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Investigating the caking phenomena of a novel dual emulsifier and fluid loss additive to establish control specifications for storage

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Abstract

We recently developed a powdered additive with excellent emulsifier and fluid loss performance (Henry et al. 2020). We learned that some similar powders under certain storage conditions can exhibit caking, which presents a problem upon storage and dispensing of products. To address this challenge, we studied the caking phenomena and endeavored to set tight control specifications.

An in-house test was developed to replicate the behaviors of the powdered additive under typical and stressed warehouse conditions. First, a statistical design of experiment (DOE) was established to examine factors of moisture content, compaction pressure, temperature, temperature cycling and storage period. These experiments demonstrated that a moisture content of > 5%, a compaction pressure of > 3 psi and elevated temperature can cause powdered additives to cake. The conclusion of the first DOE was corroborated by the result of a second experiment on a powder rheology shear cell test. The powder rheology shear cell test yields a single parameter, the flowability function, to compare the flow of powders. A flowability function value of < 2 shows impaired flow of powders. The powder rheology shear cell experiment yielded a flowability function > 3 for the powdered additive having < 5% moisture. These values also compared favorably with the flowability functions of common powder drilling fluid products.

In conclusion, we established the control specifications for the powdered additive to mitigate caking during storage. The specifications were developed with the help of an in-house test and further corroborated with the flowability function determined on the powder shear cell geometry.

Introduction

Caking is a deleterious phenomenon in which a low-moisture, free-flowing powder is transformed into lumps and then into an agglomerated solid resulting in loss of ease of handling (Aguilera et al. 1995). Caking of powder has adverse effects on solubility, mixing and dispersion, resulting in loss of products, delays in launch and consumer complaints. It causes storage and handling issues including hopper/bin arching and ratholing, resulting in no flow (Thakur et al. 2014). The cost of unproductive cake products was in an excess of 1 billion dollars in the U.S. alone in 1985 (Griffith 1991). This problem is abundantly observed in the food, feed, fertilizer, pharmaceutical and related industries (Aguilera et al. 1995). In our literature research we did not observe caking as a common phenomenon in the oilfield industry. There are many factors that need to be considered when predicting caking behavior, including cohesion, elasticity, yield stress, amorphous content, hygroscopicity, particle size, temperature, relative humidity (RH), stress, strain rate and vibration (Zafar et al. 2017). In a few articles, temperature and humidity are considered the most critical factors that influence caking (Fitzpatrick et al 2010) (Hirschberg et al. 2019).

In a particular research study (Chen et al. 2017) a parameter the critical glass transition relative humidity (RH_T) was determined for amorphous powders, polyvinylpyrrolidone and hydroxypropyl cellulose. As these powders are exposed to higher RH than the RH_T these powders exhibit rapid uptake of moisture and transform into a bonded or glassy state to undergo irreversible caking. The authors showed that with an increase in temperatures and moisture content, the powder shows a decrease in RH_T, thus increasing the chances of caking in these powders.

The literature cites quite a few methods to predict caking in powders:

1. Methods which involve cohesion between particles like the powder flow cell and powder shear cell (Anton Paar D43IA011EN-C 2021).
2. Angle of repose test (European Pharmacopoeia 6.0 2008).
3. Compressibility / Carr Index (CI) & Hausner Ratio determined from initial bulk density (ρ_{bulk}) and final tapped density (ρ_{tapped}), (European Pharmacopoeia 6.0 2008).
4. Flowability that involves discharge of flow of powder through an orifice (European Pharmacopoeia 6.0 2008).
5. Sieve methods that use a certain mesh size to quantify caking in powders (Aguilera et al. 1995).
6. Ball indentation methods to measure the hardness of cakes (Chen et al. 2017).

We recently developed a novel spray dry additive (SDA) (Henry et al. 2020) that performs exceptionally as a fluid loss additive and primary emulsifier. As the chemistry of this SDA is hygroscopic, it is prone to caking. Our previous experience with similar chemistries demonstrated that the use of anti-caking agents may be ineffective. Therefore, we took a deeper dive into the caking phenomena of the SDA to understand and mitigate it in this study.

Methods

The tapped final density (ρ_{tapped}) used to calculate the Carr Index (CI) was determined with a 250 ml cylinder and after 5000 taps on an Auto-tap instrument procured from Quantochrome.

Equilibration of samples (to achieve high moisture content) at given temperature and relative humidity (RH) was done in a EZT-570S Environmental chamber procured from Cincinnati Subzero. The drying of the samples for moisture determination was conducted in a model Binder oven typically at 105°C until constant weight was achieved.

The 2"×2", 4 mil zip lock plastic bags used for the caking DOE study were procured online from ClearBags. The statistical DOE analysis was done with JMP version 16.

The powder rheology study was conducted on an Anton Paar Modular Compact Rheometer (MCR 302) equipped with a convection temperature device (CTD 180), a humidity generator (MHG 100) and a powder shear cell. The central parts of the powder shear cell in this study were the measuring cup C-PSC32 and measuring geometry PSC32-21-9. The analysis of the powder rheology curves was done with the RheoCompass™ version 1.26 software.

Results and Discussions

Compressibility / Carr Index and Degree of Caking

Compressibility is a measure of the relative volume change a sample undergoes when pressure is applied (Anton Paar D43IA011EN-C 2021). The compressibility index (also referred Carr Index, CI) is a simple, fast, and popular method of predicting powder flow characteristics. The CI is proposed as an indirect measure of bulk density, size and shape, surface area, moisture content, and cohesiveness of powders. The CI is calculated with the below Equation 1 (European Pharmacopoeia 6.0 2008).

$$CI = 100 \times \left(\frac{\rho_{tapped} - \rho_{bulk}}{\rho_{tapped}} \right)$$

The CI determined for two lab prepared SDA samples, a caking standard and a few commercially available drilling fluid chemicals are given in Table 1 . The lab prepared SDA samples had roughly 4 – 6% moisture, were taken as is to determine the CI.

The caking phenomena is quantified in the dairy industry for milk powders and whey powders with the GEA Niro method no. A 15 a (GEA A 15a 2005). This method was followed in principle, wherein a small quantity of the sample powder was exposed to a high relative humidity of 80% in the environmental chamber for roughly 12-14 hours until equilibrium is reached. This humidified powder is then dried in Binder oven at 105°C till a constant weight is reached and after cooling in a desiccator for a few minutes it is sieved through a US # 10 (2mm sieve openings), the method gives a parameter the degree of caking calculated with the below Equation 2.

$$Degree\ of\ caking\ = \frac{100 \times weigh\ \ of\ powder\ left\ on\ sieve}{weight\ of\ powder\ used}$$

A powder sample that is very hygroscopic, typically undergoes a phase transformation and looks glassy after drying. The degree of caking determined by this method for the lab prepared SDA samples, the caking standard and a few commercially available drilling fluid chemicals is given in

Table 2.

On comparing the CI with the degree of caking we conclude that the lab prepared SDA and caking standard exhibit fair and passable flow as per CI but exhibit extreme caking as per the GEA Niro method A 15 a. The drilling fluid chemicals exhibit poor flow as per CI but exhibit non-caking behavior as per GEA Niro method A 15 a.

The GEA Niro method A15a is a pass-fail test for caking that exposes the powder to a very high humidity causing phase transformation. However, in our industrial practice a powder is typically stored under specifications to prevent caking. The CI method was also not useful in predicting the caking behavior of the powders.

The goal of this study was to determine the specifications needed to keep the powder free flowing during and after storage.

Caking study by Design of Experiments (DOE)

On review of the literature for powder caking and our consultations with oilfield experts we shortlisted the below factors that can heavily influence powder caking.

1. Moisture content of the powder
2. Humidity effects on powder
3. Temperature and temperature cycles during storage
4. Particle size, shape and charge
5. Compaction levels
6. Packaging material to limit moisture uptake
7. Duration of storage

The effect of particle size, shape and charge on powder caking was beyond the scope of this study. Our preliminary work on the reactor scale spray dryer showed that as the particle size increases the moisture content increased as given in Table 3. A high moisture in the powder increases the chance of caking (Chen et al. 2017), therefore, we aimed to produce a higher particle size with less moisture. A large particle size is preferred since a small particle size, due to its high surface area, exhibits increased cohesion with adjacent particles, leading to poor powder flow (Geldart 1975).

We developed our own method to simulate warehouse storage and to quantify the SDA powder caking: a DOE was constructed. The factors chosen for this DOE study with their high and low range are given below.

DOE Factors	Low Range	High Range
Moisture in powder, %	2.18	9.92
Temperature, °C	2	45
Compaction, psi (kpa)	1.6 (11.03)	6.5 (44.82)
Duration, days	6	90
Temperature cycle	No	Yes

The SDA samples of the DOE study were:

1. As is, samples from four batches produced on a reactor scale spray dryer with moisture contents from 2 – 4 %, refer to Table 3
2. A few lab-prepared, as is, spray dried SDA samples with moistures typically between 4 – 6 %.
    a. The D50 particle size varied between 10 and 20 µ.
3. High moisture samples of SDA # 4 (up to 7.51%) and lab prepared SDA (up to 9.92 %).
    a. These samples were produced by equilibrating, as is, samples in an environmental chamber with controlled humidity.

To simulate the bags in the warehouse, 2" × 2" zip lock 4 mil. plastic bags were used. Each zip lock bag was filled with roughly 5 - 6 g of the SDA sample. The bag opening was further sealed with masking tape to make it airtight. About 64 such bags were prepared for the DOE runs.

These SDA filled zip lock bags were compacted with multiple 2.5 and 5 lbs. weights to achieve the desired compaction pressure. A compaction of 1.6 psi simulates a stack of 20 bags (20" × 31") of 50 lbs. each whereas as a compaction of 6.5 psi simulates a stack of 3 big bags (35" × 35") of 2000 lbs. each.

The experiments at 2°C were conducted in an environmental chamber and those at 45°C were conducted in an incubation oven which housed the compaction set-up.

The experiments were conducted from 6 – 90 days and after that the bags were immediately opened and sieved on a US # 10. The degree of caking was determined for each bag using Equation 2. The data was statistically analyzed with the response surface method.

The moisture content and temperature were identified as the most significant factors for this DOE study. These same factors were identified by previous research to heavily influence powder caking (Chen et al 2017), (Fitzpatrick et al 2010) (Hirschberg et al. 2019). Both, moisture content and temperature had a P-value of 0.000. The other factors of the DOE were included for improved R^2 prediction in the model.

The summary of fit for this DOE model is shown to the right. The R^2 prediction is roughly 79% which indicates that the model has very good prediction capability.

Summary of fit	
R^2	0.870
R^2 adjusted	0.846
R^2 prediction	0.793
Observations	64

The contour plot of this DOE model is given in Figure 1, the pink shaded area is the caking region and the white area is the non-caking region. The star marker is presented in the white region that shows no-caking at a moisture content of 5% and 45°C irrespective of the compaction pressure used between 0 – 6.5 psi. The contour plot shows that at temperatures lower than 30°C no caking is observed even at 6% moisture irrespective of the compaction pressure between 0 – 6.5 psi.

In conclusion, the DOE study demonstrated that at a moisture content of 5% and temperatures ≤ 45°C, no caking is observed irrespective of the compaction pressure between 0 – 6.5 psi.

Powder Shear Cell Study

In these experiments, the powder sample was loaded into the measuring cup C-PSC32 placed within the CTD 180 on the MCR 302. The sample was then allowed to equilibrate at 30% relative humidity (RH) for 10 minutes at the temperature of interest. The 30% RH was determined as the appropriate humidity level at which minimum changes occurred in the moisture content of the powders.

The measuring geometry PSC32-21-9 is then lowered to make contact with the powder sample for the duration of the test. In the first step, a defined pre-compaction (pre-shear normal stress) is applied till it reaches steady state, then each pre-shearing step was accompanied by multiple shear-to-failure steps.

The measurement scheme for testing different powders for their flowability in this study is given in Table 4. A sample shearing diagram is shown for SDA # 3 powder in Figure 2.

At the shear-to-failure in each individual shear sequence, the maximum shear stress at the corresponding normal stress points were taken to construct the Mohr stress diagram (shear stress τ vs. normal stress σ_n) as given Figure 3 for SDA # 3 powder.

The yield locus function is obtained from this Mohr's stress diagram to give multiple co-efficient of interest (Anton Paar D43IA011EN-C 2021). For this study we will limit our discussion to the coefficient of flowability / flow function (ff_c). The ff_c interprets powder flow to compare different powders or the same powder in different conditions like temperature, humidity, compaction etc. (Anton Paar D43IA011EN-C 2021). The powder flow can be classified as below

1. $ff_c < 1$, powder does not flow
2. ff_c between 1 and 2, powder is very cohesive
3. ff_c between 2 and 4, powder is cohesive
4. $ff_c > 4$, powder is easy flowing

The ff_c was determined for the reactor scale SDA batches, the high moisture versions of SDA # 4 at 5.51% & 7.51% and commercially available drilling fluid chemicals.

In Figure 4, the ff_c of powder samples are given as determined at 25°C and 10 kpa (1.45 psi). This pre-shear normal stress simulates a stack of 20 bags over each other as discussed previously. The reactor scale powder SDA batches exhibited $ff_c > 3$, implying better flow in the cohesive region. The powder SDA # 2 had a ff_c of 3.9 implying easy to flow. The drilling fluid chemicals OGL (organophilic lignite), OCL (organophilic clay), hydrated lime and GM (ground marble) – 25µ exhibited $ff_c > 4$, imply easy flowing powders. The GM – 5µ and SDA # 4 with 7.51% moisture exhibited ff_c between 2.7 – 2.9, implying cohesive powders but still flowable.

In Figure 5, the ff_c for the powder samples are given as determined at 45°C and 20 kpa (2.90 psi). This pre-shear normal stress simulates a stack of 3 pallets, each pallet weighs 2000 lbs with dimensions 48" ×40". The DOE study in the previous section had shown that the SDA powder with moistures > 5 % exhibit caking at temperature of 45°C, hence these experiments were run at this high temperature. The reactor scale powder SDA batches 1, 2 and 3, exhibit $ff_c > 3$, whereas powder SDA # 4 exhibit ff_c of 2.8 and was more cohesive. The powder SDA # 4 with 5.51% moisture had an ff_c of 1.4, implying a very cohesive powder and poor flow whereas the powder SDA # 4 with 7.51% moisture had an ff_c of 0.4, implying a non-flowing powder. The drilling fluid chemicals OGL, hydrated lime GM – 25µ and GM – 5µ exhibit ffc > 4, implying easy flow. However, the OCL had a ffc of 1.9 implying very cohesive powder and poor flow.

From the powder shear cell study on the SDA powders, we conclude that it is imperative to limit the SDA powder moisture content to less than 5% to prevent caking and thus have better flow after storage.

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Packaging Study for the SDA

As the next step, we investigated the appropriate bag packaging material to limit absorption of moisture to the SDA powder in the bag. We consulted with a third-party bagging vendor and ran an accelerated aging study for five weeks at 45°C and 80% RH in an environmental chamber. Four different thickness of inner polyethylene-(PE) lined kraft bags were used for this study - 0.5 mil, 1 mil, 2 mil and 3 mil. Multiple bags made with these packaging materials were filled with powder SDA # 2, sealed, and placed in the environmental chamber.

Each week, a bag was weighed to determine the uptake in moisture and opened to observe its flow character. At the end of the study, it was concluded that a 3 mil PE-lined bag was the best to limit uptake of moisture. The visual flow behavior of the SDA powder from bags lined with 0.5 mil and 3 mil PE are shown as examples in Figure 6. Lumps were observed in powder from the 0.5 mil PE-lined bags, whereas the SDA powder from the 3 mil PE-lined bags was easy flowing without any lumps.

Conclusions

- The Carr Index and the degree of caking determined as per the GEA Niro method A 15a did not provide information on the specifications needed to prevent caking of SDA powder.
- The DOE study demonstrated that:
    - The SDA powder needs a moisture of < 5 % to prevent caking irrespective of the compaction pressure up to 6.5 psi and temperatures up to 45°C.
    - No caking occurs even at a moisture up to 6% for temperatures < 30°C irrespective of the compaction up to 6.5 psi.
- The powder shear cell study demonstrated that
    - The SDA powders have an $ff_c < 2$ for moisture > 5 % at 45°C and 20 kpa.
    - The SDA powders exhibit an $ff_c > 2.5$ for moisture < 5 %, irrespective of the temperature and compaction of this study.
- The bag packaging material accelerated ageing study demonstrated that a 3 mil PE lined bag limits the uptake of moisture to the SDA powder in the bag.

In conclusion, the SDA powder needs a moisture content less than 5% and preferably lower and packed in a 3 mil PE lined bag to prevent any chance of caking.

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Nomenclature

CI = *Carr / Compressibility Index*
DOE = *Design of experiments*
ffc = *Coefficient of flowability / flow function*
GM = *Ground marble*
OGL = *Organophilic lignite*
OCL = *Organophilic clay*
PE = *Polyethylene*
PSD = *Particle size distribution*
RH = *Relative humidity*
RH_T = *Critical glass transition relative humidity*
SDA = *Novel spray dry additive*
D50 = *Size in µ, known as the median diameter*
kpa = *Kilo pascal*
lbs. = *pounds*

psi =*Pounds per inch*^{2}
Pa =*Pascal, unit of stress*
μ = *microns*
ρ_{tapped} = *Final auto-tapped density*
ρ_{bulk} = *Initial bulk density*
τ = *Shear stress in Pa*
σ_n = *Normal stress in Pa*

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Tables

Table 1: Carr Index determined on auto tap instrument at 5000 taps and 23.5°C

Sample	Carr Index in %	Characterization as per European Pharmacopoeia
Lab-prepared SDA sample @ 5.78% H_2O	19	Fair flow
Lab-prepared SDA sample @ 4.45% H_2O	17	Fair flow
Caking standard	25	Passable
Hydrated Lime	37	Very poor flow
Ground marble, D50 = 5µ (GM - 5 µ)	39	Very poor flow
Ground marble, D50 = 25µ (GM - 25 µ)	36	Very poor flow
Organophilic lignite (OGL)	23	Passable
Organophilic clay (OCL)	30	Poor flow

Table 2: Degree of caking determined by adapting the GEA Niro method A15 a in principle

Sample	Degree of caking on sieve, US # 10	Standard deviation	Characterization as per GEA Niro A15a
Lab-prepared SDA sample @ 5.78% H_2O	50.0	2.8	Extreme caking
Lab-prepared SDA sample @ 4.45% H_2O	68.3	10.0	Extreme caking
Caking standard	67.3	7.4	Extreme caking
Hydrated lime	0.0	0.0	Non-caking
GM - 25 µ	0.0	0.0	Non-caking
OGL	0.0	0.0	Non-caking
OCL	0.0	0.0	Non-caking

Table 3: Moisture content and particle size distribution (PSD) of reactor scale spray dried samples

Samples	% moisture by oven method @ 105 °C	Standard deviation of % moisture @ 105 °C	PSD, D50 µ
SDA # 1	2.18	0.32	25.67
SDA # 2	2.49	0.02	32.93
SDA # 3	3.53	0.39	39.92
SDA # 4	4.05	0.4	57.47

Table 4: Overview of sample measurement conditions for testing on flowability

Temperature °C	Relative Humidity %	Pre-shear normal stress kpa (psi)	Shear-to-failure normal stress steps kpa
25	30.0	10 (1.45)	2, 4 & 6
45	30.0	20 (2.90)	4, 8 & 12

Figures

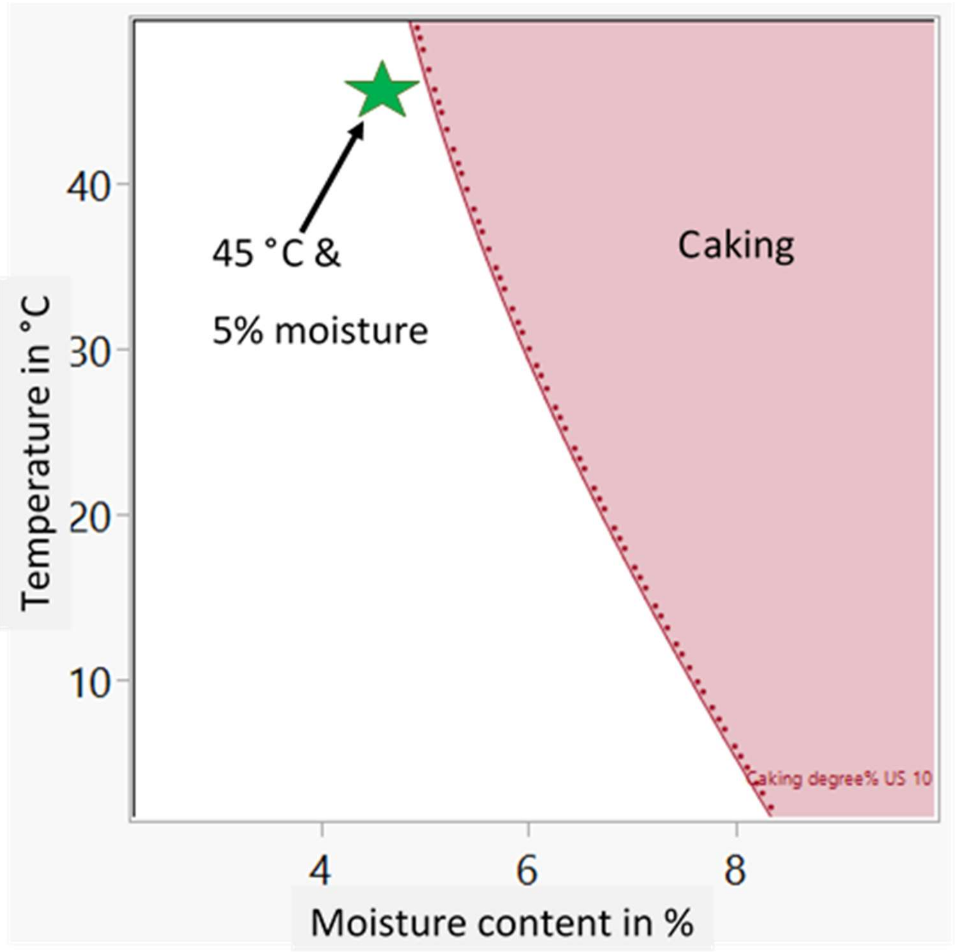

Figure 1: Contour plot of degree of caking of SDA as a function of temperature and moisture

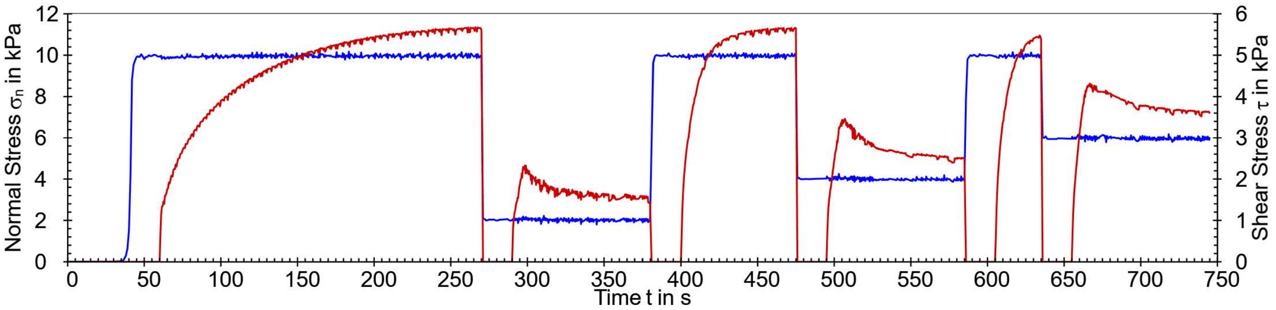

Figure 2: Shear diagram of pre-shearing at 10 kPa and intermediate shear phases (shear-to-failure) with different normal stresses at 25°C for SDA # 3. The normal stress σ_n is in blue while the red curve depicts the shear stress τ.

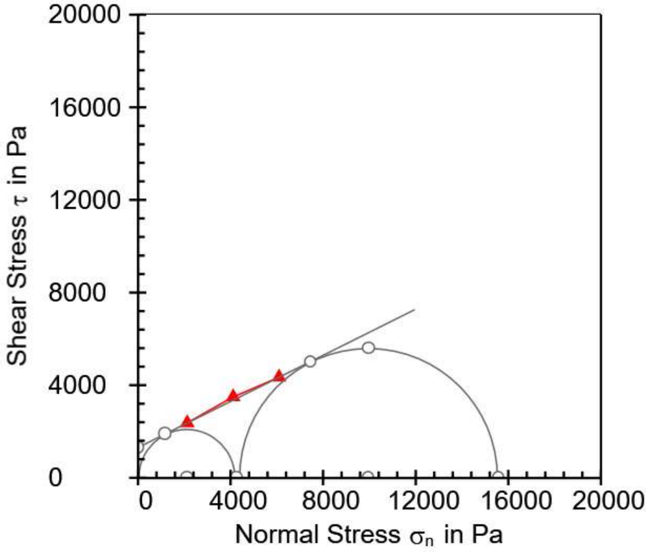

Figure 3: Mohr's stress diagram for the pre-shearing at 10 kPa of the sample measured at 25°C

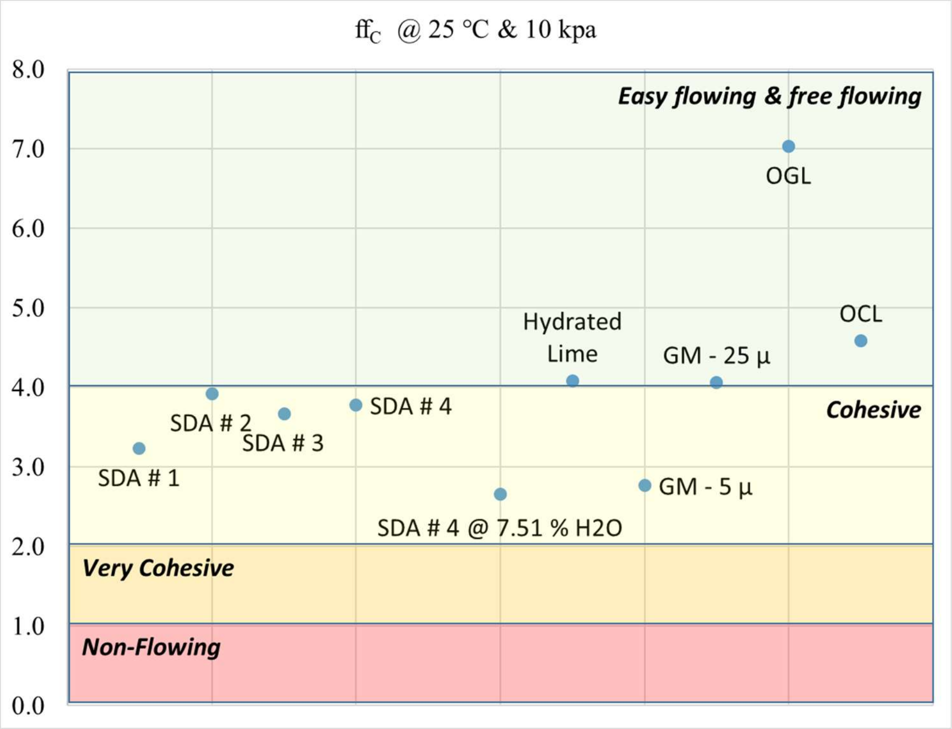

Figure 4: Flow function, ff_c (y-axis) for different category of samples (x-axis) at 25°C and pre-shear normal stress of 10 kpa (1.45 psi)

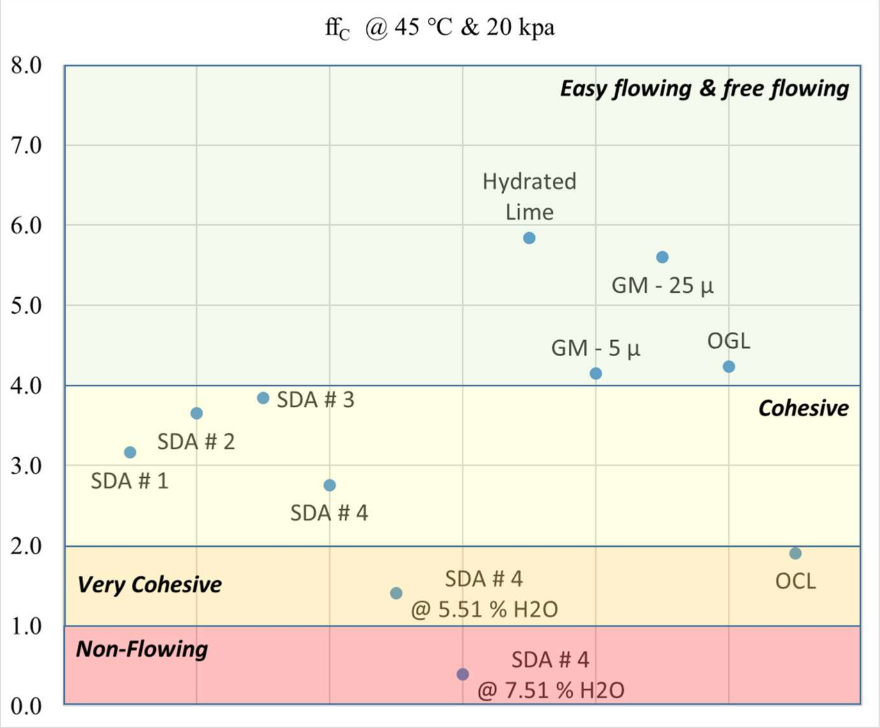

Figure 5: Flow function, ff$_c$ ((y-axis)) for different category of samples (x-axis) at 45°C and pre-shear normal stress of 20 kpa (2.90 psi)

Figure 6: Flow behavior of SDA powder after opening the bags, **A** refers to SDA powder from 0.5 mil PE lined bag and **B** refers to SDA powder from 3 mil PE-lined bag