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Effect of curing conditions on the properties of lime, lime–metakaolin and lime–zeolite mortars

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HIGHLIGHTS

- Properties of lime and lime–pozzolan mortars were affected by curing conditions.
- Semidry conditions and air access enable hardening of lime mortar and its shrinkage.
- Humid curing is a prerequisite for strength development of lime–pozzolan mortars.
- Binding potential of lime–pozzolan mortars cannot develop or is lost at dry curing.
- Addition of pozzolans slightly increased frost resistance of moist lime mortars.

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ABSTRACT

The present study was undertaken to elucidate the influence of zeolite and metakaolin addition on the compressive strength, porosity, shrinkage, and frost resistance of lime mortars cured at different humidity conditions with or without access of carbon dioxide in a period up to 1 year. The changes in mineral composition of the binders were determined by X-ray diffraction and thermogravimetric analyses. It was found that pozzolans reduced shrinkage of fresh lime mortars. These admixtures positively affected compressive strength development and frost resistance of lime–pozzolan mortars when they were cured in the environment with the relative humidity of 100%.

1. Introduction

Lime mortar is tradition binding material that was used in long period of architectural history. Lime mortars and mortars containing at least a portion of lime in the binding mixture are also used today. Limes used in different historic periods and different regions for the preparation of mortars had character of the non-hydraulic binder (air lime) or of a binder with more or less hydraulic properties (lime–pozzolan or natural hydraulic limes). Also the composition of the ancient and the newer historical mortars varied widely [1–3]. The fact that many historical structures or their fractions have been preserved up to this time confirmed durability of some of these materials. Current materials intended to be used for repair of historic structures should be comparable with the properties and the appearance of the original structure [1]. To choose suitable building material for the renewal of a construction of cultural heritage some basic principles have to be respected. These include: (a) reversibility of repair work, (b) compatibility of old and new materials, (c) minimal violation of the originality of the monument, and also some other [4]. Unsuitable use of modern building materials can cause unpredictable changes in the original structure. In the present time the lime mortars are considered generally superior to cement-based mortars for the repair of appropriate historic structures. However, lime mortars are not suitable for use in the moist environment because they lack hydraulic properties and have low frost resistance especially in non-carbonated state. Use of mortars with hydraulic properties is therefore often preferred for renovation purposes. With the growing interest in the

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conservation and repair of historic buildings there is also an increased need to understand in detail the essence of chemical reactions that are responsible for setting, hardening and durability of different binders. This knowledge can help finding application-tailored types of mortars, or modify the desired properties of lime mortars.

Significant change of material characteristics of air lime mortars can be achieved by addition of pozzolanic admixtures. Favorable properties of lime–pozzolan mortars are the result of pozzolanic reaction taking place between calcium hydroxide and pozzolanic admixture in the presence of water. Addition of a pozzolan to air lime enables the mortars to obtain hydraulic properties, resistance to water, higher compressive strength, but also durability and some resistance to weathering [1,5–10]. However, compressive strength of lime–pozzolan mortars increases usually relatively slowly over longer period of time, depending on the type of the pozzolan used. Mortars containing lime–pozzolan binder generally harden due to two mutually competing chemical processes: pozzolanic reaction and carbonation [11,12]. It is, therefore, possible to identify different reaction products in a hardened mortar, depending on the type of pozzolanic material used, curing time and type of prevailing curing environment that provides components needed for hardening processes – water, or CO_2 from the air. All these factors combined then affect the final properties of a mortar. Metakaolin and natural zeolites are two materials whose pozzolanic nature and properties are often the subject of research today.

Metakaolin (MK) is relatively very reactive pozzolanic material. Main reactive component in the metakaolin is metakaolinite ($Al_2Si_2O_7$) that is a product of thermal dehydroxylation of kaolinite in the kaolin clay. Reactive components of metakaolinite are silica (SiO_2) and alumina (Al_2O_3) that are able to react with the calcium hydroxide in the presence of water. There are numerous studies of various authors that focus on the development of properties of lime–metakaolin or cement–metakaolin mixtures and also development of products of the pozzolanic reaction between the MK and lime [10,13–27].

The main products of pozzolanic reaction that were identified in the lime–MK mixtures were C–S–H phase and hexagonal hydrated calcium aluminate phases (AFm), often including also strätlingite (C_2ASH_8). In the case when pozzolanic reaction between MK and calcium hydroxide takes place in the absence of $CaCO_3$ or CO_2 from the air the main phases identified were C–S–H or C–(A)–S–H, C_4AH_{13} (hydroxide-AFm phase) and possibly C_2ASH_8. Metastable phase of C_4AH_{13} can be converted to a stable cubic hydrogarnet, especially at higher temperature [28,29]. However, in the presence of $CaCO_3$ or CO_2 from air the carbonate-bearing AFm phases such as calcium hemicarboaluminate hydrate $C_3A{\cdot}0.5CaCO_3{\cdot}0.5Ca(OH)_2{\cdot}11.5H_2O$ (Hc) and calcium monocarboaluminate hydrate $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$ (Mc) form instead of C_4AH_{13} [30,31]. Strätlingite and calcium hydroxide are considered to be incompatible phases at normal temperatures as was reported by Matschei et al. [31], Dron [32] and Damidot and Glasser [33]. These authors suggest that strätlingite can form when there is sufficient amount of MK that can consume most or all of the calcium hydroxide content in the mixture. Development of strätlingite and other phases in the hydrating mixtures of calcium hydroxide and metakaolin or other calcined clays was described by [3,13–16,22,25,27,29,34–37] and some others.

Zeolites (Z) are crystalline hydrated aluminosilicates with a specific three-dimensional framework structure comprised of Si, Al and O atoms, where Si but also Al atoms have tetrahedral oxygen coordination. Microporous cage-like structure of zeolites has a large surface area and can accommodate various types of cations such as Na^+, K^+, Ca^{2+} and Mg^{2+}. The cations can be exchanged for others in the contact with water solution. Zeolites therefore possess excellent ion exchange capabilities. There exist a great number of zeolite minerals. Zeolitic tuffs have been used with limes already in the Roman times. Perspectives of effective use of natural zeolites as a pozzolanic additive to lime or cement composites and their pozzolanic reaction were studied by a number of authors, as for example [9,38–44]. It was confirmed that calcium hydroxide was consumed during curing of zeolites and compressive strength of tested samples significantly increased. These finding were essentially consistent with the general knowledge of other pozzolans. Perraki et al. [39] found low Ca/Si ratio in the hydration products surrounding the zeolite particles in mixes cured at 50 °C. Shellings et al. [42] found that the exchangeable cation content of clinoptilolite influenced the duration of the initial induction period and the structural evolution of the C–S–H reaction product. It was also found that the rate of pozzolanic reaction was affected by the silica and alumina active contents in zeolites. Mertens et al. [9] reported that zeolites with higher Si/Al ratios reacted faster with $Ca(OH)_2$ than Al-rich ones. Calcium aluminate hydrates beside the C–S–H phases can also be found between the products of pozzolanic reaction of zeolites.

The aim of the study was to determine the influence of ground zeolite and metakaolin addition on the properties of lime mortars and evaluate the effect of curing conditions on the final properties of mortars. Mortar specimens were cured at different humidity conditions with or without access of carbon dioxide in order to promote or prevent pozzolanic or carbonation reaction.

2. Materials and methods

2.1. Materials

Test mortars were prepared from the following materials:

(a) Natural standard silica sand with continuous grading according CEN EN 196-1.
(b) Hydrated calcium lime powder designated CL90-S according to CEN EN 459-1 was produced by Calmit, s.r.o., Tisovec, Slovakia.
(c) Ground natural zeolite from pure zeolite deposits was produced by ZEOCEM, a.s., Bystré, Slovakia. The product designated as ZeoCem Micro 50 contains, according to producer‘s data, prevailingly particle with size up to 50 μm and median size of about 10 μm. Main mineral in this zeolite is clinoptilolite. Effective pore diameter in the zeolite rock is 0.4 nm, volume of hollow spaces of the rock varies from 24% to 32%.
(d) Metakaolin was produced by Keramost a.s., Most, Czech Republic. The commercial product is designated as KM 60.

Metakaolin and zeolite were used as pozzolanic admixtures. Chemical composition of lime, zeolite and metakaolin used for mortars preparation is Table 1. Mineralogical composition of zeolite is in Table 2.

2.2. Test samples and curing conditions

Three types of binders were used for preparing the mortar specimens. Lime hydrate without any pozzolan addition was used as the first type of binder. It was used for preparing the reference specimens. Lime–zeolite and lime–metakaolin mortars were prepared with lime:pozzolan ratio 1:1. Each type of lime–pozzolan mortar was prepared with two different binder:sand ratio. Composition of all prepared mortars is in Table 3. Mortars were prepared in laboratory mixer. Water content in lime–pozzolan mortars was controlled to obtain near to equal consistency for workable mortars. Consistency of fresh mortars was determined after 7 min of mixing using flow table test according to the EN 1015-3.

Test specimens of two geometrical shapes were prepared from the mortars: (a) Cylindrical test specimens with diameter and height of 30 mm for determination of compressive strength, and (b) Prisms with size 40 × 40 × 160 mm that were fitted with glass contacts at their ends for the shrinkage testing. The forms with fresh mortars were then covered by glass plates and left covered for 4 days in a humid environment. After demolding the specimens were stored for another 3 days in the closed plastic container at relative humidity (RH) of about 100% – to achieve sufficient volume stabilization of the mortars. Then, after totally 7 days, the samples were divided into four groups and each group was then cured in four different environmental conditions, which enabled evaluating the effect of different environments on the final properties of mortars. Curing conditions were as follows: