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Complexities observed during the development of a rheological testing procedure for small cement paste samples

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COMPLEXITIES OBSERVED DURING THE DEVELOPMENT OF A RHEOLOGICAL TESTING PROCEDURE FOR SMALL CEMENT PASTE SAMPLES

by

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PUBLICATION DISSERTATION OPTION

This dissertation consists of the following four articles, formatted in the style used by the Missouri University of Science and Technology:

Paper I, found on pages 30–55 is a manuscript entitled “How do different testing procedures affect the rheological properties of cement paste?” and has been submitted to Cement and Concrete Research Journal.

Paper II, found on pages 56–80, is a manuscript entitled “Resting time effect on the rheological behavior of cement paste in the presence of superplasticizer” and is intended for submission to Cement and Concrete Research Journal

Paper III, found on pages 81–94, entitled “Challenges in Rheological Characterization of Cement Pastes Using a Parallel-Plates Geometry” has been published in the proceedings of Rheology and Processing of Construction Materials (pp. 228-236). Springer, Cham.

Paper IV, found on pages 95-116, is a manuscript entitled “Effect of sedimentation on the rheological properties of cement paste” and is intended for submission to Materials and Structures Journal.

ABSTRACT

Rheology has been widely used to describe the flow properties of fresh cement-based suspensions. The use of a rheometer to characterize these properties is not a straightforward task due to the dependency to different preparation conditions, mixing processes, testing procedures and measuring instruments employed. In addition, shear and time dependency of the material which undergoes chemical and physical particle bonding, caused by hydration of cement and flocculation. Nevertheless, the characterization and understanding of the rheological behavior of cement-based materials have become essential with the recent introduction of novel applications like digital construction in the field of civil engineering, among others. Therefore, to be able to suitably adapt such properties, to optimize and to ensure consistent performance, there is a need to accurately measure the properties and to obtain repeatable and consistent results. This research work shows how changes in the testing procedure, rheometer geometry and resting time in between measurements impact the rheological properties of cement pastes. The results indicate that the time-evolution of the rheological properties is strongly dependent on the employed procedure, and the effect is attributed to shear-enhanced hydration. Also, the resting time enhances the increase in differential viscosity and is dependent on the admixture's workability retention, as small or significant variations in the rheological properties are observed. The proper understanding of the advantages and disadvantages as well as the limitations of each geometry and procedure should be taken into account to avoid issues such as wall slip, sample spill, dryness, particles sedimentation, non-uniform shear rate applied, etc. that can be prevented.

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1. INTRODUCTION

1.1. BACKGROUND

Cement-based materials are characterized as complex suspensions with properties that are shear and time dependent due to chemical and physical particle bonding, related to the hydration of cement and flocculation [1-4]. The effect of flocculation, governed by attraction and dispersion, has been studied on cement-based materials, although many research questions still remain. The effect of hydration and early hydration product formation on rheology, and the effect of shear on breaking of hydration bonds is less known. The goal of this project is to clarify the role of early hydration of cement on the evolution of rheological properties with time, in presence of dispersing admixtures, to eludiate the mechanisms influencing the rheological properties with time.

Several researchers have studied the rheological behavior of cement-based materials, but often, results obtained are dependent on different preparation conditions, mixing processes, testing procedures and measuring instruments employed [5-8]. Although there have been several attempts to provide guidelines to ensure a proper characterization of the rheological properties, there is still not a standardized procedure. Therefore, many errors or inaccuracies may occur during the acquisition of the data and erroneous interpretation leading to incorrect conclusions. A first part of this study was to select the adequate measuring system for the sample, as well as establish a measurement procedure which could be employed to investigate the time, shear and temperature dependency of the rheological properties.

1.2. OBJECTIVES

The followings are the general and specific objectives of this research project:

1.2.1. General Objective.

The main purpose of this research work is to develop a testing procedure which can evaluate the rheological properties of a small sample of paste over an extended period of time. Therefore, it is the goal to understand and evaluate how different measuring geometries and testing parameters affect the rheological behavior of cement paste in the presence of dispersing admixtures at early age.

1.2.2. Specific Objectives.

In order to accomplish the main objective of this research project, the following objectives were proposed:

- To develop a testing procedure suitable for the material and evaluate the rheological properties examining different measuring geometries available.
- To identify and eliminate any artifacts found in previous task.
- To evaluate the effect of different testing procedures varying parameters such as: applied shear rate, time and temperature on the rheological properties of cement paste.

1.3. RESEARCH SIGNIFICANCE

The characterization and understanding of the rheological properties of cement-based materials have become essential with the recent introduction of novel applications like digital construction in the field of civil engineering. Therefore, to be able to suitably adapt such properties, there is a need to accurately measure the properties, to obtain repeatable and consistent results. To study the rheological properties of cement-based materials, different geometries are available, such as vane, parallel-plates, and coaxial cylinders. Due to its simplicity, and other factors such as: the small sample volume required, surface roughness and the variable gap that can simulate the distance between the aggregates when testing, parallel plates geometry is a common tool to use. However, there are no specific guidelines on how to select the appropriate geometry for the material that will be tested. Proper understanding of the advantages and disadvantages as well as the limitations of each geometry should be considered. Previous studies have shown evidence on how the rheological properties are significantly influenced by the variations in geometry of the test accessory, gap size and friction characteristics of the shearing surfaces as well as the squeezing velocity during gap positioning [9,10]. During the evaluation of yield stress and viscosity, sedimentation of cement particles may occur and affect the properties of the measured paste. It has been well documented that concrete and mortar may suffer stability problems (i.e. the ability of the mixture to maintain homogeneity). At the scale of cement paste, this phenomenon can still arise and depends highly on the viscosity of the medium and the density difference between cement and water. The settling of the cement particles is a consolidation process that displaces water through a dense system of cement particles resulting in bleeding. Therefore, in order to prevent gravity-induced and shear-induced sedimentation, the sample should be evaluated depending of application and the information is needed to be collected as there is not a universal testing procedure.

Several researchers have studied the rheological behavior of cement-based materials, but often, results obtained are dependent on different preparation conditions, testing procedures and measuring instruments employed [11-13,14]. The applied shear rate, the age and resting time of the sample have a strong influence on the amount of physical and chemical bonds that can be broken during the test. Consequently, rheological properties that may not resemble the rheological behavior observed during a given application may be obtained.

1.4. OUTLINE OF THE DISSERTATION

This study was divided into three tasks: (1) the development of a rheological testing procedure examining different measuring geometries, (2) elimination of artifacts during testing (3) evaluation of the proposed testing procedure on cement paste. Task 1 of the project is published in a conference proccedings. Results from Task 2 and 3 are submitted in journal publications. The dissertation is divided into four sections: introduction, literature review, results and discussion (as published), conclusions and recommendations.

INTRODUCTION: In this section is presented a brief introduction on the relevant topics and the justification as well as the objectives of this research project.

LITERATURE REVIEW: A comprehensive literature review is presented on early hydration of cement, basic concepts of rheology of cement-based materials and specific topics of interests towards the results and discussions.

RESULTS AND DISCUSSION: This section includes the content of four technical papers on the challenges in rheological characterization of cement pastes using a parallel-plates geometry. The effect of different testing procedures and resting time on the rheological behavior in the presence of superplasticizer of cement paste have been evaluated. In addition, the influence of sedimentation in on the rheological properties of cement paste has been investigated.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS: In this section is presented the summary and relevant findings of all the technical papers, as well as recommendations for future research.

1.5. LIST OF PUBLICATION/SUBMISSIONS

Peer-reviewed Conference Articles

1. Ley-Hernández, A. M., & Feys, D. (2019). "Challenges in Rheological Characterization of Cement Pastes Using a Parallel-Plates Geometry". In *Rheology and Processing of Construction Materials* (pp. 228-236). Springer, Cham.

Peer-reviewed Journal Articles

2. Ley-Hernández, A. M., Feys, D., & Kumar, A. (2020). "How do different testing procedures affect the rheological properties of cement paste?", Submitted to Cement and Concrete Research.
3. Ley-Hernández, A. M., & Feys, D., (2020). "Resting time effect on the rheological behavior of cement paste in the presence of superplasticizer", Submitted to Construction and Building Materials.
4. Ley-Hernández, A. M., & Feys, D., (2020). "Effect of sedimentation on the rheological properties of cement paste", Submitted to Materials and Structures.

Conference Proceedings

1. Ley-Hernández, A. M., Cook, R., Feys, D., & Kumar, A. (2019)," Effect of different testing procedures on the rheological properties of cement paste*", RheoCon2 Conference and SCC9 Symposium* in September 2019 in Dresden, Germany.
2. Ley-Hernández, A. M., & Feys, D., (2019). "Challenges encountered in rheological characterization of cement paste*", American Concrete Institute* in March 2019 Quebec City, Canada.

3. Ley-Hernández, A. M., & Feys, D., (2019). "Effect of sedimentation on the rheological properties of cement paste*", 10th advances in cement-based materials conference,* June 16 to 18, 2019, Urbana-Champaign, Illinois.
4. Ley-Hernández, A. M., Cook, R., Feys, D., & Kumar, A. (2018) "The link between rheological properties and degree of hydration of different PCEs on cement pastes"*, 9th advances in cement-based materials conference,* June 11 to 12, 2018, State College, Pennsylvania.

2. LITERATURE REVIEW

2.1. CEMENT HYDRATION

Cement represents about 7 to 15% of the volume of the most used construction material in the world, concrete [15]. The massive consumption of cement generates high environmental impact due to the CO_2 emissions linked to its production. In order to reduce CO_2 emissions, it is very important to understand the kinetic mechanisms behind the hydration of cement. Although, hydration of cement has been extensively investigated, reactions at very early age are still a delicate subject, particularly the so-called induction or "dormant" period which is characterized by a dramatical reduction of the rate of reaction after short and rapid initial reaction of cement in contact with water (initial dissolution). Cement is a composite material consisting mainly of ground clinker and a small amount of gypsum (calcium sulfate). The clinker is composed by four main phases, which are: alite, an impure form of C_3S; belite, an impure form of C_2S; tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF).

The hydration of cement is a very complex and important process since it involves different clinker phases, impurities and their interactions and primarily dictates the development of the microstructure and the consequent evolution of fresh and hardened properties. Cement hydration has been extensively investigated, although many detailed features are still not well understood and remains a subject of scientific debate.

The rate of hydration of pure C_3S, alite and Portland cement is generally divided in the following stages (Figure 2-1): (I) initial reaction or dissolution period, (II) induction period or slow reaction, (III) acceleration, (IV) deceleration period and (V) slow ongoing hydration period. These stages have been reported in the literature for many years. Although recent progress has been made, it is still hard to understand beginning and the ending of some stages and the controlling rate. This is due to the difficulty of isolation of the different chemical processes involved in the cement hydration. The reaction between Portland cement and water involves processes of dissolution and precipitation that causes formation of different hydrates such as: calcium silicate hydrate (C-S-H) and calcium hydroxide (CH), generally called portlandite, these two hydrates are hydration products of the reaction between C_3S, C_2S and water. While, the reaction between C_3A, C_4AF and calcium sulfate lead to the formation of ettringite and monosulfoaluminate.

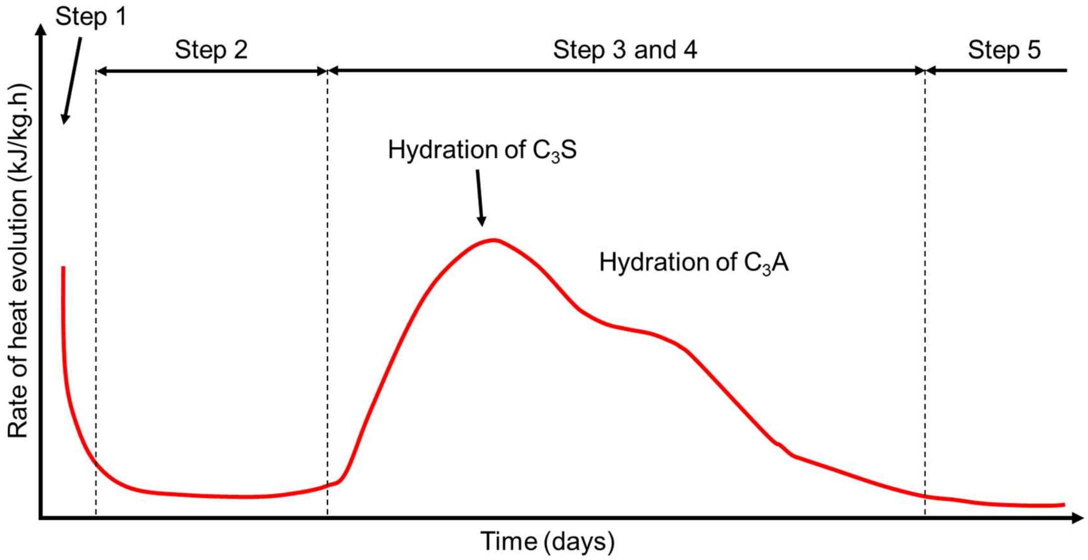

Figure 2-1.Typical heat of hydration curve of Portland cement.

To study the hydration kinetics of cement, many researchers focus on the hydration characteristic of the main hydrate tricalcium silicate (C_3S). One of the reasons is that impure C_3S (alite), constitute about 50 to 70 percent of Portland cement by mass. In addition, alite dominates the early hydration of cement that includes setting and early strength development, and it is mostly the responsible for the formation of calcium silicate hydrate gel (C-S-H) the main hydration product. Also, it is easier to understand hydration kinetics of a simpler chemical subsystem rather than a series of components and phases that makes the chemical analysis much more complex.

Within seconds of contact with water, a rapid reaction starts, and it is characterized by a large amount of heat released. Chemical analysis of the solution phases has given evidence that C_3S dissolves quickly after wetting. Subsequently, the dissolution rate of C_3S decelerates very rapidly, this transition from initial reaction to induction period has been under debate for many years and different hypothesis have been proposed but none is widely accepted. Some authors argue that the deceleration of the dissolution rate of C_3S is caused by a "protective" layer of metastable calcium silicate hydrate [C-S-H (m)] that covers the surface of alite, which does not permit the contact of alite with the solution [16]. Regardless of some evidence based on nuclear resonance reaction analysis (NRRA) that show changes in the hydrogen depth profile as a function of time, and more recent results that show formation of a layer of silicate hydrate phase that later becomes C-S-H, once the solution is sufficiently concentrated with calcium [17]. There is still a question if the layer covers C_3S completely and if it is sufficiently dense to block the further diffusion of the components. Also, there is no explanation of why at the end of the induction period the C-S-H forms rapidly. In addition, there is not sufficient experimental data that can support this theory.

Other researches assumed that C_3S dissolution rate decreased due to a "superficially hydroxylated layer" that forms on C_3S surfaces in contact with water, and the dissociation of the ions occurs slowly [17-19]. This hypothesis was adopted as an explanation of the slow dissolution of C_3S. Later, an alternative mechanism explanation for initial reaction was developed, which was based on a steady state between the diffusion of C_3S and the initial growth of C-S-H. In this theory, the dissolution rate decreases quickly when the calcium hydroxide concentration increases due to the dissolution process [17]. When the solution exceeded a critical supersaturation with respect to C-S-H, it starts to nucleate rapidly on C_3S surfaces and begin to grow due to its initial low surface area. Within minutes, equilibrium state condition is achieved in which the solution is undersaturated with respect to C_3S and supersaturated with respect to C-S-H.

Different mechanisms control the dissolution rate and depend on the saturation state of the solution. The low-solubility mineral approach has been applied to alite and have shown that the dissolution rate is affected by the initial saturation of the solution. According to the theory that was borrowed from geochemistry to explain the dissolution of the C_3S, there are three basic mechanism that promote dissolution: formation of 2D vacancy islands led by the nucleation of pits on the perfect surfaces of the crystal, etch pits formed by dislocations with the surface and step retreating at existing roughness. The triggering of these mechanisms is closely related to the undersaturation conditions and their activation energies. If the undersaturation is very large, the 2D pits can nucleate on surfaces without the presence of dislocation but the precipitation of reaction products on the surface when dealing with cementitious systems would require a high activation energy. If the undersaturation decreases, the activation energy barrier increases and the formation of etch pits on the surface becomes impossible on plain surfaces. Once the ionic activity is high and the undersaturation becomes lower than its critical value for etch pits formation, the new formation of etch pits stops and the process is controlled by the step retreat formed on the previous stage [20].

Another hypothesis for the slow reaction period is that crystallographic defects have influence on the early hydration of cement. By changing the quenching rate of the reaction of alite some researchers found that faster quenching, induced more defects resulting in a shorter induction period while other results show that by thermally treating samples at 650 ºC of alite of a narrow particle size distribution will decrease the defect density which caused a long induction period. Both results support the hypothesis that surface defects have influence on the dissolution rate and thereby the length of the induction period [20]. The hypothesis explains how defects on the surface can have an effect on the dissolution rate, but it does not explain how the initial reaction starts and how the induction period occurs and its transition to the acceleration stage.

Other theories related to nucleation and growth suggest that CH does not precipitate even if the saturation of the solutions reaches levels where CH can be formed due to the poisoning effect created by silicate ions. Once the supersaturation is such that the poisoning effect can be overcome, the CH precipitates, lowering the calcium concentration available in the solution and promoting further dissolution of the anhydrous grain. Young et al [21] proved that at the end of the induction period, the calcium concentration is almost twice what is needed to precipitate CH in water. There are reasons to believe that the subsequent precipitation of CH at the end of the induction period is more a consequence than a cause. There are experiments were CH was added to a solution of C_3S and water, the effect of the CH addition was translated in an induction period prolongation showing that the CH precipitation does not really control the rate of the reaction. On the other hand, under dilute conditions C-S-H precipitates before CH proving that indeed its role is relevant. Other authors have stated that the induction period end is driven by the nucleation and growth of the C-S-H but there is enough evidence in literature that proves that C-S-H if formed as soon as the C_3S gets in contact with water [20].

2.2. BASIC RHEOLOGY

Rheology is the science that studies the flow and deformation of matter (solid, liquid and gases). In principle, rheology includes everything related to the flow behavior in fields such as: aeronautics, hydraulics, fluid dynamics and soil mechanics. However, it is frequently restricted to study the fundamental relationship between force and deformation of materials, particularly liquids [22]. Rheological characterization is typically used to assess the quality control of raw material as well as processing conditions and final products. The main goal is to understand the interactions between different ingredients in a product and to get an insight of the structure of the samples, etc. Also, it is applicable to all the materials from dilute solutions to semi-solids such as pastes and creams, to solid polymers as well as asphalt.

Many industrial or natural materials exhibit complex rheological properties and can vary depending upon the external conditions applied, such as: stress, strain, time, temperature, etc. The internal structure of the material and the flow history are also key factors that should be taken in account when measuring or predicting such properties.

Figure 2-2 shows the flow curves of the different models that describe the flow behavior of materials. Newtonian fluid (Equation 1) describes the flow characteristics of a fluid with a simple linear relation between the shear stress τ and shear rate $\dot{\gamma}$. The flow history of this type of material has no impact and flow proportional to the existing applied shear stress.

$$\tau = \mu\dot{\gamma} \tag{1}$$

where: μ is the material viscosity.

A non-Newtonian fluid exhibits a non-linear relationship between shear stress and shear rate, which means that the viscosity is not constant at all shear rates. When the viscosity decreases with an increase in the shear rate, the fluid is called shear thinning. On the other hand, when the viscosity is increasing with increasing the shear rate, the material is shear thickening. Equation. 2 shows one of the most applied models in rheology, the "power law model", which describes the shear thinning and shear thickening behavior.

$$\tau = m\gamma^{n} \tag{2}$$

Some materials require a minimum stress to be applied before they start flowing, this stress is called yield stress (τ_0) [23]. These materials are non-Newtonian, but once it starts flowing, they behave essentially as Newtonian fluids (Equation. 3).

$$\tau = \tau_0 + \mu_p\dot{\gamma} \tag{3}$$

2.2.1. Thixotropy. It is defined as a reversible time-dependent phenomenon where the apparent viscosity continuously decreases when shear rate is applied and subsequently recovers when the shear rate is removed [23-26]. Figure 2-3 shows a simple physical explanation of thixotropy and the different motions within a system. The particle interaction forces determine the potential energy well for each particle. When the material is at, rest there is an equilibrium position that the particle tends to reach for which the energy is minimum between its neighbors (Figure 2-3 (a)). In solid regime, when the element does not overcome the energy (ΔE) given to the system, the particle does not leave the well. Once the applied stress stops, the particle comes back to the original position, which is characterized by the elastic solid behavior (Figure 2-3 (b)). In the case of the liquid regime, if the energy given to the system is higher, the particle is able to overcome this barrier and flow occurs (Figure 2-3 (c)). When a system displays thixotropy behavior, the depth (ΔE') of the potential well varies over time, increases at rest and the energy for the particle to leave the well increases (Figure 2-3 (d)) [27,28].

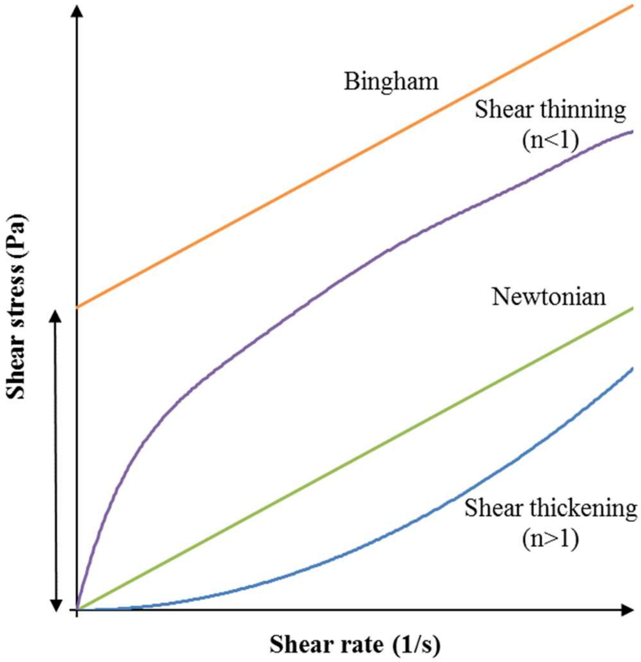

Figure 2-2. Flow curves for a Newtonian, shear thinning, shear thickening and Bingham material.

In many cementitious systems, a reversible evolution of the material rheological behavior happens during the induction period of the hydration reaction: when the material is at rest the static yield stress continuously increases over time, this evolution can be erased or broken-down by strongly shearing or remixing the paste, and the material can go back the reference state or equilibrium. This is often described as thixotropy (Figure 2-4)[29]. The generalized model to describe thixotropy in detail consists of the following equations (Equations 4 and 5), where the structural parameter λ is introduced to reflect the internal structure of the suspension. Equation 4 shows the dependency of the yield stress on the structural parameter (λ), while Equation 5 shows the rate of change of the internal structure. When the lowest shear rate for which dλ/dt can be zero [30], there is an equilibrium value of λ, which has a set of constant rheological properties over time, therefore when the shear rate is varied it will create a unique set of rheological properties of a thixotropic system [31].

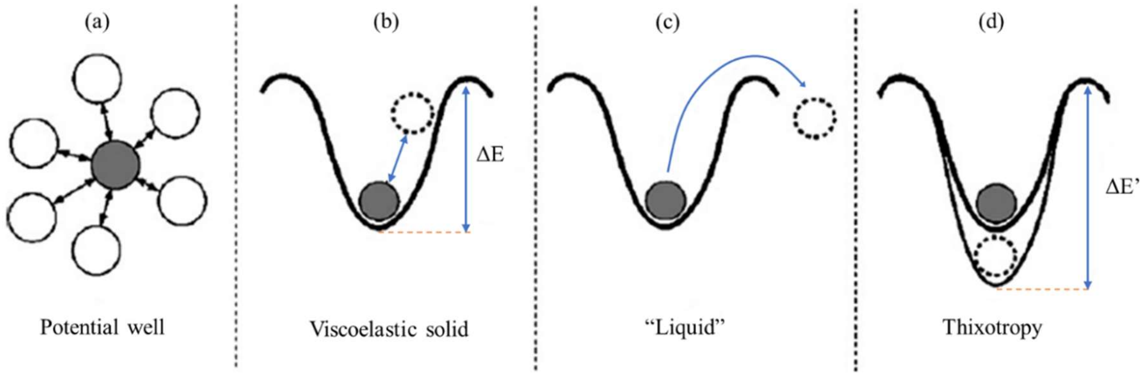

Figure 2-3. A simple physical explanation of thixotropy behavior. Adapted from [27].

$$\tau(\dot{\gamma},\lambda) = \lambda \cdot \tau_0 + \lambda \cdot K_{st} \cdot \dot{\gamma}^n + K_\infty \cdot \dot{\gamma}^n \,; \qquad (4)$$

$$\frac{d\lambda}{dt} = \underbrace{-k_1 \cdot \dot{\gamma} \cdot \lambda}_{\text{breakdown}} + \underbrace{k_2 \cdot \dot{\gamma}^m \cdot (1-\lambda)}_{\text{build-up due to shear rate}} + \underbrace{k_3 \cdot (1-\lambda)}_{\text{build-up until } \lambda=1 \text{ at rest}} \,; \qquad (5)$$

λ = 0, when the suspension is completely dispersed.

$\lambda = 1$, when the system is completely flocculated.

where: τ = *Shear stress (Pa)*

$\dot{\gamma}$ = *Shear rate (1/s)*

λ = *Structure parameter varying between 0 and 1*

K_{st} = *Consistency factor due to the structure (Pa* s^n*)*

K_{∞} = *Consistency factor at* λ*=0 (Pa* s^n*)*

k_1, k_2, k_3, m = *Factors describing changes of structure in time*

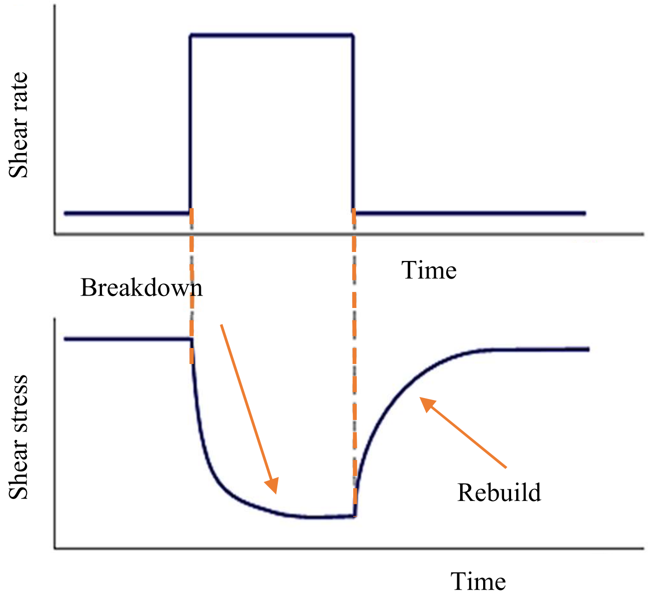

Figure 2-4. Schematic representation of a thixotropic material subjected to a shear rate.

2.2.2. Rheometry. The rheological properties can be characterized in a simple shear flow with homogenous regime of deformation, such as: imposition of constant rotational speed or constant torque which correspond to a controlled shear rate and shear stress, respectively. Different measuring systems are available i.e. cone and plate, parallel-plates, coaxial cylinders and vane. However, there are no specific guidelines on how to select the appropriate geometry for the material that will be tested. Proper understanding of the advantages and disadvantages as well as the limitations of each geometry should be considered. In the case of cement-based materials the most commonly use geometries are the following:

2.2.2.1. Parallel plates (PP). In parallel plates measuring system, the material is confined in the gap between two disks of the same axis and same radius (Figure 2-5). One plate is fixed, and shear is imposed by the rotation of the other plate.

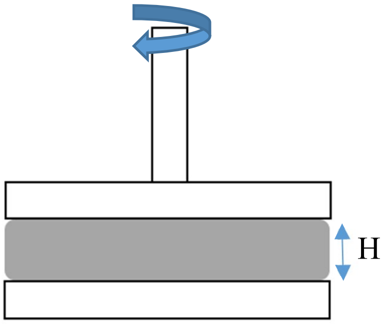

Figure 2-5. Parallel plate measuring system.

The following Reiner-Riwlin equations for parallel plates are used to transform from relative to absolute units. The intercept of torque (T) and angular velocity (**Ω**) curve (G) is transformed into yield stress (YS) using Equation 6. The plastic viscosity (PV) of the material can be determined using the slope of the curve (L) and transformed using Equation 7.

$$T = G + L\Omega$$

$$\tau_0 = \frac{3G}{2\pi R^3} \tag{6}$$

$$\mu_p = \frac{2HL}{\pi R^4} \tag{7}$$

where: T = Torque (Nm)

Ω = Angular velocity (rad/s)

τ_0 *= Yield stress (Pa)*

μ_p *= Plastic viscosity (Pa s)*

R = Radius of plate (m)

H = Gap between the plates (m)

Parallel-plates geometry is a common tool used due to its simplicity, the small sample volume required, the ease of inserting surface roughness and the variable gap to accommodate large particles. On the other hand, the shear conditions in this geometry are heterogeneous around the entire shear gap. At the edge of the plate, the shear rate is higher than the center causing sample migration out of the gap. Other issues are the drying of the sample at the edge of the plate and non-uniform temperature sample along the gap.

2.2.2.2. Concentric cylinders (CC). The material is placed into between two cylinders, in most cases the outer cylinder (cup) is fixed, and the shear is imposed by the inner cylinder (bob). The gap between the two cylinders can be narrow or wide, in the case of cement-based materials wide gap rheometers are used. Figure 2-6 shows a schematic representation of the concentric cylinder measuring system.

The Reiner-Riwlin equations for concentric cylinders transforms the parameters G and H into yield stress (Equation 8) and plastic viscosity (Equation 9), defining a linear relationship between torque (T) and rotational velocity (N), into the Bingham parameters.

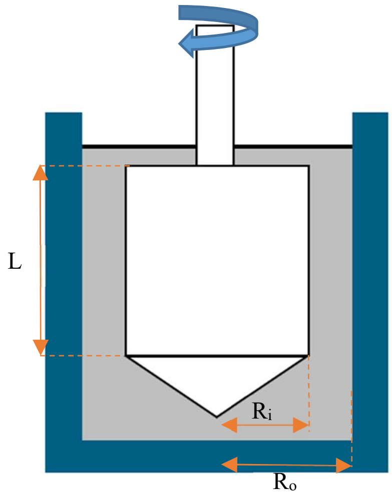

Figure 2-6. Concentric cylinders measuring system.

$$T = G + HN$$

$$\tau_0 = \frac{G \cdot (\frac{1}{R_i^2} - \frac{1}{R_0^2})}{4 \cdot \pi \cdot \ln(\frac{R_0}{R_i})} \tag{8}$$

$$\mu_p = \frac{H \cdot (\frac{1}{R_i^2} - \frac{1}{R_0^2})}{8 \cdot \pi^2 \cdot h} \tag{9}$$

where: τ_0 = *Yield stress (Pa)*

G = *from equation 5 (Nm)*

R_i = *Radius of inner cylinder (m)*

R_0 = *Radius of outer cylinder (m)*

h = *Height of inner cylinder submerged into the material (m)*

μ_p = *Plastic viscosity (Pa s)*

H = *from equation 5 (Nm s)*

Concentric cylinders geometry is also a common tool used in cement-based materials due to the following advantages: it is easy to fill the cup, the temperature of the sample can be controlled without difficulty, the transformation equations are simple, sample evaporation can be prevented easily by a cover or a solvent trap. On the other hand, a relatively large amount of sample is required, the sample can experience sedimentation and plug flow can be present.

2.2.2.3. Vane. In the vane measuring system, the sample is in between a cylinder and a vane tool that consists of thin blades centered on a shaft (Figure 2-7). The outer cylinder is fixed, and the vane is imposing the shear. In order to transform the material properties from relative units to absolute units, concentric cylinder equations can be applied, in this case the vane tool is considered a cylinder (inner cylinder). Some of the advantages are of using this measuring system are: it allows to study properties of structured materials with negligible disturbance during the insertion of the tool and avoids wall slip. On the contrary, in this geometry the vane path is not completely circular, larger sample is required and the material is not sheared evenly.

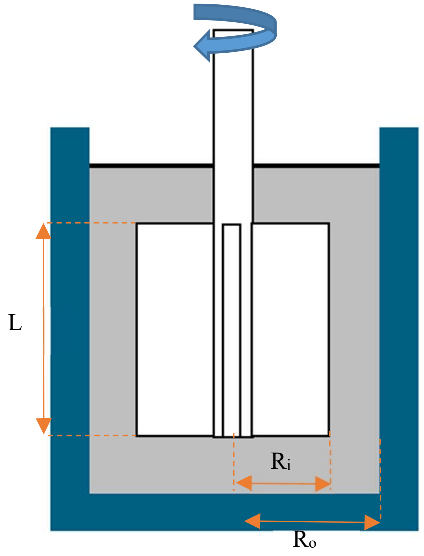

Figure 2-7. Vane measuring system.

2.3. RHEOLOGY OF SUSPENSIONS

The word “suspensions” is often used to describe a two-component system where discrete phase (particles) is suspended in a continuous fluid. The rheology of suspension systems of both non-colloidal and colloidal hard spheres varies widely depending of the nature of the individual phases and the interaction between them, such as the particle volume fraction and the particle size distribution. Particle interaction, morphology and softness also intervene in the rheological properties of the material. In general, the addition of solid particles in a suspending fluid contributes to the total stress of the suspension resulting in an increase of viscosity, even at low volume fractions [32].

Colloid refers to the dispersed phase of a biphasic system, which elements are too small to be able to see them easily using an optical microscope, usually on the size range of ~nm (10^{-9} m) to ~μm (10^{-6} m). In the case where the suspended medium, the liquid, the particles do not settle, and ordinary separation techniques cannot be applied [33]. Colloids suspended in a continuous phase are a type of mixture called “colloidal suspensions” or “colloidal dispersions”, in this mixture the continuous phase can be a solid, liquid or a gas. While the discrete phase are particles larger than simple molecules, but small enough so that the inter-particle forces are significant [33,34].

Colloidal interactions can be classified as attractive forces and repulsive forces. The van der Waals attraction arises from attraction between molecules that have been electronically or orientationally polarized by neighboring particles [34]. For electrostatic repulsion, the particles in the suspension are charged on their surface which will make other particles with the same change to repel each other. An addition of a polymer layer to the particle surface can create a barrier for other particles. This leads to a separation of two particles due to the barrier created by the polymers.

The Peclet number indicates the relative importance of the hydrodynamic forces to Brownian forces. When Pe << 1 then Brownian forces plays a significant role. In contrast, the larger the Pe-number >>1, the more important the hydrodynamic part is [23].

$$P_e = \frac{\eta_s \dot{\gamma} a^3}{k \cdot T} \tag{10}$$

where: P_e *is the particle Reynold number*

η_s *is the apparent viscosity of the suspended medium*

$\dot{\gamma}$ *is applied shear rate.*

a *is the particle radius*

k *is the Boltzmann's constant*

T *is the temperature*

For non-colloidal suspensions where Peclet number is large, particle inertia can dominate according to the Reynolds number (Re). For Re < 0.1, it is stated that the inertia forces can be neglected.

$$R_e = \frac{\rho_s \dot{\gamma} a^2}{\eta_s} \tag{11}$$

where: R_e *is the particle Reynold number*

ρ_s *is the density of the suspending medium*

η_s *is the apparent viscosity of the suspended medium*

$\dot{\gamma}$ *is applied shear rate.*

a *is the particle radius*

For non-colloidal particles ($> 1\ \mu m$), the influence of the inter-particle forces can be negligible and will not have influence on the rheological behavior of the suspension. Which means that the non-colloidal interactions are caused by the direct contact of the particles and by increasing the hydrodynamic forces between the particles.

2.3.1. Diluted Suspensions. Suspensions rheology is strongly depended on the volume fraction of the particles and the viscosity of the continuous phase. When the particles are suspended in a Newtonian fluid at a dilute concentration (ϕ < 0.05), overall viscosity is expressed by the Einstein's equation [35].

$$\eta_r = \frac{\eta}{\eta_s} = 1 + [\eta]\phi \tag{12}$$

where: η_r is the relative viscosity

η is the viscosity of the suspension

η_s is the viscosity of the suspended medium

$[\eta]$ depends on the particle shape, being 2.5 for rigid spheres.

ϕ is the volume fraction

In dilute systems where the distance between the particles is high, the dispersion viscosity is nearly independent of shear stress [33]. Also, a modest change in the particle size may not be affected greatly, as long as the flow domain is sufficiently larger than the particles. Thus, the conclusion is reached that in dilute suspension (ϕ < 0.05) modest changes in the particle size distribution are of no consequence [36].

2.3.2. Concentrated Suspensions. A concentrated regime starts with a volume fraction higher than 0.25 [37]. With the increase of the volume fraction of the suspending medium, the particles come into close contact and many interactions must be considered

[32]. Equation 12 is no longer applicable at high concentration of solids. Therefore, other models have been proposed to describe the concentration dependence of the relative viscosity of concentrated suspensions. One of the most useful expressions is the semi-empirical equation of Krieger and Dougherty for monodisperse suspensions [38]. As the particle concentration approaches ϕ_m, there is not enough fluid to lubricate the motion of the particles and the viscosity goes to infinity. Figure 2-8 shows a comparison of the dilute concentration equation and the concentrated equation.

$$\eta_r = (1 - \frac{\phi}{\phi_m})^{-[\eta]\phi_m} \tag{13}$$

where: ϕ_m *is the maximum packing fraction of particles*

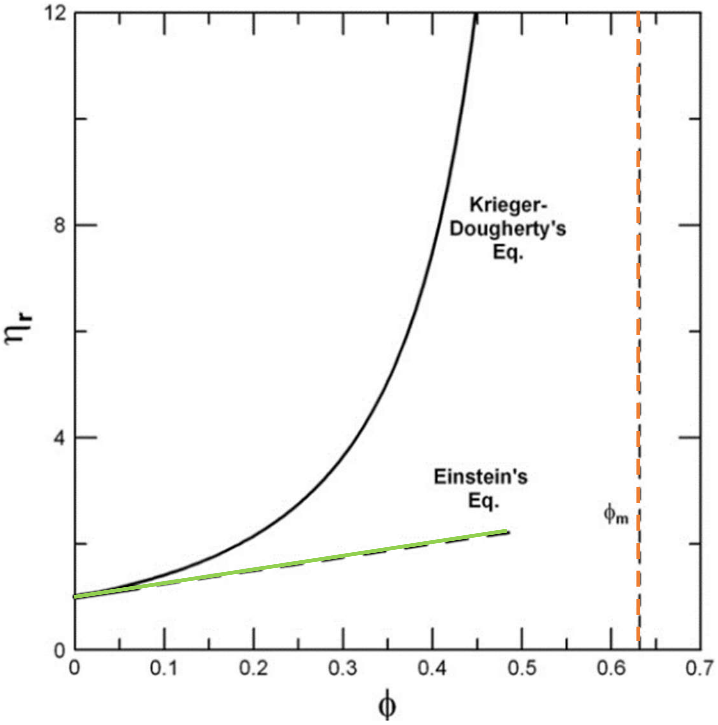

Figure 2-8. Relative viscosity vs particle volume fraction predicted by Einstein's equation. For dilute hard-spheres suspensions (Equation (12) with [η] = 2.5), and Krieger-Dougherty's equation for concentrated hard-sphere suspensions (Equation (13) with ϕ_m= 6.3). Adapted from [34].

Cement paste is categorized as a concentrated suspension since the discrete cement particles are suspended in a continuous fluid (water) and the volume fraction is higher than 0.25. Cement particles are poly-dispersed in size, with an average particle size of ≈ 20 μm. According to Wallevik et al [3], it has been demonstrated that the cement particles are as large as 40 μm and can behave as a colloidal particle. Therefore, the colloidal inter-particle forces (such as: Brownian motion, Van der Waals attraction, Electrostatic repulsion) apply to cement-based materials. Due to these inter-particle forces, immediately after cement is mixed with water, flocculation of the cement particles occurs, and early hydrates start to form preferentially at the contact points between the flocculated cement grains.

When cement begins to hydrate, C-S-H starts to form bridges (linkages) between cement particles, which can be non-permanent, these bridges restrict the flow and cause an increase in the rheological properties. As hydration progresses to the later stages, the water in the system is consumed increasing viscosity. Also, more linkages are being formed and becoming permanent, which results in the stiffening and subsequent development of strength. The stiffening (C-S-H hydrates increase dramatically the numbers of bridges forming a strong structure) of the cement paste is due to the multiplication of contacts between particles over time. In the presence of superplasticizers, the polymer adsorbs onto the cement surface changing the surface charge providing repulsion and steric hindrance preventing the cement particles from coming too close to each other. This results in an improvement in the rheological properties, due to the dispersion of the agglomerate cement and hydrating cement particles. The rheological properties of concrete determine its flow performance and therefore they are of greatly importance in transportation, placement and consolidation of concrete.

2.4. DISPERSING ADMIXTURES

The use of the first and second generation of superplasticizers (SPs), such as lignosulphonates (LS), sulphonated naphthalene formaldehyde (SNF), sulphonated melamine formaldehyde (SMF) and polynaphthalene sulphonates (PNS), brought high improvements in the fresh properties of concrete. However, due to major problems on their poor slump retention characteristics, their interaction with the cement phases, excessive retardation and air entrainment, a new generation of superplasticizer was introduced. The new generation of superplasticizers are the polycarboxylate and polyacrylates type superplasticizers, which differ substantially from the SNF and SMF type. They are derivatives of acrylic, methacrylic and maleic acids like polycarboxylates (PCs), acrylic acid and acrylic ester copolymers (CAE), cross-linked acrylic polymers (CLAPs) and polyacrylic esters (PAEs). Also, they contain much smaller number of ionic group and their spatial structure differs due to the presence of side chains [39]. The structure of comb-shaped SPs, also called polycarboxylate ethers, polycarboxylate esters or polycarboxylates (PCEs) consists of a main chain (backbone), and commonly having carboxylic groups, to which an anionic side chains made of polyethers are attached [40].

2.4.1. Polycarboxylates (PCE). The PCEs superplasticizers, also defined as high range water reducers (HRWR) modify the rheological properties of cement-based materials. This type of SPs is categorized as the “new generation” of superplasticizers and were developed in Japan around the mid-1980s [23,41]. Previous synthetic polymers were linear ionic polymers or bulky natural polymers like the LS type, while the PCE have a comb-shaped molecular architecture. PCEs molecules generally consist of an anionic backbone with mostly carboxylate groups to which side chains of polyethers are attached in a more less regular fashion as shown in Figure 2-9. The responsible for the adsorption of the PCE onto the positively charged surface of cement particles is the negatively charge backbone. The resulting charge provided by the backbone to the cement particles is much lower than the one induced by LSs, polynaphthalene sulphonates and polymelamine sulphonates (PMS) polymers and depends on the number of free carboxylic groups in the backbone. The side chains variations also play an important role, since the number of side chain and the length determines the steric repulsive forces of the PCE that is absorbed on the cement surface.

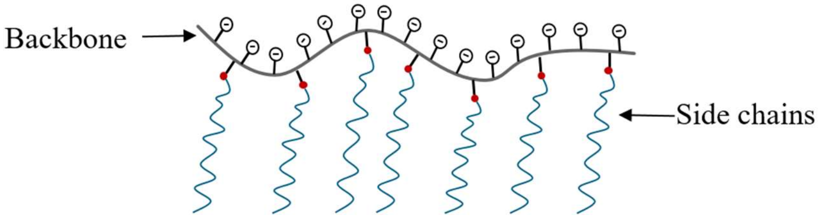

Figure 2-9. Schematic drawing of the comb-like structure of a PCE. Adapted from [42].

The PCEs main monomers that are part of the anionic component of the backbone are acrylic acid, methacrylic acid and maleic acid. Generally, in the PCE polymer polyethylene oxide (PEO), also called polyethylene glycol (PEG) is used as side chains. These side chains are attached to the backbone via ester, amide or ether bonds. The success of the PCE lies in the fact that has a broad range of possible molecular architecture, which is the main parameter that greatly affect its performance. By adapting their molecular structure enables the PCE to be used in large range of application in the construction field. The main parameters that determines the effect of the PCE properties are the following [23].

- The chemical composition of the backbone (acrylic, methacrylic, maleic, etc.)
- The length of the backbone
- Distribution and number of the side chains along the backbone
- Length of the side chain
- Chemical nature of the side chains (PEG, polypropylene oxide, etc.)
- Type of bond between the backbone and the side chain (ester, ether, amide, etc.)

The adsorption of polymers onto the cement surfaces plays an important role in cementitious systems concerning the enhancement of workability. The adsorption capability of the PCEs is controlled by molecular weight, side chain density, and side chain length of the polymers. The adsorption increases with polymer dosage until the surface of the solid particles is completely covered. PCEs with higher molecular weight, lower side chain densities and shorter side chains will adsorb more onto the cement particles. The charge density of the comb-shaped PCEs increases with the presence of a high number of free carboxylic groups, i.e. with decreasing side chain length and with decreasing side chain density [43].

2.4.2. Polynaphthalene Sulphonates (PNS). Initially, the dispersive properties of the PNS superplasticizers were discovered and patented by Tucker in 1938, but Japan in 1960s found a different application in the field of civil engineering making high slump concretes which were not able to produce with the lignosulphonates. PNS superplasticizer is a polymeric molecule formed during the sulphonation process of naphthalene, followed by a reaction of condensation using formaldehyde molecule and in the last step polysulphonic acid produced is neutralized [40,44]. The hydrophilic part of the PNS molecule is mainly sulfonic groups and the hydrophobic part is naphthalene [44]. The working mechanism of PNS is based on short-range steric repulsive forces, the presence of sulfonate groups is the responsible for negatively charge the cement surfaces (Figure 2-10). These induced repulsive forces inhibit the agglomeration of cement particles and increase the fluidity of cement pastes. One of the advantages of PNS is that their use does not interact with the stability of the pore network of entrained air. On the other hand, it does have incompatibility with low-alkali cement [42].

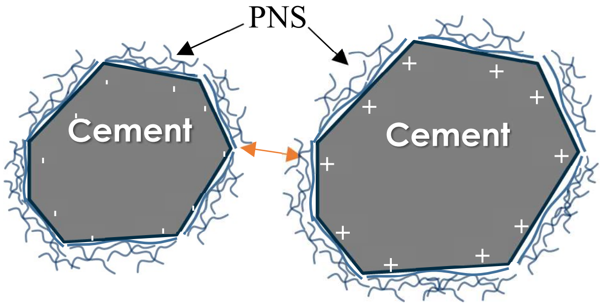

Figure 2-10. Schematic drawing of the working mechanism of PNS.

PAPER

I. HOW DO DIFFERENT TESTING PROCEDURES AFFECT THE RHEOLOGICAL PROPERTIES OF CEMENT PASTE?

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ABSTRACT

Rheological properties of cement-based materials are shear- and time dependent due to the chemical and physical particle bonding. Proper characterization of these properties is necessary to predict the behavior of concrete over time. Often, results on rheological measurements are dependent on different preparation conditions, testing procedures and measuring instruments employed. This paper explores how changes in the testing procedure impact the rheological properties of cement pastes with different superplasticizers. Three procedures with a different shear rate profile were repeatedly imposed. The last shearing for each procedure step was identical, imposing the reference state. The results indicate that the time-evolution of the rheological properties is strongly dependent on the employed procedure. It is hypothesized that, at low imposed shear rates, dissolution and precipitation of hydration products is accelerated, creating a stronger internal structure. As a result, the imposition of reference state does not guarantee full elimination of shear history.

Keywords: cement paste, rheology, testing procedure, thixotropy, time, workability loss

1. INTRODUCTION

Concrete is the most used construction material worldwide. Part of the popularity of concrete is because its fresh and hardened properties can be tailored in such a way to cover a wide range of requirements, even in the most demanding construction tasks [1]. The fresh properties of concrete are of paramount importance when it comes to placement of concrete, not to jeopardize the expected structural and durability requirements [2]. Therefore, the characterization and understanding of the rheological properties of cement-based materials have become essential, especially with the recent introduction of novel applications like digital fabrication in the field of civil engineering [3,4]. To be able to suitably adapt such properties, to optimize and to ensure consistent performance between batches, there is a need to accurately measure the properties and to obtain repeatable and consistent results. There are many empirical tests that describe the plasticity of cement-based materials, but these tests fail to measure the intrinsic rheological properties of the material [5]. However, the use of a rheometer to characterize the rheological properties of cement-based materials is not a straightforward task, due to the shear and time dependency of the material. Cement-based materials undergo chemical and physical particle bonding with time, caused by hydration of cement and flocculation [6-9]. This leads to rheological properties that are constantly evolving with time [10]. In the presence of dispersant admixtures, polymers adsorb onto the cement surfaces, altering the interaction patterns and preventing the cement particles from coming too close to each other, which reduces the formation of clusters [11-14]. This results in a change in the rheological properties, due to the dispersion of groups of cement particles.

In cementitious systems, it has been demonstrated that cement particles as large as 40 µm can behave as a colloidal particles [8]. Therefore, the colloidal inter-particle forces (such as Brownian motion, Van der Waals attraction, electrostatic and steric repulsion) apply to cement-based materials. The particle interaction forces determine the potential energy well for each particle. When the material is at rest, there is an equilibrium position that the particles tend to reach for which the energy is minimum between its neighbors. When a cement-based material displays thixotropic behavior, which happens during the induction period of the hydration reaction, the depth of the potential well increases at rest and the energy for the particle to leave the well increases [15,16]. When cement is mixed with water, flocculation of the cement particles occurs within a few seconds, and early hydrates start to form preferentially at the contact points between the flocculated cement grains [10]. Through this process, the nucleated C-S-H starts to form bridges (linkages) between cement particles. These bridges can rigidify the formed network restricting the flow and causing an increase in the rheological properties. However, with sufficient shear, some of those bridges could be broken as well [10]. The reversible evolution of the material's rheological behavior, when the cement suspension is allowed to rest, is the consequence of the physical and chemical structuration. This is often described as thixotropy. This evolution can be erased or broken-down by strongly shearing or remixing the material, to bring it back to the reference state [10,16]. A generalized model to describe thixotropy in detail consists of a structural parameter (λ) that reflects the internal structure of the suspension and influences the yield stress and viscosity. For each shear rate above the critical shear rate [17] there is an equilibrium value of the structural parameter that induces constant rheological properties over time (if no chemical reaction is present). In a thixotropic system, the measured rheological properties depend on the applied shear rate [16,18,19]. Therefore, when the shear rate is varied, it will create different unique rheological properties [20], which may not resemble the rheological behavior observed or desired for a given application. Increasing the applied shear rate decreases the equilibrium rheological properties.

Several researchers have studied the rheological behavior of cement-based materials, but often, results obtained are dependent on different preparation conditions, mixing processes, testing procedures and measuring instruments employed [21-24]. Although there have been several attempts to provide guidelines to ensure a proper characterization of the rheological properties [3,5], there is still not a standardized procedure. Consequently, many errors or inaccuracies may occur during the acquisition of the data and erroneous interpretation may lead to incorrect conclusions.

The objective of this paper is to describe a new observation on the time-dependency of the rheological properties of cement-based materials. The common assumption that imposing the reference state, by applying the highest shear rate on the sample erases all shear history [16], is countered. When applying different rheological measuring procedures on cement pastes, some differences in rheological properties are observed which are not in alignment with the currently known effects of shear-history. This paper describes the rheological procedures employed to investigate this effect, the selected cement paste mixtures, and the hypothesis that shear-induced acceleration is the most probably cause for the observed behavior.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS AND METHODS

2.1.1. Materials. The cement paste mixtures were produced with a commercially available type I/II ordinary Portland cement complying with ASTM C150/C150M, using a water-to-cement ratio (w/c) of 0.35. Four high-range water reducers were used to obtain a dispersed system with a mini-slump flow spread of 330 ± 20 mm, three different polycarboxylate-based (PCE) and one polynaphthalene sulfonate (PNS) superplasticizer. Table 1 shows the density of the cement and the different superplasticizers as well as the solid content used in this study.

Table 1. Physical properties of cement and superplasticizers used.

Material	Density (g/cm^3)	Solid content (%)
Cement	3.15	-
PCE1	1.032	25.80
PCE2	1.076	37.00
PCE3	1.080	29.50
PNS	1.190	40.94

2.1.2. Mixing Procedure. The mixtures were prepared in 0.5 l batches in a small Hobart mixer using two speed positions. The mixing sequence consisted of introducing first the water and then the cement into the bowl and wait for 30 s. The mixer was started at slow speed (140 ± 5 rpm) for 30 s to homogenize the materials. After that, the mixer was stopped for 30 s and the mixture was manually homogenized by scraping the walls of the mixing bowl. After this scraping period, the selected dispersant was added, and the mixing continued for 120 s at medium speed (285 ± 10 rpm). Immediately after mixing, the mini-slump flow of the mixture was measured, and all rheological testing was performed at 15 min after the contact with water. Table 2 shows the evaluated mix designs and average of the initial mini-slump flow of each mixture, as each employed testing procedure required a new batch of materials. The required quantities of dispersant were determined by means of trial batches.

Table 2. Evaluated mix designs. Units in g/l of paste.

Mixture	**OPC**	**Water**	**PCE 1**	**PCE 2**	**PCE 3**	**PNS**	**Initial mini-slump (mm)**
Mixture 1	1500	521	4.74				330
Mixture 2	1500	523		2.21			335
Mixture 3	1500	523			2.48		330
Mixture 4	1500	518				9.60	300

2.1.3. Rheological Measurements. The rheological measurements were performed using a concentric cylinder (CC) geometry in an Anton Paar MCR 302 rheometer at a constant temperature of 20 ºC during 150 min. For two sets of experiments, the temperature was set at 5 ºC and 35 ºC to investigate its effect on the testing procedure and formation of hydration products. A serrated cylinder was used to minimize slippage between the cylinder and the sample [3]. The inner radius of the cylinder (R_i) was 13.33 mm, outer radius (R_o) equal to 14.56 mm and the height of the vertical part of the inner cylinder is

40.00 mm. To avoid evaporation of water from the sample during the measurements, a plastic cover was placed on the top of the system.

Figures 1-3 show the details of the measuring procedure. Figure 1 shows the entire procedure over time, with the boxed part being repeated every 20 min. The details of each procedure (the content of the box), is highlighted in Figure 2 for procedures 1 and 2, and Figure 3 for procedure 3. Regardless of the procedure, a pre-shear was imposed at 15 min after the contact of water with cement and the testing procedure started at 20 min. First, the sample was pre-sheared at 15 min of age at 100 s^{-1} for 120 s to impose a reference state [3] (Figure 1). Then, a linearly decreasing shear rate ramp, from 100 s^{-1} to 10 s^{-1} was imposed over a period of 25 s. Finally, a logarithmic ramp from 10 s^{-1} to 0.1 s^{-1} was performed for 5 s (Figure 2). Procedure 1 (P1) and procedure 2 (P2) have the same shearing time but different applied shear rates (Figure 1). The purpose of procedure 1 is to investigate the shear-dependency of the sample by shearing at 20, 36, 60 and 100 s^{-1}. Each constant shear rate step had a duration of 120 s, followed by a linear decrease in the shear rate to 10 s^{-1}, over 15 s, to obtain a flow curve (Figure 2). Procedure 2 followed the same strategy, but kept the imposed shear rate constant at 100 s^{-1} at each of the four steps (Figure 2). Procedure 3 (P3) takes into consideration the time necessary to reach equilibrium in the sample at 100 s^{-1}. It only uses one shearing period, determined by preparatory tests. Table 3 shows the different durations of constant shearing for each paste. The flow curve was measured in the same way as procedure 1 and procedure 2. After performing the rheological procedure, the sample was allowed to rest for 10 min for procedure 1 and procedure 2. For procedure 3, the resting time depended on the mix design. Tests were restarted at the same times as for procedure 1 and procedure 2 (20, 40, 60, 80, 100, 120 and 140 min). It should be noted that at the end of each combination of flow curves, before each resting period, the sample was re-homogenized to avoid the effect of sedimentation on the results [25]. Figure 1 illustrates the entire imposed testing procedure with 10 min resting time followed up to 150 min, using procedure 1.

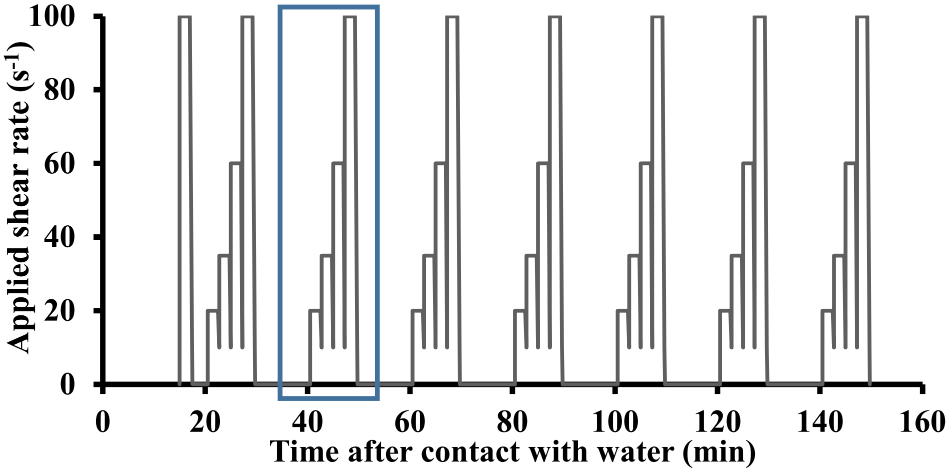

Figure 1. Testing procedure for P1 followed up to 150 min. P2 and P3 follow similar profile, but with varying shear rate profiles. Figures 2 and 3 show a magnification of the boxed (repeated)profile for procedures 1 and 2 (Fig. 2) and procedure 3 (Fig. 3) Note that the starting times for procedure 3 were identical as for procedures 1 and 2, despite differences in pre-shear time.

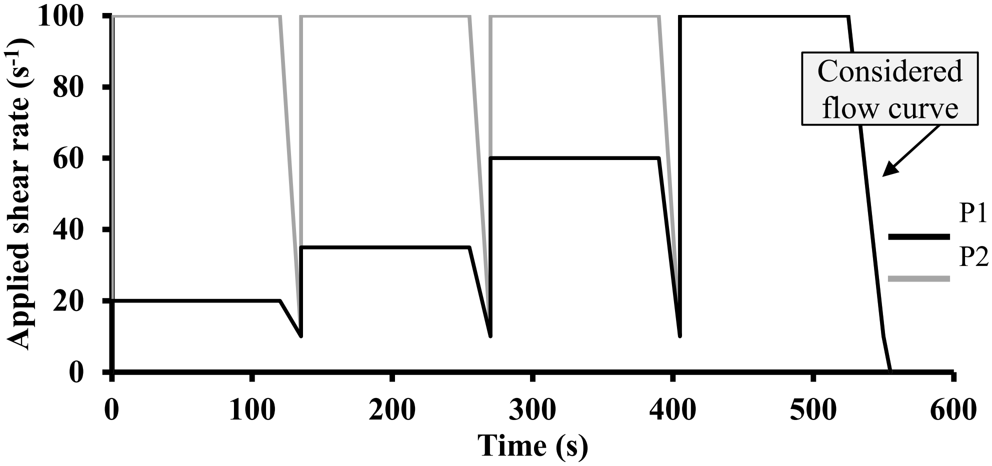

Figure 2. Rheological procedure 1 (P1) and procedure 2 (P2).

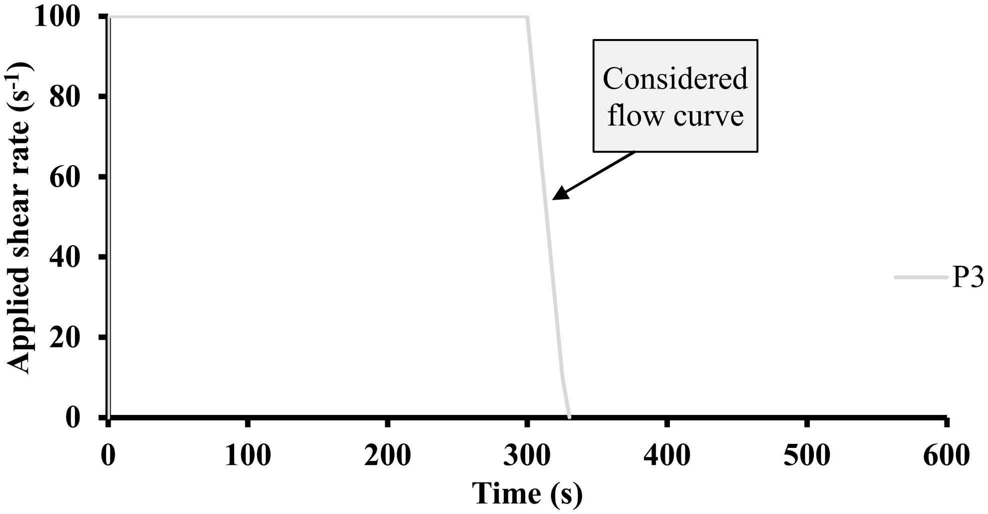

Figure 3. One step rheological procedure 3 for mixture 1 (P3). For the other mixtures, the preshear time was changed according to Table 3.

Table 3. Duration of shearing in procedure 3 to reach equilibrium for each mixture.

Mixture	Time (s)
Mixture 1	300
Mixture 2	400
Mixture 3	415
Mixture 4	390

2.2. ANALYSIS

For procedure 1 and procedure 2, the rheological properties were evaluated using the last flow curve at each time interval, at the maximum shear rate of 100 s^{-1}, while for procedure 3, these were obtained from the only flow curve measured at each time interval. The other flow curves are not considered in this paper. The analysis was done using a similar approach from [20] were a 6th order polynomial equation was fitted on the flow curve from 100 to 10 s^{-1} (Figure 4) and was differentiated to the shear rate, describing the slope (differential viscosity). The equation was then evaluated at 55 s^{-1} to obtain the differential viscosity at the median shear rate applied. Similarly, the yield stress was obtained by fitting an equation on the portion of the curve from 10 to 0.1 s^{-1} (Figure 5) and stress was evaluated at 0.1 s^{-1} to reflect the yield stress. Each yield stress, regardless of procedure, or when it was measured, was determined in the same fashion. Although, there is no physical meaning for the coefficients in the equation, it is the best strategy to be able to compare the different flow curves in the future, as the chosen curve-fit is sufficiently accurate in all shear rate ranges, regardless of the chosen maximum shear rate.

Figure 6 shows an example of the calculation of the equilibrium apparent viscosity from the pre-shear period at 100 s^{-1}, during the fourth step of procedure 1. Equation (1) was fit to the shear stress evolution with time. The equation consists of two decreasing exponential functions with different time periods to adequately capture the decreasing part of the curve. A linear increasing portion is added as some curves at lower shear rates show an increase in shear stress with time (see further). However, for all flow curves at 100 s^{-1}, there was no increase. The last parameter (E) is a constant value, which is the equilibrium value for the shear stress if no increasing part is observed. The equilibrium apparent viscosity is calculated by equation (2). The equilibrium value (E) is the extrapolation of the stress curve to infinite time, and is thus the stress value when equilibrium is fully achieved. This procedure was followed for all pre-shear curves at 15 min, at each 4th step for procedure 1 and procedure 2, and at each pre-shear in procedure 3.

$$\tau = Ae^{-Bt} + Ce^{-Dt} + m * (t - 117.5) + E \tag{1}$$

$$\eta_{app,eq} = \frac{E}{\dot{\gamma}} \tag{2}$$

where: τ *- shear stress (Pa)*

A, B, C, D *- fitting parameters*

t - time (s)

m - slope of the linear part

E- shear stress at which the slope is equal to zero (Pa).

$\dot{\gamma}$ - shear rate (s^{-1})

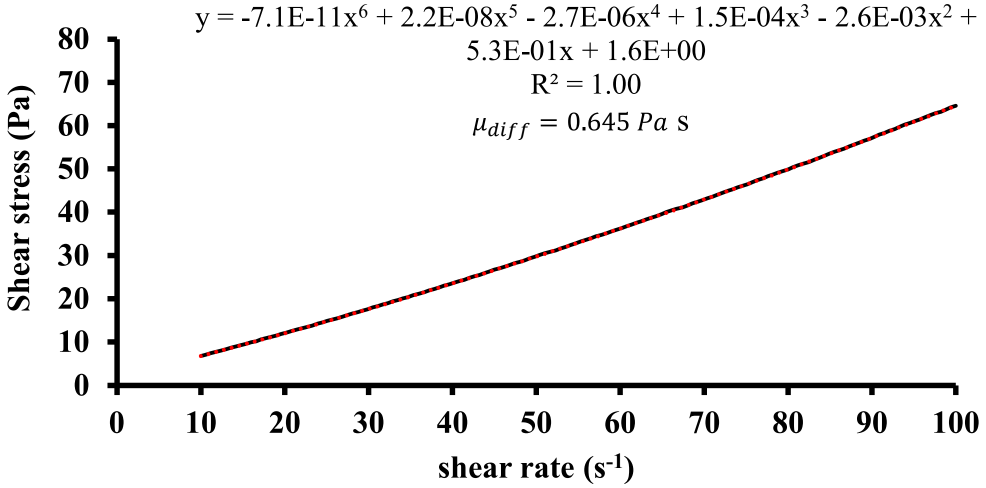

Figure 4. Shear stress and shear rate curve used to evaluate differential viscosity.

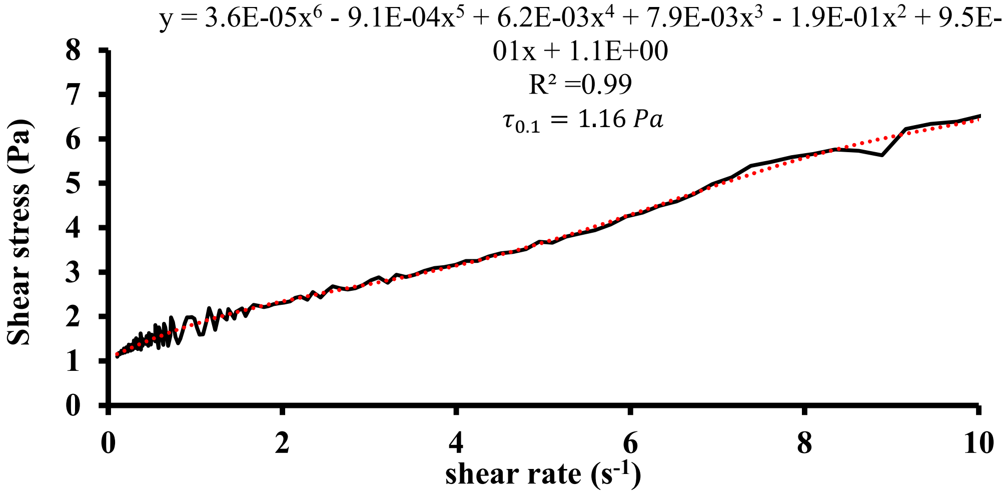

Figure 5. Shear stress and shear rate curve used to evaluate yield stress as the shear stress at 0.1 s^{-1}.

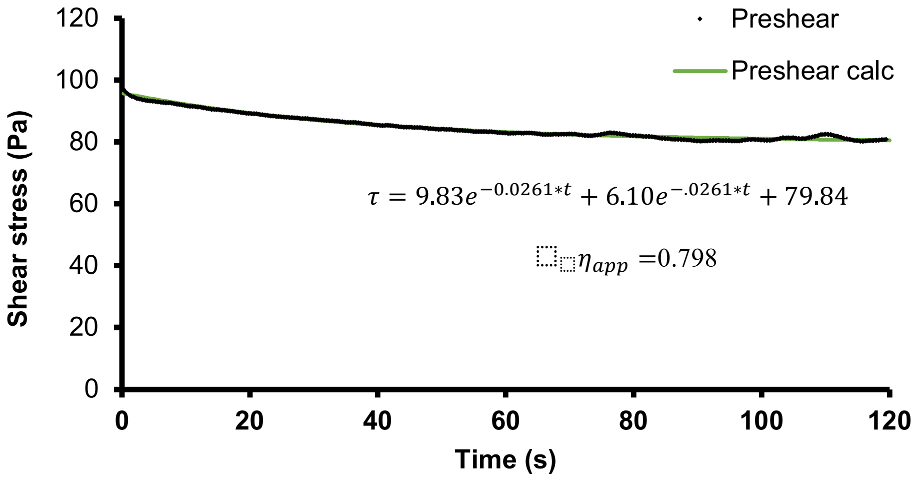

Figure 6. Example of the calculation of equilibrium apparent viscosity, which is the extrapolation of the shear stress vs. time profile to infintite time, during the pre-shear period at 100 s^{-1}.

3. RESULTS AND DISCUSSION

As mentioned in previous sections, replicates of the pastes were subjected to three different measuring procedures, and the purpose of this paper is to evaluate how the different procedures affect the rheological properties of the pastes, obtained from the flow curve at 100 s^{-1}. In theory, as 100 s^{-1} is the highest shear rate applied, one would expect the results to be identical, regardless of the applied procedure, as the imposition of the reference state should erase the shear history [16]. However, different results are observed.

3.1. OBSERVED DIFFERENCES AND SIGNIFICANCE FOR MIXTURE 1

Before starting the variation of the different parameters, 90% confidence intervals were established based on three repetitions of mixture 1 – procedure 3. The shown confidence intervals in the following figures include the evolution of the rheological properties with time using procedure 3. For all procedures, the rheological properties of the cement pastes at a certain time were normalized using the respective measurement at 15 min (pre-shear) after the contact of water with cement. The viscosity and yield stress were determined from the flow curves at 100 s^{-1} according to the procedures listed in Section 2.4.

The evolution of normalized differential viscosity and yield stress for each procedure with time, combined with the confidence interval for procedure 3, are illustrated in Figure 7 (a) and (b), respectively. No significant difference is observed between procedures 2 and 3, indicating that the cement pastes are in the same reference state at the determination of the considered flow curve. As such, the duration of the pre-shear, or the total duration of all shearing periods does not affect the rheological properties, as long as the same, constant shear rate is applied and the sample does not show sedimentation. However, the results for procedure 1 show a significant difference with procedure 3. The differential viscosity for procedure 1 is, at all times evaluated, outside of the confidence interval for procedure 3. For mixture 1, the procedure 1 yield stress does not fall outside of the confidence interval of procedure 3, but it can be seen it is higher as well.

To ensure that this is truly material behavior, the potential measurement artifacts must be addressed. At first, one can argue that the sample in procedure 1 showed sedimentation, causing a more pronounced increase in rheological properties with time [25]. Although this phenomenon is possible, it should affect the results in procedure 2 in a similar way. In fact, as the differential viscosity is lower for procedure 2 compared to procedure 1, one would expect a (slightly) faster sedimentation in the mixture tested with procedure 2 (based on Stokes' Law), and a slower sedimentation for procedure 3 due to the reduced shearing time. This is not observed. Furthermore, as mentioned before, the samples were re-homogenized before each rest period to eliminate the long-term effect of sedimentation, and the w/c was adjusted to avoid the effect of sedimentation on the results. For reference, cement pastes with a w/c = 0.45 could not be evaluated. Further discussion on sedimentation is beyond the scope of this paper.

As a second measurement artifact, it could be argued that equilibrium is not achieved in procedure 1. To counter this argument, the equilibrium apparent viscosity results are showing the same tendency as the differential viscosity: procedure 1 delivers systematically higher results compared to the other two procedures (Figure 8). So, if the pre-shear periods did not fully achieve equilibrium, even though they were chosen sufficiently long, a similar effect is observed when extrapolating the fitted pre-shear stress curve to infinite time. As such, the observed significant difference in differential viscosity between procedure 1 and procedure 3 is not the consequence of non-equilibrium.

3.1.1. Hypothesis. It is expected that the observed behavior is not a measurement artifact, but a true change in rheological properties of the material. Figures 9 and 10 show the shear stress evolution at different shear rates during the pre-shear periods for procedure 1. In the case of 20 and 35 s^{-1}, there is an initial break-down but after a few seconds, the shear stress starts to increase. While at 60 and 100 s^{-1}, only destructuration occurs. It could be argued that at each shear rate, both structuration and destructuration happens, but at higher shear rates, the destructuration is more dominant. The source of destructuration is well-known: increased shear breaks more flocculation and hydration bonds between particles. The source of structuration under shear is less well-known. At low shear rates, the material may have time to restructure, however at high shear rates, the material does not have enough time to restructure. The corresponding rate of destructuration is proportional to the applied shear rate [26]. Although shear-induced flocculation may be unlikely at 20 and 35 s^{-1}, the chance of it occurring is still latent and cannot be fully discarded. Another hypothesis, besides flocculation, that could contribute to this effect is the continuous hydration reaction. It is very plausible that shear accelerates dissolution of calcium and silicon ions. It could also be assumed that precipitation of hydration products rigidifying the formed network between the cement particles and increasing the rheological properties might be accelerated under shear. However, some of those newly formed or reinforced connections under shearing conditions are not broken at higher shear rates. Previous studies have shown the influence of shear (mixing) in the early hydration of alite and cement systems: Dollimore and Mangabhai [27] found an acceleration in the hydration kinetics by increasing the mixing time. Thomas and Jennings reported for tricalcium silicate (C_3S) systems that rapid hand mixing shortened the length of time to reach the heat evolution peak compared to pastes that underwent minimal mixing [28]. The impact of the shear rate (mixing) on hydration kinetics indicates that the thickness of the diffuse electrical boundary layer changes and that the rate of dissolution in the first minutes increases when the surface reactions are faster than the transport reactions. This results in a reduction of the length of the induction period. Whereas prior to the end of the induction period, the concentration of Ca^{2+} approaches the critical concentration at which the surface reactions slow down. In this regime mixing homogenizes the concentration in the solution and the reaction will tend to be controlled by the rate of transport of the ions from the surface to the bulk solution so the dissolution continues at a higher rate longer [29]. Han and Ferron [30] found that pastes had changes in their physical and chemical nature induced by increasing the shear intensity during mixing, such changes led to a decrease in the thickness of the diffuse double layer.

When procedure 2 is applied, which has a constant shear rate of 100 s^{-1}, lower properties are observed in spite of having the same shearing time as procedure 1. Therefore, increasing the applied shear rate in the sample is sufficient to break a portion of the internal connections, or prevent the shear-induced building of these connections, resulting in a decrease in the rheological properties [20,31]. Procedure 3, which has one extended shearing step, shows similar viscosity and yield stress in comparison with procedure 2. As such, if the shearing is applied for a sufficiently long time, the duration of the shear does not influence the results. However, if different, lower shear rates are applied, it is hypothesized that the accelerated dissolution of ions and increased precipitation rate of hydration products, which cannot be broken down under the applied shear, cause an increase in rheological properties. This causes a change in the reference state.

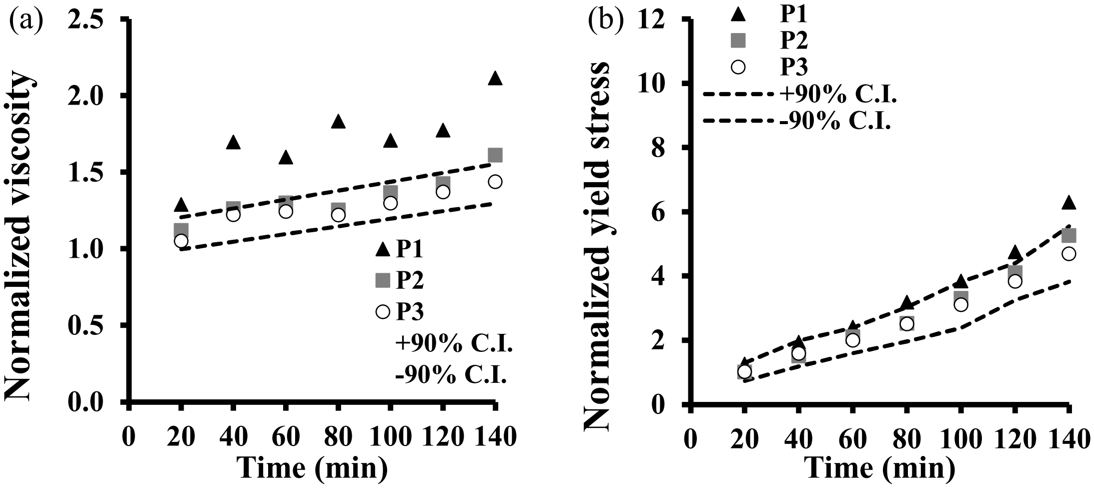

Figure 7. Confidence intervals of mixture 1 using P3. Comparison of (a) normalized viscosity and (b) normalized yield stress with the different procedures. For the viscosity, it can be observed that the results for P1 are outside the P3 confidence interval.

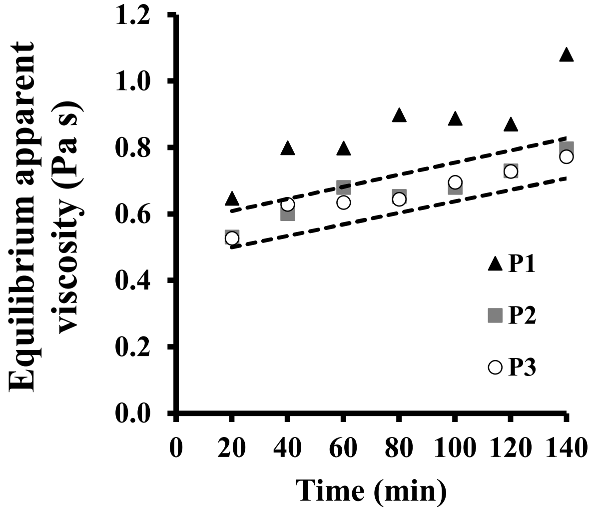

Figure 8. Confidence intervals of mixture 1 using P3. Comparison of equilibrium apparent viscosity with the different procedures. Similarly, as for the normalized (differential) viscosity, the equilibrium apparent viscosity delivers a significant difference between P1 and P3.

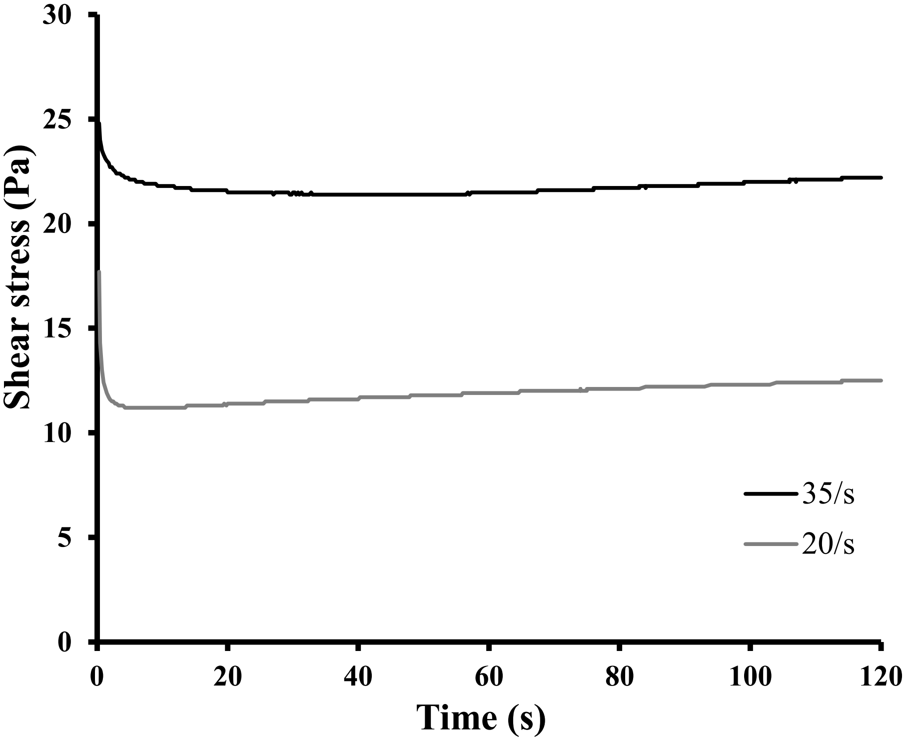

Figure 9. Shear stress evolution during pre-shear at 20 and 35 s^{-1} in P1. Beyond the initial breakdown, a slow build-up of structure is observed under shear.

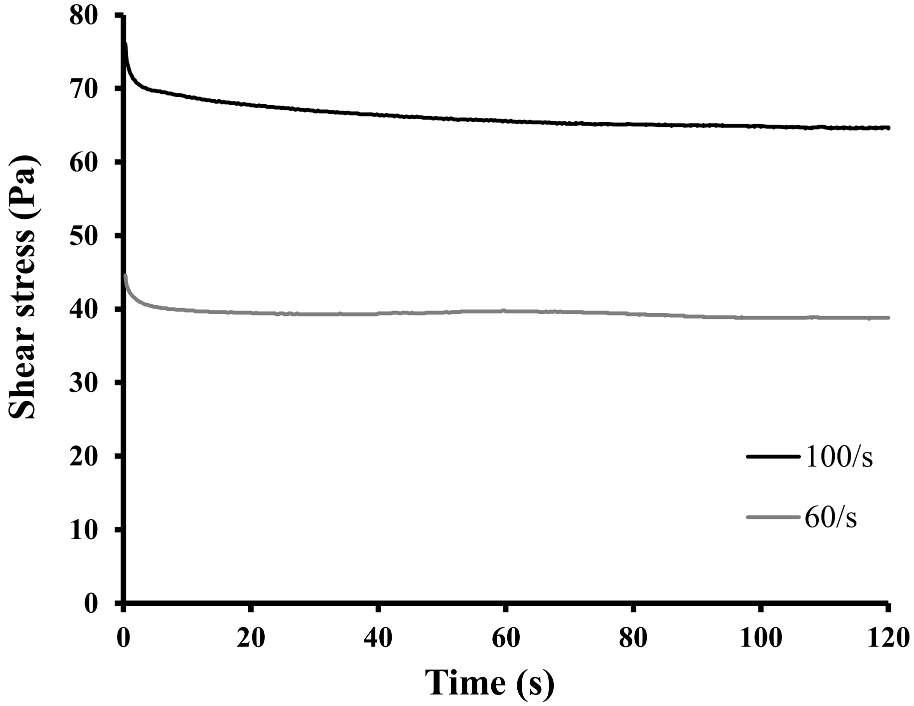

Figure 10. Shear stress evolution during pre-shear at 100 and 60 s^{-1} in P1. No build-up is observed.

3.2. PHENOMENON FOR OTHER DISPERSANTS

Figures 11, 12 and 13 show the flow behavior using the different testing procedures for mixtures 2, 3 and 4, respectively. In general, the measured differential viscosity values, determined from the flow curves at 100 s^{-1} are almost always higher for procedure 1, compared to procedures 2 and 3. The equilibrium apparent viscosities (not shown for mixtures 2, 3 and 4) follow closely the trends for the differential viscosities. Intrinsic differences can be found in the detailed evolution of the viscosity as a function of time and employed procedure, which are likely to be dependent on the working mechanism and the delay in hydration caused by each dispersant separately. In particular, the PNS mixture seems to show a less important effect on the change in viscosity due to the selected procedure, but regardless, the majority of the viscosity measurements with procedure 1 are above the other two procedures. It is well-known that, at dosages required to make mixtures with SCC consistency, PNS admixtures induce long workability windows, which could be attributed to a delay in hydration [32]. For yield stress, as can be seen in Figure 7b, the influence of the selected procedure is not as clear, as most of the procedure 1 results fall within the 90% confidence interval for procedure 3. Some differences in yield stress between procedures 1 and 2 or 3 can also be observed for mixtures 2 and 3, and no difference is seen for mixture 4. Despite the differences between the admixtures, for the viscosity, it seems that the effect of applied procedure can be observed regardless of the chosen admixture. Its occurrence as a function of time and its magnitude are though dependent on the dispersant.

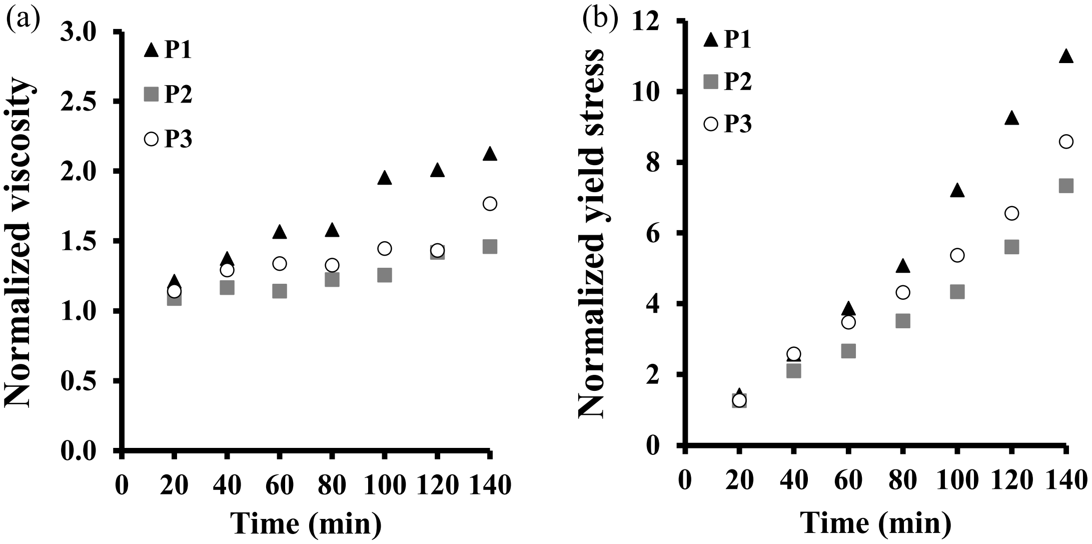

Figure 11. (a) Normalized viscosity and (b) yield stress for mixture 2 evaluated with P1, P2 and P3, showing a difference between P1 and P2/P3 as mixture 1

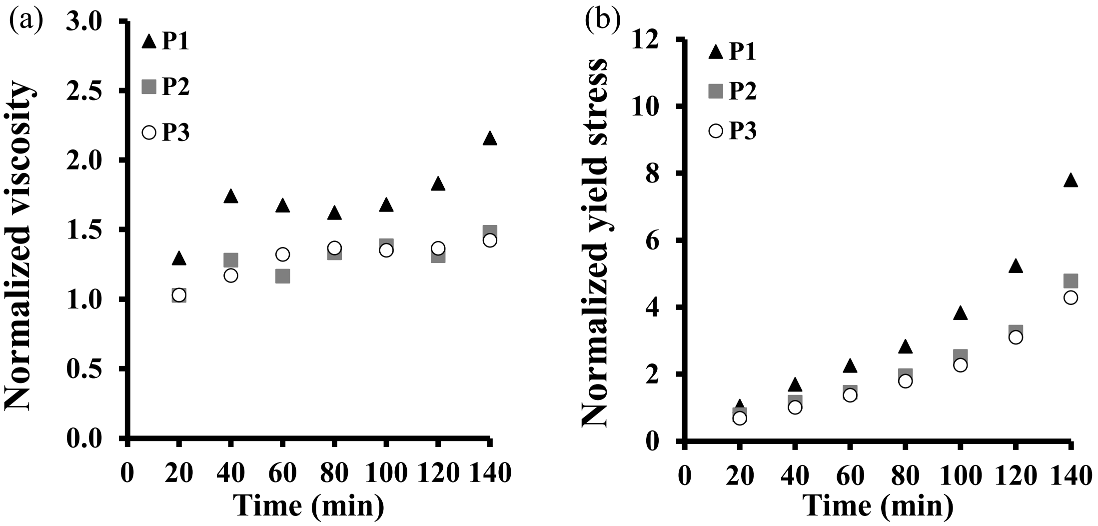

Figure 12. (a) Normalized viscosity and (b) yield stress for mixture 3 evaluated with P1, P2 and P3.

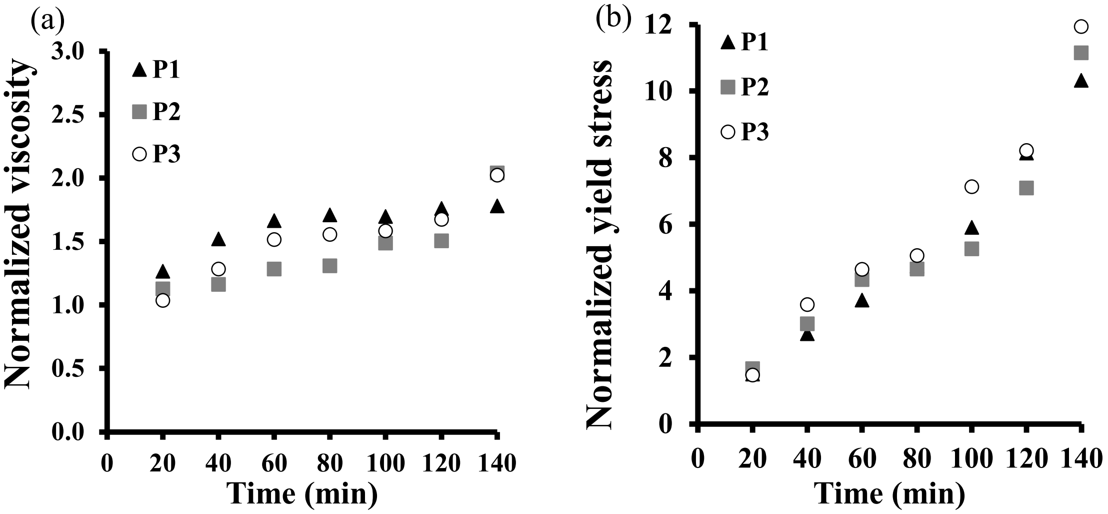

Figure 13. (a) Normalized viscosity and (b) yield stress for mixture 4 evaluated with P1, P2 and P3.

3.3. TEMPERATURE VARIATIONS

The influence of temperature was evaluated at 35 and 5°C, and compared to the results at 20°C. Figure 14 and 15 illustrate the rheological properties of mixture 1 using testing procedures 1 and 3 at 35 and 5°C, respectively. Procedure 2 was no longer executed, as no considerable differences with procedure 3 were observed. Normalized differential viscosity is more susceptible to changes in procedures at high temperature, compared to 20°C. At 100 min, also yield stress start to dramatically deviate between procedures at 35°C. It is well know that increasing temperature has an effect on the flow behavior of cement paste. It increases structural build up and accelerates hydration [33,34]. Therefore, it is expected that internal structure is more rapidly built or strengthened in between particles at low shear rate and high temperatures, restricting the flow and increasing the rheological properties faster with time. At 5°C, at which hydration is slowed down, the rheological properties do not seem to be affected by the imposed testing procedure. This could confirm the previously mentioned hypothesis that hydration contributes to the dependency of the rheological properties on the imposed testing procedure.

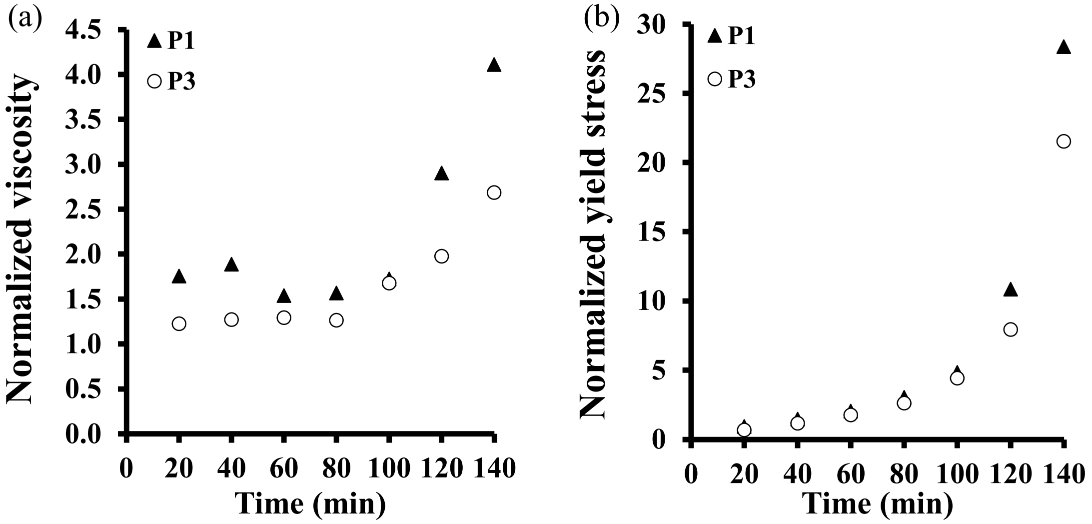

Figure 14. (a) Normalized viscosity and (b) yield stress for mixture 1 evaluated with P1 and P3 at 35 °C. Differences between procedures are more extreme, compared to 20 °C.

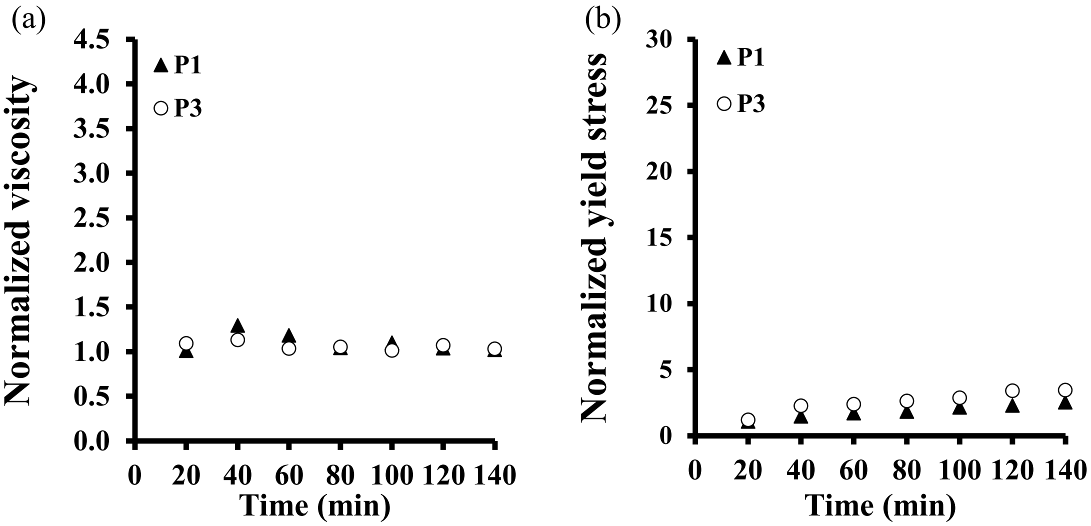

Figure 15. (a) Normalized viscosity and (b) yield stress for reference mixture evaluated with P1 and P3 at 5 °C. Almost no differences between procedures can be observed.

4. CONCLUSIONS

The effect of different testing procedures on the rheological properties of well-dispersed cement pastes was evaluated by varying the applied shear rate and time. Results show that low shear may accelerate dissolution and precipitation of hydration products, strengthening the formed network between the cement particles and consequently induce larger permanent increases in the rheological properties, especially in viscosity. The effect was observed for two different types of dispersing agents, one of which in three variations. Although differences are observed in the evolution of viscosity with time, and in the magnitude of the differences, the effect on viscosity was visible for all dispersants. This indicates the behavior is not caused by these admixtures.

At low temperature, at which hydration is slowed down, the viscosity does not seem to be affected by the imposed testing procedure, confirming that hydration does contribute to the variation of the rheological properties between the testing procedures. Also, besides hydration, shear induced flocculation may still arise at low shear rates and could be a catalyst for the hydration linkages to form.

Although the "most de-flocculated" state (reference state) was imposed in all experiments, the elimination of the shear history is not fully guaranteed. This is contrary of what is believed that this reference state can be reached when the material flow history is submitted to the highest shear rate. Therefore, the sample should be evaluated according to the intended shearing procedure for its application, since there is not a universal testing procedure.

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II. RESTING TIME EFFECT ON THE RHEOLOGICAL BEHAVIOR OF CEMENT PASTE IN PRESENCE OF SUPERPLASTICIZER

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ABSTRACT

Rheology has been widely used to describe the flow properties of fresh cement-based suspensions. Nevertheless, the effect of hydration and early hydration product formation on rheology, and the effect of shear on breaking of hydration bonds is not fully understood. From the literature it is well known that the rheological properties of cement-based materials change over time due to the chemical and physical particle bounding related to the hydration of cement and thixotropy. Therefore, the characterization of these properties has become necessary to predict with precision the behavior of concrete during placement. Superplasticizers attached to cement particles, modifying its surface charge, to improve dispersion and increase the mean distance between particles. These chemicals are used in concrete to control the flow behavior and improve the workability in practice. In this study, variations in the resting time in between testing procedures were imposed to evaluate the effects on the development of internal structure of the mixture using different PCE and PNS dispersing agents. The resting time in between measurements mainly influences viscosity but this seems to be strongly dependent on the dispersant admixture used. Dependent on the admixture's workability retention, small or significant variations in the rheological properties are observed, confirming for those observations that increased resting time enhances the increase in differential viscosity. However, the effect of the employed procedure, as two procedures were evaluated, seems to have a stronger influence on the time-evolution of the rheological properties than changing the resting time in between measurements.

Keywords: cement paste, rheology, resting time, thixotropy, workability loss, superplasticizer

1. INTRODUCTION

High range water reducers (HRWR) are often used in modern highly workable concretes to tailor their properties and satisfy a wide range of construction requirements. These concretes can show complex flow behavior that can vary depending on the external conditions applied, such as: mixing, transport and placement. These modern concrete mixtures cannot be fully characterized by empirical test methods which fail to describe the intrinsic rheological properties of the material. Therefore, accurate characterization and understanding of the rheological properties of concrete has become necessary in order to assess a proper quality control and guarantee consistent performance. However, the characterization of the rheological properties of cement-based materials is challenging due to the shear and time dependency as a result of the chemical and physical particle bonding, related to the hydration of cement and flocculation [1-4]. The internal structure of the material and the flow history are also key factors that should be taken into account when measuring or predicting such properties.

Thixotropy is described as the reversible evolution of the material flow properties in cementitious systems that often occurs during the induction period of the hydration reaction [5]. When the material is at rest, internal structure of the material continuously develops over time and this evolution can be removed or broken-down by strongly shearing or remixing the material, making the properties return to the reference point [6]. The effect of flocculation, governed by attraction and dispersion forces, has been studied on cement-based materials, although many research questions still remain. While, the effect of hydration and early hydration product formation on rheology [7,8], and the effect of shear on breaking of hydration bonds is less known.

The influence of the HRWR on the flow behavior of cement-based materials depends on various parameters such as: the type, the chemical composition and the molecular structure of the admixture, as well as the chemical composition of the cement (specially the amount of C_3A and the availability of soluble sulfates), the specific surface area, and addition of mineral or other types of admixtures [9-14]. In the case of polycarboxylate esters or polycarboxylates (PCEs), the working mechanisms are based on both electrostatic repulsion and steric hindrance. The negatively charged backbone attaches to cement particles, modifying its surface charge, while the non-adsorbing side chains induce steric repulsion by increasing the mean distance between cement particles. This improves dispersion and prevents re-agglomeration of cement particles, liberating the water trapped within the flocculated structure and thus rendering the material less viscous [15-18]. The dispersion capability of PCEs is controlled by molecular weight, side chain density, and side chain length of the polymers and plays an important role in cementitious systems concerning the enhancement of workability [19-21]. Another popular type chemical admixture are the polynaphthalene sulphonates (PNS), which are polymeric molecules formed during the sulphonation process of naphthalene, followed by a reaction of condensation using formaldehyde and neutralizing the produced polysulphonic acid [22,23]. The hydrophilic part of the PNS molecule is mainly attributed to the sulfonic groups while the hydrophobic part is the naphthalene [23]. The working mechanism of PNS is based on short-range steric repulsive forces and, the presence of sulfonate groups is the responsible for negatively charging the cement surfaces. These induced repulsive forces inhibit the agglomeration of cement particles and increase the fluidity of cement pastes. One of the advantages of PNS is that their use does not interact with the stability of the pore network of entrained air. On the other hand, it does have incompatibility with low-alkali cement [24]. The generation of steric repulsive forces of these chemical admixtures overcome the attractive interparticle forces that cause flocculation [17,25].

It is also known that the ongoing hydration in cement-based materials, even during the induction period, leads to precipitation of hydration products [26,27]. These products can gradually overgrow the used dispersing admixtures, and cause connections between particles [28]. As a result, with elapsed time, the rheological properties increase. During shear, some of these formed connections can be broken, rendering the material more fluid [6]. If the process were fully reversible, consistently shearing the same sample at different time intervals would result in constant rheological properties. However, the process is not fully reversible, and a portion of the formed connections cannot be broken for the amount of shear or energy applied to the system [29]. This causes a permanent increase in rheological properties with time, also known as the workability loss.

The workability loss is governed by the type of dispersing admixture, its dosage, and the hydration reaction, which on its turn is again influenced by the type and dosage of dispersant [7,8 ,28]. Another factor which could play a role is the amount of time between two consecutive shearing periods. It has been hypothesized that the formed connections between cement particles strengthen as a function of time [30]. This implies that a formed hydration bond between two cement particles could be reversible if short resting intervals between shearing periods are imposed, but the connection could become permanent if longer resting times are imposed. As such, measuring the workability loss of cement-based materials would be dependent on the applied procedure.

This paper investigates the above theory to see whether and to which extent variations in resting times between consecutive rheological measurements affect the rheological properties evolution with time on well-dispersed cement pastes.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS AND METHODS

2.1.1. Materials. The cement pastes used in this study were produced with three different PCEs and one PNS superplasticizer to obtain a dispersed system with a mini-slump flow spread of 330 ± 20 mm. A commercially available type I/II ordinary Portland cement was used which met ASTM C150/C150M requirements. A w/cm = 0.35 was maintained for all mixtures. The liquid portion of the dispersant was subtracted from the added water. Table 1 shows the density of the cement and the different superplasticizers as well as the solid content used in this study.

2.1.2. Mixing Procedure. The cementitious systems were prepared in a small Hobart mixer, using two speed positions, in batches of 0.5 l. First, water and cement were inserted into the bowl. After 30 s of waiting, the materials were homogenized at slow speed (140 ± 5 rpm) for 30 s. This was followed by manually homogenizing the mixture by scraping the walls of the mixing bowl for 30 s while the mixer was stopped. Then, the selected dispersant was added, and the mixing continued for 120 s at medium speed (285 ± 10 rpm). Instantly after mixing, the workability of the mixture was evaluated by means of the mini-slump flow, and all rheological testing was initiated at 15 min after the contact with water. Table 2 shows the mix designs and the initial mini-slump flow of each mixture. The reported mini-slump flows are the average of all mixtures produced for this paper. The quantities of dispersing admixture were determined by means of trial batches.

Table 1. Physical properties of cement and superplasticizers used.

Material	Density (kg/m^3)	Solid content (%)
Cement	3150	-
PCE1	1030	25.80
PCE2	1075	37.00
PCE3	1080	29.50
PNS	1190	40.94

Table 2. Evaluated mix designs. Units in g/l of paste.

Mixture	Water	OPC	Initial mini-slump (mm)	PCE1	PCE2	PCE3	PNS
M1	521	1500	330	4.74			
M2	523	1500	335		2.21		
M3	523	1500	330			2.48	
M4	518	1500	300				9.60

2.1.3. Rheological Measurements. The flow behavior of the cement pastes was evaluated with an Anton Paar MCR 302 rheometer using a serrated concentric cylinder (CC) geometry at a constant temperature of 20 ºC during 150 min. The serrated geometry was chosen in order to minimize slippage between the cylinder and the sample [31]. The inner (R_i) and outer (R_o) cylinder radius were 13.33 and 14.56 mm, respectively, and the height of the inner cylinder was 40.00 mm. A plastic cover was placed on the top of the system, to protect the sample and to avoid evaporation of water during the measurements.

First, for all mixtures and all procedures, a reference state was imposed by means of pre-shearing the sample at 100 s^{-1} for 120 s at 15 min after the contact of water with cement. Immediately after pre-shearing, a linearly decreasing ramp, from 100 s^{-1} to 10 s^{-1} was imposed over a period of 25 s. At the last part of the flow curve, a logarithmic ramp from 10 s^{-1} to 0.1 s^{-1} was performed for 5 s.

Starting at 20 min, two different testing procedures were evaluated. Procedure 1 (P1) has four steps with different applied maximum shear rates: 20, 35, 60 and 100 s^{-1}. To obtain the flow curves, each constant shear rate step of 120 s was followed by a decreasing shear rate ramp to 10 s^{-1} during 15 s, in a linear fashion (Figure 1). The second procedure, named procedure 3 (P3) only uses one shearing period and it considers the time necessary to reach equilibrium in the sample at 100 s^{-1}. The different constant shear rate step durations can be found in Table 3. The flow curve measurements were evaluated similarly to previous procedure (Figure 1). Similar tests were performed with a different procedure (procedure 2 in [32]), but the results do not show significant differences with procedure 3 and are not included in this paper.

After evaluating the rheological properties of the mixture at 20 min, the sample was allowed to rest for 10 min, 30 min or 50 min for procedure 1. While for procedure 3, the entire procedure and resting time depended on the mix design. Tests were then initiated at the same times (20, 40, 60, 80, 100, 120 or 140 min - see Table 4) as for procedure 1. The starting times of the imposed testing procedure with the different resting times are in shown Table 4. It is important to mention that at the end of each rheological procedure, before each resting period, the sample was re-homogenized to avoid the effect of sedimentation on the results [33].

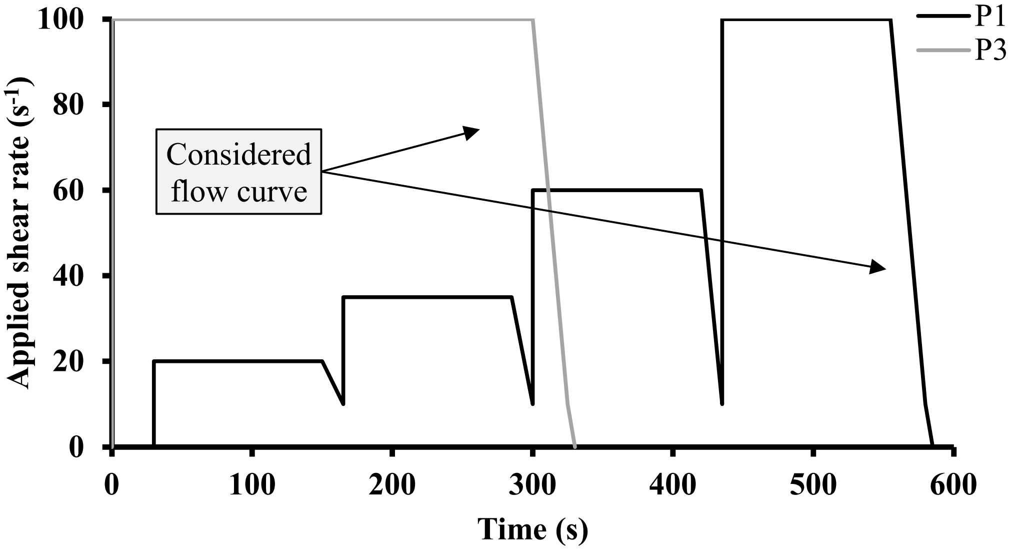

Figure 1. Rheological testing procedure 1(P1) and procedure 3 (P3).

Table 3. Duration of shearing in P3 to reach equilibrium for each mixture.

Mixture	Time (s)
M1	300
M2	400
M3	415
M4	390

Table 4. Starting time of each procedure with different resting times.

Action	10 min rest	30 min rest	50 min rest
Pre-shear + FC	15 min	15 min	15 min
P1 or P3	20 min	20 min	20 min
P1 or P3	40 min	-	-
P1 or P3	60 min	60 min	-
P1 or P3	80 min	-	80 min
P1 or P3	100 min	100 min	-
P1 or P3	120 min	-	-
P1 or P3	140 min	140 min	140 min

2.2. ANALYSIS

2.2.1. Flow Curves. To obtain the rheological properties of the studied pastes at each imposition of a procedure, the analysis was performed on the last flow curve at the maximum shear rate of 100 s^{-1} for procedure 1, and for procedure 3 on the only flow curve measured. The other flow curves are not taken into consideration in this paper. To obtain the differential viscosity, a 6th order polynomial equation was fitted on the flow curve from 100 to 10 s^{-1} (Figure 2) which was differentiated to the shear rate, describing the slope (differential viscosity). The equation was then evaluated at the average shear rate applied: which is 55 s^{-1}. In a similar way, the yield stress was obtained by fitting an equation on the portion of the curve from 10 to 0.1 s^{-1} (Figure 3) and stress was evaluated at 0.1 s^{-1}. There is no physical meaning for the coefficients in the equation, but it seems the most consistent way to express the resistance of the material to flow for the combined rheological behavior observed over all mixtures. It is the best strategy to be able to systematically describe the rheological behavior in specific shear rate ranges for all flow curves (even the ones not considered in this paper). A similar approach was followed in [30].

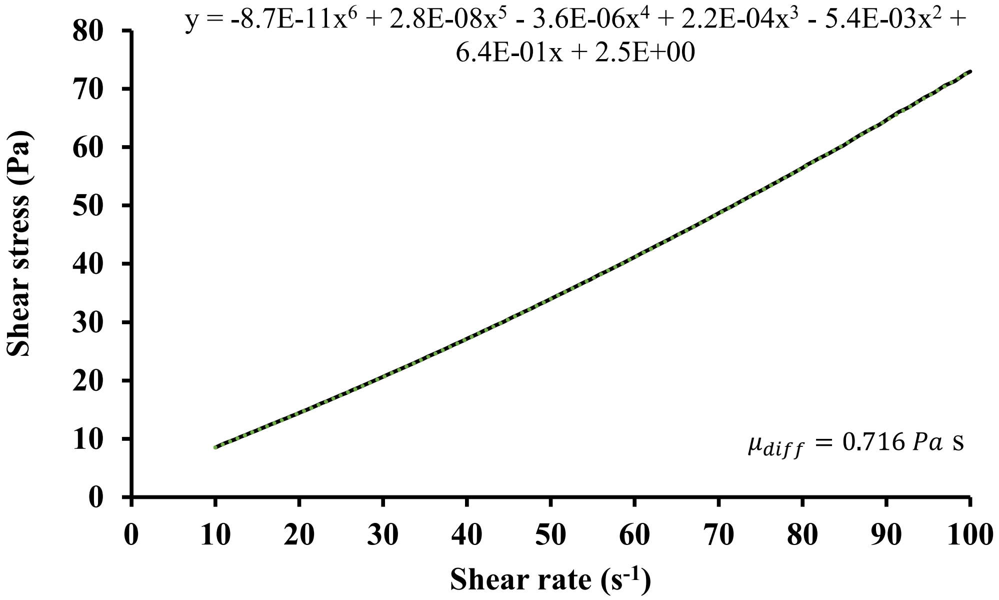

Figure 2. Shear stress and shear rate curve used to evaluate differential viscosity.

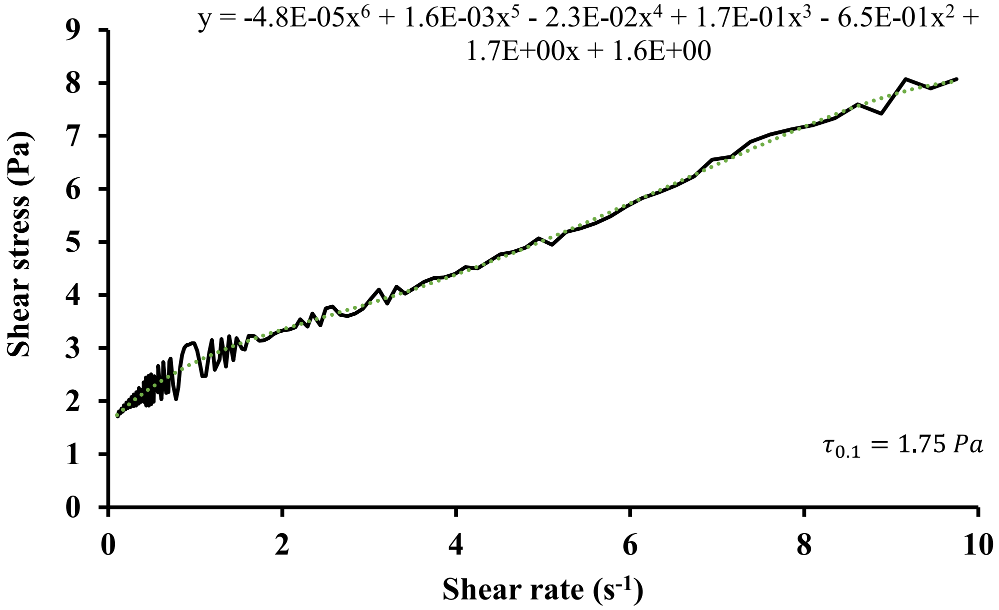

Figure 3. Shear stress and shear rate curve used to evaluate yield stress as the shear stress at 0.1 s^{-1}.

2.2.2. Pre-shear Period. The response during the pre-shear period for the cement paste samples tested with procedure 3 was also evaluated by fitting a double decreasing exponential equation on the shear stress vs. time curve (equation 1). Two parameters were extracted from each pre-shear curve: the equilibrium apparent viscosity at the end of the pre-shear period ($\eta_{app,eq}$), and the change in apparent viscosity over the pre-shear period ($\Delta\eta$). The equilibrium apparent viscosity is calculated as the constant "E" in equation 1, divided by the applied shear rate. The change in apparent viscosity is calculated as the difference between the apparent viscosity at 0.5 s during the pre-shear period, and the equilibrium value. As such, based on the values of the pre-shear period, one can compare the permanent change in rheological properties, i.e. workability loss, by investigating the evolution of $\eta_{app,eq}$ with time and different resting times, as well as the reversible portion broken during the pre-shear period, by comparing $\Delta\eta$ values. As hypothesized before, increased resting times should lead to larger changes in $\eta_{app,eq}$ with time and larger $\Delta\eta$.

$$\tau = Ae^{-Bt} + Ce^{-Dt} + E \tag{1}$$

where: τ *- shear stress (Pa)*

A, B, C, D *- fitting parameters*

t *- time (s)*

E*- shear stress at which the slope is equal to zero (Pa).*

3. RESULTS AND DISCUSSION

The differential viscosity and yield stress of the cement pastes were normalized using the respective measurement at 15 min (pre-shear) after the contact of water with cement for both procedures. Variations in the resting time in between testing procedures were imposed to evaluate the effects on the development of internal structure of the mixture using different dispersing agents such as PCEs and PNS.

3.1. EFFECT OF RESTING TIME

Figure 4 illustrates the results of mixture 1 evaluated at different resting times using procedure 3. The 90% confidence interval, determined on three repetitions of this mixture with 10 min resting time, are shown as the dashed lines. The results on viscosity are in agreement with the hypothesis that with increased resting time, more permanent structure is formed. The yield stress results seem to follow this observation, but the results are less statistically significant. Figures 5, 6 and 7 show the same results for mixtures 2 to 4. During the first 100 min in the evaluation of the different resting times, the rheological properties appear not be affected, in contrast to mixture 1. However, almost at the end of the testing around 100-140 min, where it is assumed that the effect of the superplasticizer is reduced due to overgrowing of the hydration products [34], the flow properties of the cement paste start to deviate. The reason for this apparent discrepancy at earlier age is the (unknown) workability retention mechanism of the dispersants. PCE1 is known for a lower workability retention, compared to PCE2 and 3, and with the dosage of PNS to obtain SCC-like consistency, the workability retention is known to be extensive.

Figure 8 shows the shear stress evolution of mixture 2 at 140 min with 100 s^{-1} during the pre-shear periods for procedure 3 imposing different resting periods. The results in Figure 8 and in Table 5 show the effect of the samples left to rest in between testing procedures. As known from literature, with longer resting periods, the internal structure of the material is allowed to re-structure more and build more connections in between the particles. This is reflected by the increase in $\Delta\eta$ values with increased resting time in Table 5, by comparing $\Delta\eta$ values at equal testing times. However, the results at 60 and 80 min in Table 5 do not show any significant difference between the equilibrium apparent viscosity with short (10 min) or longer (30 or 50 min) resting times for mixtures 2, 3 and 4. At 140 min, there are more noticeable differences between the equilibrium apparent viscosities as a function of resting time.

As a consequence, the permanent change in rheological properties, associated with the increase in equilibrium apparent viscosity, differential viscosity and dynamic yield stress, appears not to be affected by the employed resting times, except for mixture 1, for up to 100 min. At 140 min, some logical differences, meaning that longer resting times induce a larger increase in rheological properties, are observed for the PCE-based dispersants. This implies that, except for mixture 1, any permanent increase in rheological properties up to 100 min of age, due to hydration, is created during the 10 min resting time. Any subsequently formed connections are hypothesized to be reversible. This could be attributed to hydration connections primarily forming at near-contact points between cement particles relatively quickly [6], while other hydration bridges, formed in other locations, are not sufficiently strong to resist the 100 s^{-1} shear rate during breakdown. However, this could be a function of repulsion forces from the dispersant, surface of cement covered by the admixture and as such the admixture dosage, and the hydration reaction of the cement. Different results might be expected at lower dispersant dosages, but this is beyond the scope of this paper.

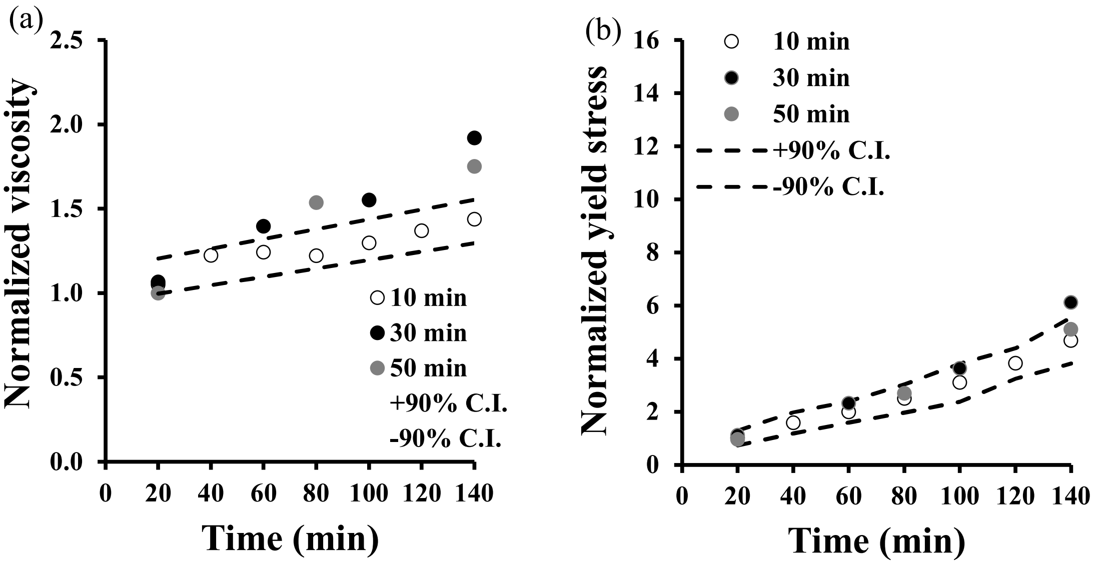

Figure 4. (a) Normalized viscosity and (b) yield stress for M1 evaluated with P3 at different resting times with confident intervals.

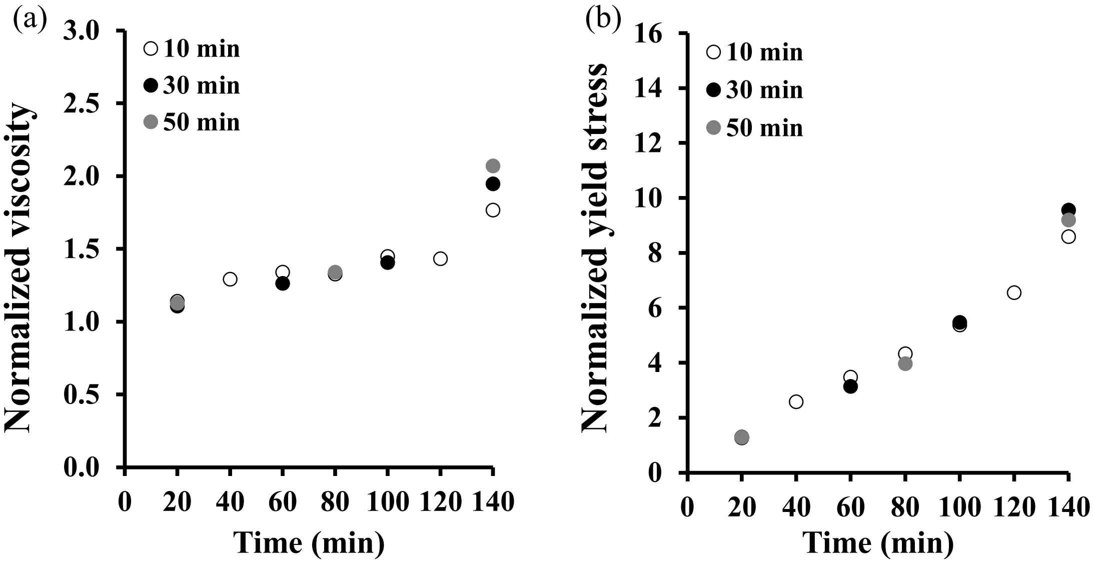

Figure 5. (a) Normalized viscosity and (b) yield stress for M2 evaluated with P3 at different resting times.

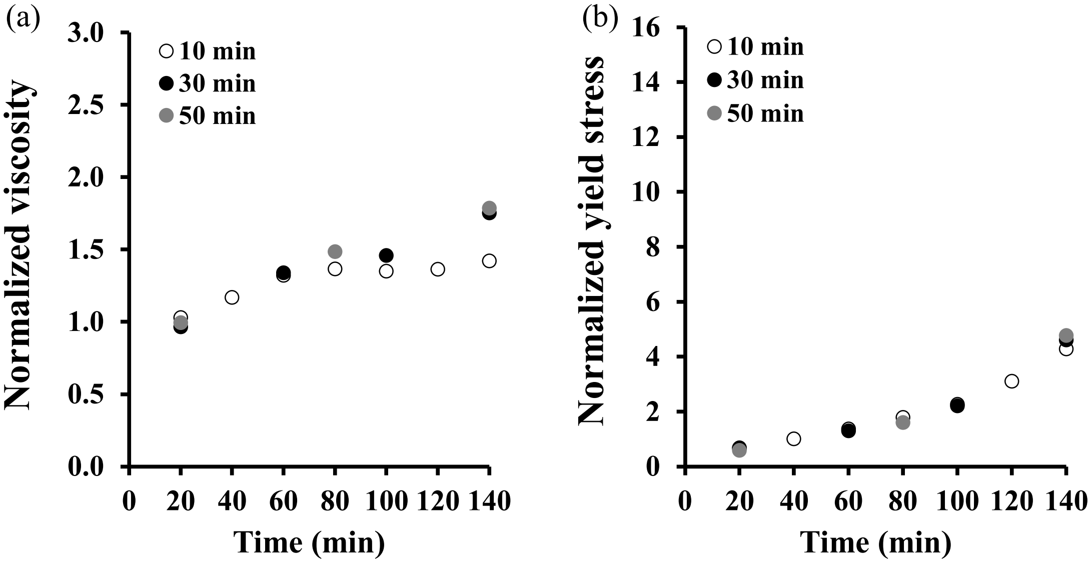

Figure 6. (a) Normalized viscosity and (b) yield stress for M3 evaluated with P3 at different resting times.

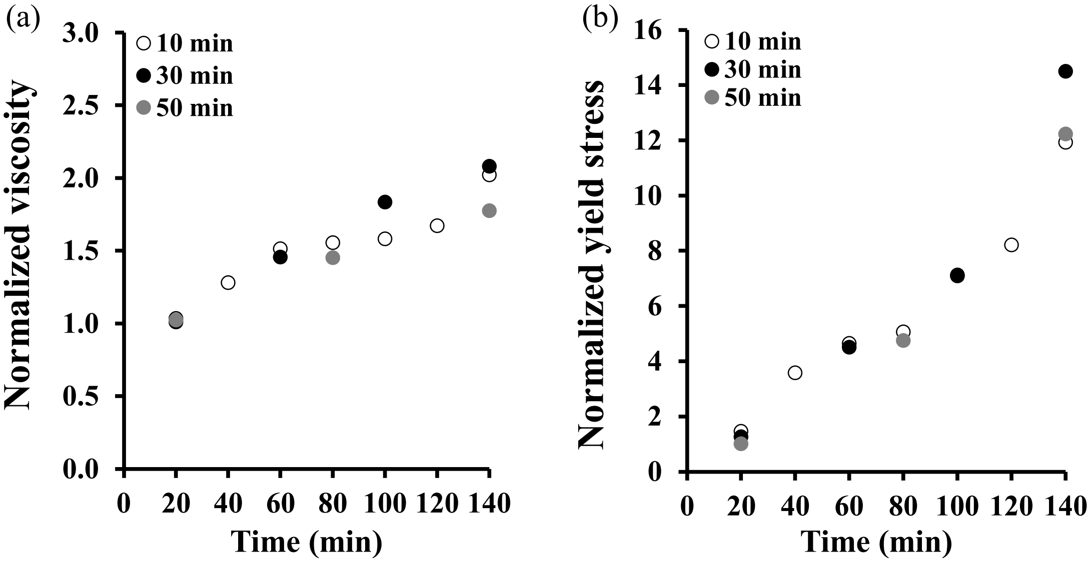

Figure 7. (a) Normalized viscosity and (b) yield stress for M4 evaluated with P3 at different resting times.

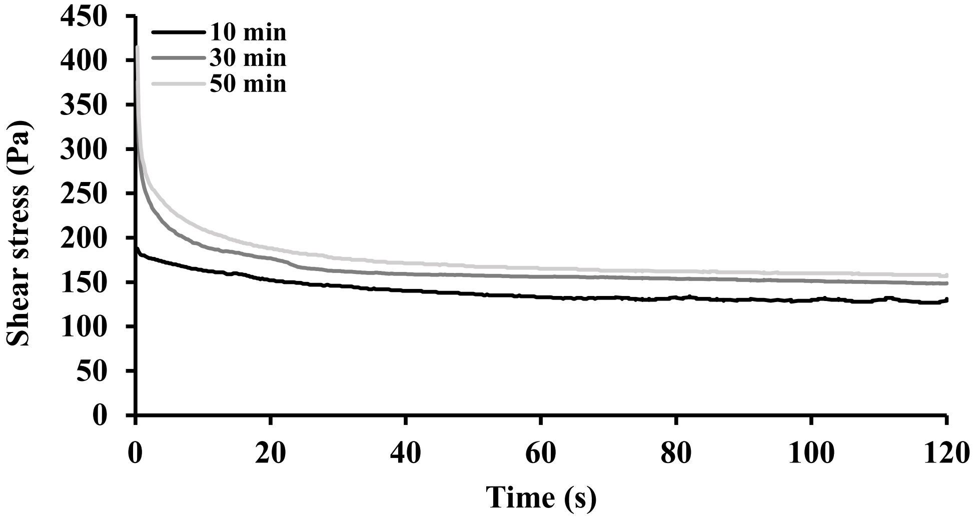

Figure 8. Shear stress evolution of M2 during pre-shear at 100 in P3 at different resting periods at a 140 min after the contact with water.

Table 5. $\Delta\eta$ and apparent viscosity of the different mixtures using P3.

	Resting time: 10 min							
Testing time (min)	**M1**		**M2**		**M3**		**M4**	
	$\Delta\eta$ (Pa s)	$\eta_{app, eq}$ (Pa s)	$\Delta\eta$ (Pa s)	$\eta_{app, eq}$ (Pa s)	$\Delta\eta$ (Pa s)	$\eta_{app, eq}$ (Pa s)	$\Delta\eta$ (Pa s)	$\eta_{app, eq}$ (Pa s)
60	0.275	0.635	0.490	0.990	0.300	0.730	0.650	1.200
80	0.238	0.644	0.439	0.991	0.284	0.766	0.663	1.297
140	0.238	0.772	0.562	1.278	0.351	0.899	1.012	1.828
	Resting time: 30 min							
Testing time (min)	**M1**		**M2**		**M3**		**M4**	
	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$
60	0.527	0.714	0.626	0.967	0.499	0.702	0.730	1.300
80	-	-	-	-	-	-	-	-
140	1.018	1.032	1.627	1.456	0.760	1.000	2.190	2.060
	Resting time: 50 min							
Testing time (min)	**M1**		**M2**		**M3**		**M4**	
	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$	$\Delta\eta$	$\eta_{app, eq}$
60	-	-	-	-	-	-	-	-
80	0.935	0.795	1.085	0.995	0.790	0.820	0.760	1.210
140	0.916	0.925	1.800	1.580	1.500	1.250	1.825	1.795

3.2. DIFFERENCES INDUCED BY THE PROCEDURE

In [32], a significant difference between the differential and equilibrium apparent viscosities and, to some extent dynamic yield stresses, was observed between procedures 1 and 3, both following the 10 min resting time protocol. These differences are observed despite shearing the sample at the same shear rate of 100 s^{-1}, assuring equilibrium, at the end of both procedures. The behavior was hypothesized to be caused by shear-enhanced dissolution and precipitation of hydration products at lower shear rates, causing the results for procedure 1 to be higher than those for procedure 3. Results from mixture 2 with different testing procedures are illustrated in Figures 9, 10 and 11 for 10, 30 and 50 min resting time protocols, respectively. These results show that, regardless of the resting time, the imposition of reference state by shearing at the highest shear rate applied on the material does not guarantee full elimination of shear history and permanent changes of the rheological properties are observed. In fact, it even seems that, for the selected mixtures, that the choice of shear rate profile has a much larger consequence on the observed changes in rheological properties with time, compared to the resting time.

When solely evaluating the data at 60 and 80 min, two comparisons can be made: based on resting time and based on procedure. The effect of the resting time is calculated by taking the ratio of the differential viscosities on measurements of the longer resting time (30 or 50 min) to the shorter resting time (10 min), both for procedures 1 and 3. This results in four values which are averaged. Similarly, the effect of the procedure can be calculated as the ratio of a measurement with procedure 1 and its equivalent measurement with procedure 3. This delivers again four values which are averaged. For example, for mixture 1, procedure 1, the normalized differential viscosity at 60 min, with a 10 min resting time was 1.6, while it was 1.856 with 30 min resting time. This gives a ratio of long-to-short resting time of 1.16 (Table 6). Similarly, the normalized differential viscosity at 60 min with 10 min resting time, using procedure 3 is 1.243, delivering a P1-to-P3 ratio of 1.29 (Table 6). Table 6 shows all ratios and averages, clearly indicating that the percent increase in differential viscosity at 60 and 80 min is larger when switching from P3 to P1 (39%, 29%, 24% and 13% for mixtures 1 through 4, respectively), than when employing a longer resting time but keeping the same procedure (19%, 3%, 5% and -2% for mixtures 1 through 4, respectively). This supports the hypothesis that, for the employed dispersants, mix designs, and testing procedures, shear-induced aggregation of cement particles delivers stronger connections leading to a faster increase in viscosity. Curiously, for mixtures 1 and 2, although the statistical significance is low, it seems that the yield stress increase with time, with procedure 1, is faster with the 10 min resting time, compared to the 30 and 50 min resting time (Figure 12). Mixtures 3 and 4 do not clearly show this effect.

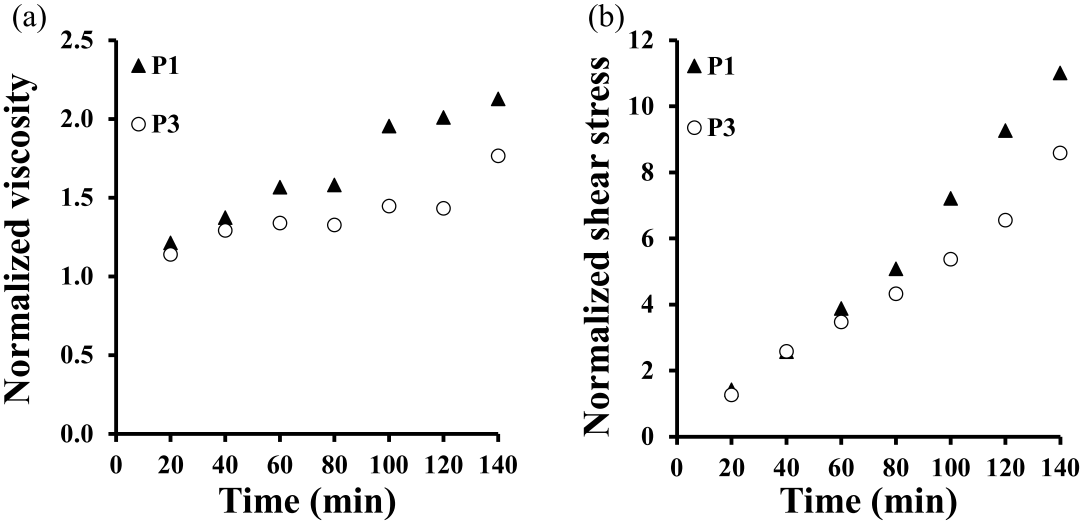

Figure 9. (a) Normalized viscosity and (b) yield stress for M2 evaluated at 10 min resting time with different testing procedures.

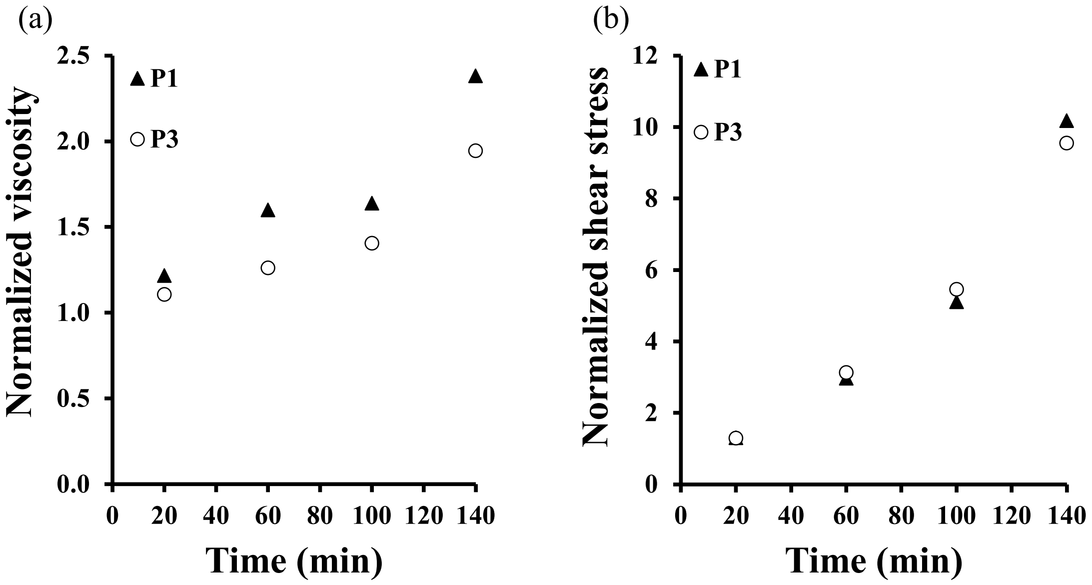

Figure 10. (a) Normalized viscosity and (b) yield stress for M2 evaluated at 30 min resting time with different testing procedures.

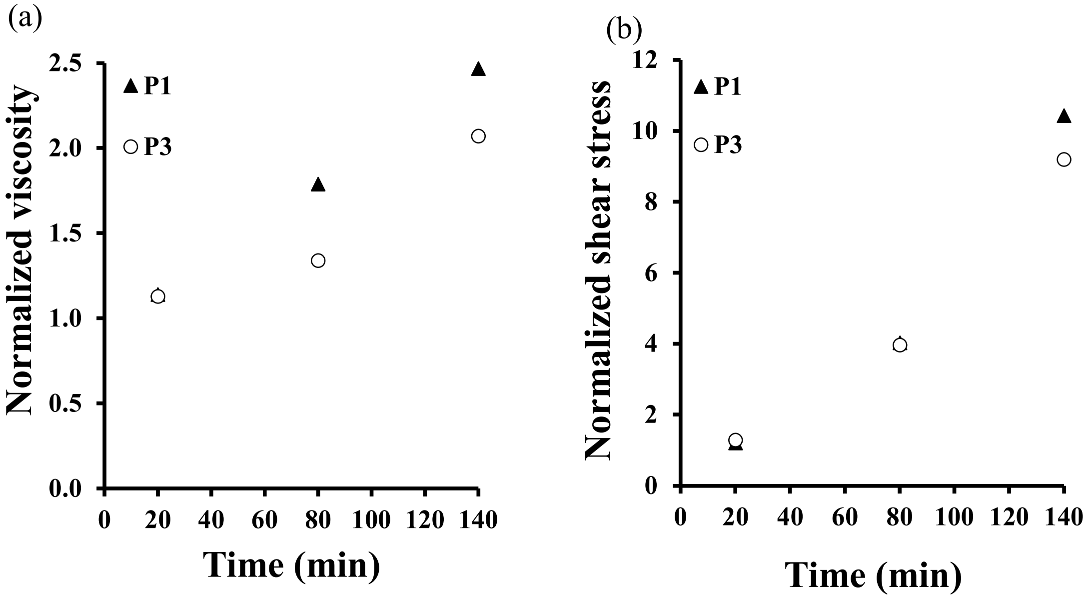

Figure 11. (a) Normalized viscosity and (b) yield stress for M2 evaluated at 50 min resting time with different testing procedures.

Table 6. Evaluation of the effect of changing procedure versus changing the resting time. Results are expressed as ratios of differential viscosities.

	Long/short: P1	**Long/short: P3**	**P1/P3: Short**	**P1/P3: Long**
M1 – 60 min	1.16	1.13	1.29	1.33
M1 – 80 min	1.21	1.26	1.51	1.44
M1 - average	1.19		1.39	
M2 – 60 min	1.02	0.94	1.17	1.27
M2 – 80 min	1.13	1.01	1.19	1.33
M2 - average	1.03		1.24	
M3 – 60 min	1.07	1.01	1.27	1.34
M3 – 80 min	1.02	1.09	1.16	1.08
M3 - average	1.05		1.21	
M4 – 60 min	0.96	0.96	1.10	1.09
M4 – 80 min	1.05	0.93	1.10	1.24
M4 - average	0.98		1.13	

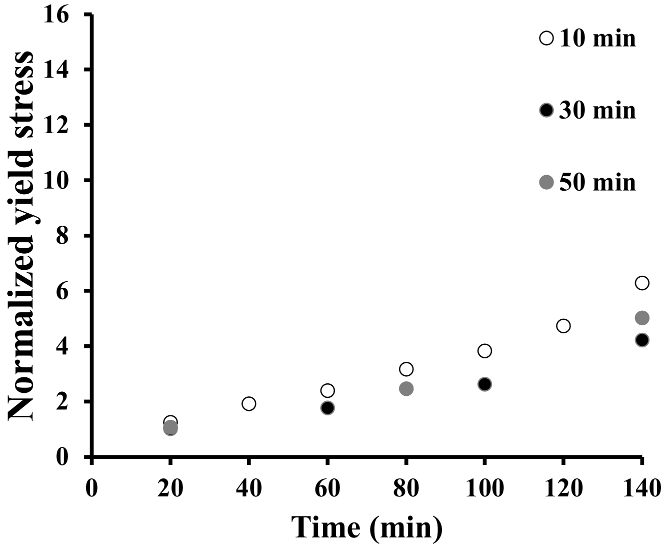

Figure 12. Normalized yield stress for M1, procedure 1, shows the opposite effect: the yield stress increases faster with time with more frequent applications of procedure 1.

4. CONCLUSIONS

The effect of different resting periods on the dynamic rheological properties of cement pastes in the presence of dispersant admixtures was evaluated with 10, 30 and 50 min resting times, to investigate to which extent resting time affects measured workability loss. Based on the results the following conclusions were drawn:

- The resting time in between measurements influences differential viscosity but this seems to be strongly dependent on the workability retention mechanisms of the used dispersing admixtures. One PCE-admixture showed a rather immediate effect. Two other PCE-admixtures only had a noticeable effect after 2 hours, and the PNS, at the dosage added, showed negligible differences.
- The dispersion mechanism of the chemical admixtures does not seem to be a factor influencing the yield stress differently when changing the resting periods.
- The shearing imposed with the different testing procedures is relatively high to break-down the structure developed during the resting periods. Analysis of the pre-shear data shows the difference in structural build-up, but a majority of the built structure is broken down, regardless of the chosen resting time.
- The above-mentioned effect on differential viscosity was noticed for a standard pre-shear + flow curve procedure (procedure 3) as well as for a more complicated procedure including different pre-shear and flow curve determinations (procedure 1). However, the significant difference between the flow curves obtained at 100 s^{-1} with the different procedures, hypothesized to be caused by shear-induced structure

formation at low shear rates, has a stronger influence on the measured properties than the resting times themselves.

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III. CHALLENGES IN RHEOLOGICAL CHARACTERIZATION OF CEMENT PASTES USING A PARALLEL-PLATES GEOMETRY

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ABSTRACT

Cement-based materials are characterized as complex suspensions that may experience a thixotropic behavior caused by physical and chemical phenomena. The characterization and understanding of the rheological properties of cement-based materials have become essential with the introduction of 3D printing in field of civil engineering. Therefore, there is a need to accurately measure such properties to obtain repeatable and consistent results. To measure the rheological properties, different geometries are available, such as vane, parallel-plates, or coaxial cylinders: These are the most used for cement-based materials. Although, there are no specific guidelines on how to select the appropriate geometry for the material that will be tested. Proper understanding of the advantages and disadvantages as well as the limitations of each geometry should be taken into account. Since parallel-plates is a common tool used to evaluate fresh cement-based materials, due to its simplicity, the small sample volume required and the variable gap that can simulate the distance between the aggregates. This paper discusses the major challenges and issues encountered when using parallel-plates geometry to measure the rheological properties of cement-based suspensions under shear. Some issues such as wall slip, sample spill, dryness, particles sedimentation, non-uniform shear rate applied, etc. can be prevented but the user should be aware of these problems.

Keywords: parallel-plates, rheology, cement-based materials, challenges

1. INTRODUCTION

Digital printing has been recently introduced into the field of civil engineering offering significant advantages, such as construction without using a formwork, which allows for a greater freedom of shape, a faster construction process and cost savings. This technology comes with engineering challenges, as some of the requirements that the formwork used to fulfill, e.g. support of the concrete, are now imposed onto the material [1]. Therefore, the proper characterization and understanding of the rheological properties of cement-based materials has become essential to successfully print the material. Cementitious pastes are characterized as complex suspensions that contain a wide particle size distribution, which are on the boundary between colloidal and non-colloidal particles. This broad distribution of polydisperse particles is influences various interaction forces depending of the size of the particles, the volume fraction in the mixture and external forces. Therefore, these pastes may experience thixotropic behavior caused by physical and chemical phenomena [2-5].

To measure the rheological properties of cement pastes, different geometries are available, such as vane, parallel-plates, or coaxial cylinders: These are the most used for cement-based materials. However, there are no specific guidelines on how to select the appropriate geometry for the material that will be tested. Proper understanding of the advantages and disadvantages as well as the limitations of each geometry should be considered. In the case of parallel-plates, which is a common tool to use to evaluate fresh cement-based materials. This due to its simplicity, the small sample volume required, surface roughness and the variable gap that can simulate the distance between the aggregates when testing. It has been shown that the rheological properties of cement-based materials are highly sensitive to variations in geometry used to test, gap size and friction characteristics of the shearing surfaces [6]. The object of this paper is to discuss some challenges encountered when using parallel-plates geometry in cement pastes.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS AND METHODS

2.1.1. Materials. A commercially available type I/II ordinary Portland cement complying with ASTM C150/C150M specifications was used to produce the cement paste mixtures with a water-to-cement ratio (w/c) of 0.45. A polycarboxylate-based superplasticizer (SP) with a solid content of 25.8 % was incorporated to obtain a dispersed system with a mini-slump flow spread of 330 ± 10 mm. The specific gravity of the cement and the SP is 3150 kg/m^3 and 1032 kg/m^3, respectively.

2.1.2. Mixing Procedure. The mixtures were prepared in 1.0 l batches in a small Hobart mixer using two speed settings. The mixing sequence consisted of introducing first the water and then the cement into the bowl and wait for 30 s. The mixer was started at slow speed (140 ± 5 rpm) for 30 s to homogenize the materials. After that, the mixer was stopped for 30 s and the mixture was manually homogenized by scraping the walls of the mixing bowl. After this scraping period, SP was added and the mixing continued for 120 s. Immediately after mixing, the mini-slump flow of the mixture was measured, and all rheological testing was performed at 15 min after the contact with water.

2.1.3. Rheological Measurements. The rheological measurements were performed at a constant temperature of 20 ºC using sandblasted parallel plates (PP) geometry, unless stated otherwise, in an Anton Paar MCR 302 rheometer. The plates were 50 mm in diameter and the gap was varied from 0.25 to 1.5 mm. Sandpaper disks (#60 grit) of 50 mm were used in some cases to minimize slippage between the plates and the sample. To avoid evaporation of water from the sample a temperature-controlled hood was typically placed on the top of the system. To compare the rheological properties measured with different geometries, a serrated concentric cylinder (CC) was used with an inner radius (R_i) of 13.33 mm, outer radius (R_o) equal to 14.56 mm and the height of the vertical part of the inner cylinder is 40.00 mm.

The testing procedure was executed at 15 min after the contact of water with cement. First, the sample was pre-sheared at 100 s^{-1} for 120 s to minimize measurements artifacts caused by breakdown of internal structure and to impose a reference state [7]. Then a linearly decreasing shear rate ramp, from 100 s^{-1} to 10 s^{-1} was imposed over a period of 30s. The rheological properties were determined using the transformation equation for parallel plates geometry. The equation (eq. 1) transforms the relative units into a relationship between shear rate and shear stress. The intercept of torque (T) and angular velocity (Ω) curve (G) is transformed into yield stress (YS) using eq 2. The plastic viscosity (PV) of the pastes was determined using the slope of the curve (L) and transformed using eq 3. Similarly, CC data was transformed using the Reiner-Riwlin for concentric cylinder equation described in [7]. Similarly, the yield stress and viscosity of the CC geometry were transformed using the Reiner-Riwlin for concentric cylinder.

$$T = G + L\Omega \tag{1}$$

$$\tau_0 = \frac{3G}{2\pi R^3} \tag{2}$$

$$\mu_p = \frac{2HL}{\pi R^4} \tag{3}$$

where: *T = Torque (Nm)*

Ω= Angular velocity (rad/s)

τ_0= yield stress (Pa)

μ_p= plastic viscosity (Pa s)

R= radius of plate (m)

H= gap between the plates (m)

3. RESULTS AND DISCUSSION

3.1. EVAPORATION OF WATER (DRYING)

A series of cement pastes mixtures were produced in a previous study [8], where the influence of using a temperature-controlled hood to prevent drying of the sample was found to be critical for prolonged testing procedures. Table 1 results for the mixtures with a water-powder ratio (w/p) of 0.35 containing slag (dose by mass 25%), silica fume (SF-5%) and attapulgite clay (Att clay-0.5%). The evolution of the rheological properties over time are expressed as the change in yield stress and plastic viscosity, from 15 to 45 min, with and without hood. The variation in the rheological properties over time is significantly smaller when the hood is engaged, except for the plain cement system. The reason of such discrepancy is unknown. The percentage change when using or omitting the hood is higher when the mixtures are composed by additional powders besides cement, this behavior can be due the increased surface area provided by the powders. Additional surface area will have a higher water demand and the effect of the evaporation will be more critical in these systems.

Table 1. Time-evolution of rheological properties of pastes with and without hood.

Mixture	**YS (Pa/min)**			**PV (Pa s/min)**		
	Hood	**No hood**	**% Change**	**Hood**	**No hood**	**% Change**
CEM	0.563	0.285	-49	0.006	0.004	-29
Slag + Att clay	0.032	0.162	407	0.003	0.010	180
SF + Att clay	0.006	0.215	3191	0.001	0.014	693
Slag + SF + Att clay	0.016	0.246	1425	0.002	0.021	888

3.2. GAP SIZE

This section discusses the effect of different gap sizes between the sandblasted parallel plates on the rheological properties of cement pastes. According to literature, the selection of the gap size to obtain consistent results should be at least an order of magnitude larger than the maximum particle size [9,10]. However, the ideal gap size depends on other factors such as the depth of the serration of the plate, shear rate and the plate diameter [11]. Figure 1 illustrates the shear stress values at a constant shear rate at 1, 0.5 and 0.25 mm gap up to 120 s, followed by a flow curve. In the case of a small gap size a liquid-solid phase segregation is critical due to the limited sample size. Therefore, the results at 0.25

mm show more scattering, which might be caused by the sensitivity to the squeeze velocity applied to the sample [12]. Table 2 show that increasing the gap size from 0.5 mm to 1 mm decreases the plastic viscosity. This can be explained as the effect of confinement of the samples is reduced when the gap size is increased. This behavior was also observed in previous studies [6,11]. Yield stress values are not reported since the models used for linear and non-linear fitting led to negative values, which have no physical meaning.

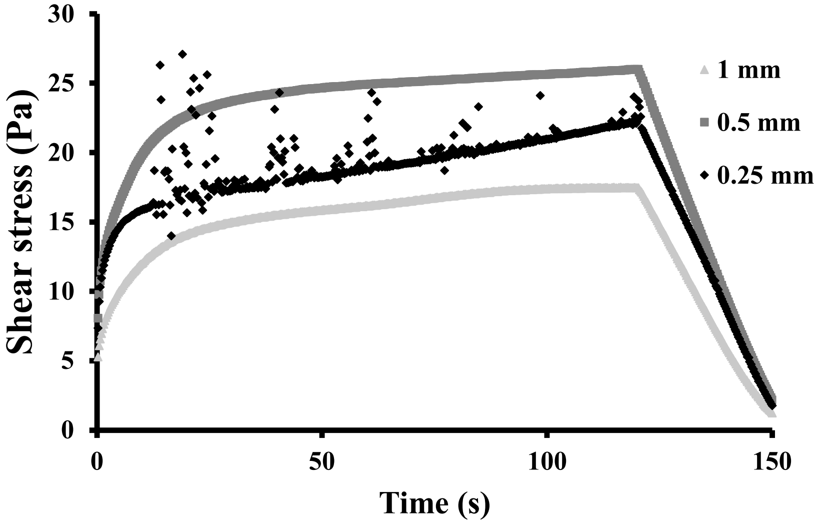

Figure 1. Shear stress vs time curve for different gap sizes with sandblasted parallel plates.

Table 2. Rheological properties using different gap size.

Gap (mm)	**PV (Pa s)**
1.0	0.188
0.5	0.269
0.25	0.234

3.3. WALL SLIP

Yield stress and viscosity measurements might be influenced by the friction between the sample and the shearing surfaces. Previous studies have shown that a smooth shearing surface increases the possibility of experiencing slippage (Figure 2 (a)) and flow localization [13-15]. Slippage occurs when cement particles move away from the smooth wall of the shearing surface, causing a decrease in particle concentration, producing a lubrication effect enhancing the flow and resulting in erroneous estimations of the rheological properties. This phenomenon is more pronounced to develop at stresses near the yield stress [16]. In order to prevent the lubrication layer to form, the use of texture or roughness on the shearing surfaces is desired (Figure 2 (b)), to a certain extent. This depends on the nature and size of the dispersed particles [6].

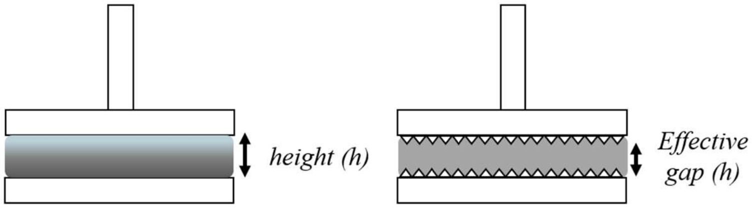

Figure 2. (a) Smooth plates (b) Serrated plates.

3.4. GEOMETRY COMPARISON AND SURFACE CONDITION

To evaluate the influence of different geometries on the rheological properties of cement pastes, two geometries were used and the average of three replicates was considered. Figure 3 shows the shear stress vs time for CC, PP and PP with sandpaper (PP-SP), and the flow curves with the different geometries. The results in Figure 3 (a), show during the pre-shear, when using the PP geometry, an increase in shear stress at a constant shear rate (100 s^{-1}), which does not agree with the literature. CC show a decreasing shear stress due to structural breakdown [7]. In order to avoid any potential slippage between the sample and the rheometer surfaces, sandpaper disks were used to increase the friction between the sample and the shearing surfaces. PP-SP shows similar behavior as CC in the pre-shear period, but the values of the rheological properties were significantly lower. The behavior of the flow curves with different geometries and surface roughness is illustrated in Figure 3 (b). The results of PP geometry show higher viscosity compared to the other systems, but the yield stress was not reported since the flow curve intercepted the shear stress axis in the negatives range. PP-SP rheological properties are lower, not agreeing with reported in previous studies [11] where viscosity increases when surfaces roughness increases. This discrepancy may be due to a measurement artifact that occurs when the true gap (h) is larger than the apparent gap (h_a) calibrated by apparent contact of the plates [17,18]. In addition, the effect of the squeezing speed during gap positioning that may alter the w/c due to a phase separation, which significantly influence the rheological properties [12]. The transformation function for the slope of the T-Ω to the plastic viscosity (equation 3) shows linear dependence on the gap size (H).

Table 3 shows the rheological properties and the standard deviation of the cement paste measured using different geometries and plate roughness.

Table 3. Rheological properties of cement paste using different geometries.

Geometry	**YS (Pa)**	**ST DEV**	**PV (Pa s)**	**ST DEV**
CC	1.654	0.072	0.160	0.001
PP	-	-	0.253	0.014
PP-SP	0.840	0.136	0.059	0.004

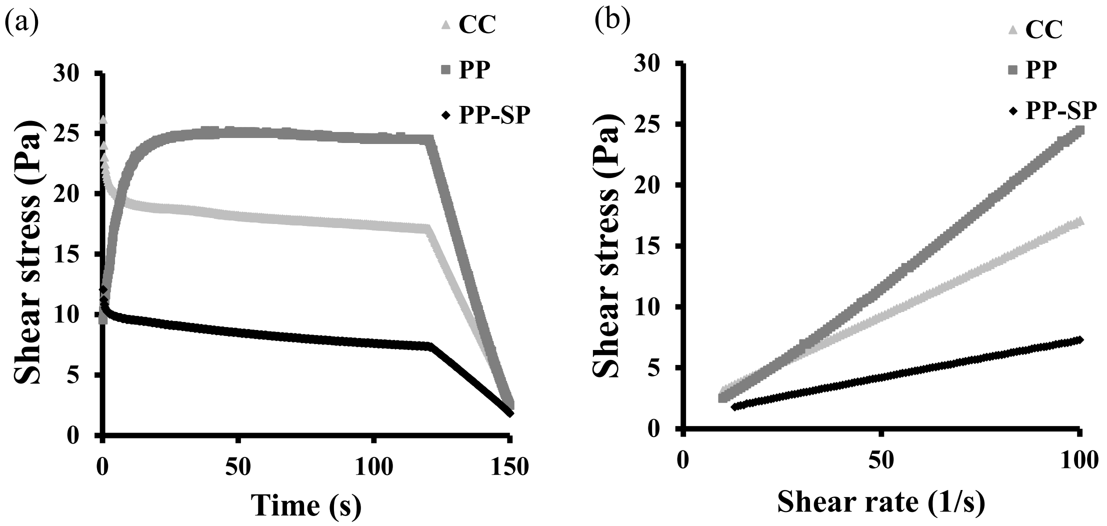

Figure 3. (a) Shear stress vs time curve - (b) Flow curves with different geometries.

3.5. OTHER CHALLENGES

Additional issues can also be included in the list of possible ways that the rheological measurements can go astray, invalidating any further interpretation of data. One important point is the sample volume. In PP geometry, torque is very sensitive to the surface contact of the sample and the shearing plates. Underfill is more susceptive than overfill to an uneven shearing of the sample, but in both cases those problems cause errors on the measurements [17]. Figure 4 (a) shows a sample spill after the testing procedure was executed. This phenomenon occurred due to a high shear rate applied to the sample (300 s^{-1}), therefore a proper shear rate must be selected that is relevant for the application of the material and leads to minimal errors. Another issue is sedimentation of the particles: When particles settle, the water in the mixture migrates to the top, causing bleeding. Figure 4 (b) illustrates a sample of cement paste exhibiting bleeding, which results in lower rheological properties. In case a sample is susceptible to bleeding, a concentric cylinder geometry is usually recommended [17], but that does not guarantee adequate measurements either.

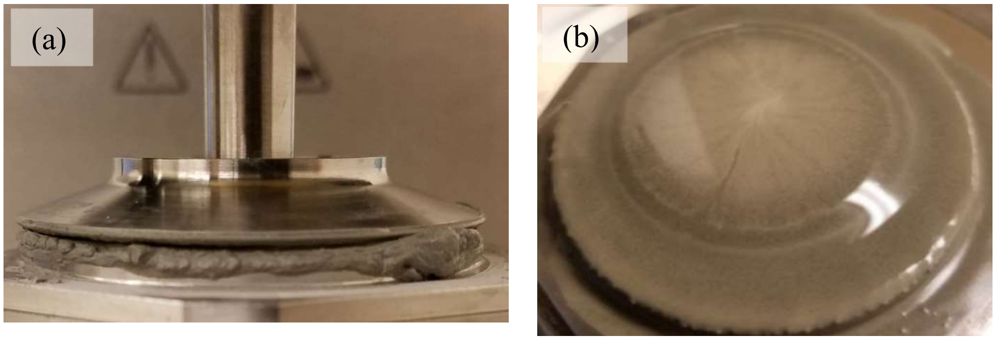

Figure 4. (a) Sample spill (b) bleeding of the sample after measuring.

4. CONCLUSIONS

Some of the challenges encountered when measuring the rheological properties of cement-based materials using parallel plates geometry are drying of the sample, varying gap size, wall slip, particle sedimentation and surface conditions. However, some of these issues are inherent to the nature of the sample. Therefore, a proper selection of the rheometer geometry and setup details is of paramount importance in order to get reliable, accurate and reproducible data.

- The evaporation of water is highly critical in systems containing additional powder due to the additional surface area, having higher demand leading to a higher rate of increase of the rheological properties over time. The use of evaporation protection, such as a temperature-controlled hood, is recommended.

- Increasing the gap size from 0.5 mm to 1 mm between the sample and the shearing surfaces, decreases the plastic viscosity, since the confinement of the particles is reduced.
- Wall slip can be prevented enhancing the texture of the shearing surfaces.
- CC geometry appeared to be more appropriate to measure the rheological properties for the cement paste with a w/c of 0.45.
- The use of PP with rough sandpaper disks may cause a measurement artifact due to inaccuracies during the determination of the gap or secondary flows.
- PP geometry is more sensitive to changes in the sample volume causing uneven shear rates and errors during the measurement. Also, it is more susceptible to obtain less repeatable rheological properties when the sample has a risk for bleeding.

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IV. EFFECT OF SEDIMENTATION ON THE RHEOLOGICAL PROPERTIES OF CEMENT PASTES

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ABSTRACT

Rheology has been widely used to describe the flow properties of fresh cement-based suspensions. Nevertheless, the characterization and understanding of the rheological behavior of cement-based materials have become essential with the recent introduction of novel applications like digital construction in the field of civil engineering, among others. It has been well documented that concrete and mortar may suffer stability problems (i.e the ability of the mixture to maintain homogeneous). At the scale of cement paste, this phenomenon can still arise and depends highly on the viscosity of the medium and the density difference between cement and water. The settling of the cement particles is a consolidation process that displaces water through a dense system of cement particles resulting in bleeding. During the evaluation of the rheological properties, sedimentation of cement particles may occur and affect the properties of the measured paste. Therefore, inaccuracies during the measurements and incorrect interpretation may occur, resulting in erroneous conclusions. This study explores the impact of sedimentation of cement particles when characterizing the rheological properties of cement paste. The w/c employed in the pastes were 0.45 and 0.35 with the addition of superplasticizer to obtain a dispersed system. The rheological properties were measured using a coaxial cylinder configuration and followed up to 180 min after the contact between cement and water. The results indicate that the time-evolution of the rheological properties is strongly affected by the settling of the cement particles.

Keywords: cement-based materials, rheology, testing procedure, sedimentation, time, workability loss

1. INTRODUCTION

Cement paste is categorized as a concentrated suspension since the discrete cement particles are suspended in a continuous fluid (water) and the solid volume fraction is higher than 0.25. Often, the cement particles, which are poly-dispersed in size with an average particle size of ≈ 20 µm, tend to settle as they are denser than the average system density. The origin of concrete and mortar stability problems (i.e. the ability of the mixture to maintain homogeneity) has been well documented [1-5]. The overall segregation resistance of concrete can be divided in two major characteristics: the ability of mortar to keep the coarse aggregate from sinking, while the stability of mortar depends on the cement paste capacity of retain the sand particles in suspension [6]. When concrete is at rest, static stability is achieved when the yield stress of the mortar in combination with the buoyancy of the coarse aggregates is sufficiently high in order to maintain the aggregates in suspension [7-9]. This process can be aided by the particle lattice effect as smaller, stable particles can keep the larger, theoretically unstable particles, in place [10-12]. On the other hand, under dynamic conditions, the viscosity is expected to have a significant role. During motion, the yield stress is exceeded, sometimes only in specific zones, which may allow aggregates to settle. Therefore, higher viscosities will help drag aggregates along with the flow and reduce the rate of sedimentation until the concrete comes to rest [13].

At the scale of cement paste, phase separation can still arise and depends highly on the viscosity of the medium and the density difference between cement and water. It may occur at rest simply because the gravity forces differ from one element to the other. It also can occur during flow, which is known as shear-induced sedimentation in yield stress fluids [14]. The settling of the cement particles is a consolidation process that displaces water through a dense system of cement particles. It is also known as bleeding [15-18]. This is a critical problem, when settling occurs, the material loses its homogeneity and this can affect its properties. The stability of a cementitious paste depends on different factors such as: constituent's properties, mix design and rheological properties including viscosity and thixotropy [19]. The general knowledge of this phenomenon is rather simple but limited in terms of its effects on rheological characterization.

The rheological properties of cement paste are strongly depended on the volume fraction of the particles, the viscosity of the continuous phase, as well as on the extent to which the particles are flocculated or dispersed [20]. The Krieger-Dougherty equation (Equation 1), which is an extension of the Einstein equation [21], describes a non-linear relationship between the relative viscosity (η_r) and the solid volume fraction (ϕ) in the suspension. When there is a decrease in the concentration of the solid particles, the relative viscosity of the suspension decreases [22]. As such, any local changes in concentration due to sedimentation will locally alter the rheological properties.

$$\eta_r = (1 - \frac{\phi}{\phi_m})^{-[\eta]\phi_m} \tag{1}$$

In contact with water, flocculation of the cement particles occurs, and early hydrates start to form preferentially at the contact points between the flocculated cement grains forming a network. The cement suspension begins to flow as soon as sufficient shear is applied to the system to overcome the network of interacting cement particles. This flow onset is defined as the yield stress. The resistance to bleeding and the yield stress of the material depend on the interactions between cement particles and the particles concentration [18,20]. Yield stress decreases as concentration and degree of flocculation decreases [20].

The settling rate of the suspended solid particles is generally calculated from the balance of gravity and drag forces. To avoid separation of the solid particles from the liquid, the only practical solution is to induce sufficient agitation to the system, which will produce some lift or dispersion forces to the particles [23]. Phase separation in cement paste may occur and affect the properties of the measured paste. Therefore, inaccuracies during the measurements and incorrect interpretation may happen, resulting in erroneous conclusions. The focus of this paper is to evaluate the impact of phase separation when characterizing the rheological properties of cement paste.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS AND METHODS

2.1.1. Materials and Mixing Procedure. The cement paste mixtures were prepared using type I/II ordinary Portland cement with a w/c of 0.35 or 0.45. To obtain a dispersed system with a mini-slump flow spread of 330 ± 10 mm, a polycarboxylate-based superplasticizer (SP) with a solid content of 25.8 % was incorporated. The specific gravity of the cement and the SP is 3150 kg/m^3 and 1032 kg/m^3, respectively. The mixing procedure was conducted as shown in the following table:

Table 1. Mixing sequence for the tested cement pastes.

Task	**Time**	
	Partial (mm:ss)	**Cumulative (mm:ss)**
Introducing water and cement in the bowl	0:30	0:30
Material homogenization at slow speed (140 ± 5 rpm)	0:30	1:00
Rest period and scrapping bowl walls	0:30	1:30
The dispersant was added and then mixed at medium speed (285 ± 10 rpm)	1:00	2:30

2.1.2. Rheological Measurements.

The rheological properties were measured using a concentric cylinders geometry with the inner (R_i) and outer (R_o) cylinder radius of 13.33 and 14.56 mm, respectively and the height of the inner cylinder of 40.00 mm. The device employed is an Anton Paar MCR 302. A special insert was created to fit the bottom of the rheometer cup (Figure 1). It created a gap of 2 mm and it had the same angle as the cone-shape of the inner cylinder. The insert was developed to enable testing of materials which have limited availability. To avoid drying of the sample, a plastic cover was placed on the top of the system during the measurements. Figure 2 shows the testing procedures used in this paper, where procedure 1 and procedure 2 have the same shearing time but different applied shear rates. Regardless of the procedure, a pre-shear was imposed at 100 s^{-1} for 120 s to impose a steady state [24] at 15 min after the contact of water with cement.

The testing procedure started at 20 min and measured every 20 min for up to 180 min. As can be seen in Figure 2, flow curves were determined after each preshear, by decreasing the shear rate linearly from the applied preshear to 10 s^{-1} in 15 s. For the last curve, a logarithmic decrease to 0.1 s^{-1} was added during 5 s.

To investigate the effect of sedimentation of the sample during the measurements, a homogenizing procedure was imposed on a portion of the executed measurements. Once the rheometer finished the testing procedure, the inner cylinder was carefully decoupled from the rheometer head. Then, the rheometer head was lifted to have enough space to homogenize the sample. Without exposing the inner cylinder to the air, to avoid drying of the cement paste stuck to the cylinder wall, a homogenizing tool was inserted and moved along the gap to re-homogenize the sample for 1 min. The tool was moved in a vertical sawing motion to re-suspend some of the sinking particles. The conical shape of the insert was helpful to be able to re-suspend the particles at the bottom of the rheometer. Finally, the rheometer head was positioned close to the inner cylinder to couple them back and the protective cap was placed back on top to avoid evaporation, the sample was left undisturbed until the next testing procedure.

2.2. ANALYSIS

The employed analysis for the rheological measurements in this study was done using the last flow curve at the maximum shear rate of 100 s^{-1} for both procedures. A 6th order polynomial was used to describe the shear stress-shear rate curve from 100-10 s^{-1} (Figure 3) and then differentiated by the shear rate to obtain a 5th order polynomial, which was evaluated at 55 s^{-1}, which is the median shear rate, to obtain the differential viscosity.

In a similar way the yield stress was acquired by fitting an equation to the curve of 10-0.1 s^{-1} (Figure 4) and then evaluated at the minimum shear rate of 0.1 s^{-1}.

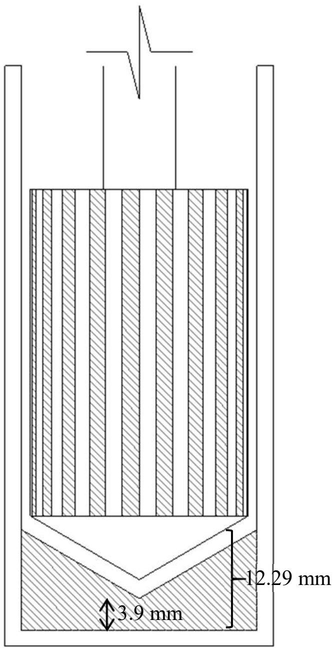

Figure 1. Layout of the rheological test set up with inset.

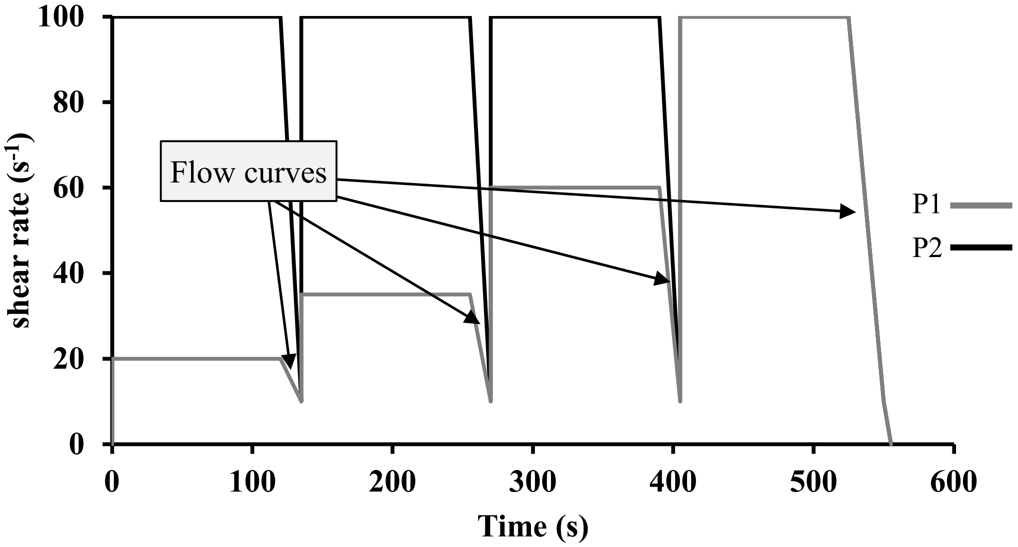

Figure 2. Rheological testing procedure, repeated every 20 min.

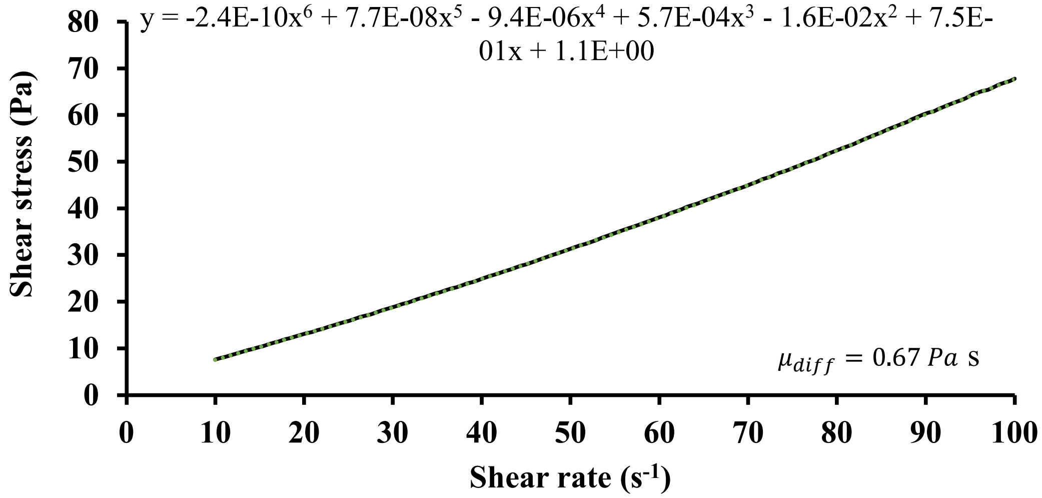

Figure 3. Shear stress and shear rate curve used to evaluate differential viscosity at 55 s^{-1}.

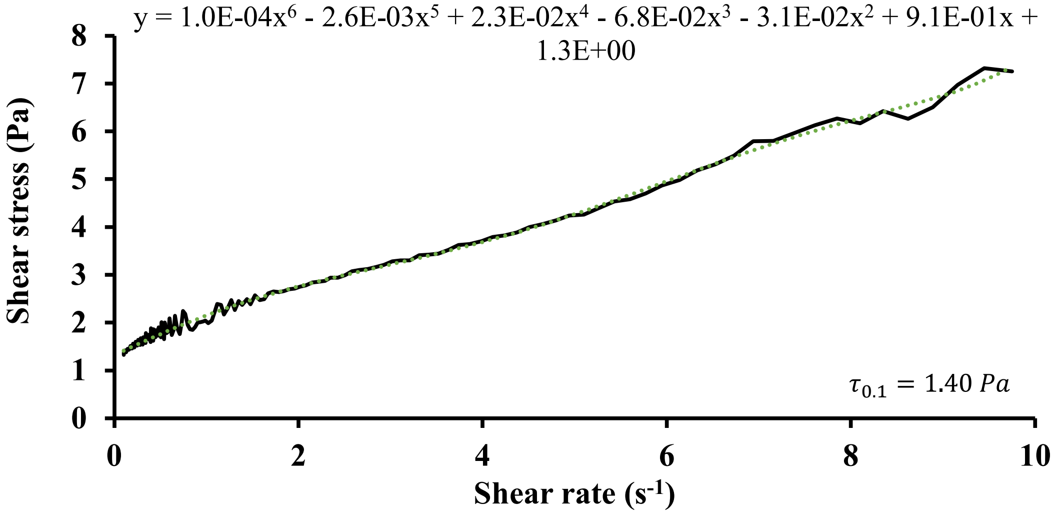

Figure 4. Shear stress and shear rate curve used to evaluate yield stress as the shear stress at 0.1 s^{-1}.

3. RESULTS AND DISCUSSION

Figure 5 to Figure 7 show the effect of sedimentation on the rheological properties of cement paste with different w/c as a function of elapsed time, when normalizing the differential viscosity or yield stress by the result obtained at 15 min. Each graph shows two replicates: a sample which is not homogenized between tests and a sample which is. Figure 5 shows the results for the mixture with w/c = 0.45 and procedure 1. Figures 6 and 7 show the results for the w/c = 0.35 mixture with procedures 1 and 2, respectively.

Results show that the change in concentration of cement particles in the rheometer gap during testing highly affects viscosity after one or two executions of the procedure. Meanwhile, the yield stress does not seem to be affected until after 120 min, except for the 0.45 w/c mixture, where a dramatically increase is observed. When procedure 2 is applied, with a constant applied shear rate of 100 s-1, lower rheological properties are observed in spite of having the same shearing time as procedure 1. Therefore, applying higher shear rate in on the sample is sufficiently to break part of the internal structure of the paste, or prevent the shear-induced building of these connections, results in lower rheological properties [25,26]. Therefore, procedure 2 displays more sedimentation of the sample compared to procedure 1. Figure 8 shows how the shear stress in the non-homogenized sample increases during the measurements with procedure 2 compared to the homogenized sample. Only the pre-shear values are shown, the flow curves were removed for clarity. The shown tests in Figure 8 are at the 4th application of the procedure, at 80 min of age. Initially, this behavior was attributed to the effect of the continuous hydration reaction, that has been observed in previous study paper at low-shear rates [27]. To confirm if the observed increase in shear stress at constant shear rate can be attributed to hydration or sedimentation, an evaluation of the rheological properties of a limestone system was done with continuous shearing through during the 10 min resting times to accelerate the sedimentation. Figure 9 shows similar behavior to the cement system, which eliminated the hydration reaction hypothesis. Also, increasing the w/c from 0.35 to 0.45 decreases viscosity of the paste due to a lower volume of particles, thus increasing the settling rate of the cement particles, leading to a much faster difference between the homogenized and non-homogenized procedures.

Figure 10 shows bleed water coming to the top while the testing procedure was in progress, while Figure 11 displays a plug of cement paste found at the bottom of the rheometer cup at the end of the test, which confirms that sedimentation happens during measurements, especially when the sample is not homogenized. Samples that were homogenized did not have a substantial amount of consolidated paste at the bottom of the cup.

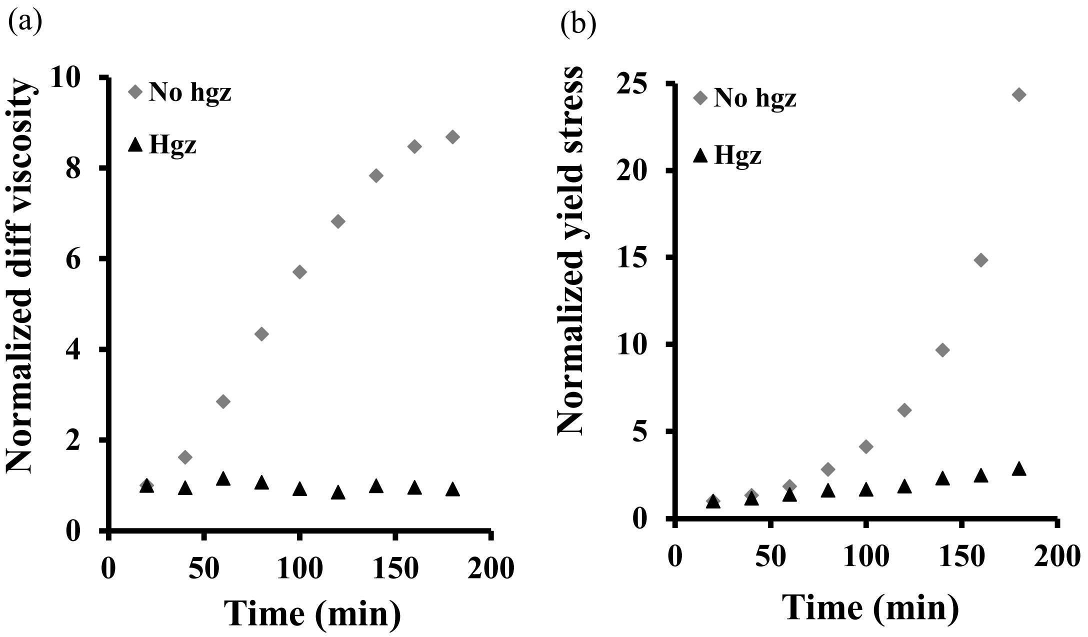

Figure 5. Evolution of normalized (a) differential viscosity and (b) yield stress of 0.45 w/c paste with and without homogenizing using procedure 1.

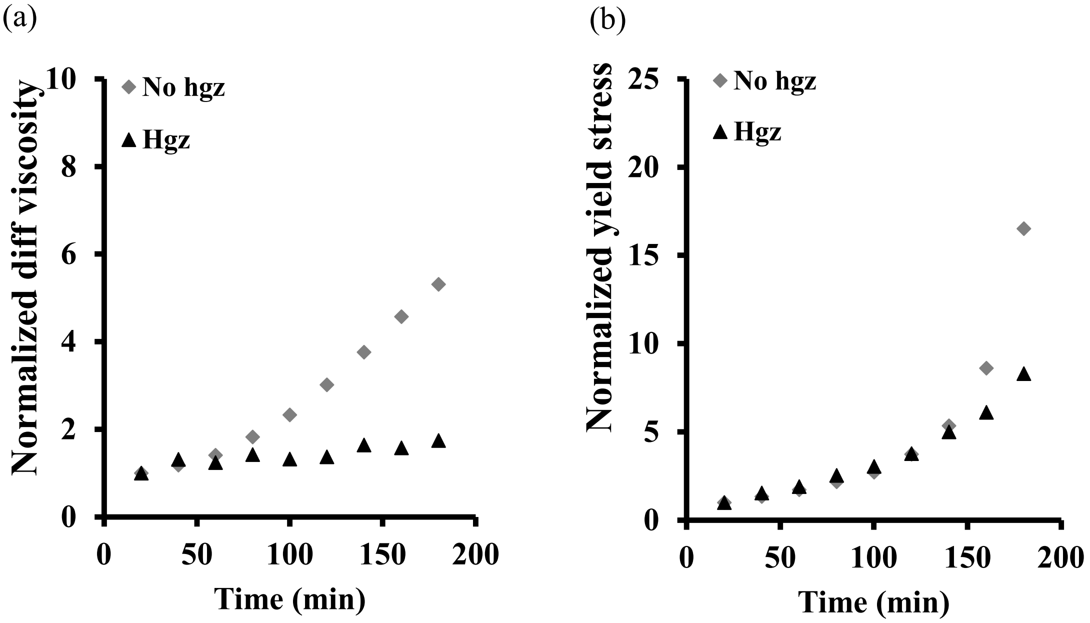

Figure 6. Evolution of normalized (a) differential viscosity and (b) yield stress of 0.35 w/c paste with and without homogenizing using procedure 1.

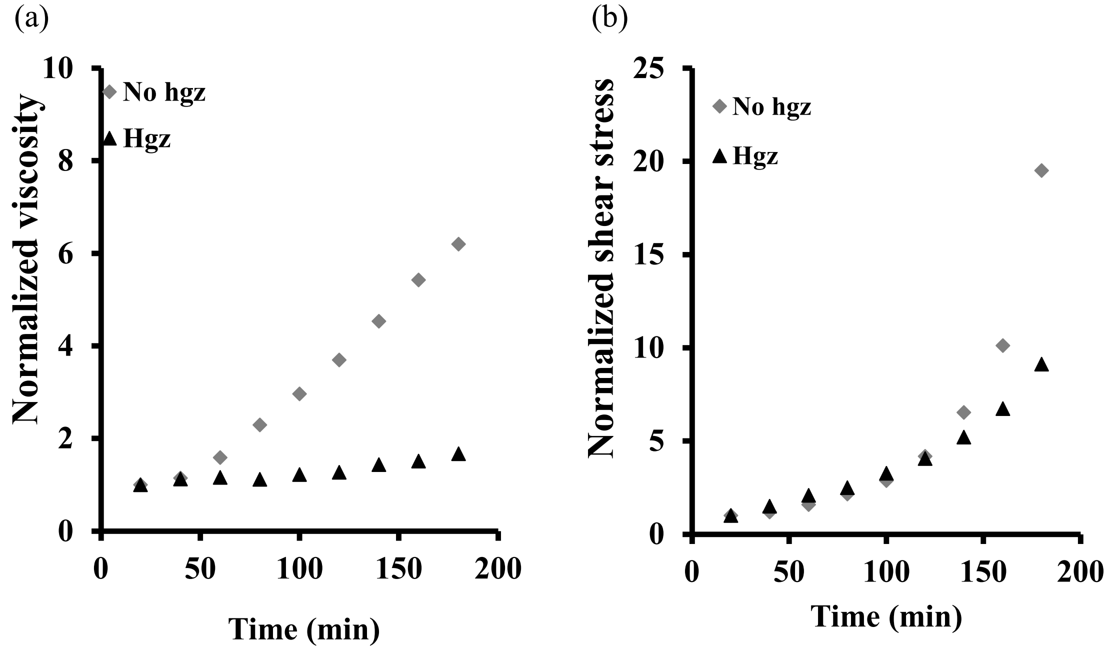

Figure 7. Evolution of normalized (a) differential viscosity and (b) yield stress of 0.35 w/c paste with and without homogenizing using procedure 2.

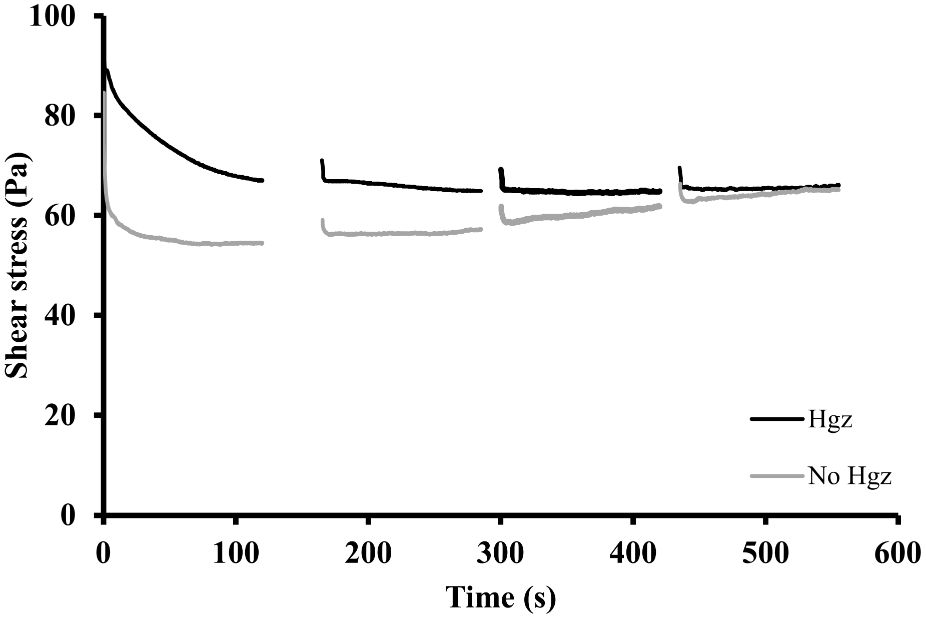

Figure 8. Shear stress evolution during the pre-shear periods of 0.35 w/c evaluated at 80 min using procedure 2 with and without homogenization.

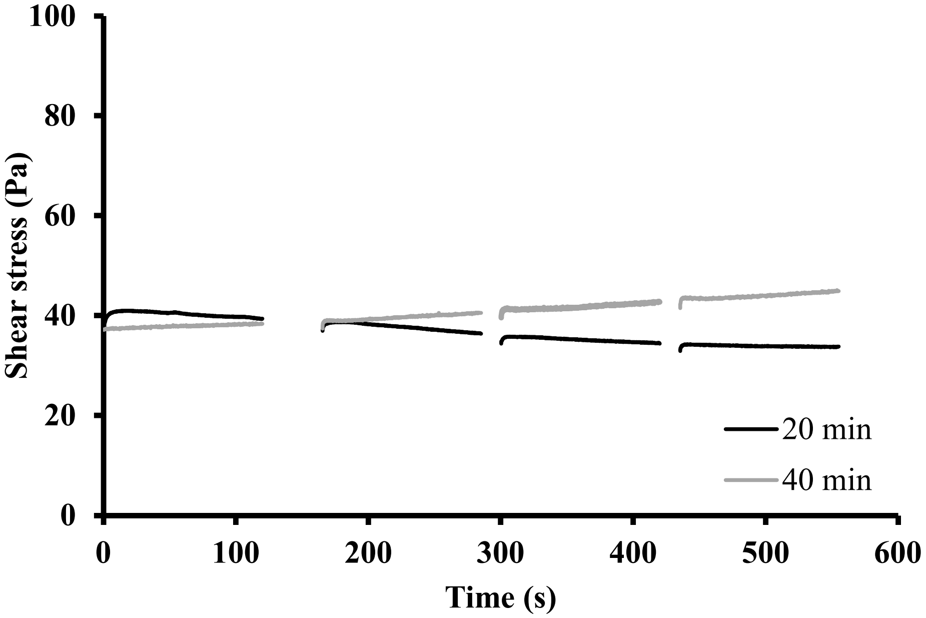

Figure 9. Shear stress evolution during the pre-shear periods of 0.35 w/c limestone system evaluated using procedure 2 with consistent shearing.

Figure 10. Bleed water at the top can be observed during test without homogenizing.

Figure 11. Plug found inside the rheometer cup after testing without homogenizing.

To evaluate the amount of bleeding water on the sample, and to confirm the presence of sedimentation, static bleeding tests were executed. A sample of the mixture was placed in a known volume (314.1 ml) and water was collected every 10 min in the first hour, then every 30 min until no more water was able to be collected. The procedure is inspired from ASTM C232 which measures the bleeding rate of concrete. According to Stokes's law, particles settle spontaneously (individually) at an equilibrium velocity that is proportional to the square of the radius of the particle. As a result, certain characteristics dominate sedimentation. Larger particles settle faster than smaller particles. If the height of the rheometer were infinitely long, there would be no consequence on the results, as the sinking particle at height h_1 would be replaced by a sinking particle coming from higher. However, due to the finite dimensions of the reservoir, three layers can be determined: On the top is a cloudy liquid (bleed water), in the middle a free sedimentation section (homogenous volume) and lastly a region of consolidated particles [28]. The volumetric proportions of these layers were calculated as follows: the percentage of bleed water was obtained using Equation 2, while the consolidated volume was calculated with Equation 3 using a maximum packing density of 0.60 [29] and the homogenous volume was determined using Equation 4. The results of the static bleeding for 0.35 and 0.45 w/c are illustrated in Figure 12. The amount of bleed water in 0.45 system is almost double than the 0.35 w/c, however the consolidated volume of cement paste is similar in both systems: between 18.5 and 20 %.

$$\%V_b = \frac{V_{cc}}{V_T} \tag{2}$$

$$\%V_c = \frac{\left(\dfrac{w_{cc}}{\dfrac{w}{c} - \dfrac{w}{c}_{\emptyset\, max}}\right) * \dfrac{w}{c}_{\emptyset\, max} + \dfrac{\dfrac{w_{cc}}{\dfrac{w}{c} - \dfrac{w}{c}_{\emptyset\, max}}}{\rho_c}}{V_T} \tag{3}$$

$$\%V_{hom} = 100 - \%V_b - \%V_c \tag{4}$$

where: $\%V_b$ *is percentage volume of bleed water*

V_{cc} *is volume of cumulative bleed water*

V_T *is total volume of the sample*

$\%V_c$ *is percentage volume consolidated*

w_{cc} *is mass of cumulative bleed water*

w/c *is water to cement ratio of the sample*

$w/c_{\emptyset\, max}$ *is the water to cement ratio of maximum packing*

ρ_c *is density of cement*

$\%V_c$ *is percentage volume homogeneous*

Based on the geometry of the rheometer with the insert, and the used sample size (13 ml), one can calculate to which extent the consolidated part interferes with the measurement. It is assumed that all bleeding and consolidation is observed at the end of the static bleeding test (at 210 min), and that the rheometer sample has consolidated and bled to the same extent. This latter statement is assumed to under-estimate the total amount of consolidated material in the rheometer, as the maximum packing density obtained when particles are sinking is different in static compared to dynamic conditions. This is caused by any network formation allowed in static conditions, which is not in dynamic conditions. Based on a consolidated volume of 18.5% to 20% of the sample volume, the consolidated zone extents to 20 - 25% of the measuring zone in this rheometer configuration. This means that the bottom 20-25% of the vertical portion of the rheometer, and the entire bottom zone of the rheometer contain the consolidated sample, affecting the measurement. As approximately half of the sample is above the measuring zone, the bleeding does not have an effect on the measurements. This explains why significant increases in rheological properties are observed when sedimentation is allowed to happen.

This method only describes the amount of sedimented material at the end of the sedimentation process. However, it is unknown when this happens in the rheometer test, as network and structure formation continuously change. Furthermore, as the network of connections is systematically broken, there is no other stabilizing force, except for viscosity. As such, cement particles will sink during the measurement, disturbing the outcome. The only thing which matters is how quickly do they sink compared to the duration of the measurement. This is governed by the overall amount of particles present in the system, and how much the smaller particles hinder the settlement of the larger. As observed in the experiments, a higher w/c results in a faster settlement of particles.

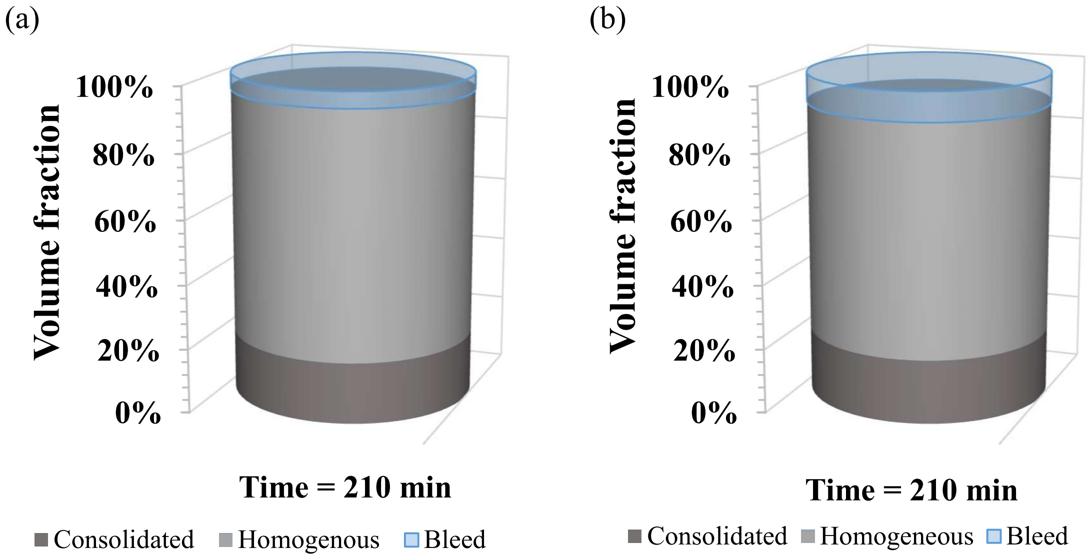

Figure 12. Static bleeding results for (a) 0.35 and (b) 0.45 w/c at the end of the test.

3.1. CONSEQUENCES

As a consequence, there is a maximum duration for which a rheological experiment is valid. This duration is dependent on the geometrical characteristics of the rheometer and the material (especially its macroscopic viscosity), but is expected to be independent of the shear rate [23]. It is also known that rheological measurements on cement-based materials typically need a pre-shear period to break down internal structure prior to assessing a flow curve. This pre-shear period should be sufficiently long to assure the reference state, but sufficiently short to prevent the effect of sedimentation. This could constitute a difficult task and the pre-shear period might need to be adjusted between mix designs to be able to accommodate both requirements simultaneously. Figure 13 shows the increase in shear stress during the pre-shear periods at 20 min of contact with water, illustrating sedimentation is happening during the measurement starting at around 200s. These results were obtained on a repeat mixture with w/c = 0.45 and with procedure 2. This is why no results with procedure 2 and w/c = 0.45 are reported, as one application of the full procedure was sufficient to invalidate any results.

Based on the authors' experience, it is recommended pre-test the material to establish the required parameters to obtain valid rheological properties. In addition, it is recommended to keep the procedure short if the sample has a risk of sedimentation of the cement particles. The sample should be evaluated depending on its application and the information is needed to be collected as there is not a universal testing procedure. Before measuring, the cement paste may be stable, but it can become unstable under the effect of shear [19,30]. The authors therefore believe that no uniform testing procedure for all cement pastes, mortars or concretes can be developed, but that a conceptual procedure with adjustable steps is necessary. Furthermore, a material which sediments quickly and needs extensive time to break down structure could exist, which would cause significant concerns to assess its properties. One potential solution is to ensure that the measuring zone of the rheometer contains only homogeneous material (if the three-layer approach is applicable), by increasing the sample height. In this way, the interference of the consolidated and bleeding zone could be postponed in time, allowing to perform longer duration experiments. On the other hand, a parallel plate geometry, for which the entire sample is in the measuring zone, would be very sensitive to sedimentation concerns.

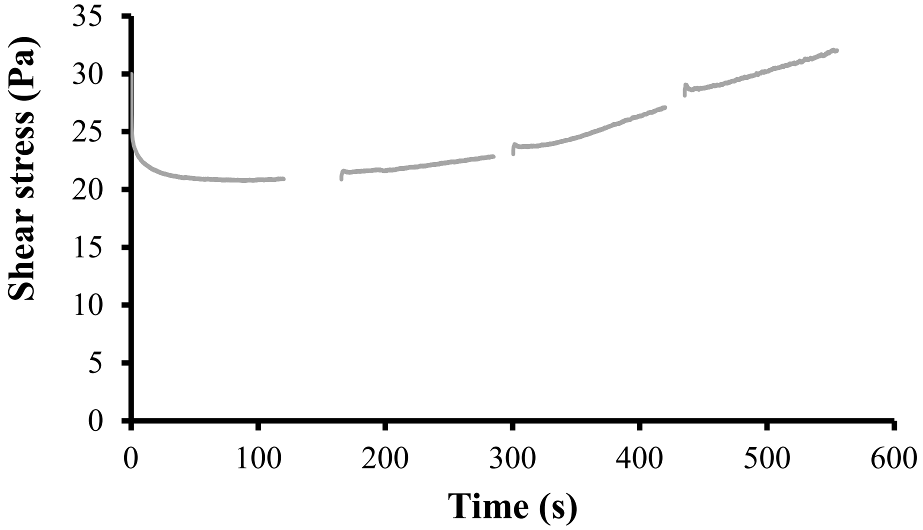

Figure 13. Shear stress evolution for 0.45 w/c during pre-shear at 100 s^{-1}.

4. CONCLUSIONS

The effect of sedimentation on the rheological properties of dispersed cement pastes were evaluated using two different shearing procedures and mixtures with two different water to cement ratios. Based on the results from this study the following conclusion were obtained:

- Results show that depletion of concentration of cement particles in the rheometer gap during testing highly affects the rheological properties when the sample is not homogenized after each measurement, specially for viscosity.

- Increasing the w/c from 0.35 to 0.45 decreases particle volume fraction, reflected by a lower viscosity of the paste, and consequently increasing the rate of sedimentation.
- Higher variations in the rheological properties are observed between the homogenized and non-homogenized sample when procedure 2 is applied. If the sample is sheared sufficiently to break part of the internal structure of the paste or to prevent the shear-induced building of these connections, this results in lower rheological properties and increasing sedimentation.
- Measuring procedures should be kept sufficiently short to avoid the effect of sedimentation, but achieving the reference state should not be neglected either. As a result, it is believed that a universal measuring procedure cannot be developed, but instead a conceptual and adaptable procedure is needed.

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SECTION

3. SUMMARY OF RESEARCH

This research was conducted to establish guidance in proper selection of the rheometer geometry and setup details as well as a suitable testing procedure that are of paramount importance in order to get reliable, accurate and reproducible data. Some of the challenges encountered when measuring the rheological properties of cement-based materials are drying of the sample, varying gap size, wall slip, particle sedimentation and surface conditions. However, some of these issues are inherent to the nature of the sample.

The first paper represented a unique up-to-date study on the effect of different testing parameters such as: applied shear stress (from 0.1 s^{-1} to 100 s^{-1}), temperature and sample age on the rheological characterization of cement pastes followed up to 180 min.

The second paper demostrasted the results of how variations in resting times between consecutive rheological measurements affect the rheological properties evolution with time on well-dispersed cement pastes.

The third paper demostrated the challenges encountered when using parallel-plates geometry in cement pastes and the importance of a proper rheometer geometry selection.

The fourth paper investigated the concequences of sedimentation on the rheological properties of dispersed cement pastes that were evaluated using two different shearing procedures and mixtures with two different water to cement ratios.

4. CONCLUSIONS, RECOMMENDATIONS AND FUTURE WORK

4.1. CONCLUSIONS

This section summarizes the conclusions from the different phases of the experimental studies that show the importance of the employed testing procedure, resting time in between measurements and rheometer geometry selected. The following conclusions are presented:

- Results show that low shear rate may accelerate dissolution and precipitation of hydration products, strengthening the formed network between the cement particles and consequently induce larger permanent increases in the rheological properties, especially in viscosity.
- At low temperature, at which hydration is slowed down, the viscosity does not seem to be affected by the imposed testing procedure, confirming that hydration does contribute to the variation in the rheological properties between the testing procedures. Also, besides hydration, shear induced flocculation may still arise at low shear rates and could be a catalyst for the hydration linkages to form.
- Although the “most de-flocculated” state (reference state) was imposed in all experiments, the elimination of the shear history is not fully guaranteed. This is contrary of what is believed that this reference state can be reached when the material flow history is submitted to the highest shear rate.
- The resting time in between measurements influences differential viscosity but this seems to be strongly dependent on the workability retention mechanisms of the used dispersing admixtures.

- The dispersion mechanism of the chemical admixtures does not seem to be a factor influencing the yield stress differently when changing the resting periods.
- The shearing imposed with the different testing procedures is relatively high to break down the structure developed during the resting periods. Analysis of the pre-shear data shows the difference in structural build-up, but a majority of the built structure is broken down, regardless of the chosen resting time.
- The results indicate that the chosen measuring procedure to determine the rheological evolution with varying shear rate and time as a larger consequence on the time-evolution of rheological properties at constant shear rate, compared to the different resting times in between measurements.
- The evaporation of water is highly critical in systems containing additional powder due to the additional surface area, having higher demand leading to a higher rate of increase of the rheological properties over time.
- Increasing the gap size from 0.5 mm to 1 mm between the sample and the shearing surfaces, decreases the plastic viscosity, since the confinement of the particles is reduced.
- Wall slip can be prevented enhancing the texture of the shearing surfaces.
- Concentric cylinders geometry appeared to be more appropriate to measure the rheological properties for the cement paste with a w/c of 0.45.
- The use of parallel plate with rough sandpaper disks may cause a measurement artifact due to inaccuracies during the determination of the gap or secondary flows.
- Parallel plate geometry is more sensitive to changes in the sample volume causing uneven shear rates and errors during the measurement. Also, it is more susceptible

to obtain less repeatable rheological properties when the sample has a risk of sedimentation.

- Results show that changes in concentration of cement particles in the rheometer gap during testing highly affects the rheological properties when the sample is not homogenized after each measurement, especially for viscosity.
- Increasing the w/c from 0.35 to 0.45 decreases concentration of the paste and consequently increasing the rate of sedimentation.
- Extensive rheological measurements on cement pastes induce the risk that sedimentation will invalidate the test results. Re-homogenizing of the sample in between testing protocols is recommended.
- Due to differences in settling rate between different cement pastes, no uniform measuring procedure, guaranteeing successful measurement of the rheological properties, can be developed. Instead, the applicability of measuring procedures should be evaluated per mix design, and adjusted if necessary.

4.2. RECOMMENDATIONS

According to the results found in this study, the following recommendations to propertly characterize the rheological properties of dispersed cementitious pastes can be made:

- The sample should be evaluated according to the intended shearing procedure for its application, since there is not a universal testing procedure.
- Measuring procedures should be kept sufficiently short to avoid the effect of sedimentation but achieving the reference state should not be neglected either. As

a result, it is believed that a universal measuring procedure cannot be developed, but instead a conceptual and adaptable procedure is needed.

- If a long measuring procedure is selected, it is recommended to homogenize the sample after each measurement to avoid the effect of sedimentation.
- The use of evaporation protection, such as a temperature-controlled hood, is recommended.
- It is recommended pre-evaluate the applicability of a measuring procedure on the material to establish the required parameters to obtain valid rheological properties.
- A material which sediments quickly and needs extensive time to break down structure could exist, which would cause significant concerns to assess its properties. One potential solution is to ensure that the measuring zone of the rheometer contains only homogeneous material, by increasing the sample height. In this way, the interference of the consolidated and bleeding zone could be postponed in time.

4.3. FUTURE WORK

- Development of guidelines to proper selection of geometry and testing procedure to evaluate the desired properties.
- Further research is needed in regards of the application of parallel plates geometry on the rheological characterization of cement paste.
- Evaluate the proposed testing procedures using a finer cement to assess the hydration contribution in the observed effects.

- Additional investigation is needed to understand the correlation between hydration kinetics and rheology, this can be done by using a simpler system such as C_3S and C_3A pastes.
- To study different particle size distribution in C3S/C3A systems and cement pastes to evaluate its effect on the rheological properties using different testing procedures.
- Evaluation on the effect of different applied shear rates on the sedimentation of cement pastes.

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VITA

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