Pergamon

Cement and Concrete Research 30 (2000) 1477–1483

CEMENT AND CONCRETE RESEARCH

Study of the shear thickening effect of superplasticizers on the rheological behaviour of cement pastes containing or not mineral additives

Martin Cyr[a,b], Claude Legrand[b,*], Michel Mouret[b]

[a]*Département de Génie Civil, Université de Sherbrooke, 2500 boul Université, Sherbrooke, Québec, Canada J1K 2R1*
[b]*Laboratoire Matériaux et Durabilité des Constructions INSA-UPS, Complexe Scientifique de Rangueil, 31077 Toulouse Cedex, France*

Received 21 December 1999; accepted 2 June 2000

Abstract

Fresh cement pastes, when dispersed by a superplasticizer acting mainly by electrostatic effect, present a viscosity that increases with the shear rate (shear thickening). When mineral additives are used, the intensity of the phenomenon depends on their nature: it can be amplified (metakaolin), unchanged (quartz, fly ashes) or reduced (silica fumes). According to the literature, shear thickening occurs when suspensions have a high solid concentration and when repulsive interactions are predominant. These conditions can be achieved in cement pastes owing to the dispersing action of superplasticizer. In that case, the shear thickening behaviour could be due to local mechanical actions created by the increased shearing forces.

Keywords: Shear thickening; Rheology; Cement pastes; Superplasticizers; Mineral additives

1. Introduction

Cement pastes, without the use of any mechanical action or superplasticizer, present a structure called "flocculent," a word coined by Powers [1], who states that "under the effects of combined interparticle forces of attraction and repulsion the grains make up floccules so concentrated that they merge into a continuous mass, thus giving the whole system the aspect of a single large floc."

The consequence of such a structure is a particular rheological behaviour that has already been described [2]. To sum up, without any vibration, cement pastes are viscoplastic. To make them flow, sufficiently strong shearing forces are necessary to break the bonds between grains that are the cause of an initial yield value. Because of the structural breakdown that occurs when this point is exceeded, the shearing forces necessary to maintain the flow at a constant rate decrease strongly during time. A good vibration periodically breaks the bonds and tends to decrease the initial yield value. It can even suppress it and, at the same time, the time-dependent behaviour.

Whether the flow is facilitated by local shear or by vibration, the apparent viscosity decreases nearly always with the increase in the strain rate (shear thinning). This property can give some interesting effects on the workability of concretes.

Legrand [3] pointed out possible causes to explain the shear thinning, especially the fact that all the bonds are not broken and that flocs can remain and be dragged by the flow. The number, size, and shape of such flocs will change as a function of the strain rate.

For some years, new products have appeared, like superplasticizers, which cause an important decrease in the initial yield value without any external mechanical action. The effect is mainly physicochemical and consists in interparticle repulsive forces that tend to change a flocculent state into a dispersed one. This results in concentrated and dispersed suspensions that can exhibit an increase in their apparent viscosity with an increase in the strain rate (shear thickening). This behaviour can induce unexpected consequences on concrete workability.

Already, a few authors have accidentally found the shear thickening behaviour when using superplasticizers and mineral additions [4–7] but the knowledge remains very partial.

* Corresponding author. Tel.: +33-5-61-55-67-05; fax: +33-5-61-55-99-49.
E-mail address: lmdc@insa-tlse.fr (C. Legrand).

0008-8846/00/$ – see front matter
PII: S0008-8846(00)00330-6

Table 1
Physicochemical properties of cement and mineral additives

	Cement	Silica fume (SF)	Metakaolin (MK)	Micronised fly ash (MFA)	Crushed quartz (Qtz)
Density	3.10	2.24	2.60	2.65	2.65
Specific surface BET (m^2/g)	1	25	23	3	6
Mean diameter (μm)	12	0.3	4	2	2
Particle shape	Angular	Spherical	Plate-like	Spherical, angular	Angular
Mineralogical compostition	C_2S, 13 C_3S, 60 C_3A, 10 C_4AF, 6 Gypsum, 5 Others, 6	Glass (99%)[a], silicium, carbide	Glass (97%)[a], anatase, phyllite	Glass (83%)[a], quartz, mullite, hematite, magnetite	Quartz

[a] Measured by XRD [9].

The objective of this paper is to experimentally point out the conditions of occurrence of the shear thickening behaviour in cement pastes. Rheological tests have been carried out varying the nature and dosage of superplasticizers and mineral additives. Some microstructural interpretations of such behaviour have then been attempted with the help of recent theories about colloidal and monodispersed suspensions.

2. Viscosimetric equipment and pastes composition

The equipment used is a modified Rotovisco RV2 (Haake). The inner rotating bob is replaced by a six-blade vane, which drags a cylindrical block of paste (to avoid slip). The gap is wide enough to allow the medium to be considered as infinite. Because of the time-dependent behaviour when the paste is at rest, a single flow curve cannot represent the complete rheological behaviour; thus, the paste is sheared at a high shear rate to get, in the sheared zone, the best structural breakdown. A pseudo flow curve is then obtained by decreasing velocities [3].

The binder is a standard OPC. The superplasticizers are commercial ones: they act by electrostatic (SP1, SP2, SP3), steric (SP4), or combined effects (SP5). The four mineral additives used have been chosen to achieve a large range of fineness, shapes and chemical compositions. All of them (silica fume, micronised fly ash, metakaolin, crushed quartz) are used in the concrete industry (Table 1).

Each test, performed at 20°C, required 2 l of paste. The pastes were mechanically mixed for 8.5 min to obtain a good dispersion of the components. The superplasticizer was added in two steps: 1/3 in the initial water and 2/3 after half time of mixing.

The outer cup can be fixed on a vibrating table and, in that case, the vanishing of the time-dependent behaviour by the vibration permits achieving a single significant flow curve. The directions for use and the equations that give the

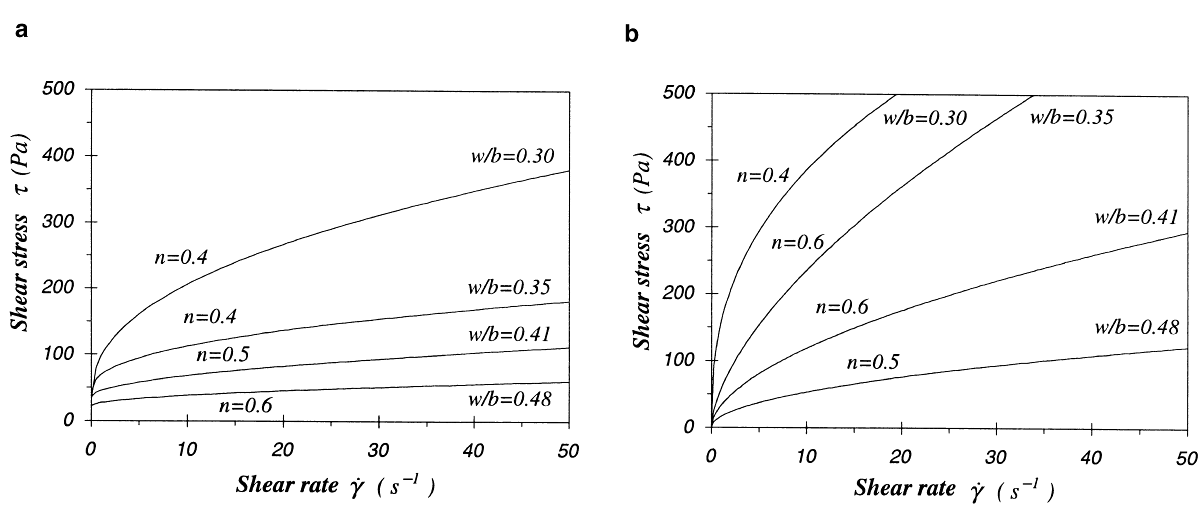

Fig. 1. Flow curves of cement pastes without superplasticizer, not vibrated (a) or vibrated (b).

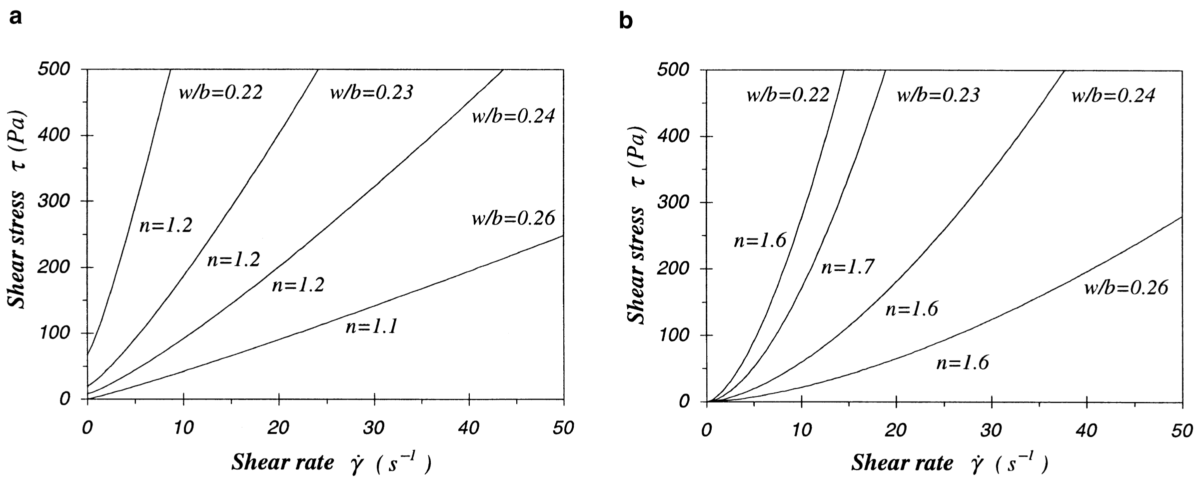

Fig. 2. Flow curves of cement pastes with 3% (liquid) of superplasticizer SP1, not vibrated (a) or vibrated (b).

shear stress τ and the strain rate $\dot{\gamma}$ have already been published [3,8].

3. Results

All the flow curves have been modelled by Herschel–Bulkley's equation ($\tau = \tau_0 + k\dot{\gamma}^n$). The exponent n characterises the behaviour of the pastes: shear thinning for $n < 1$ and shear thickening for $n > 1$.

3.1. Influence of the superplasticizer dosage

The curves in Fig. 1 illustrate the shear thinning behaviour of plain cement pastes (without superplasticizer), independently of the water content, without or with vibration.

Whatever the water to binder ratio studied, the use of the superplasticizer SP1 gives to the mixes a shear thickening behaviour, as clearly shown by Fig. 2. Some other flow curves, not presented here, have been obtained by varying the superplasticizer SP1 dosage. The variation of corresponding exponent n is depicted in Fig. 3. It can be seen that n varies clearly with the superplasticizer dosage: the rheological behaviour becomes first linear ($n \approx 1$) and then shear thickening ($n > 1$), when the amount of superplasticizer increases in the mix.

The initial yield value is strongly reduced but never vanishes completely with this type of superplasticizer (Fig. 2a). Hence, the same measurements have been realised, completing the effect of the admixture with that produced by vibrations; it is obvious that vibrations amplify the phenomenon for a given dosage of SP1 (Fig. 2b), and that it induces a very distinct evolution of n from one behaviour to another (Fig. 3b).

3.2. Influence of superplasticizer nature

All the curves of Fig. 4 have been plotted for different kinds of superplasticizers and with the same water content. The efficiency of the products is very different from one to

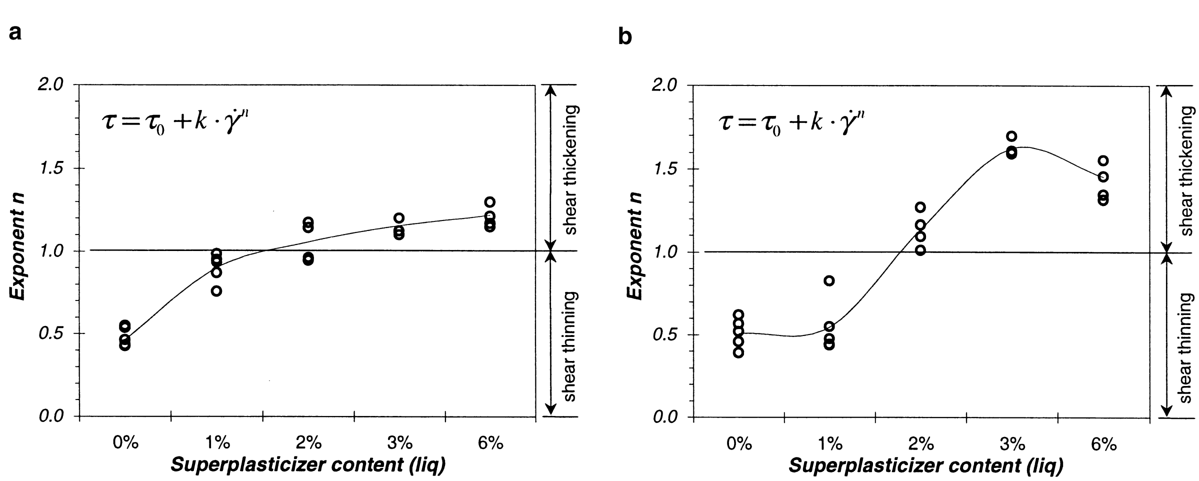

Fig. 3. Effect of superplasticizer content (SP1) on the rheological behaviour of cement pastes without (a) and with vibration (b).

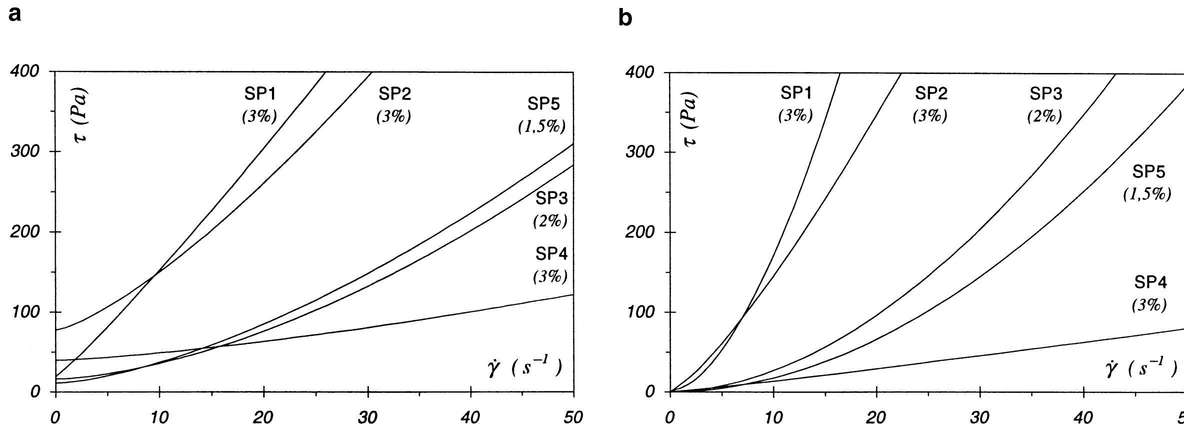

Fig. 4. Effect of superplasticizer nature on flow curves of pure cement pastes (w/b = 0.23), without (a) and with vibration (b).

another; this implies that it is quite impossible to work with the same dosage and to compare quantitatively the curves among them. Nevertheless, all of them display a plain shear thickening behaviour except for mixes made with SP4 that seem to behave like a Binghamian fluid when at rest and like a Newtonian fluid in the presence of vibrations.

3.3. Influence of mineral additives

Pastes have been realised with different proportions of mineral additives substituted to the cement (10% and 25% by mass). The water to binder ratio (w/b) was variable while the amount of superplasticizer SP1 was constant. For mixes without superplasticizer, the behaviour remains shear thinning (Fig. 5).

For pastes with superplasticizer, the behaviour varies with the mineral additive used. In the results presented in Fig. 6, only the average of different values of n (for varying w/b) has been plotted. For some products like micronised fly ashes (MFA) and quartz (Qtz), the shear thickening effect persists and n slightly increases with the increase in the proportion of these additions. For the metakaolin (MK), the phenomenon is amplified. On the contrary, with silica fumes (SF), the mix can revert to a light shear thinning behaviour.

4. Discussion

4.1. Present knowledge about shear thickening behaviour

The shear thickening behaviour was first associated, and even confused, with the phenomenon of volumetric dilatancy of coarse aggregate, originally described by Reynolds [10]. This is not the case here, where the particles are small and far from being overlapped.

All kinds of suspensions of solid particles in a fluid can show a shear thickening behaviour [11,12], if they present two particularities: the volume fraction of solids in the suspension must be very high and the suspension must be nonflocculated. This requires that the particles are mutually repelling owing to Van der Waals and electrostatic forces as in some colloidal concentrated suspensions. According to Barnes [11], the other parameters that

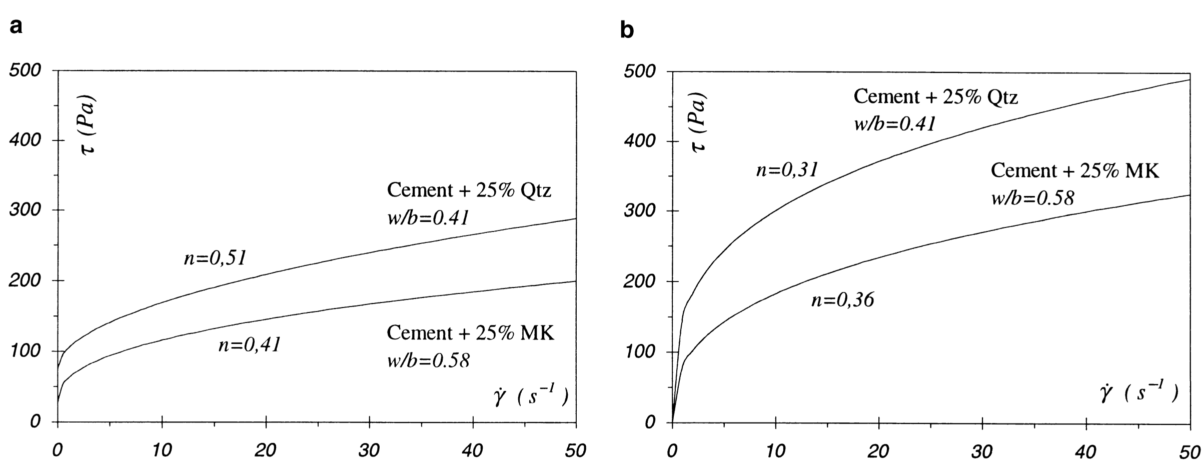

Fig. 5. Examples of flow curves of cement pastes without superplasticizer, vibrated or not, containing 25% of mineral additive (quartz and metakaolin).

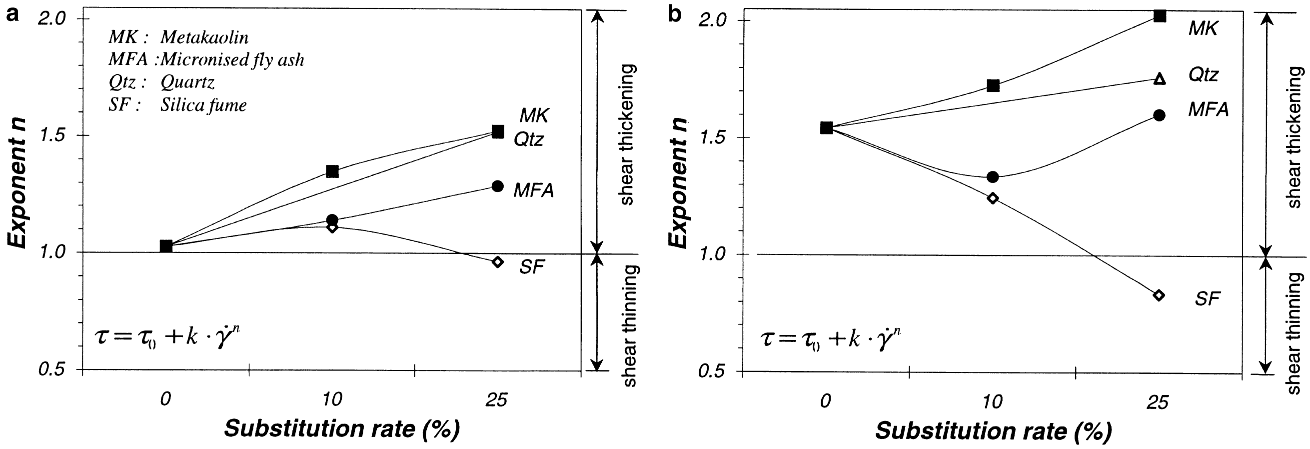

Fig. 6. Evolution of rheological behaviour of cement pastes containing mineral additives (w/b variable, 3% SPI).

control shear thickening behaviour are mostly particle shape, particle size, and particle size distribution. The effects of these parameters on shear thickening are listed in Table 2.

Various attempts have been made to provide assumptions explaining this behaviour [11–21]. Among them, two theories, developed over the last 20 years, seem to emerge. They are based on the microstructural changes of the concentrated monodispersed suspensions of colloidal particles.

The order–disorder transition theory is due to Hoffman [12,14,15], who used a combination of rheological tests and in situ light-diffraction experiments to clarify microstructural changes that occur in monodisperse suspensions during shear thickening. He found that an easy flowing state, where the particles are ordered into layers, shifts at a critical shear rate, to a disordered state where this ordering is absent. This less-ordered structure dissipates more energy while flowing due to particles "jamming," and hence the viscosity increases. The critical shear rate corresponds to a state where the hydrodynamic forces are strong enough to overcome the repulsive interparticle forces that favour the well-ordered structure.

The clustering theory is due to Bossis and Brady [16–18], who used dynamic simulations to show that the shear thickening could be the consequence of the formation of transient "hydrodynamic clusters" that jam the flow. These clusters are composed of compact groups of particles formed when the shear forces are sufficient to drive particles nearly into contact. Under these conditions, the increase in shear rate leads to an increase in the viscosity as the clusters become larger and larger. According to these researchers, no ordered state is necessary to obtain a shear thickening behaviour.

4.2. The cement pastes

It is difficult to directly transpose these theories to the material studied here, mainly because the cement particles are not fine enough to give notable colloidal properties. In spite of that, the use of superplasticizer makes possible, owing to its dispersing action, the existence of concentrated dispersed suspensions and so the occurrence of shear thickening. According to Barnes [11], the gradual occurrence of shear thickening could be due to the high polydispersity of particles.

The shear thickening behaviour in cement pastes could also be linked to the presence of superplasticizer as a physical component of the paste. It is possible that the increase of shear rate enhances the disorder, not only between the particles of cement, but within the polymeric chains of the superplasticizer.

Moreover, it is also possible that a part of the adsorbed polymer is locally torn off by the shear, this portion increasing with the shear rate. The consequences would be double:

– on one hand, a part of the polymer would come back in the free liquid, increasing its own viscosity and possibly making it shear thickening, according to Hoffman's theory;

Table 2
Parameters that control shear thickening behaviour [11]

Particle volume fraction	The severity of shear thickening depends on the particle concentration in proportion to the maximum packing fraction.
Particle–particle interaction	Shear thickening takes place only when the suspensions are deflocculated.
Particle shape	Particles that present irregular shape tend more easily to show a shear thickening behaviour.
Particle size	Suspensions that contain particles up to a few tens of micrometers can exhibit shear thickening.
Particle size distribution	Generally, the intensity of shear thickening continuously decreases as the mixture becomes more and more polydisperse.

– on the other hand, the local lack of adsorbed polymer would cause the occurrence of interparticular bonds and flocs, as in the clustering theory. Because shear thickening does not occur when mixes are made with a superplasticizer exclusively acting by steric effect, the clustering-theory seems to be reinforced.

The quantity of adsorbed product locally torn off by the shear and the capacity to flocculate depend on the specific area and the surface activity of the grains (cement and mineral additives) and also on the superplasticizer nature. As an example, Fig. 7 represents the flow curves of cementless pastes of metakaolin and silica fumes, without and with superplasticizer.

Both pastes are shear thinning when made without superplasticizer. When superplasticizer is added, the metakaolin pastes become strongly shear thickening, thus explaining why this kind of mineral additive amplifies the phenomenon when combined with cement (see Section 3.3). On the contrary, silica fume pastes with superplasticizer remain shear thinning. Note that silica fumes used as mineral additive tend to attenuate and even suppress the shear thickening (Section 3.3).

4.3. Concretes

Some tests carried out on concretes by other researchers, especially on self-compacting ones, show that the flow of such materials can be influenced by the shear thickening character of the paste [22]. This feature could be interesting in practice when concrete flows under the effect of its own weight: while flowing the increased viscosity of concrete involves an optimal filling of forms; and when concrete is just placed, a maintained high viscosity prevents static segregation (sinking of the coarse aggregate within the matrix).

Nevertheless, shear thickening could be harmful for high shear mixing and for pumped concretes. In that case, flowing would be impaired in pipes, which results in unexpected consequences, notably as far as self-compacting concrete is concerned. That is why viscosimetric tests on mixes of the

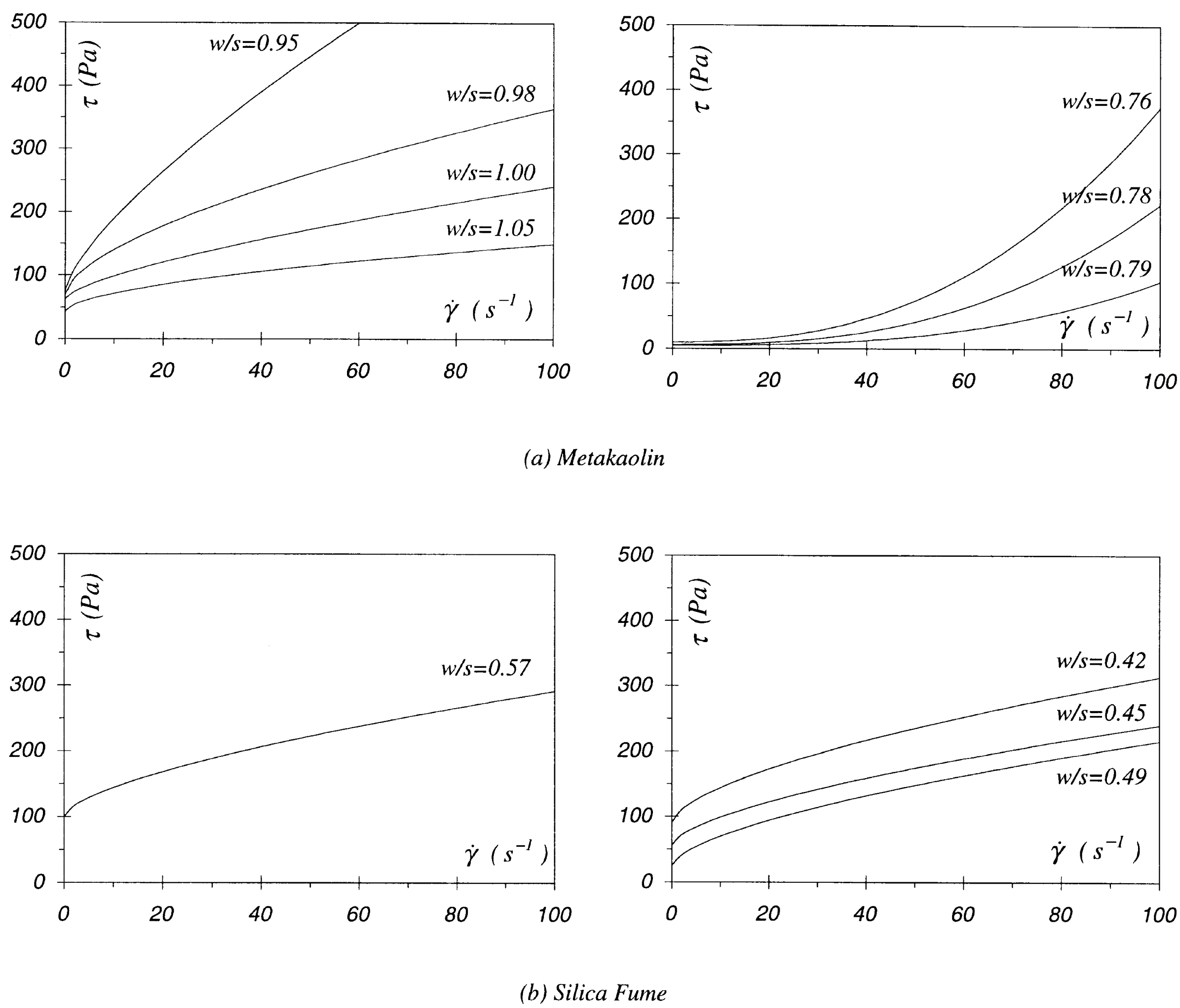

Fig. 7. Flow curves (without vibration) of mineral slurries without and with superplasticizer SPI.

fine constituents of a concrete design are necessary to anticipate the flow ability of the whole material.

5. Conclusion and prospects

Some products like superplasticizers and mineral additives are now inevitable when designing a concrete. These products can give unexpected rheological behaviour of pastes as the main phase affecting the rheology of concrete: shear thickening is often observed.

Rheological tests have been carried out to point out the conditions of occurrence of the shear thickening behaviour in cement pastes, varying nature and dosage of superplasticizer and mineral additives. The following conclusions were obtained.

1. Superplasticizers are responsible for shear thickening provided that their dispersing actions created the necessary conditions of occurrence of such a phenomenon: the suspensions must be concentrated and dispersed.

2. Mineral additives, as replacement of different amounts of cement, modify the intensity of shear thickening, depending on their nature: the phenomenon can be amplified (metakaolin), unchanged (quartz, fly ashes) or reduced (silica fumes), compared to plain cement pastes.

3. Microstructural interpretations of shear thickening behaviour can be attempted with the help of recent theories about colloidal and monodispersed suspensions, completed by local mechanical actions due to the shear effect.

References

[1] T.C. Powers, The Properties of Fresh Concrete, Wiley, New York, 1968.
[2] C. Legrand, L'état floculent des pâtes de ciment avant prise et ses conséquences sur le comportement rhéologique, Compte-rendus du 15e Colloque du Groupe Français de Rhéologie, Paris, 1980, pp. 129–135.
[3] C. Legrand, Contribution à l'étude de la rhéologie du béton frais, Mater Constr 5 (29) (1972) 275–295.
[4] T.E.R. Jones, S. Taylor, A mathematical model for the flow curve of cement paste, Mag Concr Res 29 (101) (1977) 207–212.
[5] I. Odler, U. Duckstein, Th. Becker, On the combined effect of water solubles lignosulfonates and carbonates on Portland cement and clinker pastes: 1. Physical properties, Cem Concr Res 8 (4) (1978) 469–480.
[6] D.M. Roy, K. Asaga, Rheological properties of cement mixes: III. The effect of mixing procedures on viscometric properties of mixes containing superplasticizers, Cem Concr Res 9 (6) (1979) 731–739.
[7] F. Curcio, B.A. De Angelis, Dilatant behavior of superplasticized cement pastes containing metakaolin, Cem Concr Res 28 (5) (1998) 629–634.
[8] M. Cyr, Contribution à la caractérisation des fines minérales et à la compréhension de leur rôle joué dans le comportement rhéologique des matrices cimentaires, PhD thesis, INSA de Toulouse/Université de Sherbrooke, 1999.
[9] M. Cyr, B. Husson, A. Carles-Gibergues, Détermination, par diffraction des rayons X, de la teneur en phase amorphe de certains matériaux minéraux, J Phys IV 8 (Pr5) (1998) 23–30.
[10] O. Reynolds, On the dilatancy and media composed of rigid particles in contact, Philos Mag 8 (20) (1885) 469–481.
[11] H.A. Barnes, Shear-thickening ("dilatancy") in suspensions of non-aggregating solid particles dispersed in Newtonian liquids, J Rheol 33 (2) (1989) 329–366.
[12] R.L. Hoffman, Explanations for the cause of shear thickening in concentrated colloidal suspensions, J Rheol 42 (1) (1998) 111–123.
[13] A.B. Metzner, M. Whitlock, Flow behavior of concentrated (dilatant) suspensions, Trans Soc Rheol 11 (1958) 239–254.
[14] R.L. Hoffman, Discontinuous and dilatant viscosity behavior in concentrated suspensions: I. Observations of a flow instability, Trans Soc Rheol 16 (1972) 155–173.
[15] R.L. Hoffman, Discontinuous and dilatant viscosity behavior in concentrated suspensions: II. Theory and experimental tests, J Colloid Interface Sci 46 (3) (1974) 491–506.
[16] J.F. Brady, G. Bossis, The rheology of concentrated suspensions of spheres in simple shear flow by numerical simulation, J Fluid Mech 155 (1985) 105–129.
[17] J.F. Brady, G. Bossis, Stokesian dynamics, Annu Rev Fluid Mech 20 (1988) 111–157.
[18] G. Bossis, J.F. Brady, The rheology of brownian suspensions, J Chem Phys 91 (1989) 1866–1874.
[19] D. Quemada, Modélisation structurelle du comportement rhéo-épaississant des fluides complexes. Application aux dispersions colloïdales, Cah Rheol 14 (1) (1995) 1–10.
[20] D. Quemada, I. Talbi-Boucenna, Effets rheoepaississants dans des suspensions concentrées de silice, Cah Rheol 15 (1) (1996) 245–251.
[21] W.J. Frith, P. D'Haene, R. Buscall, J. Mewis, Shear thickening in model suspensions of sterically stabilized particles, J Rheol 40 (4) (1996) 531–548.
[22] F. de Larrard, C.F. Ferraris, T. Sedran, Fresh concrete: A Herschel–Bulkley material, Mater Struct 31 (211) (1998) 494–498.