resistant to weathering. They discovered that substituting ordinary sand by sand of volcanic origin (found near Pozzuoli) caused mortar to become hydraulic. Therefore, the term “pozzolanic”

is used to refer to a type of sand which is able to make mortars hydraulic, although the binder, i.e. lime, by itself is not hydraulic. ⁽²¹⁾

Recognition of hydraulic lime, lime which is hydraulic by itself, without any additions, was made not sooner than in 16th century by Italian architect Andrea Palladio ⁽²¹⁾. In 1756 Smeaton discovered the hydraulic reactions and he acknowledged that it is the clay presence in limestone being responsible for the hydraulic properties. L.J. Vicat laid the foundation of scientific knowledge on limestone based on chemical analysis ⁽²¹⁾. He sorted limestone according to content of hydraulic oxides (SiO_2 , Al_2O_3 and Fe_2O_3) and came into conclusion that only mortars containing these oxides are stable also under the water ^(23; 18).

In 1796, the discovery that hydraulic cement could be made by calcining nodules of argillaceous limestone, known as septaria, found in certain Tertiary strata, was patented ⁽²⁴⁾. James Parker named the product obtained this way Roman cement, in a pamphlet entitled Roman cement, artificial terras and stucco (1798) ⁽²⁴⁾. Roman cement was in fact a strong hydraulic lime, since the burning temperature did not exceed 1250°C ⁽⁴⁾.

In 1811 James Frost produced and patented cement which was made by calcining an intimate mixture of chalk and clay, ground together in a wet mill. This process may be regarded as the principal forerunner of the manufacture of Portland cement. ^(24; 4)

Among the numerous patents for hydraulic cements which appeared in the early 19th century, Joseph Aspdin's patent no. 5022 dated 21 October 1824 stands out in historic importance to the others – Aspdin described his material called Portland cement. He chose the name Portland to direct people's attention to the resemblance of the colour and quality of his cement to Portland limestone, which had at that time a high reputation for quality and durability. ⁽²⁴⁾ The following year Aspdin's factory launched the first Portland cement into the British market ⁽⁴⁾.

2.3.2.1 CEMENT MORTAR

Using of cement mortar for building restoration may cause severe problems. Cement mortar reaches very high strengths (35-50 MPa, depending on the quality of cement and the type and granulometry of aggregate ⁽⁴⁾), far higher than lime mortar and some masonry materials, and generally adheres very well to bricks and stones. For this reason, as degradation progresses, it can even cause mechanical damage to original material, i.e.

cement mortar may pull out original matter (e.g. **Figure 3**). Incompatible porous structure of the cement mortar compared to weaker stones or bricks and different thermal expansion also play an important role ⁽²¹⁾. Moreover, since cement contains gypsum, it may introduce harmful sulphate salts, which cause further damage ^(15; 22; 21). However, in modern restoration practice cement is sometimes added in small quantities (5-10% by the weight of binder) into lime mortar mixtures in order to increase their final strength and to reach early strength.



Figure 3: Decomposition of mortar-stone composite sample: Surface layer of cretaceous marly chert (left) was detached by cement-hydraulic lime mortar (1:1) (right) after three sodium sulfate crystallization cycles ⁽⁷⁸⁾

2.3.2.1.1. BINDER PROPERTIES

Cement is a hydraulic binder, i.e. finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water ⁽²⁵⁾.

Cement is produced in many versions, for care of historical monuments is most commonly used the white ordinary Portland cement (OPC), which is made from white limestone with minimal content of iron oxides (less than 1 wt%) (15).

Portland cement is a mixture of compounds; none of these compounds is chemically pure substance. Chemical composition is expressed by the content of oxides of which the clinker is made. The main clinker oxides are CaO, SiO₂, Al₂O₃ and Fe₂O₃, these oxides form 96% of total components. Amount of particular oxides is expressed by empirical formulas, so called indexes, which express proportions between oxides. For example hydraulicity index is defined as:

$$I_H = \frac{SiO_2 + Al_2O_3 + Fe_2O_3}{CaO}$$

Hydraulicity index may reach values 0,45-0,55. ⁽⁴⁾

Portland cement clinker is made by sintering raw oxides, which transform to clinker minerals, which are crystalline silicates, aluminates and ferrites^(17; 4; 26).

Clinker mineral synthesis takes place at temperature over 1400°C, formation of minerals continues also during cooling down of the clinker when the final form of minerals is established. Clinker is then grounded together with gypsum, which is added as a setting rate regulator. Clinker minerals make phases called alite, belite, aluminate and aluminoferrite.^(17; 4; 26)

Following **Table 1** gives overview of clinker minerals and their chemical composition and **Table 2** the resulting chemical composition. According to EN 197-1 “Portland cement clinker shall consist of at least two-thirds by mass of calcium silicates, the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by mass (CaO)/(SiO₂) shall be not less than 2,0. The content of magnesium oxide (MgO) shall not exceed 5,0 % by mass.”⁽²⁵⁾

Table 1: Clinker minerals and their chemical composition

Clinker phase	Main phase name	Abbreviation	Chemical composition
alite	Tricalcium silicate	C ₃ S	3CaO.SiO ₂
belite	Dicalcium silicate	C ₂ S	2CaO.SiO ₂
aluminate	Tricalcium aluminate	C ₃ A	3CaO.Al ₂ O ₃
aluminoferrite	Tetracalcium aluminoferrite	C ₄ AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃
gypsum	Calciumsulphate dihydrate	-	CaSO ₄ .2H ₂ O

Table 2: Chemical composition of clinker⁽²⁷⁾

Oxide	[wt%]
CaO	58-68
Al ₂ O ₃	4-8
Fe ₂ O ₃	2-5
SiO ₂	16-26
MgO	1-4
Na ₂ O + K ₂ O	0-0,6
SO ₃	0,1-2,5

2.3.2.1.2. HARDENING PROCESS

When the cement is mixed with water, the hydration of individual clinker minerals starts. The main product is hydrosilicate gel (C-S-H phase), which defines most of the properties. The process of hydration can be divided into several phases. During the initial hydrolysis calcium, sodium and potassium sulphates dissolve in water. Calcium hydroxide is being dissolved until supersaturated solution has occurred. On the surface of the grains the ettringite is formed, which is slowing down the setting process. After the dwell period which is lasting few hours, the hydration of clinker minerals initiates, giving rise to hydrosilicate phase (C-S-H phase). Incurred C-S-H phase gradually connects individual cement grains, thus cement phase loses its plasticity and the mortar hardens. In the last phase the hydration rate decreases. The hardening rate is determined by the rate of water diffusion into so far unhydrated cement grains. After 28 days 70-90% of the mass of cement is hydrated and the incurred hardened cement mortar is practically insoluble in water. The process of cement hydration is possible to be monitored by measuring the development of hydration heat in time (see **Figure 4**).

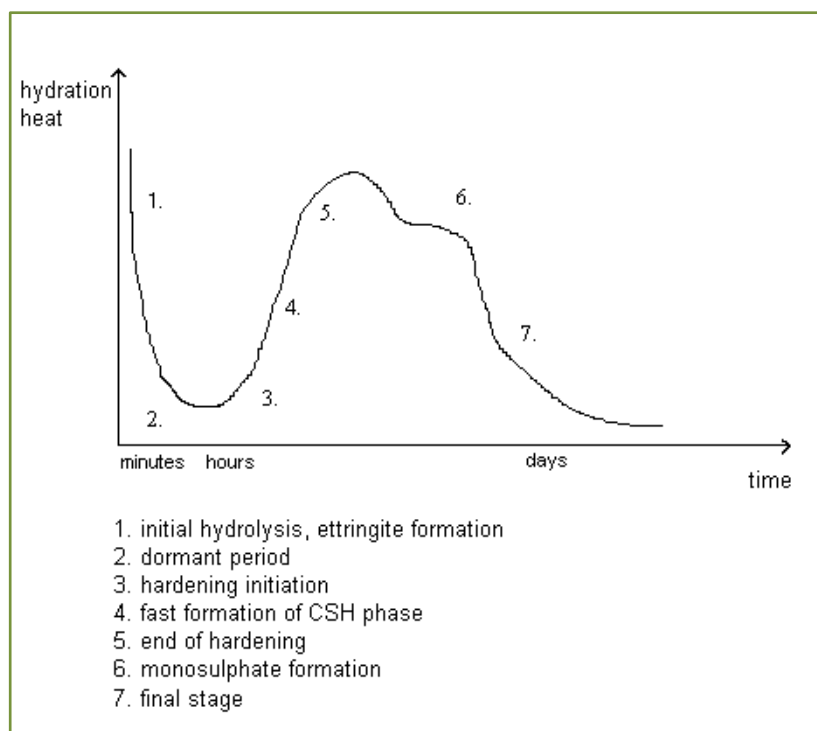


Figure 4: Hydration heat of cement

2.3.2.2 HYDRAULIC LIME MORTAR

2.3.2.2.1. BINDER PROPERTIES

Hydraulic lime lies in terms of its properties and composition in between hydrated lime and cement. Contrary to hydrated lime, hydraulic lime contains also hydraulic oxides, which enables it, after initial hardening, to harden even under water. Among hydraulic oxides belong SiO_2 , Al_2O_3 and Fe_2O_3 , which hydrate to form in water insoluble calcium silicates and aluminates ⁽¹⁴⁾. Strongly hydraulic lime contains more than 15% of hydraulic components ⁽⁴⁾. Hydraulic properties can be characterized by hydraulicity index, which is defined as ⁽²²⁾:

$$I_H = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}{\text{CaO}}$$

According to the value of the hydraulicity index, hydraulic limes can be divided as follows:

Table 3: Hydraulicity index of hydraulic limes ⁽⁴⁾

Lime	Hydraulicity index I_H
Faintly hydraulic	0,11-0,17
Medium hydraulic	0,17-0,33
Strongly hydraulic	0,33-0,59

According to EN 459-1 ⁽¹³⁾ hydraulic limes are sorted according to their compressive strength reached after 28 days of curing **Table 4:**

Table 4: Compressive strength of hydraulic mortar after 28 days ⁽²²⁾

Hydraulic lime class	Compressive strength [MPa]
HL 2	2-5
HL 3,5	3,5-10
HL 5	5-15

Hydraulic lime is produced by burning of marl or marlaceus limestone at temperature 900-1100°C. The temperature needed is dependent on the content of clay and dolomitic admixtures - the higher is its content, the lower burning temperature. During the burning

CaCO_3 and MgCO_3 (if present) decomposes, followed by reaction of CaO (and MgO) with clay and siliceous components. The final product contains free CaO , belite (C_2S), aluminite (C_3A), ferrite (C_2F), aluminoferrite (C_4AF). Further eventually CaO.MgO.SiO_2 phase rises from a part of free MgO . Contrary to cement, hydraulic lime does not contain alite (C_3S), due to the reason that the burning temperature is lower than the temperature of its formation (1250°C).^(4; 14)

2.3.2.2.2. HARDENING PROCESS

During hardening process of hydraulic lime mortar, firstly the physical-chemical processes ongoing during setting and hardening of the hydrated lime mortar are taking place (see 2.3.1.2) and secondly processes related to hydration of hydraulic components similar to cement hardening (see 2.3.2.1.2). First calcium and magnesium hydroxides are formed out of the free calcium and magnesium oxides, if the magnesium oxides are present, and then by carbonation calcium and magnesium hydroxides give rise to CaCO_3 (MgCO_3). The hydraulic components give rise to formation of C-S-H phases.^(14; 4)

Hydraulic lime is a slowly hardening binder. Depending on the content of free CaO , the initial setting time is in 0,5-2 hours from mixing the dry constituents with water, and the setting and hardening process lasts for 8-16 hours⁽⁴⁾.

Hydraulic mortars have due to their different mineralogical composition, and thus hardening process, different properties than hydrated lime mortars. Porosity of hydraulic mortars is lower than that of hydrated lime mortars, and they may reach higher mechanical strength. Hydraulic lime mortars have better adhesion to substrate comparing to hydrated limes. On the other hand, fresh hydraulic lime mortar has lower plasticity than hydrated lime mortar.^(14; 22; 21)

2.3.2.3 POZZOLANIC MORTAR

Pozzolanic mortar is a lime mortar with pozzolanic additions, which give mortar hydraulic properties. Pozzolans consist essentially of silicon dioxide (SiO_2) and often also aluminium oxide (Al_2O_3), which thanks to their amorphous, vitreous state and high specific surface area react with lime^(21; 26; 28).

The traditional pozzolans can be divided

- according their origin as:
 - Natural (only natural pozzolans from Pozzuoli in Italy can be called “pozzolana”⁽¹⁴⁾), which can be either:
 - Volcanic origin, or
 - Sedimentary rocks; or
 - Artificial (obtained from chamotte, brick dust (cocciopesto mortar)).⁽⁴⁾
- according their composition – containing amorphous silicon oxide, silicates, aluminates, ferrites.

Pozzolans do not harden themselves when mixed with water but, when finely ground and in presence of water, they react at normal ambient temperature with dissolved calcium hydroxide to form strength-developing calcium silicate and calciumaluminate hydrates, very similar to those formed in the hardening of hydraulic materials^(14; 29; 26). These compounds have the binding ability; they make strong connection between aggregate grains and are stable under water and resistant to acids.

Pozzolans’ ability to react with calcium hydroxide in water is called pozzolanic activity^(14; 4). The pozzolanic reaction is determined by the chemical and mineral composition of the pozzolan, its specific surface and the conditions of the reaction including water-binder ratio and curing time and temperature^(30; 31). Fine pozzolan having high specific surface should be therefore considered as a part of the binder. Coarse pozzolan, often porous, can be used to improve the permeability of the mortar and is then treated as a part of the aggregate⁽¹⁴⁾.

2.4 DETERIORATION OF MORTARS

Materials’ deterioration is a set of natural phenomena, which lead to change of mechanical, physical and chemical characteristics as well as to the change of appearance. According factors affecting the causing the damage it can be divided into three main categories: physical deterioration, chemical deterioration and biological deterioration.

2.4.1 PHYSICAL DETERIORATION

The main characteristic of physical deterioration is mechanical damage caused most commonly by the effects of water, temperature changes, salt crystallization, wind flow or mechanical stress to the object.

2.4.1.1 THE EFFECT OF WATER

The presence of water is necessary for the run of chemical reactions, water dissolves and transports soluble salts and it supports living and action of living organisms. Rain water flowing over surface causes erosion. ⁽¹⁵⁾

Water can get into structure in form of rain water (rain, melting snow or fog), rising from wrong isolated object foundation, water spray carried by wind from big water areas, condensed water or water which got into object during its cleaning or restoration. Water is usually not pure but in a form of salt or gas solutions (so called acid rains). Water present inside mortar structure may cause frost damage. Water increases its volume by 10% when transformed from liquid to solid state, causing pore systems damage, which may result in formation of fissures and cracks in mortar. The change of water state happens repeatedly as the temperature fluctuates around the water freezing point. Micro-cracks formed in previous freeze-thaw cycles allow water to be absorbed deeper and the damage keeps increasing ^(15; 4). In Central Europe, over 30 freeze-thaw cycles may occur per year ⁽³²⁾.

2.4.1.2 THE EFFECT OF SALTS

"I observed ... that salt exuded from the soil to such an extent as even to injure the pyramids."

- Herodotus (484 B.C.-425 B.C.), History, Book 2 (from A.E.Charola ⁽³³⁾)

Salts can originate from various sources: air pollution, de-icing salts, soil, sea spray, inappropriate treatments or interaction between building materials. Some materials may even contain salts inherently, for example Portland cement usually contains sulphates. ^(4; 33)

Salts can enter mortar or porous bodies in general only when dissolved in water. Water can enter either as a liquid or vapour. In the liquid state, two mechanisms can be operative ⁽³³⁾:

- Capillarity rise of groundwater – it is a result of the attraction of water and capillary material,
- Infiltration of rain water – requires a hydrostatic pressure and depends on the permeability of the material.

In the vapour state, water can enter through two main mechanisms⁽³³⁾:

- Condensation, of which there two types:
 - Surface condensation
 - Capillary condensation in pores
- Hygroscopicity – ability of some salts to absorb or attract moisture

Once inside the porous material, water moves through capillarity mechanism, if it is in a liquid state. When in a vapour state, transport mechanism relies on diffusion, if the water vapour is not retained by hygroscopicity. Water movement is dependent on materials porosity, pore-size distribution and environmental conditions.⁽³³⁾



Figure 5: Damage due to salt crystallization (Prague, Czech Republic)



Figure 6: Salt efflorescence on a wall (Prague, Czech Republic)

Deterioration of mortar can be rarely attributed to the presence of only one salt. The most abundant salts are chlorides, sulphates or nitrates, of calcium, sodium, potassium, magnesium and sometimes also ammonium kations. Source of chlorides are usually de-icing agents, nitrates are of organic origin. Sulphates are usually rising from groundwater but may be also a product of calcium carbonate corrosion reaction with sulphur oxides. Nitrates and sulphates can be also product of an action of some bacteria.⁽¹⁵⁾

Salt action in pores is strongly related of the amount of crystalline water they contain (Table 5). Anhydrites (NaCl, KCl, K_2SO_4 and others) are very well soluble and movable in water solution, thus they can get easily deep into mortar. When crystallizing they develop crystallization pressure having effect on surrounding material (Table 6). Into second group belong salts which crystals contain crystalline water ($CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 2H_2O$ etc.). These salts may lose crystalline water with the decrease of relative humidity in the air, forming anhydrite form, and with the increasing humidity they recrystallize. Recrystallization is accompanied with the development of hydration pressures (Table 7). These pressures are first compensated by the porous system of the material but when exceeding the mechanical strength of the material they cause damage. Another group are salts which seldom crystallize. These salts are hygroscopical, they can easily absorb water from the air, thus causing long-term wetness of the material. ^(15; 4)

In an object which is in contact with groundwater, salt solution is transported by capillary rise into the building material and moves up towards to the surface. As water evaporates, the concentration of salts in the solution increases, and finally salts precipitate. The place where salts precipitate is determined by the balance between the evaporation rate and the supply of salts into the structure. If the evaporation is slower than the salt solution supply, salts precipitate on building surface, forming so-called efflorescence (Figure 6). Efflorescence doesn't cause mechanical damage of material, but the salt crystallization on surface can be considered a visual damage. If the evaporation rate predominates the supply of the salt solution from the material, crystallization take place inside the matter causing damage to the material. The most harmful is subflorescence, which takes place when the evaporation rate and the supply of the salt solution are in an approximate equilibrium and salts crystallize beneath the surface, which may lead to bulging, scaling and spalling of the whole outer layer, causing serious damage to the material (Figure 5). After exposure of a new surface the whole process may repeat. Examples of damage due to the salt crystallization are showed in Figure 7-9.



Figure 8: Detachment of plaster due to the subflorescence



Figure 7: Example of masonry damaged due to the crystallization of salt on a frequent street in Prague, Czech Republic, where NaCl is used as a de-icing agent in winter



Figure 9: Salt crystallization on naked masonry

Barbara Lubelli in her Ph.D. thesis ⁽³⁴⁾ showed that the presence of salts (NaCl, KCl, NaNO₃ tested) in a material changes its hygric behaviour (i.e. dilation and shrinkage depending on relative humidity changes) completely and thus that damage in a salt contaminated material may originate from the shear stresses developed between areas containing different amounts of salts. In a not contaminated material dilation can be observed as RH increases and vice versa. In a salt loaded material dilation occurs during the drying phase of RH cycle, when salts crystallize, whereas shrinkage occurs during dissolution of the salts. Salt crystallizing in a form of a layer on the pore walls is able to transform stresses to the pore walls as it crystallizes and thus causing dilation of the material, leading to damage ⁽³⁴⁾.

Table 5: The solubility of some salts and the relative humidity above their saturated solutions⁽⁴⁾

Salt	Formula	Solubility [g.dm ⁻³]	RH [%]
Calcium sulphate dihydrate	CaSO ₄ .2H ₂ O	2,6	100
Potassium sulphate	K ₂ SO ₄	111	98
Potassium nitrate	KNO ₃	316	95
Sodium carbonate decahydrate	Na ₂ CO ₃ .10H ₂ O	910	92
Magnesium sulphate heptahydrate	MgSO ₄ .7H ₂ O	1170	90
Sodium sulphate decahydrate	Na ₂ SO ₄ .10H ₂ O	580	87
Potassium chloride	KCl	340	76
Sodium chloride	NaCl	360	76
Sodium nitrate	NaNO ₃	880	75
Ammonium nitrate	NH ₄ NO ₃	1920	62
Magnesium nitrate hexahydrate	Mg(NO ₃) ₂ .6H ₂ O	2850	54
Calcium nitrate tetrahydrate	Ca(NO ₃) ₂ .4H ₂ O	4300	53
Potassium carbonate dihydrate	K ₂ CO ₃ .2H ₂ O	1410	43
Magnesium chloride hexahydrate	MgCl ₂ .6H ₂ O	3050	33
Calcium chloride hexahydrate	CaCl ₂ .6H ₂ O	5360	30

Table 6: Crystallization pressures of some compounds⁽⁴⁾

Compound	Crystallization pressure [MPa]
CaSO ₄ .2H ₂ O	28,2
MgSO ₄ .2H ₂ O	10,5
Na ₂ SO ₄ .10H ₂ O	7,2
Na ₂ CO ₃ .10H ₂ O	7,8
NaCl	55,4
H ₂ O	210

Table 7: Recrystallization pressures of some salts⁽⁴⁾

Original salt	Final salt	Recrystallization pressure [MPa]
CaSO ₄ .½H ₂ O	CaSO ₄ .2H ₂ O	160
MgSO ₄ .6H ₂ O	MgSO ₄ .7H ₂ O	10
Na ₂ CO ₃ .H ₂ O	Na ₂ CO ₃ .7H ₂ O	64

2.4.2 CHEMICAL (ENVIRONMENTAL) WEATHERING

Chemical weathering is a complex system of chemical reactions, which lead to destruction of several minerals. The main causes of chemical deterioration are acid exhalants in the air and polluted rain and ground water, and to a lesser extend also

chemically active substances which may be formed as products of living organisms. The basic condition for chemical weathering is the presence of water. The main agents causing chemical weathering are sulphur, nitrogen, carbon oxides and ammonium compounds. Oxides and other gaseous exhalants are washed out from air by rain or fog to produce much diluted solutions of inorganic acids, so called acid rains ⁽¹⁵⁾. The main damage product resulting from interaction between atmosphere and building materials is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which can be either washed away due to its greater solubility, or be deposited in the material's structure ⁽²¹⁾.

2.4.2.1 DEGRADATION OF LIME MORTARS ⁽⁴⁾

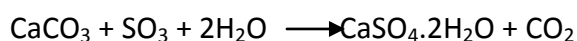
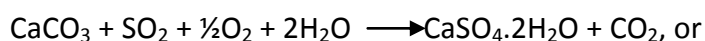
The main product of hardening of lime mortar is calcium carbonate (as described in 2.3.1.2), which is almost insoluble in water, its solubility is 1,4 mg in 100 g water at 25°C, however it has a very low resistance to action of atmospheric acid gases. Due to their effect the binder decomposes, forming usually more soluble products and these can be washed away by rainwater. By this way mortar loses binder and when the limit of cohesion is exceeded, the mortar disintegrates. Calcium carbonate may be decomposed by reaction ⁽⁴⁾

- *with aggressive carbon dioxide*, which may be dissolved in rainwater, giving rise to soluble calcium hydrogen-carbonate:



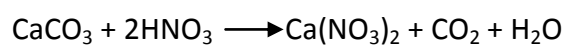
Reaction is reversible; under suitable conditions hydrogen-carbonate anion may decompose forming insoluble carbonate anion.

- *With sulphur oxides in presence of humidity* forming calcium sulphite, which further oxidises to form calcium sulphate:



The gypsum formed is of high molar volume and under appropriate humid condition may crystallize forming large crystals. The process is accompanied by development of high pressures on pores' walls, which may result in mortar's degradation.

- *With nitrogen oxides in presence of water* giving rise mostly to nitric acid, which reacts with calcium carbonate according to the following equation:



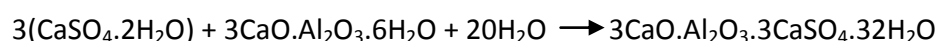
Well soluble calcium nitrate is formed (solubility 127 g in 100 g water at 20°C), which may be washed out from mortar by rainwater.

2.4.2.2 DEGRADATION OF HYDRAULIC MORTARS

The main products of hydraulic mortars hardening are C-S-H gels and hydrated calcium aluminates. These compounds are formed both in hydraulic lime mortars and hydrated lime mortars with hydraulic additions. Hydraulic binders are damaged mostly due to the effect of acid compounds present in the air. Generally degradation process is similar for all types of hydraulic binders, with the exception of cement and pure hydraulic lime containing quicklime (CaO), which degrades preferentially, giving rise to calcium hydroxide (Ca(OH)₂). In mortars whose binder is composed of both lime and hydraulic products, degradation initially runs the same way as in the lime mortars, followed by process related to the degradation of hydraulic products. ⁽⁴⁾

The main product of environmental deterioration is gypsum. In case of hydraulic mortars the presence of gypsum may lead to two damaging expansive reactions to take place ⁽²¹⁾:

- Ettringite formation

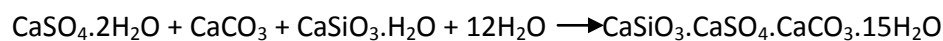


Ettringite is produced at three possible situations:

1. In first hours of binder hardening process, in this case it is not dangerous, because mortar is still in a plastic state so the expansion will not cause any damage. Usually all sulphate present in mortar is consumed.
2. Secondary ettringite – if new sulphate interacts with the calcium aluminates hydrates from the binder paste.
3. Delayed ettringite – produced in precast elements (cured in hydrothermal condition, i.e. 60°C and 95%RH), when sulphates plus water are present in the mortar.

Both secondary and delayed ettringite formation processes, which are highly expansive, lead to the total destruction of the material.

- Thaumasite formation (at low temperatures)



Thaumasite formation implies the destruction by CO_2 and sulphate attack of C-S-H gel, which is the main constituent of hydraulic binder paste. ⁽²¹⁾

2.4.3 BIOCORROSION

Mortars can be damaged also by the action of living organisms, such as bacteria, fungi, algae, mosses, lichens and also plants and animals. Besides the esthetical damages, organisms damage mortar mostly mechanically. For example lichens hyphae and plant's roots cause mechanical stress, which may lead to the destruction of a material, by its growth or by the change of water content in its fibers. Organisms also produce various compounds causing chemical deterioration. Sulphur bacteria oxidize compounds forming sulphurous acid; even 5% solution can be formed. Fungi, algae and mosses produce organic acids which cause deterioration of calcium carbonate.

2.5 NATURAL POLYMERS AS MORTAR ADMIXTURES

2.5.1 OVERVIEW OF NATURAL POLYMERS

Natural polymeric additives used for modification of lime-based mortars can be sorted into several groups according to various criteria. According to their origin as natural and synthetic additives, according to chemical composition as an organic and inorganic, and according to their effect on the properties of lime-based mortars as additives:

- Increasing strength and durability,
- Setting time regulators,
- Plasticizers,
- Aerating agents,
- Reinforcing fibrous additives,
- Water-proofing additives. ⁽⁹⁾

Following **Table 8** gives examples of natural additives for some of the groups. Some additives are listed in contradictory groups. In **Table 9**, Sickels sorts natural organic additives into historical periods in which they were used.

Table 8: The effect of natural organic additives on lime-based mortars ^(4; 9; 5; 35)

Type of additive	Natural compound
Increasing strength	Sugar, molasses, fats, fruit juices, rye dough, rice starch, gluten, curdled milk, egg white, vegetal gums, casein, cheese, blood
Setting time accelerators	Egg white, bullock's blood, sugar, hog's lard, casein, starch
Setting time reducers	Sugar, fruit juices, gluten, bullock's blood, egg white, molasses
Plasticizers	Milk, egg white, fats, sugar, rosin, dung, starch
Aerating agents	Urine, malt, beer
Waterproofing agents and sealants	Fats, oils, waxes, asphalt, sugar materials
Reinforcing fibrous materials	Animal hair, hen, straw, sea-weeds, elm bark, fibrous plants, cotton, rice paste, barley

Table 9: Historical overview of using natural polymers as an additives to lime-based mortars ^(3;9) (from L.B. Sickels, modified – I inserted the green fields based on Pliny ⁽²⁾, Alberti ⁽³⁶⁾ and Chandra ⁽⁵⁾)

		2500-2100 B.C. (Middle East) Chandra, Pliny	150 B.C. (Egypt)	46 B.C. (Vitruvius, Roman Empire)	23 A.D. (Pliny, Roman Empire)	800 A.D. (Rochester Cathedral, England)	13 th century (England)	15 th century (Alberti)	16 th century	17 th century (Plat)	18 th century (Neve&Moxon, England)	mid-18 th century	19 th century (Vicat&Smith, England)	19 th century (Burnell&periodicals, England)
proteins	eggs		█				█		█		█	█	█	█
	egg whites		█	█			█		█		█	█	█	█
	albumen		█	█			█		█		█	█	█	█
	animal glue		█								█			█
	casein		█											
	cheese											█	█	█
	milk			█	█							█	█	█
	curdled milk			█	█							█	█	█
	buttermilk											█	█	█
	malt						█		█					
	gluten						█		█			█		
	rye dough			█	█							█		
	keratin		█											
hair					█									
lipids	hog's lard			█	█						█			█
	oil				█			█					█	█
	butter				█								█	█
	suet				█								█	█
	beeswax						█		█		█	█	█	█
saccharides	sugar						█		█				█	█
	molasses												█	█
	fruit juice						█		█			█		
	fig juice		█	█	█							█		
	gum Arabic		█						█	█				█
	cotton													█
resin	vegetable resin										█			
	animal resin (shellac)													█
others	bitumen	█			█									
	blood		█	█	█				█	█	█	█	█	█
	urine		█	█	█		█		█	█	█	█	█	█
	dung						█					█		
	beer						█		█			█		
	wine				█							█		
	wort				█							█		
	fibers				█							█		
	barley				█							█		
	elm bark				█							█		
	rye dough			█	█							█		
	rice						█		█					
	size				█				█					
	saffron				█									
	vegetable juices											█		
	tannin					█								

2.5.2 OILS AND FATS

Both oils (linseed oil) and fats (hog's lard, butter) were used for the preparation of mortar. Oils and fats belong to the chemically same group of compounds - lipids; they differ in that oils are liquid at room temperature and fats are solid ⁽³⁷⁾. They were added into mortars in order to make them hydrophobic and consequently more durable against deterioration. Such mortars were used especially for pavements and in areas suffering higher contact with water and humidity, e.g. baths ⁽³⁶⁾.

2.5.2.1 THE USE OF OILS AND FATS AS AN ADMIXTURES TO MORTAR IN HISTORY

While there are quite a lot of information in literature on using natural admixtures such is proteins, saccharides and others ^(2; 38; 12; 39; 19; 40), information about linseed oil and oils and fats in general are very rare. Oils and fats are more commonly mentioned as a protective coat applied on a hardened mortar ^(41; 19; 42).

Marcus Vitruvius Pollio (later on Vitruvius) in his *Ten Books on Architecture* dated 30 B.C. mentions oil as a protective coating layer against frost:

"In order to protect the mortar from the strains of frost, every year, before winter comes, saturate it with the residue from pressing olive oil; in this way it will not admit or absorb frost." ⁽¹⁾

In a chapter about pavements he advises to seal tiles on floor with lime mixed with oil.

"When these are joined, lime tempered with oil is to be filled in... thus the lime will harden and prevent water or anything else from passing through the joints" ⁽³⁹⁾

In a newer translation:

"When the tiles are joined together, these channels should be filled with lime that has been mixed with oil, and the joins are rubbed together once they are compressed. In this way, the lime that has adhered in the channels solidifies in an interlocking pattern as it dries, and will not allow water, nor anything else, to penetrate the joints." ⁽¹⁾

Besides the oil, hog's lard is known to be used in ancient times. George P. Bankart in his *Art of the Plasterer* (1909) refers to Vitruvius: *"It has always been known to be necessary*

to toughen and regulate its (lime) setting qualities, and the ingredients in his time were: juice of figs, rye dough, hogs' lard, curdled milk, blood, etc."⁽⁴³⁾

The oldest mention about oil as an additive into mortar is by Pliny the Elder (23 A.D. - August 25, 79 A.D. (the eruption of Vesuvius)) in his *Natural History* (around 77 A.D.). He gives a recipe for a type of mortar^a called Maltha:

"Maltha is a cement prepared from fresh lime; lumps of which are quenched in wine, and then pounded with hogs' lard and figs, both of them, mollifying substances. It is the most tenacious of all cements, and surpasses stone in hardness. Before applying the maltha, the substance upon which it is used must be well rubbed with oil."⁽²⁾

Leone Batista Alberti (February 18, 1404 – April 20, 1472 in his *Ten Books on Architecture* (1452) described the theories and ideas of the Renaissance as well as his observations about ancient Roman architecture, he often refers to Vitruvius and Pliny.

Alberti states that:

"Mortar worked up with Oil, is said in Pavements to keep out every thing that is noxious."⁽³⁶⁾

And he also advises to sprinkle mortar with limewater and spread with linseed oil, because it will attain *"hardness comparable to that of glass and is unaffected by any weather"*.⁽³⁸⁾

Lauren-Brooks Sickels has made an extensive literal survey on the use of natural polymeric additives from ancient times to the 20th century in Great Britain. He reports that hog's lard was one of the natural organic additives used in England by the mid-18th century. Sickels also quotes two Indian recipes for stucco, which were both mentioned in 1837 book by Luis J. Vicat *"A Practical and Scientific Treatise on Calcareous Mortars and Cements"* (23), for stuccoes containing oil together with other organic materials.

"The fact is, that they mix the lime with a little curdled milk, with gingelli oil, and water of jaghery a course very brown sugar, which is derived from cocoa tree."⁽³⁾

^a Bostock and H.T. Riley use in their translation of Pliny term "cement", which seemed to have until the discovery of Portland cement the same meaning as a term "mortar".

Second recipe is for stucco called 'Madras'; it was added as a footnote to the first abovementioned recipe by a Madras engineer Colonel J.T. Smith, R.E. who translated that particular edition of Vicat's book.

"In about every bushel...mix the whites of ten or a dozen eggs, half a pond of ghee, (which is a butter separated from its caseous parts by melting over slow fire,) and a quart of tyre, (which is sour curd fresh prepared,) to which some add powdered balapong (or soap-stone) from a quarter to half a pound, which is said to improve the polish. But, each master bricklayer has generally a recipe of his own, which he boasts of as superior or all others. The essential ingredients, in addition to the lime and sand, seem to be the albumen (of the eggs), and the oily matter of the clarified butter, for which oil is sometimes substituted."⁽³⁾

Furthermore, Sickels reports that in 23 August 1856 issue of The Land and Building News is an article on "Mortar and Cements" which lists one Turkish cement recipe: "100 pounds of picked kilned lime...10 quarts of linseed oil, and one or two ounces of cotton."⁽³⁾

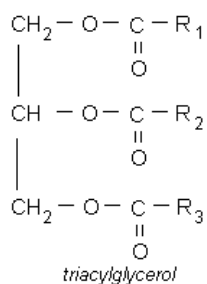
In India, between 4th and 6th century, many types of beans, flowers, pulp of fruits and various types of leaves soaked in different oils were employed in preparation of plasters used on the wall for paintings^(6; 44).

In Czech Republic, some of the Romanesque, Gothic or Baroque plasters are said to be of exceptional quality and that it might be because of an addition of various natural polymers that they have been lasting for centuries. However, as well as in other countries, recipes for mortars using improving additions were each mason's technological secret and passed only orally from generation to generation, thus there is almost no information in the literature. As for the linseed oil, in studied literature there is only a mention that it was commonly added to lime water for preparation of a finish coat of plaster in the period of Renaissance and Baroque⁽¹⁹⁾. And also that it was used for the impregnation of the plaster⁽¹⁹⁾.

In Brazil, it is said that in past whale oil was commonly used as an additive to lime mortars to increase their resistance. There are many historical buildings surviving to the present days in Brazil, however there is no evidence in literature supporting the using of whale oil for special purposes⁽⁴⁵⁾.

2.5.2.2 CHEMISTRY AND PROPERTIES OF OILS AND FATS ^(37; 46; 47; 48)

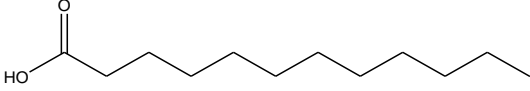
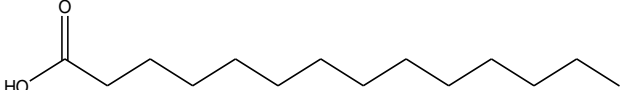
Oil and fats are naturally occurring mixtures of triacylglycerols (also called triglycerides). These are built on a glycerol framework, containing three acyl groups derived from fatty acids. They are nonpolar molecules thus they are hydrophobic. Following formula is showing a general structure of triacylglycerols ^(37; 46; 47; 48):



Where R_1 , R_2 and R_3 are acyl groups.

All three acyl groups in triacylglycerols may be the same, all three may be different, or one may be different from the other two ⁽³⁷⁾. Fatty acids forming triglycerides are of wide range as for the length of their chain as well as the degree of unsaturation, which is defined by the number of double bonds present in the chain. Saturated acids contain only single bonds between carbon atoms and are characterized by relatively high melting points. Presence of saturated acids in fats explains why they are usually solid. Unsaturated acids have at least one double bond between carbon atoms and they are thus more reactive with lower melting temperatures. Following **Table 10** lists common fatty acids present in oils. **Table 11** shows fatty acids content in some oils. ^(37; 46; 48)

Table 10: Some common fatty acids present in oils ^(37; 46)

Fatty acid	Number of carbon atoms	Number of double bonds	Structural formula
Lauric acid	12	0	
Myristic acid	14	0	

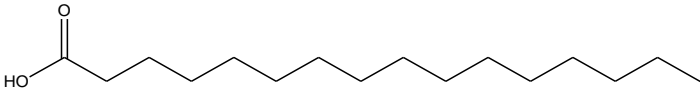
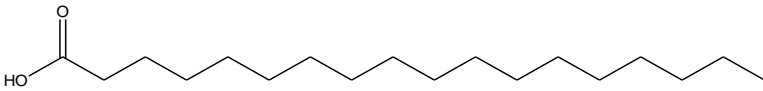
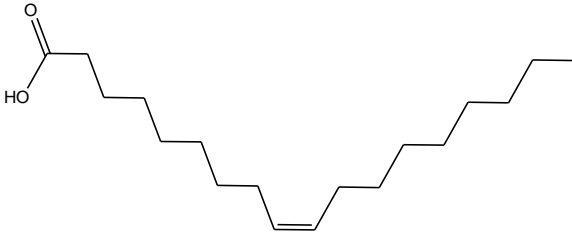
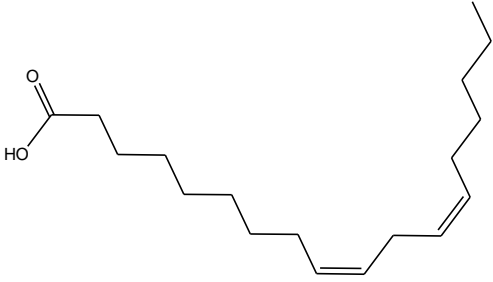
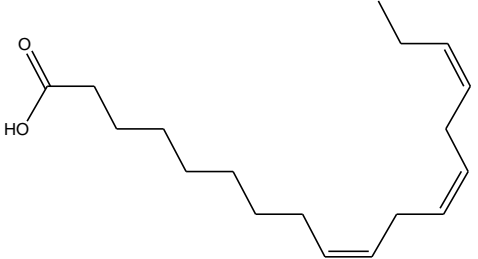
Fatty acid	Number of carbon atoms	Number of double bonds	Structural formula
Palmitic acid	16	0	
Stearic acid	18	0	
Oleic acid	18	1	
Linoleic acid	18	2	
Linolenic acid	18	3	

Table 11: Composition of some oils [wt%]^(46; 47)

	Linseed oil	Walnut oil	Poppyseed oil	Tung oil
Palmitic acid	6-7	3-7	10	3
Stearic acid	3-6	0,5-3	2	2
Oleic acid	14-24	9-30	11	11
Linoleic acid	14-19	57-76	72	15
Linolenic acid	48-60	2-16	5	3
Elaeostearic acid	0	0	0	59

The degree of unsaturation determines the speed of desiccation (polymerization initialized by air oxygen) and ability to form tough elastic film. Linseed oil is an easily siccative oil since it contains many unsaturated and polyunsaturated acyl groups. It forms elastic, transparent, and slightly yellowish touch-dry film. Oxidation reaction is accelerated by a presence of kations of some metals. Compounds of lead, manganese or cobalt are catalyzing film formation as well as its aging and degradation.^(47; 46)

2.5.2.2.1. DRYING-OUT OF OILS

Drying-out of oils is not a physical phenomena related to the evaporation of solvent, but polymerization of fatty acids in triacylglycerols initialized by oxygen. The process of oil polymerization is complicated and its mechanism has not yet been fully clarified.^(46; 47)

First step is separation of hydrogen radical from activated carbon next to a carbon with double bond^(46; 47):



Where R' is aliphatic chain and R'' is aliphatic chain ended with carboxyl group. Free radical may be formed due to the effect of light, heat, ionizing radiation or by effect of chemical initiators.

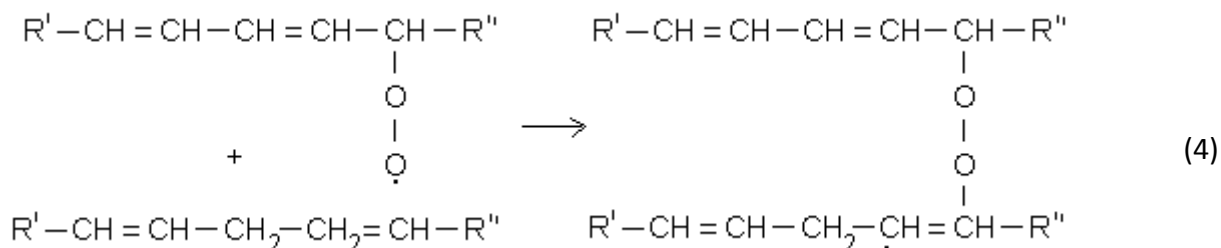
Radical (1) transforms into a more stabilized system containing conjugated double bonds^(46; 47):



This radical reacts with oxygen forming peroxide radical^(46; 47):



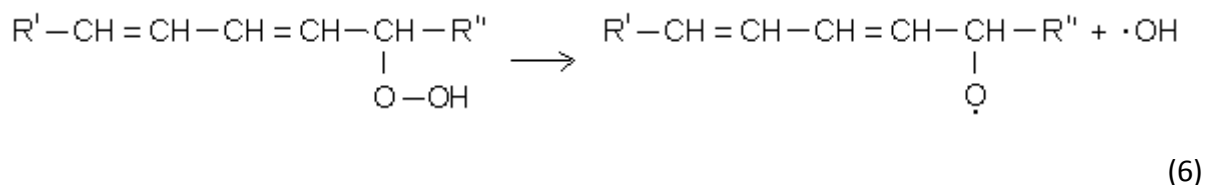
Peroxide radical (3) may react with double bonds of neighbouring acyl groups forming cross-links^(46; 47):



Alternatively, peroxide radical (3) stabilizes itself forming hydroperoxide by detaching hydrogen from another molecule^(46; 47):



These peroxide compounds (5) are unstable, they fission by the action of heat, light or kations of metals, forming peroxide, alkoxy or hydroxyl radicals^(46; 47):



Finally, alkoxy radical (6) forms again cross-links with a neighbouring double bond^(46; 47):

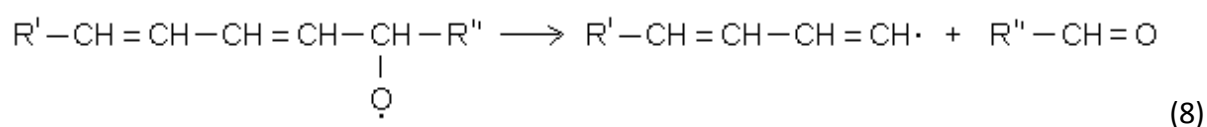


Reactions (4) and (7) lead to three-dimensional structure and are the principle of the desiccation of oils.^(46; 47)

2.5.2.2.2. OIL FILMS AGING AND DEGRADATION

Dried oil film contains cross-linked molecules of triacylglycerols. However, the polymerization reactions may continue. These following reactions lead to film degradation.

Film darkens, is losing its elasticity, cracks are formed and finally the film disintegrates. Degradation process is caused mostly by breaking labile peroxide cross-links. This leads to fission of fatty acid chains and to formation of compounds containing reactive hydroxyl, carboxyl, and carbonyl groups. These groups are formed during subsequent reactions of primarily formed hydroperoxides or alkoxy radicals. For example, saturated and unsaturated C₅-C₉ carbohydrates and various aldehydes may be formed by degradation of linoleic acid^(46; 47).



Further oxidation leads to a formation of carboxylic acids such is capronic or azelaic acid. A schematic representation of oil film structure and its degradation is shown in **Figure 10**.

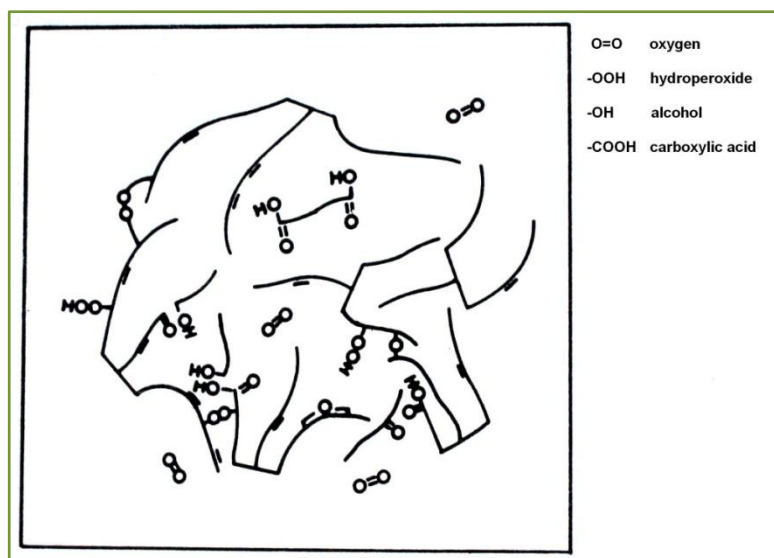


Figure 10: Structure of oil film and its degradation⁽²²⁾

Figure 11 shows process of degradation reactions of linseed and poppyseed oil films. We can observe well-known phenomena that during the degradation process the weight loss of linseed oil is lower than that of poppyseed oil films.⁽⁴⁶⁾ The reason is that linseed oil contains higher amount of unsaturated fatty acids and the higher content of double bonds leads to higher density of cross-links between the molecules. Thus, the degradation products are held bounded in the structure for a longer time, some of them permanently, and the whole degradation process is slower.⁽⁴⁶⁾

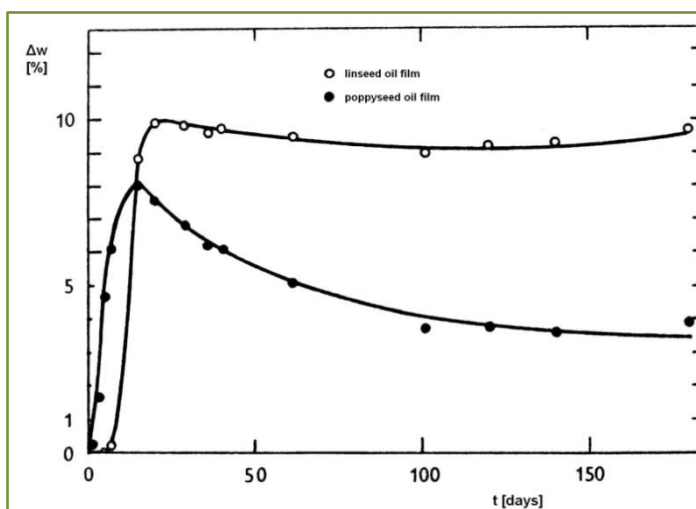
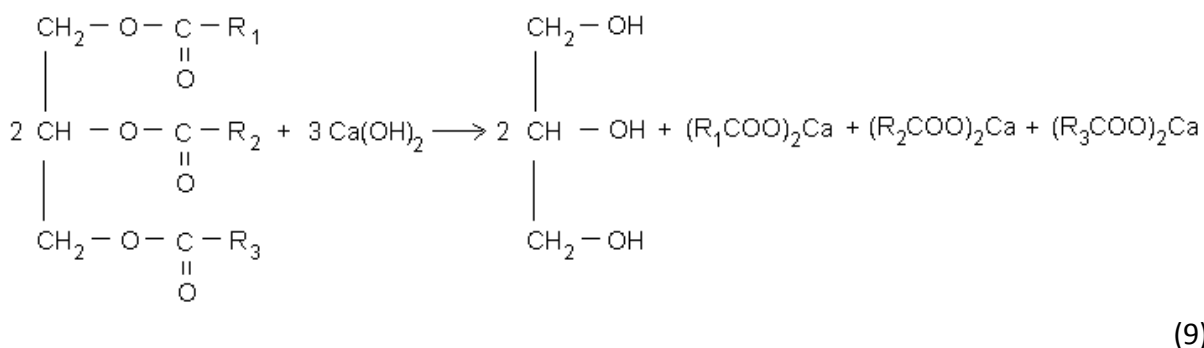


Figure 11: Weight change of linseed and poppyseed oil films aged at 20°C in time ⁽⁴⁶⁾

2.5.2.2.3. REACTION OF OIL IN BASIC ENVIRONMENT

Fresh mortar is strongly basic, with $\text{pH} > 12$. When oil is added into mortar, triacylglycerols undergo hydration resulting in formation of insoluble calcium salts of fatty acids ^(4; 49; 5; 48).



Incurred fatty acids salts are hydrophobic due to their alkyl chains the same as triacylglycerols. Due to their interaction with calcium, they are well bounded in mortar structure and the hydrophobic alkyl chain will cause mortar repellency ^(48; 49).

2.5.2.3 STUDIES ON EFFECT OF OIL ON MORTAR

While there are some mentions of using of oil as a mortar additive in literature, there are only a few studies on its actual effect.

Chandra et al. ⁽⁵⁾ studied effect of linseed, corn, and mustard oils on properties of Portland cement mortar. Flexural and compressive strength, water absorption and freeze-

salt resistance have been tested. Oils were added in 0,5% and 0,8% concentrations by the weight of cement, cement-sand ratio 1:3 mortar, samples were tested after 7 and 28 days of curing. After 28 days, addition of 0,5% did not have effect on compressive strength, while the addition of 0,8% decreased the compressive strength. Water absorption was decreased and subsequently freeze-salt resistance was increased. The effect was more apparent with higher concentration of oils. ⁽⁵⁾

Further, Justnes et al. ^(48; 49) studied effect of vegetable oils but, the same as Chandra, on cement mortar, which is not suitable for restoration purposes due to its hardness and because of the risk of introducing dangerous salts into historical structures. Authors' motivation was to develop a natural replacement of synthetic additives that can secure a sustainable development, the so-called bio-admixtures. Linseed, sunflower, olive, soya beans, peanuts, corn and rapeseeds oils were tested in 0,5% and 1,5% concentration by the weight of cement. Oils were dispersed in the mixing water by the aid of lignosulphonate. Cement-sand 1:3, w/c= 0,5. After 1 and 28 days of curing flexural and compressive strength, capillary water absorption and water vapour diffusion was tested. After 3 years of further curing at 93%RH, compressive strength, capillary water absorption, monolayer capacity and chemically bound water were measured (49). Of the strengths measured after 1 and 28 days, only compressive strength at 28 days of some oils at the highest dosage showed significant decrease. The 3-year compressive strength was reduced by 30%, but had still increased from the 28 days strength. Flexural strengths were not reduced to any larger degree than the compressive strengths. Strength didn't show clear dependence on oil dosage. Capillary water absorption was greatly reduced comparing to reference, while water vapour diffusion was only marginally reduced. Similarly to Chandra's findings, capillarity was decreasing with increasing oil concentration. Chloride intrusion was reduced to 35-66% of the reference sample, but no trends were found in-between oils. Water repellent effect lasted more than 3 years at moist conditions. Oil did not have effect on the hydration degree of cement ^(48; 49).

The two following authors tested effect of oils on the lime mortar.

Santiago and Mendonca De Oliveira tested whale oil addition in concentration of 2% and 5% by the weight of lime. Mortar was prepared in proportion lime:sand 1:3 and lime:clay:sand 1:2:1. Capillary absorption of mortars with oil was lower than that of those without oil, tested after 4 years of curing, mortars with 5% of oil had almost zero absorption.

On the other hand, mortars with oil had lower compressive strength than unmodified mortars. Authors suppose it could be because oil encapsulates the Ca(OH)_2 particles and prevents carbonation process to take place ⁽⁴⁵⁾.

Rovnaníková ⁽⁴⁾ studied an effect of various natural polymers on hydrated lime mortar. Boiled linseed oil was tested in 1%, 5% and 10% concentration by the weight of mortar mixture (0,3%, 1,7% and 3,3% by the weight of lime). Hydrated lime-sand-water ratios were in proportion 1:3:1. Author observed decreased porosity and workability of fresh mortar “due to the hydrophobicity of oil”. Hardened mortar showed lower porosity and water absorption comparing to reference. Compressive strength was significantly increased with addition of oil; however flexural strength was lower, probably because of the physical action of oil. Water vapour permeability was not affected by the oil addition. Higher additions of oil (5%, 10%) were causing slight increase in volume (1-1,5%) comparing to the reference mortar, which showed shrinkage (2,5%) ⁽⁴⁾.

In summary, the effect of oil was tested mostly on the cement mortar, which is not suitable for restoration, little is known about the effect on lime mortars. Cement mortar has different chemical composition and in consequence different properties than the lime-based mortars, so the effect of oil may be different.

Little experimental work on the effect of oil has been done. The effect of oil on some properties (strength, porosity, capillarity) has been tested, but the effect of oil on mortar's microstructure and the exact mechanism of its operation is not clearly known. Most importantly, the supposed increased resistance of lime-based mortars against deterioration has not yet been verified experimentally.

3 Experimental part

In the present study, the effect of linseed oil on the properties of six various lime-based mortars has been studied. Mortars composition has been selected with respect to composition of historical mortars (hydrated lime mortar and pozzolanic mortars⁽⁵⁰⁾), but also mortars used in modern restoration practise (hydraulic lime mortar, mortars with addition of cement) have been tested. Mortar mixtures were prepared in three different versions: unmodified and with 1% and 3% addition of linseed oil by the weight of binder.

The effect of linseed oil addition on mortars mechanical (compressive and flexural strength, dynamic modulus of elasticity) and physical properties (open porosity, water absorption through capillarity) have been studied. Changes in pore size distribution have been investigated by means of mercury intrusion porosimetry and the effect of oil addition on mortars' structure has been studied by means of scanning electron microscopy. Dispersion of oil in mortar structure was verified by observing their cross-sections under microscope with UV light, which evokes fluorescence of linseed oil. FTIR analysis of binder pastes was performed in order to examine linseed oil's possible chemical changes in mortar (formation of carboxylate salts, cross-linking of fatty acids molecules). Finally, mortars durability against salt crystallization (NaCl and Na₂SO₄) and freeze-thaw cycles was tested.

3.1 USED MATERIALS

- Lime – hydrated lime, EN ISO 9002 TUV CERT, manufacturer: CaO Hellas
- Pozzolan – natural pozzolan with very fine particles (<55µm), manufacturer: Dalkafoukis, technical sheet in Appendix I.
- Hydraulic lime – Albaria Calce Albazzana, natural hydraulic lime, without cement, light colour, binder for plasters, bedding and joint mortars. Manufacturer: Degussa Construction Chemicals spa (now BASF), technical and safety sheets in Appendices II and III.
- Cement – white cement, CEM II/A – LL 42,5N, manufacturer: TITAN
- Brick dust – manufacturer: Kourasanit
- Sand – Axios river natural sand, supplier: Tratselas S.A.

- Linseed oil – crude natural linseed oil, manufacturer: Mercola
- Potable water

3.2 EXPERIMENTAL METHODS

3.2.1 MATERIALS CHARACTERISTICS

3.2.1.1 DETERMINATION OF THE PARTICLE DENSITY OF BINDER

Real density of hydrated lime, hydraulic lime, cement, pozzolan and brick dust has been determined by pycnometer method at 20°C, ethanol has been used as an auxiliary liquid. Analysis has been done by Stavroula Konopissi at the Chemical laboratory of AUTH.

As a first step apparent volume of pycnometer has been determined:

$$V_p = \frac{m_B - m_A}{\rho_{H_2O}}, \text{ where}$$

V_p is the apparent volume of the pycnometer [m^3],

m_A is the mass of the empty pycnometer [kg],

m_B is the mass of the pycnometer filled with distilled water [kg],

ρ_{H_2O} is the density of distilled water at 20 °C, $\rho_{H_2O} = 998,23 \text{ kg}\cdot\text{m}^{-3}$.

Then the density of ethanol has been determined:

$$\rho_C = \frac{m_C - m_A}{V_p}, \text{ where}$$

ρ_C is density of ethanol at 20°C [$\text{kg}\cdot\text{m}^{-3}$],

m_C is mass of the pycnometer filled with ethanol [kg].

Particle density of analysed materials has been calculated from the following formula:

$$\rho_p = \frac{\rho_C \cdot m_D}{m_C + m_D - m_E}, \text{ where}$$

ρ_p is the particle density [$\text{kg}\cdot\text{m}^{-3}$],

m_D is the mass of the specimen [kg],

m_E is mass of the pycnometer filled with ethanol and the specimen [kg].

3.2.1.2 DETERMINATION OF LOOSE BULK DENSITY OF DRY BINDERS AND AGGREGATE

Loose bulk density of hydrated lime, hydraulic lime, pozzolan, cement and brick dust has been determined according to EN 1097-3⁽⁵¹⁾.

Loose bulk density is defined as the quotient obtained when the mass of dry aggregate filling a specified container without compaction is divided by the capacity of that container.

The loose bulk density ρ_l is calculated according to the following equation:

$$\rho_l = \frac{m_2 - m_1}{V}, \text{ where}$$

ρ_l is the loose bulk density [$\text{kg}\cdot\text{m}^{-3}$],

m_2 is the mass of the container and test specimen [kg],

m_1 is the mass of the empty container [kg],

V is the volume of the specimen [m^3].

3.2.1.3 GRAIN SIZE DISTRIBUTION

Distribution of sand and brick dust particles has been determined on mechanical sieve shaker with sieve series of ISO 3310, using sieves with a square mesh of size 8 mm, 6,3 mm, 4 mm, 2,5 mm, 1 mm, 0,5 mm, 0,2 mm, 0,1 mm, 0,075 mm and 0,063 mm. Sieving time was 10 min. Individual fractions were weighed and result plotted as a cumulative curve.

3.2.1.4 BINDER SETTING TIME DETERMINATION

Determination of initial and final setting time of hydrated lime, hydraulic lime, mixture of hydrated lime and pozzolan in proportion 1:1, mixture of hydrated lime, pozzolan and brick dust 1:0,5:0,5, mixture of hydrated lime, pozzolan and cement 1:0,9:0,1 mixture of hydrated lime, pozzolan and cement in proportion 1:0,8:0,2 and all previous binder mixtures modified by 1% and 3% per weight addition of linseed oil has been determined according to EN 196-3⁽⁵²⁾ on the Vicat apparatus.

Firstly the standard consistence was supposed to be determined. Standard consistence is characterized by the depth of penetration of plunger into binder paste, which is filled into Vicat ring placed on a glass base-plate. Standard consistence is such a proportion of binder and water that the distance between the bottom face of the plunger and the base-plate is (6 ± 1) mm. Unfortunately, it was not possible to prepare binder pastes of the standard consistence, because at this consistence binder pastes were too thick to be mixed well so it was not possible to ensure proper incorporation of oil into the binder paste.

Setting time is determined on the Vicat apparatus equipped with a steel needle. Initial setting time is defined as the time measured from zero time (mixing binder with water) at which the distance between the needle and the base-plate is (4 ± 1) mm.

Final setting time is defined as the time measured from zero time (mixing binder with water) at which needle first penetrates only 0,5 mm into the specimen.

3.2.2 PREPARATION OF MORTAR MIXTURES

Mortar mixtures were prepared using six different binding systems: hydrated lime: sand (1: 3, code L), natural hydraulic lime: sand (1: 3, code HL), hydrated lime: pozzolan: sand (1: 1: 6, code P), hydrated lime: pozzolan: brick dust: sand (1: 0,5: 0,5: 6, code B) and hydrated lime: pozzolan: cement: sand with cement in two different concentrations (1: 0,9: 0,1: 6, code C1 and 1: 0,8: 0,2: 6, code C2). Compositions were prepared in three different versions: unmodified, with 1% and 3% of linseed oil by the weight of binder. Water was added in amount needed to maintain the same workability for all mortar mixtures. Mortar mixtures have been prepared in the following way:

1. Mixing up of all dry constituents by chisel (to avoid dusting),
2. For modified mixtures: mixing oil with a bit of dry mixture (approx. 50 g) in a plastic cup, then pouring oiled powder into the dry mixture,
3. Adding water while mixing at low speed, mixing for 3 minutes,
4. Pouring water on the bottom of mixing vessel, incorporation of mortar held on vessel sides by chisel,
5. Mixing for another 3 minutes at low speed,

6. Checking consistence on a flow table (adding more water if necessary, additional mixing for approx. 1 minute),
7. Filling into the moulds.

3.2.3 PROPERTIES OF FRESH MORTARS

Fresh mortar is characterized by its water-binder ratio, consistence, and bulk density.

3.2.3.1 DETERMINATION OF WATER-BINDER RATIO

Water binder ration is defined as:

$$w/b = \frac{m_{H_2O}}{m_b}, \text{ where}$$

w/b is the water-binder ration,

m_{H_2O} is the mass of the kneading water [g],

m_b is the mass of the binder [g].

3.2.3.2 DETERMINATION OF CONSISTENCE

Consistence is a measure of the fluidity and/or wetness of the fresh mortar and gives a measure of the deformability of the fresh mortar when subjected to a certain type of stress. Consistence has been determined according to 1015-3:1999⁽⁵³⁾.

Mould of defined diameters has been placed in a centre of a flow table and filled with fresh mortar. After removing the mould, mortar has been spread out on the disc by jolting the flow table 15 times. Flow value has been measured after 15 vertical strokes of flow table by raising the flow table and allowing it to fall freely through a given height. Consistence is defined as a mean value of mortar diameter in centimetres measured in three directions.

3.2.3.3 BULK DENSITY DETERMINATION

Bulk density has been determined according to EN 1015-6:1999⁽⁵⁴⁾. Bulk density expresses the mass of defined volume of fresh mortar. It is calculated from following formula:

$$\rho_b = \frac{m_2 - m_1}{V}, \text{ where}$$

ρ_b is the bulk density of fresh mortar [$\text{kg}\cdot\text{m}^{-3}$],

m_0 is the mass of empty vessel [kg],

m_{fm} is the mass of vessel with mortar [kg],

V_{fm} is the volume of fresh mortar [m^3].

3.2.4 SAMPLES PREPARATION

Samples of shape of prisms 4 x 4 x 16 cm and cylindrical discs (\varnothing 16 cm x 2 cm) were prepared.

Internal faces of assembled moulds for preparation of prisms have been firstly lubricated with a thin layer of mineral oil to prevent adhesion of the mortar. Fresh mortar has been filled into the moulds in two approximately equal layers; each layer has been compacted by 25 strokes of the tamper. Moulds have been covered with an iron plate and stored according to EN 1015-11⁽⁵⁵⁾.

Cylindrical disc specimens were prepared in a similar way, but without lubricating the moulds by mineral oil, because that could affect water vapour permeability to be tested.

Curing conditions were as follows:

1. 5 days in the mould at (95±5)%,
2. 2 days with the mould removed at (95±5)%,
3. 11 weeks with the mould removed at (65±5)%,
4. 1 year in ambient conditions in air-conditioned room (temperature 20-25°C, 40-80% RH) – unmodified mortars and mortars with 1% oil addition only.

(95±5)%RH was reached by covering specimens in moulds and (65±5)% was obtained by placing specimens into tray with dampened cloth and partial covering of tray by plastic foil. Unfortunately, a climatic chamber was not available for curing of the specimens.

Prisms were used for experiments after 1, 3, and 12 months of curing.

Cylindrical discs for water vapour permeability test were cured for 1 month.

3.2.5 PROPERTIES OF HARDENED MORTARS

3.2.5.1 FLEXURAL STRENGTH DETERMINATION

Flexural strength has been measured according to EN 1015-11:1999⁽⁵⁵⁾ on machine by “Chemischer Laboratorium für TUNINDUSTRIE, Prof.Dr.H.Leger&E.Cramer Kom. Ges., BERLIN/WEST, Masch.Nr.12633, Bemjahr 1962”. For flexural strength determination specimen in shape of prisms (4 x 4 x 16 cm) were used. Exact prisms diameters (length, width and depth in the place of testing, i.e. half of prism) were measured before testing.

Flexural strength was calculated from following formula:

$$f = \frac{1,5 \cdot F_f \cdot l}{b \cdot d^2}, \text{ where}$$

f is the flexural strength [MPa],

F_f is the maximum load applied to the specimen [N],

l is the distance between the axes of the support rollers [mm],

b is the width of specimen [mm],

d is the depth of specimen [mm].

Flexural strength has been tested on specimens of unmodified mortars and of mortars with 1% addition of linseed oil at the age of 1, 3 and 12 months, specimens of mortars with 3% addition of oil at 1 and 3 months. Result is the mean value of 6-9 measurements.

3.2.5.2 COMPRESSIVE STRENGTH DETERMINATION

Compressive strength has been determined according to EN 1015-11:1999⁽⁵⁵⁾ on MOHR & FEDERHAUF AG instrument provided with adapter for testing of mortars. Instrument has been operated by either Michalis Papachristoforou, Dr. Maria Stefanidou or Yiannis Goutsios. Halves of prisms have been used for the testing. Compressive strength is defined by the maximum load to the specimen area:

$$c = \frac{F_C}{A}, \text{ where}$$

c is the compressive strength [MPa],

F_c is the maximum load applied to the specimen [N],

A is the area on which the load is applied [mm²].

Compressive strength has been tested on specimens of unmodified mortars and of mortars with 1% addition of linseed oil at the age of 3 and 12 months, mortars with 3% of oil addition were tested after 3 months of curing. Result is the mean value of 4-7 measurements.

3.2.5.3 DYNAMIC MODULUS OF ELASTICITY DETERMINATION

Dynamic modulus of elasticity was calculated from measured ultrasonic pulse velocity, which is influenced by those properties of the material which determine its elastic stiffness and mechanical strength. It indicates material's uniformity, presence of cracks and voids.

Ultrasonic pulse velocity in a solid material is a function of the square root of the ratio of its modulus of elasticity to its density, according to BS 1881-203^(56; 57):

$$v = \frac{L}{T} = f \left(\frac{g \cdot E_{dyn}}{\rho} \right)^{\frac{1}{2}}, \text{ where;}$$

v is the ultrasonic pulse velocity [m.s⁻¹];

L is the length of specimen [m];

T is the pulse transit time [s];

E_{dyn} is dynamic modulus of elasticity [GPa],

ρ is the density of the material [kg.m⁻³],

g is the gravity acceleration, $g = 9.81 \text{ m.s}^{-2}$.

The natural frequency of transducers was 55 kHz.

The dynamic modulus of elasticity may be then calculated by substituting the value of the pulse transit time into the equation according to BS 1881-209⁽⁵⁸⁾ to yield an approximate value for the desired resonant frequency:

$$E_{dyn} = 4.n^2.L^2.\rho.10^{-15}, \text{ where}$$

E_{dyn} is the dynamic modulus of elasticity [GPa],

n is the fundamental frequency in longitudinal mode of vibration of the specimen [Hz],

L is the length of the specimen [mm],

ρ is the density of the specimen [$\text{kg}\cdot\text{m}^{-3}$].

Dynamic modulus of elasticity has been tested on specimens of unmodified mortars and of mortars with 1% addition of linseed oil at the age of 3 and 12 months, mortars with 3% of oil addition were tested after 3 months of curing. Result is the mean value of 3 measurements.

3.2.5.4 DETERMINATION OF OPEN POROSITY, APPARENT DENSITY, WATER ABSORPTION AND PORES ACCESSIBILITY TO WATER

Open porosity and apparent density determination has been based on EN 1936:2006⁽⁵⁹⁾. Quarters of prisms of weight (100 ± 20) g were used for testing. Specimens were dried in a ventilated oven at a temperature of (65 ± 5) °C and weighed prior to the testing. The procedure was as follows:

1. Submerging specimens in distilled water for 48 hours at ambient atmospheric pressure,
2. Weighing the specimens after quick drying with a cloth at the air and also when immersed under water,
3. Submerging the specimens in distilled water for 24 hours at lowered pressure -0,85 bar compared to the atmospheric pressure (i.e. the pressure in the vacuum vessel was 16,3 kPa). Obtained pressure was higher than the pressure recommended by the standard ($(2\pm 0,7)$ kPa), also the time of air evacuation was prolonged comparing to standard (2 hours).
4. Gradually increasing the pressure in the evacuation vessel (within 10 minutes), leaving specimens for another 24 hours under water at atmospheric pressure,
5. Weighing the specimens at the air after quick drying with a cloth and also when immersed under water.

Following variables were calculated based on measured weights:

- Apparent density – ratio between the mass of the dry specimen and its apparent volume:

$$\rho_a = \frac{m_0 \cdot \rho_{H_2O}}{m_{SSD2} - m_{h2}}$$

- Water absorption after 48 hours – ratio between the mass of water in the specimen after 48 hours and the mass of dry specimen:

$$WA_{48} = \frac{m_{SSD1} - m_0}{m_0} \cdot 100$$

- Open porosity after 48 hours – ratio between the volume of the water in pores after 48 hours (volume of easily accessible pores) and the apparent volume of the specimen:

$$P_{48} = \frac{m_{h1} - m_0}{m_{SSD1} - m_{h1}} \cdot 100$$

- Water absorption - ratio between the mass of water in the specimen after vacuum evacuation and the mass of dry specimen:

$$WA = \frac{m_{SSD2} - m_0}{m_0} \cdot 100$$

- Open porosity – ratio between the volume of the water in pores after vacuum evacuation (volume of pores accessible to water) and the apparent volume of the specimen:

$$P_{H_2O} = \frac{m_{SSD2} - m_0}{m_{SSD2} - m_{h2}} \cdot 100$$

Pores accessibility to water can be expressed as the proportion of pores easily accessible to water to the total amount of opened pores⁽⁶⁰⁾:

$$C_a = \frac{P_{48}}{P_{H_2O}}$$

m_0 is the mass of the dry specimen [kg],

m_{SSD1} is the mass of the saturated surface dry specimen after 48 hours [kg],

m_{h1} is the mass of the saturated specimen after 48 hours weighed hydrostatically [kg],

m_{SSD2} is the mass of the saturated surface dry specimen after vacuum evacuation [kg],

m_{h2} is the mass of the saturated surface dry specimen after vacuum evacuation weighed hydrostatically [kg],

ρ_{H_2O} is the water density at 20 °C, $\rho_{H_2O} = 998,2 \text{ kg.m}^{-3}$,

ρ_a is the apparent density [kg.m^{-3}],

WA_{48} is the water absorption after 48 hours [%],

p_{48} is the porosity after 48 hours, i.e. porosity easily accessible to water [%],

WA is the water absorption after vacuum evacuation [%],

p_{H_2O} is the porosity accessible to water, i.e. open porosity [%],

C_a is the coefficient of pores accessibility to water.

Two samples of each mortar type were tested at the age of 1, 3, and 12 months. Result is the mean value of the two measurements.

3.2.5.5 DETERMINING OF DRYING RATE

Saturated specimens after the open porosity determination, as described in previous chapter, have been dried in a ventilated oven at 85°C. Specimens have been weighed in time intervals and the drying rate has been plotted as a function of time⁽⁶¹⁾.

3.2.5.6 PORE SIZE DISTRIBUTION

Pore size distribution has been determined by means of mercury intrusion porosimetry, through ThermoQuest mercury porosimeter utilizing the Pascal 140 and Pascal 240 units. Analyses have been done by Dr. Silvia Rescic at CNR-ICVBC in Florence, Italy. Analyse has been carried out in a range from 0,0037 μm to 150 μm pore ratio, which is the area of mesopores⁽⁶²⁾.

The porosity is defined as a ratio of vacuum space and the total volume of the material. Vacuum space is calculated as the difference between the total volume of the material and the volume of the solid portion. At CNR-ICVBC, total volume of the material

was measured by means of mercury pycnometer, and volume of the solid portion by means of the helium pycnometer.

3.2.5.7 CAPILLARY ACTION

Capillarity is characterized by the coefficient of water absorption, which expresses the initial slope of the plotted amount of water per unit surface as a function of square root of time ⁽⁶³⁾ (i.e. how much water and how quickly gets absorbed into material). Besides water, the test has been performed using also salt solution (10% by weight NaCl) to see whether the ions in water can significantly affect the process of capillary action. Coefficient of water (salt solution) absorption by capillary action has been measured using half-prism specimens of size of approximately 4 x 4 x 8 cm, as described in EN 1015-18:2002 ⁽⁶³⁾. After drying the specimens for 2 days at (65±5) °C, specimens have been immersed in 1 cm of distilled water (salt solution) by their rough surface face (after breaking the specimen when measuring the flexural strength) and the container with the specimen has been sealed to avoid evaporation. Specimens have been weighed after 10 and 90 minutes and the increase in mass determined. Coefficient of water (salt solution) absorption has been calculated according to the following formula:

$$C = 0,1 \cdot (m_{90} - m_{10}), \text{ where}$$

C is the coefficient of water (salt solution) absorption [$\text{kg}/(\text{m}^2 \cdot \text{min}^{0,5})$],

m_{10} is the mass after 10 minutes [kg],

m_{90} is the mass after 90 minutes [kg].

Two specimens of all mortar types have been tested after 1 and 3 months of curing. Mortars with 1% of oil and unmodified mortars have been tested also at the age of 1 year. Result is the mean value of two measurements.

3.2.5.8 WATER CONTACT ANGLE

Contact angle that water drop forms on material's surface defines material's hydrophobicity. It is measured as an angle between the baseline of the drop and the tangent at the drop boundary. The higher is the contact angle, the more hydrophobic is material's surface.

Water contact angle was observed on specimens of hardened binder pastes, which were of the same composition as those used for the preparation of mortars. Pictures of water drop on specimens' surfaces were taken after approximately two seconds after applying the water drop and the contact angle was compared among the different types of mortars.

3.2.5.9 WATER VAPOUR PERMEABILITY

Water vapour permeability is an important characteristic of plastering and/or rendering mortar. Vapour permeability affects mortar's ability of drying; low permeability may slow down carbonation process. "Walls that cannot "breath" trap moisture, which could cause problems with mould on interior finishes or freeze-thaw damage to the masonry".⁽⁶⁴⁾

Water vapour permeability has been tested on cylindrical disc specimens of $\varnothing 16$ cm x 2 cm, 3 specimens of each mortar type have been prepared. Each specimen was placed on an open mouth of a cup filled with silica gel and the edges were sealed so that air could not penetrate through (Figure 12). Cups with specimens were placed into climatic chamber with 75%RH and 20°C. The difference between relative humidity inside and outside the cups causes moisture to flow through the porous mortar samples from the side with higher RH (outside 75%RH) to the side with lower RH (inside $\sim 10\%$ RH). Increase in weight has been recorded in regular intervals until the diffusion equilibrium occurred. Water vapour permeability coefficient (simplified) was calculated as the amount of water vapour passed through one square meter of sample in one hour, using following formula according to NORMAL 21/85⁽⁶⁵⁾:

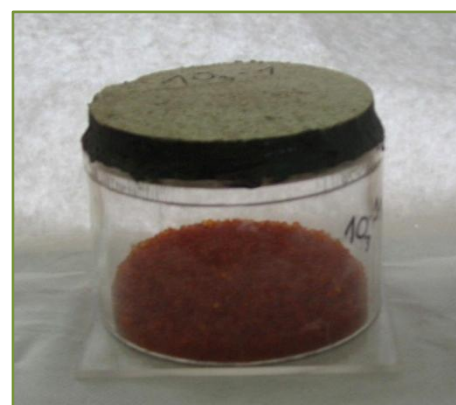


Figure 12: Specimen for water vapour permeability test

$$C_v = \frac{\Delta m}{\tau \cdot A}, \text{ where}$$

C_v is the water vapour permeability coefficient [$\text{g} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$],

τ is the time between two successive measurements [h],

A is the area of the specimen [m^2].

3.2.5.10 DEFINING THE COLOUR OF BINDER PASTES

Colour of hardened binder samples has been observed in order to ascertain whether oil addition has some effect on the colour. Binder pastes have been of the same composition as the binders in mortars, plus the 1% and 3% by weight oil addition. Colour has been determined according to Munsell soil colour charts⁽⁶⁶⁾.

3.2.5.11 RESISTANCE TO SALT CRYSTALLIZATION CYCLES

Resistance to salt crystallization has been tested in two different types of cycles. Firstly, cycle during which specimens have been allowed to absorb 10wt% NaCl solution by capillary rise for 24 hours and then dried in a ventilated oven for 2 days at $(65\pm 5)^{\circ}\text{C}$ has been tested. This cycle did not show to be sufficient enough, because specimens even after 15 cycles did not show decrease in weight, furthermore values were fluctuating (perhaps due to unstable capillary rate and/or drying temperature), so that it was not possible to compare individual mortar types in terms of their resistance.

Therefore another, more efficient, cycle has been set up, using both 10wt% NaCl and 10wt% Na_2SO_4 solution, with parameters as follows:

- 6 hours full immersion in salt solution;
- 18 hours drying in ventilated oven at 85°C (newer model of oven used).

In the first cycle NaCl has been used, since it is one of the most common salt, but in the second type of cycle also Na_2SO_4 has been used concurrently to NaCl, because Na_2SO_4 is more damaging salt than NaCl.

Drying temperature of 85°C is rather high temperature, but still lower than the drying temperature recommended by RILEM for the porosity determination ($(105\pm 5)^{\circ}\text{C}$ ⁽⁶⁷⁾), mortar microstructure should not get damaged.

Mortar quarter-prism specimens of weight $(100\pm 20)\text{g}$ were used for testing. Specimens were weighed after each cycle and the weight change as a percentage of the original weight was plotted. Damage has been monitored visually, photographically and some specimens representing three groups of mortar (unmodified, 1% and 3% linseed oil addition) has been observed under SEM after 20th cycle of sodium chloride crystallization.

Cycles have been repeated until the destruction of specimens got destroyed, but maximum 25 times. Two specimens of each mortar type have been tested.

3.2.5.12 RESISTANCE TO FREEZE-THAW CYCLES

Mortar quarter-prism specimens of weight (100 ± 20) g were used for testing. Prior to initial cycle specimens were immersed under water for 24 hours and weighed. Freeze-thaw cycles were set up as follows:

- 6 hours at temperature of -20°C ,
- 18 hours melting while immersed under the water at ambient temperature.

Specimens were weighed after each cycle and the weight change as a percentage of the original weight was plotted. Damage has been monitored visually and photographically. Cycles have been repeated until the destruction of the specimens, but maximum 25 times. Two specimens of each mortar type have been tested.

3.2.6 STUDYING OF LINSEED OIL'S BEHAVIOUR IN MORTAR STRUCTURE

3.2.6.1 OBSERVATION OF OIL IN MORTAR STRUCTURE

3.2.6.1.1. UV MICROSCOPY

Cross-section of mortar specimens were observed under an epifluorescence microscope Nikon Eclipse E 600, equipped with UV-2a filter (excitation 330-380, DM 400 nm, BA 420 nm) at CNR-ICVBC in Florence, Italy. This technique allows capturing natural or induced fluorescence of inorganic and organic materials.

3.2.6.1.2. SCANNING ELECTRON MICROSCOPY

Specimens were observed under Scanning electron microscope (SEM) JEOL JSM-840A coupled with energy dispersive spectroscopy (EDS), dual voltage 20kV, at the Laboratory of Scanning Electron Microscope at A.U.TH., Greece. The instrument was operated by Lambrini Papadopoulou.

3.2.6.2 STUDYING OF CHEMICAL CHANGES OF OIL IN A MORTAR AND OIL AGING

Plastic binder pastes of the same binders proportion as in mortars with high content of oil (30% oil, 40% water by the weight of binder) have been analysed with ATR Smart Orbit Accessory inserted into Nicolet 5700 FTIR spectrometer from Thermo Electron Corporation in the range $4000\text{-}525\text{ cm}^{-1}$ in M2ADL laboratory in Ravenna, Italy, by Elsebeth Kendix. Specimens have been analysed at the age of 2 weeks.

The drying and oxidative degradation of oils has been investigated through drying of a thin layer of oil, and also oil mixed with hydrated lime, in a ventilated oven at 60°C for 24 hours. Formed oil films have been observed under microscope with UV light (instrument described above) at CNR-ICVBC and its changes monitored photographically. Dried oil film has been analysed by FTIR-ATR in Ravenna.

4 Results

4.1 BASIC CHARACTERISTICS OF MATERIALS USED

Values of particle density determined as described in 3.2.1.1, p. 42 and loose bulk density determined as described in 3.2.1.2, p.43 of hydrated lime, hydraulic lime, cement, pozzolan and brick dust are listed in **Table 12**.

Grain size distributions of brick dust, pozzolan and sand are shown in **Figure 13-15**.

Table 12: Particle density and loose bulk density of materials used

Material	ρ_p [kg.m ⁻³]	ρ_l [kg.m ⁻³]
Hydrated lime	1961	633
Hydraulic lime	2741	937
Pozzolan	2220	420
Brick dust	2279	1147
Cement	2664	1032
Sand	-	1437

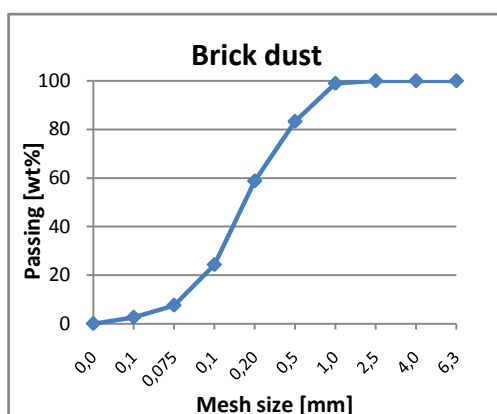
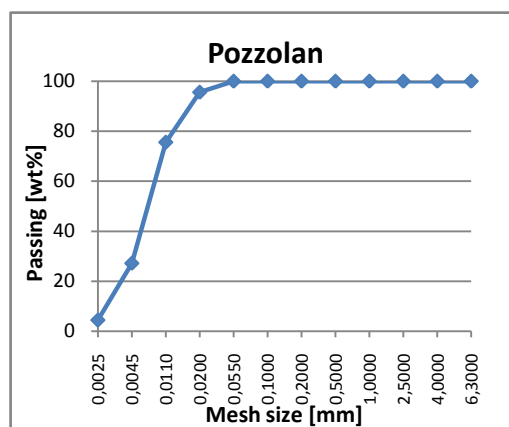
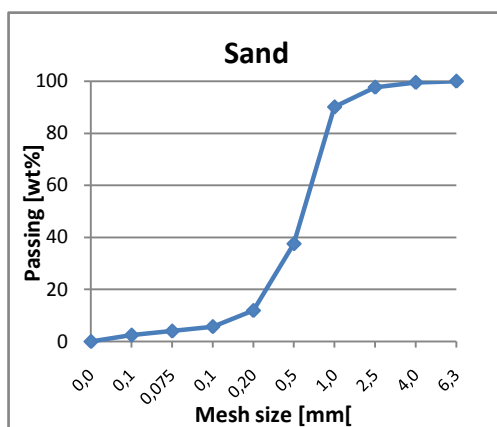


Figure 13: Grain size distribution of sand (up-left)

Figure 14: Grain size distribution of pozzolan (up-right, data provided by the manufacturer)

Figure 15: Grain size distribution of brick dust (right)

4.2 SETTING TIME DETERMINATION

Initial and final setting time has been determined as described in section 3.2.1.4., p.43, its values together with water-binder ratio of tested mixtures are listed in **Table 13**. Addition of oil does not have effect on the initial setting time. However, addition of 3% of oil is delaying the final setting time of hydraulic mortars, thus prolonging binders' setting period. The reason may be that hydrophobic oil tends to adhere to binder grains and it is thus limiting water molecules access. Oil does not have clear effect on hydrated lime setting; that may be because of its different setting time mechanism - water does not play as crucial role as for hydraulic binders.

Table 13: Setting times

code of binder*	water/binder ratio	initial setting time [hh:mm]**	final setting time [hh:mm]**	setting period [hh:mm]
L-b	0,69	2:45	12:15	9:30
LO ₁ -b	0,67	4:20	13:15	8:55
LO ₃ -b	0,64	3:10	12:55	9:45
H-b	0,42	1:25	8:50	7:25
HO ₁ -b	0,42	1:45	8:25	6:40
HO ₃ -b	0,43	1:45	12:00	10:15
P-b	0,69	3:00	15:25	12:25
PO ₁ -b	0,72	3:05	19:40	16:35
PO ₃ -b	0,77	3:05	21:00	17:55
B-b	0,64	3:40	14:50	11:10
BO ₁ -b	0,60	3:50	19:10	15:20
BO ₃ -b	0,60	4:15	21:00	16:45
C1-b	0,68	3:00	15:10	12:10
C1O ₁ -b	0,72	3:20	16:45	13:25
C1O ₃ -b	0,72	3:00	19:20	16:20
C2-b	0,74	3:30	12:20	8:50
C2O ₁ -b	0,64	2:45	12:30	9:45
C2O ₃ -b	0,64	2:45	17:40	14:55

* composition of binders is listed in *Table 14* in the following section

** accuracy is ± 10 min, only values in grey fields have accuracy ± 1 h

4.3 COMPOSITION AND PROPERTIES OF FRESH MORTARS

Compositions of prepared mortars correspond to the historic mortars (hydrated lime mortar, lime with pozzolan, lime-pozzolanic mortar with brick dust⁽⁵⁰⁾), but also mortars with new type of mortars were prepared (hydraulic lime mortar and mortars with 5% and 10%

content of cement). Composition of mortars and their properties are listed in Table 14 and Table 15.

Table 14: Composition of mortars, each mortar type has been prepared in 3 versions: unmodified, with 1% and 3% addition of linseed oil by the weight of binder

Mortar code	L	H	P	B	C1	C2
Lime dry	1		1	1	1	1
Hydraulic lime		1				
Pozzolan			1	0,5	0,9	0,8
Brick dust				0,5		
Cement					0,1	0,2
Sand	3	3	6	6	6	6

Table 15: Composition and properties of fresh mortar mixtures

mortar code	binder					admixture	aggregate	water	properties		
	hydrated lime [g]	hydraulic lime [g]	pozzolan [g]	brick dust [g]	cement [g]	linseed oil [g]	sand [g]	water [g]	w/b	consistency [cm]	bulk density [kg.m-3]
L	875	-	-	-	-	-	2625	665	0,76	14,5	1876
LO ₁	875	-	-	-	-	8,75	2625	630	0,72	15,5	1917
LO ₃	875	-	-	-	-	26,25	2625	656	0,75	15	1967
H	-	875	-	-	-	-	2625	560	0,64	15,5	1999
HO ₁	-	875	-	-	-	8,75	2625	543	0,62	14	2127
HO ₃	-	875	-	-	-	26,25	2625	560	0,64	14	1978
P	437,5	-	437,5	-	-	-	2625	726	0,83	15,5	1967
PO ₁	437,5	-	437,5	-	-	8,75	2625	683	0,78	14,5	2001
PO ₃	437,5	-	437,5	-	-	26,25	2625	735	0,84	15	1953
B	437,5	-	218,75	218,75	-	-	2625	639	0,73	15	1975
BO ₁	437,5	-	218,75	218,75	-	8,75	2625	639	0,73	15	1982
BO ₃	437,5	-	218,75	218,75	-	26,25	2625	656	0,75	15	1945
C1	437,5	-	-	393,75	43,75	-	2625	718	0,82	15,5	1957
C1O ₁	437,5	-	-	393,75	43,75	8,75	2625	683	0,78	14,5	1994
C1O ₃	437,5	-	-	393,75	43,75	26,25	2625	630	0,72	15,5	1922
C2	437,5	-	-	350	87,5	-	2625	700	0,80	15,5	2017
C2O ₁	437,5	-	-	350	87,5	8,75	2625	674	0,77	15	1954
C2O ₃	437,5	-	-	350	87,5	26,25	2625	630	0,72	15,5	1970

Table 15 shows amount of components used for preparation of one mortar dosage, which is amount of which 6-7 prisms (4 x 4 x 16 cm) or 3 disc specimens (\emptyset 16 cm x 2 cm) can be prepared. To get the desired amount of specimens, each mortar mixture has been prepared three times. Amount of dry constituents and oil has been always the same, but amount of kneading water needed to maintain the same consistency varied (\pm 5%), since the consistency of fresh mortar is affected by many factors (temperature, humidity, speed of adding water into dried constituents...). Values of water amount and fresh mortars' properties are mean value of the three values.

4.4 PROPERTIES OF HARDENED MORTARS

4.4.1 MECHANICAL PROPERTIES

Mean values of flexural strength are listed in **Table 16**, compressive strength in **Table 17**, and the mean values of dynamic modulus of elasticity are listed in **Table 18**.

Table 16: Flexural strength

Mortar code	1 month			3 months			1 year		
	flexural strength [MPa]	standard deviation [MPa]	coefficient of variation [%]	flexural strength [MPa]	standard deviation [MPa]	coefficient of variation [%]	flexural strength [MPa]	standard deviation [MPa]	coefficient of variation [%]
L	0,11	0,011	10	0,23	0,021	9	0,35	0,134	38
LO ₁	0,11	0,043	39	0,13	0,029	22	0,33	0,032	10
LO ₃	0,09	0,014	15	0,04	0,021	53	-	-	-
H	0,91	0,074	8	1,20	0,116	10	1,03	0,191	19
HO ₁	1,06	0,045	4	1,32	0,220	17	1,04	0,144	14
HO ₃	0,22	0,013	6	0,48	0,077	16	-	-	-
P	1,77	0,264	15	1,88	0,183	10	0,58	0,067	12
PO ₁	1,64	0,203	12	1,37	0,158	12	1,87	0,110	6
PO ₃	0,47	0,092	20	1,06	0,052	5	-	-	-
B	1,00	0,057	6	1,30	0,084	6	0,44	0,068	15
BO ₁	1,33	0,147	11	1,43	0,218	15	1,35	0,164	12
BO ₃	0,17	0,013	8	0,42	0,039	9	-	-	-
C1	2,00	0,102	5	1,39	0,230	16	0,71	0,115	16
C1O ₁	1,57	0,307	20	1,73	0,260	15	1,27	0,159	13
C1O ₃	0,50	0,016	3	0,18	0,071	40	-	-	-
C2	1,77	0,086	5	1,53	0,263	17	0,48	0,095	20
C2O ₁	1,49	0,102	7	1,62	0,103	6	1,34	0,063	5
C2O ₃	0,72	0,038	5	0,70	0,116	17	-	-	-

Table 17: Compressive strength

Mortar code	3 months			1 year		
	Compressive strength [MPa]	standard deviation [MPa]	coefficient of variation [%]	Compressive strength [MPa]	standard deviation [MPa]	coefficient of variation [%]
L	0,46	0,049	11	1,04	0,220	21
LO ₁	0,27	0,015	6	0,52	0,051	10
LO ₃	*			-	-	-
H	3,64	0,134	4	10,96	1,018	9
HO ₁	3,1	0,316	10	6,89	0,154	2
HO ₃	2,08	0,462	22	-	-	-
P	8,81	0,277	3	6,37	0,275	4
PO ₁	9,56	0,336	4	12,53	1,152	9
PO ₃	3,65	0,568	16	-	-	-
B	6,25	0,495	8	5,35	0,277	5
BO ₁	5,78	0,434	8	8,76	0,370	4
BO ₃	1,10	0,083	7	-	-	-
C1	8,08	0,575	7	7,89	0,713	9
C1O ₁	9,72	0,038	0	9,77	1,443	15
C1O ₃	0,84	0,206	25	-	-	-
C2	8,53	0,518	6	6,9	0,002	0
C2O ₁	10,09	0,130	1	13,21	0,412	3
C2O ₃	2,26	0,118	5	-	-	-

*below detection

Table 18: Dynamic modulus of elasticity

Mortar code	3 months			1 year		
	E_{dyn} [GPa]	standard deviation [GPa]	coefficient of variation [%]	E_{dyn} [GPa]	standard deviation [GPa]	coefficient of variation [%]
L	0,60	0,034	6	0,45	0,059	13
LO ₁	0,2	0,003	2	0,41	0,018	4
LO ₃	0,44	0,161	36	-	-	-
H	1,35	0,047	3	0,55	0,004	1
HO ₁	1,5	0,014	1	0,9	0,012	1
HO ₃	0,69	0,076	11	-	-	-
P	1,57	0,035	2	0,3	0,083	28
PO ₁	1,6	0,009	1	1,2	0,061	5
PO ₃	1,09	0,120	11	-	-	-
B	1,28	0,090	7	0,31	0,047	15
BO ₁	1,5	0,005	0	1,28	0,109	8
BO ₃	0,46	0,056	12	-	-	-
C1	1,47	0,051	3	0,52	0,066	13
C1O ₁	1,6	0,005	0	0,79	0,060	8
C1O ₃	0,52	0,017	0	-	-	-
C2	1,46	0,048	3	0,33	0,041	12
C2O ₁	1,8	0,000	0	1,33	0,111	8
C2O ₃	0,63	0,072	12	-	-	-

4.4.2 APPARENT DENSITY, OPEN POROSITY, WATER ABSORPTION AND PORES ACCESSIBILITY TO WATER

Table 19 lists apparent density, open porosity and water absorption tested after 3 months of curing, and calculated coefficient of pores' accessibility to water as described in section 3.2.5.4, p. 49. Properties of mortars cured for 1 year are listed in Table 20.

Table 19: Apparent density, water absorption, porosity measured under various conditions and coefficient of pores' accessibility to water

Mortar code	ρ [kg.m ⁻³]	WA _{48h}	p_{48} [%]	WA [%]	p_{H_2O} [%]	C_a	p_{Hg} [%]
L	1793	14	24	14	26	0,955	26
LO ₁	1759	17	19	14	25	0,751	29
LO ₃	1767	2	3	16	29	0,106	-
H	1810	14	26	17	31	0,836	24
HO ₁	1804	12	22	14	25	0,862	24
HO ₃	1800	4	7	16	28	0,256	27
P	1692	18	30	20	34	0,900	32
PO ₁	1747	16	28	16	28	1,019	28
PO ₃	1663	9	16	20	33	0,469	33
B	1739	16	27	18	31	0,899	29
BO ₁	1706	15	25	18	30	0,843	25
BO ₃	1695	4	6	18	31	0,199	-
C1	1694	17	30	19	32	0,921	28
C1O ₁	1709	16	28	17	29	0,952	27
C1O ₃	1679	11	18	18	31	0,596	-
C2	1725	17	30	19	33	0,902	22
C2O ₁	1817	16	28	16	30	0,934	25
C2O ₃	1701	7	12	17	29	0,418	24

Total porosity measured by means of mercury intrusion porosimetry is in average lower than total open porosity measured by water absorption. The reason for that is that MIP includes only range of mesopores into calculation of total porosity, while porosity measured by water absorption detects also big pores.

Table 20: Apparent density, water absorption and opened porosity, mortars 1 year old

Mortar code	ρ [kg.m ⁻³]	WA [%]	p_{H_2O} [%]
L	1810	16,7	30,2
LO ₁	1803	16,1	29,1
H	1773	13,9	24,6
HO ₁	1834	15,6	28,7
P	1727	19,0	32,7
PO ₁	1725	18,5	31,9
B	1780	16,5	29,3
BO ₁	1722	18,5	31,9
C1	1730	18,7	32,4
C1O ₁	1704	19,0	32,4
C2	1748	18,2	31,9
C2O ₁	1751	18,2	31,9

4.4.3 DRYING RATE

Mortars' drying rates expressed as a function of time are showed in **Figure 63**, p.96.

4.4.4 PORE SIZE DISTRIBUTION

Graf comparing pore size distributions of individual mortar types is presented in **Figure 25**, p. 81 and **Figure 27**, p. 82. Values of overall porosity of mesopores are listed in **Table 19** on the previous page.

4.4.5 CAPILLARY ACTION

Capillary action is expressed by the coefficient of water (salt solution) absorption, which values for various types of mortars are listed in **Table 21**.





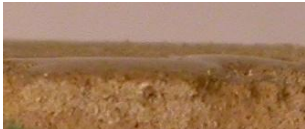



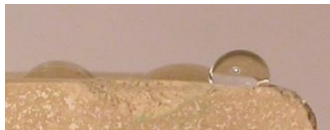
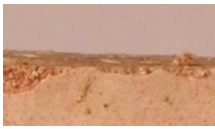





Table 21: Coefficient of water (salt solution) absorption of mortars with different content of linseed oil at different stages of curing

Mortar code	4-6 weeks		3 months		1 year	
	water	10wt% NaCl	water	10wt% NaCl	water	10wt% NaCl
L	1,51	1,51	2,06	2,00	1,59	1,61
LO ₁	0,50	0,37	0,18	0,29	0,49	0,81
LO ₃	0,02	0,03	-0,02	0,00	-	-
H	1,35	1,38	1,30	1,09	1,60	1,38
HO ₁	0,48	0,48	0,27	0,37	0,47	0,60
HO ₃	0,05	0,06	0,06	0,05	-	-
P	1,69	1,62	2,18	2,08	1,77	2,08
PO ₁	1,47	1,30	0,99	1,13	0,96	0,93
PO ₃	0,07	0,05	0,07	0,17	-	-
B	1,21	1,06	1,32	1,11	1,99	1,99
BO ₁	0,41	0,59	0,60	0,83	0,71	0,69
BO ₃	0,03	0,03	0,04	0,03	-	-
C1	1,54	1,64	1,91	1,93	1,15	1,47
C1O ₁	0,92	1,05	0,90	1,07	0,77	0,75
C1O ₃	0,31	0,25	0,47	0,30	-	-
C2	1,04	1,17	1,56	1,24	1,91	1,65
C2O ₁	0,57	0,78	0,64	0,75	0,69	0,73
C2O ₃	0,17	0,12	0,11	0,08	-	-

4.4.6 CONTACT ANGLE

Table 22 shows pictures of water drops on samples of hardened binder pastes with different oil content. It is obvious that even only 1% addition of oil by weight is significantly increasing all binders' hydrophobicity^a. Samples of binders with no oil addition absorb water drop immediately after application, but binders with oil show hydrophobic properties. The effect is the most evident on the samples of hydrated lime (code L): while water drop got immediately absorbed into the unmodified sample, sample with 1% oil addition was hydrophobic – the contact angle was nearly 90°. Sample of hydrated lime with 3% of oil (code LO₃) showed to be totally hydrophobic (cohesive forces among water molecules exceed the adsorption forces to polar surface of the material) - water drops hardly held on sample's surface, as seen on the picture below. On the other hand, 1% addition of oil has not had effect on hydraulic lime samples (code HO₁), nevertheless sample with 3% of oil addition (code HO₃) did show increased hydrophobicity.

Table 22: Contact angle on hardened binder pastes

Binder paste code	unmodified	1% linseed oil	3% linseed oil
L			
H			
P			
B			
C1			

^a The term "hydrophobic" applies according to a definition to materials on which water drop makes contact angle higher than 90°. In this thesis by the term "hydrophobicity" is meant a general ability of material to repel water.

4.4.7 COLOUR CLASSIFICATION

Colour classification of hardened binder pastes determined at the age of 1 month according to Munsell Soil Colour Charts is showed in **Table 23**.

Table 23: Munsell chart colour determination of hardened binder pastes

Binder type	unmodified	1% linseed oil	3% linseed oil
L	white GLEY 8 *	white 2,5Y 8/1 *	pale yellow 2,5Y 8/2 *
H	very pale brown 8/2 10YR	very pale brown 8/2 10YR	light grey 10YR 7/2
P	white 5YR 8/1	white 5YR 8/1	white 5YR 8/1
B	pinkish white 10R 8/2	pinkish white 10R 8/2	pink 2,5YR 8/3
C1	white 5YR 8/1	white 5YR 8/1	white 5YR 8/1

* hydrated lime samples (L) had lighter colour than listed, their actual colour was out of the Munsell chart colour range.

Linseed oil generally did not have effect on colour distinguishable by naked eye. Only hydrated lime (code L) with 3% oil showed slightly yellowish shade comparing to snow white colour of unmodified specimen.

4.4.8 WATER VAPOUR PERMEABILITY

Values of the measured coefficients of water vapour permeability are shown in **Table 24**. Unfortunately, only hydrated lime and hydraulic lime mortars with 3% of oil and unmodified ones could be tested. Other mortar samples has not been possible to test due to the failure of climatic chamber, which has not been repaired until the termination of the Episcon project. However, the addition of linseed oil does not seem to decrease water vapour permeability. Coefficient of water vapour permeability of hydrated lime mortar (code L) is at the same level for both modified and unmodified mortar; hydraulic lime mortar specimen showed to have even higher permeability when linseed oil was added.

Table 24: Coefficient of water vapour permeability

mortar code	C_v [$\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$]
L	3,997
LO ₃	3,929
H	1,404
HO ₃	2,583

4.4.9 DURABILITY

Mortars durability has been tested as their resistance to salt crystallization and freeze-thaw cycles. Mortars with 1% of oil have been tested at the age of 1 year and mortars with 3% oil addition after 1 month of curing. Resistance of both modified mortars have been compared to the reference unmodified mortar.

4.4.9.1 RESISTANCE TO SALT CRYSTALLIZATION CYCLES

Specimens' weight change after each 5 performed cycles of NaCl (Na_2SO_4) crystallization are showed in **Table 25** (NaCl) and in **Table 27** (Na_2SO_4). In **Table 27** the weight change is showed after 5th, 6th, 8th, 10th and 15th cycle, as the deterioration due to sodium sulphate crystallization is faster. **Table 26** and **Table 28** show the number of cycles of NaCl and Na_2SO_4 crystallization respectively, after which specimens have lost 5% of their weight, which can be considered a beginning of the deterioration process. If no value is listed, specimen has already fallen apart. State of specimens during and after salt crystallization cycles is documented in Appendix III.

Table 25: Resistance to NaCl crystallization cycles

Mortar code	Δm_5 [%]	Δm_{10} [%]	Δm_{15} [%]	Δm_{20} [%]	Δm_{25} [%]
L - 1 year	-4	-24	-51	-87	-94
LO ₁ -1 year	1	-4	-8	-16	-45
L -1 month	-30	-59	-79	-95	-98
LO ₃ -1 month	-5	-6	-7	-16	-17
H -1 year	4	0	-4	-9	-17
HO ₁ -1 year	3	1	-1	-8	-29
H -1 month	6	3	3	1	-16
HO ₃ -1 month	-1	-5	-12	-19	-28
P -1 year	-10	-68	-89	-91	-
PO ₁ -1 year	3	-2	-9	-23	-49
P -1 month	6	1	-3	-29	-93
PO ₃ -1 month	0	-1	-6	-11	-18
B -1 year	-12	-58	-	-	-
BO ₁ -1 year	2	-5	-17	-34	-58
B - 1 month	8	5	4	0	-29
BO ₃ - 1 month	0	-1	-4	-7	-14
C1 -1 year	0	-16	-79	-	-
C1O ₁ -1 year	4	-3	-13	-60	-84
C1 -1 month	7	5	5	-1	-46
C1O ₃ -1 month	-9	-44	-68	-81	-92
C2 -1 year	0	-11	-44	-100	-
C2O ₁ -1 year	94	-1	-9	-40	-73
C2 -1 month	9	7	9	7	-15
C2O ₃ -1 month	-1	-18	-43	-71	-90

- sample destroyed

Table 26: Beginning of deterioration due to NaCl crystallization cycles

Mortar type	1 year old		1 month old	
	unmodified	1% linseed oil	unmodified	3% linseed oil
L	6	12	2	5
H	14	19	24	10
P	4	13	16	15
B	3	9	21	18
C1	7	9	21	4
C2	8	13	24	8

Table 27: Resistance to Na₂SO₄ crystallization cycles

Mortar code	Δm_5 [%]	Δm_6 [%]	Δm_8 [%]	Δm_{10} [%]	Δm_{15} [%]
L-1 year	-75	-100	-	-	-
LO ₁ -1 year	-100	-	-	-	-
L-1 month	-95	-100	-	-	-
LO ₃ -1 month	-4	-6	36	-40	-41
H-1 year	-16	-90	-100	-	-
HO ₁ -1 year	-17	-85	-100	-	-
H-1 month	-68	-100	-	-	-
HO ₃ -1 month	-21	-61	-80	-	-
P-1 year	-92	-100	-	-	-
PO ₁ -1 year	-31	-87	-100	-	-
P-1 month	-15	-80	-	-	-
PO ₃ -1 month	-12	-95	-	-	-
B-1 year	-50	-100	-	-	-
BO ₁ -1 year	-29	-45	-93	-	-
B-1 month	-76	-96	-	-	-
BO ₃ -1 month	-2	-7	-14	-23	-72
C1-1 year	-55	-100	-	-	-
C1O ₁ -1 year	-42	-75	-	-	-
C1-1 month	-27	-100	-	-	-
C1O ₃ -1 month	-100	-	-	-	-
C2-1 year	-64	-100	-	-	-
C2O ₁ -1 year	-19	-76	-100	-	-
C2-1 month	-6	-100	-	-	-
C2O ₃ -1 month	-63	-79	-89	-97	-

- sample destroyed

Table 28: Beginning of deterioration due to Na₂SO₄ crystallization cycles

Mortar type	1 year old		1 month old	
	unmodified	1% linseed oil	unmodified	3% linseed oil
L	4	3	2	6
H	4	5	4	4
P	3	4	5	5
B	4	5	4	6
C1	4	4	5	2
C2	4	4	5	3

4.4.9.2 RESISTANCE TO FREEZE-THAW CYCLES

Specimens' weight change after each 5 performed freeze-thaw cycles are showed in **Table 29**. **Table 30** shows the number of freeze-thaw cycles, after which specimens have lost 5% of their weight, which can be considered a beginning of the deterioration process. If no value is listed, specimen has already fallen apart. State of specimens during and after freeze-thaw cycles in documented in Appendix IV.

Table 29: Resistance to freeze-thaw cycles

Mortar code	Δm_5 [%]	Δm_{10} [%]	Δm_{15} [%]	Δm_{20} [%]	Δm_{25} [%]
L-1 year	-77	-	-	-	-
LO ₁ -1 year	-54	-96	-	-	-
L-1 month	-	-	-	-	-
LO ₃ -1 month	0	-13	-29	-51	-62
H-1 year	1	-18	-50	-72	-82
HO ₁ -1 year	0	-2	-6	-12	-18
H-1 month	1	-26	-80	-99	-
HO ₃ -1 month	2	-13	-30	-46	-55
P-1 year	-21	-74	-98	-100	-
PO ₁ -1 year	-7	-25	-50	-66	-76
P-1 month	-1	-19	-40	-60	-73
PO ₃ -1 month	9	2	-28	-52	-69
B-1 year	-54	-89	-99	-	-
BO ₁ -1 year	-1	-10	-24	-38	-47
B-1 month	0	-31	-58	-71	-76
BO ₃ -1 month	3	-19	-43	-56	-63
C1-1 year	-14	-71	-100	-	-
C1O ₁ -1 year	-5	-24	-54	-68	-79
C1-1 month	0	-18	-45	-60	-70
C1O ₃ -1 month	-7	-64	-90	-99	-
C2-1 year	-13	-82	-100	-	-
C2O ₁ -1 year	-2	-16	-40	-56	-66
C2-1 month	2	-23	-56	-80	-87
C2O ₃ -1 month	5	-12	-38	-59	-70

Table 30: Beginning of deterioration due to the freeze-thaw cycles (expressed as a number of cycles after which 5% weight loss occurred)

Mortar type	1 year old		1 month old	
	unmodified	1% linseed oil	unmodified	3% linseed oil
L	3	5	1	8
H	9	13	8	8
P	3	5	7	12
B	2	8	8	8
C1	4	5	7	5
C2	4	7	8	9

4.5 OBSERVATION OF OIL IN MORTAR STRUCTURE

Mortar specimens have been observed under UV light and scanning electron microscope; pictures are showed and discussed in Chapter 5.

4.6 STUDYING OF CHEMICAL CHANGES OF OIL IN MORTAR AND OIL AGING

Figure 16 shows spectra of binder pastes with linseed oil (see 3.2.6.2, p. 56) compared to spectra of dried and fresh (M2ADL database) linseed oil film. IR vibrational assignments of raw linseed oil are listed in Table 31.

Spectrum of linseed oil shows signs of polymerization, there is a decrease in intensity of peak of isolated double bonds, meaning that some of the double-bonds have reacted to make cross-links. According to literature, triacylglycerols present in oil decompose in basic environment, giving rise to formation of fatty acids, which interact with calcium kations^(23; 48; 5; 4; 7). Nevertheless, neither free fatty acids nor calcium carboxylates have been identified in FTIR spectra⁽⁶⁸⁾.

Table 31: IR vibrational assignments of raw linseed oil⁽⁴⁷⁾

Band position [cm ⁻¹]	Intensity ^a	Assignment ^b
3011	m	$\nu(\text{C-H})=\text{CH}$
~2960	sh	$\nu_a(\text{C-H})\text{CH}_3$
2926	s	$\nu_a(\text{C-H})\text{CH}_2$
2855	s	$\nu_s(\text{C-H})\text{CH}_2$
1747	s	$\nu(\text{C=O})$
1658	w	$\nu(\text{C=C})$
1464	s	$\delta(\text{CH}_2)$

Band position [cm ⁻¹]	Intensity ^a	Assignment ^b
1418	w	wag(CH ₂)-CH ₂ -CO-O-
1378	m	wag(CH ₂)
1240	m	ν_a (C-C-O)
1164	s	ν (C-O)
1100	m	ν (O-CH ₂ -C)
723	s	γ -(CH ₂) _n -+wag(C-H)=CH

^a s: strong; m: medium; w: weak; sh: shoulder.

^b ν : stretching; δ : bending; wag: wagging; γ : rocking; _a: asymmetric; _s: symmetric.

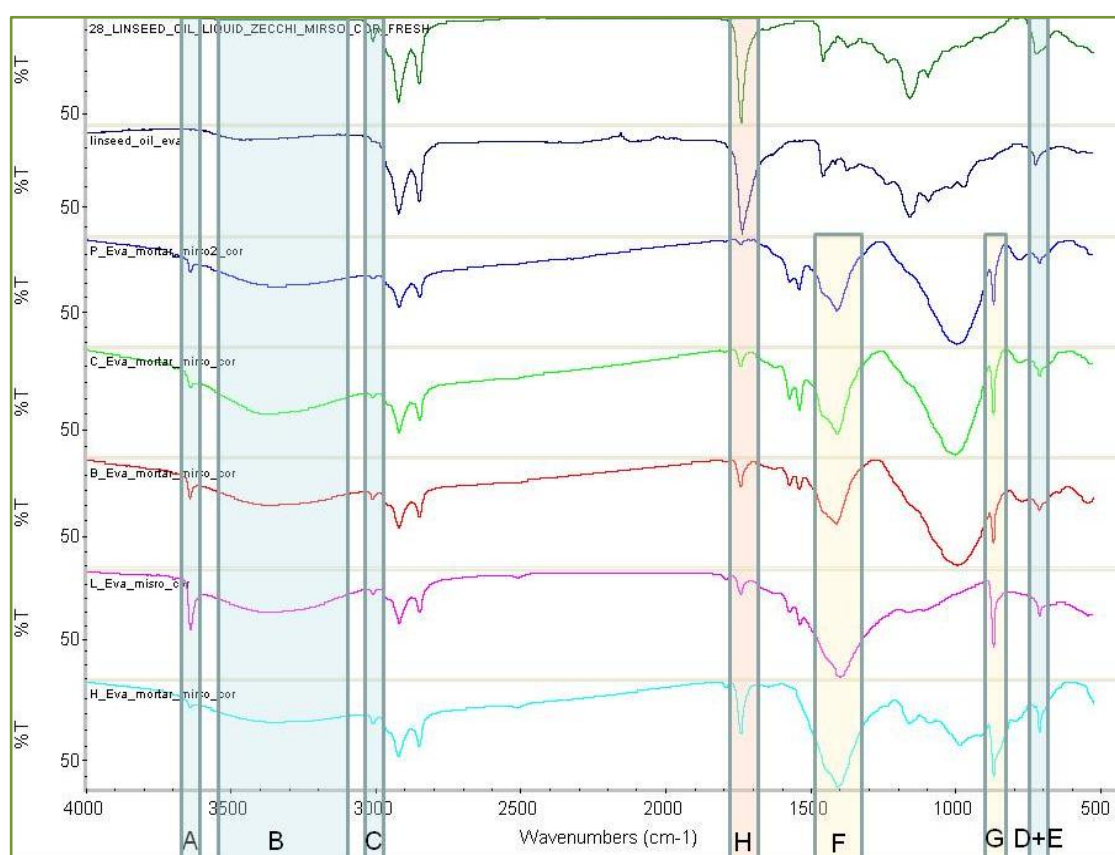


Figure 16: FTIR-ATR analysis of binder-oil pastes

Below some of the main bands are identified ^(47; 68):

- A- Sharp band at 3650 cm⁻¹ is indicative of the free -OH group stretching, i.e. not polymerised OH, probably humidity in the binder samples;
- B- Broad band centred at ca. 3430 cm⁻¹, due to hydroxyl groups which are bonded (polymerised), but it can be also humidity in the samples;

- C- 3011 cm^{-1} , alkene HC=CH stretching vibration, i.e. isolated double bonds, almost disappeared at polymerized linseed oil film;
- D- 723 cm^{-1} , long alkyl chain band $-(\text{CH}_2)_n-$, where $n \geq 4$;
- E- 712 cm^{-1} , $-\text{CO}_3$ bending vibration in calcium carbonate, D and E can be better distinguished in **Figure 17**;
- F- 1395 cm^{-1} , stretching vibration of CO_3 in calcium carbonate;
- G- 874 cm^{-1} , $-\text{CO}_3$ bending vibration in calcium carbonate;
- H- 1745 cm^{-1} , ester bond in triacylglycerol - if acids were present, the band would be lower at 1715 cm^{-1} , and if metal carboxylates were present, the band should be lower at around 1700 cm^{-1} (68).

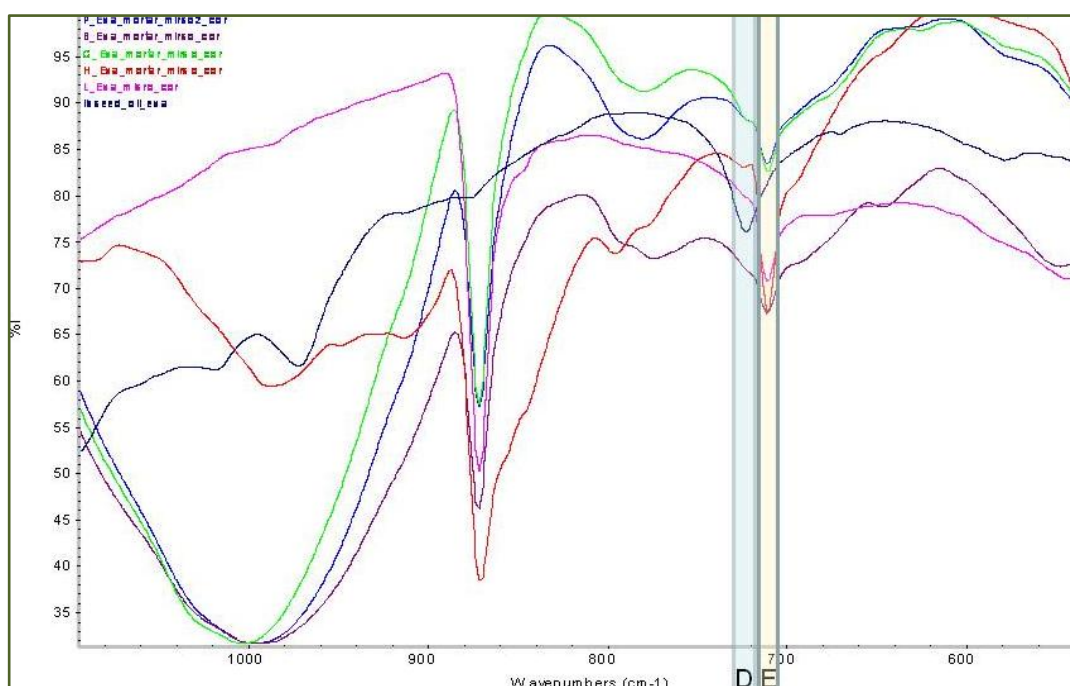


Figure 17: Linseed oil and binder pastes spectras, 500-1000 cm^{-1}

5 Discussion

5.1 THE EFFECT OF LINSEED OIL ON THE PROPERTIES OF FRESH MORTARS

The addition of linseed oil is improving fresh mortars' plasticity and workability. Modified mixtures have been generally more compact and easier to work with. Addition of 1% of linseed oil is slightly decreasing water-binder ratio while maintaining the same consistency. Nevertheless, the water-binder ratio of mortars with 3% addition of oil stayed at the same level as that of unmodified mortars. The explanation might be the fact that the mortars with 3% of oil paradoxically required higher amount of kneading water than the mortars with only 1% of oil. As the water was being added, mortar first became too compact and rather sticky, so that it required more kneading water compared to mortars with 1% oil addition to reach the same workability. Also Rovnaníková⁽⁴⁾ mentions decreased workability of fresh mortar with the oil addition. Explanation of this phenomenon could be that oil, being a hydrophobic substance, tends to soak into the solid phase, covering particles of binder and aggregate, and thus increases cohesion of binder paste. When oil is added in a little amount it improves mortar's consistency, but at higher additions of oil the increased cohesion results into very stiff mortar (particles are "glued" together) which consequently requires more kneading water to reach appropriate workability.

This explanation has been supported by preparation of hydrated lime and hydraulic lime mortar with high addition of oil - 5% by the weight of binder. Fresh mortars have been very compact, plastic and rather stiff. Increasing of water additions did not lead to increased plasticity, water was not fully mixed in mortar mass and the excess water has been being released out of the mass of mortar, making little pools in the mortar mixture. When determining the consistency by vibrations of a flow table, formation of fissures few centimetres long throughout the mass of mortar and consequent releasing of excess water has been observed. This phenomenon will later give an explanation of different effect of 1% and 3% oil addition on some properties of hardened mortars, which will be discussed later.

However, the different water-binder ratios did not affect the bulk density of fresh mortar; it stayed on the same level for all mortar mixtures.

Addition of linseed oil did have effect on setting of hydraulic mortars. While the initial setting time has not been affected by either 1% or 3% addition of linseed oil, the final setting time of mortars with oil addition has been retarded. It seems that oil does not play a role at an initial phase of setting, where there is enough water available for the hydration of hydraulic binder. But as the setting continues the water is consumed and the concentration of oil in a liquid phase increases, thus the oil droplets may block the pores and slow down the hydration ⁽⁴⁹⁾. In case of hydrated lime mortar the final setting time has not been affected as significantly, because the mechanism of hydrated lime setting and hardening is different than that of hydraulic limes, hydrated lime is air-hardening, i.e. water does not play as important role as it does in hardening of hydraulic binders, it is only a transport medium for carbon dioxide and does not directly participate in the hardening reactions.

5.2 THE EFFECT OF LINSEED OIL ON THE PROPERTIES OF HARDENED MORTARS

5.2.1 THE EFFECT OF LINSEED OIL ON THE MECHANICAL PROPERTIES OF MORTARS

Mechanical properties of mortars with 1% oil addition

Following figures show compressive strengths of mortars with 1% addition of linseed oil measured after 3 month (Figure 19) and 1 year (Figure 18) of curing.

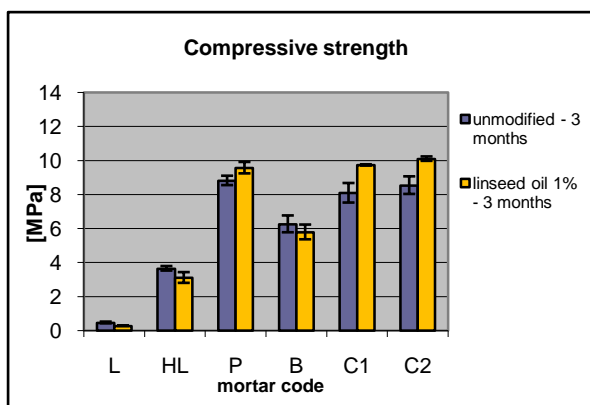


Figure 19: Compressive strength of mortars with 1% of linseed oil compared to unmodified mortars at the age of 3 months

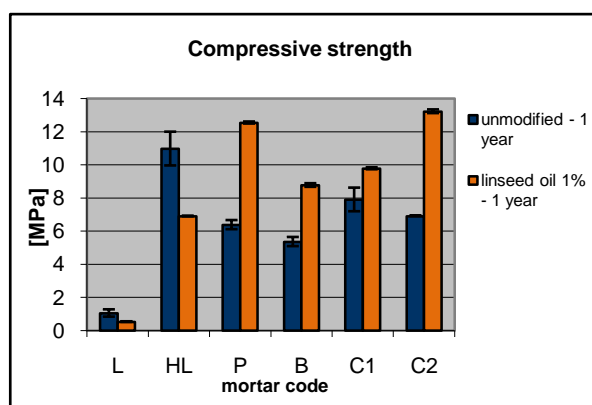


Figure 18: Compressive strength of mortars with 1% of linseed oil compared to unmodified mortars at the age of 1 year

As seen in Figure 19, oil in 1% concentration did not have significant effect on the compressive strength tested at 3 months. This is in agreement with the study of Justnes et al. ⁽⁴⁸⁾, who tested the effect of oil on cement mortar (0,5%, 1% and 1,5% by the weight of

cement), and did not observe significant changes of strengths after 1 month of curing. Albayrac et al.⁽⁶⁹⁾ studied the effect of using sunflower oil as grinding aid on the strength of cement and found a 50% decrease in compressive strength after 1 month of curing. After 1 year strength of unmodified mortars in present study stayed at the same level (except for hydraulic lime mortar which shows multiple increase), while the strength of modified mortars is increased by 30% in average. Modified mortars containing pozzolan (codes P, B, C1 and C2) developed 20%-50% higher compressive strengths comparing to the reference mortars.

Flexural strength development of mortars with 1% of oil compared to unmodified mortars is showed in **Figure 20**. All mortars were tested at the age of 1, 3 and 12 months. 1% of oil did not have effect on the flexural strength of hydrated lime mortar (code L) – strength develops gradually in time without dependence on the oil addition.

Changes of strength of both modified and unmodified hydraulic mortars at the age of 1 and 3 month are not of statistical importance.

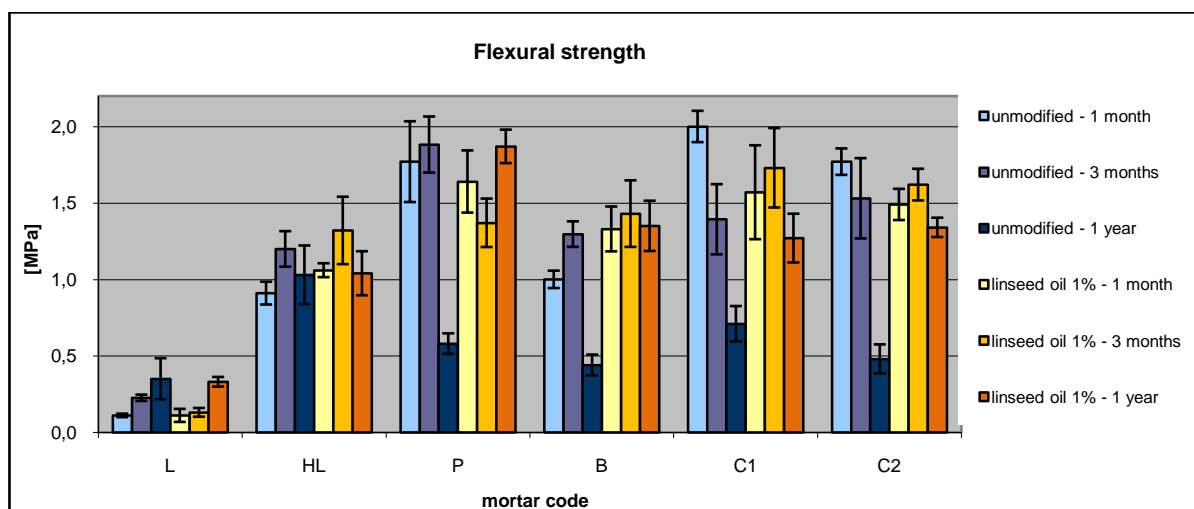


Figure 20: Flexural strength of mortars with 1% of linseed oil tested at different ages

However, as seen in the graph above, the flexural strength of unmodified mortar rapidly decreased after 1 year. Only hydrated lime mortars showed increased strength also after 1 year of curing, showing that the carbonation process has been still running. The decreased strength of hydraulic mortars can be caused by formation of microcracks due to drops in humidity in the room where the specimens were stored. Specimens were kept in controlled environment (20°C, (65±5)%RH) only during the first 3 months of curing,

afterwards they were left in ambient conditions ((25±5)°C, 40%-80%RH). The reason of increased strength of both modified and unmodified hydrated lime mortars (codes L and LO₁) might be, as mentioned before, that their curing is not that affected by the amount of humidity in the air as are the hydraulic mortars, which need water to form the C-S-H phases, while for hydrated lime mortar water vapour is a transport medium for carbon dioxide. Since neither in situ the ideal humidity level can be ensured, it is an encouraging finding that the specimens with 1% of oil maintained their flexural strength on the same level, on contrary to the unmodified mortars.

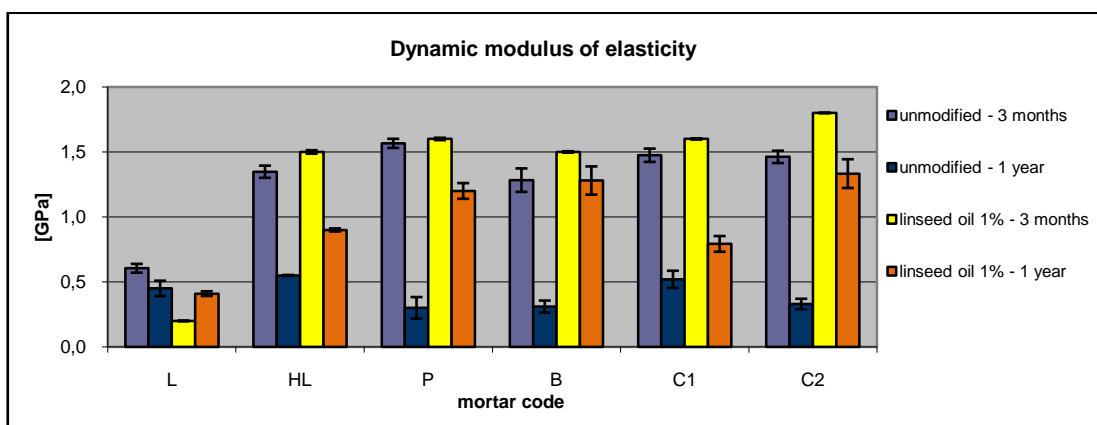


Figure 21: Dynamic modulus of elasticity of mortars with 1% oil addition

Values of dynamic modulus of elasticity (E_{dyn}) are similar to those of flexural strength. At the age of 3 month E_{dyn} of mortars with 1% oil is on the same level as the unmodified mortars, while after 1 year values of E_{dyn} are decreased. Dynamic modulus of elasticity of mortars with oil is not as much decreased as that of unmodified mortars. Unmodified mortars showed decrease by 60%, while mortars with oil only by 30%.

Based on the results of mechanical properties, it seems that linseed oil in 1% addition is protecting mortars from drying out thus enabling them to cure for a longer time.

Results of compressive strength are in agreement with the study by Rovnaníková⁽⁴⁾, who also observed increased compressive strength of lime mortars when linseed oil was added. Vikan and Justnes tested effect of oil on cement mortar⁽⁴⁹⁾. In their study, they found trends opposite to those in the present study. They found compressive strength of cement mortar with oil addition approximately 30% lower than that of the reference mortar after 3 years of curing. The reason of different results might be partially caused by the different type of mortar studied and by different mixing of oil in mortar (oil was firstly mixed with

water with the help of emulgator (lignosulphate) and then added to dried mixture, while in the present study oil was mixed with dry constituents first), which might play an important role. Authors suggest that the explanation of their lower strengths obtained might be either lower degree of cement hydration due to the blocking of micro-pores by oil droplets, or the fact that oil oxidizes as the oxygen diffuses over time through the sample to form solid saturated fatty acid. Furthermore, authors propose that carboxyl acids derivatives, occurring during decomposition of oil in basic environment and coordinating strongly with Ca-sites, might alter the hydration as they are adsorbed on cement particles by both delaying the hydration and changing the morphology of hydration products. In the present study no carboxylic acid derivatives were identified in samples of binder-oil-water pastes by means of FTIR-ATR (see sections 3.2.6.2 on p. 56 and 4.6 on p. 71). In order to support their theory, Vikan and Justnes⁽⁴⁹⁾ have measured the amount of chemically bounded water, i.e. the degree of hydration. Nevertheless, they found no trends between degree of hydration and amount of oil added into mortar. This means that their finding of decreased strength of mortars with oil is not caused by the lower degree of hydration.

Mechanical properties of mortars with 3% oil addition

The effect of 3% addition on mortars' mechanical properties is not an increased effect of 1% addition, but the opposite. Mechanical characteristics were significantly reduced when 3% of linseed oil was added. Following figures show compressive (**Figure 22**) and flexural (**Figure 23**) strengths of mortars with 3% addition of oil compared to mortars with 1% addition and unmodified, tested after 3 months of curing. Strengths of mortars with 3% of oil were decreased by approximately 65%.

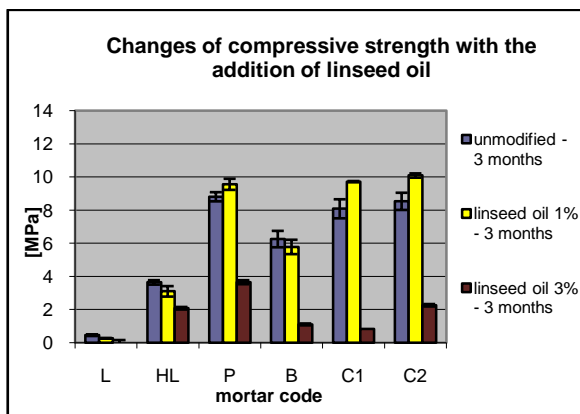


Figure 22: Changes of compressive strength with the addition of linseed oil

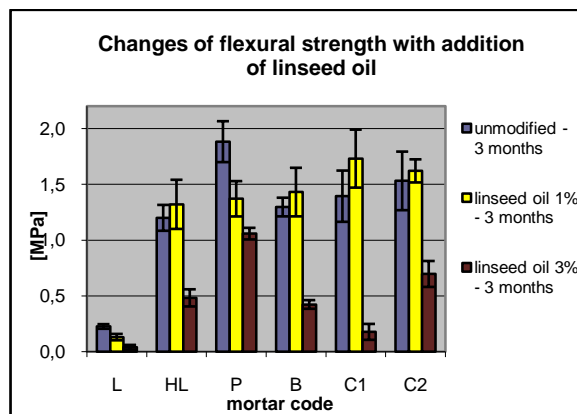


Figure 23: Changes of flexural strength with the addition of linseed oil

Theoretically, decreased strength of mortars with 3% addition of oil might be caused by various reasons, such is lower degree of carbonation, lower degree of hydration of hydraulic components and/or increased porosity of mortars with oil. Oil can be also limiting contact between grains of aggregate and binder phase. We will now discuss some of the possible factors.

First theory is that oil as a hydrophobic substance in mortar is limiting water vapour with dissolved carbon dioxide to penetrate into the mortar structure and thus causing decreased carbonation. The result of water vapour permeability test did not show lower permeability of hydrated and hydraulic mortars with the oil addition. Neither Rovnaníková⁽⁴⁾ found decreased water vapour permeability of hydrated lime mortar in her study. Justnes⁽⁴⁸⁾ studied the effect of linseed oil on the cement mortar, which has different porosity than hydrated lime mortars, but however he did not find reduced vapour diffusion coefficient of mortars with the oil addition.

The rate of carbonation was tested by phenolphthalein method. Phenolphthalein is a acidobasic indicator changing its colour depending on the pH. It has purple colour when $\text{pH} > 8,5$, like in a fresh mortar which is strongly basic, and it is colourless when $\text{pH} < 8,5$, e.i. in a carbonized mortar. As seen in Figure 24 below, mortars with 3% addition of oil (bottom) are far more carbonized than unmodified mortars, so lower carbonation is not a cause of the decreased strength of 3% oil-mortars.

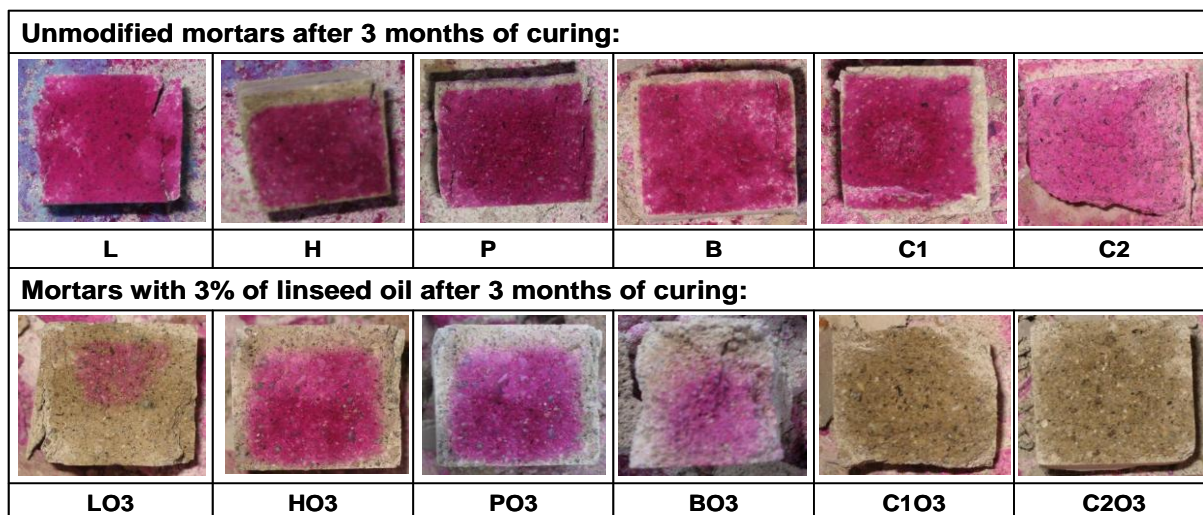


Figure 24: Rate of carbonation - phenolphthalein method

5.2.2 THE EFFECT OF LINSEED OIL ON MORTARS' POROSITY

Another theory which might be explaining the decreased strength of mortars with 3% addition of oil is that the decreased strength might have been caused by higher porosity of modified mortars. Nevertheless, results of total open porosity measurement did not show significant differences between unmodified mortars and mortars with 3% oil addition. On the other hand, as seen from the diagram of pore size distribution measured by mercury intrusion porosimetry (Figure 25), there are obvious differences between mortars with oil and unmodified mortars.

Pore size distribution of all tested mortars with 3% of oil is shifted towards bigger pore sizes. Also the calculated average pore radius indicates that mortars with 3% of oil have much bigger pores. It should be pointed out that mercury intrusion porosimetry does not measure the actual radius of the pore, but the radius of entrance into the pore, as the pressure needed to push mercury inside the pore is defined by the size of its entrance and remains the same while the whole volume of a pore is being filled. However, the mercury intrusion porosimetry gives an idea about the pore size distribution. So it can be stated that mortars with 3% of oil have seem to have higher proportion of big pores while maintaining the same level of total porosity, which might affect their mechanical properties. Furthermore, many big pores of size of about 1 mm can be observed in structure of 3% oil-mortars even by naked eye, these can be responsible for the decreased strength.

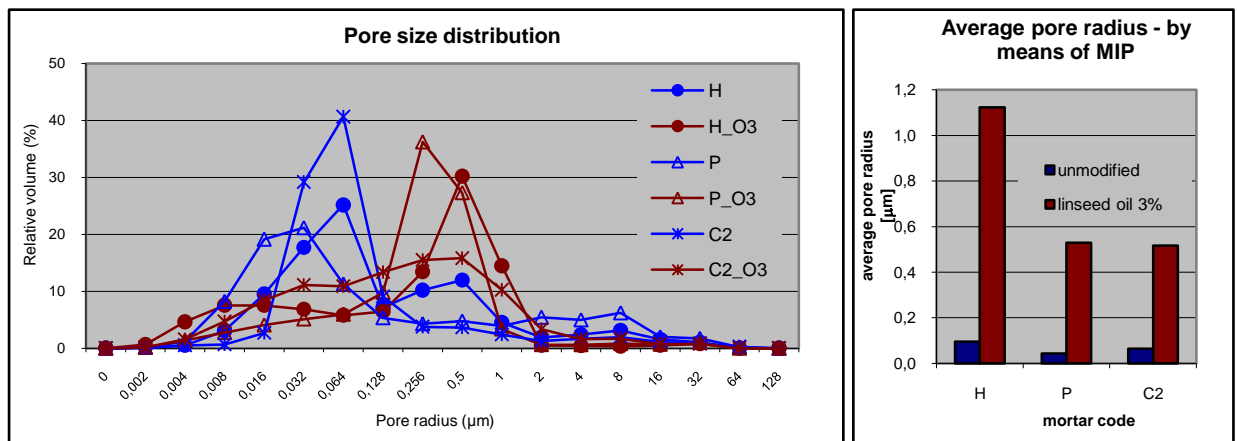


Figure 25: Pore size distribution of mortars with 3% addition of oil compared to unmodified mortars

Figure 26 (right): Average pore radius of mortars with 3% of oil compared to unmodified mortars

The higher proportion of big pores in mortar with 3% of oil is a result of its properties in a fresh state. As it was said before, in a mortar with oil addition the particles of binder covered with oil tend to coagulate, in consequence the excess water is not adsorbed by the particles of binder is being separated from the mass of mortar. The accumulation of water results in the occurrence of big pores in the hardened mortars. The effect of coagulation of binder with oil is not that strong when only 1% of oil is added, so the fresh mortar mixture does not require as much water to obtain desired workability. The fact that in mortar with little amount of oil is no excess water accumulated in the structure is possible to observe on the pore size distribution – mortars with 1% of oil has smaller pores comparing to unmodified mortars (see **Figure 27**). Both modified and unmodified hydrated lime mortars (codes L and LO₁) have generally bigger pores than hydraulic mortars, it is done by the different morphology of hydrated lime mortar (crystals of CaCO₃ in case of hydrated lime mortar compared to hydrated CSH phases of hydraulic mortars)^(22; 70), however the trend is the same, hydrated lime mortar with oil (code LO₁) has its pore size distribution slightly shifted towards smaller pores compared to the unmodified mortar (code L). Average pore ratio (**Figure 28**) of all mortars with 1% oil addition is slightly lower than that of unmodified mortars; in consequence the total open porosity will be decreased.

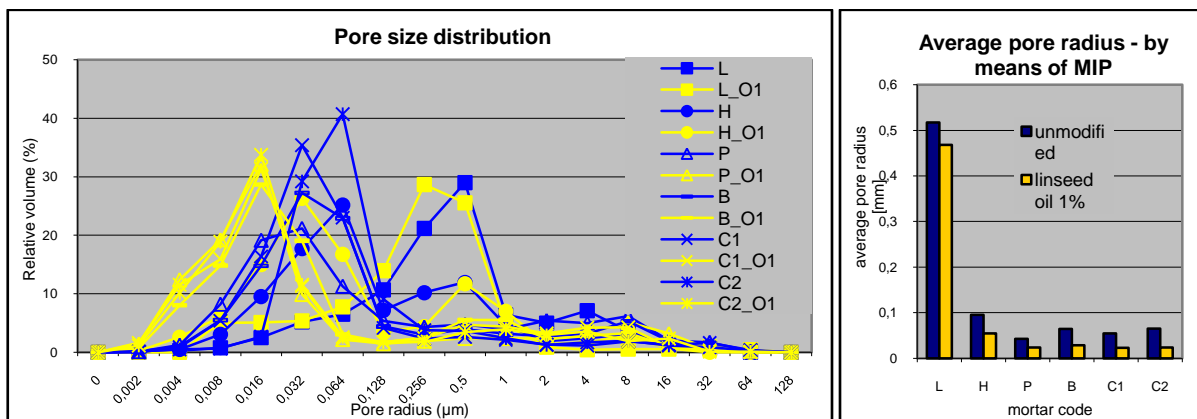


Figure 27: Pore size distribution of mortars with 1% addition of oil compared to unmodified mortars

Figure 28 (right): Average pore radius of mortars with 1% of oil compared to unmodified mortars

Changes of open porosity depending on the concentration of oil in mortars tested at the age of 3 months are shown in Figure 30. Values of open porosity of mortars after 3 months of curing are in accordance with water-binder ratio (Figure 29), confirming that higher content of water in the fresh mortars results in higher porosity of hardened mortars. As seen in the graph, porosity of mortars with 1% addition of linseed oil is slightly lower than that of unmodified mortars, while the porosity of mortars with 3% oil addition is slightly higher than the porosity of mortars with only 1% of oil.

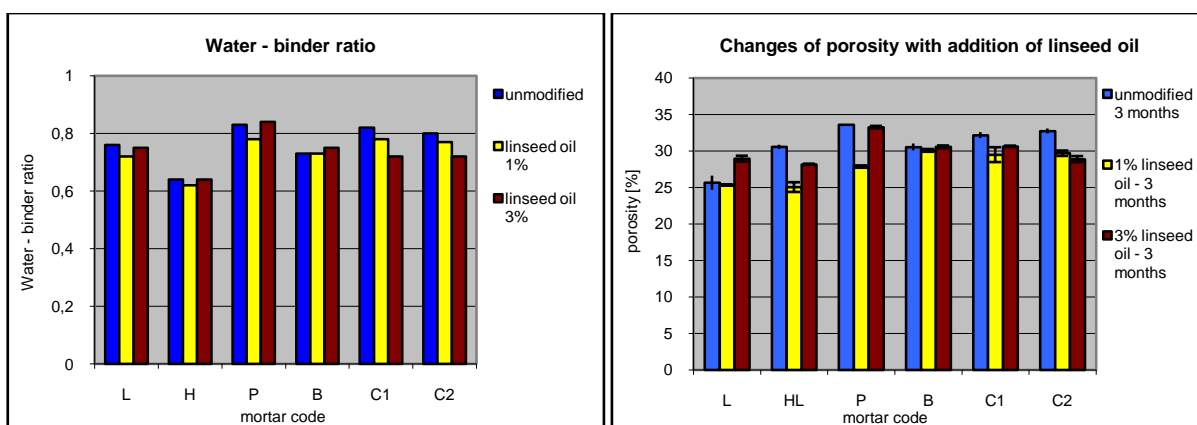


Figure 29 (left): Water-binder ratio of mortars with different amount of oil

Figure 30: Open porosity of mortars with different amount of oil

There is also a difference in the development of porosity in time. Porosity of the majority of unmodified mortars (those mortars containing pozzolan, codes P, B, C1 and C2) stays at the same level as at the age of 3 months, while the porosity of all types of mortars

with 1% of oil develops in time to reach values of unmodified mortars in 1 year, as seen in **Figure 31**. Porosity of mortars with 1% addition of oil develops for a longer time than that of unmodified mortars, confirming that humidity is kept in mortar and thus that the curing of mortars with oil is in progress for a longer time than that of unmodified mortars.

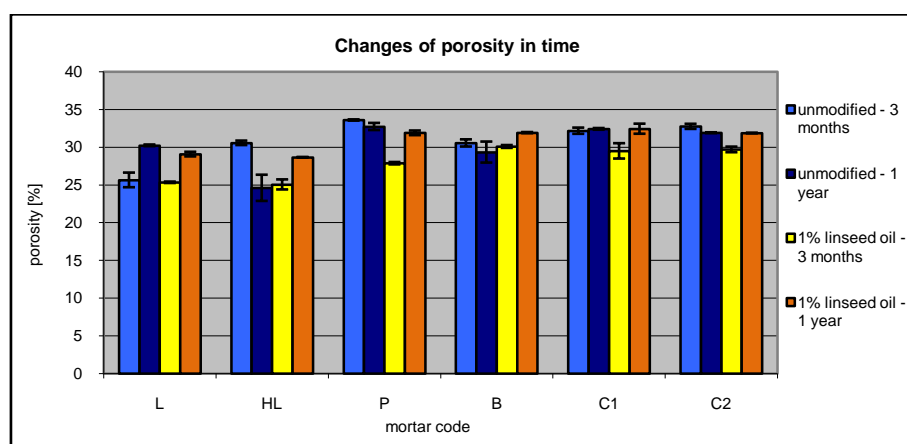


Figure 31: Changes of porosity in time

5.2.3 DISPERSION OF OIL IN THE MORTAR STRUCTURE

Samples of mortars with the addition of oil have been observed under UV light, it was supposed that the area where oil accumulates would be visible due to oil's fluorescence. On the picture of pozzolanic mortar with 3% addition of oil (**Figure 32**) some light areas can be observed, but since the same have been observed also in a sample of the same type of mortar, but with no oil (**Figure 33**), it must be concluded that those lightning areas are not due to the presence of oil. The same observations were done on the samples of all mortar types. The whole picture of the sample with 3% oil addition seem to be generally lighter, though the picture was taken under the identical conditions, with the same microscope and camera setting was used, which might mean that the oil does release fluorescence, but that the oil is very well dispersed in the structure or at least that it is not accumulated in areas big enough to be distinguishable by the microscope.

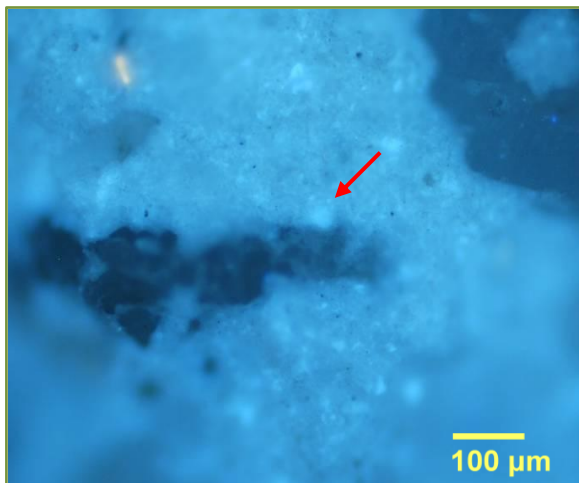


Figure 32: Pozzolanic mortar with 3% addition of linseed oil (code PO₃), observed under UV light

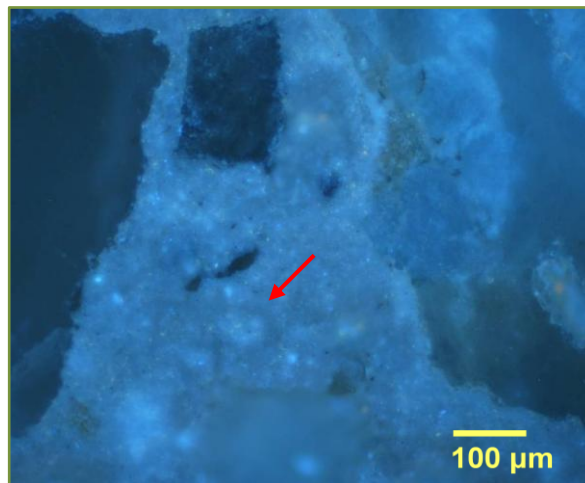


Figure 33: Unmodified pozzolanic mortar (code P), observed under UV light

However, samples made of binder mixed with oil were prepared and observed under microscope with UV light after two weeks in order to learn how intense is the fluorescence of linseed oil and accordingly whether it would be possible to observe the areas of oil accumulation, if there were any, in mortar samples at all.

As can be seen in **Figure 34**, hydrated lime-oil paste (down-right corner) has a very strong fluorescence. For a comparison reason, **Figure 35** shows the same samples observed under the normal light. As a result it can be stated that oil is very well dispersed in mortar structure, at least as well as the resolution of microscope allow to distinguish. Accordingly, the fact that tested mortars with the oil addition did not show a higher coefficient of variability than the unmodified mortars confirms the assumption that oil is very well dispersed in the mortar structure (see **Table 16-18**, p. 61).



Figure 34: Fluorescence of oil-lime paste compared to lime without oil and lime with applied oil drop

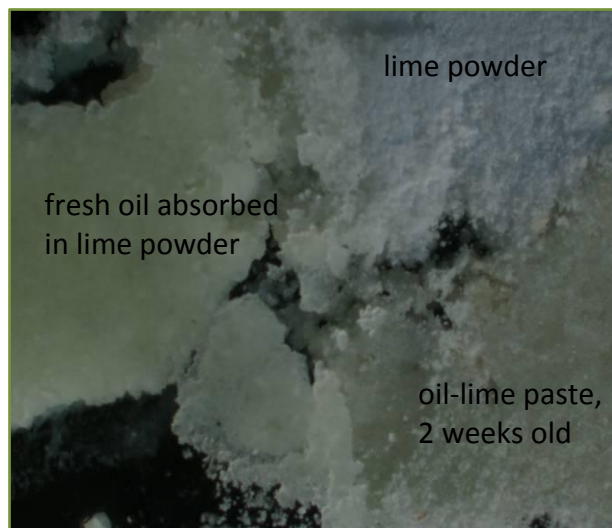


Figure 35: Oil-lime paste compared to lime without oil and lime with applied oil drop, observed under normal light

It has been observed that the fresh oil has a different colour of its fluorescence than the hydrated lime-oil paste. It could be explained by the chemical reaction that happens in a basic environment (see section 2.5.2.2.3, p.38), the triacylglycerols present in oil decompose to form fatty acids, which might have a different fluorescence.

Mortars structure has been studied more in detail by means of scanning electron microscopy, the observations will be discussed later.

5.2.4 THE EFFECT OF LINSEED OIL ON CAPILLARY ABSORPTION

As expected, linseed oil is decreasing material's ability to absorb water and this effect is the most apparent on water absorption through capillarity. Following figures show capillary coefficient of mortars tested after 1, 3 and 12 months. It can be seen that already 1% of oil is significantly decreasing capillary absorption coefficient and 3% concentration is making material to be almost hydrophobic.

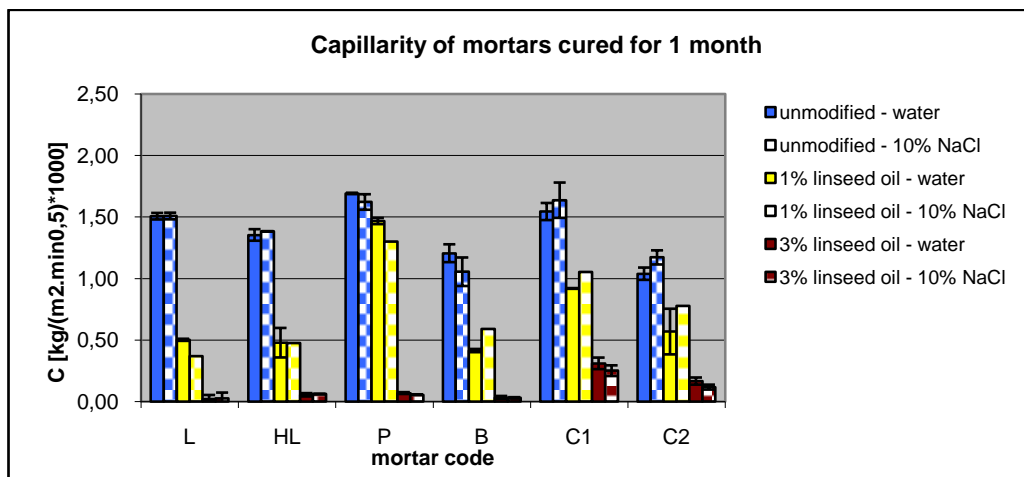


Figure 36: Capillarity of mortars cured for 1 month

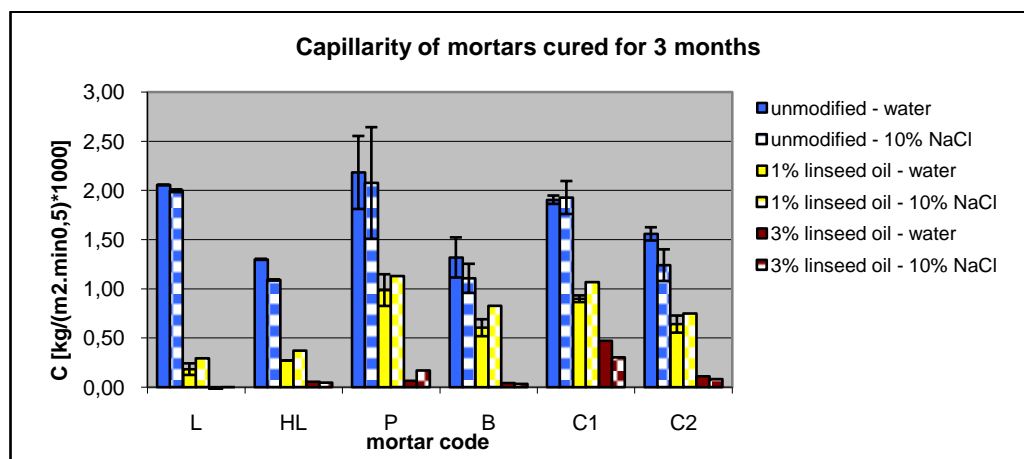


Figure 37: Capillarity of mortars cured for 3 months

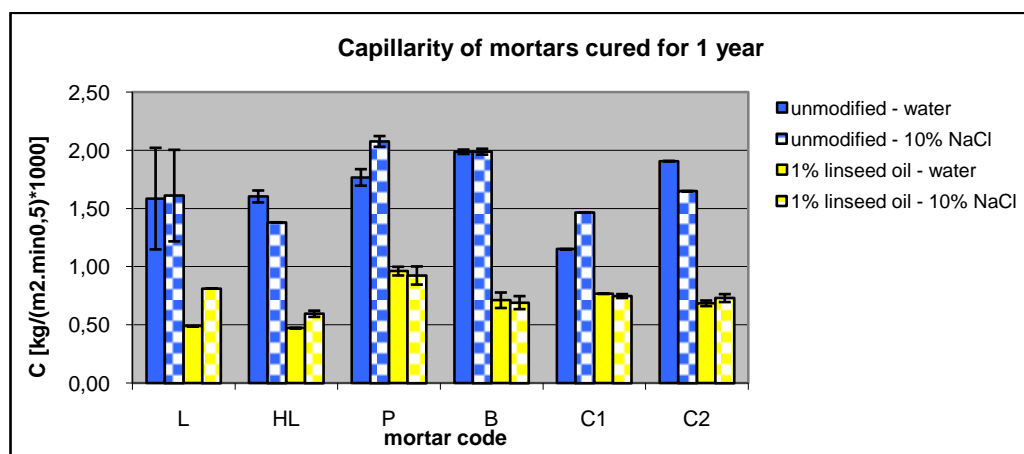


Figure 38: Capillarity of mortars cured for 1 year

As can be seen in the graphs above, the addition of only 1% of oil is already decreasing capillarity coefficient by 40-70%, and the 3% addition results in decrease of even more than 99% (see Figure 39). Hydrated lime mortar (code L) and mortar with brick dust (code B) were the most hydrophobic; their water absorption through capillarity was nearly zero.

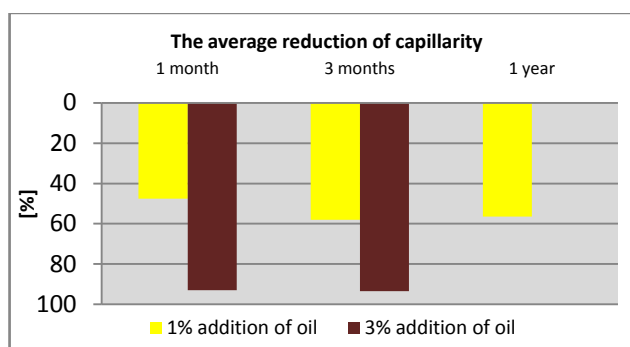


Figure 39: Average reduction of the coefficient of liquid absorption

It is been also observed that the capillarity does not change in time and that the capillarity of salt solution is not significantly different than that of water, showing that the higher density, ionic power and surface tension of the salt solution does not have significant effect on the capillarity.

Now let's take a closer look on the capillarity mechanism. Capillary rise is a phenomena resulting from the competition between adsorption forces to polar solid surface and cohesive forces among water molecules. If the adsorption forces to material surface are high enough, water can rise even against the gravity.

Capillarity may be affected by:

- Contact angle that liquid makes on a solid surface;
- Capillary pore radius;
- Pores' shape and connectivity.

The effect of oil addition on the factors listed above will be discussed in detail.

Capillary tension p_c in a cylindrical pore can be expressed by:

$$p_c = 2 \cdot \sigma \cdot \cos\theta / r \quad [\text{Pa}] \quad (10)$$

To describe the maximum capillary height for the vertical transport the influence of gravity and viscous resistance has to be considered since they are in opposition to the capillary force:

$$H_{max} = 2 \cdot \cos\theta / r \cdot \rho \cdot g \quad [\text{m}], \quad (11)$$

where r is the capillary radius [m], θ is the contact angle, σ is the surface tension of the water [$\text{N}\cdot\text{m}^{-1}$], ρ is the water density [$\text{kg}\cdot\text{m}^{-3}$], and g is the gravity force [$\text{m}\cdot\text{s}^{-2}$] ⁽⁶¹⁾.

1. contact angle

Contact angle that liquid makes on a solid surface is defined by the surface energy of the solid. As can be seen from the above equations, if the $\theta = 90^\circ$, $p_c=0$, and the adsorptive and cohesive forces are equal. If $\theta > 90^\circ$, capillary depression will occur and water will not enter the pore system unless external pressure is applied. Only if $\theta < 90^\circ$, adsorptive forces exceed cohesive forces resulting in capillary absorption ⁽⁶¹⁾.

As shown in section 4.4.6, p. 66, contact angle of water drop on a surface of binder pastes is significantly increased for all mortars, i.e. the mortars are more hydrophobic, so the capillary rise is decreased. The hydrophobicity of mortars with the oil addition is probably the most significant factor causing the decreased water absorption, however there are also other factors which might play a role.

2. capillary pore radius

Since only water molecules close to the mineral surface (pore wall) can contribute to absorption, smaller pores show a larger capillary tension. It is then valid that the smaller is the capillary pore radius, the higher will be the capillary rise.

To study pore system of a material, mercury intrusion porosimetry (MIP) is a generally accepted technique. Even though it has some disadvantages, i.e. assuming cylindrical shape of pores, the pores are not equally accessible to mercury, and in fact it measures the diameter of the entrance to the pore not the actual pore size, MIP gives an indication about the pore size distribution in the material.

As it was already shown in **Figure 26**, p. 81, the 3% addition of linseed oil is increasing average pore radius measured by means of MIP approximately ten times. Assuming some

constant proportion of pores of the capillary shape, the result is in the agreement with the theory, i.e. the capillary rise is inversely proportional to the capillary pore radius (Equations 10 and 11), thus the decrease in capillarity of mortars with 3% oil addition might be caused (besides other factors) by increased average pore radius.

The situation is not that clear for mortars with only 1% addition of linseed oil. Average pore radius of mortars with oil is slightly lower than that of unmodified mortars and as it can be seen in the pores size distribution (**Figure 27**, p. 82), mortars with 1% of have all smaller range of pores compared to unmodified mortars, so consequently, if only pore radius was concerned, the capillarity should be increased. It could mean that the pore sizes do not have a significant effect on capillarity, i.e. the effect of hydrophobicity of material plays much more important role than the pores' sizes. Alternatively, observed phenomena can be explained by the effect of absorption rate. The general equation describing transport mechanism can be derived from the Pouiseuille and La Place equation ⁽⁶¹⁾:

$$\Delta h/\Delta t = [r^2/8.\eta.h] (2.\sigma.\cos\Theta / r + \rho.g.h_0 + \rho.g.h.\cos\varphi), \text{ where} \quad (12)$$

$\Delta h/\Delta t$ is the capillary absorption rate [m.s^{-1}];

h is the distance reached by water in the capillary [m];

r is the capillary radius [m];

η is the water viscosity [Ns.m^{-2}];

σ is the surface tension of the water [N.m^{-1}];

ρ is the water density [kg.m^{-3}];

g is the gravity force [m.s^{-2}]

h_0 is the height of water above entrance pore [m];

Θ is the contact angle between water and the solid surface; and

φ is the angle with vertical direction.

The last term of the equation turns negative for φ angles larger than 90° , i.e. for capillaries that are not vertical and the previous term turns constant for horizontal transport. Thus, smaller capillaries will give rise to higher capillary rise, but larger capillaries will provide faster water absorption rate due to their larger cross-section.

According to the previous equation, the capillary rate of pores smaller than $1 \mu\text{m}$ is extremely slow, so there is practically no rise. Furthermore, in pores smaller than $0,1 \mu\text{m}$ capillary condensation takes place, which is in fact a spontaneous formation of ordered

water structures adsorbed on a mineral surface due to its electrostatic influence ⁽⁶¹⁾. In small pores (nanopores) the influence of opposite pore walls may reach through the whole pore so that the water is not in a liquid or vapour phase, but only in a phase of ordered structure, which is energetically favoured ⁽⁶¹⁾. Thus, according to Wendler and Charola, water will move by capillary transport only in pores in range from 10 μm to 1 mm ⁽⁶¹⁾. Barsottelli et al. ⁽⁶²⁾ suggest that capillary rise is most affected by the pores with radius around 1 μm .

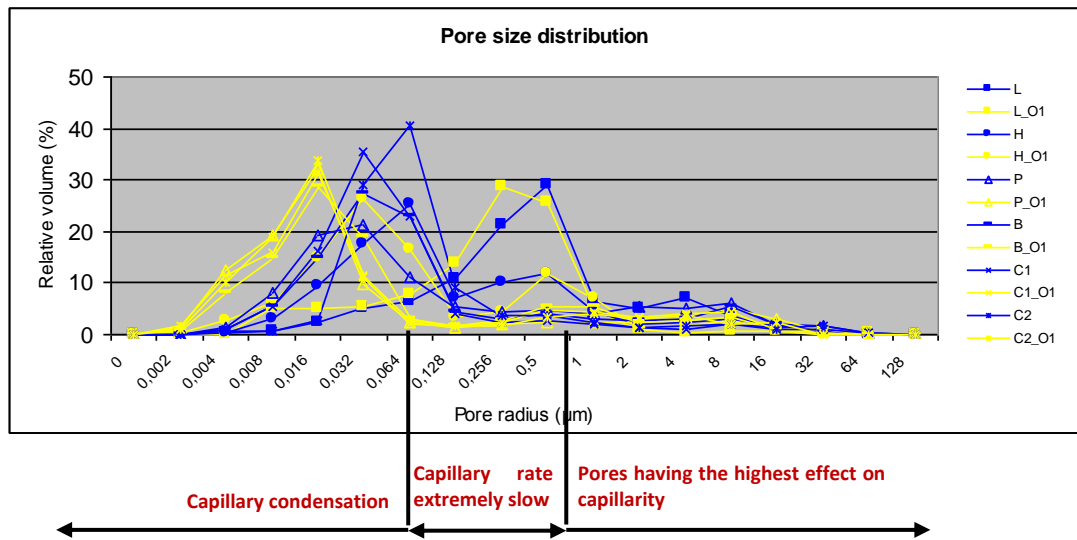


Figure 40: Pore size distribution of mortars with 1% of oil compared to unmodified mortars and the effect of pore ratio on capillary rise

In the following Figure 41-46 pore size distribution within 1 μm and 128 μm is showed, which should be the range of pores most affecting the capillarity. It must be nevertheless kept in mind that the pore size distribution is actually not showing pore ratios distribution but the distribution of pores' entrances, thus the evaluation is very rough. However, it can be seen that the unmodified mortars of the majority of mortar types have the highest proportion of pores in this range, followed by mortars with 1% of oil and the mortars with 3% of oil, in the same order as the capillarity decreases, suggesting that the capillarity might be indeed affected mostly by the pores of ratio bigger than 1 μm .

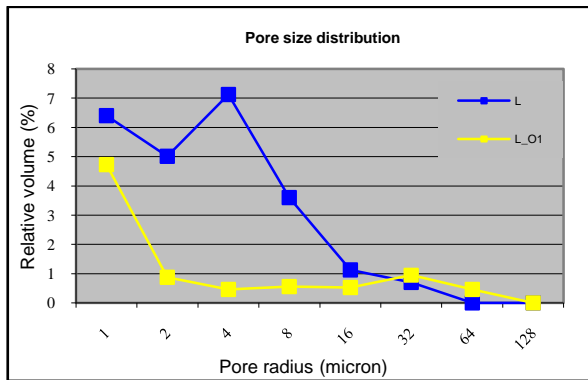


Figure 41: Pore size distribution of hydrated lime mortars

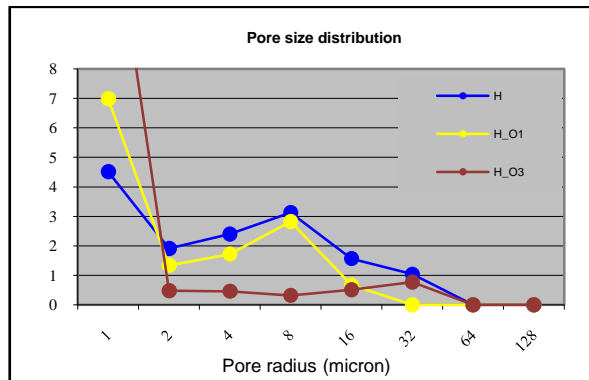


Figure 42: Pore size distribution of hydraulic lime mortars

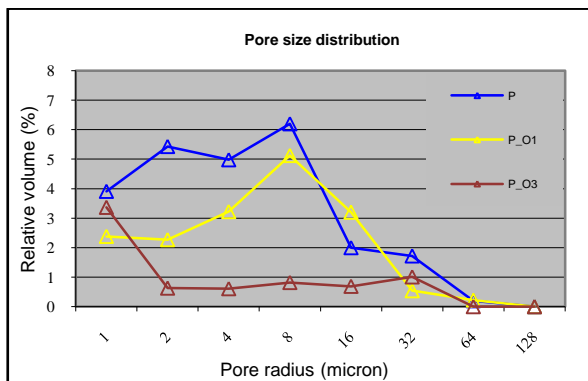


Figure 43: Pore size distribution of pozzolanic mortars

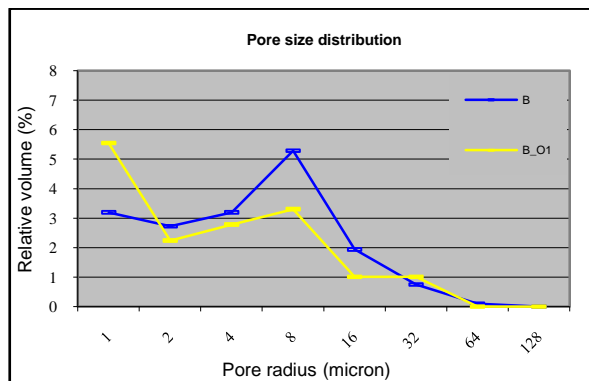


Figure 44: Pore size distribution of mortars with brick dust

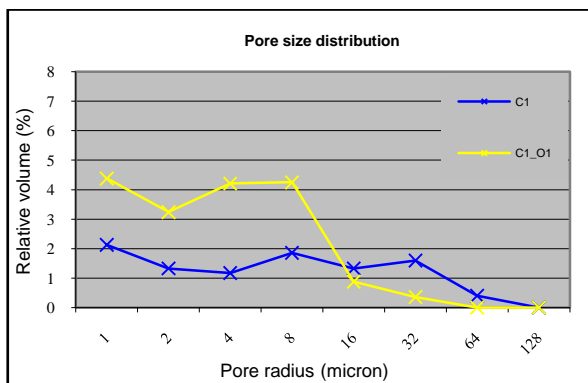


Figure 45: Pore size distribution of mortars with 5% of cement

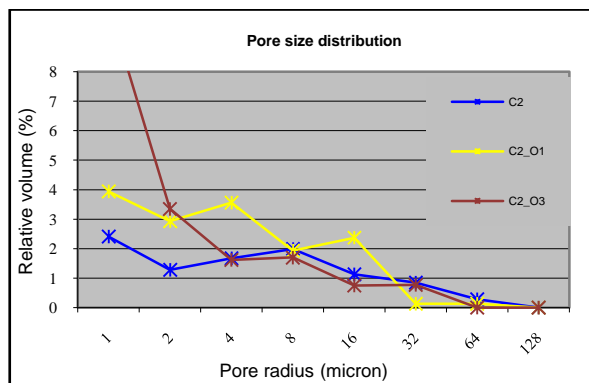


Figure 46: Pore size distribution of mortars with 10% of cement

3. pores' shape and connectivity

Finally, the last issue having effect on capillarity is the shape and connectivity of pores. The mathematical models describing the capillarity consider material to be composed of parallel vertical capillary tubes. Since the real material pore structure is of course far from the mathematical model, the absorption through capillarity will be affected by the pores' shape, i.e. the proportion of capillary pores to the cylindrical pores as the two extreme possible shapes, and the pores connectivity. The connectivity between pores can be affected by the pore structure, as well as by the effect of the oil addition into the mortar. Oil is first of all making material hydrophobic, thus the whole water movement mechanism is limited, but it is not clear whether oil is covering pores walls, filling some pores, blocking the capillaries or whether it is just evenly dispersed in the structure, without a tendency to accumulate in dependence on pore system.

In order to understand better the mortar structure and the effect of the addition of linseed oil on it, mortars samples have been observed under the scanning electron microscopy (SEM). The resolution of SEM images does not allow observing pores' shapes in detail, however there were general differences in the appearance of the mortars. As seen in **Figure 49-61**, unmodified mortars have sharp clear structure, while the mortars with oil addition have all smoother texture. In unmodified hydraulic mortars (codes H, P, B, C1 and C2) crystals have been observed. These crystals are probably various calcium silicates and aluminates and are not present in hydrated lime mortar (code L) because it contains only calcium carbonate. EDX analyses made in the points marked in figures below are listed in **Table 32**. In mortars with the oil addition those crystals have not been observed anymore.

The SEM observation suggests that there is a thin oil film evenly spread in mortars structure, covering the grains of binder and it seems that it is also limiting the formation of crystals in hydraulic mortars.

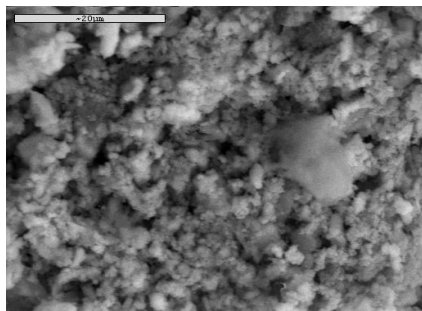


Figure 47: Hydrated lime mortar (code L)

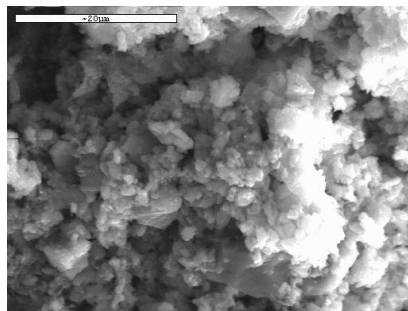


Figure 48: Hydrated lime mortar with 1% oil addition (code LO₁)

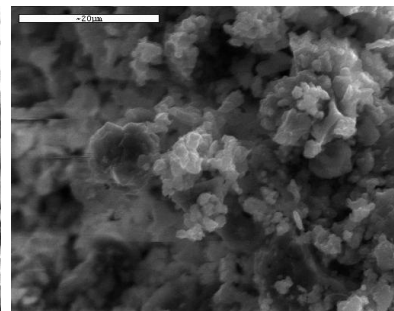


Figure 49: Hydrated lime mortar with 3% oil addition (code LO₃)

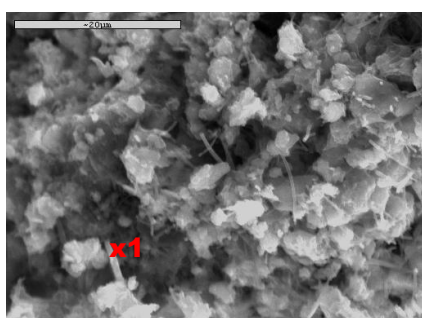


Figure 50: Hydraulic lime mortar (code H)

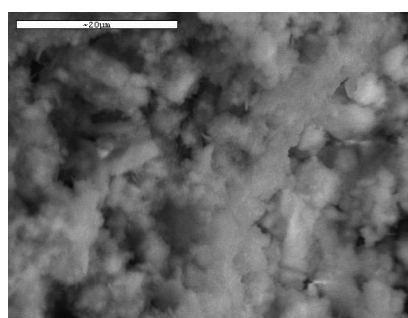


Figure 51: Hydraulic lime mortar with 1% oil addition (code HO₁)

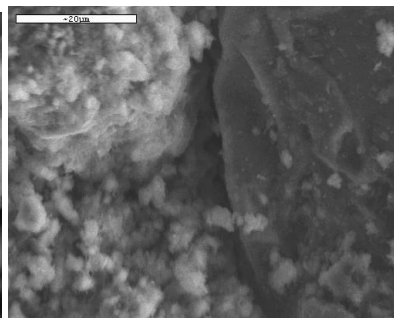


Figure 52: Hydraulic lime mortar with 1% oil addition (code HO₃)- oil does not seem to be accumulated at the edge of aggregate grain (on right)

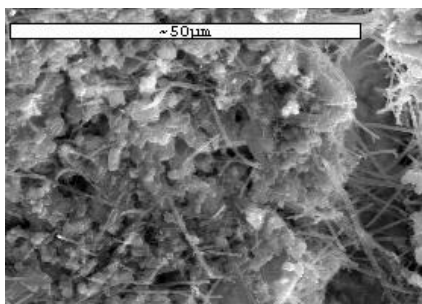


Figure 53: Pozzolanic mortar (code P)

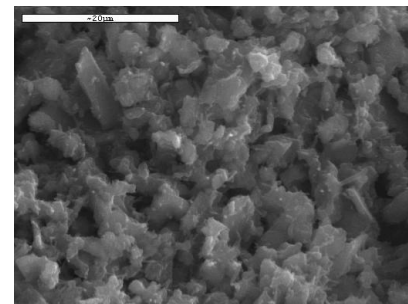


Figure 54: Pozzolanic mortar with 3% oil addition (code PO₃)

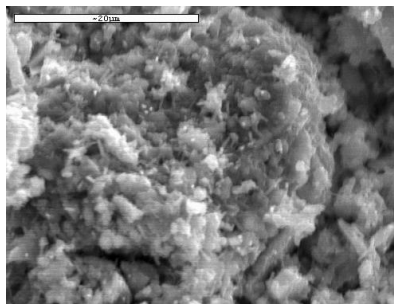


Figure 55: Pozzolanic mortar with 3% oil addition (code PO₃)

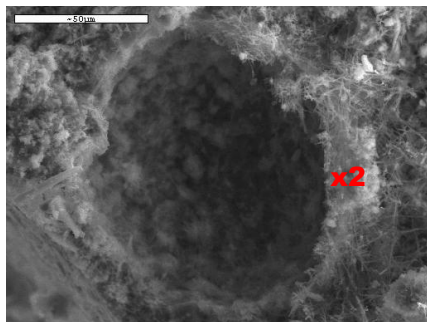


Figure 56: Big pore in the mortar with brick dust (code B)

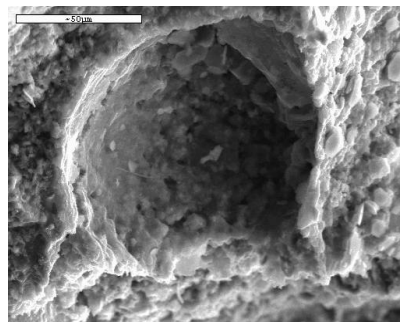


Figure 57: Big pore in a brick dust mortar with 1% oil addition (code BO₁)-smoother edges of the pore

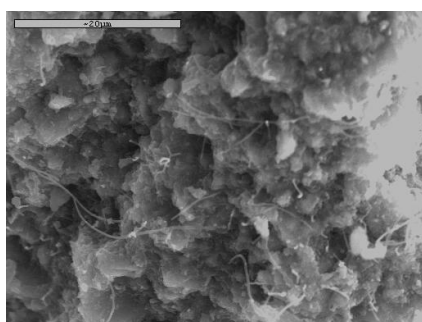


Figure 58: Cement mortar (5% of cement, code C1)

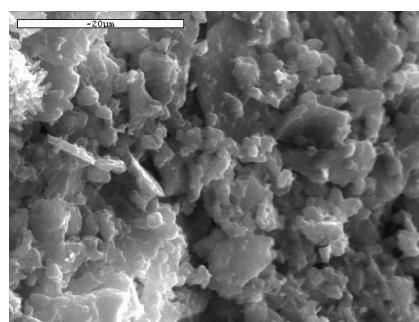


Figure 59: Cement mortar (5% of cement) with 1% oil addition (code C2O₁)

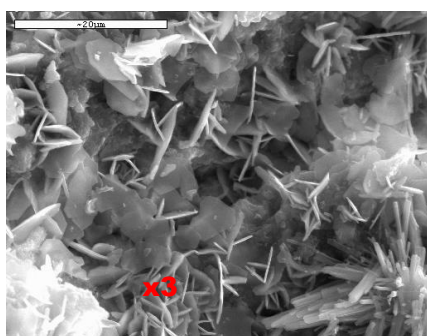


Figure 60: Cement mortar (10% of cement, code C2)

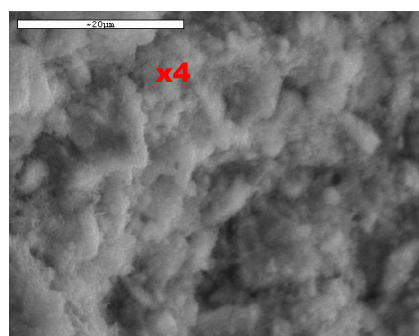


Figure 61: Cement mortar (10% of cement) with 1% oil addition (code C2O₁)

Table 32: EDX analysis of mortar specimens

Place of analysis/Element [wt%]	O	Al	Si	S	Cl	K	Ca	Fe
x1 in Figure 50	55,70	3,80	4,70	-	-	-	31,25	4,56
x2 in Figure 56	29,11	4,73	15,28	1,80	-	-	41,25	4,59
x3 in Figure 60	58,20	5,71	8,50	1,09	1,65	0,67	24,16	-
x4 in Figure 61	61,59	2,67	12,96	0,42	0,18	1,19	20,98	-

As a next step, the effect of linseed oil addition on the connectivity between pores has been investigated by measuring the ease with which water gets into pore structure. Open porosity has been determined by water absorption firstly after 48 hours of full immersion of the specimens under normal pressure, and then after applying vacuum (described more in detail in the section 3.2.5.4, p.49). Values of opened porosities measured under normal conditions were plotted as percentages of the values of porosities measured under vacuum (see Figure 62), giving an idea about the proportion of volume of the pores easily accessible to water to the volume of those hardly accessible to water.

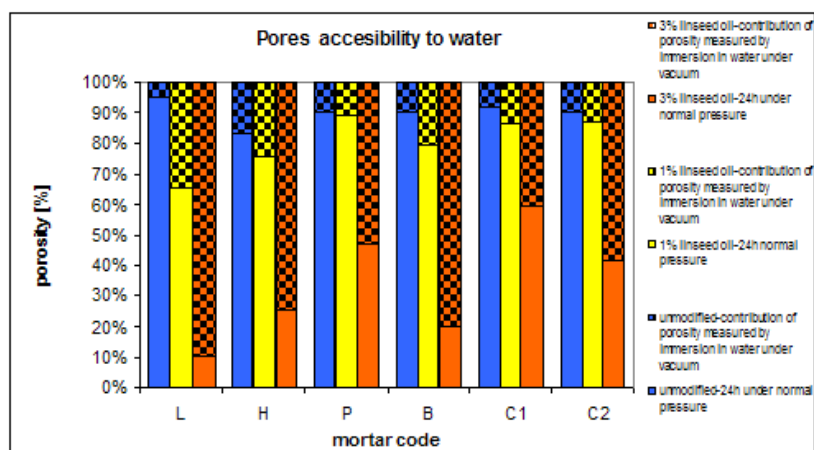


Figure 62: Pores accessibility to water

It is obvious that mortars with oil have higher volume of pores hardly accessible to water. While the unmodified mortars have around 90% of pores filled by water already by absorption under normal conditions, for mortars with 1% of oil addition it is 80% and in case of mortars with 3% of oil addition it is only 30% of pores, which are easily accessible to water. The effect of oil addition is the most prominent in case of hydrated lime mortar

(code L). The proportion of pores hardly accessible to water decreased from 95% to only 65% when 1% of oil was added, and to 10% for the mortars with 3% oil addition, meaning that only 10% of pores are accessible to water under normal conditions.

To summarize the discussion about capillarity, it can be stated that linseed oil is decreasing the capillarity by various mechanisms. It makes a thin film spread evenly in mortar's structure, covering the grains of binder, which results in the decreased connectivity between pores and thus limited water transport. Furthermore, the linseed oil's addition is also changing the pore size distribution in a way which decreases the capillary transport.

The ease with which water gets into material is a crucial factor affecting mortar's durability. Hirshwald stated already in 1908⁽⁶⁰⁾ that materials having more than 80% of pores easily accessible to water are likely to suffer damage due to the freeze-thaw cycles. Based on the obtained results, the addition of oil into mortar is expected to improve mortar's durability.

5.2.5 THE EFFECT OF LINSEED OIL ON THE RATE OF DRYING

Once the water gets into material, it is important to know how quickly it will get out. Rate of drying has been tested on saturated specimens of hardened mortar and, as seen in **Figure 63** in which the change of moisture content is plotted as a function of time, the results did not show any effect of oil on the drying rate.

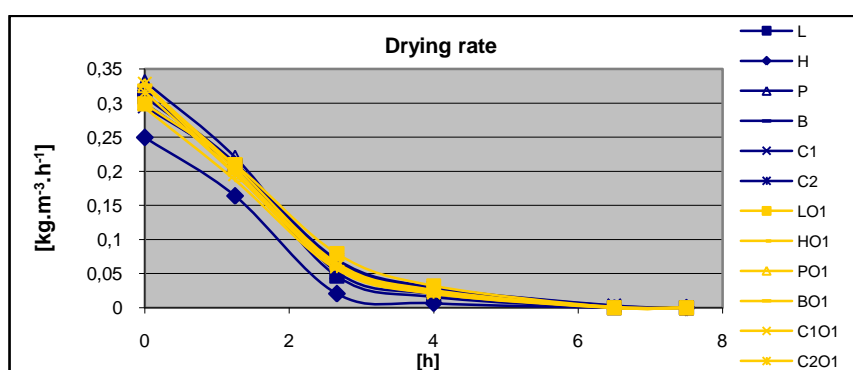


Figure 63: Drying rate of mortars with 1% addition of linseed oil compared to unmodified mortars

In the first stage of drying evaporation takes place from the exposed surface and the drying rate is constant (this stage is not seen in the graph), as long as the liquid water is supplied to the surface by capillary transport. The rate in this stage depends only on the

external conditions and it will stay constant until the moisture content within the porous material can no longer sustain capillary transport (critical moisture content). In the second stage drying rate decreases and will be result of combination of different processes happening due to the heterogeneity of material. In area with small capillary pores it can still be controlled by capillary transport, but in other areas having higher number of large pores the drying rate will depend on the water evaporation from the remaining liquid water front and subsequent vapour diffusion. The third stage begins when no liquid water is left and the drying rate is controlled by the diffusion of water vapour to the surface and its diffusion or convection from the surface. The rate is very slow, nearly constant, while the moisture content of the materials tends towards the hygroscopic moisture content.⁽⁶¹⁾

The addition of oil might take effect in the second and third stage of drying, when the attraction of water molecules to the mineral surface is involved. If the oil was limiting the adsorption of water molecules to the polar material, drying of modified mortars would be faster. On the other hand, oil might be locking water in very small pores and then the drying of modified mortars would be slower than that of unmodified. Nevertheless, no differences between modified and unmodified mortars were observed. Perhaps the method is not very sensible to detect the changes on microscopical level.

However, the important conclusion to be made is that the addition of oil is not slowing down the process of drying, i.e. the water evaporation from mortar structure, so that the modified mortar does not tend to retain humidity.

5.2.6 THE EFFECT OF LINSEED OIL ON MORTARS' DURABILITY

The durability is the most important characteristic of building materials in general. Durability of mortar is a consequence of all previously discussed properties, bringing theoretical presumptions a bit closer to practical applications.

Resistance to salt crystallization cycles

Resistance to the crystallization of two types of salts has been tested – sodium chloride and sodium sulphate.

Resistance to NaCl crystallization

In Figure 64 can be seen that the 1% addition of linseed oil significantly improves mortars' resistance to salt crystallization, tested after 1 year of curing. After 25 cycles all unmodified mortars, except for the hydraulic lime mortar (code H), are totally destroyed, while mortars with 1% addition of linseed oil show 30%-80% weight loss.

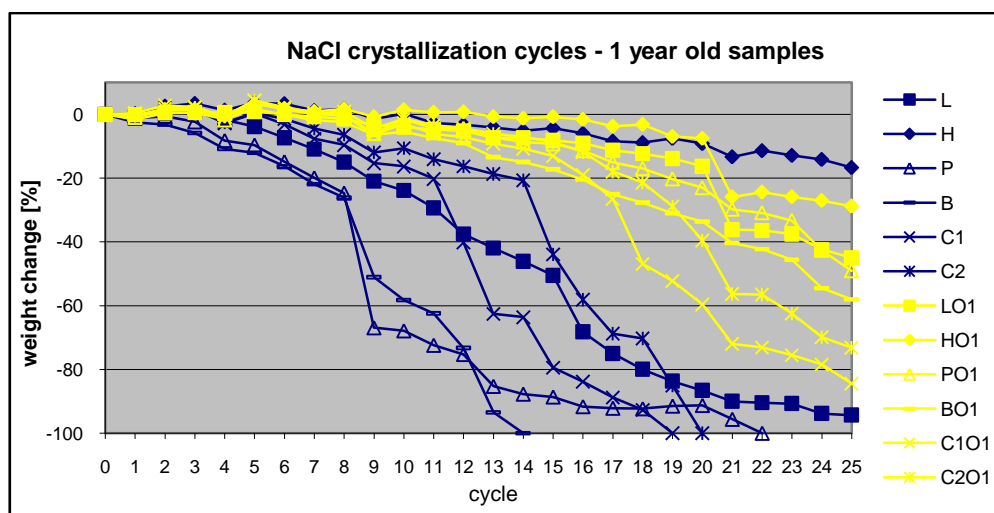


Figure 64: Resistance of 1 year old mortars to NaCl crystallization cycles – mortars with 1% addition of oil compared to unmodified mortars^a

Hydrated lime mortars (codes L and LO₁) belong to the most resistant mortars, even though its mechanical strength was the lowest. On the other hand, mortars with cement addition (codes C1, C1O₁ and C2, C2O₁; cement is added to hydrated lime mortars in order to increase their strength) show quite low resistance compared to other mortars. In case of hydrated lime mortars with the oil addition, their high resistance could be explained by their lowest capillarity. But this explanation fails for the unmodified mortar. Another reason could be their different pore size distribution compared to hydraulic mortars, i.e. that hydrated lime mortars have bigger pores than hydraulic mortars. Or another hypothesis which might explain the high resistance of hydrated lime mortars to salt crystallization is that sodium chloride may have an effect of a sort of reinforcement, after it accumulates in pores, supporting the mortar's structure. Very resistant lime mortars have been observed on old

^a drops in weight of mortars of codes L, LO₁, H, HO₁, P and PO₁ after 20th cycle are caused by taking samples for SEM analysis (code L – one of the two specimens has been used as a whole)

light-houses (19th century), which mortars are fully loaded with salts and suffering frequent wetting-drying cycles, though they are well resistant to damage⁽⁷¹⁾.

Mortars with 1% of linseed oil seem to get deteriorated in a different way than the unmodified mortars (see **Figure 65**). Unmodified mortars got usually broken apart into pieces after occurrence of cracks formed throughout the structure, as can be seen on the drops in their weight in the graph (**Figure 64**), while mortars with 1% oil addition lose their weight more continually. As can be seen on the following pictures, unmodified mortar samples have deep fractures throughout the mass from which they later decompose, mortar with oil lose their surface gradually by surface scaling and powdering.

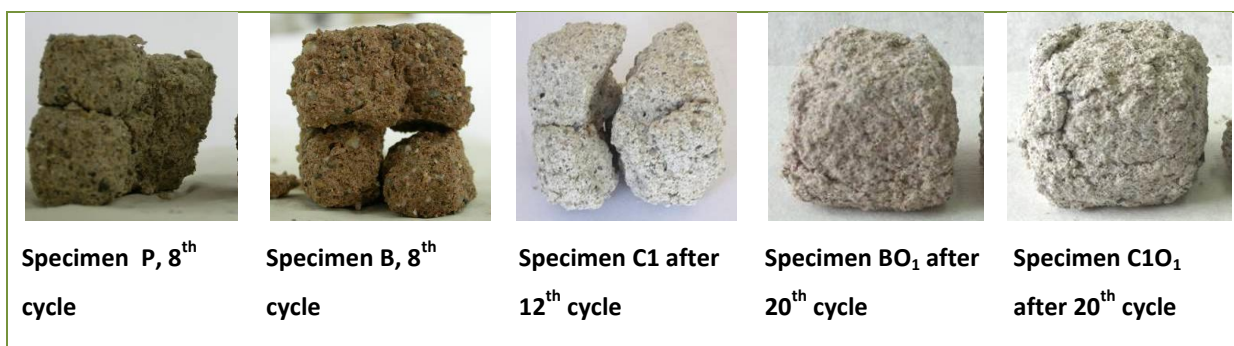


Figure 65: The damage pattern of unmodified mortars (codes P, B and C1) and mortars with 1% addition of linseed oil (codes BO₁ and C1O₁)

Specimens of some mortar types (codes H, HO₁, P and PO₁) have been observed under the scanning electron microscope in order to enlighten the different damage pattern of mortars with the oil addition. As can be seen on the figures bellow, besides to NaCl precipitation, in samples of unmodified mortars areas where mortar's surface seems to be covered by a smooth layer have been found, EDX analyses (**Table 33**) indicates present of NaCl.

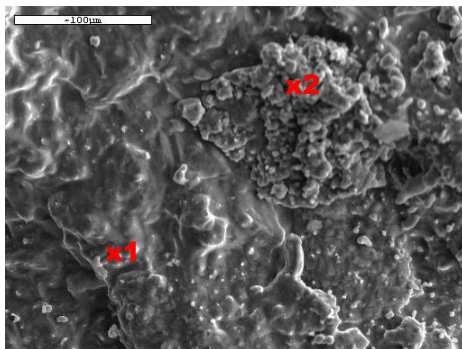


Figure 66: Hydraulic lime mortar (code H) after twenty NaCl crystallization cycles performed (SEM)

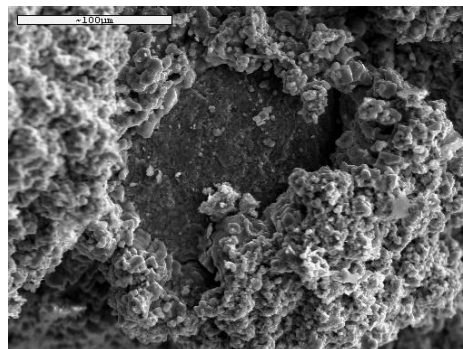


Figure 67: Hydraulic lime mortar with 1% oil addition (code HO₁) after twenty NaCl crystallization cycles performed (SEM)

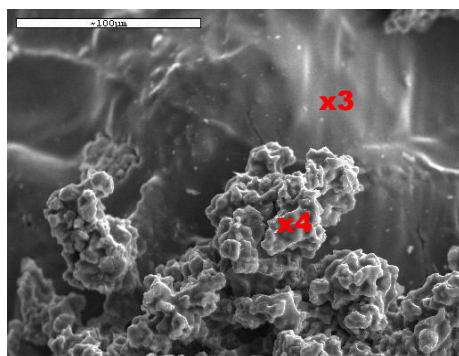


Figure 68: Pozzolanic mortar (code P) after twenty NaCl crystallization cycles performed (SEM)



Figure 69: Pozzolanic mortar with 1% oil addition (code PO₁) after twenty NaCl crystallization cycles performed (SEM)

Table 33: EDX analysis of mortar specimens after twenty NaCl crystallization cycles performed

Element [wt%]/ Place of analysis	O	Na	Mg	Si	Cl	Ca
x1 in Figure 66	9,28	22,98	0,03	0,82	62,75	4,19
x2 in Figure 66	-	42,68	0,14	-	57,08	0,11
x3 in Figure 68	-	42,09	0,02	0,11	57,68	0,07
x4 in Figure 68	-	36,76	0,06	0,07	63,10	0,03

It seems that salt makes a crust on the surface of unmodified mortars. This crust has not been observed in specimens of mortar with 1% addition of oil, as if the oil in mortar was preventing crystals adhesion to mortar mass and thus affecting the damage pattern of

modified mortars. However, this crust has not been observed in hydrated lime mortar (code L) and only three mortar types out of six types have been studied.

Resistance to sodium chloride crystallization of mortars with 3% addition of oil is shown in Figure 70.

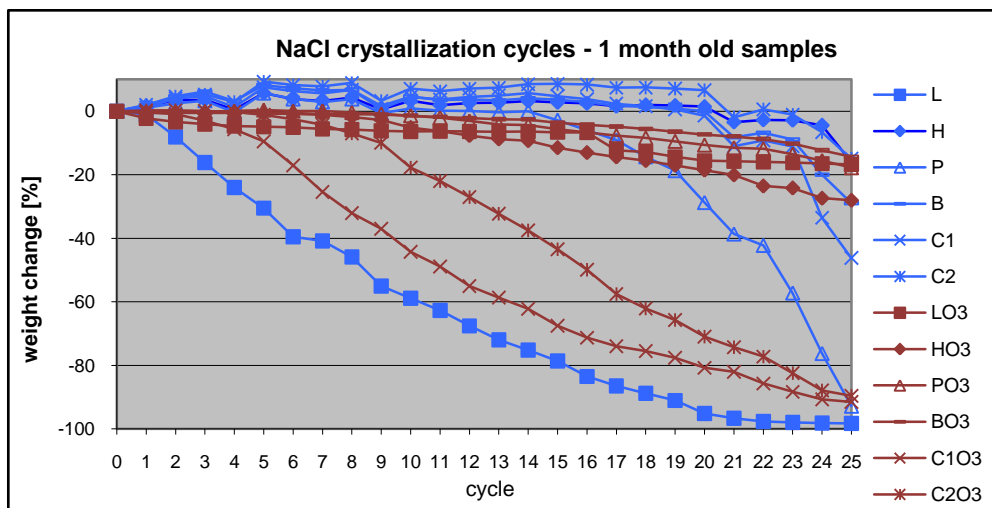


Figure 70: Resistance of 1 month old mortars to NaCl crystallization cycles – mortars with 3% addition of oil compared to unmodified mortars

Specimens of mortars with 3% addition of oil tested after 1 month of curing are more resistant than those with only 1% oil tested at the age of 1 year. Specimens of unmodified mortars firstly had increased in their weight due to the accumulation of salts; this lasted until approximately 20th cycle, and then started to lose their weight rapidly as the damage have been proceeding. Mortars with 3% of oil have been losing their weight gradually; there was not the weight increase in the first cycles as in the case of unmodified mortars - that is because they have not absorbed much of salt solution due to their hydrophobicity. From the same reason their damage has been proceeding only slowly, as they have been losing only the surface layer (Figure 71). Unmodified hydrated lime mortar tested after 1 month of curing is significantly less resistant to damage than that cured for 1 year, that is because it has not yet been carbonated as much as mortar after 1 year of curing. In case of mortars with 3% of oil the mechanical strength does not play a role in their resistance, because the hydrophobicity is a much more important factor. Hydraulic unmodified mortars 1 month old are generally more resistant than those tested at the age of 1 year. The reason is that the

unmodified mortars lost their strength probably because of formation of microcracks due to improper curing conditions, as it has been already mentioned before.



Figure 71: Specimen after 6 hours of full immersion into a salt solution - solution penetration only into depth of approx. 3 mm

On the pictures in **Figure 71** can be seen that unmodified mortars contained cracks after the testing, showing that higher damage occurred compared to the mortars with 3% of linseed oil even though the weight loss is not that significant yet.

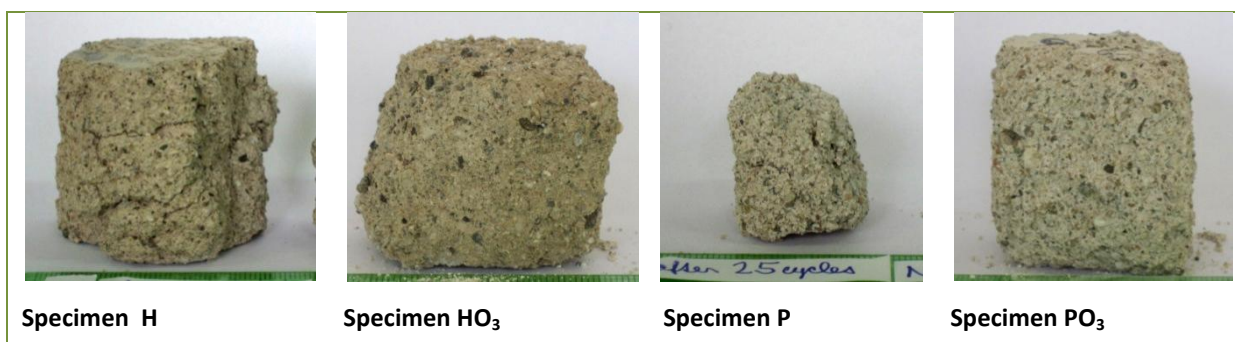


Figure 72: State of the specimens of mortars with 3% addition of oil and unmodified mortars after 25 NaCl crystallization cycles, tested after 1 month of curing

Resistance to Na_2SO_4 crystallization

To accelerate damage due to the salt crystallization, 10 wt% sodium sulphate solution has been used for testing besides the sodium chloride solution of the same concentration. Indeed, as seen in **Figure 73** and **Figure 74**, the damage takes place much faster than that due to the sodium chloride crystallization. The reason for that is that the damage is caused by not only crystallization pressures like in the case of NaCl, but also by high hydration pressures accompanying conversion of anhydrous phase of sodium sulphate (thenardite Na_2SO_4) into the hydrated phase (mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), taking place when the dried specimens are immersed into salt solution (hydration heat can be felt, the solution is warmed-up).

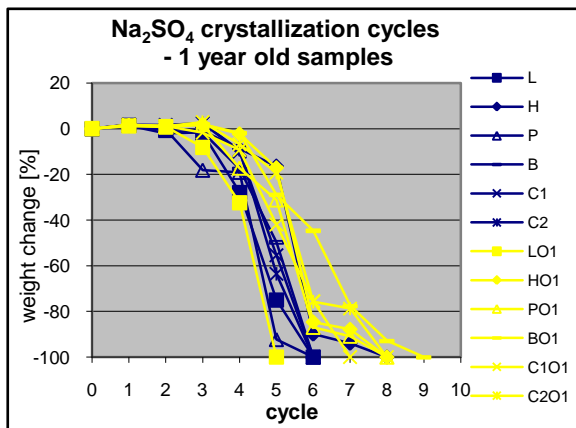


Figure 73: Resistance of 1 year old mortars to Na₂SO₄ crystallization cycles – mortars with 1% addition of oil compared to unmodified mortars

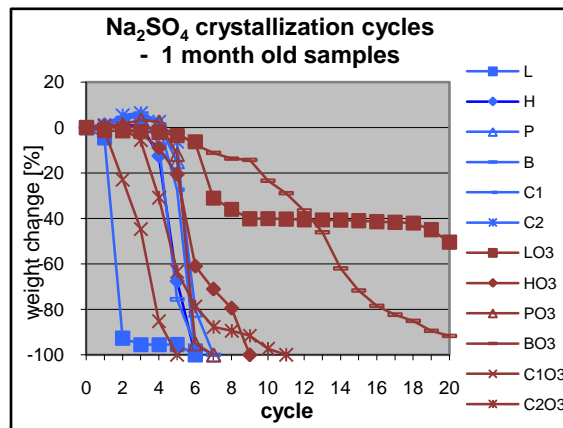


Figure 74: Resistance of 1 month old mortars to Na₂SO₄ crystallization cycles – mortars with 3% addition of oil compared to unmodified mortars

The process of damage due to sodium sulphate crystallization is rather too fast so that it is harder to compare weight loss of various types of mortars. However the result is in accordance with the resistance to NaCl crystallization cycles – mortars with the addition of linseed oil are showing higher durability. Interesting phenomena has been observed on the hydrated lime (code LO₃) and brick dust (code BO₃) mortars with 3% addition of oil. Specimens of these mortars stayed with almost no weight loss for ten more crystallization cycles while all the other specimens have been already destroyed. These mortars both show excellent hydrophobity and for that reason salt solution does not penetrate into their structure thus cannot cause any damage, even though they have a very little strength. Damage takes place only by losing a thin powder layer from their surface when moved out of salt solution, as can be seen in **Figure 75**.



Figure 75: Specimens of hydrated lime and brick dust mortars in sodium sulphate solution - specimens are hydrophobic, they lose surface powder layer

Resistance to freeze-thaw cycles

Improved durability of mortars with linseed oil addition has been confirmed also by testing their freeze-thaw resistance. Following **Figure 76** shows resistance of mortars with 1% linseed oil addition compared to unmodified mortars.

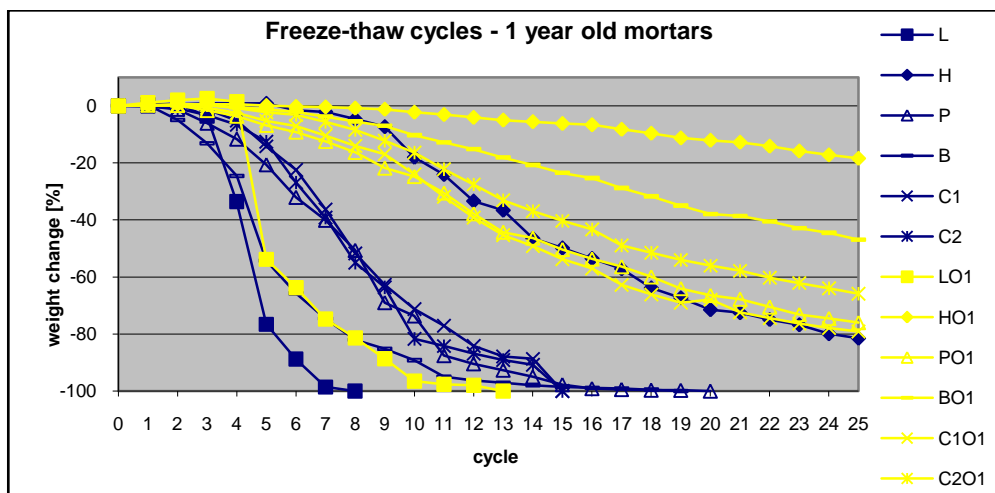


Figure 76: Resistance of 1 year old mortars to freeze-thaw cycles – mortars with 1% addition of oil compared to unmodified mortars

All modified mortars are more durable than the unmodified ones. The resistance to freeze-thaw cycles corresponds to the mechanical strengths of mortars. Hydraulic lime mortars (codes H and HO₁) are the most durable, that is in agreement with their highest strength caused by the highest content of hydraulic components among all mortar types. On the other hand, hydrated lime mortars (codes L and LO₁) are the least durable, which is in contrary to their quite high resistance to salinity tested at the same age. However the damage mechanism is different than that of salt damage and thus different factors are playing a role in mortars' resistance.

Following **Figure 77** shows resistance to freeze-thaw cycles of mortar with 3% addition of oil, tested after 1 month of curing.

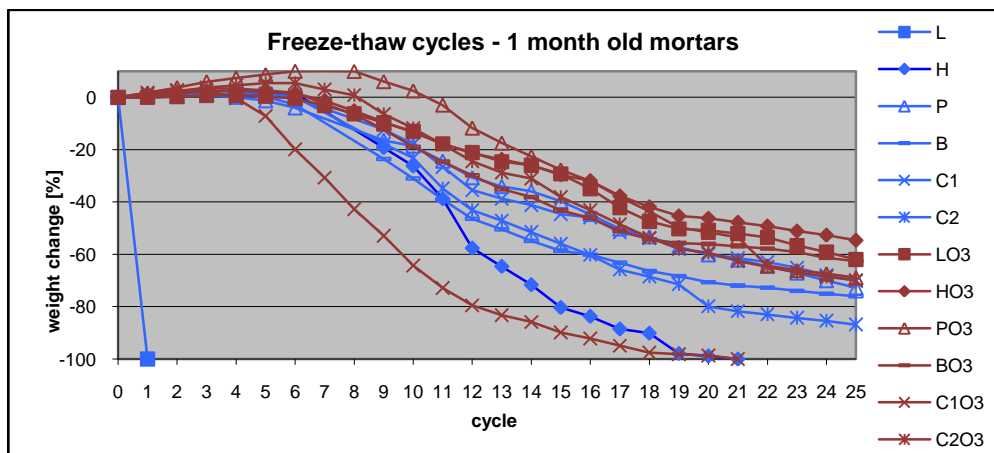


Figure 77: Resistance of 1 month old mortars to freeze-thaw cycles – mortars with 3% addition of oil compared to unmodified mortars

Resistance to freeze-thaw cycles of mortars with 3% oil addition has been improved as well as those with 1% oil addition comparing to unmodified mortars tested at the same age, though the difference between modified and unmodified mortar is not as remarkable as in the case of mortars with 1% oil addition. The reason for that is probably that none of the mortars have been carbonated at this age and that the strength obtained by carbonation plays more important role than the effect of oil addition. Hydrated lime mortar decomposed due to its low strength already after the first cycle.

Cement mortar with 3% oil addition (code C1O₃) showed significantly lower resistance than the other mortars. The decreased resistance might have been partially affected by biological deterioration of mortars. Signs of moulds were observed on a surface of two out of twelve specimens of this mortar type. Biological deterioration is a threat related to the use of natural organic materials, moulds develop when suitable temperature and relative humidity occurs, provided that they have nutrients, which can be oil in this case. Growing of moulds is connected with development of pressures which may lead to damage of the material. It is possible that the development of moulds, which might have not yet been visible, might be one of the factors which caused the decrease in strength of all mortars with 3% addition of oil. However no moulds were found on any other specimens and in outdoor conditions moulds are less likely to occur. Nevertheless it should be kept in mind that higher concentration of natural additives is increasing the risk of biological deterioration.

In contrary to damage mechanisms observed at mortars subjected to salinity test, there seems to be no difference between the way of damage of modified and unmodified mortars due to the freeze-thaw cycles. Mortars have been losing weight gradually by surface powdering and scaling, specimens have been losing compactness and cohesion due to the binder phase which seemed to be washing out. No formation of crack as in the case of the salinity resistance test has been observed.

Following pictures document the damage mechanism due to the freeze-thaw cycles.



Figure 78: Formation of crack due to freeze on the surface of a specimen (code C1O₁)



Figure 79: Surface scaling due to freeze-thaw cycling (sample BO₃)

6 Conclusions

6.1 THE EFFECT OF THE ADDITION OF LINSEED OIL ON MORTARS PROPERTIES AND THE MECHANISM OF ITS OPERATION

In the present study, the effect of linseed oil on the properties of lime-based mortars has been studied. Oil was added in two different concentrations – 1% and 3% by the weight of binder – into six various lime-based mortar mixtures, which composition has been selected with respect to composition of historical mortars, but also mortars used in modern restoration practise have been tested.

Addition of linseed oil showed to have different effect on some properties of hardened mortars depending on the amount added. The effect of 1% and 3% addition of oil on the mechanical properties of mortars has been contradictory. Addition of 1% of linseed oil is improving mortars' strength, but the strength of mortars with 3% addition of oil is dramatically reduced comparing to unmodified mortars. The explanation of the decreased strength of mortars with 3% oil addition might be that oil is limiting contact between binder phase and the grains of aggregate, but could be also related to the effect of oil on the properties of fresh mortar. Oil seems to increase cohesion among the grains of binder and by this way increasing the consistency of a mortar. In 1% addition the effect is positive – the cohesion between binder grains leads to increased consistency, which is still sufficient for required workability. The water/binder ratio is thus slightly decreased and so is the final total porosity of hardened mortars. But in 3% addition of oil the cohesion among grains of binder is higher, so the consistency of a mortar is too high and thus higher amount of kneading water is needed to reach required plasticity and workability. But this “extra” water is not incorporated evenly in mortar mixture because of the hydrophobicity of binder-aggregate paste (oil does not allow more water to be mixed in), and hence the pore size distribution of hardened mortar is affected. In other words, for a given concentration of oil in mortar there is only a limited amount of water that can be evenly mixed into fresh mortar. Excess water is segregated out of mortar mass or, if locked in mortar structure, results in a formation of big pores in the hardened mortar, but without affecting the total porosity

significantly. For mortars with 1% addition of oil the effect is the opposite, mortars have higher proportion of small pores compared to unmodified mortars.

Oil addition is mitigating water transport in mortar structure, both in a micro- and macro- scale. It delays final setting time, because of blocking the pores and thus slowing down the penetration of water molecules to grains of binder. 1% addition of oil is slowing down the hydration of hydraulic components, but it is not decreasing the final hydration degree. Later within the range of months the effect of oil addition on the water transport is positive. Oil in 1% addition seems to be prolonging curing process (compressive strength of modified mortar increased after 1 year while reference mortar stayed at the same level) and preventing mortar to dry-out (flexural strength of unmodified mortar at the age of 1 year decreased while that of mortar with 1% of oil stayed at the same level as at the age of 3 months). On contrary, in case of mortars with 3% addition of oil there are probably other predominant effects, like worse contact between binder and aggregate grains due to oil or the high proportion of big pores in the structure, as mentioned before, which resulted in the decreased strength. Water vapour permeability does not seem to be affected by the addition of oil and the degree of carbonation of mortar with either oil addition has not been decreased, mortars with 3% addition of oil have been even more carbonated than unmodified mortars, which is in accordance with the highest proportion of big pores causing higher permeability.

As expected, oil addition is decreasing mortars' ability to absorb liquid water, and this effect is the most apparent on the results of water absorption through capillarity. Already 1% addition of oil is decreasing the coefficient of capillarity significantly and 3% addition of linseed oil results in decreasing the value of capillary coefficient by approximately 90%. Decreased capillarity is probably first of all caused by the hydrophobic effect of linseed oil, mortars with oil addition show increased water contact angle, but may be also affected by the changes in pore size distribution in mortars due to the addition of oil.

Furthermore, the addition of oil into the mortar was found to be significantly decreasing the amount of pores which are easily accessible to water; after immersion of mortars specimens with 1% and 3% oil addition for 48 hours under water under normal pressure, water filled 80% and 30% respectively of the total volume of opened pores comparing to 90% easily accessible pores of unmodified mortar.

Pores accessibility to water is together with the strength of the material a crucial characteristic determining mortars' resistance to deterioration. Indeed, the durability of mortars with oil addition has been significantly improved. Modified mortars showed higher resistance to damage due to both salt crystallization and freeze-thaw cycles. For example specimens of mortars with 1% addition of oil suffered in average only 40% weight loss when all the unmodified mortars had been already decomposed, i.e. the difference in weight loss between modified and unmodified mortars at the end of testing made 60%. The situation is similar for the freeze-thaw testing; the difference in weight loss between modified and unmodified mortars after 25 performed cycles was 55%.

In summary, the low addition of linseed oil (1%) has proved to have positive effect on mortars' properties. It improves mechanical characteristics and limits water absorption into mortar without affecting the total open porosity or decreasing degree of carbonation. On the other hand, the addition of linseed oil in 3% by the weight of binder does not have a positive effect on the quality of mortars. Mortars with this content of oil are almost hydrophobic, but their mechanical characteristics are markedly decreased. Mortars with linseed oil in both concentrations showed significantly improved resistance to salt crystallization and freeze-thaw cycles.

On the base of the above mentioned reasons, the addition of one percent of linseed oil can be taken into consideration in the design of mortars meant to repair or replace historic mortars.

6.2 SUGGESTIONS FOR FURTHER RESEARCH

Satisfactory results have been obtained by blending the oil with the dried constituents of mortar prior to adding water. However the effect of different ways of mixing the oil into mortar (blending the oil with water first, eventually with the addition of emulsifier, effect of different periods and intensities of mixing) might be interesting to study in detail.

Addition of 1% of linseed oil is unambiguously improving mortars' properties tested on small specimens in laboratory. In the next step mortars' durability should be tested in outdoor conditions, applied on a stone or brick masonry. It is important to study the influence of linseed oil addition on mortar's adhesion to different types of substrate.

Furthermore, the effect of mortars with oil addition on the mechanism of transport of humidity and salts in a complex system of masonry should be studied.

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Appendix I: *Technical sheet of pozzolan*

VOLCANIC TERRA

Description

Volcanic Terra is a natural volcanic pozzolan for the restoration of monuments and traditional buildings and the construction of new buildings with higher durability.

TECHNICAL FEATURES

CHEMICAL FEATURES

- Chemical reaction (ENV 955-4)

	SiO₂	Al₂O₃	Fe₂O₃	MgO	CaO	Na₂O	K₂O	LOI
(%)	68.29	15.60	1.56	0.95	1.40	1.81	3.03	5.58

- Soluble salts

	SO₄²⁻	Mg²⁺	Ca²⁺	K⁺	Na⁺
(%)	0.270	0.024	0.057	0.020	0.057

PHYSICAL FEATURES

- Physical humidity: 1,27 % (ISO 5017)
- Apparent special weight: 430 Kg/m³ (ISO 5017)
- Real special weight: 2400 Kg/m³ (ISO 5017)
- Special surface: 36,31 m²/g
- Grain measurement: 100 % <55 µm, 95.6 % <20 µm, 75.6 <11 µm, 27.2 % <4.5 µm, 4.5 % <2.5 µm

Features of pozzolan

Definition of pozzolan: 7,3 N/mm²

Drastic silicon: 34,45 %

Mineral features

The material is in amorphous crystal structure.

The tests have been carried out in laboratories of EKEPI SA

Storage

The product must be stored up in covered and dry place.

Appendix II: *Technical sheet of hydraulic lime*

ALBARIA CALCE ALBAZZANA

Powdered natural hydraulic lime

Description

ALBARIA CALCE "ALBAZZANA" is a powdered natural hydraulic lime obtained by calcining selected marly limestone. It is heated in traditional kilns at low temperature (900°C) following a practice in accordance with the historical tradition.

Fields of application

The product is a binder of great historical value, specifically designed to be mixed with local sand directly on site, obtaining mortar suited to:

- laying brick, stone and tufa walls;
- reconstructing vacant parts;
- filling of joints of brick, stone and tufa walls;
- internal and external plastering.

Benefits

Thanks to its capacity of transpiration and the absence of water-soluble salts, ALBARIA CALCE "ALBAZZANA" is the best advisable binder to prepare mortar for historical building restoration. ALBARIA CALCE "ALBAZZANA" presents a soft light brown-pink colour that gives a natural appearance to facing plaster, especially if the colour of the mixed sand softens more the tonality.

Method of use

"Albazzana" lime should be mixed with the right amount of local sand, without adding other cement agents that may compromise purity and transpiration of the executed work.

Mix sand, lime and clean water in the cement mixer. It is recommended finishing plasters obtained with ALBARIA CALCE "ALBAZZANA" with stuccoes or paintings of confirmed transpiration qualities.

Protect from heavy rain during setting time.

Do not use the product with temperatures below +5°C or above +35°C.

Technical characteristics of the product

Aspect	Powder
Colour	Light brown – pink
Setting time	start 10 h end 30 h at +20°C
Compressive strength of mortar	30 kg/cm ² at 90 days
Average particle size	25 µm
Water-soluble salts	Conductivity < 500 µS/cm
Admixtures	Absent
Pigments	Absent
Reaction to fire	Class 0 (Fireproof)

Dosage

The sand-lime ratio varies from 3:1 to 2.5:1 depending on the sand particle size; fine sand requires a larger amount of lime.

Packs

25 kg bags on 1500 Kg pallets.

The material can be stored in a covered, dry place for up to 12 months.



The Chemical Company

Specification item

Mortar mix: 450 Kg of natural hydraulic lime type ALBARIA CALCE "ALBAZZANA" and 1 m³ of clean sand.

The natural hydraulic lime, called "Albazzana", is obtained by calcining at low temperature (900°C) selected marly limestone in traditional kilns.

Technical specifications of the binder are:

- Setting time: starts after 10 hours, end after 30 hours at 20°C;
- Compressive strength of mortar: 30 kg/cm at 90 days;
- Average particle size of the binder: 25 µm;
- Water-soluble salts:
- Conductivity < 500 µS/cm;
- Admixtures: absent;
- Pigments: absent.
- Color of the binder must be its natural light brown – pink.

Safety norms

The product comes with a safety sheet

ALBARIA is a registered trademark of the group.

BASF Construction Chemicals Italia Spa has been working since 16/12/1992 with a certificated Quality System to UNI-EN ISO 9001. The Environmental Management System is also certificated to UNI EN ISO 14001.

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This publication supersedes all others.
September 2006



ANALYTICAL DEPARTMENT

Sample	NATURAL HYDRAULIC LIME ALBAZZANA
Requested by	R & D
Operator	G.B.

Loss to ignition		18,10 %
Silicon dioxide	(SiO₂)	21,05%
Calcium oxide	(CaO)	57,50%
Magnesium oxide	(MgO)	0,42%
Iron oxide	(Fe₂O₃)	1,21%
Aluminium oxide	(Al₂O₃)	1,19%
Sodium oxide	(Na₂O)	0,12%
Potassium oxide	(K₂O)	0,10%
Sulphates	(SO₃)	0,11%
Total oxides		99,80%




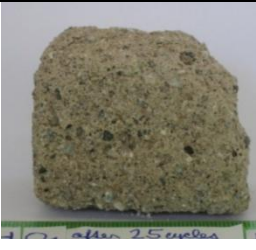







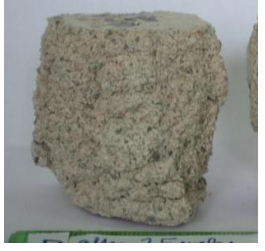
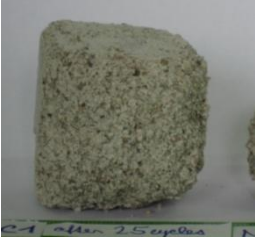




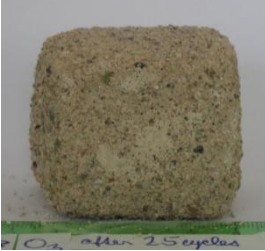
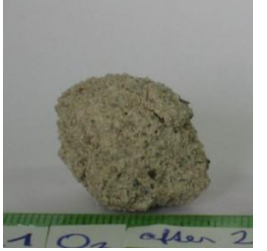

Material	microS/ cm	Calcium %	Sodium %	Potassiu m %	Magnesi m %	Chloride %	Nitrate %
Calce albazzana	1105	10,67	0,04	0,06	0,005	0,02	0,01
Maximum limits ICR	10000	2.0-10.0	0,10	0,15	0,06	0,10	0,10

* Conductibility according to method Normal 13/83 (0.1000 g. sample in distilled 100 ml water)

** Ionic chromatography according to method Normal 26/87
















Appendix III: *Resistance to salinity*

Documentation of the state of the specimens after 25 performed NaCl crystallization cycles

	L	H	P	B	C1	C2
Unmodified - 1 year old			Both specimens destroyed	Both specimens destroyed	Both specimens destroyed	Both specimens destroyed
Linseed oil 1% - 1 year old						
Unmodified - 1 month old						
Linseed oil 3% - 1 month old						

Appendix IV: *Resistance to freeze-thaw cycles*

Documentation of the state of the specimens after 25 performed freeze-thaw cycles

	L	H	P	B	C1	C2
Unmodified - 1 year old	<i>Both specimens destroyed</i>		<i>Both specimens destroyed</i>	<i>Both specimens destroyed</i>	<i>Both specimens destroyed</i>	<i>Both specimens destroyed</i>
Linseed oil 1% - 1 year old	<i>Both specimens destroyed</i>					
Unmodified - 1 month old	<i>Both specimens destroyed</i>					
Linseed oil 3% - 1 month old					<i>Both specimens destroyed</i>	