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The effect of microwave on the crystallization process of magnesium carbonate from aqueous solutions

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ABSTRACT

The effect of microwave on reactive crystallization is investigated with magnesium carbonate as the working substance. In the experiments, magnesium carbonate is precipitated by mixing aqueous magnesium sulfate and sodium carbonate solutions in a MSMPR crystallizer located in a microwave reactor. A population balance model along with crystallization kinetics is formulated to assess the influence of microwave energy input on nucleation, growth, agglomeration and breakage during crystallization process. A general high order moment method of classes (HMMC) framework is applied to solve the model numerically. The results show that crystallization kinetics parameters, including the nucleation rate constant (k_n), the growth rate constant (k_g), the exponent of growth rate (g) and the collision efficiency (Ψ_{ag}) change significantly due to mass transfer enhancement in microwave field. Meanwhile, the exponent of nucleation (n) and the breakage rate constant (k_{br}) remain constant or only change slightly. It is further discovered that the crystal suspension attenuates the microwave effect during crystallization process.

1. Introduction

Microwave is a radio wave with a frequency ranging from 300 MHz to 300 GHz [1]. During the last two decades, microwave becomes an efficient and suitable tool in various industrial processes, such as synthesis and processing of chemical materials [2,3].

Recently, microwave also has attracted considerable attention as a new way to control crystallization process. Asakuma and Miura found growth rate of crystals is improved by microwave field in the anti-solvent crystallization. They claimed that the applied microwave can enhance the diffusion coefficient which governs the liquid to solid mass transfer during crystal growth [4]. Gordon et al. realized that microwave can introduce a fast and uniform nucleation to crystallization system [5]. In addition, the microwave field was also found to change the size and morphology of crystal products [6,7]. In order to achieve a higher yield of crystal products, Rizzuti et al. and Serrano et al. applied the microwave radiation to the crystallization process [8,9]. Wu et al. and Hart et al. found that microwave field can promote the phase transform of crystal [10,11]. Tian et al., Mahmoud et al. and Aquino et al. concluded that microwave can be used to speed up crystal growth during crystallization process [12,13,14]. Asakuma and Miura found that microwave can accelerate the crystal precipitation and control the crystal size [4]. The microwave effect on crystallization has also been reported to change the degree of crystallization [15,16].

When microwave propagates through a liquid medium, its energy will not only cause temperature increase but also initiate an electromagnetic effect that accelerates the movement and the collision rate of the molecules in the reaction system. As a result, the nucleation and growth of crystals could be improved. Microwave is widely thought to enhance the rate of mass transfer [4,17,18,19]. Meanwhile, Janney et al. and Wilson et al. found that the diffusion coefficients increase in the presence of the microwave electromagnetic effect as well [20,21]. Li et al. found that diffusion acceleration is the main reason for the increase of nucleation rate [22], and the diffusivity enhancement (D_{AB}- D_{AB0}) with energy input (E) follows the Arrhenius law.

Despite the fact that microwave has been proven to be an effective method to control crystallization process, to our knowledge, the quantitative study of microwave effect on crystallization kinetics is limited. The aim of this study is to investigate the influence of microwave on the crystallization mechanisms of inorganic salts in a water-based system by analyzing the variation of crystallization kinetic parameters in microwave field. Magnesium carbonate ($MgCO_3$) crystals, a typical inorganic salt, were precipitated from the aqueous solution in a laboratory MSMPR crystallizer settled in the cavity of microwave reactor. The experiments were carried out under fixed temperature and various microwave power inputs. A population balance model considering nucleation, growth, agglomeration and breakage was constructed and solved with high order moment method of classes (HMMC). [23,24]

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The crystallization kinetic parameters, including the nucleation rate constant (k_n), the exponent of nucleation (n), the growth rate constant (k_g), the exponent of growth rate (g) and the breakage rate constant (k_{br}), were fitted against experimental data. The mechanisms of the microwave effecting on kinetic parameters were discussed as well.

2. Theory

Crystallization is a solid–liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. The particle size distribution (PSD) depends on the processes that create new particles ("birth" processes) and destroy existing particles ("death" processes). Birth of new particles can occur due to breakage or splitting, agglomeration and nucleation. Breakage and agglomeration also contribute to death processes [25]. Nucleation, growth and agglomeration are dominated by liquid to solid mass transfer while breakage is mainly affected by turbulent intensity [26]. As previously mentioned, the diffusion coefficient of mass transfer could be significantly influenced by the microwave field. Therefore, the PSD of crystal products may be changed greatly by microwave.

There are three different classes of materials in microwave field: insulators, which are not affected by microwaves, conductors (such as metals) which reflect the energy, but do not heat, and dielectrics (polar molecules, ions) which absorb the energy [27]. With the increase of the weight fraction of inorganic salt, the microwave absorption properties are enhanced, which leads to the enhancement of dielectric and magnetic losses in the solution [28]. In this case, the increase of inorganic salt suspension density may shield the microwave effect on mass transfer during crystallization process. Thus, the influence of microwave energy input on kinetic parameters needs to be analyzed quantitatively to understand the mechanism of crystal formation in microwave field.

In the steady-state crystallization system, the mass balance equation for Mg^{2+} in the liquid phase can be calculated as:

$$Q_{in}c_{in} - R_c V_{disp} - Q_{out}c_{Mg} = 0 \tag{1}$$

where c_{in} is the concentration of Mg^{2+} in the inflow; c_{Mg} is the concentration of Mg^{2+} in the solution and outflow; Q_{in} and Q_{out} are inflow rate and outflow rate; V_{disp} is the volume of dispersion. The terms on the left hand side are: 1) liquid feed, 2) crystal mass deposition rate, 3) liquid outlet. The crystal mass deposition rate (R_c) can be calculated as: [29]

$$R_c = f_v \rho_{MgCO_3} {L_0}^3 J_N + f_s \rho_{MgCO_3} m_2 G/2 \tag{2}$$

where f_v is the volume shape factor and f_s are the surface shape factor, ρ_{MgCO3} is the density of $MgCO_3$, L_0 is primary crystal size and m_2 is 2nd-order moment of size distribution obtained by solving the population balance equation.

Based on the consideration of 'birth' and 'death' processes, a general form of the population balance equation expressed in particle size as the internal coordinate for an MSMPR crystallizer in the presence of agglomeration and breakage can be written as [26]:

$$\dot{n}(L)_{in} - \dot{n}(L)_{out} + \frac{\partial}{\partial L}[G(L)n(L)] + J_n = B_{ag}(L) - D_{ag}(L) + B_{br}(L) - D_{br}(L) \tag{3}$$

The terms on the left-hand side are: flow of particles into the control volume, flow of particles out from the control volume, growth along internal coordinate and primary nucleation. The terms on the right-hand side are: birth term by agglomeration, death term by agglomeration, birth term by breakage and death term by breakage. To numerically solve this population balance equation, a general high-order moment method of classes (HMMC) framework is applied in this paper [23,24]. It is based on conservation of an arbitrary number of moments in the numerical discretization.

After discretizing the internal coordinate space into a finite number of size class (NC) and counting the number density of particles (Y) belonging to each class, the continuous population balance equation becomes: [23,24].

$$\begin{aligned} &\frac{1}{V_{disp}} Q_{in} Y_{i,in} - \frac{1}{V_{disp}} Q_{out} Y_{i,out} + \sum_{j=1}^{NC} \xi(L_i, L_j) G(L_j) Y_j + \Omega(L_i) = \\ &\sum_{j=1}^{NC} B(L_i, L_j) g(L_j) Y_j + \sum_{j=1}^{NC} \sum_{k=1}^{NC} \chi(L_i, L_j, L_k) F(L_j, L_k) Y_j Y_k \\ &- g(L_i) Y_i - Y_i \sum_{j=1}^{NC} F(L_i, L_j) Y_j \end{aligned} \tag{4}$$

where i, j and k are the indices of particle size class; Y_i is the particle number density of class i; g (L, λ) is the breakage frequency; F (L, λ) is the agglomeration frequency; $B(L_i, L_j)$ is the breakage table, that determines the contribution of breakage event of particles in j-th class to particles number in i-th class; $\chi(L_i, L_j, L_k)$ is the agglomeration table, that describes the contribution of agglomeration event of particles in j-th and k-th class to particles number in i-th class; $\xi(L_i, L_j)$ is the growth table, that represents the contribution of growth event of particles in j-th class to particles number in i-th class; $\Omega(L_i)$ is the nucleation table. In this work, $Y_{i,in}$ is zero since there is no crystals in the inflow. In addition, particle number density in the outflow ($Y_{i,out}$) is equal to the tank averaged particle number density (Y_i) due to the typical assumption of well mixing in MSMPR crystallizers. [30].

In stirred tank reactor, the nucleation and growth rates of $MgCO_3$ can be calculated with power-law functions: [31]

$$J_N = k_n (S)^n \tag{5}$$

$$G = k_g (S)^g \tag{6}$$

where J_N is the primary nucleation rate; k_n is the nucleation constant; n is the exponent of nucleation; G is the crystal growth rate; k_g is the growth rate constant; g is the exponent of growth and S is the supersaturation.

In the dilute binary solution with charged ions of Mg^{2+} and CO_3^{2-}, S can be presented as: [32]

$$S = \sqrt{c_{Mg} c_{CO_3}} - \sqrt{K_{sp,MgCO_3}} \tag{7}$$

where c is the concentration of components in the liquid phase; K_{sp} is the solubility product of the new formed crystals [26].

The crystal agglomeration often occurs along with primary nucleation and crystal growth under relatively high supersaturation during reactive crystallization. Besides the properties of surrounding solution, the crystals agglomeration depends on particle-particle and particle-fluid interactions, particle morphology and fluid mixing. Generally, three steps are needed to obtain agglomerates: (a) the collision of two particles, (b) a sufficient time interval during which the two particles stay together with the help of the flow, and (c) the adherence of the two particles caused by supersaturation [26].

The agglomeration rate, $F(L_i, L_j)$, is initially governed by a variety of effect, such as attractive force (Van der Waals theory) and repulsive force (DLVO theory). This balance is significantly influenced by the ionic strength of the solution. Another major effect is due to hydrodynamics or viscous interaction, which tends to hinder the approach of colliding particles. The agglomeration rate can be expressed as the product of collision frequency function and the collision efficiency: [33,34]

$$F(L_i, L_j) = \left(\frac{2 k_B T}{3\mu} \frac{(L_i + L_j)^2}{L_i L_j} + 1.29 \left(\frac{\varepsilon}{\nu} \right)^{1/2} (L_i + L_j)^3 \right) \psi_{ag} \tag{8}$$