Original research or treatment paper

Non-structural injection grouts with reduced water content: Changes induced by the partial substitution of water with alcohol

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Conventional grouting – used to stabilise delaminated plaster – typically involves the use of water as suspension medium. Water can be dangerous when water-sensitive original materials are present and can cause the solubilisation of salts, leading to their re-crystallisation on drying. Ethyl alcohol is a less effective solvent for soluble salts and generally does not affect the original materials. This is the reason why it was used as a partial substitute for water in grout preparations in the present research. Three water–ethyl alcohol-based grouts were compared with the correspondent water-based grout. The working properties and performance characteristics of the injection grouts with reduced water content were measured to assess their suitability for use on historic plasters.

Keywords: Grout, Wall painting, Delamination, Soluble salts, Alcohol, Water, Working properties, Performance characteristics

Introduction

Wall paintings are complex, multi-layered porous systems and often suffer from lack of adhesion between different plaster layers. This problem can be stabilised with injection grouting, introducing a compatible adhesive material with bulking properties (Griffin, 2004; Rickerby *et al.*, 2010, p. 471).

Injection grouting is a crucial remedial intervention which can potentially prevent the total loss of the plaster. However, since generally both the problem and the intervention are not visible, it is difficult to assess the efficacy of grouting. Moreover, this intervention involves the introduction of a large amount of material in the wall painting system and it is completely irreversible, since injection grouts introduced cannot be removed and – when set – become a non-extractable part of the wall (Rickerby *et al.*, 2010, p. 472).

The intervention typically involves the introduction of large amounts of water. Before grouting, during pre-wetting, water is introduced to clear the cavity and to saturate the void internal surfaces with the aim of reducing the absorption of the water contained in the grout mix. To increase wetting and reduce the overall provision of water, pre-wetting is often performed with a solution of water and alcohol.

Lime-/hydraulic lime-based injection grouts (typically chosen for stabilisation of lime-based wall paintings for a matter of compatibility with original materials) are usually prepared with water as suspension medium. Technical data sheets for commercial pre-mixed grouts suggest the addition of water to the dry mix in amounts comprised between 70 and 180% (mL/g of solid).¹ This water plays a role in the setting/hardening mechanism and in the improvement of injectability, but its presence can be problematic. In fact, it has been shown that excessive water leads to unstable grouts prone to segregation and bleeding and to greater shrinkage upon setting (Bicer-Şimşir et al., 2009). Moreover, water in the porous wall system causes the dissolution of soluble salts, leading to the harmful phenomenon of their re-crystallisation when water evaporates. Contamination by soluble salts and cycles of salt solubilisation and re-crystallisation are common deterioration mechanisms for porous building materials including decorated plasters (Arnold & Zehnder, 1991, p. 114).

The objective of this research was to evaluate possible reduction of water in grouts to avoid, or at least

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¹Technical data sheets of some pre-mixed grouts largely used in Italy.

reduce, the problems mentioned above. To that end, two pre-mixed commercial grouts and one grout designed in our laboratory were tested for their working properties and performance characteristics, replacing in their suspension medium different proportions of water with ethyl alcohol. For each grout individually, it was intended to compare the performances of mixtures prepared with 100% water vs. the same grout prepared with water–ethyl alcohol.

Materials, mixtures, and testing programme

In this study, three injection grouts were evaluated: two pre-mixed commercial grouts with hydraulic lime as binder (in this paper they will be called grouts A and B) and one grout designed in our laboratory with slaked lime as binder (it will be called grout C). These three grouts were prepared using as suspension medium only water (reference mixtures) or water and ethyl alcohol in different proportions: 50 to 50 and 25 to 75.

Two pre-mixed commercial grouts (PLM A - grout A – and LEDAN RI.STAT BASE B – grout B) were selected among several options available on the market. The two pre-mixed grouts chosen are widely used by conservators in Italy and elsewhere. According to a technical report (Università degli Studi di Trento - Dipartimento Ingegneria dei Materiali, 2006), PLM A is composed of 'desalted hydraulic lime; ventilated quartzite, micro fine clays and talc; melamine formaldehyde-based superplasticisers, inorganic shrinkage balancers, cellulose etherbased water retainers'. According to the technical data sheet, LEDAN RI.STAT BASE B is composed of 'natural lime and special hydraulic binders with low-soluble salts content, pozzolan, ventilated perlite, plasticising-, water retaining-, and air-entraining-admixtures'.

The third grout (C) was formulated with the following components (all parts in volume): 1 part of slaked lime, 1.5 parts of quartz sand ($\emptyset < 740 \,\mu\text{m}$), 1 part of pozzolan (pozzolana flegrea), 0.6 parts of ammonium carbonate, and 0.1 parts of a plasticiser, which slaked lime used in this research is composed of ca. 50% $Ca(OH)_2$ – ca. 50% water (in weight), which has been gravimetrically determined. For sake of simplicity the slaked lime was considered as a solid in the volume-mass percentages calculations in the rest of the paper. A pozzolan was added to allow the development of strength through the lime-pozzolan reaction (Lea, 1973, pp. 426-29). The plasticiser used was Sika Viscocrete-2S (Sika AG) with polycarboxylates modified in water (2,2-methylaminoethanol, L+lactic acid). Ammonium carbonate, which releases carbon dioxide through the following auto-decomposition

reaction

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O_3$$

was added to provide carbon dioxide to help carbonation in the deficiency of air in the void space.

As it is known, carbon dioxide is required in the carbonation reaction, which occurs in the presence of water

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Ammonium carbonate and bicarbonate were considered as possible additives for autogenous grouts, which have a compound producing CO_2 in an alkaline medium, and thus enhancing carbonation (Baglioni *et al.*, 1997).²

The materials tested included grouting mixtures prepared with water and with water and ethyl alcohol mixed in different proportions. Alcohols have the polar hydroxyl group (–OH) and a non-polar chain, therefore they are less effective solvents for ionic substances (e.g. for soluble salts) when compared to water. An alcohol with a short chain (such as ethyl alcohol) was selected as a substitute for water because of its miscibility with water and because it is a poor solvent for salts (Kolker & de Pablo, 1996; Pinho & Macedo, 2005).³

The volume-mass percentages of suspension medium (mL suspension medium/g dry pre-mixed grout) used for the research are considerably lower than the water amounts suggested in the technical data sheets: they are 65% for PLM A and 70% for LEDAN RI.STAT BASE B (while the respective technical sheets indicate up to 80% for PLM A and 100–120% for LEDAN). The volume-mass percentages were determined by preliminary tests; different amounts of suspension medium were added, always aiming to use the minimum water amount. For each of the mixture trials, injectability of the fluid material and cohesion of the hardened material were qualitatively assessed. For each grout typology, the percentage of suspension medium was determined, with several

²Decomposition of ammonium carbonate is much faster at higher pH than in water with pH = 7. Since pH of Ca(OH)₂ is between 11.5 and 12.5, CO₂ release in the presence of Ca(OH)₂ is quick. This reaction probably provides a high amount of CO₂ in a short time, but CaCO₃ crystals do not have time for developing and as a result the grout is weak, as noticed in Baglioni *et al.* (1997). Nevertheless, promising tests using ammonium carbonate to accelerate carbonation in lime-based plaster samples were carried out by Prof. M. Matteini and G. Botticelli (Matteini, 2011). Moreover, according to the previously mentioned observations, a pozzolan was added to allow the development of strength through the pozzolanic reaction.

³Kolker and de Pablo (1996) calculated the solubility of some salts in ternary systems containing two solvents and a soluble salt. In this study, the solubility of NaCl, KCl, KBr, and KNO₃ in mixed water–ethyl alcohol solvent was determined and they found that solubility progressively decreases when the ethyl alcohol weight percentage increases in the binary solvent: the more the ethyl alcohol (and thus the less the water), the lower the salt solubility. Pinho and Macedo (2005) found that solubility of NaBr and KCl is much lower in ethyl alcohol than in water; moreover, in ternary systems water–ethyl alcohol–NaBr/KCl, the more the ethyl alcohol (and again the less the water), the lower the salt solubility.

Mixture name	Suspension medium	Inert filler
Grout PLM A: 65% dilution (n	nl/g dry A)+40% inert filler (g/g dry A)	
A65/100	100% water	No
A65/100F	100% water	Yes
A65/25F	25% water – 75% ethyl alcohol	Yes
Grout LEDAN RISTAT BASE	B: 70% dilution (ml/g dry B)+70% inert filler (g/g dry B)	
B70/100	100% water	No
B70/100F	100% water	Yes
B70/50F	50% water – 50% ethyl alcohol	Yes
B70/25F	25% water – 75% ethyl alcohol	Yes
Mixture name	Suspension medium	Dilution (mL/g slaked lime)
Grout C		
C60/100	100% water	60%
C60/50	50% water – 50% ethyl alcohol	60%
C70/25	25% water – 75% ethyl alcohol	70%
Considering e.g. AXX/YYF:		
A = grout A		
XX = dilution (mL of liquid)	g of dry pre-mixed commercial grout or slaked lime)	
YY = water percentage of t	the total volume of mixing liquid	
F = filler addition		

Table 1 Grout mixtures and proportions

'trial and error' tests, to obtain suitable injectability and cohesion while keeping the least amount of water in grouts prepared with water and ethyl alcohol. Once determined, the percentage of suspension medium chosen for grout A and B was consistently used.

To obtain a cohesive and stable grout, PLM A and LEDAN RI.STAT BASE B required the addition of a filler (quartz sand) when mixed with water and ethyl alcohol. This is because the addition of alcohol determined a collapse of the samples while drying. Quartz sand was chosen because it is inert and non-porous, therefore not reacting with the other grout components, but just acting as a filler.

The three suspension media selected were: 100% water ('reference grouts' representing the conventional grout mixtures), 50% water -50% ethyl alcohol, 25% water -75% ethyl alcohol.

For all grouts, 75% water – 25% ethyl alcohol was not considered because the water amount would not have been significantly reduced to achieve the objectives of the research. PLM A mixed with 50% water – 50% ethyl alcohol was not tested because in all samples deep cracks (clearly visible during specimen drying) formed and grout cohesion was therefore unsuitable. This is obviously not desirable in an injection grout to be used on site. For all grouts, 100% ethyl alcohol was not considered because all grouts (especially those with hydraulic binder) require a certain amount of water to set and harden (Pecchioni *et al.*, 2008, p. 58; Cizer *et al.*, 2012).

The final formulations of the mixtures in terms of dilution (% of suspension medium used) and in

terms of the water–ethyl alcohol proportion used as suspension medium are provided in Table 1. This table also indicates the amount of filler (F) added to grouts PLM A and LEDAN RI.STAT BASE B.

Grout C was prepared using two dilutions (60 and 70% mL/g of slaked lime, see Table 1) to obtain suitable fluidity.

Testing procedures and results

Working properties concern the properties of the grout in the fluid state and refer to its short-term behaviour during the intervention; performance characteristics, instead, concern material properties in the hardened state and over time (long-term performance) and they are fundamental to the stability of the wall painting (Rickerby *et al.*, 2010, pp. 473–74). For this reason, in general, and also in grout design, performance criteria must be defined first (Cather, 2006, p. 92) while the working properties must be consistent with the performance requirements.

Working properties tested were injectability, fluidity, expansion, bleeding, and setting time. Performance characteristics tested were water vapour diffusion and capillary water absorption, porosity parameters, flexural and compressive strength, adhesion (pull-off test) and cohesion (direct tensile strength), shrinkage, and performance of grouts injected into replicas simulating a void between plaster layers. For each test three samples were tested and the average of the values obtained is reported in this paper.

For simplicity's sake, both in the next paragraphs and in the tables, PLM A is called A, LEDAN RI.STAT BASE B is called B, and the grout with separate components is called C (see Table 1 for the name and composition of each mixture tested).

Working properties

Injectability with syringe

In this paper, injectability is considered to be the ability of an injection grout to pass through the opening of a syringe (Griffin, 2004).

All mixtures were qualitatively evaluated by placing 10 mL of grout into a 100 mL syringe (with 3 mm diameter exit) and applying the same pressure on the syringe siphon by hand to push the grouts through the syringe. Based on the amount of material passing through in a certain time interval (3 seconds), the grouts are categorised as easy (more than 25 mL material passed through in 3 seconds), feasible (between 25 and 15 mL material passed through in 3 seconds), and difficult (less than 15 mL material passed through in 3 seconds) to inject. As expected from preliminary tests, all grouts were found to be easy to inject except for B70/50F, which was classified as feasible to inject.

Fluidity

Fluidity of grouts was qualitatively evaluated by letting the grouts flow through vertical channels carved on a porous plastered tile, previously pre-wetted (Biçer-Şimşir & Rainer, 2013, pp. 75–77). 10 mL of each grout were injected with a syringe at the top of the channel. 10 mL of each grout were also injected on the smooth surface of the tile (not in the channel). Once the grout, had stopped flowing, the flowing time and distance reached were measured (Fig. 1).

Grouts were also assessed on a non-porous substrate, a sheet of glass, to determine the influence of the support on grout flow. Fluidity within each group was evaluated by comparing distance reached (cm) and flow time (s), and classified as low (grout flow distance <100 mm), medium (100–200 mm), or high (>200 mm) (Biçer-Şimşir & Rainer, 2013). Generally, all grouts have medium-to-high flow. The only grout with an unsatisfactory fluidity (low) is B70/50F. Grouts prepared with water and ethyl alcohol flowed slower than those prepared with only water.

Expansion and bleeding (Standard ASTM C940–10a, modified)

The standard ASTM C 940–10a procedure was followed, with a modification regarding the volume of grout used, which was reduced from 800 ± 10 to 250 ± 10 mL. Evaluation of expansion and bleeding was carried out in a closed graduated cylinder (in non-allowed evaporation conditions). Expansion is the volume increase in the freshly mixed injection grout, while bleeding is the separation of the liquid from the solid.



Figure 1 Fluidity test.

Final expansion (E) is calculated by

$$E = (V_g - V_0) / V_0 \times 100,$$

where V_0 is the initial volume (mL) and V_g is the final volume of the grout (mL).

Final bleeding (FB) is calculated by

$$\mathbf{FB} = V_{\mathbf{W}}/V_0 \times 100,$$

where V_0 is the initial volume (mL), and V_W is the volume of decanted liquid (mL).

All grouts tested have no bleeding and no expansion with the exception of grout A65/100, which has 1% expansion.

Setting time (Standard UNI EN 196–3, modified) Before discussing this test, it is important to keep in mind that the terms *hardening* and *setting* have different meanings in conservation and in materials technology fields.⁴ In this research, the 'materials technology concept' is adopted and the standard UNI EN 196–3 (Vicat needle) for cements is used, given that there are no specific tests for injection grouts.⁵ In this research, the height of the sample was reduced from 40 to 20 mm to have a more realistic thickness considering the voids usually found in wall paintings.

Setting end results vary between ca. one day to 12 days and are listed in Table 2.

Grouts A have setting ends between two and three days, whereas grouts B ends between one and two

⁴In materials technology, *setting* concerns the initial stiffening of the paste (cement, plaster, etc.) and its consequential resistance to the Vicat needle penetration. By convention, setting is explained as two arbitrarily chosen points in the process, initial setting and final setting (which can be measured with standard UNI EN 196-3). *Hardening* concerns the development of measurable strength of the paste, it starts when setting ends and continues much longer. For cementitious systems, *hardening* is considered to reach ca. 80% of its cementing potential after 28 days at specific conditions (20°C and with RH>90%). Properties of specimens are usually measured after 28 days of standard curing. In conservation, *setting* is used to describe the entire process, which usually involves carbonation and hydraulic hardening processes when lime and pozzolanic materials or hydraulic binders are present. *Hardening* is part of the setting process, but clear and objective definitions are not shared.

⁵Biçer-Şimşir & Rainer (2013, pp. 58–61) propose a modification of the standard (ASTM C 953) which consists in retarding the start of the measure from three to eight hours.

Table 2 Setting time

Mixture name	Final setting time (in days)
A65/100	2.2
A65/100F	2.1
A65/25F	2.8
B70/100	0.9
B70/100F	0.9
B70/50F	2.2
B70/25F	1.1
C60/100	11.7
C60/50	9.7
C70/25	3.7

days. Ethyl alcohol seems to have a slight retardant effect for both grouts A and B (as already observed in Ramachandran & Beaudoin, 1987). Grouts C, as expected, have longer setting times, but in this case, the addition of ethyl alcohol has the effect of reducing significantly the setting time from ca. 12 days (C60/100) to less than four days (C70/25), opposite of the effect seen for grouts A and B.

Given that ethyl alcohol is more volatile than water, water-ethyl alcohol-based grouts undergo faster suspension medium evaporation than only water-added grouts. However, for grouts A and B this faster evaporation did not shorten the setting time of water-ethyl alcohol grouts compared to grouts prepared just with water.

Grouts C were covered with a plastic film to impede access of CO_2 of the air. It was possible in this way to qualitatively assess the 'autogenous setting' due to CO_2 release from ammonium carbonate autodecomposition (even if lime-pozzolan reaction contributes to the setting in the long term).

Performance characteristics

Grouts specimens were stored at 65-70% RH and 20-23°C and tested 28 days after their preparation.

Water vapour diffusion (Standard UNI EN 12086 modified)⁶ and capillary water absorption (Standard DIN 52617-A)

The water vapour diffusion test determines the diffusion resistance factor (μ) of a certain material. The lower the μ the easier the passage of the water vapour through the material. Water vapour diffusion samples are cylinders with diameter of 100 mm and height of 20 mm. For this test, the specimen is positioned on top of a cup containing a hygroscopic salt (anhydrous CaCl₂), the edges of the specimen are sealed, the system is placed in a controlled environment (at 20°C and 50% RH), and it is weighed at regular time intervals. The water vapour goes through the specimen due to the RH gradient between the high external RH and the low RH in the cup. The rate of weight increase indicates the resistance to water vapour diffusion through the grout specimen.

Capillary absorption instead quantifies the amount of liquid water absorbed by the grout over time. Capillary absorption samples are cylinders with diameter of 50 mm and height of 20 mm. The specimen sides are sealed, so that the water can be absorbed only from the lower surface. The base of the dry specimen is placed in contact with water and the specimen is weighed at defined time intervals.

Results of water vapour diffusion factor (μ) and capillary water absorption (W) are reported in Table 3.

All the tested grouts have $\mu \le 16$ and these values are comparable with those obtained for lime-based mortars prepared in the lab. It was found that limebased plasters prepared in the lab (lime putty-sand 1:2 in volume) have $8 < \mu < 15$ (Jornet & Romer, 2008; Jornet *et al.*, 2012). The addition of a filler clearly increases the water vapour diffusion factor (compare A65/100 with A65/100F and B70/100 with B70/100F). To assess the influence of ethyl alcohol on water vapour diffusion for grouts A and B, comparison should be made between those prepared with a filler addition, i.e. A65/100F with A65/25F and B70/100F with B70/25F.

In general, the results show that grouts prepared with the highest amount of ethyl alcohol have μ lower than their reference ($\mu_{A65/25F} < \mu_{A65/100F}$; $\mu_{B70/25F} < \mu_{B70/100F}$; $\mu_{C70/25} < \mu_{C60/100}$), i.e. the higher presence of ethyl alcohol (or the lower presence of water) seems to result in an easier water vapour diffusion through the grout.

The amount of capillary water absorbed by the grouts at the end of the test (after 24 hours) varies between 6.1 and 8.7 kg/m² and lies within the range of those obtained for lime-based plasters tested in the lab. Capillary absorption of some specific lime-based plasters tested in the lab (lime putty–sand 1:2 and 1:3) is $4.83 < W_{24} < 6.04$ (Jornet & Romer, 2008). The addition of a filler clearly reduces the amount of water absorbed (compare A65/100 with A65/100F and B70/100 with B70/100F).

More significant variations are observed when absorption after 10 minutes is considered (Table 3); the amount of capillary water absorption of all grouts A and all grouts C is very high, with no significant difference between mixtures with water and with water–ethyl alcohol. While for grouts B water absorption is lower with the exception of the B mixture with the highest ethyl alcohol percentage (B70/25F).

⁶The principal reference for this test is standard UNI EN 12086. Modifications were based on standards DIN 52 615, SIA 279, SIA V280.

Mixture name	μ (diff resistance factor)	$W_{10^{1}}$ (kg/m ²) (capillary water absorption after 10 minutes)	W _{24hr} (kg/m ²) (capillary water absorption after 24 hours)
A65/100	7	8.1	8.7
A65/100F	12	6.4	7.3
A65/25F	11	5.9	6.3
B70/100	11	2.3	7.1
B70/100F	16	1.2	6.2
B70/50F	14	2.4	6.1
B70/25F	11	6.5	6.9
C60/100	9	6.1	6.3
C60/50	10	6.8	7.0
C70/25	7	6.2	6.5

Table 3	Water va	pour diffusion	and capillar	y water absor	ption parameters
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Table 4 Porosity parameters and density

Mixture name	<i>n</i> (%) (total porosity)	U _E (%) (capillary porosity)	LP (%) (air pores)	qw (g/m ² h) (coefficient of permeability)	d (g/cm ³) (density)
A65/100	57.6	47.5	10.0	9.4	1.1
A65/100F	50.3	41.6	8.7	9.1	1.3
A65/25F	46.5	39.7	6.7	8.1	1.4
B70/100	61.0	41.0	19.9	7.0	1.0
B70/100F	52.1	35.0	17.2	8.0	1.2
B70/50F	48.2	35.8	12.4	7.9	1.3
B70/25F	47.2	34.3	12.9	6.3	1.3
C60/100	44.9	39.1	5.0	6.9	1.5
C60/50	44.8	41.5	3.3	7.7	1.5
C70/25	45.7	43.7	2.0	7.6	1.4

Porosity (Standard SIA 262/1)

For all grouts, the total porosity (n), the capillary porosity (U_E) , and the amount of air pores (LP) were determined together with the permeability coefficient (qw). Starting from a known weight, these parameters are determined by measuring the specimen weight increase-due to water absorption-at different stages. Vacuum is used to fill the pores not filled by capillarity, this allowing the assessment of the amount of air pores (LP). Porosity samples are cylinders with diameter of 50 mm and height of 20 mm.

The results of porosity measurements are reported in Table 4, together with the relative density of the grouts. Total porosity, capillary porosity, and air pores parameters are also shown in Fig. 2. All the tested grouts have a high total porosity which varies between ca. 44.8 and 61.0%. All values are higher than the porosity of many other building materials, including rocks, bricks, and plasters.⁷

The addition of a filler clearly reduces the total porosity, the capillarity porosity, and the amount of air pores (compare A65/100 with A65/100F and B70/100 with B70/100F) and increases the density.

In grouts A and B, the substitution of water with ethyl alcohol seems to slightly reduce the porosity parameters. On the other hand, in grout C the substitution of water with ethyl alcohol produces an increase in capillary porosity (U_E) and a decrease in air pores percentage (LP).

Data obtained for grouts B do not show the expected proportional correlation between capillary water absorption (W_{10} , and W_{24hr} , Table 3) and porosity parameters (Table 4). In particular, the capillary absorption coefficient increases significantly with the increase in ethyl alcohol used in the mixture (after 10 minutes B70/25F absorbs much more than B70/ 100). This, however, does not correspond to an increase in capillary porosity of the same amount. This behaviour may be explained considering that the speed of the capillary absorption depends not only on the capillary porosity percentage but also on the dimensions and the distribution of the capillary pores (not determined in the testing procedure used). In addition, B70/25F has a lower percentage of air pores compared to B70/100F: as air pores slow absorption down, the lower percentage of air pores

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⁷Sandstone n = 14-22%, limestone and marbles n = 7-20% (Weber *et al.*, 1983, p. 49); bricks 18.8% < n < 42.6% (Dondi *et al.*, 2003); plasters lime-sand 1:2 and 1:3 30.5 < n < 38.3% (Jornet & Romer, 2008; Jornet *et al.*, 2012); plasters NHL and crushed stones 1:2 and 1:3 24.72% < n < 27.20% (Lanas *et al.*, 2004).



Figure 2 Porosity parameters.

may correspond to a faster absorption of B70/25F compared to B70/100F.

Another cause for this behaviour could be the presence of chemical admixtures (not specified in the premixed product technical data), which may be responsible for the initial slow absorptive behaviour in grouts B prepared with more water. The addition of ethyl alcohol to the mix may reduce this initial effect, maybe due to an interaction between ethyl alcohol and the chemical admixtures.

Among grouts A, grouts with higher capillary porosity absorb faster. Even if they have a high percentage of air pores, the absorption is not significantly reduced. A65/100 is the grout with the highest capillary porosity (47.5%), but also with the highest percentage of air pores (10%). It still absorbs very fast, probably because the high capillary porosity counteracts the presence of air pores.

Grouts C have similar total porosity values among them. They all absorb a high amount of water in the first minutes because of their high capillary porosity and their relatively low amount of air pores. For these grouts, the reduction in air pores corresponds with an increase in the capillary porosity, while capillary water absorption coefficient remains almost unchanged.

The density of both references grouts A and B (A65/100 and B70/100) is lower than the density of the corresponding mixtures prepared with filler addition (A65/100F and B70/100F). As expected the presence of sand increases the densities.

For both grouts A and B with filler addition, the mixtures prepared with ethyl alcohol have a higher density than those prepared only with water (i.e. A65/25F density is higher than A65/100F density; B70/50F and B70/25F densities are higher than B70/100F density). These results are in agreement with the measured decrease in porosity when ethyl alcohol content increases. On the contrary, grout C prepared with ethyl alcohol (C70/25) has lower density and higher capillary porosity than grout C prepared just with water (C70/100).

Mechanical strength (Standard UNI EN 1015/11) Flexural and compressive strengths of the grouts A and B were evaluated on 28-day-old samples. Flexural and compressive strength of lime-based grout C were not tested, because samples were still too weak after 28 days and broke when demoulded. Samples for flexural strength test are prisms, 20 mm high, 20 mm wide, and 80 mm long. Samples for compressive strength are cubes $20 \times 20 \times 20$ mm. These dimensions, corresponding to half of those used in standard procedures, better represent the void volumes usually found in wall paintings.

Results are listed in Table 5 together with strength data-found in the literature-of plasters with different binders. All grouts B have higher flexural and compressive strengths than the NHL-based plaster references from the literature. Values obtained for grouts A lay within the reference values (≤ 1.7 and 5.6 N/mm², respectively). The results for both A and B show a wide range of values within the same mix, probably because of the reduced size of the samples.

The addition of ethyl alcohol seems to reduce flexural strength and increase compressive strength. However, results significantly vary within the same mix, therefore no conclusions can be drawn regarding alcohol influence.

The addition of a filler increases both the flexural and the compressive strength: compare A65/100 with A65/100F and compare B70/100 with B70/ 100F. This expected result can be explained by the fact that although the mixtures have the same dilution (mL suspension medium/g dry pre-mixed grout), when the filler is added the water to binder ratio is reduced, with the consequent increase in mechanical strength.

Adhesion (pull-off – Standard UNI EN 1015/12) and cohesion (direct tensile strength – Standard DIN 1048–2)

Adhesion is determined as maximum tensile strength with direct load (pull-off) perpendicular to the surface of the tested material applied on a support (the support should be selected depending on the material to test). In this research, a lime-sand plaster support was chosen, to simulate historic plasters. As described in Fig. 3, the plaster layer support (slaked lime-sand 1:3 in volume) was applied on a brick tile and allowed to harden. A perimetric boundary was positioned around this support and the fluid grout was poured on the plaster to reach a thickness of 12 mm. Before the grout was completely set, circular incisions - 50 mm of diameter - were made with a coring device, from the surface down to the brick. Steel plugs were attached to the upper part of the grout (corresponding to the circular incision) and

Table 5	Flexural, o	compressive,	direct tensile	strengths,	pull-off test	t data
	/					

				P	ull-off test
Mixture name	σ _f (N/mm²) (flexural strength)	σ_{c} (N/mm ²) (compressive strength)	σ _t (N/mm ²) (direct tensile strength)	σ _f (N/mm²) (failure force)	Location of failure
A65/100	1.2 ± 0.3	1.7 ± 0.4	0.2 ± 0.0	0.2 ± 0.0	Within the grout
A65/100F	1.5 ± 0.2	3.1 ± 0.5	0.2 ± 0.0	0.2 ± 0.0	Within the grout
A65/25F	0.9 ± 0.6	3.6 ± 0.3	0.5 ± 0.1	0.5 ± 0.1	Within the grout
B70/100	3.1 ± 0.1	6.1 ± 1.2	0.6 ± 0.3	0.3 ± 0.0	Plaster-brick interface
B70/100F	3.3 ± 0.4	7.1 ± 1.4	0.6 ± 0.2	0.4 ± 0.1	Within the plaster
B70/50F	2.3 ± 0.2	6.3 ± 0.6	0.6 ± 0.1	0.4 ± 0.0	Plaster-brick interface
B70/25F	2.6 ± 0.4	7.2 ± 0.7	0.3 ± 0.1	0.3 ± 0.1	Plaster-brick interface
C60/100	-	-	0.0 ± 0.0	0.0 ± 0.0	Within the grout
C60/50	-	-	0.0 ± 0.0	0.0 ± 0.0	Within the grout
C70/25	-	-	0.0 ± 0.0	0.0 ± 0.0	Within the grout
Plasters					
NHL5:sand 1:2 (Lanas <i>et al.</i> , 2004)	1.2-1.7 ca*	4–5.4 ca*			
NHL5:sand 1:3 (Lanas <i>et al.</i> , 2004)	0.5–1.0 ca*	2.5–5.6 ca*			
Lime:sand 1:2 (Jornet <i>et al.</i> , 2012)	0.2–0.4	0.5–1.1			
Lime:sand 1:3, (Jornet <i>et al.</i> , 2012)	0.6	0.9			

*In Lanas et al. (2004), no tables are provided, but graphs.

torn away perpendicularly to the surface. A dynamometer was used to measure the maximum force applied before failure occurs.

This test provides information about the tensile strength of the material described and adhesion (bond strength) between these materials. In the tests performed in this research, the failure occurred in different positions.

In grouts A and C, the failure was located within the grout. This indicates that tensile strength of grouts A and C is lower than both adhesion between grout and plaster, and tensile strength of the underlying plaster.

In grouts B, the failure occurred at the interface between the plaster and the brick tile or within the plaster. This indicates that bond strength between



Figure 3 Cross section of the plaster tile for the adhesion pull-off test.

grouts B and plaster is higher than both adhesion between plaster and brick tile, and tensile strength of the underlying plaster. Failure force and location are reported in Table 5.

The internal cohesion of the grouts was determined testing their direct tensile strength, following the DIN 1048–2 standard. Two metal plugs are glued with an epoxy resin to the grout specimen, one on its upper surface and one on its lower surface. The two plugs are then pulled perpendicularly to the sample surface in the two opposite directions. The strength (σ_t) is measured according to $\sigma_t = F/S$, where F is the force applied (N) and S the surface of the specimen (mm²). Samples are cylinders with diameter of 50 mm and height of 20 mm.

Results are listed in Table 5 and show that filler addition does not affect the tensile strength. The addition of ethyl alcohol (and the corresponding reduction of water) affects the tensile strength values of grouts B decreasing them for B70/25F (while they remain unchanged for B70/50); ethyl alcohol addition increases tensile strength values for grout A (A65/25F).

Thus, there is no consistent correlation between the amount of ethyl alcohol and tensile strength. As expected, lime-based grouts C values are very low (ca. 0) and much lower than those of the hydraulic grouts. In general, the erratic variations in mechanical properties are difficult to explain due to the fact that PLM A and LEDAN RI.STAT BASE B formulations are only partially known.

Shrinkage

The shrinkage test measures the dimensional variations of the grout, starting 24 hours after its preparation and continuing until shrinkage stops. A shrinkage test for grouts was recently developed (Biçer-Şimşir & Rainer, 2013, pp. 23–27), but in this research shrinkage was evaluated by measuring the variation in length of prism-shaped samples (100 mm long). The measuring device had a precision of 0.01 mm. Results of shrinkage measurements and the days needed to reach a stable situation are reported in Table 6.

As it could be expected, the addition of a filler tends to reduce shrinkage. This is particularly evident for grouts B (compare B70/100 with B70/100F). The addition of ethyl alcohol (and the corresponding reduction of water) affects the values of grouts A and B in an opposite way: increasing shrinkage for grouts A and significantly decreasing it for grouts B. Therefore, again, the influence of ethyl alcohol does not have a clear trend.

Shrinkage was not measured for grouts C, because samples handling was not possible 24 hours after preparation, due to the lack of strength development. However, some indication about shrinkage of grouts C was obtained by examining replicas in cross section (see below *Injection into replicas*).

Injection into replicas

Replicas simulating a void between plaster layers were prepared to reproduce a real case situation. A delamination between two plaster layers was created using the following procedure: the first plaster layer (slaked lime-sand 1:3 by volume) was applied on a brick tile; on this plaster, in the middle of the tile, small cylinders of dry ice were stacked together in the shape of a truncated pyramid (Fig. 4). The second plaster layer (slaked lime-sand 1:2) was applied on the dry-ice cylinders. As the dry-ice sublimes, an empty void between the two plaster layers is created.

Table 6 Shrinkage

Mixture name	Shrinkage (‰)	Constant conditions after-days
A65/100	0.69	12
A65/100F	0.67	17
A65/25F	1.50	16
B70/100	1.53	14
B70/100F	1.25	10
B70/50F	0.83	7
B70/25F	0.28	8



Figure 4 Dry-ice cylinders stacked in the shape of a truncated pyramid on the first plaster layer.

The CO_2 released may also contribute to the carbonation of the plasters. These replicas were allowed to set and harden for 90 days.

The injections were performed in the replicas kept in a vertical position to simulate a wall, after pre-wetting the internal surfaces of the void with a water and of ethyl alcohol solution (1:3 by volume); after 10 minutes grouts were injected into the void. After 90 days, replicas were cut and their cross sections were observed (Fig. 5).

The reference mix (100% water, no filler) and the corresponding grout with maximum percentage of ethyl alcohol (i.e. A65/100 and A65/25F, B70/100 and B70/25F, and C60/100 and C70/25) were injected into replicas. The replicas were cut and visually evaluated: all grouts considered showed good adhesion to the internal walls of the void.

Conclusions and final discussion

The properties of three grouts – prepared with water and with water and ethyl alcohol – were qualitatively



Figure 5 Cross section of a replica with C70/25. Red line indicates the boundary between the grout and the plastered layers. The visible discontinuities are limited in length and superficial, i.e. they do not pass through the grout, and seem not to affect the grout adhesion to the rendered layers.

and quantitatively evaluated, following standards and procedures adapted to injection grouts.

Before discussing the results, it is important to remember that the formulation of grouts to be used on cultural heritage requires knowledge of the composition and characteristics of the historic layers to be reconnected. Properties such as low shrinkage, good cohesion, and adhesion, as well as good injectability and low-salt content are always required for grouts. Other properties, such as mechanical strength, adhesion, water vapour diffusion, capillary absorption and porosity should be tailored to the case study under consideration. The objective of this research was not to formulate injection grouts with defined characteristics for a specific case study, but to assess if the tested grouts prepared with a reduced amount of water had basic properties for use. Further, the three grouts selected for this investigation are indeed different in formulation: therefore our results cannot be used to compare the grouts (A with B with C), but rather to compare each grout individually with its waterreduced counterpart.

The results of this study can be summarised as follows:

- PLM A: Compared with grout A65/100 mixed with only water as suspension medium, grout A65/25F (water and ethyl alcohol 1:3) is satisfactorily injectable, has no bleeding, high porosity, high water vapour diffusion, and high capillary water absorption. A65/25F has also a good internal cohesion and good adhesion to the lab plaster support considered in the pull-off test. The substitution of water with ethyl alcohol affects the mechanical strength, reducing flexural strength and increasing compressive and tensile strengths. Although ethyl alcohol increases setting time and shrinkage, the resulting mixture (A65/25F) is suitable both in terms of setting time (barely 14 hours longer than the reference)⁸ and shrinkage (as shown in the injection replica).
- LEDAN RI.STAT BASE B: Grout B70/50F (water and ethyl alcohol 1:1) is not satisfactorily injectable. It has porosity and capillary absorption similar to grout B70/25F, but water vapour diffusion is lower than grout B70/25F. Grout B70/25F (water and ethyl alcohol 1:3) can be easily injected and it has no bleeding. Compared with grout B70/100 mixed with only water as suspension medium, grout B70/ 25F has still high total porosity, high water vapour diffusion, and low shrinkage. It has high capillary water absorption and slightly higher setting time than the reference grout B70/100 (barely five hours higher than B70/100).⁸ As seen for grouts A, ethyl alcohol affects mechanical strength, but not consistently. B70/25F shows good cohesion. Adhesion to

the plaster support considered is higher than the cohesion of the plaster itself, where failure occurs during the pull-off test. In general, grouts B have mechanical properties significantly higher than those of limebased mortars tested in the lab (Jornet *et al.*, 2012). Overall the performances of grout B70/25F (water and ethyl alcohol 1:3) are more suitable for grouting than those of grout B70/50F (water and ethyl alcohol 1:1), with the further advantage of having less water.

• Grouts C: All grouts C have good injectability and fluidity (aided by the addition of plasticiser). Grout C70/25 (water and ethyl alcohol 1:3) has a shorter setting time than the reference grout C60/100 (100% water). Water vapour diffusion resistance factor, coefficient of capillary absorption, and total porosity parameters are not significantly influenced by the presence of alcohol, except the air pore content which decreases and the capillarity porosity which increases when the ethyl alcohol content increases. Mechanical strength of grouts C is lower than the strength of lime-based mortars, but their internal cohesion is sufficient to effectively fill a void, as shown in the replicas test. This test also showed no shrinkage and good adhesion of all grouts C to the plaster.

Given that the performances of grout C60/50F and grout C70/25F are similar, grout C70/25F mixed with less water would be preferable.

Overall, ethyl alcohol affects grout properties, even if the trend observed in the different groups is not always consistent. The results of our research showed, however, that grouts mixed with water and ethyl alcohol are characterised by adequate shrinkage, porosity, cohesion, and adhesion, as well as good injectability, and therefore they are potentially suitable for *in situ* implementation. However, before using ethyl alcohol as a substitute for water, preliminary tests should be performed to determine the compatibility with the original materials to be treated.

It is not possible to thoroughly interpret the influence of ethyl alcohol on mixture performances because commercial grouts formulations are not fully provided. It can reasonably be assumed that ethyl alcohol interacts with the chemical admixtures present in the commercial products. The lack of knowledge about the components of the mixtures A and B tested has been a limitation of this research.

Although the results are encouraging, the influence of suspension media other than water on the properties of grout should be further investigated. Further research should focus on mixtures of known composition using different binders (slaked lime with and without pozzolanic addition, and hydraulic lime) in addition to fillers, other suspension media (alternative to water) and, if required, chemical admixtures to obtain desirable properties for cultural heritage preservation. The on-going PhD research work of the first author is covering some of these aspects.

⁸In conservation practice, when working under constrains on site, it is important that the grout fulfils relatively rapidly its stabilising function, i.e. not remaining too long in a fluid state. The increase in setting time of five hours (for B70/25F) and 14 hours (for A65/25F) when using alcohol is negligible in conservation practice.

Manufacturers and suppliers

- PLM A, C.T.S. Suisse SA, Via Carvarina, 1, 6807 Taverne (TI), Switzerland, http://www.ctseurope. com/
- LEDAN RI.STAT BASE B, Tecnoedile Toscana srl, Strada Statale dei Monti Lepini 14, 04100 Latina, Italy, http://www.tecnoediletoscana.it/
- Slaked lime: Grassello Candor 48 months aged, Adriatica Legami srl, Str. Statale 16 Km 855,500–72015 Fasano di Brindisi (BR), Italy, http:// www.calceviva.it/
- Milled quartz sand up to 740 μm, Carlo Bernasconi AG, Riedbachstrasse 51–3027 Bern, Switzerland.
- Pozzolana flegrea, 80078 Pozzuoli (NA), Italy, sample taken by the University 'Federico II' of Naples (Italy), Science Department, Faculty of Mathematics, Physics and Natural Sciences.
- Ammonium carbonate, CTS srl, C.T.S. Suisse SA, Via Carvarina, 1, 6807 Taverne (TI), Switzerland, http://www.ctseurope.com/
- Ethyl alcohol, Emanuele Centonze SA, Via Luigi Favre 16, 6828 Balerna (Chiasso), Switzerland, http://www.ecsa.ch/en
- Plasticiser: Sika Viscocrete-2S, Sika AG, Zugerstrasse 50, 6341 Baar, Switzerland, http://www.sika.com/

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Standards

ASTM C940-10a	1981. Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory, USA
DIN 1048-2	1991. Prüfverfahren für Beton; Festbeton in Bauwerken und Bauteilen
DIN 52617-A	1987. Bestimmung des Wasseraufnahmekoeffizienten von Baustoffen, Beuth Verlag GmbH, Berlin
DIN 52615	1987. Wärmeschutztechnische Prüfungen–Bestimmung der Wasserdampfdurchlässigkeit von Bau–und Dämmstoffen
SIA 262/1	2003. Perméabilité à l'eau, Construction en Béton–Spécifications complémentaires, Société suisse des ingénieurs et des architectes, Zurich

SIA 279	2001. Matériaux de construction isolants
SIA V280	1996. Kunststoff-Dichtungsbahnen (Polymer-Di)
UNI EN 196–3	1996. Methods of Testing Cements–Part 3, Determination of Setting Times and Soundness
UNI EN 1015/11	1999. Methods of Test for Mortar for Masonry–Part 11, Determination of Flexural and Compressive Strength of Hardened Mortar, Milano
UNI EN 1015/12	2002. Methods of Test for Mortar for Masonry–Determination of Adhesive Strength to Hardened Rendering and Plastering Mortars on Substrates
UNI EN 12086	Water Vapour Resistance (Z)

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