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Experimental study of nano-modified lime-based grouts

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Abstract

Grouts are fluid mixtures of binders with water, for the filling and strengthening of masonry or the consolidation and preservation of mortar stratification. In this paper, totally 15 compositions of lime-based grout mixtures containing admixtures and silica nano-particles were designed, manufactured and experimentally tested in order to evaluate their properties in fresh (fluidity, permeability, volume stability) and hardened state (shrinkage deformations, mechanical strength). Conclusive remarks were attained regarding the influence of silica nano-particles in grouts performance.

Key words: *Binders, Nano-particles, Masonry*

1. Introduction

Grouts are fluid mixtures of binders with water, for the filling and strengthening of masonry or the consolidation and preservation of mortar stratification (Papayianni, *et al.*, 2010). They started to be used during the 80's and since then a lot of research has been done for improving their properties and performance (Ferragni, *et al.*, 1985; Penelis, *et al.*, 1988; Binda, *et al.*, 1994; Binda, *et al.*, 1997; Toumbakari, 2002; Eriksson, *et al.*, 2004; Vintzileou and Miltiadou-Fezans, 2008; Bras, *et al.*, 2012).

To this direction, the use of additives and/or admixtures has showed positive effects provided that proper selection and proportioning of binders is made, so as high performance and compatibility with the old masonry materials to be achieved. The addition of silica nano-particles can enhance their properties since they decrease the Ca/Si of C-S-H compounds and increase the mean silicate chain length, leading to a C-S-H matrix of long-term stability (Gaitero, *et al.*, 2008; Hui, *et al.*, 2004). The common practice for the consolidation of historic mortar surface layers such as in case of murals, floor-wall mosaics, renders was the use of ready mixed (usually cement based) binders or of synthetic resins.

In this paper, totally 15 compositions of lime-based grouts, containing admixtures and silica nano-particles were designed, manufactured and experimentally tested in order to evaluate their properties in fresh and hardened state. The effect of silica nano-particles in grouts' properties was studied, leading to conclusions about their pros and cons, as well as the measures for limiting their disadvantages.

The binding system lime+pozzolan was selected, since the majority of old mortars found in

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monuments and historic buildings of Greece were made of lime+pozzolan (Papayianni, 2004; Pachta, 2011). Therefore, in order to fulfil the principle of compatibility, retaining the matrix of historic mortars, the tested grouts were also based in lime+pozzolan.

2. Experimental

2.1. Materials

Powder hydrated lime was used, as well as two natural and milled (to increase their fineness) pozzolanic materials (a volcanic material from the island of Milos and a diatomite). White cement was added in a low percentage (10–15% w/w of binders), in order to increase the early strength development and stability of the mixtures. For comparison reasons hydraulic lime was also used. Two types of fumed nano-silica of different gradation were added in various percentages (0.5 and 1% w/w of binders), in order to estimate the most effective proportion in the mixture. To reduce the water demand, a superplasticizer of polycarboxilic basis was added in a proportion of 1 w/w of binders and 2.5% w/w of binders. Additionally a retarder was also used (in a proportion of 0.5% w/w of binders), in order to preserve grouts fluidity, 1 h after their manufacture.

Some of the characteristics of the binders and additives used are shown in Table 1.

The proportions of the grout mixtures are given in Table 2.

2.2. Apparatus and procedures

For grouts mixing, a high speed mixer (up to 8000 rpm) was used, for a total period of 5 minutes, starting with low speed and gradually increased up to 8000 rpm. Three triplets of 4 × 4 × 16 cm steel moulds were sealed and filled with fresh grouts and cured at climatic chamber of 90% RH and 20°C, up to the testing dates. In order to evaluate their performance, grout mixtures were tested at fresh and hardened state (28 days after their manufacture), as following:

Fresh state: Flow time measured by Marsh cone at 0 and 1 h after mixing (ASTM C939-87), Penetrability by using sand-column test (NORM NFP 18-891, 1986) filled with sand 2–4 mm, Volume stability 24 hours after mixing, by using filled with grouts cylindrical containers (DIN 4227 Teil 5 standards).

Hardened state: Differential thermal analysis (DTA-TG), Shrinkage deformations (ISO1920-8:2007), Dynamic Modulus of Elasticity (ASTM C597-71), Flexural and Compressive strength (ASTM C191-81).

Additionally, samples of grout and sand, coming out from the sand column penetrability test were put in a cubic matrix (4 × 4 × 4 cm) and were subjected to compressive strength test at 28 days.

3. Results and discussion

3.1. Fresh state test results

The test results concerning fluidity, penetrability and volume stability are presented in Table 3. From their evaluation, the following conclusions can be asserted regarding the lime+pozzolan mixtures (series A):

The increase of superplasticizer's proportion from 1% w/w (composition A_1) to 2.5% w/w (composition A_2) influences positively the fresh

Table 1.
Characteristics of the constituents of the grouts

Constituents	App. Spec. density	Specific surface area (m2/g)	Pozzol index ASTMC311:77 (MPa)	Particle size analysis percentage of grains (μm) d (0.9)	d (0.5)
Lime powder	2.471	2.250	—	10.8	3.09
Pozzolan	2.403	1.820	10.5	11.6	4.3
Diatomite	2.425	1.070	9.0	59.8	13.9
White Cement	3.100	1.030	—	57.9	17.0
Limestone filler	2.846	0.408	—	152.9	47.5
Fumed nano-silica Type A (150 nm)	2.20	170.0	—	—	—
Fumed nano-silica Type B (14 nm)	2.20	200.0	—	—	—

Table 2.
Constituents and proportions of grout compositions

	Binders (parts by weight)					Fumed nano-silica % by mass		Admixtures % by mass		
Code Nr	Lime powder	Pozzolan	Diatomite	White Cement	Hydraulic lime	Type A (150 nm)	Type B (14 nm)	Super plasticizer	Retarder	W/B
A_1	1	1						1	0.5	1.09
A_2	1	1						2.5	0.5	1.14
A_3	1	1				1		1	0.5	1.18
A_4	1	1					1	1	0.5	1.43
A_5	1	1					1	2.5	0.5	1.29
A_6	1	1					0.5	2.5	0.5	1.14
B_1	1		1					1	0.5	0.86
B_2	1		1			1		1	0.5	1.03
C1	1	0.8		0.2				2.5	0.5	1.07
C_2	1	0.8		0.2			0.5	2.5	0.5	1.14
C_3	1	0.8		0.2			1	2.5	0.5	1.12
D_1	1	0.7		0.3				1	0.5	0.97
D_2	1	0.7		0.3		1		1	0.5	1.24
E_1					1			1	0.5	0.61
E_2					1	1		1	0.5	0.59

Table 3.
Fresh state properties of grout mixtures

Code Nr	Flow time (sec)		Pene trability (sec)	Volume stability (%)
	0h	1h		
A1	10.19	12.99	6.47	0.9
A2	10.08	9.95	2.70	0.8
A3	9.80	9.89	1.41	0.2
A4	9.89	9.96	2.04	3.10
A5	10.39	9.99	3.22	1.70
A6	10.56	10.38	3.28	3.70
B1	9.48	8.96	2.86	11.9
B2	10.51	10.23	0.92	6.8
C1	10.35	10.28	3.31	2.0
C2	10.12	10.03	3.26	1.50
C3	10.20	10.07	3.20	3.50
D1	10.26	11.79	2.10	0.6
D2	10.13	13.77	1.20	0.3
E1	9.33	9.84	3.41	0.7
E2	10.59	10.23	2.68	0.3

state properties, since flow time 1 h after mixing, penetration time and volume stability are decreased.

The addition of fumed nano-silica type A (150 nm) (composition A_3) in a percentage of 1% w/w, shows positive effect at fresh state properties, since flow time 1 h after mixing, penetration time and volume stability are decreased.

The addition of fumed nano-silica type B (14 nm) (composition A_4) in a percentage of 1% w/w, increases significantly the W/B ratio (approximately 30%). Flow time (1 h after mixing) and penetration time is decreased, while volume stability is increased (however under the experimental acceptable limit of 5%). The increase of superplastricizer's proportion to 2.5% w/w (composition A_5), contributes to the reduction of the W/B ratio, the 1h after mixing flow time, as well as of the volume stability. The reduction of fumed nano-silica proportion (0.5% w/w), in accordance with the increase of superplasticizer (2.5% w/w) (composition A_6) shows similar results, keeping however volume stability in higher levels.

Regarding the lime+diatomite mixtures (series B), the addition of fumed nano-silica type A (150 nm) at a proportion of 1% w/w (composition B_2), also improves the fresh state properties of the mixture and especially penetrability and volume stability (reduction almost to the half).

In the lime+pozzolan+white cement mixtures (series C), the addition of fumed nano-silica type B (14 nm) at a proportion of 0.5% and 1% w/w (compositions C_2, C_3), does not seem to influence significantly the fresh state properties of the mixtures. When the white cement proportion is increased to 15% (series D), fumed nano-silica affects negatively the 1 h after mixing flow time and positively the penetrability and volume stability.

Finally, the addition of fumed nano-silica type A (150 nm) at a hydraulic lime mixture (series E) affects positively all fresh state properties.

Generally, it could be said that the addition of fumed nano-silica and especially of the type A (150 nm), affects positively the fresh state properties of the mixtures. The negative effect of fumed nano-silica addition (concerning mainly the W/B ratio increase) can be limited with the increase of superplasticizer proportion from 1% to 2.5% w/w.

3.2. Hardened state test results

The test results concerning shrinkage deformations of specimens by measuring their volume change for 14 days after demoulding, are depicted in Figure 1. From the evaluation of results it is shown that for series A (lime+pozzolan), the increase of superplasticizer proportion from 1% to 2.5% w/w (compositions A_1, A_2) increases the shrinkage of the specimens. The addition of fumed nano-silica type A (composition A_3) seems to stabilize the specimens' volume change. However, the addition of fumed nano-silica type B (150 nm) (compositions A_4–A_5) seems to induce shrinkage, which is more intense when 1% w/w of fumed nano-silica and 2.5% w/w of superplasticizer are used.

Similarly the use of fumed nano-silica type A seems to reduce volume changes in all other compositions (B_2: lime+diatomite, E_2: hydraulic lime), meanwhile it seems that it has a negative effect in the mixture lime+pozzolan+white cement (composition D_2). The use of fumed nano-silica type B in the mixture lime+pozzolan+white cement and especially when 0.5% w/w is used (composition C_2) seems to reduce volume changes.

Conclusively, it seems that the addition of fumed nano-silica type A (150 nm) tends to improve shrinkage deformations, while the fumed nano-silica type B (14 nm) has a positive effect when it is combined with a high proportion of superplasticizer (2.5% w/w).

The test results (Table 4, Figures 2) regarding the rate of carbonation (evaluated by DTA-TG method) of series A (lime+pozzolan) showed that the addition of fumed nano-silica and specifically of Type B (14 nm) (composition A4) tend to increase the rate of carbonation of the mixtures.

Results at hardened state concerning dynamic modulus of elasticity, flexural and compressive strength (both of prisms and of cubic specimens with sand) are presented in Table 5 and Figure 3. From their evaluation the following conclusions can be asserted:

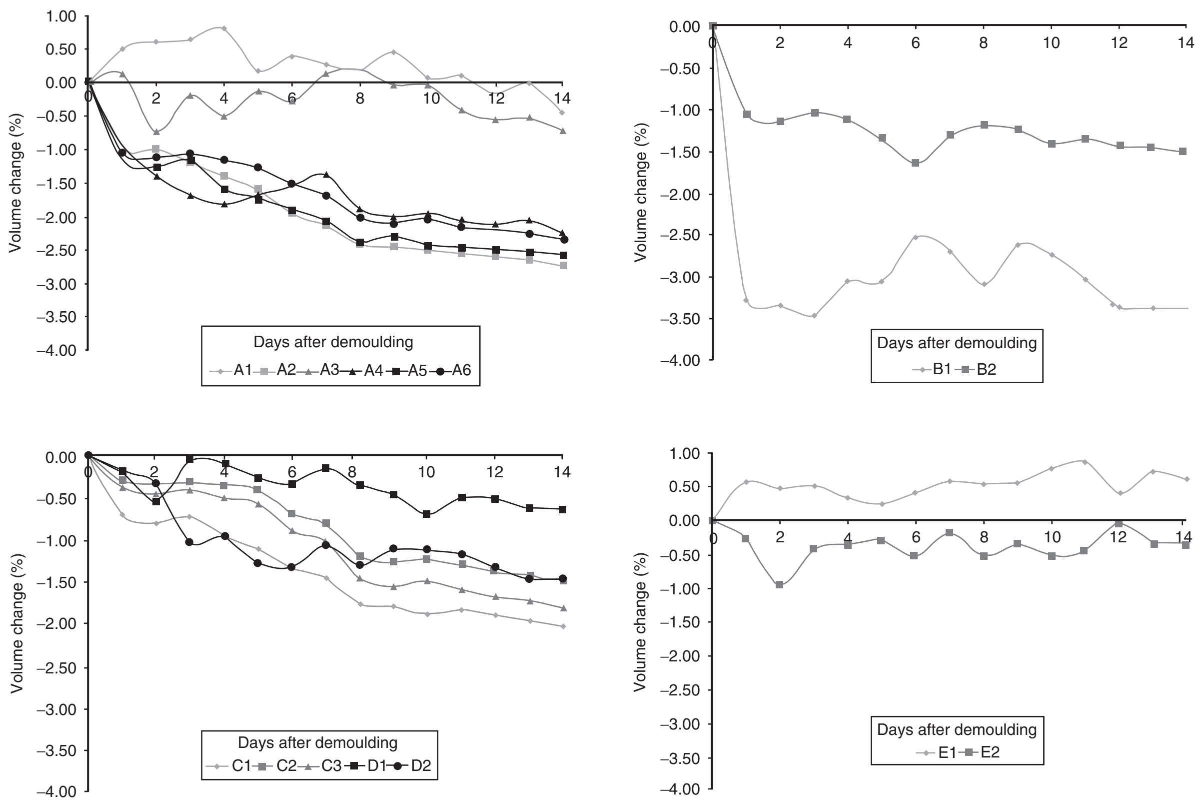

Fig. 1. Shrinkage deformations (volume change) of grout specimens after demoulding.

Table 4.
Proportions of $Ca(OH)_2$ and $CaCO_3$ in A series grouts at 28 and 60 days from their manufacture

Code Nr	$Ca(OH)_2$ (%)			$CaCO_3$ (%)		
	28d	60d	Decrease	28d	60d	Increase
A_1	8,37	7,24	13,5	30,75	31,11	1,2
A_3	7,19	6,44	10,4	23,59	28,70	21,7
A_4	6,10	3,44	43,6	25,09	31,25	24,6

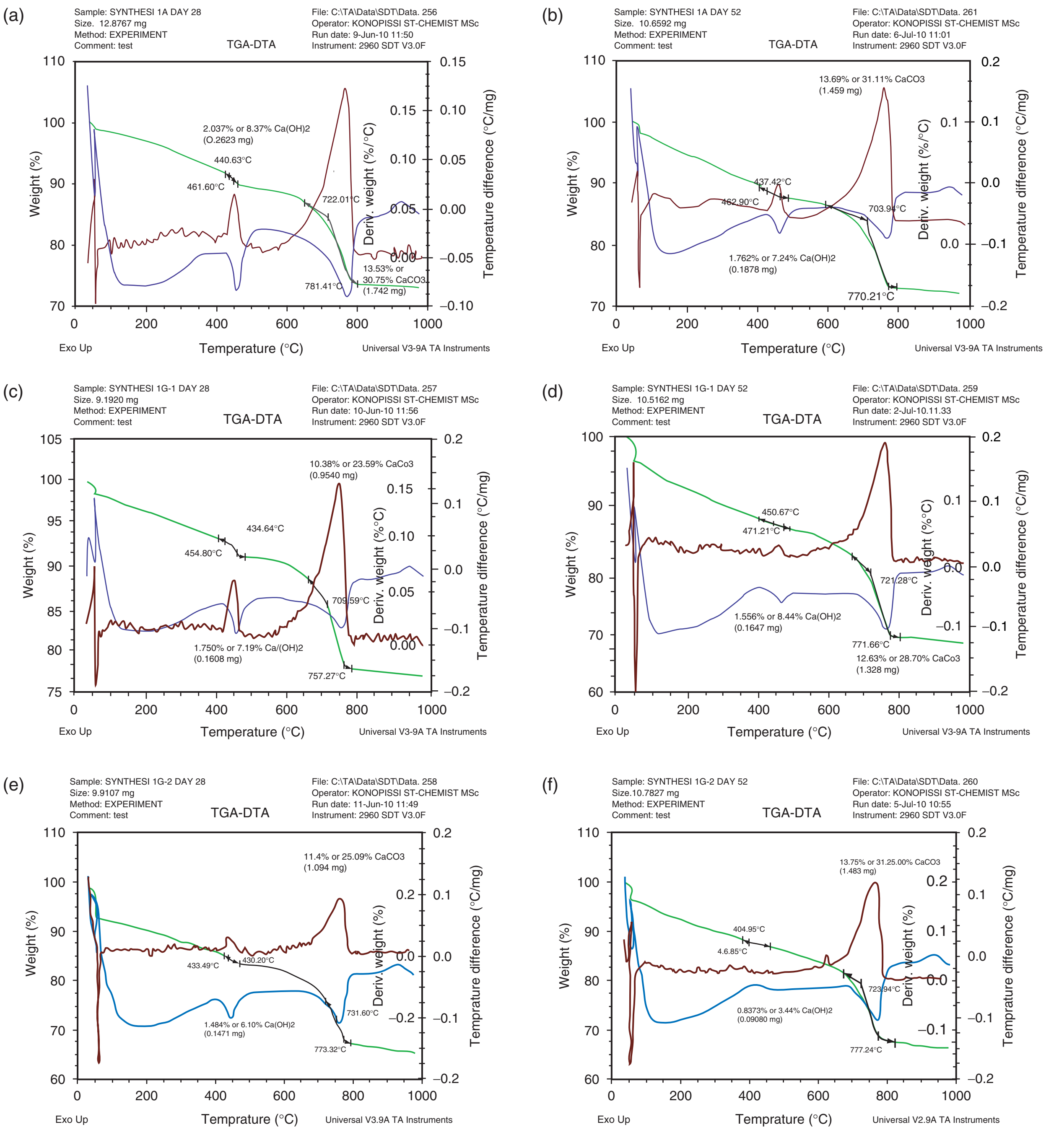

Fig. 2. DTA-TG diagrams of mixtures at 28 and 60 days. a) A_1-28d, b) A_1-60d, c) A_3-28d, d) A_3- 60d, e) A_4-28d, d) A_4- 60d.

Table 5.
Hardened state properties of grout mixtures at 28 days

Code Nr	Dynamic modulus of elasticity (GPa)	Flexural strength (MPa)	Compressive strength (MPa)	
			Prismatic specimens	Cubic specimens with sand
A_1	0.046	0.76	2.24	1.15
A_2	0.029	0.47	0.61	0.74
A_3	0.033	0.74	1.96	0.71
A_4	0.030	0.67	1.40	0.59
A_5	0.022	0.55	0.70	0.95
A_6	0.031	0.30	0.62	0.79
B_1	0.019	0.58	1.17	0.90
B_2	0.017	0.51	0.72	0.69
C_1	0.038	0.45	0.74	0.87
C_2	0.021	0.39	0.73	0.87
C_3	0.027	0.41	0.79	1.01
D_1	0.049	1.09	2.64	1.64
D_2	0.032	0.70	1.46	0.99
E_1	0.046	1.15	1.76	1.76
E_2	0.055	1.20	2.58	2.93

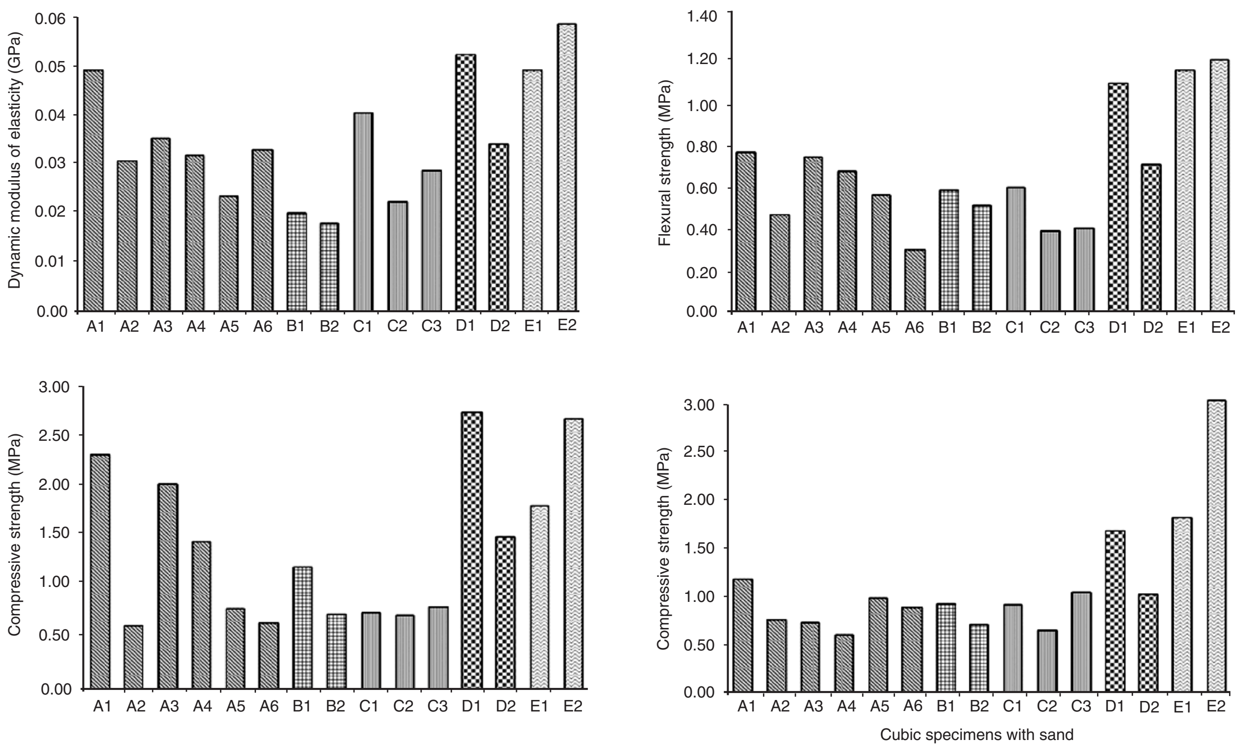

Fig. 3. Mechanical characteristics of grout specimens at 28 days.

By increasing the proportion of superplasticizer from 1% to 2.5% w/w (compositions A_1, A_2), mechanical properties and especially compressive strength are significantly decreased. When fumed nano-silica type A (150 nm) is used with a superplasticizer of 1% w/w (composition A_3), dynamic modulus of elasticity is reduced in a percentage of 28%, flexural strength is almost the same, while compressive strength is reduced in a percentage of 12%. Compressive strength of the cubic samples with sand specimens is also decreased in a percentage of 38%.

The addition of fumed nano-silica type B (composition A_4) leads to a higher decrease of mechanical properties. However, when 1% w/w nano-silica is used with 2.5% w/w of superplasticizer (composition A_5) mechanical properties seem to increase (σf: 17%, σc: 15%) and especially the compressive strength of the cubes with sand specimens (28%). The reduction of the nano-silica proportion to 0.5% w/w (composition A_6) leads to a decrease of mechanical characteristics.

When adding fumed nano-silica type A (150 nm) in lime+diatomite mixture (composition B_2) mechanical properties are reduced. When adding fumed nano-silica type B (14 nm) in series C (lime+ pozzolan + white cement+2.5% w/w superplasticizer) no significant changes of mechanical properties are shown, except for the compressive strength of the cubes with sand specimens (C_3) which is increased in a percentage of 16%.

In series D (lime+pozzolan+white cement+ 1% w/w superplasticizer), fumed nano-silica type A (150 nm) lead to a decrease of mechanical properties, while in series E (hydraulic lime+1% w/w superplasticizer) a significant increase of strength is observed (σ_f: 4%, σ_c: 30%, σ_c cubic: 40%).

By resuming all experimental remarks the following conclusions can be asserted:

The addition of fumed nano-silica and especially of type A (150 nm) affects positively the fresh state properties of the mixtures (fluidity 1h after mixing, penetrability, volume stability). The negative effect of type B (14 nm) addition concerning the W/B ratio increase can be limited with the increase of superplasticizer proportion from 1% to 2.5% w/w.

The addition of fumed nano-silica type A (150 nm) tends to improve the shrinkage deformations of the grout specimens, while type B (14 nm) addition has positive effect when it is combined with a high proportion of superplasticizer (2.5% w/w).

The addition of fumed nano-silica and especially type B (14 nm) tends to increase the rate of carbonation of the grout mixtures.

The addition of fumed nano-silica type B (14 nm) improves the mechanical properties of grout mixtures when it is combined with a high proportion of superplasticizer (2.5% w/w), while type A (150 nm) tends to improve the mechanical properties of hydraulic lime-based grout mixtures. In all cases the strength of the cubic specimens with sand is increased, showing their intense adhesive character.

4. Conclusions

The use of additives and admixtures has proved that can contribute to the improvement of the fresh and hardened state properties of lime-based grouts and ensure their efficacy in the consolidation of historic masonries. According to the results of this study, the use of fumed nano-silica seems to have positive effect on the performance of the tested grout mixtures under specific conditions. Gradation seems to be a significant factor for their performance, since, according to results, the lower gradation (type B) needs higher quantity of superplasticizer to overscale the disadvantage of low strength.

Taking into account the evaluation of results, as well as the main disadvantage of nano-particles which is their high cost, it is believed that their use can be focused in strengthening the interlayer connection of mortar stratification found in historic surface architectural members (murals, wall-floor mosaics, renders). In these cases the fresh state properties of grouts, as well as their adhesion capability are the most significant, while lower quantities of materials are generally needed. As it is shown from this preliminary study, fresh state properties of grouts are significantly improved, while their adhesion capacity with sand seems also to be improved. In this sense, it is concluded that the study of nano-modified lime-based grouts can open a new field of investigation for the consolidation and conservation of decorative structural historic members.

References

Binda L., Modena C., Baronio G. and Gelmi A., 1994. Experimental qualification of injection admixtures used for repair and strengthening of stone masonry walls. In: Proc. 10th International Brick and Block Masonry Conference, Calgary Canada. 539–548.

Binda L., Modena C., Baronio G. and Abbaneo S., 1997. Repair and investigation techniques for stone masonry walls. *Construction and Building Marerials* **11(3)**, 133–142.

Bras A., Fernando M.A. and Henriques F., 2012. Natural hydraulic lime based grouts-the selection of grout injection parameters for masonry consolidation. *Construction and Building Materials* **26**, 135–144

Eriksson M., Friedrich M. and Vorschulze C., 2004. Variations in the rheology and penetrability of cement-based grouts-an experimental study. *Cement and Concrete Research* **34**, 1111 –1119.

Ferragni D., Forti M., Malliet J., Teutonico J.M. and Torraca G., 1985. In situ consolidation of wall and floor mosaics by means of injection grouting techniques. *Conservation in Situ Mosaics* **3**, 83–101.

Gaitero J.J., Campillo J. and Guerrero A., 2008. Reduction of the calcium leaching rate of cement paste by addition of silica nanoparticles. *Cement and Concrete Research* **28**, 1112–1118.

Li H., Xiao H.J., Yuan J., Ou J.P., 2004. Microstructure of cement mortar with nanoparticles. *Composites* **B35**, 185–189.

Pachta V., 2011. Study of the technological evolution of mortars. PhD Thesis, Aristotle University of Thessaloniki.

Papayianni I., 2004. Design of compatible repair materials for the restoration of monuments. *Int. Journal for Restoration* **1(6)**, 623–636.

Papayianni I., Stefanidou M. and Pachta V., 2010. Grouts for injection of historical masonries: influence of the binding system and other additions on the properties of the matrix. In: Proc. 2nd Historic Mortars Conference and Rilem TC 203-RHM 'Repair Mortars For Historic Masonry', RILEM Publications SARL, 1123–1134.

Penelis G., Karaveziroglou M. and Papayianni I., 1988. Grouts for repairing and strengthening old masonry structures. In: Proc. International Conference on Structural Repair and Maintenance of Historic Buildings. Computational Mechanics Publications, Basel, 179–188.

Toubakari E., 2002. Lime-pozzolan-cement grouts and their structural effects on composite masonry walls. PhD thesis, Katholieke Uneversiteit Leuven.

Vintzileou E. and Miltiadou-Fezans A., 2008. Mechanical properties of three-leaf stone masonry grouted with ternary or hydraulic lime-based grouts. *Engineering Structures* **30**, 2265–2276.