The Effect of Agglomeration on the Emission of Particles from Nanopowders Flow

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This paper suggests an original method to evaluate the possible emission of particles from a nanopowder submitted to a shear stress in dense phase and the resulting degree of agglomeration of the particles released. The method is based upon the monitoring of the rheological signature of the nanopowders, thanks to a powder rheometer. As a function of the increasing shear rate, the powder flow will evolve from the newtonian state (dense powder) to the coulombian state (dense rheofluidified phase). If the shear rate is high enough, the powder will be set in suspension and the kinetic state (a leaner dense phase submitted to particles collisions) will be reached. The shear stress in this state is dependent on the particle or the agglomerate diameter for cohesive powders, which can be then calculated from rheograms. Carbon black and silica nanopowders have been tested and compared to other experiments carried out on non cohesive glass beads microparticles, chosen as reference. For the different glass beads powders, the average value of their "agglomerate" diameter is 12% different of the primary diameter, indicating agglomeration of less than two particles. Nanometric agglomerates were found to be of hundred micrometers diameter. That is in line with the high tendency of the nanoparticles to agglomerate. This work can be used to evaluate the current safety tests, such as Hartmann's tube or 20 L sphere apparatuses, to verify whether the standard equipment for microparticles is suitable for the use of nanoparticles. This is linked to research projects like NanoSafe 2.

1. Introduction

The increase of the use of nanotechnology in research and in industry has led to evaluate the risks related to the nanomaterials. As specified in the Recommendation of the European Directive in 2011, a nanomaterial is a material, which has been formed accidentally or has been manufactured […], whose at least 50 % of the particles have one or more dimensions between 1 and 100 nm.

The risk assessment of nanopowders implies the evaluation of the risks linked to powder materials at the nanometric size. Indeed, the toxicity and the inflammation and explosion risks are directly affected by the reactivity of the powder and its dispersion in a carrier fluid (air, water...).

But nanoparticles tend to easily agglomerate (Mishra, 2012), leading to modification of reactivity, dispersion and toxicity of the powder by the modification of the surface properties.

This study will focus on the effect of agglomeration on the emission of particles from nanopowders flows. Due to agglomeration, the nanopowder will be composed of agglomerates, whose size depends on the material and on the interaction forces involved. When submitted to a shear, the nanopowder will then be able to emit agglomerates and the monitoring of the rheological signature of the powder is a way to characterize their size and the solicitation necessary to emit them.

2. The agglomeration effect

Two particles, whether micro or nanometric are submitted to attractive and repulsive forces. Agglomeration occurs when the attractive forces are predominant and the smaller the particle size is, the higher these forces are. This explains why agglomeration plays an important role for nanoparticles.

According to ISO TS27687 2008 an agglomerateagglomerate is a collection of loosely bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components. The standard adds that the forces holding agglomerate together are weak forces, for example Van der Waals forces, as well as simple physical entanglement.

The terms agglomerate and aggregate are often assimilated, but as also explained in ISO TS27687 2008, an aggregate is made of particle comprising strongly bonded of fused particles. As a consequence, aggregation is often considered as a non-reversible phenomenon.

Agglomerates are brittle structures, which can be broken down and rebuilt depending on the strength of the external solicitations. They can be described by the number and the arrangement of the particles, which they contained.

2.1 Physical characteristics of an agglomerate

The number of particles within an agglomerate, n_{agg}, is linked (Gmachowski, 2002) by Equation 1 to the diameter of gyration d_g of the agglomerate. d_g is a mathematic concept equal to the root mean square distance between each particle of the agglomerate and the centre of gravity of this one.

$$n_{agg} = k_f \left(\frac{2+D_f}{D_f} \right)^{D_f/2} \left(\frac{d_g}{d_p} \right)^{D_f} \tag{1}$$

d_p is the diameter of each particles. Hess (1986) proposed, as explained in Equation 2, a relation between the diameter of gyration and the diameter of the sphere circumscribed on the agglomerate, d_{agg}.

$$\frac{d_{agg}}{d_g} = \left(\frac{2+D_f}{D_f} \right)^{1/2} \tag{2}$$

D_f, the fractal dimension, and k_f, the structure factor, are two parameters describing the sphericity of the agglomerates, and as a consequence are an information about the arrangement between the particles within the agglomerate. k_f is a coefficient between 0 and 1 and D_f between 1 and 3. The closer to 3 the fractal dimension will be, the more spherical the agglomerate will be. The structure factor is given by Equation 3 (Gmachowski, 2002).

$$k_f = \left[\left(1.56 - \left(1.728 - \frac{D_f}{2} \right)^2 \right)^{1/2} - 0.228 \right]^{D_f} \tag{3}$$

The inner porosity of an agglomerate can then be linked to d_{agg} and n_{agg} according to Equation 4.

$$e_{agg} = n_{agg} \left(\frac{d_p}{d_{agg}} \right)^3 \tag{4}$$

2.2 The agglomeration stress

As explained in ISO TS27687 2008, the particles within an agglomerate are linked with weak forces: Van der Waals, electrostatic, capillary and magnetic forces. For dry suspension and particles without dipole moment, the interaction forces can be limited to the first two ones. Van der Waals forces are inversely proportional to d_p^2, although electrostatic forces are inversely proportional to d_p. As a consequence, Van der Waals forces will be predominant for short distance and will ensure cohesion within the agglomerate.

Debrincat et al. (2008) proposed an agglomeration stress, defined by Rumpf, depending on Van der Waals forces and on the agglomerate porosity, as explained in Equation 5.

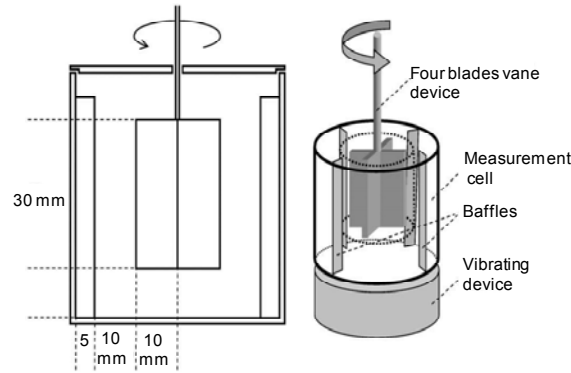$$\Gamma_{agg} = \frac{1-e_{agg}}{e_{agg}} * \frac{F_{VdW}}{2d_p^2} \tag{5}$$

Figure 1: Measurement cell (Madariaga et al., 2009)

3. Nanopowder rheology

3.1 Description of the powder rheometer

The experiments have been led with a powder rheometer, which applies shear within a measurement cell. An induction motors supplies a torque and an optical sensor measures the angular rate. Both parameters are respectively proportional to the shear stress and the shear rate. In this paper, the evolution of shear stress versus shear rate has been monitored.

The powder-powder shear is applied with a four blades vane device and baffles within the cell avoid a powder-tank shear on the inner surface of the cell.

The cell, described in figure 1, is submitted to mechanical vibration, with variable frequencies and amplitudes. The vibrating device has two objectives in the case of this study. On first, it allows to induce a Brownian motion within the powder, in order to access to all the spatial configurations of the particles. Indeed, the rheological properties are dependent on the way the powder is loaded and the assurance of the ergodicity of the system is necessary to have an average of these rheological properties. Secondly, in the case of nanoparticles, the strength of the powder within the cell can be high enough to avoid flowing at low shear rates and shear stress is then too high to be measured. The vibrations allow the powder to flow at low shear rates.

3.2 The three states of flow

A powder submitted to an external solicitation, as a shear rate, can be described by different states. Silica powder flows like a liquid if it is slightly poured, whereas the powder will behave as a gas if it is highly agitated.

The rheological approach is a good way to follow these behaviours. As shown in figure 2, the state of flow of the powder will then change with the increasing shear rate. The newtonian state describes a state of a dense powder (similar to a pseudo solid). The coulombian state corresponds to a dense rheofluidified phase (similar to a viscous liquid) and the kinetic state to a less and less dense phase submitted to particles collisions.

The newtonian state corresponds to a state in which the viscosity tends to a constant value. This is the case when the shear rate $\dot{\gamma}$ is much lower than the critical shear rate $\dot{\gamma}_c$. In the same way, when the shear rate is higher than $\dot{\gamma}_c$, the shear stress tends to a constant value σ_f. This is in accordance with the inverse proportionality of the viscosity in frictional (or coulombian) state. This evolution of the viscosity in newtonian and coulombian states is figured by Equation 6 (Marchal and Choplin, 2004):

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{\eta_0}{1 + \frac{\dot{\gamma}}{\dot{\gamma}_c}} \tag{6}$$

At kinetic state, the shear stress increases again and is dependent on the square of the shear rate and on the agglomerate diameter. A first evaluation (Andreotti et al., 2011) is Equation (7) :

$$\sigma = \frac{\rho_{agg} d_{agg}^2}{\left(\frac{1-e_0}{1-e_{app}}\right)^{1/3} - 1} \dot{\gamma}^2 \tag{7}$$

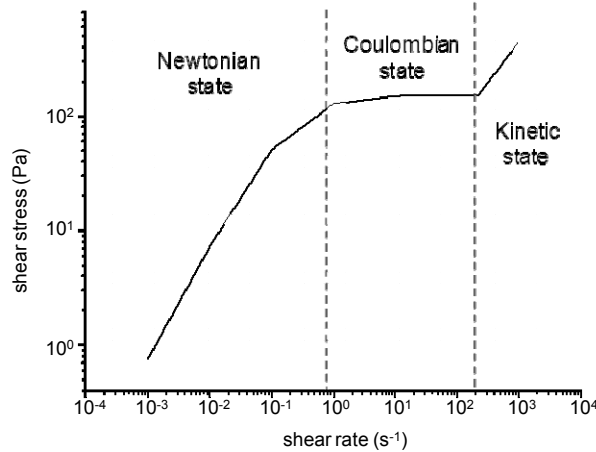e_0 and e_{app} are the porosity of the compact powder and the apparent porosity.

Figure 2: The three flow states

The principle of d_{agg} calculation from rheological data lays on the use of the transition regime between coulombian and kinetic states. In Equation 7, in order to calculate d_{agg}, it is necessary to evaluate the apparent porosity, the agglomerate density and the shear rate and stress. Before the kinetic state, the apparent porosity does not change, whereas it is decreasing when the powder is setting on suspension. This value is linked to the inner porosity of the agglomerates and to the total porosity e_b (porosity inter- and intra-agglomerates), following Equation 8. The compact powder porosity has been evaluated to the random close packing, 0.36 (Lochmann et al., 2006).

$$1 - e_{app} = \frac{1-e_b}{1-e_{agg}} \tag{8}$$

Moreover, knowing that the agglomerate porosity and density are linked, the agglomerate diameter d_{agg} can be expressed in Equation 9.

$$d_{agg} = \sqrt{\frac{\sigma_f}{\dot{\gamma}_f{}^2 \rho_p}\left[\left(\frac{1-e_0}{1-e_b}\right)^{1/3}\left(1-e_{agg}\right)^{-2/3} - \left(1-e_{agg}\right)^{-1}\right]} \tag{9}$$

4. Experimental results

4.1 Experimental protocol

The experiments have been conducted with nanometric and micrometric powders, whose properties are presented in table 1. Four nanopowders are presented in this paper: three carbon black powders, with particle diameters of 25, 30 and 330 nm (Corax N115, Printex XE2 and Thermal Black, DEGUSSA) and a hydrophilic silica powder, made up of 12 nm particles (Aerosil A200, DEGUSSA).

The powder is charged in the rheometer cell and the volume of shear powder V_b is 54.4 cm^3. During each test, the evolution of the shear stress versus the shear rate is monitored. The values of shear rate and stress at the limit between coulombian and kinetic states are then taken down.

In order to compare the values for the nanopowders, other rheological tests have been conducted with micrometric glass powders with diameters of 0.33, 0.5, 0.8 and 1 mm, which are not agglomerated.

Table 1: Material and bulk properties of the tested powders

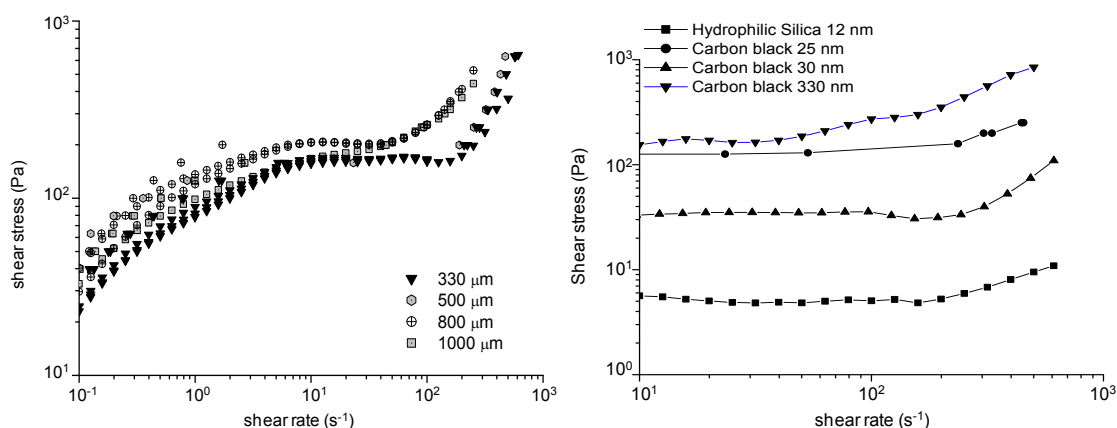|	c.b. 25 nm	c.b. 30 nm	c.b. 330 nm	silica 12 nm	glass 0.33 mm	glass 0.50 mm	glass 0.80 mm	glass 1 mm
material density (kg.m^{-3})	2,050	2,350	1,830	2,200	2,700	2,700	2,700	2,700
sheared mass (g)	21.6	7.32	42.3	2.61	84.0	84.2	87.4	91.2
bulk density (kg.m^{-3})	397.1	134.6	777.6	47.98	1544.1	1,547.8	1606.6	1,676.5
total porosity	0.81	0.64	0.57	0.98	0.43	0.43	0.40	0.38

Figure 3: Shear stress versus shear rate for glass beads powders and nanometric powders

4.2 Rheological behaviour of the tested powders

Equation 10 can be used on first for glass beads. In this case, the agglomerate density will be null and the agglomerate diameter must be equal to the particle diameter. Table 2 presents the values of agglomerate porosity and of the shear stress and rate at the limit between coulombian and kinetic state.

The values of the "agglomerate" diameter are on average 12 % lower than the primary diameter, confirming that the particles do not agglomerate and considering that these values are strongly dependent on e_0, which is generally given with experimental errors.

For the tested nanopowders, e_{agg} must be calculated in order to access to the value of d_{agg}. In regard of Equation 8, the agglomerate porosity is linked to the apparent porosity. A hypothesis has then been made: knowing that each powder is vibrated before the shear test in order to avoid the effect of the load in the cell, it is estimated that the apparent porosity of the nanopowder is equal to the apparent porosity (and the total porosity) of the glass beads powder. As a consequence, an average of e_{app} for the nanopowders is 0.425.The agglomerate porosity and diameter can then been calculated.

Table 2: Material and bulk properties of the tested powders

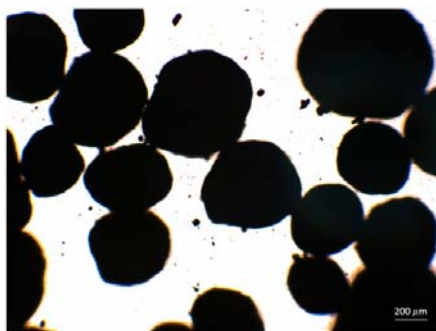|	c.b. 25 nm	c.b. 30 nm	c.b. 330 nm	silica 12 nm	glass 0.33 mm	glass 0.50 mm	glass 0.80 mm	glass 1 mm
σ_f (Pa)	154	35.6	178	5.04	168	203	206	204
$\dot{\gamma}_c$ (s⁻¹)	160	287	100	193	198	170	90	60
e_{agg}	0.66	0.90	0.26	0.96	0	0	0	0
d_{agg} (µm)	704	361	668	234	323	414	720	813
n_{agg} (*10⁹)	14, 768	1, 575	2.12	7, 168	-	-	-	-
agglomeration stress (Pa)	3, 536	636.8	1, 532	575.6	-	-	-	-

Figure 4: Optical microscopy observation of 25 nm carbon black

An observation with an optical microscope of 25 nm carbon black, as shown in figure 4, presents agglomerates from 416 to 850 µm. In table 2, the value of d_{agg} is 704 µm. Knowing that this value, in comparison with glass beads, can vary with a small fluctuation of the initial porosity, it can be concluded that the microscopic observation is in the same order of magnitude as the theoretical calculation. It is all the more difficult to compare with microscopic observations since these tests tend to apply a stress on the powder, which can change the size distribution.

Finally, assuming that Van der Waals forces decrease when the particle diameter increases (Fortes et al., 1998), the agglomeration stress for the different nanopowders has been calculated. It appears that 30 nm carbon black and silica agglomerates are the more brittle. It must not be interpreted as an agglomerate diameter inverse dependence of the agglomeration stress. Indeed, for two agglomerates with the same inner porosity, the highest one will be the more brittle one. In the case of this study, 30 nm carbon black and silica agglomerates are the more brittle, due to the high porosity of these agglomerates.

5. Conclusions

The effect of agglomeration on the emission of particles from nanopowders flow has then been studied with the use of a powder rheometer. Depending on the mechanical solicitation, the powder follows three different flow states. The first two states, newtonian and coulombian, depend on the cohesion of the particles and the third state, the kinetic state, is dependent on the size of the agglomerates, which are emitted. This size is defined as the diameter of the sphere circumscribed on the agglomerate. The agglomerate diameter and porosity are two characteristics, which allow defining the strength of an agglomerate. The agglomerate stress decreases with the increasing diameter and porosity.

The values of the shear rate and stress at the limit between coulombian and kinetic states allow calculating the agglomerate diameter. The method has been used on first for micrometric glass beads powders, which cannot be agglomerated. This diameter must then be equal to the particle diameter of the glass beads. The results give a difference of 12 % between the calculated and particle diameters, which is in accordance with the hypothesis made on the initial porosity of the compact powder. Assuming that the porosity intra-agglomerates for nanopowders is the same as the apparent porosity of the tested glass beads, the agglomerate diameter for carbon black and hydrophilic silica nanopowders have been calculated.

The physical characteristics of the agglomerates, which are emitted by the mechanical solicitation of the rheometer, are then defined and their agglomeration stress can be calculated. This stress is highly dependent on the inner porosity and the agglomerates are all the more brittle that they are porous.

This work is then a method to assess the state of agglomeration for suspensions of nanoparticles submitted to a rheological shear stress. The safety tests with apparatuses such as Hartmann's tube and 20 L sphere use nozzles to suspend the powder, which is then submitted to shear. It is essential to estimate the effect of these nozzles to the particle-size distribution in order to confirm or not the values of the explosion characteristics actually displayed in literature for nanoparticles.

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