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MIX DESIGN AND PERFORMANCE EVALUATION OF GROUTS WITH SUPERFINE NATURAL POZZOLAN

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ABSTRACT

In this paper the first results of a research program for the optimization of the mix design of hydraulic lime pozzolanic grouts evaluated through rheological, mechanical and durability tests, are presented. Two different types of superfine natural pozzolans, commercially available as μ-silica, W and B type, based on volcanic glass of rhyolitic composition, were used as pozzolanic additives (10%) to a commercial natural hydraulic lime (NHL5 of St Astier), in order to prepare grouts of high injectability, suitable for the strengthening of stone masonry historic structures. The evaluation of the grouts injectability capacity was first performed by fluidity, penetrability and stability tests. Flexural and compressive strength tests were subsequently carried out together with drying shrinkage test, for the physical-mechanical characterization of a series of grout mixtures, selected on the basis of their satisfactory injectabilitry characteristics. The selected grouts were also exposed to 10% sodium sulphate solution, in order to record their durability behavior, regarding the salt crystallization. The until now experimental results show that the use of this superfine natural pozzolan leads to injectable grouts with an improvement of the compressive strength, compared to the pure commercial hydraulic lime based grout. Furthermore, grout mixes containing pozzolan, presented better resistance to salt crystallization, in comparison to the samples that did not contain pozzolan. Especially, the mixtures with W-type pozzolan demonstrated the best mechanical performance and resistance to salt crystallization. However the strength and durability results present some differences in comparison with those obtained in the literature. Nevertheless, the research is still in progress in order to better clarify the present results and fully investigate the beneficial effect of substituting a part of hydraulic lime with the aforementioned pozzolanic materials, in terms of injectability, strength and durability requirements.

Keywords: *Grout, Natural pozzolan, Injectability, Mechanical characteristics, Durability*

1. INTRODUCTION

Hydraulic lime-based grouts (hydraulic lime with or without a pozzolanic material) seem to offer a promising alternative to the ternary grouts (with limited cement content) due to their similarity with the in situ materials and their mechanical efficiency for the structural restoration of stone masonry

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[1-3]. Systematic studies of grouts using a series of commercial hydraulic limes have proven that this type of grouts constitute a reliable alternative to higher strength ternary cementitious grouts [4-6].

For the mix design of hydraulic grouts of high injectability, specific criteria, which link the estimated nominal minimum width of voids to be filled (W_{nom}) with basic properties of the grout composition, have been proposed in the literature [7-9]. Based on these criteria and using commercial materials, one can prepare hydraulic grouts injectable in voids and cracks of a nominal minimum width of 0.1-0.2 mm or higher. For lower nominal minimum widths, which correspond to very fine silt or clay, the penetrability of hydraulic grouts cannot be satisfactory. That is why when an important percentage of clay and silt is present as loose material, a successful injection cannot be assured [5, 7].

In this framework, a comparative study was undertaken for the design of grouts injectable in voids and cracks of nominal minimum width Wnom ~200 μm using a natural pozzolan, as an additive to a commercial hydraulic lime. Injectability and durability characteristics, as well as mechanical properties, the most important parameters that influence the performance of the grouts, are examined and used for the selection of the optimal compositions on the basis of the aforementioned mix design criteria.

2. EXPERIMENTAL WORK

Superfine natural pozzolan, commercially available as μ-silica type W and B, was used as a pozzolanic additive to the commercial natural hydraulic lime NHL5 (St Astier). Natural Pozzolan, is a pure natural amorphous aluminosilicate mineral, occurring in Milos Island (Greece). Chemical and a qualitative mineralogical composition, are given in Tables 1 and 2, respectively. It was found that natural pozzolan contains more than 70.0% of silica (SiO_2) and 12.0-15.0% of amorphous alumina (Al_2O_3) and it occurs in amorphous glassy state of 95.0%, at least. More details and performance characteristics of the material are given elsewhere [10]. Hydraulic lime NHL5 is produced from an argillaceous limestone with siliceous content. It contains mainly calcite, Portlandite and calcium silicates. Chemical and a qualitative mineralogical analysis, are also given in Tables 1 and 2, respectively. Laser grain size analysis of the materials are given in Table 3. Natural pozzolan has a mean size of approx. 1,28-1,4 μm and both types have a high specific surface measured using the method of N_2 BET (3,0 and ~20,0 m^2/gr, respectively), as a result of their initial mechanical activation by physical process.

Table 1 Chemical analysis of Pozzolan and Natural Hydraulic Lime

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	L.O.I
Natural Pozzolan	71,57	13,81	1,01	0,50	0,71	3,33	4,03	5,04
NHL5	18,57	2,35	0,66	2,37	59,70	0,06	0,39	16,41

Table 2 Mineralogical analysis of Pozzolan and Hydraulic binder

	Natural Pozzolan	**NHL5**
Quartz	√√	√√
Illite	√	
Feldspar	√√	
Calcite – $CaCO_3$		√√√
Calcium Silicate – C_2S		√√√
Portlandite – CH		√√√
Calcium Aluminum Oxides- C_3A, CA		√

Finally, two types of superplasticizers of Domylco Ltd, CH 174 and SPL, were used together with tap water in various percentages for the dispersion of the solid materials and the preparation of grouts. They were compared, since they act differently. More specifically, CH 174 creates, in addition to its electrostatic action, molecular chains around the particles, which leads to less friction surfaces in between them. The action of SPL is mainly electrostatic and the better rheological behaviour of the mix is a result of the developed repulsion forces in between the charged particles. Both superplasticizers comply with EN 934-2 t. 3.1, 3.2, A.S.T.M. C494 type A&F and ASTM C1017.

Based on the grain size analysis presented in Table 3, the diameter corresponding to 85% passing and to the 99% passing of the solid phase of a grout consisting of neat natural hydraulic lime fulfil the penetrability grading criteria for voids and cracks of nominal minimum width Wnom ~ 200μm (i.e. $d_{85} <$ Wnom/5 = 40 μm and $d_{99} <$ Wnom/2 = 100 μm, respectively) [8].

Table 3 Grain size analysis characteristics of pozzolan and hydraulic lime

		Undersize (μm) of volume fractions (%)		
		d_{50}	d_{85}	d_{99}
Natural Pozzolan	*W-type*	1,42	14,22	25,04
	B-type	1,28	9,15	14,15
NHL5		10,00	27,00	50,00

As the objective of this research is to compare the characteristics of grouts with a solid phase composed by 90% of NHL5 and 10% of natural pozzolan to those of grouts of neat NHL5, the design of all compositions was performed with the aim to ensure high injectability under low pressure, in cracks of the aforementioned Wnom ~ 200 μm.

To this end the performance of the mixtures, in terms of penetrability, fluidity and stability characteristics was examined for various water to solid ratios with and without superplasticizer. Grout penetrability was measured using the standardized sand column test [NF P18-891 and EN 1771], with siliceous sand varying from 1,25 mm to 2,50 mm, which corresponds to voids of 0,2-0,4 mm, and to a W_{nom}=205 μm [8]. Grouts are considered to exhibit high penetrability, when the time (T_{36}) the grout takes to reach the upper part of the column (36 cm), is less than 50.0 sec and the grout comes out of the column and flows to an adjacent recipient [9]. Fluidity was measured through the Marsh cone test (ASTM C939-87 or NF P 18-358). Satisfactory fluidity of the grout mixtures is considered to be achieved, when the fluidity factor (based on measurements with a Marsh cone with a nozzle diameter d = 3 mm) is higher than $0,7 \times 10^{3}$ mm/s and the total efflux time of 500.0 ml of grout is less than 45 sec (based on measurements with a Marsh cone with a nozzle diameter d = 4,7 mm) [9]. In addition to adequate penetrability and fluidity properties, stability of the suspension, i.e. ability to preserve homogeneity, was examined. A grout is considered stable when it has no segregation and it presents low bleeding, with a maximum acceptable limit of 5% (measured according to NF P18-359) [7].

In order to reach similar injectability for all grout mixes keeping the same water to solids ratio, the use of an adequate superplastisizer was necessary especially for the grouts containing NHL5 and natural Pozzolan. The selection of the water to solids ratio and of the type and content of superplasticizer was performed on the basis of a preliminary study for all the solid phases studied. All the grouts were mixed using an ultrasound mixer (1000W, 28KHz), with a mechanical agitation of low turbulence (approximately 300 rpm). Total mixing time was 2 minutes for the neat hydraulic lime grout and 4 minutes for the binary grouts of hydraulic lime associated with natural Pozzolan (2 min/solid component) [7].

In Table 4 are shown the grout mixtures selected on the basis of their satisfactory injectabilitry characteristics. The first two mixes (G0.5 and Gs) contain a solid phase consisting of neat hydraulic lime NHL5 and have the same W/S = 0,825. They differ only concerning the type and percentage of superplisticizer: G0.5 contains 0,5% of CHEM 174 and Gs 0,75% of superplasticizer SPL. In the next four mixes (GW10, GW10s, GB10 and GB10s) 10% natural Pozzolan μ-silica, type W and B respectively, were added, together with superplasticizer in similar percentages for each type, as those used for the first two mixes. The water to solids ratio in these four mixes is also the same with that used in the first two grouts (G0.5 and Gs) where neat hydraulic lime was used. This was one of the objectives of the research in this preliminary phase, in order to facilitate the comparison of mixtures with and without Pozzolan, in terms of strength and durability characteristics where the water content plays an important role.

Table 4 Grout design mixes

Grout composition	Composition (% w/w)					
	NHL5	μ-silica/W	μ-silica/B	Superplasticizer CH174 (*)	Superplasticizer SPL (*)	Water
G0.5	100			0,50		82,50
Gs	100	-	-	-	0,75	82,50
GW10	90	10	-	0,50	-	82,50
GW10s	90	10	-	-	0,75	82,50
GB10	90	-	10	0,50	-	82,50
GB10s	90	-	10	-	0,75	82,50

(*) of the solid phase of the grout.

For the above selected grouts of similar injectability, additional testing has been carried out. Flexural strength and compressive strength at 28, 90 and 180 days were measured in specimens 40 × 40 × 160 mm and 40 × 40 × 40 mm, respectively [EN196-1]. Drying Shrinkage was also evaluated, according to ASTM C596 and EN 196-3. Finally, after 90 days of curing, samples 40 × 40 × 40 mm from the selected grout mixes have been tested for evaluating their durability, regarding the salt crystallization resistance [3]. According to the procedure (RILEM V 1.b), dried samples were immersed in a 10% w/v Na_2SO_4 solution for two hours, removed and patted dry, and then dried in the oven for 20 hours. After drying, they were placed in the desiccator and left to cool for 2 hours. This 24 hour test cycle of immersion, drying, and cooling was repeated 15 times. The samples were photographed and weighed after every second cycle and after the fifteenth (final) cycle (when survived). At the end of the salt immersion cycling, the surviving samples are placed in a container filled with tap water. This tap water was replenished daily for a week. The samples were then dried until they reached constant weight, weighed and photographed at the end of this procedure. Weighting indicated the effect of salt crystallization to the grouts consistency.

This test attempts to simulate salt crystallization within the material and to record the destructive effect of sodium sulphate re-crystallization on the tested samples. As it is well known, when salts re-crystallize they expand within the material and cracking occurs, which gradually causes collapse. Even though this testing procedure simulates extreme weathering cycles that the grout formulation may not be subjected to, it establishes a comparative index of durability across samples based on their specific variables.

3. RESULTS AND DISCUSSION

Table 5, shows the injectability characteristics of the selected grouts, (i.e.: the time T36 in sand column 1,25/2,5 mm (voids 0,2-0,4, Wnom = 205 μm) is given for characterizing penetrability; the fluidity factor (based on measurements with a Marsh cone with a nozzle diameter d = 3 mm) and the total efflux time of 500.0 ml of grout (based on measurements with a Marsh cone with a nozzle diameter d = 4,7 mm) are given for characterizing fluidity; finally bleeding values are included for characterizing stability, taking into account that all the composition selected did not present segregation.

All selected grout compositions satisfy the injectability criteria, set in the literature [7-9], in terms of penetrability, fluidity and stability characteristics, and present a similar high injectability capacity for common water to solid ratio of 0,825. For all grouts, when superplasticizer CH174 is added, the optimum content seems to be 0.50%, while when superplasticizer SPL is added, the optimum content is 0.75 %. Nevertheless the research is still in progress and a more detailed investigation is taken place regarding the optimisation of water and superplasticizer content, as well as the percentages of NHL5 and natural pozzolan.

Table 5 Penetrability, fluidity and stability characteristics, for the selected grout mixes

Grout Mixtures	Penetrability	Stability	Fluidity Marsh cone test		
	T36 (sec) Sand column test 1,25/2,5mm, Wnom=205µm	Bleeding (%)	t $_{d=3mm}$ (sec) (100ml of grout)	Fluidity Factor (*10^3 mm/sec)	t $_{d=4,7mm}$ (sec) (500ml of grout)
G0.5	25,15	2,00	19,84	0,71	27,43
Gs	12,91	2,00	16,58	0,85	24,40
GW10	9,72	2,00	15,36	0,92	22,99
GW10s	16,39	2,00	17,11	0,83	25,30
GB10	15,97	1,75	19,39	0,73	26,46
GB10s	15,05	2,50	18,41	0,77	26,22

Five of the above selected mixes, namely, Gs, GW10, GW10s, GB10 and GB10s were further studied for their physical, mechanical and durability behaviour. Table 6 includes the results for the flexural and compressive strength at various ages, as well as for the drying shrinkage of the designed grouts. Fig.1 presents the results of flexural strength and Fig. 2 those of compressive strength, respectively. As it is shown, the addition of natural pozzolan improves the flexural and compressive strength of the grouts and its positive effect becomes clearer after the age of 90 days. Little differences are reported between the two types of superplasticizer, as well as between the two types of µ-silica type. The addition of µ-silica, type B, seems to be more influential on strength development compared to type W. Since there is no difference in the chemical composition between the two types, the difference in the mechanical properties of the mixes, could be attributed to its finer characteristics.

However it has to be noted that the results obtained are not comparative with those presented in the literature for grouts composed by neat hydraulic lime (NHL5 St Astier) with or without superplasticizer for similar W/S ratio and with totally similar mixing and test procedures [4, 5]. In fact the strength values were higher than those obtained in the current experiments. Nevertheless, the research is still in progress using a new batch of the same type of hydraulic lime and this phenomenon will be further examined, as it has impact not only to the mechanical characteristics of NHL5 (st Astier) grouts but also on those of the 90% NHL5 and 10% natural Pozzolan ones. Subsequently, the beneficial effect of the pozzolan on strength and durability properties, is possibly underestimated.

Table 6 Flexural strength, compressive strength and drying shrinkage of the selected grout mixes

Sample	Flexural Strength (MPa)			Compression Strength (MPa)			Shrinkage (mm)
	28	90	180	28	90	180	
Gs	0,5	0,7	0,5	1,6	2,0	2,0	0,2360
GW10	0,5	0,8	0,7	1,7	2,5	2,8	0,1400
GW10s	0,6	0,6	0,7	1,7	2,9	2,8	0,1650
GB10	0,5	0,8	0,6	1,8	2,8	3,2	0,0780
GB10s	0,7	0,7	0,6	1,8	2,7	3,4	0,0625

Drying shrinkage results are also shown in Fig. 3. Drying shrinkage is reported reduced by 30 to 75%, for the grouts with µ-silica, compared to pure NHL mix (Gs).

Fig. 4 shows the results of weighting of the grout specimens at the age of 90 days, after several cycles of exposure in the salt solution. For all specimens, it is observed that during the first 4 cycles, the weight is increased, due to salt re-crystallisation. After the 4th cycle, the weight of the specimens did not further increase, except of that of GW10. In Fig. 5, where pictures of the samples are presented after 6 cycles of exposure, it is shown that only the specimens with µ-silica W-type (GW10, GW10s, have been remained compact, proving the better resistance to salt crystallization.

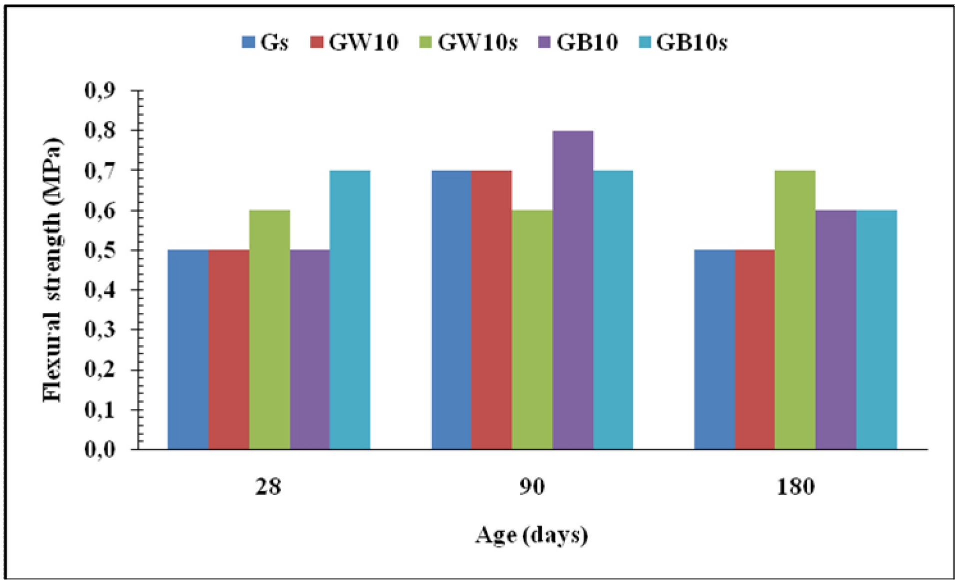

Fig. 1 Flexural strength of grout specimens at various ages, in relation to the type of natural pozzolan

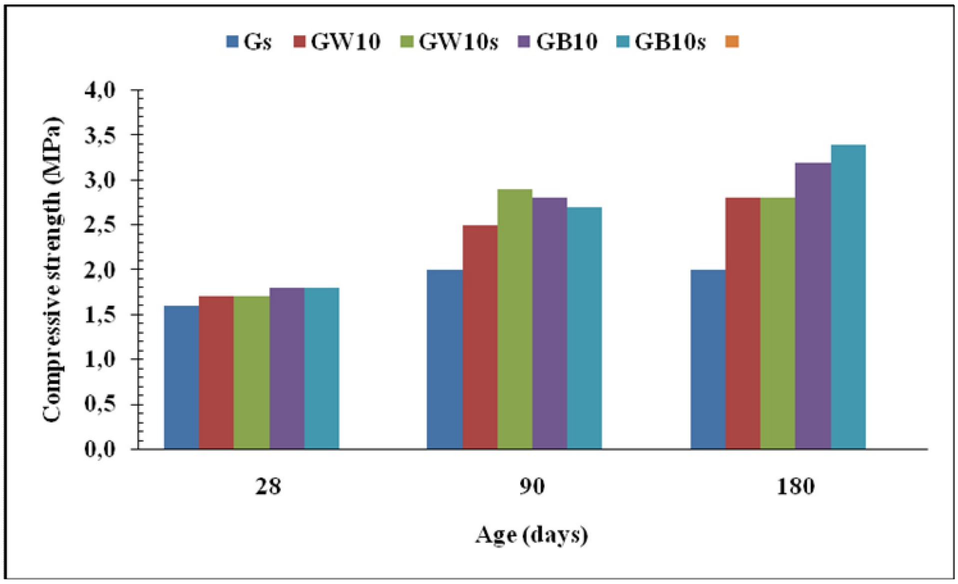

Fig. 2 Compressive strength of grout specimens at various ages, in relation to the type of natural pozzolan

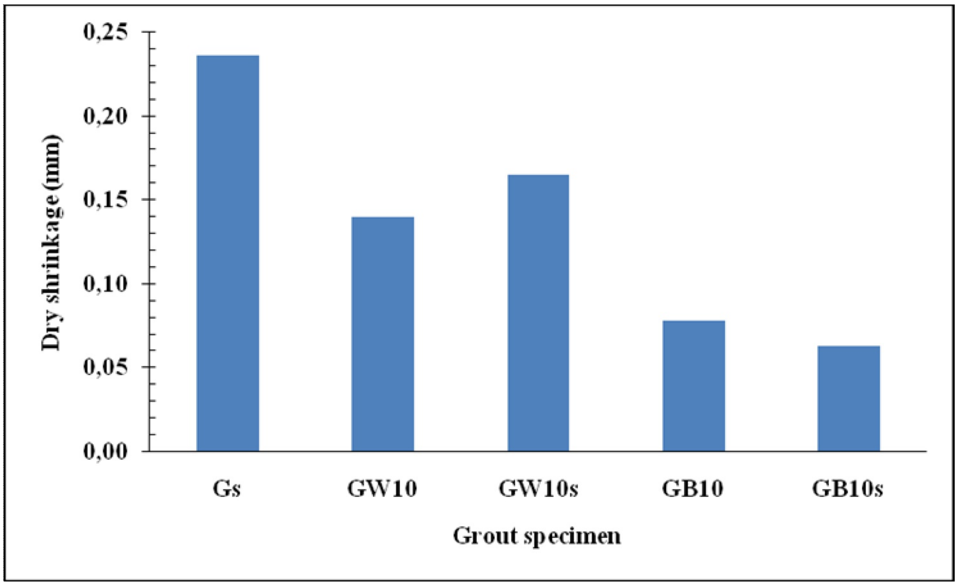

Fig. 3 Drying shrinkage of grout specimens, in relation to the type of natural pozzolan and superplastisizer

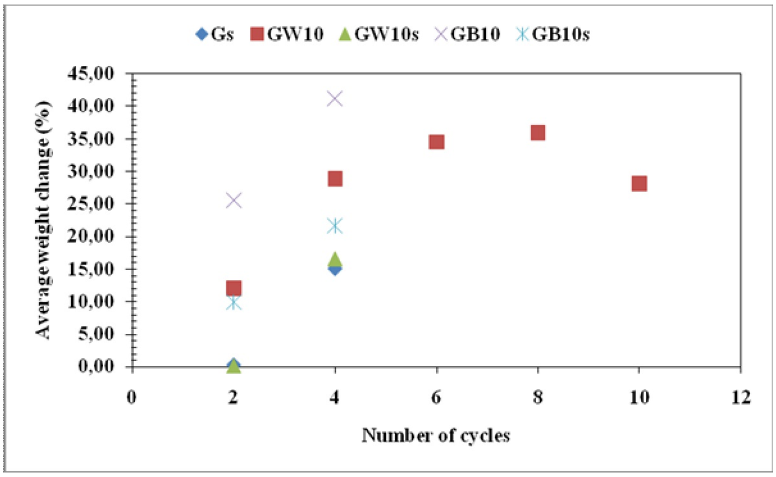

Fig. 4 Weight change of grout specimens, in realtion to the number of exposion cycles

Fig. 5 Photographs of grout specimens after six (6) cycles of exposure

4. CONCLUSION

The following conclusions are drawn from this study:

- The mixtures with natural pozzolan μ-silica, type W and B, satisfy the requirements for injectable grouts. Five mixtures were selected to be tested as far as their strength and durability characteristics are concern.
- The strength development of the grouts is favoured by the addition of natural pozzolan μ-silica, compared to the grout made with neat hydraulic lime.
- Drying shrinkage is reported reduced for the grouts with μ-silica.
- Durability behaviour of the specimens was reported weak, even though the exposure conditions are considered intense. These results concern both for the specimens with NHL5 only and those of NHL5 and pozzolan. However mixtures with μ-silica W-type (GW10 and GW10s) proved better resistance to salt crystallization, compared to the grout with neat NHL5 or the grouts with μ-silica B-type.
- The research is still in progress in order to better clarify the presented strength and durability results in comparison with those obtained in the literature, and fully investigate the beneficial effect of substituting a part of hydraulic lime with the aforementioned pozzolanic materials, in terms of injectability, strength and durability requirements.

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