Calibration of rheometers for cementitious materials

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Abstract The calibration of rheometers to determine the rheological properties of cementitious materials ranging from cement paste to concrete cannot be done using standard oils as they are cost prohibitive and do not possess sufficient granularity to test slip phenomena near the fluid wall interface. From American Concrete Institute Committee 238 discussions and two international testing campaigns, it became clear that there is a need for a reference material specifically designed to assess the rheological properties of such granular materials. A newly developed series of reference materials, composed of corn syrup solution, fine limestone powder and glass beads, is presented here. Glass beads of 1 mm and 10 mm represent the sand and coarse aggregates respectively, while the mixture of corn syrup solution and limestone represents the paste. These systems simulating cement paste, mortar and concrete were tested using both rheological measurements and modelling. The synergy between experiment and modeling allowed for the elucidation of an effective slippage phenomenon near the moving surface, and suggested possibilities to reduce it. This paper explores what kind of measurements would be most suitable for the development of the reference materials as well as the results obtained using various rheometer geometries, such as parallel plate, coaxial, vane and double spiral geometries. A critical analysis of the measurement techniques is presented.

Keywords: Rheology, Rheometers, Reference Materials

Introduction

Since 1990s, the concrete technical community, and especially the American Concrete Institute (ACI) have debated the best methods to measure the rheological properties of concrete. There were already a few concrete rheometers available commercially, but they were not widely accepted by practitioners. One major obstacle was identified to be the lack of analytical equations and the lack of calibration or reference materials, which could be used to compare results obtained from various rheometers. Two international tests (2000 and 2003) were organized to bring all the concrete rheometers in one laboratory [1, 2] and test them on the same concrete. The goal was to determine correlation functions between the rheometers. The conclusion was that any pair of rheometer measurements can be correlated and that all rheometers ranked the concretes in the same order as per the plastic viscosity or yield stress. The idea to use standard oils, with and without particles, was discussed but the cost was found extreme. Also the oils are Newtonian materials and thus do not represent a concrete behaviour.

This result was encouraging, but finding a correlation function for each pair of rheometers would have required a large number of tests to be statistically valid for validation. This was not logistically and economically feasible, as another solution is needed. The idea of reference materials was investigated and will be discussed in the present work.

Background

It is well known that commercially available concrete rheometers are designed with a different geometry: coaxial (BML[1]), vane (ICAR, Two-point test, IBB, CAD), parallel plate (BTRHEOM). However, most rheometers are based on the principle to shear a fluid between two surfaces in order to measure the viscosity Analytical solution to calculate the shear rate and shear stress from the torque and rotational speed based on an ideal Newtonian fluid and perfect 'stick' boundary conditions at the walls, are known for coaxial and parallel plate rheometers with the assumption that the gap between the two surfaces is small. According to this model, the velocity profile of the fluid suspension should decrease linearly between the moving surface and the stationary surface [3]. Concrete is not a Newtonian material, exhibiting strong shear thinning near the rheometer wall that is often interpreted as 'slip' based on an interpretation of the fluid based on an effective Newtonian fluid model; further, the gap of concrete rheometers must be large enough to accommodate the coarse aggregate particles. Thus, some analytical solutions and calibration were developed for concrete rheometers but are often limited to idealized fluid models Instead, numerical methods are then required to realistically model flow in these materials. The ACI 238 (Workability of concrete) Committee came to the consensus that a reference material would be needed to calibrate the rheometers. Various options were discussed, such as particles in oil or carbopol [4] or calcium carbonate paste [5]. It was clear that the new reference materials matrix should be similar to cement paste, but should not hydrate, should be non-segregating, and should not change properties for any reason for at least several days.

[1] Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement or recommendation by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

NIST researchers proposed an aqueous solution of corn syrup with fine limestone as the particles [6] as a cement paste reference material. This paste, to which spherical particles of various sizes could be added, would be utilized as the basis for a mortar and concrete reference material. A summary of the properties and development of three reference materials like cement paste, mortar and concrete will be presented below.

Materials used

Three Standard Reference Materials (SRMs) have been developed based on the size scale of the particles in each level of composite: cement paste, mortar, and concrete. Typically, a cement paste is defined as having a Newtonian medium containing particles less than 100 µm in size. Mortar is created by adding small aggregates, such as sand, to the paste. In this study, 1 mm diameter glass beads were added to the paste. For the concrete, 10 mm glass beads were added to the mortar mixture.

The Newtonian medium for the paste is an aqueous solution of corn syrup of 159 cP ± 5 cP (1000 cP = 1 Pa·s) [7]. The corn syrup was a commercially available 100 % glucose. The limestone has a density of 2724 kg/m^3 ± 15 kg/m^3 by helium pycnometer and a median particle size of 17.3 µm ± 0.6 µm. The full distribution measured by laser diffraction in IPA is shown in Figure 1. More details on the materials can be found in [7].

The glass beads are nominally 1 mm in diameter with a density of 2465 kg/m^3 ± 3 kg/m^3 by the ASTM C188-09 test method. Their sphericity was examined and measured using both light microscope and X-ray Computed Tomography. Results showed that some of the beads were deformed, i.e., not spherical or two beads attached together. The number fraction of such beads were found to be between 1 % (Light microscope) to 4 % (X-ray Tomography) of the sample population. More details on how the measurements were conducted are described elsewhere [8].

The glass beads for the concrete were nominally 10 mm in diameter. A random selection of 103 beads was selected for shape analysis via a combination of X-ray CT and spherical harmonic analysis, a procedure similar to that used for the 1 mm beads. Images were taken at a pixel size of about 30 µm. The images were segmented into binary images, stacked into a three dimensional structure, and then the individual particles were fit to a spherical harmonic series [9]. Various shape parameters were computed for each particle and collected to give a statistical picture of the glass bead shape [10,11]. Shape analysis results will be detailed in the upcoming report [12].

The composition of each of the mixtures is detailed in the reports [7, 8, 12] and in the certificates that accompany each standard reference material. The paste is called SRM 2492 and it is now available as a package: 200 g of corn syrup, 63.16 g of distilled water and 458.1 g of limestone powder. All the constituents, except the water, are provided in the SRM 2492 box. The mortar or SRM 2493 is essentially a box containing the same materials and amounts for SRM 2492 with an additional bottle of 1 mm beads. The beads are added after the paste mixture is completed according to the specification in the certificate, to achieve either 20 % or 40 % by volume. The concrete mixture or SRM 2497 is packaged in two 5-gal buckets that contain enough material to produce about 20 L of mixture. Again, all the constituents are provided but the water. At this time, SRM 2492 is available, while SRM 2493 and SRM 2497 are packaged but the reports and certificates are in progress. It is expected that they will be available for purchase by summer 2016.

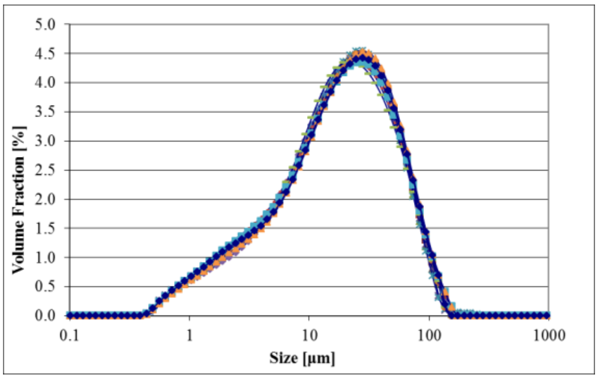

Figure 1: Particle size distribution of 12 limestones specimens, from 12 containers randomly selected [7]

Testing

The three SRMs were tested using rotational rheometers and modelling to determine their rheological parameters. The flow curves are approximated by the Bingham model and the values of yield stress and plastic viscosity are calculated. The viscosity is also provided as a function of the shear rate. The experimental part of this research was supported by a computerized simulation model which was developed to test the flow of these materials in various rotational rheometer geometries. The model directly simulates many particles being sheared in a liquid medium, so it computationally intensive and operates in a parallel mode using hundreds or thousands of processors.

The rheological properties of SRM 2492 [13] were measured using serrated parallel plates (35 mm in diameter) (Figure 2). As this SRM contains water, precautions were taken to avoid evaporation during the experiment, by using a small enclosure around the shearing plates as shown in Figure 2D, containing also a wet sponge. The gap between the two parallel plates was 0.600 mm ± 0.001 mm (one standard deviation). The temperature of the rheometer was maintained at 23 °C ± 0.5 °C during all tests via controlled water bath. The material was nominally sheared at 0.01 s^{-1} for 150 s before starting the Bingham test. The Bingham test consisted of increasing the nominal shear rate from 0.1 s^{-1} to 50 s^{-1} (15 points in total) and then decreasing shear rate from 50 s^{-1} to 0.1 s^{-1} (20 points in total). Both linear and logarithmic scales were used and the flow curves were calculated using the down curves. At each point the shear rate was maintained at the desired value until a stable value (less than 5 % change over a period of time automatically determined by the computer) of the torque was reached, but for a time not to exceed 30 s, to limit the duration of the testing time.

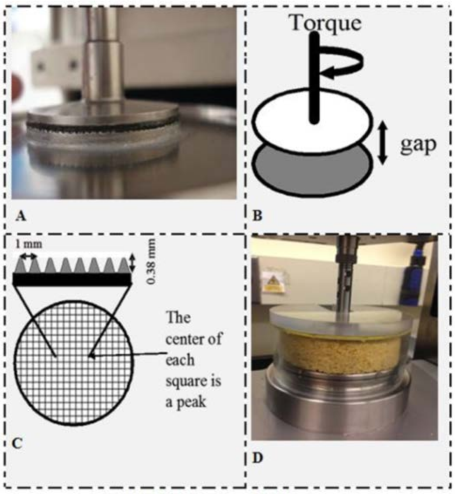

Figure 2: Parallel Plate Rheometer [7]: a) actual serrated plates used; (b) schematic of system showing top plate is subjected to torque; (c) details about serrations of the plates; (d) evaporation trap for sample

The rheological properties of SRM 2493 (paste with 1 mm beads) were measured using a coaxial rheometer with three different spindles: coaxial serrated, six-blade vane and a double helical spiral (Figure 3). The container was a cylinder with a 43 mm diameter and a height of 100 mm. The walls of the containers had the same serration as the coaxial spindle. The test protocol consisted of ramping 15 steps up from 0.1 rpm (0.0105 rad/s) to 100 rpm (10.47 rad/s) and 20 steps back down to 0.1 rpm (0.0105 rad/s). All tests were done on three concentrations of beads in the amounts of 0 %, 20 % and 40 % by volume. The 0 % concentration material is essentially the SRM 2492 and was used as a reference. The data collected consisted of the measured torque (Γ) [N·m] and rotational speed (N) [rpm or rad/s]. The SRM 2492 certified Bingham parameters, yield stress and plastic viscosity, were obtained in fundamental units (Pa and Pa·s), thus they were used to calculate the calibration factors to convert the measurements in the coaxial rheometer from N·m·s and N·m to Pa·s and Pa respectively [7]. This transformation was used as the basis for all measurements with a specific spindle. Figure 4 shows the representation of the viscosity as a function of the shear rate for all spindles and paste with no beads. As this SRM 2492 is used as calibration, all curves were collapsed on the SRM 2492 curve.

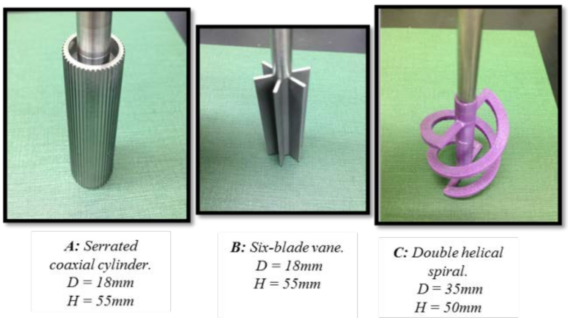

Figure 3: Three rheometry types were used for testing SRM 2493

SRM 2497 (the mortar with added 10 mm beads) data were obtained using a rotation rheometer with two geometries: 4-blade vane and helical spindle. Figure 5 shows a picture of the spindles. The same procedure was applied as for SRM 2493, the paste and then the mortar was tested and finally the concrete with the 10 mm beads. The data from these tests are in progress and thus cannot be presented here, but the same procedure will be applied. The paste and the mortar can be used as references to convert the torque and the rotational speed into shear stress and shear rate, expressed in fundamental units.

Model

The computational approach utilized in this work for modelling suspension flow is based on the Smoothed Particle Hydrodynamics (SPH) method. A full description of this approach is beyond the scope of this paper. A detailed description of this model, including dependent references is given in ref [14]. For this paper, SPH is a Lagrangian formulation of the Navier Stokes equations and is well-suited to model non-Newtonian fluids and the motion of rigid bodies. This approach has been modified to include lubrication forces in order to properly model interactions between solid inclusions when they are in very close proximity. A Lee-Edwards boundary condition is used to model Couette flow in the simulation cell, which contains a matrix fluid and spherical inclusions. The constitutive equation (viscosity vs. shear rate) of the matrix fluid used in these simulations is matched to that used in the experiments by fitting the original paste SRM data. For an applied rate of strain, the volume-averaged stress is determined. From this quantity, the viscosity is determined by dividing the volume average stress by the shear rate.

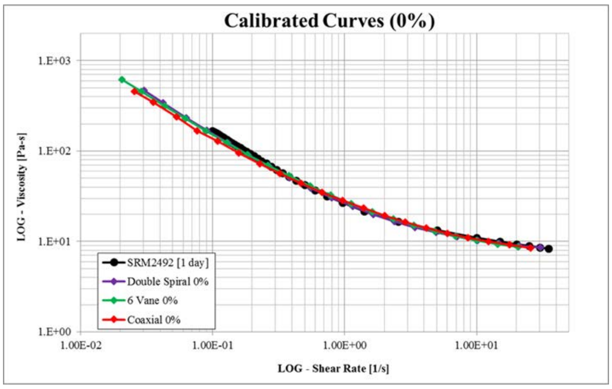

*Figure 4***:** Flow curve comparison of the calibrated 0% flow curves for all three geometries. The flow curves are compared to their reference curve shown in black, which were the SRM 2492 certified values.

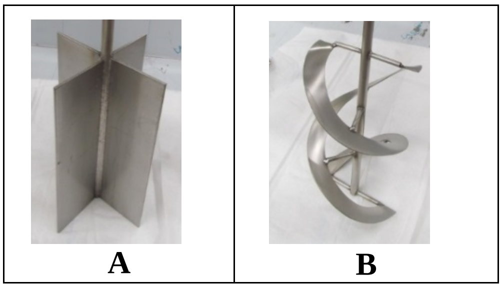

Figure 5: Picture of the spindles for the concrete rheometer: A) Vane; B) double spiral. Both have a length of 180 mm and a diameter of 110 mm.

Results and Discussion

To obtain certified values for the SRM 2492 an experimental design tested 12 mixtures which were prepared and tested at 1 d, 3 d and 7 d [7]. After a statistical analysis of the data, the Bingham parameters were calculated as well as the viscosity vs. shear rate curves. As all the measurements were done using serrated parallel plates, the plastic viscosity and yield stress were obtained in fundamental units. It was found that from 7 d, the material deteriorated due to bacteria growth. Studies are underway at NIST to determine the best biocide that could curtail the bacteria growth for a longer period of at least one month. Important criteria for the biocide are that it would not affect the rheological properties and would not be toxic to humans.

Twelve samples of SRM 2493 were tested, again at 0 %, 20 % and 40 % concentration of beads (1 mm in diameter) by volume. The Bingham parameters and the viscosity vs shear rate were calculated from the data using statistical analysis. To obtain the results in fundamental units the data at 0 % were used as calibration of the rheometer. Then the addition of the beads increased the viscosity. Figure 6 shows an example of the data obtained with the model and the 3 spindles. In this figure, at 0 % concentration (no beads) only the data obtained for the model are shown for clarity.

It is clear that the addition of beads increased the viscosity at the high shear rate by a factor of about 6.7 in the model, while the spiral reaches a factor of about 4.1 and the vane or coaxial are around a factor of only 3 (table I). The uncertainty calculation will be provided in the final report for SRM 2493 [12]. Several observations can be made:

- The viscosity of the spiral is closer to the model data then the other two. This could imply that there is slippage at the surface of coaxial, despite the serration, and the vane.
- The coaxial and the vane also could induce migration of the particles to the container walls, thereby causing a lower value of the viscosity. This was clearly observed for the 10 mm beads in concrete.
- The vane and spiral data are very similar implying that both spindles experience some slippage.
- The model has the highest viscosity probably due to the ideal condition of the simulation: no wall slippage or 'stick' boundary conditions, the concentration of beads is at all times constant, since no migration is possible, and there is no free surface that could lead to dilatancy.

Thus, from this data it could be implied that the spiral-vane, although it has a viscosity value that is still lower than the model, this rheometer exhibits the least effective slippage near the rheometer walls.

The SRM 2497 (concrete) is still in development for both the model and the data. But it was observed during the tests that the large 10 mm beads were migrating to the container wall when the vane was used. On the other hand, the spiral did not cause such a migration to the walls of the container. This migration might be mitigated in real concretes due a wider range distribution of the aggregates size. Potentially, reference materials with a wide range of beads size could be developed in the future.

Conclusions

In this paper, development of SRMs for calibration of rheometer was described. The difficulty and novelty was to use non-Newtonian materials with particles up to 10 mm in diameter to simulate paste, mortar and concrete. Use of such SRMs can help evaluate measurement artefacts on rheometers designed for such materials. Ultimately, calibration of the rheometers will allow the calibration of rheometers for cement materials should allow the determination of rheological properties in fundamental units.

Table I: Ratio of the viscosity at 40 % and at 0 % beads concentration, at the rotational speed of 100 rpm [10.47 rad/s].

Geometry	*Model*	*Spiral*	*Vane*	*Coaxial*
Relative viscosity 40 % to 0 % Ratio	***6.7***	***4.1***	***3.3***	***3.2***

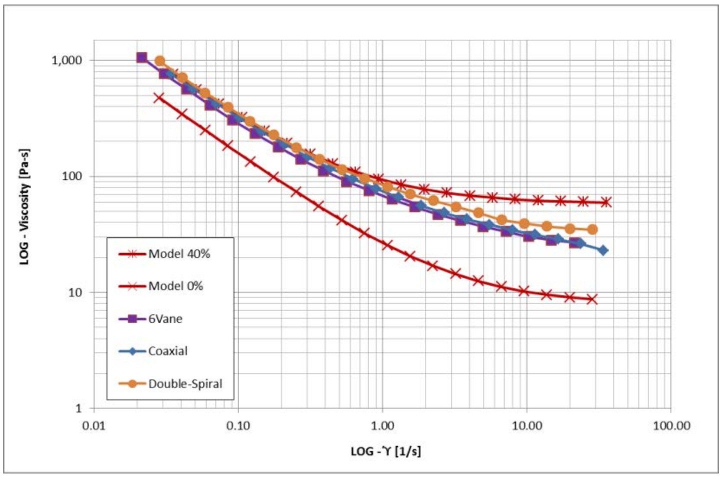

Figure 6: Viscosity curve as a function of the shear rate obtained with a mortar at a concentration of 40 % by volume of glass beads. The model data are also represented here. The uncertainty is estimated 10 % of the viscosity. Full discussion on the uncertainty will be in the full report [9].

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