Development of Standard Reference Materials for Rheological Measurements of Cement-Based Materials

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ABSTRACT:
Rotational rheometers are routinely used for homogeneous materials, but their usage for characterization of a granular fluid like concrete is a relatively new phenomenon. As measurements with rheometers can involve flow in a complex geometry, it is important that they are calibrated with a reference material or an SRM. NIST has produced an SRM for cement paste (SRM 2492) as the first step for the development of a reference material for concrete rheometers. The second step is the development of a reference material for mortar, composed of the SRM 2492 with added spherical beads. Here, material properties, such as viscosity, cannot be measured in fundamental units with certainty, thus modeling was used to determine the plastic viscosity of the SRM mortar which in turn could be compared with experiments. This paper will present the process used to develop the mortar reference material. Measurements and modeling will be presented.

Keywords: Reference materials, calibration, mortar, paste

1. INTRODUCTION

Self-consolidating concrete (SCC) is defined by American Concrete Institute (ACI) terminology for its ability to flow and consolidate under its own weight without vibration. Therefore, the rheological properties of SCC are the most essential parameters that determine successful placement and consolidation. In the past 10 to15 years, concrete rheometers were built to measure such properties. It was found by two international round-robin tests[1,2] that different concrete rheometers do not provide the same viscosity or yield stress value while measuring the same concrete batch. Nevertheless, they rank different concrete mixtures in the same order. Thus, the rheological properties of a concrete can only be specified relative to the rheometer used. This is not an optimal approach for developing specifications and codes that require viscosity or yield stress for general usage instead of the slump or slump flow that is currently used.

Thus, discussion in ACI 238 committee, *Workability of Fresh Concrete*, led to the consensus that a reference material needs to be developed. This material must be similar to concrete (e.g., containing aggregates). The NIST approach, presented here, was to develop a reference material having similar rheological properties as cement paste and then add fine aggregates to simulate mortar and then add coarse aggregates to approximate concrete. The Standard Reference Material (SRM) for paste rheology was developed and it is composed of a solution of corn syrup and limestone fine powder (SRM 2492)[3]. The next step, presented here, is the development of the SRM for mortar rheology. While the rheological properties of a SRM paste can be measured accurately using a laboratory rheometer, the mortar SRM properties cannot be measured with certainty because mortar rheometers cannot be properly calibrated with oil. Therefore, a model was developed to determine the rheological properties to be assigned to the mortar SRM. The goal is that these SRMs will be used to calibrate rheometers to be used to measure mortar or concrete, allowing all rheometers to report data normalized to the same material values.

2. BACKGROUND

2.1 Rheological measurements

Rheological properties are typically measured using rotational rheometers that essentially shear a material between two surfaces. Usually one surface is stationary and the other is rotating. Various geometries could be used. For this report, we used a vane and a coaxial configuration. Rheological measurements typically produce a shear stress vs. shear rate plot. In cases where the geometry of the rheometer does not allow a direct calculation of the shear stress and shear rate in fundamental units, as for a vane, the rotational speeds and the resulting torques are plotted[10].

Viscosity[4] is defined as the ratio of the shear stress to the shear rate at a given shear rate. For a Newtonian fluid, it is also equal to the slope of the fitted line of the shear stress-shear rate plot, going through zero, as the relationship is linear. But most granular fluids, such as mortar and concrete, are non-Newtonian. Their most notable characteristic is that they exhibit a yield stress, which is the stress needed to initiate deformation or flow of the material. The two most common methods for measuring this behavior are the stress growth method and the extrapolation from the Bingham test method[5, 6].

Most researchers use the method based on the Bingham equation (Eq. (1)) to determine the plastic viscosity and the yield stress. This procedure implies that the plastic viscosity is defined as the slope of the shear stress-shear rate curve and the yield stress is the intercept of the curve at zero shear rate. This point is generally not directly measured, so this constitutes an extrapolation (Figure 1). The Bingham rheological parameters, yield stress and plastic viscosity, will characterize the flow curve within a range of shear rates, as shown in Figure 1 and equation[4] (1).

$$\tau = \tau_B + \mu_{pl}\dot{\gamma} \qquad \textbf{(1)}$$

where τ = shear stress, τ_B = Bingham yield stress, μ_{pl} = plastic viscosity, and $\dot{\gamma}$= shear rate.

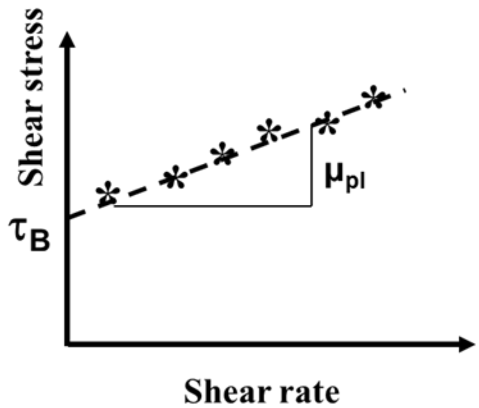

Figure 1: Bingham model and calculation of the plastic viscosity and yield stress.

2.2 Model overview

The computational model of fluid flow utilized for this work is based on a Smoothed Particle Hydrodynamics approach[7,8], and Lucy[9,10] that is a Lagrangian formulation of the Generalized Navier-Stokes equations. The Lagrangian formulation is preferred because this approach can give us more flexibility in handling moving boundaries. This approach can account for a spatially varying viscosity that is, for example, dependent on the local shear rates. While details of the model are beyond the scope of this paper, we briefly describe some of its features. The time evolution of a fluid is represented as a set of particles, located at r_p, carrying local flow information (velocity, density). These particles undergo motion in response to effective “interparticle” forces that are defined by a discretized version of an integral representation of the general Navier-Stokes equations[11]:

$$\frac{\partial \rho}{\partial t} = -\rho \nabla v \qquad \textbf{(2)}$$

and

$$\rho \frac{\partial v_i}{\partial t} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_k}\left[\mu\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\nabla v\right)\right] + \frac{\partial}{\partial x_i}(\zeta \nabla v). \qquad \textbf{(3)}$$

Here, ρ is the fluid density, $\boldsymbol{P}$ is pressure, v is velocity, μ and ζ are the shear and bulk viscosities respectively.
In these equations the bulk and shear viscosities cannot be taken outside the gradient operator because they can vary in space. The discretization form is very similar in structure to a molecular dynamics simulation and indeed can be related to other approaches like dissipative particle dynamics. Lubrication forces are also included in this model to account for behavior of dense suspensions where there are many solid inclusions in close contact. The lubrication forces have been modified such that the viscosity is dependent on the local shear rate between neighboring sphere surfaces. This approach has been demonstrated to recover simple analytic solutions of flow fields of pipe flow for non-Newtonian fluids and agrees well with experimental data of relative viscosities of suspensions having a Newtonian and non-Newtonian fluid matrix. The full details of this model are given elsewhere[7].

3. EXPERIMENTAL WORK

Reference materials were prepared as stated in the SRM certificate[12] and beads were added to simulate mortar reference material.

3.1 Materials and mix proportions

SRM 2492 is composed of pure corn syrup, water and limestone. The corn syrup is used as supplied by the manufacturer. Its density measured at NIST is 1427 kg/m^3 ± 5 kg/m^3, with a water content of 18.6 % ± 0.2 % by mass fraction, and its chemical composition is 100 % glucose.

The limestone powders were analyzed to determine mineralogical, chemical, and physical characteristics. Table 1 and Figure 2 show some physical properties and the particle size distributions, respectively. The particle size distribution (PSD) was measured using laser diffraction with either water or isopropanol (IPA) as the suspension media. It should be noted that there is little difference, suggesting that the particles are well dispersed in either medium.

The proportions of the SRM 2492 are shown in the certificate[12] and are:

- Corn Syrup: 200 g
- Distilled water: 63.16 g
- Limestone: 458.1 g

The rheological values associated with this material were determined at NIST after a statistical experimental design and are described in a report[13].

Table 1 - Properties of the limestone used [3].

Density [kg/m^3]	BET surface [m^2/g]	*Phases [%]*					
		calcite	*dolomite*	*quartz*	*tremolite*	*talc*	*chlorite*
2755 ± 5	1.56 ± 0.04	75 ± 2.6	20 ± 2.1	0.8 ± 0.7	2 ± 0.8	0.8 ± 0.2	0.7 ± 0.7

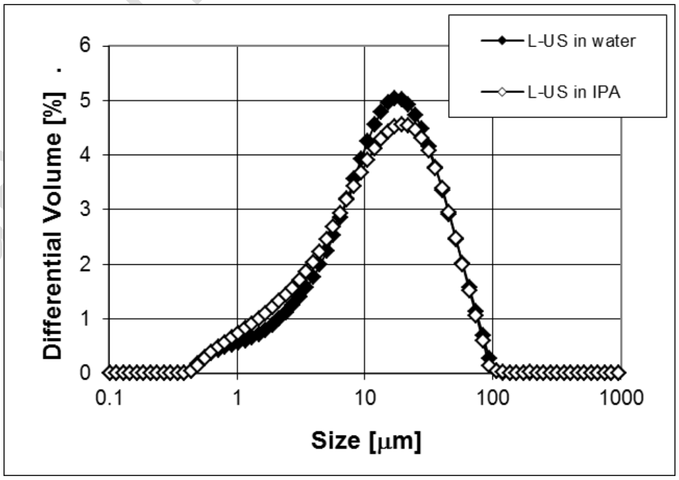

Figure 2 - Particle size distribution of the limestone

Glass beads with diameters, reported by their manufacturer, of 0.50 mm to 0.60 mm were used as aggregates for creating the mortar reference material. Figure 3 shows the distribution of the size of the beads, which was measured using laser diffraction assuming an index of refraction of 1.52.

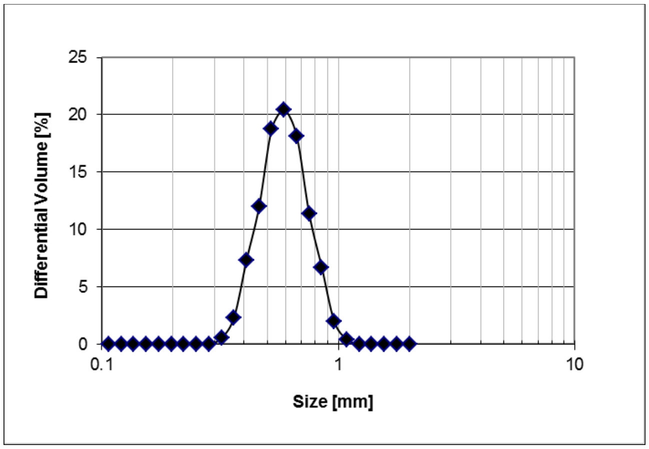

Figure 3: Beads size distribution

The SRM 2492 is prepared by the operator using the procedure described in ASTM C1738 and it is designed to have stable rheological properties for 7 days. The mortar is prepared by adding the beads to the SRM 2492 in the proportions desired. In this paper, the volume fractions used were 0 %, 20 %, 30 %, and 40 %.

3.2 Experimental set-up

The rheological measurements were performed using a coaxial rheometer that was shear rate (rotational speed) controlled. The speed ranges were (a) 0.12 rad/s to 5.2 rad/s with 10 points measured, and (b) 5.2 rad/s to 0.1 rad/s with15 points measured. At each point the rotational speed was maintained for 20 s to ensure equilibrium. In the future other shear rate range should be investigated.

The coaxial rheometer was composed of a bob manufactured at NIST that rotates within a container of 43 mm in diameter. The bob is shown in Figure 4[14]. The gap between the bob and the container was of 4.9 mm, and an overall bob diameter of 33.2 mm. The length of the bob is 69.4 mm (Figure 4). The bob was made of plastic covered with waterproof sand paper grit 100. The diameter of the bob was measured with the cover of the sand paper.

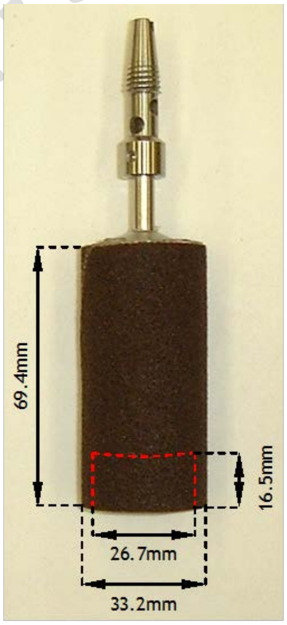

Figure 4 – Bob used in the coaxial rheometer. The red dashed line show the hollow bottom designed to have an air pocket at the bottom to ensure no interference of the bottom surface.

4. RESULTS AND DISCUSSION

4.1 Results of the experimental testing

The data collected for each test at each concentration were interpreted using a Bingham model to infer the plastic viscosity and the yield stress. In this paper, only the plastic viscosity value will be considered. To facilitate comparison with the modeling results, Figure 5 shows the torque versus angular velocity as measured for the various concentrations of beads. As expected, the applied torque increases with volume fraction of beads and with angular velocity.

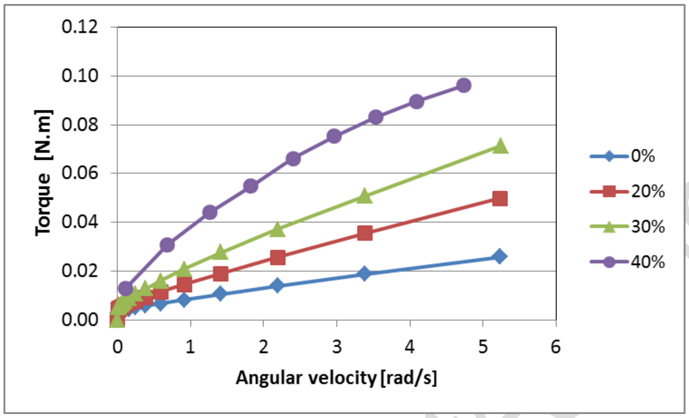

Figure 5: Torque vs. shear rate as measured with the coaxial rheometer. The experimental uncertainty is about 10%.

4.2 Modeling of the mortar and paste SRM

To simulate a candidate SRM mortar, the rheological properties of a matrix fluid were first determined. From evaluation of the experimental data of this SRM 2492 paste, the following empirical function $\mu = (0.135 + (\frac{1-e^{-\dot{\gamma}^{.15}}}{\dot{\gamma}})$ for viscosity vs. shear rate fit the experimental data reasonably well (Figure 6). This fluid actually has a divergent viscosity in the limit of zero shear rates. To avoid this divergence the viscosity was modified by setting $\gamma' = \gamma + 0.001$. This small offset should have a minimal impact at the shear rates investigated.

After establishing the constitutive relation for the matrix fluid (SRM 2492 for paste), a set of mono size spheres at volume fractions of 20 %, 30 %, and 40 % were added to the paste to simulate mortar. The systems (matrix + spheres) were sheared to obtain couette flow at various shear rates . Figure 7 shows the viscosity vs. shear rate for each of the volume fraction mixtures. The simulated viscosity was determined by calculating the average stress throughout the sheared material and dividing it by the macroscopic shear rate. As seen in Figure 7, the simulation is able to correctly recover the input viscosity function that is based on the SRM paste. The analytical calculation of the rheological parameters with a material including large aggregates, such as the spheres is not known. Thus, the implication is that there is no rheometer that can measure the values in fundamental units. Hence the set of curves from Figure 7 could constitute the “true” rheological properties of the SRM mortar.

Nevertheless, any simulation must be validated. Therefore, the simulation results were compared with experimental results with the same volume concentration of spheres in SRM 2492 (Figure 8). Clearly, there is a fairly good agreement between the simulation and experimental data. It should be noted that in general the experimental values have a tendency to be lower than the simulation. This can possibly be attributed to slippage at the rotor or the container during the experimental measurements. Further, this slippage could be due to the fact that the beads are significantly larger than the roughness of the sand paper. We plan to repeat these tests, using a serrated cup and rotor. In particular, it seems that the sand paper used for the rotor is not sufficient to avoid slippage (Figure 4).

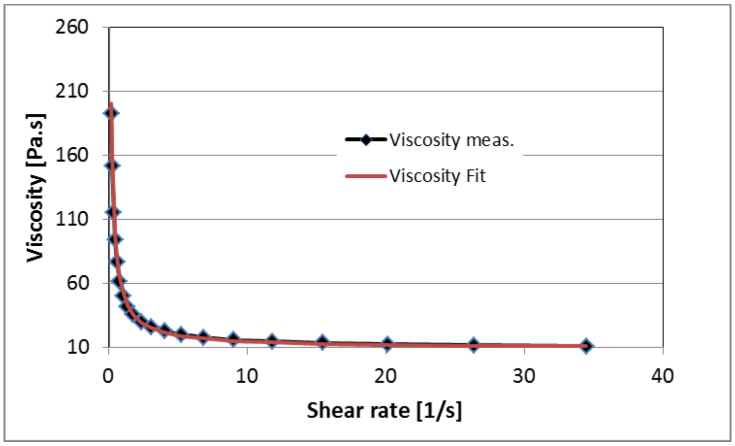

Figure 6: Experimental measurement of the SRM viscosity using a coaxial rheometer along with the fit using the empirical function for the viscosity (see text). The experimental uncertainty is about 10%.

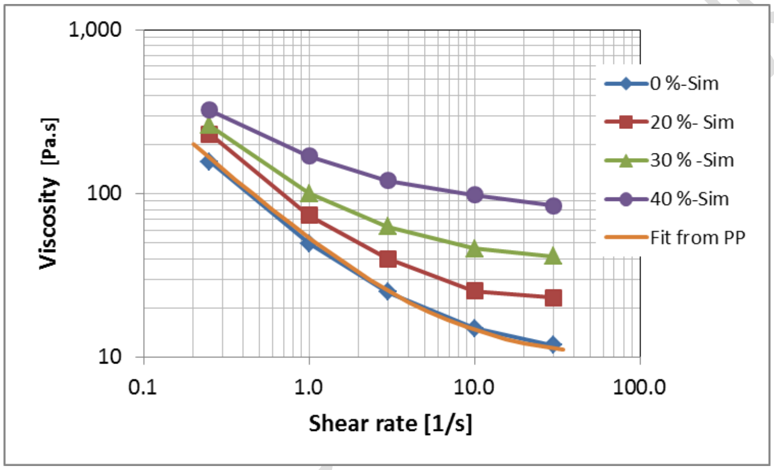

Figure 7: Simulated mortar viscosity vs. shear rate for various volume fractions of aggregate. From the legend: *Sim* = simulation results; *Fit from PP* = Fit from parallel plate measurements.

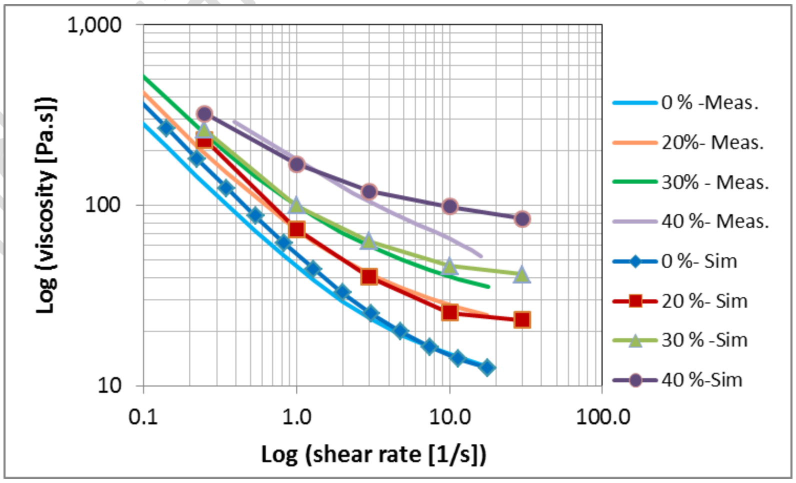

Figure 8: Comparison between measurements and simulation using the coaxial geometry. From the legend: *Sim* = simulation results; *Meas.* = Results from experimental data shown in Figure 6.

4.3 Simulation of flow in other rheometer geometries

In practice, a vane rheometer is often used to determine the rheological properties of granular fluids like mortar and concrete because it is thought that the vane blade couples the rotor to the fluid better than a cylinder, especially one that is not serrated. No theoretical solution for a full three-dimensional vane rheometer exists, so it is a challenge to relate the measured torque and angular velocity to the actual constitutive equation describing the viscosity vs. shear rate of the fluid. However, a solution does exist for a theoretical two dimensional (zero thickness) vane (Sherwood and Atkinson (SA)[16]), which predicts that the measured viscosity, μ_m, from the vane rheometer is $\mu_m = \left(1 - \frac{1}{n}\right)\mu$. Here n is the number of blades on the vane, μ is the actual fluid viscosity of the fluid. This strategy suggests that the response from a vane rheometer can be approximated using a similar modification of the theoretical equation for the coaxial rheometer:

$$\mu = \frac{\mu_m}{1-\frac{1}{n}} = \frac{1}{1-\frac{1}{n}}\left(\frac{T(\Omega)}{\Omega}\frac{R_0^2 - R_i^2}{4\pi H R_0^2 R_i^2}\right). \quad \textbf{(4)}$$

In equation (4), T is the applied torque; the dimensions of the simulated vane are R_o=22 mm for the outer radius, R_i=11 mm for the blade radius, H=16 mm for the blade height; and Ω is the angular velocity of the vane. Using equation (4) with n=4, the value $\mu_m / \mu = 0.73$ was obtained, in good agreement with the theoretical value of 0.75. However, these results are dependent on the vane blade thickness. The ratio of the blade thickness to radius was selected as 0.0627, 0.0727, 0.0910, yielding viscosities of $\mu_m/\mu = 0.73$, 0.79, 0.82 respectively. The agreement is quite good with the idealized prediction of zero thickness blade of 0.75. Experiments performed by Ovarlez et al.[15] obtained results that were about 10 % higher than the prediction of Sherwood and Atkinson[16] for the case of n=6. Perhaps the higher value is a consequence of the ratio of blade thickness to radius which was equal to 0.15 in the experiment of Ovarlez et al.[15] Hence there is a tendency to over predict the viscosity even when correcting for n. However, discrepancies were only about 10 % which can be quite good for many applications.

The full vane rheometer is next modeled such that the vane has finite length, the blade thickness-to-radius ratio is 0.091, and there is a shaft. Repeating the same simulation as above, it was found that μ_m was equal to 0.9μ, which is quite similar to the actual viscosity of the fluid. In this case, there is an additional contribution of the drag at the top and the bottom of the blades as well as the narrow shaft. Surprisingly, these additional contributions allowed the vane rheometer to produce close values of fluid viscosity for this rheometer design. Values obtained by Olvarez[15] with n=6 are similar to our results.

4.4 Suspension modeling

The viscosity of a non-Newtonian fluid using a full 3D vane rheometer simulation will now be discussed. Here the matrix fluid is the same as the SRM, but the shear rate is offset (see section 4.2) to illustrate how the maximum viscosity can be capped at low shear rates. Figure 9 shows the theoretical viscosity of the paste as a function of shear rate. Simulation of the paste viscosity is in good agreement and indeed as in the case of the Newtonian fluid about 90 % that of the theoretical value. Adding the spheres produced a higher viscosity as expected and shown in Figure 9. In the future, an actual SRM paste will be modeled and compared to experiment with the same rheometer design.

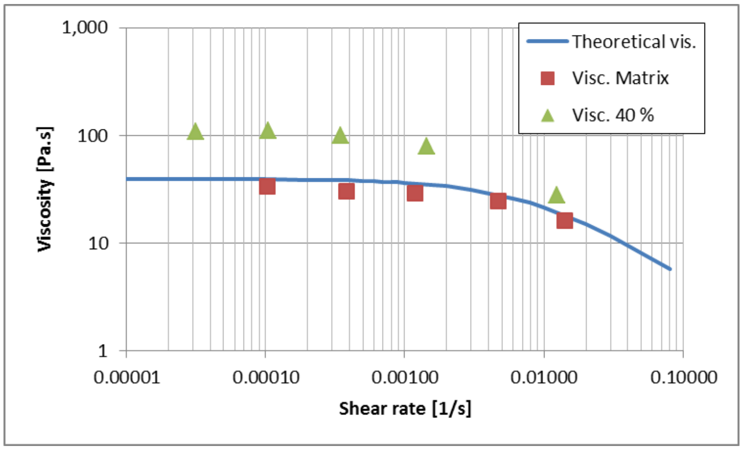

Figure 9: Viscosity simulated using a vane geometry. The matrix (0% beads) and 40 % volume fraction were simulated with the theoretical viscosity.

5. CONCLUSIONS

A Standard Reference Material (SRM) was developed to simulate the rheological properties of paste and it was used as a basis to initiate development of a mortar rheology SRM. The SRM mortar is made from the paste SRM by adding spherical glass beads. To determine its rheological properties in fundamental units, it was necessary to develop a computational model and to validate it with experimental measurements. This paper presents the preliminary results both from the simulation and from the experimental tests. The agreement between the model and the experimental data is reasonably good, providing validation to this approach. Nevertheless, the small discrepancies need to be further investigated by ensuring that no slippage occurs during experimental tests and that the model holds with other bead volume fraction and other beads diameters. Also, this approach needs to be validated with the other rheometer geometries frequently used such as the vane.

6. ACKNOWLEDGEMENTS

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