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Shear hydrophobic flocculation and flotation of ultrafine Anshan hematite using sodium oleate

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Abstract: Effects of stirring speed and time, pH and sodium oleate concentration on the shear hydrophobic flocculation of ultrafine Anshan hematite with sodium oleate as the surfactant were discussed. The results show that these parameters significantly affect the shear hydrophobic flocculation of ultrafine hematite. The optimum conditions for the flocculation are: stirring speed 1 400 r/min, flocculation time 20 min, pH 9 and sodium oleate concentration 3.94×10^{-4} mol/L; the flotation recovery of hematite flocs is remarkably high compared with non flocculated ultrafine hematite. According to the extended DLVO theory, the total interaction potential of Anshan ultrafine hematite was determined. The calculation results indicate that the hydrophobic flocculation state of the ultrafine hematite-sodium oleate system is mainly dominated by electric double layer repulsive interaction potential and hydrophobic interaction potential. A mechanical agitation is required to impart particles a kinetic energy to overcome potential barrier between them due to the existence of electric double layer repulsive interaction potential. Those particles further approach to form flocs due to the significant increase of the hydrophobic interaction potential.

Key words: sodium oleate; ultrafine hematite; shear hydrophobic flocculation; extended DLVO theory

1 Introduction

The separation efficiencies of ultrafine minerals by flotation are very low due to their small mass, huge specific surface area and low collision efficiency between the particles and bubbles during flotation. The enhancement of their apparent sizes by aggregation or flocculation is an effective way to increase their flotation efficiency.

For understanding the flocculation or dispersion of ultrafine mineral suspensions in flotation, the existence of remarkable deviations between the experimental results and the theoretical explanations by the DLVO theory has been found in which the potential energies of particle-particle interaction only comprise of van der Waals attractive energy and electric double layer energy. The extended DLVO theory with a hydrophobic interaction energy U_{HI} is considered to be more suitable for understanding the hydrophobic flocculation in flotation. According to the extended DLVO theory, the essential condition for the aggregation of particles is that the hydrophobic interaction energy U_{HI} surpasses the electric double layer energy U_{R}. Meanwhile, the kinetic energy of particles imparted by stirring suspension is an important factor to overcome the energy barrier of surface when particles approach for aggregation. That is, the hydrophobic flocculation of particles is determined by the conditions of particle surface chemistry and hydrodynamic interactions.

In recent two decades, the mechanisms of the hydrophobic flocculation of ultrafine minerals have been investigated with various kinds of minerals involving numerous parameters including original particle size and concentration, pH, surfactant type, hydrocarbon chain length and concentration, agitation strength and flocculation time, dispersant type and concentration, structure of tank and type of impeller, etc.

The investigation methods of shear hydrophobic flocculation can be divided into surface chemistry and hydrodynamic approaches. The surface chemistry method is based on the extended DLVO theory and effects of above parameters on hydrophobic flocculation are studied by Zeta potential, contact angle and other measurements of particle surface. The shear flocculation characteristics of celestite（$SrSO_4$）mineral using sodium dodecyl sulfate (SDS), Aero 845, sodium oleate and tallow amine acetate (TAA) as the surfactants was

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investigated by OZKAN et al[1−2]. The effective variables involved suspension pH, surfactant concentration, stirring speed and time. Meanwhile, the effects of sodium silicate, sodium phosphate and sodium polyphosphate used as inorganic dispersants on the shear flocculation extent of celestite were also studied. For the shear flocculation experiments at pH=11 by preaddition of calcium or magnesium ions into the suspensions at the concentrations above 0.05 mmol/L, the shear flocculation of celestite was promoted. AKDEMIR and HICYILMAS[3] examined the effects of pH, sodium oleate concentration, stirrer speed and flocculation time on the chromite fines aggregation by stirring after the particle surfaces were made hydrophobic using sodium oleate. AKDEMIR[4] presented a study on the shear flocculation of fine hematite (38 μm) using dodecylamine acetate and Aero 801 (a mixture of petroleum sulfonate and mineral oil) as the collectors. The effects of pH, collector concentration and stirring speed were investigated. PASCOE and DOHERTY[5] investigated the separation of ultrafine hematite (<10 mm) from quartz with sodium oleate as the selective flocculant. The main factors affecting hematite floc size were found to be oleate concentration, pH, shear rate and agitation time. SONG et al[6] studied the floc flotation of galena and sphalerite fines (<20 μm) and analyzed the effects of pH, potassium amyl xanthate concentration, addition of kerosene and agitation strength on the floc flotation. SONG et al[7−8] also investigated the hydrophobic flocculation of sphalerite fines in aqueous suspensions induced by ethyl and amyl xanthates using laser diffraction, electrophoretic light scattering and contact angle measurements. The investigation included studying the effects of hydrocarbon chain length of xanthate ions, xanthate concentration, pH, original particle size and stirring strength, and approaching the mechanisms of the hydrophobic flocculation. QIU et al[9] studied the adsorption of sodium oleate on the surface of cassiterite and quartz and the conditions of the interaction and aggregation between cassiterite particles, quartz particles and cassiterite-quartz particles in the presence of sodium oleate were determined according to the extended DLVO theory.

Most of the studies are related to the surface chemistry of the process. The another way to investigate the hydrophobic flocculation of ultrafine minerals is the dynamic method. That is, the effects of the hydrodynamic parameters of suspensions on the hydrophobic flocculation during stirring are investigated. The aggregation and flotation of hematite and wolframite were investigated by HU et al[10] through particle size analysis, flotation tests and measurement of energy input based on hydrodynamic interactions. The studies on the effects of particle size, agitating speed and time, and structure of agitation tank on aggregation and flotation showed the importance of hydrodynamic interactions in aggregation and flotation. The kinetics of particle aggregation, including coagulation and hydrophobic flocculation, in turbulent flow, was studied by LU et al[11]. It was discovered by both theoretical analysis and experimental result that the macroscopic kinetic model of particle aggregation is closely correlated with the microscopic particle-particle interaction. PATIL et al[12] used a lumped population balance model (PBM) to understand the effects of different parameters on the kinetics of floc coalescence and breakage processes in shear flocculation. The results showed that the flocculation rate decreases with the increase in shear rate and the breakage rate is approximately proportional to the 0.7 power of the volume of the floc. High concentrations of sodium oleate reduce the floc strength and the presence of modifiers like sodium carbonate and sodium silicate decreases the flocculation rate. The studies by GRANO[13] showed that the physical conditions for effective flotation of fine (<9 μm) and coarse (>53 μm) particles differ substantially, suggesting that a specific hydrodynamic environment will favor a high flotation rate for fine galena, which may be detrimental to the recovery of coarse galena, and vice versa. A fundamental flotation model was applied to quantifying differences in the flotation rate of the various size particles with impeller rotational speed. Furthermore, the effects of gravity and slurry rheology on the aggregative stability and coagulation were studied[14−18].

For the most hematite concentrators in Anshan area of China, the low recovery of ultrafine hematite particles in the concentrates by the present flowsheets has caused the high iron grade of tailings (16%−20%) and a large amount of iron is lost to the tailings in the form of liberated or associated ultrafine hematite particles. The investigations of the shear hydrophobic flocculation of ultrafine Anshan hematite carried out are limited. In the present study, the effects of sodium oleate concentration, stirring speed and time and pH on the floc size and flotation were discussed based on the experiments by Zeta potential measurements and flocculation image analysis. According to the extended DLVO theory, the total interaction potential between particles of the hematite-sodium oleate system was determined, including electric double layer repulsive potential, van der Waals attractive potential, hydrophobic interaction potential and hydrocarbon chain association potential.

2 Materials and methods

2.1 Preparation of sample

The mine ore taken from Qidashan mine, Anshan area, was crushed to the size less than 2 mm and then ground to the size less than 0.15 mm. The sample was further enriched using a shaking table and then the concentrate was finely ground. The finely ground sample has the size of d_{50}=4.15 μm and the specific area of 25 998 cm^2/cm^3.

The size distribution and the elemental analysis results of the sample are shown in Fig.1 and Table 1, respectively.

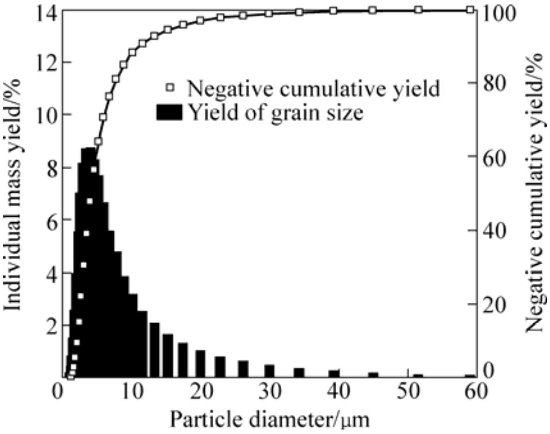

Fig.1 Size distribution of sample for flocculation and flotation experiments

Table 1 Elemental analysis results of experimental sample (mass fraction, %)

TFe	FeO	SiO_2	Al_2O_3	MgO	CaO	P
68.07	0.25	2.19	0.15	0.08	0.07	<0.005

2.2 Flocculation experiments

The flocculation experiments were carried out in a 200 mL-beaker using 6.00 g solid sample and 100 mL distilled water. Dilute NaOH or H_2SO_4 was used to adjust pH. A variable-speed stirrer with a maximum speed of 4 000 r/min was used.

First, the solid and distilled water were mixed in the beaker by stirring at low speed for 3 min. Then, the pH of suspension was adjusted by adding dilute NaOH or H_2SO_4, and sodium oleate was added. The adsorption of surfactant on the particle surface was promoted by stirring for 2 min at low speed. The hydrophobic flocs were formed by stirring and recorded by a digital camera.

The flotation experiments were carried out at a hanging cell flotation machine using 6.00 g hematite sample and 100 mL distilled water. Dilute NaOH or H_2SO_4 was used to adjust pH. Flotation time was 5 min.

2.3 Mean flocs size calculation

The flocs feature was observed and the diameters of all counted flocs were measured with a biological microscope. The mean size was calculated statistically by following equation: $d=\dfrac{\sum(d_1+\cdots+d_i+\cdots+d_n)}{n}$.

2.4 Zeta potential measurements

Zeta potentials of hematite particles were determined with an electrophoretic apparatus. 100 mg hematite sample and 50 mL distilled water were added in a beaker. Dilute NaOH or H_2SO_4 was used to adjust pH and the suspensions were agitated for 5 min. A small amount of suspensions were taken for the measurements of Zeta potentials at the electrophoretic apparatus.

The curve of the Zeta potentials of hematite versus pH is shown in Fig.2.

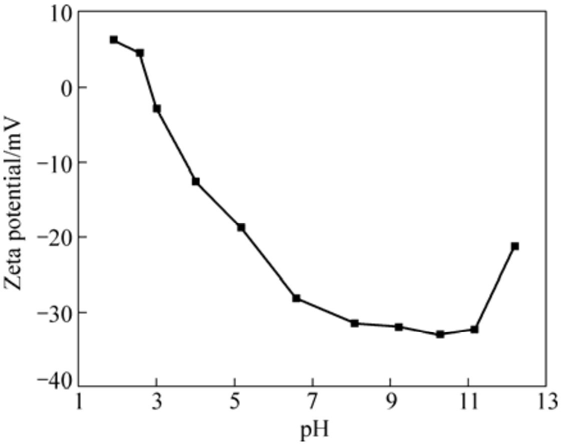

Fig.2 Zeta potentials of hematite vs pH

3 Results and discussion

3.1 Effects of stirring speed and time

The flocculation features at different stirring speeds under the flocculation condition of stirring time 20 min, pH 9 and sodium oleate concentration 0.394 mmol/L are shown in Fig.3.

The effects of stirring speeds on the mean size and the flotation recovery of hematite flocs are shown in Figs.4 and 5, respectively.

From Fig.3, it is found that the suspension has light brown color at the stirring speeds of 600 and 800 r/min, meaning that there are a lot of non flocculated ultrafine hematite particles in the suspension. When the stirring speed increases to 1 000 r/min, flocs appear in the suspension; the number and the size of flocs significantly increase when the stirring speed reaches 1 400 r/min. Fig.4 shows that the mean size of flocs increases with the increase of stirring speed. However, the mean size obviously decreases and the number of flocs may still increases when the stirring speed exceeds 1 400 r/min. The ruptures of the large flocs occur at high stirring speeds over 1 400 r/min.

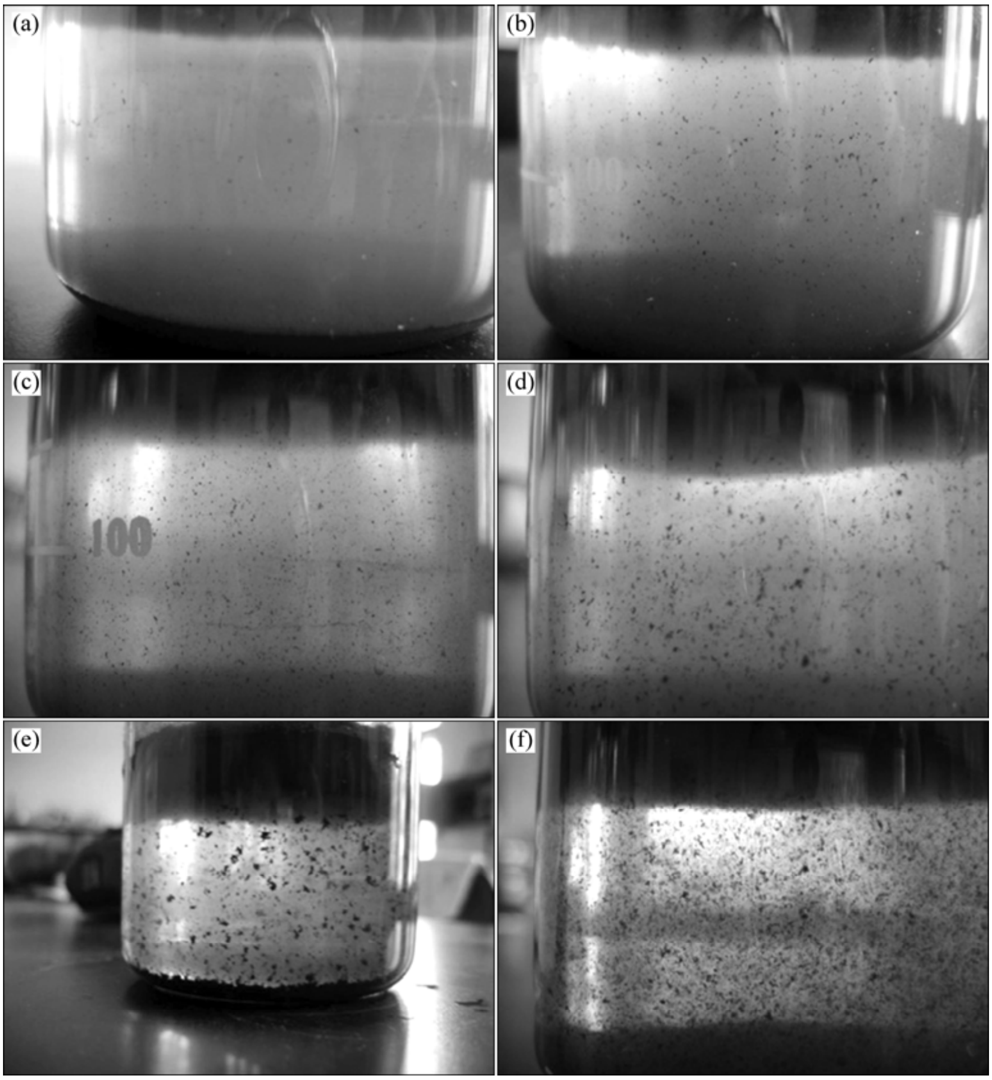

Fig.3 Flocculation features at different stirring speeds (flocculation time 20 min, pH 9 and sodium oleate concentration 0.394 mmol/L): (a) 600 r/min; (b) 800 r/min; (c) 1 000 r/min; (d) 1 200 r/min; (e) 1 400 r/min; (f) 1 600 r/min

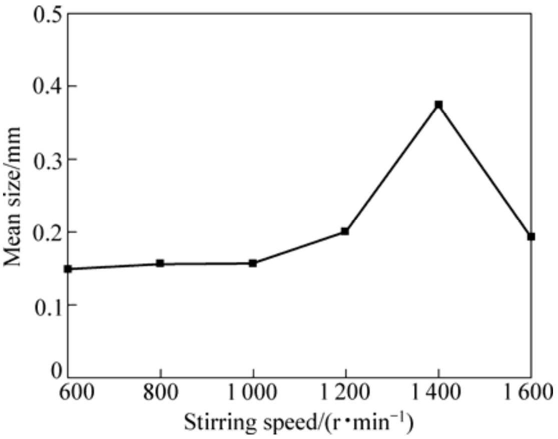

Fig.4 Stirring speed vs mean size of flocs

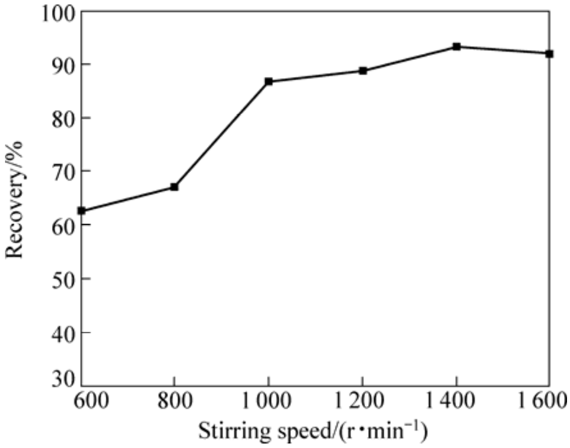

Fig.5 Stirring speed vs flotation recovery of flocs

The similar conclusions were obtained by other researchers. The studies of WARREN[19] and OZKAN[1] showed that flocs growing and flocs rupturing take place simultaneously in the shear flocculation process and therefore, floc strength must be greater than floc rupture force for increase of floc size. The higher stirring strength than optimum value causes flocs to rupture, and therefore, flocs break up into small pieces. The results by MANNING and DYER[20] indicated that increasing turbidity (showing the extent of flocculation) at low shear levels encouraged floc growth, but the effect of increasing turbulent shear (0.35 N/m^2) together with increasing concentration in suspension causes disruption rather than enhancing the flocculation process. At shear rate up to 0.35 N/m^2, the largest size and settling velocity of flocs were produced at high concentrations, whereas disruption rate above 0.35 N/m^2 caused smaller flocs at higher concentrations.

The flocculation features and the mean sizes of flocs at different stirring time under the flocculation conditions of stirring speed 1 400 r/min, pH 9 and sodium oleate concentration 0.394 mmol/L are shown in Figs.6 and 7. It can be found from Fig.6 that flocculation takes place when the stirring time is 10 min or above. The flocculation becomes more and more obvious as the stirring time increases until the time exceeds 25 min at which the flocculation weakens obviously. Fig.7 shows that the flocs size significantly increases with increasing the stirring time from 5 min to 10 min and reaches the maximum at the time of 20 min, and then decreases when the time exceeds 20 min. This phenomenon indicates that the processes of flocs growing (from 5 to 10 min) and flocs rupturing (from 20 to 25 min) of the ultrafine hematite particles are quick.

From Fig.5 it is shown that the flotation recovery significantly increases with the increase of stirring speed from 600 r/min to 1 000 r/min and as the stirring speed continuously increases from 1 000 r/min to 1 400 r/min, the flotation recovery of flocs increases slowly although the size of flocs increases quickly. By comparing Figs.4 and 5, when the stirring speed increases from 1 400 to 1 600 r/min, the mean size of flocs reduces quickly but the flotation recovery of flocs remains at the almost same value. Above phenomena prove that the flotation recovery of flocs not only depends on the mean size of flocs but also on the flocs number. When the stirring speed reaches 1 600 r/min, the flotation recovery of flocs

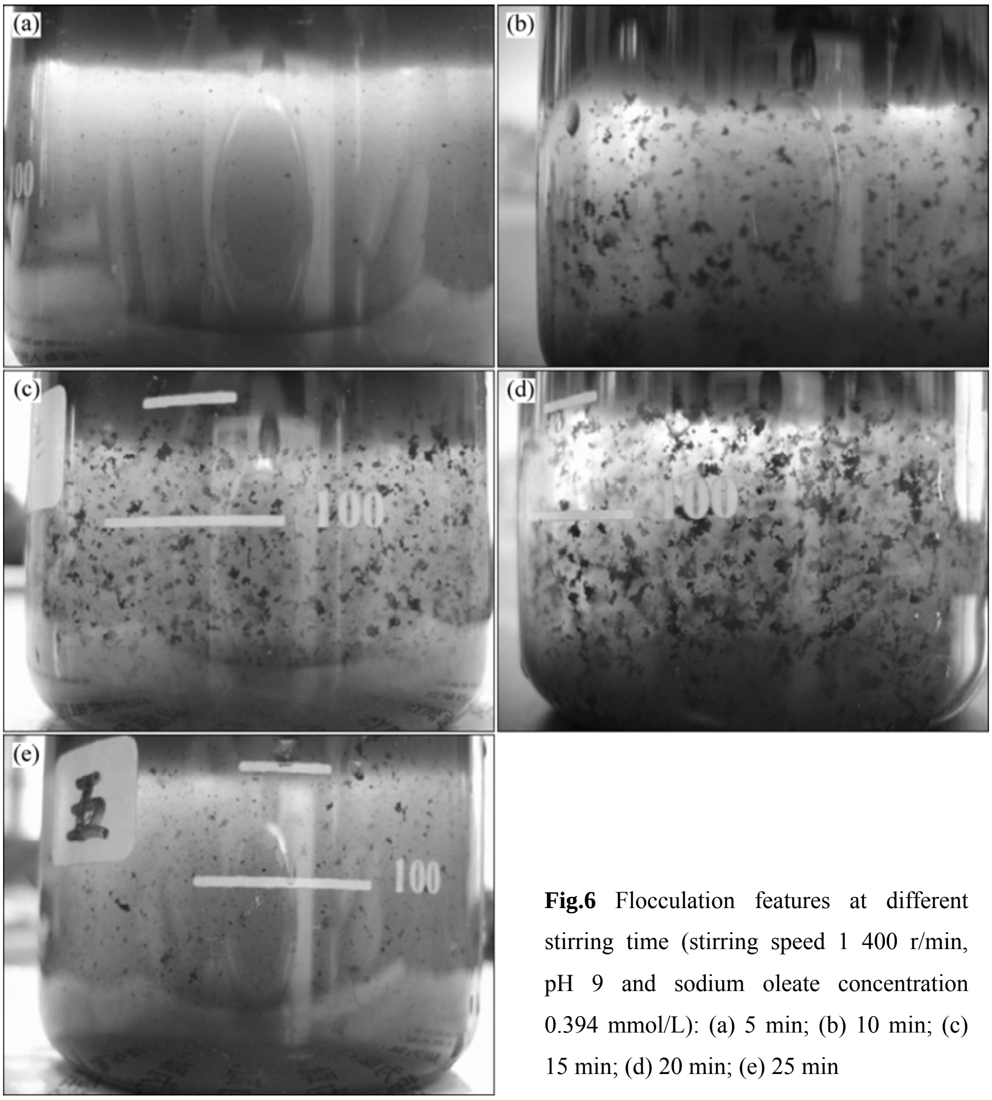

Fig.6 Flocculation features at different stirring time (stirring speed 1 400 r/min, pH 9 and sodium oleate concentration 0.394 mmol/L): (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 25 min

still remains at high value although the floc size decreases significantly because the number of flocs increases. Figs.7 and 8 show the effects of flocculation time on the floc size and the flotation recovery of flocs. It can be found that both the floc size and flotation recovery reach the maximum when the flocculation time is 20 min; and the flocs are ruptured when the time increases to 25 min but no significant change takes place for the flotation recovery.

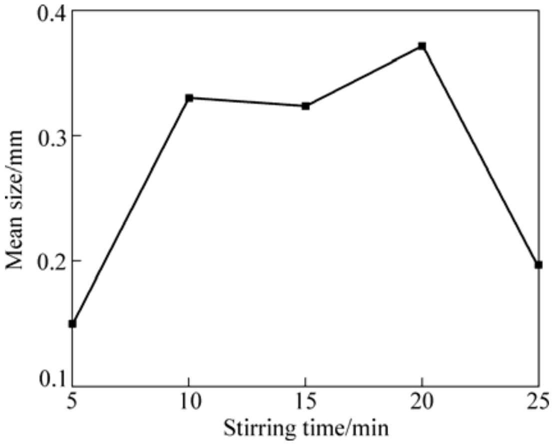

Fig.7 Mean size of flocs vs stirring time

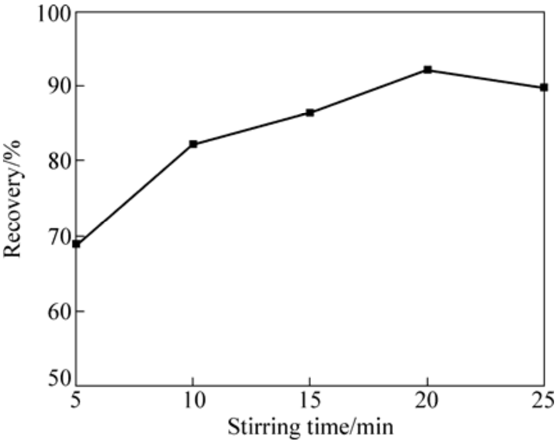

Fig.8 Flotation recovery vs stirring time

The most studies[1, 6−8, 19, 21] on the shear hydrophobic flocculation show that an optimum stirring speed exists at which the floc size is the maximum and the value of the optimum stirring speed depends on the hydrophobicity and electric potential of particle surface, original size and shear rate and type, etc. The dynamic energy of particles is provided by shear to overcome the energy barrier between particles which is proportional to the surface electric potential. Therefore, the minimum shear strength for the formation of flocs decreases with the decrease of surface charge. Additionally, the strength of flocs increases with the decrease of original size of particles, the original size is smaller and the shear rate necessary for flocculation is higher[6].

For the same reason, an optimum flocculation time (stirring time) exists at which the floc size is the maximum and the value of the optimum time depends on the hydrophobicity, electric charge of particle surface, original size, shear rate and type, etc. The minimum flocculation time for the formation of flocs increases with the increase of surface charge. Meanwhile, the flocculation time depends on the stirring speed, and the lower the stirring speed, the longer the flocculation time[1].

3.2 Effects of pH

The flocculation features at different values of pH are shown in Fig.9 under the flocculation conditions of stirring speed 1 400 r/min, flocculation time 20 min, and sodium oleate concentration 0.394 mmol/L. The effects of pH on the floc size and the flotation recovery of hematite flocs are shown in Figs.10 and 11.

Figs.9 and 10 show that the flocculation of ultrafine hematite induced by sodium oleate takes place in the wide range of pH (2.5−11.0). The extent of flocculation at the low pH of 2.5−3.0 is slightly higher than that at the middle pH of 5.0−8.0 and the floc size increases significantly with the increase of pH when pH is higher than 8. The floc size reaches the maximum at pH 9 and decreases significantly at strong alkaline condition (pH >10).

As shown in Fig.11, the flotation recoveries of hematite flocs are higher than those of non flocculated hematite in the wide pH range of 2.0−11.0. Particularly, the flotation recoveries of hematite flocs increase significantly compared with non flocculation. However, the optimum values of pH for the flocculated and non flocculated hematite flotation are the same and at about 9. By comparing Fig.10 with Fig.11, it can be seen that although the floc size decreases obviously when pH is higher than 9, the flotation recovery remains the same value. The study of PASCOE and DOHERTY[5] on the separation of flocculated fine hematite (<10 μm) from quartz using sodium oletae indicated that the flocs induced by sodium oleate can be easily floated.

Additionally, the results of Zeta potential measurement (Fig.2) indicate that Zeta potential increases with the increase of pH. Therefore, from Figs.10 and 11, the main reason that the floc size significantly increases when pH is higher than 8 is considered the remarkable increase of particle surface hydrophobicity. However, although the extent of flocculation decreases under high alkaline condition (pH>9), no significant change for the flotation recovery of flocs takes place, which can be explained that the

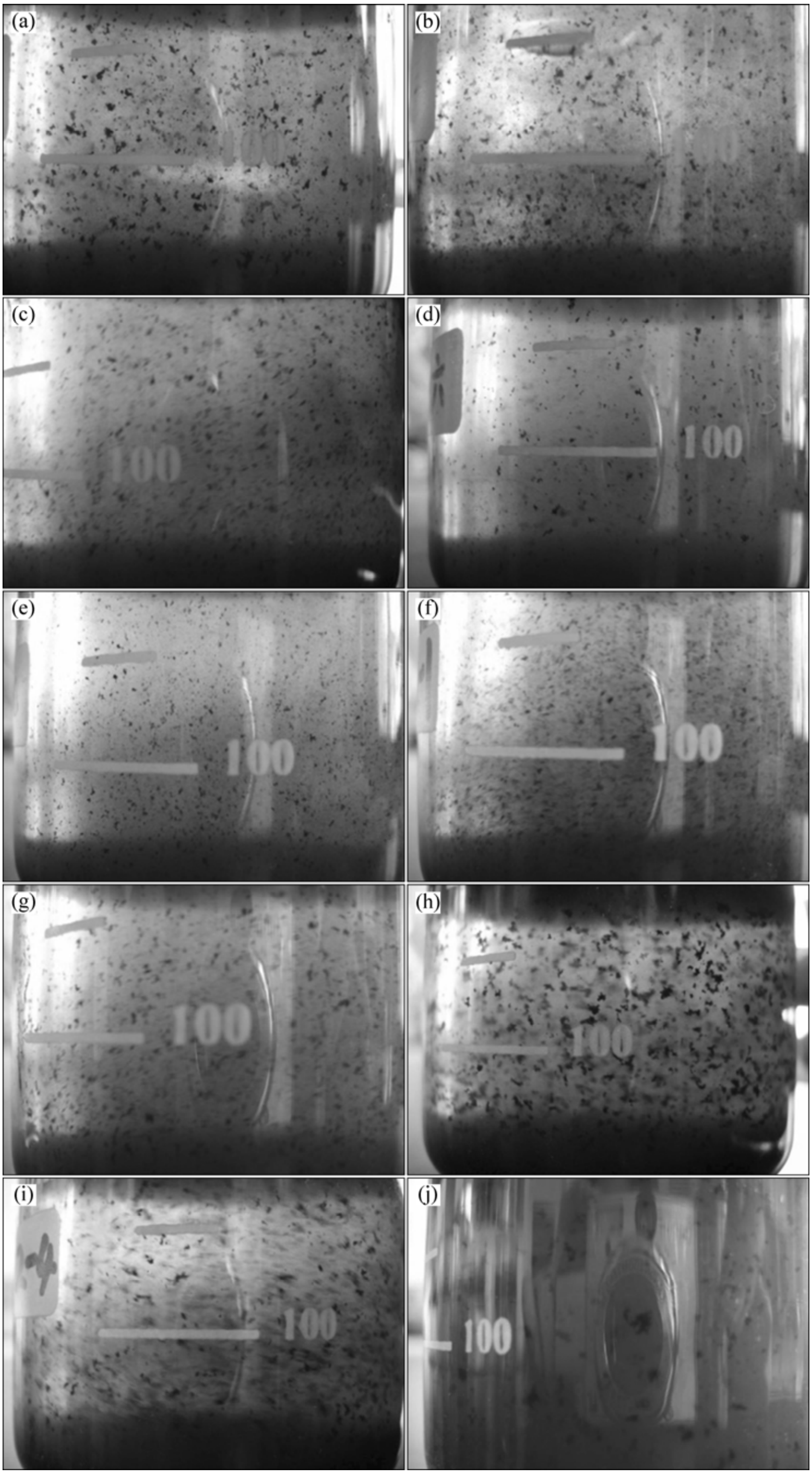

Fig.9 Flocculation features at different pH values (stirring speed 1 400 r/min, flocculation time 20 min, and sodium oleate concentration 0.394 mmol/L): (a) pH=2.5; (b) pH=3; (c) pH=4; (d) pH=5; (e) pH=6; (f) pH=7; (g) pH=8; (h) pH=9; (i) pH=10; (j) pH=11

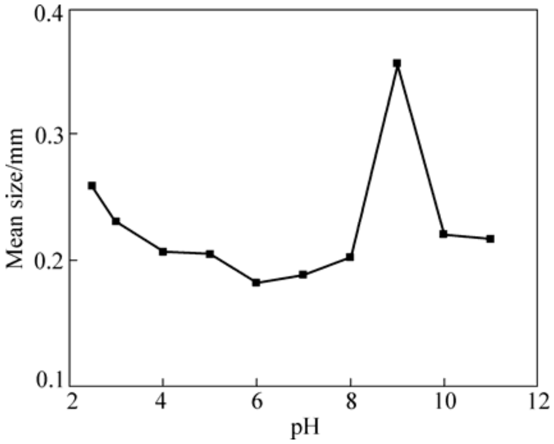

Fig.10 Mean size vs pH

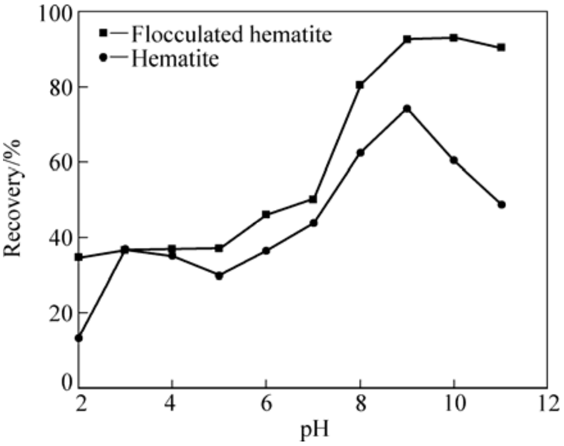

Fig.11 Flotation recovery of flocs vs pH

hydrophobicity required for the flocculation is higher than that for flotation because a static electric force presents between particles. In other words, the hydrophobicity of particle surface is large enough for flotation but not for the formation of flocculation.

Fig.11 also shows that unlike the flocculated hematite the flotation recovery of non flocculated hematite decreases significantly when pH is higher than 9. This phenomenon can be considered because the size of non flocculated particles is so small that the floating efficiency is very low due to the low collision efficiency between particles and bubbles during flotation.

According to the solution chemistry of sodium oleate[22], there is an equilibrium between the molecules of oleic acid and the oleate ions in solution, and the critical pH is 8.6, that is, pH=8.6. When pH<8.6, the sodium oleate exists mainly in the form of oleic acid molecules; when pH=8.6, there are both oleic acid molecules and sodium oleate ions; and when pH>8.6 the sodium oleate exists mainly in the form of oleate ions. Theoretically, the concentration of oleate ions reaches an maximum at pH=8.6, which is why the hydrophobicity of hematite surface in the presence of sodium oleate is the maximum at pH=9.0. The concentration of OH^- increases quickly as pH increases further. The competition of adsorption on the particles between OH— and RCOO— takes place, which causes the reduction of the adsorption of RCOO— on the particle surface of hematite and the hydrophobicity of particle surface decreases.

3.3 Effects of sodium oleate concentration

The flocculation features at different concentrations of sodium oleate are shown in Fig.12 under the flocculation condition of stirring speed 1 400 r/min, flocculation time 20 min, and pH 9. The effects of sodium oleate concentration on the floc size and the flotation recovery of hematite flocs are shown in Figs.13 and 14 respectively.

From Figs.12 and 13 it can be seen that the hydrophobic flocculation of ultrafine hematite occurs in the experimental range of sodium oleate concentration of 0.197−0.591 mmol/L and the optimum concentration is 0.394 mmol/L at which the size of flocs is the maximum. Figs.13 and 14 show that when the concentration of sodium oleate is lower than 0.296 mmol/L, the sizes of flocs are small and the flotation recoveries of flocculated and non flocculated hematite are similar. As the concentration of sodium oleate is larger than 0.296 mmol/L, both the size and the flotation recovery of flocs increase significantly but the flotation recovery of non flocculated hematite increases slightly. The size and flotation recovery of flocs reach the maximum values at the concentration of sodium oleate of 0.394 mmol/L. However, they decrease significantly when the concentration of sodium oleate is larger than 0.394 mmol/L.

Fig.14 also shows that as the concentration of sodium oleate is larger than 0.296 mmol/L, the flotation recovery of flocculated hematite is remarkably higher than that of non flocculated hematite; and as the concentration of sodium oleate is larger than 0.394 mmol/L, the flotation recovery of flocculated hematite decreases slightly but no change takes place for the flotation recovery of non flocculated hematite.

When the adsorption of sodium oleate on mineral surface takes place with increasing the concentration, the oleate assembles on the mineral surface sequentially in the forms of monomolecular layer, aggregation and micelle. The concentration at which the micelle starts to form is called the critical micelle concentration indicated by CMC. The CMC of sodium oleate is 0.187 mmol/L. In this study, because the concentrations of sodium oleate for the flocculation and flotation experiments are greater

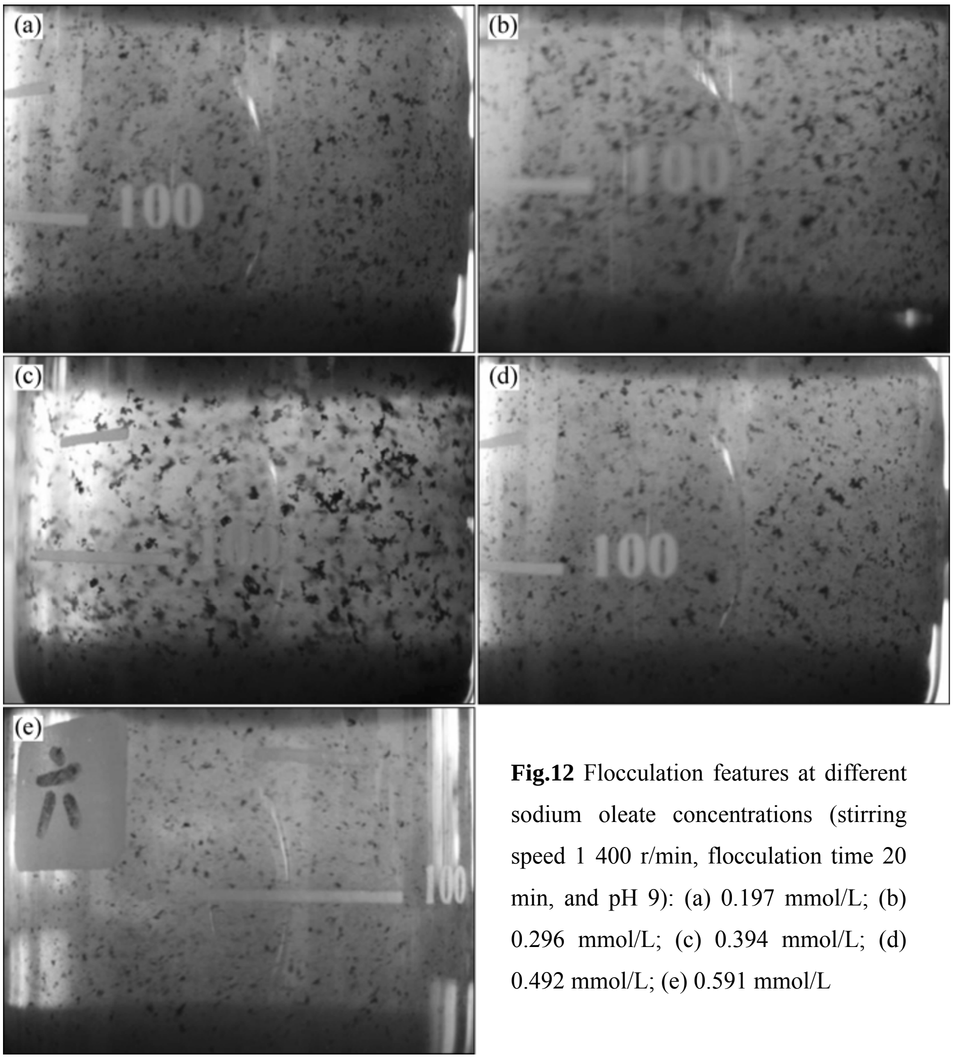

Fig.12 Flocculation features at different sodium oleate concentrations (stirring speed 1 400 r/min, flocculation time 20 min, and pH 9): (a) 0.197 mmol/L; (b) 0.296 mmol/L; (c) 0.394 mmol/L; (d) 0.492 mmol/L; (e) 0.591 mmol/L

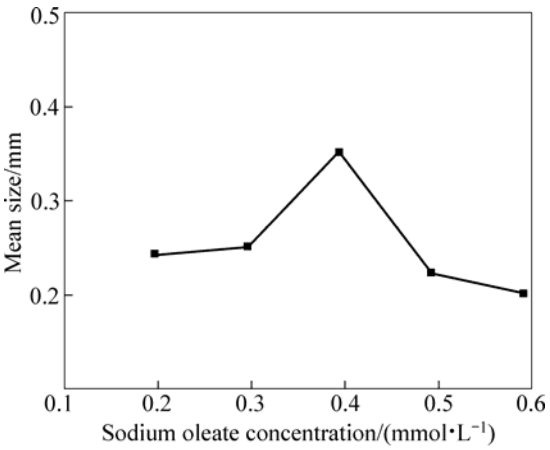

Fig.13 Mean size vs sodium oleate concentration

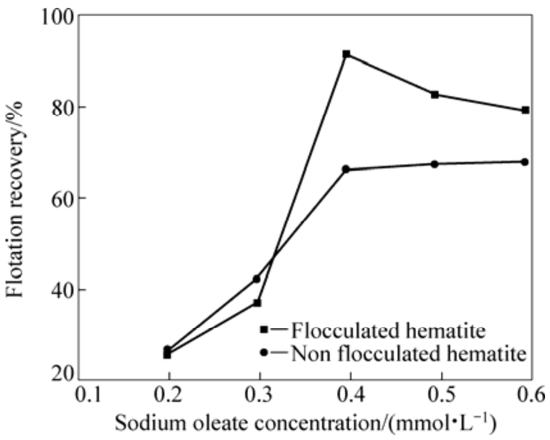

Fig.14 Flotation recovery of flocs vs sodium oleate concentration

than the CMC, there are sodium oleate micelles formed on the hematite particle surface under the conditions of experiments. PASCOE and DOHERTY[5] investigated the process of shear hydrophobic flocculation of ultrafine hematite using sodium oleate in the broad range of sodium oleate concentrations ($1-1\times10^{-3}$ mmol/L). The study shows that hematite flocs are produced only when the solubility of oleic acid is exceeded and an oil-in-water emulsion is formed. Floc size increases with the increase of the concentration of insoluble oleic acid, suggesting that oleic acid droplets can form directly on the mineral surface, and these droplets have an important role in the flocculation process.

However, in this study when the concentration of sodium oleate in pulp exceeds 0.394 mmol/L, both the floc size and flotation recovery decrease significantly with the increase of sodium oleate concentration. This proves that overly oil-in-water emulsions formed are adverse for the flocculation of ultrafine hematite.

4 Determination of total potential of interaction between hydrophobic particles of hematite

4.1 Total potential of interaction between hydrophobic particles

According to EDLVO theory, the total potential of interaction between hydrophobic particles is

$$U_T=U_A+U_R+U_{HI}+U'_{HI} \tag{1}$$

where U_T is the total potential of interaction between hydrophobic particles; U_A is van der Waals attractive potential; U_R is electric double layer repulsive interaction potential; U_{HI} is hydrophobic interaction potential; U'_{HI} is hydrocarbon chain association potential.

For two spherical particles of same material and radius (r), the van der Waals attractive potential between them is

$$U_A=-\frac{Ar}{12H} \tag{2}$$

where A is Hamaker or the material characteristic constant; H is the shortest distance between particles.

Eq.(2) is suitable for the case of the sizes of particle being much larger than their distance.

Hamaker constant is determinant for U_A and can be calculated by

$$A=\pi^2 c\rho^2=\pi^2\rho^2\frac{3\alpha_0^2 h_0 v}{4(4\pi\varepsilon_0)^2} \tag{3}$$

where ρ is density of particles，kg/m^3; c is coefficient of chromatic dispersion interaction energy; α_0 is atomic polarizability, c^{2}m^2/J; h_0 is Planck constant, 6.626×10^{-34} J·s; v is electronic rotation frequency, for Bohr atom, $v=3.3\times10^{15}$ s^{-1}; $h_0v=2.2\times10^{-18}$ J.

For spherical particles, when the distance between particles is larger than the thickness of an electric double layer, the repulsive interaction potential is

$$U_R=\frac{1}{2}\varepsilon r\Phi_0^2\ln[1+\exp(-\kappa H)] \tag{4}$$

where r is radius of particles, m; k is Boltzmann constant, 1.38×10^{-23} J/K; Φ_0 is surface potential of particles, V; ε is permittivity of solution, F/m; κ is thickness of electric double layer, m^{-1}.

$$\kappa=\left(\frac{8\pi e^2 nZ^2}{\varepsilon kT}\right)^{1/2} \tag{5}$$

where n is ion number in solution, m^{-3}; T is temperature, K; Z is ion valence in solution; e is electronic charge, 1.602×10^{-19} C.

To date there has not been a theoretical model to calculate the hydrophobic interaction potential, an empirical equation obtained by direct measurements is as follows[22]:

$$U_{HI}=-Crh_0\exp\left(-\frac{H}{H_0}\right) \tag{6}$$

where C is constant, N/m, $C=2.51\times10^{-3}k_1$ (k_1 is hydrophobic coefficient, related to contact angle θ, $k_1=\frac{\exp(\theta/100)-1}{e-1}$); H_0 is attenuation length，m.

The surface hydrophobicity of particles is induced by the adsorption of surfactants on the particle surface. If the density of the adsorption layer of surfactants on the surface of induced hydrophobic particles is small or the coverage rate is smaller than 50% and approaching particles are close to the length within two times surfactant ion length ($L<H<2L$), the hydrocarbon chains on the particle surface will associate each other at certain short distance and a hydrocarbon chain association potential arises[22].

Because the active points of adsorption on the surface of mineral particles are not homogenous, the coverage rates of surfactants adsorbing on the surface of induced hydrophobic mineral particles are usually small, 10%−30%. Therefore, in terms of the interaction between induced hydrophobic mineral particles the hydrocarbon chain association potential cannot be neglected. The hydrocarbon chain association potential can be calculated by[22]

$$U'_{HI}=\pi K_2 s\Phi\frac{r^2\sigma n_c}{(r+L)^3-r^3}\left(L-\frac{H}{2}\right)^2(6r+4L+H),$$

$$L\le H\le 2L \tag{7}$$

where Φ is standard free energy change per unit of —CH$_2$ during hydrophobic association in water solution, J; K_2 is pre-association constant, $0\le K_2\le 1$; s is association degree, $0<s<1$; n_c is number of — CH$_2$ on the hydrocarbon chains of surfactants; σ is area adsorption density of sodium oleate molecules on the particle surface, m^{-2}.

In terms of induced hydrophobic particles, because the adsorption densities of surfactants on particle surface are relatively low, the association degree can be supposed to be 0.5 and the pre-association constant to be 1. Therefore,

$$U'_{\mathrm{HI}} = -6.97\times10^{-21}\frac{r^2\sigma n_{\mathrm{c}}}{(r+L)^3-r^3}\left(L-\frac{H}{2}\right)^2(6r+4L+H),$$

$$L \le H \le 2L \qquad (8)$$

4.2 Calculation of total potential of interaction between hydrophobic particles

The data used for the calculation of total potential of interaction between hydrophobic hematite particles are listed in Table 2 and the calculation results are listed in Table 3.

The relationships between the interaction potentials of ultrafine hydrophobic hematite particles induced by sodium oleate and the distance between their surfaces are shown in Fig.15. From Fig.15, the trends of various potentials of interaction between hematite particles are very different. When the distance between particles is larger than 20 nm, the interaction potential of electric double layer is dominant and the value of the total potential is positive. However, when the particles approach closer each other, the attractive hydrophobic interaction potential increases more significantly than the repulsive interaction potential of electric double layer with the distance between particles, and dominates the total interaction potential. At the distance of 30−40 nm, a small potential barrier exists. That is, a hydrodynamic force is required by mechanical agitation to give the particles sufficient kinetic energy to overcome the potential barrier. Due to the strong hydrophobic interaction potential, the total interaction potential between particles becomes obviously attractive as long as the kinetic energy of particles acquired by mechanical agitation exceeds the potential barrier. The particles will approach further to form flocs. Fig.15 also shows that the hydrocarbon chain association potential increases very significantly and it becomes much larger than other potentials at the distance near the surface of particles where a deep potential valley presents. When those particles approach so close each other, tight and not easily ruptured flocs would be formed. The study of WARREN[21] indicated that the length that the hydrophobic particles can approach each other depends on the surface electric charge, hydrophobic force and original size as well. PASCOE and DOHERTY[5] also found that the stronger the hydrocarbon chain association and hydrophobic forces are, the smaller the original size is, and the stronger the flocs formed are.

Table 2 Data used for calculation of total potential of interaction between hydrophobic hematite particles

Parameter	Value
Absolute temperature/K	293
Length of sodium oleate molecule, L/nm	1.3
Number of —CH_2 on hydrocarbon chains of sodium oleate n_{c}	16
Pre-association constant K_2	1
Association degree s	0.5
Area adsorption density of sodium oleate molecules on particle surface, σ/m^{-2}	6.21×10^{17}
Permittivity of solution, ε/($F\cdot m^{-1}$)	7.172×10^{-10}
Zeta potential of particle surface, φ_0/V	-31.2×10^{-3}
Debye constant, κ/m^{-1}	3×10^{7}
Hamaker constant, A/J	0.22×10^{-20}
Mean particle radius, r/m	$2.713\ 45\times10^{-6}$
Constant, C/($N\cdot m^{-1}$)	10.329×10^{-4}
Attenuation length, H_0/m	5.1×10^{-9}

Table 3 Calculation results of total potential of interaction between hydrophobic hematite particles

H/nm	U_{A}/ 10^{-19} J	U_{R}/ 10^{-19} J	U_{HI}/ 10^{-19} J	H'_{HI}/ 10^{-19} J	U_{T}/ 10^{-19} J
1.0	−4.97	6.42	−117.49		
1.3	−3.83	6.38	−110.78	−1 221.36	−1329.59
2.0	−2.49	6.29	−96.57	−260.18	−352.95
2.6	−1.91	6.20	−85.85	0	−81.56
4.0	−1.24	6.01	−65.24		−60.47
6.0	−0.83	5.75	−44.08		−39.16
8.0	−0.62	5.50	−29.78		−24.9
10.0	−0.50	5.25	−20.12		−15.37
20.0	−0.25	4.14	−2.83		1.06
30.0	−0.17	3.23	−0.40		2.66
40.0	−0.12	2.49	0.06		2.43
50.0	−0.10	1.91	0		1.81
100.0	−0.05	0.46	0		0.41

5 Conclusions

1) The investigation of the shear hydrophobic flocculation and flotation of Anshan ultrafine hematite taken from Qidashan Mine shows that stirring speed and flocculation time, pH of suspension and sodium oleate concentration significantly affect the shear hydrophobic flocculation of ultrafine hematite using sodium oleate as the surfactant. The optimum conditions for the flocculation are: stirring speed 1 400 r/min, flocculation time 20 min, pH 9 and sodium oleate concentration 0.394 mmol/L, at which the average sizes of flocs are the maximum.

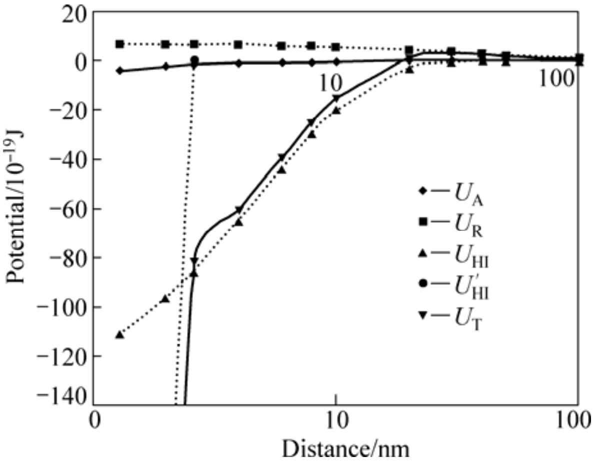

Fig.15 Curves of interaction potentials of ultrafine hydrophobic hematite particles induced using sodium oleate vs distance between them

2) The flotation recovery of hematite flocs is remarkably higher than that of non flocculated ultrafine hematite and basically proportional to the size of flocs, that is, the larger the mean size of flocs are, the higher the flotation recovery is. However, after the flocs are formed, the rupturing of flocs by increasing stirring speed and flocculation time does not influence the flotation recovery significantly.

3) According to the extended DLVO theory, the total interaction potential of Anshan ultrafine hematite was found based on the calculations of the van der Waals attractive potential, electric double layer repulsive interaction potential, hydrophobic interaction potential and hydrocarbon chain association potential. The calculation results indicated that the hydrophobic flocculation state of the ultrafine hematite-sodium oleate system is mainly dominated by electric double layer repulsive interaction potential and hydrophobic interaction potential. A mechanical agitation is required to overcome a potential barrier at the distance of about 20 nm between particles due to the existence of electric double layer repulsive interaction potential. The particles approach further to form flocs due to the significant increase of the hydrophobic interaction potential.

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鞍山微细赤铁矿的油酸钠诱导剪切疏水絮凝和浮选

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摘　要：讨论搅拌速度、絮凝时间、矿浆 pH 值和油酸钠浓度等对鞍山微细赤铁矿的油酸钠诱导剪切疏水絮凝和浮选的影响。结果表明：剪切搅拌速度、絮凝时间、矿浆 pH 和油酸钠浓度对该系统疏水性絮凝均有显著影响; 最佳疏水絮凝条件为：剪切搅拌速度 1 400 r/min、剪切搅拌时间 20 min、矿浆 pH=9 和油酸钠浓度 3.94×10^{-4} mol/L；絮凝浮选回收率比未絮凝浮选的有明显提高。根据扩展 DLVO 理论，计算出油酸钠诱导疏水微细赤铁矿颗粒的总相互作用势能，证实该系统的疏水絮凝状态主要受颗粒间双电层排斥能和疏水作用势能支配，双电层排斥能使颗粒间的作用存在能垒，机械搅拌使颗粒获得动能克服能垒，随着颗粒的进一步靠近，颗粒间疏水作用势能显著增大，引起颗粒团聚。

关键词：油酸钠；微细赤铁矿；剪切疏水絮凝；扩展 DLVO 理论

(Edited by YANG Hua)