Rheology of Fresh Cement Paste

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ABSTRACT

Fresh cement paste exhibits a yield stress and structural breakdown as well as some viscoelastic behaviour. Experimental problems can arise from slippage and sedimentation during testing and the structural breakdown makes the material shear history dependent.

INTRODUCTION

The rheology of fresh (i.e. before setting) cement paste is widely studied for both fundamental and practical technological reasons. The chemical reactions between cement and water show a dormant period before setting which makes it possible to handle, pump, mould and compact cement-based materials which then harden in place. Cement paste is used industrially in its own right e.g. for grouting and oilwell cementing. It is a constituent of concrete and may therefore provide information on that material. Effects of admixtures and other variables on concrete may be predicted from smaller scale tests of their effects on cement paste. Its study may give information on the structure of cement-water systems to complement that provided by other methods - for instance rheological and chemical methods may be used in parallel. Finally, unlike fresh concrete, cement paste is fine grained and amenable to study in commercially available rotational viscometers using well established measuring geometries.

This paper is a brief review of the main features of the rheology of cement paste.

RHEOLOGICAL MEASUREMENTS

Cement based materials exhibit both liquid and solid-like behaviour. For flow and remoulding the liquid-like behaviour may be considered to be more important and may be measured in a variety of viscometers, both rotating and tubular. That they also have solid-like behaviour is evident from the observation that they will stand unsupported in a pile without flowing under their own weight. This is evidence for a yield stress which arises from the interparticle forces. Tattersall and Banfill discuss viscometers for cement paste.[1] An indication of solid-like properties can also be obtained from penetrometers [2], vanes [3], and the pulse shearometer [4], where the shear modulus can be determined from the velocity of propagation of a shear wave. Finally, oscillatory rotational and translational shear, enabling the elastic and viscous components of the material's response to be separated, and stress relaxation methods have all been used to a limited extent [5-8].

GENERAL FEATURES OF THE RHEOLOGY

Flow curves

Shear stress-shear rate flow curves have been fitted to several different models[9] the common feature of which is an intercept on the stress axis, indicating a yield stress. This yield stress can be confirmed in a controlled stress rheometer[10]. In a systematic investigation using a coaxial cylinders viscometer, Banfill and Saunders[11] showed that the shape of the hysteresis loop depends on the time to complete the up and down test cycle. As cycle time increased the shape progressed from those showing structural breakdown through double loops to those showing structural buildup. They ascribed the changes to the competition between shear-induced breakdown and hydration-induced buildup but Hattori and Izumi[12] explained the effect in terms of the competition between coagulation and deflocculation processes.

Mixing and handling

Structure in a cement paste can be broken down by mixing before testing as well as by shear in the test, in both cases reducing the measured yield stress and plastic viscosity. The amount of work done during mixing can be quantified from the shear stress and shear rate and relationships with rheology have been published[10,13].

Structural breakdown

Cement paste gets thinner as it is sheared and its structure breaks down, but the hysteresis loops cannot be analysed to probe the nature of the structure through kinetic studies. At constant shear rate the shear stress decays exponentially with time[14] to an equilibrium value which may be about 10% of the initial value, the excess shear stress being used to break the structure down. The inverse effect occurs at constant shear stress[10]. After breakdown the paste stiffens with time but possesses a yield stress throughout. Thus the structure involves at least two types of interaction, one which is irreversibly destroyed by shearing and one which is both immediately and reversibly reformed when shearing stops.

Viscoelastic behaviour

Oscillatory shear is advantageous for cement paste because the amplitude is small enough not to cause structural breakdown. In the early stages of hydration the loss modulus is higher than the storage modulus but the latter increases faster with time as solid-like behaviour dominates. In cement-polymer latex blends the behaviour becomes progressively more elastic as the proportion of polymer increases[7].

Effect of paste composition

Much experimental data have been published on the effects of paste composition on rheological parameters, including

- water/cement ratio
- age, temperature and cement fineness
- cement type - portland, oilwell, white, aluminous
- cement composition and hydration
- effects of admixtures and polymer latexes
- effects of other cementitious materials - flyash, slag, limestone, microsilica.

EXPERIMENTAL PROBLEMS

Banfill[9] reviewed the main experimental problems facing investigators of cement paste rheology as follows.

Reproducibility

Discrepancies between the numerical results obtained by different workers can be accounted for by a failure to appreciate the importance of standardising such details as mixing technique and shear rates during testing. Structural breakdown during mixing and testing may reduce the measured values by up to 75% and as some authors give no useful information about procedures, it is impossible to draw meaningful comparisons.

Wall slippage

Mannheimer[15] first demonstrated convincingly that slippage at the smooth walls of the viscometer could result in an underestimate of the rheological parameters to as low as 15% of their true values. However, the slippage layer, caused by the separation of water, is very thin and difficult to observe directly. Nobody has yet shown that it does not occur with the roughened surfaces which are normally used, although it has been found that the yield stress behaviour is much more clear cut when rough surfaces are used[10].

Sedimentation

At high water contents gravitational and centrifugal separation is possible and this can cause errors. When measurement geometries with angled blades are used the vertical concentration gradient is much smaller and with an interrupted helical impeller water /cement ratios up to 1.0 can be tested[16].

Plug flow

Plug flow occurs when the shear stress does not exceed the yield stress everywhere in the sample and some part of it does not flow. Experimental conditions can be chosen to eliminate it, but Tattersall and Dimond[17] found that the semi-logarithmic plot obtained in experiments on structural breakdown at constant shear rate often consisted of two straight intersecting lines. It was only when they filmed the flow of paste in a dummy coaxial cylinders viscometer that they discovered the hitherto unknown existence of a solid plug adjacent to the outer cylinder.

When smooth cylinders were used this plug slid round slowly until it broke up and shearing flow started across the whole gap. The time at which this occurred corresponded to the intersection between the two parts of the semi-logarithmic plot. Using serrated cylinders the plug remained intact until the end of the experiment and there was no discontinuity in the data. No satisfactory explanation for this anomalous plug flow has been offered but its existence casts doubt on all experimental data where full shearing flow has not been confirmed visually.

MICROSTRUCTURAL INTERPRETATION

Any proposed structural model must take into account the instantaneous formation of a skin or membrane of hydrated minerals around cement particles in water[18]. The yield stress can be accounted for by the usual interparticle Van der Waals attraction and electrical double layer repulsion effects, but the irreversibly destroyed structure is much stronger than this. Tattersall and Banfill[1] proposed that when dry cement powder first comes into contact with water the hydrated skin or membrane may form around pairs or groups of particles. When the skin is broken by the action of shear and particles separate, that region of one particle which was in contact with other particles is exposed and hydrates to heal the broken skin. The links cannot then reform in the same way when the structure is at rest because of this healing, i.e. the breakdown of the skin linkage is irreversible. In this model, then, the breakable structure is due to membrane bridges while the yield stress is due to flocculation forces. If other factors remain constant the ratio between the yield stress before the structure has been broken and that of a fully broken paste should be the same as the ratio between the strength of a membrane bridge and that of the flocculated linkage. Even though a membrane bridge is made up of poorly crystalline material, its strength will approach that of a typical chemical bond between atoms (200-500 kJ/mol). However, a flocculated linkage is much weaker, consisting primarily of the van der Waals force of attraction (20-40 kJ/mol). (In this situation 1 mol consists of 6 x 10^{23} individual bonds between atoms). The yield stress of a cement paste would therefore be expected to decrease through one order of magnitude when the structure due to membrane bridges is destroyed. That this is just the amount by which the initial and equilibrium shear stresses differ is strong evidence in support of the model.

Referring to the original proposition[14] that the excess shear stress is used in breaking down the structure it ought to be possible to relate the work done in breaking the structure down to equilibrium to the energy required to rupture all the membrane bridges which existed at the start of shearing. It would be reasonable to suppose that the bond energy in membrane bridges would be constant and that the total energy input as a result of the shear work done would be related to the proportion of the surface area of the cement which participates in forming the bridges. A preliminary consideration of the work done yielded realistic numerical data in support of this notion[19].

CONCLUSION

While further work is needed to establish
(i) the form of the structure in cement pastes,
(ii) the origin of the anomalous plug flow,
(iii) the experimental conditions needed to obviate slippage in viscometers,
for the present it is recommended that the following experimental guidelines be followed:
(i) the paste should be visually examined during the experiment to confirm that complete shearing flow is happening,
(ii) the surfaces of the viscomenter measuring geometry should be roughened,
(iii) if high water/cement ratios are unavoidable, mixer type geometries with angled blades should be used to obviate sedimentation,
(iv) sole reliance should not be placed upon hysteresis loop measurements.

REFERENCES

1. Tattersall, G.H. and Banfill, P.F.G., (1983) "Rheology of fresh concrete", Pitman. London, pp356.
2. Bombled, J.P., (1970) "A rheograph for studying the rheology of stiff pastes: application to cement setting", *Rev. des Mater. de Const.* (673), 256-277.
3. Barnes, H.A. and Carnali, J.O., (1991) "The use of vanes to determine yield stress",

J. Rheology, **34**(6), 841-866.
4. Gregory, T., (1987) "The measurement of early strength development in polymer modified cement pastes", in Proc. 5th Int. Congr. Polymers in Concrete, (Staynes, B.W. ed), Brighton Polytechnic, 205-208.
5. Cusens, A.R. and Harris, J., (1973) "A rheological study of fresh cement pastes", Proc RILEM Seminar on Fresh Concrete, Leeds, **1**, 2.8-1 - 2.8-34.
6. Jones, T.E.R., Brindley, G.I., Patel, B.C., (1976) Hydraulic cement pastes: structure and properties, Cement and Concrete Association, Slough, Publ. 15.121, 135-149.
7. O'Keefe, S.J., (1991) "Rheological properties of polymer modified cement pastes", PhD thesis, Bristol Polytechnic.
8. Banfill, P.F.G., Carter, R.E. and Weaver, P., (1991) "Simultaneous rheological and kinetic measurements on cement pastes", *Cem. Concr. Res.* **21**, 1148-1154.
9. Banfill, P.F.G., (1990) "The rheology of cement paste: progress since 1973", in Properties of Fresh Concrete, (Wierig, H-J. ed), Chapman and Hall, London, 3-9.
10. Banfill, P.F.G. and Kitching, D.R. (1991) "Use of a controlled stress rheometer to study the yield stress of oilwell cement slurries", in Rheology of Fresh Cement and Concrete (Banfill P.F.G. ed), Spon, London, 125-136.
11. Banfill, P.F.G. and Saunders, D.C., (1981) "On the viscometric examination of cement pastes", *Cem.Concr.Res.* **11**, 363-370.
12. Hattori, K. and Izumi, K. (1991) "A new viscosity equation for non-Newtonian suspensions and its application", in Rheology of Fresh Cement and Concrete (Banfill P.F.G. ed), Spon, London, 83-92.
13. Orban, J., Parcevaux, P. and Guillot, D. (1986) "Influence of shear history on the rheological properties of oilwell cement slurries", in Proc. 8th Int. Congr. on Chemistry of Cement, **6**, 243-247.
14. Tattersall, G.H. (1955) "The rheology of portland cement paste", *Brit.J.Appl.Phys.* **6**, 165-167.
15. Mannheimer, R.J. (1983) "Effect of slip on flow properties of cement slurries can flaw resistance calculations", *Oil and Gas J.* Dec 5, 144-147.
16. Bhatty, J.I. and Banfill, P.F.G. (1982) "Sedimentation behaviour of cement pastes subject to continuous shear in rotational viscometers", *Cem.Concr.Res.* **12**, 69-78.
17. Tattersall, G.H. and Dimond, C.R. (1976) Hydraulic cement pastes: structure and properties, Cement and Concrete Association, Slough, Publ. 15.121, 118-133.
18. Taylor, H.F.W. (1990) "Cement chemistry", Academic Press, London, 221.
19. Banfill, P.F.G. (1992) "Structural breakdown and the rheology of cement mortar", in Theoretical and applied rheology: Proc. XIth Int.Congr., (Moldenaers, P. and Keunings, R. ed.), 790-792.