Cement and Concrete Research 40 (2010) 77–84

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Steady state flow of cement suspensions: A micromechanical state of the art

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ARTICLE INFO

Article history:
Received 20 May 2009
Accepted 28 August 2009

Keywords:
Admixture (D)
Particles
Rheology (A)
Shear thickening
Yield stress

ABSTRACT

Fresh cementitious pastes can be viewed as suspensions of particles of many different sizes (from several tens of nm to 100 μm) in a continuous fluid phase. This broad poly-dispersity implies that various interactions such as surface forces (or colloidal interactions), Brownian forces, hydrodynamic forces or various contact forces between particles interplay. Depending on the volume fraction of the particles in the mixture, the use of admixtures or the magnitude of either the applied stress or strain rate, one or several of these interactions dominate. Our objective here is not to quantitatively predict rheology of cement pastes but rather to understand and classify the situations where, depending on composition and processing, one or other of the physical phenomena will control the macroscopic behavior. The result of this analysis is a conceptual diagram of predominant interactions in flowing cementitious suspensions under simple shear, as a function of shear rate and solid fraction.

1. Introduction

The vast family of industrial cementitious materials presents such a variety of rheological behaviors that their classification seems unattainable. This is even more so for the possibility to predict, if only qualitatively, their response in practical processing conditions. However, achieving such predictive capabilities would be extremely useful since the quality of placing (or shaping) is crucial to obtain the best possible properties of the hardened materials. This holds for ordinary concrete, roller compacted concrete, self compacting concrete, self leveling concretes, overlay mortars, injection grouts. For all these materials, improper processing and/or placing such as segregation, excessive bleeding, incomplete formwork filling, air bubble void, *etc.* will lead to defects that greatly affect strength after setting and more importantly durability.

It is our opinion that a better understanding and classification of the basic principles that govern the fresh state properties of cementitious materials will contribute to avoiding such problems. Our objective in this paper is to propose a general framework for such a classification. Although we do not resolve or address detailed processing problems of all fresh cementitious materials, we provide here general guidelines to identify the physical parameters which govern the macroscopic rheological behavior. In doing so, we hope this rheological classification will contribute to progress in the materials science of cementitious materials, whereby we summarize materials science by “the study of how microstructure controls properties and how processing and composition control microstructure”.

2. Background

Let us first recall that apparent viscosity is defined as the ratio between instantaneous shear stress and shear rate. As an example, this rheological parameter may be used to roughly evaluate the time needed to empty a truck or fill a given formwork [1]. Depending on their mix-proportioning and the considered range of shear rates, cementitious materials may display, in steady state flow, either Newtonian (*i.e.* constant apparent viscosity), shear thinning (*i.e.* decreasing apparent viscosity with shear rate) or shear thickening behavior (*i.e.* increasing apparent viscosity with shear rate). In the case of a pumped concrete, the pumping pressure will thus depend on the mix proportioning and on the pumping rate.

Moreover, most cementitious materials display a yield stress that should be overcome to initiate flow from rest, and below which the flow stops during casting. The first part of this definition of yield stress is very relevant for other industrial materials such as paint or ketchup where the initiation or non initiation of flow is clearly essential. For cementitious materials, cases where non initiation of flow are desired include so-called zero slump concrete or shotcrete where, after spraying, it is clearly desired that the material should stay on the wall in thick layers rather than flow down. However, in most cases of industrial interest, the yield stress of cementitious materials would be more pertinently defined in terms of the shear stress below which the material stops flowing. For example, in the case of concrete, if this yield stress is too high, it may prevent the filling of a given formwork [2]. Indeed, the stress generated by gravity during casting decreases until it becomes equal to the yield stress, at which point the flow stops [3]. Apart from the macroscopic yield stress of concrete, the yield stress of the constitutive paste formed by water and fine particles such as cement, fly-ash, slag, silica fume and other fine fillers is also important in most practical situations. For example, the value of the yield

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doi:10.1016/j.cemconres.2009.08.026

stress of the cement paste determines whether sedimentation of the coarsest elements [4,5] of the concrete may occur. Indeed, sedimentation is avoided when the gravity forces, generated by the density difference between an individual coarse grain and the cement paste, are too small to overcome the yield stress of the cement paste. Moreover, as shown in [6], there is a strong correlation between the yield stress of the cement paste and the yield stress of the associated concrete.

Finally, another major aspect of the rheology of cementitious systems is its dependence on the flow history of the material. For example, the yield stress of a concrete left at rest or slowly sheared significantly increases with time. This leads to what is often described as "workability loss". Some of the structural changes responsible for the evolution of rheological properties are reversible: their effects are erased by mixing or by any type of strong shearing which brings the system back to a previous structural state. These reversible changes, often dominant on short observation times, are generally described as thixotropy [7–16]. Other changes, in particular consequences of the hydration phenomenon, are irreversible [17–19] and thus contribute to the long term evolution of material properties (towards the solid state) even if they take place on longer time scales than thixotropy. We will however in this paper only focus on steady state properties of the material.

3. Review of interactions and basic implications on the rheological behavior

Despite the variety of parameters and the complexity of physical phenomena governing rheology, we show, in this paper, that it is possible to identify a few major trends and propose a rough classification of cementitious materials. For example, depending on the amount of water mixed with a given cement powder, the obtained suspension either behaves as an almost Newtonian fluid (cement grout) or presents a yield stress [20]. Moreover, cement suspensions may display shear thinning, Newtonian and shear thickening behaviors [21,22] depending on the applied shear rate. Of course, a possible classification can emerge only from a detailed study of the physical phenomena governing the material response, aiming at understanding how they emerge from the mixture components and their interactions.

If fresh cement pastes can be viewed as suspensions of particles of many different sizes (from several nm to 100 µm) in a continuous fluid phase, this broad poly-dispersity implies that various interactions interplay. We can at least identify four main types of interactions:

(i) Surface forces (or colloidal interactions).
(ii) Brownian forces.
(iii) Hydrodynamic forces.
(iv) Various contact forces between particles.

Depending on the size of the particles, on their volume fraction in the mixture and on external forces (*e.g.* the magnitude of either the applied stress or strain rate), one or several of these interactions dominate [23]. Our objective here is not to quantitatively predict rheology of cement pastes but rather to understand and classify the situations where, depending on composition and processing, one or the other physical phenomena will control the macroscopic behavior. In this respect, we follow Coussot and Ancey [24], who proposed a conceptual diagram of predominant interactions in flowing concentrated suspensions under simple shear, as a function of shear rate and solid fraction. We will make here the following assumptions and choices:

(i) Since cementitious materials are always broadly poly-disperse, the question of defining a characteristic particle size d is delicate. Here, we shall use a characteristic average particle size and overlook the exact granular distribution [25,26].
(ii) The amount of each solid component as well as the total solid amount in the mixture are given by their volume fractions ϕ (*i.e.* the ratio of the volume of solid to the total sample volume). Unlike the weight fraction, ϕ is of critical importance for evaluating the rheo-physical properties as it is directly related to the geometrical packing of the suspension.
(iii) Only stable mixtures are considered (*i.e.* sedimentation will not be dealt with specifically).

In practice, cement pastes are yield stress fluids. Their yielding behavior basically takes the form of a flow curve such as the one shown in Fig. 1. The stress tends to a finite value at low shear rates. This is the minimum value of the applied stress (the yield stress τ_0) needed to initiate flow. At high shear rates, their viscosities tend towards a constant value (note the plateau in Fig. 1 (right)).

We will recall here that yield stress corresponds to the energy that has to be applied to the system in order to break a network of interaction between particles. It originates from colloidal and contact interactions between particles and depends on the volume fraction and nature of the solid particles. It is affected by the presence of plasticizers.

We will also recall that, in the flow regime, the macroscopic viscosity of the mixture (higher than the viscosity of the suspending fluid) results from a complex interplay between hydrodynamic, colloidal and contact forces involved in the motion of the suspended cement grains.

A Bingham type relation ($\tau = \tau_0 + \mu_p\dot{\gamma}$) where μ_p is the plastic viscosity is often used to describe the shear thinning behavior at low and intermediate shear rates of cement pastes (See Fig. 1). On the basis of this observation, it is possible to evaluate the macroscopic relative importance of the yield stress and the viscosity from the value of the following dimensionless empirical number:

$$\Gamma = \frac{\mu_p\dot{\gamma}}{\tau_0} \qquad (1)$$

It is then possible to determine a critical value of the shear rate $\dot{\gamma}_0(\Gamma = 1)$ above which the effect of the yield stress on the flow behavior can be neglected. For $\dot{\gamma} < \dot{\gamma}_0$, a shear thinning behavior is observed. For $\dot{\gamma} \gg \dot{\gamma}_0$, a plateau is expected. We could expect roughly that, below $\dot{\gamma}_0$, the macroscopic response is dominated by the behavior of the network

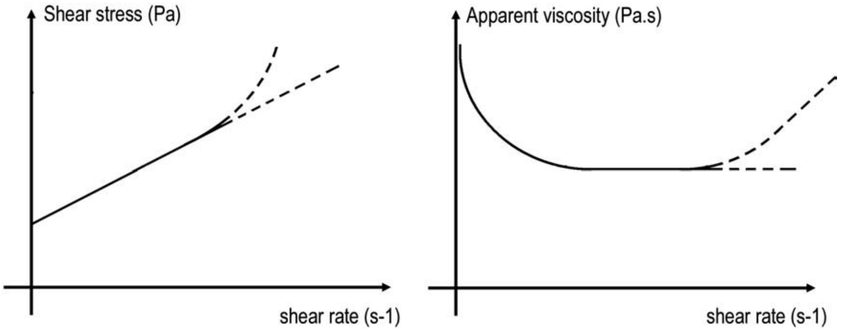

Fig. 1. Typical shear stress vs. shear rate (left) or apparent viscosity vs. shear rate (right) for cementitious materials. The dashed lines represent two different possible behaviors depending on the mix proportions and the range of shear rates.

of particle interactions while, above $\dot{\gamma}_0$, hydrodynamic effects progressively become predominant. However, as it will be described further in this paper, this simple scheme may be perturbed by the inertia of the particles at high shear rates and shear thickening behavior such as the one shown in Fig. 1 may be observed.

In the first part of this paper, we will focus on the yield stress behavior of cement suspensions and on the transition between rest and flow. In the second part, we will describe what happens when the material flows. Finally, in a third part, we will propose a rheo-physical classification of cement suspensions which will gather in a synthetic way most of the results presented here.

4. Components and interactions within a cement suspension

Water is the only liquid component in the mixture and, if the effects of the admixtures [21] are neglected, we shall consider that its Newtonian viscosity μ_0 is of the order of that of pure water at 20 °C ($\mu_0 = 1$ mPa s). Solid cement particles, the density ρ_p of which is about 3100 kg/m^3, are suspended in this fluid. Their size ranges approximately from 1 µm to 100 µm. We shall, in the following, for the sake of simplicity consider that the characteristic size of cement grains d is around 10 µm [23]. We shall also consider that the water to cement ratio W/C in modern cement suspensions varies between 0.20 and 0.60. This range covers cement grouts and cement pastes and, for the lowest values, this assumes that, often, a super-plasticizer will be added to the mixture to make it workable. The solid volume fraction of such a cement paste is $\phi = (1 + \rho_p W / \rho_w C)^{-1}$ and thus ranges from 0.35 to 0.60.

Several types of non-contact interactions occur within a cementitious suspension [23]. At short distance, cement particles interact via (generally attractive) van der Waals forces [27]. Also, there are electrostatic forces that result from the presence of adsorbed ions at the surface of the particles [28]. Polymer additives, present in many modern cementitious materials, can induce steric hindrance [29–31], which is believed to predominate over electrostatic repulsion. Each of these different interactions introduces non-contact forces between particles, the magnitude of which depend primarily on their separation distance. Repulsive electrostatic forces alone are generally insufficient alone to prevent agglomeration due to van der Waals forces and steric hindrance or additional electrostatic repulsion from polymers is needed to disperse the cement particles as recently observed in [30].

However, it has to be kept in mind that cement particles smaller than a few µm as any other small particles in nature or industry may be subjected to significant random (Brownian) motions, which *e.g.* causes them to diffuse through the suspending liquid. In order to estimate the relative magnitude of the Brownian over inter-particle forces, we introduce a dimensionless number [24]:

$$N_r = \frac{\Phi_0}{kT} \tag{2}$$

where Φ_0 is an energy which characterizes the strength of the inter-particle interactions and kT is the typical energy associated with thermal agitation (k is the Boltzmann constant and T the absolute temperature). Non-contact interactions are negligible compared to thermal agitation if N_r is much smaller than 1. In the particular case of non retarded van der Waals interaction, which were shown to dominate the other colloidal interactions in the case of cement pastes and therefore dictate the inter-particle distance [31,32], Φ_0 can be written as [26]:

$$\Phi_0 \cong \frac{A_0 a^*}{12H} \tag{3}$$

where a^* is the radius of curvature of the "contact" points, H is the surface to surface separation distance at "contact" points (see Fig. 2) and A_0 is the Hamaker constant [26]. It can be noted that H is strongly affected by polymers and, even in cases without any polymers, can never equal zero because of very short range repulsive electrostatic forces.

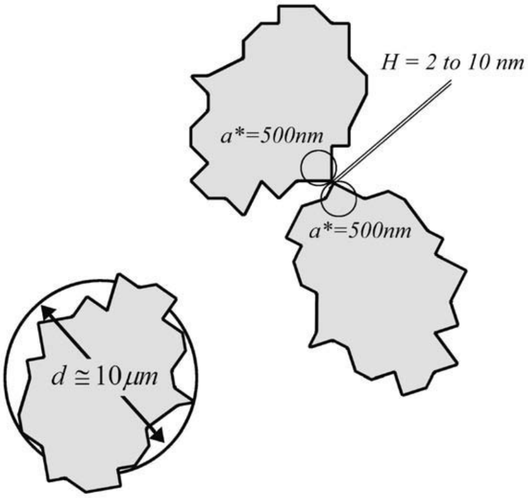

Fig. 2. Average diameter, radius of curvature and surface to surface separation distance at "contact" points.

Let us estimate N_r in the case of cement paste. kT at room temperature is of order $4 \cdot 10^{-21}$ J. The Hamaker constant value for C_3S is of the order of $1.6 \cdot 10^{-20}$ J [27]. N_r is therefore of order $a^* / 3H$, where we emphasize that a^* is determined by the shape of the particles and not by their radius [26]. The values of H that may be found in the literature [26,33] are of the order of 2 nm for flocculated systems and 10 nm for totally dispersed systems. The estimated value of a^* for cement particles is of the order of 500 nm. A value for a^* of the order of 20 nm was estimated for alumina particles [26]. This value is probably substantially larger for cement particles that are about 20 times larger than those alumina particles. We might therefore assume a^* to be rather in the range of 500 nm. These values leave N_r of order 10^2 for flocculated systems and 10 for totally dispersed ones.

This value suggests that, for flocculated systems, Brownian effects only play a minor role and are dominated by the van der Waals attractive inter-particle forces. Of course, quantifying precisely the role of Brownian motion, especially in totally dispersed pastes, is an interesting and open question which will require further studies but, as a first approximation, it is reasonable to think of cementitious materials under the assumption that, if two particles are brought into contact by thermal agitation or shear, they cannot be separated by thermal agitation. Each cement particle will then interact with a few neighbors and stay in the vicinity of their neighbors. The formation and destruction of contacts between particles and in general structural changes can of course result from shear, as will be discussed later.

Note, however, that many experiments show that rheology of cementitious suspensions strongly depends on temperature. For example, it was found in [18] that the increase of the yield stress of a cement paste with time is accelerated when the temperature increases. This temperature dependence is proof that some thermally activated processes are at work. The estimate above however suggests that Brownian motion plays only a minor role in this temperature dependence. We should thus expect that other mechanisms are involved. In particular, we can think of physico-chemical processes affecting the inter-particle bond strength. Some of these processes correspond to the chemical formation of bonds between cement particles in close contact (*e.g.* hydration reaction) although many other phenomena might be involved. These processes should also be related to the work by Banfill et al. or Otsubo et al. [17,19] where the long term evolution of the apparent viscosity of the material is attributed to the hydration process. But formation of chemical bonds may also be involved in thixotropy (*i.e.* reversible evolution). Indeed, if the chemical bonds are weak enough, they are likely to be broken by shear.

Their formation is hence not incompatible with a macroscopic reversible evolution.

It should also be noted that modern cementitious materials such as Self Compacting Concretes (SCC) or “green” concretes may contain particles from alternative powders far smaller than cement particles (a factor 10 is not uncommon). These smaller particle sizes may result in smaller value of N_r, whereby Brownian motion may have an influence. It was indeed noted in [34] that substituting a volume of cement by finer particles in a cementitious system reduces bleeding. This effect may be explained by the fact that, for small values of N_r, flocculation in the suspension at rest should become reversible (*i.e.* thermal agitation can separate particles in contact). By reducing the amount of flocs which are prone to sedimentation, cement suspensions should become more stable. To this end, we should also add that the fine fraction from the broad particle size distribution of cement can be expected to play a similar role. Although in small amounts, the role of these particles could be quite important.

The following simple scheme should be kept in mind when considering a cementitious suspension at rest. Because of Brownian motion, cement particles diffuse through the liquid and may get close enough for the van der Waal attractive forces to strongly increase and dominate electrostatic repulsion. As Brownian motion is not able to separate the particles, they agglomerate. In order to prevent this situation from occurring, water reducing admixtures may be used. They can be seen as molecules which get adsorbed at the surface of cement grains and, through steric hindrance or electrostatic effects, increase the average inter-particle distance and therefore decrease the magnitude of the attractive van der Waal forces.

5. The yield stress

5.1. Interactions network

In order to support a finite amount of stress without flow, the suspension must possess an internal network of particles with attractive interactions either via direct contacts or via colloidal forces. An extreme situation occurs in very dilute suspensions (for large *W*/*C*) when there is no direct contact between particles and when particles are sufficiently far apart so that the above-mentioned colloidal interactions are negligible. In this case, we must expect that the suspension is essentially Newtonian just as the water in which the particles are suspended. This situation was encountered in [35] where, below a critical value of *W*/*C*, the measured behavior of the tested cement pastes was purely Newtonian. The critical solid fraction value below which the suspension does not display any yield stress at all varies according to the physicochemical properties of the cement powder and to the nature and amount of the additives used in the mixture. It can be defined as the percolation volume fraction ϕ_{perc} above which a network of colloidal interactions appears in the material. Values ranging between 20 and 40% depending on the sensitivity of the yield stress measurements can be found in the literature [21,26]. These values correspond to water to cement ratio between 0.6 and 1.2.

When cementitious materials exhibit a yield stress, it is because of the network of attractive particle–particle interactions, which allows the suspension to support finite amount of stress without flowing. Macroscopic flow is achieved as soon as the stress applied to the system overcomes what can be supported by the attractive network of particle interactions. Yield stress is thus dictated by the structure of the interaction network. Accumulated experimental and numerical evidence show that network breakage occurs when its initial shape has been sufficiently modified, namely for a critical deformation γ_c [36–39], which only weakly depends on the details of the interaction forces. This critical deformation and the yield stress are related by $\tau_0 = G\gamma_c$ where *G* is the shear elastic modulus as long as we assume a linear elastic behavior in the solid regime below the yield stress. Note, here, that there is an ambiguity in the literature concerning the value of the critical deformation of cement pastes. When Papo and Piani [40] or Schmidt and Schlegel [41] study the transition from rest to flow, they measure a critical deformation of the order of several % while other studies using oscillary rheometry point towards values of the order of few hundredths of % [42,43]. Caution should however be exerted about this second value, which is defined by a change in shear modulus in oscillatory rheometry and not by a true measurement of the flow onset. As a consequence, these lowest values are inconsistent with studies of yielding in networks of interacting particles [37–39]. Moreover, this γ_c cannot be related to the yield stress (for the flow onset) using the relation $\tau_0 = G\gamma_c$. We expect that the change of shear modulus observed in oscillatory rheometry results from minute changes in the particle/particle contacts. In particular, the breakage of an interparticle bond that has a range of a couple nm with respect to particles that are on the order of 10 µm would give the critical deformation in the range of a few hundredths of %. This does not mean however that the system begins to flow. Indeed and in contrast, the value of several % is however related to large structural changes corresponding to the actual reorganization of the particle network at flow onset.

Many observations [21,23,25–27,33] concur that yield stress increases with volume fraction and, for all practical purposes, diverges when ϕ reaches a critical packing fraction ϕ_{div}. In fact, as ϕ increases, the soft repulsive interactions between cement particles (polymer layers, electrostatic forces…) are progressively less capable of sustaining the normal forces and direct contacts between rigid cement grains are increased. Since the cement grains are very rigid, high levels of stress are required to further compress the network of rigid grain–grain contact, hence the apparent divergence of stress at ϕ_{div}. More insights of this quantity come from studies of packing of rigid particles.

5.2. Packing of rigid particles

It is known that stable packing of rigid particles is observed only above a critical packing fraction ϕ_c, which can be associated to a percolation process of particles in contact (cf. Fig. 3). Experimental and numerical results indicate that, for uniform spheres, ϕ_c (the so-called Random Loose Packing (RLP) fraction) should be situated around 0.5 [44]. There exists also a dense packing fraction ϕ_m (the close packing fraction), which is a geometric property of packing of non interacting rigid particles (cf. Fig. 3). Both ϕ_c and ϕ_m are directly related to the poly-dispersity and shapes of the constitutive particles. For example, for identical spheres, ϕ_m is of the order of 0.64. As it will be shown below, although they may be difficult to measure in the case of cement pastes, ϕ_c and ϕ_m are major characteristics of a cement suspension [35].

In the general case of poly-disperse granular materials, Hu and de Larrard [45] have proposed a semi-empirical relation predicting ϕ_m in

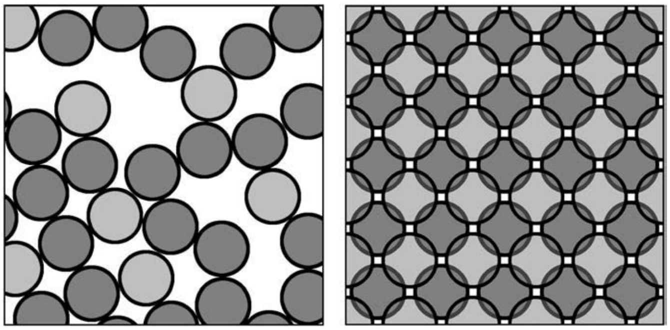

Fig. 3. Packing of rigid particles. (left) random loose packing fraction for which a contact network appears in the granular materials (of order 0.55 for uniform spheres). (right) dense packing fraction (of order 0.64 for uniform spheres).

terms of the diameter of smallest and largest particles in a granular system $\phi_m = 1-0.45(d_{min}/d_{max})^{0.19}$. The ratio between the smallest and largest grains in cement powders being of the order of 100, ϕ_m, according to the above relation, should thus be of the order of 80%. This estimate is weakened for cement by the somewhat arbitrary limit put on the particle size distributions. Furthermore, if, for the same cement, one uses the full compressible packing model of de Larrard [46] assuming each particle class can pack individually to 65%, then, the maximum packing of cement is only slightly larger than identical spheres in random configuration and about 68%. Moreover, it can be noted that it is possible to determine experimentally the maximum packing of cement suspensions by filter pressing [33,47]. This technique involves pressing out the liquid of a suspension over a filter and measuring the compaction obtained as a function of applied pressure.

Note that, like ϕ_m, ϕ_c should also increase in the case of poly-disperse particles. In fact, experimental observations [6,15] even suggest that the ratio ϕ_c/ϕ_m (equal to 0.85 for mono-disperse spheres) is roughly constant for many different poly-dispersity and particle shapes. This can be understood because the average distance between particles scales with $(\phi/\phi_m)^{-1/3}$ [46] and hence packing properties primarily depends on ϕ/ϕ_m.

Between ϕ_c and ϕ_m, there thus exists a continuous network of rigid particles in contact. At these high solid volume fractions, the particles have to push their neighbors to initiate their motion. The densely packed material volume must expand in order to make space for the encaged grains to pass over each other. Since this phenomenon is intimately related to a crowding effect which tends to dilate the granular network, it has been referred to as dilatancy. If this dilatancy is prevented, the crowding shows up via the emergence of normal forces [47,48].

In the case of rigid spheres, numerical and experimental observations [49] seem to suggest that the critical packing fraction for which yield stress diverges $\phi_{div} \cong \phi_m$. For our practical purposes, we could expect this relation to hold in the case of cement suspensions. However, we must be cautious that this is no longer correct if flocculation occurs. Indeed, as cement particles form flocs entrapping water, they constitute larger apparent particles. The volume of these aggregates (cement grains + entrapped water) is higher than the volume of the dispersed cement grains, hence the effective solid fraction of the flocs $\phi_{floc} > \phi$. For this reason, the divergence of the yield stress will be observed for a solid fraction of the powder $\phi_{div} < \phi_m$. In this particular case, ϕ_{div} provides an indirect measurement of maximum packing fraction ϕ_m^{floc} for the flocculated system. The relevant quantity to characterize the particle network becomes in this case ϕ/ϕ_{div} to be compared with 0.85.

This rough picture is consistent with the measurements by Mansoutre et al. [47] of normal forces for C_3S pastes without any admixtures with $\phi_{div} = 0.45$ in a parallel plate rheometer. They observed three regimes: for solid volume fractions lower than 0.38, no normal forces were measured; for volume fractions between 0.38 and 0.41, normal forces were measured that increase with the solid content; above 0.41, large fluctuations of the normal forces were measured. It can be noticed that, in this paper, the transition for which a contact network appears corresponds to a reduced volume fraction of 0.38/0.45 = 0.84, which is very close to the critical reduced volume fraction defined above. The large fluctuations measured in the parallel plate rheometer may be explained by the fact that, at these high solid contents, the crowding effect may become very strong and the granular nature of the flow (potential formation of granular arches within the testing device) dominate the measured behavior.

5.3. The YODEL, a Yield stress mODEL for suspensions

Recent progress on the prediction of the yield stress from mix design for colloidal particles suspension has come from studies of the yield stress of metal oxide suspensions as a function of particles size, volume fraction of solids and pH [25,50]. A first principle analysis of yield stress has recently been proposed [26]. It successfully quantifies the main parametric dependencies observed experimentally by Zhou et al. [25,50] and can be extended to polydisperse powder mixes [51]. The basic expression is written as:

$$\tau_0 \cong \frac{A_0 a^*}{d^2 H^2} f_\sigma^* \frac{\phi^2(\phi-\phi_{perc})}{\phi_m(\phi_m-\phi)} \tag{4}$$

where d is the median cement particle diameter, f_σ^* is an explicit function of particle size distribution that is equal to unity for monodisperse systems. This relation captures the fact that the yield stress decreases with increasing adsorbed layer thickness [32] (it may be worth noting that, in the case of steric stabilization, it was found that, at full surface coverage of the particles, the yields stress scales with the $-6/5$ power of the side chain length of poly-carboxylate super-plasticizers [33]). In this model, the volume fraction for which the yield stress diverges is estimated as the dense packing fraction. It should be kept in mind that this should not apply in the case of strongly flocculated systems for which $\phi_{div} \neq \phi_m$ (*i.e.* cement pastes without water reducing admixtures) and where the breakage probability used in the model derivation would no longer hold.

6. Flow of cement pastes

6.1. Viscous regime and solid volume fraction

It is common for many suspensions to present a macroscopic viscous behavior over some intermediate range of $\dot{\gamma}$. Although rarely seen for cement pastes even at high shear rates, this is clearly the case of cement grouts [35]. This macroscopic viscous behavior is a property of non Brownian suspensions of spheres at low shear rates and is expected on general grounds when the interactions are essentially mediated by a Newtonian interstitial fluid [49]. Even in this apparently simple case, the viscosity is a complicated function of the volume fraction.

For low values of ϕ, say, simple analytical relations such as Einstein relation can be applied:

$$\mu = \mu_0(1 + 2.5\phi) \tag{5}$$

The above relation holds in general for volume fractions lower than 5%, which, in the case of cement pastes, corresponds to a *W*/*C* ratio higher than 6, a situation which is never encountered in practice.

For larger values of ϕ, experimental observations show that the apparent viscosity deviates significantly from the Einstein relation and eventually diverges, just like the yield stress when the solid volume fraction tends towards ϕ_{div} (we assume here that the divergence of the yield stress and viscosity occur at the same ϕ_{div}; we are not aware of any data which would invalidate this assumption). Various empirical expressions have been proposed, the most famous one being the Krieger–Dougherty equation [52]. The general form of all these equations is the following:

$$\mu = \mu_0\left(1-\frac{\phi}{\phi_{div}}\right)^{-q} \tag{6}$$

The specific microscopic processes responsible for this behavior are still a matter of debate. Clearly, as ϕ increases, at intermediate volume fractions, energy dissipation progressively concentrates in strongly sheared fluid layers between neighboring particles. Moreover, above ϕ_c (see Section 5.2.), actual particle/particle contacts exist and contribute to the macroscopic stress. The value of the viscosity near ϕ_{div} hence results from the interplay between hydrodynamics inside the interstitial fluid and occasional contacts between particles. For more on this topic, see [49].

The specific values of q and ϕ_{div} are also matter of debate (it echoes the discussion on yield stress and ϕ_{div} in Section 5.2.). In its most famous form, the Krieger–Dougherty equation, Eq. (6) is written with $q = 2.5\phi_{\mathrm{div}}$ for spheres so that it matches Eq. (5) at low volume fractions while capturing the divergence near ϕ_{div}. Recent studies suggest instead that q takes on the simple value $q = 2$ for spheres [49]. The actual value of q may also depend on particle shape, some studies suggesting $q > 2$ for non spherical particles. This question however requires further studies using modern rheological tools.

As discussed in Section 5.2., if there is no flocculation of the particles, $\phi_{\mathrm{div}} = \phi_{\mathrm{m}}$ with ϕ_{m} the maximum packing volume fraction of the cement powder. However, small values of ϕ_{div} are often found in the literature. For example, Mansoutre et al. [47] measured the apparent viscosity μ of C_3S pastes at a shear rate of 100 s^{-1} in a parallel plate rheometer and represented the data with the help of Eq. (6). They observed $\phi_{\mathrm{div}} = 0.45$, which is low compared to traditional expectations for ϕ_{m} based on geometrical packing. It confirms the strongly flocculated structure of the materials studied, which were indeed prepared without any superplasticizer. Contrarily, Struble and Sun [35] carried out similar experiments on fully dispersed cement pastes. They obtained values of ϕ_{div} between 0.64 and 0.80 depending on the type of cement tested and the shear rate at which the apparent viscosity was determined. In this particular case or in other studies on dispersed cement pastes [21], the value of ϕ_{div} extrapolated from Eq. (6) is consistent with the maximum solid volume fraction of the powder. It can be noted that, in the case of cement pastes, fitted values of q are often of order 4 and therefore higher that the value of 2 for spherical particles. This may be explained by the fact that cement particles are not spherical [35,47]. It is also worth noting that, since cement particles are not spherical, they tend to align with the shear direction during flow, which might show up as higher apparent values of ϕ_{div}.

In the case of SCC or "green" concretes, a large fraction of the cement powder is replaced by various alternative powders. Some of these powders may reduce the apparent viscosity of the mixture at a given volume solid fraction: in fact, these fine powders increase the value of ϕ_{m} (and therefore ϕ_{div}) in dispersed systems by improving the particle size distribution [53,54]. It can be shown, in the particular case of mixtures of two granular species, that ϕ_{m} reaches a maximum for optimal proportions and relative diameters. However, as any other colloidal particles, some of these alternative powders may develop non-contact interactions, which can even be stronger than the interactions between cement particles themselves. This was for example the case for the silica fumes (average diameter: 0.1 µm) tested in [35,53]. Even if these particles theoretically increase the value of maximum geometrical packing ϕ_{m}, this effect is counterbalanced by an increase in the strength of the network of attractive inter-particle forces which may lead to a decrease of ϕ_{div} because of cement grains flocculation.

6.2. Dimensional analysis

The previous discussion shows that, even in the situations when particle–particle interactions are only due to viscous forces within the interstitial fluid, they may result in a complex rheology. In this case, it is understood that, as ϕ increases, the gap between particles becomes increasingly smaller. Therefore, the fluid layers between neighboring particles are more strongly sheared which leads to higher energy dissipation. The level of stress in the suspension is proportional to the average local shear rate in the gaps multiplied by the Newtonian viscosity of the interstitial fluid. The stress associated with these viscous forces is thus expected to scale as $\tau_{\mathrm{v}} \approx \mu_0 \dot{\gamma} f_{\mathrm{v}}(\phi)$ [55] where $f_{\mathrm{v}}(\phi) \rightarrow 1$ when $\phi \rightarrow 0$ and diverges at ϕ_{div}.

To construct a broader classification of cement pastes, we need to take other effects into account, in particular colloidal, Brownian forces and particle inertia. As we previously discussed, Brownian forces are generally irrelevant to cement pastes because they are dominated by interparticular colloidal forces. This is a consequence of the "large" particle sizes. The typical inter-particle colloidal force within a cement paste is of order $A^0 a^* / H^2$ [26] (see also Eq. (3)). This translates into colloidal stresses of order $\tau_{\mathrm{c}} = A_0 a^* f_{\mathrm{c}}(\phi) / d^2 H^2$, which dominates all other interactions near the yield stress. $f_{\mathrm{c}}(\phi)$ diverges at ϕ_{div} (see also Eq. (4)).

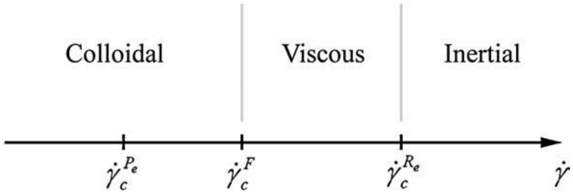

Fig. 4. Transition between colloidal, viscous and inertial regimes as a function of the shear rate for suspensions of rigid cement particles with attractive van Der Waals forces.

Particle inertia (kinetic energy) also contributes to stresses. It has been much studied in the case of dry granular flows where it controls the scaling of stress with strain rates. It is found that inertial stress is of the form $\tau_{\mathrm{i}} \approx \rho_{\mathrm{p}} d^2 \dot{\gamma}^2 f_{\mathrm{i}}(\phi)$ where the function $f_{\mathrm{i}}(\phi)$ also diverges at ϕ_{div} [55].

These stress values measure the respective contributions of viscous, colloidal and inertial forces to the macroscopic stress. Regimes of dominance of either type of interactions can be identified by introducing once again dimensionless ratios of these.

In order to characterize the scale of van Der Waals forces *versus* viscous forces, we introduce the flow number:

$$N_{\mathrm{F}} = \frac{\tau_{\mathrm{v}}}{\tau_{\mathrm{c}}} = \left(\frac{\mu_0 \dot{\gamma} d^2 H^2}{A_0 a^*}\right)\left(\frac{f_{\mathrm{v}}(\phi)}{f_{\mathrm{c}}(\phi)}\right) \tag{7}$$

Likewise, a particular Reynolds number characterizes the scale of inertial forces *versus* viscous forces.

$$\mathbf{Re}_{\dot{\gamma}} = \frac{\tau_{\mathrm{i}}}{\tau_{\mathrm{v}}} = \left(\frac{\rho_{\mathrm{p}} \dot{\gamma} d^2}{\mu_0}\right)\left(\frac{f_{\mathrm{i}}(\phi)}{f_{\mathrm{v}}(\phi)}\right) \tag{8}$$

The values $N_{\mathrm{F}}(\phi) = 1$ and $\mathbf{Re}_{\dot{\gamma}}(\phi) = 1$ define two critical shear rates $\dot{\gamma}_{\mathrm{c}}^{\mathrm{F}}$ and $\dot{\gamma}_{\mathrm{c}}^{\mathrm{R_e}}$, which respectively correspond to transitions from colloidal to viscous and from viscous to inertial regimes as sketched in Fig. 4.

The critical shear rate $\dot{\gamma}_{\mathrm{c}}^{\mathrm{F}}$, which separates a regime dominated by a network of attractive colloidal interactions and a regime dominated by hydrodynamic viscous forces, can be written as

$$\dot{\gamma}_{\mathrm{c}}^{\mathrm{F}} = \left(\frac{A_0 a^*}{\mu_0 d^2 H^2}\right)\left(\frac{f_{\mathrm{c}}(\phi)}{f_{\mathrm{v}}(\phi)}\right) \tag{9}$$

It is of the order of $10^4 f_{\mathrm{cv}}(\phi)$ for flocculated systems and $10^2 f_{\mathrm{cv}}(\phi)$ for dispersed ones with $f_{\mathrm{cv}}(\phi)$ an unknown function of the volume fraction which tends towards 0 when $\phi \rightarrow \phi_{\mathrm{perc}}$.

The critical shear rate $\dot{\gamma}_{\mathrm{c}}^{\mathrm{Re}}$, which separates a regime dominated by hydrodynamic viscous forces and a regime dominated by the inertia of the particles, can be written as

$$\dot{\gamma}_{\mathrm{c}}^{\mathrm{Re}} = \left(\frac{\mu_0}{\rho_{\mathrm{p}} d^2}\right)\left(\frac{f_{\mathrm{v}}(\phi)}{f_{\mathrm{i}}(\phi)}\right) \cong 10^3 f_{\mathrm{vi}}(\phi) \tag{10}$$

where $f_{\mathrm{vi}}(\phi)$ is an unknown function of the volume fraction which tends towards 1 for dilute cement suspensions. It has to be kept in mind that the pre-factors in the above expressions are rough order of magnitudes that should be considered with care as they should strongly vary, for instance, with the use of a super-plasticizer. Moreover, according to the parameters of the system, the two critical shear rates $\dot{\gamma}_{\mathrm{c}}^{\mathrm{F}}$ and $\dot{\gamma}_{\mathrm{c}}^{\mathrm{Re}}$ in Fig. 4 could be inverted and the viscous regime could disappear.

6.3. Shear thickening and shear thinning behavior

A large body of literature focuses on the shear thickening of suspensions of non interacting particles. In this case, shear thickening can be related to the so called "hydro-cluster" mechanism originally proposed by Brady and Bossis or various other types of order-disorder transitions [49,56,57]. These theories describe the competition between Brownian motion, which tends to homogeneously distribute the particles in the suspending fluid, and viscous effects, which tend to gather particles in structured clusters. The Peclet number $Pe_{\dot{\gamma}} = \mu_0 d^3 \dot{\gamma} / kT$ measures the ratio between viscous and Brownian forces. The above theories predict a typically sharp transition to shear thickening at a finite Peclet number, which shows up as a jump of the viscosity at some critical shear rate. As shown in Section 4 of this paper, N_r being large, we cannot expect these mechanisms to be relevant in the case of cement pastes. This is further confirmed by the fact that $Pe_{\dot{\gamma}} = 1$ defines a critical shear rate $\dot{\gamma}_c^{Pe} = kT / \mu_0 d^3$ (see Fig. 4), which corresponds to transitions from Brownian to viscous and that typical values for this critical shear rate, in the case of cement pastes, are of the order of $10^{-3}\,s^{-1}$, far below the range of shear rates for which shear thickening of cement pastes can be measured.

Instead, we expect the macroscopic behavior of cement pastes to be characterized by two transitions: macroscopic shear thinning resulting from the transition between a colloidal and viscous regime, and shear thickening corresponding to the transition between a viscous and inertial regime. The first transition should occur around $\dot{\gamma}_c^F$ whereas the second transition to shear thickening should occur around $\dot{\gamma}_c^{Re}$.

This gives us more insight about the function $f_{vi}(\phi)$. It can indeed be noted from literature that no shear thickening can be spotted up to $1000\,s^{-1}$ in the case of dilute systems such as cement grouts with average W/C equal to 0.6 [58,59] whereas shear thickening can be spotted for shear rates as low as $10\,s^{-1}$ for cement pastes with W/C = 0.22 [60] or $150\,s^{-1}$ for W/C = 0.3 [22]. This means that the function $f_{vi}(\phi)$ seems to strongly decrease with the volume fraction.

Moreover, it can be rigorously shown that, in the inertial regime ($\dot{\gamma} > \dot{\gamma}_c^{Re}$), stresses scale as $\dot{\gamma}^2$ [55], hence $\mu \approx \dot{\gamma}$ in the shear thickening regime (cf. Fig.1). However, it can be noted that trying to fit any power law curve on any data in the high shear rates range should probably lead to $\dot{\gamma}^n$ scaling with $1 < n < 2$ and the power 2 scaling should only be measured when inertia totally dominates all other interactions in the suspension. Let us stress that, at high shear rates, the inertial forces are however no longer balanced by viscous forces but by contact forces between quasi-rigid particles. There have been a lot of misinterpretations of this type of $\dot{\gamma}^2$ scaling in the literature. In particular, it has been wrongly attributed to the dominance of particle/particle collisions (*i.e.* contacts of duration far shorter than $1/\dot{\gamma}$). Let us only insist here on the fact that, depending on the solid volume fraction, transient force chains (*i.e.* sustained contacts) may be present at high strain rates and may significantly contribute to macroscopic stresses. It can moreover be noted that these chains may lead to spurious shear thickening behavior due to the formation of shear resistant structures when the flow characteristic length becomes of the order of the size of these structures [60]. It seems possible to reduce the effect of this shear thickening by a lubrication of the contacts between particles although this is a still a very open research area [61]. Finally, according to the expression of $\dot{\gamma}_c^{Re}$, increasing the viscosity of the interstitial fluid by using viscosity enhancing admixtures for example could in principle prevent the hydrodynamic shear thickening as the laminar viscous dissipation in the interstitial fluid would dominate the inertia of particles.

7. Rheophysical classification of cement pastes

Let us now recall the main results of this paper:

(i) Brownian motion does not affect the rheological behavior of cement pastes as its effect is always dominated by the effect of van der Waals forces. Brownian motion cannot therefore be the origin of shear thickening.
(ii) There exists a critical volume fraction ϕ_{perc} below which there are no direct contacts nor distance interactions between the particles and above which the suspension displays a yield stress.
(iii) There exists a critical volume fraction ϕ_{div} above which the yield stress and the viscosity diverge. This critical fraction depends on the degree and/or strength of flocculation of the suspension.
(iv) There exists a transition volume fraction of the order of $0.85\phi_{div}$ which separates suspensions in which the yield stress is mainly due to a van der Waals interactions network and suspensions in which the yield stress is mainly due to a direct contacts network.
(v) The van der Waals forces dominate the hydrodynamic forces in the low strain rate regime and give rise to a shear thinning macroscopic behavior.
(vi) Hydrodynamic forces dominate at intermediate strain rates.
(vii) Particle inertia dominates the high strain rates response and may lead to shear thickening ($\mu \approx \dot{\gamma}$).
(viii) The transitions between these regimes are governed by critical strain rates that depend on the particle average size, the fluid viscosity, the cement density and the intensity of the van Der Waals forces.

All the information above can be gathered in a conceptual diagram such as Fig. 5 in which all the characteristics of the cement suspension are fixed apart from the shear rate and the reduced cement volume fraction. The boundaries between the different zones in Fig. 5 are plotted as straight lines for the sake of simplicity. It has to be noted that the existence of the grey zone in Fig. 5 could be debatable as, at these high volume fractions, effects both due to inertia and direct contact network are very strong and the transition between shear thinning and shear thickening behavior could be direct with no intermediate Newtonian regime. The existence of this regime has however been observed in the case of polystyrene beads in Newtonian oil [49].

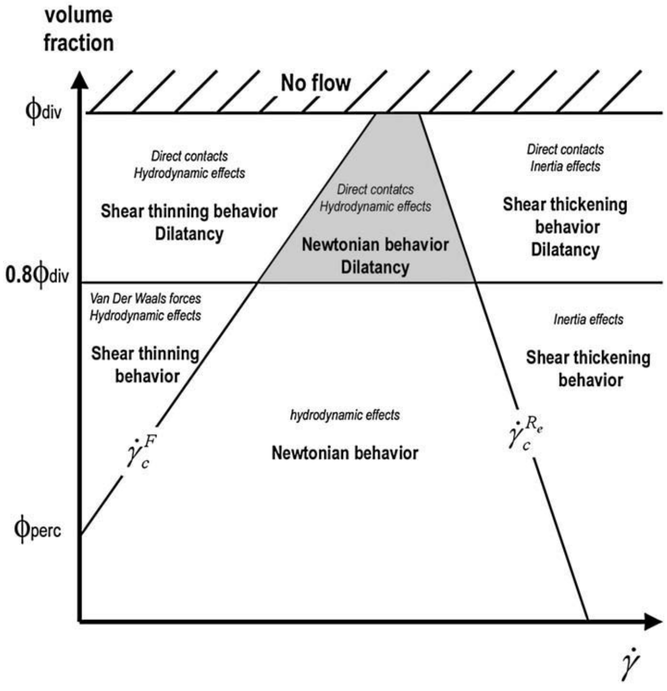

Fig. 5. Rheo-physical classification of cement suspensions. All the characteristics of the cement suspensions are fixed apart from the shear rate and the solid volume fraction. The dominating physical phenomena (italic) are indicated above their macroscopic consequences on the rheological behavior (bold).

Further research is needed to introduce more quantitative values in this diagram that remains very qualitative. In particular, the ability to understand and quantify the transitions between the different flow regimes appears to be a major challenge. In this task it can be expected that advanced rheology simulations will play a growing role [62].

Acknowledgements

The authors wish to thank the French competitiveness cluster Advancity and the Region Île de France for their financial help. Support from the Agence Nationale de la Recherche (ANR) is also acknowledged (Grant No. ANR-05-JCJC-0214).

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