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Original Research Paper

Potassium chloride caking tendency: A parametric study of cake break energy

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ABSTRACT

Undesired particulate agglomeration can create powder flow issues during manufacturing. Potassium chloride (KCl), a commercial product used in powder form as a potassium source, is known to agglomerate. The main objective is to develop a method to assess KCl agglomeration, then use it to understand its driving forces and the phenomena taking place. Based on industrial data in pharmaceutical manufacturing, the following 5 parameters are considered as critical in terms of agglomeration: conditioning humidity, conditioning time, drying, applied pressure and particle size. Beakers containing 40 g of original or ground KCl powder are compacted under specific humidity conditions in a bell jar. Once the beakers are conditioned, agglomerate hardness tests evaluate agglomeration extent by correlating it with the energy required for powder penetration. This energy is calculated from force-distance curves. The results show that the Area Under the force vs distance Curve (AUC) is a good indicator of agglomeration extent. Thus, the AUC is a scalar and has units of work. Based on AUC analysis, the highest agglomeration is found in conditioning humidity of 85% relative humidity (RH), original particle size, drying and conditioning time of 16 h. The agglomeration of original versus ground particle size powders is further investigated over time in a conditioning test. Preliminary tests validate our method and indicate that KCl premixing with other materials can solve agglomeration problems encountered during manufacturing processes as KCl-particle-particle interactions per unit volume are reduced.

1. Introduction

1.1. Context of the work

Particulate agglomeration is an undesired phenomenon during transport, storage and feeding [1] of powders as the presence of agglomerates can trigger asymmetric dose distribution of active pharmaceutical ingredients [2]. Caking is relevant and worthy of investigation in the fertilizer, detergent, chemical, food and pharmaceutical industries. Prevention, or minimization, of such agglomerates often requires investigation and considerable technical effort [1]. In the pharmaceutical industry, to prevent the formation of agglomerates, costly and time-consuming corrective actions need to be taken, such as batch rejection once agglomerates are uncovered or, in some cases, re-processing by sieving to ensure batch homogeneity. Industrial practice and qualitative consideration of attraction forces show that the parameters influencing material agglomeration under storage conditions are: chemical composition/nature of powders, impurity and moisture content, porosity, hygroscopicity, particle surface area, size and morphology, degree of crystallinity, material temperature, storage temperature and humidity, column pressure exerted in storage, and storage time [3]. Therefore, a parametric study of the effect of these parameters on the agglomeration is required.

The potassium chloride is one of the materials presenting significant agglomeration issues in the manufacturing process. Potassium chloride is globally used for treating hypokalemia (low level of potassium in blood serum) and as an electrolyte replenisher. In our study, it is used as a potassium source in multivitamin products with a mass fraction of around 10%. The main objective of this work is to better understand KCl (potassium chloride granular, Mallinckrodt Chemicals) agglomeration mechanisms through

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parametric study using a penetration test and a humidity chamber. These results may contribute to solving agglomeration issues during storage and blending of marketed pharmaceutical blends.

1.2. Literature review on KCl

1.2.1. Hygroscopic properties

Hygroscopicity is a key physical condition that affects material properties during handling and storage [3]. Water solubility and critical relative humidity (CRH) are both related to material hygroscopicity. As KCl has water solubility of 0.355 kg/L at 25 °C [4], it is classified as highly soluble. CRH is the minimum ambient relative humidity (RH) at which materials absorb moisture. The CRH of KCl is 70–80%RH at 30 °C [3]. CRH tends to decrease with rising temperature.

Potash particles (composed of mainly the salt KCl and with small surface fractions of NaCl and $MgCl_2$) are hygroscopic for an ambient air relative humidity higher than 52% [5]. Water condensation occurs at RH higher than 52%. At higher relative humidity (typically more than 75%RH), moisture content can exceed 3%w/w and yields to KCl dissolution [5]. Pyne et al. [6] studied the rate of water vapour uptake by potash; their results showed that there are two regions, from 60%RH, a significant moisture accumulation begins and from 84%RH, moisture accumulation is intensified [6]. Peng [7] reports that the moisture accumulation onset may correspond to the dissolution of $MgCl_2$ and NaCl. Thus, in our case, with pure KCl, moisture accumulation should start at around 52%RH and upon reaching 84%RH potassium chloride dissolution begins.

1.2.2. Agglomeration mechanism

Cleaver [8] studied the formation and growth of crystal bridges as a function of load size, temperature cycles, relative humidity and storage time. They report that fine graded particles yield larger and stronger cakes [8]; supersaturation promotes crystal growth on surface [9]. Humidity is expected to have a major impact on salt-like and hygroscopic materials; storage time and pressure should have significant impacts as well.

Setting aside the capillary forces, the extent KCl agglomeration is mainly driven by the formation of solid bridges between particles. Solid bridges occur through various mechanisms, such as: (a) chemical reactions; (b) partial melting followed by subsequent solidification, and (c) partial dissolution with subsequent crystallization [10–12]. In the case of KCl agglomeration, mechanisms (a) and (b) are not relevant because neither chemical reaction is taking place nor are there temperature levels high enough to yield melting. According to the KCl-H_2O phase diagram [13], illustrated in Fig. 1, no hydrated KCl phases occur. Hence, mechanism (c), partial dissolution and recrystallization [3], is considered as the main other agglomeration mechanism.

Fluctuations in atmospheric RH are the driving force of this mechanism [14]. First, surface KCl is dissolved by absorbed moisture, resulting in the formation of liquid bridges. Second, KCl in these liquid bridges crystallizes in interstices between adjacent particles, generating solid bridges. The organization of such solid bridges is attributed to the powder's hygroscopic properties [3,15]. The amount of water absorbed depends on particle-specific characteristics, mainly particle shape, size, stacking and porosity [16]. It is a mass-transfer, rate-dependent process which is linearly proportional to available specific surfaces. Isothermal water absorption and desorption are determined by exposure of powder to different RH environments until equilibrium is reached [17]. Since capillary force intensity depends on absorbed water, hygroscopicity is directly related to such forces [18].

Wang [19] presented a simple geometric relationship for the mass of salt recrystallized near contact points between particles in a bed that gives cake strength σ directly proportional to initial moisture content X_i and solid fraction in a potash particle bed ε_s and inversely proportional to the square of the mean particle diameter d_{pm} [19]:

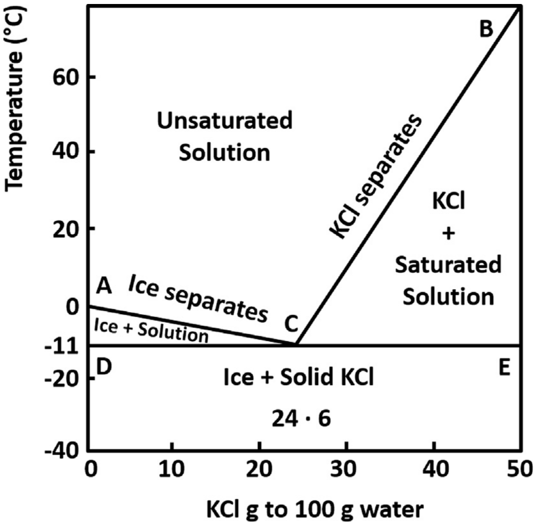

Fig. 1. KCl-H_2O phase diagram (redrawn from Pronk [13]).

$$\sigma \,\alpha \left(\frac{\varepsilon_s X_i \rho_s}{\pi \rho_w}\right) d_{pm}^{-2} \tag{1.1}$$

where ρ_s is the real density of a potash particle (kg/m^3), and ρ_w the density of water (kg/m^3).

Thompson [20] and Tanaka [21] gave a power relationship between cake strength which is assumed to increase with a power of drying time constant and exponent cake index "a" as presented in Eq. (1.2). The value of "a" was estimated by Thompson [20] to be in range 0.1–1 and by Tanaka [21] to be equal to 0.5. Wang [22] studied with a centrifugal method the cake strength of potash fertilizer (majority of KCl with small fractions of NaCl and $KMgCl_3 * 6H_2O$, i.e., less than 2% of each). The following linear correlation for cake strength (kPa) of potash has been developed [19]:

$$\sigma \,\alpha\, t_c^{a=0.4} \times X_i \times d_{pm}^{-2} \left(\overset{0.4}{min} \cdot \mathrm{mm}^{-2}\right) \tag{1.2}$$

This correlation is valuable for producers of potash to improve quality control and reduce caking. Cake strength should increase as function of solid fraction, drying time, initial moisture and decrease with particle size [19].This correlation is valid for initial moisture from 0.25% to 6% (w/w), for particles with diameters between 0.85 and 3.35 mm and drying time ranging between 7 and 1900 min.

As potash main component is KCl, its caking tendency is supposed to be similar to KCl. In our study, the d_{50} of the original KCl is 353.9 µm and that of ground KCl is 48.4 µm; both are significantly lower than those of the previous studies and, consequently, may behave very differently.

1.2.3. Agglomeration quantification methods

Agglomerates can be characterized by various measurement techniques [23]. Calvert [40] presented a summary of the caking test methods available (Table 1). Mechanical testing methods characterizing agglomerates have certain limitations because of their sensitivity to anisotropy and porosity [23]. Such measurements include tensile strength [24], yield strength, fracture toughness and attrition [23]. They include different characterization methods such as shear cell [27,28], uniaxial compression [29,30], tensile testing [25,26,31,32], caking tester [33,34] and penetration testing

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