Particle and Powder Flow Properties- Part II

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Topics/Outline

• Sampling (Wassgren)
• Particle size (Wassgren)
• Granular Material (Valverde/Castellanos)
• Particle-Particle Interactions
• Dry Particle Coating – Nano-additives
• Cohesion, Flow and Roles of Nano-additives (Valverde/Castellanos)
• Cohesion/Flow Characterization using several powder testers (Dave, Sanchez-Quintanilla, Valverde, Wassgren)
• Contact Modeling – Influence of Nano-additives (Yuhua Chen and Dave)
• Appendices
  – Plasticity Theory for Powders (Sanchez-Quintanilla)
  – Mechanical Properties (Hancock and Morris)
  – Review on Powder Testing Equipment (Sanchez-Quintanilla, Lauren Beach, Yuhua Chen, Laila Jallo)
• Reading material
  – Key papers as PDF files

* Names in blue are students who assisted with notes
Relevance for testing

There is not a single physical model capable of explaining the behaviour of a granular material in the four dynamical regimes

THUS

✓ A single testing device can not given meaningful results for the flowability of a powder all the four regimes

✓ Before committing time for testing, the dynamical regime of the powder in the plant process needs to be identified.

✓ A testing device in which the powder is in the same dynamical regime as in the plant process must be selected.

Types of testers

• Shear tests
  In these tests the stresses applied to the powder are controlled to ensure the velocities of the particles are small and the powder is always in the plastic regime
  They are the only tests backed by a well established physical theory

• Rheometers
  They borrow methods and ideas developed for fluid testing, but they lack the backing of a physical theory because the fluid mechanics does not directly apply to powders

• Tests based on mechanical stability
  In these tests the stresses applied to the powder are not controlled. Therefore, the powder may experiment transitions from the plastic regime to the granular or the fluidized regime

• Tests based on the solid fraction
• Tests based in fluidization
  These tests determine the properties of the sample in the fluidized regime
Tests based on mechanical stability

In this type of tests the stresses inside granular material are driven to the yield condition in an uncontrolled way and it is allowed to flow until the stresses are relaxed and the flow stops.

- Because the initiation of the flow is determined by the plastic yield condition, the results of these tests is influenced by the flowability of the powder in the plastic regime.

- However, since the velocities attained in the flow are not controlled, it may happen that the material enters the inertial or fluidization regimes. Hence the flowability of the powder in these regimes may affect the results of the test.

There are two types of this tests: tests based on avalanches and tests based on the angle of repose.

Angle of Repose

- Poured angle of repose
  - Pour a powder from some elevation onto a flat plate and measure the angle that the powder slope makes with respect to the horizontal.

- The angle of repose is does not have a unique value, especially for cohesive powders.
Angle of Repose...

- **Angle of fall**
  - the angle of repose for a powder mound that has been impacted

- **Angle of spatula**
  - the angle of repose for a powder that has been formed by lifting a spatula out of a bed of powder

- **Dynamic angle of repose**
  - the angle of repose for a continuously avalanching powder
    - this concept is utilized in several testers - Kaye, Muzzio, etc.

Angle of repose

The tests based on the angle of repose characterise the flowability of a powder by the angle of the free surface of the material when the granular flow stops under different configurations.

Example of configurations:
- Conical pile
- Hopper discharge
- Tumbler

- When the unconfined yield strength of the material is not negligible, the stability of the free surface depends on the consolidation stresses acting on the surface.
- Since the consolidation stresses depend on the geometry and scale of the test, for cohesive materials these tests show scale and geometry dependence

No real problems can be solved by only knowing the angle of repose
Angle of Repose...

- Segregated powder blends may have different angles of repose at different locations in the bed.

- A smaller angle of repose generally implies better flow characteristics.
- Angle of repose as a measure of flowability is most useful (only) for free flowing powders.
  - Hiestand (1991) states that “for pharmaceutical materials the angle of repose [as a flowability measure] is satisfactory only with powders whose flow characteristics are so good that one seldom needs the measurement.”

<table>
<thead>
<tr>
<th>Material</th>
<th>Angle of Repose [deg.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>34 ± 1 (Lavoie et al., 2002)</td>
</tr>
<tr>
<td>Sucrose</td>
<td>35 ± 1 (Lavoie et al., 2002)</td>
</tr>
<tr>
<td>Lactose 100</td>
<td>38 ± 2 (Lavoie et al., 2002)</td>
</tr>
<tr>
<td>Lactose 325</td>
<td>41 ± 1 (Lavoie et al., 2002)</td>
</tr>
</tbody>
</table>

Results using the Angle of Repose (I)


**Apparatus:** PharmaTest Flow-time and Cone Angle Tester

**Materials used:**

Ordered mixtures of a carrier (Pharmatose 325M, $d_p = 50 \mu m$), intermediately sized particles (Pharmatose 450M, $d_p = 20 \mu m$) and micronized lactose ($d_p = 2 \mu m$)

**Conclusions:**

- The more cohesive powders, as determined by other techniques, have a higher angle of repose.
- For the most cohesive powders, the differences between the angle of repose tend to decrease
- There is a linear correlation between angle of repose and the modified Hausner Ratio
Results for the Angle of Repose (II)

• Räsänen et al. AAPS PharmSciTech 2003; 4 (4) Article 53

**Apparatus:** Custom made: Funnel discharging into a plate

**Materials used:**
Active ingredient: paracetamol
Excipients: microcrystalline cellulose (MCC, Avicel PH101, PH102 and PH200 and a mixture of MCC101/MCC200 (75%/25%) and silicified micro-crystalline cellulose

**Conclusions:**

✔ The angle of repose increases with increasing concentration of the poorest flowing ingredient (paracetamol).

✗ For the largest concentrations of paracetamol, the angle of repose tends to a plateau (implies that one cannot really get very meaningful results for very cohesive powders)

✔ Samples with larger angles of repose showed larger minimum fluidization velocity and increasingly poorer fluidization in a fluidized bed

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**A New Device**

**Schematic of AOR Equipment**

**Magnetically Assisted Particle Flow (MAPF):**
Use magnetic particles to agitate host powders, inducing flow.
**Parameters Studied**

- Height from which the powder is dropped
- Mass of powder
- Magnetic field strength (field voltage)
- Hopper/funnel position within magnetic field
- Mass of magnets
- Outlet area of hopper/funnel
- Outlet mesh size
- Effects of different powders

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**Examples of piles obtained using this device**

*False angle of repose*

Clean heaps are obtained - no false peaks are observed
Material Studied: Cornstarch
AOR as a function of height of fall

AOR as a function of applied voltage (related to magnetic field strength)
Angle of Repose as a function of mass of cornstarch through hopper

AOR as a function of the powder mass

Mass of corn starch through hopper (grams)

AOR as a function of hopper/funnel position within the magnetic field

Distance between bottom of hopper and electromagnet base(cm)

Angle of Repose as a function of hopper position in the magnetic field
Angle of Repose as a function of mass of magnets

AOR versus mass of magnets (mass of powder is fixed)

AOR versus flow rate
**AOR versus outlet mesh size**

![Graph showing AOR versus outlet mesh size](image)

**AOR for different powders as a function of particle size**

![Graph showing AOR for different powders](image)

Angle of repose versus particle size
Comparison between MAPF and a Mechanically Vibrated Hopper

<table>
<thead>
<tr>
<th>Mass of Cornstarch</th>
<th>AOR MAPF (degrees)</th>
<th>AOR Vibrated Hopper (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 grams</td>
<td>58</td>
<td>56</td>
</tr>
<tr>
<td>10 grams</td>
<td>62</td>
<td>65</td>
</tr>
</tbody>
</table>

Values obtained for experiment comparing AOR for vibrated hopper and MAPF hopper.

Comparison of piles obtained using MAPF and Vibration

Piles using MAPF

Piles using Hosakawa Micron Tester
Summary

- An AOR measurement device based on Magnetically Assisted Powder Flow System allows for “erasing the memory of the previous state”
- It provides clean heaps with sharp boundaries, thus gives precise values for AOR, eliminating false peaks
- It is easy to operate thereby reducing errors due to inexperienced operators
- High degree of reproducibility of results is obtained
- Tests require very little time

Angle of repose (AOR) to indicate flow improvements from nano-additives

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AOR of Coated Cornstarch with R972
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Yuhua Chen (NJIT)
Carr Indices (Carr, 1965)

- Two indices: “flowability” and “floodability”
- **Flowability** is a measure of a powder’s ability to flow freely.
- **Floodability** is a measure of a powder’s tendency to fluidize in air and produce liquid-like flow.

- Measured using the Hosokawa Powder Tester

Hosokawa Powder Tester

The Hosokawa powder tester is a multi-test apparatus, that measures:

- Cohesion Index: Defined as the relative amounts of solid remaining in three sieves of 74, 149 and 250 μm meshsize after sieving for a definite time.
- Angle of Spatula: Obtained taken upwards a plate immersed in the powder (i.e. the angle of repose at the plate).

- Angle of Fall
- Angle of Repose
- Compressibility (i.e. Carr Index)
- Aerated Bulk Density and Packed Bulk Density
- Uniformity: characterizes the width of the particle size distribution

Flowability is determined from a combination of all results.

According to Schwedes, it can only be used as a very rough classification of bulk solids behavior.
Carr Indices

- Carr’s flowability index is an empirically derived score that combines measurements of a powder’s:
  - angle of repose
  - compressibility
  - angle of spatula, and
  - either cohesion or coefficient of uniformity
- $0 \leq \text{Flowability} \leq 100$ with 100 indicating excellent flow qualities

Carr Indices...

- Compressibility is the relative change in bulk density of a powder that is “tapped” and “aerated”:
  \[
  \text{compressibility} = \frac{\rho_T - \rho_A}{\rho_T}
  \]
  where $\rho_A$ and $\rho_T$ are the aerated and tapped bulk densities (density = mass of the powder/total volume occupied by the powder as the bulk or bed)
- The aerated bulk density, $\rho_A$, is the bulk density of the powder sifted into a containing vessel
  - in practice $\rho_A$ is the most loosely packed bulk density rather than an aerated density
Tests based on density

Tests that measure the density are based on the fact that in cohesive powders, the attractive forces between particles can stabilise arrangements of particles with solid fractions smaller than those found in non-cohesive powders.

Because of this, if a cohesive powder is gently poured in a container, its solid fraction (defined as the ratio of the volume of the powder or solid and the total volume occupied by the powder bed) \( \phi_{\text{loose}} \) would be on the lower end of the range attainable for that powder.

If the container is tapped, the acceleration on the taps causes a consolidation stress on the powder that rearranges the particles into a larger solid fraction \( \phi_{\text{tapped}} \).

The result of the test is usually given in terms of the tapped solid fraction \( \phi_{\text{tapped}} \), the ratio \( \phi_{\text{tapped}}/\phi_{\text{loose}} \) (Housner ratio) or \( (\phi_{\text{tapped}} - \phi_{\text{loose}})/\phi_{\text{tapped}} \times 100 \) (Carr index).

Typically, the higher \( \phi_{\text{tapped}}/\phi_{\text{loose}} \) and the lower \( \phi_{\text{tapped}} \) the poorer is the flowability of the powder.

Tapped density- Caution

• The tapped bulk density, \( \rho_T \), is the bulk density obtained while subjecting the powder to a prescribed series of taps.
  – The tapped bulk density has been shown to increase with the number of taps (Yu and Hall, 1994). For example:

\[
\rho_n = \rho_0 - (\rho_0 - \rho_\infty) \exp\left(-\frac{nT}{T}\right)
\]

where \( \rho_n \) is the bulk density after \( n \) taps, \( \rho_\infty \) is the asymptotic bulk density, \( \rho_0 \) is the initial bulk density, and \( T \) is a time constant.

  – The tapped bulk density is also a function of the tapping style (Abdullah and Geldart, 1999).
Amplitude=0.025mm

Amplitude=0.05mm
Amplitude=0.075mm

Flow Improvement Correlates Well with Packing Density (Vibrated Packing)
Another Representation of the Vibrated Bed Packing Results

![Vibrated bed results](image)

**Carr Indices...**

- Powders with significant frictional and cohesive interactions (which tend to decrease flowability) will have a larger difference in their tapped and aerated bulk densities.

- Increasing compressibility generally implies decreasing flowability (table from Hiestand, 1991):

<table>
<thead>
<tr>
<th>Subjective Flowability</th>
<th>Compressibility [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>excellent</td>
<td>5 – 10</td>
</tr>
<tr>
<td>good</td>
<td>11 – 15</td>
</tr>
<tr>
<td>fair</td>
<td>16 – 20</td>
</tr>
<tr>
<td>passable</td>
<td>21 – 25</td>
</tr>
<tr>
<td>poor</td>
<td>26 – 31</td>
</tr>
<tr>
<td>very poor</td>
<td>32 – 37</td>
</tr>
<tr>
<td>exceeding poor</td>
<td>38 – 45</td>
</tr>
</tbody>
</table>
Carr Indices...

- Carr quantified a powder’s cohesion by measuring the mass of powder retained on three vibrating, stacked screens.
  - The screen mesh sizes are a function of the powder’s working bulk density ($\rho_W = \rho_A + (\rho_T - \rho_A)\text{compressibility}$):
    - $160 < \rho_W < 400 \text{ kg/m}^3$: 40, 60, 100 mesh
    - $400 < \rho_W < 960 \text{ kg/m}^3$: 60, 100, 200 mesh
    - $960 < \rho_W < 1440 \text{ kg/m}^3$: 100, 200, 325 mesh
  - Start with 2 g of -200 mesh material on the top screen.
  - The vibration duration increases with decreasing $\rho_W$.
  - The cohesion of a powder is given by:
    
    $n_1 = \text{floor}(\text{mass on top screen}/0.1 \text{ g})$
    
    $n_2 = \text{floor}(\text{mass on middle screen}/0.1 \text{ g})$
    
    $n_3 = \text{floor}(\text{mass on bottom screen}/0.1 \text{ g})$

    $\text{cohesion} = 5n_1 + 3n_2 + n_3$

    Decreasing cohesion implies increasing flowability.

Carr Indices...

- The uniformity coefficient is used in place of cohesion for larger sized (i.e. granular or coarse) materials.
- Uniformity is defined as the ratio of the width of sieve opening that passes 60% of the material (by mass) to the width of sieve opening that passes 10% of the material.

$$\text{uniformity} \equiv \frac{d_{60}}{d_{10}}$$

- Increasing uniformity implies increasing flowability.
Carr Indices...

- The flowability index is determined from an empirical formula based on the behavior of >2,800 dry materials (Carr, 1965).

<table>
<thead>
<tr>
<th>Flowability and Performance</th>
<th>Angle of Repose</th>
<th>Compressibility</th>
<th>Angle of Spatula</th>
<th>Uniformity Coeff.</th>
<th>Cohesion**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent, 90 - 100 pts</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Poor, 70 - 80 pts</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Very poor, 60 - 70 pts</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Passable, 60 - 80 pts</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Borderline, Material may hang up</td>
<td>60 - 100 pts</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Poor, 40 - 50 pts</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Must agitate, Vibrate</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Very poor, 0 - 20 pts</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Agitate more promptly</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Very, very poor, 0 - 10 pts</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
</tbody>
</table>

* Used with granular and powdered granular materials.
** Used with powders or where an effective cohesion cannot be measured.

Carr Indices...

- Floodability is an empirically derived score that combines measurements of a powder’s:
  - flowability
  - angle of fall
  - angle of difference
  - dispersibility

- $0 \leq \text{floodability} \leq 100$ with 100 indicating the material is very floodable
Carr Indices…

- **Angle of difference** is the difference between the angle of repose and the angle of fall.

\[(\text{angle of difference}) \equiv (\text{angle of repose}) - (\text{angle of fall})\]

- A floodable material typically has a small angle of fall since air trapped within the heap of powder causes the material to fluidize when the base is impacted.

- The larger the angle of difference, the more likely the material will be floodable.

Carr Indices…

- **Dispersibility** is a measure of the scattering and dusting characteristics of a powder.
  - The more dispersible a material is, the more floodable it is.

- Dispersibility is measured by dropping a 10 g sample of material en masse through a 4 in. diameter, 13 in. long cylinder from a height of 24 in. above a watch glass (which in turn is located 4 in. from the bottom of the cylinder). The material remaining on the watch glass is weighed and the dispersibility is given by:

\[\text{dispersibility} \equiv 10 \times \left[10 - (\text{mass remaining, in grams})\right]\]
Carr Indices...

- The floodability index is determined from an empirical formula (Carr, 1965).

<table>
<thead>
<tr>
<th>Floodability and Performance</th>
<th>Flooability</th>
<th>Angle of Fall</th>
<th>Angle of Difference</th>
<th>Dispensability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very floodable, 30 - 180 pts</td>
<td>50 - 56</td>
<td>20 - 24</td>
<td>24 - 26</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Positive rotary seal</td>
<td>55 - 66</td>
<td>20 - 22</td>
<td>22 - 25</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Floodable, 60 - 79 pts</td>
<td>50 - 69</td>
<td>20 - 22</td>
<td>22 - 25</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Be necessary</td>
<td>45 - 55</td>
<td>19 - 22</td>
<td>22 - 25</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Inclined to flood, 40 - 59 pts</td>
<td>35 - 45</td>
<td>20 - 24</td>
<td>24 - 26</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Rotary seal is desirable</td>
<td>35 - 45</td>
<td>20 - 24</td>
<td>24 - 26</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Rotary seal probably needed</td>
<td>31 - 39</td>
<td>20 - 24</td>
<td>24 - 26</td>
<td>25 - 30</td>
</tr>
<tr>
<td>depending on drop velocity</td>
<td>30 - 50</td>
<td>19 - 22</td>
<td>22 - 25</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Rotary seal will not be needed</td>
<td>25 - 35</td>
<td>19 - 22</td>
<td>22 - 25</td>
<td>25 - 30</td>
</tr>
</tbody>
</table>

Carr Indices...

- Standards related to measuring Carr Indices:
  - USP 24 / NF 19: <616> Bulk and Tapped Density
Hausner Ratio (Hausner, 1967)

- Perhaps the most commonly used quantities to determine flowability
- Defined as the ratio of the tapped bulk density to the aerated bulk density:

\[
\text{Hausner ratio} \equiv \frac{\rho_T}{\rho_A}
\]

- Directly related to the compressibility:

\[
\text{HR} \equiv \frac{\rho_T}{\rho_A} = \frac{1}{1 - \frac{\rho_T - \rho_A}{\rho_A}} = \frac{1}{1 - (\text{compressibility})}
\]

Subjective Flowability Compressibility [%] Hausner Ratio

- excellent 5 – 10 1.05 – 1.11
- good 11 – 15 1.12 – 1.18
- fair 16 – 20 1.19 – 1.25
- passable 21 – 25 1.27 – 1.33
- poor 26 – 31 1.35 – 1.45
- very poor 32 – 37 1.47 – 1.59
- exceedingly poor 38 – 45 1.61 – 1.82

(Table adapted from Hiestand, 1991.)

- HR can also be used to distinguish between Geldart Group A (aeratable, easy-to-fluidize, HR < 1.25) and Group C (cohesive, difficult-to-fluidize, HR > 1.4) powders. Powders with 1.25 < HR < 1.4 are Group AC (transitional) powders (Geldart et al., 1984).
Hausner Ratio...

- The Hausner ratio (i.e. compressibility) has been known to give erroneous flowability results:
  
  - If the cohesion strength is greater than the tapping strength, the initial packing arrangement may not change $\Rightarrow$ HR small indicating good flowability when in fact the flowability is poor (Li et al., 2004; Lavoie et al., 2002). Example: MCC 103
  
  - If the cohesion is significant, the initial packing may already have a large initial bulk density so tapping won’t decrease it significantly $\Rightarrow$ HR small indicating good flowability when in fact the flowability is poor (Li et al., 2004).
  
  - Non-cohesive, angular particles may pack loosely initially but small perturbations result in significant re-packing $\Rightarrow$ HR large indicating poor flowability when in fact the flowability is good (Li et al., 2004). Example: pre-gelatinized starch
  
  - Other erroneous results: stearic acid (HR indicates poor flowability when in fact the flowability is very poor) (Li et al., 2004)

### Table: Hausner Ratio and Flowability

<table>
<thead>
<tr>
<th>Material</th>
<th>Hausner Ratio</th>
<th>Flowability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td>1.04 (Lavoie et al., 2002)</td>
<td>excellent</td>
</tr>
<tr>
<td>Sucrose</td>
<td>1.10 (Lavoie et al., 2002)</td>
<td>excellent</td>
</tr>
<tr>
<td>Povidone</td>
<td>1.13 (Li et al., 2004)</td>
<td>good</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1.15 (Lavoie et al., 2002)</td>
<td>good</td>
</tr>
<tr>
<td>MCC 103</td>
<td>1.19 (Lavoie et al., 2002)</td>
<td>fair</td>
</tr>
<tr>
<td>Lactose 100</td>
<td>1.20 (Lavoie et al., 2002)</td>
<td>fair</td>
</tr>
<tr>
<td>MCC 105</td>
<td>1.22 (Lavoie et al., 2002)</td>
<td>passable</td>
</tr>
<tr>
<td>Lactose 300</td>
<td>1.23 (Lavoie et al., 2002)</td>
<td>passable</td>
</tr>
<tr>
<td>Maltodextrin</td>
<td>1.24 (Lavoie et al., 2002)</td>
<td>passable</td>
</tr>
<tr>
<td>Avicel PH-102</td>
<td>1.26 (Schussele and Bauer-Brandl, 2003)</td>
<td>poor</td>
</tr>
<tr>
<td>Avicel PH-101</td>
<td>1.28 – 1.29 (Sinka et al., 2004)</td>
<td>poor</td>
</tr>
<tr>
<td>Avicel PH-102</td>
<td>1.29 (Sinka et al., 2004)</td>
<td>poor</td>
</tr>
<tr>
<td>Starch 1500</td>
<td>1.29 (Schussele and Bauer-Brandl, 2003)</td>
<td>poor</td>
</tr>
<tr>
<td>Paracetamol</td>
<td>1.39 (Li et al., 2004)</td>
<td>exceedingly poor</td>
</tr>
<tr>
<td>Magnesium stearate</td>
<td>1.39 (Li et al., 2004)</td>
<td>exceedingly poor</td>
</tr>
<tr>
<td>Lactose 200</td>
<td>1.41 (Lavoie et al., 2002)</td>
<td>exceedingly poor</td>
</tr>
</tbody>
</table>
Hausner ratio/Compressed Bulk Density


**Materials used:**
Ordered mixtures of a carrier (Pharmatose 325M, \(d_p \approx 50 \mu m\)), intermediate sized particles (Pharmatose 450M, \(d_p \approx 20 \mu m\)) and micronized lactose (\(d_p \approx 2 \mu m\))

**Apparatus:** GeoPyc 1360 from Micromeritics

**Composition of ordered mixtures**

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Pharmatose 325M, % w/w</th>
<th>Pharmatose 450M, % w/w</th>
<th>Micronized lactose, % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100:0)</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(95:5)</td>
<td>95</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>(95:2.5:2.5)</td>
<td>95</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>(90:7.5:2.5)</td>
<td>90</td>
<td>7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>(95:0:5)</td>
<td>95</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>(90:5:5)</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>(90:2.5:7.5)</td>
<td>90</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>(85:7.5:7.5)</td>
<td>85</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>(80:10:10)</td>
<td>80</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**Conclusions:**

✓ Poured bulk density decreases with increased amounts of lactose.

✗ If density is measured after a compression of 35 KPa, the values are larger than the tapped density. Hausner Ratio is calculated as compressed bulk density (CBD) over poured density.

✓ The Hausner Ratio discriminates well between the investigated mixtures, increasing with and increase of micronized particles

✗ The Hausner Ratio levels out at about 1.5 for the most cohesive powders

✓ Comparing the measured density with the theoretical density of the mixture gives insight into the arrangements of the particles

---

**Hausner Ratio**


**Apparatus:** VanKel tapping device fitted with a 100 ml glass measuring cylinder

**Materials used:**

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean volume diameter (µm)</th>
<th>10th % size (µm)</th>
<th>50th % size (µm)</th>
<th>90th % size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>632</td>
<td>424</td>
<td>629</td>
<td>851</td>
</tr>
<tr>
<td>Aerosil petrolatum</td>
<td>3.38</td>
<td>61</td>
<td>294</td>
<td>683</td>
</tr>
<tr>
<td>Aspartame</td>
<td>12</td>
<td>1</td>
<td>5</td>
<td>26</td>
</tr>
<tr>
<td>Stecchino sodium</td>
<td>20</td>
<td>2</td>
<td>11</td>
<td>40</td>
</tr>
</tbody>
</table>

**Conclusions:**

✓ Solid fraction measurements can discriminate the effect of the size and shape of the particles: large rounded shaped particles can be tapped to a much higher solid fraction than the small irregularly shaped particles

✓ Results are comparable to those obtained with the Aeroflow, although the rank order for both methods is not the same
Avalanche Flowability Index

- Powder sample placed inside a slowly rotating drum
  - Avalanches detected photoelectrically
  - Measures mean avalanche time and scatter in avalanche time
  - Typical drum diameter = 150 mm and rotation speed = 1/3 – 1/2 rpm (typically just test at one speed)
  - Operator independent \(\Rightarrow\) more repeatable
  - Powder is in a dynamic, rather than static, state

Figure from the TSI Aero-Flow Powder Flowability Analyzer Model 3250 Specifications Sheet.
Avalanche Flowability Index…

- Shorter, more reproducible avalanche times $\Rightarrow$ better flowability
- Smaller scatter $\Rightarrow$ smaller cohesion

- Lavoie et al. (2002) propose testing at multiple drum speeds and define the following indices:

  \[
  \text{Flowability Index} \equiv \frac{1}{n} \sum_{i=1}^{n} \sigma_i, \quad \text{where } n \text{ is the number of different speeds tested}, \quad \sigma_i \text{ is the standard deviation of the time between avalanches at speed test } i, \quad \text{and } m_i \text{ is the mean time between avalanches at speed test } i.
  \]

  \[
  \text{Cohesion Index} \equiv \frac{1}{n} \sum_{i=1}^{n} m_i, \quad \text{where } m_i \text{ is the mean time between avalanches at speed test } i.
  \]

- The time between avalanches is proportional to the drum speed (Lavoie et al., 2002) so the proposed indices are artificially weighted toward the slower speed values. The indices would be more useful if the time between avalanches were normalized by the drum rotation period before calculating standard deviations and means.

Avalanche Flowability Index…

- Issues (Thalberg et al., 2004):
  - Need to use a rough boundary surface (e.g. sand paper or mesh) to prevent slipping at the drum walls
  - Need to minimize electrostatic forces at the observation windows to prevent erroneous light obscuration due to sticking particles
  - Gives errors if agglomerates form since the time between agglomerate avalanches rather than particle avalanches
  - Not recommended for cohesive powders.
Tests based on avalanches

The tests based on avalanches characterise the flowability of a powder by measuring the time interval between avalanches in a rotating drum.

The shorter the time between avalanches, the better the flowability of the powder.

Example: Aeroflow®, TSI Instruments

Review on results using the Aeroflow (I)


Materials used:

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle morphology</th>
<th>True density (g cm⁻³)</th>
<th>Median particle size (μm)</th>
<th>10th percentile size (μm)</th>
<th>90th percentile size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid</td>
<td>Equant crystals</td>
<td>1.66</td>
<td>249</td>
<td>33</td>
<td>479</td>
</tr>
<tr>
<td>Citric acid</td>
<td>Equant crystals</td>
<td>1.00</td>
<td>388</td>
<td>195</td>
<td>585</td>
</tr>
<tr>
<td>Croscarmellose sodium</td>
<td>Elongated twisted fibres</td>
<td>1.55</td>
<td>42³</td>
<td>18⁴</td>
<td>114⁴</td>
</tr>
<tr>
<td>Hydroxypropyl cellulose</td>
<td>Fragmented fibres</td>
<td>1.21</td>
<td>85</td>
<td>12</td>
<td>247</td>
</tr>
<tr>
<td>Lactose anhydrous</td>
<td>Equant crystals</td>
<td>1.50</td>
<td>136</td>
<td>12</td>
<td>324</td>
</tr>
</tbody>
</table>

* Particle size parameters for this material are only approximate because of the elongated nature of the particle.

Conclusions:

✔ For cohesive powders, the numbers of avalanches per time was less than that of less cohesive powders.

✔ Positive correlation with the results of a benchmark method (the simplified shear cell)

✗ However, the average time between avalanches and the width of the distributions of the avalanche times do not arrange the materials in the same order from more cohesive to less cohesive.
Review on results using the Aeroflow (II)

Lee et al. *AAPS PharmSciTech*, 2000; 1 (3) article 21

**Materials used:**

- Microcrystalline cellulose, $d_v = 70.51 \mu m$ (Avicel PH 101®, $d_v = 70.51 \mu m$)
- Avicel PH 102®, $d_v = 115.03 \mu m$
- Lactose monohydrate crystals, $d_v = 144.21 \mu m$
- Lactose monohydrate "Fast-Flo", $d_v = 99.29 \mu m$
- Pregelatinized maize starch, $d_v = 77.84 \mu m$
- Calcium phosphate, dibasic anhydrous, $d_v = 14.72 \mu m$

**Conclusions:**

- ✓ The powders exhibited four behaviors: rolling (Flow category 1), slumping (FC2), slipping (FC3), cataracting (FC4). As the value of the flow category increased, the powder flow became worse.
- ✗ Determination of flow properties cannot be based solely on strange attractor plots, mean time to avalanche or scatter. A combination of visual observation of the type of motion with the numerical values appears more accurate.
- ✓ The flow behaviour determined with the aeroflow and with the critical orifice diameter method and Carr compressibility tend to show the same

Review on results using the Aeroflow (III)


**Materials used:**

- Ordered mixtures of a carrier (Pharmatose 325M, $d_v = 50 \mu m$), intermediate sized particles (Pharmatose 450M, $d_v = 20 \mu m$), and micronized lactose ($d_v = 2 \mu m$)

**Conclusions:**

- ✓ Short and reproducible times between avalanches indicate a good flowability, while long and/or irregular times indicate poor flowability.
- ✗ Care must be taken to avoid sliding of powder and powder adhering to the glass walls, which give false avalanches.
- ✗ The AeroFlow is suitable for ordered mixtures with 5% micronized lactose or less, but cannot discriminate between the more cohesive powders.
- ✗ Cohesive powders may display short times between avalanches due to aggregate formation and thereby wrongly be assessed as having good flow.
Review on results using the Aeroflow (IV)


Materials used:

Batches containing approximately 15% of active pharmaceutical ingredient (API), fillers, binders, and lubricant (2%)

The author does not give details about the components

Conclusions:

✓ An index of the bulk flow of the material is provided by the time between avalanches.

✓ The scatter of the data provides an index of the cohesivity, which is related to the irregularity of the flow.

✓ Short and reproducible times between avalanches, i.e., low mean time and scatter, indicate better flow properties.

✓ The rank order correlation was similar with all the tested techniques (Hausner ratio, uniaxial tester, powder rheometer, Jenike tester) and reflected the behavior during processing of the powder mixtures.

Rheometers

Rheometers characterize the powder flowability by measuring the force, torque or powder needed to maintain the movement of a impeller in the powder

Example: Freeman FT4 Powder Rheometer®

• The FT4 forces a twisted blade along a helical path through a powder sample, causing a flow inside the powder.

• Samples are prepared for testing by a conditioning process in which the blade causes gentle displacement of the powder to establish a reproducible packing density.

• In a test, the blade digs into the sample compressing the powder. The axial and rotational forces acting on the blade are measured continuously to derive the work done, or energy consumed, in displacing the powder.

• The basic flowability energy (BFE) is defined as the energy required to complete a standard test and it is regarded as a measure of the rheological properties of the powder.
**(Freeman) Powder Rheometer**

- FT4 Powder Rheometer
- Rotating blade moved helically in a cylinder containing powder
- Measure energy required to drive the blade
  - "The basic flowability energy [BFE] is therefore the energy required to displace a constant volume [of] conditioned powder at a given flow pattern and flow rate."
  (http://www.freemantech.co.uk/)
- Other related measures:
  - stability index: the factor by which the BFE changes during repeated testing
  - flow rate index: The factor by which the energy requirement is changed when the flow rate is reduced by a factor of 10.
  - compaction index: The factor by which the BFE is increased when the powder is consolidated.

**Review on results on Rheometers**


**Apparatus:** Freeman FT4 Powder Rheometer

**Materials used:**

- Batches containing approximately 15% of active pharmaceutical ingredient (API), fillers, binders, and lubricant (2%)
- The author does not give details about the components

**Conclusions:**

- There was a noticeable change in the rheological behavior if the test was repeated several times, although results are reproducible using fresh samples
- For some samples results were rate independent while for others not
- The basic flowability index changes with the density of the sample when it is compacted or aerated, reflecting the change in rheological properties with the consolidation acting on the sample
- Rank order of the materials according to flowability in agreement with other techniques
Review on results on Rheometers

• Navaneethan et al. AAPS PharmSciTech 2005; 6 (3)

**Apparatus:** ManUmit Powder Rheometer combined with Texture Technologies TA.XT2i Texture Analyzer

**Materials used:**
- Metronidazole, colloidal bismuth citrate, and tetracycline hydrochloride, as active ingredients
- Excipient: microcrystalline cellulose
- Binder: PVP and croscarmellose sodium
- Lubricant: magnesium stearate at different concentrations

**Conclusions:**
- The test can discriminate the effect of different amounts of lubrication and give an optimum concentration of lubricant
- Apart from the basic flowability index, the presence of peaks in the torque acting on the blade and its frequency is an indication of powder flowability
- For powders with large amounts of entrapped air or coarse characteristics, the correlation between basic flowability index and flowability may fail

Hall Flow Meter

The Hall Flow meter measures the flowability of a powder measuring the rate of discharge Q of the powder from funnels with different orifice size

Typically, the higher the rate of discharge Q the better the flowability of the powder
Flow Through an Orifice...

- Similar, but more simplified, than the Jenike minimum outlet diameter analysis.
- Does not represent powder behavior under dynamic conditions (Lavoie et al., 2002)
- A flowing powder could become non-flowing when forced through small openings (Lavoie et al., 2002)

<table>
<thead>
<tr>
<th>Material</th>
<th>Minimum Diameter for Flow [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>5</td>
</tr>
<tr>
<td>Lactose 100</td>
<td>17</td>
</tr>
<tr>
<td>Lactose 325</td>
<td>19</td>
</tr>
<tr>
<td>Lactose 200</td>
<td>29</td>
</tr>
<tr>
<td>MCC 105</td>
<td>&gt; 34</td>
</tr>
</tbody>
</table>

Funnel Flow


**Apparatus:** Sotax Powder Flow Tester FT 300 and European Pharmacopoeia’s funnel based flowability test

**Materials used:**
- Tablettose™ 80, Tablettose™ 100, Fujicalin™, Emcompress™ Dihydrat, Avicel™ PH-102, Starch 1500™

**Conclusions:**

- No significant difference found between free flowing materials
- Vibrating the funnel can be used to induce flow in the most cohesive materials, that otherwise cannot be tested
- Due to widely different bulk densities of powders, the expression of flowability in terms of time per mass may in some cases not match the macroscopic flow qualities. It is proposed that "volume-flowability" is a better description.
Shear Cells

- Used to measure a powder’s yield strength as a function of the pressure used to compact the powder.
- Usually performed as a quasi-static test, *i.e.* at incipient yield
- Measurements can be used in design, not simply for comparisons
- Typically used in the design of hoppers and bins

Shear Cells...

- An example: The Jenike Shear Cell
**Shear Cells**

- **Procedure:**
  - Base and ring assemblies are filled and the lid is placed on the particulate material. A consolidating load, resulting in a stress of $\sigma_c$, is applied to the lid in order to compress the material. The material now has a bulk density, $\rho_b$.
  - The consolidating lid is removed and a new normal load is applied. The material is now sheared by applying a shear force to the lid/ring assembly. The material may expand or contract depending on the applied normal load. The normal load under which the material volume does not change (referred to as the end-point load) and the corresponding shear stress are noted.
  - The shear cell is emptied and a new sample is prepared following the procedure outlined in the first step using the same consolidating load. Now a new normal load, which is less than the end-point load, is applied to the lid and the shear stress required to just shear the material is noted. This procedure is repeated several times for different applied normal loads; all of which are smaller than the consolidating load.
  - Steps are repeated for different consolidating loads.

---

**Jenike Yield Loci (JYL)** are the values of the shear stress required to initiate movement in the material as a function of the applied normal stress for different consolidating stresses.

![Graph showing Jenike Yield Loci (JYL)](image)

- Data points for different consolidating stresses
- * (gives different initial $\rho_b$)
- End-point stresses (stresses at which no changes in $\rho_b$ occur)
Shear Cells…

- The unconfined yield strength, $f_c$, is the maximum stress that a powder's free surface can withstand before failing (i.e. flowing).

![Diagram showing unconfined yield strength and compacting stress](image)

Mohr’s circle corresponding to the unconfined yield strength

Mohr’s circle corresponding to the compaction stress
Shear Cells…

- A material flow function (mff) is the relationship between a powder’s unconfined yield strength, $f_C$, and the compacting stress, $\sigma_1$.

Shear Cells…

- The effective internal friction angle, $\delta$, is the angle of the line that is tangent to the end-point load Mohr's circles.
Shear Cells...

- The flow function, $ff$, is the inverse of the slope of the $mff$: $ff = \sigma_1/f_c$
  - $ff < 1$ hardened
  - $1 < ff < 2$ very cohesive
  - $2 < ff < 4$ cohesive
  - $4 < ff < 10$ easy flowing
  - $10 < ff$ free flowing

Review on results from Shear Testers (I)


**Apparatus:** custom made annular shear cell.

**Materials used:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean volume diameter (µm)</th>
<th>Particle shape</th>
<th>Powder density (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel PH-101</td>
<td>52</td>
<td>rod-shaped</td>
<td>0.35</td>
</tr>
<tr>
<td>Avicel PH-102</td>
<td>96</td>
<td>rounded</td>
<td>0.30</td>
</tr>
<tr>
<td>Avicel PH-200</td>
<td>290</td>
<td>agglomerates</td>
<td>0.46</td>
</tr>
<tr>
<td>Anh. Lactose</td>
<td>121</td>
<td>irregular</td>
<td>0.75</td>
</tr>
<tr>
<td>Erimengras</td>
<td>141</td>
<td>irregular</td>
<td>1.09</td>
</tr>
<tr>
<td>Pearlitol SD 200</td>
<td>195</td>
<td>rounded</td>
<td>0.44</td>
</tr>
<tr>
<td>Super-Tab</td>
<td>76</td>
<td>rounded</td>
<td>0.55</td>
</tr>
<tr>
<td>Anh. Theophylline</td>
<td>84</td>
<td>irregular</td>
<td>0.77</td>
</tr>
<tr>
<td>Theophyllina H$_2$O</td>
<td>—</td>
<td>needle shaped</td>
<td>0.54</td>
</tr>
</tbody>
</table>

**Measured magnitudes:**

Cohesion, angle of internal friction $\phi$, effective angle of internal friction $\delta$, flow factor FF and shear index $n$.

**Conclusions:**

- In some cases it was found that the ranking of powders was different when different indices like $\phi$, FF, and $n$ were used.
- The ranking of powders using shear analysis was different from other flow methods (Carr index, funnel flow).
- For this shear cell, instrument and process parameters are of significant importance and need to be standarized.
Review on results from shear testers (II)


**Materials used:**
- Batches containing approximately 15% of active pharmaceutical ingredient (API), fillers, binders, and lubricant (2%)
- The author does not give details about the components

**Apparatus:** Jenike shear cell and uniaxial compression tester.

- Typical stresses: 3.8 KPa for Jenike tester and 80 KPa for the uniaxial compression tester

**Conclusions:**
- ✓ The results of the uniaxial tester are useful for measuring tableting characteristics
- ✗ The results of the Jenike tester do not give much information about tableting characteristics
- ✓ Rank order correlation for both testers similar than the obtained using the FT4 Powder Rheometer, the Aeroflow and the Houssner ratio

Review on results from Shear Testers (III)


**Apparatus:** Johansson indizicer and uniaxial press Lloyd LR30K

**Materials used:**
- Three direct compression excipients: Avicel PH 102, Starch 1500, and Pharmatose DCL 21
- Three drug substances: SRX1, SRX2 CP (CP: Coarse Particles) and SRX2 FP (FP: Fine Particles), SRX1 and SRX2 being two different polymorphs of the same drug substance.

**Measured magnitudes:** Packing coefficient, flow function

**Conclusions:**
- ✓ Using the flow function the apparatus discriminates between materials with poor flow properties
- ✗ On the contrary, using the flow function the apparatus does not discriminate between materials with free flowing properties
- ✗ The packing coefficient combines several material properties, such as particle shape, particle size distribution, interaction between particles, electrostaticity, as well as flow properties to which it can be linked.
Review on results from Shear Testers (IV)


Apparatus: custom made uniaxial tester

Materials used:
Ordered mixtures of a carrier (Pharmatose 325M, \(d_p \approx 50 \mu m\)), intermediate sized particles (Pharmatose 450M, \(d_p \approx 20 \mu m\)) and micronized lactose (\(d_p \approx 2 \mu m\))

Conclusions:

× The tester cannot discriminate between ordered mixtures with good flowability.

✓ On the other hand, the tester seems suitable for assessment of more cohesive powders.

Measured magnitudes: yield strength

Correlation Between Flowability Indices

• Lindberg et al. (2004) found that rank order correlation was similar between the Hausner ratio, avalanching, powder rheometry, uniaxial compression, and Jenike shear cell

• Thalberg et al. (2004) found that there was a linear correlation between the Hausner ratio and angle of repose (for materials that weren’t too cohesive); uniaxial compression only suited for more cohesive materials
Factors Affecting Flowability

- **Particle size**
  - affects ratio of inter-particle attractive and inertial forces
- **Particle size distribution**
  - more uniform size distribution $\Rightarrow$ lower bulk density $\Rightarrow$ easier to shear
- **Particle shape**
  - mechanical interlocking of particles
  - more spherical $\Rightarrow$ better flow
- **Particle surface roughness**
  - affects the significance of attractive forces
  - smooth surfaces $\Rightarrow$ surfaces can get closer $\Rightarrow$ stronger van der Waals forces
  - rough surfaces $\Rightarrow$ greater surface energy $\Rightarrow$ stronger electrostatic forces

Principal Contributor: Wassgren
Factors Affecting Flowability

- Interstitial air
  - larger permeability $\Rightarrow$ air can easily infiltrate gaps when bulk expands under shear
  - fluidized powder easily flows
- Moisture
  - low moisture $\Rightarrow$ increases electrostatic forces
  - high moisture $\Rightarrow$ increases capillary forces

The Sevilla Powder Tester (SPT)

- Any reliable device to measure powder properties should be able to erase powder memory. Otherwise results are history-dependent
- This can be achieved by driving the powder into a highly expanded fluidization state
Preconditioning (fluidization) of fine cohesive powders

- Fine cohesive powders are difficult to fluidize (Geldart C)
- Classical Geldart C classification does not refer to an intrinsic property of the powder
- Pre-conditioning process to achieve uniform fluidization are available or have to be developed. They need to be applied before any measurement
- Examples: Coupling gas flow with: vibration, magnetic assistance, acoustic excitation and/or centrifugal force (Pfeffer, Nam, Dave, Liu, Quevedo, Yu, Zhao:US2006086834 patent)

• For xerographic toners, coated cornstarch, silica nano-particles…strong shaking is enough.
• Note that shallow beds are employed

For micron-sized particles memory is erased when inter-particle contacts are broken to the level of individual particles

Fluidization of Dry-Coated Fine Powders

- Fluidization Behavior Comparison

Raw Cornstarch
Size: 15 micron

0.1% R972 Coated Cornstarch
Size: 15 micron
The Sevilla Powder Tester (SPT)

Gas velocity: $v_g$

Gas Pressure Drop:
(load or unload)

$\sigma_c = W \pm \Delta p \sigma_l$

Ultrasonic:

Bed height $H$, packing fraction $\varphi$, settling velocity $v_s$

Developed from the work of A.T. Perez, A. Ramos, JM Valverde, MAS Quintanilla, A Castellanos (U. Seville), MA Morgan, F Genovesse, PK Watson (Xerox Co.). Principal Contributor: Valverde
Powder tester: Experimental procedure

1. Material is fluidized to be initialized
2. The gas flow is reduced and the powder collapses
3. The powder is pressed or decompressed by the gas
4. The ultrasonic sensor measures the porosity
5. The gas flow breaks the powder bed to measure its tensile stress

Powder Tester: Measured variables

- **Consolidation stress.** Calculated from the mass $m$, the filter area $A$ and the pressure drop $\Delta p$ as:
  \[
  \sigma_c = \frac{mg}{A} \pm \Delta p
  \]
  The sign of $\Delta p$ depends on whether the gas flow consolidates the powder or holds part of its weight

- **Solid fraction.** Calculated from the mass $m$, the particle density $\rho$, the filter area $A$ and the height $H$ measured by the ultrasound sensor as:
  \[
  \phi = \frac{m}{\rho HA}
  \]

- **Tensile strength.** The difference between the maximum value of the pressure drop and the weight per unit area during the rupture process
  \[
  \sigma_t = \Delta p_{\text{max}} - \frac{mg}{A}
  \]

- **Powder resistance to the gas flow.** The slope of the linear relationship between pressure drop $\Delta p$ and superficial gas velocity $U$

Principal Contributor: Valverde
Breaking takes place at the bottom

\[
\frac{d\sigma}{dx} = \rho_p \phi g - \frac{dp}{dx}, \quad \frac{dp}{dx} = \frac{E \mu \phi^2}{d_p^2 (1 - \phi)^3} v_p
\]

\[
\sigma(x) = \rho_p \phi g \left( 1 - \frac{10 \phi_0 g x}{(1 - \phi_0)^3 v_p} \right) \quad (E=180)
\]

\[
v_p = \frac{1}{18} \frac{\rho_p g d_p^2}{\mu}
\]

We systematically observe a layer of powder that remains adhered to the gas distributor.

The tensile stress from SPT

The cohesivity of a powder is characterised by the plot of its tensile strength, \( \sigma_t \), as a function of the consolidation stress, \( \sigma_c \).

Additionally, the tester provides the solid fraction of the powder versus the consolidation stress in uniaxial compression.

The smaller the tensile strength for a given consolidation, the better the powder will flow in the plastic regime.
Over-weight consolidation and under-weight consolidation by gas flow

Checks

Tensile yield stress measured by increasing quasi-statically the gas flow (solid triangle) and by imposing instantaneous values (void triangles) of the gas flow represented in the horizontal axis.

Increase of 1 cc/min in 3 sec is good enough for quasi-static condition.

Wall effects are negligible if bed height is kept low.

Tensile yield stress versus consolidation stress. Data obtained for toner with 0.4%wt of additive obtained with different bed diameters (4.09 cm, 4.72 cm, 5.08 cm, 8.0 cm) and with a rectangular bed.

Principal Contributor: Valverde
Tensile yield stress as a function of the consolidation stress for an experimental xerographic toner with 0.2% wt concentration by weight of additive. The data from different tests using consolidation by gas (two tests with samples of different masses) and centrifuging in a bed with a metallic gas distributor are plotted jointly with data obtained in a bed with a ceramic gas distributor where consolidation was increased by adding new mass to the sample.

Using different techniques of consolidation. One of them consists of adding mass to the sample contained in a cylindrical bed (diameter $D=5.08$ cm). The other way of consolidation consists of centrifuging the bed. With the technique of adding mass, wall effects are not negligible for around 200 Pa, corresponding to bed heights typically larger than the bed diameter.

Minimum accuracy is needed

- Gas velocity accuracy 0.01 mm/s
- Gas pressure drop accuracy 2 Pa
- Bed height accuracy 0.1 mm
**Essential requirements:**

- Pre-conditioning procedure (assisted fluidization) to **erase powder memory**
- **Shallow beds** to avoid wall effects
- **Accuracy** of the measuring devices

**Viscosity (consolidation time) effects on interparticle contacts**

Tensile stress as a function of the **time during which the powder is consolidated.** Examples are shown for TA toner particles with different surface Aerosil coverage and subjected to different load forces (indicated in parenthesis)
Powders that flow well pack well

Effect of surface additive and particle size

In the old days, the xerographic industry did not have powder flow related problems…
Effect of gel content in host particle

Sevilla Powder Tester measurements of Xerox 6500 and Canon CLC500 Toners

Example of use in industry. Powder flowability may be inferred from the state diagram.
Two samples of different color (magenta and cyan) of the commercial xerographic toner Canon CLC700.

The points of time $T_n$ at which an avalanche occurs are represented against the points of time $T_{n+1}$ of the next avalanche.

Average particle volume fraction as a function of the consolidation stress.

The SPT as a research tool on contact forces.

First derived by Rumpf for a monodisperse packing of hard spheres, wherein the distribution of stresses is isotropic and homogeneous.

The estimated forces are well correlated to forces between individual particles measured by AFM, although for low consolidation stress particle agglomeration must be considered.

Contact forces directly measured with the AFM, predicted by the modified Maugis-Pollock equation ($w = 0.07$ J/m², $\nu = 1/3$, $E = 6$ GPa, and $H = 0.3$ GPa), estimated by means of the Rumpf equation and forces estimated by means of the modified Rumpf equation. The powder tested has 10% of surface additive coverage and 12.7 μm particle size.
Theory on contact forces

Taking into account the Hertz solution for elastic solids the critical load for the initiation of plastic yield within the bulk is \( P_Y \approx \pi d_a^2 Y^3/6E^2 \) where \( d_a \) is the asperity size, \( E \) is the Young modulus and \( Y \) is the yield strength.

Attractive forces contribute to an effective load \( P_0 \) on the contact and, in the absence of external loading, may originate by their own plastic deformation if \( P_0 > P_Y \).

For zero external load the equivalent Hertzian load due to attractive forces is \( P_0 \approx \pi w d_a \) (Derjaguin et al. 1975; Johnson et al. 1971), where \( w \) is the adhesion energy.

Thus we estimate that attractive forces would induce a plastic deformation \((P_0 > P_Y)\) if \( d_a < \frac{6wE^2}{\pi Y^3} \).

For polymer-polymer contacts (typically \( w \approx 0.07 \text{ J/m}^2, \ E \approx 6 \text{ GPa}, \ Y \approx 0.1 \text{ GPa} \)) we get \( d_a < 1 \mu \text{m} \) for the critical asperity size below which plastic deformation is present. This value is clearly larger than our typical asperity size. Thus the elastic limit is well exceeded due to the presence of attractive forces alone.

In the regime where the whole area of contact deforms plastically (fully plastic regime), the modified Maugis-Pollock equation gives an estimate of the interparticle adhesion force \( F_t \) as a function of the interparticle load force \( F_c \):

\[
F_t = \frac{3\sqrt{\pi}}{4} \frac{wE}{(1 - v^2)^{3/2}} \left( F_c + \frac{\pi w d_a}{2} \right) H
\]

\( H \) is the contact hardness.

Effect of surface additives, size hardness, etc on interparticle forces can be estimated

- 100% SAC of 8nm silica nanoparticles on host 7 microns toner particle
- 20% SAC of 40nm silica nanoparticles on host 7 microns toner particle

- The size of silica nanoparticle agglomerates determines asperity size
- The %SAC controls contact hardness

Principal Contributor: Valverde
Estimated Interparticle Forces

\[ \sigma = \frac{2F}{\pi d_o^2} \quad \text{(Rumpf eq.)} \]

\[ \xi = \frac{\pi}{2} (1 - d) \gamma \quad \text{(coordination no.)} \]

ASPERITY SIZE \( d_o \)

\[ F_s \propto \frac{W}{R^{1/2}} \sqrt{F_r + \pi w d_o} \quad \text{(plastic contact)} \]

AGING

The SPT to measure the yield locus

\[ \tau \approx \rho g h_0 \sin(\theta) \]

\[ \sigma \approx \rho g h_0 \cos(\theta) - \Delta P(v_s) \]

Coulomb yield locus at low consolidations
Summary- SPT

• Advantages of the Sevilla Powder Tester are i) results are operator-insensitive since measurements are automatically taken, and ii) fluidization provides a convenient method to have the sample in a reproducible initial state that lacks memory of previous processes.

• Every step in the process is determined by gas flow, and by means of a set of valves and flow controllers, the entire process runs by a computer. The measurements involving gas flow velocity, pressure difference, and bed height are accessed by the same computer, and from these sets of measurements, the values of consolidation stress, average particle volume fraction, and uniaxial tensile yield stress are automatically calculated.

• An upward/downward-directed gas flow is used for deconsolidating/consolidating the powder, and an ultrasonic device measures the bed height giving an average value of the particle volume fraction.

• The usefulness of the SPT is not just restricted to flowability diagnosis. Our experimental work shows that the tester is a powerful instrument of research in powder technology.

Cohesion Reduction by Nano Coating:
Theoretical Considerations

The equation above gives the contact force between two coated particles having one guest particle between the two.

Here $A$ is the Hamaker constant for these materials, and $h_o$ is the atomic scale separation between the two contacting surfaces.

If two particles are not coated, then van der Waal’s attraction force between them is given by the above equation

Hence the ratio between the two cohesive forces (coated and uncoated particles) is as below, assuming $d$ is much smaller than $D$:

$$
\frac{P_{\text{coated}}}{P_{\text{uncoated}}} = \frac{2 d}{D} \approx \frac{d}{D}
$$
Reminder: Van der Waal’s Interactions between Various Geometries

Interaction energies are given for various geometries.

\[ A = \text{Hamaker constant} \]

\[ D = \text{Separation between the bodies, } 1.65 - 4A^* \]

For two equal spheres of radius, \( R \)

\[ F(D) = -\frac{AR}{12D^{13}} \]

Force between two spheres can be given by:

\[ F(D) = -\frac{A}{6D^2} \left( \frac{R_1R_2}{R_1 + R_2} \right) \]

\( \text{For two crossed cylinders} \)

\[ F(D) = -\frac{AR}{12D^{13}} \]

Modeling of Adhesion Force of Group C Powders

- **Rumpf Model**

\[ F_{ad} = \frac{A}{12z_0^2} \left[ \frac{dD}{d + D} + \frac{D}{(1 + d / 2z_0)^2} \right] \]

- Asperity is considered as a hemisphere centered on the contact surface
- Adhesion force comprises two parts—“contact” and “noncontact” force
- Does not take into account the effect of deformation and surface asperity distribution

Principal Contributor: Chen
Modeling of Adhesion Force of Cohesive Powders

- **Sandwich Model**

\[
F_{0c} = F^\alpha + F^\delta = \frac{AD}{12(2z_0 + d')} + \frac{A(D_1 + D_2')}{12z_0^2}
\]

- Adhesion force consists of two terms
- If the asperity is less than 10nm, the surface can be treated as smooth
- If the asperity is more than 0.1um the asperity-particle attraction is dominant
- Does not consider the deformation and surface asperity distribution

Modeling of Adhesion Force of Group C Powders

- **Rabinovich Model**

\[
F_{ad} = \frac{AD}{12z_0^2} \left[ \frac{1}{1 + \frac{1.6 D k_r m s}{\lambda^2}} + \frac{1}{1 + \frac{k_r m s}{z_0}} \right]
\]

- Adhesion force has two components
- Asperity is treated as a hemisphere centered below the contact surface
- The rms roughness is applied instead of the radius of asperity
- The model is valid for small asperity and large peak-peak distance \(\lambda / rms \geq 14.5\)
Modeling of Adhesion Force of Group C Powders

- Mei’s Model

\[
\frac{P_{\text{coated}}}{P_{\text{uncoated}}} = \frac{2R_f}{R_1}
\]

- Adhesion force model is based on surface energy and has only one part
- The adhesion force is reduced dramatically by dry particle coating
- Does not consider the guest particle distribution

\[
f_R = \frac{2R_f}{R_1}
\]

\[R_f\] Radius of guest particle
\[R_1\] Radius of host particle
\[P_{\text{coated}}\] Adhesion force between coated particles
\[P_{\text{uncoated}}\] Adhesion force between uncoated particles

Modeling of Adhesion Force of Group C Powders

- Comparison of the Current Models

Rabinovich model provides the largest adhesion force. Mei’s model provides the smallest.
Rumpf, sandwich and modified rumpf model have the same results.
These plots indicate that there exists a certain asperity size to where the adhesion force takes a minimum value (this will give us the direction on choosing guest particles when we use dry coating to reduce adhesion force).
Modeling of Adhesion Force of Group C Powders

N1, N2, N3 are the centers of guest particles respectively.
C1 and C2 are the centers of two host particles.
R is the radius of contact circle formed by three guest particles.
L is the lateral length of equilateral triangle with three guest particles on vertexes.
H is the distance between centers of host particles.

\[ F_{ad} = \frac{A}{12z_0^2} \frac{3dD}{d+D} + \frac{A}{12H_0^2} \frac{DD}{D+D} \Rightarrow F_{ad} = \frac{Ad}{4z_0^2} + \frac{A}{2} \left( \frac{1 + \frac{d}{D}}{D} - \frac{1.21}{SAC} \frac{d}{D} \right) \frac{1}{D^2} \]

The distance between two host particles \( H_0 \) is calculated by:
\[ H_0 = H - (2z_0 + D) + H - D \]

The distance between center of two host particles \( H \) is calculated by:
\[ R' = \left( \frac{D + d}{2} \right)^{\frac{3}{2}} - \left( \frac{H_0}{2} \right)^{\frac{3}{2}} \Rightarrow R' = \frac{D + d}{2} - \left( \frac{D + H_0}{2} \right)^{\frac{3}{2}} \]
Radius of contact triangle \( S \) is derived from the area of contact circle \( S \)
\[ S = \frac{2\sqrt{3}}{4} R' \]
Assuming that guest particles are evenly and individually distributed on host particle surface, \( S \) could be deduced from the number of guest particles by
\[ N = \frac{\pi D^3}{25} - 2\frac{\pi d^3}{9\rho} \]
The number of guest particles \( N \) can be derived form the Surface Area Coverage (SAC) or weight ratio of guest particles respectively by:
\[ SAC = \frac{N \times d^2}{4D + D} \times 100\% = \frac{N \times d^2}{4D + D} \times 100\% \quad \text{or} \quad \chi_n = \frac{(N \rho_d)}{(D \rho_H)(N \rho_d) + 100\%} \]
Finally, the \( H_0 \) is:
\[ H_0 = \left( \frac{D + d}{2} \right)^{\frac{3}{2}} - \frac{1.21}{SAC} \frac{d}{D} \frac{1}{D^2} \]
Cohesive Force for the Coated Particles as a Function of SAC

Cohesive Force for the Coated Particles as a Function of Guest Particle Size
Powder Testing of Functionalized Powders

• **Functionalization**
  – Modifying properties of powder
    • Dry coating
      – MAIC (Magnetically Assisted Impaction Coating)
      – Hybridizer

• **Characterize powders both before and after modification**
  – Sevilla Powder Tester
  – Hosokawa Powder Tester
    • Carr Indices
  – Vibrated Packing density

The following materials were used:
  • Host particles:
    - Cornstarch, diameter $D \sim 15 \, \mu m$, density $\rho_h = 1.55 \, g/cm^3$
    - Acetaminophen (APAP), diameter $D \sim 50 \, \mu m$, $\rho_h = 1.29 \, g/cm^3$
    - Tolmetin Sodium dihydrate, diameter $D \sim 120 \, \mu m$

  • Guest particles:
    - Silica R972, diameter $d = 16 \, nm$, density $\rho_g = 2.55 \, g/cm^3$, hydrophobic

Powders used in the experiment are processed in Magnetically Assisted Impact Coater (MAIC).
Characterization: Packed Density

Motivation: While SPT provides very useful data on flowability such as the tensile strength and packed density as a function of consolidation stress, it cannot work well with powders that cannot be fluidized well. Hence a new approach is required for measuring packed density.

• Useful as a test of flowability improvement
• Under the same consolidation stress, a more flowable powder will have a higher solid fraction upon packing
  – Under the same consolidation stress, a less flowable powder will have a lower solid fraction than another
• Testing has been done with cornstarch and varying amounts of additive processed in the MAIC under standard conditions

Packed Density Apparatus
Packed Density Apparatus

- Material fluidized to initialize and clear history of the powder
- Material is given time to randomly settle
- Frequency is set to 60 Hz
- Acceleration velocity ranged from 0.5 to 4g in 0.5g increments
- Time cumulatively increased by a minute for each test as the acceleration velocity is increased
- Ultrasound measures the height of the powder and is translated into solid fraction based on the weight of the powder

Packed Density Controller Program

- Totally automated setup with continuous testing

Labworks automated software to control the vibration setup

Winspan program for ultrasonic height sensor
Packed Density Results

- As additive amount increases, solid fraction increases for each consolidation stress
- With 0.5% R972+ Cornstarch, upon vibration, solid fraction nears that of random close packing of a sphere
  - Coated cornstarch, approximately 16 micron in size begins to behave similarly to a 100 micron round glass sphere.
- However, 2% and 5% R972+ Cornstarch do not follow the trend
  - These percentages are over the percentage additive needed for 100% surface area coverage using the MAIC
  - Excess silica might be interfering with the packing.
Packed Density Results (Cornstarch)

Solid Fraction vs Apparent Weight

Packed Density Results (APIs)

Solid Fraction with Increasing Acceleration
Active Ingredients
1. Which flow regime(s) is(are) addressed by the Sevilla Powder Tester? What part of the Yield Surface does the SPT measurements provide?

2. Derive the following equation for estimate of cohesion reduction due to nano-coating.

\[
\frac{P_{\text{coated}}}{P_{\text{uncoated}}} = 2 \frac{d}{D} \approx \frac{d}{D}
\]

3. Reading assignment: Valverde JM et al: The tensile strength of cohesive powders and its relationship to consolidation, free volume and cohesivity, Powder Tech. 97 (1998) 237-245. (a) Explain Fig 9. (b) What can we learn about the capability of the SPT as a flowability measurement device from the results such as those of Fig 12?