REFERENCE MATERIALS FOR RHEOMETERS AND THE FLOW TABLE

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Abstract

Oil is the most used standard material for the calibration of rheometers. Other products are used to calibrate flow devices, i.e., the flow table is calibrated using a mixture of oil and silica powder. The oil is a Newtonian liquid while the oil-silica powder mixture is a non-Newtonian fluid. Using this material as a reference material for cement paste and adding aggregates to scale up to concrete has the drawback that it is hard to clean a large rheometer full of an oil mixture. This paper will present two aspects of the development of a reference material for rheometers and for the ASTM flow table. First, the flow table calibration will be analyzed using an approach based on fundamental rheological measurements and characterization of the components (oil and silica powder). Second, the development of a biodegradable reference material would be discussed. The combination of these two topics would illustrate the difficulties of the measurement and development of a granular reference material.

1. INTRODUCTION

Rotational rheometers are used for determining the flow properties of a variety of materials including suspensions. Normally, they are calibrated by using standard oils of known viscosity. The kinematic viscosities of these oils are determined by reference to the water viscosity established by international consensus in 1953 [1] as described in ISO-3666 [2]. The National Institute of Standards and Technology (NIST) in 1954 [1] conducted a study to compare two techniques, the Bingham viscometer and the Cannon Master Viscometers (both based on capillary flow), that are still used for determining the viscosity values of standard oils today. These oils are expensive and therefore cannot be used for large containers such as concrete rheometers.

Some concrete rheometers use a cheaper oil that has a known viscosity as measured using a calibrated rheometer. In 2003, a high viscosity polydimethylsiloxane fluid , with a nominal viscosity according to the manufacturer of 29.1 Pa·s and measured at NIST at 24.4 °C ± 0.4 °C as 29.5 Pa·s ± 0.6 Pa·s, was used with concrete rheometers [3]. It was shown that not all the rheometers were able to measure the oil due to specific shear patterns and slippage on the shearing surfaces. On the other hand, Ferraris et al. [4] calibrated various rotational rheometer geometries using oil and successfully determined a correction factor for a rheometer geometry used for mortar. The oil is a Newtonian material while cement paste is non-Newtonian fluid with a yield stress. Usually oil does not experience slippage on the wall of the shearing planes while suspensions do.

The characteristics should be: 1) no particle sedimentation in the medium at least for the duration of the test; 2) linear stress response to shear rates over a large range; 3) rheological and chemical properties not changing over at least a period of weeks, with no chemical reactions between the medium and the particles; and 4) a yield stress sufficient to avoid sedimentation of added sand and coarse aggregates. Then a multiphase approach would consist of developing a paste that can be measured with a conventional rheometer, then developing a mortar by adding sand and then producing a reference material for concrete by adding coarse aggregates. The rheological parameters of mortar and concrete would be determined from the paste by a combination of simulation and experimental measurements. The simulation would allow the calculation of the viscosity of the suspensions (mortar or concrete) from the medium viscosity (cement paste) with various aggregates concentrations, aggregates size distribution, and particle shape. Therefore, a granular material seems to be the best suited to fulfill all the requirements above to be used as a reference material. Unfortunately such a material does not exist for concrete.

Some granular materials exist as reference materials for use on specific standard tests, such as the flow table (ASTM C230 [5]). In this case, the reference material is a mixture of oil and finely ground silica sand. The mixture must have a yield stress so that it can be placed in the conical mold and not flow under its own weight when the cone is removed, but flow only when the table is dropped.

In this paper, the development of a new granular material for paste rheometers and the characterization of the current reference material for the flow table will be presented.

2. MATERIALS

The materials used for the flow table reference material are a mineral oil (FTO) that is commercially available, with nominal kinematic viscosity between 65.8 cSt to 71.0 cSt at 40 °C. The density is 873 kg/m^3 ± 0.5 kg/m^3 at 23 °C and the viscosity is 0.159 Pa.s ± 0.001 Pa.s (coaxial rheometer) as measured at NIST. The silica powder is graded standard sand (ASTM C778 [6]) that is ground for 20 h in a ball mill to a mean particle diameter of 5.8 µm. The mixture used here is 31 % by volume of silica powder. A vegetable oil (VO), with a viscosity of 0.055 Pa.s ± 0.001 Pa.s (coaxial rheometer) and density of 920 kg/m^3 ± 0.5 kg/m^3 at 23 °C, was also used to determine the influence of the medium on the flow properties.

The materials for a new proposed reference material to simulate cement paste are a mixture of corn syrup and fine ground limestone and water. Corn Syrup (CS-US) is, according to the manufacturer, pure corn syrup with no additives. Its density measured at NIST was 1431 kg/m^3 ± 0.5 kg/m^3. The limestone (L-US) has a density of 2755 kg/m^3 ± 0.5 kg/m^3. It is also referred to, by the manufacturer, as micro-limestone flour obtained by sieving with a #325 sieve (45 µm opening).

3. EXPERIMENTAL SET-UP

The rotational rheometer used is equipped with a parallel plate geometry. The plates are 35 mm in diameter and serrated [4]. The gap between the two plates was 0.4 mm unless otherwise stated. To measure the rheological parameters by the Bingham method, the material was sheared with a shear rate of 0.1 s^{-1} for 200 s, then after a period of rest of 30 s, the shear rate was increased from 0.1 s^{-1} to 50 s^{-1} and then decreased back to 0.1 s^{-1}. The induced shear stresses were measured, corresponding to 15 levels of shear rates on the up curve and 20 levels on the down curve. Each measured point was recorded after the shear stress reached equilibrium or after 20 s, whichever occurs first. The descending data were linearly fit, and the slope and intercept were calculated.

A standard flow table as described in ASTM C230 [5] was used to determine the relationship between the flow and the characteristics of the reference material used as measured with the rheometer. The flow table is designed to determine the consistency of mortars. A brief description will be given here. The flow table is a brass frustum of a cone placed on top of a brass table attached to a device that would allow the table to be lifted and dropped at regular intervals from a specific height. To perform the test, the frustum is placed at the center of the table, filled with the material, and lifted to form a cone of the material. The material does not flow under its own weight. Then the table is lifted and dropped 25 times. Under such an action, the material flows and forms a patty. Four diameters of the patty are measured using a special caliper and added up to represent the flow table value. The larger the number, the higher is the consistency of the material.

4. RESULTS AND DISCUSSION

4.1 Paste reference material

As stated in the introduction, the characteristics for a reference material of cement paste should be: 1) no particle sedimentation in the medium at least for the duration of the test; 2) linear stress response to shear rates in a large range; 3) rheological and chemical properties not changing over at least a period of weeks, with no-chemical reactions between the medium and the particles; and 4) a sufficient yield stress to avoid sedimentation of added sand and coarse aggregates.

The reference material selected here is a mixture of 76 % by mass of aqueous solution of corn syrup and limestone at 48 % by volume that shows no sedimentation. Figure 1 shows that stress-shear curve, whether mixed by hand or with a high shear blender, was linear up to 50 s^{-1} shear rate. This shear rate value should be high enough to match that in concrete the shear rate during placement is about 40 s^{-1} [7]. It should also be noted that no hysteresis is present in the flow curves (Figure 1).

Figure 2 shows the evolution of the properties over time as well as repeatability of the measurements of the rheological parameters. Two identical mixtures were prepared and half of each was stored at 23 °C while the other half was stored at 6 °C. The rheological parameters of the mixtures were then measured after different elapsed times. It can be seen that there was less change over 2 months of storage at 6 °C than at 23 °C. Also, the repeatability was sufficient. So there is good time stability if the material is stored at 6 °C between tests.

The material has a yield stress above 50 Pa. The yield stress necessary to avoid segregation depends on the density and size of the particles placed in the mixture. Saak et al. [8] have show experimentally that a yield stress over 60 Pa could prevent sedimentation with aggregates. As the suggested material has a yield stress of at least 90 Pa, it should be high enough to prevent sedimentation of aggregates are added to simulate mortar or concrete.

In summary, it seems that all the four characteristics stated above for a reference material are met using a mixture of corn syrup, water and limestone at 48 % by volume. These are nevertheless preliminary data and they should be confirmed. The detailed development of this material will be described in a future paper.

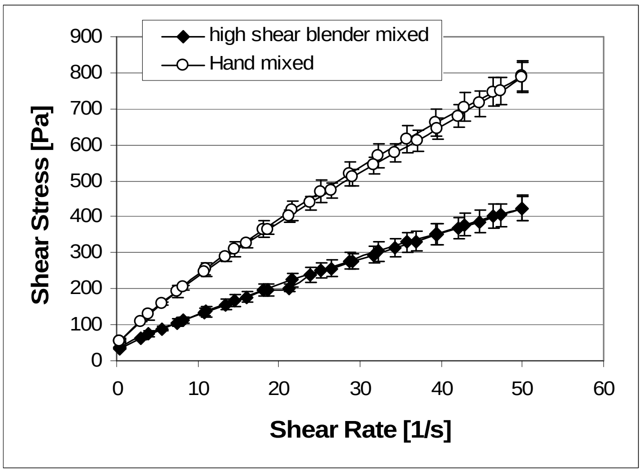

Figure 1: Flow curves of the mixture of corn syrup and limestone mixed by hand and by the high shear blender. The uncertainty bars are one standard deviation from three measurements for each test.

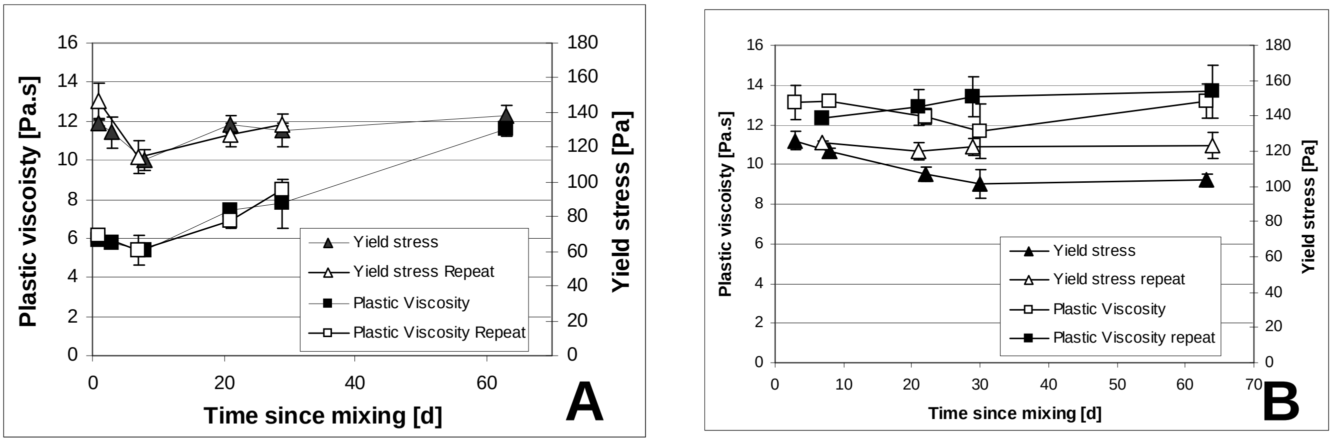

Figure 2: Influence of time and temperature on the rheological properties of the corn syrup suspension. A) at 23 °C; B) at 6 °C. The uncertainty bars are one standard deviation from three measurements for each test.

4.2 Reference material for the flow table

The reference material for the flow table has been developed in the past by trial and error and historical knowledge. The results obtained should be about 110 % ± 5 % (as read on the caliper) using a standard caliper on a flow table that is well maintained by the Cement and Concrete Reference Laboratory (CCRL). The proportions of the mixture of oil and ground silica are adjusted to obtain that value. It would be more reliable if the properties of the silica, such as particle size distribution, of the oil such a viscosity and of the mixture rheological properties would be determined using fundamental measurements. For instance the influence of the oil viscosity on the mixture viscosity could be clearly determined as well as the influence on the amount of silica sand. This reference material does not need to have the same characteristics than the reference material used for rheometer. It should have a yield stress not to flow under its own weight when the mold is lifted and a viscosity that allow flowing under external force to a certain size patty. Obviously, no segregation of the suspension during the test should occur.

Figure 3 shows the rheometer results obtained with two oils (FTO and VO) and two concentrations in silica (48 % and 32 % by volume). The values measured with the flow tables are indicated on Figure 3 as well. The yield stress was high enough to ensure that the cone of material did not flow on its own for the VO-silica suspension at 48% volume concentration, but the flow was not as high as the reference material (88 % instead of 100 %). So from the rheological characteristics shown in Table 1, it could be inferred that a 21 Pa yield stress is enough to conduct the test as the material can be demolded from the frustum without flowing under its own weight. On the other hand, to increase the flow to 110 % as desired for the flow table standard, both suspensions would require a decrease in viscosity, so that the material would flow to a larger patty. To increase the patty, one solution would be to increase the oil content. An increase in oil content will certainly increase the flow table value but also decrease the viscosity and yield stress of the material. A decrease of yield stress for the FTO suspension will not affect the requirement of the material not flowing under its own weight. On the other hand, a decrease of the yield stress for the VO suspension would probably results in a material that will flow under its own weight as the yield stress would be too low. Therefore, it could be stated that a full characterization of the flow table reference material requires an optimization of both the yield stress and the plastic viscosity. From these preliminary tests, the minimum yield stress could be determined to be 21 Pa. But the range of acceptable viscosities was not as yet determined.

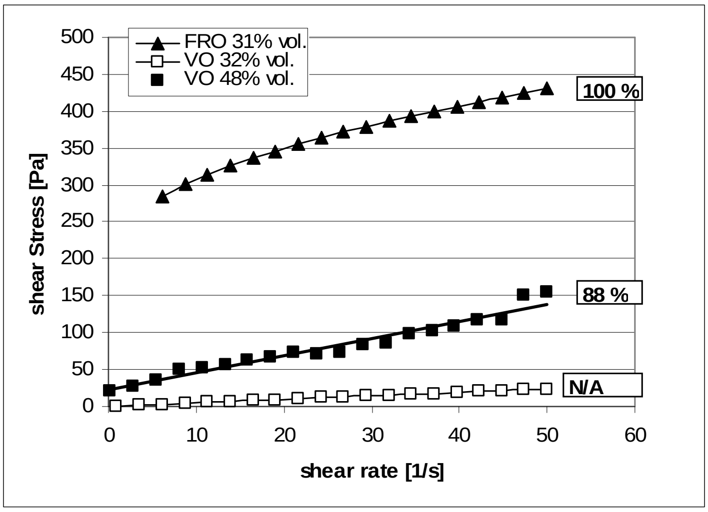

Figure 3: Comparison of shear stress-shear rate curves for the two oils considered. In the boxes, the values of the flow table tests are indicated (N/A implies that the material flowed under its own weight)

Table 1: Rheological parameters for the oil silica suspensions used for the flow table. Uncertainty is estimated to about 10%.

	Bingham yield stress [Pa]	Plastic viscosity [Pa.s]
VO suspension at 32 % volume	0	0.48
VO suspension at 48 % volume	21	2.3
FTO suspension at 31 % volume	280	3.2

5. CONCLUSION

In conclusion, the availability of reference materials whose values are determined with calibrated instruments in fundamental units is paramount. Two cases have been discussed here: 1) reference materials for rheometers and 2) development of reference material for empirical test such as the flow table. The characteristics requirements of both materials are not identical as discussed.

In the first case, the reference material for rheometer needs to have clearly defined four properties that were found to be fulfilled using a suspension for an aqueous solution of corn syrup (76 % by mass) and finely ground limestone 48 % by volume. The mixture was found to be stable over time, especially if stored at 6 °C between usage, have a yield stress above 60 Pa that is sufficient to prevent aggregates sedimentation, a linear stress-shear rate curve up to at least 50 s^{-1} shear rate (higher than shear rates in concrete during placement), and no sedimentation of the suspension.

In the second case, the reference material for flow table is already in use and therefore the composition known. The minimum yield stress to avoid flow of the material under its own weight was determined to be 21 Pa. Further study need to be conducted to determine the range of acceptable viscosities. Then the material performance could be determined from a rheometer even if the one reference flow table is damaged.

In both cases, further development and research is needed to completely develop and characterize reference materials. More detailed study will be presented in future papers.

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