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Hydrophobic Flocculation of Galena Fines in Aqueous Suspensions

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The hydrophobic flocculation of galena fines induced by potassium amyl xanthate (PAX) in aqueous suspensions has been studied using laser diffraction, electrophoretic light scattering, contact angle, and microflotation measurements. The measurements were performed on <2 μm, 2–5 μm, 5–10 μm, and <30 μm size galena by varying several parameters, including PAX concentration, pH, original particle size, kerosene concentration, and suspension stirring. The experimental results have demonstrated that the hydrophobic flocculation was closely correlated with the particle hydrophobicity, but was not lowered upon increasing the particle surface charges due to PAX adsorption, which is contrary to the DLVO theory. This flocculation has been observed to increase with a reduction of the original particle size and an increase in kerosene concentration, and to require sufficient stirring strength and magnitudes of kinetic energy input to achieve the maximum aggregation degree. From the microflotation results, it has been found that the flotation response of galena fines is markedly improved due to the formation of hydrophobic flocs, suggesting that floc flotation is a promising means to recover galena in the fine size range. © 2000 Academic Press

Key Words: **hydrophobic flocculation; galena fines; contact angle; zeta potential; floc size; floc flotation; nonpolar oil enhancement.**

INTRODUCTION

The aggregative stability of colloidal or fine particle suspensions is due to the existence of an energy barrier to prevent the proximity of particles. According to the Derjaguin–Landau–Verway–Overbeek (DLVO) theory (1, 2), the barrier arises as a result of the electric double layer and van der Waals interactions. Hence, the states of fine particle suspensions change sensitively upon particle surface charges. However, this theory does not apply to hydrophobic particles in aqueous suspensions. For instance, a strong aggregation resulted in the aqueous suspension of naturally hydrophobic coal fines with −60 mV zeta potential (3). This phenomenon has been considered to result from the hydrophobic interaction between the particles, so it is called "hydrophobic flocculation." The hydrophobic force has been observed by direct force measurements to exist between hydrophobic surfaces in aqueous solutions (4–9). This force is found to be 1 or 2 orders of magnitude larger than the DLVO forces in short surface separation ranges. Accordingly, the hydrophobic interaction substantially reduces the energy barrier and increases the primary energy valley, leading to a powerful aggregation.

Hydrophobic flocculation is usually induced by surfactants upon their adsorption to impart hydrophobicity to the particles. For example, a colloidal silica suspension tended toward aggregation when a sufficient amount of tetradecylpyridinium bromide (a cationic surfactant) was present (10). In this instance, the aggregation occurred not only due to the hydrophobic attraction between the particles, but also due to the hydrocarbon chain association (or hydrophobic association) when the surfactant adsorption layers on particles contact each other (11–13). The hydrophobic association depends on the carbon number of adsorbed surfactant chains. For oleate ion adsorbed layers, it ranges from $1000kT$ to $10000kT$ (k is the Boltzmann constant; T is the absolute temperature) in the surface separation of the two molecule lengths according to potential energy computations (11, 13). Considering this effect, long-chain surfactants were suggested to be required for obtaining a good hydrophobic flocculation (14). As of yet, few reports in the literature have concerned the hydrophobic flocculation of fine particles induced by surfactants with less than 10 carbons.

During past two decades, numerous investigations have concerned the hydrophobic flocculation of minerals fines in aqueous suspensions, including scheelite (15), apatite (16, 17), rhodochrosite (11), and wolframite (18) fines induced by sodium oleate, hematite fines by sodium dodecyl sulfate and sodium oleate (12, 19–21), and quartz fines by dodecylamine (22), to name just a few. These investigations have shown that for mineral hydrophobic flocculation, particle hydrophobicity is the dominant factor, and a strong suspension stirring is required to provide the particles with sufficient kinetic energy to overcome the energy barrier. Through these studies, hydrophobic flocculation has found its application in the beneficiation of mineral fines. As is known, mineral flotation response substantially falls when the mineral particles are present in the fine size range because of the collapse of the probability of collision and adhesion of solid particles to air bubbles (23–25). By applying hydrophobic flocculation to mineral fines, the poor flotation response could be greatly improved by increasing the size of floated particles (26).

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For instance, fine scheelite fines had a much higher flotation rate in the form of hydrophobic flocs than as individual particles (27). This process has gotten the term floc flotation, including shear flocculation flotation, carrier flotation, and emulsion flotation. A detailed description of this can be found elsewhere (28, 29).

However, few researchers have dealt with the hydrophobic flocculation and the floc flotation of metallic sulfide minerals. In the present study, we attempt to characterize the hydrophobic flocculation behaviors of galena fines induced by potassium amyl xanthate (a short hydrocarbon chain surfactant). The objectives are to study the mechanism and to correlate the flocculation with various parameters, including potassium amyl xanthate concentration, pH, original particle size, suspension stirring, kerosene addition, contact angle, and zeta potential. In this work, degrees of aggregation were estimated through the size distributions and volumetric mean diameters of flocs that were obtained by laser diffraction measurements, and zeta potentials were obtained using electrophoretic light scattering measurements. Both techniques have been widely used in the research and development of macromolecules and colloids. Also, the floc flotation of galena fines induced by potassium amyl xanthate was investigated using a Hollimond flotation tube, in order to find the possibility of the hydrophobic flocculation applying to the beneficiation of galena fines.

EXPERIMENTAL

Materials

The galena sample used in this work was from the Naica mine, in Chihuahua, Mexico. The chunk galena was crushed by a hand hammer, and then was purified by hand sorting. Several pieces of galena were cut to obtain rectangles of 3 cm length and 1 cm width for contact angle measurements. The rest was finely ground using a vibrating cup mill, followed by size classification to obtain four size fractions (<2 μm, 2–5 μm, 5–10 μm, and <30 μm) using gravity sedimentation. The size distributions of the former three samples are illustrated in Fig. 1. The last one was measured to have a volumetric mean diameter (d_{50}) of 5.6 μm, and was used for floc flotation tests. The final galena samples were assayed to have a purity of 97.4–98.2%.

The potassium amyl xanthate (PAX) used in this work was from the Industria Quimica de Mexico, and was purified in our laboratory as follows. The xanthate powders were first dissolved in acetone, followed by filtration. Next, the filtrate was mixed with amyl ether, and then filtrated. The last filter cake was the purified PAX. The kerosene (50 mg/ml hexane) used in this study was from Fisher Scientific, and was used without further purification. The hydrochloric acid and sodium hydroxide from J. T. Baker with analyzed purity were used to adjust the pH.

The water used was distilled first, and then treated by passing over resin beds and a 0.2 μm filter. The residue conductivity of the water was less than 1 μS/cm.

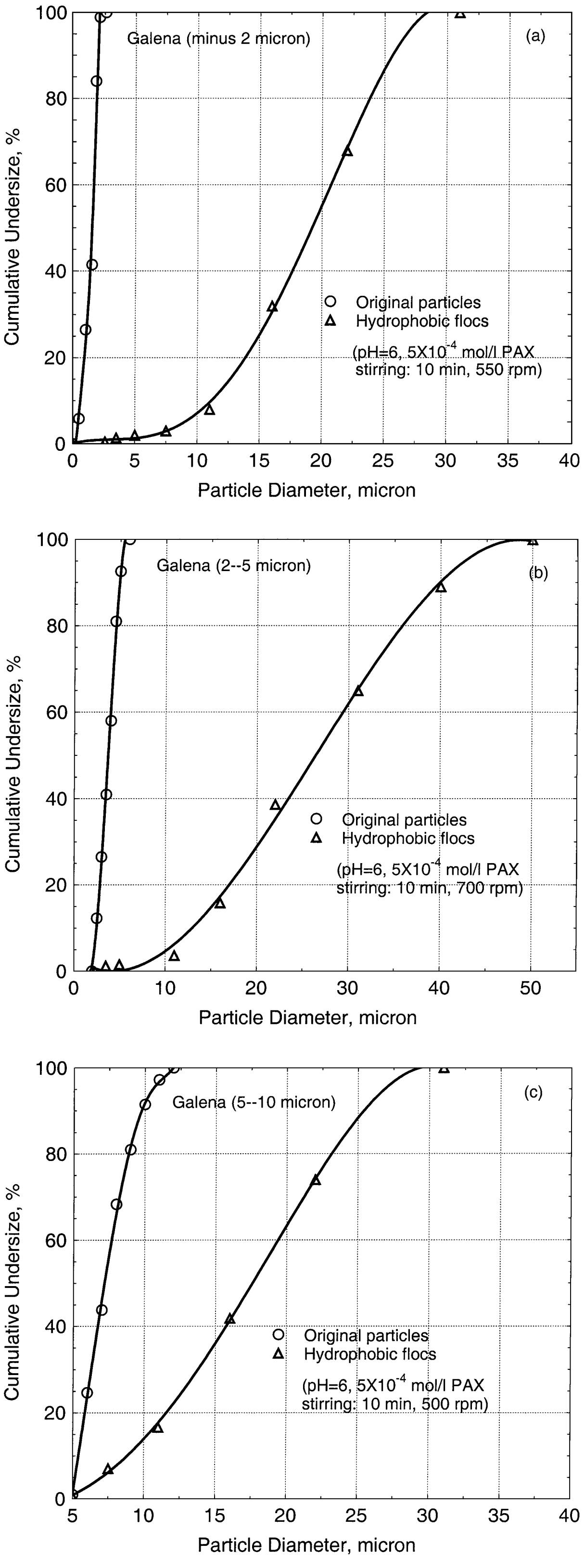

FIG. 1. Size distribution of fine galena particles before and after hydrophobic flocculation induced by potassium amyl xanthate. (a) <2 μm galena; (b) 2–5 μm galena; (c) 5–10 μm galena.

Hydrophobic Flocculation

The hydrophobic flocculation of galena fines in aqueous suspensions was performed in a mixing tank of 10 cm inner diameter and four 1 cm width baffles. The mixing head was connected with a Servodyne mixer controller, and the shaft was equipped with an S-shaped impeller of 6 cm width and 2 cm height. Galena fine suspensions with 1 g of galena and 100 ml of water were first adjusted for pH using hydrochloric acid or sodium hydroxide solution, and then were strongly conditioned at a given stirring speed for a given duration in the presence of PAX. Sometimes kerosene, a common nonpolar oil with a medium density and viscosity, was added together with the xanthate. After that, the suspension was transferred to the particle size analyzer for floc size measurements or to the Hollimond flotation tube for microflotation.

Determination of Floc Size

A Shimadzu SALD-1100 laser diffraction particle size analyzer with a semiconductor laser as the light source was used to determine the size distributions of original and flocculated galena particles in the present study. This instrument reports the optical diameter instead of the equivalent Stokes diameter. In order to protect flocs from breaking during the measurements, ultrasonic treatment was not applied to the suspensions.

Zeta Potential Measurement

The zeta potentials were obtained using a Coulter Delsa 440SX instrument, which performs a simultaneous four-angle electrophoretic light scattering measurement using a rectangular capillary cell. A detailed description of the instrument can be found elsewhere (30, 31). In this study, the measurements were performed using an electric field of 16–19 V/cm and a frequency range of 500 Hz with a duration of 100 s (2 s on and 1 s off sequence, alternating the electric field polarity) at both the upper and lower stationary planes. The temperature through the whole measurement was kept at $25.0 \pm 0.1^\circ$C.

Aggregation Degree

Besides floc size, the dispersion and aggregation of galena suspensions were also evaluated on the basis of the aggregation degree (E), which is represented as (32)

$$E = \frac{N_0 - N}{N}, \tag{1}$$

where N_0 and N are the particle number concentrations in suspensions before and after aggregation, respectively. The higher the aggregation degree, the more powerful the aggregation. In this study, the volumetric mean diameters of galena fines before and after aggregation were used to calculate aggregation degrees. Considering one floc, $N = 1$, and N_0 can be given by

$$N_0 = P_\mathrm{f}\frac{V_\mathrm{f}}{V_0}, \tag{2}$$

where P_f is floc porosity, and V_f and V_0 are the volumes of the floc and the original particle, respectively. In the event that both the original particle and floc are spheres, Eq. [1] can be written as

$$E = P_\mathrm{f}\frac{d_\mathrm{f}^3}{d_0^3} - 1, \tag{3}$$

where d_f and d_0 are the volumetric mean diameters of the floc and the original particle, respectively. Unlike loose polymer flocs, hydrophobic flocs have a more compact structure, resulting in a floc porosity of about 0.5 (33). In this paper, the floc porosity was supposed to be 0.5 for all cases.

Contact Angle Measurement

The contact angles were determined using a Rame-Hart NRL-100-00 contact angle goniometer. The galena surface, which was polished using fine sandpaper and cloth, was first immersed in a given concentration of PAX solution for 10 min, and then was transferred to the measurement cell. Next, a small air bubble was made on the surface immersed in water to obtain a solid/water/gas interface, followed by the determination of contact angle.

Microflotation

The microflotation of galena fines and flocs was performed in a Hollimond flotation tube with nitrogen as the bubble source. Flocculated or dispersed galena suspensions were first transferred to the tube, and diluted to a volume of 130 ml. Next, under a nitrogen gas flow rate of 29.2 ml/min, the flotation was carried out for 1 min. The floated and nonfloated products were filtered and then dried, respectively. The flotability was obtained by taking the total weight of the two products divided by the floated product weight.

Preparation of Kerosene Emulsion

In this work, kerosene was added into suspensions in the form of an emulsion. The kerosene emulsion was made by 10 min ultrasonic treatment of a kerosene–water mixture (1 g and 48.75 ml of water). The volumetric mean diameter of the oil droplets in the emulsion was measured to be 0.5 μm using the Coulter Delsa 440SX instrument.

RESULTS AND DISCUSSIONS

Hydrophobic Flocculation of Galena Fines

The size distributions of the <2 μm, 2–5 μm, and 5–10 μm galena before and after the hydrophobic flocculation induced by potassium amyl xanthate are shown in Fig. 1. For the measurements of the galena particles in dispersion, a sufficient amount of sodium hexametaphosphate was used to prevent coagulation. As can be seen, the three galena samples had the optical size ranges of <2.6 μm, 2–6 μm, and 5–13.8 μm, respectively, and had volumetric mean diameters of 1.5 μm, 3.9 μm, and 7.1 μm, respectively (it is noted that optical diameter is slightly different from Stokes equivalent diameter). It is clear that the hydrophobic flocculation greatly increased the apparent size of the galena fines. Panel A of Fig. 1 shows that over 95% of the flocs were in the size range of 10–30 μm, while the original particles were <2.6 μm. The 50% and 80% volumetric diameters (d_{50} and d_{80}) were 18.9 μm and 23.4 μm, respectively, in comparison to 1.5 μm and 2.0 μm for the original particles. The flocs were over 10-fold larger than the original particles. Panel B of Fig. 1 illustrates that the maximum floc diameter was 50 μm. Hydrophobic flocculation increased the size to $d_{50} = 26.2$ μm and $d_{80} = 35.8$ μm from $d_{50} = 3.9$ μm and $d_{80} = 4.8$ μm, respectively. Clearly, powerful hydrophobic flocculation happened to the <2 μm and 2–5 μm galena fines. However, the hydrophobic flocculation of 5–10 μm galena was much weaker, as shown in panel C of Fig. 1. The flocs ($d_{50} = 15.3$ μm and $d_{80} = 26.1$ μm) were only about 2-fold as large as the original particles ($d_{50} = 7.1$ μm and $d_{80} = 8.8$ μm), which were even smaller than those formed by the <2 μm galena.

Effect of Original Particle Size

From Fig. 1, it is clear that the hydrophobic flocculation of galena fines is closely correlated with the size of original particles. This effect was also investigated through the measurement of aggregation degree as a function of pH. The results are illustrated in Fig. 2. As already stated, the aggregation degree is related to the particle number in flocs. The larger the aggregation degree, the more particles in flocs. It can be seen from this graph that the most powerful hydrophobic flocculation occurred with the <2 μm galena. The finer the original particles, the more powerful the hydrophobic flocculation. At pH 6, the aggregation degree for the <2 μm galena was 1 and 3 orders of magnitude larger than those for the 2–5 μm and the 5–10 μm galena, respectively. A floc formed by <2 μm galena contained about 1200 original particles, in comparison to 6 original particles in one formed by 5–10 μm galena. It might be speculated that no hydrophobic flocculation happens to the coarser galena particles in aqueous suspensions.

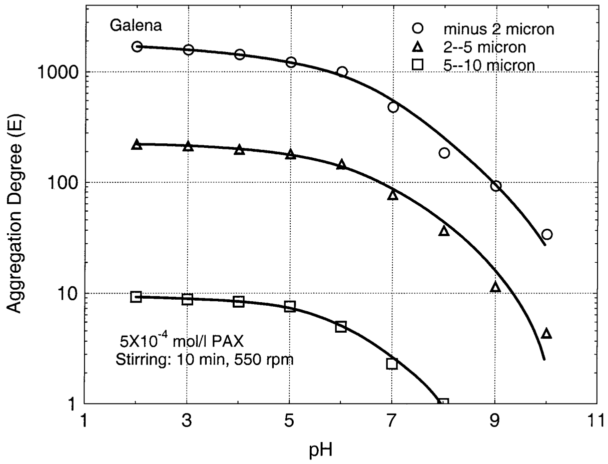

FIG. 2. Aggregation degree of the hydrophobic flocculation of the three galena samples (<2 μm, 2–5 μm, and 5–10 μm) induced by potassium amyl xanthate as a function of pH.

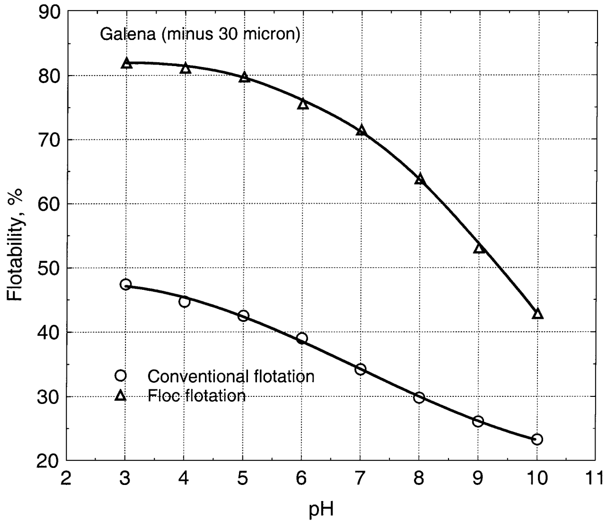

FIG. 3. Flotability of galena flocs induced by potassium amyl xanthate as a function of pH. The results from the conventional flotation are also presented. Test conditions: for conventional flotation, pH 8, 10^{-4} mol/l potassium amyl xanthate, and mild suspension stirring with a magnetic stirrer; for floc flotation, pH 8, 10^{-4} mol/l potassium amyl xanthate, suspension stirring with 700 rpm for 20 min in the mixing tank.

The foregoing results have demonstrated that original particle size is a notable factor for hydrophobic flocculation. Although there are a few reports on the hydrophobic flocculation of fine particles in a narrow size range (22, 34), there is little information on the effect of original particle. This effect might be related to many variables, namely flocculation kinetics, gravitational force, surfactant adsorption, surface charges, particles collision frequency, etc. The exploration of the mechanism of this effect should be an interesting theoretical subject, which will be our future research topic.

Effect of pH

Figure 2 also shows the effect of pH on the hydrophobic flocculation of galena fines induced by PAX. As is noted, the aggregation degrees increased with decreasing pH. This increase was much more marked under alkaline conditions than acidic conditions, and became very slight at pH less than 5. For the <2 μm galena, the aggregation degree at pH 2 was over 40-fold larger than that at pH 10. Also, the three aggregation degree vs pH curves have a similar shape, although there is a big difference in the values.

The flotability of galena flocs induced by PAX as a function of pH is shown in Fig. 3, in which the results from the conventional flotation of the same galena sample under the same reagent conditions are also given. For the conventional flotation, the suspensions before being transferred to the Hollimond tube were only mildly conditioned with a magnetic stirrer together

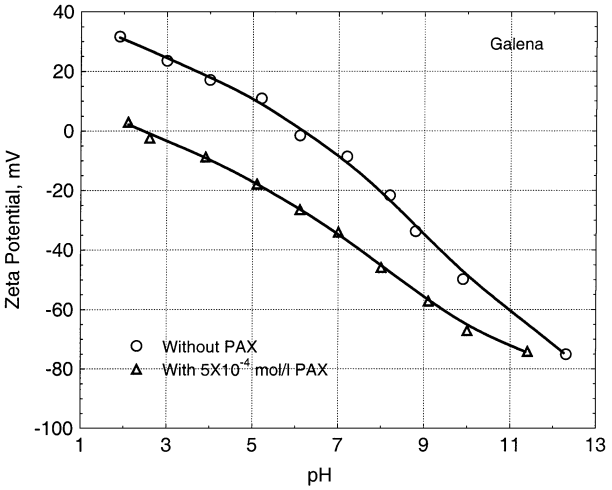

FIG. 4. Zeta potential of galena particles as a function of pH in the absence and in the presence of potassium amyl xanthate.

with PAX. As is noted, the flotation response of the galena fines was markedly improved due to the formation of hydrophobic flocs. The floc flotation increased the flotability over 30% in the range of pH 3 to 7 when 10^{-4} mol/l PAX was present, in comparison to the conventional flotation. These results indicate that floc flotation is a very effective means to recover galena fines. This graph also shows that the floc flotability increased sharply with decreasing pH, similar to the dependence of the hydrophobic flocculation on pH. Clearly, floc flotation closely correlates with the aggregation degrees of the corresponding hydrophobic flocculation or the size of the flocs.

The zeta potentials of galena fines were measured as a function of pH in the presence and in the absence of PAX. The results are illustrated in Fig. 4. It shows that the isoelectric point (IEP) of galena in aqueous solutions was at pH 6.1. In the presence of 5×10^{-4} mol/l PAX, the IEP shifted to pH 2.3, and the zeta potentials became more negative. As is known, the adsorption of PAX on galena is due to the chemical forces between the polar group of the xanthate and the lead on the surfaces (35). This adsorption (chemical adsorption) occurs in the Stern plane, resulting in a more negative zeta potential (36, 37). The adsorption density is proportional to the difference in the zeta potentials in the presence and in the absence of PAX (38). The greater the difference, the higher the adsorption density. Hence, from Fig. 4, it can be speculated that the adsorption density of PAX on the galena was almost a constant under acidic conditions, and decreased with increasing pH until reaching zero around pH 12 under alkaline conditions.

Potassium amyl xanthate ions adsorb on galena surfaces with their hydrocarbon chains orientated toward the bulk suspension, rendering the surfaces hydrophobic. The higher the adsorption density, the more hydrophobic are the surfaces rendered. Figure 5 shows the contact angles of galena surfaces as a function of pH in the presence and in the absence of PAX. Indeed, the presence of 10^{-4} mol/l PAX greatly increased the galena contact angles. This increase was about 35 degrees under acidic conditions, and decreased with increasing pH under alkaline conditions, which is in a good agreement with the PAX adsorption density on the galena mentioned above.

By superimposing Fig. 5 on Figs. 2 and 3, it can be seen that the hydrophobic flocculation of galena fines induced by PAX closely correlated with the contact angles of the galena surfaces, because the contact angle vs pH curve is similar in shape to the aggregation degree vs pH and floc flotability vs pH curves. The greater the galena contact angle, the more powerful the hydrophobic flocculation and the higher the floc flotability. These observations indicate that the galena hydrophobicity (which is usually represented by contact angle) is a dominant factor for the hydrophobic flocculation. From the point of view of surface forces, the particle hydrophobicity effect is due to the fact that elevating the contact angles of the surfaces increases the hydrophobic attractive force (39, 40), and thereby the hydrophobic flocculation.

The collapses of the hydrophobic flocculation and floc flotability of the galena fines under alkaline conditions (see Figs. 2 and 3) should be due not only to the decline of the contact angle (see Fig. 5), but also to the sharp increase of the surface charges (see Fig. 4). According to the DLVO theory (2), the electrical double-layer repulsion is proportional to the square of the surface charge, so that the repulsion between PAX-adsorbed galena fines substantially increases with increasing pH, resulting in a much higher energy barrier. Hence, although the contact angle did not strongly decrease, the hydrophobic flocculation under alkaline conditions fell substantially.

Effect of Potassium Amyl Xanthate Concentration

The volumetric mean diameter of the galena flocs as a function of PAX concentration at pH 8 is shown in Fig. 6. As can be noted, for the two galena samples, the floc size increased with

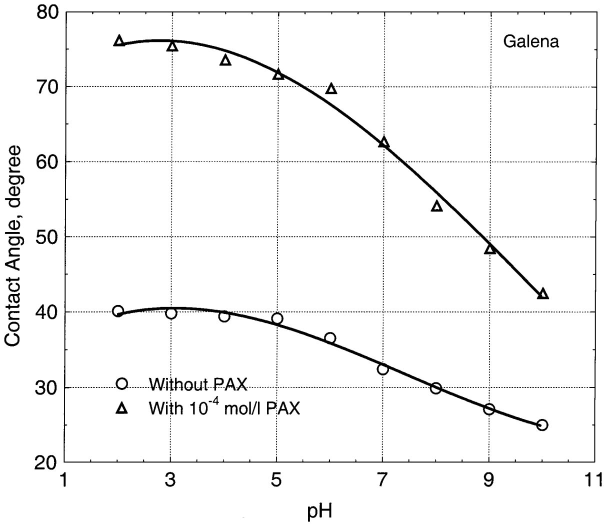

FIG. 5. Contact angle of galena as a function of pH in the absence and in the presence of potassium amyl xanthate.

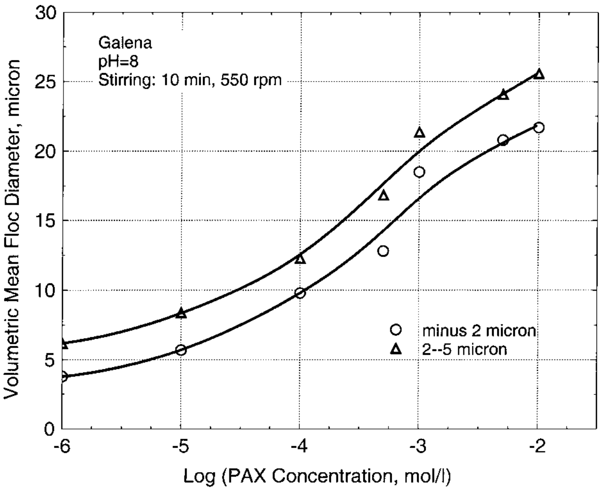

FIG. 6. Volumetric mean diameter of galena flocs as a function of potassium amyl xanthate concentration at pH 8.

increasing PAX concentration. This increase appeared to be mild in the low-concentration range, and to be strong in the high-concentration range.

Figure 7 illustrates the flotability of the galena as a function of PAX concentration at pH 8. It shows that the floc flotability sharply increased with increasing PAX concentration until reaching complete flotation at 2×10^{-3} mol/l, and then flattened out. This result coincided with that obtained from galena conventional flotation as reported by Fuerstenau (41).

The zeta potentials and contact angles of galena particles were also measured as functions of PAX concentration at pH 8. The results are shown in Fig. 8. As can be seen, the galena contact angles substantially increased and the zeta potentials dramatically went down to a large negative value with increasing PAX concentration. As already stated, these observations are attributed to the adsorption of PAX on galena surfaces. The adsorption density increased with increasing PAX concentration, raising the increases of the contact angle and the zeta potential in absolute value.

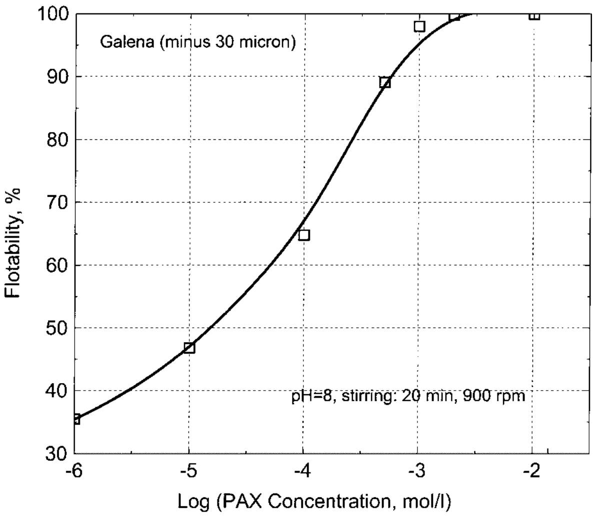

FIG. 7. Flotability of galena flocs as a function of potassium amyl xanthate concentration at pH 8.

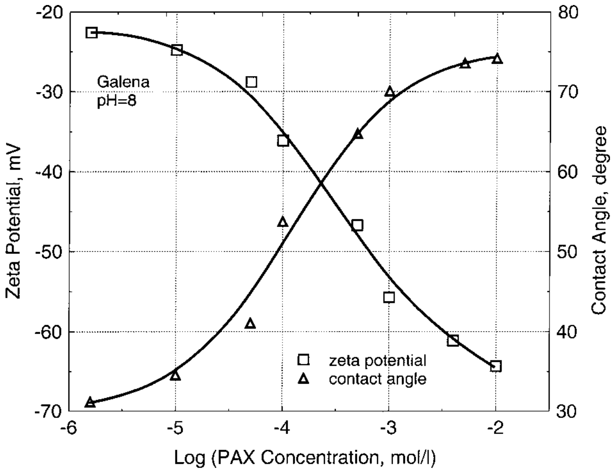

FIG. 8. Zeta potential and contact angle of galena particles as a function of potassium amyl xanthate concentration at pH 8.

From the results presented in the three graphs, it is clear that the hydrophobic flocculation and the floc flotation of the galena fines had responses to the change of PAX concentration quite similar to that of the galena contact angle, suggesting a close correlation between the hydrophobic flocculation and the particle hydrophobicity. However, no correlation between the flocculation and the zeta potential is found. As already stated, the electric double-layer interaction between particles resulting from particle surface charges prevents fine particles from aggregating. The greater the surface charge, the higher the energy barrier. In the case of PAX adsorption on galena, the hydrophobic flocculation of the galena fines was not depressed, but was enhanced upon increasing the surface charges, which is contrary to the DLVO theory. This observation may be due to the fact that the PAX adsorption on galena increased the hydrophobic attraction much more strongly than the electric double-layer repulsion.

Effect of Suspension Stirring

The kinetic energy input for the hydrophobic flocculation of galena fines was provided mechanically in a stirred tank in this work. As is known, the stirring strength in a mixing system is mainly determined by stirring revolutions if the impeller, tank, slurry volume, and solid concentration are constants (15), and the magnitude of kinetic energy input is determined by stirring duration if stirring strength is constant. In this study, therefore, the stirring speed and stirring duration influencing the hydrophobic flocculation were investigated.

The volumetric mean diameters of galena flocs induced by 5×10^{-4} mol/l PAX as a function of stirring speed at pH 6 is shown in Fig. 9. As can be noted, for the two galena samples, the volumetric mean floc diameter increased with increasing stirring speed until it reached a maximum, and then declined, indicating that a sufficient stirring strength is required to achieve the

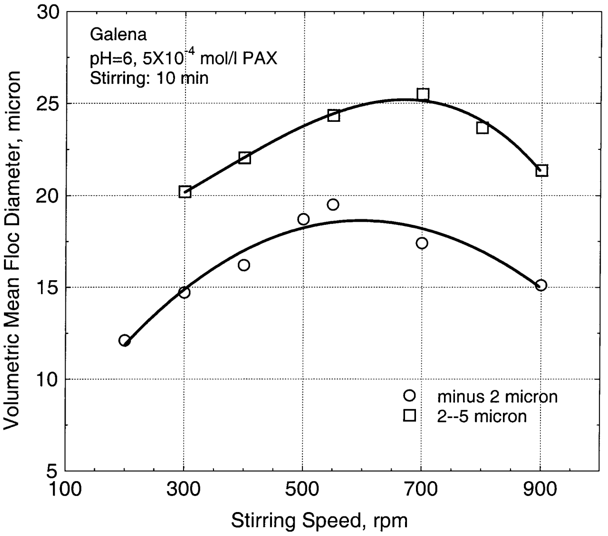

FIG. 9. Volumetric mean diameter of galena flocs induced by potassium amyl xanthate as a function of the stirring speed at pH 6.

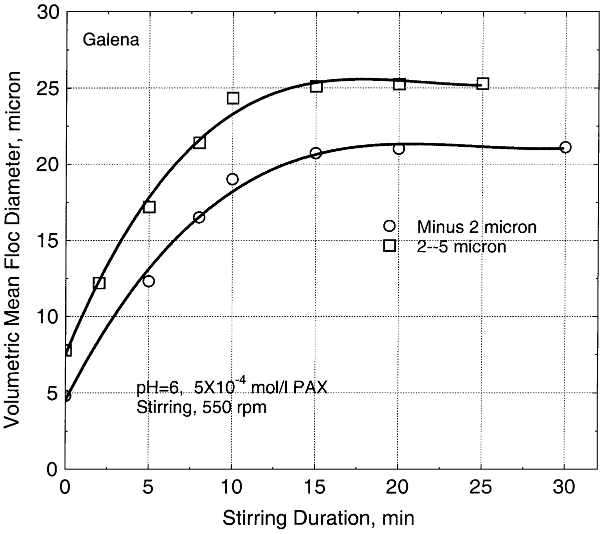

FIG. 10. Volumetric mean diameter of galena flocs induced by potassium amyl xanthate as a function of the stirring duration at pH 6.

maximum aggregation degree of the hydrophobic flocculation. The critical stirring speed at which the peak appeared is around 550 rpm for <2 μm galena and 700 rpm for 2–5 μm galena. Clearly, the galena flocs could sustain great floc-rupture forces and keep growing under high stirring strengths. The decline of the flocculation after the critical speeds indicates that the flocs were ruptured into small pieces due to the strong shear and strain forces resulting from high-speed suspension stirring (22). On one hand, hydrophobic flocculation requires a high stirring strength to provide the particles enough kinetic energy to overcome the energy barrier. On the other hand, too high stirring strength causes flocs to rupture. Thus, the optimum stirring strength has to be applied to fine particle suspensions to obtain the maximum degree of hydrophobic flocculation. In an hydrophobic flocculation process the trends of flocs growing and flocs rupturing occur simultaneously. If floc strength is greater than floc rupture force, floc size increases; if the reverse, flocs break up into small pieces. The floc strength correlates with the interactions between particles (hydrophobic attraction, hydrophobic association, electric double-layer repulsion, van der Waals interaction, etc.), and is a constant for a given system. The floc rupture forces increase with increasing stirring strength. In the case shown in Fig. 9, before the critical stirring speed the floc rupture forces were smaller than the floc strength, and thus the hydrophobic flocculation was stimulated by increasing the stirring speed. After the critical speed, however, the floc rupture forces had the advantage over the floc strength, resulting in flocs rupturing.

Figure 10 illustrates the volumetric mean diameters of galena flocs induced by 5×10^{-4} mol/l PAX as a function of stirring duration at pH 6. It shows that for the two galena samples, the volumetric mean floc diameter sharply increased with increasing stirring duration until reaching a plateau. The critical stirring duration at which the volumetric mean floc diameter started to be a constant is about 15 min for <2 μm galena and 10 min for 2–5 μm galena. This result suggests that a sufficient magnitude of kinetic energy input is required to achieve the maximum degree of hydrophobic flocculation. In this system, the stirring strength was fixed, so that increasing the stirring duration did not increase the floc rupture forces, and thus the aggregation degree was unchanged after reaching a maximum. Such a phenomenon was also observed in the hydrophobic flocculation of scheelite (15) and hematite fines (12) in aqueous suspensions.

The effect of the suspension stirring on the floc flotation of the galena fines was also investigated through microflotation. Figures 11 and 12 show the flotability of galena flocs induced by PAX as a function of the stirring speed and stirring duration

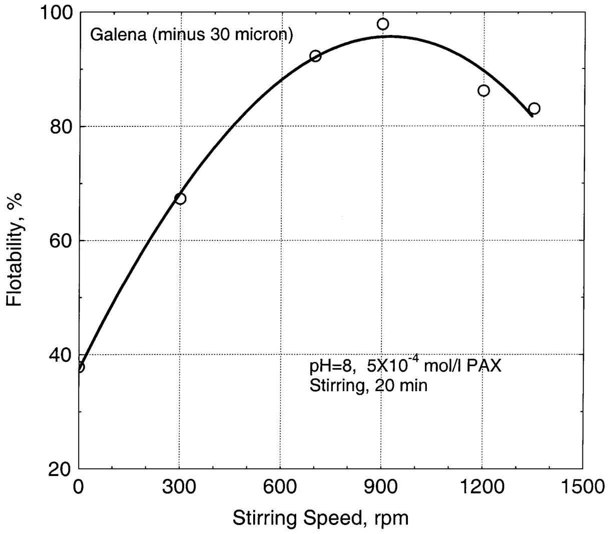

FIG. 11. Flotability of galena flocs induced by potassium amyl xanthate as a function of the stirring speed at pH 8.

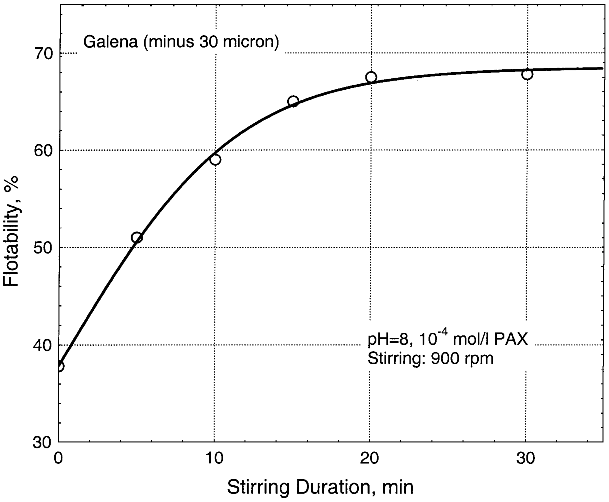

FIG. 12. Flotability of galena flocs induced by potassium amyl xanthate as a function of the stirring duration at pH 8.

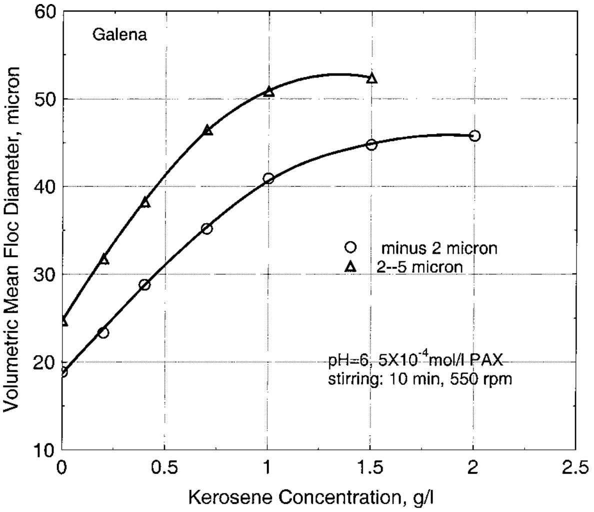

FIG. 13. Volumetric mean diameter of galena flocs induced by potassium amyl xanthate as a function of kerosene concentration at pH 6.

at pH 8, respectively. From Fig. 11, a peak with 89% flotability can be observed around a stirring speed of 900 rpm. After that speed, the floc flotability declined. Figure 12 shows that the floc flotability strongly increased with increasing stirring duration until reaching a maximum around 20 min and then flattened out. The floc flotation could not be improved by further prolonging the stirring duration. It seems obvious that the stirring speed and duration influenced the floc flotation in a manner quite similar to their influence on the volumetric mean diameters of galena flocs, as given in Figs. 9 and 10.

In the system shown in Fig. 7, the improvement of the floc flotability is due to both floc size and floc hydrophobicity increasing. However, in the systems shown in Figs. 11 and 12, the stirring speed and duration influence the floc flotation only through influencing the floc size. Thus, the results given in Figs. 9–12 could provide information on the relationship between floc size and floc flotability. From these results, it is clear that the floc flotation of galena fines closely depends on the size of the flocs. The bigger the flocs, the higher the floc flotability. According to the theoretical studies on flotation kinetics, the flotation rate constant (k) depending on particle size can be expressed by (42, 43)

$$k \propto d_{\mathrm{p}}^{n}, \qquad [4]$$

where d_{p} is the particle diameter and n is the empirical constant, $1.5 < n < 2$. This means that the flotation rate is proportional to the particle size. Clearly, the same principle also applies to the floc flotation of galena fines. Hydrophobic flocs might interact with air bubbles differently from individual particles, leading to a different value of n for floc flotation. Although numerous investigations have considered the effect of particle size on flotation rate, there is little information about the relationship between floc flotation rate and floc size. This study may give results about many variables such as floc structure and shape, which will be an interesting research subject.

Effect of Nonpolar Oil Addition

The volumetric mean diameters of galena flocs induced by PAX as a function of kerosene concentration are shown in Fig. 13. As can be noted, the floc size increased with increasing kerosene concentration. This increase was very strong at low kerosene concentrations, and became mild at high kerosene concentrations. With 1 g/l kerosene, the volumetric mean floc diameters increased from 18.9 μm to 40.9 μm for the <2 μm galena and from 24.8 μm to 50.9 μm for the 2–5 μm galena. It is clear that the hydrophobic flocculation of galena fines is substantially enhanced by kerosene addition.

The flotability of the galena flocs as a function of kerosene concentration is illustrated in Fig. 14. It can be seen that the

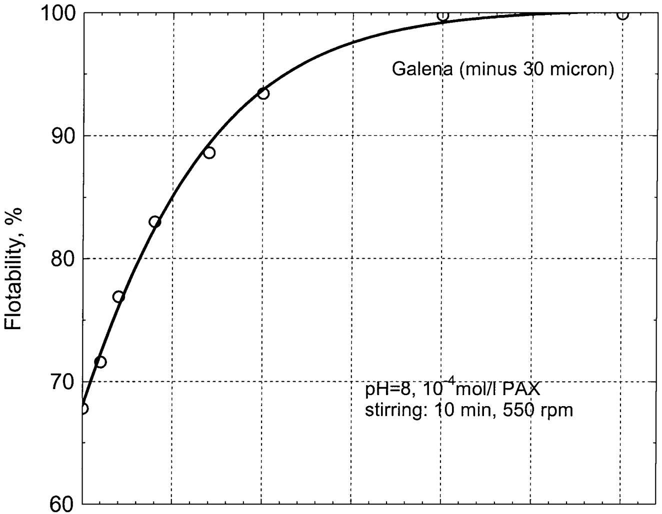

FIG. 14. Flotability of galena flocs induced by potassium amyl xanthate as a function of kerosene concentration at pH 8.

floc flotability strongly increased with increasing kerosene concentration until reaching complete flotation at 200 mg/l, and then flattened out. The floc flotability without kerosene was 67%. Clearly, the floc flotation was markedly improved due to kerosene addition. Also, it shows that kerosene replaced a large amount of PAX addition, because to obtain complete flotation of the galena fines, 2×10^{-3} mol/l PAX was needed when it was used alone (see Fig. 7), while only 10^{-4} mol/l PAX was needed when 200 mg/l kerosene was added. The difference in the PAX addition is 319.2 mg/l. It is clear that using kerosene to enhance the floc flotation gives a large savings in operating cost because kerosene is much cheaper than PAX. From the point of view of flotation principle, the kerosene improvement of the floc flotation is attributed not only to the increase of floc size, but also to the increase of floc hydrophobicity and floc–air bubble adhesion.

Nonpolar oil enhancement of hydrophobic flocculation is due to the formation of oil films on the hydrophobic particles to increase the particle hydrophobicity and the bridging of the particles (44–46). In the case of surfactant-induced hydrophobic flocculation, the oil films extend the surfactant adsorption layer on the particle surfaces, leading the interaction between the particles to actually occur between the oil surfaces, instead of the surfactant adsorption layers. Thus, the hydrophobic association between surfactant-adsorbed particles is hidden by the aggregation of oil films on interacting particles. This effect would be especially important for the hydrophobic flocculation of fine particles induced by short hydrocarbon chain surfactants, such as the hydrophobic flocculation of galena fines induced by potassium amyl xanthate. As already stated, short hydrocarbon chain surfactants induce a weaker hydrophobic association, and thereby a weaker hydrophobic flocculation, in comparison to long hydrocarbon chain surfactants. With nonpolar oil involved in the hydrophobic flocculation, this disadvantage could be avoided, because the thickness of oil films on particles is always much greater than surfactant molecule length, leading the interaction between the particles to be independent of the hydrocarbon chain length of adsorbing surfactants. Accordingly, it can be expected that the nonpolar oil enhancement of hydrophobic flocculation may be much stronger for that induced by short hydrocarbon chain surfactants than for that induced by long hydrocarbon chain surfactants.

CONCLUSIONS

(1) In the present study, we have demonstrated that the hydrophobic flocculation of galena fines in aqueous suspensions could be induced by potassium amyl xanthate (a short hydrocarbon chain surfactant) upon its adsorption to impart hydrophobicity to the particles and sufficient kinetic energy input, and could be greatly enhanced by addition of a small amount of kerosene. This hydrophobic flocculation has been found to closely correlate with the hydrophobicity (or contact angle) of galena particles. The more hydrophobic the galena particles, the more powerful the hydrophobic flocculation. However, it is not lowered by increasing the surface charges due to potassium amyl xanthate adsorption, which is contrary to the DLVO theory.

(2) The flotation response of galena fines is markedly improved due to the formation of hydrophobic flocs. The floc flotation strongly correlates with the size of the flocs, and is enhanced by addition of a small amount of kerosene that allows large savings in operating costs. This enhancement might be more marked for the hydrophobic flocculation induced by a short hydrocarbon chain surfactant than a long hydrocarbon chain surfactant.

(3) This hydrophobic flocculation is strongly influenced by the size of the original galena particles. The finer the original galena, the more powerful the hydrophobic flocculation.

(4) Sufficient stirring strength and magnitude of kinetic energy input are required to achieve the maximum degree of the hydrophobic flocculation. Prolonging the stirring duration does not increase the stirring strength, leading to a constant aggregation degree after a critical stirring duration.

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