REFERENCE MATERIALS FOR RHEOMETERS AND THE FLOW TABLE

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Abstract

Oil is the most frequently used standard material for the calibration of rheometers. Other products are used to calibrate flow devices; e.g., the flow table is calibrated using a fluid composed of oil and silica powder. The oil is a Newtonian fluid, while the oil-silica powder mixture is non-Newtonian. Using this mixture of oil-silica powder 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 International (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 non-toxic reference material will be discussed. The combination of these two topics would illustrate the challenges involved in the measurement and development of a granular reference material.

1. INTRODUCTION

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

Some concrete rheometers use a cheaper oil with a known viscosity as measured using a calibrated rheometer. In 2003, a high viscosity polydimethylsiloxane fluid with a nominal viscosity of 29.1 Pa·s (per the manufacturer) and a NIST measured viscosity of 29.5 Pa·s ± 0.6 Pa·s at 24.4 °C ± 0.4 °C as, 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 standard 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 of a non-Newtonian rheological reference material for cement paste should be: 1) no particle sedimentation in the medium for the duration of the test; 2) linear Bingham stress response to shear rates over a large range; 3) rheological and chemical properties unchanged 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.

This kind of reference material will be used to represent the cement paste in concrete. To develop a reference material for concrete rheometers, a multiphase approach will be necessary. The paste with the characteristics described above can be measured with a conventional rheometer. Then a mortar reference would be developed by adding sand, and a reference material for concrete would be produced by adding coarse aggregates. The rheological parameters of mortar and concrete would be determined from the paste by a combination of computer 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 aggregate concentrations, aggregate 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. However, 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 mold 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 consists of a mineral oil (FTO) that is commercially available, with nominal kinematic viscosity between $65.8 \cdot 10^{-6}$ m^2/s (65.4 cSt) to $71.0 \cdot 10^{-6}$ m^2/s (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. It also consists of a 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 to produce silica powder. 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, also was used to determine the influence of the medium on the flow properties.

The materials for a 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 a micro-limestone flour obtained by sieving with a #325 sieve (45 μm opening).

3. EXPERIMENTAL SET-UP

The rotational rheometer used is equipped with 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 initial shear rate was 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 occurred 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. Only a very 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 (with units described by the standard ASTM C230; it is zero for no flow and a maximum flow of 160 %) and added up to represent the flow table value. The larger the number, the higher is the consistency (workability) 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 as follows: 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 unchanged 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 concentration aqueous solution of corn syrup and limestone at 48 % by volume that shows no sedimentation. Figure 1 shows that the stress-shear curve, for the material sheared with the high shear blender is approximately Bingham up to 50 s^{-1} shear rate. The material sheared by hand also follows a Bingham function between 10 s^{-1} to 50 s^{-1}. The high shear blender allows a better dispersion of the limestone as expected. This shear rate value should be high enough to match that in concrete during placement. Saak et al. [7] stated that the shear rate during placement is about 40 s^{-1}. It also should 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 could be seen that there was less change over 2 months of storage at 6 °C than at 23 °C. Also, the repeatability was sufficient. Therefore, 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 shown experimentally that a yield stress over 60 Pa could prevent sedimentation of aggregates. As the suggested material has a yield stress of at least 90 Pa, it should be high enough to prevent sedimentation of aggregates that are added to simulate mortar or concrete.

In summary, it seems that all four of the stated characteristics of an ideal reference material have been met using a mixture of corn syrup, water, and limestone at 48 % by volume. These are nevertheless preliminary data, and should be confirmed. Detailed characterization of this material will be described in a future paper.

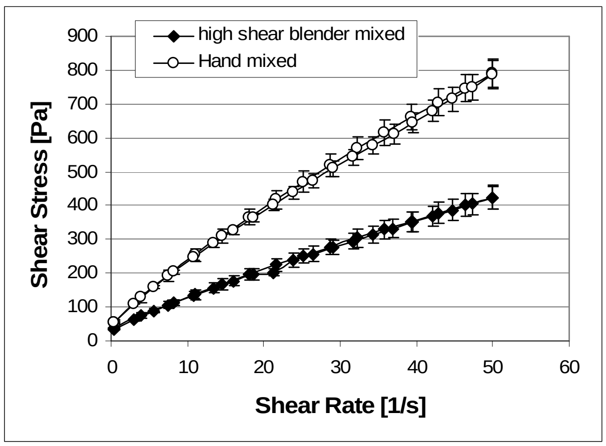

Figure 1: Flow curves of the mixture of corn syrup and limestone mixed by hand and by the high shear blender. The uncertainty bars are one standard deviation from three measurements for each test.

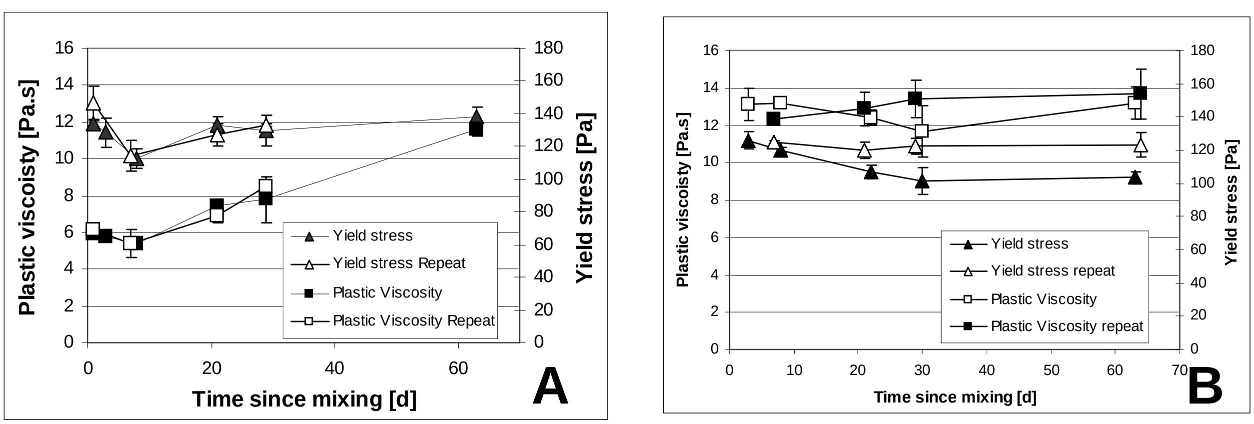

Figure 2: Influence of time and temperature on the rheological properties of the corn syrup suspension. A) at 23 °C; B) at 6 °C. The uncertainty bars are one standard deviation from three measurements for each test.

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), the oil (such a viscosity), and the mixture's rheological properties would be determined using fundamental measurements. For instance, the influence of the oil viscosity on the mixture viscosity could be determined clearly as well as the influence on the amount of silica sand. This reference material does not need to have the same characteristics as the reference material used for rheometer. It should have a yield stress so that it does not flow under its own weight when the mold is lifted and it should have a viscosity that would allow the flow under an external force to a certain size patty. Obviously, segregation of the suspension during the test should not 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 %). Therefore, 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 diameter of the 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 result in a material that will flow under its own weight, as a result of a too low yield stress. 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. The range of acceptable viscosities has not yet been determined.

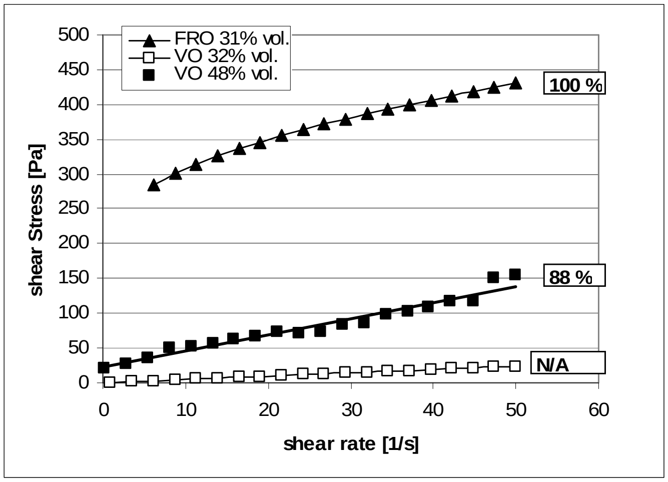

Figure 3: Comparison of shear stress-shear rate curves for the two oils considered. In the boxes, the values of the flow table tests are indicated (N/A implies that the material flowed under its own weight).

Table 1: Rheological parameters for the oil silica suspensions used for the flow table. Standard 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

The availability of reference materials whose values are determined using 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 characteristic requirements of both materials are not identical as discussed.

In the first case, the reference material for the rheometer needs to have four clearly defined 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, having a yield stress above 60 Pa that was sufficient to prevent aggregates sedimentation, having 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 is known. The minimum yield stress to avoid flow of the material under its own weight was determined to be 21 Pa. Further study needs 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 research will be needed to completely develop and characterize reference materials. A more detailed results will be presented in future papers.

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