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Review

Rheology of Natural Hydraulic Lime Grouts for Conservation of Stone Masonry—Influence of Compositional and Processing Parameters

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Abstract: This review provides an overview of the recent progress in the field of the rheology of grouts for historic masonry consolidation. During the last two decades, significant research has been devoted on the grouting technique for stone masonry consolidation but most results are scattered by scientific papers, congress communications, and thesis. This paper compiles and briefly demonstrates the effect of several intrinsic and extrinsic parameters, such as admixtures, additions, pressure, temperature, and measuring instrumentation, on the rheological performance of natural hydraulic lime-based grouts.

Keywords: grout; rheology; natural hydraulic lime; masonry; consolidation

1. Introduction

Grouting is generally used as a means of changing or improving the masonry's load bearing capacity to vertical and horizontal actions. A commonly used method for grouting is the grout injection, whereby the grout material, i.e., the suspension of binder particles in an aqueous medium, is forced by pressure into voids and fractures of stone masonry wall (Figure 1). It has been largely used in Europe, since the beginning of the twentieth century for consolidation of stone masonry walls, particularly in seismic areas [1–6].

Grouting is an invisible retrofitting technique, which is an advantage when working on historic buildings. On the other hand, it is an irreversible technique, which means that a badly designed grout can lead to regrettable consolidation failures [7,8]. Cement based grouts are the most widely used reinforcing material in concrete structures. However, it is not suitable for consolidation works of stone masonry buildings and the main reasons are the mechanical strength and rigidity (higher modulus of elasticity) of cement, which results in poor compatibility with the masonry characteristics in mechanical, physical, and chemical aspects. In this sense, the natural hydraulic lime (NHL) is today the most commonly used material for grouting operations in historic masonry buildings because of its moderate mechanical strength, water vapor permeability and chemical compatibility with traditional materials found in old masonry walls [7,9].

Depending on the prevailing masonry conditions, grouts with different characteristics must be designed [10–12]. Although, most grout' characteristics like penetrability, rheology, mechanical strength, stability, and durability are characteristics that need measurement techniques and standards, many of which have yet to be undertaken. Nevertheless, when it comes to penetrability and rheology of natural hydraulic lime-based grouts, several research works have been done in the last decades [13–19]. Among the various grouts characteristics, fluidity appears as one of the most determinant characteristics in the grouting performance, since it is important to ensure that the grout can flow and fill well the cracks and voids in the masonry core.

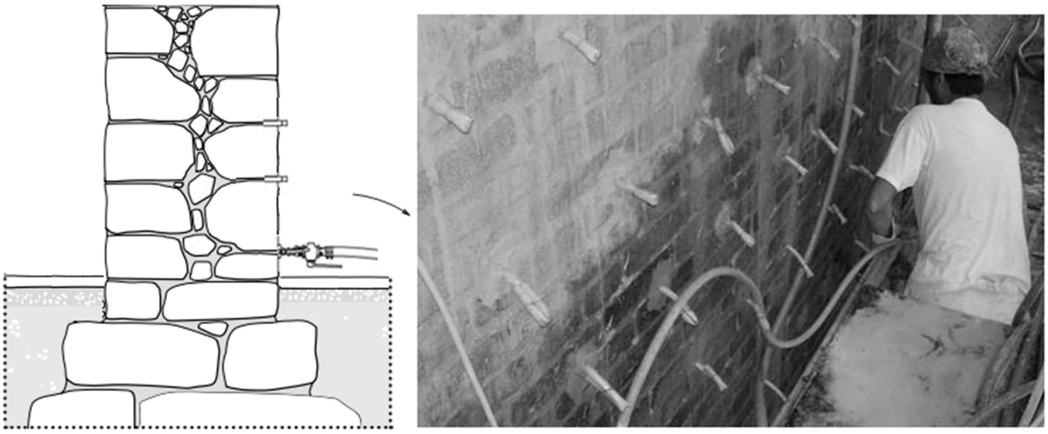


Figure 1. Detail of the grout injection on a stone masonry wall.

NHL-based grout is a suspension of particles in water and the NHL is the element that gives the grout its binder character. However, different elements, currently used by the cement and concrete industries, can be added to the grout, to either optimize its performance or lower the cost. In fact, it is the suspended particles that have an important contribution on the rheological behavior of the grout [20,21]. The particles will influence the flow properties and set a limit to void size that can be penetrated. Notwithstanding, apart from the penetration issues due to particle size, understanding and controlling the rheology of the grout is essential for a successful grouting intervention. The knowledge will, under the prevailing conditions, facilitate the choice of additive, admixtures, grouting pressure, and temperature. The present paper reviews the current knowledge concerning the measurements of the rheological properties of NHL-based grouts, with emphasis on a contribution of different factors, additives, and admixtures on the rheology of injection grouts.

2. Rheology of Natural Hydraulic Lime Grouts

Rheology plays an important role in injection grouts since it provides valuable data about the influence of composition, temperature, pressure, resting time, among others, on flowability of grouts. The rheological behavior of NHL-based grouts is a difficult task since it can be considered a complex system due to simultaneous interactions between the two phases and also between the particles themselves. Moreover, the fresh behavior is also influenced by the hydration of the NHL; despite considering that the hydration of lime during the dormant period is practically stationary, it will inevitably lead to changes in the rheological properties with time.

2.1. Yield Stress

The interactions between the particles in a suspension (like a grout) result in a yield stress value. The presence of yield stress means that under static conditions, the grout essentially acts as a solid and will continue acting as a solid until the stress reaches the shear force needed to overcome the internal bonding between the particles. This yield stress (also called static yield stress) can thus be regarded as the property that represents the transition between solid and liquid behavior [22,23]. This behavior can also be characterized by the flow curves, resulting from the relation between shear stress (τ) and shear rate ($\dot{\gamma}$) under simple steady shear; so the yield stress is equal to the intersection point on the stress axis, as shown in Figure 2.

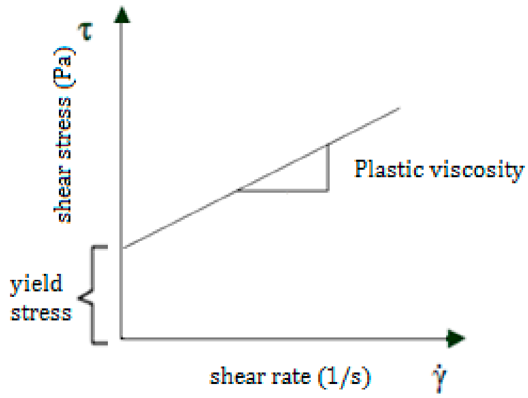


Figure 2. Example of a flow curve of a fluid with yield stress.

In addition to a yield stress, cementitious grout compositions display another peculiarity, which is the change of its properties during time, namely due to hydration. Therefore, from a practical point of view, the grout fluidity is not only a function of the instantaneous shear rate but also presents time-dependent behavior. Shaking or shearing the grouts causes a gradual breakdown of its microstructure, which is recovered when the grout is at rest. A reversible and time-dependent microstructure defines thixotropy that will be discussed below. Nevertheless, this behavior causes several challenges in defining the yield stress as a constant property since different measuring protocols, history of shear, and type of geometry lead to different yield stress results [24,25]. Thus, to solve these issues, two yield stress values, namely static and dynamic yield stress, were proposed [26,27]. The static yield stress has already been defined above, while the dynamic yield stress can be seen as the yield stress when the grout is subjected to shear and is in a fully broken down state. Rahman et al. [28] measured the yield stress of cement-based grout considering the effect of thixotropy and hydration. In the same work, it was shown that there exists a critical shear rate range, below which there is a transition from the dynamic to the static yield stress, which should be taken into account for grout design. It should be noted, however, that despite the importance of yield stress in cementitious suspensions design, no standard methods are yet available to determine the yield stress of grouts.

2.2. Thixotropy

Thixotropy is a gradual decrease of the viscosity under constant shear stress followed by a gradual recovery of structure when the stress is removed [29,30]. Thixotropy should not be confused with shear thinning. When a material is shear thinning it changes the microstructure instantly while in a thixotropic material the microstructure does change (by breaking down or building up) and such changes take time [29,30]. It can be said that thixotropy is due to the structure degradation resulting from rupturing flocs or linked particles when the grout is sheared. When the shearing stress is removed, the grout microstructure rebuilds and is eventually restored to its original condition [31,32]. According to Billberg [30] with today's knowledge of microstructural changes it is probably safe to say that shear thinning materials are also thixotropic since it always takes time, even limited, to create the re-grouping of the microstructural elements to result in shear thinning.

A quantitative measurement of thixotropy can be performed in several ways. The most apparent characteristic of a thixotropic system is the hysteresis loop, which is formed by the up-and down-curves of the flow curve [23,33]. If the grout is thixotropic, the resulting two curves (up and down curves) do not coincide, as shown in Figure 3. The degree of thixotropic behavior can be quantified by the area of the hysteresis loop, which indicates a breakdown of structure that does not reform immediately when the stress is removed or reduced.

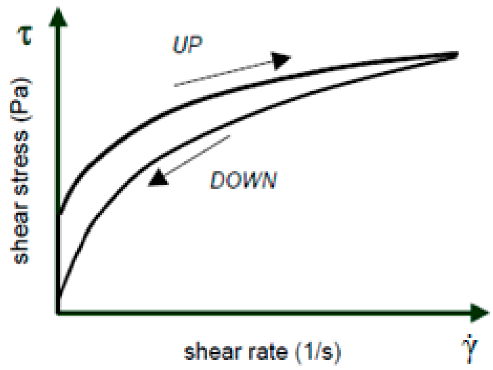


Figure 3. Illustration of thixotropic behavior.

2.3. Rheological Models

The injection grouts are often referred to as non-Newtonian, thixotropic, and in possession of a yield stress [14,34–36]. This non-Newtonian behavior can be attributed to mechanisms in which the shear stress orients the suspended binder particles in opposition to the randomizing effects of Brownian motion [14,37–39]. The rheological behavior of cementitious suspensions is often approximated by a rheological model, incorporating various rheological parameters. The typical model used for NHL grouts have to take into account the yield stress. The yield stress value will limit the penetration distance that the grout will reach at a certain injection pressure. A review of the literature shows that several mathematical models have been proposed for the behavior of the injection grouts. Some of the more widely used models include Bingham, Modified Bingham, Casson, Herschel Bulkley, and Power Law, as shown in Table 1.

Table 1. Rheological models used for describing the flow curve of injection grouts.

Model	Equation	Description	Parameters
Bingham	$\tau = \tau_0 + \eta_p \dot{\gamma}$	Yield and linear	τ_0 = yield stress, η_p = plastic viscosity
Modified Bingham	$\tau = \tau_0 + \eta_p \dot{\gamma} + c\dot{\gamma}^2$	Yield and nonlinear	τ_0 = yield stress, η_p = plastic viscosity, c = constant
Herschel-Bulkley	$\tau = \tau_0 + k\dot{\gamma}^n$	Shear thinning	τ_0 = yield stress, k = consistency, n = power law index
Power law	$\tau = k\dot{\gamma}^n$	Shear thinning	k = consistency; n = power law index
Casson	$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta . \dot{\gamma}}$	Linear between the square root of shear stress and the square root of the shear rate	τ_0 = yield stress, η = viscosity

The simplest model including a yield stress is the Bingham model which is a two parameter model widely used in the injection grouts. The grout behavior has been modeled with Bingham model by several authors [40–44]. However, for injection grouts that exhibit a pronounced shear thinning behavior, and according to several studies [14,20,45,46], the modified Bingham model or the Herchel–Bulkley leads to better fittings especially at very low shear rates. The Hershel–Bulkley model is an extension of the Bingham model to include shear rate dependence by replacing the plastic viscosity term (in the Bingham model) with the power law expression, where k is the consistency ($Pa.s^n$) and n is the flow behavior index (dimensionless) [47]. Non-linear relations between shear stress and shear rate can be described by the power law model. However, care should be taken in the use of this model outside the range of the data used to define it. For instance, the power law model fails at high shear rates, where the viscosity approaches a constant value. This weakness of the power law model can be rectified by the use of other models which can fit different parts of the flow curve.

The Casson model is a structure based model traditionally used to describe the flow of viscoelastic fluids [48]. This model has a more gradual transition from Newtonian to the yield region. Taking into account the testimonies of various authors [14,18,49,50] the geometry and morphology of the flow channels in the core of the masonry that is to be consolidated is very difficult to define, so the development of sophisticated rheological models may not be justified when most of the time the Bingham model is the model used because the cementitious suspensions in general follows this equation fairly well and the two parameters in the Bingham model, yielding stress and viscosity, can be determined. In this sense, it can be concluded that researchers have not agreed upon a rheological model which satisfactorily describes the flow of injection grouts. Many researchers [25,51,52] are in effect using the Bingham model due to its simplicity.

It should be mentioned, however, that there are some practical difficulties in using theses classical rheological models especially in computational simulations of viscoplastic materials, due to their intrinsic singularities [53]. All rheological models presented in Table 1 are discontinuous, which means that for flow field of viscoplastic suspensions it is often required to develop numerical techniques to track down yielded/unyielded regions in flow fields. In this sense, regularized versions of the original rheological models have been proposed and are often used for the simulations of viscoplastic flows, such as the Bingham–Papanastasiou model (equation 1) proposed by Papanastasiou [54].

$$\tau = \eta_p \dot{\gamma} + \tau_0 \left[1 - exp\left(-m.\dot{\gamma}\right)\right], \tag{1}$$

where m is a non-rheological parameter acting on yield stress term.

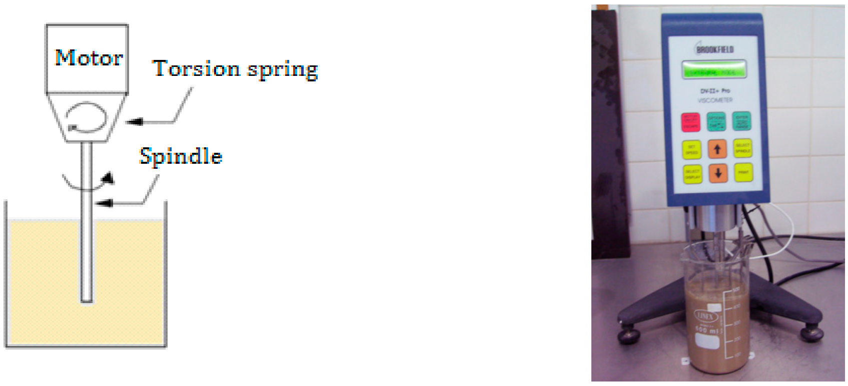
This regularized model rendered the original discontinuous Bingham viscoplastic model as a purely viscous one by introducing into a continuation parameter, which facilitates the solution process and is valid for all rates of deformation.

3. Rheological Measurements Apparatus

The rheological characterization of injection grouts can be challenging because of the need for suitable devices as well as measurement procedures and data analysis appropriate to each grout composition [27,55]. Below, a summary is given of each general method along with descriptions of common measurement devices and geometries.

3.1. Viscometer

The viscometers measure the grout apparent viscosity as a function of rotation speeds by driving a measurement tool (called spindle), immersed in the test sample (Figure 4a). According to Hackley and Ferraris [56] the viscous drag of the sample against the spindle causes the spring to deflect, and this deflection is correlated with torque. The calculated shear rate depends on the rotation speed, the tool geometry and the size and shape of the sample container. Furthermore, the conversion factors are needed to calculate shear stress vs. shear rate curve and are typically pre-calibrated for specific tool and container geometries [57,58]. Despite some limitations that are often pointed to viscometers (for example related to the range of shear rates, accuracy in measurements and inability to perform some types of measurements) these devices can be used to measure the typical rheological properties of injection grouts. Previous studies [14,59] where the effect of mixing procedures on some fresh properties of hydraulic grout, including the rheological ones, were conducted using a Brookfield viscometer (Figure 4b).

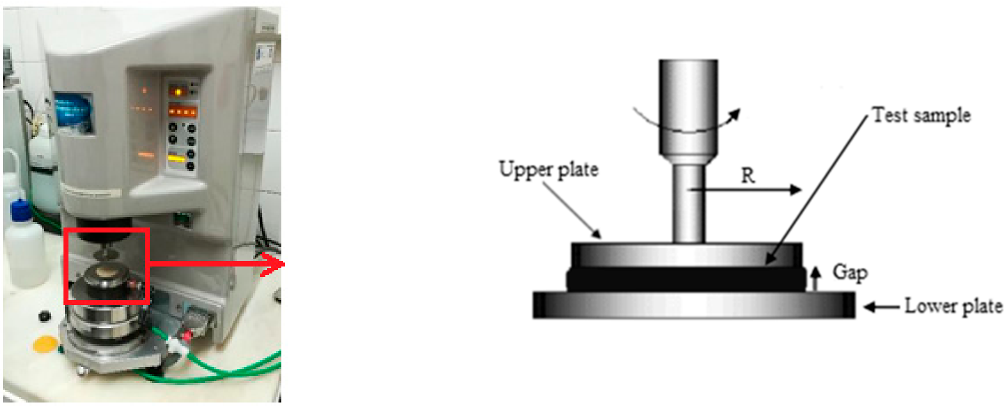


(**a**) (**b**)

Figure 4. Viscometer: (**a**) Schematic diagram of a Brookfield-type viscometer; (**b**) Brookfield viscometer LV DV-II + PRO with spindle immersed in the sample.

3.2. Rotational Rheometer

These kind of devices (Figure 5a) are of higher precision when compared with viscometers and are some of the most commonly used devices for measuring the rheological properties of cementitious pastes and grouts. The basic rotational system consists of four parts: (i) a measurement tool with a well-defined geometry, (ii) a device to apply a constant torque or rotation speed to the tool over a wide range of shear stress or shear rate values, (iii) a device to determine the stress or shear rate response and (iv) the temperature unit control for the test sample and tool. Depending on the design specifications, rheometers may also include built-in corrections or compensations for inertia and temperature fluctuations during measurements. The measurement of the forces and torques acting on the geometry yields the stresses, and the ratio of shear stress to the shear rate (which is related with the rotation speed) gives the apparent viscosity.



(**a**) (**b**)

Figure 5. Rheometer: (**a**) Rotational rheometer; (**b**) Illustration of parallel plates geometry.

Most rheometers are based on the relative rotation about a common axis of three alternative tool geometries: concentric cylinder, cone and plate, or parallel plates. In concentric cylinder geometry, either the inner, outer, or both cylinders may rotate, depending on instrument design. The test material is maintained in the annulus between the cylinder surfaces. The large surface area of this geometry improves sensitivity when measuring samples with low viscosity. Furthermore, it allows good thermal control and when this geometry is used in conjunction with solvent traps, the sample evaporation can be minimized.

On the other hand, a concentric cylinder generally requires greater sample volumes than the others geometries. The cone and plate geometry consists of an inverted cone in near contact with a lower plate. The geometry advantages are that only a small sample is required, the shear rate is constant all over the gap, and the shear fracture is minimized because of the small free surface. The parallel plate geometry (see Figure 5b) can be considered a simplified version of the cone and plate, having an angle of 0°. The test sample is constrained in the narrow gap between the two surfaces. An advantage of the parallel-disk geometry is that the gap height can easily be changed, even without reloading the sample. One disadvantage when compared to the cone and plate geometry is the fact that the shear rate varies with the radius of the plate. However, the parallel plate geometry is more suitable than the cone and plate for large particles, since the gap is fixed in the cone and plate and is very small (the order of tens of microns in the top of the truncated cone) [60]. Measuring grouts with large particle sizes can then be problematic because of the limited small gap size of the cone and plate geometry.

3.3. Ultrasound Velocity Profiling Method

The in-line rheological instruments appear as a response to the ever-increasing demand for the development of rheometers capable of dealing with complex fluids. The in-line measurement techniques that combine the ultrasound velocity profiling (UVP) method with the pressure difference (PD) measurements (also known as UVP+PD) belongs to the non-invasive rheological measurement techniques, which has been investigated and applied on the characterization of cement grouts [43,61,62].

The UVP+PD measurement method is based on the emission of pulsed ultrasound bursts and echo reception. This method determines the relative time lags of the echoes received between successive emitted pulses [63,64]. The time lags are related to the speed of the moving fluid. The UVP+PD method contrasts with conventional off-line rheometers, in which a data fitting is required to determine the rheological behavior and the velocity profiles. One of the greatest advantages of the UVP+PD method is the determination of the true rheological properties using the non-model approach [62]. This means that common unreliable determination of rheological properties due to the influence on the microstructure of the measuring geometry can be avoided with this non-invasive measurement method. It was evidenced by Håkansson and Rahman [65] that the UVP+PD technique can also be used for continuous monitoring of grout concentrations, which will confirm the water/cement ratio of the grout and thereby act as a quality control. The potential of UVP+PD as rheometric method for measuring the rheological properties of cement-based grouts has been studied and demonstrated in several works carried out at the Royal Institute of Technology in Sweden [43,62,63,65].

3.4. Marsh Cone and Slump Test

The Marsh cone is a simple instrument (see Figure 6) that initially started to be used in the oil industry to measure the flow performance of drill muds in the field. The instrument is currently used in the construction industry to empirically measure fluidity of consolidation grouts or pastes for preplaced-aggregate concrete as specified in the standard ASTM C939:02 [66]. Based on this standard from the time it takes a certain volume to flow out of the cone, the flow properties can be estimated. In order to improve the physical significance of the Marsh cone test some authors suggest that the grout fluidity (especially in very fluid grouts) should be evaluated using a modified Marsh cone having an outlet diameter of 5 mm [17,50]. However, the only property that can be measured with the Marsh cone is the fluidity, which is an empirical measurement since the physical parameter "viscosity" is not in fact determined. In this sense, mathematical models were proposed by Baltazar & Henriques [67] that allow predicting the rheological properties of the grout just by performing the Marsh cone test on field. The proposed models can be very useful to streamline the grout design methodology since these models are able to calculate a physical parameter (e.g., viscosity) instead of an empirical one (e.g., fluidity).

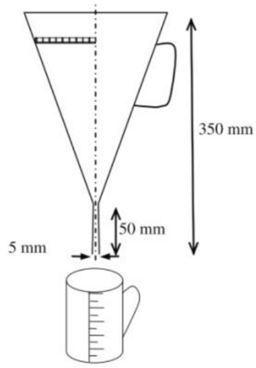
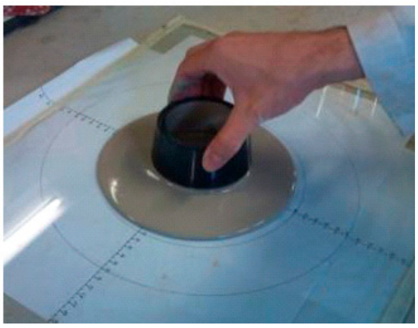


Figure 6. Illustration of the Marsh cone apparatus.

Despite the Marsh cone has been extensively used to make rapid measurements, its accuracy still raises some controversy. However, the growing development of computational fluid dynamics, has prompted several attempts of numerical and analytical simulation of Marsh cone flows [25,42,68,69]. Nowadays, it is already possible to predict the flow of some fluids through the Marsh cone as an alternative to the experiments. Notwithstanding, according to Sadrizadeh et al. [70] limited investigations with numerical and analytical calculations have been done, thus further investigation is needed to develop an easy, fast, and reliable fluid viscosity analysis in terms of numerical and analytical calculations of the Marsh cone.

The slump test is another common method to quantify the fluidity of cementitious mixtures. This measurement technique is used extensively for the evaluation of self compacting concrete due to the low yield stress of such materials. The modus operandi is the following: the cone is laid on a horizontal glass surface. After the careful placing of the grout into the cone, to avoid bubble formation and grout overflow, the cone is vertically lifted (Figure 7a). After lifting the cone, the grout flows by gravity and the slump occurs. The grout will flow while the local stress is higher than the material yield stress. The spread diameter is measured when the flow stops. Each spread diameter value is the mean of two measurements along two perpendicular directions (Figure 7b). The spread at stoppage is directly linked to the yield value, which may even be calculated. In fact, the relation between yield value and slump has been studied by Hu [71] or Christensen [72]. More recently Roussel et al. [73] proposed another approach, the mini-cone test, which is very suitable for yield stress measurements of cement pastes and grouts. From a practical point of view, it is desirable to perform "in site" measurements, whereby the significant rheological properties are measured during the grouting operations. In this sense, the research work should be guided in this direction.



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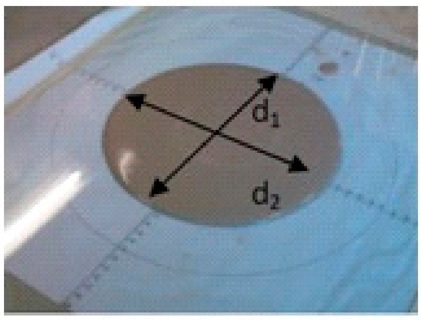

(**b**)

Figure 7. Slump test, (**a**) Lift the cone; (**b**) Spread sample at stoppage.

3.5. Important Features Affecting the Rheological Measurements of Grouts

During rheological measurements many disturbing effects may arise. They often reflect the changes that are happening in the microstructure of the sample. For instance, particle suspension sedimentation and migration of particles can significantly alter the stress distribution and thus the measured torque [60]. Other disturbing effects are experimental problems pertaining to the geometry type. For instance, when using a smooth metallic shearing surface, wall slip can occur (the called slippage).

A substantial source of problems may arise due to the presence of a wall, since a wall modifies the particle arrangement. This phenomenon called particle depletion involves a decrease in particle concentration close to the wall, which leads to the development of a lubricated fluid layer close to the solid boundary and to the slipping of the bulk. This is consequence of several factors, such as hydrodynamic, viscoelastic, chemical and gravitacional forces acting on the disperse phase [74]. Depending on the grout properties, there may be interactions between the metallic surface of the geometry and the constituents of the suspension. This is particularly problematic for particle suspensions like injection grouts; the presence of a solid boundary may alter the local structure within the liquid, thus producing local viscosity, and may lead to an under-evaluation of apparent viscosity and an improper evaluation of yield stress, as demonstrated in [75].

Other important factors that influence the rheological measurement is the lack of reaching a state of equilibrium of shear stress at each shear rate (steady state). During measurements this is one of the main problems in obtaining precise data on grout parameters like the yield stress and plastic viscosity. This can be a problem when a linear change in rate of shear is applied. This would not be a problem when testing Newtonian liquid, but when testing a very thixotropic and non-Newtonian suspension like NHL-grouts, it can influence the measurement significantly [76,77].

4. Intrinsic and Extrinsic Factors That Influence the Grouts' Rheology

NHL-based grouts are complex suspensions and there are several intrinsic and extrinsic factors that can influence the rheological behavior of injection grouts, such as: chemical admixtures, mineral additions, particle size distribution, particles shape, volume fraction of particles, temperature, pressure, etc. Different factors and materials that have been reported in several research works, which should be taken into account in the grout design, are briefly outlined in this review in order to highlight their contribution on the rheology of the injection grouts.

4.1. High Range Water Reducer

High range water reducers (HRWRs) like superplasticizers have a significant influence on the rheology of the grout, since they are capable of reducing the water contents by 30% or, for the same water content, will improve the fluidity of the grout [78]. The most available HRWR is based upon the polycarboxylates, which are high molecular weight polymers. The HRWR will disperse the binder agglomerates into primary particles and give them a negatively charged surface leading to repulsion between the particles, which causes a reduction of yield stress and plastic viscosity values [20,21,35]. Different works have shown that the HRWRs effect is only pronounced to dosages around 1% of the binder weight and their efficiency is also a function of their own chemical composition [18,30].

Nevertheless, other authors [79] suggested that some HRWR, when used at higher dosages, have the reverse effect. A higher dosage worsens the fluidity and consequently the injecatbility of the mixture [79–81]. Furthermore, it must be highlighted that the HRWR effect is dependent on the moment at which the HRWR is added during the mixing stage and its action is limited (ranging from 30–60 min). Baltazar et al. [59] concluded that adding the HRWR 10 min after the beginning of the mixing improves the grout fluidity. Other studies [51,82,83] for cement-based systems corroborate this result, showing that the delay in the addition of HRWR improves the effectiveness of the particles dispersing, when compared to an addition without delay. As the delay addition leads to a lower amount of HRWR being intercalated in diverse hydration products [84], a higher amount of HRWR will be available for an effective dispersion of binder particles.

4.2. Water

Water is one of the main elements that assures fluidity of the grout and enables the hydration of the NHL components. The determination of proper water dosage, i.e., the water/solids ratio (w/s), is an important aspect. The w/s ratio has a similar behavior of the HRWR since high water content gives improved flow and injectability [85,86]. However, simple addition of water to make the grout more fluid is an inappropriate decision because a higher w/s ratio decreases the mechanical properties of the hardened grout and will increase the shrinkage deformation as well as the free water amount that might cause instability of the grout.

Grouts for consolidation of old masonry buildings have a w/s ratio in the range of 0.5-1.5 [4], which is dependent on the presence of admixtures (like HRWR) and/or additives. In the same field, Bras [14] studied the optimization of hydraulic lime grout with a w/b ratio in the range 0.6–0.8. In the case of permeation grouting, the typical water/cement ratios are 0.6 to 1.0 [61,62].

4.3. Silica Fume

Silica fume is an ultrafine powder that works as pozzolan and is a by-product of the silicon metal production using electric arc furnaces. The addition of silica fume will contribute to the formation of additional C–S–H (calcium silicate hydrate), and it is expected that the small and spherical silica fume particles will fill the voids between binder particles and produce a ball-bearing effect [87–89].

On the other hand, the addition of silica fume leads to some difficulties regarding the workability of the cementitious materials, requiring the presence of HRWR to minimize these problems. According to Kadri et al. [90], the influence of silica fume on workability is a complex issue since the silica fume increases the volume concentration of the solid phase and also the specific surface; besides, it should be mentioned that silica fume, HRWR and binder constituents will interact with each other as a function of its concentrations.

This complex contribution was confirmed in previous studies, for instance Baltazar et al. [21] concluded that silica fume has an adverse effect on the rheological properties of grouts; the yield stress increases exponentially with the increasing of the content of silica fume and the use of HRWR is indispensable. A similar behavior was also observed on the results of Park et al. [91] that reported that flow resistance of cementitious-based suspensions increases with increasing silica fume dosage. Moreover, Vikan et al. [92] and Zhang & Han [93] concluded that the effect of silica fume on the rheology of cementitious materials depends on the dispersion ability of the HRWR used. Despite some rheological issues, the use of silica fume will enhance the stability which leads to less risk for grout settlement [14,27].

Knowing that a reduced workability is associated with a high water demand when silica fume is used, a recent research work [94] put forward a pretreatment with a polydimethylsiloxane solution for ordinary silica fume in order to obtain a silica fume with hydrophobic behavior to be used in injection grouts. Therefore, this study found that the majority of fluidity and workability problems of injection grouts may be easily overcome with hydrophobic silica fume. The idea can be explained by the combined effect of hydrophobicity and the spherical shape of the silica fume particles, which cause a pure ball-bearing action between the bigger and elongated NHL particles.

Different dosages of silica fume (0, 10, 20, and 30% as replacement of NHL in weight percentage) were tested, revealing that the rheological properties of grouts containing hydrophobic silica fume are significantly improved [94]. Silica fume has a strong impact on the shear thinning behavior of NHL grouts and the presence of hydrophobic silica fume leads to a more Newtonian behavior. The grouts containing 10 wt% of hydrophobic silica fume showed the best rheological performance. Additionally, hydrophobic silica fume has made the hardened grout hydrophobic as well, which significantly contributed to a higher durability of grouts. Therefore, this result should be considered in a consolidation intervention, whenever problems of rising dampness must be also solved. This way, both problems can be overcome with a lower number of physical interventions on the building.

4.4. Fly Ash

Fly ash is a by-product of coal burning from thermal electric power plants and is widely used in the concrete manufacture. It is a very fine powder that can react with calcium hydroxide ($Ca(OH)_2$) or in other words it has a pozzolanic reactivity and consequently it must be used with hydraulic binders such as cement and hydraulic lime, which produce $Ca(OH)_2$. Fly ashes have been used in cementitious-based systems since they improve the durability [95] and contribute to mechanical strength development by both the pozzolanic and filler effect [96,97].

Besides that, the replacement of a certain amount of binder by fly ash will reduce the costs and the environmental impacts [98]. Mirza et al. [99] reported the improvement of stability and the reduction of drying shrinkage in cementitious grouts proportioned by fly ash. A reduced shrinkage of injection grouts is desirable since it interfaces between the grout and the original materials of the masonry.

Sonebi [100] demonstrated that the small size and spherical shape of fly ash particles increase the grout density and reduces the yield stress values due to the ball bearing effect between the binder particles, which reduces the friction forces and consequently reduces the shear stress needed to start the flow. Similar trends of higher fluidity in the presence of fly ash were observed by Baltazar et al. [34].

4.5. Ambient Temperature

In general, a decrease in temperature leads to an increase in viscosity and vice versa, approximately following the Arrhenius relationship [22]. This is also true for hydraulic grouts and seems to be equally true for the yield stress. Bras [14], Baltazar et al. [20] and Jorne et al. [35] have focused on the effect of temperature (ranging from 5 °C to 40 °C) on the rheological properties of hydraulic grouts. From the results presented by these authors, it is clear that the rheological behavior of the hydraulic grout is a strong function of temperature. Yield stress is slightly influenced by temperatures between 5 °C and 20 °C and tends to a higher value with temperature increase. Plastic viscosity decreases between 5 °C and 20 °C but shows an incremental increase between 20 °C and 40 °C, which means a workability loss. The decrease of viscosity with the increase of temperature can be attributed to an increase in the Brownian motion of the particles, which partially weakens the interactions between agglomerates and keeps the particles away from each other. Based on the conclusion of these authors, the ambient temperature of 20 °C is the one that leads to the best grout rheological behavior and consequently the most suitable for performing the masonry injection [14,20,35].

As a consequence of the temperature dependence it is obvious that the rheological properties must be measured at the temperature that will be prevailing in the application site. Moreover, it should be noted that it is not only the ambient temperature that influences the rheology but also the temperature rise due to hydration reactions and shearing induced in high-shear mixers.

4.6. Nano-Silica

There have been progressive developments in the field of nanotechnology, which enabled the manufacture of nanoscale materials (e.g., nanosilica, carbon nanotubes, etc.) that can be incorporated in a cementitious systems [101]. With more studies on the behavior of cement-based systems incorporating nanoscale particles, a better understanding of such composites can be gained and contribute to producing cementitious materials with improved overall performance. Nanoparticles of silica can fill the spaces between/within layers of C–S–H, acting as a nanofiller.

Furthermore, the pozzolanic reaction of nanosilica with calcium hydroxide produces secondary C–S–H, resulting in a higher densification of the matrix, which improves the strength and durability of the material [102]. Other studies [103–105] also reported that the inclusion of nanosilica modifies fresh and hardened properties of cementitious materials compared to conventional mineral additions (at microscale). For example, relative to silica fume, nanosilica shortened the setting time of hydraulic binder mixture and reduced bleeding water and segregation in a more meaningful way. Baltazar et al. [106] investigated the effect of nanosilica dosages from 0 to 3.5 wt%, by mass of binder, on NHL-based grouts prepared with w/s of 0.5 and a HRWR dosage ranging from 0.8 to 1.6 wt%. In the same study they reported that the yield stress increased considerably when the nanosilica dosage increased; however, the effect on plastic viscosity was less pronounced. It was also observed that higher nanosilica dosage (>1.5 wt%) significantly affects the rheological performance of grouts, which compromises the expected injection capacity; thus, it is recommended that the use of nanosilica is always accompanied by the incorporation of a superplasticizer. Senff et al. [103] also concluded that the fluidity of cement pastes and mortars is reduced when incorporating high nanosilica dosages.

Moreover, it is believed that the reduced particle size of nanosilica (even at lower dosages) can contribute to overcome most of the grout's penetrability problems (like the so-called blockage phenomenon). It is known that grout's penetrability problems are due to the grain size characteristics of the solid phase of the grout [4,17,50]. Unfortunately, the uses of these materials to get a specific grading of the solid phase is difficult to implement and supervise on site, which in addition to higher difficulties in the mixing procedure, are real setbacks to the use of these materials. To make these grouts injectable a specific mixing procedure is essential and the use of the ultrasonic mixing procedure is crucial. An ultrasonic mixing time of around ten min (the first five with only the nanoparticles and the other five with NHL included) was set ideal to deflocculate the grain elements and obtain the appropriate fluidity of the mixtures [106].

4.7. Injection Pressure and Resting Time

A proper choice of the injection pressure is of great importance in grouting operations since it is the injection pressure that guarantees the sufficient shear rates within the injection pipes in order to cause a reduction of the grout viscosity. Nevertheless, very high pressure should not be adopted to avoid an excessive outward pressure loading, which could endanger the stability of the structure or cause fewer attached stones to blow from the surface. Thus, the pressure must be limited to a few bars in order to avoid any damage with the weakened masonry. It can be found in the literature [5,107,108] that grout injection for old masonry consolidation should be made with a pressure in the range of 0.2–1.5 bar.

The results presented by Baltazar et al. [20] clearly show the influence of injection pressure on the rheological properties of grouts, using a rotational rheometer equipped with a high pressure cell. The analysis of these results reveals that an increase of the yield stress as well as of the viscosity occurs with the increase of pressure. Moreover, this study also shows that almost no difference exists between the rheological properties of the grout at pressure of 0.5 bar (above the atmospheric pressure) and the one at atmospheric pressure. The biggest difference in rheological parameters was observed for pressures above 0.5 bar. Thus, considering these conclusions and the fact that the injection pressure should be limited to a few bars to avoid the masonry disruption, the injection pressure around 0.5 bar is recommended for the grouting operation of stone masonry [20,109]. These results emphasize how harmful it is to increase the injection pressure to overcome some injectability difficulties, which is caused by several phenomena such as grout blockage. It is worth highlight that the phenomenon behind the blocking is mainly due to particles or agglomerates that get stuck at constrictions [110,111]. Either the solid particle size is too big to allow them to go through the pores or there is segregation. The binder particles deposit themselves at the opening of the pores, producing a "cork" that hinders the injection. Moreover, an experimental program presented by Binda [112] showed that the injection pressure of grout (although it is based on another binder than NHL) should not be higher than 0.6 bar, to optimize the diffusion and penetration of the grout.

As previously mentioned, NHL-based grouts can be considered as thixotropic materials, since they show a shear thinning and time dependent behavior. During shearing of hydraulic lime grout, the weak interparticle bonds are broken by the mechanical stress and the network among them breaks down into separate agglomerates (structural breakdown). If the grout is at rest, the particles will start to flocculate into agglomerates again (structural build-up), leading to a loss of workability. In earlier investigations [14,20] NHL-based grouts were sheared using a rotational rheometer and parallel-plates at a constant shear rate of 1 s^{-1} after different resting times and the initial shear stress was plotted as a function of resting time. The initial shear stress can illustrate the intensity of interactions between particles agglomerates in the grout before shearing takes place (solid-like particle structure). Furthermore, the rate of increase of the initial shear stress, also known as the flocculation rate [14], was used in thixotropic evaluation and it is a measure of the forces acting between particles, namely the electrostatic forces and Van der Waals attractive forces [60]. Alongside the results of different works [14,20,35], it is clear that the initial shear stress rate increases linearly with resting time, which means more flocculation, which leads to workability loss according to the PFI-theory [36]. Moreover, the grout flocculation rate is of particularly relevance during a grouting operation, since it may reduce the injectability up to 59% [35]. Taking these statements into account it is recommended not to exceed 10 min and 60 min of resting time (before injection) for grouts without HRWR and with HRWR, respectively.

Nevertheless, it is important to note that the grout flocculation can be a way to solve some issues after injection. For example, when grouts are at rest in the masonry core, gravity can promote sedimentation of grout particles at rest. Thus, a higher flocculation rate can be useful since it will increase the interparticles bonds (structural build-up) which can be sufficient to prevent the particles from settling [113]. This may seem somewhat contradictory considering what has been said previously but from a practical point of view it is desirable to have grout with low flocculation rate before its injection and with a high flocculation rate after its application. Some research works [25,113] were found on this subject but in the field of self compacting concrete. Summarizing, care should be taken during the whole grouting operation, namely to avoid stops during injection and to restrict the resting time between the mixing and the injection in order to prevent flocculation, which causes a considerable reduction on grout injectability and, consequently, compromises the efficiency of the consolidation operation.

5. Conclusions

Despite the widespread use of NHL-based grouts for structural consolidation and repair of historic masonry structures, research works on the subject are still insufficient. The lack of information and fundamental understanding of the mechanics underlying the effect of some constituents and factors emphasizes the importance of continuing to study this subject in order to contribute to the optimization of the grout injection technique and to avoid new damage in historic masonry as a consequence of bad practices. In this sense, some important aspects need further study, for example: (i) to study how the slippage phenomenon, which is frequently observed in the rheological measurements, influences the flow and penetration length of the grout in practice; (ii) since significant properties are continuously changing during the grouting operation, it would also be interesting and desirable to perform "in-line" measurements (i.e., under real injection conditions) in order to provide a fuller assessment of the rheological performance of grouts. Nevertheless, and considering the review made, the following aspects stand out:

- NHL-based injection grouts are often referred to as non-Newtonian, thixotropic, and possess a yield stress. This non-Newtonian behavior can be attributed to mechanisms in which the shear stress orients the suspended binder particles in opposition to the randomizing effects of the Brownian motion.
- A non linear relationship between shear stress and shear rate implies that a shear thinning relationship like a Herschel–Bulkley model should be adequate. However, in most grouting applications a simple model like the Bingham one is used as it contains the fundamental properties, yield stress, and plastic viscosity.
- Due to the complex nature of hydraulic binders, the rheological characterization of NHL-based grouts is challenging. Therefore, it is important that standard protocols are developed in order to allow the results comparison. Brookfield viscometers or rotational rheometers have been successfully used to characterize the rheology of the injection grouts. However, several details

should be taken into account, such as the type of geometry and other phenomena that may affect the accuracy of the measurements, such as wall slip and segregation.

- The incorporation of HRWR will cause a reduction of yield stress and viscosity values. Several studies have shown that their effect is only pronounced to an amount around 1% of the binder weight. Nevertheless, a higher value worsens the fluidity and consequently the injectability of the mixture. Furthermore, it must be highlighted that the HRWR effect is dependent on the moment that the HRWR is added to during the mixing stage.
- High water content improves the flow and injectability of the grouts. However, a simple addition of water to make the grout more fluid is inappropriate. Grouts for consolidation of old masonry buildings should have a w/s ratio of around 0.5–1.5, the dosage of water depending on the presence of HRWR and ultra fine materials such as silica fume.
- The use of fly ash additions, besides improving the mechanical properties, has a significant influence on the rheology of the grouts. For instance, the small size and spherical shape of fly ash particles increases the grout density and reduces the yield stress values due to the ball bearing effect, which reduces the friction forces and consequently reduces the shear stress needed to start the flow.
- The addition of silica fume leads to some difficulties regarding the rheological properties of grouts and the use of HRWR is indispensable. However, a pretreatment with a polydimethylsiloxane applied on ordinary silica fume was a proposed solution to mitigate the rheological disadvantages of this material.
- The reduced particle size of nanosilica (even at lower dosages) may contribute to overcome most of grout's penetrability problems (like the so-called blockage phenomenon). Nevertheless, the uses of these materials require a different mixing procedure.
- An ambient temperature of 20 °C is the one that leads to the best grout rheological behavior and consequently the most suitable for performing the masonry injection. The injection pressure around 0.5 bar is recommended for grouting operation. Moreover, a low resting time (less 10 min) is desired, especially in the cases of grouts with low HRWR amount.

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