EXPERIMENTAL CHARACTERISATION OF INJECTION GROUTS
INCORPORATING HYDROPHOBIC SILICA FUME

Luis G. Baltazar1*, Fernando M.A. Henriques2, Douglas Rocha3 and Maria T. Cidade4

1 Departamento de Engenharia Civil, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
2 Departamento de Engenharia Civil, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
3 Departamento de Engenharia Civil, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
4 Departamento de Ciência dos Materiais e Cenimat/I3N, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.

* Corresponding author. Tel.: +351 21 2948580; E-mail addresses: luis.baltazar@fct.unl.pt

ABSTRACT

The present paper put forward a new hydrophobic silica fume and assesses their contribution on the performance improvement of grouts for stone masonry consolidation. The experiments were conducted using different dosages of hydrophobic silica fume with natural hydraulic lime grouts in the presence of a polycarboxylate-based high range water reducer. Results revealed that the effects of hydrophobic silica fume on properties of natural hydraulic lime grouts optimise the use of ordinary silica fume. Remarkable rheological performance was obtained in the presence of hydrophobic silica fume: the plastic viscosity and yield stress were reduced compared with the ordinary silica fume. On mechanical strength aspects it was found that hydrophobic silica fume slightly affect the flexural and compressive strength; however the values obtained are suitable for the old stone masonry consolidation purposed. It was also observed that water capillarity was substantially reduced, namely due to the water repellent behaviour of hardened grouts. This study suggests that the promising effectiveness of this new silica fume on injection grouts open the way to be used in many other applications.

Keywords: Masonry; Grout; Rheology; Natural hydraulic lime; Hydrophobic silica fume.
INTRODUCTION

Stone masonry is a simple and durable constructive technique that is present in the large majority of old buildings in many urban centres in Europe. However, these masonries exhibit a non-monolithic behaviour which increases their vulnerability against several damaging actions, like seismic events (Binda et al., 1997). Grout injection is an effective technique to repair and consolidate stone masonry walls by improving the cohesion between the masonry elements (Corradi et al., 2002; Chaudhry, 2007). Grouts should be well designed in order to have adequate performance (i.e. considerable fluidity and penetrability). The use of ultra-fine materials, such as silica fume, in cementitious materials is one of the main trends in development of materials with improved performance (Artelt and Garcia 2008; Sobolev et al. 2016).

Silica fume is a by-product of the smelting process in the electrometallurgy industry, which has been mainly used in cementitious materials as a binder replacement. The effect of silica fume on cementitious materials is now well known. Several studies (Wei-Hsing, 1997; Shannag, 2000) have shown that the properties of cementitious materials can be improved in the presence of silica fume. Although, the use of silica fume should not be indiscriminate in order to take full advantage of its properties. Previous studies have shown that silica fume can have harmful effects on rheology of injection grouts (Park et al., 2005; Baltazar et al., 2013), which result in grouts with low flowability.

Knowing that the decrease of grout workability is associated with the high water demand of ordinary silica fume, the authors of this paper put forward a pre-treatment with poly(dimethylsiloxane) (PDMS) solution on ordinary silica fume in order to get a silica fume with hydrophobic behaviour. PDMS is a polymer belonging to the family of silicones. One of the first applications of PDMS was in analytical chemistry, mostly in sample preparation
techniques (Seethapathy and Górecki, 2012). However, over the last decades, the applications
of PDMS have expanded into different areas, such as in the manufacture of textiles, personal
care products, or acting as additive to provide desirable properties in polish formulations,
water proofers and other surface treatments (Lecomte et al., 2013).

It is expected that the majority of fluidity and penetrability problems of injection grouts may
be easily overtaken with hydrophobic silica fume. This can be explained by the combined
effect of hydrophobicity and spherical shape of silica fume particles that cause a pure ball-
bearing action between the bigger and elongated natural hydraulic lime (NHL) particles. The
choice of NHL as binder is a consequence of its compatibility with pre-existing materials in
old masonries. According to other authors (Ballantyne, 1996; Binda et al., 2006; Biçer-Şimşir
et al., 2009) the NHL binders are widely agreed to be the most compatible material for the
conservation of heritage buildings. It should be noted, however, that the major advantage of
hydrophobic silica fume over other materials (that also led to improved hydrophobicity) is
that besides to obtain hardened hydrophobic grouts, which improve their performance from
durability point of view, the fresh properties, namely the rheological ones, are expected to be
improved as well.

This work provides insight into the influence of hydrophobic silica fume on the rheological
properties of NHL-based grouts with different concentrations of silica fume (10%, 20% and
30% replacement by NHL mass). Furthermore, the effects of this new silica fume on the
stability, water absorption, porosity, pore size distribution, pozzolanic reactions and
mechanical strength of NHL-based grouts were also evaluated.
MATERIALS AND GROUTS COMPOSITION

Materials characteristics

A NHL from Secil-Martigança produced according with the European Standard EN459-1:2010 was used in the experiments, with nominal strength of 5 MPa and specific surface of 9400 cm²/g (blaine specific surface). The density of this NHL is of 2.7 g/cm³. The silica fume used was an undensified silica fume produced by MAPEI. The specific surface of this silica fume is of 17.5 m²/g (BET method). The particle size is comprehended between 2 and 30 μm, 80% being below 10 μm. The chemical properties of both NHL and silica fume are listed in table 1. Polycarboxylate-based high range water reducers (HRWR) produced by BASF according to ASTM C494-05 Type F was used. It has a specific gravity, pH, chloride content, charge and solid content of 1.05, 8, <0.10%, anionic and 28-32%, respectively. The PDMS used has a density, appearance, viscosity, and volatile content of 0.97 g/cm³, liquid/paste aspect, 0.5 Pa.s and <1.0%, respectively. PDMS is a polymeric organic silicon composed of repeating monomer [SiO(CH₃)₂] units, with trimethylsilane groups as terminal units, as shown in Fig. 1. Previous studies (Lecomte et al., 2007; Lucquiaud et al., 2014; Roos et al., 2008) demonstrate that due to its high flexibility, low surface tension, resistance to ageing agents, high hydrophobicity, chemical inertness and good gas permeability, PDMS became a material of great benefit in the field of hydrophobic treatment of construction materials, such as mortars, concrete, tiles, etc. In addition to the above characteristics, the water solubility and reduced cost of PDMS, compared to that for the equivalent materials, make it appropriate for the coating treatment of silica fume.

Grouts composition and silica fume pre-treatment

A comparison between two types of silica fume was made, namely ordinary silica fume and the hydrophobic one. In order to carry out the hydrophobic treatment the following procedure
was adopted: first the PDMS was diluted in deionised water in a ratio of 1:7 (by weight) using a high shear mixer. Then, the silica fume was immersed in the PDMS solution and stirred for 10 min, followed by a resting period of 30 min. After this, the silica fume was filtered and placed in an oven at 60 °C until constant mass was achieved. The temperature of 60 °C was adopted because it is the optimal temperature to evaporate the water from the impregnated silica fume without damaging the polymer (Löters, et al., 1997). Finally the dry silica fume was ground and sieved in order to remove any lumps and to get a homogeneous powder.

Different dosages were tested for both types of silica fume (0%, 10%, 20%, and 30% as replacement of NHL in weight percentage). All grouts were made with HRWR to maintain constant water content, since this is the parameter that potentially provides more changes on fresh and hardened properties of grouts. The HRWR was incorporated in weight percentage of total NHL binder. The compositions of the NHL-based grouts are shown in table 2. The HRWR dosage was kept constant at the value of 0.8% when the hydrophobic silica fume is used as result of its reduced water demand (this will be further discussed in the next section).

Grouts were prepared at room temperature of 20 ± 2 °C and a relative humidity of 60 ± 2 %. For the preparation of grouts ordinary tap water was used. The silica fume was added and mixed with the dry NHL separately to ensure a homogeneous distribution before being transferred to the mechanical mixer. The mixture procedure adopted was the following: the whole powder (NHL + silica fume) is added to 70 % of the total mix water and mixed for 10 min. The remaining water (with diluted HRWR) is added within 30 s (without stopping the mixer). After all materials had been added, the mixture was maintained for an additional 3 min. Other studies (Aiad, 2003) have shown that the delay of 10 min on the HRWR addition improves the effectiveness of its dispersing action.
Preliminary tests

A set of preliminary flow tests was made to assess the appropriate dosage of HRWR in order to get grouts with satisfactory injectability. To do so, some grout’s injectability criteria already established in the literature was taken into account (Miltiadou-Fezans and Tassios, 2012). The fluidity factor (FF) proposed by Miltiadou and Tassios (2012) and a targeted porous medium with a representative diameter of orifices of 0.108 mm to be injected were considered (Miltiadou-Fezans, 1990). Flow tests on Marsh cone with 6 mm nozzle-diameter was performed to determine the FF and, consequently, the HRWR dosage that leads to a FF higher than the one associated to the nominal orifice width ($W_{nom}$) of 0.108 mm. Higher FF values are associated with greater injectability. In the scope of these preliminary tests (table 2) a HRWR dosage of 0.8% showed a satisfactory fluidity for the reference grout and those with hydrophobic silica fume to be injected in the reference porous media. Regarding the grouts containing ordinary silica fume it was necessary to increase the HRWR up to a content of 1.5% to obtain a proper FF.

EXPERIMENTAL PROCEDURES

Rheological measurements

Rheological properties were evaluated with a Bohlin Gemini HR$^{nano}$ rotational rheometer, equipped with parallel-plate geometry. The diameter of the geometry was 40 mm and the gap was set to 2 mm. To avoid the undesirable influence from mechanical histories, fresh samples were subjected to a pre-shearing at an identical shear rate of 1 s$^{-1}$ for 1 min and left standing for an additional 1 min before measurements took place. Then, the sample was subjected to a stepped ramp with shear rates from 1 to 100 s$^{-1}$. Each shear rate was applied long enough in order to ensure the attendance of the steady state. All grout samples were analysed with a constant temperature of 20 ºC, maintained by means of a temperature unit control. According
to Baltazar et al. (2015) the NHL grout’s rheological behaviour can be modelled fairly well using the Bingham model Eq. (1).

\[ \tau = \tau_0 + \eta \times \dot{\gamma} \]  

(1)

where: \( \tau \) is the shear stress (Pa), \( \tau_0 \) is the yield stress (Pa), \( \eta \) is the plastic viscosity (Pa.s) and \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)). In order to better characterise the shear-thinning behaviour of NHL grouts, the power-law model Eq. (2) was fitted to the experimental data in order to get the flow index.

\[ \eta = k \times \dot{\gamma}^{n-1} \]  

(2)

where: \( k \) is the consistency coefficient (Pa.s\(^n\)), \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)) and \( n \) is the flow index which characterises shear-thinning behaviour of grouts.

**Bleeding**

The bleeding test was based on ASTM C 940. After mixing, a 1000 ml glass graduated cylinder was filled with 800 ml of grout and covered to prevent water evaporation. For each grout, the thickness of the bleeding water was measured after complete sedimentation. The final bleeding was calculated using the Eq. (3).

\[ \text{Final bleeding (\%) } = \frac{V_w}{V_i} \times 100 \]  

(3)

where \( V_w \) is the volume of bleed water (ml) measured 120 min after the end of the mixing and \( V_i \) is the volume of grout sample at beginning of test (ml).

**Flexural and compressive strength**

Flexural and compressive strength were determined with five samples of each grout composition. The strength tests were done following standard EN 1015-11:1999. Flexural and
Compressive strengths were obtained using a universal traction machine Zwick Z050 with a 2 kN load cell and a deformation rate of 0.2 mm/min and a load cell of 50 kN and deformation rate of 0.7 mm/min for flexural and compressive test, respectively.

_Water absorption by capillarity_

The test of water absorption by capillarity was performed based on the European standard EN 1015-18:2002. For each grout, three samples (40 x 40 x 160 mm) previously cured for 28 days were used. The samples were vertically placed in a watertight box with water depth of 2 mm that was kept constant and the box was covered to maintain constant hygrothermal conditions. The grout specimens were weighted after 5, 10, 15, 30 min and at each hour during the first 6h of testing, and then weighted every 24 h. The capillary water absorption coefficient was determined by the angular coefficient of the linear part of the capillary absorption curve (i.e. absorbed water mass per unit of the surface vs. time).

_Open porosity, density and pore size distribution_

Open porosity was measured by total saturation with water of five samples of each grout under vacuum and hydrostatic weighting based on the European Standard EN 1936:2006. Samples were dried and placed under vacuum for 24 h, then maintained under vacuum but immersed in water for another 24h and finally left for 24h immersed at ambient pressure. After this procedure the samples were hydrostatically and saturated weighted. In order to better understand the previous results, the fresh density was measured after mixing by following the ASTM C138. Pore size distribution was conducted on grout samples using a Micromeritics’ AutoPore IV 9500 Series mercury intrusion porosimeter (MIP). The pressure required to intrude mercury into the sample’s pores is inversely proportional to the size of the pores; in this study a measuring pressure ranging from 0.003 to 207 MPa was adopted.
**Contact angle measurements**

The grout wettability was characterised with measurements of the grouts contact angles determined using a sessile drop method described by Leelamanie and Karube (2012), using a Goniometer KSV instrument. Contact angle measurements were performed as follows: a droplet of water was carefully dispensed onto the grout samples and an image of the droplet making contact with the grout surface was captured by a video camera. The image was subsequently processed with software to determine the contact angle.

**Thermogravimetric analysis**

The grout samples to be analysed by thermogravimetry (TG) were dried and ground. 1g sample was used in all tests performed. TG analyses were performed using a NETZSCH 449 F3 Jupiter thermogravimetric analyser. The experimental conditions were: N₂ gas dynamic atmosphere (40 ml/min); heating rate (40 ºC/min) and an alumina top-opened crucible. The samples were heated from room temperature to 1000 ºC at a constant rate. The TG test was conducted at the maturity age of 28 days.

**RESULTS AND DISCUSSION**

**Yield stress and plastic viscosity**

Rheological properties of injection grouts are decisive parameters since they affect the fresh performance and therefore the success of the consolidation operation. Thus, the yield stress, plastic viscosity and flow index were determined to compare grouts to each other. The knowledge of the yield stress enables to understand if a fluid will flow or not, since it represents that threshold. This important property affects the flow behaviour of the grout and its capacity to flow inside the masonry inner core. Plastic viscosity is associated with the flow resistance once flow is initiated. Fig. 2 presents the evolution of the yield stress and plastic viscosity, respectively, according to the silica fume used and its dosage. A smaller yield stress
and plastic viscosity is better than larger ones. From the rheological parameter results it is clear that as the ordinary silica fume dosage increases the grout becomes less workable. Even for the lowest dosage of silica fume (10 wt%) it can be observed that yield stress and plastic viscosity increased regarding the reference grout (without silica fume). The addition of silica fume leads to an increase of specific surface, causing higher adsorption of mixing water resulting in a decrease of grout flowability and therefore a lower injectability (Toumbakari, 2002; Assaad and Daou 2014; Khayat et al., 2008). This behaviour is dependent on the solid volume fraction, meaning that when the silica fume dosage exceeds a threshold value, and according with the Krieger-Dougherty equation, an increase in the inter-particle friction occurs (Struble and Sun, 1995; Phan et al., 2006). In other words, the introduction of small-sized silica fume particles is the source of additional surface area resulting in an increase of contact forces among fine particles leading to an easier coagulation due to interparticle interactions (Van-der-Waal’s interactions). The penetration capacity of such grouts is significantly decreased, making its injection at low pressure rather difficult. Thus, for a required penetrability performance, the water content of the grout must increase with detrimental effects on the fresh grout stability and hardened properties of grout.

As mentioned, a good flowability (i.e. grouts with lower plastic viscosity and yield stress) is preferred for injection purposes. The results illustrate that the rheological properties of grouts containing silica fume with hydrophobic treatment are significantly improved when compared to the ones of grouts containing ordinary silica fume. It is worth mentioning that grouts containing hydrophobic silica fume were found to have lower plastic viscosity values than the grout without silica fume. This is due to the fact that hydrophobic silica fume acts as fine aggregates (with reduced absorption of water) whose small-spherical shape particles fill the spaces made by the large and long shape particles of hydraulic lime binder imposing a ball
bearing effect, which reduce the friction forces between lime particles and therefore an improvement of grout flowability.

Flow index

The flow index ($n$) is dimensionless and reflects the kind of flow behaviour (Cao et al., 2016). If $n > 1$, the grout is shear thickening; while $n < 1$ the grout is shear thinning. For the case of a Newtonian grout ($n = 1$). Fig. 3 shows the evolution of the flow index calculated from the power-law model for different silica fume type and dosages. Most grout compositions tested presented a shear-thinning behaviour, which means that $n$ is lower than 1. A shear-thinning behaviour means that if flow velocity decreases during grout injection it leads to a viscosity increase (which is not desirable); thus $n$ value should be closer to 1 in terms of injection grouts.

For the grouts tested, when the dosage of silica fume increases, the $n$ index decreases. Indeed, the higher adsorption of water by silica fume explains this decrease. However, for grouts with hydrophobic silica fume, fluidity index are always higher than the grouts with ordinary silica fume. In fact, for grout containing 10 wt% of hydrophobic silica fume, flow index was found to be very close to 1 which means a quasi Newtonian behaviour or in other words a grout whose viscosity is not dependent on the injection pressure. Baronio et al. (1992) carried out an experimental program with masonries of different dimensions with cracks and voids irregularly distributed that showed that it was difficult to conduct the injections with a constant pressure. A grout exhibiting quasi-Newtonian behaviour enables an easier flow inside the porous medium, even when velocity decreases during injection, since viscosity will not change. Thus, on the basis of these results, it can be concluded that the presence of hydrophobic silica fume is useful to improve the rheological performance of injection grouts as result of the combined effect of its spherical shape and water repellence.
**Bleeding**

The results obtained for the bleeding evaluation are presented in Fig. 4, where it can be seen that all grouts are stable. According to Toumbakari (2002) and Lambardi (1985) a grout is considered stable when the final bleeding is less than 5%. Nevertheless, the results show differences between grouts with ordinary and hydrophobic silica fume. Thanks to the hydrophobic behaviour of the later the bleeding increases as consequence of higher amount of free water available in the mixture. The best results were obtained by the grout with ordinary silica fume which presented no bleeding. These results can be explained by a higher specific surface and a higher interstitial water retention that is offered by the ordinary silica fume compared to the hydrophobic one.

**Mechanical strength**

Compressive and flexural strength are good indicators of the quality of grout in hardened state. Fig. 5 and 6 present flexural and compressive strength values respectively. From the flexural strength results, it is clear that it increases when NHL is replaced by silica fume. A significant increase of flexural strength is observed when 10 wt% silica fume is added to the grout. However, the increase of 10 to 30 wt% in silica fume dosage does not present further improvement. In regard to the grouts with hydrophobic silica fume, it is clear that the flexural strength is always lower than the ones with ordinary silica fume.

Concerning compressive strength, it increases with increasing of ordinary silica fume dosage; the explanation for this behaviour is based on the high amorphous silicon dioxide contend of silica fume that reacts with the Ca(OH)$_2$ and results in the formation of additional calcium silicate hydrate structures (Shihada and Arafa, 2010; Khana and Siddique, 2011). From Fig. 6 it can be seen that the compressive strength values decrease with increasing dosage of hydrophobic silica fume, which is probably caused by the fact that hydrophobic silica fume has little or no pozzolanic reactivity. In addition, grouts in which NHL is replaced by
hydrophobic silica fume will not have enough silicate content (i.e. less NHL) to hydrate and
reach the compressive strength value of the reference grout. Another explanation for the
mechanical strength loss is based on the increase of grout’s open porosity in the presence of
hydrophobic silica fume (see further section). Note, however, that the compressive strength is
less determinant that flexural strength to get a successful consolidation process since the latter
are responsible to promote the adherence between grout and masonry elements (Jorne et al.,
2015). In addition, the typical compressive stress in old masonry is in range of 1 to 2.5 MPa
(Corradi et al. 2002; 2008) and all the analysed grout’s compositions have higher compressive
strength. Moreover, according to Valluzi et al. (2004) who assessed masonry walls through
compressive testing before and after grout injections, and despite the difference in the grout
compressive strengths, the strength gains in the walls were similar.

Open porosity

In order to better understand the mechanical strength results, the grout’s open porosity was
determined by the hydrostatic method. It should be highlighted, however, that the open
porosity of grouts with hydrophobic silica fume was also determined using the MIP method,
once in the hydrostatic method, the water repellence of grouts with hydrophobic silica fume
might block the entrance of water into some pores resulting in lower open porosity. As it can
be seen from Fig. 7 the values of open porosity obtained using the MIP method are higher
since the pressure used with mercury is able to overcome the surface energy of the
hydrophobic pore surfaces. Fig. 7 shows that there is a decrease of the grout porosity for
increasing dosage of ordinary silica fume. As expected the presence of silica fume decreases
the porosity, increasing the packing density, which explains the compressive strength
evolution. The same trend is not detected in hydrophobic silica fume, since when the
hydrophobic silica fume content increases the open porosity also increases. The authors
believe that this behaviour is due to combined effect of higher entrained air (as shown by the
fresh density values in Fig. 7) in the fresh grout, promoted by the hydrophobic silica fume, and the lower amount of hydration products as result of the lower pozzolanic effect of this kind of silica fume.

**Thermogravimetry**

The thermographs presented in Fig. 8 indicate that the peak of the decarbonation of CaCO$_3$ (peak around 900 °C) decreases with increasing replacement of lime by silica fume (this occurs for both silica fume types). As expected the amount of CaCO$_3$ decreases with decreasing amount of lime available to hydrate. However, differences between both silica fume types can be detected on the peak around 500 °C (i.e. dehydroxylation of calcium hydroxide). The derivative thermogravimetry (dTG) curves of the ordinary silica fume show that this silica fume reduces the Ca(OH)$_2$ content as illustrated by the lower Ca(OH)$_2$ peaks for higher silica fume dosage; this is attributed to the reaction of silica fume with Ca(OH)$_2$ leading to the formation of C-S-H. In contrast, in grouts with hydrophobic silica fume, the content of Ca(OH)$_2$ is only slightly affected, which corroborates the results of the mechanical strength in the previous section.

**Water absorption by capillarity**

The results of water absorption coefficient are presented in Fig. 9. According to this figure, there is a decrease of water capillary coefficient with increasing of the ordinary silica fume dosage. This comes from the fact that ordinary silica fume contributes to pore-size refinement and matrix densification and, consequently, the capillary pores are reduced. A major decrease until 10 wt% of silica fume can be seen. Above 10 wt% of ordinary silica fume there are no significant differences in water capillary coefficient; notwithstanding a slight tendency to decrease can be observed. These results indicate that there can be no advantage in using higher dosages than 10 wt%.
Regarding the grouts containing hydrophobic silica fume, the water capillary coefficient values are lower than the ones presented when the ordinary silica fume is used. The reason behind this is that hydrophobic silica fume has turned the hardened grout also hydrophobic. Those results can be explained by evaluating the wetting behaviour of hardened grouts through contact angle measurements. As the grout samples have a flat and rigid surface the water drops were placed directly over the surface of the sample. The results obtained for the contact angle measurements are presented in table 3. These results are averages of four measurements and the standard deviation is given between parentheses. It can be noted that the contact angle increases in the presence of hydrophobic silica fume. In fact, the grout with hydrophobic silica fume can also be considered as having hydrophobic properties (quasi non-wettable) since the contact angle is higher than 90º (see Fig. 10). This is in fact a promising behaviour from a durability point of view, since typically water transport soluble salts in old masonries which will induce destructive crystallization/dissolution cycles and in this case the hydrophobic performance of the grouts prevents or minimises that risk. Furthermore it should be noted that this hydrophobic behaviour does not compromise water vapour permeability.

**Pore size distribution**

The pore structure is a major component of the microstructure that affect mechanical strength and capillarity of hardened cementitious materials (Perraton et al., 1988). Thus, the microstructure of the grouts was examined using MIP to assess the influence of type and dosage of silica fume on the pore size distribution, at the age of 28 days. The MIP results (Fig. 11) show that there are differences among the grouts related to pore size distribution; however the majority of pore volume in all compositions is in the range of capillary pores (i.e. mesopores). As expected, the use of ordinary silica fume led to a pore diameter reduction. In Fig. 11a the comparison of the reference grout (0% ref.) with the one with silica fume dosage of 30wt% shows that there is a decrease of capillary pore size from 1 μm to 0.1 μm. This is
due to the fact that ordinary silica fume contributes to the formation of additional pozzolanic products that fill the pore spaces and therefore refines the pore structure. These results are consistent with the water capillarity shown in Fig. 9. In the case of hydrophobic silica fume (see Fig. 11b) it also shifts the pore size distribution to smaller diameter; although this reduction is much less pronounced than in the case of ordinary silica fume. It can be therefore observed that the grout with 30wt% of hydrophobic silica fume presented some pores greater than 1 μm (macropores range). The authors believe that these macropores might be assigned to shrinkage cracks due to the low strength of this grout composition.

CONCLUSIONS

This paper focuses on the influence of hydrophobic silica fume and its dosage on the properties of NHL-based grouts, namely rheological and mechanical properties, pozzolanic reactivity, water transport and microstructure. From the results obtained, the following conclusions can be deduced:

- The rheological properties of grouts containing hydrophobic silica fume are significantly improved. The grout containing 10wt% of hydrophobic silica fume showed the best rheological performance (lower plastic viscosity, lower yield stress and flow index close to 1).

- The hydrophobic silica fume acts as fine aggregates, filling the spaces between the long shape particles of hydraulic lime, and imposing a pure ball bearing effect, which improves the grout flowability by reducing the friction forces between lime particles.

- Silica fume has a strong impact on the shear-thinning behaviour of NHL grouts: the presence of hydrophobic silica fume leads to a more Newtonian behaviour. This can be seen as an advantage for grout’s flow and injectability performance.
The bleeding phenomenon slightly increases when hydrophobic silica fume is used, however, all grout compositions tested had an acceptable stability i.e. bleeding less than 5%.

Mechanical strength is somewhat affected by the hydrophobic silica fume. Notwithstanding, the compressive strength values obtained are still suitable, with compressive stresses in the range of the ones (1-2.5 MPa) typically found in old stone masonry.

The thermogravimetric analyses indicates that hydrophobic silica fume does not fully react with Ca(OH)$_2$ in the presence of water to produce additional pozzolanic products.

The water capillary coefficient is remarkably reduced when hydrophobic silica fume is used. The main reason behind this is that hydrophobic silica fume has turned the hardened grout also hydrophobic, as showed by the contact angle measurements.

Both types of silica fume tested lead to a reduction of pores size when dosage is increased (with the exception of hydrophobic silica fume at 30wt%). Nevertheless, it was observed that there is a decrease of the grout porosity with increasing dosage of ordinary silica fume and an opposite trend for hydrophobic silica fume as a result of entrained air during mixing.

This study suggests that the hydrophobic silica fume can be used to improve the performance of NHL grouts for consolidation of old stone masonries. It is clear, however, that additional characterisation of the contribution of this kind of silica fume in grout injection processes are needed. Anyway, the results of this study open the way to the manufacture of other materials like mortars, using the promising effectiveness of hydrophobic silica fume on improving rheological behaviour and durability by granting remarkable water transport properties.
Acknowledgments

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References


**Table 1.** Chemical composition of hydraulic lime and silica fume

<table>
<thead>
<tr>
<th>Formula</th>
<th>Hydraulic lime (%)</th>
<th>Silica fume (%)</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>2.00</td>
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<td>CaO</td>
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<tr>
<td>Free lime (%)</td>
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Table 2. Compositions of tested NHL grouts and its fluidity factor

<table>
<thead>
<tr>
<th>Grout No.</th>
<th>Amount of lime (%)</th>
<th>Ordinary Silica fume (wt%)</th>
<th>Hydrophobic Silica fume (wt%)</th>
<th>w/b</th>
<th>HRWR (wt%)</th>
<th>FF $x10^3$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>II</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td>III</td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>0.5</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>IV</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>0.5</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>V</td>
<td>90</td>
<td>-</td>
<td>10</td>
<td>0.5</td>
<td>0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>VI</td>
<td>80</td>
<td>-</td>
<td>20</td>
<td>0.5</td>
<td>0.8</td>
<td>2.7</td>
</tr>
<tr>
<td>VII</td>
<td>70</td>
<td>-</td>
<td>30</td>
<td>0.5</td>
<td>0.8</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Table 3. The contact angle between the hardened grout samples and water

<table>
<thead>
<tr>
<th>Grout designation</th>
<th>$\theta^{\text{SDM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grout without silica fume</td>
<td>28.5° (2.1)</td>
</tr>
<tr>
<td>Grout with ordinary silica fume = 20%</td>
<td>41.3° (2.6)</td>
</tr>
<tr>
<td>Grout with hydrophobic silica fume = 20%</td>
<td>108° (1.4)</td>
</tr>
</tbody>
</table>
Fig 2

Click here to download Figure Fig. 2.pdf
Stable if the bleed is less than 5%
Dehydroxylation of Ca(OH)$_2$
Fig 11(a)

Click here to download Figure Fig. 11(a).pdf
Fig 11(b) Click here to download Figure Fig. 11(b).pdf
Figure 1 The structural units of PDMS

Figure 2. Evolution of yield stress ($\tau_0$) and plastic viscosity ($\eta$) according to the dosage and type of silica fume

Figure 3. Evolution of the flow index ($n$) with the dosage and type of silica fume

Figure 4. Final bleeding of each grout composition studied

Figure 5. Evolution of flexural strength of hardened grout with the dosage and type of silica fume studied

Figure 6. Evolution of compressive strength of hardened grout with the dosage and type of silica fume studied

Figure 7. Evolution of open porosity of hardened grout and fresh density with dosage and type of silica fume studied

Figure 8. Thermogravimetric analysis of grouts: (a) ordinary silica fume; (b) hydrophobic silica fume

Figure 9. Water absorption coefficient due to capillary of hardened grout for the different dosage and the silica fume studied

Figure 10. The contact angle between the hardened grout with hydrophobic silica fume and the water drop

Figure 11. Differential pore volume as function pores size diameter of grouts: (a) ordinary silica fume (b) hydrophobic silica fume