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Population balance modeling of precipitated calcium carbonate (PCC) flocculation induced by cationic starches

Xiang Wang

Weifang University of Science & Technology, 166 Xueyuan Road, Shouguang, Shandong 262700, China

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ABSTRACT

In order to predict and control the flocculation process, it is necessary to develop quantitative model which can describe aggregation, breakage and restructure phenomenon. In this paper, population balance equation was employed to model the PCC flocculation process. Energy dissipation rate was calculated to evaluate the floc strength. It was found, compared to the low charge density starch, the high charge density starch resulted in lower collision efficiency, lower restructure rate and stronger flocs (indicated by higher energy dissipation rate). The higher the temperature, the lower the energy dissipation rate was needed to break the flocs. The addition of NaCl did not show effect on the collision efficiency for both high and low charge density starches, but weaker flocs were formed and more prominent restructure rate was observed at higher NaCl concentration. The collision efficiency decreased with the increase of the shear rate for both starches. At higher starch dosage, lower energy dissipation rate could break the flocs and higher restructure rate was observed.

1. Introduction

The precipitated calcium carbonate (PCC) flocculation and the resulted floc size, structure and strength are important for the waste water treatment, water treatment, papermaking, and mineral recovery, etc. (Sang et al., 2012; Sang and Xiao, 2008). The stronger the bonding between the particles, the higher the floc strength (Tang et al., 2001). Greater number of interparticle bond can result in more compact floc structure and stronger flocs (Hermawan et al., 2003, 2004). Static light scattering/diffraction (SLS), real time fluorescent video imaging, image analysis, photometric dispersion analysis (PDA) and scanning electron microscopy (SEM) was employed to investigate the floc structure of PCC aggregates induced by different polymers (Gaudreault et al., 2009). High shear generally produced small, weak and less reversible flocs (Gaudreault et al., 2009). High polymer dosages usually produced larger flocs than those produced at low chemical dosages (Gaudreault et al., 2009). However, very little is known about the details of floc strength and structure which affect the filtration rate and settability due to the fragile nature of flocs. It has not developed a satisfactory technique to quantify floc strength (Jarvis et al., 2005; Yeung and Pelton, 1996). In order to predict and control the flocculation process, it necessitates the development of a model which can describe flocculation mechanisms. Since the population balance model was first proposed by Smoluchowski (von Smoluchowski, 1917), it has found wide applications in describing the nucleation (Gooch and Hounslow, 1996; Hounslow et al., 1988; McCoy, 2002; Qamar et al., 2009), crystallization (Gooch and Hounslow, 1996; Hounslow et al., 2005), and flocculation process (Bramley et al., 1996; Hamalainen and Hamalainen, 2010; Kramer and Clark, 1999; Selomulya et al., 2003; Somasundaran and Runkana, 2003; Spicer and Pratsinis, 1996), etc. Compared to branched cationic polyacrylamide, linear cationic polyacrylamide resulted in higher collision efficiency and restructure rate during PCC flocculation process (Antunes et al., 2010). Aggregation rate was calculated through population balance modeling without considering the floc structure change (Ding et al., 2006). The mass fractal change was taken into account in the population balance modeling of PCC flocculation to make it closer to the actual case (Sang and Englezos, 2012a, 2012b).

Though lots of work has been conducted to model the flocculation process using population balance model, the relationships between these parameters and the experimental conditions were not well established. The objective of this work is to investigate the effect of cationic starch with different charge densities on the collision efficiency, floc strength and restructure rate in order to control the flocculation process and manipulate the floc properties.

2. Materials and methods

2.1. Materials

Two cationic starches with different charge densities (Starch 1, charge density = 0.26 meq/g; Starch 2, charge density = 1.01 meq/g, average molecular mass = 3 million Da for both starches) produced by Guangxi State Farms Mingyang Biochemical Group, Inc. (China)

E-mail address: 2008wangxiang@163.com.

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were used for the PCC flocculation. The charge density was determined by colloidal titration with particle charge detector (PCD, Mütek, Herrsching, Germany) using potassium polyvinylsulfate (PVSK) solution as a titrant. The cationic substituent of the starches is quaternary ammonium. NaCl was used as the background electrolyte. Acid-tolerant PCC obtained from Chenming Group, Shouguang, China was used. This PCC has a negative zeta potential -20 ± 5 mV and a pH of 8.7 ± 0.1 at 0.002 wt.%. The PCC has an average particle size of 2.53 μm measured with Malvern Mastersizer 2000.

2.2. Flocculation experiment

The flocculation experiments were conducted in a beaker and using water bath to control the temperature. During the experiment, 0.30 g PCC was added to 600 mL water to get 0.05 wt.% PCC suspension and then continuously circulated to the Mastersizer 2000 (Malvern Instruments Inc., Malvern, UK) with a peristaltic pump for floc size measurement. The pump was placed downstream of the Mastersizer 2000 to avoid the breakage of flocs by pump stress.

2.3. Population balance model

The population balance equation describes the rate of change of the particle number concentration in section i is shown in Eq. (1) (Hounslow et al., 1988):

$$\begin{aligned}\frac{dN_i}{dt} &= N_{i-1}\sum_{j=1}^{i-2} 2^{j-i+1}\alpha_{i-1,j}\beta_{i-1,j}N_j + \frac{1}{2}\alpha_{i-1,i-1}\beta_{i-1,i-1}N_{i-1}^2 \\ &-N_i\sum_{j=1}^{i-1} 2^{j-1}\alpha_{i,j}\beta_{i,j}N_j - N_i\sum_{j=i}^{i\max}\alpha_{i,j}\beta_{i,j}N_j \\ &-S_iN_i + \sum_{j=i}^{i\max}\Gamma_{i,j}S_jN_j\end{aligned} \tag{1}$$

where N_i is the number concentration of particles in section i, $\alpha_{i,j}$ is the collision efficiency, and $\beta_{i,j}$ is the collision frequency for the particles in sections i and j. The number concentration of primary particles is used as the initial condition for the population balance equation. Fragmentation rate S_j was used to describe the floc breakage rate. The distribution of floc fragments in interval i from the break-up of flocs in interval j was described by the breakage distribution function Γ_{ij}. The first two terms on the right hand side of Eq. (1) represent the aggregation birth of floc of size, i. The third and fourth terms represent the death of floc of size, i due to aggregation. The fifth term is the death of floc of size, i. The sixth term is the breakage birth of floc of size, i, by breakage of larger flocs in interval j.

2.3.1. Collision efficiency

Collision efficiency has been mostly employed as a fitting parameter for population balance equation. It is a function of the interaction forces between particles that depend on the type of polymer used. Eq. (2) was used to describe the collision efficiency for particles in section i and j (Bonanomi et al., 2004; Selomulya et al., 2003).

$$\alpha_{i,j} = \frac{\exp\left(-0.1\left(1-\frac{i}{j}\right)\right)^2}{(i\times j)^{0.1}} \times \alpha_{\max} \tag{2}$$

Maximum collision efficiency $\alpha_{\max}$ was considered to be 1.

2.3.2. Collision frequency

Particle–particle, particle–floc and floc–floc collisions resulted in the formation of flocs. Mass fractal dimension of flocs is incorporating into the collision frequency factor to take account of the irregularity of flocs. The rate of flocculation is primarily a function of collision frequency, which depends strongly on particle collision radius. The thicker the adsorbed layer at the solid–liquid interface, the larger the collision frequency (Runkana et al., 2006).

Without considering the settling and inertial effects and only considering binary collisions, the overall collision frequency can be calculated as follows (Swift and Friedlander, 1964):

$$\beta_{ij} = \beta_{ij,perikinetic} + \beta_{ij,orthokinetic}. \tag{3}$$

The binary collision frequency between particles because of Brownian motion is estimated by Eq. (4) (Saffman and Turner, 1956):

$$\beta_{ij,perikinetic} = \left(\frac{2k_BT}{3\mu}\right)\frac{(R_{ci}+R_{cj})^2}{R_{ci}R_{cj}} \tag{4}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and μ is the dynamic viscosity. This mechanism is dominant for small particles (<1 μm). The collision frequency for orthokinetic coagulation is given by the Eq. (5) (Saffman and Turner, 1956):

$$\beta_{ij,orthokinetic} = 1.294\left(\frac{\varepsilon}{\nu}\right)^{1/2}(R_{ci}+R_{cj})^3 \tag{5}$$

where ε (m^2/s^3) is the average energy dissipation rate, υ is the kinematic viscosity (m^2/s), R_{ci} and R_{cj} (m) are the effective collision radius.

2.3.3. Energy dissipation rate

The energy dissipation rate is the rate of the turbulence energy absorbed by breaking the flocs down into smaller particles. The energy dissipation rate required for floc breakage is inversely proportional to the floc size. It is expressed as the kinetic energy per unit mass per second (m^2/s^3).

A semi-empirical exponential kernel which correlates the fragmentation rate S_i and the critical energy dissipation rate were employed in the model through Eq. (6) (Kusters, 1991):

$$S_i = \left(\frac{4}{15\pi}\right)^{1/2}\left(\frac{\varepsilon}{\nu}\right)^{1/2}\exp\left(\frac{-\varepsilon_{ci}}{\varepsilon}\right) \tag{6}$$

where ε_{ci} is the critical energy dissipation rate (Shirazi et al., 2003).

2.3.4. Breakage distribution function

Binary breakage, ternary breakage and normal breakage have been proposed for the population balance model. Previous work showed the application of any type of the breakage functions results in similar final floc size distributions (Spicer and Pratsinis, 1996). For simplicity, the binary breakage distribution function was adopted and is expressed as follows (Spicer and Pratsinis, 1996).

$$\begin{aligned}\Gamma_{ij} &= \frac{V_j}{V_i} = 2 \ \text{ for } \ j = i+1 \\ \Gamma_{ij} &= 0 \ \text{ for } \ j \neq i+1\end{aligned} \tag{7}$$

The number concentration of particles in the intervals (N_i) was used to estimate the volume mean diameter $d_{4,3}$ (m) (Kusters, 1991):

$$d_{4,3} = \frac{\Sigma N_i D_i^4}{\Sigma N_i D_i^3}. \tag{8}$$

The characteristic floc diameter (m) in interval i is calculated as

$$D_i = \left(2^{\frac{i-1}{d_f}}\right)d_0 \tag{9}$$

where the primary particle size $d_0 = 0.25$ μm, $d_f = 1.70$ are obtained using the Malvern Mastersizer 2000.