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Monte Carlo simulation of the induction time and particle size distribution in the nucleation of calcium carbonate

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ABSTRACT

In water treatment, the crystallization of insoluble salts may produce a large number of fines, thereby increasing the turbidity and reducing the treatment efficiency. The induction time (t_{ind}) is a crucial indicator of nucleation during crystallization. Previous studies have predicted t_{ind} using an aggregation model (AM) proposed by Qian (QIAN-AM), which ignores cluster breakup during nucleus formation. The present study incorporated a hypothesized "binary breakup" mechanism into the AM, thus creating an aggregation–breakup model (ABM). This ABM was combined with a multi-Monte Carlo method (MMC–ABM) and applied to simulate the nucleation of calcium carbonate. Compared with the QIAN-AM and MMC–AM, the MMC–ABM showed improved accuracy, especially at high supersaturation conditions. Moreover, the MMC–ABM was used to predict the particle size distribution during nucleation and to simulate t_{ind} for a water-softening reactor. The simulation suggested that the nucleation in the reactor was faster than the macromixing; in this case, a large number of fines would form before homogeneous mixing, which would make the subsequent sedimentation process difficult. Therefore, effective control of the dosing point supersaturation is crucial to improving the performance of the reactor.

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1. Introduction

The crystallization of insoluble salts is widely performed in water treatment processes such as water softening, the recovery of heavy metals, and the removal of phosphate and fluoride [1]. Crystallization involves several processes, including heterogeneous nucleation, homogeneous nucleation, surface growth, etc. Homogeneous nucleation results in the formation of a large number of fines, and thus increases the water turbidity, thereby reducing the efficiency of the crystallization process [2]. Investigating the mechanisms of formation of these particles might provide valuable information that could improve our understanding of the nucleation process, and help to optimize reactor designs. The classical theory of homogeneous nucleation says that when the solution is supersaturated, the monomers in the solution start to coagulate and form clusters. If the size of a cluster exceeds a critical size (g_c), a nucleus forms and the subsequent growth of the nucleus leads to a crystal. The time interval between the establishment of supersaturation and the onset of nucleation is defined as the induction time (t_{ind}) [3]. For a crystallization reactor, if t_{ind} is less than the mixing time of the reactor, a large number of fines will be produced, which adversely affects the subsequent sedimentation process.

Previous studies have investigated the effects of various influences (supersaturation (S_a), temperature, inorganic salts, organic compounds) on t_{ind}, several experimental methods and theoretical models have been developed [4–7]. Of these, the aggregation model proposed by Qian and Botsaris (QIAN-AM) has been the most widely used to describe cluster aggregation during crystallization. The QIAN-AM assumes that only g-mers are initially present, which aggregate to form 2g-mers. The 2g-mers subsequently aggregate to give 4g-mers, until clusters with the critical nuclei (g_c-mers) are formed. In this model, g_c and t_{ind} can be expressed by Eqs. (1) and (2), respectively:

$$g_c = \frac{32\pi V_m^2 \delta^3}{3(kT \ln S_a)^3}, \tag{1}$$

$$t_{ind} = \left\{\frac{3\eta}{4kT}\right\}\left\{n_1^{-1}\exp\left[-\bar{g}\ln S_a + \frac{\delta}{kT}(4\pi)^{1/3}(3\bar{g}V_m)^{2/3}\right]\right\} \times \left\{\frac{32\pi V_m^2\delta^3}{3\bar{g}(kT\ln S_a)^3} - 1\right\}. \tag{2}$$

For simplification, the QIAN-AM assumes that clusters of insoluble salts are structurally stable, and not easily broken. This simplification, however, results in errors in the simulation. For example, Tai and Chien [8] observed errors greater than 20% in their modeling of crystallization at 298 K.

The present study combines the aggregation model (AM) with a "binary random breakup" hypothesis to build a new aggregation–breakup model (ABM). Using the Monte Carlo algorithm to solve the ABM, this model is capable of predicting the induction time (t_{ind}) and the particle size distribution (PSD).

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2. Methods

2.1. Aggregation–breakup model

According to Smoluchowski's aggregation model [9,10], the rate of aggregation can be expressed by Eq. (3):

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k}\beta(i,j)n_i n_j - \sum_{i=1}^{\infty}\beta(i,k)n_i n_j \tag{3}$$

where the first term on the right-hand side represents the cluster formation (each collision is counted twice; thus, a factor of 1/2 is applied), and the second term on the right-hand side represents the cluster disappearance. Because clusters form via inter-particle collisions, their formation is assumed to be a second-order reaction with respect to the particle density. In typical aggregation processes, particle–particle collisions occur via three mechanisms: Brownian motion, fluid shear, and differential sedimentation. The rectilinear collision frequency functions for Brownian motion (β_{Br}), fluid shear (β_{Sh}), and differential sedimentation (β_{DS}) are given [9] by Eqs. (4)–(6):

$$\text{Brownian motion}: \quad \beta_{Br}(i,j) = \left(\frac{2kT}{3\mu}\right)\left(\frac{1}{d_i}+\frac{1}{d_j}\right)\left(d_i+d_j\right), \tag{4}$$

$$\text{Fluid shear}: \quad \beta_{Sh}(i,j) = \left(\frac{G}{6}\right)\left(d_i+d_j\right)^3, \tag{5}$$

$$\text{Differential sedimentation}: \beta_{DS}(i,j) = \left(\frac{2kT}{3\mu}\right)\left(\rho_p-\rho_l\right)\left(d_i+d_j\right)^3\left|d_i-d_j\right|. \tag{6}$$

According to Han's curve model [9], the overall frequency of inter-particle collisions can be expressed by Eq. (7):

$$\beta(i,j) = \alpha(i,j)\left(\beta_{Br}(i,j)+\beta_{Sh}(i,j)+\beta_{DS}(i,j)\right) \tag{7}$$

where α (i, j) is a correction coefficient for inter-particle collision.

$$\alpha(i,j) = 1.03 \times \exp\left(\frac{-38.4}{RT}\right) \tag{8}$$

Particle breakup refers to the fragmentation (under external forces) of a parent particle into several daughter particles. The breakup rate of a parent particle is related to its size. After a breakup event, the particle number increases, but the overall particle mass is conserved [11–13]. The "binary random breakup" model hypothesizes that each parent cluster (i.e., particle) [n_{i+j}, $(i+j \geq 2)$] randomly fragments into two daughter clusters (n_i and n_j). The sizes of n_i and n_j are random, and the overall mass is conserved. This is in contrast to cluster aggregation, where cluster breakup is a first-order reaction with respect to the cluster density. The net rate of n_i formation is given [14] by Eq. (8):

$$\frac{dn_i}{dt} = -k_b n_i + 2\sum_{j=1}^{\infty}\frac{k_b n_{i+j}}{(i+j-1)} \tag{9}$$

where the first and second terms on the right-hand side represent the breakage death and the breakage birth, respectively. It is assumed that one large cluster breaks into two smaller clusters with a breakage rate coefficient, k_b, which, in general, depends upon the cluster size.

$$k_b = 9122 \times \exp\left(\frac{-50}{RT}\right)(N-1) \tag{10}$$

2.2. Multi-Monte Carlo simulation

A particle system undergoes complex events such as aggregation and breakup, and a population balance equation (PBE) can be introduced to describe the microscopic behavior of particles and their size distribution. The population balance is a statement of continuity that is based on the number density function. To simplify the solution process, previous studies have focused on cluster aggregation while ignoring cluster breakup [15].

The present study uses an improved time-driven multi-Monte Carlo (MMC) method to solve the PBE [16,17]. In this method, possible events are considered for all particles during an appropriate time interval (assuming that all events are mutually independent). The MMC method introduces the concept of a "weighted fictitious particle" to conserve the volume of the computational domain and the number of fictitious particles within it. It is assumed that real particles that have the same or similar volume have the same properties, and hence exhibit the same behavior; thus, the evolution of these fictitious particles represents the evolution of real particles in the computational domain. In this model, the treatment of particle aggregation involves judging the likelihood of an aggregation event, choosing the aggregation partner, and dealing with the consequences of aggregation. Each breakup event involves only one parent particle. Treatment of a particle breakup involves judging the likelihood of a breakup event, and dealing with its consequences. After selecting the parent particle, the parameters are first calculated for one daughter particle (Daughter 1), using a random number and the size of the parent particle (i.e., the number of constituent molecules). The parameters of the other daughter particle (Daughter 2) are then determined based on the conservation of mass. One important point in treating the breakage event is to keep the total number of fictitious particles constant. Some measures to achieve this are adopted as follows: Daughter 1 is stored at the position of the parent particle and Daughter 2 is merged with a fictitious particle that has the same or a similar size as Daughter 2.

Although the total number of real particles fluctuates continuously with the occurrence of the aggregation event and the breakage event, the total number fictitious particles remains constant by means of the adjustment of the weight of those related fictitious particles. In addition, the volume of the computational domain is conserved.

In the MMC method, the particle aggregation event and the breakage event can be decoupled within a sufficiently small time step Δt. That is, the evolution is decomposed into two distinct processes: an aggregation event and a breakage event. Time step Δt should be less than or equal to the minimum aggregation time scale (min ($t_{i,aggre}$)), and it should also be less than or equal to the minimum breakage time (min ($t_{i,brk}$)), that is:

$$\Delta t \leq \alpha \min\left\{\frac{1}{\max_{i=1,\ldots N_t}(C_i)}, \frac{1}{\max_{i=1,\ldots N_t}(S_i)}\right\}$$

where C_i is the total aggregation probability of fictitious particle i in unit time; S_i is the breakage rate of fictitious particle i in unit time; and $\alpha = 0.05$.

The number-average degree of clustering (N_{av}) is defined as the ratio of the total number of molecules to the total number of clusters in a crystallization system. At the inception of the reaction, these two numbers are equal and, therefore, $N_{av} = 1$. With subsequent cluster formation, the clusters increase in size, but decrease in number. As a result, N_{av} gradually increases to become equal to g_c. The time required for N_{av} to reach g_c is defined as t_{ind} [14].

3. Results

The nucleation of calcium carbonate was simulated via the MMC method for both the AM and ABM (abbreviated as MMC–AM and

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