

Aggregate size distributions in sweep flocculation

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Abstract

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The evolution of aggregate size distributions resulting from sweep flocculation has been investigated using laser light scattering technique. By measuring the (volume) distributions of floc size, it is possible to distinguish clearly among floc formation, growth and breakage. Sweep flocculation of stable kaolin suspensions with ferric chloride under conditions of the rapid/slow mixing protocol produces uni-modal size distributions. The size distribution is shifted to larger floc size especially during the rapid mixing step. The variation of the distributions is also shown in the plot of cumulative percent finer against floc size. From this plot, the distributions maintain the same S-shape curves over the range of the mixing intensities/times studied. A parallel shift of the curves indicates that self-preserving size distribution occurred in this flocculation. It is suggested that some parameters from mathematical functions derived from the curves could be used to construct a model and predict the flocculating performance. These parameters will be useful for a water treatment process selection, design criteria, and process control strategies. Thus the use of these parameters should be employed in any further study.

Key words : aggregate size distribution, S-shape curve, self-preserving size distribution, sweep flocculation

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บทคัดย่อ

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การกระจายขนาดของกลุ่มอนุภาคที่เกาะกลุ่มแบบตะกอนตกจม

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วัตถุประสงค์ของการวิจัยนี้คือ ศึกษาการเปลี่ยนแปลงการกระจายขนาดของกลุ่มอนุภาคที่เกิดจากการเกาะกลุ่มแบบตะกอนตกจม โดยอาศัยวิธีการวัดขนาดและการกระจายขนาดด้วยหลักการกระเจิงแสงเลเซอร์ ผลการวัดการเปลี่ยนแปลงการกระจายขนาด สามารถแยกระบุถึง ช่วงก่อกำเนิด เดิบโต และแตกย่อยของกลุ่มอนุภาคอย่างชัดเจน พบว่าการเกาะกลุ่มของอนุภาคดินขาวที่เดิมดำรงอยู่ในสภาวะกระจัดกระจายทั่วไป ด้วยสารละลายเหล็กคลอไรด์ ภายใต้สภาวะเงื่อนไขการกวนแบบมาตรฐานเร็วแล้วช้า ทำให้เกิดการกระจายขนาดแบบหนึ่งโหมดทั้งหมด และการกระจายขนาดแบบนี้จะเปลี่ยนเป็นการกระจายขนาดของกลุ่มอนุภาคที่มีขนาดใหญ่ขึ้นอย่างรวดเร็ว โดยเฉพาะอย่างยิ่งในช่วงของการกวนของผสมอย่างรวดเร็วในช่วงสั้น ๆ พร้อมกันนี้ การเปลี่ยนแปลงของการกระจายขนาดได้ถูกแสดงในพล็อตระหว่างเปอร์เซ็นต์น้ำหนักสะสมของส่วนละเอียดและขนาดกลุ่มอนุภาค จากพล็อตนี้พบว่า การกระจายขนาดมีรูปแบบการกระจายตัวแบบโค้งรูปตัวเอส ทุกช่วงความเร็วของการกวนและเวลาที่ศึกษา การเปลี่ยนแปลงแบบขนานของเส้นโค้งการกระจายแบบเอส บ่งบอกถึงภาวะการกระจายแบบคงรูปร่างเดิมที่เกิดขึ้นในการเกาะกลุ่มแบบนี้ มีข้อเสนอแนะว่าพารามิเตอร์บางตัวจากฟังก์ชันคณิตศาสตร์ของการกระจายแบบโค้งเอส สามารถนำมาใช้สร้างแบบจำลอง และทำนายประสิทธิภาพของกรรมวิธีเกาะกลุ่มแบบตะกอนตกจม พารามิเตอร์เหล่านี้ อาจเป็นประโยชน์สำหรับการเลือก ออกแบบ และควบคุมกระบวนการบำบัดน้ำ ดังนั้นควรศึกษาเพิ่มเติมเกี่ยวกับการประยุกต์ใช้ประโยชน์จากพารามิเตอร์เหล่านี้

ภาควิชาวิศวกรรมเหมืองแร่ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเชียงใหม่ อำเภอเมือง จังหวัดเชียงใหม่ 50200

Aggregation of fine particles in aqueous media can be achieved by flocculation. The generic term of flocculation can be defined as a process of aggregation by any kinds of mechanisms involved. Flocculation can be attained by the following mechanisms; approach to the point of zero charge (PZC), electrical double layer compression, charge-patch neutralization, polymer bridging, hydrophobic interaction, and enmeshment within sweep floc -- sweep flocculation.

Sweep flocculation is a non-selective aggregation of colloidal size particles within the flocs. Sweep flocs can be described as large aggregates of aluminum hydroxide; $Al(OH)_3$, or ferric hydroxide; $Fe(OH)_3$ that are formed when alum or a ferric salt (coagulant) is added to water. It has been found that sweep flocs formed in any conventional water treatment process are positively charged (Dempsey, 1987). For example, the PZC of $Al(OH)_3$ and $Fe(OH)_3$ is about 8.5 (David and Leckie, 1978). The colloids of clay minerals

abundantly found in the wastewater are negatively charged. For example, the PZC of silica and kaolin is about 2 and 4 respectively (Fuerstenau and Fuerstenau, 1982). As a result, the colloidal particles are electrostatically attached to the sweep flocs in the neutral pH water. In addition soluble contaminants, e.g. arsenate, chromate, mercury, cadmium, etc. can adsorb on the sweep flocs, and be removed from the wastewater.

Since conventional raw water treatment is oriented toward the removal of turbidity caused by colloidal size particles suspended in water, many flocculation processes have been designed to minimize the value of turbidity in the finished water. Most investigators in the water treatment field use residual turbidity as a parameter to measure the effectiveness of the flocculation process. O'Melia (1978) noted that turbidity may not be the best parameter for evaluation of process effectiveness, and measurement of particle number and particle size distribution should be used to

understand and control the removal of the suspended particles. Kavanaugh *et al.* (1980) has reviewed the importance of using particle number and particle size distribution as the direct performance criteria. They found that these criteria were useful in the selection of a water treatment process, for design criteria, and for process control strategies. Lawler and Wilkes (1984) have also shown that particle number and particle size distribution are important criteria to measure and predict flocculation performance. These criteria can be used to measure the performance of the actual process used in a water softening plant. However, the measurement of these criteria using electrical sensing technique of a modified Coulter Counter is difficult, time-consuming and prone to sampling errors. Rattanakawin (2003), Rattanakawin and Hogg (2001) used the light scattering technique of Microtrac X-100 Tri Laser Particle Size Analyzer to successfully evaluate aggregate (floc) size distributions resulting from hydrophobic and polymeric flocculation respectively. Therefore volumetric floc size distribution obtained from the Microtrac X-100 will be further used to monitor the change in size distribution of sweep flocculation in this study.

Materials and Methods

The experimental method of sweep flocculation was adapted from the work of Rattanakawin and Hogg (2001). Kaolin was used as the model mineral in this flocculation study. Hydrite R kaolin was obtained from Dry Branch Kaolin Company. This kaolin has a median particle size of $0.34 \mu\text{m}$ and point of zero charge of 2.40 (Suharyono, 1996).

The kaolin was dispersed in distilled water at 0.01 wt.% solids in the 800 ml standard mixing tank. The dispersion step included mechanical agitation for 5 min. at a mean shear rate (G_{mean}) of 1000 sec.^{-1} by mechanical stirrer, ultrasonic dispersion for 15 sec. at 35% amplitude with the ultrasonic probe followed by additional mechanical agitation for 5 min. During the last five-minute agitation period, the suspension pH was adjusted with sodium hydroxide (NaOH) to pH 7. After that

initial floc size distribution of the kaolin in the suspension was measured using the Microtrac X-100.

An aqueous solution of FeCl_3 was added to the kaolin suspension to achieve the dosage of 50 mg FeCl_3 per liter of suspension along with the adjustment of the suspension pH to pH 7 using NaOH, with agitation at G_{mean} of 1000 sec.^{-1} . The suspension was first agitated at 1000 sec.^{-1} for 0.5 min. in the rapid mixing step. This rapid mixing protocol is normally used in a typical turbine (back-mix) reactor (AWWARF, 1989). After that the suspension was agitated continuously at 60 sec.^{-1} in the slow mixing step with varying times. The sampling times of sweep flocs were set to be 0.5, 1, 2, 3, 4, 5, 10, 15 and 20 min. respectively. The floc samples were drawn from the mixing tank and transferred into the feeder tank of the modified Microtrac (Rattanakawin and Hogg, 2001). Then the floc size distribution of the samples was measured using the Microtrac X-100.

Results and Discussion

Floc size distribution obtained from the light scattering technique was used to evaluate the mechanisms of sweep flocculation. The evolution of floc size distribution as a result of a combination of rapid/slow mixing times is shown in Figure 1. It can be seen that all the floc size distributions show a uni-modal characteristic. The distribution progresses rapidly to the larger floc size in the rapid mixing step with mixing intensity of 1000 sec.^{-1} for 0.5 min. In the slow mixing step, at a mixing intensity of 60 sec.^{-1} , the distributions become coarser and reach the largest floc size at 10 min. After this time, continued slow mixing reverses the process and the distribution shifts back to the smaller size.

This result indicated that sweep flocs are produced at high formation rate in the rapid mixing step as also noted by Amirtharajah and Mills, 1982. The growth of the sweep floc is continuously increased in the slow mixing step up until the floc breakage dominates. It is intuitive that the sweep flocs are weak and prone to breakage. For this

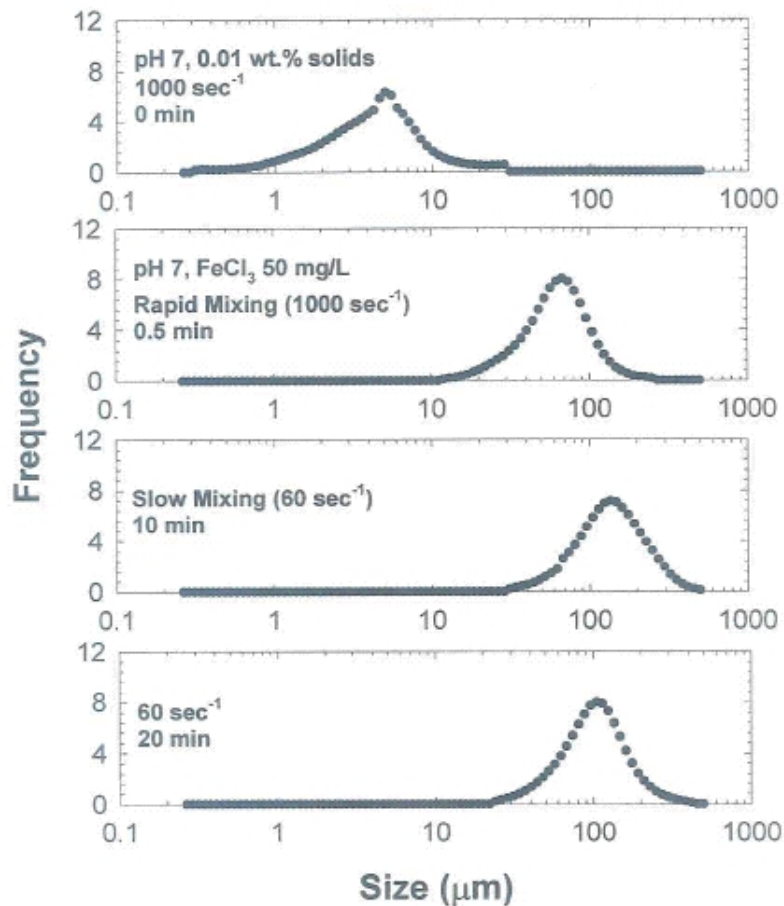


Figure 1. The evolution of floc size distributions as a function of rapid/slow mixing intensity and time for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg/L ferric chloride, and rapid-mixed at 1000 sec⁻¹ for 0.5 minute followed by slow mixing at 60 sec⁻¹ for varying times in the 800 mL standard mixing tank.

reason the rapid/slow mixing scheme is always employed in any sweep flocculation.

The variation of floc size distributions as a function of a combination of rapid/slow mixing time is shown in the cumulative percent finer versus floc size curves in Figure 2. Interestingly, the S-shape curves are shifted in a parallel manner with the mixing times. The parallel shift of these curves implies the development of the so-called self-preserving size distributions. To confirm the self-preserving size form, the normalized curve of cumulative percent finer as a function of dimensionless floc size (d/d_{50}) is plotted and shown in Figure 3. It can be seen that all the curves

are lumped into one single curve. The dimensionless d/d_{50} is not a function of mixing times. This confirmation leads to the conclusion that the sweep flocculation in this study indeed produces self-preserving size distributions. The self-preserving size distribution obtained during flocculation has been observed by many researchers (Wang and Friedlander, 1967; Sastry, 1975 and Hunt, 1982).

In the absence of uniform size distribution of particles, the number size distribution of aquatic suspensions is often found to follow some form of a mathematical function e.g. power function (Lawler *et al.*, 1980). If the volumetric distributions of floc size progress with the same function

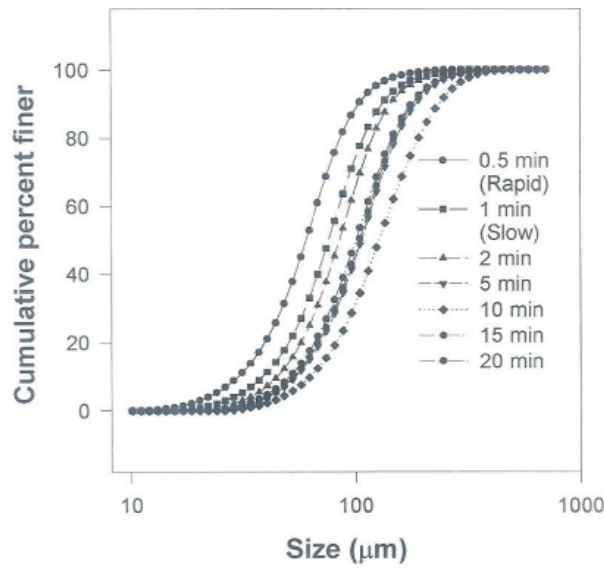


Figure 2. The variation of floc size distributions (cumulative percent finer against size) as a function of rapid/slow mixing intensity and time for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg/L ferric chloride, and rapid-mixed at 1000 sec⁻¹ for 0.5 minute followed by slow mixing at 60 sec⁻¹ for varying times in the 800 mL standard mixing tank.

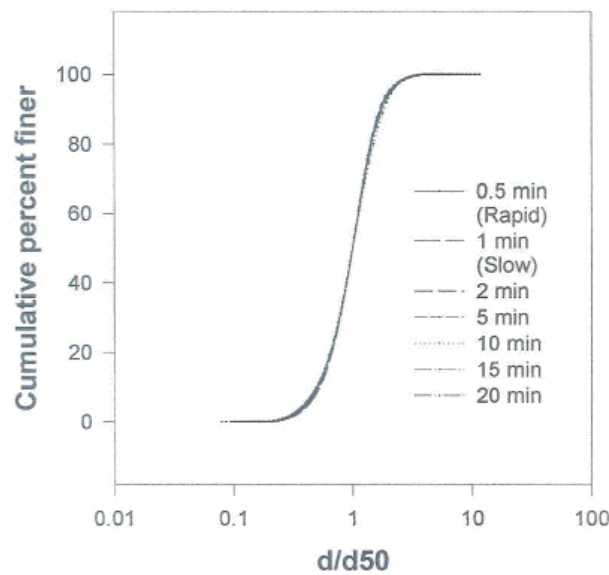


Figure 3. Normalized curves of cumulative percent finer as a function of dimensionless floc size (d/d_{50}) with various mixing intensities and times for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg/L ferric chloride, and rapid-mixed at 1000 sec⁻¹ for 0.5 minute followed by slow mixing at 60 sec⁻¹ for varying times in the 800 mL standard mixing tank.

during sweep flocculation as shown in Figure 2, it is possible to use some parameters of this function to construct a model and predict the flocculating performance. The construction of the model from the number distributions of floc size to evaluate the effects of various raw water characteristics and design parameters on the performance of water treatment plant has been developed at length by Lawler *et al.* (1980).

Due to the lack of the coagulation theory of particles with continuous size distribution, the early flocculation models can be obtained empirically from laboratory or pilot plant studies. By verifying of the existence of the self-preserving size distribution, it is possible to simplify the classic Smoluchowski (1917) population balance model of the particles with broad size distribution. Hogg *et al.* (1990), for example, derived the simplified population balance model for simultaneous floc growth and breakage by assuming that the self-preserving size distribution occurs in a flocculation process. This simplified model was appropriate for measuring the flocculating performance of fine-particle suspensions by continuous addition of polymer to an agitated suspension. Together with an expression relating the effects of process variables on the model parameters: agglomeration and breakage rate constants, the model can be used to establish criteria for equipment selection and process design.

Conclusions and Recommendations

Volumetric floc size distribution obtained from light scattering technique is very useful to study the sweep flocculation of kaolin suspensions. By monitoring the distributions of floc size, it is possible to distinguish clearly among floc formation, growth and breakage. The floc size distribution maintains the same S-shape characteristic over the range of rapid/slow mixing times. Parameters from the function may be used to construct a mathematical model and predict the flocculating performance. Therefore further construction of the model from the distribution is suggested. The parallel shift of the S-shape curves

indicates that self-preserving size distribution occurred in this sweep flocculation. The finding of the self-similar distribution may be used to simplify the derivation of standard population balance model.

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