# THE RHEOLOGY OF FRESH CEMENT AND CONCRETE – A REVIEW

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## 1.0 ABSTRACT

The rheology of fresh cement, mortar and concrete is described and selected features of the behaviour of these materials are interpreted from a rheological perspective, making use of research results from the past 20 years.

## 2.0 INTRODUCTION

The hard, strong and durable cement–based product required by the user is only achieved following a period of plasticity but the attention paid to its fresh properties is small, despite the far–reaching effects of inadequate fresh performance. Pumping, spreading, moulding and compaction all depend on rheology and thanks to an increasingly scientific approach it is becoming possible to predict fresh properties, design and select materials and model processes to achieve the required performance. Rheology is now seriously considered by users, rather than being seen as an inconvenient and rather specialised branch of cement science.

This paper aims to review selected developments in our understanding of the rheology of cement based materials since about 1980. During this period a comprehensive book [1], and proceedings of several conferences at which rheology of cement–based materials have played a major part[2,3,4,5] have appeared. In addition, papers on cement and concrete have been published in most of the rheology conferences (for example, the International Congress of Rheology and the conferences of the European Society of Rheology (both every 4 years)).

## 3.0 RHEOLOGY

Rheology is the science of the deformation and flow of matter, and the emphasis on flow means that it is concerned with the relationships between stress, strain, rate of strain, and time. Publication of accessible introductory texts [6,7] has helped to overcome perceptions of the difficulty of rheology with its often mathematically complex relationships. Flow is concerned with the relative movement of adjacent elements of liquid and in shear flows liquid elements flow over or past each other, while in extensional flows elements flow towards or away from each other. In a shear flow imaginary parallel layers of liquid move in response to a shear stress to produce a velocity gradient, which is referred to as the shear rate, equivalent to the rate of increase of shear strain. Elongational or stretching flows are rarely found in cement systems but there may be some elongation at the entry or exit of a pipe. They will not be considered further here. The rich variety of material behaviour can be characterised in various ways, of which the flow curve showing how shear stress and shear rate are related is very common, but equally data may be presented as the variation of viscosity (the ratio of shear stress to shear rate) with shear rate or time.

The Deborah number, defined as $De = t_r/t_o$, gives an indication of whether solid–like (elastic) or liquid–like (viscous) behaviour is likely for a particular material. When the relaxation time $t_r$ is similar to a time characteristic of the experimental measurement $t_o$ the material exhibits both types

of behaviour and the material is said to be viscoelastic. Such behaviour is shown by dispersions of solids in water, since the interparticle forces resulting from surface charges and the electrical double layer (see Appendix) cause $t_r$ to be in the range $10^{-4}$ to $10^4$ seconds which is comfortably within the range of most laboratory instruments. Obviously long time–scale measurements are irrelevant for cement systems because they set before the measurement can be completed. In the flow and remoulding of cement–based materials the liquid–like behaviour is likely to be more important and can be measured in a variety of viscometers, both rotating and tubular. Well established formulae enable shear stress and shear rate to be calculated from the torque and speed of rotation respectively in a rotational viscometer, or from pressure drop and flow rate in a tube.

Clearly there are also many situations where solid–like behaviour is important. Cement–based materials are able to stand unsupported without flowing under their own gravity and during setting they develop strength and stiffness. The simplest analysis involving solid–like behaviour is that of the Bingham model

$$\tau = \tau_o + \mu \dot{\gamma} \qquad\qquad (1)$$

where the material is an elastic solid at shear stress $\tau < \tau_o$, the yield stress, but flows at higher stresses, ($\mu$ is the plastic viscosity, $\dot{\gamma}$ the shear rate). The yield stress is a consequence of the interparticle forces, but these links are often broken irreversibly by shear and the measured shear stress is found to depend on time and previous shear history as well as on shear rate. An indication of yield stress can be obtained from controlled stress rheometers [8] where the shear stress to initiate flow is measured; from penetrometers [9] in which the force needed to insert a needle into the material is measured; from vanes [10] where the shear stress to overcome the internal structure and set the material in motion is measured; and the pulse shearometer [11] where the shear modulus can be determined from the velocity of propagation of a shear wave. Finally, oscillatory rotational and translational shear, enabling the elastic and viscous components of the material's response to be separated, and stress relaxation methods have all been used to a limited extent [12,13,14]. These have given information on the structure in the cement–water system.

In concentrated dispersions of solid in liquid, like cement systems, the proximity of particles gives rise to strong interactions, the strength of which depend on the shape of the particles, their size distribution, their concentration, their surface properties and the composition of the liquid. Commonly there is a net attraction which causes flocculation – the consequence of randomly moving particles coming together and sticking (see Appendix). The size and architecture of the flocs play a major role in the rheology of the dispersion, with vigorous shearing reducing the flocs to the primary particles accompanied by a reduced resistance to flow, often followed by reflocculation and thickening when the dispersion comes to rest. These shear–induced changes in microstructure take time and, if fully reversible are called thixotropy, but in cement systems it is better to refer to the two processes as structural breakdown and build–up. Their existence means that the rheology of cement systems is best studied in experiments where the shear rate is held constant until equilibrium is reached, but it will be shown below that progress can nevertheless be made from other approaches. Despite considerable advances in computational modelling of liquid rheology resulting from increases in computer power, it is not yet possible to model from first principles the flow of suspensions as complex as cement systems [15] but success can be anticipated in the next decade.

## 4.0 CEMENT–BASED MATERIALS – TESTING METHODS

There are well–established rules for the sizes of apparatus and sample to ensure that rheological measurements are reliable, chiefly that any gap must be 10 times the size of the largest particles and that the ratio of outer cylinder radius to inner must be less than 1.2. For coarse granular materials like concrete this means that a coaxial cylinders viscometer is impracticably large, requiring a

sample volume of 2.5m$^3$ [1], whereas a specially designed one for mortar is feasible [16,17] and cement pastes are well within the capability of any of the wide range of laboratory instruments available commercially. These principles are equally applicable to other geometries and mean, for example, that the cone and plate viscometer cannot be used for suspensions because the gap is zero under the apex of the cone. This led to the development of the truncated and annular plate and cone geometries [8].

## 4.1 Solutions for fresh concrete

Because of the impracticability of using a coaxial cylinders viscometer of anything like ideal dimensions for fresh concrete, Tattersall and co−workers developed a highly successful and practical apparatus in which an interrupted helical impeller rotates in a cylindrical bowl of fresh concrete and the behaviour is analysed using the theory of mixing [1]. This has been developed further by Domone and Banfill [18] and the current computer assisted model of the Two−point apparatus is available commercially [19]. Following calibration it can deliver the yield stress and plastic viscosity of fresh concrete in fundamental units.

Other, broadly equivalent, approaches to the measurement of fresh concrete rheology have produced the IBB rheometer [20], the BML rheometer [21] and the BTRHEOM [22]. These instruments were developed in different countries and the question naturally arose as to whether the results can be compared. The first attempt to answer this was a programme of comparisons achieved by bringing all four instruments together at a single location with a fifth, the Cemagref−IMG [23], a large (0.5m$^3$) coaxial cylinders instrument used as a standard, all under the sponsorship of the American Concrete Institute [24]. While each instrument characterised fresh concrete as a Bingham material and the yield stresses and plastic viscosities measured on the 12 concretes tested remained in the same rank order, the results fell into two groups. The Cemagref−IMG and BTRHEOM agreed well, and the Two−point and BML agreed well, with the second group giving a generally lower yield stress. Pairwise correlations were highly significant and enable the result of one test to be predicted from another. Since the BTRHEOM uses parallel plates, the Cemagref−IMG uses coaxial cylinders, the Two−point uses an interrupted helix rotating in a cylinder and the BML uses coaxial cylinders this agreement is encouraging.

## 4.2 Solutions for mortar

Mortar can be considered to be fresh concrete without the coarse aggregate and its testing has attractions for the study of the effects of ingredients at small scale. A coaxial cylinders viscometer, while feasible, proved to be inconvenient and Banfill described the use of the Viskomat as a small calibrated mixer for mortar testing [25]. More recently Jin [26] used a scaled down interrupted helix (like the Two−point impeller) in an extensive study of the mortar fraction for design of self compacting concrete and demonstrated that its rheology could be predicted with a high degree of certainty from tests on the rheology of the mortar.

## 4.3 Progress with cement paste

Experimental challenges for testing cement pastes and slurries are the risks of slippage at the walls of the viscometer, sedimentation of the particles and plug flow. Depletion of particles at the viscometer surface can result in a thin (<1μm) layer of water which facilitates bulk flow of the sample, superimposed upon the shearing flow within the rest of the material. The result is an underestimate of the stiffness of the sample [27]. The slip can be avoided using a roughened surface and Mannheimer [28] showed convincingly that slippage reduced measured yield stress by 85%. This is supported by comparisons between smooth coaxial cylinders and a vane−in−cup apparatus: slippage in the former reduced the measured yield stress by 50% but oscillatory measurements at lower stresses were indistinguishable [29]. However, proof that slippage does not occur with roughened surfaces above the yield stress has been elusive. At the high water contents representative of concrete, the particles in cement pastes may separate gravitationally and centrifugally and this can cause errors. When measurement geometries include devices to keep the

paste homogeneous the results are much more satisfactory. These include angled blades to lift the particles [30], recirculating pumps [31], blades with interlocking fingers [32] and more conventional mixers [33]. The problem of plug flow, when the shear stress does not exceed the yield stress everywhere in the sample and some part of the sample does not shear, was first raised by Tattersall and Dimond [34] but has never been satisfactorily resolved. They found that hitherto irreconcilable anomalies in breakdown measurements were explained when filming the flow in the gap of a coaxial cylinders viscometer revealed that a solid plug of paste formed and was either stationary (rough cylinders) or slid round slowly (smooth cylinders). No satisfactory explanation has ever been offered for this anomalous plug flow but its existence casts doubt on all experimental data where full shearing flow has not been confirmed visually.

## 5.0 CEMENT–BASED MATERIALS – RHEOLOGICAL RESULTS

It might be expected that the rheology of the more complex material, concrete, containing a wider range of particle sizes, would be more complicated than that of one of its constituent materials, cement paste, but in fact fresh concrete has proved to be simpler and considerable practical progress has been made with it and, more recently, with mortars.

### 5.1 Concretes
Much work has been done on the effects on the rheology of concrete of mix constituents and their relative proportions, cement properties and admixtures and cement blending agents [1,17,20,21,35]. Concrete conforms to the Bingham model and does not show structural breakdown over the range of shear rates used in the test. Yield stress and plastic viscosity vary in a complex fashion with composition and this makes rheology measurement a versatile way of controlling the quality of fresh concrete production: tests carried out on the fresh concrete can show up changes in the mix composition which may have implications for the concrete's hardened properties and performance in use [35]. With the recent advent of self–compacting concrete, characterised by a very low yield stress, it has been found that the thickeners used to prevent segregation in use by raising the viscosity of the water also change the flow curve from the normal Bingham behaviour to Herschel–Bulkeley type behaviour (see below) [26].

### 5.2 Mortars
Mortars undergo structural breakdown and measured data are sensitive to the previous shear history of the sample, but the equilibrium flow curve conforms to the Bingham model [25] The effects of composition are similar to those observed in fresh concrete and mortar tests can be used as small scale predictors of concrete rheology [26, also Banfill, unpublished].

### 5.3 Cement pastes
There are qualitative and quantitative disagreements between the results for cement paste reported by different research workers. The flow curve has been reported to fit several different mathematical forms, all of which indicate the existence of a yield stress:

Bingham [1] $\qquad$ $\tau = \tau_o + \mu \dot{\gamma}$ $\qquad$ (1)

Herschel–Bulkley [7] $\qquad$ $\tau = \tau_o + A \dot{\gamma}^B$ $\qquad$ (2)

Robertson–Stiff [6] $\qquad$ $\tau = A(\dot{\gamma} + B)^C$
(3)

Modified Bingham [36] $\qquad$ $\tau = \tau_o + \mu \dot{\gamma} + B \dot{\gamma}^2$ $\qquad$ (4)

Casson [7] $\qquad ?\tau = ?\tau_o + ?(\mu\dot{\gamma})$ $\qquad\qquad\qquad$ (5)

De Kee [36] $\qquad \tau = \tau_o + \mu\dot{\gamma}e^{-A\dot{\gamma}}$ $\qquad\qquad\qquad$ (6)

Yahia and Khayat [36] $\qquad \tau = \tau_o + 2?(\tau_o\mu\dot{\gamma}e^{-A\dot{\gamma}})$ $\qquad\qquad$ (7)

where A, B and C are constants.

Additionally the numerical values reported for the rheological parameters cover a very wide range, which cannot be wholly explained by variations in the materials used. It can only be accounted for by accepting that differences in experimental technique and apparatus of different workers have a much greater effect than has been generally realised. Differences in the shear history at the time of test, undetected plug flow and slippage at the smooth surfaces of a viscometer could all combine to give experimental variations as large as those reported. However, there is general agreement on two fundamental qualitative aspects of the behaviour of cement pastes.

First, the material breaks down during the test and hysteresis loops with the downcurve falling to lower stresses than the upcurve are obtained when the flow curve is determined over a short cycle time. The shape changes systematically with increasing cycle time through loops with a crossover point to loops showing structural build up [37], attributable to chemical reaction during the course of the test, but Hattori and Izumi [38] explained the effect in terms of the competition between coagulation and deflocculation processes. The apparent need to fit the range of models in equations 1−7 may be the result of not allowing for the possibility of structural breakdown during the test.

Second, the material has a yield stress which decreases, in line with reductions in the apparent viscosity indicated by the rest of the curve, as the total amount of shearing energy experienced by the paste increases. Thus successive hysteresis loops fall to progressively lower values of torque in a coaxial cylinders viscometer [39], yield stress and plastic viscosity fall to an equilibrium value as the time of mechanical mixing is increased [40] and the effect can be quantified in terms of the total shear energy received by the sample prior to the test [41,42]. This structural breakdown has been amply confirmed by experiments carried out under both continuous steady shear rate and continuous steady stress. In the former the relationship between shear stress and time is affected by the shear rate in the experiment and was explained theoretically by Tattersall [39] using a linkage theory, in which the links between particles are broken by the work done in shearing the paste.

Space precludes description of the large amount of work carried out on the effect of experimental variables on the rheological parameters of cement pastes. It is sufficient to note that investigations have included paste concentration (water/cement ratio or % solids) cement composition (portland cements) and fineness, aluminous cement, oilwell cement, non−shrinking cement, flyash, silica fume, slags, chemical admixtures, polymer latexes, and effects of age and temperature [1,43].

### 5.4 Comparison of cement pastes, mortar and concrete

Table 1 shows that there is a trend in the rheological properties of cement−based materials, as quoted in the literature, which can be explained semiquantitatively by the presence of aggregate in the coarser grained materials. The flow properties of suspensions are governed by the interfaces between solid and water and, in terms of the surface area of contact, the dominant contribution is due to the cement−water interface. This is progressively diluted by the presence of aggregate. Thus, for example in one comparison, two cements which gave pastes whose rheological parameters differed by a factor of two produced concretes of indistinguishable flow behaviour [1].

The yield stress and plastic viscosity increase as the maximum particle size increases. This is because in a typical concrete at least 50% by volume is in the form of aggregate which is capable of

withstanding the applied stresses without deformation: consequently the yield stress is higher, a point confirmed by the increase with increasing aggregate content in concrete [1]. The increased plastic viscosity is partly due to the increased interparticle contact and surface interlocking, as demonstrated by the fact that for two concretes with the same yield stress containing rounded and angular coarse aggregates, the plastic viscosity of the latter is higher. It is also partly due to the inability of the aggregate to be sheared: when an overall shear rate $\dot{\gamma}$ is applied to an imaginary concrete consisting of aggregate and paste 50:50 per cent by volume, the shear rate within the solid aggregate particles is zero and that in the paste is $5\dot{\gamma}$. This higher shear rate results in a higher stress and resistance to flow in the paste which in turn accounts for the increase in measured plastic viscosity of the bulk material.

Table 1. Rheology of cement paste, mortar and concrete

| Material | Cement paste, grout | Mortar | Flowing concrete | Self–compacting concrete | Concrete |
|---|---|---|---|---|---|
| Yield stress N/m$^2$ | 10–100 | 80–400 | 400 | 50–200 | 500–2000 |
| Plastic viscosity Ns/m$^2$ | 0.01–1 | 1–3 | 20 | 20–100 | 50–100 |
| Structural breakdown | Significant | Slight | None | None | None |

In contrast, the yield stress and plastic viscosity of cement paste increase as the cement gets finer [44], which reflects the dominance of the water–cement interface in this system. Evidently the influence of particle size is a surface area effect in fine grained pastes and a simple volume effect in the coarser grained concretes. Perhaps further work on particles suspended in dispersions will suggest the particle size range where the change from one influence to the other occurs.[45]

The trend in structural breakdown behaviour may be explained qualitatively in a similar way. The work of shearing done on a material in unit time is proportional to the square of the shear rate. Structural breakdown experiments on cement paste show that the breakdown resulting from this work is rapid at first and complete in a few minutes and also that the rate of decay is proportional to the square of the shear rate. Thus in the 50:50 concrete mentioned above the total shear work done on the paste by the end of a three minute mixing period at a mean shear rate of 10 sec$^{-1}$ is equivalent to that done in a viscometer in 45 seconds at 100 sec$^{-1}$ or 12 seconds at 200 sec$^{-1}$. This is enough to give almost complete breakdown and explains the absence of structural breakdown when concrete is tested: all the breakable structure has been broken down before the material leaves the mixer. Furthermore, the higher the aggregate content, the higher the shear rate in the paste and the more complete the breakdown at the end of mixing.

## 6.0 A STRUCTURAL MODEL

Any proposed structural model must be able to explain the irreversible breakdown which occurs on shearing cement–based systems, and which is different from thixotropic behaviour. Such a model is shown in Figure 1 [1,46], in which the yield stress can be accounted for by the usual Van der Waals attraction (see Appendix) and electrical double layer repulsion effects. These result in links between particles reforming reversibly when the particles come to rest, but the irreversibly destroyed structure is much stronger than this. When dry cement powder first comes into contact with water the hydrated skin or membrane may form around pairs or groups of particles. When the skin is broken by the action of shear and the particles separate, that region of one particle which was in contact with other particles is exposed and hydrates to heal the broken skin. Because of this healing these links cannot then reform in the same way when the structure comes to rest, i.e. the breakdown

of skin linkage is irreversible. This model is consistent with both the instantaneous formation of a protective layer on cement [47], and the notion of links between particles first proposed by Tattersall [39].
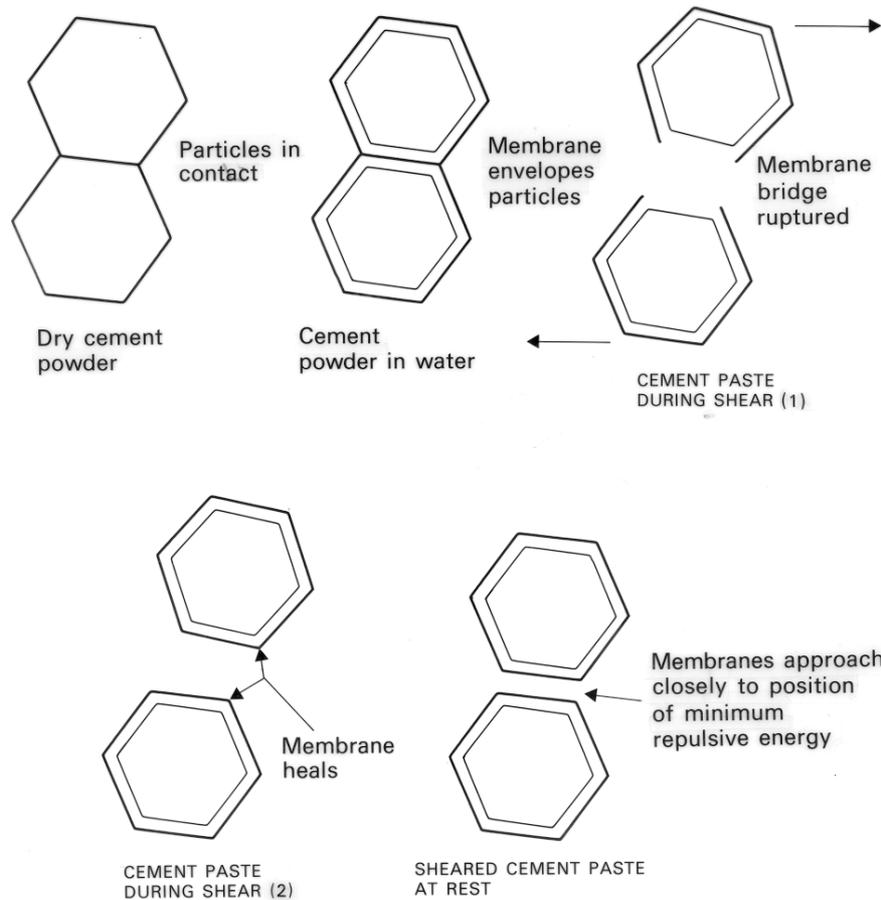


Figure 1. A structural model for the shear induced breakdown in cement systems.

## 7.0 MODELS FOR PARTICULAR SITUATIONS

### 7.1 Pumping
Transport of fresh concrete by pumping through pipes to the point of placement has been used since the 1930s and is an obvious candidate for rheological study, to help select pumping equipment and conditions. Pipe flow of a Bingham material is well characterised and the variation of shear stress from a maximum value at the wall of the pipe to zero at the centre line means that a plug of solid unsheared material moves surrounded by a zone of shearing flow from which pressure−flow rate equations have been derived [1,7]. However, this assumes that the material is homogeneous, whereas pumped concrete actually forms a layer of paste which lubricates the wall and facilitates flow. Therefore the pumpability of a concrete is mainly governed by its ability to form and maintain this layer under the pumping conditions and an acceptance test has been developed [48]. In fact, practical problems with blockage of pipework have meant that most pumping trials have had to be done at full scale, which is both costly and inconvenient.

Kaplan found that the pressure loss−flow rate relationship is independent of pressure for saturated concretes and formulated the wall lubrication law as follows [49]

$$\tau_i = \tau_{oi} + \eta V \tag{8}$$

where $\tau_i$ is the shear stress at the interface, $\tau_{oi}$ the interfacial yield stress, $\eta$ the interfacial viscosity and V is the speed of the boundary layer. The full pressure loss–flow rate relationship with its zones of shearing and lubricated flow depends on these parameters and on the rheological constants for the material, which he measured by the BTRHEOM apparatus [22]. He determined the interfacial parameters in a modified version of the apparatus using smooth cylinders to promote slippage (a so–called tribometer) and performed 36 full scale pumping tests in an experimental loop 150m long with pipe of 125mm diameter using a range of concretes (ordinary, high performance, self compacting and air–entrained). This innovative use of slippage measurements produced a model which was able to predict the pressure–flow relationship with a high degree of accuracy and therefore can be used for pumping system design.

A point of obvious interest is whether there is any relationship between the interfacial parameters and the bulk values: clearly there is no reason to expect one since the interfacial parameters depend on the ability of the concrete to establish and maintain a lubricating layer. In fact, Kaplan obtained excellent numerical agreement between the interfacial values from the tribometer and from the pumping tests, with $\tau_{oi}$ in the range 0–150 Pa and $\eta$ 300–1200 Pa.s/m, the former being considerably lower than the corresponding bulk yield stresses of 300–2000 Pa. There was a broad positive correlation between $\tau_{oi}$ and $\tau_o$ for about half of the tested concretes but there were some extreme outliers in both directions, especially for some high yield stress concretes which had zero interfacial yield stress. There was no correlation between interfacial viscosity and the plastic viscosity of the concrete. These results confirm that while bulk rheology has a part to play in the flow of concrete in pumping the dominant lubricating effect is influenced by other properties of the concrete

### 7.2 Interactions at the surface of formwork
A related problem requiring a knowledge of friction at a concrete–wall interface is the pressure on formwork, which is lower than the equivalent hydrostatic pressure because of the yield stress within the material and the friction at the wall [50], but empirical predictions underestimate the actual pressures measured for modern highly fluid concretes. Friction between steel and fresh concrete was measured in a tribometer based upon moving a steel plate between opposed pressurised cylinders filled with concrete which exert a known stress normal to the surface [51,52,53]. Applying the coefficient of friction between steel and concrete determined in this apparatus enabled preliminary estimates of the formwork pressures exerted by fluid and self compacting concrete to be compared with those measured in full size formwork up to 12 metres high. This confirmed the complexity of the factors affecting formwork pressure and showed that it is about 25% less than hydrostatic for a self–compacting concrete, but the contribution of friction depends on surface roughness, concrete rheology and particle size distribution. Unfortunately information on the rheology of the concrete used is not available (only slump and slump flow were measured) but Vanhove found that the friction stress (equivalent to $\tau_i$ in equation 8) is independent of velocity and roughly proportional to the normal stress, from which the coefficient of friction can be determined for use in pressure calculations. Vanhove's friction stress and Kaplan's $\tau_i$ can be compared only if Vanhove's data is extrapolated a long way to zero normal stress, an unreliable process. However, there is no doubt that this fundamental work on friction has the potential to contribute to the understanding of this important practical area.

### 7.3 Vibrational compaction
Vibration is the most popular means of compacting fresh concrete into formwork and around reinforcement and there is an extensive literature on the effects of such features as frequency, amplitude and acceleration, but several recent papers have significantly advanced understanding. Practically vibration removes the yield stress of fresh concrete which then flows under its own weight [54,55] and the important characteristic of the vibration is the peak velocity. The fluidity of vibrated concrete, defined as the reciprocal of its low shear rate viscosity, is proportional to peak vibrational velocity up to a critical value, above which it is constant, and the viscosity of the

vibrated concrete is proportional to the plastic viscosity of the unvibrated concrete [56]. This work enabled the effect of vibration to be defined phenomenologically but a more rigorous investigation was recently completed by Teixeira et al [57].

They studied the propagation of vibration through analysing the effects of shear and compressive waveforms on the oscillatory flow of fresh concrete and concluded that there is a liquid region near the vibrator, where the flow is controlled by the shear waveform and in which hydrodynamic theory may be used in the calculations. Beyond this, there is a solid region where the motion is controlled by compressive waveforms and structural vibration theory is used in the predictions. The interface between the liquid and solid regions corresponds in practical terms to the radius of action of the vibrator. This wave propagation analysis was validated experimentally and was able to predict correctly the rapid decay of vibration near the source, a phenomenon that has previously been attributed to cavitation [58]. A software solution enabled the radius of action to be predicted from yield stress, plastic viscosity, density and the vibrational parameters and while experimental work on a range of concretes confirmed that the radius of action decreases linearly as yield stress increases, the measured and calculated values differ significantly for stiff concretes. These findings are encouraging and suggest that solution of the fresh concrete vibration problem may be near.

### 7.4 The action of superplasticisers
It has long been established that superplasticisers can have spectacular but sometimes unpredictable effects on the rheology of cement systems. The yield stress of cement and concrete are reduced to very low values by the dispersion of flocculated cement particles [1]. However, the progress of the hydration reactions causes stiffening (slump loss) and this can be a serious practical problem. Based on an extensive review of experimental data, Flatt and Houst proposed that there are three components of the behaviour of the superplasticiser added to the system [59].

The first part is consumed by intercalation, coprecipitation or micellization (see Appendix) within the hydrating cement minerals, forming an organo−mineral phase. These chemical reactions during the formation of AFt and C−S−H, mean the admixture is no longer available for dispersing flocs and are most important in the first minutes after addition, when the precipitation rate of AFt is highest, governed by the availability of sulphate. As a consequence, at the same addition level a cement with a high degree of consumption will have less favourable rheology than an otherwise identical cement but with a low degree of consumption. Delayed addition can reduce this consumption, especially for long chain polyelectrolyte polymers, which are trapped in the organo−mineral phase, but has less effect on polymers with side chains extending through the surface hydration layers into the solution.

The second part is available for adsorption at the surface of cement particles and is effective in dispersing the flocs, but the adsorbed amount is not easily measured since current analytical methods are based on the amount removed from solution and this cannot distinguish between admixture consumed in the first part (above) and adsorbed on surfaces. Consequently the dispersive power of superplasticisers and their effect on rheology can only be evaluated using model powders which do not react or under conditions of full surface coverage in cements. The third part consists of the superplasticiser which remains dissolved in the aqueous phase and may play a part in dispersing cement particles [60], but has otherwise been ignored in experimental studies. They point out that too little attention has been paid to differentiating adsorption from consumption in the interpretation of data. Work on tailoring improved superplasticisers, based on these considerations, is currently in progress [61].

### 8.0 CONCLUSIONS AND FUTURE POSSIBILITIES

Rheology is important because of the scope it offers for characterising fresh cement paste, grout, mortar and concrete, and for understanding how they perform in practical applications. Without satisfactory fresh properties it is unlikely that the desirable properties of the hardened materials can be achieved. Their rheology is dominated by the structure that exists in the cement paste, but in mortar and concrete the structure has been partially or fully broken down during mixing. As a result they conform closely to the Bingham model and their behaviour during pumping, vibration and in formwork can be explained by reference to that model.

Reliable instruments for testing the coarser grained materials are available and experience in comparing the data is growing. In contrast there remain apparently conflicting results for cement pastes, which are probably due to the different experimental techniques used by different workers. The important effects of shear history, mixing energy and wall slippage on the results obtained in viscometers are only now being generally understood.

Building upon our current understanding of the rheology of fresh cement and concrete the future developments are likely to be incremental in the following areas:

- Steady increases in computing power and better algorithms will improve the modelling of more complex systems. A numerical model for the rheology of cement paste can be anticipated soon.
- The rheological modelling of practical situations will enable better tailoring of solutions in fields such as pumping, vibration, self–compacting flow, efficient grouting of voids and estimation of formwork pressures.
- There will always be a need for production quality control testing of rheology and inter–comparisons between the different instruments can be expected to enable a common basis of agreement to be established.
- Rheology will continue to be a product development tool as new materials become available and require objective and discriminating evaluation

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**APPENDIX: GLOSSARY OF TERMS**

Co–precipitation: The precipitation of one substance from solution, encouraged by the tiny solid nuclei which form during precipitation of another. Both substances precipitate together.

Electrical double layer: A model for the situation at a charged solid surface in solution where ions of opposite charge are attracted to the surface, but try to diffuse away to remain uniformly distributed in the solution, resulting in two plates of an electric condenser – the charged surface and a balancing charge in solution spread over a short distance from the surface.

Flocculation: The process by which particles in a suspension are mutually attracted by a combination of van der Waals and electrostatic forces, stick together to form agglomerates and either settle out of the suspension as flocs or form a three–dimensional network throughout the suspension.

Intercalation: The incorporation of molecules of one substance into the crystal lattice of a solid as it precipitates from solution.

Micellization: A process where polymer molecules with both hydrophobic and hydrophilic parts (such as detergents) group together in aqueous solution such that the hydrophobic parts associate to form regions from which water is excluded. The hydrophilic parts remain on the outer surface to maximise their interaction with the water. There is a critical concentration above which the dissolved polymer mostly exists as micelles and is therefore unavailable for active dispersion of the solid.

Van der Waals attraction: Weak forces of attraction between any pair of molecules due to oscillations in the charge distribution inside the individual atoms which produce electrostatic forces. When two solid surfaces are brought close together, all the atoms in the surface zones contribute to the forces of attraction, which are then large enough to be measurable.