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Synthetic zeolite pellets incorporated to air lime–metakaolin mortars: Mechanical properties

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HIGHLIGHTS

- Synthetic fine and coarse zeolite pellets were added to air lime–metakaolin mortars.
- Synthetic zeolite pellets promote the development of pozzolanic phases.
- With the curing age both fine and coarse zeolite pellets improve mechanical strengths.

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ABSTRACT

In this study synthetic fine and coarse zeolite pellets were chosen in the development of air lime–metakaolin mortars for repairing ancient masonry to be used in conservation and restoration of cultural heritage. Synthetic zeolite was used due to their particular water adsorption properties and act as an artificial pozzolan promoting the development of hydraulic phases.

Physical, chemical, mineralogical and microstructural tests were accomplished to characterize the materials used in mortars' preparation.

Flexural, compressive strength and dynamic modulus of elasticity tests were performed in mortars at 28, 90 and 180 days of curing. Incorporation of both fine and coarse zeolite pellets caused improvement of mechanical strength of mortars. The highest flexural strength value (~0.5 MPa) was achieved in both mortars with fine zeolites pellets at 90 days and 20 and 30 wt.% metakaolin, and coarse zeolite pellets at 180 days and 30 wt.% metakaolin as lime replacement. 1.0 MPa was the highest compressive strength value obtained at 180 days for mortars with both fine zeolite pellets and coarse zeolite pellets, with 20 and 30 wt.% of metakaolin, respectively.

Elasticity modulus ranged from 2.3 GPa to 3.9 GPa confirming the high deformation capability of these mortars.

Zeolite pellets type A is a promise synthetic material that could be successfully used in air lime–metakaolin render mortars for applications in the conservation and restoration of cultural heritage.

1. Introduction

The use of natural and artificial pozzolans as supplementary binder materials is widespread throughout the world in order to develop durable and high-performance mortars and concrete. Slag, fly ash, silica fume, rice husk ash, metakaolin, diatomite, zeolite, among others, are being used as blended admixtures.

Natural zeolites have been widely used as supplementary cementitious materials [1]. In the cement industry they are used as natural pozzolan in some regions of the world. In lime mortars, the behaviour of natural zeolites has been studied for a long time. The presence of authigenic zeolites has been detected in ancient Roman mortars cured in aggressive marine environment [47]. The formation of mineral phases on the pozzolan–lime–water system was reported by García et al. [17]. Mertens et al. [27] have studied the parameters that affect the pozzolanic reactions of common natural zeolites with lime. The pozzolanic reaction of lime with natural zeolites was also studied by Snellings et al. [38], Snellings et al. [37] and Moropoulou et al. [29]. The use of natural

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zeolite in a saturated lime solution at 40 °C was studied in order to determine its pozzolanic activity [46]. Studies related with the incorporation of synthetic zeolites in air lime and air lime–metakaolin mortars are scarce. Andrejkovičová et al. [2] explained the evolution of flexural and compressive strength, and dynamic elasticity modulus of air lime mortars with fine and coarse zeolite pellets up to 180 days of curing time.

Zeolites are hydrated crystalline aluminosilicate materials with three-dimensional skeletal structure that occur in nature, but can be synthetically manufactured for presenting highly porous microstructure promoted by a network of channels and interconnected voids. The frameworks are composed by repeated silicon tetrahedrons $[SiO4]^{4-}$, that can be substituted by alumina $[AlO4]^{5-}$ in variable proportions. This structure is linked by sharing of oxygen atoms, whereas exchangeable alkaline and alkaline-earth metals compensate for the resulting charge deficit [25].

Molecular sieves are "tailored" synthetic zeolites which due to their precise pore size and shape, molecular polarity and chemical composition have developed selective adsorption properties, based on surface molecular scale phenomena in which gas or liquid molecules are attracted to the internal volume of the porous solid.

The diameter of the open structure typically ranges between 3 to 10 Angstrom [40] and determines the size of the molecules which can be adsorbed, such as NH_3, H_2O and H_2. One of the most common molecular sieves is the "type A" framework or "Linde Type A – LTA" (Fig. 1), where the 3 Å, 4 Å, and 5 Å open-window diameter in α-cage is obtained with potassium (K-LTA), sodium (Na-LTA), and calcium (Ca-LTA) cation inclusion, respectively [24]. Zeolite type A is a synthetic zeolite widespread over the world and its cost is usually lower than other synthetic zeolites.

In many common adsorbent applications coarse spherical agglomerates or pellets of zeolites (Fig. 2) are manufactured, where the pellet contains, in addition to the zeolite material with diameter about 1–4 μm, a binder of an amorphous aluminosilicate (typically, kaolin or bentonite) or alumina. This palletized material has a high adsorbent capacity and presents high potential to be incorporated in mortars enabling adsorbed water to the system, since its structure contains inter-macropores that are inside the pellet and intra-micropores within the zeolitic material (Fig. 2). According to Muller et al. [30], the maximum water adsorption capacity for dry Na-A zeolite powder is 28 wt.% while Hunger et al. [20] present an experimental value around 25.5 wt.%. Whereby, in pellet form it is expected that this property exceeds 30 wt.% value.

The main aim of this study was to evaluate the behaviour of synthetic coarse and fine zeolite pellets incorporated in air lime–metakaolin mortars for repairing ancient masonry (render mortar) with compatible mechanical properties to be used in conservation and restoration of cultural heritage.

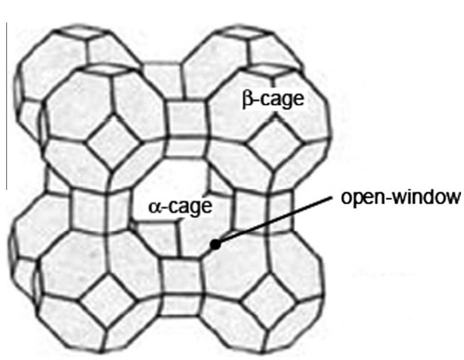

Fig. 1. Zeolite type A framework (modified from Baerlocher et al. [5]).

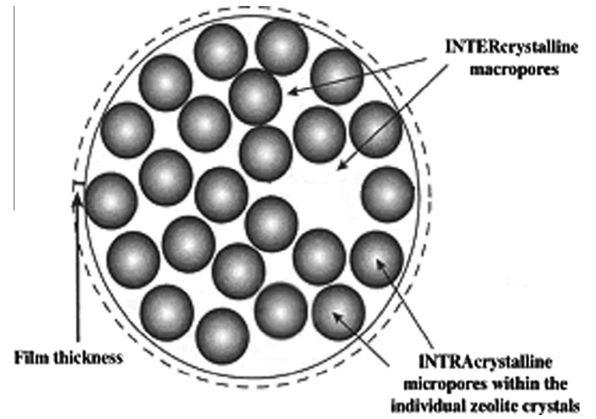

Fig. 2. Schematic diagram of a zeolitic pellet (adapted from [43]).

A secondary aim of the work was to check the validity of the experimental modified Chapelle test to evaluate the pozzolanic activity of synthetic zeolite pellets.

2. Materials and methods

Mortars were formulated with powdered commercial air lime (AL) CL 90 (Calcidrata, Portugal) and siliceous river sand. Mortars were prepared with air lime/sand volumetric ratio of 1:3. Air lime binder was replaced by: (a) 10, 20 and 30 wt.% of commercial metakaolin (MK) (C. Condestável, Portugal) and (b) the same mortar compositions in which air lime was substituted by 5 wt.% of coarse and fine synthetic zeolite pellets Phonosorb 551 (Grace Davison, USA).

The coarse zeolite (CZ) pellets used in the mortar compositions correspond to the commercial synthetic material presented in bead (pellet) form, while the fine zeolite (FZ) pellets were obtained in laboratory by dry grinding (milling) the commercial coarse zeolite pellets in a Ceramic Instruments mill (S2-1000-M) with porcelain jars and alumina balls, during 15 min.

Table 1 present the references and the compositions of the mortars are marked in the text.

Particle size distribution of fine materials was performed with X-ray grain size analyser Sedigraph 5100 from Micromeritics, following the standard [9].

The mortar samples for XRD and STA analysis were sieved trough 0.150 mm sieve in order to eliminate the coarse materials, namely quartz presented in river sand.

The mineralogical composition of the mortars on powder random oriented samples was determined by X-ray diffraction (XRD) analysis using a Philips X'Pert diffractometer equipped with Cu Kα radiation. The crystalline phases were identified by comparison with the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

The chemical composition (major elements) was obtained by X-ray fluorescence (XRF) spectrometry using a Panalytical Axios X-ray fluorescence spectrometer. Loss on ignition was determined by heating the samples in an electrical kiln at 1000 °C during 3 h.

Ammonium acetate saturation method was used to determine the cation exchange capacity according Molina and Poole [28].

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out as simultaneously thermal analysis (STA) on a SETARAM TGA 92 thermobalance, under argon atmosphere (3 l/h) between ≈20 °C and 1000 °C, with a heating rate of 10 °C/min.

Table 1
Composition of mortars.

Mortar	Metakaolin (wt.%)	Zeolite (wt.%)
AL	–	–
AL10MK	10	–
AL20MK	20	–
AL30MK	30	–
FZAL	–	5
FZAL10MK	10	5
FZAL20MK	20	5
FZAL30MK	30	5
CZAL	–	5
CZAL10MK	10	5
CZAL20MK	20	5
CZAL30MK	30	5