fluids

MDPI

Review

Rheological Behavior of Fresh Cement Pastes

Francisco-José Rubio-Hernández

Departamento de Física Aplicada II, Universidad de Málaga, 29071 Málaga, Spain; fjrubio@uma.es;
Tel.: +34-951-952-296

Received: 7 November 2018; Accepted: 7 December 2018; Published: 11 December 2018

check for updates

Abstract: Rheology of a concrete is mainly controlled by the rheological behavior of its cement paste. This is the main practical reason for the extensive research activity observed during 70 years in this research subfield. In this brief review, some areas of the research on the rheological behavior of fresh cement pastes (mixture method influence, microstructure analysis, mineral additions influence, chemical additives influence, blended cements behavior, viscoelastic behavior, flow models, and flow behavior analysis with alternative methods) are examined.

Keywords: cement pastes; rheology; particle suspensions

1. Introduction

Concrete can be dealt with as a dispersion of gravel (around 20 mm diameter) in mortar, and mortar can be dealt with as a dispersion of sand (around 1 mm diameter) in cement paste. So, cement paste that is a dispersion of cement particles (around 10 µm) in water, is the fluid media where aggregate particles (sand and gravel) are dispersed.

Interest in gaining information about the rheological behavior of fresh cement pastes (RBFCP) is mainly due to the role played by this phase in concrete and mortar formulations. Tattersall firstly pointed to this field of research in 1955 [1], enhancing the fact that this is a non-Newtonian fluid. More precisely, he assumed a relationship between thixotropic behavior of the cement paste and the performance of the vibration process commonly used when the concrete is placed. Although a direct connection between cement paste and concrete rheology can be questioned [2] due to the effect of the shape and grain size distribution of coarse aggregates, the subject left open the search for possible relationships between both materials [3]. In this line, Ferraris and Gaidis [4] studied the rheology of the paste with parallel plate geometry (Figure 1) in an attempt to simulate the effect of coarse aggregate on the rheological behavior of pastes.

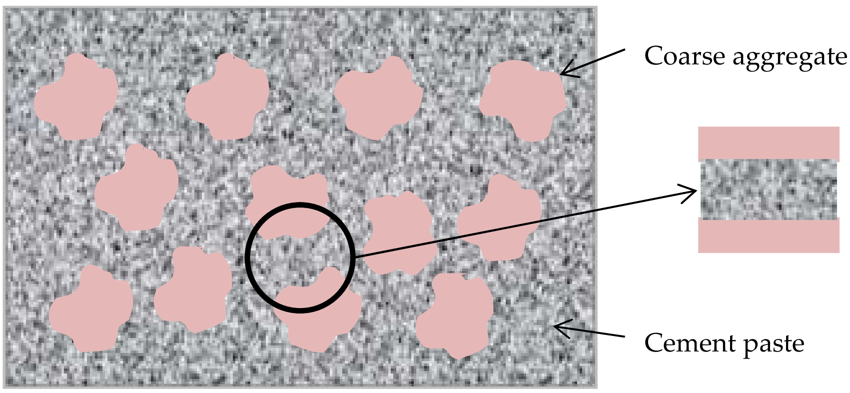

Figure 1. Cement paste flow in concrete is directly influenced by the action of coarse aggregate [4].

Interest in the study of fresh cement paste rheological behavior is founded in the assumption that concrete rheology is mainly determined by cement paste rheology [4]. Considering that the hydration reaction of cement starts at the first contact between cement and water, and continues when the rheological studies are usually made (10–60 min after), it is reasonably expected that rheometric work with fresh cement pastes faces a variety of challenges. Even if it is assumed that during the dormant period the hydration of cement is basically stopped, additional problems associated with rheological measurements of cement pastes can be listed. Banfill [5,6] pointed to possible reasons for these problems. Concretely, (a) discrepancies in time-dependent viscosity curves are usually reported, that can be due to variable competition between shear-induced breakdown and by-hydration build-up of structure when the design of hysteresis loops is modified; (b) the rheological results depend on the mixing and handling protocol, probably due to the decrease of the yield stress with vigorous mixing; (c) slippage of pastes at the walls of the rotor can certainly be overcome with roughened surfaces, but it is not possible to determine to which extension; and (d) particle sedimentation during measurement can be neglected when helical impeller or similar are used, or when the water/cement ratio is kept below 0.4 with conventional geometries. All these problems can be overcome with a good experimental design, however plug flow due to the existence of a range of stresses in the bulk of the material, some of them with values lower than yield stress, is described as an unsolved problem [5,6].

It can be affirmed that the experimental study of the rheological behavior of fresh cement pastes is a difficult task [5,6]. Generally, this is due to several factors and conditions that have certain influence on the response of the material. We can include physical factors like water/cement ratio or the morphology of cement grains, mineralogical factors like cement composition, chemical factors like structural modifications due to hydration processes, mixing conditions like the type of stirrer, or measurement conditions like experimental procedures.

The first interest for the study of RBFCP was initially practical; i.e., it was motivated by the necessity to control and predict the rheological behavior of the concrete obtained when sand and gravel are added to the cement paste. But, also, this study is interesting from a fundamental point of view. This is because cement pastes are particle dispersions featured by a decisive hydration chemical activity, which generates products of the reaction that form a gel phase interconnecting the core of cement particles. It is easy to understand that a material with such a brand mark had been wide and deeply studied. Different aspects of these particle suspensions have attracted the interest of researchers. Some of them will be briefly described in this review:

a) Mixture method influence.
b) Microstructure analysis.
c) Mineral additions influence.
d) Chemical additives influence.
e) Blended cements behavior.
f) Viscoelastic behavior.
g) Flow models.
h) Flow behavior analysis with alternative methods.

2. Mixture Method Influence

The purpose of cement paste mixing processes is to reduce the size of particle clusters in order to make effective the wetting of each individual cement particle. Additionally, specific interest in the study of the mixture method influence on cement paste rheology is justified by the fact that cement paste forms part of the medium where aggregates are dispersed. Certainly, when concrete flows cement paste is mixed similarly to that which occurs in a laboratory stirrer. Therefore, it is of capital importance to determine the influence of mixing procedure on cement paste rheology, because it has been clearly demonstrated that the mixing procedure to obtain the cement paste has a direct influence on its rheological behaviour. This is probably due to the fact that different water–cement contacts (in number and quality) can be obtained when the mixture is agitated or mixed following different methods. Consequently, several research studies have been undertaken with the objective of achieving an optimal mixing protocol, specifically referring to the reproducibility and repeatability of the rheological results. In this line, Jones and Taylor [7] obtained rheological reproducible results applying vibration to cement pastes that had been previously mixed by hand. Yang and Jennings [8] investigated the effect of low and high mixing procedures on the peak stress value, which was obtained when a constant shear rate was applied to samples just after they were at rest along different time intervals. These authors observed that peak stress values were directly related to the size of agglomerates, and concluded that the lack of hydration of the inner particles of the agglomerates is a determinant source of microstructural defects. Additionally, they proposed a new empirical parameter, the limiting gap, as a measure of the degree of mixing. As the shear stress increases when the gap reduces, the limiting gap was defined as the gap that separates the two plates of plate–plate geometries just when the shear stress was three times higher than the shear stress measured at high gaps. Although some correlation between limiting gap and microstructure was induced, the utility of this parameter is still open to discussion. Williams et al. [9] used, in a very detailed work, plastic viscosity and the area enclosed by the up and down curves of the hysteresis loop to compare the effect of several mixing methods (hand-, paddle-, high-shear-, and concrete-mixed) on the degree of structure remaining in the cement paste. Results confirmed, as is reasonably expected, that the structure be comparatively much more broken down when the mixed method was more vigorous. Additionally, they obtained similar effects for concrete- and high-shear mixed pastes; a result that suggests that, in concrete, cement paste is highly sheared by aggregates (see Figure 1). Therefore, it could be concluded that standard initially used to prepare cement paste samples [10] is not adequate to simulate the ball-milling effect of aggregates in concrete [8]. Then, another standard [11] for the preparation of cement pastes was introduced. The capability of both standards to influence on structural and rheological properties of cement pastes was evaluated by Han and Ferron [12]. These authors obtained an unexpected result. They observed that the mixing intensity had much more influence on the yield stress and the plastic viscosity for pastes formulated with chemical additives and lower particle concentration (higher water/cement ratio). Their results were clearly counterintuitive because, while a decrease in both rheological parameters was expected with the increase of the mixing intensity, the opposite result was found using the ASTM C1738 protocol [11]. The discrepancy was especially high when plasticizers form part of the cement paste formulation. Han and Ferron [12] pointed out that if, certainly, the vigorous mixing breaks particle agglomerates, it also accelerates the cement hydration. Then, a hindering effect of the plasticizer agent due to the high velocity of mixing, which leads to a decrease in the extent of the steric diffuse double layer that surrounds cement particle and promotes particle agglomeration, was claimed [12,13].

The main conclusion of this research area is that the mixing protocol applied to cement pastes preparation is not a trivial issue. It should be intensive and lengthy enough to break all particle agglomerates, but limited by the possibility of provoking the opposite effect, especially when chemical additives form part of the cement paste formulation.

3. Microstructure Analysis

Breakdown of structure due to shear and rebuilding of structure-at-rest are phenomena of technical interest in cement paste applications. The contact of cement pastes with water gives place to a process of coagulation starting from a completely dispersed state. A gel layer of calcium silicate hydrate (C-S-H) progressively surrounds cement particles, the process being very slow during the dormant or induction period [14]. This phase initiates around 10 min after the first contact between cement and water. During the induction period, fresh cement pastes can be properly analyzed from a rheological point of view [15]. It is worth distinguishing when fresh cement pastes are studied between reversible and irreversible microstructure evolutions. Reversible evolution of the cement paste microstructure (breaking or building) can only be claimed when colloidal interactions between cement particles are taken into account. Hydration of cement particles is always connected to irreversible processes. Fortunately, during the dormant period of the cement hydration, this reaction can be slow enough to assume that chemical changes in cement pastes are negligible. However, it is important to consider that these effects are not fully absent during rheological measurements. Hydration products generate particle flocs that, finally, lead to the formation of clusters or 3D networks formed by aggregates of flocculated cement particles [16]. If we consider only reversible evolution of the microstructure, the picture can be described as follows. Initially, when the network immobilizes the liquid phase, cement pastes behave in a solid-like way, and only when the stress achieves a threshold value, or yield stress, due to the action of shear, does the structural breakdown begin. The increasing of shear rate results in further deflocculation, i.e., the apparent viscosity will decrease with shear. This is the basis for the concrete vibration technique that is applied after placing, which makes that previous stiff material can after flow easily. Therefore, lower water/cement ratios can be used in concrete formulations, and higher strength of the set concrete can, consequently, be obtained. So, it is justified why an understanding of both, reversible (thixotropy) and irreversible (setting) breakdown of structure of cement pastes, is of major importance: simply due to the role-played by cement pastes when a vibratory force is applied in the placing of concrete [1,17].

First studies of the time evolution of the microstructure of Portland cement pastes [1] showed that an exponential decrease of the torque with time, when a step-up in shear rate is applied to samples, fits reasonably well experimental results,

$$M = M_e + (M_o - M_e)e^{-kt} \tag{1}$$

In Equation (1), M is the torque at time t, k is the rate for the stress decay, and M_o and M_e are the initial and the equilibrium torque values, respectively (see Figure 2). Tattersall's results [1] showed that k increases with the angular velocity of the rotor. The area under the torque-time curve (Figure 1) can be used as a measure of pastes workability [17] because it is directly related to the net energy input or work done by the rotor to (i) overcome viscous forces, (ii) breaking the structure, and (iii) maintaining broken the structure [1].

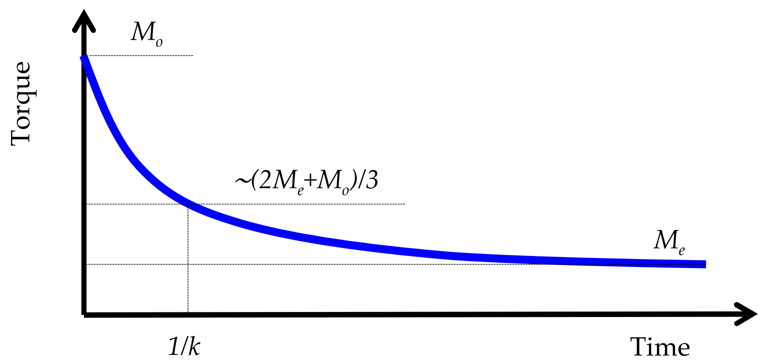

Figure 2. Schematic plot of the evolution with time of the torque after a step-up in angular velocity according with Tattersall [1].

Bouras et al. [18] found that the sum of two exponentials fitted better stress decay with time due to breakdown microstructure, when pastes contain some viscosity-modifying admixture (polysaccharide). They justified their result as due to the existence of two relaxation times for the rebuilding of microstructure. The first one is related to particle–particle interconnections as usual, and the second one refers to the alignment and disentanglement under flow of admixture molecules. Then, using Cheng and Evans' general thixotropic microstructural model [19], the kinetics equation for the structural parameter λ should be expressed as,

$$\frac{d\lambda}{dt} = \frac{1}{T_a} + \frac{1}{T_b} - \lambda\dot{\gamma} \tag{2}$$

In Equation (2), T_a is the characteristic time for cement particles aggregation, T_b is the characteristic time for the admixture entanglement, and $\dot{\gamma}$ is the shear rate. However, when Bouras et al. [18] analyzed the microstructure rebuilt process assumed that, experimentally, stress increases exponentially with time, avoiding the use of Equation (2) that predicts a linear increase of the stress with time.

Irreversible time-evolution of the microstructure is observed during the setting of cement pastes due to the hydration chemical reaction is the dominant effect. It has been observed that in this case the increase in the viscosity with time, which is partially attributed to shear-induced aggregation, is opposite to that which could be expected, faster with increasing organic additives concentration [20]. These processes are dominated by the hydration of cement particles and fall out of the scope of the rheological analysis proposed in this review. However, it is worth distinguishing between the irreversible, or aging due to hydration, and the reversible part, or thixotropy, of the transient behavior of cement pastes, as mentioned above. This is important to avoid misinterpretations of the experimental results. For example, Roussel [21] proposed a thixotropic model for cement pastes. He started from the assumption of the experimental results summarized in Equation (1) although he attributed it to Lapasin et al. [22] instead of Tattersal [1]. Then, Roussel used Cheng and Evans' general microstructure thixotropic model [19] and assumed that the material restructuration occurs in a natural way at an unique constant rate $1/T$, although maintaining the idea that the destructuration is proportional to the existing structure and to the shear rate,

$$\frac{d\lambda}{dt} = \frac{1}{T} - \alpha\lambda\dot{\gamma} \tag{3}$$

Roussel assumption predicts, as Bouras et al. [18], unrealistic linear increase of the microstructure-at-rest. When shear rate is zero,

$$\frac{d\lambda}{dt} = \frac{1}{T} \tag{4}$$

Solving Equation (4),

$$\lambda = \frac{t}{T} + \lambda_o \tag{5}$$

However, experimental tests have demonstrated that the microstructure-at-rest increases exponentially until a maximum (reversible) structure is achieved [18,23]. This result is opposite to which Equation (5) predicts [21].

Very recently, Ma et al. [24] have proposed a kinetics equation for the rebuilt process, which expresses restoration of an equilibrium state from a non-equilibrium condition, i.e.,

$$\frac{d\lambda}{dt} = -\frac{1}{T}(\lambda - \lambda_e) \tag{6}$$

In Equation (6) $\lambda_e > \lambda$ represents the structure of the paste at equilibrium. Effectively, solving Equation (6) a most realistic exponential evolution of the microstructure towards the rest equilibrium state is obtained (Figure 3),

$$\lambda = \lambda_e + (\lambda_o - \lambda_e)e^{-t/T} \tag{7}$$

It is worth noting that experimental results by Ma et al. [24] supported the existence of two structural levels (particle flocs and C-S-H nucleation) in cement pastes, which were previously pointed out by Roussel et al. [25].

Summarizing, fresh cement pastes are concentrated particle suspensions in which particle-particle interaction is not only governed by colloidal and hydrodynamic forces, but also steric (admixtures) and products of the hydration reaction (C-S-H) play a specific role for the development of microstructures. These aspects of cement particle interactions make the study of the microstructural evolution of cement pastes with time (thixotropy) especially interesting.

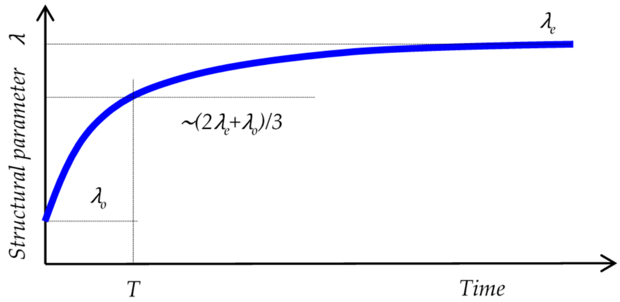

Figure 3. Schematic plot of the evolution with time of the atructure at rest according with Ma et al. [24].

4. Mineral Additions Influence

The flow behavior of cement pastes is characterized by a variety of rheological parameters. It is a task of major importance to determine the influence of the cement properties, and of mineral and chemical additions on these parameters. So, a lot of work has been done with the aim to determine correlations between different geometric, physical and chemical modifications of cement pastes with their rheological properties.

Some results corresponding to this research sub-area refer to the yield stress value. For example, it has been observed that the yield stress increases with the specific surface area of cement particles and the water/cement ratio [26]. Ivanov et al. [27] obtained an increasing dependence of the yield stress and the plastic viscosity with a variety of factors; concretely, they observed that the yield stress is more dependent according to the following succession, superplasticizer > addition of silica fume > water/cement ratio; while the plastic viscosity is dependent in the following succession, water/cement ratio > superplasticizer > addition of silica fume. Nehdi et al. [28] observed that the replacement of cement with limestone filler slightly increased the yield stress of cement paste with added plasticizer, but its plastic viscosity decreased. Latter, Rubio-Hernández et al. [23] observed that when the limestone filler concentration is lower than 3% weight the opposite effect appears, i.e., the yield stress decreases and the plastic viscosity increases.

It is reasonably expected that the different factors on which the rheological behavior of cement pastes is dependent, interact among them giving place to complex dependencies. Then, it is necessary to define combinations of them. So, Wong and Kwan [29] considered the effect of the excess water to solid surface area ratio on the rheological properties of cement pastes. In this way, water content, packing density and solid surface area effects were simultaneously considered. They found that yield stress and plastic viscosity versus excess water/solid surface area ratio curves overlap when this parameter was higher than 0.05 μm, while at lower values the yield stress and the plastic viscosity curves separate, distinguishing between pastes with and without silica fume, i.e., the rheology of cement pastes also depends on silica fume content at the lower water/solid surface area ratios.

One of the technical applications pursued by means of mineral additions is the design of highly concentrated suspensions with moderate yield stress and plastic viscosity values [30]. To this end, advantages resulting from the use of bimodal suspensions have been considered. This strategy can be useful to improve the performance of, for example, extruded materials [31]. For example, bimodal suspensions of cement and clay particles showed higher yield stress values than those obtained for the original cement suspension, despite the maximum packing fraction practically did not vary [32]. This apparently contradictory result was justified as due to the water adsorption of clays, which eliminates lubricant water phase and increases the effective size of clay particles [33]. Fine mineral additions like limestone, silica fume, fly ash, etc. increase maximum packing fraction with good lubricant effect, and the resulting cement pastes can serve as the base for self-compacting concrete design [33]. However, not only the particle size but also the geometric shape have a determinant effect on the cement paste and, consequently, on the concrete fluidity. So, when fly ash particles of spherical shape substituted amorphous cement particles, the viscosity or consistency of fresh cement pastes decreases, and even lower yield stress values can be obtained although the water/binder ratio decreases [34]. Nevertheless, high dosages of fly ash can lead to fluidity loss due to its high specific surface area, which provokes higher water demand and admixture consumption. The combined effects of spherical shape and high polydispersity of fly ash added to cement pastes can enhance the results before pointed out, i.e., for a given solid volume fraction, the plastic viscosity increases and the yield stress decreases with particle polydispersity [35]. In the last sense, the main objective pursued adding fine mineral additions with a high polydispersity index is to reduce, as low as possible, water/binder ratio in order to obtain optimal conditions for the production of high-strength and high-performance concretes [36]. Sometimes, mineral additions are used in combination with chemical additives (superplasticizers) [37]. The objective is to reduce water demand maintaining workability and strength at hardened state. Not all mineral additions can be used to this end. For example, this can be achieved using fly ash but not limestone [38] or nano-$CaCO_3$ [39].

Summarizing, mineral additions are used to improve hardened properties of cementitious materials maintaining or refining fresh state behaviour. Two main types of mineral additions are used, with and without pozzolanic activity. The first type will be specifically considered in part 6 when advances in blended cement are reviewed. The main characteristics of mineral additions without pozzolanic activity that have an influence on the rheology of cement pastes are size, shape and particle polydispersity. In both cases, combined action of mineral additions with plasticizers gives place to cement paste formulations optimal for high-performance concretes design.

5. Chemical Admixtures Influence

There are two most important effects that the presence of chemical additives has on the rheology of fresh cement pastes,

a) the increase of the duration of the dormant period [40], because hydration reaction of cement slows down [41], allowing considering cement pastes as a chemically stable suspension during longer time intervals [42],
b) and the modification of its viscosity [43,44].

The type of chemical additive is determinant for the observation of different rheological behaviors. Specifically, polysaccharide gums increase the viscosity of pastes, enhance rebuilt-up kinetics at rest, and increase the yield stress [18], the effect being much more significant at low than at high shear rates [43]. So, the cement paste will be stable against sedimentation at rest and resistive to solid–liquid separation, but will flow easily when, for example, being pumped.

Sometimes, counterintuitive effects, like a decrease of the viscosity of cement paste when the viscosity of the interstitial liquid phase is increased due to the addition of a chemical admixture, are also observed. This phenomenon has been justified by the lubricant action of the liquid phase with respect to solid particles [45], which is higher when the admixture viscosity is higher [46].

Whatever the case is, the performance of a chemical additive is determined by its compatibility with cements, i.e., the adsorption capability of each type of cement particles [44,47], and temperature [48]. Bonen and Sarkar [49] analyzed the adsorption capacity of sodium salt of polynaphthalene sulfonate superplasticizer by different cement types, and concluded that cement fineness and superplasticizer molecular weight are the main factors determining the adsorption capacity of pastes. Bessaies-Bey et al. [50] studied polyacrylamide adsorption on cement particles, and observed the formation of polymer micro-gels that not only adsorb on particles but also bridge them increasing consequently the yield stress of the cement paste. Then, Mukhopadhyay and Jang [51] proposed a rheological method to quantify cement-admixture incompatibilities. They measured the time evolution of the yield stress and plastic viscosity of pastes and justified, combined with heat of hydration evolution data, that incompatibility of the admixture corresponded to a rate of change of yield stress lower than 14 Pa/h and a rate of change of plastic viscosity lower than 0.02 Pas/h.

Two main types of chemical admixtures can be distinguished, viscosity-modifying admixtures, which increase the viscosity of cement pastes [43,44], and superplasticizers, which disperse cement particles [52,53].

In order to design adequate formulations of cementitious materials, the optimal dosage of chemical admixtures must be determined [54–56]. Sometimes, this does not coincide with that recommended by the producer [57] or is clearly dependent on physical conditions of the cement paste, as temperature [58]. Moreover, incompatibilities before cited between cement and chemical admixtures should be well established to avoid problems in fluidity [58]. In fact, the same chemical admixture can show a different performance when added to different cement types [59]. It appears that polycarboxylate type superplasticizer have the best compatibility with a wider variety of cements [60]. So, the study of this kind of superplasticizers has extended to consider a variety of molecular conformations due to the incorporation of different hydrophobic groups to the polycarboxylate molecule [61].

Another aspect that must be considered when several chemical admixtures are simultaneously used in the formulation of the same cement paste is its synergic effect [62–65]. For example, it was observed that a polysaccharide viscosity-modifying agent (Welan Gum) has a higher influence on rheological properties of cement pastes formulated with an ester polycarboxylate superplasticizer than when it was formulated with an ether polycarboxylate [66]. Nanoclay enhances or modifies [24] thixotropy behavior of cement pastes with polycarboxylate ether superplasticizer [67]. Hydroxypropyl-methyl cellulose ether [68] and polyacrylic acid [69] acts opposite to the dispersive capability of polycarboxylate type superplasticizers. The presence of other mineral additions, as borax, in order to retard cement paste setting must be analyzed in depth due to the negative effect that can induce in the adsorption of superplasticizer molecules onto the particle surface [70]. On the other hand, specific plasticizer and viscosity-modifying admixture concentrations are necessary to achieve the best rheological performance of cement pastes [30]. Although polycarboxylates are more effective than lignosulfonates, i.e., a lower concentration of polycarboxylates is necessary to obtain the same yield stress and consistency reductions, when they are combined, lignosulfonates adsorption onto the cement particle surface is dominant [71], although limited by the amount of C_3A in the composition of the clinker from which the cement powder is obtained [72].

Viscosity-modifying admixture of starch type can give place to different viscous behavior at low (shear-thinning) and high (shear-thickening) shear rates. These opposite behaviours have been ascribed to disentanglement and alignment of admixture molecules at low shear, and the increase of repulsive interparticle forces at high shear [73].

Summarizing, two main types of chemical admixtures are used to modify cement paste rheological behavior, viscosity-modifying admixtures and superplasticizers. The first are used to improve stability of pastes against sedimentation and bleeding, while superplasticizers increase the dormant period and allow for reduction of water content, which leads to higher strength when pastes set. Synergic effects must be carefully considered when different chemical admixtures are tested.

6. Blended Cements Behavior

Although the term blended cements generally refers to materials obtained when the ligand phase is obtained with water added to the mixture of cement and another material in different states of aggregation [74–76], here we will limit the definition to materials that are obtained when cement is partially substituted by another solid phase. This last can or cannot show pozzolanic activity. The term "binder" is used for the mixture cement + solid addition. It is widely accepted that particle morphology [77] and pozzolanic activity [78] of binders are the main features that determine their influence on the rheological behaviour of blend cement pastes.

Limestone filler and silica fume are two examples of solid substitutions without pozzolanic activity. It has been observed that the substitution of cement by limestone filler, maintaining constant the water/binder ratio, increases the yield stress and decreases the plastic viscosity of pastes [28]. Then, the stability at rest of cement pastes is enhanced, although the increase of the segregation of the phases can be an undesirable consequence. It has been also observed that the particle morphology of limestone has much more influence on the rheological behavior of pastes than its chemical composition [79].

Activated kaolinite (metakaolin) is a widely used example of the solid phase with pozzolanic activity [80]. The yield stress of blended pastes increases when the amount of activated kaolin increases [81] or the pozzolanic activation of kaolinite is enhanced [82]. Even then it can give to cement paste adequate characteristics for use in self-compacting concrete formulation [83]. Fly ash is another binder extensively used due to its pozzolanic activity. The origin of fly ash can be the combustion of fuel [34] or different biomasses [84]. In both cases, the regular shape of particles is a characteristic demanded for the optimal rheological behavior of pastes.

The use of natural pozzolans (mixtures of volcanic ash and pumice powder) as partial substitution of Portland cement has been shown to be an economic and very useful alternative in volcanic zones. Again, the yield stress increases and the plastic viscosity decreases with cement substitution. This variation of the rheological parameters has been justified by using a model that treats fresh volcanic cement pastes as suspensions of particles in a fluid phase formed by water and the gel resulting from the chemical hydration reaction of cement [78].

Blended cements contribute to the reduction of CO_2 emissions that result from cement production, and help to conserve the environment when waste solid materials are used. These are two important reasons that justify the interest for this research area that can be added to the increase of concrete durability thanks to improving the resistance to salts, freeze-thaw and carbonation effects.

7. Viscoelastic Behaviour

The objective of the rheological studies of cement pastes is to obtain rheological parameters with some practical meaning. This has traditionally been the case with viscosity, yield stress, and plastic viscosity, which are related to workability, fluidity and resistance to segregation, respectively. However, these rheological parameters account only for the viscous behaviour of the pastes. Additionally, time dependence of viscosity (thixotropy) is used to quantify microstructure changes, which is information useful to avoid, for example, cold joints in sequential casting applications. Moreover, viscoelastic studies are considered when useful knowledge for practical applications is obtained, i.e., on workability [57], microstructural evolution [85,86], and pumping [87].

Creep-recovery tests have been used for cement pastes to determine with much more precision the yield stress value. This is the stress value that limits the transition from viscoelastic solid-like to liquid-like behaviour [88,89].

Small-amplitude oscillatory shear applied to cement pastes has been shown to be the main evolution of the microstructure of the paste occuring just after the first contact of the cement with water [85,86]; the linear viscoelastic behaviour is limited by lower shear strain values when the water/cement ratio increases [88]. Moreover, as is reasonably expected, the storage modulus also decreases when the water/cement ratio increases [90]. Large-amplitude oscillatory shear will be of interest when the meaning for the results is proposed.

8. Flow Models

As cement pastes need, in general, for a threshold shear stress to be surpassed in order to observe flow, viscoplastic models [26,57,91–97] have been largely used to describe shear-stress-shear-rate or steady flow curves (Table 1). Some confusion results from the use of ramp flow curves (non-steady) to fit or describe new viscoplastic models [98]. Whatever the case, the influence of cement paste composition (cement type, water/cement ratio, type and concentration of different additions and admixtures, etc.) on the value of the model parameters, has been the subject of a large number of publications [2,27,59,99–101]. For example, Jones and Taylor [7] proposed a model based on Robertson–Stiff's to relate the flow curve of cement pastes to water/cement ratio,

$$\tau = (aw + b)\left\{\dot{\gamma} + (cw + d)\right\}^{\left(\frac{r}{w} + se^{-w}\right)} \tag{8}$$

where w is the water/cement ratio, and a, b, c, d, r, and s are constants to be determined. However, this 6-parameter model is capable for describing only qualitatively shear-stress-shear-rate-water/cement-ratio curves [7].

Table 1. Viscoplastic models used for describing steady flow curve of cement pastes.

Model Name	Equation	Reference
Bingham	$\tau = \tau_y + \eta_p \dot{\gamma}$	[90]
Modified Bingham	$\tau = \tau_y + \eta_p \dot{\gamma} + c\dot{\gamma}^2$	[91]
Herschel–Bulkley	$\tau = \tau_y + K\dot{\gamma}^n$	[92]
Robertson–Stiff	$\tau = A(C + \dot{\gamma})^B$	[93]
Karam	$\tau = Aexp(k\phi)(\dot{\gamma}_o - \dot{\gamma})$	[94]
Casson	$\tau = \tau_y + \eta_\infty \dot{\gamma} + 2\sqrt{\tau_y \eta_\infty}\sqrt{\dot{\gamma}}$	[95]
Modified Casson	$\tau^m = \tau_y^m + \eta_\infty \dot{\gamma}^m$	[96]
Papo–Piani	$\tau = \tau_y + \eta_p \dot{\gamma} + K\dot{\gamma}^n$	[57]
Vom Berg	$\dot{\gamma} = Bsinh\left(\frac{\tau - \tau_y}{A}\right)$	[97]

The responses of cementitious materials to flow after rest state cycles have been also modeled [102].

9. Flow Behavior Analysis with Alternative Methods

It has been recognized the influence of the measurement device on the results of rheological testing. A study on concentric cylindrical geometries [103] lead to acknowledge that the surfaces in contact with cement pastes must be roughness to avoid wall-slip phenomena, and the gap between rotor and stator must be large enough to guarantee laminar and homogeneous flow of the fluid. The use of cone-plate geometry to obtain rheological data is not appropriate due to the size of cement particles (10–100 µm) despite, surprisingly, some authors affirming the reproducibility of the results when the gap was the same order than particle size [7].

The sedimentation of cement grains is one of the most important problems that must be avoided to obtain valid results. With the aim to reduce its negative impact on rheological measurements, alternatives to rotational rheometers have been explored. For example, the turning-tube viscometer [104] avoids cement grain sedimentation, although rheometric measurements are relative, i.e., it does not supply absolute or fundamental rheological parameters.

Squeeze flow has been also used to characterize rheologically cement pastes [105]. However, it is necessary to assume a variety of simplifications in the experimental procedure (infinite volume of the sample, neglecting buoyancy force on the top plate, and neglecting of stress due to friction) to obtain results with some physical meaning. Despite squeeze and shear experiments results did not coincide [104], it is a valuable technique to mimic the flow conditions experienced by the cement paste in the inner granular space of concretes [106].

The inclined plane test has been shown to be a valuable way to infer rheological characteristics of cement pastes [107]. Shear stress-shear rate curves show reasonable agreement with those obtained with conventional rotational rheometers but what is most remarkable is that they allow us to show directly that the yield stress increases with the time that the sample is at rest before the test was made.

Extrusion is used in the formation of cement pastes. To determine the conditions that maintain constant the shape and cohesion of the extruder, specific studies complementary to rotational rheometry must be undertaken. Another reason for the use of this technique is the possibility to test materials with very low water/binder ratios [108]. In this respect, the presence of fly ash reduces the value of the extrusion load due to the lower size and the spherical shape of fly ash particles gives place to a lubricant effect [31].

Flow measurements at high pressure conditions can be made with specific cells that can be coupled to conventional rotational rheometers. They are designed to simulate pumping processes [109].

10. Conclusions

Interest in gaining information about the rheological behavior of fresh cement pastes (RBFCP) is mainly due to the role played by this phase in concrete and mortar formulations. Moreover, as cement pastes are particle dispersions featured by a decisive hydration chemical activity, which generates products from the reaction that form a gel phase interconnecting the core of cement particles, academic interest in the study of this material has also given rise to a variety of research sub-fields on RBFCP. Briefly, the state of the art can be summarized as follows:

a) The mixing protocol applied to cement paste preparation is not a trivial issue. It should be intensive and lengthy enough to break all particle agglomerates, but limited by the possibility of provoking the opposite effect, especially when chemical additives form part of the cement paste formulation.
b) Fresh cement pastes are concentrated particle suspensions in which particle–particle interactions are governed by colloidal, steric, and hydrodynamic forces, and also by products of the hydration reaction (C–S–H).
a) The combined action of mineral additions with plasticizers gives rise to cement paste formulations optimal for high-performance concrete design.
d) Viscosity-modifying admixtures and superplasticizers are used to improve the stability of pastes against sedimentation and bleeding, and to increase the duration of the dormant period and allow for a reduction in water content. Synergic effects must be carefully considered when different chemical admixtures are jointly tested.
e) Studies on blended cements are justified by the benefits on the environment and the possibility to develop new and improved concrete formulations.
f) Viscoelastic studies on cement pastes need to be properly justified, giving practical meaning to the rheological parameters thus obtained.
g) Cement paste is a viscoplastic material. In this case, the rheological parameters commonly analyzed, the yield stress and the plastic viscosity, are related to practical uses. This is because steady viscous flow studies have traditionally been undertaken.
h) Sedimentation and wall slip are two error sources in rheological tests. Then, new experimental methods must be developed that, in addition, can inform us about other flow cement pastes characteristics.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflicts of interest.

References

1. Tattersall, G.H. The rheology of Portland cement pastes. *Br. J. Appl. Phys.* **1955**, *6*, 165–167. [CrossRef]
2. Tattersall, G.H.; Banfill, P.F.G. *The Rheology of Fresh Concrete*; Pitman Advanced Publishing Program: Boston, MA, USA, 1983; ISBN 978-0273085584.
3. Struble, L.; Szecsy, R.; Lei, W.G.; Sun, G.K. Rheology of cement paste and concrete. *Cem. Concr. Aggr.* **1998**, *20*, 269–277. [CrossRef]
4. Ferraris, C.F.; Gaidis, J.M. Connection between the Rheology of concrete and Rheology of cement paste. *ACI Mater. J.* **1992**, *89*, 388–393. [CrossRef]
5. Banfill, P.F.G. The Rheology of cement paste: Progress since 1973. In *Properties of Fresh Concrete, Proceedings of the International RILEM Colloquium, Leeds, UK, 22–24 March 1973*; Wierig, H.J., Ed.; Taylor & Francis: New York, NY, USA, 1990; pp. 3–9.
6. Banfill, P.F.G. The Rheology of fresh cement and concrete-A review. In Proceedings of the 11th International Cement Chemistry Congress, Durban, UK, 11–16 May 2003.
7. Jones, T.E.R.; Taylor, S. A mathematical model relating the flow curve of a cement paste to its water/cement ratio. *Mag. Concr. Res.* **1977**, *29*, 207–212. [CrossRef]

8. Yang, M.; Jennings, H.M. Influences of mixing methods on the microstructure and rheological behavior of cement paste. *Adv. Cem. Based Mater.* **1995**, *2*, 70–78. [CrossRef]
9. Williams, D.A.; Saak, A.W.; Jennings, H.M. The influence of mixing on the rheology of fresh cement paste. *Cem. Concr. Res.* **1999**, *29*, 1491–1496. [CrossRef]
10. ASTM C305-14. *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*; ASTM International: West Conshohocken, PA, USA, 2014.
11. ASTM C1738/C1738M-18. *Standard Practice for High-Shear Mixing of Hydraulic Cement Pastes*; ASTM International: West Conshohocken, PA, USA, 2018.
12. Han, D.; Ferron, R.D. Effect of mixing method on microstructure and rheology of cement paste. *Constr. Build. Mater.* **2015**, *93*, 278–288. [CrossRef]
13. Han, D.; Ferron, R.D. Influence of high mixing intensity on rheology, hydration, and microstructure of fresh state cement paste. *Cem. Concr. Res.* **2016**, *84*, 95–106. [CrossRef]
14. RILEM Committee 68-MMH. The hydratium of tricalcium silicate. *Mater. Struct.* **1984**, *17*, 457–468. [CrossRef]
15. Lei, W.G.; Struble, L.J. Microstructure and flow behavior of fresh cement paste. *J. Am. Ceram. Soc.* **1997**, *80*, 2021–2028. [CrossRef]
16. Jiang, W.; Roy, D.M. Microstructure and flow behavior of fresh cement paste. In *Flow and Microstructure of Dense Suspensions*; Struble, L.J., Zukoski, C.F., Maitland, G.C., Eds.; MRS Online Proceedings Library Archive: Warrendale, PA, USA, 1993; Volume 289, pp. 161–166.
17. Nessim, A.A.; Wajda, R.L. The rheology of cement pastes and fresh mortars. *Mag. Concr. Res.* **1965**, *17*, 59–68. [CrossRef]
18. Bouras, R.; Chaouche, M.; Kaci, S. Influence of viscosity-modifying admixtures on the thixotropic behaviour of cement pastes. *Appl. Rheol.* **2008**, *18*, 1–8. [CrossRef]
19. Cheng, D.H.; Evans, F. Phenomenological characterization of the rheological behaviour of inelastic reversible thixotropic and antithixotropic fluids. *Br. J. Appl. Phys.* **1965**, *16*, 1599–1617. [CrossRef]
20. Otsubo, Y.; Miyai, S.; Umeya, K. Time-dependent flow of cement pastes. *Cem. Concr. Res.* **1980**, *10*, 631–638. [CrossRef]
21. Roussel, N. Steady and transient flow behaviour of fresh cement pastes. *Cem. Concr. Res.* **2005**, *35*, 1656–1664. [CrossRef]
22. Lapasin, R.; Longo, V.; Rajgelj, S. Thixotropic behaviour of cement pastes. *Cem. Concr. Res.* **1979**, *9*, 309–318. [CrossRef]
23. Rubio-Hernández, F.J.; Morales-Alcalde, J.M.; Gómez-Merino, A.I. Limestone filler/cement ratio effect on the flow behaviour of a SCC cement paste. *Adv. Cem. Res.* **2013**, *25*, 262–272. [CrossRef]
24. Ma, S.; Qian, Y.; Kawashima, S. Experimental and modeling study on the non-linear structural buil-up of fresh cement pastes incorporating viscosity modifying admixtures. *Cem. Concr. Res.* **2018**, *108*, 1–9. [CrossRef]
25. Roussel, N.; Ovarlez, G.; Garrault, S.; Brumaud, C. The origins of thixotropy of fresh cement pastes. *Cem. Concr. Res.* **2012**, *42*, 148–157. [CrossRef]
26. Vom Berg, W. Inflkuence of specific surface and concentration of solids upon the flow behaviour of cement pastes. *Mag. Concr. Res.* **1979**, *31*, 211–216. [CrossRef]
27. Ivanov, Y.P.; Roshavelov, T.T. Flow behaviour of modified cement pastes. *Cem. Concr. Res.* **1993**, *23*, 803–810. [CrossRef]
28. Nehdi, M.; Mindess, S.; Aïtcin, P.C. Statistical modeling on the microfiller effect on the rheology of composite cement pastes. *Adv. Cem. Res.* **1997**, *9*, 37–46. [CrossRef]
29. Wong, H.H.C.; Kwan, A.K.H. Rheology of cement paste: Role of excess water to solid surface area ratio. *J. Mater. Civ. Eng.* **2008**, *20*, 189–197. [CrossRef]
30. Martins, R.M.; Bombard, A.J.F. Rheology of fresh cement paste with superplasticizer and nanosilica admixtures studied by response surface methodology. *Mater. Struct.* **2012**, *45*, 905–921. [CrossRef]
31. Micaelli, F.; Lanos, C.; Levita, G. Rheology and extrusion of cement-fly ashes pastes. In Proceedings of the XVth International Congress on Rheology, the Society of Rheology 80th Annual Meeting, Monterey, CA, USA, 3–8 August 2008; Co, A., Leal, L.G., Colby, R.H., Giacomm, A.J., Eds.; Amerivan Institute of Physics: College Park, MD, USA, 2008; pp. 665–667.
32. Tregger, N.A.; Pakula, M.E.; Shah, S.P. Influence of clays on the rheology of cement pastes. *Cem. Concr. Res.* **2010**, *40*, 384–391. [CrossRef]

33. Diamantonis, N.; Marinos, I.; Katsiotis, M.S.; Sakellariou, A.; Papathanasiou, A.; Kaloidas, V.; Katsioti, M. Investigations about the influence of fine additives on the viscosity of cement paste for self-compacting concrete. *Constr. Build. Mater.* **2010**, *24*, 1518–1522. [CrossRef]
34. Rubio-Hernández, F.J.; Cerezo-Aizpún, I.; Velázquez-Navarro, J.F. Mineral additives geometry influence in cement pastes flow. *Adv. Cem. Res.* **2011**, *23*, 55–60. [CrossRef]
35. Bentz, D.P.; Ferraris, C.F.; Galler, M.A.; Hansen, A.S.; Guynn, J.M. Influence of particle size distributions on yield stress and viscosity of cement-fly ash pastes. *Cem. Concr. Res.* **2012**, *42*, 404–409. [CrossRef]
36. Kwan, A.K.H.; Chen, J.J. Roles of packing density and water film thickness in rheology and strength of cement paste. *J. Adv. Concr. Technol.* **2012**, *10*, 332–344. [CrossRef]
37. Stefancic, M.; Mladenovic, A.; Bellotto, M.; Jereb, V.; Zavrsnik, L. Particle packing and rheology of cement pastes at different replacement levels of cement by α-Al_2O_3 submicron particles. *Constr. Build. Mater.* **2017**, *139*, 256–266. [CrossRef]
38. Burgos-Montes, O.; Alonso, M.M.; Puertas, F. Viscosity and water demand of limestone- and fly ash-blended cement pastes in the presence of superplasticisers. *Constr. Build. Mater.* **2013**, *48*, 417–423. [CrossRef]
39. Sun, R.; Zhao, Z.; Huang, D.; Xin, G.; Wei, S.; Ge, Z. Effect of fly ash and nano-$CaCO_3$ on the viscosity of cement paste. *Appl. Mech. Mater.* **2013**, *357–360*, 968–971. [CrossRef]
40. Simard, M.A.; Nkinamubanzi, P.C.; Jolicoeur, C.; Perraton, D.; Aïtcin, P.C. Calorimetry, rheology and compressive strength of superplasticized cement pastes. *Cem. Concr. Res.* **1993**, *23*, 939–950. [CrossRef]
41. Ltifi, M.; Guefrech, A.; Mounanga, P. Effects of sodium tripolyphosphate on the rheology and hydration rate of Portland cement pastes. *Adv. Cem. Res.* **2012**, *24*, 325–335. [CrossRef]
42. Mikanovic, N.; Jolicoeur, C. Influence of superplasticizers on the rheology and stability of limestone and cement pastes. *Cem. Concr. Res.* **2008**, *38*, 907–919. [CrossRef]
43. Ghio, V.A.; Monteiro, P.J.M.; Demsetz, L.A. The rheology of fresh cement paste containing polysaccharide gums. *Cem. Concr. Res.* **1994**, *24*, 243–249. [CrossRef]
44. Lachemi, M.; Hossain, K.M.A.; Lambros, V.; Nkinamubanzi, P.C.; Bouzoubaa, N. Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste. *Cem. Concr. Res.* **2004**, *34*, 185–193. [CrossRef]
45. Hot, J.; Besdsaies-Bey, H.; Brumaud, C.; Duc, M.; Castella, C.; Roussel, N. Adsorbing polymers and viscosity of cement pastes. *Cem. Concr. Res.* **2014**, *63*, 12–19. [CrossRef]
46. Lombois-Burger, H.; Colombet, P.; Halary, J.L.; Van Damme, H. On the frictional contribution to the viscosity of cement and silica pastes in the presence of adsorbing and non adsorbing polymers. *Cem. Concr. Res.* **2008**, *38*, 1306–1314. [CrossRef]
47. Colombo, A.; Geiker, M.R.; Justnes, H.; Lauten, R.A.; De Weerdt, K. On the effect of calcium lignosulfonate on the rheology and setting time of cement paste. *Cem. Concr. Res.* **2017**, *100*, 435–444. [CrossRef]
48. Vicar, H. Influence of temperature, cement and plasticizer type on the rheology of paste. In Proceedings of the Second International Symposium on Design, Performance and Use of Self-Consolidating Concrete, Beijing, China, 5–7 June 2009.
49. Bonen, D.; Sarkar, S.L. The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss. *Cem. Concr. Res.* **1995**, *25*, 1423–1434. [CrossRef]
50. Bessaies-Bey, H.; Baumann, R.; Schmitz, M.; Radler, M.; Roussel, N. Effect of polyacrylamide on rheology of fresh cement pastes. *Cem. Concr. Res.* **2015**, *76*, 98–106. [CrossRef]
51. Mukhopadhyay, A.K.; Jang, S. Predicting cement-admixture incompatibilities with cement paste rheology. *Transp. Res. Rec. J Transp. Res. B* **2012**, *2290*, 19–29. [CrossRef]
52. Struble, L.; Sun, G.K. Viscosity of Portyland cement paste as a function of concentration. *Adv. Cem. Based Mater.* **1995**, *2*, 62–69. [CrossRef]
53. Houst, Y.F.; Flatt, R.J.; Bowen, P.; Hofmann, H.; Mäder, U.; Widmer, J.; Sulser, U.; Bürge, T.A. Influence of superplasticizer adsorption on the rheology of cement paste. In Proceedings of the International Conference "The Role of Chemical Admixtures in High Performance Concrete", Monterrey, Mexico, 21–26 March 1999; Cabrera, J.G., Rivera-Villareal, R., Eds.; RILEM Publications S.A.R.L.: Cachan, France, 1999; pp. 387–402.
54. Jayasree, C.; Gettu, R. Experimental study of the flow behaviour of superplasticized cement paste. *Mater. Struct.* **2008**, *41*, 1581–1593. [CrossRef]
55. Kwan, A.K.H.; Chen, J.J.; Fung, W.W.S. Effects of superplasticiser on rheology and cohesiveness of CSF cement paste. *Adv. Cem. Res.* **2012**, *24*, 125–137. [CrossRef]

56. Liu, J.; Wang, K.; Zhang, Q.; Han, F.; Sha, J.; Liu, J. Influence of superplasticizer dosage on the viscosity of cement paste with low water-binder ratio. *Constr. Build. Mater.* **2017**, *149*, 359–366. [CrossRef]
57. Papo, A.; Piani, L. Flow behaviour of fresh Portland cement pastes. *Part. Sci. Technol.* **2004**, *22*, 201–212. [CrossRef]
58. John, E.; Gettu, R. Effect of temperatura on fflow properties of superplasticized cement paste. *ACI Mater. J.* **2014**, *111*, 67–76.
59. Papo, A.; Piani, L.; Ceccon, L.; Novelli, V. Flow behavior of fresh very high strength Portland cement pastes. *Part. Sci. Technol.* **2010**, *28*, 74–85. [CrossRef]
60. Hanehara, S.; Yamada, K. Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology. *Cem. Concr. Res.* **1999**, *29*, 1159–1165. [CrossRef]
61. Shu, X.; Zhao, H.; Wang, X.; Zhang, Q.; Yang, Y.; Ran, Q.; Liu, J. Effect of hydrophobic units of polycarboxylate superplasticizer on the flow behavior of cement paste. *J. Disp. Sci. Technol.* **2017**, *38*, 256–264. [CrossRef]
62. Ouyang, J.; Han, B.; Cao, Y.; Zhou, W.; Li, W.; Shah, S.P. The role and interaction of superplasticizer and emulsifier in fresh cement asphalt emulsion paste through rheology study. *Constr. Build. Mater.* **2016**, *125*, 643–653. [CrossRef]
63. Yuan, Q.; Liu, W.T.; Wang, C.; Deng, D.H.; Liu, Z.Q.; Long, G.C. Coupled effect of viscosity enhancing admixtures and superplasticizers on rheological behavior of cement paste. *J. Cent. South Univ.* **2017**, *24*, 2172–2179. [CrossRef]
64. Tan, H.; Zuo, F.; Ma, B.; Guo, Y.; Li, X.; Mei, J. Effect of competitive adsorption between sodium gluconate and polycarboxylate superplasticizer on rheology of cement paste. *Constr. Build. Mater.* **2017**, *144*, 338–346. [CrossRef]
65. Reales, O.A.M.; Jaramillo, Y.P.A.; Botero, J.C.O.; Delgado, C.A.; Quintero, J.H.; Filho, R.D.T. Influence of MWCNT/surfactant dispersions on the rheology of Portland cement pastes. *Cem. Concr. Res.* **2018**, *107*, 101–109. [CrossRef]
66. Wang, D.; Liu, Z.; Wu, Z.; Xiong, W.; Zuo, Y. Effect of viscosity modifying agents on the rheology properties of cement paste with polycarboxylate superplasticizer. In Proceedings of the Second International Symposium on Design, Performance and Use of Self-Consolidating Concrete, Beijing, China, 5–7 June 2009.
67. Qian, Y.; De Schutter, G. Enhancing thixotropy of fresh cement pastes with nanoclay in presence of polycarboxylate ether superplasticizer (PCE). *Cem. Concr. Res.* **2018**. [CrossRef]
68. Ma, B.; Peng, Y.; Tan, H.; Jian, S.; Zhi, Z.; Guo, Y.; Qi, H.; Zhang, T.; He, X. Effect of hydroxypropyl-methyl cellulose ether on rheology of cement paste plasticized by polycarboxylate superplasticizer. *Constr. Build. Mater.* **2018**, *160*, 341–350. [CrossRef]
69. Ma, B.; Peng, Y.; Tan, H.; Lv, Z.; Deng, X. Effect of polyacrylic acid on rheology of cement paste plasticized by polycarboxylate superplasticizer. *Materials* **2018**, *11*, 1081. [CrossRef]
70. Tan, H.; Guo, Y.; Zuo, F.; Jian, S.; Ma, B.; Zhi, Z. Effect of borax on rheology of calcium sulphoaluminate cement paste in the presence of polycarboxylate superplasticizer. *Constr. Build. Mater.* **2017**, *139*, 277–285. [CrossRef]
71. Rubio-Hernández, F.J.; Moreno-Lechado, S.; Velázquez-Navarro, J.F. Experimental study on the influence of two different additives onto the flow behaviour of a fresh cement paste. *Adv. Cem. Res.* **2011**, *23*, 255–263. [CrossRef]
72. Ng, S.; Justnes, H. Influence of lignosulfonate on the early age rheology and hydration characteristics of cement pastes. *J. Sustain. Cem.-Based Mater.* **2015**, *4*, 15–24. [CrossRef]
73. Bouras, R.; Kaci, A.; Chaouche, M. Influence of viscosity modifying admixtures on the rheological behavior of cement and mortar pastes. *Korea-Aust. Rheol. J.* **2012**, *24*, 35–44. [CrossRef]
74. Ouyang, J.; Tan, Y. Rheology of fresh cement asphalt emulsion pastes. *Constr. Build. Mater.* **2015**, *80*, 236–243. [CrossRef]
75. Ouyang, J.; Corr, D.J.; Shah, S.P.; Asce, M. Factors influencing the Rheology of fresh cement asphalt emulsion paste. *J. Mater. Civ. Eng.* **2016**, *28*, 1–9. [CrossRef]
76. Ouyang, J.; Tan, Y.; Corr, D.J.; Shah, S.P. Viscosity prediction of fresh cement asphalt emulsion pastes. *Mater. Struct.* **2017**, *50*, 59–69. [CrossRef]

77. Mehdipour, I.; Khayat, K.H. Effect of particle-size distribution and specific surface area of different binder systems on packing density and flow characteristics of cement paste. *Cem. Concr. Comp.* **2017**, *78*, 120–131. [CrossRef]
78. Páez-Flor, N.M.; Rubio-Hernández, F.J.; Velázquez-Navarro, J.F. Steady viscous flow of some commercial Andean volcanic Portland cement pastes. *Adv. Cem. Res.* **2017**, *29*, 438–449. [CrossRef]
79. Sébaïbi, Y.; Dheilly, R.M.; Quéneudec, M. A study of the viscosity of lime-cement paste: Influence of the physic-chemical characteristics of lime. *Constr. Build. Mater.* **2004**, *18*, 653–660. [CrossRef]
80. Favier, A.; Hot, J.; Habert, G.; Roussel, N.; De Lacaillerie, J.B.D. Flow properties of MK-based geopolymers pastes. A comparative study with standard Portland cement pastes. *Soft Matter* **2014**, *10*, 1134–1141. [CrossRef]
81. Janotka, I.; Puertas, F.; Palacios, M.; Kuliffayová, M.; Varga, C. Metakaolin sand-blended-cement pastes: Rheology, hydration process and mechanical properties. *Constr. Build. Mater.* **2010**, *24*, 791–802. [CrossRef]
82. Banfill, P.F.G.; Rodríguez, O.; de Rojas, M.I.S.; Frías, M. Effect of activation conditions of a kaolinite based waste on rheology of blended cement pastes. *Cem. Concr. Res.* **2009**, *39*, 843–848. [CrossRef]
83. Safi, B.; Benmounah, A.; Saidi, M. Rheology and zeta potential of cement pastes containing calcined slit and ground granulated blast-furnace slag. *Mater. Constr.* **2011**, *61*, 353–370. [CrossRef]
84. Rissanen, J.; Ohenoja, K.; Kinnunen, P.; Romagnoli, M.; Illikainen, M. Milling of peat-wood fly ash: Effect on water demand of mortar and rheology of cement paste. *Constr. Build. Mater.* **2018**, *180*, 143–153. [CrossRef]
85. Nachbaur, L.; Mutin, J.C.; Nonat, A.; Choplin, L. Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting. *Cem. Concr. Res.* **2001**, *31*, 183–192. [CrossRef]
86. Páez-Flor, N.M.; Rubio-Hernández, F.J.; Velázquez-Navarro, J.F. Microstructure-at-rest evolution and steady viscous flow behavior of fresh natural pozzolanic cement pastes. *Constr. Build. Mater.* **2018**. [CrossRef]
87. Choi, M.; Park, K.; Oh, T. Viscoelastic properties of fresh cement paste to study the flow behavior. *Int. J. Concr. Struct. Mater.* **2016**, *10*, S65–S74. [CrossRef]
88. Struble, L.J.; Schultz, M.A. Using creep and recovery to study flow behavior of fresh cement paste. *Cem. Concr. Res.* **1993**, *23*, 1369–1379. [CrossRef]
89. Nehdi, M.; Martini, S.A. Estimating time and temperature dependent yield stress of cement paste using oscillatory rheology and generic algorithms. *Cem. Concr. Res.* **2009**, *39*, 1007–1016. [CrossRef]
90. Schultz, M.A.; Struble, L.J. Use of oscillatory shear to study flow behavior of fresh cement paste. *Cem. Concr. Res.* **1993**, *23*, 273–282. [CrossRef]
91. Bingham, E.C. *Fluidity and Plasticity*; McGraw-Hill Book Co. Inc.: New York, NY, USA, 1922; p. 440.
92. Feys, D.; Verhoeven, R.; De Schutter, G. Evaluation of time independent rheological models applicable to fresh self-compacting concrete. *Appl. Rheol.* **2007**, *17*, 1–10.
93. Herschel, W.H.; Bulkley, R. Measurement of consistency as applied to rubber-benzene solutions. *Am. Soc. Test. Proc.* **1926**, *26*, 621.
94. Robertson, R.E.; Stiff, H.A. An improved mathematic model for relating shear stress to shear rate in drilling fluids and cement slurries. *J. Soc. Pet. Eng.* **1976**, *16*, 31–36. [CrossRef]
95. Karam, G.N. Theoretical and empirical modeling of the rheology of fresh cement pastes. *Mater. Res. Soc. Symp. Proc.* **1993**, *289*, 167–172. [CrossRef]
96. Casson, N. A flow equation for pigment oil suspensions of the printing ink type. In *Rheology of Disperse Systems*; Mill, C.C., Ed.; Pergamon Press: London, UK, 1959; pp. 84–102.
97. Matsumoto, T.; Takashima, A.; Masuda, T.; Onogi, S. A modified Casson equation for dispersions. *Trans. Soc. Rheol.* **1970**, *14*, 617–620. [CrossRef]
98. Wessel, R.; Ball, R.C. Fractal aggregates and gels in shear flow. *Phys. Rev. A* **1992**, *46*, R3008. [CrossRef]
99. Michaels, A.S.; Bolger, J.C. The plastic flow behavior of flocculated kaolin suspensions. *Ind. Eng. Chem. Fundam.* **1962**, *1*, 153–162. [CrossRef]
100. Thomas, D.G. Transport characteristics of suspensions VII. Relation of hindered-settling floc characteristics to rheological parameters. *AIChE J.* **1963**, *9*, 310–316. [CrossRef]
101. Thomas, D.G. Turbulent disruption of flocs in small particle size suspensions. *AIChE J.* **1964**, *10*, 517–523. [CrossRef]
102. Chandler, H.W.; Macphee, D.E. A model for the flow of cement pastes. *Cem. Concr. Res.* **2003**, *33*, 265–270. [CrossRef]

103. Lapasin, R.; Papo, A.; Rajgelj, S. Flow behavior of fresh cement pastes. A comparison of different rheological instruments and techniques. *Cem. Concr. Res.* **1983**, *13*, 349–356. [CrossRef]
104. Hopkins, C.J.; Cabrera, J.G. The turning-tube viscometer: An instrument to measure the flow behaviour of cement-pfa pastes. *Mag. Concr. Res.* **1985**, *37*, 101–106. [CrossRef]
105. Min, B.H.; Erwin, L.; Jennings, H.M. Rheological behaviour of fresh cement paste as measured by squeeze flow. *J. Mater. Sci.* **1994**, *29*, 1374–1381. [CrossRef]
106. Phan, T.H.; Chaouche, M. Rheology and stability of self-compacting concrete cement pastes. *Appl. Rheol.* **2005**, *15*, 336–343.
107. Jarny, S.; Roussel, N.; Le Roy, R.; Coussot, P. Thixotropic behavior of fresh cement pastes from inclined plane flow measurements. *Appl. Rheol.* **2008**, *18*, 1–8.
108. Zhou, X.; Li, Z.; Fan, M.; Chen, H. Rheology of semi-solid fresh cement pastes and mortars in orifice extrusion. *Cem. Concr. Comp.* **2013**, *37*, 304–311. [CrossRef]
109. Kim, J.H.; Kwon, S.H.; Kawashima, S.; Yim, H.J. Rheology of cement paste under high pressure. *Cem. Concr. Comp.* **2017**, *77*, 60–67. [CrossRef]