



Review

A review of bulk powder caking

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ABSTRACT

The handling and storage of bulk powders is common in many industries such as detergent, pharmaceutical, bulk chemical and food. A lot of materials are susceptible to changes with time that may lead to bulk powder caking, resulting in an unmanageable powder and process downtime, which impacts upon profitability. In this review the current state of the art related to powder caking is explored. The relevant interparticle interactions are discussed with respect to elastic and plastic deformations and the development of liquid and solid bridges due to capillary condensation, sintering and solvent evaporation. The environmental, i.e. temperature and humidity, and the mechanical conditions can heavily influence the transformation of a bulk powder and a number of studies are available that attempt to relate these conditions to caking. A significant amount of work related to the caking behaviour of amorphous powders is available in the literature. Amorphous materials are susceptible to caking due to environmental conditions influencing the glass transition temperature. Once the temperature of amorphous powders exceeds the glass transition, viscous flow occurs and cake strength increases. Crystalline solids may undergo transformations leading to caking. It can take a considerable time and cyclic environmental conditions for caking to occur. However, little research focuses on cyclic conditions and there is limited predictive capability. Finally the options available for attempting to reduce caking propensity are briefly covered and a section that discusses the available caking test methods is given.

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1. Introduction

The undesirable transformation of bulk powders, such as caking and deliquescence is a common problem in a number of industries including detergent, food, fertiliser, pharmaceutical and chemical. By definition, powder caking may be viewed as the detrimental aggregation of particles, which transforms a readily free-flowing powder into a coherent solid. The amount of caked material can vary from large lumps, which willingly break up when stressed, to the irreversible fusion of particles that are no longer representative of the original material. The environmental and mechanical conditions a material experiences can considerably influence bulk powder transformation. In certain conditions, a material may be so hygroscopic that it deliquesces. Obviously caking and deliquescence can be a significant problem that may lead to a loss of material functionality and a lower quality product [1]. This could have a large impact on profitability.

Bulk powder caking is a very challenging topic because there are many reported mechanisms that may lead to powder transformation and few studies have taken a holistic view of the subject [2]. Griffith [3] provided a very useful and practical overview of caking and broadly classified the subject into four groups: (a) mechanical; (b) chemical; (c) plastic-flow; and (d) electrical. There are many features that need to be considered when understanding caking propensity. Intrinsic factors such as cohesion, elasticity, yield stress, amorphous content, hygroscopicity, particle size and many others will inevitably influence caking behaviour; however, extrinsic factors such as temperature, humidity, stress, strain rate, vibration may also heavily influence caking. This makes it very difficult to reliably predict how a powder will behave. This is especially the case when the timescale for a powder to cake is so long that extrapolation of laboratory data is common.

In this review, the current state of the art and the experimental approaches available for investigating bulk powder caking are addressed. A summary of relevant particle interactions, contact mechanics, caking mechanisms and dynamics is given. Finally, a section detailing the commonly used experimental test methods is provided.

2. Particle interactions

Powders may experience a variety of interparticle forces and these have been classified according to their relative magnitudes, from strongest to weakest: (a) solid bridges; (b) liquid bridges; (c) van der Waals; (d) electrostatics; and (e) magnetic [4]. There are extensive reviews of theories and experimental studies available in the literature related to interparticle forces [5–13]; consequently, it is unnecessary to focus on these interactions in great detail, but rather discuss literature that is relevant to caking. Forces such as van der Waals, electrostatics and liquid bridges serve to bring particles into contact; however, without extrinsic factors, it is unlikely these forces will spontaneously lead to cake formation.

2.1. van der Waals

There are different classes of van der Waals force and more detail is available in the literature [7,12]. The dispersion force is due to local polarisation within molecules caused by random fluctuations in electrons and is consequently transient and induced; these are regarded as non-specific interactions. Specific van der Waals forces are due to interaction between molecules with permanent dipoles.

2.2. Electrostatic forces

The science of electrostatics is in itself highly challenging as there are many mechanisms that influence particulate behaviour [14]. Electrostatic forces may be responsible for particle deposition of airborne particles on processing walls, which may promote powder make-up; however, there is little evidence suggesting that electrostatic forces play a significant long term role on powder caking. A possible explanation for this is that the potential difference between particles dissipates much more rapidly compared to the time required for caking [2]. However, in the presence of electric fields, particles adhere strongly to each other due to the electro-clamping phenomenon [15].

On the other hand, electrical caking has been implicated as a possible mechanism that may lead to caking; although the cake strength is typically relatively weak [3]. For example, the application of a mechanical stress can induce a charge polarisation in crystals, known as the piezoelectric effect, which can promote caking; pyroelectric caking can occur as a result of charge polarisation due to heating or cooling crystalline materials; and finally, ferroelectric caking may happen when crystals are placed in an electric field.

2.3. Liquid bridge forces

It is recognised that liquid plays a pivotal role in bulk powder caking and may be present between particles as a result of condensation from vapour, or because it is intentionally added, for example, as a binder. A more detailed review of capillary forces has been made by Seville et al. [16]. Capillary forces are an initial mechanism that may lead to subsequent cake formation and there are many studies that investigate the relationship between agglomerate strength and interparticle forces [17–24].

The capillary force, depicted in Fig. 2.1, is positive, as long as the liquid wets the solid particles. For particles typically smaller than 1 mm in diameter, the two components of the capillary force are the reduced hydrostatic pressure and the axial surface tension, and the resulting capillary force, F_c , is

$$F_c = \frac{2\pi R\gamma}{1 + \tan\left(\frac{\beta}{2}\right)} \quad (2.1)$$

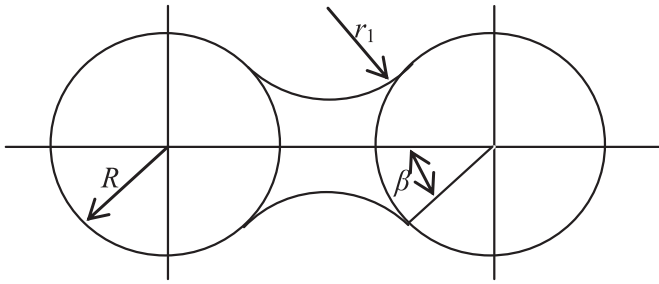


Fig. 2.1. Illustration of a liquid bridge.

where R is the particle radius, γ is the interfacial surface tension between the liquid and air, and β is the bridge half-angle. Due to a reduction in the pressure difference between the liquid in the bridge and the surroundings as the concave radius, r_1 , increases, the capillary force decreases as the bridge volume, represented by β , increases.

If the contact area is significantly smaller than the radius of the particles, Eq. (2.1) between two equal sized spheres reduces to

$$F_c = 2\pi R\gamma \tag{2.2}$$

In the case where the liquid does not completely wet the spheres, Eq. (2.2) is modified to include the contact angle, ϑ ,

$$F_c = 2\pi R\gamma \cos\vartheta \tag{2.3}$$

The above equations for liquid bridges represent a static force and will vary as the particle separates. As the two particles move apart, the force will be influenced by the liquid viscosity and the separation rate. Additionally, as the particles separate it has been observed by Cleaver and Tyrell [25] using atomic force microscopy (AFM) that liquid may feed into a bridge from the film coating the particles, which increases the bridge volume.

2.4. Contact mechanics

Contact mechanics between particles is an important area that should not be ignored when considering bulk powder transformations. Whatever the bonding mechanism that initially binds particles, the key parameter affecting the interparticle force is the size of the contact area. Particles may deform either elastically or plastically, meaning the particle will fully recover or is permanently deformed, respectively. In addition, the role of particle roughness should be considered. In the sections below, particle contact mechanics related to bulk caking are summarised. For more detail regarding particle contact mechanics, a number of reviews are available (e.g. [16,26,27]).

2.4.1. Elastic deformation

A particle that deforms elastically will fully recover once the applied stress is removed. An exception to this statement is when elastically deformed surfaces are in contact for a significant time that the contact permanently bonds due to molecular rearrangement, which is time and strain rate dependent [8]. This type of bonding is likely to yield weak cakes because elastically deformed contacts have adequate residual elastic strain energy which would assist bond rupture.

The force, P_{off} , necessary to separate elastically deformed particle contacts and the contact area can be calculated using the well-established JKR model [9],

$$P_{off} = \frac{3}{2}\pi\Gamma R^* \tag{2.4}$$

where Γ is the interface energy and R^* is the reduced radius, both are defined in the below equations.

$$\Gamma = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2.5}$$

$$\frac{1}{R^*} = \frac{1}{R_1} + \frac{1}{R_2} \tag{2.6}$$

where γ_1 and γ_2 are the surface energies of two particles made of different materials, γ_{12} is the interaction energy between the surfaces and R_1 and R_2 are the radii of the two particles, respectively. For surfaces of the same material, γ_{12} is zero and, therefore, $\Gamma = 2\gamma$.

2.4.2. Plastic deformation

If a contact deforms plastically the material will not be able to fully recover, which will lead to higher contact areas and, consequently, higher adhesion forces that may lead to cake formation. A contact will plastically deform when the contact stress is greater than the yield stress of the material. The extent of plastic deformation does not have to be significant for it to lead to a dramatic increase in bulk powder strength [28].

The model of Maugis and Pollock [29] has been successfully used to predict the contact diameter, D , from a plastic contact between two spheres,

$$D^2 = \frac{4Wd}{3Y} \tag{2.7}$$

where W is the work of adhesion, d is particle diameter and Y is yield stress. The above model is related to normal contact deformation; however, it is common for contacts to deform plastically due to shear deformation, which may be more effective at increasing the interparticle contact area [30]. Cleaver and Looi [31] successfully applied Eq. (2.7) to predict the onset of a plastic contact. Within this study AFM was used to investigate the adhesion of polystyrene spheres as a function of applied load. It should be noted that smaller particles are more likely to deform plastically. This is due to the adhesive force between particles being directly proportional to particle diameter; however, contact area is proportional to $d^{4/3}$ and, therefore, the contact area decreases at a faster rate than the adhesive force.

2.4.3. Surface roughness

An interesting feature of particles is that their surfaces are not perfectly smooth, but have asperities that invariably influence particle-particle interactions. Contact adhesion is related to the contact area and the nature of the asperity contact, i.e. if two asperity peaks are in contact or if the asperity fits into a trough of the other particle. This may lead to a smaller or larger area as opposed to smooth surfaces. Another feature of surface roughness is that asperities influence the stress acting at the contact and capillary condensation therein. Landi et al. [32] suggest that even for relatively smooth glass beads water condenses mainly on rough surfaces of the particles, influencing the interparticle capillary forces. This coupled with high stresses may lead to plastic deformation of the asperities, which will increase the overall strength of the powder as compared to its initial state. If the condensed liquid engulfs surface features at high levels of relative humidity, it can change the way the contact behaves by reducing the influence of van der Waals attraction. This would lead to adhesion being dominated by liquid bridges [19,31]. Consequently, the influence of surface roughness should not be ignored when considering bulk powder transformations.

2.5. Solid bridge formation

As categorised by Simons [4], solid bridges form very strong particle interactions and it is these interactions that are crucial to forming strong bulk powder cakes. In contrast to van der Waals, electrostatics and liquid bridges, solid bridges form a continuous solid connection and

can arise from a number of mechanisms including sintering, melting-solidification, dissolution-crystallisation, chemical reactions and the solidification of a binder.

2.5.1. Sintering

The coalescence of particles is driven by the system minimising the surface free energy by reducing the surface area [26]. The interparticle contact time and applied stress are regarded as important parameters that lead to solid bridges by sintering [33]. The ratio of the contact spot area to the original surface area of the sphere can be taken as the amount of sintering, *S.R.*,

$$S.R. = \left(\frac{a}{2d}\right)^2 \quad (2.8)$$

where *a* is the contact spot diameter. If Eq. (2.8) is scaled according to the coordination number of the assembly, an estimate of bulk powder sintering is calculated. However, such an approach would need to consider the distribution of contact areas that would exist in the sample.

It is possible for sintering to occur in elastic contacts and the extent of caking can be estimated from the JKR theory [9]. When the resistance to deformation is elastic, the equilibrium contact size is a balance between the adhesive force and the elastic restoring force. However, it is not expected that caking through elastic sintering will be a major mechanism driving cake formation.

As previously discussed, the contact area due to plastic deformation is greater compared to an elastic system; consequently, sintering due to plastic deformation is more significant in caking. The theory of Maugis and Pollock [29] can be used to estimate the sintered fraction, using the common approximation that hardness, $H = 3Y$, where *Y* is yield stress,

$$S.R. = \frac{12W}{Hd} \quad (2.9)$$

where *W* is the work of adhesion. The development of a plastic contact area is assumed to be instantaneous; however, in some cases the contact may develop over time due to viscous flow of the particles. On a bulk scale this is referred to as creep. The theory that describes viscous contacts is given by Frenkel [34]. The increase in contact area, based on the contact diameter, *D*, between particles increases with contact time, *t*, but is inversely proportional to the contact viscosity, η :

$$D^2 = \frac{3tWd}{2\eta} \quad (2.10)$$

As particles coalesce it leads to irreversible densification of the bulk powder. Kendall [26] states that the extent of shrinkage is over predicted using Eq. (2.10) due to the presence of stable agglomerates, which resist viscous flow. Current understanding of viscous contacts is that residual stresses in the system, that would otherwise promote bond rupture, dissipate, which encourages the formation of cakes [28]. Viscous contacts are common with amorphous powders that are above the glass transition temperature; due to a decrease in contact viscosity (i.e. an increase in molecular mobility).

In addition to the sintering mechanisms already highlighted, Kendall [26] discusses five other mechanisms that also play a role in cake formation: solid-state diffusion, grain boundary diffusion, surface diffusion, gas phase transport and liquid layer transport. These are summarised in Fig. 2.2.

Herring [35] demonstrated that each diffusion mechanism responds differently with respect to the time of the process and the particle diameter. The following relationship may be used as a scaling rule depending on the mechanism,

$$\frac{t_2}{t_1} = \left(\frac{d_2}{d_1}\right)^n \quad (2.11)$$

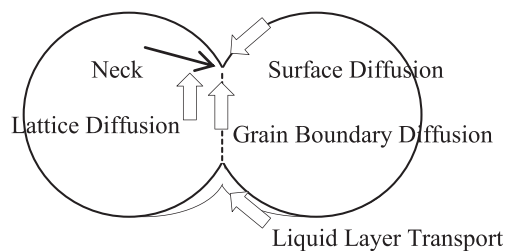


Fig. 2.2. A summary of different diffusion mechanisms for crystalline particle sintering [26].

where *n* is an index that depends on the mechanism: 1 for viscous flow, 3 for bulk diffusion and 4 for grain boundary diffusion.

2.5.2. Solvent evaporation

If a liquid bridge exists between particles and the liquid contains a solute material, it is possible that the solute solidifies and creates a solid bridge upon liquid evaporation. It is common that the solid bridge is due to a soluble component in the original powder. The solubility of constituent particles is shown to influence granular strength by comparing lactose assemblies exposed to ethanol and water [36]. The granules formed in ethanol had a lower strength than those produced in water. Lactose is insoluble in ethanol; however, due to lactose being soluble in water this leads to dissolution and re-crystallisation, which promotes solid bridge formation. Listiohadhi et al. [37–40] suggested that storage below 33% relative humidity is sufficient to prevent severe caking in dairy powders, whilst milling causes the formation of more hygroscopic amorphous lactose and stronger caking tendency. The caking characteristics of powders generally depend on the type of lactose polymorph [41]. The caking and stickiness of different water-soluble powders are discussed by Palzer and Sommer [42]. In addition, crystal expansion between particles has been identified for lactose and mannitol [43], and for sodium carbonate [44]. The dilation of the bridge leads to a recorded negative force as the bridge forces the particles apart, which could serve to compress a confined powder.

Langlet et al. [45] focused on the kinetics of dissolution followed by evaporative-recrystallisation of sodium chloride powder as the cause of caking, showing that the rate of dissolution is proportional to the difference between the imposed relative humidity *RH* and the deliquescence *RH* and follows a model based on the kinetic theory of gases.

Tardos and Gupta [44] investigated polymer bridge strength between two surfaces using an aqueous solution of carbowax (PEG 350). An amorphous structure between the surfaces was formed, which comprised of a number of strong polymeric strands that tended to rupture during bridge formation. The influence of bridge volume was studied and smaller bridges exhibited higher strength per unit mass than larger bridges.

In a lot of cases, powders will contain many components that will impact on the caking behaviour of the system. Mixed component systems have been found to be very complex; Bika et al. [36] determined the bond strength from granule uniaxial compression tests and found that the compatibility between components affected the cake strength. In fact, it has been suggested that an incompatibility between components may reduce caking propensity. Farber et al. [43] modified a texture analyser to accommodate two glass slides, between which a solid bridge was formed; this approach was used to directly measure solid bridge strength. Bridges that were formed from pure lactose or mannitol were relatively weak because they were polycrystalline and brittle, which implied a large number of defects that allowed for crack propagation. The bridge strength greatly increased when small amounts of HPC, HPMC and PVP were added to the system. This is in apparent contradiction to the study by Bika et al. [36]; but the difference is most likely due to different methods of producing bridges and determining bridge strength.

The discussion thus far has been related to the formation of bridges that remain in a state of equilibrium; however, it is likely that bridges will evolve with time. Bagster [46] investigated the shear strength of sugar samples that had been time consolidated for up to 16 weeks. Before storage, the samples were free-flowing; however, during storage the shear strength increased and had a maximum after around 30 days and then at 80 days. Using scanning electron microscopy, the bridge morphology was evaluated. It was suggested that bridge strength decreased due to the presence of cracks in the bridge as a result of micro-crystallinity. Subsequently, these cracks would “heal”, and the shear strength would increase.

Surface modification and caking with time during constant temperature and humidity conditions has also been observed for boric acid crystals [47,48]. In this case, the surface changes were attributed to Ostwald ripening. Atomic force microscopy was used to identify crystal growth by the dissolution of convex sub-micron surface features into the liquid, which leads to a supersaturated layer. It is expected that other water soluble systems will exhibit Ostwald surface modification.

3. Amorphous powders

Amorphous materials are complex and exist in a meta-stable state [49,50]. They possess a glass transition temperature, T_g , that can heavily influence the caking propensity of a material. Above the glass transition temperature amorphous powders exist as liquid-like rubbers; however, below the glass transition temperature they behave in a rigid, glassy manner [51,52]. Molecules within an amorphous material possess a mobility, which implies that viscous flow of the material can occur and will be more pronounced above the glass transition; inevitably, this will increase the extent of caking and is a common mechanism. To exacerbate the situation, the presence of moisture in amorphous materials acts as a plasticiser and reduces the glass transition temperature [1]. A material may exhibit substantial caking tendencies above the glass transition and this can occur by raising either the environmental temperature or by increasing moisture content. Amorphous powders are common within the food industry and a review of stickiness in foods is given by Adhikari et al. [53] and Ruan et al. [54].

3.1. Glass transition temperature

Below the glass transition temperature, in the glassy state, the viscosity of a solid is expected to exceed 10^{12} Pa [49,55]; therefore, the molecular movement is restricted. At the glass transition temperature, the material undergoes a dramatic reduction in viscosity to between 10^6 and 10^8 Pa [55]; furthermore, other properties of the material change, including:

- increase in free molecular volume;
- decrease in elastic and plastic moduli;
- increase in heat capacity;
- increase in thermal expansion coefficient;
- increase in dielectric coefficient.

Water has a glass transition temperature of -135 °C. If a secondary material has a higher glass transition temperature and is mixed with water, the secondary materials glass transition temperature reduces. The mixture glass transition temperature, T_{gm} , is commonly predicted by the Gordon and Taylor equation [56]:

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (3.1)$$

where T_{g1} and T_{g2} are the glass transition temperatures of components 1 and 2, respectively, k is a constant and w_1 and w_2 are taken as the mass fractions of the components [55]. Eq. (3.1) can be adapted for mixtures consisting of more than two materials. It has been suggested that k may

be predicted from the ratio of the change in specific heat capacity between the glassy and rubbery states [57,58],

$$k = \frac{\Delta C_{p2}}{\Delta C_{p1}} \quad (3.2)$$

Typical values of k are given by Roos [50].

Above the glass transition temperature, the material viscosity can be predicted by the Williams-Landel-Ferry (WLF) equation,

$$\log \frac{\mu}{\mu_g} = \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \quad (3.3)$$

where μ is the viscosity at temperature T , μ_g is the viscosity at temperature T_g , and C_1 and C_2 are constants with common values being 17.44 K and 51.6 K, respectively [49,50]. The WLF equation describes the increase in molecular movement above the glass transition temperature and can be used to predict crystallisation time as a function of temperature elevation ($T - T_g$).

A simple mechanistic model was introduced by Downton et al. [55] to describe the condition of viscous flow of material between the particles. It is assumed the flow between the particles is driven by surface tension,

$$\mu = \frac{x \gamma \tau}{K d} \quad (3.4)$$

where μ is the critical viscosity required for sticking, x is a proportionality constant with an assumed value of unity, γ is the surface tension, τ is the contact time and K is the fraction of particle diameter required as a bridge for a sufficiently strong bond [49]. The above can be extended to predict caking times. The mechanism of viscous flow caking of amorphous powders was also observed by Lloyd et al. [59]. The onset of viscous flow of the particles was detected by observing an increase in bulk density and the driving force of caking of amorphous materials by viscous flow is $T - T_g$. Similar observations have been reported by Fitzpatrick et al. [60], Paterson et al. [61] and Foster et al. [62].

3.2. Viscous flow kinetics

The WLF model is a powerful relationship that relates the change in viscosity or relaxation time to $T - T_g$ for an amorphous solid above its glass transition temperature. Aguilera et al. [1] coupled the water sorption isotherm with the Gordon Taylor equation (Eq. (3.1)) to give the relationship between water content and glass transition temperature. Aguilera et al. [1] used the WLF equation in the following form:

$$\log \frac{\tau}{\tau_g} = \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \quad (3.5)$$

where τ is the relaxation time at temperature T and τ_g is the relaxation time at the glass transition temperature. Caking studies on hydrolysed fish protein were conducted by exposing thin layers of powder to various conditions of relative humidity and temperature. The caking index, $\Phi(t)$, was measured by the fraction of material retained on a sieve of a suitable mesh size. The following first order equation was used

$$1 - \frac{\Phi(t)}{100} = \exp\left(-\frac{t - t_d}{\tau}\right) \quad (3.6)$$

In Eq. (3.6), t_d is the delay time, which is intended to account for the time required for moisture diffusion onto the outer layers of the particles. Aguilera et al. [1] suggests that knowledge of the sorption isotherm, glass transition versus moisture content and a WLF plot of relaxation times can be used as a useful prediction of the rate of caking.

Eq. (3.7) enables the calculation of the ratio between the diameter of the sintered bridge, x , and the particle diameter, a , in terms of the

surface tension, γ , the applied force between the particles, F_t , the viscosity, μ , and the contact time, t [34].

$$\left(\frac{x}{a}\right)^2 = \left(\frac{4\gamma}{5a} + \frac{2F_t}{5\pi a^2}\right) \frac{t}{\mu} \quad (3.7)$$

Palzer [33] coupled the WLF model with Eq. (3.7) and derived the following equation for the necessary sintering contact time:

$$t = \left(\frac{5a^2\pi}{4\gamma a\pi + 2F_t}\right) \mu \left(\frac{x}{a}\right)^2 10^{\frac{C(T-T_g)}{[B+(T-T_g)]}} \quad (3.8)$$

Eq. (3.8) was shown to give a good agreement with experimental data for the time required for caking [33]. This approach provides a useful tool for predicting the stability of a powdered material, which cakes through a mechanism of sintering by viscous flow. Hartmann and Palzer [63] showed that the average sintering bridge diameter, calculated from Eq. (3.8), can qualitatively be related to the unconfined yield strength measured by a ring shear cell. Haider et al. [64] developed a theoretical approach for the prediction of the contact zone formation between two individual particles. However, fitting of the stress relaxation curves with a three-parameter viscoelastic kinetic model is required. Stress relaxation curves are also shown to be an indirect measurement of caking potential by Kingsly et al. [65].

3.3. The effect of composition

A minor change in a component within a complex mixture can lead to significant changes in the final product [3]. It is advisable to identify which material is problematic and substitute them with more agreeable components; however, this is not always an option and the ability to understand the impact of components on a mixture is desirable.

For mixtures of amorphous materials it is possible to use the multi-component version of the Gordon and Taylor equation to predict the glass transition temperature for the mixture:

$$T_g = \frac{\sum_1^n w_i \Delta C_{pi} T_{gi}}{\sum_1^n w_i \Delta C_{pi} T_{gi}} \quad (3.9)$$

For the above equation to be applicable, the components should be effectively mixed on a molecular scale; but there is no evidence this approach is suitable for a blend of different powders.

Work by Foster et al. [62] investigated the effect of milk fat dairy powders containing amorphous lactose and showed that if sufficient fat was present at the particle surface, caking would occur by crystallisation of the fat. Perez and Flores [66] showed that high fat content in spray dried soymilk reduced flowability. Contrary, Fitzpatrick et al. [60] demonstrated that the presence of fat reduced the tendency for caking of the amorphous material because the hydrophobic fat inhibited formation of aqueous capillary bridges. These two emphasise the difficulty with understanding caking mechanisms, on one hand crystallising fat increased caking and on the other hand its hydrophobic nature reduced caking.

4. Caking dynamics

Bulk powders may undergo transformations with time and this is a dynamic process complicated by changing environmental and mechanical conditions. Majority of studies available in the literature are based on constant environmental conditions. It is common for heat and mass transfer effects to be neglected; however, caking is heavily influenced by temperature and water content profiles within the bulk material, or between the surroundings and the bulk. If these profiles are understood, they could be linked to cake formation and strength. This has been conceptualised by Fitzpatrick et al. [60] with respect to amorphous materials and has been recreated in Fig. 4.1.

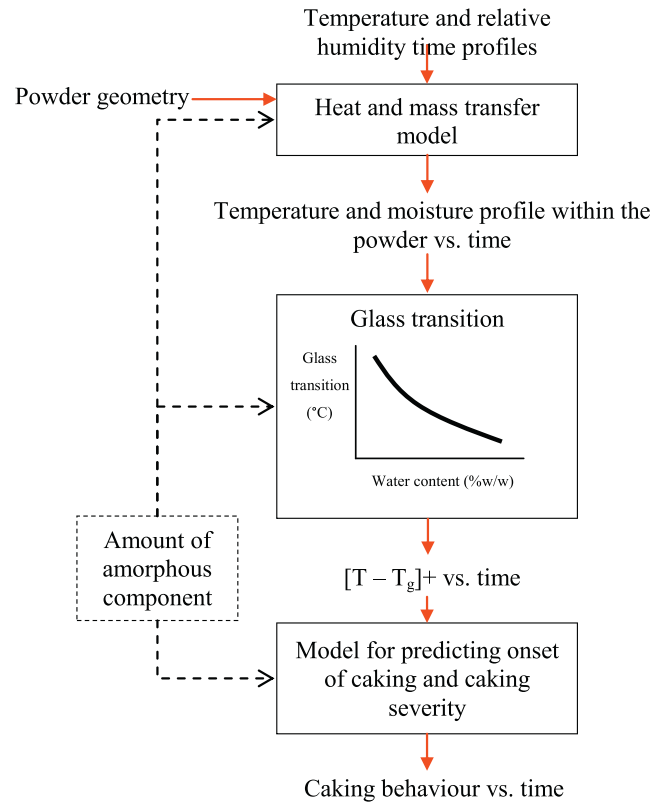


Fig. 4.1. Schematic illustration for predicting amorphous powder caking behaviour with time [60].

Johanson and Paul [67] studied the influence of temperature cycling on a range of soluble materials including common salt and sucrose. When the samples were stored in a sealed container for 1.5 days at constant temperature, the salt formed a strong cake. The transformation was attributed to moisture redistribution until equilibrium was reached. Temperature cycling for salt showed a linear increase in cake strength with the number of cycles. In contrast, sucrose reached its maximum cake strength after one cycle. Similarly, Cleaver et al. [48] showed a steady increase in caking index with number of temperature cycles between 20 °C and 40 °C. It was observed that caking was more extensive for particles <250 μm; also a steady increase in cake strength was observed at constant temperature storage in sealed containers. This steady increase was attributed to preferential dissolution of sub-micron surface features; this has been referred to as Ostwald caking.

4.1. Heat and mass transfer models

There are relatively few studies investigating the dependency of caking with transfer of mass and heat; however, those that do incorporate transfer models have focused on powders that form solid bridges through dissolution and re-crystallisation. It is important to remember that materials which cake through viscous flow or sintering are also influenced by temperature and moisture content; consequently, heat and mass transfer is equally important in these systems.

Tanaker [24] investigated the formation of crystal bridges by the dissolution of the solid and the subsequent evaporation of water from the capillary bridge. The following relationship was derived,

$$\frac{b}{R} = 0.82 \left[\left\{ \frac{8\varepsilon}{3(1-\varepsilon_c)} \right\} C_s \left(\frac{a'}{100} \right) X^{1-X} \right]^{\frac{1}{4}} \quad (4.1)$$

where b is the radius of the narrowest portion of the recrystallised solid bridge, R is the particle radius, ε_c is the porosity of the re-crystallised bridge and C_s is the saturation concentration of the solute in solution.

A relationship between b/R and tensile strength of an agglomerate was developed, which gave the strength of a fully developed cake; however, this approach does not consider time dependency. Tanaker [24] investigated the influence of compaction load, temperature, moisture content and time on the caking behaviour of sodium chloride; the above model showed reasonably good agreement to the experimental data; however, Eq. (4.1) requires further validation with more materials.

The diffusion of vapour into a powder at constant temperature was investigated by Tardos and Gupta [44] and Tardos et al. [68]. The diffusion equation for one dimensional ingress was used to calculate moisture distribution and total water as a function of time. It was shown that water uptake was very sensitive to the isotherm form. For several systems of detergent and inorganic materials, it was shown that the solid phase moisture content reached equilibrium rapidly. Over narrow ranges of RH change, the water adsorption isotherm can be considered linear, which means Henry's law is applicable; consequently, an analytical solution to the diffusion equation can be obtained giving an expression for the dimensionless vapour phase concentration, φ , as

$$\varphi = \frac{c - c_i}{c_o - c_i} = 1 - \operatorname{erf} \left[\frac{\zeta}{\sqrt{D_{eq}t}} \right] \quad (4.2)$$

where c represents the water concentration in the vapour phase, with the subscript i corresponding to the initial concentration at time $t = 0$, and the subscript o the maximum or reference value of the concentration. ζ is the depth below the powder surface and D_{eq} is the equivalent diffusion coefficient that defines physical characteristics of the system. This equation was used to determine the depth of penetration of moisture into the powder. Percolation of conditioned air through the sample is a much more effective method for rapid sample equilibration, as shown by Tardos et al. [68], whereby equilibrium was reached around an order of magnitude more rapidly than if the air was stagnant. During diffusion, the system porosity may change due to capillary bridges and particles may undergo swelling, amorphous collapse or phase transition due to water of crystallisation.

The heat and mass transfer within sugar storage silos has been experimentally and theoretically studied by Rastikian and Capart [69]. With knowledge of the water sorption isotherm and thermal conductivity, a modelling approach was developed that brought together a heat and mass balance equation. Axial distributions of temperature, sucrose water content and air humidity were determined for a simulated "maturation" process. The mass transfer coefficient was calculated by comparing experimental and calculated values of sugar moisture and air humidity. The coefficient was shown to vary during the maturation process, increasing exponentially with sucrose moisture content. Using this modelling approach, regions within the silo were identified as a risk for caking due to the relative humidity exceeding 80%. The high humidity in these regions was due to cold wall temperatures; consequently, Rastikian and Capart [69] made suggestions to prevent caking of sucrose, i.e. good thermal insulation of the wall, a sufficient air flow rate and a relative humidity of the air not exceeding 75%. It is important to note that this work is based on forced convection through the system and may not be applicable to cases when diffusive transfer or natural convection is present.

Leaper et al. [70] considered caking of sugar in big bag containers. The heat transfer was only in the radial direction and was driven by a temperature difference between the surroundings and the walls. The modelling technique evaluated temperature changes experienced by an axial core of material using a finite difference method. A reasonable agreement with experimental data obtained from a big bag study was found. The temperature profile was then used as a tool to predict the solids moisture content and relative humidity of the interstitial air. The relationship between solids moisture content and the relative humidity was obtained by fitting empirical equations to measured

water adsorption isotherm data. Comparison of the predicted bound water with that measured in a 1-dimensional caking box was favourable. The fresh sugar samples had been exposed at one end to a temperature of 10 °C for 12 h, after which the temperature was changed to 30 °C and moisture content at specific penetration distances were taken after a further 12 h. This work demonstrated a reasonable prediction of temperature and moisture content profiles by use of a relatively simplistic approach.

Christakis et al. [17] followed the work of Leaper et al. [70] and considered the case of humidity cycling in the form of a square wave to impose wetting and drying cycles within the powder. Heat and mass transfer equations were solved using a 3-dimensional, unstructured finite volume method. It was considered that during a wetting cycle material would dissolve and re-crystallise into solid bridges during drying. The correlation of Tanaker [24] was used to estimate the radius of crystal bridges and the well-established model by Rumpf [22] was used to calculate the tensile strength of the cake. The model by Christakis et al. [17] was compared with data collected by Leaper et al. [70] and a good agreement between the experimental and predicted tensile strength was shown. Using the model, the effect of maximum relative humidity, the intervals of oscillations and the effect of bed voidage on the tensile strength were investigated. It was demonstrated that both the relative humidity and voidage had a significant effect on the predicted tensile strength.

Specht [71] used a finite element method based within the COMSOL Multiphysics software to investigate caking by moisture migration whilst modelling temperature and moisture content profiles. The contribution of natural convection to the moisture transport by comparing the predicted temperature profiles with and without the convection term was evaluated. Natural convection in a cell was shown to be the dominant mode of heat transfer through evaluating the magnitude of the Peclet number. The diffusion in to the cell was predicted using the temperature profile; hence, the moisture content as a function of space and time was calculated. Sodium carbonate formed solid bridges between particles by dissolution and re-crystallisation in its monohydrate form. In addition, Specht [71] suggested the contact force distribution within a powder bed will heavily influence the cake strength. The influence of force chains was evaluated using the discrete element method (DEM). The concept of "granularity" was used, which is the spacing between the major force chains, to evaluate the strength of the powder. An inverse dependence between granularity and consolidation stress was observed through the simulation work.

Billings et al. [72] have studied the caking of sucrose due to capillary condensation in humid environment. Billings and Paterson [73] used a mass and heat transfer model to predict the onset of caking of sucrose. The approach investigates moisture migration in a sample due to temperature differences and suggests that migration can significantly influence caking propensity. Full details of the model are given by Bronlund and Paterson [74]. This model is useful for predicting possible caking conditions if there is knowledge of the water activity and the hot and cold temperature conditions the powder experiences.

5. Caking reduction

Through understanding the powder being handled and its interaction with other components, sensible precautions can be taken to mitigate caking; however, knowledge of the dominating caking mechanisms is not always known and may be difficult to ascertain. A number of common sense approaches are available that may reduce the caking propensity of a material:

1. decreasing the fines content of the powder;
2. minimising moisture content;
3. identifying the major caking component and identify if an alternative is available;

4. reducing temperature and humidity cycling where appropriate;
5. reducing consolidation load where appropriate.

To be effective at minimising caking it is beneficial to understand the prevailing caking mechanisms and the role of material properties and process conditions. In addition to the above approaches, caking can be reduced by using anti-caking additives [75].

5.1. Caking reduction additives

Caking propensity can be reduced through use of suitable additives and operate by a variety of mechanisms. Adhikari et al. [53] provide a nice summary of common flow conditioners used in food systems as well as various methods used to reduce stickiness in spray-drying operations. Aguilera et al. [1] give a good overview of caking additive mechanisms, which include:

1. competing with a host powder for available moisture. These materials are usually porous with a high capacity for moisture adsorption;
2. acting as a surface barrier between the host particles, preventing the formation of liquid bridges, decreasing inter-particle friction, dissipating electrostatic forces, or inhibiting crystal growth of solid bridges;
3. increasing the glass transition temperature of the amorphous phase, usually by adding a high molecular weight material;
4. forming a moisture protective barrier on the surface of hygroscopic powders by using, for example, lipids.

The effectiveness of a variety of inorganic inhibitors on the caking behaviour of different industrial materials, including salt, sugar, milk powder and a fertiliser, has been studied [76]. The inhibitors included tricalcium phosphate, magnesium carbonate, calcium silicate, calcium sulphate, starch and kaolin. Calcium stearate and silicon dioxide have also proved to be effective in reducing moisture sorption [77,78] in single deliquescent food ingredients (sodium chloride, sucrose, fructose, and citric acid) and binary systems (sodium chloride blended with sucrose, fructose, or citric acid). The effect of inhibitor particle size was studied and it was shown that finer particles were more effective at the same mass concentration, which is assumed to be due to a greater surface coverage. In this regard, it was found that pulverization of juice powder with powdered cane sugar as anticaking agent is effective for reducing caking and hygroscopicity of the product [79]. In this instance, the anticaking mechanism is physical separation.

Further studies have concluded that approaches may be taken that restricts the growth of crystal bridges between particles; consequently reducing the caking tendency. Chen and Chou [80] investigated the effect of surfactants on the caking of ammonium perchlorate and showed that lauryl amine and sodium dodecyl sulphate were both effective. In this case the surfactants did not affect the amount of water adsorbed by the material; but rather inhibited the growth of crystal bridges. Similar evidence was observed by Hansen et al. [81] for potash treated with an amine, and by Komunjer and Affolter [82] for ammonium nitrate treated with fuchsine acid.

6. Caking test methods

A number of caking test methods are available and range from simplistic approaches, such as dropping a 50 kg bag of fertiliser from waist height and quantifying the extent of caking by the amount of free flowing material [83], to more complex methods such as shear cell testing. Most approaches available tend to inform the operator whether a product has caked or not, but provide no predictive capability. The lack of instrumentation and control used undermines data reliability and minimises the information obtainable from the test. Finally the large sample size may be

impractical, especially for high-value or hazardous materials. Cleaver [2] states the attributes of an ideal caking test are:

- provides predictive indication of caking extent and intensity;
- maximises useful information by appropriate instrumentation;
- minimises random error through careful parameter control;
- uses a minimum quantity of sample.

An important attribute of a caking test is the ability to predict whether caking will occur in the future. The challenge of accelerating caking is that it may be necessary to increase moisture content and/or temperature, or use a compressive force that is excessively large. Changing the conditions the material is exposed to can have a profound effect on the phase chemistry of the material; consequently, accelerating caking may lead to misleading information. The aim of a rapid test should allow for prediction of caking propensity whilst remaining within the parametric envelope for normal operation. The extrapolation from accelerated caking test data to predict caking requires detailed knowledge of the relevant material properties and their response to changes in moisture content and temperature whilst under realistic levels of compressive stress.

6.1. Mechanical test methods

A variety of mechanical test methods are available for investigating the flow behaviour of bulk powders and these can be used for evaluating caking behaviour. In this section a brief overview of the techniques employed for caking is given.

6.1.1. Shear cell testing

Shear cells have been used for many years to determine bulk powder flow properties [84]. Three main classes of shear cell are available, the Jenike shear cell, the annular shear cell and the Pechl shear cell; the latter two being rotational devices with infinite shear strain [85].

Shear cells have been used by a number of researchers to study the caking and flow behaviour of powders [46,86–88]. In order to control the environment (temperature and relative humidity), the shear cell is usually placed in an environmental chamber [60,86,87]. The ability to control temperature and relative humidity whilst a sample is under a compressive stress makes the shear cell a good candidate for predictive caking tests.

6.1.2. Uniaxial compression testing

Uniaxial compression is used to form a cylindrical column of material that has been compressed axially. After consolidation the confining walls are removed and the column is in an unconfined state around its circumference; subsequently, a load is reapplied to the sample and the measured stress at failure is taken as the unconfined yield strength.

A uniaxial tester has been developed for caking studies and the test procedure by Weigl et al. [89]. Prior to testing, the sample is conditioned at a constant temperature, humidity and compression for a specified time. The cylindrical confining walls are porous to allow moisture migration, but whether thermal and moisture equilibrium is achieved is unknown. This approach is useful for comparing caking tendency of similar materials; however, with this conditioning approach it may require abnormally high environmental or mechanical conditions to accelerate caking in a reasonable timescale. An interesting conclusion from the work of Weigl et al. [89] is that the uniaxial caking test procedure needs to be very closely specified and adhered to if consistent and meaningful results are to be achieved. More recently, a similar approach has been followed by Calvert et al. [90], having accelerated caking facility by percolating humid air through the packed powder bed (see below).

The technique of uniaxial cake strength testing is based on materials failing in a plastic, ductile manner; however, caked material may exhibit more brittle failure and the underlying assumptions and associated stress analysis for plastic deformation may not be valid. An additional

problem associated with the uniaxial tester is the aspect ratio of the bed. The height to diameter ratio should be >1 and likely close to 2 in order that the gradient of the slip plane passes through the side of the cake; although, large bed heights may lead to a non-uniform stress field. The following equation is used to calculate the slip plane angle,

$$\alpha = 45^\circ + \frac{\varphi}{2} \quad (6.1)$$

where φ is the angle of internal friction of the powder [88]. Care should also be taken when removing the caked powder from the confining cylinder; if the cake is weak, removal may damage the sample.

Wahl et al. [91] employed a modified design of uniaxial tester with the walls of the measurement cell made of porous, sintered material to allow fast diffusion of moisture through the cell walls towards the sample. To minimise wall friction, the sample is positioned on top of a stand and enclosed by walls which “hang” from the sample.

Thakur et al. [92] conducted an experimental and numerical study of the packing, compression, and caking behaviour of spray dried detergent (SDD) powders using an extended uniaxial tester (Edinburgh Powder Tester-EPT). It was found that higher moisture content leads to lower bulk porosity but higher compressibility and cake strength. A discrete element method (DEM) approach, based on a simplified contact model, was also employed and proved capable of capturing the compression behaviour reasonably. However, the importance of considering a time-dependent inter-particle cohesion force in the contact model has been stressed elsewhere [93].

Another new method developed by Calvert et al. [90] for assessing powder caking propensity based on uniaxial compression is the Environmental Caking Rig (ECR), where an accelerated caking process is used. A schematic illustration of the ECR is given in Fig. 6.1. This test method uses conditioning air, which percolates through the powder sample to rapidly equilibrate the bulk sample with the desired environmental condition. The powder is compacted using dead weights and the caking tester is placed in an environmental controlled chamber, where the temperature, relative humidity at the inlet and outlet of the powder bed and the rate of compaction are recorded. The caking propensity of highly hygroscopic and deliquescent powders has been investigated, where the effect of different environmental conditions on the consolidation and development of cake strength at realistic storage conditions have been delineated. A linear relationship is shown to prevail between the cake strength and the extent of bulk deformation.

6.1.3. Tensile testing

Pietsch et al. [20] used a tensile tester; however, it is experimentally very challenging due to difficulties in applying the tensile load to the specimen and controlling the failure plane location. Tensile testing was also used by Nikolakakis and Pilpel [94] to investigate the effect of particle size and shape, and by Pierrat and Caram [18] to study the effect of water content. It has not become a widely used approach to study caking, due to its difficulties, and its advantage is overshadowed by the ease of use of other techniques such as the shear cell.

6.1.4. The ICI caking test

Thompson [95] developed the ICI caking test to eradicate the shortcomings of the high aspect ratio uniaxial testers, as mentioned in the previous section. A shallow, sealed mould, lined with a polythene sheet, to produce the cake by application of pneumatic pressure was developed. The tester was placed under isothermal conditions and a displacement transducer was used to monitor the shrinkage of the specimen during caking; this is an important phenomenon of caking, as investigated by Lloyd et al. [59] and Walker et al. [96]. After compression the top cover of the tester and a circular plug underneath the sample are removed. The load on top of the sample is reapplied until a plug of material is displaced. The pressure at which this occurs is related to the degree of powder caking. It was reported that the repeatability with this approach was typically within 5%. The tester has been used to study the effect of storage temperature, time, load and moisture content on fertiliser samples, which led to useful empirical relationships. A similar test was developed by Fitzpatrick et al. [97,98], where the cake strength was determined from the force required to displace a plug of caked material. The measured cake strength correlated well with the flow function values obtained by the ring shear tester, and a relationship between the two techniques based on a scale factor has been proposed [99].

6.1.5. Creep testing

It is useful to monitor the change in volume of a sample as a function of time as a means of understanding the effect of storage time and environmental conditions on caking. The inline determination of cake thickness can, for example, be determined by a pressure-displacement measurement [100]. Creep testing was adopted by Walker et al. [96] for granular fertilisers using the ICI caking tester. Investigating the effect of load and time allowed for comparisons between creep rates, which were used to predict the future condition of the material. Walker et al. [96] concluded that the strength of a powder was directly proportional to the reduction in voidage due to plastic creep and they recommended determining empirical constants for each material.

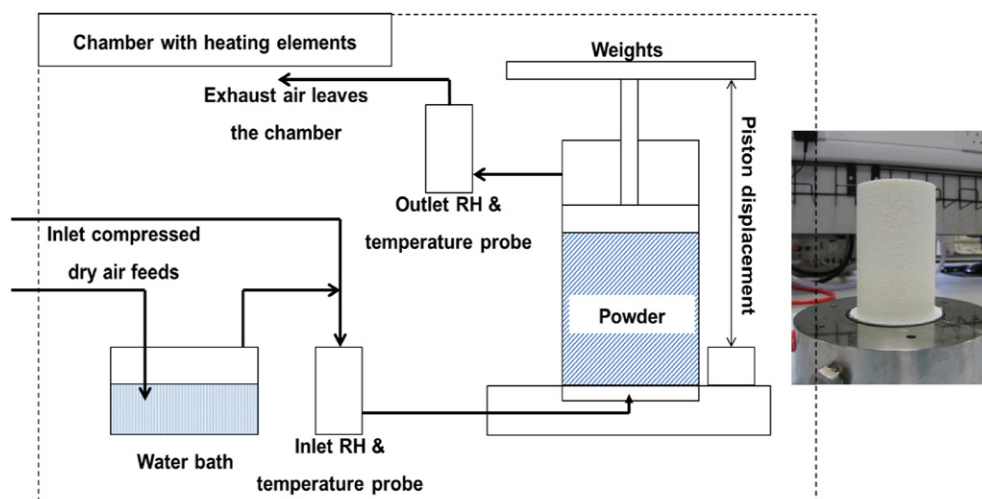


Fig. 6.1. A schematic illustration of ECR setup [90].

If the various creep mechanisms are understood, creep testing is a promising predictive tool for evaluating caking propensity. The assessment of creep is relatively quick and could be used to predict by extrapolation the future behaviour of powders.

6.1.6. Penetration testing

Knight and Johnson [101] developed a penetration test method that considered the unconfined yield strength, f_c , of a powder to be related to the measured force, F , and the penetration depth, d , by the following relationship:

$$f_c = a_{fc} \frac{F}{d^2} \quad (6.2)$$

where a_{fc} is a constant that is related to the dynamic coefficient of friction between the indenter and the powder and the dynamic angle of internal friction for the powder. The test method is illustrated in Fig. 6.2.

For a range of powders a good comparison with unconfined yield strength measurements from shear cell tests were observed when a_{fc} was equal to 1.4. This approach shows promise for investigating the caking propensity of powders. The method is intended for materials that fail plastically; if brittle failure is observed, the results would have to be interpreted using fracture toughness.

Penetration testing has been used specifically for investigating caking propensity by Ozkan et al. [102] and Ozkan et al. [104]. The samples were subjected to controlled temperature, consolidation and time and when the load is removed the penetration force was measured using an Instron mechanical tester. This approach is empirical and was used for comparison between different conditions and powders. An improved methodology for measuring penetration behaviour of powders has been developed by Hassanpour and Ghadiri [103], Pasha et al. [105], and Zafar et al. [106] to characterise the flowability of cohesive powders and is depicted in Fig. 6.3. In this method, the resistance to bulk plastic deformation (hardness), representing the material flow stress, is obtained from the ratio of the maximum indentation load to the projected area of the impression, which is calculated from the indenter diameter and the penetration depth. One major advantage of the ball indentation technique compared to conventional methods for assessing powder behaviour is that a sample size of only a few mm³ of material is required. Another significant advantage of this method is its sensitivity and ability to detect the onset of caking very quickly. The caking kinetics can be determined as a function of the exposed temperature, humidity and applied stress. The technique measures free

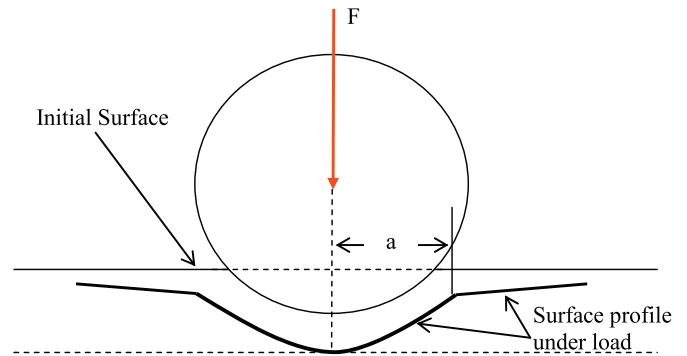


Fig. 6.3. Geometry for measurement of indentation hardness of weak powder compacts [103].

surface caking, where the internal bulk powder would not yet have caked. It has recently been used in the study of surface caking of pharmaceutical excipients by Chen et al. [107], who have shown that the onset of caking is readily detected by changes in the surface hardness.

6.1.7. Powder rheometer

Powder rheometry has been used in more recent years for assessing powder behaviour. One of the well-known testers is the FT4 Powder Rheometer by Freeman Technology, Tewkesbury, UK. This method determines bulk powder behaviour under dynamic conditions and has been used by many researchers mainly to measure powder flowability (e.g. [108–110]). Chávez Montes et al. [111] used FT4 Powder Rheometer for investigating caking of cocoa powders, for which the energy required to move the rotating blade down into the caked powder was measured and compared with that for breaking of the cake using a uniaxial tester. Both test methods were able to differentiate between samples; however, with the FT4 Rheometer it is possible to assess a broader range of environmental conditions. Furthermore, FT4 Rheometer can quantify caking as a function of height whilst most of the other techniques provide an average value for the whole sample for caking assessment [112].

6.2. Alternative test methods

A number of alternative methods are available for evaluating the caking behaviour of powders. Sensory analysis or sieving is employed

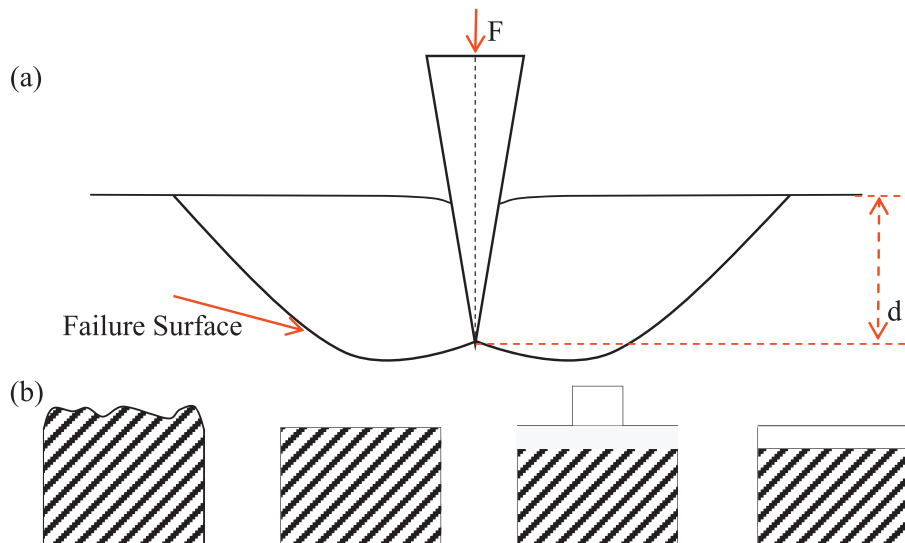


Fig. 6.2. (a) Cross section of failure surface for a conical indenter penetrating an unconfined powder; (b) sample preparation method [101].

in the food industry [113]. Sieves, in particular, can be used to classify the degree of caking. Ordinarily a free flowing material will pass through a sieve aperture that is larger than the constituent particles. If the material has caked, a certain percentage of the material will not pass. The caking index test is given as the mass fraction of material that is retained on the sieve. A number of researchers have successfully used the caking index such as Irani et al. [76] to quantify the performance of anti-caking additives, by Aguilera et al. [1] to quantify the effect of storage time when investigating caking kinetics, and by Cleaver et al. [48] in an attempt to develop an accelerated caking test. The caking index test should be treated with caution, it is rapid and simple, but it is not possible to make meaningful comparisons between caking indices measured for different materials.

The blow tester was developed to measure the cohesiveness and caking of dairy powders [61,114]. The powder is first conditioned by air at a controlled humidity and temperature. Once the powder is conditioned, an impinging jet of air is introduced to the powder surface. The velocity of the air is gradually increased until a channel is cut through the powder; the flow rate that this occurs is related to the cohesiveness or cake strength of the material.

The accepted mechanism for caking of materials above their glass transition temperature is by viscous flow of the particles in contact. A sticking point tester was developed by Lazar et al. [115]. The viscosity required for particle sticking has been explored by Downton et al. [55] by conducting sticking point experiments for fructose and sucrose powders. Sticking point tests involve continuous stirring of a powder in a sealed vessel whilst slowly increasing the temperature. The sticky point is observed by a sudden increase in the torque required for stirring. The sticking point temperature decreases dramatically with an increase in water content. It is important to note that sticking point measurements occur in the order of seconds, whereas caking occurs over significantly longer timescales; consequently, viscous flow may occur at lower temperatures and water content in reality. This was demonstrated by Foster et al. [62] for amorphous sugar particles at lower values of $T - T_g$, provided that sufficient time is given for the bonds to form.

An optical probe method has been reported by Lockemann [116]. This approach investigates the change in optical properties of a free flowing powder as cohesion increases. In some studies, methods to investigate the contact behaviour between two individual particles have been developed [64,117]. A light microscope equipped with a digital camera is used to observe the caking mechanism between two particles [117]. In other studies [64,91], distance-controlled contact experiments between two particles are performed to measure the evolving sintered bridge diameter by means of a digital microscope. A load cell is also used to record the induced compressive force, its relaxation and the resulting cohesion on separation between the tested particles. Nuclear Magnetic Resonance (NMR) studies have been used to study caking behaviour in foods [118–120]. NMR detects the changes in molecular mobility and the amplitude of molecular vibrations; consequently, it can be used to observe the glass transitions in amorphous materials.

7. Conclusions

Bulk powder caking is a challenging phenomenon that affects a wide range of materials and a variety of mechanisms are responsible for the onset of caking transformation; consequently, it is difficult to recommend a solution that will suit all powders. To successfully predict caking propensity it is vital that the underlying mechanisms that are driving the change are understood and to do this it is critical that the single particle behaviour is understood and linked to the bulk material.

A significant amount of work is available in the literature that focuses on improving the science of caking with a lot of effort devoted to amorphous materials. This is simply due to the glass transition being a common driving force within materials that leads to a caked product. In addition, a lot of studies have investigated the impact of environmental

and mechanical conditions on a powder; however, in most instances the samples are subjected to constant environmental conditions. In reality powders within a supply chain experience environmental changes that lead to thermal and moisture gradients within the bulk. This is an area within the literature that should be further investigated to understand the evolution of bridging between particles.

There are a number of test methods available that provide empirical understanding of caking, but limited predictive ability. There is a need to develop a new experimental device that provides reproducible results and enables future predictions.

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