ROLUL MATERIALELOR FINE ÎN TEHNOLOGIA MORTARELOR PE BAZĂ DE VAR

THE ROLE OF FINES IN LIME-BASED MORTAR'S TECHNOLOGY

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Binders are one of the basic constituent of mortars that plays an important role to their mechanical behavior and their behavior in physico-chemical interactions with the environment. The type, the quantity and the fineness of the binders result in different properties in the setting and in the hardening stage of mortars.

In the present paper very fine materials in the scale of nano were added to conventional binders such as lime and natural pozzolan. Properties of workability of the fresh mixtures, compression strength and porosity of the harden specimens were recorded in combination with structural observations using Scanning Electron Microscopy (SEM). Also, pore size distribution properties were recorded using Mercury Intrusion Porosimetry (M.I.P.). Based on the results, structural changes have been observed in nano-modified structures and early-age strength has been achieved in pozzolan mixtures. Pores, larger than 10μm have been reduced in mixtures with nanoparticles. The research is a precursor for the influence of nanoparticles to macro-scale properties of repair, lime-based mortars.

Lianții reprezintă unul din constituienții de bază ai mortarelor, care joacă un rol important în comportarea mecanică a lor şi în interacțiile fizico-chimice cu mediul. Natura, cantitatea şi finețea lianților au ca rezultat comportări diferite în perioada de priză şi întărire a mortarelor.

În lucrarea prezentă, s-au considerat adaosuri de materiale foarte fine, la scara nano, la lianți convenționali, cum ar fi varul şi puzzolanele naturale. Lucrabilitatea amestecurilor proaspăt preparate, rezistența la compresiune şi porozitatea probelor întărite au fost considerate în corelare cu particularitățile structurale, apreciate prin Microscipie Electronică Scanning (SEM). De asemenea, au fost determinate caracteristici de distribuție a porilor, utilizând Porozimetria cu Intruziune cu Mercur (MIP). Rezultatele au arătat modificări structurale ale compozițiilor liante aditivate cu materiale nano, amestecurile cu conținut de puzzolană dezvoltând rezistențe mecanice la perioade scurte de întărire. Pori, mai mari de 10μm au fost reduşi în amestecurile cu nanoparticole. Cercetarea reprezintă o fază incipientă referitoare la influența nanoparticulelor asupra proprietăților la scara macro, ale unor mortare pe bază de var, destinate lucrărilor de reparații.

Keywords: *D. mortars, B. nanoheterogenous structure*

1. Introduction

Mortars are diachronic building materials which dated from the first effort of human beings to build a dwelling. They are mainly used for bonding pieces of solid pieces of stone or brick, for protective or decorative covering or for making floors or substrates. The easy preparation of the mortar mixture, its plasticity and its property to harden with time makes it an indispensable building material up to nowadays. As binders, local available materials were usually used [1]. They were generally of low potential strength. The use of fine materials as fillers for making mortars stronger and impermeable was common practice in the past although old masons did not know about colloidal, they used them by preparing well-slaked lime putty or by using clay which grains are usually less than 2nm for mortar mixtures. In the form of gels they also added natural polymers to make mortar mixtures more flowable or resistant to weathering [2]. The use of inorganic or organic additives is also known as an effort to improve mortar's performance or properties [3].

In old mortars after grinding and sieving, the fraction below 75μm was 5-10% w.w. in structural mortars and a little higher in renders and plasters [4]. These fine materials are mainly attributed to the binders used. Because of the high porosity of the old mortars, when they wanted to make relatively impervious surfaces, the technique of applying successive mortar layers of lower aggregate size was used [5]. Surface was often painted with lime wash and natural pigments.

In the field of protecting and consolidating the monuments and historical buildings, the open question is how to repair with compatible to old fabric materials, which will additionally be resistant to deterioration factors [6].

The new materials, devices and methods of nanotechnology, are the much promising tools for the protection of the skin of the historical structures which suffered from the heavily polluted environment and climatic changes. Nano-scale particle could modify the microstructure of materials so as the macro-level properties and behavior (such as porosity and strength) to be enhanced for the benefit of the longevity of monumental heritage.

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Provided that the systematic analysis of old mortars proposed by RILEM TC-COM 167 has been followed and the mechanism of deterioration has been recognized and understood, numerous data which should be evaluated so as to lead to material's proportioning arise.

In order to proceed to the design of repair mortars compatible with existing structure but also durable (in environmental and other aggressive agents) first concern is to decide upon the binders used to be as close to the authentic ones in terms of composition, strength and porosity level and proportion in relation to the aggregates. The available in the market binders and their quality criteria are of primer importance. Usually, natural pozzolans are of low reactivity due to the low content in amorphous silica. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Grinding and milling are common practices in order to upgrade the raw materials.

The development of nanotechnology has led to the ability to produce nano-sized particles of predictable size ranges and of high purity. The reactive capacity of few of these materials and their pozzolanic activity has been tested in cement pastes showing its effect in properties like workability, strength and hydration rate [7,8].

2. Experimental part

Materials and Methods

Different trial mixtures have been produced in the laboratory using lime binder, natural pozzolana, $Ca(OH)_2$ in a colloidal form and average grain size 150nm (CaLoSil IP-25) and SiO_2 of 14nm grain size nanoparticles (Sigma Aldrich). The composition of the mixtures is shown in Table 1 and the properties of the materials used are gathered in Table 2. SiO_2 nano-particles were added when natural pozzolan was used in 0.3 and 0.5% w.w. of binders and $Ca(OH)_2$ was used in pure lime pastes in 3%w.w. of lime (Table1).

In order to achieve homogeneous mixing, ultrasounds were applied for 15 minutes in the solution of water and nano-particles using Hydro2000MU, Masterisizer2000. The water/binder (w/b) ratio was kept almost constant and different consistency was recorded by Vicat. SEM (JEOL 840A JSM) was used for structural observations and MIP (Poresmaster Macro, Quantachrome) was used for pore size distribution measurements. Compressive strength was recorded according to EN 1015-11:1999 and porosity was measured by water absorption techniques (RILEM CPC 11.3).

Results

In both lime and lime-pozzolan pastes the addition of nano-particles render mixtures more workable as it is shown in Table1.

The addition of superplastisizer (mixture P3) reduces the w/b ratio and at the same time assists towards good workability.

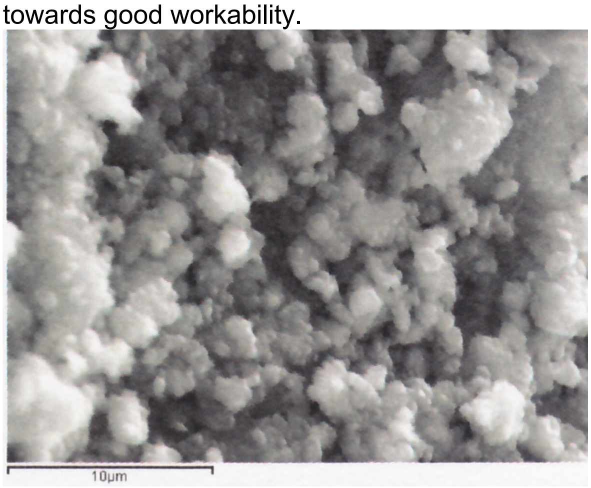

Fig. 1 - SEM micrograph of net lime paste after 28 days of hardening / *Imagine SEM a pastei de var după 28 zile de întărire.*

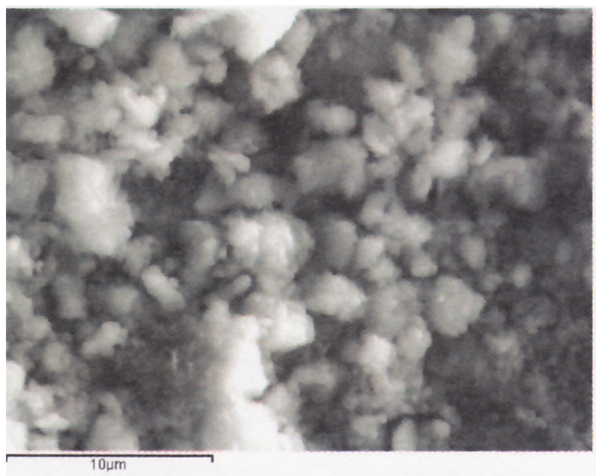

Fig 2 - SEM micrograph of lime paste with colloidal calcium hydroxide after 28 days of hardening / *Imagine SEM a pastei de var, cu adaos de $Ca(OH)_2$ coloidal.*

Table1

Composition of the paste mixtures in parts per weight / *Compoziții ale amestecurilor tip pastă în părți gravimetrice*

	Lime powder *Var pulbere*	Pozzolan *Puzzolană*	Nano- SiO_2	Nano-$Ca(OH)_2$	w/b *apă/liant*	Vicat (mm)
L	1	-	-	-	0.700	12
L1	1	-	-	3%	0.690	0
P	1	1	-	-	0.700	6
P1	1	1	0.3%	-	0.700	2
P2	1	1	0.5%	-	0.700	12
P3*	1	1	0.3%	-	0.650	3

* In composition P3 superplasizer was added in 1%w.w. of binders / *P_3 conține superplastifiant – 1% gravim. față de liant*

**Nanoparticles were added as percentage by weight of the binders / *Nanoparticulele au fost adăugate ca % gravim. față de liant*

In the case of lime pastes, SEM analysis showed more compact structure in the specimens with colloidal (Fig. 1 and 2). In early ages it was impossible to measure the strength and porosity of lime pastes as they were still very soft but at the age of 28 days an increase in compressive strength and at the same time a reduction of porosity was observed in nano-modified pastes (Table 3).

In mixtures with combination of lime, natural pozzolan and SiO_2 nanoparticles, an increase in early-gained strength was observed and a reduction of porosity as shown in Table 4.Composition P1 with 0.3%w.w. nano-SiO_2 is characterized by a stable increase of strength by time while P2 with 0.5%w.w. nano-SiO_2 at the age of 3 days has higher strength in relation to P1 but

Table 2

Characteristics of materials used for the pastes / *Caracteristicile materialelor utilizate la prepararea pastelor*

	Lime powder *Var pulbere*	Pozzolan *Puzzolană*	Nano-SiO_2	Nano-$Ca(OH)_2$
Specific gravity (g/cm^3) *Greutate specifică*	2.471	2.403	2.20	-
Avg. particle size *Dimensiunea medie a particulei*	10.8μm	11.6μm	14nm	150nm
Specific Surface Area (m^2/g) *Aria suprafeței specifice*	2.25	1.82	200	-
Pozzolanicity index (MPa) *Index de puzzolanicitate* (ASTMC311 :77)	-	10.5	-	-

Table 3

Properties of specimens / *Proprietățile probelor*

	Compressive strength, *Rezisteța la compresiune* MPa			Porosity % *Porozitatea* (RILEM CPC11.3)	Specific gravity, *Greutatea specifică* g/cm^3
	3-d	7-d	28-d	28-d	
L	-	-	1.43	54.22	0.95
L1	-	-	1.54	53.44	0.95

Table 4

Properties of specimens / *Proprietățile probelor*

	Compressive strength, *Rezistenta la compresiune* MPa			Porosity *Porozitatea* %	Specific gravity, *Greutatea specifică* g/cm^3
	3-d	7-d	28-d	28-d	
P	0.45	1.150	3□69	71.82	1.26
P1	0.55	1.54	3.70	59.74	1.08
P2	0.64	1.45	3.61	45.89	0.79
P3	0.70	2.70	6.20	31.25	1.35

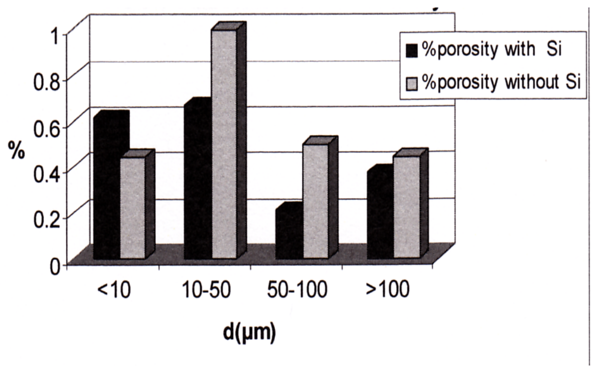

Fig. 3 -. Pore size distribution by Mercury Intrusion Porosimetry in pozzolanic pastes / *Distribuția dimensională a porilor (Porozimetrie cu mercur) în paste puzzolanice.*

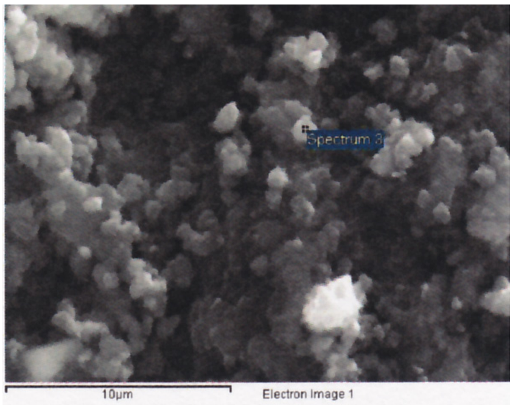

Fig. 4 - SEM micrograph of lime-pozzolan paste without nano-particles after 28 days of hardening / *Imagine SEM a pastei de var-puzzolană, fără nanoparticule după 28 de zile de întărire.*

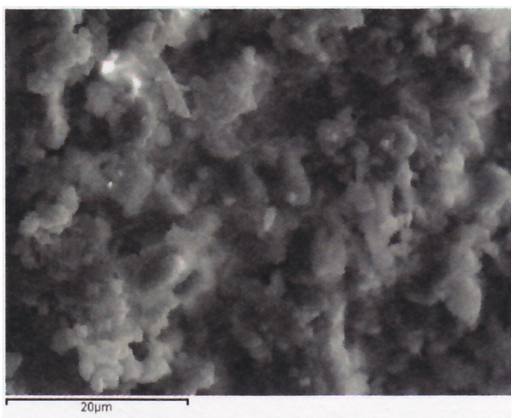

Fig. 5 - SEM micrograph of lime-pozzolan paste with 0.3%nano-particles after 28 days of hardening / *Imagine SEM a pastei de var - puzzolană,cu 0,3 % nanoparticule.*

this is inverted at further ages. This parameter needs further investigation especially as porosity seems to be reduced in specimens with increasing larger than 10μm when nanoparticles were added (Fig.3). Structural observation of the specimens indicates the reduction of porosity as more compact structure is observed in specimens with nanoparticles (Fig.4 and 5). EDX analysis performed in six positions of each sample shows the average content of Si is higher when SiO_2 nanoparticles have been used (Table 5). Considerable strength increase (and at the same time reduction of porosity) was observed in P3 composition in the different ages tested, where superplastisizer was also added in 1% w.w. of binders.

3. Conclusions

Fine materials have an important role in the properties of mortars both in fresh and in hardening stage. The addition of SiO_2 nanoparticles in lime-pozzolan pastes improves the workability of the mixtures and provokes structural changes by filling pores with diameter larger than 10μm. It also makes the structure denser. An increase in silicon content was observed when SiO_2 nanoparticles were added, resulting in increasing the compressive strength. This increase was considerably important (63% higher in relation to the net sample at 28 days) when superplastisizer was added.

The addition of colloidal calcium hydroxide proved positive for the fluidity and the reduction of the porosity. Also, a small strength increase was recorded at 28 days test.

percentage of nanoparticles (Table 4). Pore size distribution by Mercury Intrusion Porosimetry indicates the reduction of pores with diameter

This research work is indicative that nano-products are challenging in the field of repair mortars in order to increase the reactivity of the binders and produce high strength lime-based mortars. Therefore, it seems that nano-scale particles could modify macro level properties for the benefit of historic mortars which are used for repair interventions.

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