ORIGINAL ARTICLE

Aggregate size distributions in hydrophobic flocculation

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Abstract

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The evolution of aggregate (floc) size distributions resulting from hydrophobic flocculation has been investigated using a laser light scattering technique. By measuring floc size distributions it is possible to distinguish clearly among floc formation, growth and breakage. Hydrophobic flocculation of hematite suspensions with sodium oleate under a variety of agitating conditions produces uni-modal size distributions. The size distribution of the primary particles is shifted to larger floc sizes when the dispersed suspension is coagulated by pH adjustment. By adding sodium oleate to the pre-coagulated suspension, the distribution progresses further to the larger size. However, prolonged agitation degrades the formed flocs, regressing the distribution to the smaller size. Median floc size derived from the distribution is also used as performance criterion. The median floc size increases rapidly at the initial stage of the flocculation, and decreases with the extended agitation time and intensity. Relatively weak flocs are produced which may be due to the low dosage of sodium oleate used in this flocculation study. It is suggested that further investigation should focus on optimum reagent dosage and non-polar oil addition to strengthen these weak flocs.

Key words : aggregate size distribution, hydrophobic flocculation

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บทคัดย่อ

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การกระจายขนาดของกลุ่มอนุภาคที่เกาะกลุ่มแบบไฮโดรโฟบิก

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วัตถุประสงค์ของการวิจัยนี้คือ ศึกษาการเปลี่ยนแปลงการกระจายขนาดของกลุ่มอนุภาคที่เกิดจากการเกาะกลุ่มแบบไฮโดรโฟบิก โดยอาศัยวิธีการวัดขนาดและการกระจายขนาดด้วยหลักการกระเจิงแสงเลเซอร์ ผลการวัดการเปลี่ยนแปลงการกระจายขนาด สามารถแยกระบุถึงช่วงก่อกำเนิด เติบโต และแตกย่อยของกลุ่มอนุภาคอย่างชัดเจน พบว่าการเกาะกลุ่มของอนุภาคแร่ฮีมาไทต์ในสารละลายโซเดียมโอลิเอต ภายใต้สภาวะเงื่อนไขการกวนต่าง ๆ ทำให้เกิดการกระจายขนาดแบบหนึ่งโหมด (Unimodal) ทั้งหมด แต่การกระจายขนาดแบบนี้ จะเปลี่ยนเป็นการกระจายขนาดของกลุ่มอนุภาคที่มีขนาดใหญ่ขึ้น เมื่อมีการปรับสภาพความเป็นกรด-ด่างของของผสมอนุภาคที่เดิมดำรงอยู่ในสภาวะกระจัดกระจายทั่วไปในสารละลายฯ การเติมโซเดียมโอลิเอตลงไปในของผสมที่ปรับสภาพแล้วยิ่งทำให้การกระจายขนาดอยู่ในช่วงที่มีขนาดของกลุ่มอนุภาคใหญ่ขึ้น อย่างไรก็ตามการกวนของผสมนานขึ้น ทำให้เกิดการแตกย่อยของกลุ่มอนุภาค สังเกตได้จากการกระจายขนาดจะอยู่ในช่วงที่มีขนาดของกลุ่มอนุภาคเล็กลง ขนาดมัธยฐาน (median) ของกลุ่มอนุภาคที่ได้มาจากการกระจายขนาดแบบหนึ่งโหมด สามารถนำมาใช้เป็นเกณฑ์วัดประสิทธิภาพของการเกาะกลุ่มแบบไฮโดรโฟบิก ขนาดมัธยฐานจะใหญ่ขึ้นอย่างรวดเร็วในช่วงแรกของการเกาะกลุ่มและมีขนาดเล็กลงเมื่อเพิ่มเวลาและความแรงในการกวนของผสม สรุปได้ว่ากลุ่มอนุภาคที่เกิดจากการเกาะกลุ่มแบบไฮโดรโฟบิกในการวิจัยครั้งนี้ มีความแข็งแรงน้อย สาเหตุอาจมาจากปริมาณโซเดียมโอลิเอตที่ใช้น้อยเกินไป ดังนั้นควรศึกษาเพิ่มเติมเกี่ยวกับปริมาณโซเดียมโอลิเอตที่เหมาะสม และการเติมน้ำมันลงไปในของผสม อาจช่วยเพิ่มความแข็งแรงของกลุ่มอนุภาคนี้ได้

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, electrical double layer compression, charge-patch neutralization, polymer bridging, and hydrophobic interaction, etc.

Hydrophobic interaction arises when surfactants with amphiphilic character adsorb to the surfaces of hydrophilic particles. Under these circumstances, the surfactant molecules typically align in a monolayer structure with their hydrophilic entities bound to the particle surfaces, and their hydrophobic (hydrocarbon) chains facing into suspension. The particle surfaces then assume some of the hydrophobic characteristics of the hydrocarbon chain. When the surfactant coated particles interact, a strong attractive force occurs due to hydrophobic attraction. This aggregation mechanism is termed hydrophobic flocculation (Song *et al.*, 2001). In addition, agglomeration of hydrophobic particles suspended in water with liquid hydrocarbons (oils) or hydrophobic flocculants is also referred to as hydrophobic flocculation (Laskowski, 1992 and Laskowski, 2000).

Hydrophobic flocculation is a process for selectively aggregating fine particles of one mineral from others in a suspension. Therefore this process has potential as a means of upgrading low-grade, fine-grained minerals from gangues. The fine minerals suspended in an aqueous solution of surfactant are formed into flocs by applying a shear field of sufficient magnitude. These formed flocs are readily for subsequent flotation process. Therefore the surfactant should be one that renders the mineral surfaces hydrophobic.

Surfactants frequently used as flotation collectors are suitable for this flocculation process.

The use of flotation collectors as mineral flocculants gives promising results in the investigations of semi-soluble salt minerals such as scheelite (Koh *et al.*, 1986; and Patil *et al.*, 2001), fluorite (Sivamohan, 1988), and apatite (Wang and Heiskanen, 1992). Investigations of insoluble oxide minerals include cassiterite (Warren, 1982 and Bilgen *et al.*, 1994), quartz (Raju *et al.*, 1991), and hematite (Fuerstenau *et al.*, 1988; Wang and Heiskanen, 1992; and Pascoe and Doherty, 1997).

While such investigations have provided some useful information for a beneficiation of fine minerals, the hydrophobic flocculation mechanism itself e.g. floc formation, growth and breakage has not been explained in details. Rattanakawin and Hogg (2001) has shown that aggregate size distribution and its derivatives are useful parameters in describing the flocculation of fine particles via the mechanism of approach to the point of zero charge, electrical double layer compression, charge-patch neutralization, polymer bridging. The aggregate (floc) size distribution directly measures the various sizes of flocs existing in a flocculation process. The size of individual primary particles and flocs is actually a fundamental and dynamic property of the process. Moreover, the size distribution depends upon the flocculating conditions. Therefore, the distribution may be considered more or less as a real-time representation of the flocculation kinetics. In the other words, the mechanisms of any flocculation process could be observed by monitoring the change in the floc size distributions. The objective of this study is to describe the mechanism of the hydrophobic flocculation using floc size distribution and median floc size as measuring criteria.

Experimental Setup

The experimental setup used in hydrophobic flocculation study was similar to that used by Rattanakawin and Hogg (2001). The flocculation experiments were conducted in the 800 ml standard mixing tank. This tank was equipped with a six flat blade turbine driven by a mixer head model 50000-40, and controlled by a mixer controller model 50000-00 (Cole-Parmer Instrument Co.).

Acid or base for pH control was added to a dispersed suspension by means of an eye-dropper. The suspension pH was monitored using a pH meter (Orion model SA520, Orion Research Incorporated). A pipette was used to add surfactant in this research. To obtain an adequate mixing in the standard mixing tank, the surfactant was introduced through the pipette which placed between two baffles and the stirrer shaft near the turbine blade. This was a region of high turbulence in which mixing could proceed rapidly (Lu *et al.*, 1998). The sampling system employed a 5 mm diameter pipette of wide mouth eye-dropper with the tapered tip cut off to permit large flocs to be collected without breakage. Gibbs and Konwar (1982) found that if the pipette openings are less than 2 mm, it might modify the floc size distribution in certain mineral flocs.

Experimental Procedure

The experimental procedure of hydrophobic flocculation of hematite was adapted from the work of Pascoe and Doherty (1997). Synthetic hematite obtained from the J.T. Baker Chemical Co. was used in this study. The median particle size of the hematite was 0.566 µm measured using the Microtrac X-100 Tri Laser Particle Size Analyzer (Leeds & Northrup). The point of zero charge of hematite in aqueous solution is about pH 8.4±0.1 (Farinato and Dubin, 1999). The synthetic hematite was dispersed in distilled water at 1 wt.% solids in the standard mixing tank. The dispersion step included mechanical agitation for 5 minutes at 500 rpm by mixer, and ultrasonic dispersion for 15 second at 35% amplitude with an ultrasonic probe (Sonic & Materials Inc., Model Vibra Cell) followed by additional mechanical agitation for 5 minutes. To obtain good dispersion the suspension pH was adjusted with sodium hydroxide to pH 10.5 during the last five-minute agitation before the reagent was added.

Sodium oleate (NaOl) purchased from the

J.T. Baker Chemical Co. was used as a flocculating agent. An alkaline solution of NaOl at pH 10.5 was added to the hematite suspension to achieve the dosage of 50 mg NaOl per liter of suspension. After that the suspension pH was adjusted to pH 8 with hydrochloric acid and separately agitated at 500, 1000 or 1500 rpm in a continuous manner. Then the floc size distribution was measured using the modified Microtrac X-100 (Rattanakawin and Hogg, 2001). Essentially, the floc samples were drawn from the 800 ml mixing tank and transferred into the 1250 ml feeder tank of the modified Microtrac. The sampling times were 1, 5, 10, 15 and 20 minutes respectively. The floc size distributions obtained from the modified Microtrac were used to describe the mechanisms of floc formation, growth and breakage. An important derivative of the distribution - median floc size - was used to measure flocculating performance.

Results and Discussion

Three series of hydrophobic flocculation experiments were done to assess the effect of agitation time and intensity on floc size distribution. As an example, the evolution of floc size distributions as a function of agitation time for a 1 wt.% hematite suspension, flocculated at pH 8 with 50 mg/l sodium oleate and agitated at 1000 rpm in the 800 ml standard mixing tank is shown in Figure 1. It can be seen that unimodal size distributions are consistently observed in this flocculation. This type of distributions was readily noticed by Rattanakawin and Hogg (2001) who studied the flocculation of the dispersed alumina suspensions with inorganic salts and polymeric coagulant. The size distribution of the primary particles is shifted to larger floc sizes when the dispersed hematite suspension is coagulated by adjusting the suspension pH from 10.5 to 8. By adding 50 mg/l sodium oleate to the pre-coagulated suspension and agitating for 1 minute, the distribution progresses further to the larger size. However, prolonged agitation up to 20 minutes degrades the formed flocs, regressing the distribution to the smaller size. The development of floc size distributions with the agitation intensities of 500 and 1500 rpm follows the same distribution characteristics as that of the 1000 rpm condition.

The flocculation results can be summarized using median floc size as a performance criterion. Figure 2 is a plot of median floc size against agitation times with various agitation intensities. It can be first seen that the floc sizes increase rapidly at a very short time (1 minute) and then decrease with the prolonged times up to 20 minutes. Secondly, increasing the agitation intensity decreases the floc sizes. It appears that the floc sizes approach the equilibrium sizes resulting from the balance between growth and breakage of flocs under agitation environment. These results indicate that weak flocs are initially generated at high floc formation and growth rates. The rate of floc growth is dominated by floc breakage rate at longer agitation times and higher agitation intensity.

An understanding of the mechanism of hydrophobic flocculation of hematite with sodium oleate is especially important to explain the above results. Pascoe and Doherty (1997) proposed the mechanism involved in this flocculation as follows: (a) the oleate ion chemically adsorbs onto the hematite surface (Gong *et al.*, 1991); (b) oleic acid droplets form both on the mineral surface and in the bulk solution; (c) collision between oleate/oleic acid coated particles and other oleic acid droplets produces floc formation; and (d) floc growth and breakage occur until a dynamic equilibrium is reached. From this proposed mechanism, it can be implied that there are many physical and chemical variables affecting the performance of this flocculation process. The variables include suspension pH, oleate concentration, hematite concentration, agitation time and intensity.

The suspension pH affects both the aggregating states of hematite particles and oleate species distributed in the bulk solution. Obviously hematite particles are coagulated by approach to the point of zero charge at pH 8. Insoluble oleic acid concentration increases by two orders of magnitude when the pH is reduced from pH 10.5 to 8 (Pascoe and Doherty, 1997). The concentration of this species also increases with sodium oleate concen-

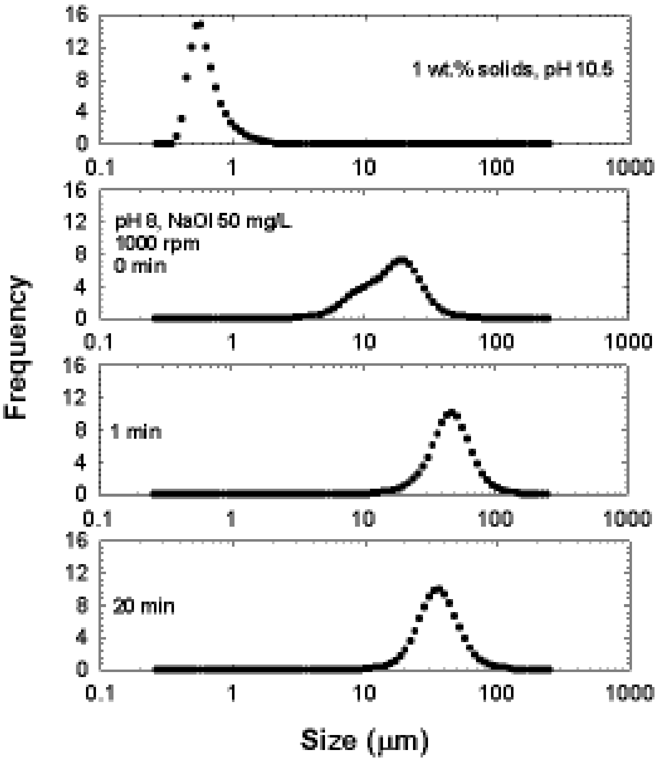

Figure 1 The evolution of floc size distributions as a function of agitation time for 1 wt.% hematite suspension, flocculated at pH 8 with 50 mg/l sodium oleate and agitated at 1000 rpm in the 800 ml standard mixing tank.

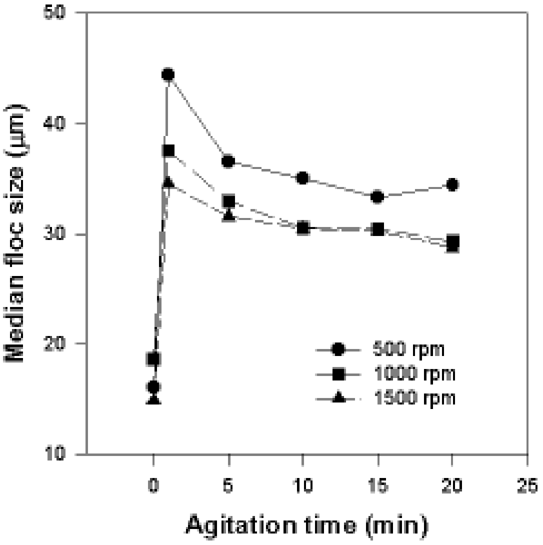

Figure 2 Median floc size as a function of agitation time for various agitation intensities in hydrophobic flocculation of 1 wt.% hematite suspension at pH 8 with 50 mg/l sodium oleate in the 800 ml standard mixing tank.

tration. Hematite content in the suspension may have an influence on sodium oleate dosage used in this type of flocculation. Agitation time and intensity mostly affect the floc growth and breakage process. Patil *et al.* (2001) found that the rate of flocculation of scheelite in sodium oleate solution decreases with increasing shear rate due to the breakage process.

From the above understanding, the results in Figure 2 may be readily discussed. The formation of hematite flocs is very fast because precoagulated hematite particles are formed at pH 8. Increasing the concentration of insoluble oleic acid (oil phase) by adjusting the pH from 10.5 to 8 enhances floc formation and growth due to the increased development of oil bridges. Koh *et al.* (1985) suggested that capillary condensation and liquid bridge bond the hydrophobic particles together in shear flocculation. Therefore the strength of the formed flocs depends upon the amount of the insoluble oleic acid generated. With a small amount of the oleic acid, only a few pendular bridges can form between the hematite particles. Funicular and capillary states of bridging occur with increasing amount of oleic acid. The floc strength should reach its peak near the capillary region. The lower resistance of hematite flocs to breakage over the range of agitation times and intensity studied is in contrast to the result of Pascoe and Doherty (1997). They found that the hematite flocs produced with sodium oleate resisted breakage under the same flocculation conditions studied here. However, the sodium oleate dosage used was six times higher compared to this study. Therefore the weak flocs formed with low dosage of this reagent were prone to break with the increasing agitation time and intensity. The strength of these weak flocs could be greatly enhanced by adding nonpolar oil to this flocculated hematite suspension as noticed by Song *et al.* (1999) who study the effect of nonpolar oil on hydrophobic flocculation of hematite and rhodochrosite fines. The enhancement of floc strength is attributed to an increase in oil bridges between the hematite flocs.

Conclusions and Recommendations

Synthetic hematite responds to hydrophobic flocculation in aqueous solutions of sodium oleate (NaOl). The floc size increases rapidly at the initial stage of this flocculation, and decreases with the extended agitation time and intensity. It can be concluded that weak hematite flocs were produced in this study. This inefficient production may be due to the low NaOl dosage used. These weak flocs are not expected to withstand the highly turbulent conditions found in the subsequence flotation process. Therefore, the optimum dosage of NaOl used in this hydrophobic flocculation should be further investigated. The dosage can be investigated in terms of both milligrams of NaOl per liter of suspension, and milligrams of NaOl per gram of hematite in the case of high hematite contents in the suspension. The use of nonpolar oil together with NaOl is also suggested for future studies.

Even though the hydrophobic flocculation of a single mineral system of hematite was successfully investigated, additional studies are needed to examine the multi-mineral systems normally found in the mineral industry. The median floc size obtained from the unimodal size distribution, is a useful parameter to measure the flocculating performance of this single-mineral system. However, multi-modal size distributions are expected to be found in the flocculation of multi-mineral systems (Sis, 2001). The complexity of the size distributions generated in multi-mineral systems may limit the use of floc size distribution and its derivatives as the direct performance criteria. However, combination of the size data with indirect criteria such as percent yield and grade of the flocculated mineral obtained from the subsequent flotation process could be used to evaluate the hydrophobic flocculating performance.

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