Caking of Bulk Solids and its Prevention

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Caking occurs when powders such as detergents, fertilizers, food powders, pharmaceutical formulations, and salts agglomerate when stored at rest. Caking problems can be challenging to solve, as agglomeration is not immediately evident. A product may be easy flowing during packaging; yet customers will report that the received powder has lumps. Operators who had no problems discharging powder from a silo when the plant was operating continuously may find that powder will not discharge after it had been shut down over a weekend.

The best metric for quantifying caking is not necessarily apparent. Those in charge of addressing a caking problem may attempt to measure the number of lumps in a container of powder. Alternatively, the size distribution of the lumps is noted. The investigator will quickly realize that the strength of the agglomerated material is important to measure, but how to measure it is not. Any program initiated to find the causes of caking is unlikely to be successful if a response to a change in a control variable is not quantifiable.

The consequences of unintended agglomeration are never pleasant. Caking may lead to customer dissatisfaction, followed by a decline of sales or a reduction in productivity when returned product must be reworked. Caking can subject plant personnel to dangerous situations when caked material in a silo collapses. This article will summarize the primary causes of caking and how appropriate actions can be taken to solve caking problems.

Caking mechanisms

Caking results when the magnitude of inter-particle forces increase over time. The adhesive forces are primarily van der Waals forces, polar interactions, and those associated with liquid bridges (when moisture is present). van der Waals' forces include all intermolecular forces that act between electrically neutral molecules. Polar interactions occur when the adjacent particles contain regions that are permanently electron-rich or electron poor. van der Waals forces and polar interactions increase as the distance between particles decrease. Both forces are proportional to particle size.

The likelihood of caking, however, generally decreases with increasing particle size. To understand the effect of particle size on agglomeration of powders, consider the experiment illustrated in Figure 1 where a compact of powder having a platen area equal to A and comprised of particles having a diameter d [1]. The tensile strength σ_T is then determined by measuring the force required to cause the compact to fail and dividing that value by the platen area.

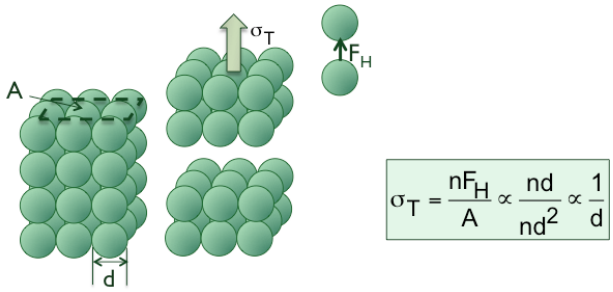

Figure 1. Tensile strength experiment.

Assuming that this force is equal to the sum of the adhesive forces at the individual particle contacts, each equal to F_H and letting the number of contacts equal n, then

$$\sigma_T = \frac{nF_H}{A} \tag{1}$$

The number of particle contacts is proportional to the platen area and inversely proportional to the square of the particle diameter, that is

$$n \propto \frac{A}{d^2} \tag{2}$$

and

$$\sigma_T = \frac{nF_H}{A} \propto \frac{nF_H}{nd^2} \propto \frac{d}{d^2} \propto \frac{1}{d} \tag{3}$$

Hence, although inter-particles forces increase with particle diameter, the strength of a powder decreases with increasing particle size.

With some bulk materials, plastic creep may occur if impurities, which act as a plasticizer, are present or if there is an elevation in temperature. Plastic creep is illustrated in Figure 2. Plastic creep is the tendency of a material to deform when under consolidation. Plastic creep can be severe in powders that are subjected high temperatures for long periods of time, especially when they are above their glass transition temperature or at their melting point.

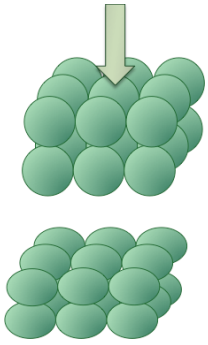

Figure 2. Plastic creep.

Liquid bridging occurs when moisture accumulates at the contact points between adjacent particles. The likelihood of liquid bridging can often be inferred from a powder's moisture sorption isotherm, which relates relative humidity (RH) and equilibrium moisture content. An example of a Type II isotherm [2], which has the sigmoidal shape characteristic of many powders prone to caking, is shown in Figure 3.

As shown in Figure 3, the first region is at low relative humidity where the moisture isotherm is linear. In this region, water molecules are adsorbed until a monolayer is formed. The effect of moisture on caking is generally negligible when moisture levels are very low. As relative humidity increases, multilayer adsorption takes place as a result of hydrogen bonding. In this second region, the slope of the isotherm is initially shallow but steepens with increasing relative humidity. As

moisture uptake increases, the particles become surrounded by moisture. If the solids are water soluble, the layer of moisture can be viscous, and the powder may become cohesive.

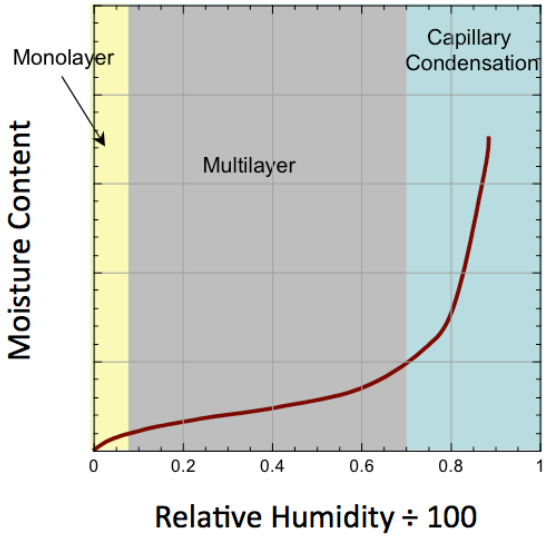

Figure 3. Type II moisture isotherm.

The third region occurs at high RH, where the equilibrium moisture content increases dramatically. In this region, most of the incremental condensation takes place at the contact points between particles. This phenomenon is known as capillary condensation. Capillary condensation is accompanied by liquid bridging, which results in strong forces between particles. This leads to powders that can cake over time. If soluble matter exists in the liquid bridges, and if the liquid evaporates, then strong, solid bridges may form.

Strength of course also depends on the pressure or stress exerted on the powder during storage. The stress on the solids in cylinder increases with bed height. If a powder is packaged in a container with rigid walls, the stress profile is not linear. It depends on the height and cross-sectional area of the container and the friction between the powder and the container walls. The Janssen equation can be used to calculate the pressure profile in a container with vertical side walls (such as cylinder or a box):

$$P = \frac{\rho_b g R_H}{k\mu_w}\left[1 - \exp\left(-\frac{k\mu_w z}{R_H}\right)\right] \tag{4}$$

where P is the vertical solids pressure, ρ_b is the bulk density of the powder, g is equal to the acceleration due to gravity, k is equal to the Janssen coefficient (approximately 0.4 for many materials), μ_w is the wall friction coefficient, R_H is the hydraulic radius of the container, and z is the distance from the top surface of the bulk material. Inspection of the Janssen equation shows that unlike a liquid where the pressure will increase linearly with depth, the solids pressure profile will be asymptotic with a maximum pressure that depends on its diameter.

Quantifying caking

To quantify caking, a test procedure in which the effect of control variables on caking can be measured using small samples offers several advantages. A test in which the temperature, relative humidity, and consolidation pressures used during the test should simulate those expected when a

powder is stored should be one that quantifies the strength of the resultant cake. Results then can be confidently applied because the tests conducted on a small sample will replicate conditions in larger-scale containers or storage vessels.

The strength that a material gains when stored at rest is best measured by shear cell testing [3]. Schematics of direct and annular shear cell testers are shown in Figure 4. The tests are described completely by ASTM D-6128 [4] and ASTM D-6773 [5]. A sample of powder is placed in a cell and then pre-sheared, *i.e.*, consolidated by applying a normal stress and then shearing it until the measured shear stress is steady. Next, the shear step is conducted, in which a reduced load is applied, and the sample is again sheared until it fails. The pre-shear and shear steps are then repeated at the same pre-shear consolidation level and a using a range of shear-step reduced normal stresses.

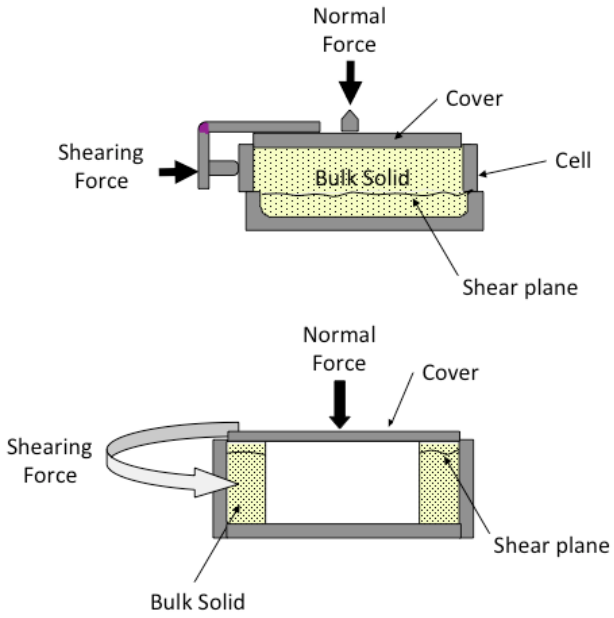

Figure 4. Jenike direct shear cell tester (above) and Schulze ring shear tester (below).

The pre-shear step establishes a consolidation state that replicates the pressures that would be experienced at a particular position in a storage container or vessel. The shear step determines the stress required to cause a consolidated material to fail. From the test results, the major consolidation stress and unconfined yield strength are determined. The major consolidation stress describes the state of stress that was used to consolidate the sample during the pre-shear step, which includes contributions of the normal and shear stresses present in the cell during the pre-shear step. The unconfined yield strength is a measure of the cohesive strength that the powder gained due to its consolidation during the pre-shear step. By conducting the test over a range of consolidation states, the material's Flow Function, which is the relationship between consolidation pressure and the cohesive strength of the material, can be established.

If a material has caked during storage, its cohesive strength, as described by its Time Flow Function, will be greater. The time Flow Function, which is the relationship between consolidation pressure and the material's cohesive strength after it has been stored at rest, is determined in a manner similar to that used to measure its instantaneous Flow Function. When conducting a time test, the sample is kept in a consolidated state after the pre-shear step for the time of interest and then sheared until failure. When the measured cohesive strength of a powder is greater after storage at rest than during continuous flow, this is an indication that caking is likely to occur under the test conditions.

Shear cell testers can also be used to measure the material's wall friction, which is required if the solids stress in a rigid container must be calculated. Wall friction is measured by following the method described in ASTM D-6128 [1]. To measure wall friction, the sample is placed inside a cell on a flat coupon of wall material. A normal load is then applied to the powder, and the shear stress that is required for the sample to flow along the wall is measured. The friction coefficient is the ratio of the shear stress to the normal stress. Because it is a function of normal pressure, the test is repeated over a range of normal loads.

Some materials exhibit plastic creep, which is the tendency of a solid material to slowly deform permanently under the influence of a mechanical stress. The engineering strain is defined as the ratio of total deformation to the initial dimension of the material body in which the forces are being applied. Because bulk density can be measured during a shear cell test, ε, can be calculated from:

$$\varepsilon = \rho_{b0}\left(\frac{1}{\rho_{bt}} - \frac{1}{\rho_{b0}}\right) \tag{5}$$

where ρ_{b0} and ρ_{bt} are the initial bulk density and bulk density after time at rest, respectively.

Figure 5 is an example of instantaneous and time Flow Functions for a pharmaceutical powder. Note that during continuous flow, this powder has low cohesive strength over a range of consolidation pressures. However, when this material is stored, it becomes very cohesive, especially when subjected to high consolidation pressures as indicated by a time Flow Function that lies well above the continuous Flow Function.

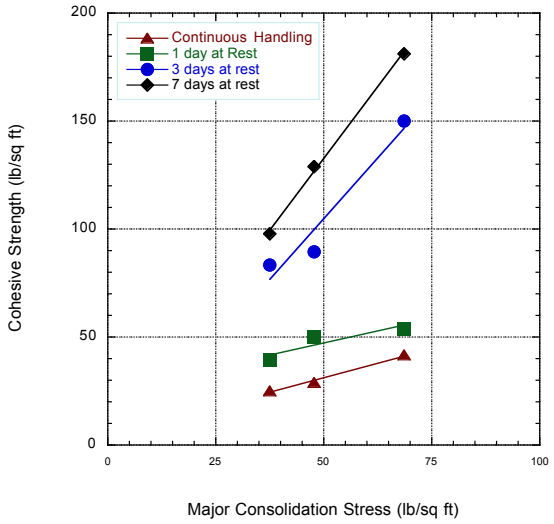

Figure 5. Cohesive strength of a pharmaceutical powder.

Figure 6 illustrates how the cohesive strength of the material stored at a consolidation pressure of 50 lb/sq ft increases with time. (50 lb/sq ft is the solids stress at the bottom of a standard 55-gal drum as calculated by the Janssen equation using an average bulk density of 26 lb/cu ft and a wall friction coefficient of 0.4). The results show that the strength of the material increases rapidly at first, but then the rate of increase decreases over time.

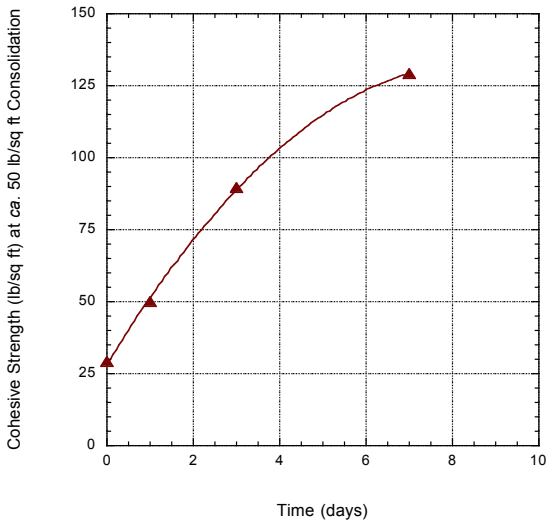

Figure 6. Strength of a pharmaceutical powder versus time, consolidation pressure equals 50 lb/sq ft.

Investigating the causes of caking

Tackling a powder caking problem entails the following steps:

1. A hypothesis based on possible mechanisms behind caking is developed.
2. Potential process control variables or product specifications are identified.
3. Investigations are conducted in which control variables or product specifications are adjusted and samples of powder are collected.
4. The samples are tested to quantify caking.

Preliminary tests to characterize the powder can be performed to help select process variables or product specifications to be investigated. These tests include moisture sorption, surface energy, differential scanning calorimetry, and particle size. For example, if a product is known to be hygroscopic, a program to determine the effect of moisture content or relative humidity should be performed. If a package of powder is expected to be stored for an extended time in a warehouse with no temperature controls, an investigation in which materials are stored over a range of temperatures should be conducted.

How shear cell testing can be used to investigate caking problems is best described by example.

Effect of particle size

Although this may seem contradictory, intentional agglomeration, or granulation, is commonly used in certain industries to prevent unintentional agglomeration or caking. The reasoning behind this approach is that cake strength is a function of the number and strength of contact points per unit volume. Granulation decreases the number of contact points, thereby decreasing the potential strength of a cake that may form and reducing the tendency for this to occur.

The results from strength tests performed on samples of fine salt and granulated salt are given in Figure 7. The fine salt was very cohesive, and its strength increased after only eight hours under

consolidation at rest. By increasing its median particle size from 10 μm to 100 μm, the salt becomes non-cohesive and remains non-cohesive when stored at rest.

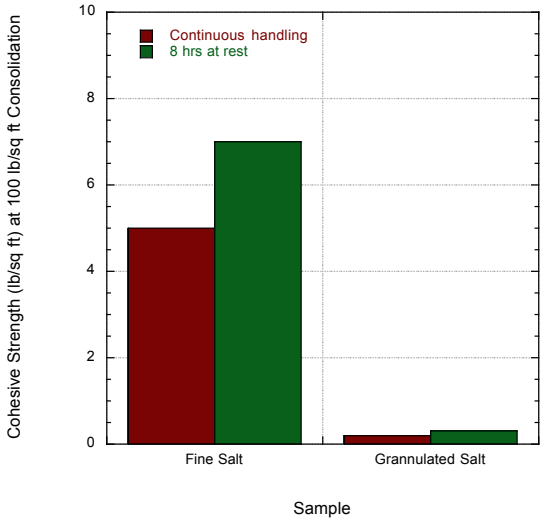

Figure 7. Effect of particle size on the strength of a salt.

Effect of moisture content

The presence of water in a powder can cause caking for two reasons.

1. Water often acts as a plasticizer, which can cause the powder particles to deform when under stress.
2. At high moisture levels, water can accumulate at the particle contact points, leading to liquid bridging. If the water then evaporates and the solid is water-soluble, solid bridges, which are exceptionally strong, may form.

Figure 8 illustrates the plasticizing effect of water on a powdered nutritional product. Because water acts as a plasticizer for this material, exposure to high relative humidity results in plastic creep. Deformation of the powder particles increases the inter-particle contact area and decreases the distance between particles. Hence, the strength of the powder increases when the material is stored in humid environments. Packaging that is impervious to water is required for storing this product.

Liquid bridging can take place if the air that surrounds a powder approaches its critical relative humidity (ERH). A powder's ERH is indicated when the slope of its moisture isotherm begins to steepen greatly. The moisture isotherm of the sample of lactose shown in Figure 8 suggests that its ERH is approximately 80 percent. At equilibrium, the moisture content of this powder is 0.05 percent (dry basis).

Caking tests confirmed that lactose exposed to 80 percent relative humidity indeed had high strength. A moisture specification of 0.05 percent would appear to be acceptable. Any specification based on equilibrium moisture content, however, should account for the possibility of moisture migration.
Moisture migration

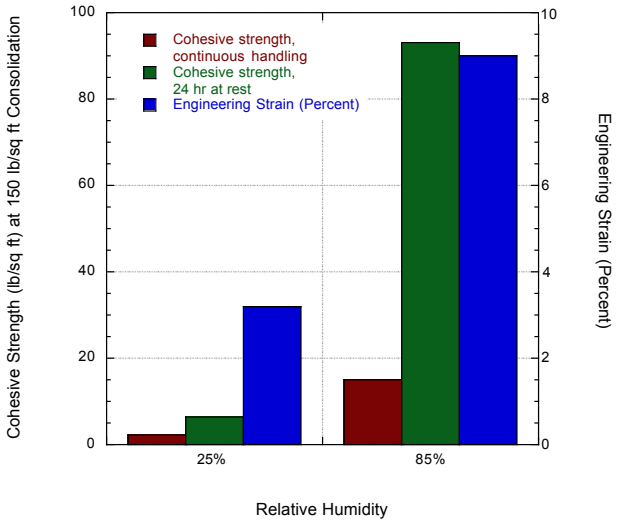

Figure 8. Effect of moisture content on the engineering strain and cohesive strength of a nutritional powder.

occurs when a temperature gradient exists during packaging, storage, or transit of powders.

The mechanism of caking due to moisture migration is as follows:

- Relative humidity of interstitial air at warm boundary decreases.
- As a consequence, moisture desorbs from the warmer solid as the solids and interstitial air are no longer in equilibrium.
- The *absolute* humidity of interstitial air increases.
- The driving force in gas phase leads to moisture migration toward interior, which has a lower absolute humidity.
- The relative humidity of cooler interstitial air increases.
- Moisture adsorbs onto solids in interior in an effort to re-establish equilibrium.

Moisture migration is illustrated Figure 9.

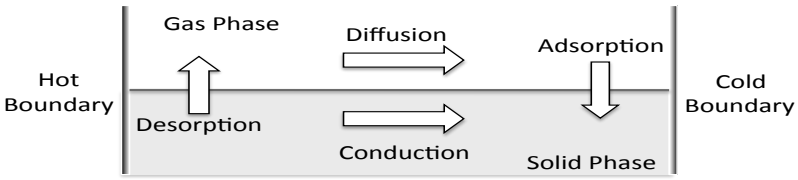

Figure 9. Schematic describing moisture migration.

An analysis can be formed to determine the moisture distribution in the bulk solid that will take place if a temperature gradient is imposed. The analysis assumes that the temperature gradient

remains constant, which is not true, and therefore allows a conservative view of possible conditions that can exist if temperature differences were to exist for an extended time.

The analysis is as follows. If a powder were exposed to a warm surface (temperature = T_H) and a cool surface (temperature = T_C), the temperature profile at steady state would be given by:

$$T = T_C + (T_H - T_C)z \tag{6}$$

where z is the distance from the colder boundary. At steady state, a constant *absolute* humidity H_{SS} will be reached.

The activity a_w is related to absolute humidity by:

$$a_w = \left(\frac{H_{SS}}{\frac{18}{29} + H_{SS}} \right) \frac{P}{P_w^{sat}} \tag{7}$$

where P_w^{sat} is the vapor pressure of pure water and P is the absolute pressure. Since the vapor pressure is a function of temperature and a temperature gradient exists in the powder bed, the activity, *i.e.*, the relative humidity of the interstitial air expressed as a fraction, is a function of its location in the bed.

From sorption tests, the relationship between the solid's equilibrium moisture content X and activity is known. For ease of calculations, the data can be fit to a model by regression. The GAB (Guggenheim, Anderson, de Boer) model [6] is appropriate for lactose:

$$X = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{8}$$

where X is the moisture content of the powder (dry basis), and X_m, C, K are constants determined by regression. The parameter X_m is related to the powder's monolayer content.

Once steady-state has been reached an equilibrium moisture content profile will exist in the powder bed. As the amount of moisture in the gas phase is very small compared to that in the solid, the total amount of moisture in the solid after migration can be assumed equal to the initial solid moisture content X_0, *i.e.*,

$$\bar{X} = \int_z X(z)\,dz = X_0$$

The system of equations can be used to determine critical moisture content or CRH of a powder. Results of the analysis conducted for a sample of lactose in a container having hot and cold boundaries of 72°F and 100°F, respectively are given in Figure 10. The analysis shows that to ensure that the moisture content of this sample of lactose does not exceed 0.05 percent moisture, which would result in caking, its initial moisture content must be no greater than 0.031 percent if it is exposed to 100°F.

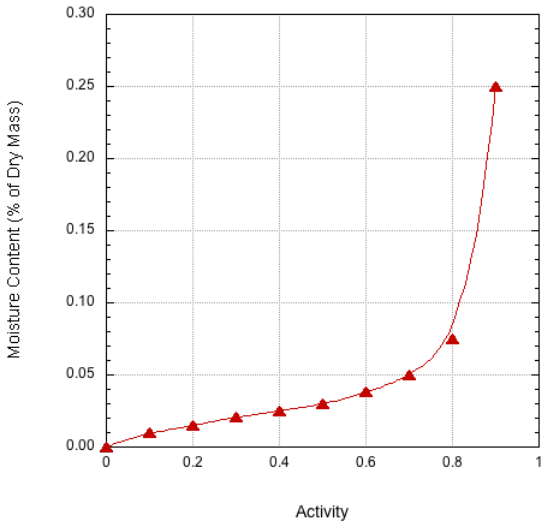

Figure 10. Moisture sorption isotherm of a grade of lactose.

Effect of composition

Frequently, the cause of caking is due to impurities in the powder, especially if they act as plasticizers that soften the particles. Figure 11 compares the strength of a sample of powder before and after it was washed with water. Removing impurities, in this case, residual solvent, which softened the powder particles, was effective in reducing the material's strength.

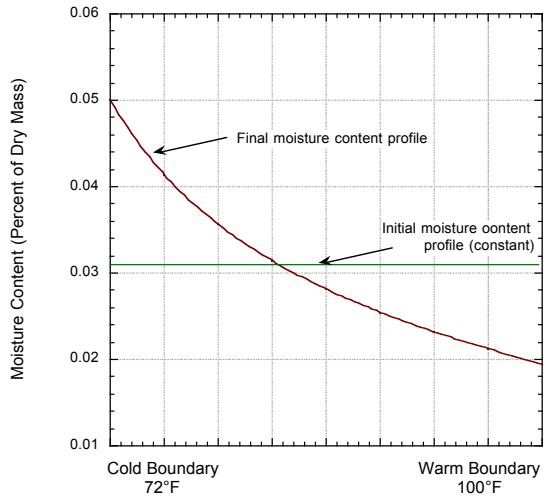

Figure 11. Moisture content profile of a container of lactose subject to a temperature gradient.

There are cases where the addition of another component to a bulk solid will reduce caking. When permissible, addition of a flow aid such as a parting agent can reduce the occurrence of caking. Parting agents are generally sub-micron in size and reduce the cohesive strength of a bulk material by increasing the distance between adjacent powder particles. In most cases, only a small amount of

flow aid (typically less than 1%) needs to be added to be effective. Figure 11 also shows the effect of adding 0.5 percent fumed silica to the same powder.

Effect of temperature

High temperatures often are the cause of caking of bulk solids, even those comprised of pellets that are typically free flowing. Tests were conducted on a sample of low-molecular-weight pellets were conducted over a range of temperatures. Results are summarized in Figure 12.

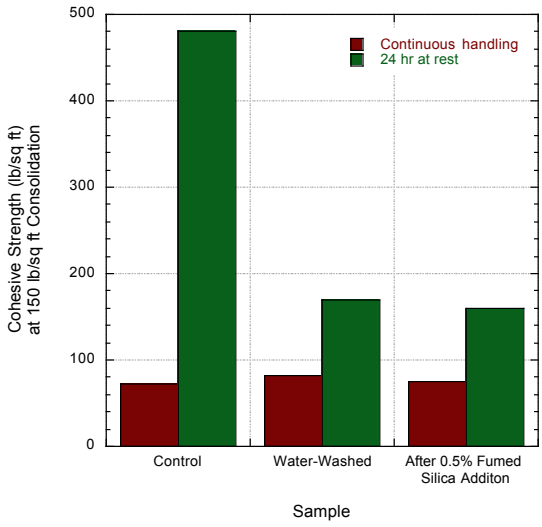

Figure 12. Effect of composition on the cohesive strength of an organic acid powder.

Tests were conducted on a sample of low-molecular-weight polymer pellets over a range of temperatures. Results are summarized in Figure 13. The test results suggest that the glass-transition temperature of the polymer lies between 140°F and 170°F. At a temperature within this range, the polymer begins to soften and plastic creep takes place. Note that if the temperature is cooled to room temperature after it had been heated to 170°F, the cohesive strength of the pellets after cooling is extremely high, suggesting that annealing had taken place.

The polymer was pelletized by melt extrusion followed by water-cooling. To prevent the pellets from agglomerating during storage, an additional cooling step is required to ensure that its packaging temperature is well below its glass transition temperature.

Effect of packaging

Cohesive strength depends on the stress imparted onto the powder, *i.e.*, the higher the applied stress, the higher the strength of a cohesive powder. The stress on a powder stored inside a container of constant cross-section depends on the container height, diameter, and wall friction, as described by the Janssen equation.

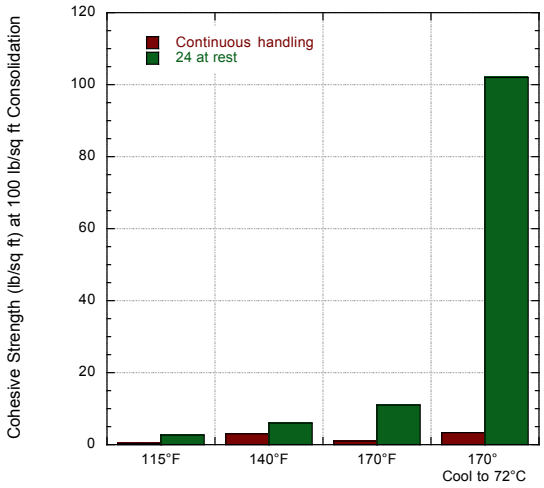

Figure 13. Effect of temperature on the cohesive strength of a sample of low-molecular-weight polymer pellets.

Test results shown in Figure 5 along with bulk density and wall friction measurements were used to calculate the solids stress profiles and cohesive strength of powder stored in 10, 15, 30, and 55-gallon drums. Figure 14 shows the solids stress at the bottom of each drum and the cohesive strength of this powder after seven days storage. The strength of the consolidated material is reduced when it is packaged in smaller containers. Because the solids stress in containers that have smaller diameters and shorter heights is reduced, powders packaged in smaller containers are less likely to cake.

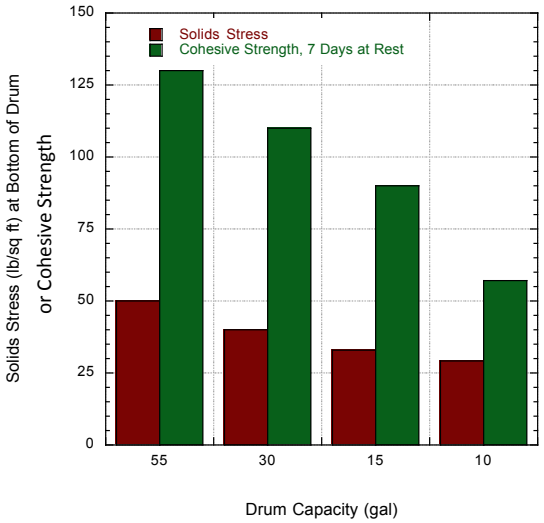

Figure 14. Effect of container size on solids stress and cohesive strength of a pharmaceutical powder.

Final remarks

Having a test method that allows quantitative rather than qualitative comparisons of test results in a relatively short period of time makes attacking powder caking problems much less intimidating. Because shear cell tests simulate conditions for which a powder will be exposed during storage, investigators can be confident in the results. By understanding the mechanisms behind caking, identifying key process control variables and product specifications, and initiating a program where the gain in cohesive strength of a powder over time can be predicted by obtaining small samples, caking problems can be successfully remedied.

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