RHEOLOGY OF FRESH CEMENT AND CONCRETE

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ABSTRACT

Cement-based materials are of enormous technological importance and their satisfactory performance depends on being able to transport and mould them in the freshly mixed state. This article describes the rheology of fresh cement, mortar, concrete and related products in the context of practical situations, and deals with testing and measurement, together with the main features of their behaviour. It explores the links between rheology and technology, and identifies areas where these are weak and could benefit from further experimental and computational effort.

KEYWORDS: Cement; concrete; mortar; grout; composites; rheometry; viscoelasticity; thixotropy; modelling;

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1. INTRODUCTION AND SCOPE

Portland cement is one of the leading manufactured commodities in the world. It is the principal inorganic binder, used in all kinds of products, and major fields of use are:

- Primary construction materials, mass and reinforced concrete, whether precast in a factory, cast in situ or sprayed onto a substrate
- Precast units for masonry (bricks, blocks and artificial stone)
- Masonry mortar for bedding the units
- Floor, wall and roof finishes, either applied plastic or precast as units
- Grout, pumped into fissured or porous ground strata to seal and strengthen, or around prepacked aggregate in an alternative form of in situ concrete construction
- Oil well cement, pumped into the annulus around the production pipe to seal against the surrounding strata
- Adhesive for ceramic tiles etc.

It so dominates the field of hydraulic binders (i.e. those capable of setting and hardening under water) that it is usually referred to simply as cement. For the purposes of this review it is taken to be a finely ground inorganic powder, produced by firing limestone and clay at around 1400°C and grinding the resulting cooled clinker with gypsum. It reacts with water (i.e. hydrates) to form a plastic paste that sets (developing rigidity in a few hours) and hardens (developing compressive strength over several months), and retains its strength and stability even under water. Mortar also contains sand or other fine aggregate and concrete additionally contains coarse aggregate - gravel or crushed rock up to 20-40 mm in size, depending on local practice. In the period before setting (typically up to a couple of hours), the material is said to be "fresh" and the hard, strong and durable product required by the user is only achieved later. Despite the far-reaching effects of inadequate fresh performance - for instance, the voids in poorly compacted concrete permit aqueous solutions from the environment to penetrate and corrode steel reinforcing bars - the attention paid to its fresh properties, generically termed 'workability', is surprisingly small.

Important processes are transporting, pumping, pouring, injection, spraying, spreading, self-levelling, hand trowelling, moulding and compaction. These all depend on the rheology of the material and a list of specific factors for consideration in these processes would include

- Flow and frictional resistance against surfaces
- Adhesion
- Resistance to segregation
- Resistance to settlement and the formation of bleeding water
- Low water content to obtain high strength and durability
- Resistance to sagging under self weight on a wall or inclined surface
- Low pressure on the temporary formwork erected to support a wall or other component.

Thanks to an increasingly scientific approach in recent years it is becoming possible to predict fresh properties, to design and select materials and to model processes to achieve the required performance. As a result rheology has become a term recognised by technologists but not necessarily understood. The situation mirrors that in the coatings industry described by Eley who stated that: "to fully realise the hoped-for benefit of rheological analysis, a robust link must be established between rheology and technology." [1]. As will become evident, that link is not fully established for cement based materials.

This paper aims to review our current understanding of the rheology of cement-based materials. It does not deal with soil mechanics or plasticity theory approaches. After a short historical and practical outline, which aims to help readers unfamiliar with these materials, the cement-water system is introduced. Testing methods are then described, followed by a survey of the main results. These results are then applied in the context of various practical applications. The review concludes with a discussion of modelling and prediction methods.

2. HISTORICAL AND PRACTICAL PERSPECTIVE

Even though the Romans used concrete extensively and various lime-based binders were developed in the 18th century, culminating in the first patent for Portland cement in 1824, it was the work of Abrams in the 1920s that set down some basic principles of the technology of concrete, in the sense of an appropriately proportioned mixture of cement, sand, gravel or crushed rock, and water. He established the eponymous rule that the strength of hardened concrete is inversely proportional to the water/cement ratio, thus showing that the higher water contents needed to give more easily workable concrete had a negative effect on strength. This is a result of the pore space left behind by the consumption of water during hydration of the cement: the higher the water content the higher the porosity and the lower the strength. Controlling workability therefore helps to control strength and other hardened properties.

The need to define and control the properties and performance of materials is part of technological development and the rheology of cement-based materials is no exception to this process. Applying Kelvin's condition to the meaning of "understand", namely that a phenomenon is not properly understood unless it can be measured, three levels of understanding may be identified. These may or may not coincide with a chronological progression. Considering the phenomenon of workability, in level 1, the property is described in comparative terms only, using subjective assessments such as "stiff". In level 2, a quantitative numerical scale based on an empirical measurement, such as slump, is established. In level 3, the property is rigorously defined in terms of physical constants, derived from the fundamental quantities of mass, length and time, which describe the material itself and do not depend on the circumstances of the test or the use of the material. This last level involves the use of sound scientific methods, such as rheology, in which physical and analytical models are developed and applied to the situation under consideration.

In the case of fresh concrete, because of a failure to progress to level 3 and gain a rigorous understanding of its flow properties, workability measurement remained stuck in level 2 for many decades. This level is characterised by the enormous number of test methods developed, many of which are of a very restricted range of applicability. In fact, the situation was so unsatisfactory that Tattersall wrote in 1976 that "at present, the most reliable method of measurement [of workability] is subjective judgement by an experienced mixer [operator] … it remains common experience for two concretes giving identical slump (or other test) values to behave quite differently" [2].

In the case of paste and grout, the mixture of cement and water which not only forms the matrix in concrete but is also pumped into voids in structures or rock / soil to consolidate them, the material lends itself more readily to study in the kind of apparatus that might be found in rheology laboratories. Consequently a higher level of understanding was achieved earlier by people experienced in rheological methods. Unfortunately the relative complexity of the behaviour observed discouraged the very workers who could make significant advances, with the result that they published one or two papers and then moved on to study easier materials. Thus, early work was based on the empirical application of instruments developed for other purposes [3-8].

The 1950s saw the first rheological investigation, with an attempt at theoretical understanding, [9-12] and an eventual appreciation of the importance of thixotropy or structural breakdown, and the consequent restricted applicability of flow curves / hysteresis loops [13]. A microstructural model for breakdown [14] was followed by experimental confirmation [15] and an eventual model for the yield stress of suspensions, including cement pastes [16].

Abrams recognised the need to control the workability of the fresh concrete and was using the term consistency in his 1920s work on the mix design of concrete. He is credited with the widespread adoption of the slump test, which had been reported earlier by Chapman, and a version is now standardised by the relevant authorities in virtually all countries. Abrams' work predated developments in rheology, which became recognised as a scientific subject in its own right in the 1930s, and concrete technology, in particular the development of processing methods for the fresh concrete, developed faster than the understanding of the material. Consequently processes such as vibrational compaction and pumping were both well established long before the first research studies on vibration [3] and pumping [17].

Empirical tests for fresh concrete have been developed almost continuously from the 1920s up to the present day, but development of rigorous definition and understanding can be charted as follows. Early experiments measured the drag or torque exerted on a body immersed in the concrete [18-20]. By the 1970s, measurements with a rotating vane or coaxial cylinders had been made and some theoretical understanding attempted [19, 21-23]. Practical difficulties with coaxial cylinders, which need to meet strict dimensional criteria, led Tattersall to adopt the approach, tried earlier [24-26], of measuring the power requirements during mixing, with a view to deriving a flow curve from the data. Success with this led to the development of a practical test method (the two-point test) that could be employed both in the lab and on site and to the body of work described in 1983 by Tattersall and Banfill [14]. Arguably, this first brought to the attention of concrete technologists the rheology of fresh concrete as an important subject worthy of serious consideration, offering benefits in understanding of properties, production and quality control, linked to the availability of a commercial apparatus. Tattersall repeatedly argued the advantages of two-point testing of fresh concrete workability over the single point empirical test methods that had been employed to date (see section 3) [2, 14, 27, 28], but it is a matter of regret that when self-compacting concrete was introduced in the early 1990s, concrete technologists immediately addressed the problem of its characterisation by introducing new single point tests, sometimes quite complex, and rheology was left to catch up [29]. The issue of characterisation and specification is particularly important given the internationalisation of concrete practice because self-compacting concrete technology differs between countries regarding the materials and mixes used and measurements of yield stress and plastic viscosity in the correct units offer the only real way of harmonisation.

Developments in materials and processing, such as flowing and self-compacting concrete with the aid of the dispersing admixtures which had become common since the 1970s, extended the range of concrete rheology needing to be measured, and led to other test methods based upon rheological principles but with better adapted sensitivity [30-32]. The need for measurements of rheology to be independent of the test method used (the requirement of level 3 mentioned above) led to a programme of comparative tests that are still in progress [33, 34] and are relevant for international harmonisation. Other milestones are the arrival of powerful computing which, on the one hand, enables rheometers to have computer control and data collection and, on the other, facilitates numerical modelling of the flow of complex mixtures of particles and suspensions.

A similar process of development of empirical test methods was followed for mortar, which is a material in its own right, used for bedding bricks, blocks or stone in masonry construction, as well as being used extensively in laboratory tests as model concrete. Many of the rheological investigations on concrete also tested mortar as part of the programme, but workers found that apparatus developed for concrete was not sufficiently sensitive for testing mortar. Banfill [35] appears to have been the first to report a coaxial cylinders apparatus for mortar and he subsequently extended the use of the ViscoCorder [36] and its engineered successor, the Viskomat, to determine the rheology of mortar [37, 38].

Some of the points in this, necessarily brief, historical review will be amplified later in this paper.

3. THE INADEQUACY OF SINGLE POINT TESTS

A rheological readership should not need to be reminded of the inadequacy of single point tests for complex fluids, so only a brief outline will be given here. A single point test, as its name implies, measures the flow of a fluid under a single set of conditions. The conditions might be simple, such as flow out of a funnel under gravity and slumping under self-weight, or subject to complicated intricacies of design or construction, but in essence either a property related to shear rate (in a possibly complex way) is measured at a single applied load which is related in some way to shear stress, or vice versa. No matter how elaborate the treatment of the data this single point measurement only gives an indication of the apparent viscosity η_{app} of the fluid at the shear rate $\dot{\gamma}$ in question and this apparent viscosity is the slope of the straight line from the point to the origin of a shear stress-shear rate graph:

$$\eta_{app} = \tau / \dot{\gamma} \qquad \text{..........} \ (1)$$

It can only give the right result if the fluid itself is a Newtonian liquid, because this has a flow curve which is a straight line passing through the origin.

Since most cement-based materials, not least fresh concrete, possess a yield stress this assumption of Newtonian behaviour is incorrect. Even so, there are two conditions under which a single point test can be helpful. Firstly, if the shear rate in the test exactly matches the shear rate in the process of interest, then the measurement from the test will place concretes in the correct rank order of their performance in that process. Secondly, if the only variable that can affect the rheology of the concrete affects the whole flow curve in the same way, then again the measurement will place the concrete in the correct rank order. Neither of these conditions apply in practice, firstly because neither the shear rate in the test nor the shear rate in the process are known, and secondly because most composition variables affect the rheology in a more complicated way than that described. In support of this, every experienced technologist can tell tales of concretes which give identical results in the slump test but perform completely differently when being placed in moulds and examples later in this paper show that composition can have very complicated effects on rheology.

Because the concrete mixes that Tattersall tested conformed to the Bingham model he named this the two-point principle [27], and developed the two-point test, since unambiguous definition of a Bingham material requires measurements at a minimum of two points. There are an infinite number of Bingham lines that can pass through a single point on the shear stress-shear rate graph, while only one straight line can pass through two points. In practice all "two-point tests" for concrete make measurements at a large number of different shear rates so strictly speaking the term is a misnomer. The recent history of the subject has been marked by attempts to get this two point message across to technologists, who are wedded to the perceived robustness and convenience of single point tests, regardless of the demonstrable advantages of a more sophisticated approach.

4. THE CEMENT – WATER SYSTEM

Consideration of rheology requires a recognition that fresh cement-based materials are highly concentrated suspensions of solid particles in liquid. Particles of dry cement clinker are not homogeneous, and each one may consist of four major mineral components, tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium alumino-ferrite, all of which react with water. Tricalcium aluminate (and to a lesser extent the alumino-ferrite) reacts with water so fast that it has to be retarded by the addition of gypsum (calcium sulfate), which produces calcium sulfoaluminate until all the gypsum has been consumed. The quantity of gypsum (about 4% of the cement) is tailored to ensure that it is consumed at about the same time as the tricalcium silicate sets occurs. Tricalcium silicate reacts over a few days and dicalcium silicate reacts slowly (over several months) and both contribute to strength development. The hydration of cement proceeds in four stages [39, 40]:

(i) An initial rapid reaction between the anhydrous minerals and water, dissolving calcium and hydroxyl ions from the surface and leading to the formation of a gelatinous, poorly crystalline skin over the particles, which probably consists of mixed calcium silicate hydrate and calcium sulfoaluminate, and which is visible within a few seconds and fully formed in a few minutes [15, 41];

(ii) a slow reaction, lasting two or more hours, which is hindered by the presence of the skin, acting as a diffusion barrier, during which the concentrations of calcium and hydroxyl rise until the water becomes supersaturated with respect to calcium hydroxide;

(iii) a fast reaction, where calcium silicate hydrate and calcium hydroxide crystals grow and interlock over a period of 6-12 hours;

(iv) a period of decelerating reaction, where diffusion of water to unreacted minerals controls the rate, the latter are nearly consumed and free space for crystallisation of hydration products is limited.

It is the existence of stages (i) and (ii) that permits fresh cement products to be moulded and cast in practice and these are the stages that are of major interest to rheologists. While stage (ii) is often referred to as the dormant period, hydration is continuing, albeit at a low rate, and as a result the rheology changes continuously from the time of mixing. Setting occurs at some point after the start of stage (iii) and can be conceptualised as the growth and interlocking of needle-like crystals of calcium sulfoaluminate and calcium silicate hydrate. Even now the exact mechanism of cement hydration and setting is a matter of debate, but it is clear that fresh cement and concrete is a chemically reacting system and that rheology is useful for studying the factors affecting the fresh system, the changes with time during stage (ii) and the transition towards the set product. Because of the presence of the hydration skin around cement particles the fresh properties are relatively insensitive to variations in the chemical composition of the cement clinker, but low concentrations of water soluble species can have significant effects.

Engineers tend to refer to the water/cement ratio, and in practice this varies from about 0.3 by weight, slightly above the minimum water content required for hydration, up to 0.7, above which the product tends to be too porous for acceptable durability. This corresponds to solids volume concentrations up to about 50% in a cement paste and up to 85% in a concrete made with 20mm coarse aggregate. Cement is typically ground to particle sizes from 0.1 to 50 μm, sand is 150 μm to 5mm and coarse aggregate up to 20 or even 40 mm depending on local practice. At such concentrations the proximity of particles gives rise to strong interactions, the strength of which depends on the shape of the particles, their size distribution, their concentration, their surface properties and the composition of the liquid. While cement particles are not small enough for the system to be considered colloidal, the general principles of colloid science [42] can be applied. Commonly there is a net attraction which causes flocculation - the consequence of randomly moving particles coming together and sticking. 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 are time dependent and there is disagreement over the extent to which it is justified to refer to them in cement systems as thixotropy (see section 6.2.2). Finally, the presence of dispersing admixtures can separate the flocs with dramatic effects on the rheology, and a considerable body of knowledge and experience in their use has built up [43, 44].

5. CEMENT-BASED MATERIALS - TESTING METHODS

5.1 General considerations

Ordinary everyday observation confirms that fresh cement-based materials are able to stand unsupported without flowing under their own weight (as in the slump test) and the simplest analysis for this behaviour is the Bingham model:

$$\tau = \tau_o + \mu\dot{\gamma}\,, \qquad \text{..........} (2)$$

where the material can support shear stresses $\tau < \tau_o$, the yield stress, without flowing but flows at higher stresses, (μ is the plastic viscosity, $\dot{\gamma}$ the shear rate). Even though the existence of the yield stress has been questioned on the grounds that it is merely a very high viscosity at very low shear rate [45], it has practical significance for cement systems because it is difficult to characterise such a high viscosity in the time available before setting. Thus cement systems are yield stress fluids and the yield stress is a consequence of the interparticle forces, and links between particles are broken by shearing so the measured yield stress depends upon time and previous shear history. An indication of yield stress can be obtained from controlled stress rotational rheometers [46] where the shear stress to initiate flow is measured; from penetrometers and compressive testing [47, 48] in which the force needed to insert a needle into, or to squeeze, the material is measured; from vanes [49] where the shear stress to overcome the internal structure and set the material in motion is measured; from capillary tube measurements [50-52] where the shear stress required to start flow is measured; and from specialised methods like the raise-pipe [53], in which the fluid rises up a small diameter vertical pipe and stops when the wall shear stress equals the yield stress. Solid-like behaviour at low stresses / small strains can be studied by shear wave propagation using instruments able to measure the elastic moduli [54-57] and by measuring viscoelasticity. Oscillatory rotational and translational shear, enabling the elastic and viscous components of the material's response to be separated [58-62], and stress relaxation methods [58, 63, 64], have all been used to a limited extent. At stresses above the yield stress cement based materials flow and rotational, capillary and translational measurement methods have all been used to determine the plastic viscosity. From all this work information on the structure in the cement-water system has been gathered.

Coarse granular materials pose difficulties in measurement. 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 in coaxial cylinders the ratio of outer to inner cylinder radius must be as near 1.0 as possible. For concrete this means that a coaxial cylinders viscometer is impracticably large, requiring a sample volume of 2.5m^3 [14], whereas one specially designed for mortar is feasible [35, 65]. Cement pastes are of course well within the capability of any of the wide range of laboratory bench top instruments available commercially. These principles are equally applicable to other geometries and mean, for example, that the cone-and-plate cannot be used for cement pastes because particles jam in the zero gap under the apex of the cone and this led to the development of the truncated cone and the annular plate and cone geometries [46].

5.2 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. The behaviour is analysed [14] using the theory of mixing based on the Metzner-Otto approach of assuming that the mean effective shear rate is proportional to the speed of rotation of the impeller [66]. This has been developed further by Domone and Banfill [30] and the current computer assisted model of the Two-point apparatus is available commercially [67]. Following calibration with a series of Newtonian and power law liquids it can deliver the yield stress and plastic viscosity of fresh concrete in fundamental units. However, its simple and robust torque measurement system imposes sensitivity limitations which cause difficulties with the new generation of self-compacting concretes, that have a low yield stress compared to ordinary concretes.

Other, broadly equivalent, approaches to the measurement of fresh concrete rheology have produced the BML rheometer using deeply ribbed coaxial cylinders [31], the IBB rheometer using a planetary motion impeller [68] and the BTRHEOM using parallel plates [32]. 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 [69], a large ($0.5m^3$) coaxial cylinders instrument used as a standard, all under the sponsorship of the American Concrete Institute [33]. While each instrument characterises fresh concrete as a Bingham material and the yield stresses and plastic viscosities measured on the 12 test concretes remain in the same rank order, the values themselves differ between instruments, although pair-wise correlations are highly significant and can be used to predict the result of one test from another. A second programme of comparisons took place in 2003 but unfortunately the results left the origin of the differences unresolved [34]. Clearly our understanding has not yet reached level 3 on the scale mentioned earlier because the measured properties of fresh concrete are not yet fully independent of the measurement method.

The alternative approach of using tube instead of rotational rheometry has been neglected until recently. Roshavelov reports a vertical tube viscometer of appropriate dimensions for concrete testing [52, 70] from which the rheology can be determined using the Buckingham-Reiner equation (section 5.7.2). While the reported values for concrete are similar to those obtained from rotational rheometry, it would be particularly interesting to include this instrument in any further comparisons of the type described above.

5.3 Solutions for mortar

Mortar (i.e binder, sand and water) can be considered to be fresh concrete without the coarse aggregate and its testing has attractions for the economical study of the effects of ingredients at small scale. A coaxial cylinders viscometer, while feasible, proved to be inconvenient in use [65] and Banfill developed the use of the Viskomat as a small calibrated mixer for mortar testing [37]. The validity of the calibration procedure, first developed for concrete [14], is confirmed by tests linking yield stress measurements to those obtained from flow spread tests [71]. Jin [72] used a scaled down interrupted helix (similar to the Two-point impeller for concrete) 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. OH Wallevik persevered with the coaxial cylinders approach and developed the Con-Tec rheometer [73] for mortar, a smaller version of his successful BML design for concrete and which uses similar deeply ribbed cylinders to minimise slippage. It is described and analysed in depth by JE Wallevik [74]. The only other commercially available rotational instrument is the Paar Physica KMS system, which uses an offset ball of 10mm diameter describing a circular path of radius 25mm through the mortar [75]. This is claimed to give good results for pastes and mortars [76], but there is insufficient experience available to be able to draw conclusions.

5.3 Progress with cement paste

Experimental challenges for testing cement pastes and slurries, as with other concentrated suspensions, are the risks of slippage at the walls of the viscometer, of sedimentation of the particles and of 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. The slip can be avoided using a roughened surface or, by sacrificing data at higher shear rates, by using a vane-in-cup apparatus [77, 78]. Mannheimer [79] shows convincingly that slippage reduces measured yield stress by 85% while Banfill and Kitching observe a 90% reduction [46]. Mannheimer [51] uses the twin-tube viscometer [80] to investigate slip in more detail and obtains excellent agreement with coaxial cylinders viscometers, when the latter data is corrected for wall slip, while the agreement with large scale measurements in a flow loop is less convincing. He points out the need for the different tube sizes to have approximately the same surface roughness. This is supported by comparisons between smooth coaxial cylinders and the vane [81]: slippage in the former appears as a series of saw-tooth steps in the progressive increase in shear stress at constant (slow) speed of rotation. When the cylinder slips the stress decreases instantaneously before continuing to increase, but never reaches the true yield stress. This effect reduces the measured yield stress by 50-75% compared to that measured by the vane. In contrast oscillatory measurements of complex modulus at stresses lower than the yield stress are indistinguishable in the two geometries, suggesting that slippage is not a problem in this situation [81]. Despite this confirmation that slippage occurs with smooth cylinders, proof that slippage does not occur with roughened surfaces above the yield stress has been elusive, until recent Magnetic Resonance Imaging measurements of liquid velocity profiles [82]. These show that cement pastes do not slip at surfaces to which sandpaper has been glued. It is normally recommended that the asperities in roughened surfaces should have a characteristic depth equal to the maximum size of the particles in the material to be tested. Despite these well established recommendations, work with smooth surfaces is still published [83, 84] and it can be noted that the Fann viscometer specified for testing oil well cement slurries uses smooth coaxial cylinders [85]. Clearly, the conclusions from such experiments run the risk of being flawed.

When using the high water/cement ratios representative of concrete, the particles in cement pastes may separate gravitationally and centrifugally and this can cause errors. Gravitational sedimentation in the annulus of coaxial cylinders produces a vertical concentration gradient. In a typical cement, sedimentation occurs at all water/cement ratios above 0.28 and can overestimate the yield stress and plastic viscosity by 15-20% at 0.4 and by as much as 400-800% at 0.7 [86]. When measurement geometries include devices to keep the paste homogeneous the results are much more satisfactory. These include angled blades to lift the particles [86, 87], recirculating pumps [88], blades with interlocking fingers [89] and more conventional mixers [90]. The angled blades of the interrupted helix impeller raise the threshold water/cement ratio for sedimentation to 0.4, and reduce the error at 0.7 to less than 5% [86]. Set against these advantages is the possibility that the rotational Reynolds number established by the latter impeller in a low viscosity paste, for which sedimentation may be a problem, could be in the turbulent zone [87]. In the gap of parallel plate or cone and plate instruments, sedimentation leads to formation of a layer of bleeding water under the upper member which gives the problem of slippage mentioned above. Indeed, it is possible to imagine that severe sedimentation could negate any surface roughening because particles settle beyond the reach of the asperities. Clearly, the experienced rheologist will take appropriate precautions for the system being studied but unfamiliar materials can trap the unwary. I have seen Bingham flow curves with negative yield stresses reported in good faith where the cement was so heavily dosed with a dispersing agent that the paste was unstable and the particles dropped clear of the measuring blades during the test. Despite all this knowledge and experience, again, work at high water/cement ratio where sedimentation would be a problem sometimes still appears [91].

Centrifugal separation in cement pastes is considered by Wesche et al [92] and in mortar and concrete by Wallevik [74], who discuss the likely effect on measured values. Noting that concrete segregates radially, Wallevik concludes that, because the centripetal acceleration in the test being used is about one-tenth of gravitational acceleration and the concrete is completely stable to particle segregation under its own weight, particle-particle contact must be causing radial migration. He also shows that the coarse particle migration in concrete is influenced by the ratio of the yield stress to the plastic viscosity. Experiments on self-compacting concrete, for which the value of this ratio is low, could give an insight into this behaviour [74].

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 [93]. They report that hitherto irreconcilable anomalies in breakdown measurements are explained by high speed filming of the flow in the gap of a coaxial cylinders viscometer which reveals that a solid plug of paste forms and is either stationary (in rough cylinders) or slides round slowly (in smooth cylinders). The plug is present even when the Reiner-Rivlin equation predicts its absence. No satisfactory explanation is offered for this anomalous plug flow, but its observation casts doubt on all experimental data where full shearing flow has not been confirmed visually, i.e. in enclosed viscometer geometries.

5.4 Compressive rheology

This is the term increasingly given to the study of rheology under uniaxial compression and an extensive review by de Kretser et al [94] describes the analysis of systems involving sedimentation under self weight and externally applied compression. The former is relevant to the situation where the fully compacted material is stationary after compaction or injection and before setting, and the separation of water due to sedimentation is undesirable. The latter is relevant to the work of the mason. Meeten's relatively simple squeeze-flow apparatus [95] employs a constant squeezing force between two plates and measures the velocities of approach and spread from which yield stress and plastic viscosity of a Bingham material can be calculated. Cardoso et al [96] describe a similar apparatus in which the top plate approaches a fixed bottom plate on which a bed of mortar is placed. Toutou et al, as described in [97], propose a parallel plate plastometer, which differs from the above because the specimen is of height/diameter ratio 1.0 and is squeezed between plates of the same diameter. These demonstrations of the feasibility of the method suggest that it could be a potentially fertile field for further development. The same considerations of surface roughness and the potential for slippage apply to these compressive geometries as apply to the rotational systems discussed in section 5.3.

5.5 Viscoelasticity

Initially motivated by a desire to understand vibrational compaction of fresh concrete (section 8.3), work on the oscillatory shear response of cement pastes soon showed that it could shed light on the solid-like properties of the material at stresses below the yield stress. Following advances in rheometer design a particular benefit is that viscoelastic measurements can play a role in studying the evolution of properties with time from fresh to set paste. In this respect, oscillatory shear at low amplitudes is very useful because changes in the dynamic moduli can be observed without disturbing the microstructure of the material.

When pastes are subjected to oscillatory shear in a parallel plate rotational rheometer, small amplitude oscillations imposed on one plate are transmitted to the other as a torque, which also oscillates but is generally out of phase with the applied oscillations by a phase angle δ, which is between 0 and 90°. The shear stress varies as a function of time t according to

$$\tau(t) = \gamma_o (G' \sin\omega t + G'' \cos\omega t) \qquad \text{..........(3)}$$

where G' is the storage modulus and G'' is the loss modulus. The storage modulus represents the elastic or in-phase component of stress and the loss modulus represents the liquid or out-of-phase component of stress. The two moduli combine to form the complex modulus

$$G^* = G' + iG'' \qquad \text{..........(4)}$$

For an ideal solid there is no loss because the material is perfectly elastic and $G'' = 0$, so $G^* = G'$ while for an ideal liquid there is no rigidity and $G' = 0$, so $G^* = G''$. In both a viscoelastic solid and a viscoelastic liquid a frequency sweep typically reveals a high frequency plateau in G' where the modulus is independent of frequency, the linear viscoelastic region, and it is important to work at frequencies in this region. At high frequency the material is being oscillated faster than its relaxation time (the time required for the stress to relax to *1/e* of its original value at the end of a period of steady flow) and the sample cannot relax between oscillations. Therefore the structure stores some residual energy, independent of the viscous nature of the sample. At low frequency the material is being oscillated slower than the relaxation time, the sample is able to relax between cycles and there is no residual energy stored in the sample. At low frequency the storage modulus of a viscoelastic liquid has a value characteristic of a liquid, while a viscoelastic solid has a value characteristic of that material. The ratio G''/ G' is $\tan\delta$, the phase angle, and can be visualised as the relative proportion of viscous to elastic properties.

If frequency is kept constant and strain amplitude is increased in a strain sweep, the behaviour changes at a critical strain. In a flocculated suspension such as cement paste, particles are able to recover elastically at low strains, and the material acts as a solid, with G' independent of strain, and the structural integrity of the flocculated network is maintained. Above the critical strain particles are not able to recover elastically and the material acts as a viscoelastic liquid.

Stress relaxation methods involve a sudden application of a small strain to a material, which is held constant while the decrease in the resulting stress is observed over time. The relaxation modulus is the ratio of the stress to the applied strain, and its variation can be fitted to a suitable viscoelastic model. Either just the initial and equilibrium (long term) values are measured or the whole curve is fitted by computer to an exponential decay model with one or more relaxation times, estimated as a spectrum [98]. Likewise, in creep tests a sudden application of a stress results in a progressively increasing strain, which is measured over time. In this case the compliance is the ratio of strain to stress, and can be fitted to a viscoelastic model.

From all this it is clear that oscillatory, relaxation and creep measurements of a cement paste have the potential to show a progression with time towards more solid-like behaviour as setting occurs and the structure becomes more rigid.

In rotational rheometry, coaxial cylinders [58, 60, 61, 63, 90, 99, 100], parallel plates [62] and a helical ribbon mixer geometry [90] all give satisfactory results, subject to the concerns discussed in section 5.3. In translational rheometry, small amplitude oscillations applied to a disposable blade also give useful data [59]. Not all workers give information on the linear viscoelastic region, but those that do so report the critical strain for cement paste to be 1×10^{-4} [60, 63], 5×10^{-5} to 2×10^{-4} [61] and 3×10^{-4} [90], values which are typically at, or just above, the lower limit of capacity of the instruments available. Equally, values for the lower frequency limit are given as 0.1 Hz [90] and 0.2 [60, 63], with other work reported at fixed values of 0.69 [100] and 2.5 Hz [61]. Schultz and Struble comment on the need to compromise on the instrument set-up between a high enough torque measuring capacity for the relatively viscous pastes and the sensitivity required for studying changes with time [60].

Gregory and O'Keefe report stress relaxation methods, focussing on polymer latex blended cement pastes [54, 58, 99]. Struble and Schultz report creep recovery behaviour of cement paste [64]. In both cases the modulus and compliance vary with time and confirm the methods' utility for studying the build up of structure associated with continuing hydration leading to setting. The creep experiments show that cement paste undergoes a sharp transition from solid-like behaviour at low applied stress to liquid-like behaviour at higher stress and the stress level associated with this transition approximates to the yield stress determined by other means.

5.6 Extensional flow

Investigations of the extensional flow of cement based materials are scarce, which suggests that either extensional flow is not considered to be of importance or it is too difficult to measure with such a coarse granular material. There is likely to be an extensional component to the flow of material through constrictions or other changes of section in pipeline flow situations but no treatments of this appear to have been made. There is an extensional component to the squeeze flow measured in the squeeze flow geometry (section 5.4) and to the remoulding that occurs in slump and slump flow tests (section 5.7). Indeed, Piau [101] points out that extensional stresses must always be taken into account when evaluating complex flows of viscoplastic materials [102] and that the absence of any extensional tress parameter in one-dimensional models can only result in the violation of the laws of continuum mechanics, and in the equations obtained being wrong. Clearly this field invites research but the experimental challenges should not be underestimated.

5.7 Empirical test methods

Over 100 empirical tests for concrete, mortar, grout and cement slurry have been developed and many have been standardised by national bodies. They are all single point tests, as discussed above, and involve flow, slump or spread under gravity or as a result of jolting, remoulding under vibration, penetration of a probe, compaction, or deformation. They were commonly developed on the unsound basis of attempting to provide a close imitation of practical conditions. None is satisfactory rheologically and, apart from those that have been adopted in a standard, most of them have been used only by the inventor. However, some, notably the slump and spread tests, are in such widespread use in industry that attempts have been made to analyse their performance in rheological terms and relate the results to the rheology of the material.

5.7.1 Remoulding tests

It is only natural to seek empirical relationships between the results of established or standardised tests and rheology, if only to enable technologists who have a "feel" for a concrete of 100 mm slump to be comfortable with the data from rheological testing, and correlations have been quoted by many workers. Tattersall [103] postulates that the empirical tests in the British Standard each operate at a mean effective shear rate and that the measurement is a simple function of the shear stress at that shear rate. For example, in the slump test the material is stationary when the measurement is made so it is reasonable to assume that the shear rate is very low or zero. Slump values would therefore be expected to correlate negatively with yield stress, as has indeed been reported [23, 104]. The effective shear rate in tests which involve some degree of remoulding would be expected to be higher and the result would correlate with apparent viscosity at a non-zero shear rate. This hypothesis is supported by examination of a number of datasets [14, 103] where two point test results are presented alongside empirical test results, but also, more importantly, an equation linking the results of empirical tests to each other is obtained by eliminating the two point values. A very high level of agreement with this equation is found for over 300 different published results given by six different workers. The important conclusion from the analysis is that if the British Standard tests, involving compaction and vibration, can be related to the two point test by assigning each of them a characteristic rate of shear, then conversely, the two point test, which involves a stirring process, is capable of assessing the behaviour of concrete in a compacting process and in a vibration process. It also suggests that it should be possible to label any practical process with its own characteristic effective shear rate. This vindicates the use of rotational rheology tests for assessing cement based materials for use in practical situations.

The relationship between slump and yield stress attracts attention because the slump test is a cheap and simple piece of equipment. Murata gives a model to predict yield stress of concrete from the conical slump test [105], subsequently used on different materials [106], extended to the cylindrical geometry [107], and extended again to consider the spread area of the slumped material [108]. Discrepancies between the data for conical and cylindrical slump moulds are addressed in later papers [101, 109, 110] by considering the details of the flow taking place as the mould is lifted and the material slides down the wall and spreads across the base plate. The key challenge for researchers is to model all aspects of the behaviour, including the final shape of the slumped heap, and figure 1 shows the latter after the mould has been lifted in both the conical and cylindrical cases. In general, depending on the stiffness of the material, two equations are needed in order to express the dimensionless yield stress $\tau_o / \rho g H_0$ in terms of slump s, where τ_o is the yield stress, ρ the density, g the acceleration due to gravity and H_0 the initial (unslumped) height.

For low slump materials

$$\tau_o / \rho g H_0 = K_1 f_1 \, (1 - s/H_0) \qquad \text{..........(5)}$$

where f_1 is either a simple proportionality constant [110] or a polynomial of third degree [101] and K_1 is a constant.

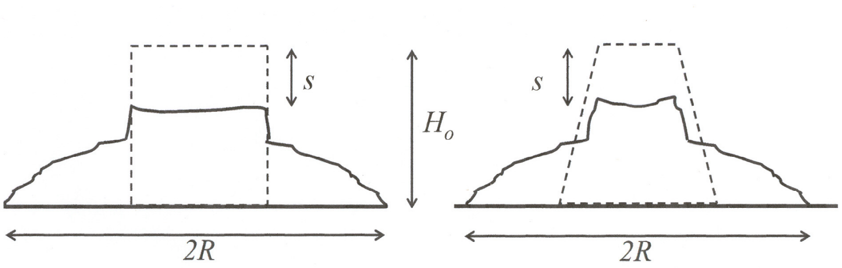


Figure 1: The shape of the slumped heap after removal of the mould (shown dotted) in the cylindrical and conical slump, mini-slump and spread tests, with the measurement parameters shown.

For high slump materials [110]:

$$\tau_o/\rho g H_0 = K_2 H_0^{1.5}(1-s/H_0)^{2.5}, \qquad ....(6)$$

and [101]:

$$\tau_o/\rho g H_0 = K_3 (f_2 (s/H_0))^{2.5}, \qquad ....(7)$$

where f_2 is a sixth degree polynomial and K_2 and K_3 are constants.

The ASTM mini-slump cone, a 50mm diameter, 50mm high cone of the same aspect ratio as the slump test, is quite widely used in industry for assessing cement pastes and filled products [111]. The parameter of interest is the radius R of the spread "pancake" obtained when the mould is lifted and the material spreads across the horizontal base plate (Figure 1). This is related to the yield stress as follows [112]:

$$\tau_o = 1.747\rho V^2 R^{-5} - \Gamma R^2/V, \qquad ....(8)$$

where V is the sample volume and Γ is a constant linked to the liquid-vapour interfacial energy and the wetting angle of the material on the plate. The other symbols have the same meaning as above.

This area is clearly poised for future development but Piau points out that the lack of accurate experimental data for testing the models is a hindrance [101].

5.7.2 Flow tests

Originally developed to assess the viscosity of oils [113], the Marsh cone is very commonly used for quality control of grouts for all void filling purposes. Strictly speaking the Marsh cone is just one of a family of efflux cones, where the time taken for a known quantity of grout to flow out of a conical funnel through a short straight pipe is measured. The dimensions vary somewhat but those specified for grout for pre-stressed concrete tendons [114] are an orifice diameter of 10 mm and a capacity of 1.8 litres, of which the time taken for 1 litre to discharge is measured. Although it can be assumed to measure the apparent viscosity of the fluid, the cone has two limits: for low viscosity fluids there is no relation between viscosity and efflux time, while for fluids with a yield stress there may be no flow at all if the yield stress is too high [115]. The governing relation for the efflux of a Bingham material with yield stress τ_o and plastic viscosity μ through an orifice of radius R is the Buckingham-Reiner equation

$$Q = \frac{\pi R^4}{8\mu l}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) \qquad \text{..........(9)}$$

where Q is the rate of flow, P the pressure gradient driving the flow and p the minimum pressure at which flow begins. This equation applies to both the conical and cylindrical parts of the apparatus and the total flow is a combination of the two. Roussel and Leroy present the full equations for both the purely viscous and the Bingham cases [115] and conclude that the equations for the latter cannot be solved analytically but that numerical simulation permits the efflux time to be predicted from the Bingham parameters with good agreement. They suggest that using two different cones could have merit as a simple quality control test for field measurements of yield stress and plastic viscosity of grouts (within ±15-30% prediction error) without the need to set up a rheometer on site.

In principle, Roussel and Leroy's analysis can be applied to all the empirical efflux tests that have been proposed for self-compacting concrete. The V-funnel is a parallel sided rectangular funnel, which tapers from 75 × 515 mm at the top to 75 × 65 mm at the bottom [116]. The Orimet is a vertical pipe of 80 mm internal diameter [117]. The L-box consists of a vertical box of rectangular section (100 × 200 mm) with a 150 mm high opening in one side at the bottom where concrete can discharge sideways through a grid of bars into a horizontal trough [118]. In each case the time taken for a quantity of concrete to discharge, either fully or sufficiently to reach a certain distance from the opening with the L-box, under gravity is measured. If these tests can be put on a sounder footing by rheological analysis in the same way as the Marsh cone, the criticisms made in section 2 could, to a certain extent, be answered. Indeed, progress has been made with the L-box using a simulation based on a finite element method formulation of the Navier-Stokes equation [119]. However, it should also be borne in mind that these empirical tests have experimental limitations in terms of sensitivity, discrimination, and testing errors, and that it is still true that testing rheology is a more fundamentally sound approach to the assessment of self-compacting concrete. Finally, evidence that simplicity is not incompatible with a sound rheological basis is demonstrated by the tube viscometer of Roshavelov [52, 70], which is designed to exploit equation (9) for fresh concrete.

6. CEMENT-BASED MATERIALS - RHEOLOGICAL RESULTS

It might be expected that the rheology of the more complex material, concrete, with its 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 by treating it as a quasi-homogeneous continuum. In this section it will be considered first, before a more detailed discussion of cement paste. Finally mortar, which shows intermediate features and is often used as a model material to study trends of composition without the sometimes confusing effects of variations in coarse aggregates, will be discussed.

6.1 Concretes

Much work reports the effects of mix constituents - cement, other cementitious materials like fly ash, aggregates and admixtures - and their relative proportions and characteristics [14, 28, 31, 120-124]. There is general agreement that concrete conforms to the Bingham model and does not show structural breakdown over the range of shear rates used in the common test methods. For example, figure 2 shows the effect of water / cement ratio on yield stress and plastic viscosity. These trends can be shown conveniently on a graph of yield stress against plastic viscosity as in figure 3. Originated by Bloomer [125], this form of presentation is useful because yield stress and plastic viscosity vary in a complex fashion with composition as shown in figure 4. The trends shown in figure 4 are built up from data in the style of figures 2 and 3 and in each case the direction of the arrowhead shows the effect of increasing the amount

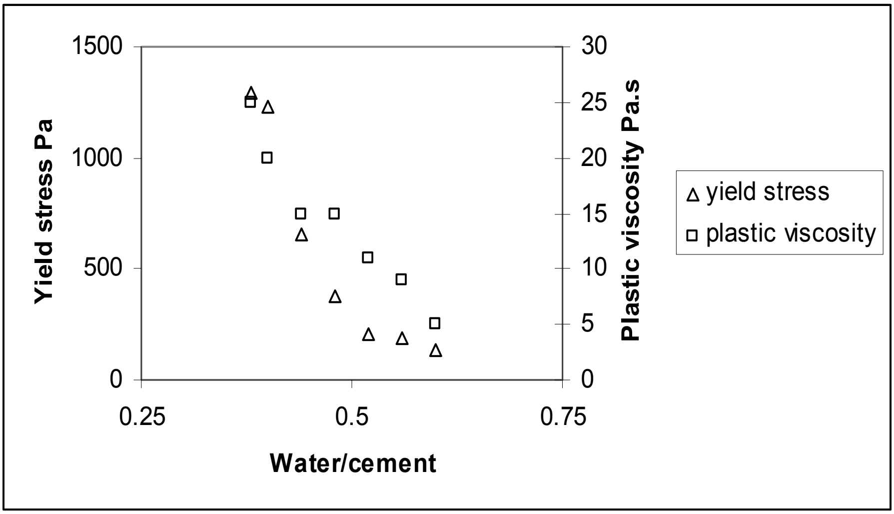


Figure 2: Effect of water/cement ratio on yield stress and plastic viscosity of fresh concrete [30].

of the appropriate ingredient. The trends are generally additive, and for example the effect of using a dispersing admixture to reduce the water content of fresh concrete is shown in figure 5. These admixtures are discussed further in section 6.2.4.

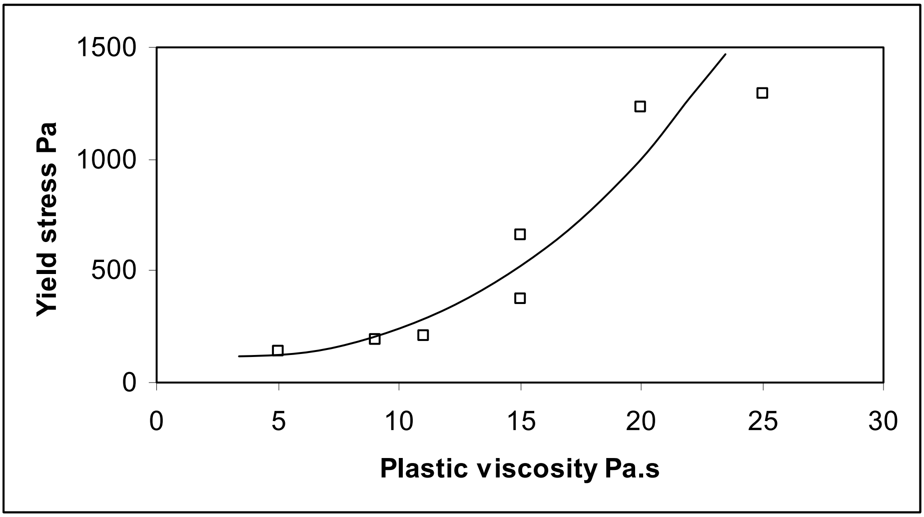


Figure 3: Yield stress vs plastic viscosity graph for the data in figure 2.

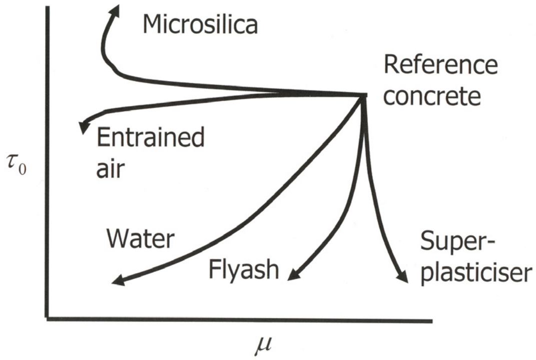


Figure 4: The direction of the change in rheology of a typical concrete caused by an increase in the amount of the parameter noted is shown by the arrows.

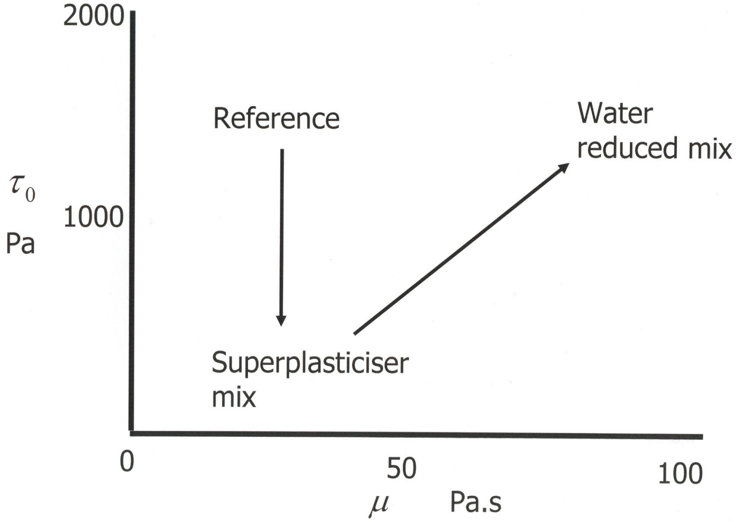


Figure 5: Rheology of water-reduced concrete produced with a superplasticiser at approximately constant slump, which implies constant yield stress. Addition of superplasticiser reduces yield stress but does not change plastic viscosity. Water reduction to regain the original slump increases both yield stress and plastic viscosity, resulting in a mix which, in extreme cases, is very sticky and hard to work.

This complexity 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 [28]. This is discussed further in section 8.5.

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 Bingham to Herschel-Bulkley type behaviour

$$\tau = \tau_o + A\dot{\gamma}^B, \qquad \text{..........(10)}$$

with the consistency index B changing from less than 1 (shear thinning) to more than 1 (shear thickening) as the superplasticiser content increases [72, 126, 127]. Researchers need to keep this in mind when studying the rheology of these types of concrete [128].

6.2 Cement pastes/slurries/grouts

There is an enormous volume of reported work on pastes, slurries and grouts, with some disagreements over fundamentals, which will be highlighted where appropriate.

6.2.1 Flow curves

The flow curve has been reported to fit several different mathematical forms, all of which, except the Quemada model, indicate the existence of a yield stress by requiring an intercept on the shear stress axis. These are listed as follows, together with a representative reference to work in which they are used:

Bingham [14, 98] $\tau = \tau_o + \mu\dot{\gamma}$; .... (2)

Herschel-Bulkley [129] $\tau = \tau_o + A\dot{\gamma}^{B}$; ....(10)

Robertson-Stiff [130] $\tau = A(\dot{\gamma} + B)^{C}$; ....(11)

Modified Bingham [131] $\tau = \tau_o + \mu\dot{\gamma} + B\dot{\gamma}^{2}$; ....(12)

Casson [132] $\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\mu\dot{\gamma}}$; ....(13)

De Kee [131] $\tau = \tau_o + \mu\dot{\gamma}\, e^{-A\dot{\gamma}}$; ....(14)

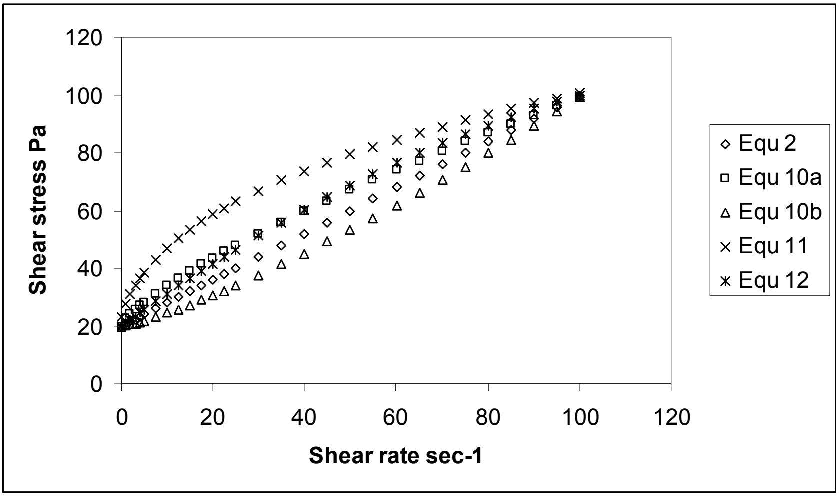
Yahia and Khayat [131] $\tau = \tau_0 + 2\sqrt{\tau_0\mu\dot{\gamma}e^{-A\gamma}}$ ....(15)

Quemada [133] $\tau = \left(\dfrac{1+\sqrt{(A\gamma)}}{B+C\sqrt{(A\gamma)}}\right)^{2}\dot{\gamma}$ ....(16)

Vom Berg [134] $\tau = \tau_o + A\sinh^{-1}(B\dot{\gamma})$ ....(17)

where A, B and C are constants, which in some cases include material parameters. Figure 6 shows the form of these flow curve models, using values (Table 1) chosen to give $\tau = 20$ and about 100 Pa at $\dot{\gamma} = 0$ and 100 sec^{-1} respectively. There is an obvious case for standardisation [135], but, as discussed in the rest of this section, this is not simple.

Many workers report the variation of rheological parameters with water/cement ratio and one compilation of data for yield stress is shown in figure 7 [14], showing the typical log-linear form of the relationship. The striking thing about this figure is the very wide range of values – at 0.45 water/cement ratio yield stresses span a 20-fold range. These results were all obtained with industrial cements, which are not sufficiently different in their chemical composition and fineness as to be able to explain this variation, so the implication is that there are unexplained variations related to differences in measurement technique. Centrifugal separation, sedimentation, undetected plug flow and slippage at the smooth surfaces of a viscometer could contribute to experimental variations as large as those reported, but the major source of error is likely to stem from the fact that cement paste is subject to structural breakdown.



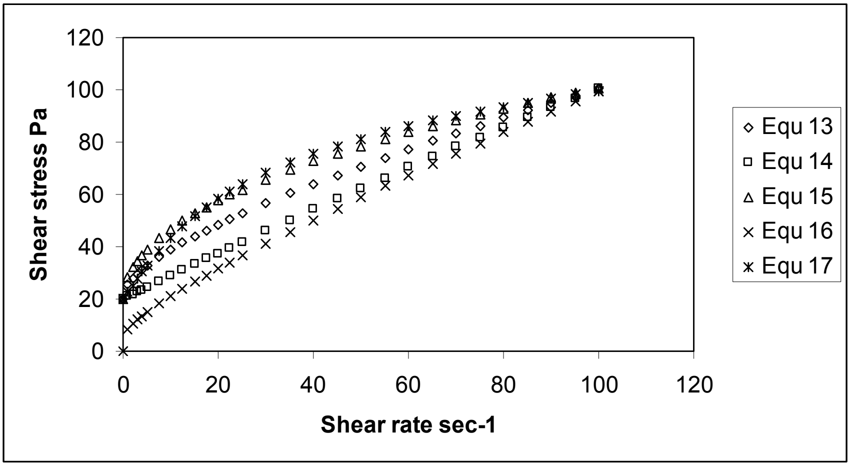


Figure 6. Shapes of the flow curves produced by the various models of equations (2), (10)-(17).

Eqn:	2	10a	10b	11	12	13	14	15	16	17
τ_o	20	20	20	-	20	20	20	20	-	20
μ	0.8	-	-	-	1.15	0.31	0.89	0.9	-	-
A	-	2.5	0.25	20	-	-	10^{-3}	10^{-3}	0.14	26.5
B	-	0.75	1.25	1.5	-0.0035	-	-	-	10^{-4}	0.1
C	-	-	-	0.35	-	-	-	-	0.14	-

Table 1: Parameters used in the various equations to generate figure 6.

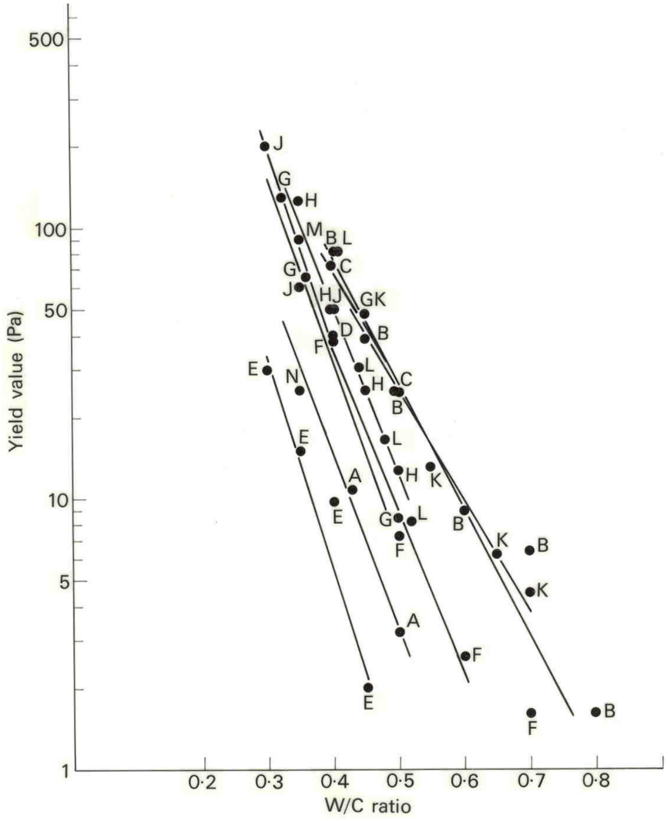
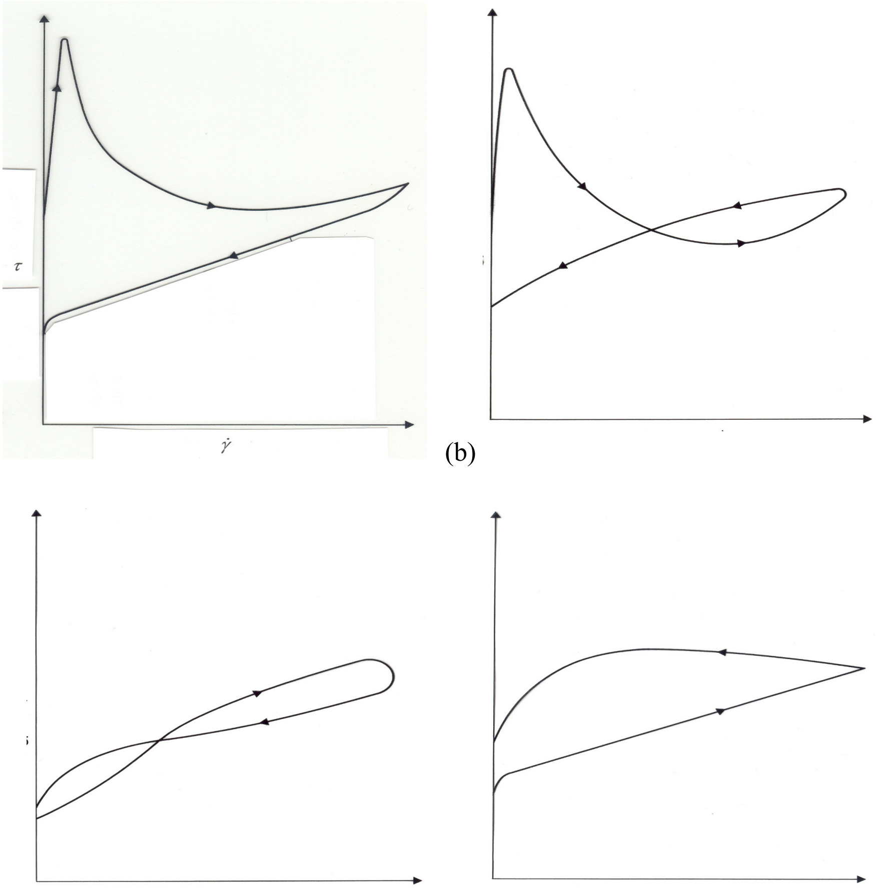


Figure 7: Effect of water/cement ratio on yield stress of cement paste [14]. Each letter denotes a different series of published data: A [257], B [11], C [258], D [50], E [130], F [134], G [259], H [260], J [261, 262], K [171], L [263], M [149].

6.2.2 Structural breakdown and thixotropy

Cement paste breaks down while being tested to obtain the flow curve and hysteresis loops where the down-curve falls to lower stresses than the up-curve are obtained when a short cycle time is used. However, the shape changes systematically with increasing cycle time, through loops with a crossover point to loops showing structural build up (figure 8), attributable to chemical reaction during the course of the test [136].



(a) (b)

(c) (d)

Figure 8. Hysteresis loops obtained with cement pastes at increasing cycle times. Type (a) is always obtained at cycle times of 2 minutes or less, while type (d) appears at times of 36 minutes or more, depending on the cement [136].

Hattori and Izumi [13] explain the effect in terms of the competition between coagulation and deflocculation processes. Their theory deals with the coagulation of cement particles in a paste due to the surface forces of attraction, as a result of which work is required to separate them. This coagulation is considered as either reversible, where the association is a relatively short-lived because the power available in the sheared suspension is sufficient to separate the particles, or permanent where it is insufficient. The individual connections, called junctions, influence the apparent viscosity at time *t* and shear rate $\dot{\gamma}$ according to:

$$\eta_{HI} = B_3 \left[\frac{n_3 \left[U_0 \left(\dot{\gamma} H t^2 + 1 \right) + Ht \right]}{\left(Ht + 1 \right)\left(\dot{\gamma} t + 1 \right)} \right]^{2/3} , \qquad \text{………(18)}$$

where B_3 is the coefficient of friction between particles, n_3 is the number of primary (uncoagulated) particles in unit volume, U_0 is the initial degree of coagulation defined as the ratio of the number of junctions to the number of particles and *H* is the coagulation rate. *H* is of course affected by the attraction between particles and by the continuing hydration of the individual particles. This equation can reproduce the different hysteresis loop shapes in figure 8 [137].

Thixotropy is defined as a decrease in viscosity when shear is applied, followed by a gradual recovery when shear is removed. This implies either a reduction in shear stress at constant shear rate or an increase in shear rate at constant shear stress. The effect is time dependent, in contrast to shear thinning where the viscosity decreases as the shear rate or stress increases, leading to a pseudoplastic (power law with index less than 1) flow curve which is independent of the time of shearing [138]. This distinction has caused some confusion among technologists as shown by the following statement in a recent paper: “Mixtures containing [viscosity modifying agent] exhibit shear thinning behaviour whereby apparent viscosity decreases with the increase in shear rate. Such a mixture (paste, mortar or concrete) is typically thixotropic where the viscosity build up is accelerated due to the association and entanglement of polymer chains … at a low shear rate that can further inhibit flow and increase viscosity.” [139]

In so-called structural kinetics models to describe thixotropic behaviour [140] the variable viscosity arises from a variable microstructure, defined by a scalar structure parameter λ, whose kinetics govern the time-dependent behaviour [141, 142]. $\lambda = 1$ defines the completely built up structure and $\lambda = 0$ defines the fully destroyed structure. As shown in figure 9, for a material conforming to the Bingham model, there is an infinite number of straight lines (some examples denoted a-d) corresponding to the various levels of λ between 0 and 1. The difficulty facing the experimentalist seeking to determine yield stress and plastic viscosity of such a material from a flow curve is that λ changes during the course of the measurement. λ may be near to 1 at the start (although it may be considerably less than 1 if the sample has been exposed to significant pre-shearing before the experiment) and decreases towards but may not necessarily reach 0 at the end of the experiment. This means that during the course of the experiment the Bingham parameters decrease and the measured curves describe a loop (shown by the dashed curve dropping from line a to line b in figure 9). Because

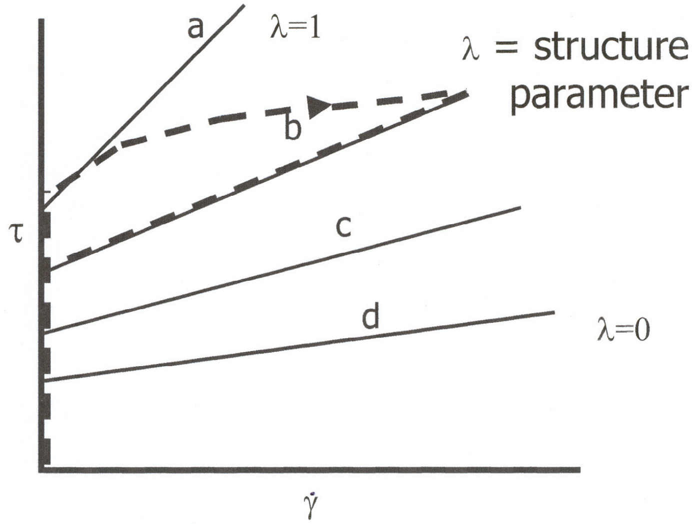


Figure 9: The origin of hysteresis loops in Bingham materials which show structural breakdown or thixotropy.

of this, and the uncertainty of the initial value of λ, the only reliable flow curve is the one for which $\lambda = 0$, i.e. after complete structural breakdown. This can only be achieved by shearing until a steady state is achieved [141]. Information on the structural kinetics can only be obtained under steady shear conditions and, even then, collecting information on the very early stages of the process is limited by the speed of response of the measuring system [143].

In the early work on cement pastes [9-12], and as confirmed later [144], there is no indication of build-up or recovery during the timescale of the experiment: ordinary pastes only stiffen over a long time and this is reflected in the progressive movement of the equilibrium flow curve towards higher shear stresses. This leads to the conclusion that thixotropy is the wrong term to use. Indeed Legrand [145] uses the term "partial thixotropy" and the assumption that all build-up is due to the progress of hydration leads to the use of continuous shear as a means of monitoring hydration and the effects of accelerating and retarding admixtures [146]. In contrast, the Hattori-Izumi theory suggests that the true situation is one in which thixotropic recovery occurs alongside chemical build-up due to hydration and is especially significant with systems containing dispersing admixtures where the cement is highly deflocculated. When such pastes are subjected to steady rotational shear conditions in which the shear rate is increased and decreased stepwise but held constant during each step, the

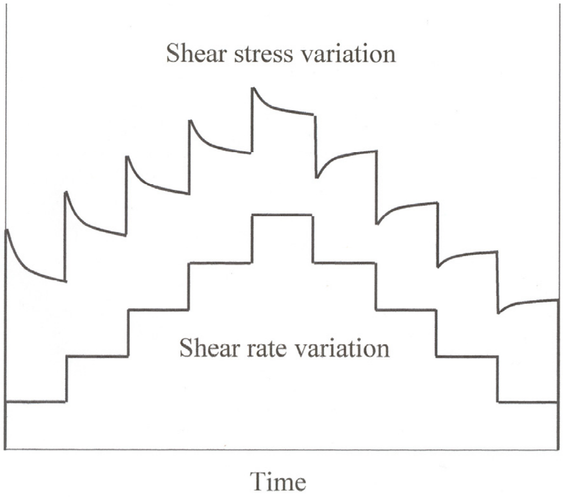


Figure 10: Variation of shear stress in a thixotropic material subjected to a stepwise increase and decrease in shear rate.

shear stress decreases to an equilibrium value during the up-curve but *increases* to an equilibrium value during the down-curve (as shown schematically in figure 10 [74, 142]. This is observed with self-compacting concrete, in which the cement is typically highly dispersed with admixtures (see section 6.2.4), and is a complicating factor in rheological measurements on this material [147, 148]. There is a conceptual problem with attempting to distinguish between thixotropy and structural build-up due to hydration because the structure parameter λ cannot be greater than 1, so in principle only structure that existed at the start of the experiment can be rebuilt. If the continuing structural build-up due to hydration is ascribed to thixotropic rebuild λ is likely to rise above 1. There is perhaps a case for modifying λ to include a term which additionally takes account of the early age kinetics of hydration, but this approach has not yet been tried.

After noting the hysteresis loop, the second obvious observation is that the yield stress, determined by the mathematical relationship chosen from the list in section 6.2.1, decreases as the total amount of shearing energy experienced by the paste increases, i.e the paste is shear history dependent. Thus successive hysteresis loops fall to progressively lower values of torque in a coaxial cylinders viscometer [10], yield stress and plastic viscosity fall to an equilibrium value as the time of mechanical mixing is increased [149] and the effect can be quantified in terms of the total shear energy received by the sample prior to the test [150-152]. This structural breakdown has been amply confirmed by experiments carried out under both continuous steady shear rate and continuous steady stress conditions.

There is practical significance in the existence of thixotropy in cement systems. Rapid structural build-up is advantageous to reduce the pressure exerted by self-compacting concrete on formwork (see section 8.2). The rapid stiffening of sprayed concrete helps prevent it slumping from the substrate before setting (see section 8.1.1) [153, 154]. Finally, it can be exploited in the formulation of high build repair materials which might need to be placed onto the underside of concrete beams or slabs.

In conclusion, the perceived need of different workers to fit the range of models in equations (2) and (10)-(17) to the flow curve data may be the result of not allowing for the possibility of structural breakdown during the test. Breakdown imposes time-dependent behaviour on a Bingham flow curve, resulting in a curved shear stress vs shear rate graph. When this is combined with the availability of curve fitting software in computer controlled rheometers, tempting possibilities open up to the investigator. When the shapes of the model flow curves in figure 6 are compared it is not difficult to imagine that experimental data with any degree of scatter could give a good fit to more than one model flow curve. In fact it has long been known that it is possible to generate an infinite range of shapes of hysteresis loops [141]. Additionally, of course, the down-curve of a partially broken down paste looks very like a Herschel-Bulkley curve with $B > 1$. The effect of structural breakdown acting through the shear history of the samples may also contribute to the wide range of yield stresses shown in figure 7. Differences between the prior mixing intensity, time and shear rates in the test will ensure that the structure parameter λ varies over a wide range [149-152].

6.2.3 Effects of composition

Space precludes extensive description of the vast amount of work reported on the effect of experimental variables on the rheological parameters of cement pastes. It is sufficient to note that investigations include the following:

- paste concentration, whether expressed as water/cement ratio (see section 6.2.1) or % solids [156],
- age and temperature [11, 47, 55, 61, 157-159],
- cement composition and fineness[11, 120, 121, 134, 160-162],
- alternative cements, such as belite cement [163], aluminous cement [164-166], oil well cement [167], non-shrinking cement [168], and magnesia phosphate cement [169, 170]
- supplementary cementing materials, such as flyash [171-177], silica fume [31, 126, 176-179], metakaolin [126, 175] and ground granulated blastfurnace slag [177, 180, 181], including those activated by alkali [182],
- presence and type of chemical admixtures (see section 6.2.4), and
- presence of polymer latex [54, 58, 83, 84, 99].

In every case data on the important material or physical factors are reported, but in some cases incomplete information on the test procedure is given.

6.2.4 Effects of rheology modifying admixtures

Admixtures, defined as materials added in very small amounts to modify the properties of the basic cement-water-aggregate system in some way, have been used for many years [43,44]. Only those whose main effect is to change the rheology will be discussed here, and accelerators, retarders, waterproofers etc will not be considered.

Water soluble dispersing agents deflocculate the cement particle network and it has long been established that this reduces the yield stress of cement and concrete [14]. Early admixtures were lignosulfonates (LS), based on the by-product of wood pulping for paper production, but impurities in these products retard the hydration of cement. So-called superplasticisers are synthetic sulfonated melamine- or naphthalene-formaldehyde polymers (SMFC and SNFC), which can be added at sufficient concentrations to reduce the yield stress of cement paste to zero without causing excessive retardation. Optimising their performance is limited to relatively coarse control of molecular size, but the more recent advent of polycarboxylate (PC) based superplasticisers offers the possibility of tailoring the polymer to optimise performance. Superplasticisers are attractive to the engineer, offering free flowing mixes at acceptable water content and hence strength, or alternatively mixes of similar workability at a water content reduced by as much as 30-35% and therefore much higher strength. However, their spectacular effects on the rheology of cement systems are sometimes unpredictable [183]. A particular problem is their effect on the progress of the hydration reactions causing premature stiffening (or slump loss), sometimes linked to the time of addition and the duration of mixing, and these can cause serious practical problems.

LS, SMFC and SNFC admixtures all adsorb at the surface of cement particles through their sulfonate groups and their deflocculating effect is attributed both to electrostatic repulsion due to the negative surface charge that they produce and to the physical size of a layer of adsorbate on the cement particles, preventing particles approaching closely enough to stick. There is a correlation between the amount adsorbed and the reduction in yield stress [184], with sufficiently high concentrations being able to separate the cement into individual particles [185]. Analytical methods estimate the amount adsorbed by measuring the amount removed from solution and this apparent adsorption could be due to two things [186]. Part of the admixture is incorporated as an organo-mineral phase within the hydrating cement minerals where its effect is lost (accounting for the stiffening with time) and part remains available for adsorption at the surface of cement particles and is therefore effective in dispersing the flocs. However, analysing the amount removed from solution cannot differentiate the two parts and too little attention has been paid to this in the interpretation of data [186]. A third part of the admixture remains dissolved in the aqueous phase and may play a part in dispersing cement particles [187], but has otherwise been ignored in experimental studies.

Since PC admixtures can be tailored, fundamental studies of the behaviour of well-characterised superplasticisers in solution and in contact with both model powders and well-characterised cements improve our understanding and have the potential to lead to new optimised products [188]. PC admixtures consist of a main

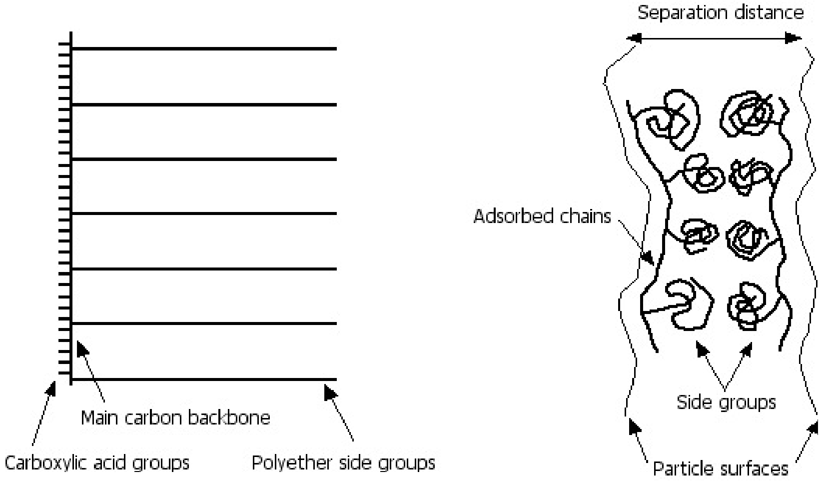


Figure 11: Chemical structure of a comb-like polycarboxylate admixture and its mechanism of steric stabilisation.

polymer backbone of carbon atoms to which carboxylic acid and long chain polyether side groups are attached. The polymer is essentially a polyacrylic acid, the carboxylic acid groups of which have been reacted with polyethylene oxide / polypropylene oxide molecules to form a comb-like structure (figure 11). Changing details of the polymerisation process enables the producer to vary the backbone length (hence molecular weight), the ratio of carboxylic acid to ether groups (hence the relative anionic/non-ionic proportion), and the length of the side chain (hence the thickness of the adsorbed layer). The anionic carboxylic acid groups adsorb on to the cement particles, providing electrostatic repulsion, while the non-ionic ether groups do not adsorb but are free to dangle in the solution. When two polymer-covered particle surfaces approach, the reduction in entropy that would result from mixing the dangling chains together makes this process thermodynamically unfavourable so the particles repel each other (figure 11). The combination of a shorter polymer backbone and longer/more numerous ether side chains makes for greater and more long lasting workability improvements [189].

Yield stress and, to a lesser extent, plastic viscosity decrease with increasing superplasticiser concentration and above a critical concentration the flow is essentially Newtonian [149, 187], where the interparticle attraction is overwhelmed by the presence of the admixture. This effect is paralleled by changes in the viscoelastic response (section 6.6) [190]. The powerful effect of PC admixtures means that as little as 0.3% polymer by weight of cement is needed and this can pose problems with quality control, because the rheology of the mix is very sensitive to errors in the added amount.

The time of addition of the superplasticiser has a significant effect on its efficiency [43, 44] and this is due to its incorporation into the organo-mineral phase [186]. Adding admixture pre-dissolved in the mixing water results in some of it being bound in the hydration skin as it forms, whereas addition delayed by a few minutes is sufficient for the skin to have already formed, so more of the admixture remains available for adsorption, bringing about better dispersion from the same amount added. It is suggested that PC admixtures are less prone to this because, even if the backbone is bound into the hydration skin, the long side chain ether groups can still dangle in the solution and cause repulsion [186].

The other group of admixtures with a significant effect on the rheology of cement and concrete are the air-entraining agents, which are added to provide resistance to the action of frost. They incorporate small air bubbles into the mix by modifying the surface tension of the water and aligning themselves at the air-water interface with their non-ionic tail oriented towards the air and their anionic head oriented into the water [43, 44]. When the concrete has hardened the bubbles provide chambers into which the stress developed by water freezing can be released, protecting the concrete from damage. The spherical bubbles have relatively little effect on the strength of the fresh cement system at rest (hence only a small effect on yield stress) but they strongly influence the flow of the system by acting as "ball bearings" to allow larger particles to move past each other more easily [14]. This explains the trend of increasing air content on rheology shown in the yield stress – plastic viscosity graph (figure 4).

Our understanding of the effects of rheology modifying admixtures is now at quite a high level and it can be expected that they will play an increasing role in the design and production of the engineered cement-based materials of the future.

6.3 Mortars

Mortars exhibit behaviour intermediate between those of concrete and of cement paste. They undergo structural breakdown and the measured data are sensitive to the previous shear history of the sample, but the equilibrium flow curve conforms to the Bingham model [37]. Much work has been done on the effects of composition, which are similar to those observed in fresh concrete, to the extent that mortar tests get pragmatic use as small scale predictors of concrete rheology [72]. An example of this is shown in figure 12, where a yield stress – plastic viscosity plot for concrete is compared with one for the "concrete equivalent mortar" i.e. one made with the same ingredients but omitting the coarse aggregate. The trends of increasing silica fume and metakaolin content on the rheology are similar between the two. Some justification of this approach is given by Toutou and Roussel [191] in a multi-scale study which successfully places mortar and concrete on the same scale of yield stress against solids volume concentration, but is unable to place cement paste because of the colloidal scale interactions between cement particles.

Prediction of concrete rheology from tests on concrete equivalent mortar is not

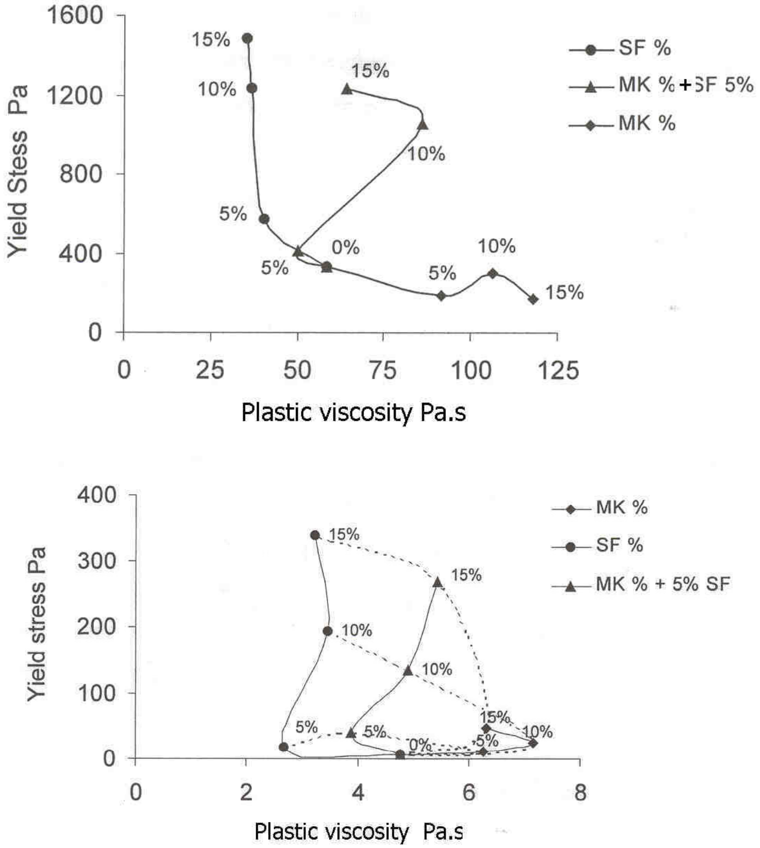


Figure 12: Yield stress vs plastic viscosity graphs produced for concrete (above) and concrete equivalent mortar (below) containing silica fume (SF) and metakaolin (MK) (Amin and Banfill, unpublished).

without its pitfalls and figure 13 shows the correlations for yield stress and plastic viscosity of concrete and mortar containing different superplasticisers.

There is a strong correlation for yield stress but not for plastic viscosity and this is attributed to poor control of the amount of entrained air in the mortar [74]. Air content is constant at 2% by volume in the concretes but varies between 0.5 and 5% in the equivalent mortars. As shown in figure 4 entrained air has a significant effect on plastic viscosity but relatively little on yield stress, so this variation accounts for the poor correlation for plastic viscosity in figure 13. A similar effect of the sensitivity of rheology to variations in air content is seen in the context of concrete production control [192].

Of course, mortar for masonry is a material in its own right and mortar sands may contain widely varying amounts of very fine particles and clay contaminants. The effect of very fine particles on workability and water demand depends on their nature, as a sand containing 8% silt behaves very differently from one containing 8% clay. Banfill [193] tested mortars made with thirty sands, containing 0 - 12.1 % passing a

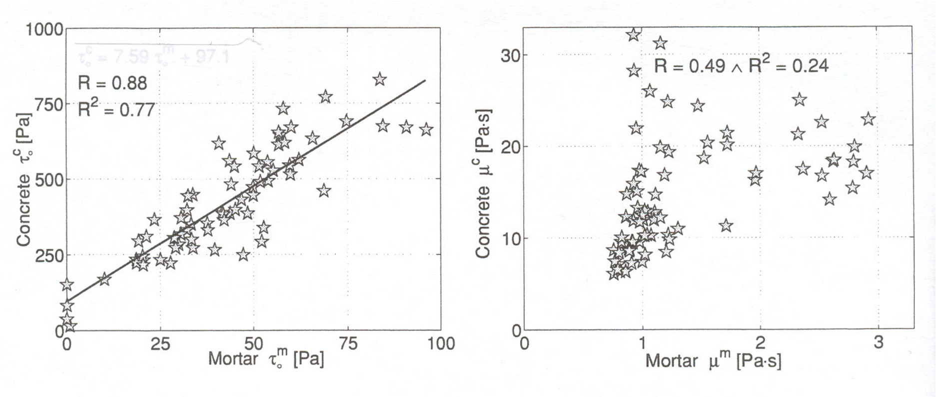


Figure 13. Correlations between yield stress (left) and plastic viscosity (right) measured on concrete and its constituent mortar [74].

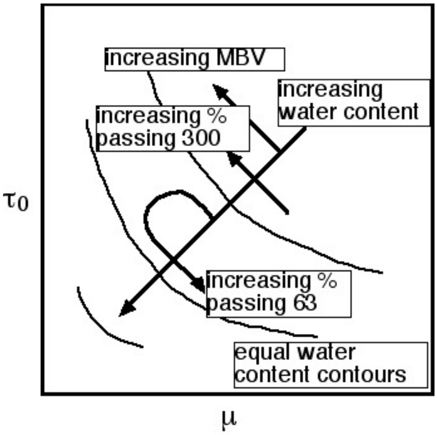


Figure 14: Summary of the effect of fineness parameters on the rheology of fresh mortar [193].

63µm sieve and with a Methylene Blue Value (MBV) of 0 - 5.24 g dye adsorbed per kg sand. The MBV classifies the amount and activity of the clay present.

The results confirm that the fineness parameters affect rheology in different ways and the effects are summarised in figure 14, where the curved lines are contours of approximately equal water content. Increasing MBV increases the water demand and changes the sensitivity to water content. In terms of figure 14 increasing MBV at constant water content moves the point upwards and to the left, but because yield stress is the parameter which dominates the overall level of workability this new point corresponds to a stiffer mortar to which more water must be added. As a consequence the water needed to achieve the original workability increases. This behaviour probably reflects the role of the very fine clay particles, whose high surface area needs a lot of water to form a continuous film and whose absorbency soaks up water for swelling. These two features account for the high yield stress, but once the mortar is flowing the fine particles act as lubricant in the spaces between the coarser sand particles and the plastic viscosity is then relatively insensitive to water content.

Overall grading, expressed as the percentage passing 300µm, changes the water demand and the rheology, as expected from previous work [194], in just the same way and for analogous reasons as MBV. The effect of percentage passing 63µm has less confidence because of shortage of data. The complexity of figure 14 shows that responding to a change in fineness by changing the water content might result in a mortar which behaves entirely differently, and this could have implications for the quality control of production.

Finally, the addition of fibres to a brittle cement matrix, such as a mortar, results in a composite with enhanced ductility, improved impact resistance and increased toughness. In addition, carbon fibres influence the electrical properties of the composite which could, potentially, make it a smart material. Despite this interest there is little information of the influence of fibre additions on the rheology, in the context of ease of moulding. Carbon fibre reinforced mortar conforms to the Bingham model and increasing fibre volume, length and concentration increase both the yield stress and the plastic viscosity of mortar [195, also Banfill et al, submitted]. Fibre reinforced composites are likely to be extruded and the process and related material properties are considered in section 8.1.3.

6.4 Comparisons between cement paste, mortar and concrete

Table 2 shows that there is a trend in the rheological properties of cement-based materials, as quoted in the literature, which can be explained, at least semi-quantitatively, 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 that of the cement-water interface. This is progressively diluted by the presence of aggregate. Thus, for example, in one comparison two cements, which give pastes whose rheological parameters differ by a factor of two, produce concretes of indistinguishable flow behaviour [14].

	Cement paste, grout	Mortar	Flowing concrete	Self-compacting concrete	Concrete
Yield stress (Pa)	10-100	80-400	400	50-200	500-2000
Plastic viscosity (Pa.s)	0.01-1	1-3	20	20-100	50-100
Structural breakdown	Very significant	Present	None	None	None

Table 2: Rheology of cement paste, mortar and concrete (shear tests)

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 withstands the applied stresses without deformation: consequently the yield stress is higher, a point confirmed by the increase with increasing aggregate content in concrete [14]. 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 at 50:50 per cent by volume, the shear rate within the solid aggregate particles is zero and the velocity gradient in the paste may be up to $5\dot{\gamma}$. Wallevik expresses this explicitly for the mortar fraction (0-2 mm) in concrete (16 mm maximum particle size) and concludes that the shear rate in the mortar is $4\dot{\gamma}$ [74]. These higher shear rates result in a higher stress and resistance to flow in the matrix which in turn accounts for the increase in measured plastic viscosity of the bulk material.

In contrast, the yield stress and plastic viscosity of cement paste increase as the cement gets finer [134], 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. Further work on particles suspended in dispersions has the potential to suggest the particle size range where the change from one influence to the other occurs [196].

The shear history of concrete starts in the mixer and using a simple geometrical model, Chopin estimates the mean overall shear rate in three typical concrete mixers of 0.08, 0.3 and 1.0 m^3 capacity to be in the range 10-20 sec^{-1} [155]. This can account qualitatively for the trend in structural breakdown behaviour in table 2. The work of shearing done on a material in unit time is proportional to the square of the shear rate [46]. 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 [9, 10]. 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 overall shear rate of 20 sec^{-1} is equivalent to that done in a viscometer in 180 seconds at 100 sec^{-1} or in 45 seconds at 200 sec^{-1}. This is enough to give almost complete breakdown to equilibrium [9, 10] 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.

In contrast to these simple concretes, flowing, high-performance and self-compacting concretes require significantly longer mixing times because the tailored recipe of powders that are used to optimise their properties takes time to be wetted and dispersed by the admixtures [197]. Consequently, if production has not achieved complete mixing these concretes may arrive at the point of use with some residual structure and their hardened properties may be impaired [155].

6.5 Compressive rheology

There is very little data on squeeze-flow behaviour in the literature. In assessing the suitability of this mode of testing, Meeten gives results for a range of materials, but none are based on cement [198]. Compressive yield stress and rotational yield stress agree satisfactorily for many pastes and gels but for others the compressive yield stress in much lower. Min et al report on cement pastes but find no agreement between squeeze-flow and shear measurements [48]. Cardoso et al show force-displacement-time data for mortars in squeeze-flow but do not derive any actual values of rheological parameters [96]. In contrast, the plastometer [97] gives satisfactory quantitative results for cement paste and mortar for which the plasticity threshold value, representing the stress above which the material will flow, is 15-40 kPa, and is relatively independent of geometry and rate of loading, and also varies in a sensible manner with composition. Similar values (3-40 kPa) for the bulk yield stress of paste in an extrusion process, in which the plastometer is designed to be applied, have been obtained [199] (see section 8.1.3).

Since shear rheometry is suitable for less stiff materials than compressive and extrusion rheometry, it is difficult to draw direct comparisons. However, yield stresses of 3-40 kPa obtained in compression or extrusion on fibre-reinforced pastes of 0.25-0.3 water/cement ratio seem reasonably consistent with those of 50-200 Pa in unreinforced pastes of 0.3 water/cement ratio obtained in rotational measurements. More work is needed to show that compressive and shear rheometry are measuring equivalent properties.

6.6 Viscoelasticity

Comparisons between the values of the viscoelastic parameters observed and identifying the effect of cement paste variables are hampered by the same differences in paste preparation technique as for steady shear rheometry, and there is not yet sufficient data for more than preliminary conclusions about trends to be drawn. Nevertheless, cement paste is clearly viscoelastic.

In oscillatory shear, with hand mixed pastes, G' and G'' decrease from 2 x 10^6 and 2 x 10^5 Pa respectively at 0.28 water/cement [90] to 500 and 1000 Pa respectively at 0.40 water/cement [59]. With high, but undefined, shear mixing G' and G'' decrease from 80 and 210 Pa respectively at 0.39 water/cement [58] to 50 and 80 respectively at 0.44 water/cement [62]. However, with the very high shear mixing of 920 sec^{-1} for 45 sec [60] G' and G'' are substantially unchanged at 10-20 x 10^{-3} over the range 0.40 to 0.50 water/cement ratio, while at 0.60 the values are 400 and 200 Pa respectively [200]. It appears from this that G' and G'' decrease with increasing water/cement ratio and with increasing shear mixing energy. Increasing concentration of superplasticiser reduces both G' and G'' at least 100-fold up to a critical level beyond which there is little further effect (see section 6.2.4) but the zero concentration values are not given [190]. Residual elasticity at high concentrations is accompanied by slight shear thickening, which is attributed to entanglement of the polymer chains in this particular admixture.

In creep, there is a clear change in behaviour above a critical stress level: at lower stress the behaviour is characteristic of a viscoelastic solid with a retarded elastic strain while at higher stress the strain increases continuously and almost linearly with time, with no recovery when the stress is removed – behaviour characteristic of a liquid [64]. This transition occurs over a narrow stress range at levels of a few Pa, which are close to the yield stress determined both by oscillatory shear and by controlled stress rheometry of flow curves fitted to the Herschel-Bulkley model. Furthermore the apparent viscosities above the yield stress estimated by creep and flow curves agree closely. Once again there is a trend of decreasing stress at the solid-liquid transition (yield stress) and of decreasing apparent viscosity with increasing water/cement ratio

The variation with time is of interest because viscoelasticity measurements offer the possibility of monitoring the progress towards setting. Struble and Lei report sequentially repeated creep/recovery measurements on a cement paste where great care was taken to prevent flow and consequent structural breakdown [63]. The yield stress rises slowly to about 100 Pa (0.45 water/cement ratio) over 120 minutes followed by a rapid increase to 1000 Pa at 150 minutes from mixing. The transition is clearly defined and, for the same cement used, coincides accurately with the setting time, as defined by a needle penetrometer, and with the end of the dormant period (see section 4), as defined by acceleration in the rate of heat evolution seen in a conduction calorimeter.

In oscillatory shear the time dependent changes are clearly visible and move earlier or later depending on the presence of accelerators or retarders, superplasticisers falling into the latter category [59, 61]. These changes are shown schematically in figure 15. The trend towards solid-like behaviour shown by viscoelasticity measurements is mirrored by changes in the microstructure of the evolving paste, visible under the Environmental Scanning Electron Microscope, but no more than a preliminary understanding of the features has been attempted [61, 62].

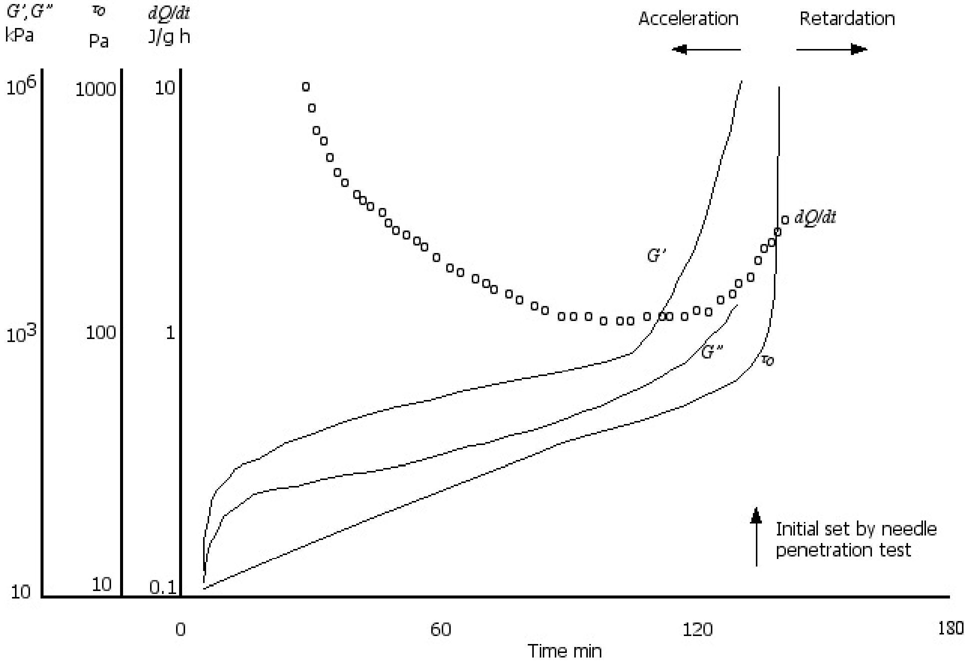


Figure 15: A composite graph showing the variation in viscoelastic parameters and yield stress with time in a hydrating cement paste [61, 63].

In stress relaxation, both initial and equilibrium modulus increase with time as the paste becomes more solid-like. Presence of polymer latex accelerates this process, while in oscillatory shear the storage and loss moduli both increase with time but the latex retards the process [99]. No convincing explanation is offered for this but Gregory and O'Keefe consider that the latex strengthens the flocculated network of cement particles while interfering with the hydration processes.

All this rich variety of the viscoelastic response of cement pastes suggests a complex area worthy of further study, with possibilities of probing the structural development and interparticle interactions in more detail.

7. A STRUCTURAL MODEL

Any proposed structural model must be able to explain the structural breakdown that occurs on shearing cement-based systems. When subjected to continuous steady shear the relationship between shear stress and time is affected by the shear rate in the experiment, and this was explained theoretically by Tattersall [10], using a linkage theory, in which the links between particles are broken by the work done in shearing the paste. Such a model is shown in figure 16 [14], in which the yield stress can be accounted for by the interparticle forces of attraction. These result in links between particles reforming reversibly when the paste comes to rest, but the irreversibly destroyed structure is much stronger than this, as shown by the initial yield stress being about 10 times the equilibrium value reached after shearing. This is explained by proposing that when dry cement powder first comes into contact with water the hydrated skin or membrane forms 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 much stronger 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 [15], and the notion of links or junctions between particles [10, 13].

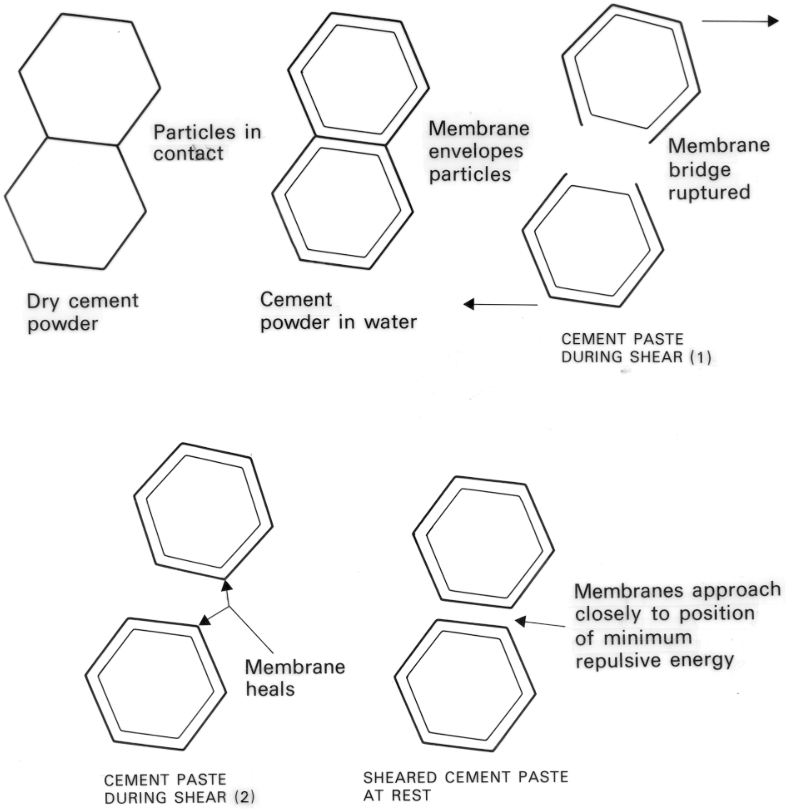


Figure 16: A structural model for the shear induced breakdown in cement systems.

8. APPLICATIONS TO PARTICULAR SITUATIONS

8.1 Pumping and related flow situations

8.1.1 Concrete

Transport of fresh concrete by pumping through pipes to the point of placement has been used since the 1930s and, given current trends towards greater mechanisation of site work, interest can only increase. It is an obvious candidate for rheological study, to help select pumping equipment and appropriate mixes. 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 [14, 98]. However, this assumes that the material is homogeneous, whereas pumped concrete actually forms a layer of paste which lubricates the wall and facilitates flow. Nomograms relating flow velocity and pressure in a practical concrete pumping operation assume that the flow of the concrete is entirely due to the lubricating layer [201], while proof of this is claimed [23] because the yield stress of the concrete used gives a value of the plug radius larger than the radius of the pipe. Therefore the pumpability of a concrete is mainly governed by its ability to form and maintain this layer under the pumping conditions and acceptance criteria are available [202].

Kaplan explicitly tackles the lubricating layer slippage. The pressure loss-flow rate relationship is independent of pressure for saturated concretes and the wall lubrication law is as follows [203, 204]:

$$\tau_i = \tau_{oi} + \eta V \,, \qquad \text{.........(19)}$$

where τ_i is the shear stress at the interface, τ_{oi} the interfacial yield stress, η 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, measured by the BTRHEOM apparatus [32]. 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 leads to a model which is able to predict the pressure-flow relationship with a high degree of accuracy and therefore can be used for design of pumping systems [204].

A point of rheological 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, and on the properties of that layer. In fact, Kaplan obtained excellent numerical agreement between the interfacial values from the tribometer and from the pumping tests, with τ_{oi} in the range 0-150 Pa and η 300-1200 Pa.s/m. The interfacial yield stresses of 0-150 Pa are considerably lower than the corresponding bulk yield stresses of 300-2000 Pa. There is a broad positive correlation between τ_{oi} and τ_o for about half of the tested concretes but there are some extreme outliers in both directions, especially for some high yield stress concretes which have zero interfacial yield stress. There is 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, and elucidating these effects is a topic for further research. In contrast to this intentional determination of slippage, the tube viscometer [52, 70] includes a series of ribs inside the flow tube specifically to minimise the risk of slippage and optimise bulk yield stress and plastic viscosity measurement.

Pumping performance is also important for the production of satisfactory sprayed concrete (gunite or shotcrete) which is used in such diverse situations as repair and reinstatement of fire damaged concrete, construction of concrete sculpture, stabilisation and strengthening of ground strata in tunnelling, and the production of free flowing surfaces for artificial watercourses. In the wet process the freshly mixed concrete is delivered under pressure to the nozzle, while in the dry process the dry ingredients are delivered to the nozzle and sprayed together with the water, which emerges from a separate nozzle so that the concrete only exists for the short time between the nozzle and the background. The wet process is evaluated by Austin et al [153, 205] and the dry process by Jolin et al [154, 206] who relate rheological measurements to a model of such requirements as non-sagging, layer build-up, rebound from the surface and nozzle efflux speed.

8.1.2 Grout and oil well cement

Both grouting and oil well cementing are applications where the materials must be pumped through complex annular spaces, which they must completely fill before hardening. It might be expected that flow would be simpler in the finer grained grout than in concrete, but again, slippage at the wall is found to be a significant problem.

The pipe flow equations are well established [14, 98, 207-209] from which pressure losses and flow rates for fluids of all types in different cross-sectional geometries can be derived. Jefferis describes the impossibility of physically modelling grout flow in a pre-stressing duct from its measured properties [57]. It is necessary to match the shear rate, the Reynolds number and the Hedstrom number [210] in model and prototype, which requires density, yield stress and plastic viscosity to be the same in both. For a fixed grout rheology, equality of shear rate and the two dimensionless groups can only be achieved if the annular gap is held constant, which, of course, defeats the object of the modelling exercise. Therefore it is, in principle, not possible to use scale models for grout flow investigation.

Nevertheless, many workers have attempted the task of predicting pipe flow from laboratory measurements on grout or cement slurry. A common starting point is the Metzner-Reed model [211], which is substantially independent of the rheology of the fluid and relates wall shear stress to apparent shear rate. Raffle [50, 212] presents results in this form and gives a start-up wall shear stress relationship for a number of pipes and cement slurries. Bannister [213] and Mannheimer [51] find that it necessary to introduce a wall slip velocity to correct the Metzner-Reed flow model to account for the variation in results for different tube diameters and uses Mooney's [214] method to analyse the slip in coaxial cylinders. The pressure drop in pipe flow predicted from the coaxial cylinder data is not always a good fit to the experimental data, which implies that other factors are playing a part. Haimoni suggests that the confused state of the literature on this point is due to the complexity of cement suspensions [167]. Suspensions may undergo phase separation or structural change when sheared and most workers either ignore the latter or eliminate it by using the completely broken down material. For a material with a yield stress or which takes a significant time to break down to equilibrium this assumption may lead to serious errors. Haimoni goes on to develop a new prediction method which involves establishing a similar flow in a coaxial cylinders viscometer to that in the pipe and makes the assumption that the sheared and unsheared layers (i.e. the plug and the sheared zone outside it) in both systems are similar. He justifies this on the basis that the curvature of large cylinders and large pipes approaches the parallel plate situation, and obtains reasonable agreement for pipes of diameter 19.5 and 34.5 mm.

Finally, it should be mentioned that grout is also used in pre-placed aggregate concrete, where the formwork is packed with aggregate and grout pumped into the gaps between particles. In this case the average shear rate of the flow can be estimated from the flow velocity through the imaginary flow channel whose nominal radius is determined from permeability measurements [215, 216]. Not only rheology of the grout but also the hydraulic parameters of the pre-packed bed must be known in order to ensure successful grouting in this application.

This section has shown that rheological properties of grouts and cement slurries tend to be of secondary importance compared to the existence of slippage layers, and that this is another area where a robust link between rheology and technology has yet to be established.

8.1.3 Extrusion

Boards, blocks and other products of regular cross-section are commonly produced by extrusion processes, and the science of extrusion flows in pastes and other concentrated suspensions is well developed [217]. In any process, paste is forced by a ram from a reservoir barrel into a die land of diameter *D* and length *L*. As it flows forward, with mean velocity *V,* it extends in the flow direction and its cross-section decreases. In the die land the material flows as a plug with only a thin lubricating layer at the wall, within which viscous effects are significant. The overall pressure drop, when the reservoir is a cylinder of diameter D_o, is given by [217]:

$$P = 2\left(\tau_{ob} + \alpha V\right)\ln\left(\frac{D_o}{D}\right) + 4\left(\tau_{ol} + \beta V\right)\left(\frac{L}{D}\right) \qquad \text{.........(20)}$$

where τ_{ob} is the bulk yield stress of the material, τ_{ol} is the lubricating layer yield stress and α and β are factors characterising the effect of velocity on the stresses. It is sometimes necessary to extend this four-parameter model to six parameters to take account of non-linearity of behaviour. In this situation αV becomes αV^m and βV becomes βV^n. In equation (20), τ_{ob}, α and m are associated with flow from the reservoir into the die land and τ_{ol}, β and n with flow along the die land.

The six-parameter model applies satisfactorily to the extrusion of fibre-reinforced cement composites of low water/binder ratio (0.25-0.33) [199, 218]. Bulk yield stress is 3-40 kPa for paste [199] and 100-700 kPa for mortar (< 600µm particles) [218], and the layer yield stress is 0.1-1 and 10-50 kPa respectively. The bulk yield stress is significantly increased by increasing concentrations of fibres, while the lubricating layer is relatively unaffected. Both are reduced by increasing water content and the values reported are consistent with the yield stresses determined in rotational rheometers, taking into account the lower water contents used in the extrusion tests. Extrusion experiments are therefore appropriate for stiff composites and the results can be applied to industrial process situations [217].

8.2 Interactions at the surface of formwork

A problem related to pumping which requires knowledge of the friction at a concrete-wall interface is the pressure on formwork - the timber, metal or other mould into which concrete is poured and which must support it until it is strong enough to support itself. This is a significant engineering design problem, where failure has expensive consequences. In traditional concrete this pressure is much lower than the equivalent hydrostatic pressure because of the yield stress within the material and the friction at the wall. As a result satisfactory empirical predictions are available [219]. However, for modern highly fluid concrete, including self compacting concrete, these predictions underestimate the actual pressures and for safety's sake the full hydrostatic pressure has to be assumed. In the case of 12 metres of fresh concrete of density 2300 kg/m^3 this is 270 kPa.

Using Janssen's theory of silo-stored granular media [220], Vanhove developed an equation for the pressure on formwork, requiring information on the yield stress, internal friction coefficient and the friction coefficient between concrete and formwork. This requires measurements of the friction between steel and fresh concrete and this can be done 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 [221-223]. Applying the coefficient of friction between steel and concrete so determined enables preliminary estimates of the formwork pressures exerted by fluid and self compacting concrete to be calculated. For the 12 metres of concrete and formwork above, the calculated pressure is 190 kPa, in good agreement with the measured value [224, 225]. Thus formwork pressure is about 30% less than hydrostatic for a self-compacting concrete, but the contribution of friction depends on surface roughness, concrete rheology and particle size distribution. These agree with other field observations [226-228]. Unfortunately information on the rheology of the concrete used in the work is not available (only slump and slump flow were measured) but Vanhove reports that the friction stress (equivalent to τ_i in equation (19)) 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 [229]. Vanhove's friction stress and Kaplan's τ_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.

Finally, it may be pointed out that there is a potentially significant role to be played by thixotropy in reducing the pressure on formwork, because the rapid build up of yield stress enables the concrete to support itself within the formwork sooner after placing and this permits more rapid placement and faster production. The formulators of self-compacting concrete therefore strive to confer some thixotropic behaviour on the fresh material by appropriate choice of admixtures, in addition to achieving a low yield stress. This is considered in a series of papers by Assaad et al [230-232].

8.3 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 factors as frequency, amplitude and acceleration [233], but several recent papers have significantly advanced understanding. Practically, vibration appears to remove the yield stress of fresh concrete, which then flows under its own weight [234, 235] 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 [236]. This work enables the effect of vibration to be defined phenomenologically, but a more rigorous investigation is reported by Teixeira et al [237]. By analysing the effects of shear and compressive waveforms on the oscillatory flow of fresh concrete they conclude 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 experimentally validated wave propagation analysis can predict correctly the rapid decay of vibration near the source, a phenomenon that has previously been attributed to cavitation [238]. A software solution enables 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 confirms 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. Unfortunately the technological stimulus to such work is weakening because the advent of self-compacting concrete renders the vibrational compaction of fresh concrete obsolescent [239].

8.4 Trowelling

Trowelling is a very common process in spreading mortar over a substrate and the behaviour of mortar under the trowel can be analysed in terms of the Bingham model. Naniwa [240] reports a trowellability apparatus, in which a trowel passes over a bed of fresh mortar and the various forces are measured (see figure 17). The blade is held at a shallow angle to the mortar bed (of thickness E) and moves with velocity v over the surface, generating forces F_t and F_n respectively parallel and perpendicular to the bed. If the mortar is a Bingham material and there is no slip under the trowel it is easily shown that:

$$F_t \cos\theta = a + b\,(v/E), \qquad \text{.........(21)}$$

where a and b are proportional to yield stress and plastic viscosity respectively. Naniwa presents a graph of F_t against v for a series of six mortars, each giving a straight line intercepting the force axis at a value greater than zero. From the limited information given in the paper the intercepts suggest yield stresses of 80-400 Pa, which agree well with the values given in Table 2. However, one problem is that the same mortar should give the same intercept regardless of the value of E, but this is not the case and this could be attributed to the existence of slippage layers under the trowel. This interesting work does not seem to have been followed up.

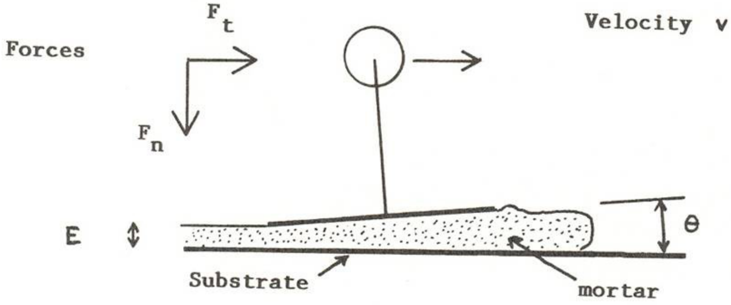


Figure 17: The forces and flow during trowelling.

8.5 Rheological quality control

The complexity of the effects of concrete composition variables (water, microsilica, flyash and superplasticiser content, etc) on the measured rheology may seem to be inconvenient but this section discusses ways of employing this complexity in the fields of production quality control and concrete mix design. A typical feature of any significant concreting projects is that the production of the concrete (possibly thousands of m^3) involves many batches of material to be supplied from the mixing plant, possibly by the ready-mixed concrete truckload of 5-10 m^3. It is impossible to test every batch but a sufficient sample is required in order to ensure that the concrete remains fit for the job, bearing in mind that the composition, particle size distribution and relative proportions of all the ingredients may change with time. Rheology can identify changes occurring during the course of production and give almost immediate information without having to wait for the concrete to harden, which is the normal practice [28].

An example of the quality control possibilities is given in figure 18, which shows the results of 11 batches of flowing concrete, containing a superplasticiser, produced on a site in the UK and tested with the two-point test by the site staff. The first obvious point is that the concrete is very variable but it is clear that most of the points lie along a trend line that is consistent with normal production where the only variable is the amount of water added to the concrete, as shown by figure 4. Point A is an extreme member of that range and the simplest explanation for this point is that far too much water was added. Point C differs from the rest of the set only by having a much higher yield stress: its plastic viscosity is similar. From figure 4 this is

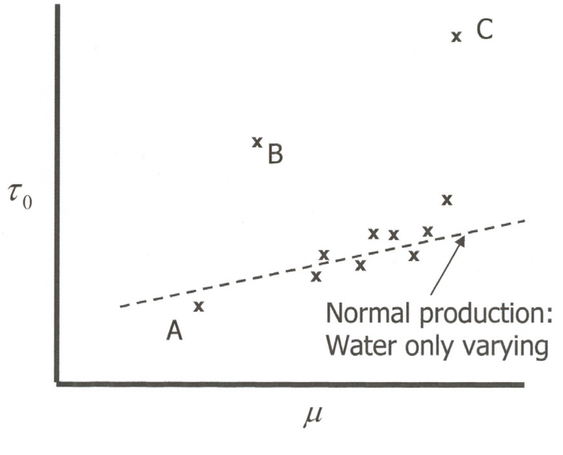


Figure 18: The results of 11 batches of concrete, produced and tested on site.

characteristic of a failure to add sufficient superplasticiser. Point B could have been due to a change in the content or nature (particle size distribution or shape, texture etc) of the sand for that single mix. When these deductions were discussed with the project manager he was able to confirm that batch C did indeed contain less superplasticiser (by deliberate decision) and that there had been a new consignment of sand during the course of production, though he was not able to identify which batch(es) might have been affected. Other possibilities of rheological quality control are shown by Tattersall [28, 192] using data obtained during concrete production, but additional value can be obtained from preliminary testing of the specified concrete to establish the effects of the possible variations in composition for that particular mix. In that case the causes of observed variations can be assigned with a fair degree of confidence [28].

8.6 Rheology and mix design

Concrete mix design is a grand name for the process of using the accumulated knowledge of the effects of the relative proportions of concrete ingredients in order to choose proportions that will give the desired properties for the task in hand [241]. As has been mentioned, concrete is typically optimised for its hardened properties – strength, durability, impermeability, fire resistance etc – with the fresh properties given little detailed attention, apart from applying a body of experience of the levels of slump or flow that are satisfactory for particular requirements. However, in more highly engineered concrete, such as self-compacting concrete, rheology is paramount and the challenge here is to design concrete mixes with a low yield stress. The difficulty with a low yield stress is that the concrete is prone to segregation, with the fine matrix filtering through the coarse particles, and it is necessary to thicken the fine matrix. Various solutions have been tried, such as:

(i) very high powder contents using inert powders to minimise the cost and the generation of heat during hydration;

(ii) water soluble thickeners to raise the viscosity of the water;

(iii) entrained air bubbles;

(iv) a combination of these.

The rheology of self-compacting concrete is likely to be different depending upon which solution has been adopted and in a recent project this caused a problem because material was supplied on the basis of approach (i) when the team assumed (rather than explicitly specified) that it would be designed according to approach (ii).

Rheological mix design can be understood as the application of information such as that presented in figure 4 to achieve the desired rheology. A combination of on-the-job experience of self-compacting concrete and the use of empirical tests alongside rheology testing of Icelandic and other materials with the BML rheometer [31] produces the zone of optimum performance shown in figure 19 [242, 243]. The method involves making trial mixes and adjusting them following the principles of figure 4 until the concrete falls within the zone of acceptable behaviour. It can be noted that a low yield stress and a low plastic viscosity together is not a satisfactory

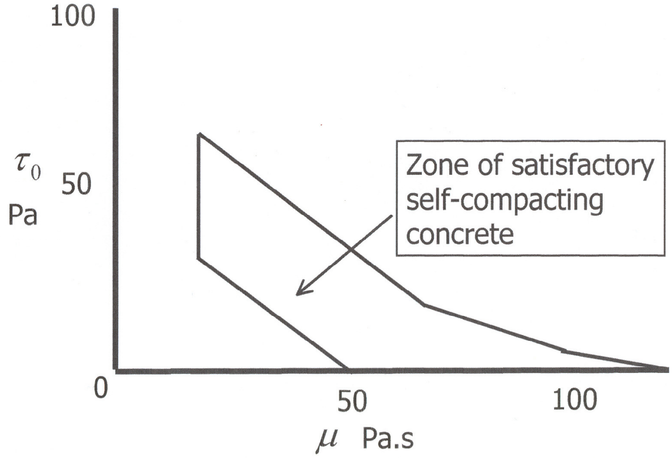


Figure 19: Self-compacting concrete has a satisfactory combination of yield stress and plastic viscosity within the zone indicated [242, 243].

combination: this gives the segregation mentioned above. A low yield stress concrete must have a high plastic viscosity, but there are upper limits to the acceptable values of both parameters, otherwise the concrete is not self-compacting.

With this application of rheology to mix design, concrete technology can be seen to have entered the modern era, but there is still one missing link: the zone of acceptability was defined by experience of the performance of concrete on the job, rather than an understanding of the rheological requirements of that job.

9. MODELLING AND SIMULATION

The question of whether it is possible to predict the rheology of cement and concrete from first principles is an obvious one to ask, and the wider one of predicting the rheology of concentrated suspensions which could be of general applicability to a range of practical situations has attracted the attention of many researchers [244-247]. Interparticle forces arising from dispersion forces, electrostatic interactions between charged surfaces, and the steric forces from species (especially polymers) adsorbed on particle surfaces all have to be taken into account, as well as volume fraction, maximum packing, percolation threshold, particle size and size distribution. Hydrodynamic interactions and the way particles “dance” around each other when put into motion by shear forces are also important. There are thus two aspects to the task: firstly to model the stress levels required to overcome the interparticle forces to start the flow (i.e. the yield stress) and secondly to model the flow behaviour at higher stresses (i.e. the apparent viscosity). A preliminary attempt to model these in concrete based on linear viscoelasticity and the classical theory of composite materials supported by experimental measurements with the BML rheometer, shows that the volume concentration, aspect ratio, angularity and surface texture of the coarse aggregate within the fine matrix affect both the yield stress and plastic viscosity [248].

9.1 Yield stress prediction

Flatt and Bowen propose a yield stress model for particles forming an attractive network [16], which makes a significant contribution. It links these physical parameters to the shear stress needed to break down the network sufficiently for it yield, and successfully accounts for all the variables except maximum packing fraction and minimum interparticle separation distance, which have to be left as fitting parameters. Even so, the values of these last two parameters required for satisfactory fitting to the experimental data on various ceramic suspensions are in good agreement with direct measurements using other techniques. They derive a basic expression for yield stress as a function of particle volume fraction ϕ:

$$\tau_o = m_1 \frac{\phi^2 \left(\phi - \phi_o\right)}{\phi_{\max}\left(\phi_{\max} - \phi\right)}, \qquad \text{.........(22)}$$

where $\phi_{\max}$ is the maximum packing fraction and ϕ_o is the percolation threshold. m_1 is a term incorporating everything that is not dependent on volume fraction, given by:

$$m_1 = \frac{1.8}{\pi^4}\left(\frac{G_{\max}}{R_{v,50}}\right) F_{\sigma,\Delta}, \qquad \text{.........(23)}$$

where $G_{\max}$ is the maximum attractive interparticle force, $R_{v,50}$ is the median particle radius calculated on a volume basis, and $F_{\sigma,\Delta}$ is a function of the coordination number which gives the number of contacts between particles in the suspension and which depends on the relative particle size in the interacting particle doublet. $F_{\sigma,\Delta}$ is defined as:

$$F_{\sigma,\Delta} = \frac{1}{2}\sum_{k=1}^{m} \phi_k \sum_{l=k}^{m} C_{k,l,\phi} \frac{\Delta v_{k,l}}{b_k^3} g_{k,l}. \qquad \text{.........(24)}$$

The first summation in equation (24) is over the volume fractions of each particle size, the second summation is over the coordination numbers of particles *l* around each particle *k* and $\Delta v_{k,l}$ represents the increase in apparent solids volume as a result of each particle *k-l* contact, all of which are evaluated explicitly from geometrical considerations.

While the original aim of the work [16] is stated as being to model cement suspensions in order to understand the behaviour of superplasticisers, they are able to test the model only on well-characterised ceramic materials because the required fundamental parameters for cements are not available. Despite this, the maximum packing fraction $\phi_{\max}$ turns out to be more than just a fitting parameter: it is a physical parameter that can be measured experimentally, in their case by filter pressing experiments on the model ceramic suspension, which give very good agreement. The quest for the remaining fundamental data also includes an assessment of the attractive forces in cements [248]. Overall, the model accurately predicts the dependence of yield stress on solids volume fraction. However, it predicts the correct scaling of yield stress with particle size only if it is assumed that the radius of curvature at the point of contact is the characteristic parameter of the powder being considered, rather than the radius of curvature of the whole particle, which is a function of its particle size, and they give microscopic evidence that this is a reasonable assumption.

9.2 Viscosity prediction

The basis of viscosity (and, by analogy, plastic viscosity) prediction stems from Einstein's equation [249]:

$$\eta = \eta_s\left(1+2.5\phi\right), \qquad \text{........(25)}$$

where η is the viscosity of the suspension and η_s is the viscosity of the solvent, and which applies to dilute suspensions of spheres, but is a considerable underestimate for suspensions of practical significance. Other more elaborate equations have been used [250] and satisfactory fitting, albeit requiring a maximum packing fraction $\phi_{\max}$, is given by the Krieger-Dougherty (K-D) equation [251] (see also figure (20)):

$$\eta = \eta_s\left(1-\frac{\phi}{\phi_{\max}}\right)^{-[\eta]\phi_{\max}} \qquad \text{........(26)}$$

$[\eta]$ is referred to as the intrinsic viscosity and increases from 2.5 for spheres to higher values for asymmetric particles, such as the > 9 quoted for glass rods [250]. For cement pastes experimental data gives a good fit with $[\eta]$ and $\phi_{\max}$ in the range 4.5-6.8 and 0.64-0.80 respectively [156]. In the cased of concrete, coarse aggregate particle shape is considered in more detail by Geiker et al [124], whose model involves packing densities and shape factors, which have a different effect on yield stress from that on apparent viscosity, using the Herschel-Bulkley equation.

A particular difficulty with the K-D equation is the distinction between the solid and the solvent and definition of their respective properties. In cement paste, the solvent is obviously water, whereas in concrete the question is whether it is the water, the cement-water paste, or the cement-water-fine aggregate suspension, because these three cases give very different values of solids volume fraction and relative viscosity. Note that figure (20) shows the variation for coarse aggregate dispersed in mortar and shows a good fit. Ferraris and Martys [252] present data for simulated particle size distributions in comparison to experimental measurements of fresh concrete in rheometers, both of which fit a trend of relative viscosity against volume concentration of coarse aggregate which follows the K-D form, although their curve is drawn in order to "aid the eye" rather than explicitly as a best fit.

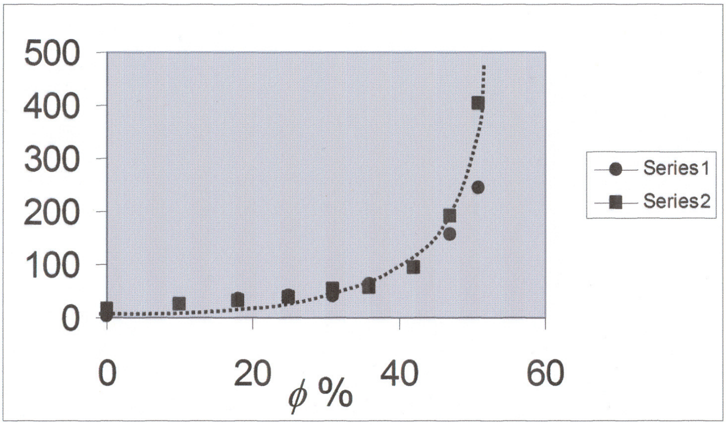


Figure 20: The variation of plastic viscosity of concrete with increasing coarse aggregate content, relative to the plastic viscosity of its constituent mortar, showing the best fit of the Krieger-Dougherty equation (Banfill and Swift, unpublished).

9.3 Flow simulation

All flows involve motion and for suspensions this requires considerable computing power. While simulation is a mature science in homogeneous fluids, simulation of the flow of suspensions is difficult because of the need to track the boundaries between the liquid and solid phases. Dissipative particle dynamics (DPD) offers the ability to do this without having to continuously update the computational grid as the flow occurs, and is therefore much more economical in computer processing. It has been developed from a method of modelling colloidal suspensions [253, 254] which gives qualitative agreement with experimental data to one which has produced very realistic flows of complex materials like fresh concrete [255]. DPD is examined in detail by Martys [256], who notes that the interactions between particles are described by three types of forces. The conservative force is a central force derived from an attraction-repulsion potential. The dissipative force is proportional to the difference in velocity between particles and acts to slow down their relative motion, producing a viscous effect. The random force helps reproduce the temperature of the system while also producing a viscous effect. DPD equations can reproduce Navier-Stokes and lattice Boltzmann hydrodynamic equations. Inclusions, such as coarse aggregate particles, are modelled by grouping a subset of the DPD particles in the shape of the particle and then constraining the equations so that they move together. The total forces and the resulting rotation and translation are determined from the interactions with other particles and the rigid body moves realistically in the flow. Flow of a concrete-like suspension between reinforcing bars has been successfully simulated [256]. Clearly, DPD offers a glimpse of the future of fresh concrete flow simulation, and has the potential to link rheology and industrial practice.

10. 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 in many practical situations can be explained by reference to that model. This provides links between rheology and technology, which can be exploited.

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. Despite this, the knowledge and understanding gained allows rheology to be used for quality control and product development.

Areas which need further experimental and computational effort to develop stronger links between science and technology are as follows:

- Viscoelastic behaviour in relation to microstructure and properties;
- Compressive rheology and stability with respect to bleeding and compaction;
- Extensional flow in relevant geometries;
- Prediction of properties from fundamental principles and material characteristics;
- Modelling of flow situations in general and of empirical test methods in particular;

Finally, there will always be a need for quality control testing through rheology and further inter-comparisons between the different instruments are needed to enable a common basis of agreement to be established.

REFERENCES

1. Eley, R R, “Applied rheology in the protective and decorative coatings industry”, Rheology Reviews (2005) 173-240.
2. Tattersall, G H, “The workability of fresh concrete”, Viewpoint Publications, Cement and Concrete Association, Slough, (1976).
3. L’Hermite, R, “The rheology of fresh concrete and vibration”, Publication Technique No 2, CERILH, Paris, (1948).
4. Roller, P S, “Plastic flow of dispersions and a new approach to the study of plasticity”, J. Phys. Chem., 43(4) (1939) 457-489.
5. Roller, P S, “Theory and measurement of plasticity and workability of mortars”, Proc. Amer. Soc. Testing Materials, 42 (1942) 750-761.
6. Mason, P, J. “A compression testing instrument for use with pastes”, Sci. Instruments, 30(1) (1953) 418-421.
7. Auerbach, R, “Vibration-Viscosimetrie”, Koll. Zeitschr., 82(1) (1938) 24-25 (in German).
8. Walz, K, “Ruttebeton”, Wilhelm Ernst, Berlin, (1948) (in German).
9. Tattersall, G H, “Structural breakdown of cement paste at constant rate of shear”, Nature, 175 (4447) (1954) 166.
10. Tattersall, G H, “The rheology of portland cement pastes”, Brit. J. App. Phys., 6 (1955) 165-167.
11. Ish-Shalom, M and Greenberg, S A, “The rheology of fresh Portland cement pastes”, in Proc. 4th Intl. Symp. on the Chemistry of Cement, Monograph 43, National Bureau of Standards, Washington DC, 2 (1960) 731-748.
12. Nessim, A A and Wajda, R L, “The rheology of cement pastes and fresh mortars”, Mag. Concr. Res., 17 (1965) 59-68.
13. Hattori, K and Izumi, K, “A rheological expression of coagulation rate theory, Parts 1-3”, J. Dispersion Sci. Technol., 3 (1982) 129-193.
14. Tattersall, G H and Banfill, P F G “The rheology of fresh concrete”, Pitman, London, (1983).
15. Sujata, K and Jennings, H M, “Formation of a protective layer during the hydration of cement”, J. Amer. Ceram. Soc., 75 (1992) 1669-1673.
16. Flatt, R J and Bowen, P, “Yodel: A yield stress model for suspensions”, J. Amer. Ceram. Soc., 89 (2006) 1244-1256.
17. Kaiser, O, “Das Pumpen von Beton”, Dissertation Technische Hochschule, Stuttgart (1939) (in German).
18. L’Hermite, R, “Recent research on concrete”, Ann. des Trav. Publics de Belgique, 50 (1949) 481-512.

19. Ritchie, A G B, “The vane method of measuring the mobility of fresh concrete”, paper presented to Conference of British Society of Rheology, (1967).

20. Komlos, K, “Penetrator for testing of concrete mix workability”, Stavebnicky Casopis, 14 (1966) 571-572.

21. Uzomaka, O J, “A concrete rheometer and its application for a rheological study of concrete mixes”, Rheol. Acta, 13 (1974) 12-21.

22. Murata, J and Kikukawa, H, “Studies on rheological analysis of fresh concrete”, in “Fresh Concrete: Important Properties and their Measurement”, Proc. of a RILEM seminar, Leeds, 1 (1973) 1.2.1-33.

23. Morinaga, S, “Pumpability of concrete and pumping pressure in pipelines”, in “Fresh Concrete: Important Properties and their Measurement”, Proc. of a RILEM seminar, Leeds, 1 (1973) 7.3.1-39.

24. Purrington, W F and Loring, H C, “The determination of the workability of concrete”, Proc. Amer. Soc. Testing Materials, 28 Part II (1928) 499-504.

25. Purrington, W F and Loring, H C, “Further studies on the workability of concrete”, Proc. Amer. Soc. Testing Materials, 30 Part II (1930) 654-673.

26. Harrison, O J, “An investigation into the relationship between concrete workability and the pressures in the hydraulic systems of truck mixers”, Ready Mixed Concrete (UK) Ltd., Feltham, Middlesex, Technical Report No 27 (1964).

27. Tattersall, G H, “The rationale of a two-point workability test”, Mag. Concr. Res., 25 (1973) 169-172.

28. Tattersall, G H, “Workability and quality control of concrete”, Spon, London, (1991).

29. Skårendahl, A and Petersson, O (Editors) “First international RILEM symposium on self-compacting concrete”, Spon, London, (1999).

30. Domone, P L J, Xu Yongmo and Banfill, P F G, “Developments of the two-point workability test for high-performance concrete”, Mag. Concr. Res., 51 (1999) 171-180.

31. Wallevik, O H, “The rheology of fresh concrete and its application on concrete with and without silica fume”. Dr.ing. Thesis NTH Trondheim, Norway (1990).

32. Hu, C and De Larrard. F R, “The rheology of fresh high-performance concrete”, Cem. Concr. Res., 26 (1996) 283-294.

33. Ferraris, C F and Brower, L E, (Editors) “Comparison of concrete rheometers: International tests at LCPC (Nantes, France) in October 2000”, NIST, Gaithersburg, NISTIR 6819 (2001).

34. Ferraris, C F and Brower, L E, (Editors) “Comparison of concrete rheometers: International tests at MB (Cleveland OH, USA) in May 2003”, NIST, Gaithersburg, NISTIR 7154 (2004).

35. Banfill, P F G, “Feasibility study of a coaxial cylinders viscometer for mortar”, Cem. Concr. Res., 17 (1987) 329-33.

36. Banfill, P F G, “The rheology of fresh mortar”, Mag. Concr. Res., 43 (1991) 13-21.

37. Banfill, P F G, “Rheological methods for assessing the flow properties of mortar and related materials”, Construction and Building Materials, 8 (1994) 43-50.

38. http://www.schleibinger.com (accessed 28/2/06).

39. Bye, G C, “Portland cement - composition, production and properties”, Thomas Telford, London (1999).

40. Hewlett, P C, (Editor), “Lea’s chemistry of cement and concrete”, Arnold, London, (1999).

41. Trettin, R, “Reactivity and mechanism of hydration of cement phases”, in Proc. 10th Intl. Congr. on Chemistry of Cement, 1997, Gothenburg, vol 2 paper no 2ii050, 8 pp.

42. Hunter, R J, “Foundations of colloid science”, vols 1 and 2, University Press, Oxford, (1987).

43. Ramachandran, V S, (Editor), “Concrete admixtures handbook”, Noyes publications, New Jersey, USA, (1996).

44. Edmeades, R M and Hewlett, P C, in “Lea’s chemistry of cement and concrete”, (Editor: Hewlett, P C), Arnold, London, (1998) 837-896.

45. Barnes, H A and Walters, K, “The yield stress myth?”, Rheol. Acta, 24 (1985) 323-326.

46. Banfill, P F G and Kitching, D R, “Use of a controlled stress rheometer to study the yield value of oilwell cement slurries”, in “The rheology of fresh cement and concrete”, (Editor: Banfill, P F G), Spon, London, (1991), 125-136.

47. Bombled, J P, “A rheograph for studying the rheology of stiff pastes: application to cement setting”, Révue des Matériaux de Construction, 673 (1970) 256-277.

48. Min, B H, Erwin, L and Jennings, H M, “Rheological behaviour of fresh cement paste as measured by squeeze flow”, J. Mat. Sci. 29 (1994) 1374-1381.

49. Barnes, H A and Carnali, J O, “The vane-in-cup as a novel rheometer geometry for shear-thinning and thixotropic materials”, J. Rheol., 34 (1991) 841-866.

50. Raffle, J F and King, A, “The effect of cellulose ethers and lignosulphonates on the settling and flow properties of cement suspensions”, J. Phys. D: App. Phys., 10 (1977) 33-41.

51. Mannheimer, R J, “Laminar and turbulent flow of cement slurries in large diameter pipe – a comparison with laboratory viscometers”, in “Rheology of Fresh Cement and Concrete”, (Editor: Banfill, P F G), Spon, (1991) 147-158.

52. Roshavelov, T T, “New viscometer for measuring flow properties of fluid concrete”, ACI Materials Journal, 102 (2005) 397-404.

53. Håkansson, U “Rheology of fresh cement-based grouts”. Ph. D. Thesis, Royal Institute of Technology, Stockholm (1993).

54. Gregory, T, “The measurement of early strength development in polymer modified cement pastes”, in Proc. 5th Int. Congr. on polymers in concrete, Brighton, (1987) 205-208.

55. Casson, R B J, Domone, P L J, Scrivener, K, Jennings, H M, Gillham, C J and Pratt, P L, “The measurement of early strength development in polymer modified cement pastes”, in “Concrete rheology”, Materials Research Society Symposium M, (Editor: Skalny, J P), (1982) 66-75.

56. Arnaud, L, “Rheological characterization of heterogeneous materials with evolving properties”, J. Materials in Civil Engineering, May/June (2003), 255-265.

57. Domone, P L J and Jefferis, S A, “Structural grouts”, Blackie, London (1994).

58. O’Keefe, S J, “Rheological properties of polymer modified cement pastes”. Ph. D. Thesis Bristol Polytechnic (1991).

59. Banfill, P F G, Carter, R E and Weaver P, “Simultaneous rheological and kinetic measurements on cement pastes”, Cem. Concr. Res., 21 (1991) 1148-1151.

60. Schultz, M A and Struble, L J, “The use of oscillatory shear to study flow behaviour of fresh cement paste”, Cem. Concr. Res., 23 (1993) 273-282.

61. Winnefeld, F and Holzer, L, “Monitoring early cement hydration by rheological measurements”, in Proc. 11th Intl. Congr. on the Chemistry of Cement, Durban, South Africa, (2003) 330-339.

62. Vlachou, P-V and Piau, J-M, “The influence of the shear field on the microstructural and chemical evolution of an oil well cement slurry and its rheometric effect”, Cem. Concr. Res. 27 (1997) 869-881.

63. Struble, L J and Lei, W-G, “Rheological changes associated with setting of cement paste”, Advanced Cement Based Materials, 2 (1995) 224-230.

64. Struble, L J and Schultz, M A, “Using creep and recovery to study flow behaviour of fresh cement paste”, Cem. Concr. Res. 23 (1993) 1369-1379.

65. Banfill, P F G, “A coaxial cylinders viscometer for mortar: design and experimental validation”, in “Rheology of Fresh Cement and Concrete”, (Editor: Banfill, P F G), Spon, (1991) 217-226.

66. Metzner, A B and Otto, R E, “Agitation of non-Newtonian fluids”, J. Amer. Inst. Chem. Engineers, 3 (1957) 3-10.

67. Celsum Technologies, http://www.celsum.com (accessed 28/2/06).

68. Beaupré, D, “Rheology of high performance shotcrete”. Ph. D. Thesis, University of British Columbia, (1994).

69. Coussot, P, “Rhéologie des boues et laves torrentielles - étude de dispersions et suspensions concentrées”. Ph. D. Thesis Institut National Polytechnique de Grenoble, (1993) (in French).

70. Roshavelov, T T, “Prediction of fresh concrete flow behaviour based on analytical model for mixture proportioning”, Cem. Concr. Res., 35 (2005) 831-835.

71. Flatt, R J, Larosa, D and Roussel, N, “Linking yield stress measurements: Spread test versus Viskomat”, Cem. Concr. Res., 36 (2005) 99-109.

72. Jin, J, “Properties of mortar for self-compacting concrete”. Ph. D. Thesis, University of London, (2002).

73. http://www.contec.is (accessed 28/2/06).

74. Wallevik, J E, “Rheology of particle suspensions”. Dr.ing-avhandling Thesis NTNU Trondheim, Norway: (2003).

75. Läuger, J, Müller, M and Tyrach, J, “A new ball measuring system for large particle suspensions”, Applied Rheology July/August (1999) 145-147.

76. Paar Physica, application note 99074, (2000).

77. Haimoni, A and Hannant, D J, “Developments in the shear vane test to measure the gel strength of oil well cement slurry”, Adv. Cem. Res., 1 (1988) 221-229.

78. Keating, J and Hannant, D J, “The effect of rotation rate on gel strength and dynamic yield strength of thixotropic oil well cements measured using a shear vane”, J. Rheol. 33 (1989) 1011-1020.

79. Mannheimer, R J, “Effect of slip on flow properties of cement slurries can flaw resistance calculations”, Oil and Gas Journal, December 5, (1983), 144-147.

80. Gleissle, W and Windhab, E, “The ‘twin capillary’, a simple device to separate shear and slip flow of fluids”, Experiments in Fluids, 3 (1985) 177-180.

81. Saak, A W, Jennings, H M and Shah, S P, “The influence of wall slip on yield stress and viscoelastic measurements of cement paste”, Cem. Concr. Res., 31 (2001) 205-212.

82. Jarny, S, Roussel, N, Rodts, S, Bertrand, F, Le Roy, R and Coussot, P, “Rheological behavior of cement pastes from MRI velocimetry”, Cem. Concr. Res., 35 (2005) 1873-1881.

83. Allan, M L, “Rheology of latex-modified grouts”, Cem. Concr. Res., 27 (1997) 1875-1884.

84. Odler, I and Liang, N, “Properties and development of the microstructure in cement pastes modified by a styrene-butadiene co-polymer”, Adv. Cem. Res. 15 (2003) 1-8.

85. API Specification, Materials and testing for well cements, American Petroleum Institute, Houston, Specification 10 (1990).

86. Bhatty, J I and Banfill, P F G, “Sedimentation behaviour of cement pastes subject to continuous shear in rotational viscometers”, Cem. Concr. Res., 12 (1982) 69-78.

87. Gill, S M and Banfill, P F G, “The viscometric examination of cement pastes with interrupted helical impellers”, Adv. Cem. Res., 1 (1987) 92-98.

88. Meeten, G H, “Rheometer”, British Patent Application UK 9026294.0, (1990).

89. Vlachou, V and Piau, J-M, “A new tool for the rheometric study of oil well cement slurries and other settling suspensions”, Cem. Concr. Res., 30 (2000) 1551-1557.

90. Nachbaur, L, Mutin, J C, Nonat, A and Choplin L, “Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting”, Cem. Concr. Res., 31 (2001) 183-192.

91. Banfill, P F G, confidential referee’s report on a manuscript recently submitted to a journal.

92. Wesche, K, Flatten, H and Vom Berg, W, “On the influence of separations on the rheological investigations of cement paste and mortar in the rotational rheometer”, in “Fresh Concrete: Important Properties and their Measurement”, Proc. of a RILEM Seminar, Leeds, (1973) 2.10-1 to 2.10-11.

93. Tattersall, G H and Dimond, C R, “The use of the coaxial cylinders viscometer to measure the rheological properties of cement pastes”, in “Hydraulic cement pastes: structure and properties”, Cement and Concrete Association, Slough, 15.121, (1976) 118-133.

94. De Kretser, R G, Boger, D V and Scales, P J, “Compressive rheology; an overview”, Rheology Reviews (2003) 125-165.

95. Meeten, G H, “The squeeze flow rheometer: how to make one”, Bull. Brit. Soc. Rheol., 45 (2002) 58-65.

96. Cardoso, F A, Pileggi, R G and John, V M, “Rheological characterisation of mortars using a squeeze-flow test”, in Proc. 6th Brazilian and 1st International

Symposium on Mortar Technology, (Editors: Cincotto, M A and Roman, H R), Florianopolis, (2005) 121-143 (in Portuguese).

97. Alfani, R and Guerrini, G L, "Rheological test methods for the characterisation of extrudable cement-based materials – a review", Materials and Structures 38 (2005) 239-247.

98. Barnes, H A, "A handbook of elementary rheology", Institute of Non-Newtonian Fluid Mechanics, University of Wales, (2000).

99. Gregory, T and O'Keefe, S J, "Rheological measurements on fresh polymer-modified cement pastes", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991) 69-79.

100. Saasen, A, Marken, C, Blomberg, N, Dawson, J and Rogers, M, "Viscoelastic properties of oilfield cement slurries", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991), 170-178.

101. Piau, J-M, "Axisymmetric slump and spreading of cohesive plastic soft materials: a yield stress measurement by consisto-rheometry", J. Rheol., 49 (2005) 1253-1276.

102. Piau, J-M, "Flow of a yield stress fluid in a long domain. Application to flow on an inclined plane", J. Rheol., 40 (1996) 711-723.

103. Tattersall, G H, "Relationships between the British Standard tests for workability and the two point test", Mag. Concr. Res., 28 (1976) 143-147.

104. Scullion, T, "The measurement of the workability of fresh concrete", M.A. Thesis University of Sheffield (1975).

105. Murata, J, "Flow and deformation of fresh concrete", Materials and Structures 17 (1984) 117-129.

106. Showalter, W R and Christensen, G, "Toward a rationalisation of the slump test for fresh concrete: comparisons of calculations and experiments", J. Rheol., 42 (1998) 865-870.

107. Pashias, N, Boger, D V, Summers, J and Glenister, D J, "A fifty-cent rheometer for yield stress measurement", J. Rheol., 40 (1996) 1179-1189.

108. Saak, A W, Jennings, H M and Shah, S P, "A generalized approach for the determination of yield stress by slump and slump flow", Cem. Concr. Res., 34 (2004) 363-371.

109. Roussel, N, "Three-dimensional numerical simulations of slump tests", Trans. Nordic Rheol. Soc., 12 (2004) 55-62.

110. Roussel, N and Coussot, P, "'Fifty cent rheometer' for yield stress measurements: From slump to spreading flow", J. Rheol., 49 (2005) 705-718.

111. Kantro, D L, "Influence of water-reducing admixtures on properties of cement paste – a miniature slump test", Cement Concrete and Aggregates, 2 (1980) 95-102.

112. Roussel, N, Stefani, C and Leroy, R, “From mini-cone test to Abrams cone test: measurement of cement based materials yield stress using slump tests”, Cem. Concr. Res., 35 (2005) 817-822.

113. Barnes, H A, “Viscosity”, Institute of Non-Newtonian Fluid Mechanics, University of Wales, (2002).

114. British Standards Institution, “Grout for prestressing tendons: test methods”, BS-EN 445 (1997).

115. Roussel, N and Leroy, R, “The Marsh cone: a test or a rheological apparatus?”, Cem. Concr. Res., 35 (2005) 823-830.

116. Ozawa, K, Sakata, N and Okamura, H, “Evaluation of self-compactibility of fresh concrete using the funnel test”, Proc. JSCE Concrete Library International, 25 (1995) 61-70.

117. Bartos, P J M, “Workability of flowing concrete: assessment by a free orifice rheometer”, Concrete, 12(10) (1978) 28-30.

118. Billberg, P “Self-compacting concrete for civil engineering structures - the Swedish experience”, CBI Report 2:99, Stockholm (1999).

119. Thrane, L N, Szabo, P, Geiker, M, Glavind, M and Stang, H, “Simulation of the test method “L-box” for self-compacting concrete”, Trans. Nordic Rheol. Soc. 12 (2004) 47-54.

120. Yeoh, A-K, “The effect of cement properties on the workability of concrete”, M.A. Thesis, University of Sheffield (1982).

121. Mork, J H, “Rheology of fresh concrete: Its relationship to the relative content of cement, gypsum and hemihydrate” Ph. D. Thesis NTNU Trondheim, Dr.-ing. thesis (1994).

122. Mørtsell, E “Effect of constituent materials on the rheology of fresh concrete” Ph. D. Thesis NTNU Trondheim, Dr.-ing. Thesis (1996).

123. Wallevik, O H and Gjørv, OE, in “Properties of fresh concrete”, (Editor: Wierig, H J) (1990) 213-224.

124. Geiker, M R, Brandl, M, Thrane, L N and Nielsen, L F, “On the effect of coarse aggregate fraction and shape on the rheological properties of self-compacting concrete”, Cement, Concrete and Aggregates, 24 (2002) 3-6.

125. Bloomer, S J, “Further development of the two-point test for the measurement of the workability of concrete”. Ph. D. Thesis University of Sheffield (1979).

126. Cyr, M, Legrand, C and Mouret, M, “Study of the shear thickening effect of superplasticisers on the rheological behaviour of cement pastes containing or not mineral additives”, Cem. Concr. Res., 30 (2000) 1477-1483.

127. Mouret, M and Cyr, M, “Discussion of reference 148”, Cem. Concr. Res., 33 (2003) 1901-1903.

128. De Larrard, F, Ferraris, C F and Sedran, T, "Properties and development of the microstructure in cement pastes modified by a styrene-butadiene co-polymer", Materials and Structures, 31 (1998) 494-498.

129. Herschel, W H and Bulkley, R, "Consistency measurements of rubber benzene solutions", Kolloid-Z. 39 (1926) 291-300 (in German).

130. Jones, T E R and Taylor, S, "A mathematical model for the flow of cement paste", Mag. Concr. Res., 31 (1979) 211-216.

131. Yahia, A and Khayat, K H, "Analytical models for estimating yield stress of high performance pseudoplastic grout", Cem. Concr. Res., 31 (2001), 731-738.

132. Casson, W, "A flow equation for pigment-oil suspensions of the printing ink type", in "Rheology of disperse systems", (Editor: Mill, C C), Pergamon, London, (1959).

133. Quemada, D, "Models for rheological behaviour of concentrated disperse media under shear", in Proc. of XIth Intl. Congr. on Rheology, Acapulco, Mexico (1984) 571-582.

134. Vom Berg, W, "Influence of specific surface and concentration of solids upon the flow behaviour of cement pastes", Mag. Concr. Res., 31 211-216 1979.

135. Nehdi, M and Rahman, M-A, "Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction", Cem. Concr. Res., 34 (2004) 1993-2007.

136. Banfill, P F G and Saunders, D C, "On the viscometric examination of cement pastes", Cem. Concr. Res., 11 (1981) 363-370.

137. Hattori, K and Izumi, K, "A new viscosity equation for non-Newtonian suspensions and its application", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991) 83-92.

138. BS 5168:1975, "Glossary of rheological terms", British Standards Institution, London, (1975).

139. Lachemi, M, Hossain, K M A, Lambros, V, Nkinamubanzi, P-C and Bouzoubaa, N, "Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste", Cem. Concr. Res., 34 (2004) 185-193.

140. Mewis, J, "Thixotropy - General review", J. Non-Newt. Fluid Mech., 6 (1979) 1-20.

141. Cheng, D C H and Evans F, "Phenomenological characterisation of the rheological behaviour of inelastic reversible thixotropic and anti-thixotropic fluids", Brit. J. App. Phys., 16 (1964) 1599-1617.

142. Roussel, N, "Steady and transient flow behaviour of fresh cement pastes", Cem. Concr. Res., 35 (2005) 1656-1664.

143. Dullaert, K and Mewis, J, "Thixotropy: build-up and breakdown curves during flow", J. Rheol., 49 (2005) 1213-1230.

144. Lapasin, R, Longo, V and Rajgelj, S, "Thixotropic behaviour of cement pastes", Cem. Concr. Res, 9 (1979) 309-318.

145. Legrand, C, "Discussion of theme VI", in Proc. of 7th Intl. Congr. on the Chemistry of Cement, Editions Septima, Paris, IV, (1980), 124.

146. Bhatty, J I and Banfill, P F G, "A viscometric method of monitoring the effect of retarding admixtures on setting of cement pastes", Cem. Concr. Res., 14 (1984) 64-72.

147. Ghezal, A F and Khayat, K H, "Pseudoplastic and thixotropic properties of SCC equivalent mortar made with various admixtures", in "Self compacting concrete", Proceedings of the 3rd International RILEM Symposium, PRO33, RILEM, Paris, (2003), 69-83.

148. Geiker, M R, Brandl, M, Thrane, L N, Bager, D H and Wallevik, O, "The effect of measuring procedure on the apparent rheological properties of self-compacting concrete", Cem. Concr. Res., 32 (2002) 1791-1795.

149. Banfill, P F G, "A viscometric study of cement pastes including a note on experimental techniques", Mag. Concr. Res., 33 (1981) 37-47.

150. Orban, J, Parcevaux, P and Guillot, D, "Influence of shear history on the rheological properties of oil well cement slurries", in Proc. 8th Intl. Congr. on the Chemistry of Cement, Rio de Janeiro, Brazil, 6 (1986) 243-247.

151. Hibbert, A P, Kellingray, D J and Vidick, B, "Effect of mixing energy levels during batch mixing of cement slurries", SPE Drilling and Completion, 10 March (1995) 49-52.

152. Hodne, H, Saasen, A, O'Hagan, A B and Wick, S O, "Effects of time and shear energy on the rheological behaviour of oilwell cement slurries", Cem. Concr. Res., 30 (2000) 1759-1766.

153. Austin, S A, Goodier, C I and Robins, P J, "Low-volume wet-process sprayed concrete: pumping and spraying", Materials and Structures, 38 (2005) 229-237.

154. Jolin, M, Beaupré, D and Mindess, S, "Tests to characterise properties of fresh dry-mix shotcrete", Cem. Concr. Res., 29 (1999) 753-760.

155. Chopin, D, "Malaxage des bétons à haute performances et des bétons auto-plaçants – optimisation du temps de fabrication". Ph. D. Thesis Ecole Nationale des Ponts et Chaussées (2003) (in French).

156. Struble, L J and Sun, G-K, "Viscosity of portland cement paste as a function of concentration", Advanced Cement Based Materials, 2 (1995) 62-69.

157. Kellingray, D S, Greaves, C and Dallimer, R P, "High temperature and high pressure rheology of oilwell cement slurries", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991) 159-169.

158. Domone, P L J and Thurairatnam, H, "The effect of water/cement ratio, plasticisers and temperature on the rheology of cement grouts", Adv. Cem. Res., 1 (1988) 195-206.

159. Petit, J-Y, Wirquin, E and Duthoit, B, "Influence of temperature on yield value of highly flowable micromortars made with sulfonate based superplasticisers", Cem. Concr. Res., 35 (2005) 256-266.

160. Grzeszczyk, S and Kucharska, L, "The influence of chemical composition of cement on the rheological properties", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991) 27-36.

161. Greenberg, S A and Meyer, L M, "Rheology of fresh portland cement pastes - influence of calcium sulphates", Highway Research Record, 3 (1963) 9-29.

162. Bombled, J P, "Influence of sulphates on the rheological behaviour of cement pastes and their evolution", in Proc. of 7th Intl. Congr. on the Chemistry of Cements, vol 3, Editions Septima, Paris, VI (1980) 164-169.

163. Grzeszczyk, S, "Rheological properties of belite cement pastes", Adv. Cem. Res., 6 (1994) 155-159.

164. Banfill, P F G and Gill, S M, "The rheology of aluminous cement pastes", in Proc. of 8th Intl. Congr. on Chemistry of Cement, Rio de Janeiro, Brazil, IV, (1986), 223-227.

165. Banfill, P F G and Gill, S M, "Superplasticisers for Ciment Fondu: Part 1 Effects on rheological properties of fresh paste and mortar", Adv. Cem. Res., 5 (1993) 131-138.

166. Chappuis, J, "Rheology of aluminous cement pastes", in Proc. 10th Intl. Congr. on Rheology (Editor: Uhlherr, P T), Sydney, 1 (1988) 247-249.

167. Haimoni, A M, "Rheology of a specific oilwell cement". Ph. D. Thesis University of Surrey (1987).

168. Banfill, P F G and Rudzinski, L R, "The rheological behaviour of non-shrinking cement pastes", Adv. Cem. Res., 1 (1987) 45-51.

169. Frantzis, P and Baggott, R, "Effect of vibration on the rheological characteristics of magnesia phosphate and ordinary portland cement slurries", Cem. Concr. Res. 26 (1996) 387-395.

170. Frantzis, P and Baggott, R, "Rheological characteristics of retarded magnesia phosphate cement", Cem. Concr. Res. 27 (1997) 1155-1166.

171. Ivanov, Y and Zacharieva, S, "Influence of fly ash on the rheology of cement pastes", in Proc. 7th Intl. Congr. on the Chemistry of Cement, Paris, Editions Septima, III, VI (1980) 103-107.

172. Sybertz, F and Reick P, "Effect of fly as on the rheological properties of cement paste", in "Rheology of Fresh Cement and Concrete", (Editor: Banfill, P F G), Spon, (1991) 13-22.

173. Banfill, P F G, “An experimental study of the effect of pfa on the rheology of fresh concrete and cement paste”, in Proc. of Intl. Symp. on the use of PFA in concrete, Leeds (Editors: Cabrera J G and Cusens, A R), (1982) 161-171.

174. Rudzinski, L R, “The effect of fly ashes on the rheological behaviour of cement pastes”, Matériaux et Constructions, 17 (1984) 369-373.

175. Ferraris, C F, Obla, K H and Hill, R, “The influence of mineral admixtures on the rheology of cement paste and concrete”, Cem. Concr. Res., 31 (2001) 245-255.

176. Xiong Zhang and Jihong Han, “The effect of ultra-fine admixture on the rheological property of cement paste”, Cem. Concr. Res. 30 (2000) 827-830.

177. Park, C K, Noh, M H and Park, T H, “Rheological properties of cementitious materials containing mineral admixtures”, Cem. Concr. Res., 35 (2005) 842-849.

178. Kucharska, L and Moczko, M, “Influence of silica fume on the rheological properties of the matrices of high-performance concretes”, Adv. Cem. Res., 6 (1994) 139-145.

179. Justnes, H and Vikan, H, “Effect of silica fume on rheology of cementitious paste”, SINTEF, Trondheim, Norway, Report STF22 A04600 (2004).

180. Wu Xuequan and Roy, D M, “Slag cement utilisation: Rheological properties and related characterisation”, Cem. Concr. Res., 14 (1984) 521-528.

181. Atzeni, C, Massidda, L and Sanna, U, “Relationship between rheology and workability of cement mixes containing blastfurnace slag”, Silicates Industriels, 51 (1986) 5-9.

182. Palomo, A, Banfill, P F G, Fernandez-Jiminez A and Swift, D.S., “Properties of alkali-activated fly ashes determined from rheological measurements”, Adv. Cem. Res., 17(4) (2005) 143-151.

183. Aïtcin, P-C, Jolicoeur, C and MacGregor, J G, “Superplasticisers: How they work and why they occasionally don’t”, Concrete International, 16 (5) (1994) 45-52.

184. Björnström, J and Chandra, S, “Effect of superplasticisers on the rheological properties of cements”, 36 (2003) 685-692.

185. Paillère, A M and Briquet, Ph, “Influence of fluidifying synthetic resins on the rheology and deformation of cement pastes before and during setting”, in Proc. 7th Intl. Congr. on Chemistry of Cements, Paris, Editions Septima, 3 VI (1980) 186-191.

186. Flatt, R J and Houst, Y F, “A simplified view on chemical effects perturbing the action of superplasticisers”, Cem. Concr. Res., 31 (2001) 1169-1176.

187. Lewis, J A, Matsuyama, H, Kirby, G, Morissette, S and Young, J F, “Polyelectrolyte effects on the rheological properties of concentrated cement suspensions”, J. Amer. Ceram. Soc., 83 (2000) 1905-1913.

188. Kauppi, A, Banfill, P F G, Bowen, P, Petersen, B G, Houst, Y F, Lafuma, F, Maeder, U, Reknes, K, Schober, I and Swift, D S, “Improved superplasticisers for high performance concrete”, in Proc. 11th Intl. Congr. on the Chemistry of Cement, Durban, South Africa, 2 (2003) 528-536.

189. Sugiyama, T, Ohta, A, Uomoto, T, “The dispersing mechanism and applications of polycarboxylate-based superplasticisers”, in Proc. 11th Intl. Congr. on the Chemistry of Cement, Durban, South Africa, (2003) 560-568.

190. Papo, A and Piani, L, “Effect of various superplasticisers on the rheological properties of Portland cement pastes”, Cem. Concr. Res. 34 (2004) 2097-2101.

191. Toutou, Z and Roussel, N, “Multi scale experimental study of concrete rheology: from water scale to gravel scale”, Materials and Structures (2006) in press.

192. Tattersall, G H, “Applications of rheological measurements to practical control of concrete”, in “Rheology of Fresh Cement and Concrete”, (Editor: Banfill, P F G), Spon, 1991, 270-280

193. Banfill, P F G, “Influence of fine materials in sand on the rheology of fresh mortar”, in “Utilising ready mix concrete and mortar”, (Editors: Dhir, R K and Limbachiya, M C) Thomas Telford, London, (1999) 412-420.

194. Banfill, P F G, “Applications of rheology in mortar production”, Proc. British Masonry Society, 7 (1995) 7-12.

195. Ponikiewski, T and Szwabowski, J, “Effects of fibres on the rheological and mechanical properties of reinforced mortar”, in Proc. 6th Brazilian and 1st International Symposium on Mortar Technology, (Editors: Cincotto, M A and Roman, H R), Florianopolis, Brazil, (2005) 331-340.

196. Ancey, C and Jorrot, H, “Yield stress for particle suspensions within a clay dispersion”, J. Rheol., 45 (2001) 297-319.

197. Chopin, D, De Larrard, F and Cazacliu, B, “Why do HPC and SCC require a longer mixing time?”, Cem. Concr. Res. 34 (2004) 2237-2243.

198. Meeten, G H, “Constant-force squeeze flow of soft solids”, Rheol. Acta, 41 (2002) 557-566.

199. Zhou, X and Li, Z, “Characterisation of rheology of fresh fiber reinforced cementitious composites through ram extrusion”, Materials and Structures 38 (2005) 17-24.

200. Struble, L J, Sun, G-K and Lei, W-G, “Changes in oscillatory shear behavior of portland cement paste during early hydration”, Concrete Science and Engineering, 2 (2000) 141-149.

201. Weber, R, “The transport of concrete by pipeline”, translated by C. van Amerongen, Cement and Concrete Association Translation 129, Slough, (1968).

202. Kaplan, D, De Larrard, F and Sedran, T, “Avoiding blockages in concrete pumping process”, ACI Materials Journal, 102 (2005) 183-191.

203. Kaplan, D, “Pompage des bétons”. Ph. D. Thesis Ecole Nationale des Ponts et Chaussées, Paris (2001) (in French).

204. Kaplan, D, De Larrard, F and Sedran, T, “Design of concrete pumping circuit”, ACI Materials Journal, 102 (2005) 110-117.

205. Austin, S A, Robins, P J and Goodier, C I, “The rheological performance of wet-process sprayed mortars”, Mag. Concr. Res., 51 (1999) 341-352.

206. Jolin, M, Beaupré, D and Mindess, S, “Rheology of dry mix shotcrete”, Concrete Science and Engineering, 3 (2001) 195-201.

207. Govier, G W and Aziz, K, “The flow of complex mixtures in pipes”, Van Nostrand Reinhold, New York (1972).

208. Van Wazer, J R, Lyons, J W, Kim, K Y and Colwell, R E, “Viscosity and flow measurement: a laboratory handbook of rheology”, Interscience, New York (1963).

209. Bird, R B, Stewart, W E and Lightfoot, E N, “Transport phenomena”, Wiley, New York (1960).

210. Hedstrom, B O A, “Flow of plastic materials in pipes”, Ind. Eng. Chem., 44 (1952) 651-656.

211. Metzner, A B and Reed, R C, American Institute of Chemical Engineers Journal, 1 (1955) 434-450.

212. Raffle, J F, in Proc. 2nd Int. Conf. on Hydraulic transport of solids in pipes, Cranfield, UK, paper C2 (1972).

213. Bannister, C E, “Rheological evaluation of cement slurries - methods and models”, J. Society of Petroleum Engineers, 9284 (1980) 1-16.

214. Mooney, M, “Explicit formulas for slip and fluidity”, J. Rheol., 2 (1931) 210-220.

215. Swaddiwudhipong, S, Zhang, J and Lee, S L, “Prepacked grouting process in concrete construction”, J. Materials in Civil Engineering, Nov/Dec (2003), 567-576.

216. Zhang, J, Swaddiwudhipong, S and Lee, S L, “Parametric study on cement grout and aggregate media for preplaced aggregate grouting”, J. Testing and Evaluation, 32 (2004), 120-130.

217. Benbow, J J and Bridgwater, J, “Paste flow and extrusion”, Clarendon Press, Oxford, (1993).

218. Srinavasan, R, Deford, D and Shah, S P, “The use of extrusion rheometry in the development of extruded fiber-reinforced cement composites”, Concrete Science and Engineering, 1 (1999) 26-36.

219. Gardner, N J, “Pressure of concrete on formwork, a review”, J. Amer. Concr. Inst., 82 (1985) 744-753.

220. Janssen, H A, “Versuche űber getreidedruck in silozellen”, VDI Z., 39 (1885) 1045-1049 (in German).

221. Djelal, C, “Designing and perfecting a tribometer for the study of friction of a concentrated clay-water mixture against a metallic surface”, Materials and Structures, 34 (2000) 51-58.

222. Vanhove, Y, “Contribution à l’étude du frottement du béton autoplacant contre une surface metallique - application aux poussées contre les coffrages”. Ph.D. Thesis Université d’Artois, Béthune, (2002) (in French).

223. Vanhove, Y, Djelal, C and Magnin, A “Influence of fresh concrete granular phase on the friction stress at the interface concrete/metallic wall”, in Proc. 13th Intl. Congr. on Rheology, Cambridge, 2 (2000) 418-420.

224. Vanhove, Y and Djelal, C, “Formwork pressures with self-compacting concrete”, Concr. Mag., (2002) 22-23.

225. Vié, D, Djelal, C, Vanhove, Y and Magnin, A, “The pressure of self-compacting concrete”, Ann. Batim. Trav. Publics, 6 (2001) 5-13.

226. Billberg, P, “Form pressure generated by self-compacting concrete”, in “Self compacting concrete”, Proceedings of the 3rd International RILEM Symposium, PRO33, RILEM, Paris, (2003), 271-280.

227. Brameshuber, W and Uebachs, S, “Investigations on the formwork pressure using self-compacting concrete”, in “Self compacting concrete”, Proceedings of the 3rd International RILEM Symposium, PRO33, RILEM, Paris, (2003), 281-287.

228. Leemann, A and Hoffmann, C, “Pressure of self-compacting concrete on the formwork”, in “Self compacting concrete”, Proceedings of the 3rd International RILEM Symposium, PRO33, RILEM, Paris, (2003), 288-295.

229. Djelal, C, Vanhove, Y and Magnin, A, “Tribological behaviour of self compacting concrete”, Cem. Concr. Res., 34 (2004) 821-828.

230. Assaad, J, Khayat, K H and Mesbah, H, “Variation of formwork pressure with thixotropy of self-consolidating concrete”, ACI Materials Journal, 100 (2003) 29-37.

231. Assaad, J and Khayat, K H, “Kinetics of formwork pressure drop of self-consolidating concrete containing various types and contents of binder”, Cem. Concr. Res., 35 (2005) 1522-1530.

232. Assaad, J and Khayat, K H, “Formwork pressure of self-consolidating concrete made with various binder types and contents”, ACI Materials Journal, 102 (2005) 215-223.

233. ACI Committee 309 “Guide for consolidation of concrete”, American Concrete Institute, Detroit, ACI 309R-05, (2005).

234. Tattersall, G H and Baker, P H, “The effect of vibration on the rheological properties of fresh concrete”, Mag. Concr. Res., 40 (1988) 79-89.

235. Tattersall, G H and Baker, P H, “An investigation into the effect of vibration on the workability of fresh concrete using a vertical pipe apparatus”, Mag. Concr. Res., 41 (1989) 3-9.

236. Banfill, P F G, Xu Yongmo and Domone, P L J, “Relationship between the rheology of unvibrated fresh concrete and its flow under vibration in a vertical pipe apparatus”, Mag. Concr. Res., 51 (1999) 181-190.

237. Teixeira, M A O M, Craik, R J M and Banfill, P F G, “Vibrational processing of fresh concrete: predicting fluidification from rheological behaviour”, in Proc. 13th Intl. Congr. on Rheology, 4 (2000)133-135.

238. ACI Committee 309, “Behaviour of fresh concrete during vibration”, American Concrete Institute, Detroit, (1993).

239. The Concrete Society, “Self compacting concrete - a review”, Technical Report 62, Crowthorne, (2005).

240. Naniwa, R, “Application du mortier en monocouche épaisse à la construction et à la reparation”, in Proceedings of the 9th CIB Congress, Stockholm, 2 (1983) 565-577 (in French).

241. De Larrard, F “Concrete mixture proportioning: a scientific approach”, Spon, London, (1999).

242. Wallevik, O H, in “Self compacting concrete”, Proceedings of the 3rd International RILEM Symposium, PRO33, RILEM, Paris, (2003), 23-31.

243. Nielssen, I, “Rheological mix design of self-compacting concrete”. M. Phil. Thesis, Heriot-Watt University, (2004).

244. Buscall, R, McGowan, I J, Mills, P D A, Stewart, R F, Sutton, D, White, L R and Yates, G E, “The rheology of strongly flocculated suspensions”, J. Non-Newtonian Fluid Mech., 24 (1987) 183-202.

245. Kapur, P C, Scales, P J, Boger, D V and Healy, T W, “Yield stress of suspensions loaded with size distributed particles”, Amer. Inst. Chemical Engineers J., 43 (1997) 1171-1179.

246. Scales, P J, Johnson, S B, Healy, T W and Kapur, P C, “Shear yield stress of partially flocculated colloidal suspensions”, Amer. Inst. Chemical Engineers J., 44 (1998) 538-544.

247. Zhou, Z, Solomon, M J, Scales, P J and Boger, D V, “The yield stress of concentrated flocculated suspensions of size distributed particles”, J. Rheol., 43 (1999) 651-671

248. Flatt, R J, “Dispersion forces in cement suspensions”, Cem. Concr. Res., 34 (2004) 399-404.

249. Einstein, A, “Eine neue Bestimmung der Molekuldimension”, Ann. Physik. 19 (1906) 289-306 (in German).

250. Barnes, H A, Hutton, J F and Walters, K, “An introduction to rheology”, Elsevier, Amsterdam (1989).

251. Krieger, I M and Dougherty, T J, “A mechanism for non-Newtonian flow in suspensions of rigid spheres”, Trans. Soc. Rheol., 20 (1959) 137-152.

252. Ferraris, C R and Martys, N, “Relating fresh concrete viscosity measurements from different rheometers”, J. Res. Natl. Inst. Stand. Technol., 108 (2003) 229-234.

253. Hoogerbrugge, P J and Koelman, J M V A, “Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics”, Europhys. Lett., 30 (1992) 155-160.

254. Koelman, J M V A and Hoogerbrugge, P J, “Dynamic simulations of hard sphere suspensions under steady shear”, Europhys. Lett., 31 (1993) 363-368.

255. Flatt, R J, Martys, N and Bergstrom, L, “The rheology of cementitious materials”, MRS Bull., May (2004) 314-318.

256. Martys, N S, “Study of a dissipative particle dynamics based approach for modelling suspensions”, J. Rheol., 49 (2005) 401-424.

257. Lobanov, V P, “The visco-plastic properties of building mortars”, Kolloidnii Zhurnal, 12(5) (1950) 352-358 (Library Communication no 579, Garston, Building Research Station).

258. Pierzchala, H, “Rheologische Eigenschaften an Portlandzementpasten”, Tonindustrie Zeitschrift und Keramische Rundschau, 94(8) (1970) 331-336 (in German).

259. Bombled, J P, “Influence of sulphates on the rheological behaviour of cement pastes and their evolution”, in Proc. of 7th Intl. Congr. on the Chemistry of Cement, Editions Septima, Paris, III, VI (1980) 164-169.

260. Ivanov, Y and Stanoeva, E, “Influence of cement composition and other factors on the rheological behaviour of cement pastes”, Silicates Industriels, 44 (1979) 199-203.

261. Roy, D M and Asaga, K, “Rheological properties of cement mixes: IV Effects of superplasticisers on viscosity and yield stress”, Cem. Concr. Res., 10 (1980) 287-295.

262. Roy, D M and Asaga, K, “Rheological properties of cement mixes: V The effects of time on viscometric properties of mixes containing superplasticisers; conclusions”, Cem. Concr. Res., 10 (1980) 337-344.

263. Dimond, C R, Unpublished internal report, University of Sheffield, (1980).