

Hydraulicity and Mechanical Properties of Mortars Manufactured with a Commercial Zeolite

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ABSTRACT

Further to a recent exploratory investigation on the possible use of cheap, commercially available, synthetic zeolites as pozzolanic addition to portland cement, the present study aims at characterizing a low-silica sodium zeolite, named Na-A, as possible component of hydraulic lime mortars. In order to evaluate the action played by the zeolite in developing hydraulicity and mechanical properties, three lime-zeolite mortars with different ratios of the two components were prepared and characterized in terms of compositional features and mechanical and physical properties. The pozzolanic activity of the zeolitic addition was also evaluated by measuring the amount of free lime in experimental pastes, as a function of ageing time.

The main results worked out are: (a) zeolite addition gives rise to a clear benefit on compressive strengths of the hardened mortars; (b) hardening is rapid, as more than 60% of the final compressive strengths is developed after only 7 days; (c) lime/zeolite ratio does not affect to a great extent porosity and water absorption of the manufactured mortars; (d) mortars containing equal amounts of lime and zeolite show the best performances, either from a compositional point of view (absence of unreacted zeolite) or from mechanical and porosimetric properties, also in comparison to an analogous, non-zeolitic, commercial mortar.

INTRODUCTION

The survival of many monuments of Roman times (or before) is mainly connected to the excellent properties, in terms of mechanical resistance and durability, of the peculiar binders used for their construction. These binders, called hydraulic lime mortars, are made of mixtures of lime and reactive silico-aluminates. Hydraulicity is connected to the property of these mixtures to give rise to compounds, namely, hydrated calcium silicates and aluminates, able to harden in both aerial and aqueous environments [Taylor, 1990].

The ability to react with lime is typical of pozzolan, an unconsolidated, mostly glassy, rock of volcanic origin, widespread especially in central-southern Italy. Many natural or artificial products, possessing this property, are said to have “pozzolanic activity”. These materials have been used in the last hundred years and are being used today mostly for manufacturing pozzolanic cements. Natural, zeolite-rich volcanic tuffs [Sersale, 1995] are among these materials and are used as pozzolan in several European and extra-European countries [Colella et al., 2001]. Today, the great availability of some cheap synthetic zeolites has drawn the attention on the possibility of their use as pozzolanic addition to portland cement [Caputo et al., 2008].

The increasing attention for restoration and conservation of monuments and buildings of historical and/or architectural relevance and a major sensitivity for environmental problems (reduction of CO₂ emissions in atmosphere) has re-awaked the interest for lime-based binders and, in particular, hydraulic lime. It has therefore been considered useful to investigate on the possibility to use a cheap commercial zeolite, named Na-A [Caputo et al., 2008], to obtain hydraulic lime mortars. Hydraulicity and mechanical resistance of the hardened mortars have been selected as the main parameters to evaluate the prepared materials.

A peculiar care has been paid in the selection of the method to evaluate pozzolanic activity [Surana and Joshi, 1988]. The official test accepted by the European Standards [Fratini, 1949; 1950; European Committee for Standardization, 1994] is based on a hydrothermal treatment of portland clinker-pozzolan-gypsum pastes. Ca²⁺ and OH⁻ concentration in solution is assumed as an indicator of the presence/absence of “free lime” in the solid and therefore of the effectiveness of the pozzolanic action. Actually, this test has been demonstrated to fail in giving a reliable information on the presence of residual Ca(OH)₂ in hardened pastes [Liguori et al., 2004]. On the contrary, thermoanalytical methods, based on TG/DTG, DTA and DSC measurements [Perraki et al., 2005], seem to be more consistent and have been adopted in the present study. Apart from reliability, these methods give also quantitative results, as they allow to estimate the amount of residual Ca(OH)₂ from its decomposition in the temperature range 400–500°C. In addition, following the kinetics of lime disappearance helps to give an estimation of the time needed to develop the pozzolanic action [Kontori et al., 2009].

EXPERIMENTAL

Materials

A sample of synthetic sodium zeolite A (Na-A) was provided by Sasol Italy. This material, named Vegobond 4A and marketed as detergent builder, contains roughly 80% zeolite, having a mean grain size of about 10 μm. X-ray diffraction analysis (XRD, see next section) demonstrated that no other crystalline phases were present in the sample. The residual 20% should therefore be constituted by an amorphous unreacted silico-aluminate phase, which is normally used as starting mixture for zeolite production.

A sample of natural pozzolan, coming from a quarry in Barile (Rionero in Vulture, Potenza, south Italy), was used as reference in the pozzolanicity test.

The chemical composition of these two materials was determined as follows. After grinding, a weighted sample was first calcined (loss on ignition was roughly 22% and 2% for zeolite and pozzolan, respectively), then subjected to digestion, under microwave-induced heating (Perkin-Elmer Multiwave 3000 oven), in a standard solution prepared by mixing 1 ml of HCl, 1 ml of HNO₃ and 4 ml of HF. After addition of H₃BO₃ (24 ml) to attain fluoride complexation, the solution was analyzed by ICP atomic emission spectrophotometry (ICP-OES, Perkin-Elmer Optima 2100 DV). Table 1 reports the chemical compositions obtained.

Table 1. Oxide composition of ignited Na-A and pozzolan (%)

Oxide	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	MgO	CaO	K ₂ O	TiO ₂
Na-A	43.60	33.01	23.33	-	-	-	-	-
Pozzolan	61.04	19.83	3.54	3.96	0.89	2.62	7.63	0.47

A commercial sample of lime was utilized in all the experiments. Its composition, estimated by thermogravimetry (TG, see the following section) was as follows: Ca(OH)₂ 88.5%, CaCO₃

5.7% plus impurities. A commercial dolomitic sand (dolomite 94%; quartz 6%), with a mean grain size < 0,35 mm, was used as aggregate.

Three different hydraulic lime mortars were prepared, mixing together the commercial lime, the Na-A zeolite, the commercial dolomitic sand and distilled water. An ordinary lime mortar was also prepared as reference. The selected liquid-to-solid weight ratio was 0.30. Table 2 summarizes the compositions of the mortars, which were labelled as $M_{x/(100-x)}$, being x the lime percent in the mixture lime-zeolite. A commercial, non-zeolitic, fine mixture for mortar preparation, which is largely used for surface finishing, was employed as reference.

Table 2 – Composition of the prepared mortars

Mortars	Lime (g)	Zeolite Na-A (g)	Aggregate (g)	Distilled water (g)
$M_{35/65}$	350	650	2000	910
$M_{50/50}$	500	500	2000	910
$M_{65/35}$	650	350	2000	910
$M_{100/0}$	1000	-	2000	910

Methods

To test the pozzolanic activity of zeolite Na-A, several samples of a lime-zeolite blend, containing equal weight amounts of the two components, were prepared. Enough water was added to the blends in order to obtain a solid-to-liquid ratio of 1.40. After a careful mixing, the pastes were cured in sealed polyethylene containers at room temperature. The hardened pastes were collected after time intervals of 3, 7, 14, 28, 60, and 90 days, ground, vacuum dried, to stop further hydration, and lastly stored in sealed containers until analysis.

TG analyses (Netzsch STA409 PCLuxx apparatus; alumina crucibles; N_2 gas flow; heating rate: $10^\circ\text{C}/\text{min}$) of pastes and mortars were carried out in the temperature range $25\text{-}1000^\circ\text{C}$. The weight loss of pastes in the range $400\text{-}500^\circ\text{C}$, due to the dehydration of $\text{Ca}(\text{OH})_2$, was taken as a measure of advancement of pozzolanic reaction.

Mortars were manufactured and mechanically characterized following the prescriptions of the European UNI EN 1015-11 standard [European Committee for Standardization, 2007]. Accordingly, they were cast in $4 \times 4 \times 16$ cm prismatic moulds, compacted and cured at 20°C and R.H. = 95% for 7 days, and afterwards at the same temperature, but at R.H. = 65%, for the following 21 days. Flexural and compressive strengths measurements were carried out using a MTS instrument (MTS Alliance RT/50) and each value was obtained as a mean of three determinations.

The advancement of the hardening reactions was monitored by XRD (Philips PW 1730 apparatus, rad. $\text{CuK}\alpha 1$) on powdered and vacuum dried specimens, withdrawn from the fragments of the mechanical tests.

Some physical properties were also determined, in particular, the porosity accessible to water, defined as the ratio of the volume of the pores accessible to water to the bulk volume of the sample, the real density and the bulk density. All these parameters were measured according to the RILEM prescriptions [RILEM, 1980a; 1980b].

RESULTS AND DISCUSSION

Figure 1 shows the results of the TG analysis on the hardened lime-zeolite Na-A or lime-pozzolan pastes after curing for 3, 7, 14, 28, 60 and 90 days. Data are presented in form of kinetics plots, reporting water loss percent in the $400\text{-}500^\circ\text{C}$ range, connected to lime dehydration. Loss is proportional to residual $\text{Ca}(\text{OH})_2$ content and is therefore an indirect

measure of the advancement of pozzolanic reaction. Inspecting the figure points out that, at a parity of weight, zeolite Na-A is more reactive than natural pozzolan. In fact, the zeolitic material (a) presents a faster kinetics than pozzolan in the early stages of the reaction, as can be deduced from the initial slope of the curves, (b) is able to fix more than 45% of the initial lime in only three days, and (c) presents a larger capacity to fix lime also for longer curing times. Considering the composition of the two pozzolanic materials (see Table 1), in particular the higher $\text{SiO}_2 + \text{Al}_2\text{O}_3$ content in pozzolan than in zeolite, it can be deduced that zeolite has a major intrinsic reactivity with lime, possibly due to its “open” structure [Sersale, 1995; Liguori et al., 2004]. Note, however, that the reactivity of the investigated material may depend, at least partially, by the presence of an amorphous phase (see Experimental), which had an undoubted ability to act as pozzolan.

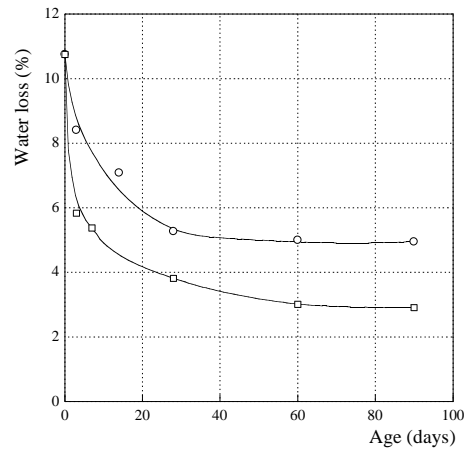


Figure 1. Water loss of lime-Na-A (O) and lime-pozzolan (□) pastes at different curing times, due to dehydration of unreacted $\text{Ca}(\text{OH})_2$.

Thermal analyses carried out on the hydraulic mortars prepared with different amount of zeolite Na-A, confirmed the satisfactory reactivity of the zeolite towards lime. In fact, no residual free lime was detected in mortar $M_{35/65}$ after 7 days ageing, while just a trace of lime (less than 5%) was observed in mortars $M_{50/50}$ and $M_{65/35}$. Accordingly Fig. 2, reporting the DTG curves of the three mortars in the temperature range corresponding to dehydration of hydrated calcium silicates and aluminates [Taylor, 1990], shows the different contents of these phases in the hardened mortars, increasing from the mortar $M_{65/35}$ to the mortar $M_{35/65}$.

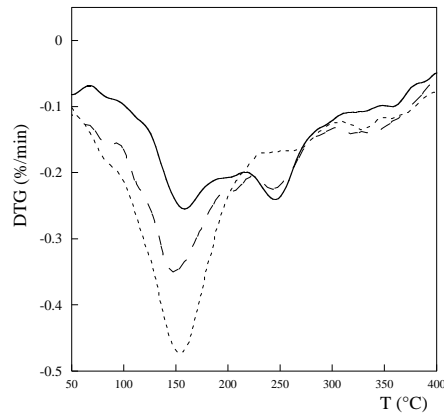


Figure 2. DTG curves of the hardened mortars $M_{65/35}$ (continuous line), $M_{50/50}$ (dashed line) and $M_{35/65}$ (dotted line) after 28 days curing.

Figure 3 shows some representative TG and DTG curves of zeolite-lime mortars after 28 days curing. No endothermic peaks related to the $\text{Ca}(\text{OH})_2$ decomposition is present in the temperature range 400-500°C, what might mean that all lime has reacted. Nevertheless there is a mass loss in the range 600-700°C, especially evident in the $M_{65/35}$ and $M_{50/50}$ mortars (see arrow in Fig. 3), corresponding to CO_2 loss following to thermal decomposition of CaCO_3 [Kontori et al., 2009]. The presence of CaCO_3 is mostly due to a partial carbonation of $\text{Ca}(\text{OH})_2$, that can take place accidentally during the preparation of blends and/or during the grinding of the hardened mortars previous to TG analysis. This mass loss is therefore a sign that not all lime has been fixed: some of it underwent carbonation, which might have prevented lime from reacting exhaustively.

The other endothermic effect, present in the 700-800°C temperature range, must be attributed to the decomposition of the dolomitic aggregate, as demonstrated by comparison with a thermogram of the original material.

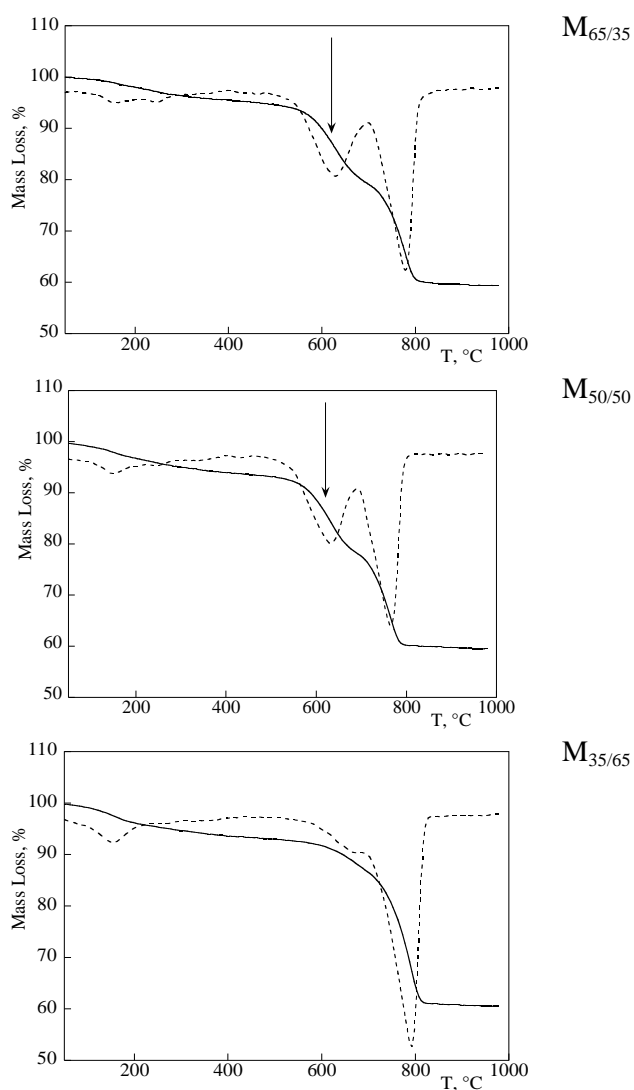


Figure 3. TG analysis profiles (continuous line) and DTG curves (dotted line) of the three mortars after 28 days curing.

Figure 4 reports the X-ray diffractograms of the three mortars after 7 days and 28 days curing. Phases present in all the diffractograms are: dolomite (aggregate), quartz (impurity of aggregate) and calcite (present in the original lime and/or formed by carbonation of the residual lime). Zeolite peaks are hardly detectable in the patterns after 7 days curing (arrows indicate the most intense reflections). They are, however, more clearly visible in the pattern of the mortar $M_{35/65}$, in which zeolite is likely in excess, compared to lime. After 28 days curing zeolite is still present only in the mortar $M_{35/65}$. As expected, no silicate phases are detectable, because of their amorphous nature. Unexpectedly, no peaks of hydrated calcium aluminates were detected [Snellings et al., 2009]. No explanations can be proposed at present for this absence.

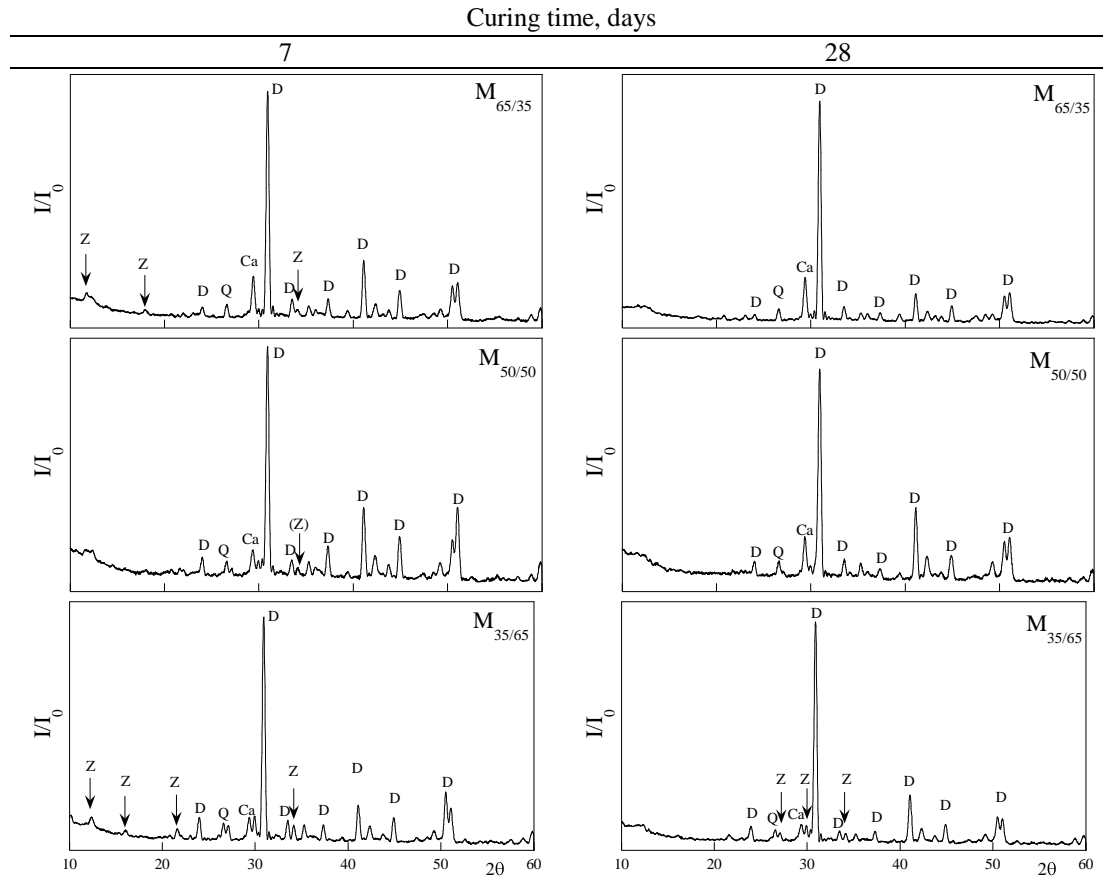


Figure 4. X-ray diffraction patterns of the three different mortars at different curing time. Z = Na-A; D = dolomite; Q = quartz; Ca = calcite.

Table 3 – Mechanical resistances of hardened mortars

Mortars	Compressive strength [N/mm ²]		Flexural strength [N/mm ²]	
	7 days	28 days	7 days	28 days
$M_{35/65}$	2.3	3.9	*	*
$M_{50/50}$	5.6	6.5	0.8	0.9
$M_{65/35}$	3.7	5.4	*	1.2
$M_{100/0}$	0.9	1.7	*	*
Commercial [§]	4.0-6.0	8.0-10.0	0.5-1.0	1.0-1.5

[§] Values of mechanical strengths provided by the manufacturer. * Not measurable value.

These considerations are fully confirmed by the mechanical behaviour of the mortars, which is summarized in Table 3. The following observations can be worked out:

- comparing the pozzolanic mortars to the reference lime mortar, points out that zeolite addition produces a decided benefit on compressive strengths;
- more than 60% of final compressive strengths are developed after only 7 days;
- mortar M_{50/50} shows the best performances, due to the abundant presence of hydraulic compounds (see Fig. 2) and to the absence of unreacted zeolites (which has no or negligible mechanical resistances compared to hydraulic compounds, and therefore represents the “weak point” of the mortars).

Table 4 reports some data concerning the physical characterization of the hardened mortars, with a particular attention to porosity and water absorption. The evaluation of these parameters is of great importance. In fact, on one side, too high values of porosity may affect negatively the mechanical resistances, on the other, porosity with the connected permeability represents a necessary requirement of mortars employed in restoration and conservation to make easier water vapour transpiration.

Table 4 – Physical parameters of hardened mortars after 28 days curing

Mortars	Porosity (%)	Water absorption (%)	Real density (g/cm ³)	Apparent density (g/cm ³)
M _{35/65}	41.3	27.8	2.53	1.49
M _{50/50}	41.1	27.1	2.57	1.51
M _{65/35}	42.8	28.3	2.65	1.51
Commercial	38.8	24.8	2.56	1.56

Inspecting the values reported in the Table 4 points out that zeolite/lime ratio does not markedly affect the physical behaviour of the mortars. All experimental mortars exhibit porosity and permeability slightly higher than the commercial mortar. This is probably due to the higher liquid-to-solid ratio used in this study (about 0.30) than that suggested for the commercial product (about 0.24). An overall evaluation of the data in Table 4 points out that the mortar M_{50/50} exhibits the best performances also in terms of porosity and water absorption.

CONCLUSIONS

The present study, based mostly on a thermogravimetric analysis of experimental lime-zeolite pastes and mortars, pointed out the good prospects of use of the cheap commercial zeolite Na-A as pozzolanic material. Zeolite Na-A exhibits, in fact, a good reactivity towards lime, even better than pozzolan itself. Mortars prepared with this material, gave rise to mechanical and physical performances comparable to those of a commercial, non-zeolitic, hydraulic lime mortar.

Performances attained are of great interest, e.g., the fast hardening (more than 60% of the compressive strength after 28 days curing were developed after only 7 days). Lime/zeolite ratio proved to not affect to a great extent porosity and permeability. Overall characterization evidenced that the best performance was attained with mortars containing comparable weight amounts of lime and zeolite. More research is, however, needed to obtain an optimization of the lime/zeolite ratio, also in terms of scale-up.

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