PASTE LIANTE DE TIP PUZZOLANĂ – VAR, NANOMODIFICATE
NANO-MODIFIED LIME-POZZOLANA PASTES

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Repair mortars based on lime known as "traditional" mortars have been applied the last decades in monuments and historic buildings as the best solution in terms of compatibility. However, problems of durability have been arising due to their weak structure and easy fracture pattern. In order to improve their durability, the new developed tools of nanotechnology are tested in order to strengthen the structure of repair mortars and restrict the durability problems. In the present work, nano-SiO_2 of approximately 14nm in diameter is added in lime- natural pozzolana binders, which are the most common used binders of the "traditional" mortars, in different percentages in order to study the micro and nano structure of the produced pastes using Scanning and Transmission Electron Microscopy. Additionally, their mechanical and physical properties are tested from 3 up to the age of 28 days. From the study derives that nano-modified lime-pozzolana binders have a dense structure with reduced large pores and increased strength. Additionally, the catalytic role of nano-particles to crystal formation is confirmed.

Mortarele pe bază de var, cunoscute sub numele de mortare tradiționale, au fost folosite în ultimele decenii în restaurarea monumentelor şi clădirilor istorice, ca cea mai bună soluție din punct de vedere al compatibilității. Cu toate acestea, există probleme de durabilitate, generate de structura lor – fără rezistență mecanică, uşor de fracturat. Pentru a îmbunătăți durabilitatea, sunt folosite instrumentele nanotehnologiei, în scopul consolidării structurii mortarelor de reparații şi minimizării problemelor de durabilitate. Sistemele liante de tip puzzolane naturale – var sunt cel mai des folosite ca mortare tradiționale. În lucrarea de față, în pastele liante de tip puzzolane naturale – var, se adaugă nano-SiO_2 cu diametru de aproximativ 14nm, în diferite proporții, cu scopul de a studia micro şi nano structura pastei folosind microscopia electronică de baleiaj şi microscopia electronică de transmisie. În plus, proprietățile mecanice şi fizice ale pastelor studiate vor fi determinate pentru o perioadă de timp între 3 şi 28 de zile. Din datele experimentale rezultă că lianții de tip puzzolană-var, nanomodificați au o structură densă, cu un număr redus de pori mari şi rezistență mecanică mărită. În plus, este confirmat rolul de catalizator al nano-particulelor la formarea cristalelor este confirmată.

Keywords: *nano-SiO_2; lime-pozzolana pastes; strength; SEM; TEM*

1. Introduction

Interventions in monuments and historic buildings usually concern replacement of missing or deteriorating mortars or parts of stones, filling cracks, cleaning and consolidating decayed materials. The characteristics of the old building materials are guidelines for the design and application of the new repair materials [1,2]. Old mortars of excellent durability are usually based on a combination of lime and pozzolana as binding agents and present a well developed porous microstructure which retains a small quantity of water [3]. The long-term application of lime-based mortars in repair works of monuments and historic buildings accented the durability problems in respect to their cracking tendency, porosity increase and strength reduction in time [4].

In order to restrict these problems different techniques for upgrading the raw materials used for the production of repair mortars by grinding gave some positive results [5]. Advanced binding systems as well as additives / admixtures of nowadays result in high performance and long life materials [6].

Nowadays, the emerging field of nanotechnology also provides materials and techniques which have been tested for the protection of surfaces in monuments with positive results in terms of water resistance [7,8]. The most common tested nano-particles are TiO_2, SiO_2, Al_2O_3, and carbon nanotubes. Attempts to add nano-particles in cement mortars were encouraging in terms of improving structural and mechanical properties [9-11]. Few studies have been published though, relating to nano-particles and lime-based mortars in order to investigate strength development and structural changes [12-14].

The main purpose of this work is to report the effect of nano-SiO_2 added as admixture in lime-pozzolana pastes, on compressive strength, porosity, and structure.

2. Experimental study

2.1. Materials and Methods

Detailed analysis has been done on the raw materials used for the production of pastes of

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normal consistency according to EN196-3:1994. Hydrated lime and natural pozzolana were used in all the samples in 1:1 proportion by weight. Nano-SiO_2 of 14nm was added after mixing with pre-weighted quantity of water (200ml) under ultrasounds for 10minutes, using HYDRO 2000MU Mastersizer2000 system in order to restrict agglomeration. The nano-SiO_2 used was commercial available from the Sigma Aldrich company. This water quantity was also used in the mixture. The distribution of the binders' grain sizes was recorded using Scirocco Mastersizer 2000 particle analyzer by Malvern and the fineness, the density and the surface area of these materials are

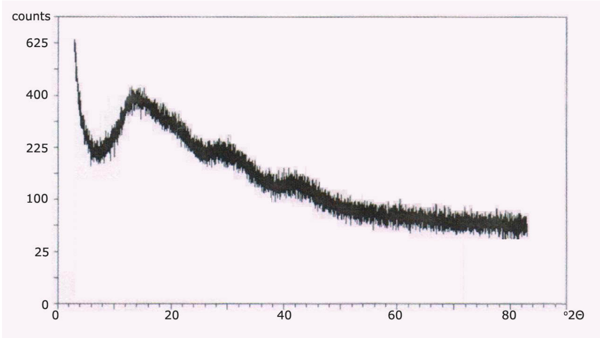

Fig.1 - XRD pattern of nano-SiO_2 / *Spectrul de difracție al razelor X pentru nano-SiO_2.*

Table1

Properties of materials used for the preparation of pastes / *Proprietăți ale materialelor folosite pentru obținerea pastelor*

	Lime powder *Calcar*	Natural pozzolana *Puzzolană naturală*	Nano-SiO_2
Density g/cm^3 / *Densitate g/cm^3*	2.471	2.403	2.200
Average particle size *Dimensiunea medie de particulă*	10.8μm	11.6μm	14nm
Specific Surface Area (m^2/g) *Suprafața specifică* (m^2/g)	2.25	1.82	200
Pozzolanicity index (MPa) (ASTMC311:77) Indicele de puzzolanicitate (MPa) (ASTMC311:77)	-	10.5	-
$Ca(OH)_2$ content / *Cantitatea de $Ca(OH)_2$*	75%	-	-

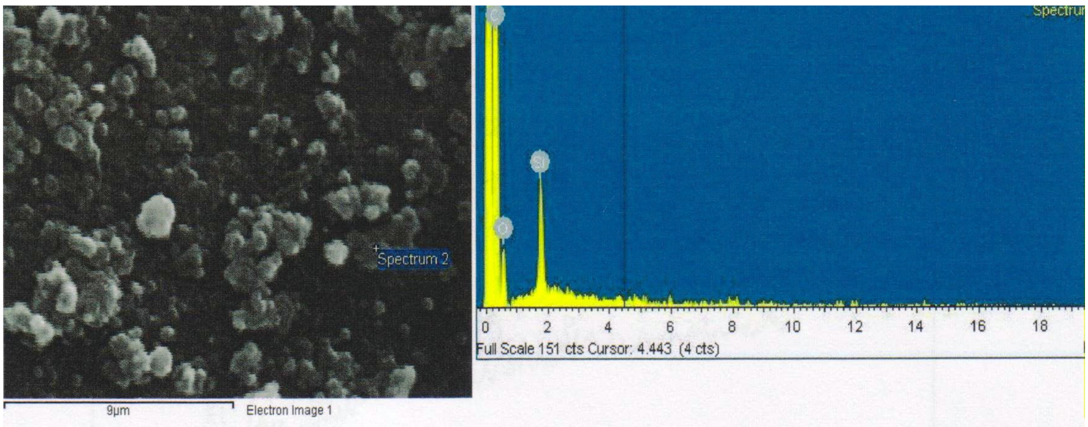

Fig.2 - SEM image of nano-SiO_2 particles and EDX analysis shows the presence of Si and the size of the agglomerates / *Imagine SEM şi analiza EDX a particulelor nano-SiO_2 care atestă prezența Si precum şi mărimea aglomeratelor.*

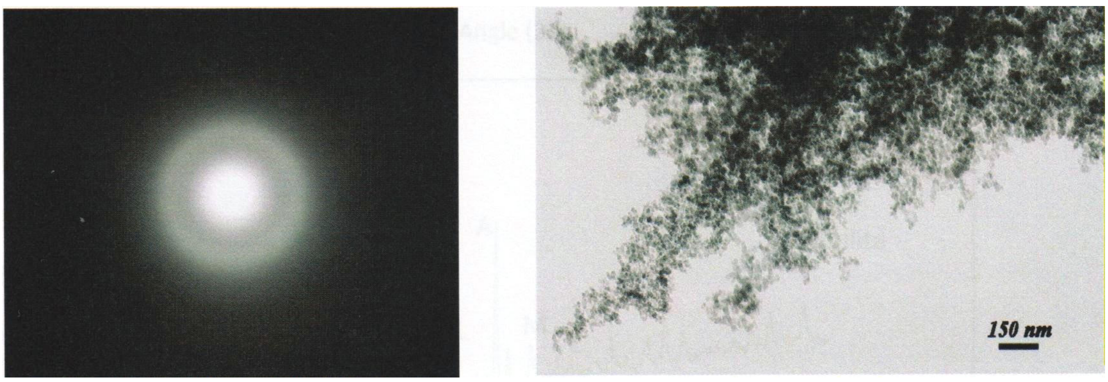

Fig. 3 - (left): SAED pattern from nanoSiO_2 sample, (right): Bright Field(BF) image, showing the structure of the nanosilica / *Difracție de electroni pe arie selectată (stanga) şi imagine TEM în câmp luminos (dreapta) pentru nano-SiO_2.*

recorded in Table1. Also, Mercury intrusion porosimetry (M.I.P.) (Macro, Quantachrome) was applied in the samples at the age of 28 days and thermogravimetric analysis (DTA-TG) was performed in nitrogen environment from 50 up to 1000^{o}C with a temperature increase of 10^{o}C/min.

Additional tests were performed in nano-grains trying to find their morphology and composition. Powder XRD analysis (XRD) was performed using a Philips PW 1710 diffractometer with Ni-filtered CuKa radiation. The samples were scanned from 3–83° 2θ at a scanning speed of 1.2°/min-1(Fig.1). The analysis revealed that it is a 100% amorphous material [15].

Scanning electron microscopic observation (S.E.M.) by JEOL 840A JSM showed agglomeration of the grains and verified the silicon content through an energy-dispersive X-ray spectroscopy (EDX) (Fig.2).

The use of transition electron microscopy (T.E.M.) (JEOL 120CX) also verifies the amorphous nature of the nano-grains as the typical appearance of selected area electron diffraction (SAED) pattern is a diffusible intensity ring (Fig.3).

2.2 Results and Discussion

The mixtures produced were tested using the Vicat method in terms of workability and indicating the normal consistency of the pastes. Paste specimens 2.5x2.5x10cm were formed and cured in humid environment, until tested, according to EN 459-2. From the W/B ratio it is obvious that there is an increased demand in water when the amount of nanosilica was increased. The results are presented in Table2.

The compressive strength was recorded for reference and modified samples from 3 days up to 28 days (Fig. 4). There is a continious strength increase indicating that the pozzolanaic reaction and the carbonation are taking place and also nanomodified samples present higher strength almost in all ages tested showing that nanoparticles can have a drastic role in the paste.

The porosity and pore size distribution was measured by Mercury Intrusion Porosimetry (M.I.P.) and the total porosity was increased for the modified samples. This tension can be related to the increased water content in those samples (Fig.5). The pores of diameter larger than 100μm though are restricted in nano-modified samples probably because capillary pores of that diameter were blocked due to the structural changes performed. Taking into account the significant role of porosity in mechanical properties [16] it can be assumed that by reducing the water content in the modified samples (possibly by adding superplasticizers) improved mechanical properties can be expected. The reduced amount of total porosity is also in agreement with the higher strength recorded as these properties are inversely proportional.

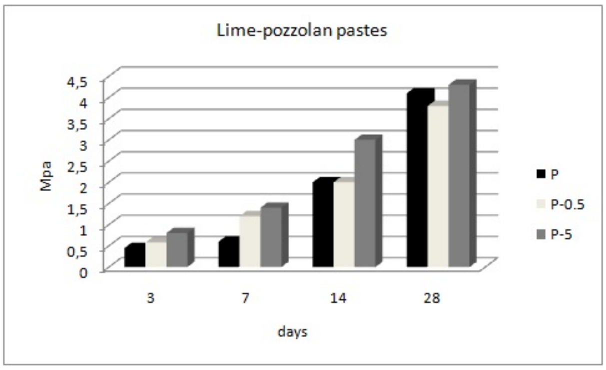

Fig.4 - Evolution of compressive strength in lime-pozzolana pastes / *Evoluția rezistențelor mecanice la compresiune a pastelor de calcar – puzzolană.*

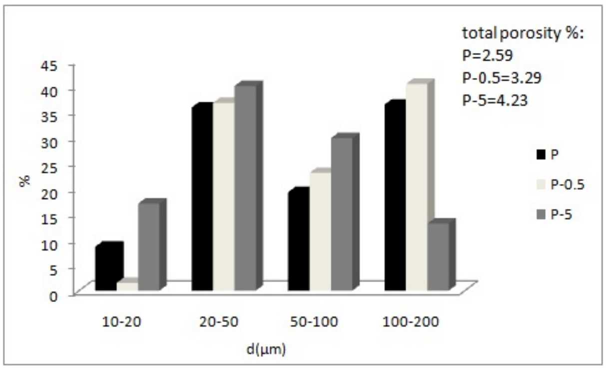

Fig.5 - Porosity and pore size distribution by M.I.P. at the age of 28 days / *Porozitatea şi distribuția dimensiunii porilor, determinată prin porozimetrie cu mercur, la un timp de întărire de 28 de zile.*

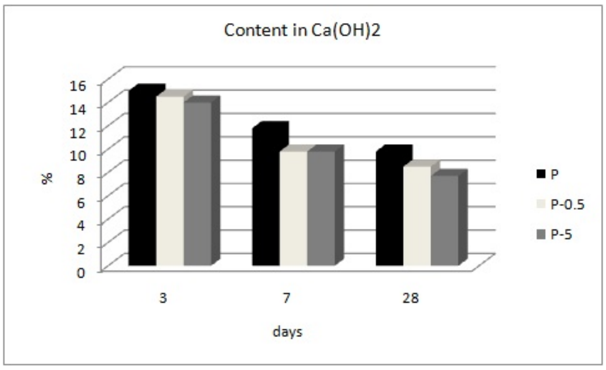

Fig.6 - $Ca(OH)_2$ content assessed by DTA-TG at the age of 28 days / *Proporția de $Ca(OH)_2$ determinată prin ATD-TG, la un timp de întărire de 28 de zile.*

Table2

Properties of lime-pozzolana pastes (the proportion is in parts per weight)
Proprietățile pastelor calcar – puzzolană (proporțiile sunt date în părți per greutate)

Sample *Probă*	Lime *Calcar*	Pozzolana *Puzzolană*	Nano-SiO_2 (%w.w binders) *(% grav. raportate la amestecul liant*	W/B a/c	Vicat mm
P	1	1	-	0.658	11
P-0.5	1	1	0.5	0.680	8
P-5	1	1	5	0.800	10

The content in $Ca(OH)_2$ was measured by thermogravimetric analysis (DTA-TG) and from Fig.6 it can be concluded that the $Ca(OH)_2$ is reduced in nano-modified samples presumably due to the active pozzolanaic reaction by the addition of nano-silica. This is also in aggreement with the increased strength recorded in modified pastes.

In relation to the structure, the observation by SEM at the age of 28 days reveals that there is a difference in the crystal size between the modified and non-modified samples (Fig. 7, 8) but the chemical composition of the portlandite crystals and the crystals with Ca-Si-Al composition formed was the same as it was measured by EDX analysis. All those crystals are larger in size in the nano-modified samples as recorded below probably because the nano-particles act as nucleus of crystalization and crystals are early formed.

The above observation was testified by transmission electron microscopy (T.E.M.)

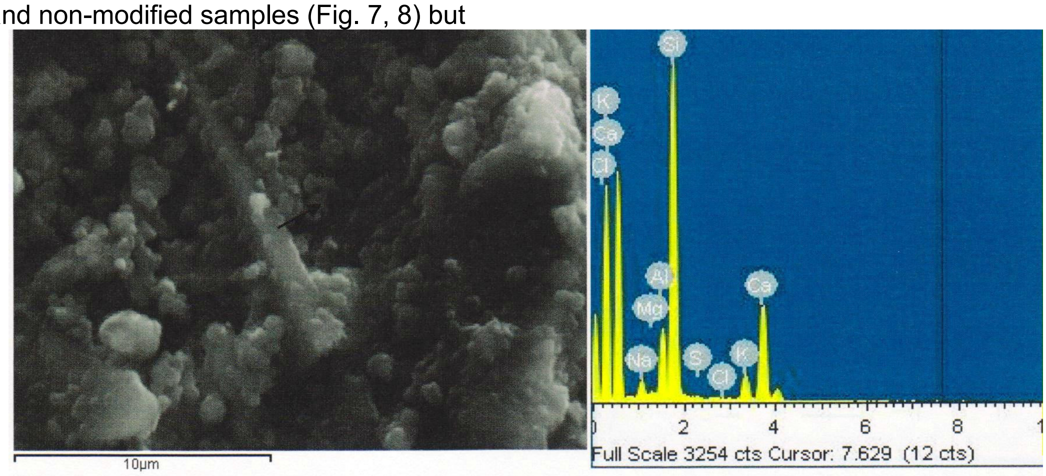

Fig.7 - SEM-EDX analysis on a lime-pozzolana sample without nanoparticles / *Analiza SEM-EDX pe probă calcar – puzzolană fără nanoparticule.*

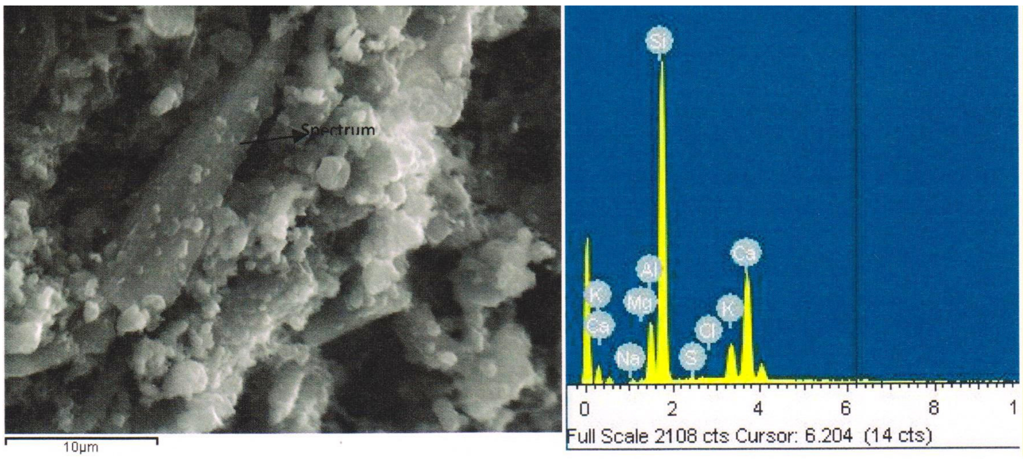

Fig.8 - SEM-EDX analysis on a lime-pozzolana sample with 0.5%nano-SiO_2 / *Analiza SEM-EDX pe probă calcar – puzzolană cu 0,5% nano-SiO_2.*

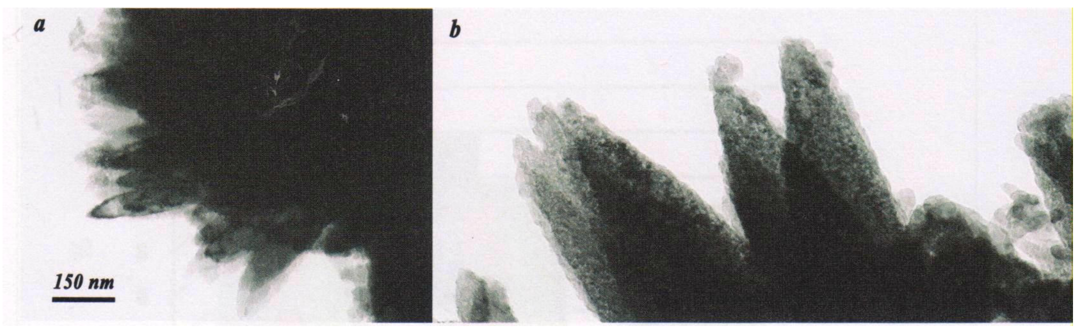

Fig.9 - Bright Field (BF) TEM images of the two samples (a for P and b for P-0.5), showing the difference in Ca-Si-Al crystals size. The scale bar to the left of the image stands for both a and b images / *Imagini TEM în câmp luminos pentru probele P (a) şi P-0,5 (b), care relevă diferențele dimensionale între cristalele Ca-Si-Al. Scala din imaginea (a) este valabilă şi pentru imaginea (b).*

measurements after detailed study of the structure using samples suitable for electron microscopy observations, which were prepared using the traditional techniques, including further disagglomeration of the powder material with medical blade and gluing on copper grids. At the age of 28 days, the average crystal size in samples without nanoparticles was measured to be 600nm while in the modified with 0.5% nano-SiO_2 the crystal size ranged from 800nm to 1.2μm. The Dark Field (DF) images also suggested the existence of smaller crystals up to 12nm which were probably SiO_2 (Fig.9). In both cases sharp needle–like crystals were formed.

3. Conclusions

Lime and pozzolana are the main binders of “traditional” mortars which are considered suitable for interventions of old historic structures. The role of fine materials in the properties of the mortars is crucial and the subject has been studied previously [17]. In order to face some of their drawbacks such as slow rate of strength development and fracture pattern, nano-SiO_2 was added as admixture in two different ratios. The addition of nano-SiO_2 particles up to 5% w/w of binders mixture, contributed to the formation of large crystals of Ca-Si composition indicating their role as nuclei for crystallization. Also, a reduced amount of $Ca(OH)_2$ was assessed by DTA-TG analysis in nano-modified samples indicating an acceleration in carbonation process. This property assisted towards the formation of a dense structure of reduced pores of diameter larger than 100μm and also to higher strength.

REFERENCES

1. I. Papayianni, A holistic way of studying mortars and bricks of ancient masonry for manufacturing compatible repair materials,’ Proceedings of the 4th International Symposium on the Conservation of Monuments in the Mediterranean, Rhodes, May 6-11, 1997, 265.
2. A. Moropoulou, A. Bakolas, and K. Bisbikou, Investigation of the technology of historic mortars, Journal of Cultural Heritage 2000, **1**, 45.
3. B. Middendorf, G. Baronio, K. Callebaut, and J.J. Hughes, Chemical–mineralogical and investigations of old mortars, Proceedings of an international RILEM-workshop historic mortars: characteristics and tests , Paisley, 2000, 53.
4. I.Papayianni, M. Stefanidou, and S. Konopissi, Pathology symptoms of lime-based repair mortars” Proceedings HMC 1st Historical mortars Conference, Lisbon (proceedings in CD), 2008.
5. E.F. Irassar, D. Violini, V.F. Rahhal, C. Milanesi, M.A. Trezza and V.L. Bonavetti, Influence of limestone content, gypsum content and fineness on early age properties of Portland limestone cement produced by inter-grinding, Cement and Concrete Composites 2011, **33** (2), 192.
6. V.M. Malhotra, and P.K. Mehta, High-Performance, High-Volume Fly Ash Concrete Supplementary Cementing Materials for Sustainable Development, Inc., Ottawa, Canada, 2002, 101.
7. P. Baglioni, and R. Giorgi, Soft and hard nanomaterials for restoration and conservation of cultural heritage, Soft matter 2006, **2**, 293.
8. A. Ershad-Langroudi, and A. Rahimi, Synthesis and characterization of nano silica-based coatings for protection of antique articles, International Journal of Nanotechnology, 2009, **6**, 915.
9. B-W. Jo, C-H. Kim, G-H. Tae, J-B. Park, Characteristics of cement mortar with nano- SiO_2 particles, Construction and Building Materials 2007, **21**(6)1351.
10. K. Sobolev, et. al., Engineering of SiO_2 nanoparticles for optimal performance in nano cement-based materials” Editors: Z. Bittnar, P.J.M. Bartos, J.Nemecek, V. Smilauer, J. Zeman Nanotechnology in Construction: Proceedings of the NICOM3 Prague, 2009, 139.
11. Z.S. Metaxa, M.S. Konsta-Gdoutos, and S.P. Shah, Carbon Nanotubes Reinforced Concrete, Nanotechnology of Concrete: The Next Big Thing Is Small ACI Editors: Konstantin Sobolev, Mahmoud Reda Taha SP-267-2, 2009.
12. M. Dracky M. S. Slizova, and G. Ziegenbalg, A Nano Approach to Consolidation of Degraded Historic Lime Mortars, Journal of Nano Research 2009, **8**, 13.
13. M. Stefanidou, I. Papayianni, I. Zyganitidis, Th. Altantzis, Ch. B. Lioutas, E. Pavlidou, and S. Logothetidis, Nanotechnology and Lime-pozzolana Mortars: On the Modification of Their Physical, Structural and Mechanical Properties by the Addition of SiO_2 Nanoparticles, 8th International Conference on Nanosciences & Nanotechnologies, Thessaloniki, 2009, 14.
14. P. Maravelaki, E. Lionakis, C. Kapridaki, and A. Verganelaki, Physico-chemical characterization of hydraulic mortars containing nano-titania for restoration applications 8th International Conference on Nanosciences & Nanotechnologies, Thessaloniki, 2011, 14.
15. N. Kantiranis, A. Stergiou, A. Fillipidis, and A. Drakoulis, Calculation of the percentage of amorphous material using PXRD patterns 10th Inter. Congress Industrial minerals and rocks, Geochemistry, Environmental Geology Thessaloniki, 2004, 446.
16. I. Papayianni, and M. Stefanidou, Strength-porosity relationships in Lime- Pozzolana mortars, Construction and Building Materials, November, 2006, **20** (9), 700.
17. I. Papayianni, and M. Stefanidou, The role of fines in lime-based mortar’s technology, Romanian Journal of Materials, 2011, **41** (1), 26.

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