AIR LIME MORTARS WITH INCORPORATION OF SEPIOLITE AND SYNTHETIC ZEOLITE PELLETS

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ABSTRACT
The requirements of conservators who take care of historical monuments are that the materials for rehabilitation of old renders should have a composition as similar to the historical materials as possible and should provide improvement in durability. Fine and coarse sepiolite and synthetic zeolite pellets were chosen as additives in the development of lime mortars for conservation work, due to their unique adsorption properties providing water to the mortar system and acting as water reservoirs in conditions of low humidity. Flexural and compressive strength and the dynamic modulus of elasticity were studied at 28, 90 and 180 days of curing. Addition of both fine and coarse sepiolite and zeolite pellets caused improvement of mechanical strength of mortars, clearly evident at later ages of curing. Elasticity modulus ranged from 2.3 GPa to 3.6 GPa relating to a high deformation capability of mortars and confirming their suitability for use in conservation work.

KEYWORDS: lime, mortar, sepiolite, synthetic zeolite pellets

1. INTRODUCTION

Lime mortars were developed in ancient times and used by the Roman civilization throughout its Empire and calcium hydroxide or slaked lime has been, since then, a current binder in mortars (Velosa et al., 2007). With the discovery of hydraulic binders, during the mid-18th century, lime was gradually replaced by hydraulic lime and finally by cement (19th/20th century) (Martínez-Ramírez et al., 1995). The use of Portland cement-based mortars for conservation and restoration purposes has been criticized because of its high salts content, excessive stiffness and strength, setting shrinkage and cracking susceptibility (Feilden, 1982; Maravelaki-Kalaitzaki et al., 2003). At the same time, the adhesion of Portland cement-based mortars to the old historic supports is generally inadequate and these mortars have lower open porosity than the lime based ones and therefore lower water vapour permeability. Because of this, and in order to result in better compatibility with the historic masonry supports, lime-based mortars are proposed as the best restoration mortar choice (Sepulcre-Aguilar and Hernández-Olivarez, 2010; Veiga et al., 2010). Air lime is the most adequate binder; however it encloses some problems such as specific execution techniques, slow setting, inability to harden under water and lack of durability.

The main objective of this study is to develop new repair mortars used especially as renders for historical buildings fulfilling compatibility requirements and with higher mechanical properties. Sepiolite and a zeolite pellets were chosen as additives for lime mortars due to their unique adsorption properties – retaining moisture in mortar system after the mortar mix and application, by acting as water reservoirs.

Sepiolite is a clay mineral with structural formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$. It exhibits a microfibrous morphology with a particle length of 2–10 μm. The properties of the sepiolite are closely related to its structure which is made up of layers of tetrahedrons of silicon linked by oxygen atoms to a central octahedral plane of magnesium atoms. The silicon tetrahedrons are inverted every six units, which causes formation of longitudinal channels with dimensions of 3.6 x 10.6 Å. These channels are called zeolitic, giving the sepiolite a high specific surface area close to 340 m²/g, that is expressed in its admirable adsorptive and absorptive properties. In addition, sepiolite has high volume stability (it does not swell) and considerable chemical and structural

stability in strongly basic media (Martínez-Ramírez et al., 1996). Sepiolite particles, when dispersed in the mortar slurry, form an interacting network in which the components of the system are homogeneously distributed. The network is stabilized by the weak forces provided by hydrogen bonds that can be re-configured due to the shear existing during mixing steps. This change allows getting highly viscous gels that sharply reduce the apparent viscosity, when some energy is supplied to the system (Kang et al., 2008).

There are recently only few studies related to an addition of sepiolite to mortars. Martínez-Ramírez et al. (1995, 1998a, 1998b) used sepiolite to develop lime mortars with biocide characteristics and noted that sepiolite plus biocide decrease reaction between mortar and "acid rain" media with pH = 3.5. Authors have found out that incorporation of sepiolite below 5 % in weight into the mortar does not affect the mechanical behaviour of the mortar; but there is a reduction of its mechanical strength when 10 % of lime is substituted. Sepulcre-Aguilar and Hernández-Olivarez (2010) stated that thermally activated sepiolite in metakaolin-lime mortars avoids a C_4AH_{13} phase formation what results in a strength decrease of 66% compared to metakaolin-lime mortars only. Sepiolite has been used to provide the required rheology for a high quality corrugated fiber–cement piece (Pérez and Álvarez, 1988) and also improves both flexural and compressive strength because of the network structure induced within the cement matrix (Kavas et al., 2004). The addition of sepiolite to Portland cement mortar reduces the crack width and crack length notably (Kang et al., 2008).

Zeolites are hydrated crystalline aluminosilicates $\{M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O\}$ where n is the charge of cation M, and the values of x, y and z depend on the type of zeolite, having a three-dimensional skeletal structure based on repeated units of SiO_4 and AlO_4 tetrahedra. They may occur either in nature or be manufactured synthetically (Colella et al., 2001). Molecular sieves are a certain kind of synthetic zeolites, which due to their precise size and pore shape, molecular polarity and chemical composition, have developed particular selective adsorption properties, based on a surface molecular scale phenomenon in which gas or liquid molecules are attracted to the internal volume of the porous solid. The diameter of the open-window in the α-cage structure, typically ranging between 3 and 10 Å (Szostak, 1989), can be as small as NH_3, H_2O and H_2 molecules and determines the size of the molecules which can be adsorbed or released (Kresge and Dhingra, 2004). One of the most common molecular sieve types is the "A" structure, where the 3Å, 4Å, and 5Å opening diameter pore is obtained with a potassium (K^+), sodium (Na^+), and calcium (Ca^{2+}) cation, respectively (Kresge and Dhingra, 2004). Zeolites are pozzolanic materials characterized by lime adsorption values between 134 and 224 mg CaO/g. The highly porous structure of the typical natural zeolite raw material provides a large reaction surface for interaction with $Ca(OH)_2$ (Tong and Fang, 1983). Zeolitic tuffs have been widely used, as admixtures with lime, in construction since Roman times. Poon et al. (1999) reported that natural zeolite is a pozzolanic material, with reactivity between that of silica fume and fly ash. Caputo et al. (2008) have studied the pozzolanic activity of synthetic zeolite A and zeolite X in portland cement mortars and concluded that both types of zeolites provide pozzolanic activity and zeolite A reacts more easily when compared to zeolite X.

In scientific studies performed on the usability of natural zeolite especially as a cement blend material, strength development and other properties of cements depending on the percentage of zeolite blend ratios were examined and results were found positive (Poon et al., 1999; Janotka et al., 2003; Perraki et al., 2003; Canpolat et al., 2004). However there is no systematic study about lime mortars containing natural or synthetic zeolites.

Seok-Kyun et al. (2009) used zeolite to develop effective anti-fungal mortars. Research of Haile et al. (2008) confirmed that zeolites functionalized with heavy metals exhibit both antimicrobial characteristics and resistance to biologically produced sulphuric acid attack in mortars. Natural zeolites also prevent the undesirable expansion due to alkali aggregate reaction and sulfate attack (Janotka and Števula, 1998).

2. MATERIALS, MORTAR COMPOSITIONS AND CONDITIONING

Mortars were formulated with powdered commercial air lime CL 90 (AL) (Portuguese origin) and siliceous river sand. Mortars were prepared with air lime/sand volumetric ratio of 1:3. The weight loss for portlandite and calcite presented in air lime was 8.2 wt. % and 29.7 wt. %, respectively. Lime binder was replaced by 5 % of fine and coarse commercial sepiolite (Spanish origin) and fine and coarse commercial synthetic zeolite pellets (Grace Davison, USA). Individual specimens are in the text marked as follows (Table 1).

The added water was calculated in relation to required consistency (i.e. similar flow table values of around 130 mm), which corresponds to appropriate workability for this type of mortars. 19 % of water, considering total mortar mass, was added to air lime mortar. Forasmuch sepiolite and zeolite pellets have high specific surface areas and consequently

Table 1 Composition of mortars.

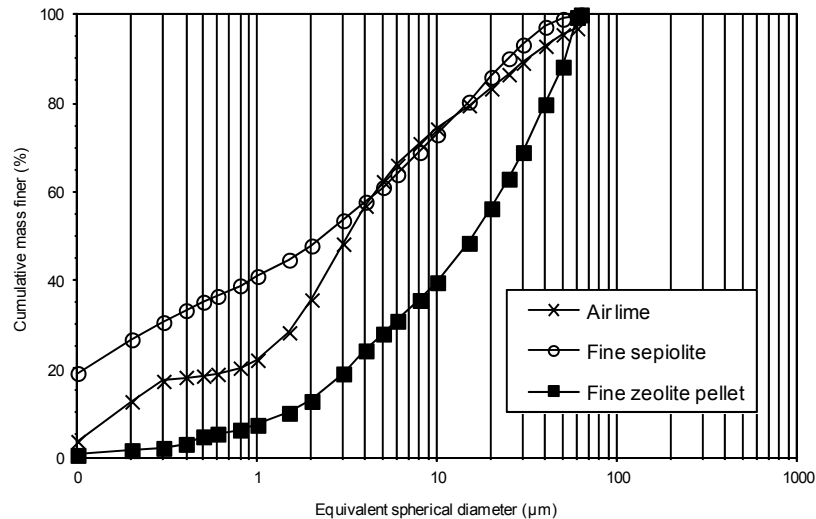| Reference	Materials
AL	air lime + sand
FSAL	fine sepiolite + air lime + sand
CSAL	coarse sepiolite + air lime + sand
FZAL	fine zeolite pellet + air lime + sand
CZAL	coarse zeolite pellet + air lime + sand

Fig. 1 Particle size distribution of air lime, fine sepiolite and fine zeolite pellets.

higher water demand, 23.3 % and 21.1 % of water was necessary to add to fine/coarse sepiolite and zeolite mortars, respectively. Mortar prisms 40 × 40 × 160 mm were prepared and conditioned in a climatic chamber following the Standard EN 1015-11 (1999). Specimens were stored in moulds for the first 2 days in a chamber at 20±2 ºC with a relative humidity of 95±5 % and 5 days at the same temperature, but at a relative humidity of 65±5 %. After removing the moulds, specimens were maintained at a relative humidity of 65±5 % and cured up to an age of 28, 90 and 180 days.

3. METHODS

The fine size material was obtained by dry grinding the commercial coarse (beads) zeolite pellets in a Ceramic Instruments mill (S2-1000-M) with porcelain jars and alumina balls, during 15 minutes.

Particle size distribution of fine materials was performed with X-ray grain size analyser Sedigraph 5100 from Micromeritics, following the BS 3406-2 (1986).

The mineralogical composition of the specimens was determined using a Philips X'Pert diffractometer equipped with CuKα radiation. The mortar samples for XRD analysis were sieved through 0.150 mm sieve in order to eliminate the coarse aggregate materials, namely quartz present in river sand.

The chemical composition (major elements) was analyzed using a Panalytical Axios X-ray fluorescence spectrometer. Loss on ignition was determined by heating the samples in an electrical kiln at 1000 ºC during 3 hours.

The specific gravity of the mortars was carried out with paraffin method (uncohesive samples) according to Bardet (1997).

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 ºC and 1000 ºC, with a heating rate of 10 ºC/min.

The microstructural and chemical homogeneity was analysed by scanning electronic microscopy, SEM/EDS (Hitachi SU 70 coupled with EDAX Bruker AXS detector).

The specific surface area analysis was accomplished in Micromeritics Gemini 2.0 equipment according to the BET method (Brunauer et al., 1938).

Total specific surface area of the materials was determined using ethylene glycol monoethyl ether (EGME) retention according to Novák and Číčel (1970).

The pozzolanic measurements were performed using the Chapelle modified test according to NF P 18-513 (2010).

Flexural and compressive strength testing was performed following the Standard EN 1015-11 (1999) on ELE Multiplex 50-E equipment, with a ring load of 3 kN. Three probes were used to measure flexural strength and 6 probes were used to measure compressive strength.

The dynamic modulus of elasticity was determined based on the fundamental longitudinal resonant frequency following the BS 1881-209 (1990).

4. RESULTS AND DISCUSSION

4.1. *CHARACTERIZATION OF MATERIALS USED FOR MORTAR PREPARATION*

4.1.1. *PARTICLE SIZE DISTRIBUTION*

Particle size distributions for air lime, fine sepiolite and fine zeolite pellets are reported in Figure 1. D50 values of air lime, fine sepiolite and fine zeolite pellets are 3.2, 2.4 μm and 16.0 μm, respectively. The coarse sepiolite presents a particle size range distribution from 0.2 - 1.1 mm and the coarse zeolite pellets (beads) between 1.2 - 2.5 mm.
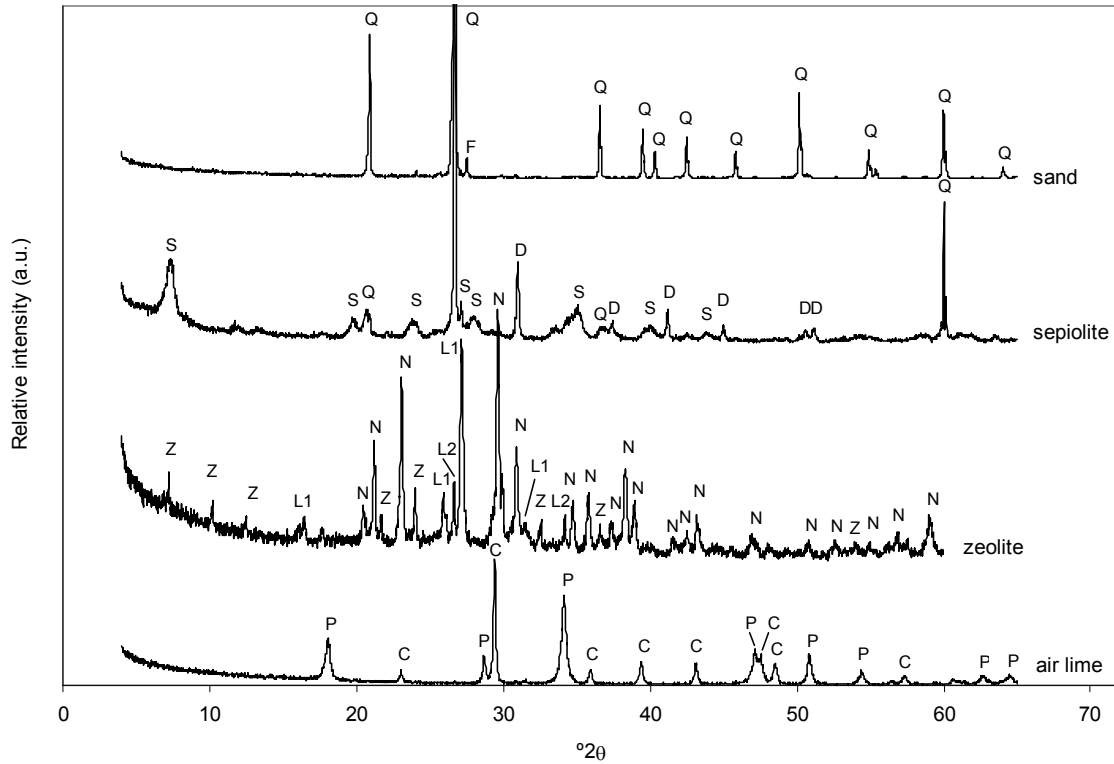
Fig. 2 X-ray diffraction of random oriented materials used for mortars preparation.
(Q-quartz, F-feldspar, S-sepiolite, D-dolomite, Z-zeolite type A, N-nepheline, L1-leucite, L2-leucite, P-portlandite, C-calcite)

Table 2 Chemical analyses of materials used for mortars preparation.

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	P$_2$O$_5$	L.O.I.*
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
sand	96.22	2.17	0.19	0.01	nd**	0.02	nd	1.15	0.14	0.02	0.49
air lime	nd	nd	0.09	0.01	0.16	62.24	nd	0.01	0.03	0.01	38.12
sepiolite	56.62	4.22	1.29	0.04	19.28	4.85	nd	0.96	0.19	0.06	12.58
zeolite pellets	48.69	27.52	1.60	0.04	3.44	0.70	7.06	8.94	0.22	0.07	1.71

* Loss on ignition
** nd - not detected

4.1.2. X-RAY DIFFRACTION

The mineralogical analysis reveals that sand is mainly composed by quartz (ICDD PDF 05-0490), as major mineral, with traces of K-feldspar (ICDD PDF 19-0932). Sepiolite pattern shows that sepiolite (ICDD PDF 02-0034) is the major component associated with dolomite (ICDD PDF 11-0078) and quartz (ICDD PDF 05-0490) impurity. The synthetic zeolite pellets are composed by potassium-sodium zeolite type A (ICDD PDF 76-6495), nepheline (ICDD PDF 78-8388) and leucite (1: ICDD PDF 13-2785 and 2: ICDD PDF 06-5428). Portlandite (ICDD PDF 02-0968) and calcite (ICDD PDF 04-0636) are the phases identified in the air lime, being the calcite due to carbonation of Ca(OH)$_2$.

4.1.3. CHEMICAL ANALYSIS

The chemical compositions of the materials used in mortar preparation are presented in Table 2. Air lime, as expected, has as major element CaO, attributed in XRD analysis to portlandite and calcite (Fig. 2) and high loss on ignition (~38 %) due to the release of H$_2$O from portlandite and CO$_2$ from calcite. Sand presents a high amount of SiO$_2$ related with quartz and lower quantity of Al$_2$O$_3$ and K$_2$O related with alkali feldspar, both identified in XRD analysis (Fig. 2). Sepiolite sample shows increased amount of MgO and CaO which is a consequence of the dolomite admixture confirmed in its XRD patterns (Fig. 2). The zeolite used in this study, commercialized in bead (pellet) form, is a synthetic

Table 3 Specific gravity of materials used for mortars preparation.

Sample	Specific gravity (kg.m^{-3})
sand	1470
air lime	460
fine sepiolite	530
coarse sepiolite	680
fine zeolite pellets	1140
coarse zeolite pellets	1290

Table 4 Properties of the fine and coarse adsorbent materials.

	SSA^a (BET) (m^2/g)	TSA^b (EGME) (m^2/g)	Chapelle modified (mg Ca(OH)$_2$/g pozzolan)
fine sepiolite	77	390	90
coarse sepiolite	20	430	120
fine zeolite pellets	0.8	25	340
coarse zeolite pellets	2.2	63	110

a- Specific surface area
b- Total surface area

potassium-sodium material (Table 2), which is in agreement with the mineral composition (Fig. 2)

4.1.4. SPECIFIC GRAVITY

Specific gravities of materials used for mortars' preparation are reported in Table 3. The highest value was achieved by sand with 1470 kg.m^{-3} as its particles range between 0.125 – 0.5 mm, with D50 = 0.36 mm.

Values for fine and coarse zeolite pellets are approximately about 100 % higher compared to fine and coarse sepiolite. The finest material used for mortar preparation is air lime with specific gravity value of 460 kg.m^{-3}.

4.1.5. CHEMICAL PROPERTIES

Table 4 presents chemical properties and the pozzolanic activity of the adsorbent materials for both fine and coarse size.

Specific surface area (*SSA*) by BET method presented very low values: 0.8 and 2.2 m^2/g for both fine and coarse zeolite pellets, respectively. This is due to the capacity of these molecular sieves to adsorb polar molecules instead of nitrogen, because these materials are used as desiccants in insulated glass, which is in the inner air space filled with this gas. Coarse sepiolite has *SSA* value in accordance with the range (95-400 m^2/g) reported by Hibino et al. (1995). The low result of *SSA* for fine sepiolte (77 m^2/g) shows that the structure of the sepiolite fibers surface is changed by the grinding and the number of surface micro-pores decrease (Vučelić et al., 2002).

Total surface areas (*TSA*), which include external and internal surfaces, of fine and coarse sepiolites are considerably higher compared to fine and coarse zeolite pellets. *TSA* of coarse sepiolite and zeolite increased of 10 % and 150 % compared to fine sepiolite and zeolite, respectively (Table 4). Lower *TSA* values for coarse and fine zeolite pellets are due to the fact that ethylene glycol monoethyl ether (EGME) molecules ($C_4H_{10}O_2$) are physically adsorbed in the exterior of the β-cage structure of these materials, as their size is bigger compared to NH_3 or H_2O molecules, which can be adsorbed also in the

inner α-cage structure of the zeolite type A. By other hand, the feldspathoids presented in the pellets do not have capacity to adsorb EGME. This implies that the amount of EGME adsorbed is also correlated with the exterior surface of the zeolite type A and thereby the *TSA* values are underestimated.

It is noticed that coarse sepiolite has higher pozzolanic activity then fine sepiolite, by opposition to zeolite pellets (Table 4). This is related to the higher specific surface of the coarse sepiolite, as it is one of the factors that promotes a better pozzolanic reaction. Pozzolanic activity for coarse and fine zeolite pellets with values 110 and 340 mg Ca(OH)$_2$/g pozzolan, respectively, are lower than the values of 555 and 640 mg Ca(OH)$_2$/g pozzolan reported by Perraki et al. (2003, 2010) for natural pozzolans. This behaviour is related with the presence of feldspathoids in the pelletized material.

### 4.2. CHARACTERIZATION OF MORTARS

4.2.1. THERMOGRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL THERMAL ANALYSIS (DTA)

Figures 3A and 3B report the DTA curves of FSAL/CSAL and FZAL/CZAL mortars from 28 to 180 days of curing, respectively. DTA curves show in all admixtures two not well-resolved endothermic peaks around 150 ºC and 250-265 ºC, namely at 28 and 90 days in FZAL/CZAL mortars. Based in the study of Ubbriaco and Tasselli (1998), the first peak can be attributed to the dehydratation of hydrated calcium monocarboaluminate ($C_4A\overline{C}H_{11}$) and the second one to C_4AH_{13}. Also in FSAL/CSAL mortars, another endothermic peak is clearly resolved at 180 days nearly 400 ºC. This could be attributed to brucite or hydromagnesite formation at higher curing ages, since sepiolite has a magnesium compound present in its composition.

Also, we cannot exclude the formation of hydrated amorphous calcium silicates or calcium silicate aluminates that could explain the endothermic signals observed in sepiolite and zeolite mortars until 400 ºC at 180 days.
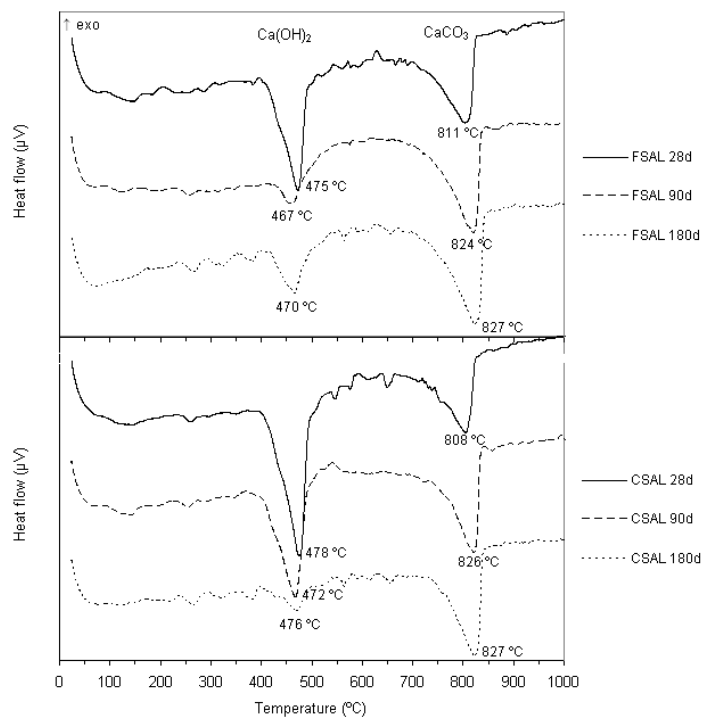
3A
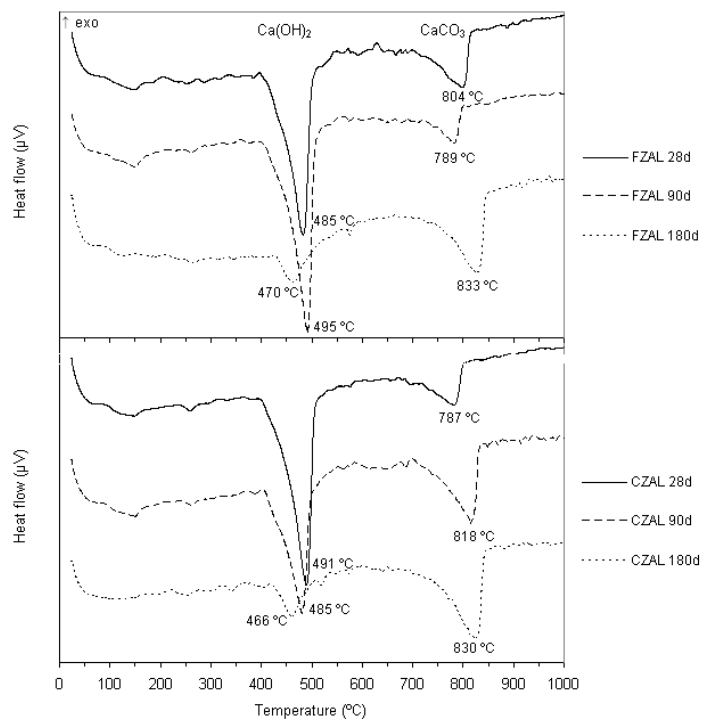
3B

Fig. 3   DTA of mortars at 28, 90 and 180 days.
         A) fine and coarse sepiolite mortars,
         B) fine and coarse zeolite pellets mortars.

Table 5 Weight loss of the portlandite and calcite in the mortar admixtures.

Curing time	FSAL		CSAL		FZAL		CZAL	
(days)	Portlandite (%)	Calcite (%)	Portlandite (%)	Calcite (%)	Portlandite (%)	Calcite (%)	Portlandite (%)	Calcite (%)
28	4.2	13.7	6.6	14.2	7.8	11.5	9.6	9.4
90	2.1	17.8	5.6	19.6	10.4	10.3	6.4	16.1
180	2.5	18.8	1.6	19.4	2.0	16.0	2.5	21.2

From 28 to 180 days, two large endothermic peaks can be observed, assigned to portlandite and calcite in the temperature ranges of 466 ºC (CZAL at 180 days) to 495 ºC (FZAL at 90 days) and 787 ºC (CZAL at 28 days) to 833 ºC (FZAL at 180 days), respectively.

The portlandite and calcite mortars content, calculated from the weight losses obtained by TGA due to portlandite and calcite decompositions are presented in Table 5. At 28 days, zeolite pellets admixtures present higher weight loss of portlandite (7.8% for fine and 9.6 % for coarse) than the sepiolite admixtures (4.2 % for fine and 6.6 % for coarse). By opposition, the sepiolite mortars show higher calcite weight loss (13.7 % for fine and 14.2 % for coarse) than zeolite pellets admixtures (11.5 % for fine and 9.4 % for coarse). The same tendency is observed at 90 days. The results suggest faster carbonation of sepiolite admixtures.

From 28 to 90 days, in FZAL mortar, an unexpected behaviour related with an increase of portlandite (2.6 %) and a decrease of calcite (1.2 %) occurs. This behaviour can be related with pozzolanic activity of fine zeolite pellets, where calcium is consumed by the creation of stable calcium aluminium silicates and on the other hand, possible decomposition of metastable phase-calcium aluminium hydrate, promoting liberation of portlandite to the system (Gameiro et al., 2011). At 180 days, all the mortars still contain traces of unreacted portlandite ranging from 1.6 % (CSAL) to 2.5 % (FSAL, CZAL).

4.2.2. SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy observations allow a further insight into the mortars' composition and morphology. Figures 4A-4F illustrate microstructures of individual mortars. Figures 4A and 4B show a typical calcitic lime mortar matrix. Addition of sepiolite and/or zeolite pellets (Figs. 4C-4F) causes microstructural changes of mortars. Needle shaped fine and coarse particles of sepiolite connect individual components producing a denser framework and improve compactness of the mortar system (Fig. 4C, 4D). Fine zeolite pellets create mosaic shaped flakes of calcium aluminium silicate, developed in the pozzolanic reaction of Ca(OH)$_2$ and zeolite pellets (Fig. 4E). Formation of a new

pozzolanic phase was also confirmed by EDS analysis (Fig. 4G). The mosaic shaped flakes are observed in CZAL mortar, too, but predominantly in FZAL mortar. In addition, coarse zeolite pellets in AL mortar provide conditions, in which fan-shaped clusters of aragonite are formed (Fig. 4F). Crystallization of aragonite in mortars or concretes depends on experimental conditions (Martínez-Ramírez et al., 2003; Taylor 1997) and its creation is not a very frequent phenomenon. Taylor (1997) states that CaCO$_3$ precipitates as aragonite rather than calcite in presence of Mg^{2+} ions and according to Roques and Girou (1974) carbonation with high carbon dioxide concentration leads to the formation of aragonite crystals. Chemical analysis (Table 2) shows that zeolite pellets contain 3.44 % of exchangeable MgO, which could be an appropriate environment for aragonite creation.

4.3. MECHANICAL PROPERTIES

4.3.1. FLEXURAL STRENGTH

Figures 5A and 5B present the results of flexural strengths (R_f) of individual mortars at 28, 90 and 180 days. Although it is well known that sepiolite slows down the carbonation process (Martínez-Ramírez et al., 1995), the small length of sepiolite fibers and their acicular morphology resulted in improved flexural resistance compared to AL mortars only. Addition of fine and coarse sepiolite caused an increase of flexural strength values compared to AL mortar by 14 and 50 % and 23 and 35 % at 28 and 90 days, respectively (Fig. 5A). At 180 days, the flexural strength continues to show a slight increase for all studied mortars compared to values at 90 days.

Addition of FZ and CZ to AL mortars did not influence the flexural strength at 28 days noticeably (Fig. 5B). It is a result of high portlandite occurrence and thus slower carbonation in FZAL and CZAL mortars which is confirmed in their TGA-DTA analysis (Fig. 3B, Table 5). FZ caused an improvement of R_f compared to AL mortar of about 8%. However, the pozzolanic activity of fine zeolite pellets (Table 4) became evident at 90 days, when there is an increase of R_f for FZAL of about 62% in comparison with AL mortar. Coarse zeolite pellets addition has a similar effect as coarse sepiolite addition to AL mortar at 90 days with R_f values of
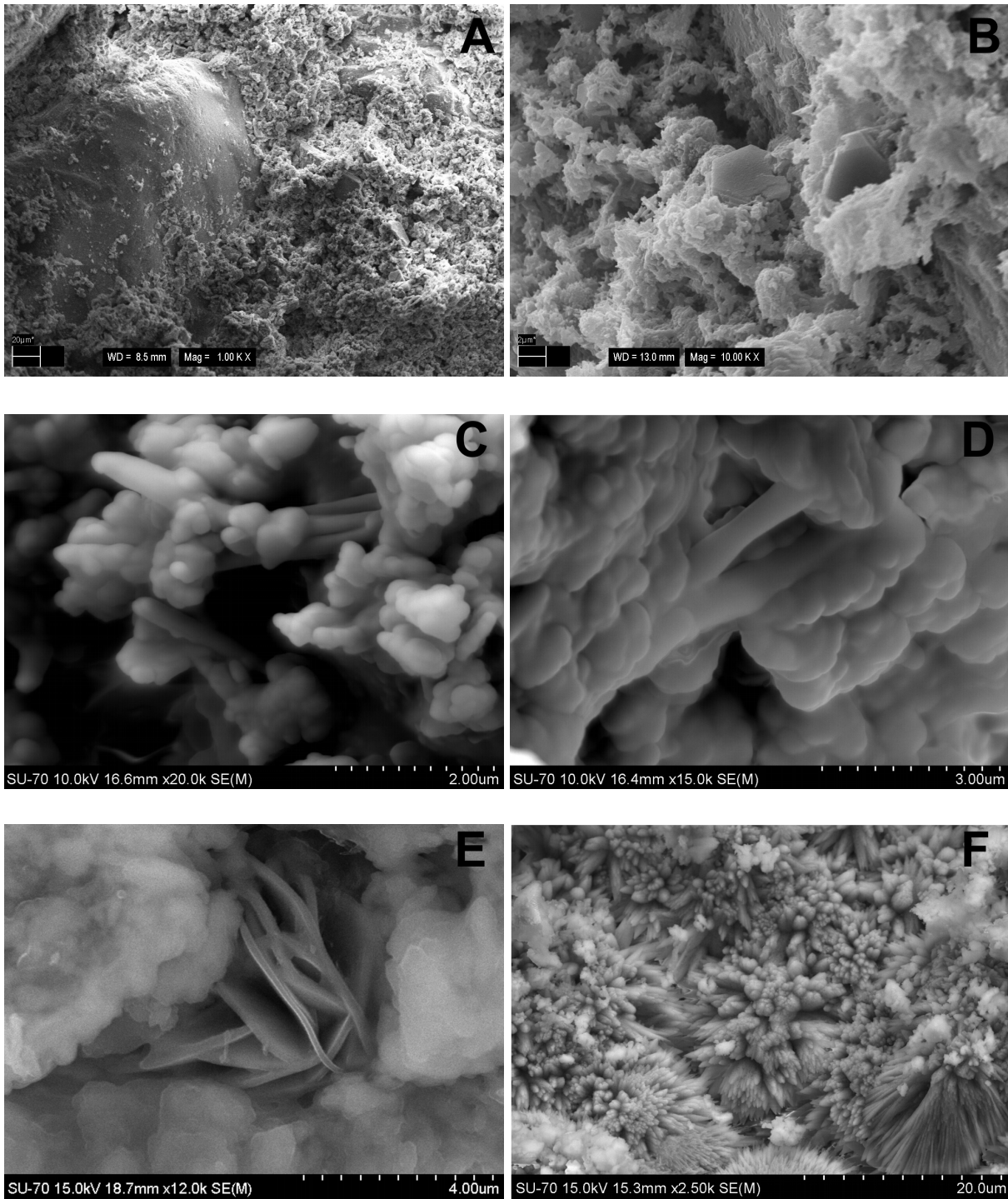
Fig. 4   SEM images of mortars at 90 days.
       A) AL, microstructure of lime matrix on sand grain,
       B) AL, detail on portlandite structure,
       C) FSAL, sepiolite needles in mortar matrix,
       D) CSAL, sepiolite particles in lime bulk,
       E) FZAL, formation of calcium aluminium silicate,
       F) CZAL, fan-shaped clusters of aragonite.
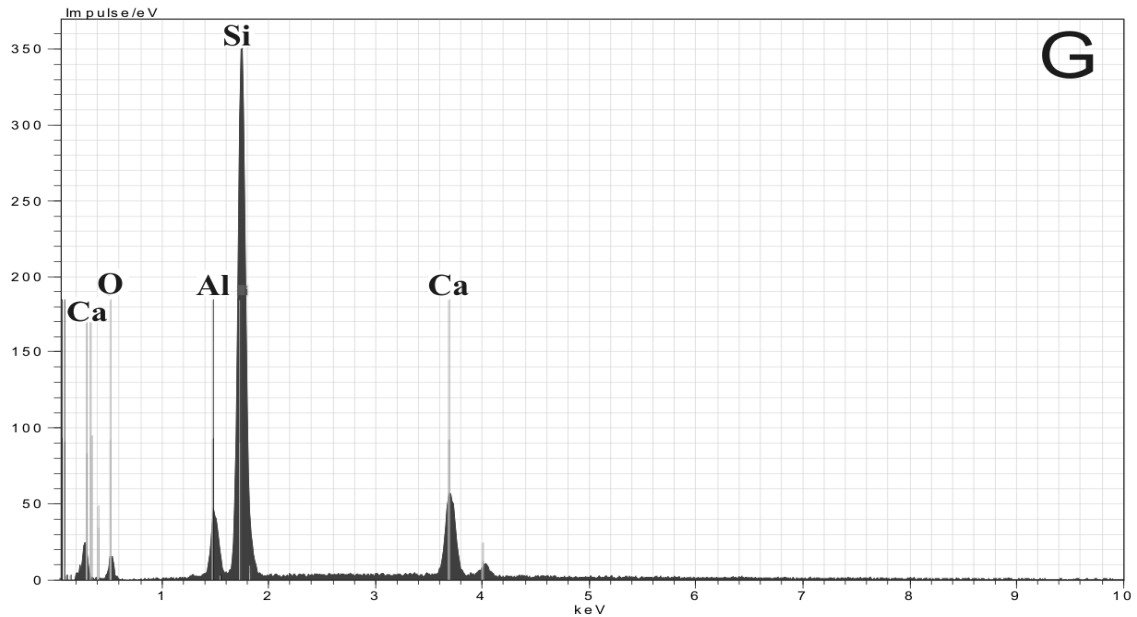
Fig. 4   SEM images of mortars at 90 days.
        G) EDS analysis of Figure 5E.

0.33 and 0.35 MPa, respectively (Fig. 5A, 5B). At 180 days, zeolite mortars display a similar trend as sepiolite mortars. FZAL mortar shows the highest flexural strength (0.44 MPa) from all the mortars at 180 days (Fig. 5B).

4.3.2.   COMPRESSIVE STRENGTH

Compressive strength (R_c) values of the mortars at 28, 90 and 180 days are reported in Figures 6A and 6B. With the increase of curing time, higher values of compressive strength are observed as in the case of flexural strength (Figs. 5A, 5B).

Sepiolite mortars show a similar trend to that of flexural strength (Fig. 5A, 6A) and the highest R_c is attained by CSAL and followed by FSAL mortar at all ages of curing. The diffusivity of mortar for gaseous carbon dioxide in air depends on the openness of the porous structure and thus on the presence of water in the pores (Van Balen, 2005). Coarse sepiolite provides more pore spaces in the mortar matrix causing the creation of greater $CaCO_3$ crystals on the surface of the mortars compared to FSAL; therefore compressive strength of CSAL reaches higher values (Martínez-Ramírez et al., 1995). A more compact structure and lower open porosity of FSAL slow the carbonation process in comparison with CSAL and this results in similar values of R_c for AL and FSAL mortars at 28 days. Nevertheless, addition of fine sepiolite improves R_c of AL mortar of 19 % and 13 % at 90 and 180 days of curing, respectively. Due to the creation of needle shaped particles promoting interlocking of mortar components (Fig. 4D), incorporation of CS to AL mortar manifested in a vast increment of compressive strength around 75 % compared to AL at 180 days (Fig. 6A).

Incorporation of FZ and CZ to AL mortar causes a raise of R_c values about 37 and 47 % compared to AL mortar at 28 days, respectively (Fig. 6B). The addition of CS and CZ to AL at 28 days has the same effect (Figs. 6A, 6B). Substantial increase of R_c was reached at 90 days for FZAL and CZAL mortars of about 54 and 72 % when compared to AL, respectively. This is a very interesting finding considering that FZAL and CZAL, in the same way as CSAL, still contain a significant amount of unreacted portlandite even at 90 days (Table 5). Portlandite occurrence in mortars provides the opportunity for the carbonation and ensures the mortar system with high mechanical resistance at later ages. This can be confirmed by 12 and 14 % increase of compressive strength for FZAL and CZAL from 90 to 180 days. On the other hand, formation of mosaic shaped calcium aluminium silicate in zeolite pellets mortars (Fig. 4E) also contributes to improved mechanical properties of zeolite mortars.

Addition of coarse sepiolite and zeolite pellets at 180 days to AL mortar resulted in comparable R_c of about 0.8 MPa (Figs. 6A, 6B). Coarse materials (sepiolite/zeolite) in AL mortars cause higher R_c values than fine materials and lowest values are characteristic for AL mortars without admixtures.

As was noticed above about the influence of coarse sepiolite addition to mortar, which provides more open pore spaces compared to fine sepiolite, the same phenomenon is found with the addition of coarse and fine zeolite pellets. However, addition of FZ
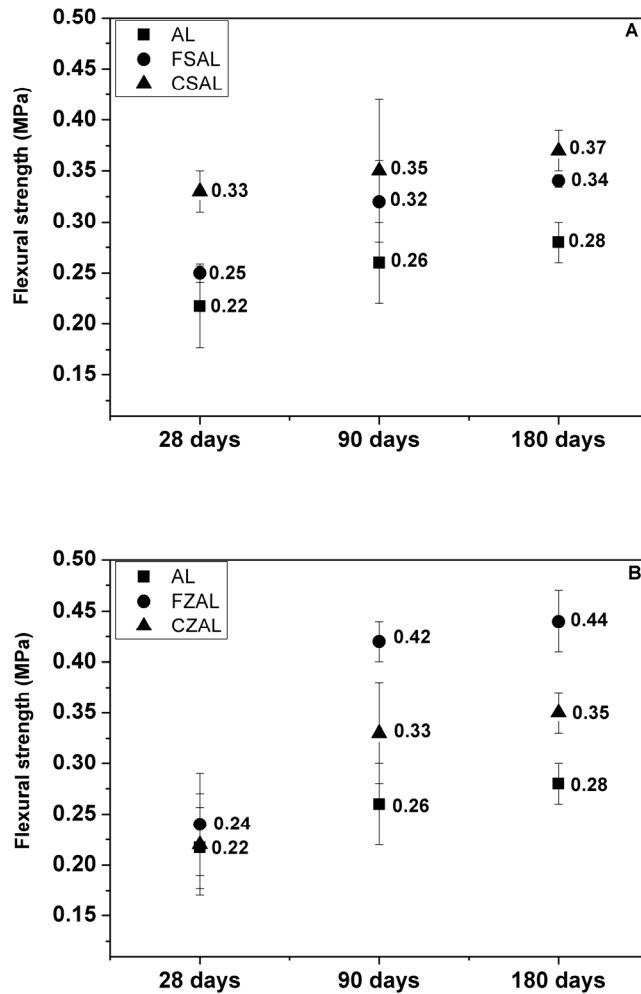
Fig. 5   Flexural strength of mortars at 28, 90 and 180 days.
            A) comparison of AL with FSAL and CSAL mortars,
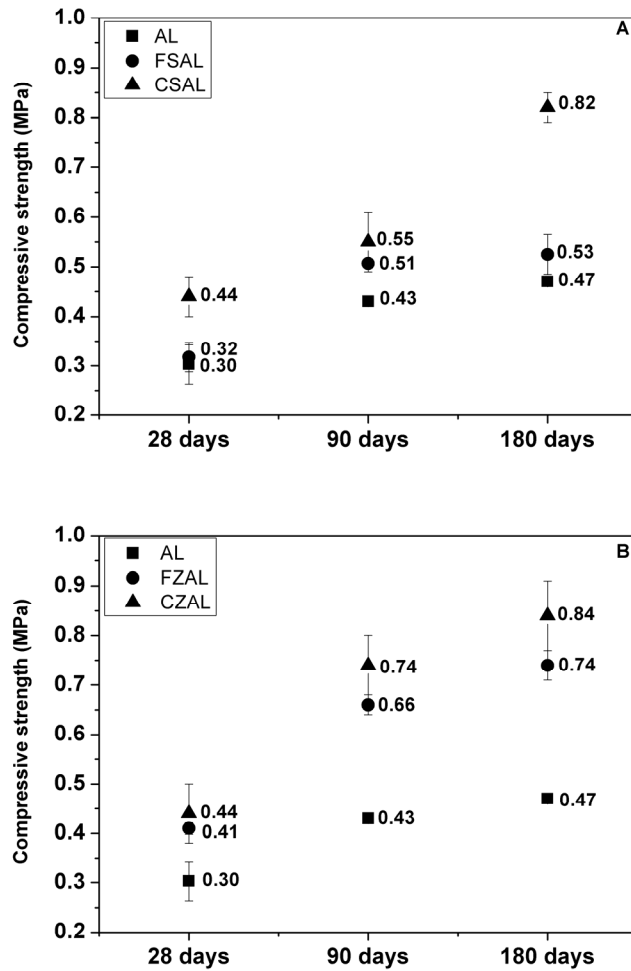   B) comparison of AL with FZAL and CZAL mortars.

provides higher flexural, but lower compressive strength compared to CZAL during all ages of curing (Figs. 5B, 6B). The decrease in flexural strength of CZAL in comparison with FZAL is partially due to zeolite-paste interface fragility, especially evident in the bigger particles, following a rupture scheme similar to that of common aggregate/binder interface. Moreover, according to Ventolà et al. (2011), the growth of crystals of aragonite may help to improve the consistency of the mortar and result in better compressive strength as it is in the case of CZAL mortar.

It can be concluded that coarse and/or fine sepiolite and zeolite pellets incorporation in air lime mortar retards the carbonation process at early ages of curing; however, the final values of mechanical strength are due to continuous and slower carbonation

and changes in mortar microstructure, higher in comparison with AL mortar.

4.3.3. ELASTICITY MODULUS

Figures 7A and 7B present the results of elasticity modulus (E) of all tested samples at 28, 90 and 180 days. With opposition to mechanical properties, a significant increase of E with curing time is not desired, as renders with high elastic modulus have low deformation capability and are therefore unadapted for use in conservation work. Elasticity modulus of all tested mortars is low as required, ranging from 2.3 to 3.6 GPa. At 28 days of curing, there are no considerable differences between particular sets of mortars. Values of elasticity modulus vary from 2.3-2.7 GPa. The upward trend in E values with age is evident in AL, FZAL and CZAL mortars

Fig. 6 Compressive strength of mortars at 28, 90 and 180 days.
A) comparison of AL with FSAL and CSAL mortars,
B) comparison of AL with FZAL and CZAL mortars.

(Fig. 7B). Elasticity modulus of FSAL and CSAL at 28 and 90 days stays without significant change with values of about 2.33 and 2.65 GPa, respectively (Fig. 7A). From 90 to 180 days, E values of all the mortars increase. The highest E value is reached by AL mortar in both ages of curing with values 3.13 (90 days) and 3.60 GPa (180 days), while sepiolite and zeolite pellets additions have diminishing effect on elasticity modulus compared to AL, as desired (Figs. 7A, 7B).

5. CONCLUSIONS

Addition of fine and coarse sepiolite and fine and coarse zeolite pellets to lime mortars provided the following results:

A   Their high specific surface area influences overall compatibility of the mortar matrix. Sepiolite and zeolite pellets slow the carbonation process of mortars as was confirmed by portlandite appearance in their TGA-DTA graphs at 90 and 180 days. Nevertheless, this phenomenon did not affect mechanical resistance of blended mortars in a negative way.

B   The mechanical properties of mortars containing fine and coarse sepiolite and fine and coarse zeolite pellets are higher than those of lime mortars especially at 90 and 180 days of curing. Some pozzolanic activity of fine/coarse zeolite pellets results in higher mechanical resistance values compared to fine/coarse sepiolite. Increased specific surface area and Chapelle modified test values of coarse sepiolite are reflected in the higher compressive and flexural strengths compared to fine sepiolite mortar.

C   Differences in microstructure of blended mortars were observed. Needle shaped fine and coarse particles of sepiolite connect individual components of lime mortar producing a denser framework. Fine zeolite pellets create mosaic shaped flakes of calcium aluminium silicate
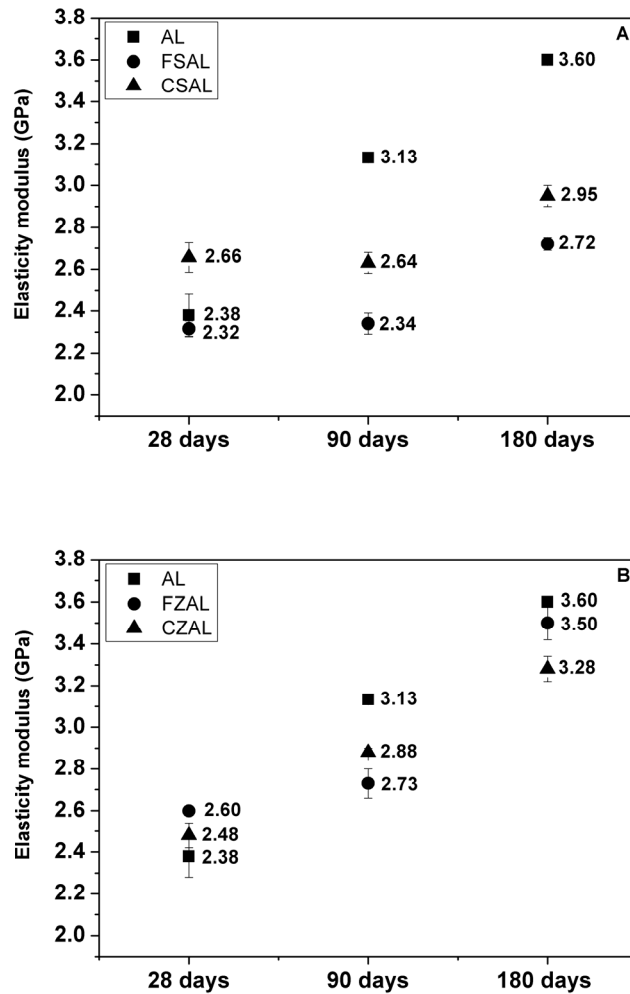
Fig. 7   Elasticity modulus of mortars at 28, 90 and 180 days.
A) comparison of AL with FSAL and CSAL mortars,
B) comparison of AL with FZAL and CZAL mortars.

developed in pozzolanic reaction and coarse zeolite in air lime mortar provides conditions, in which fan-shaped clusters of aragonite are formed.

D   Elasticity   modulus ranges from 2.3 GPa to 3.6 GPa, meaning that mortars have high deformation capability and are therefore suitable for use in conservation work.

Both fine and coarse forms of sepiolite and zeolite pellets additions to the lime mortar produced an improvement of mortar properties, which makes them promising materials for the repair of ancient masonry and could be successfully used for applications in the conservation and restoration of cultural heritage.

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