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LESSONS LEARNED, AND PITFALLS TO AVOID IN MODERN RHEOMETRY

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ABSTRACT: Rheometry is the measurement of rheological properties. Rheometry is essential to understanding and quantifying the flow behaviour of non-Newtonian fluids. Results may differ from one research group to another, or from machine to machine. We will address discrepancies that may arise from the conversion of the machine's rotational velocity to physical shear rate, ill-defined protocols, the occurrence of wall slip, (bottom) gap size variations, and differences in sample preparation. We confine ourselves to materials consisting of fine colloidal constituents, which form a homogenous carrier fluid with eventual coarse material augmenting the rheology, but are inert by themselves and prone to jamming your rheometer or may settle during the rheometric measurement. Wall slip may occur in rheometry, especially in smooth-walled geometries. Wall slip transpires when the composition of the mixture near the wall differs from that in the interior. A method to identify wall slip in rheometry involves comparing flow curves obtained from various geometrical dimensions, such as pipe/capillary diameter, sheared gap size, or radical testing with vane. Coarse constituents may promote wall slip, but surprisingly, we also encountered it in natural fluid mud without coarse particles. Measurements show that the narrow bottom gap, the mechanical default of the concerned rheometer using vanes, impacts results. The application of dedicated protocols to measure specific properties is another crucial aspect that is emphasized in this paper.

KEY WORDS: rheometry, measuring elements, conversion factors, wall slip, bottom gap, sample preparation.

1. INTRODUCTION

Rheology is important for the flow of particulate slurries in diverse industries and natural systems. Our applications are mainly found in Deltaic natural mud, clay suspensions in subsoil infrastructural activities, in resource industry slurries.

Deltares purchased their current main rheometer (Haake Mars 1) in 2015, after a CV100 that had meant a lot to our theoretical developments, services to industries, and research disciplines, had broken down. It meant a change from Couette to Searle type, the possibility of CSS mode testing, and the availability of a diversity of programmable and combinable protocols. The size and type of measurement elements were also different. Gradually, we adapted our protocols to the new possibilities. This was sped up by the joining of the second author in 2017, who came with skills and experience in relating the newly available protocols to particular aspects of rheology, gained by utilizing a similar modern instrument.

Rheometry can be conducted at different levels of detail. Our rheology finds its application in advice and consulting, in calculation models for free surface flows, in pipe flow, and in applied theoretical developments. With application in mind, it occurs regularly that it is asked for simple rheology, or simple rheology is proposed. This might be a pitfall, when you do not know what you are looking for. The current contribution might help to avoid known pitfalls and to obtain meaningful results, with an effort matching the adjective “simple”.

The material that is being encountered in a hydrodynamic/geotechnical institute’s work, that is eligible for rheometry, often consists of clays, silts, and sands. The clays introduce a non-Newtonian character because of the flocculated structure that changes with shear rate. Flocculated structure also changes with time because of the clay platelet's attractive charges. The flocculated clays (merged partly with silt) determine the base rheology, and sand augments this rheology. Hence, particle size distribution is important not only to rheological constitutive modeling, but also to the choice of measuring elements.

In the majority of our work, which is eligible for rheometry, we are facing high concentrations of clay. We acknowledge the different colloidial activities of clay minerals affecting rheology, and we follow and confirm existing theories stating that the rheology decreases with water content, and calibrate.

The growth and decay of the floc structure of clay aggregates introduces (reversible) time-dependance. Hence, we distinguish between unremoulded and remoulded conditions. Usually, the remoulded flow curve is needed, with initial strength being sheared away, corroborating the state-of-the-art flow models. On a number of occasions, the unremoulded conditions are important: for slow transient processes, and stability of the materials. It is rarely included in flow calculations.

2. THEORY

2.1. RHEOLOGICAL CONCEPTS IN CHARACTERIZING

Colloid structure may provide strength, and the material may yield. Definition, determination of yield points, and existence of non-Newtonian materials are debated in the literature, Barnes (2007). The yield point is defined as the lowest shear stress value above which the material will act as a fluid and below which it behaves like a very soft solid matter. This definition is subjective, because the boundary between the fluid-like and solid-like state is not discrete but continuous. Under different rheometry protocols, other yield points may appear. The transition direction (i.e., from fluid-like to solid-like or vice versa) is important. This is why, in materials with time-dependent strength (thixotropic), at least two different yield points can be distinguished. Engineering applications may require knowledge of various yield points, depending on the application. The principal yield points are as follows:

- The static yield stress (SYS): defined as the minimum stress required for initiating the (shear) flow in a stagnant material under stress.
- The dynamic yield stress (DYS): defined as the minimum stress required for maintaining a given material in flow.

Time-independent materials have unique flow curves. However, the flow behaviour of time-dependent materials may vary depending on their shear and resting history, resulting in different flow curves.

In applications for fluid flow, conditions' at very low shear rates, where shear stresses are below SYS and DYS, are not so relevant. Under those conditions elasticity becomes dominant, as oscillatory rheometry shows. Beyond yielding, the relation between shear rate and shear stress needs to be quantified, i.e., the flow curve.

Other points of relevance are the Bingham yield stress (BYS) and the dynamic Peak Shear Stress (PSS). Utilizing a Bingham model description, the plastic viscosity μ_∞ is the relevant parameter characterising the slope of the remoulded flow curve.

2.2. CSS AND CSR PROTOCOLS

In roto-viscometry two main operational modes are distinguished:

- the controlled shear rate (CSR) mode, in which the torque required to rotate a measuring element is measured at a pre-set speed or range of speeds. The measured torque values are then converted into shear stresses;
- the controlled shear stress (CSS) mode, in which the resulting rotational speed of a measuring element is measured at a pre-set shear stress or range of shear stresses, utilizing the same conversion. The measured rotational speeds are converted into shear rates.

Using these two operational modes, an infinite number of "rheological protocols" can be developed varying, the magnitude, duration, and sequence of the main variable in each mode. Two commonly used rheological protocols are illustrated in Figure 1 and typical results are given in Figure 2:

- CSS ramp-up-constant-down: shear stress (torque) increases stepwise (or continually) from a value close to zero to a predefined maximum shear stress within a user defined time window, followed by a constant shear stress at the maximum shear stress for a pre-set time, then shear stress is reduced again stepwise (or continually) to zero (Figure 1a). Throughout this shear stress (torque) loop, the shear rate is continuously measured.
- CSR ramp-up-constant-down: shear rate ascents stepwise (or continually) to a maximum shear rate during a predefined time, then is kept constant at the maximum shear rate for a given time, after which it descends stepwise (or continually) to a standstill (Figure 1b). Throughout this shear rate loop, the corresponding shear stress (torque) is continuously measured.

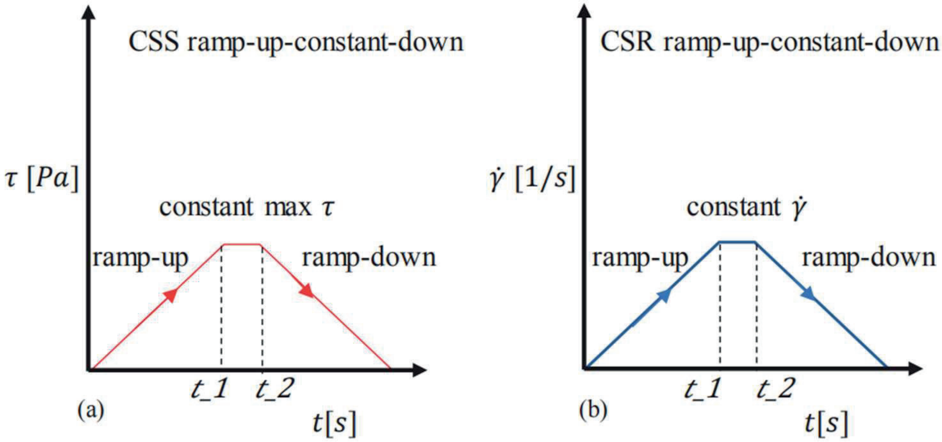

Figure 1 Definition sketch of two different protocols, τ = shear stress, $\dot{\gamma}$ = shear rate, Meshkati et al. (2021).

An infinite number of small steps can be applied in modern rheometers (a linear or logarithmic course with time can be programmed, we usually apply linear).

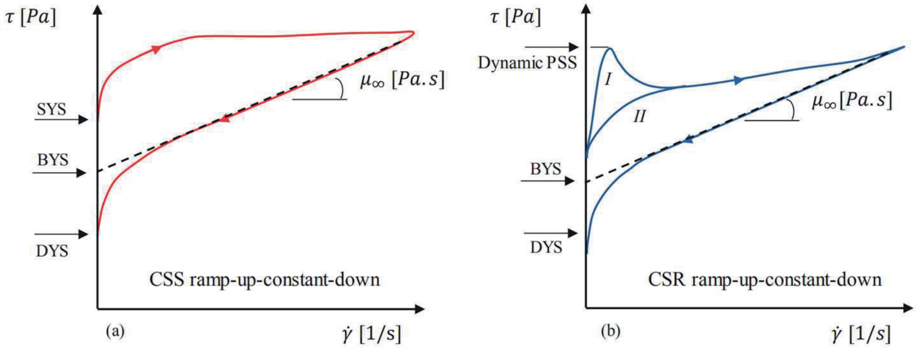

Figure 2 Rheological properties obtained with CSS and CSR protocols, Meshkati et al (2021)

2.3. CHOICE OF ELEMENTS

Rheometry can be conducted with measuring elements like, Figure 3; BC bob-cup (concentric cylinder geometry), PP parallel-plate, CP cone-plate, VB vane-in-bucket (Fisher et al., 2007), VC vane-in-cup (Barnes and Carnali, 1990), in a variety of geometrical dimensions. Of these, the cone-plate has the best-defined shear profile, but is very sensitive to the slightest grain. The horizontal plate orientation has the drawback that shear settling sand will lead to a weakened layer under the top plate. The bob-cup has a reasonable, well-defined shear rate, although not strictly uniform across the annular gap, but has some tolerance for shear settling sand. The vane comes with an ill-defined shear rate, but under certain conditions / protocol it can give meaningful results. The vane is least affected by the presence of sand.

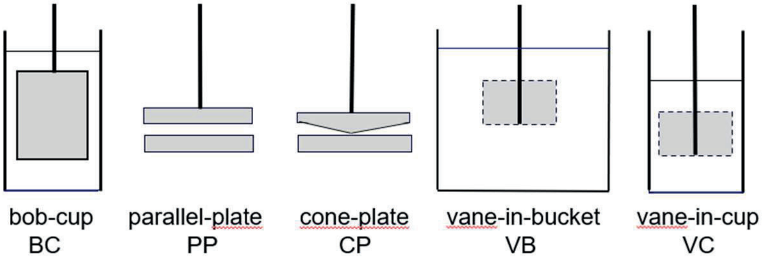

Figure 3 Examples of common type of measuring elements in rotoviscometry

2.4. SHEAR STRESS - SHEAR RATE IN CONCENTRIC CYLINDER GEOM.

In concentric cylinder rheometry the shear stress varies with radius, because of mechanical balance. Shear stress decreases outward because of torque. In the case of Newtonian fluid, this leads to a slightly varying shear rate across the annular gap. In case of the yield stress fluid tested close to the yield stress, this may lead to stagnant layers at the outer cylinder. There exist methodologies to eventually correct for that. For bob-cup, the Haake applies a set of conditions pertaining (wall shear stress, shear rate) to the bob's surface.

In geometrical configurations, a compromise is needed. Small gap to radius ratios are preferable to approach true Couette shear flow. But gap size cannot be too small because that might interfere with floc size of the clay aggregates.

It is further worth mentioning that during the course of our work, we came across an inconsistency upon application of a vane. The rotoviscometer displays, and digitally outputs shear rate in [1/s]. Applied formula to convert from the machines' rotational velocity Ω to fluid shear rate $\dot{\gamma} = M\Omega$ are documented in the associated manual, Thermo Scientific (2014). The manual states that for vanes M=1 is utilized, because the shear rate with a vane is ill-defined. So, it actually outputs its rotational velocity [rad/s], but on the machines' software and in digital output [1/s] is confusingly given for unit. Those are of course not the same. Therefore, utilizing a virtual effective bob approximation, Talmon and Meshkati (2022), we postprocess vane data-according to the same formula $M=2\delta^2/(\delta^2-1)$ as for the bob-cup system: where δ = diameter cup/diameter bob. For vane FL22 M=5.8 and for vane FL16 M=3.5, when these elements are applied in the Din CC 27 cup.

So, in every direct plot of vane element results (e.g., given by the machine's software, but also in reported results, Ma et al. (2021), Shakeel (2022)), rotational velocity [rad/s] is displayed instead of shear rate [1/s]. This also affects reported viscosities and hampers interpretation.

2.5. SHEAR STRESS AND SHEAR RATE IN PIPE FLOW

Like in rotoviscometry, the reference for conversions is the Newtonian fluid. In the laminar flow of a Newtonian fluid, the shear rate at the wall is 8U/D. This is called the bulk shear rate. However, with non-Newtonian shear thinning fluids, the wall shear rate is higher. If we plot wall shear stress (determined from the measured pressure drop) vs. bulk shear rate, we have created a pseudo-rheogram. Mooney (1931) gives a procedure to estimate the true wall shear rate from such a pseudo-rheogram, utilizing the local slope of such a flow curve. We have applied this method in the ARM pipeviscometer, van Wijk et al., (2023). Built as an inverted U-loop, the ARM has a vertical orientation to prevent sand from settling in measurement sections. Compensated for measured density, the results of the three different pipe diameters available in the ARM collapse onto one flow curve, and the measurements correspond well with associated rotoviscometric measurements.

Instead of the Rabinowich Mooney transformation procedure, it is also possible to fit the non-linear analytical solution to the data (velocity and pressure drop combinations). Chryss et al. (2019) used the extended Buckingham equation (Govier Aziz 1977) to find the values of the three rheological parameters of the Hershel Bulkley model.

2.6. WALL SLIP CORRECTION

Wall slip occurs when the composition of the mixture at the wall is not exactly the same as in the interior of the mixture, Cloiture and Bonnecaze (2017). Checking for wall slip requires measurement at different pipe diameters at the same wall shear stress, or if driven by the same pressure difference; with $\Delta z/D$=constant, after which a Mooney (1931) analysis can be performed. Figure 4 portrays the principle: for three different pipe diameters evaluated at the same wall shear stress, the circular data points indicate wall slip with slip velocity v_s, while the square data points show zero wall slip.

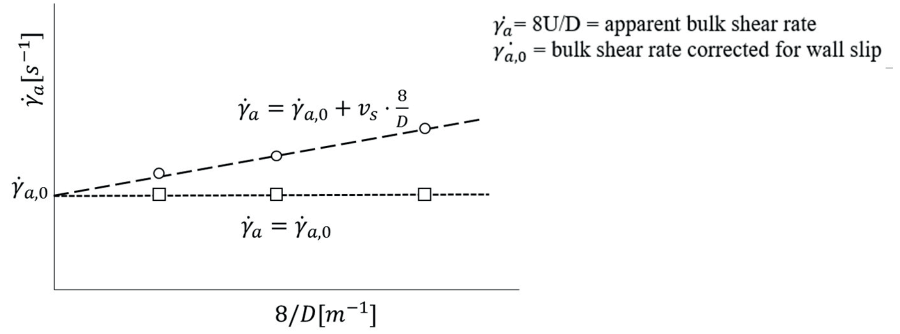

Figure 4 Plotting for correction for wall slip and calculation of wall slip velocity. If for the same wall shear stress, the (bulk) shear rate varies, there is wall slip. By fitting the true bulk shear rate is found at the vertical axis and the wall slip velocity v_s follows from the slope of the fit.

Intersection with the vertical axis is the sought-after bulk shear rate 8U/D. Because the thickness of the wall slip layer is assumed to be governed by shear stress and not by pipe diameter, wall slip becomes negligible for infinite pipe sizes. This principle is not limited to pipes, it can also be applied to other geometrical variations: e.g., gap size in parallel-plate rotoviscometry.

An effective way to verify the occurrence of wall-slip in rotoviscometry with elements having well defined shear rates, is to additionally conduct tests with a vane (Barnes and Carnali 1990, Boger et al., 2008, Buscall et al., 1993.

3. EXPERIENCES

3.1. SAMPLE PREPARATION & COMPOSITE PROTOCOL

Sample preparation and handling are important and will definitely be different between different individuals. It will mainly affect the measured unremoulded state properties, as per definition, in the remoulded state, initial conditions are lost. We only experienced, in some kaolinite/illite materials, an increase in strength during rheometry. It is suspected that the material was not mixed sufficiently intense during preparation.

We may adhere to a strict separation of CSS and CSR protocols. With thixotropic materials however, it is convenient to have a CSS for ramp-up and a CSR for down-ramp. It is illustrated in Figure 5. The SYS is measured in the CSS ramp-up and the remoulded flow curve in the CSR ramp-down. Such a composite protocol might reduce the number of tests, but some repeats will be necessary, and the max shears stress of CSS ramp-up might not be estimated correctly: SYS is not reached. When in CSS the imposed shear stress is higher than SYS, depending on material, the element might commence running at a high rotational velocity, not being able to find equilibrium, a max shear rate is however imposed. Depending on dynamics, major transient excursions may be present in the raw data, which is no reason for worry since this is not part of the controlled measurement and is rejected in analysis.

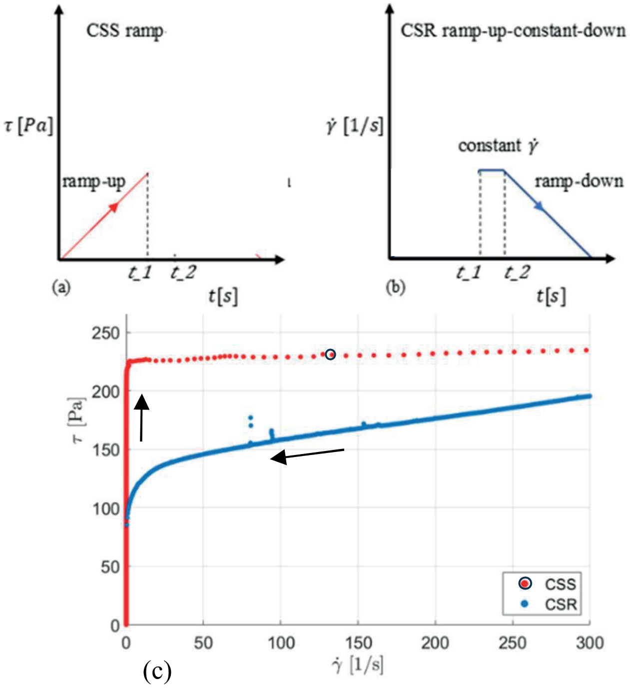

Figure 5 Example of composite protocol and result: a) & b) composite protocol, c) example: shear stress as function of shear rate, van Rees (2022).

3.2. SAND JAMMING

A problem in the rheometry of non-Newtonian mixtures with sand is the jamming of the instrument. Particularly, bob-cup elements are sensitive to it.

In CSR mode, the torque will show peaks, but rotation continues. In that case spiky signals results, of which the lower bound is the required flow curve. In CSS mode, however, upon jamming, the torque remains the same, but the rotation stops. Figure 6 shows the jamming of a vane in CSS mode. Afterwards, comparing with other data, it is concluded that at first, the instrument tried to follow the unremoulded branch (at 15 Pa), got stuck, freed itself at higher torque, but got stuck again. This repeated until the apparatus broke loose and started to rotate fast, trying to find equilibrium. This measurement happened to be the first of a series, and it made the researchers wonder, what is the static yield stress? The same graph also contains the remoulded flow curve, measured by CSR, still some sand peaking, but stresses are remarkably lower than the initial CSS data.

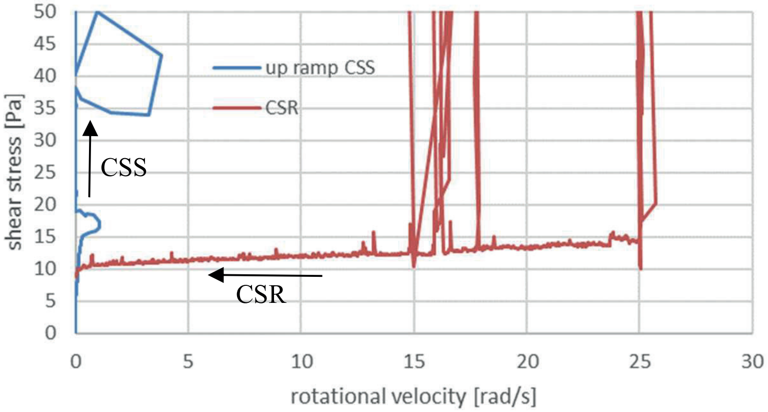

Figure 6 Example of sand jamming(s) with vane FL22, Asian mud.

3.3. WALL SLIP

The rheology of the material is not well measured if wall slip occurs. Rotoviscometric testing with different measuring elements might reveal wall-slippage with certain elements. The vane element is least prone to wall slip. Rheometric wall-slip is not specific to industrial slurries and appears in natural (fluid) mud as well, mostly found in harbours and estuaries, and its characterization is important too. In natural (fluid) muds, contrary to industrial muds, coarse solids are absent. However, similarly, (clay) colloids govern their non-Newtonian flow characteristics. We elaborate on wall-slip in some existing resource industry rheometry data and compare them with typical recent results of fluid mud rheology, Talmon & Meshkati (2022). Applying a grooved bob instead of a smooth cylinder did not help much. The wall slip is illustrated in some of the data in the next Section.

3.4. CONFINEMENT

Small gap size may increase shear stresses because of confinement, this is seen in Figure 7, which occurs for a 1 mm gap PP-element. Apparently, the gap size is smaller than the correlation distance of structure within the fluid. Jamming effects emerge. So, the higher shear stresses for the 1 mm gap, for shear rates <5 [1/s], indicate that the unsheared clay aggregates may have a size of 1 to 2 mm.

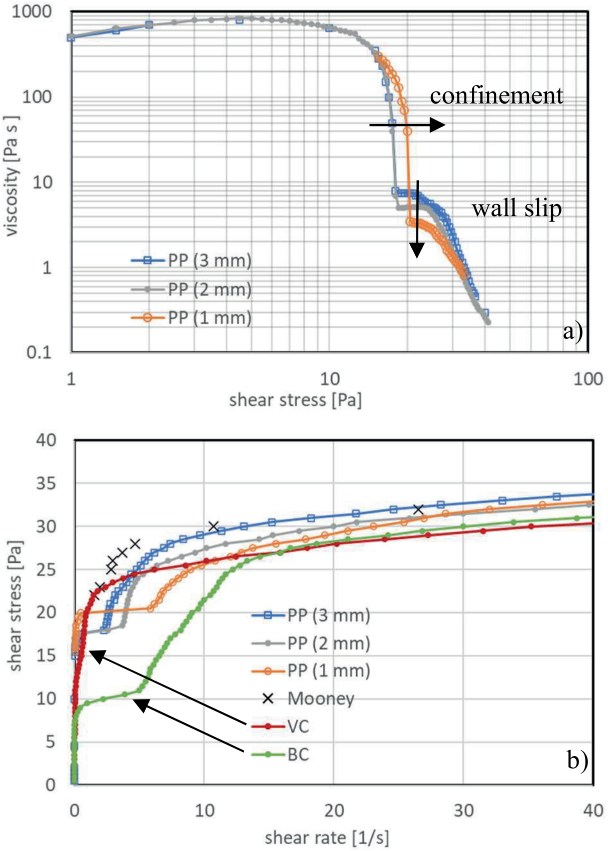

Figure 7 Confinement effect and wall slip in parallel-plate including Mooney wall slip correction, after Talmon and Meshkati (2022).

Figure 7 also reveals a wall slip. The flow curves for the 3 different gap distances are shifted. We applied the Mooney wall slip correction procedure. As seen in Figure 7, this projects the data back to lower shear rates, close to the vane results. This demonstrates that a vane is a better element for this type of mixture. Note that parallel plate outputs calculate shear stress at the rim, overestimating yield stress in fluids.

The graph also includes a bob-cup measurement, which gives an entirely different result, revealing impressive wall-slip (performing worst of all).

3.5. BOTTOM GAP

To examine SYS values as a function of bottom gap size, we computed SYS as the mean shear stress at incipient motion (between 0.1 and 0.2 [1/s]). This is just after yielding, where shear stress is representative of yielding. As can be seen, in Figure 8, SYS values decrease with the bottom gap size. Hence, application at 1 or a couple of millimetres above the bottom of the cup gives a too high value.

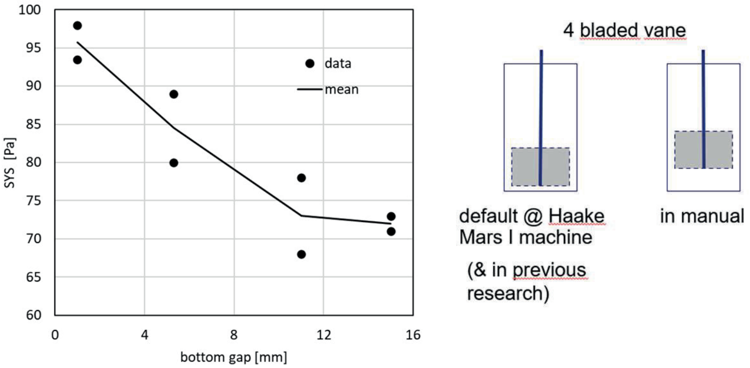

Figure 8 SYS value as a function of bottom gap using the FL22 vane-in-cup geometry for unconsolidated Calandkanaal mud, after van Rees (2022).

It is better to follow the manufacturer's manual. Only in case where available sample volumes are small, less sample material is needed when a vane is applied close to the bottom, it may be interesting to investigate this further.

4. CONCLUSIONS

It is exciting to see that wall-slip does not only occur in the case of dispersed coarse particles, but also in the absence of those.

It is necessary to check the results of viscometers: not every element gives the shear rate that you expect it to give (a pitfall). Beyond the low shear wall slip region, flow curves coincide much better.

We encountered the rarely identified confinement effect.

We show, the otherwise not quantified, influence of bottom clearance in vane-in-cup rheometry: closer to the bottom, greater shear stresses: e.g. the pitfall of not consulting formal information.

We are inclined to use the vane-in-cup more often: less problems with sand, but also a radical suppression of wall slip at low shear rates, which would occur with the better defined bob-cup geometry (pitfall: the idea that a bob-cup gives better defined rheometry, is basically true, but not at low shear rates: where it is risky).

Simple rheometry exists, but you need to know what you are looking for and why. This overview might help to choose the protocol and element that suit you the best.

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