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RHEOLOGICAL CHARACTERISTICS OF RETARDED MAGNESIA PHOSPHATE CEMENT

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ABSTRACT

The rheological characteristics of rapid setting magnesia phosphate-based slurries determined with a rotating viscometer incorporating an interrupted helical impeller are reported. The investigations also included an evaluation of the effect of test specimen dimensions and comparisons with an ordinary Portland cement based reference slurry. The test procedure adopted comprised measuring the stress response to three repetitive speed cycles undertaken over a 15 minutes period immediately after slurry preparation. The results are assessed in the practical context of the use of retarded slurry to infiltrate a steel fiber reinforcing array. An empirical treatment of the data is presented which provides the basis for assessing the influence of viscosity during vibratory infiltration as well as providing some insight into hysteresis phenomena and test procedure. © *1997 Elsevier Science Ltd*

Introduction

The deterioration of highway pavements, roads and motorways, airport runways, bridge decks, marine and other concrete structures presents serious problems requiring substantial expenditure to eradicate. A major factor is the time of repair which can interrupt the use of the structures for a considerable time if traditional materials are used. This delay can be reduced by utilizing non-traditional very rapid strengthening cements (1-6). The very rapid strength development of magnesia phosphate cement accompanied by good bonding to old concrete provides the basis for a material for the rapid repair of concrete structures. The infiltration of magnesia phosphate slurries into aggregate arrays is a proven method of rapid bulk repair (7) and the extension of this approach to infiltration into fiber arrays enables cementitious materials with high toughness to be utilized for repair. Such composites produced from normal cements are already used as structural and repair materials (8).

The inclusion of high volume fractions of steel fiber in a cementitious matrix produces significant increases in the stress and strain to the limit of proportionality, flexural strength, tensile strength and strain to failure, all of which contribute to very large increases in energy absorbing capacity (9-12). It is not possible to fabricate the relatively high fiber volume fraction composites necessary with conventional concrete bulk mixing procedures and slurry infiltration into a fiber array is a convenient practical solution. Effective slurry infiltration is therefore an essential requirement for successful fabrication. In the case of magnesia phosphate slurries it is also necessary to incorporate vibration to assist penetration as well as delaying the setting period using retarders particularly when infiltrating high fiber volume fraction arrays.

In order to optimize infiltration the rheology of the slurry needs to be characterized. A considerable amount of work has been undertaken on the flow properties of normal setting concretes and mortars. Banfill (13-16) and Tattersall (17) have developed techniques for characterization and have identified the key phenomena involved. A significant amount of work has also been undertaken on cement pastes addressing a variety of factors of influence (13-19). In the case of magnesia phosphate cements and mortars, rapid strengthening is accompanied by rapid setting and the rheological parameters are changing too rapidly for conventional measurement. An additional problem with such systems is the highly exothermic setting period which necessitates special techniques to establish the temperature dependence of phenomena.

The approach adopted in the present paper was to employ a helical impeller to allow measurement of the rheological behavior using rotational speed cycling via impeller speed variation. The helix viscometer was used because of the rapid setting nature of the cement system (in order to eliminate the effects of rapid particle packing at the cylinder surfaces of the coaxial cylinders viscometer) and because it eliminates the problems of slippage associated with the coaxial cylinders viscometer (where the shear stresses developed are much higher than in the helix viscometer because of the narrow gap), accepting that, this method does not allow the determination of rheological parameters in fundamental scientific units. Another advantage is that while measurements are taken place all readings of torque, temperature and time can be recorded.

The slurry performance was compared with that of an ordinary Portland cement based slurry of proven infiltrability into densely packed steel fibre arrays. The overall objective was to obtain baseline data from which to build eventually a model of the infiltration process.

Experimental Procedure

Materials. Two types of cement were used: a rapid strengthening magnesia phosphate, ASR-1, supplied by FEB, and an ordinary Portland cement, supplied by Blue Circle Ltd. The ASR-1 contained a proportion of very fine aggregate and required the addition of a retarder to increase the setting time from 4 minutes to up to 15 minutes, sufficient to obtain measurements. Three different retarders were assessed, all at 2% weight of the cement, namely sodium tetraborate, ($Na_2B_4O_7 10H_2O$), boric acid (H_3BO_3) and NaK-tartrate ($C_4H_4O_6NaK$) subsequently referred to as NaK. The water to solids ratio was 0.17 as recommended by the manufacturer. In the case of the OPC system a blend of 60 parts by weight of cement and 40 parts by weight of silica flour (BM500) was used at a liquid-solids ratio of 0.3. The liquid included 11% by volume of superplasticizer (Conplast 430).

Equipment and Experimental Procedure. The viscometer used was the Haake Rotovisco RV2 with MK 500 torque measuring head (19, 20). Two sizes of sample container were used, one of internal diameter 36 mm and 118 mm height giving an annular gap between the extremities of the impeller blades and the internal wall of approximately 5 mm, and the other of internal diameter 82 mm and height 110 mm providing a 28 mm annular gap. The normal rotating internal cylinder was replaced by an interrupted helical impeller for the small sample container (as shown in Fig. 1) and the same impeller connected to the rheometer via an extended arm for the large sample container. A Comark 2007 digital thermometer was used to monitor temperature changes in the larger sample container at two locations, just below the slurry surface and in the middle of the slurry. For every cycle the rotational speed was increased linearly to 500 rpm and then decreased to zero by means of the PG 142 external programmer. The time to complete one cycle was set to 4 minutes. A Bryans 2500 x/y recorder was used to plot the loops obtained from each cycle in terms of torque against speed, the torque then converted into shear stress from the calibration of the instrument.

Individual batches of slurry were prepared in a standard fashion. The water (including the superplasticizer in the case of the ordinary cement) was placed in the bowl of an orbital mixer. The cement plus either the appropriate amount of the retarder powder (in the case of the ASR-1 cement) or the appropriate amount of silica (in the case of OPC) were added and mixed for 30 seconds at medium speed followed by 1 minute at high speed. The slurry was then transferred to the sample container which was filled to the top. The small sample container was then assembled in the viscometer. In the case of the large sample container, the extended helical impeller was lowered into the container.

Each fresh slurry sample was subjected to three cycles with 0.5 minutes fluid rest time between them. The tests commenced 2 minutes after mixing and the total time to complete a test (that is three cycles) was about 15 minutes. The average plastic viscosity was calculated from the slope of the linear parts of the hysteresis loops. All tests were repeated three times using fresh samples.

Results

Large Sample Container.

Magnesia Phosphate With Borax/Boric Acid Retarder. Fig. 2 shows typical hysteresis loops obtained with time using the ASR-1 cement with 2% addition of borax or boric acid as retarders. Similar families of loops were obtained for both retarders. The stress levels at decreasing speeds were found to be higher than those at increasing speeds and the upward going curve was concave towards the stress axis. The downward going part of the curves was found to be linear but the slope of the line changed at about 275 rpm in the case of loop A whereas there was no change in gradient with loops B and C. Average viscosity values were calculated from the slopes of the linear sections of the hysteresis loops (using the average slope in the case of those with two gradients) from the chart recordings of the x/y plotter and the calibration factor of the instrument (19, 20).

Magnesia Phosphate With NaK Retarder. The NaK retarder at 2% addition resulted in a Vicat setting time of about 7 minutes and only one full cycle and one part cycle could be performed, as shown in Fig. 3, before the test had to be discontinued. The hysteresis loop obtained from the full cycle test had a more pronounced curve on the upward going part of the cycle than with the other two retarders and a linear downward going return to zero stress.

OPC Based Slurry. The same three cycles were applied to the OPC/BM 500/Conplast 430 system but only one loop is shown in Fig. 4 as the three loops were identical, the stress upward going curve was concave towards the stress axis. The downward going curve for

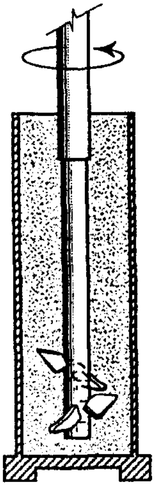

FIG. 1.
Schematic diagram of interrupted helical impeller and small sample container.

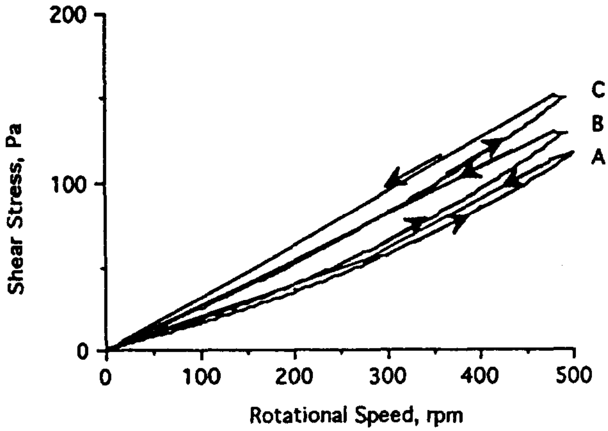

FIG. 2.
Successive hysteresis loops for the ASR-1 2% borax and boric acid cement systems within the 15 minutes time interval (large container).

decreasing speeds was linear but the slope of the line changed at about 275 rpm. The loop was essentially the same as loop A with the borax and boric acid retarders.

Temperature Changes. The results from the temperature measurements during testing with the large sample container are shown in Fig. 5. It can be seen that there was a 10°C increase (from 21 to 31°C) in the temperature of the magnesia phosphate slurry with 2% borax or boric acid at the centre of the slurry (and 5°C increase in the small container not shown in Fig. 5).

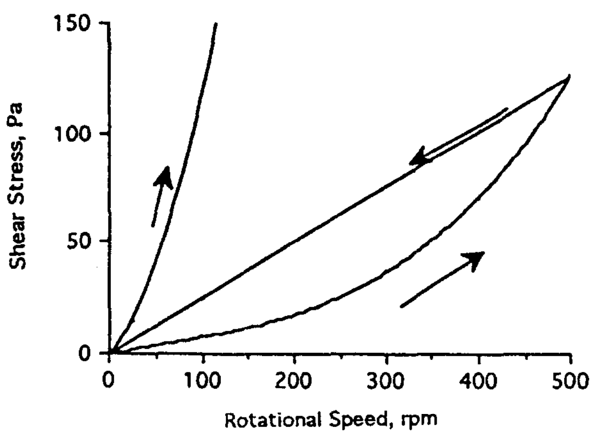

FIG. 3.
Hysteresis loops for the ASR-1 2% NaK system within the 15 minutes time interval (large container).

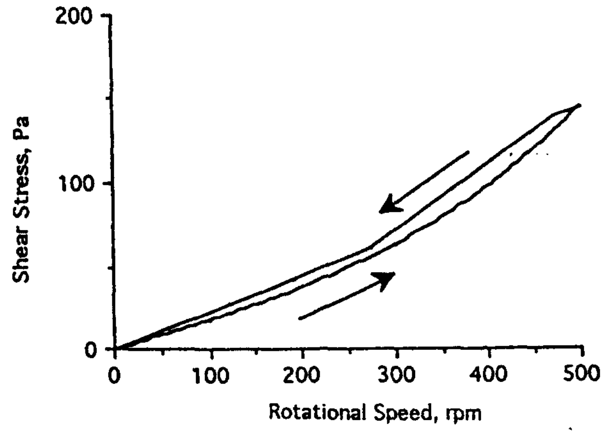

FIG. 4.
Hysteresis loop for the OPC/BM 500/Conplast 430 cement system within the 15 minutes time interval (large container).

Small Sample Container.

Magnesia Phosphate With Borax/Boric Acid Retarder. Three different cycles were obtained with increasing time with these two systems as shown in Fig. 6. Cycle A had a two part upward going section and lower stress levels in the downward going curve which was slightly concave to the speed axis. Cycle B showed no hysteresis with the same two part linear regions with both increasing and decreasing speeds. Cycle C produced a hysteresis loop with a two part linear upward going region but with higher stress levels in the downward going curve which was also concave to the speed axis.

Magnesia Phosphate With NaK Retarder. All three cycles were obtained with the small sample container apparatus, that is setting took longer than in the large sample container.

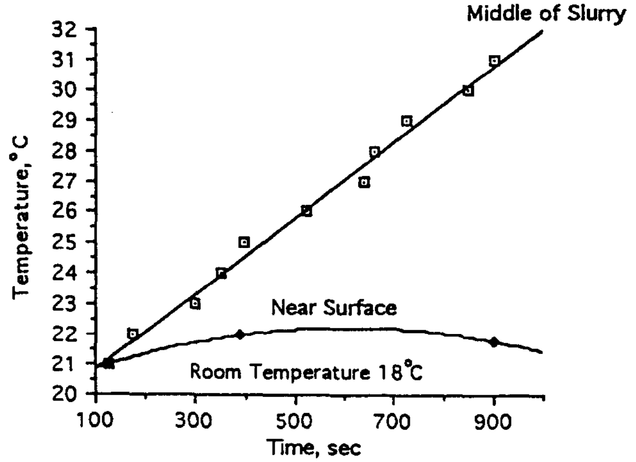

FIG. 5.
Temperature increases in the magnesia phosphate slurry (with 2% borax or boric acid).

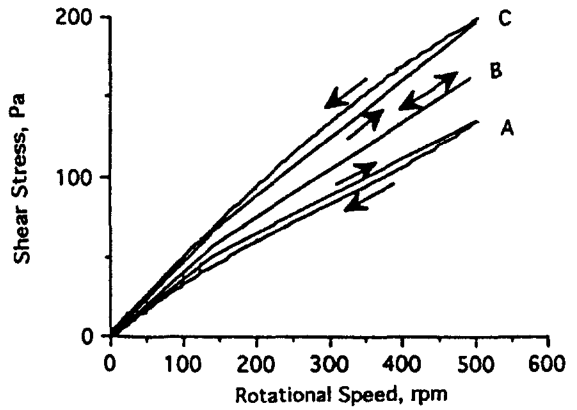

FIG. 6.
Successive hysteresis loops of the ASR-1 2% Borax and Boric Acid systems within the 15 minutes interval (small container).

The three hysteresis loops are shown in Fig. 7. They are similar to loop C in Fig. 6 with increasing stress differences accompanying increasing time.

OPC Based Slurry. Fig. 8 shows the hysteresis loop obtained for the OPC/BM500/Conplast430 cement system. This loop was unchanged for each of the three times of test and lower stress levels were obtained in the second half cycle with the curve concave towards the stress axis.

Discussion

The results can be considered from two aspects, firstly with regard to the main objective of providing a measure of rheological behaviour relevant to the practical problem of infiltration and secondly as to whether any insight is provided into the rheology of cementitious slurries.

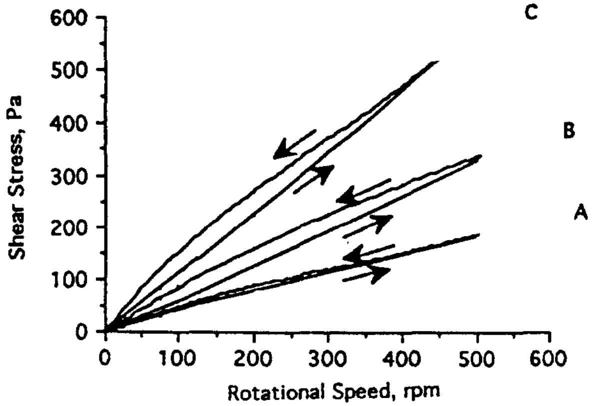

FIG. 7.
Hysteresis loops of the ASR-1 2% NaK system within the 15 minutes time interval (small container).

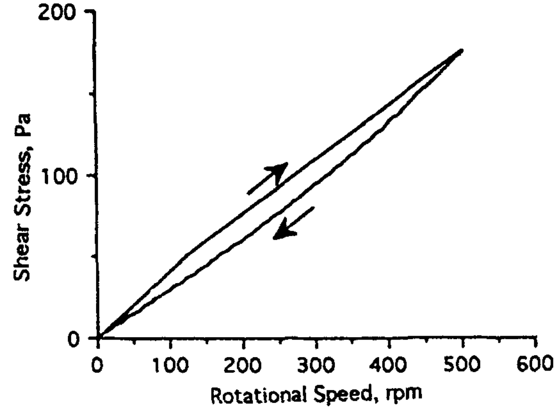

FIG. 8.
Hysteresis loops obtained for the OPC/BM 500/Conplast 430 cement system within the 15 minutes time interval (small container).

Empirical Characterization. Examination of Fig. 2-4 and 6-8 indicates that to a first approximation apart from the very rapid setting composition there is a linear relationship between stress and speed albeit with two different gradients in some instances and either upward or downward depending upon the size of the slurry container. In order to make quantitative comparisons within the data the average gradient of the linear regions of the various curves was used to calculate viscosity.

Fig. 9 illustrates the time dependencies of the viscosity of the cement systems as measured in the large sample container. The viscosity is plotted against time where time is measured from the completion of mixing to the completion of a speed cycle.

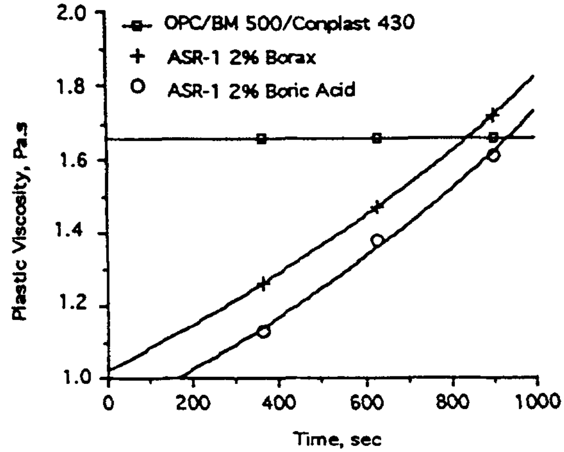

FIG. 9.
Time dependence of viscosity measured in the large container.

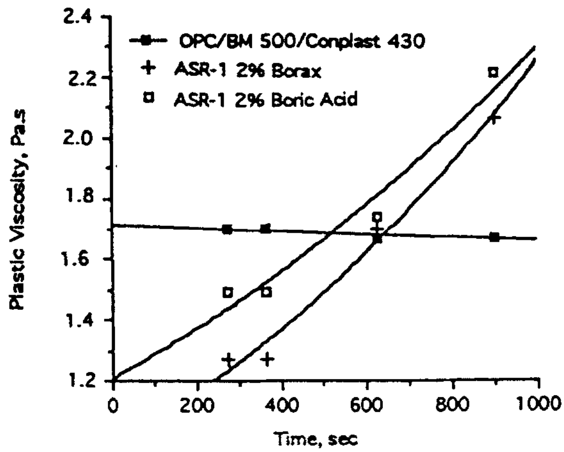

FIG. 10.
Time dependence of viscosity measured in the small container without NaK system.

It can be seen that the viscosity values of the ASR-1 systems increase with increasing time with a dependency of the form

$$\eta = A\ 10^{kt}\ \mathrm{Pa.s}$$

where A = 1.02 and k = 0.00025 for the 2% borax and A = 0.9 and k = 0.00028 for the 2% boric acid systems, η = viscosity and t = time.

Similar relationships were obtained from the small sample container data, Fig. 10 and 11, where k = 0.00036, 0.00028, 0.00088 for the borax, boric acid and NaK systems respectively.

In the case of the OPC system there was no change with time over the 15 minutes period of the tests with the large sample container and a slight reduction with the small container and the same final numerical value was obtained in both cases. The viscosity values of the OPC system can be considered as a minimum requirement for successful infiltration since it has been used successfully to infiltrate a fine steel fibre array of 15% fibre volume fraction (21).

The viscosity values of the ASR-1 borax and boric acid systems were considerably lower than those of the OPC system initially and the cross over point occurred at 15 minutes with the large sample container and 10 minutes with the smaller sample container.

The ASR-1/NaK system was only comparable with the OPC system initially and subsequently was higher.

The analysis therefore provides three pieces of helpful information concerning possible infiltration behaviour of magnesia phosphate slurries:

- Sufficiently low viscosity values can be obtained at the technically most effective water/solids ratio of 0.17.
- The time available for infiltration will be dependent upon the nature of the infiltrating system, in particular upon the levels of shear stress introduced in the infiltrating fluid.
- The repetitive cycle test method provides the basis for further optimisation of mix proportions with respect to the viscosity contribution to infiltration performance.

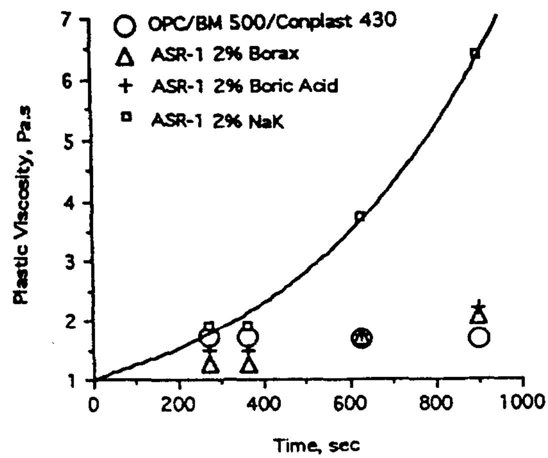

FIG. 11.
Time dependence of viscosity measured in the small container including NaK system.

Rheological Phenomena. It is clear that given the nature of the rapidly changing structure of the magnesia phosphate slurry during the test, its changing temperature and the complicated flow geometry associated with the test method, there is no possibility of ever achieving the equilibrium conditions necessary to identify basic properties. Interpretation of the data is therefore test specific and limited in general application. However it is thought that, qualitatively, it provides useful indicators to phenomena associated with cement slurry behaviour.

Absence of Yield Stress. The one common feature of every curve recorded was the absence of a yield stress with both magnesia phosphate and OPC. In the case of OPC this observation is in agreement in principle with data in the literature which shows that the presence of sufficient superplasticizer reduces the yield value to essentially zero (22-25). It also shows that the presence of substantial amounts of very fine aggregate does not produce any residual yield in contrast to the influence of the presence of coarse aggregate which does (23, 26). The incorporation of fly ash in cement pastes has been shown (27) to reduce the yield stress and since the silica flour in the OPC mix was of finer size (average diameter 4 microns) the results perhaps indicate the completion of a trend.

No results have been reported in the literature for retarded magnesia phosphate slurries. The present data show an absence of yield even as setting approaches with the compositions evaluated. The expectation was that yield should have occurred eventually but even the semi-retarded material tested into the setting stage showed no yield at the beginning of the cycle whilst the material was still fluid. This was attributed to the time sequence of testing, that is at no time was the bulk of the slurry at rest for more than 30 seconds, hence any structural build-up of reaction products was inhibited.

Detail of Curves/Hysteresis Loops. Although the various hysteresis loops obtained were not wide they were all reproducible. The loops obtained from the tests with the large sample container were all of the same form and all indicated slight shear thickening with increasing speeds and higher stress levels at comparable speeds with decreasing speed cycling. Such curves are indicative of slight structural build-up as the rate of agitation reduced. The effect of time was to increase the resistance to flow at all speeds in the case of the magnesia phosphate system indicating some build-up of structure occurring during the testing period but insufficient to develop yield stress. A yield stress was not detected because of the very rapid transition from the viscous to the solid state (see Fig. 3). In the case of OPC there were no detectable changes presumably because measurements were made during the dormant period of hydration (19, 24, 28).

The results with the small sample container were substantially different in detail from those with the large container. All upward curves exhibited shear thinning but the downward going curve varied from lying to the right of the upward curve type "A" to lying to the left type "B". In the case of the borax and boric acid retarded magnesia phosphates the transition occurred after about 6.5 minutes from mixing. In the case of the ASR-1 NaK system, Fig. 8, the first type of loop was absent and much higher stress levels were observed than with the more effective retarders. The OPC curve was the reverse of that obtained with the large sample container and the downward curve significantly different to all of the magnesia phosphate curves. Overall the detail of the curves relate to the extent to which the build-up of structure via nucleation and crystal growth due to the increase in the amount of reaction product is inhibited by the agitation of the test regime. In the small container the agitation (in this case speed cycling) at a given speed of rotation is greater than in the large container because of the closeness of the wall. A systematic pattern is discernible with the magnesia phosphate curves with the changing relative position of the downward curve relating to whether structural build-up or breakdown was dominant (that is in the early stages type "A" curves are obtained indicating breakdown overcoming build-up whereas in the closing stages, type "C" curves are observed with build-up overcoming breakdown).

The values of the viscosity calculated using the small sample container were higher than those calculated using the larger sample container. This was attributed to the effect of the wall (rather than the effect of temperature) but in this case it is thought that the actual rotational speeds are larger than indicated by the instrument hence overestimating the viscosity. To avoid the influence of the wall it is recommended that the inner diameter of the sample container should be at least 4 times the diameter of the rotor (13, 14). In the present tests the inner diameter of the large sample container was 3.1 times that of the rotor and 1.4 times in the case of the small sample container.

Finally, it is worth commenting that although the method of obtaining the data was intended to facilitate the inhibition of structural build-up simply to allow testing of the magnesia phosphate it demonstrates the point made (29) that the agitation imposed by some test regimes do not provide data for modelling quantitatively infiltration at low slurry flow rates. The authors have reported empirical flow tests designed to provide such information for a gravitational infiltration process (30).

Comparison of Data With Literature Values. It can be seen that, within a time period of about 10.5 minutes after mixing, the viscosity values of the ASR-1 systems were lower than those of the OPC based system, but increased thereafter.

Hysteresis loops are frequently used to characterize cement slurry and grout rheologies (31). The duration of the loop has been found to change the response of the slurry from shear thinning at short cycle times to shear thickening at long cycle times. At intermediate cycle times the curves may cross and double or treble loops have been observed (19). In this investigation the time to complete a loop was kept constant at 4 minutes but three loops were obtained over an extended time period. The changes in behaviour can be attributed to the influence of setting phenomena on viscosity and hence enable a measure of the performance limitations to be made. The repetitive fixed loop time method also identifies clearly the influence of specimen size on flow behaviour.

The numerical values obtained for the viscosity of the OPC based system lay in the range 1.66-1.73 Pa.s. These values agree with those reported in the literature for cement pastes and mortars, which lie in the ranges 0.01-1 MPa.s for neat cement pastes and 0.86-5 MPa.s for conventional mortars (13, 16, 31, 32).

Conclusions

The rheological behaviour of magnesia phosphate slurries with setting times of the order of 15 minutes have been effectively characterized by means of helix viscometry.

Average plastic viscosity values were obtained from three consecutive cycles undertaken over the setting period which ranged below and above those of OPC based reference slurries depending critically upon the age of the mix. No yield stress was observed.

There was a significant specimen size influence on the rheological behaviour of both the magnesia phosphate and the OPC slurries. In the case of tests in the larger sized slurry container shear thickening behavior was observed whereas with the smaller container shear thinning occurred. Higher viscosity values were obtained with the smaller sized samples but this was considered to be due to the greater actual agitation imposed on the slurry due to a wall effect.

The setting time of the rapid strengthening cement was increased in the small sample tests which was attributed to the inhibition of structural build-up by the test procedure.

Overall it has been shown that the early viscosity of the rapid strengthening cement based slurry was lower than that of a reference OPC based slurry and hence should effectively infiltrate fibre arrays infiltrated by the OPC slurry across the range of speeds evaluated.

An empirical relationship based on the experimental observations provides the basis for optimising the slurry composition with regard to the time available for successful infiltration.

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