



Design and mechanism of the formation of spherical KCl particles using cooling crystallization without additives

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ABSTRACT

Potassium chloride crystals are cubic, which often leads to caking and greatly limits their applications. This caking can be overcome by modifying the crystal shape toward sphericity. Spherical particles have a high anti-caking ability and flowability. In this work, spherical KCl particles were prepared using a simple cooling crystallization process designed to function without additives. Among the four main processes in the crystallization of spherical particles, i.e., nucleation, growth, agglomeration, and attrition, agglomeration is the greatest contributor to the formation of spherical KCl particles, which were prepared following the principle that the adhesion force must be larger than the dispersion force. The adhesion free energy between KCl particles and solvents (i.e., water, *n*-hexane, formamide, diazomethane, methanol, ethanol, ethyl acetate, ethylene glycol, and dimethyl sulfoxide) was calculated using the Lifshitz–van der Waals acid–base approach, and water was found to be the most appropriate solvent because of its attractive interaction with the crystals. According to the relationship between the adhesion force and dispersion forces, we found that the stirring rate should be lower than 1300 rpm. Additionally, the effects of stirring rate and cooling rate on the KCl products were investigated and optimized, and the optimal conditions were found to be 400–500 rpm and 10–15 min/°C, respectively. All of the spherical KCl products prepared under the optimal conditions show a better morphology, flowability, and anti-caking performance than the original crystals.

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1. Introduction

Potassium chloride (KCl) is a metal halide salt composed of potassium and chloride. It is commonly used as a fertilizer because the growth of many plants is limited by their potassium intake. As a chemical feedstock, it is used for the manufacture of potassium hydroxide and potassium metal. Beyond that, it has broad applications in general science, medicine, lethal injection, and food processing [1]. Such extensive applications are dependent on the properties of KCl. However, pure KCl is highly hygroscopic because of its low deliquescence point (at humidities of 0% and 2%, the deliquescence transition point of chemically pure KCl located at around 84% RH and 74% RH, respectively) [2,3]. As a consequence, caking is inevitable, accompanied by a loss of product flowability. The cubic crystal habit [4] of KCl results in a large contact area between particles when packing. Capillary condensation,

thus, easily develops, followed by the formation of a large crystal bridge as a result of caking or densification, which can cause serious problems during separation, processing, storage, and transportation, and may lead to a loss of material functionality, thus seriously hindering the growth of the potassium chloride industry [5].

Many of the crystalline characteristics and environmental factors have a significant impact on the anti-caking properties, such as the critical humidity value of the material, particle geometry, and ambient temperature. Most of these variables, however, are unchangeable or uncontrollable. Although anticaking agents are usually used to prevent caking, they cause consequent environmental problems. Thus, only the particle size and shape, which are considered to be important factors for caking characteristics, are accessible and can be manipulated [6]. Previous studies have shown that crystals with smaller particle sizes cake first and form strong crystal bridges easily [7]. Spherical crystals exhibit the lowest contact area between crystals and, thus, the weakest capillary force; therefore, they form liquid bridges slowly and have better anti-caking characteristics and flowability [8]. Specifically, spherical KCl, when used in bathing supplies, such as bath salts, provides more rolling friction with the body and avoids scratching while ensuring efficacy.

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Furthermore, the specific performance of spherical KCl crystals makes it possible to use them as additives in bathing and medical supplies.

In spite of the many advantages of spherical crystals, existing techniques for spherical crystallization are limited. This is due to the high cost of these techniques, which derives from the extreme operating conditions or their adverse environmental effects as a result of the extensive use of organic solvents or additives [9,10]. The preparation of micro-spherical lactose, for instance, requires supercritical carbon dioxide as solvent [11]. If these strict or high-cost operating conditions are applied to the preparation of inexpensive potassium chloride, the process will become economically unviable. From the literature to date, no simple and low-cost method for the preparation of spherical KCl has been reported. Therefore, developing a crystallization process without additives, under mild conditions, and with high-quality products, is the biggest challenge and innovation in this work. Another innovation in this paper is that the spherical crystallization process for KCl was designed rather than prepared by a trial-and-error method. The critical parameters, such as the solvent, stirring rate, and cooling rate in this design process were determined through theoretical calculations and optimized with a relatively small number of experiments. These theoretical calculations are based on the adhesion free energy and adhesion force by the Lifshitz–van der Waals acid-base theory, shear stress, and dispersion forces by an empirical equation.

2. Theory

2.1. Design of the spherical KCl crystallization process

The most common techniques used to form spherical crystals are spherical agglomeration and quasi-emulsion solvent diffusion, both of which need a complex solvent system. The solvent system involves a good solvent that dissolves the compound, an antisolvent to generate the required supersaturation, and a third solvent called the bridging liquid for the former method or an emulsifier for the latter [12,13]. Other methods that do not require a complex solvent system often require strict operating conditions. However, some authors have reported successful morphology control that requires no habit modifier or bridging assisted by the mother liquor [14]. In this case, simple evaporation is used to prepare spherical crystals. Thus, we would like to gain a deeper insight into the underlying mechanism of such a simple process.

The overall design process for spherical KCl particles is shown in Fig. 1. The mechanism involves nucleation, growth, agglomeration, and attrition, in which agglomeration is the most critical step. The intrinsic key factors corresponding to nucleation, growth, and agglomeration are solubility, adhesion, and dispersion forces, respectively. Solvent, cooling rate, and stirring rate are the controllable macro variables in this work. Only when the adhesion force is larger than dispersion force between crystals can agglomeration occur. The adhesion force provided by solvents is characterized by the adhesion free energy based on the Lifshitz–van der Waals acid–base theory, and the dispersion force provided by agitation is characterized by the shear stress. The solvent of interest is determined by comparing the adhesion free energy of different solvents. Then, the relative magnitude of the aforementioned two forces provides a guideline to choose a stirring rate. With respect to nucleation and growth, the solubility of KCl is critical. The effect of the cooling rate on the products could be interpreted in terms of the supersaturation with time and temperature. As for attrition, it is directly related to stirring, which also affects the properties of products, which can be interpreted in terms of the shear stress. Furthermore, the stirring rate and cooling rate are optimized in subsequent crystallization experiments. Spherical agglomerates of crystals are eventually formed if all the process parameters are set appropriately.

2.2. Adhesion free energy

The adhesion free energy between particles immersed in a liquid can be estimated as

$$\Delta G_{SLS} = -2\gamma_{SL} \quad (1)$$

where ΔG_{SLS} is the adhesion free energy per unit area between two solid surfaces immersed in a liquid, and γ_{SL} is the surface free energy between solid and liquid [15]. A positive value of the adhesion free energy suggests repulsion between the particles, whereas a negative value indicates attraction [16].

For the solid/liquid interface, Eq. (1) can be further developed using the Lifshitz–van der Waals acid–base theory proposed by van Oss et al. [17].

$$\Delta G_{SLS} = -2 \left[\left(\sqrt{\gamma_S^{IW}} - \sqrt{\gamma_L^{IW}} \right)^2 + 2 \left(\sqrt{\gamma_S^+ \gamma_S^-} + \sqrt{\gamma_L^+ \gamma_L^-} - \sqrt{\gamma_S^+ \gamma_L^-} - \sqrt{\gamma_S^- \gamma_L^+} \right) \right] \quad (2)$$

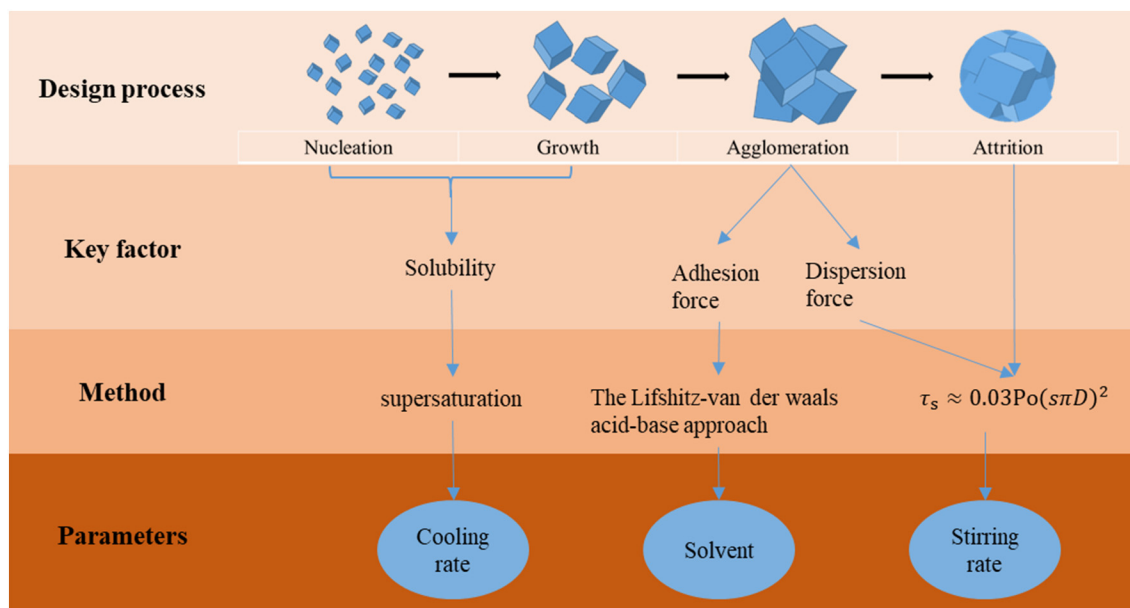


Fig. 1. Design process of spherical KCl particles.

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