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SIMULTANEOUS HYDROPHOBIC AND MAGNETIC FLOCCULATION OF FINE PARAMAGNETIC MINERAL PARTICLES IN AQUEOUS SUSPENSION

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Abstract

Flocculation of fine paramagnetic particles rendered hydrophobic by absorption of surfactants in external magnetic field in aqueous suspension, called simultaneous hydrophobic and magnetic flocculation (SHMF), has been studied through a theoretical approach and experiments. All interactions between fine paramagnetic particles in the case of SHMF are being discussed in this paper. Through extension of the classical DLVO theory, the theory of stability of fine particles in aqueous suspension in the case of SHMF is proposed. Potential energies of interaction between fine rhodochrosite particles rendered hydrophobic by absorption of sodium oleate in external magnetic field have been calculated from the theory. Experimental results of SHMF of fine rhodochrosite and siderite particles showed that SHMF exhibits much stronger and faster aggregation then either hydrophobic or magnetic flocculation alone. Two examples of SHMF applied to fine particle processing are given.

INTRODUCTION

Flocculation can be classified into three main categories: polymeric flocculation which is caused by a bridging action of a polymeric flocculant [1]; hydrophobic flocculation which results from hydrophobic interaction of attraction between hydrophobic particles in an aqueous suspension [2,3]; magnetic flocculation which

is caused by magnetic attraction between ferromagnetic or weakly magnetic particles in an external magnetic field [4]. Owing to high selectivity, hydrophobic and magnetic flocculation have recently attracted considerable attention in various scientific and technological fields.

Hydrophobic flocculation as applied in mineral processing has a history of about forty years. Several techniques of fine particle processing such as carrier flotation, oil agglomeration, emulsion flotation and shear flotation are based on selective hydrophobic flocculation of fine mineral particles. It features compact structure of flocs, hydrophobic surfaces of flocs and low moisture content. Moreover, it has a high selectivity; that is only hydrophobic particles are aggregated and hydrophilic particles remain dispersed in a suspension.

Since early 1980s, numerous theoretical approaches to hydrophobic flocculation have been made. It is known that the degree of hydrophobicity of particle surfaces is the dominant parameter affecting hydrophobic flocculation [2, 5], and the high mechanical energy input is an important parameter [6, 7]. Besides, hydrophobic flocculation of fine hydrophobic particles in aqueous solution can be enhanced by addition of non–polar oil emulsion [8].

With development of high magnetic field technology, magnetic flocculation of weakly magnetic particles in a aqueous suspension became possible. In 1976, Watson [9] firstly proposed a possibility of exploiting magnetic flocculation of weakly magnetic particles. In 1979 Hencl and Svoboda [10] described their research results into magnetic flocculation of weakly magnetic particles as applied to mineral processing. Afterwards, Svoboda [11] deduced a formula for calculating potential energy of magnetic attraction between weakly magnetic particles in an external magnetic field, and established the theory of stability in the case of magnetic flocculation.

Van Kleef and his colleagues derived an expression of magnetic attractive force between weakly magnetic particles in an external magnetic field [12], studied the kinetics of formation of binary particle flocs in a magnetic field [13], and found a way for evaluating threshold value of magnetic field strength for magnetic flocculation of paramagnetic particles through a special experiment. Moreover, they used the magnetic flocculation technique to efficiently separate fine rhodochrosite and quartz mixture [14].

Magnetic flocs of fine weakly magnetic particles posses a long chain and loose structure which has been observed experimentally [15]. Such flocs are not good enough to be practically utilised. On the other hand, to produce significant magnetic flocculation of fine weakly magnetic particles in aqueous suspension, external magnetic field of a very high strength is needed. From the economic and technological point of view at the present time, it is difficult to be applied in industry. These disadvantages result in the fact that magnetic flocculation of fine weakly magnetic particles is not an efficient and economical method of aggregation.

On the other hand, hydrophobic flocculation, in some cases, needs to be enhanced by physical treatment in order to strengthen selectivity of aggregation. For example, separation between some fine oxide mineral particles with hydrophobic flocculation is not easy because good collectors with high selectivity are hard to find. Accordingly, we think that hydrophobic flocculation and magnetic flocculation should be joined so that they could enhance one another.

This process can be realised by mixing a suspension of fine weakly magnetic particles rendered hydrophobic by the adsorption of proper collectors in an external magnetic field. We call it a simultaneous hydrophobic and magnetic flocculation (SHMF). SHMF would exhibit advantages of both hydrophobic flocculation and magnetic flocculation, and could provide a satisfactory selective flocculation with higher selectivity and stronger aggregation behaviour.

Objectives of the present work are to approach theoretically and experimentally the aggregation behaviour of simultaneous hydrophobic and magnetic flocculation of fine paramagnetic particles in an aqueous suspension, and to explore a possibility of SHMF applied to processing of fine mineral particles. We shall endeavour to estimate quantitatively the potential energies of interaction between hydrophobic particles in a magnetic field, and finally to establish a theory of stability of a suspension of fine paramagnetic particles in the case of SHMF.

THEORY

For simultaneous hydrophobic and magnetic flocculation the theory of stability of a suspension can be established through an extension of the classical DLVO

theory.

Magnetic Interactions

Magnetic Interaction Between Paramagnetic Particles

Van Kleef et al. [12] derived an expression of the magnetic attractive force between paramagnetic particles in an external magnetic field. It is expressed as follows:

$$F_{mp} = -\frac{2\pi\chi_p^2 B_0^2 a^6}{3\mu_0 r^4}(1 + 3\cos 2\theta_p) \tag{1}$$

where χ_p is the volume magnetic susceptibility of particles, B_0 is the external magnetic field strength, a is the radius of particle, μ_0 is magnetic permeability of vacuum, r is the polar radius and θ_p is the polar angle.

In order to obtain an expression of the potential energy of the magnetic interaction between weakly magnetic particles in aqueous suspension (U_{mo}), we integrate F_{mp} over r in eq. (1):

$$U_{mp} = \int_R^\infty F_{mp} dr = -\frac{2\pi\chi_p^2 B_0^2 a^6}{9\mu_0 R^3}(1 + 3\cos 2\theta_p) \tag{2}$$

If we take average value of θ_p, i.e. $\theta_p = 45^o$, then eq. (12) can be simplified to:

$$U_{mp} = -\frac{2\pi\chi_p^2 B_0^2 a^6}{9\mu_0 R^3} \tag{3}$$

where R is the distance between the particle centres, i.e. $R = h + 2a$, where h is the nearest distance between the particles.

Magnetic Interaction Between a Ferromagnetic and Paramagnetic Particles

Aggregation of ferromagnetic and paramagnetic particles in an external magnetic field is a common phenomenon and is utilised in mineral processing, such as magnetic seed technique. In our early paper [16] we derived a formula for calculating the magnetic attractive force between ferromagnetic and paramagnetic particles in external magnetic field. The force is written in the form:

$$F_{Mf}(r) = -\frac{4\pi^2}{9} b^3 a^3 (\chi_p - \chi_w) M \left[\frac{3B_0(2\cos^2\theta_0 - \sin^2\theta_0)}{r^4} + \frac{4\pi a^3 M \mu_0 (3\cos^2\theta_0 + 1)}{r^7} \right] \quad (4)$$

where M is the magnetisation of ferromagnetic particles, b is the radius of a ferromagnetic particle, χ_p and χ_w are the volume magnetic susceptibilities of paramagnetic particles and water, respectively. Compared with volume magnetic susceptibility of paramagnetic particles, χ_w can be ignored, i.e. $\chi_p - \chi_w \approx \chi_p$. If we take the average value of θ_0, i.e. $\theta_0 = 45^o$, then eq. (4) can be simplified as:

$$F_{Mf}(r) = -\frac{2\pi^2}{9} b^3 a^3 \chi_p M \left[\frac{3B_0}{r^4} + \frac{20\pi a^3 M \mu_0}{r^7} \right] \quad (5)$$

We integrate $F_{Mf}(r)$ over r in eq. (5) and obtain:

$$U_{Mf} = \int_R^\infty F_{Mf}(r)dr = -\frac{2}{27} \pi^2 a^3 b^3 \chi_p M \left[\frac{3B_0}{R^3} + \frac{10\pi a^3 M \mu_0}{R^6} \right] \quad (6)$$

Expression for the potential energy of magnetic interaction between ferromagnetic and paramagnetic particle in an external magnetic field is derived.

Hydrophobic Interactions

Hydrophobic interaction is perhaps most simply defined as a tendency of apolar chain of hydrophobic particles to aggregate when immersed in water. It depends on hydrophobicity of particle surfaces. Since Isrealachvili [17] directly measured the hydrophobic force acting between two mica surfaces rendered hydrophobic by the adsorption of hexadecyltrimethylammonium bromide in water in early 1980s, it has been given worldwide interest.

There have been many attempts [18 to 20] to provide a theoretical model or explanation for hydrophobic interaction. However, no satisfactory achievement has been made so far. Many researchers have been studying direct measurement of hydrophobic force with various hydrophobic surfaces [21 to 27]. all of them have discovered that the hydrophobic force obeys exponential relationship to the separation distance, and can be expressed in the form:

$$F_{HI} = -f_0 a \exp\left[-\frac{h}{h_0}\right] \tag{7}$$

where F_{HI} is the hydrophobic force, f_0 is the empirical parameter of the hydrophobic force, h_0 is the decay length. Up to now, all authors have used the empirical exponential function for hydrophobic force.

Table 1 The empirical parameter and the decay length of the hydrophobic force between two particle surfaces in water determined with surface force apparatus

particle	Hydrophobic surfaces	Contact angle	f_o (Nm^{-1})	h_o (nm)	Valid distance (nm)	Researchers	Reference
Mica	CTAB	65°	0.14	1.03	0 ~ 10	Israelachvili	(21)
	DHDAA	95°	0.056	1.4	0 ~ 15	Pashley	(22)
	DDOA	94°	0.36	1.2	0 ~ 7	Christenson	(23)
		94°	6.6×10^{-3}	5.5	> 7	Christenson	(23)
	F-surfactant	113°	2.3×10^{-3}	16	> 30	Christenson	(24)
	PA		1.5×10^{-3}	62	> 75	Kurihara	(25)
Quartz	DMDCHS	100°	2.51×10^{-3}	12.2	20 ~ 60	Rabinovich	(26)

CTAB=cetyltrimethylammonium bromide; DHDAA=dihexadecyldimethylammonium acetate; DDOA=dioctadecyldimethylammonium ions; DMDCHS=dimethyldichlorosilane; PA=polymeric ammonium surfactant

Table 1 summarises the values of these two parameters obtained by several researchers through measurements in their laboratories. Each exponential function is valid only in a particular region of the separation distance.

We integrate F_{HI} in eq. (7) over h to obtain the potential energy of the hydrophobic interaction between particles in an aqueous suspension as follows:

$$U_{HI} = -f_0 a h_0 \exp\left(-\frac{h}{h_0}\right) \tag{8}$$

Additionally, if particles are rendered hydrophobic by adsorption of surfactants on their surfaces, there will be an interaction of hydrocarbon chain association present. Lu and Song [3] provided a detailed discussion of this problem. An expression of the potential energy of the hydrocarbon chain association in relation to the distance between particles can be written as ($\delta \leq h \leq 2\delta$):

$$U'_{HI} = 1.08kT\pi CS\frac{a^2\sigma n_c}{(a+\delta)^3 - a^3}\left(\delta - \frac{h}{2}\right)^2(6a+h+4\delta) \tag{9}$$

where U'_{HI} is the potential energy of hydrocarbon chain association, k is the Boltzmann constant, T is the absolute temperature, C is the coefficient of preassociation, S is the grade of association; $0 \leq S \leq 1$; σ is the average surface distribution density of adsorbed surfactant molecules, n_c is the carbon number of the hydrocarbon chain, δ is the thickness of the adsorbed layer and is equal to the length of the adsorbed molecules.

Total Potential Energy Change of SHMF

The total potential energy of interaction of particles in the case of simultaneous hydrophobic and magnetic flocculation can be written as:

$$U_T = U_R + U_A + U_M + U_{HI} + U'_{HI} \tag{10}$$

where U_M could be either U_{Mp} or U_{Mf}; U_R is the potential energy of interaction of

electric double layer, U_A is the potential energy of van der Waals interaction. for two spherical particles of equal radius, U_R can be expressed as follows ($\kappa a \gg 1$):

$$U_R = \tfrac{1}{2}\epsilon a \psi_0^2 \ln [1 + \exp(-\kappa h)] \tag{11}$$

where ϵ is the absolute dielectric constant of medium, ψ_0 is the potential on the surface of a particles, and κ is the Debye–Huckel reciprocal length. U_A can be expressed as:

$$U_A = -\frac{A_{123}\ a}{12h} \tag{12}$$

where A_{123} is the Hamaker constant of particles in water. Theory of stability of suspension in the case of simultaneous hydrophobic and magnetic flocculation has thus been established.

CALCULATION OF THE POTENTIAL ENERGY

The potential energy of interaction between rhodochrosite particles rendered hydrophobic by adsorption of sodium oleate have been calculated from eqs. (11), (12), (3), (8) and (9). In the calculation of the potential energy of the hydrophobic interaction we chose the values of empirical parameters obtained by Robinovich and Derjaguin [26]. Therefore, eq. (8) becomes:

$$U_{HI} = -2.51\times10^{-3}\ a h_0 \exp\left(-\frac{h}{h_0}\right) \tag{13}$$

$$h_0 = 12.2 \pm 1.0 \text{ nm}$$

It has been known that the hydrophobic interaction force and the decay length depend on the degree of hydrophobicity and the range of distance for which the interaction force appears to increase with the contact angle [26]. Hence, for particles with the contact angle of less than 100^0, the expression of hydrophobic interaction (eq. (10)) must be revised by introducing a coefficient of incomplete surface hydrophobicity k_1. Thus, eq. (13) becomes:

$$U_{HI} = -k_1 f_0 a h_0' \exp\left(-\frac{h}{h_0'}\right) \tag{14}$$

$$h_0' = k_1 h_0 = k_1(12.2 \pm 1.0)\ \text{nm} \tag{15}$$

where $O \leq k_1 \leq 1$.

In our previous paper [5] we gave an expression for determining k_1 through experimental results. It can be written in the form:

$$k_1 = \frac{\exp\left(\frac{\theta}{100} - 1\right)}{e - 1} \tag{16}$$

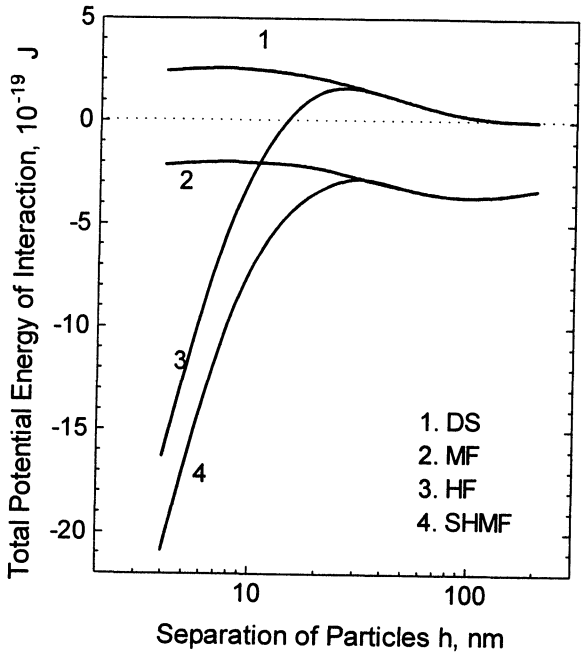


Fig. 1 Curves of total potential energy of interaction between fine rhodochrosite particles in aqueous suspension (B_0=0.8 T, θ=52°). DS: DLVO theory, $U_T = U_R + U_A$. MF: magnetic flocculation model, $U_T = U_R + U_A + U_M$. HF: hydrophobic flocculation model, $U_T = U_R + U_A + U_{HI} + U_{HI}'$. SHMF: SHMF model, $U_T = U_R + U_A + U_M + U_{HI} + U_{HI}'$.

Data used in the calculation are: the particle radius $a = 0.889$ μm, Hamaker constant of rhodochrosite particles in water $A_{131} = 0.43\times10^{-20}$J, specific surface area of particles 0.67322 m^2g^{-1}, the carbon number of NaOl $n_c = 17$, length of NaOl molecule $\delta = 1.3$ nm, grade of association S = 0.5, coefficient of preassociation C = 1, zeta potential $\zeta = -40$ mV. As a result of the calculation, we have obtained curves of the total potential energy of interaction between fine rhodochrosite particles. These curves are shown in Figures 1, 2 and 3.

Figure 1 illustrates four curves of the total potential energy of interaction in the cases of dispersion, magnetic flocculation, hydrophobic flocculation and SHMF. Without considering hydrophobic and magnetic interaction, classical DLVO theory proclaims that particles expel each other and that no aggregation exists in the suspension. If the magnetic interaction is taken into account, the curve will mode down in parallel with the curve Ds. In our situation, the curve of magnetic flocculation is in the negative of the potential energy throughout the entire separation distance. This means that magnetic flocculation exists in the suspension.

However, the valley in the potential energy curve is too small so that the aggregation degree under this condition will be weak and the magnetic flocs will not have sufficient strength to resist breakup. As we know, the curve of the total potential energy, in the case of hydrophobic flocculation has a small potential energy barrier and a very deep potential energy valley. In our situation, the depth of the valley is 621×10^{-19} J. Such a deep potential energy valley is able to make the hydrophobic flocs strong enough against breakup and enables them to grow.

For the SHMF, both hydrophobic and magnetic interactions are taken into account, besides the electric double layer and van der Waals interactions. In can be seen from Fig. 1 that the curve of the total potential energy of SHMF is completely located in the negative area and that is has a very deep potential energy valley. It exhibits both features of the two kinds of flocculation, namely no potential barrier of magnetic flocculation and deep potential energy valley of hydrophobic flocculation.

The shape of the curve demonstrates that SHMF does not need very high mechanical energy input to be produced, and its aggregation degree would be much stronger. In our situation, the curve of the total potential energy of SHMF has a

potential valley with 634×10^{-19} J, which is able to allow the flocs to grow to a relatively large size. Consequently, from the viewpoint of the curve of the total potential energy, SHMF is much easier to be generated and has a much stronger and more rapid aggregation than the hydrophobic and magnetic flocculation alone.

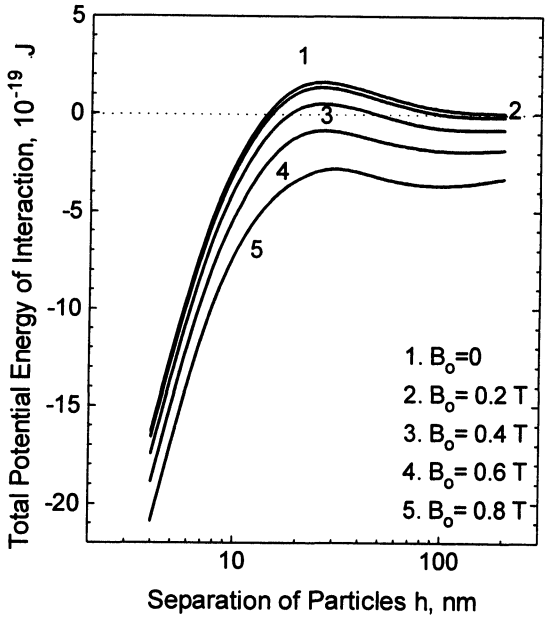


Fig. 2 Curves of the total potential energy of interaction between fine rhodochrosite particles in the case of SHMF at various magnetic field strengths

Relationship between the magnetic field strength and the total potential energy curves of fine rhodochrosite particles in the case of SHMF is shown in Fig. 2. As the magnetic field increases, the potential energy barrier gradually flattens out and for $B_0 > 0.4$ T the potential energy curve enters completely the negative area. The higher is the magnetic field strength, the further is the curve from zero potential energy line. Obviously, the action of the magnetic field in SHMF is mainly to reduce the value of the potential energy barrier, and eventually to make it disappear. To impose an external magnetic field to a suspension, even though the field strength is low, is very helpful to the hydrophobic flocculation of weakly magnetic particles in aqueous suspension.

Relationship between contact angle of particle surfaces and the total potential energy curves of fine rhodochrosite particles in the case of SHMF is illustrated in Fig. 3. The graph shows that as the contact angle increases, the right–hand side of the curve is unchanged while the left–hand side region moves sharply downwards to form a deep potential energy valley. The higher the contact angle, the deeper is the valley. If the hydrophobicity of the particle surfaces is weak, e.g. $\theta = 15^o$, the aggregation behaviour of SHMF will be the same as for magnetic flocculation alone (in Fig. 3, the curve at $\theta = 15^o$ is superimposed on curve at $\theta = 0^o$). We can conclude that the hydrophobicity of the mineral particle surfaces is a dominant parameter affecting simultaneous hydrophobic and magnetic flocculation, just like the hydrophobic flocculation.

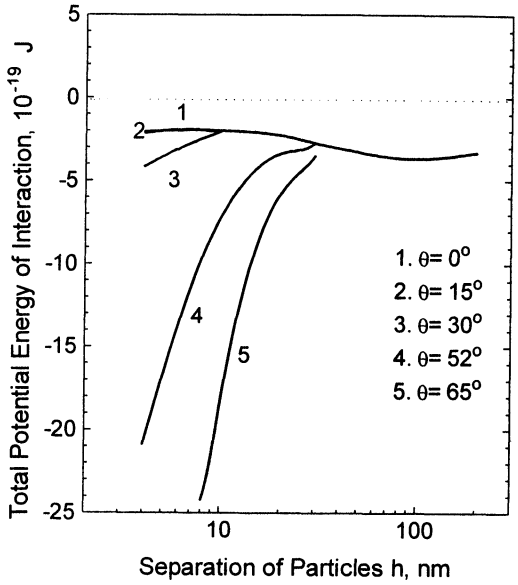


Fig. 3 Curves of the total potential energy of interaction between fine rhodochrosite particles in the case of SHMF at various contact angles of the particle surfaces.

SAMPLES AND EXPERIMENTS

Mineral samples used in this study were rhodochrosite and siderite. Chunky specimens were broken by hammer and purified by gravitational concentration in deionised water. Then, they were ground to less than 30 μm in a porcelain ball

mill. Purity was 94.81% $MnCO_3$ for rhodochrosite and 82.74% $FeCO_3$ for siderite. Size distribution (d_{50}) of rhodochrosite and siderite samples was 2.25 μm and 6.65 μm, respectively, while the average volume diameters were 1.798 μm and 3.830 μm, respectively. The volume magnetic susceptibilities of the rhodochrosite and siderite samples were 3.83×10^{-9} (SI) and 3.15×10^{-9} (SI), respectively.

Simultaneous hydrophobic and magnetic flocculation of fine mineral particles in aqueous suspension was produced in a mixing tank equipped with four baggles in an external magnetic field, with addition of a proper amount of sodium oleate by a given time of stirring. The aggregation–dispersion behaviour was evaluated by a refitted electronic balance for sedimentation analysis, and expressed by the aggregation efficiency E_a. Detailed description of this procedure can be found in our previous paper [3].

The contact angle of mineral particle surfaces treated in a sodium oleate solution of a given concentration was determined by using the tilting plate method in which a contact point of the air/water/solid interface was observed and the angle was measured in a microscope.

The floc size was determined by sedimentation analysis and using stokes formula. It is well known that density of flocs is much smaller than density of the original particles and is difficult to be determined. We propose a new concept, namely the compact floc diameter d_w to describe the floc size. Density of the original particles is used in the calculation of Stokes diameter of the flocs. d_w of the flocs means that all fine particles comprising the floc are from crushing the original particles of the same size.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 4 and 5 illustrate the compact floc size distribution of fine rhodochrosite and siderite particles in aqueous suspension in the case of dispersion, magnetic flocculation, hydrophobic flocculation and SHMF. It can be seen from the diagram that SHMF has much stronger and more rapid aggregation than either hydrophobic flocculation or magnetic flocculation. An order of the aggregation rate is SHMF > hydrophobic flocculation > magnetic flocculation. The experimental

results are in good accordance with conclusion obtained by quantitative evaluation of the potential energy mentioned above.

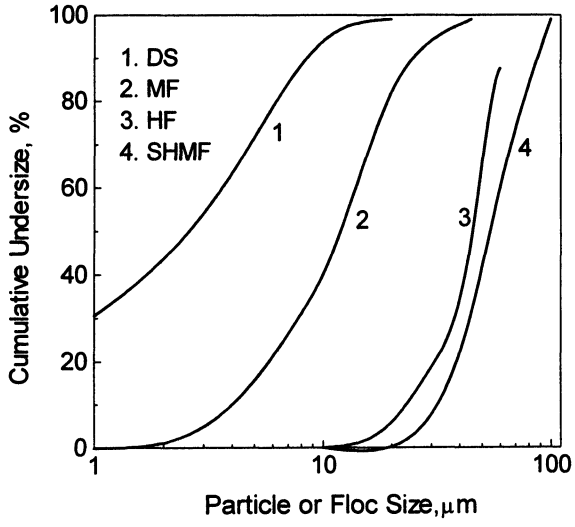


Fig. 4 Compact floc size distribution of fine rhodochrosite in aqueous suspension in the case of SHMF, hydrophobic flocculation, magnetic flocculation and dispersion. DS: dispersion, sodium hexamethaphosphate 5 mg/ℓ, MF: magnetic flocculation, B_0=0.85 T; HF: hydrophobic flocculation, θ = 33°, kerosene 15 mg/ℓ: SHMF: θ=33°, kerosene 15 mg/ℓ, B_0=0.85 T.

Figure 4 shows that the volume mean diameter d_{w50} of the original particles, magnetic flocs, hydrophobic flocs and the SHMF flocs of fine rhodochrosite are 2.3 μm, 13.5 μm, 46 μm and 55.5 μm, respectively. In magnetic flocculation at B = 0.85 T the particles were aggregated from 2.3 μm to 13.5 μm, only, in d_{w50}. Such a weak aggregation is not qualified to be used for a separation process alone.

SHMF generated very strong aggregation. After SHMF, particles smaller than 20 μm in a suspension were about to disappear and the floc size d_{w50} reached 55.5 μm which is bigger by 10 μm than the hydrophobic flocs. Considering the concept of of compact floc size, the floc of 55.5 μm consists of over than 14 000 original particles. With scanning electronic microscope we observed that the maximum SHMF flocs

of fine rhodochrosite was about 1000 μm in diameter in our experiments. Such large flocs are in the region of optimum size for conventional flotation and magnetic separation and even some gravity separation. Hence, SHMF could be utilised in processing of fine mineral particles.

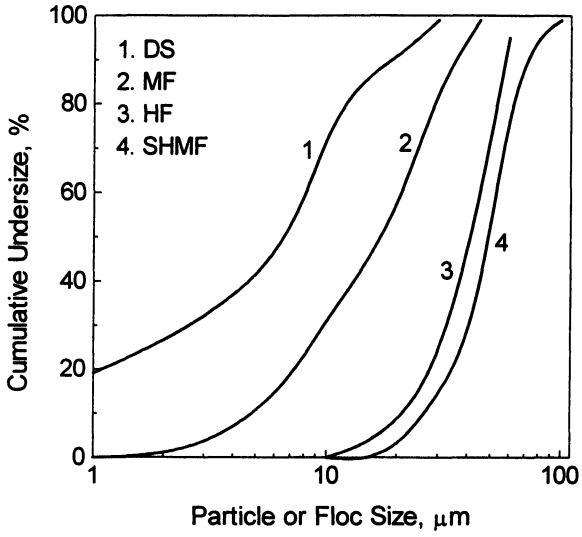
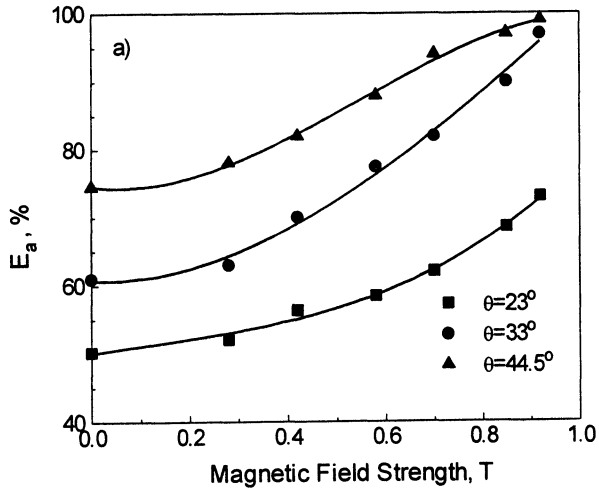


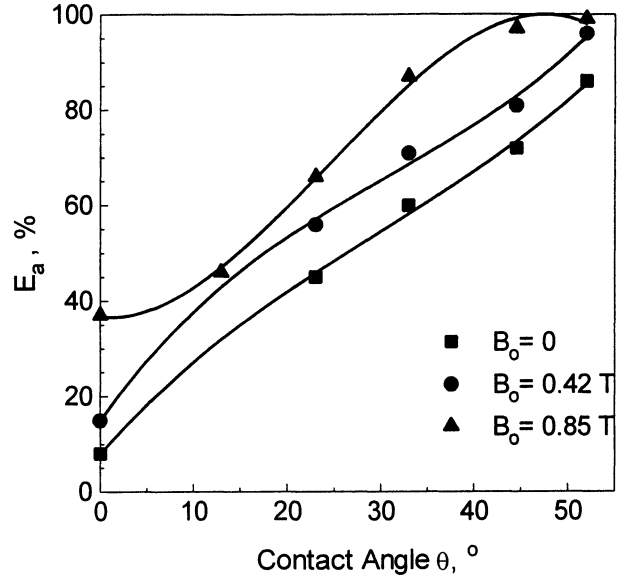
Fig. 5 Compact floc size distribution of fine siderite in aqueous suspension in the case of SHMF, hydrophobic flocculation, magnetic flocculation and dispersion. DS: dispersion, sodium hexametaphosphate 3 mg/ℓ, MF: magnetic flocculation, B_0 = 0.93 T; HF: hydrophobic flocculation, θ = 40°, kerosene 12 mg/ℓ; SHMF: θ = 40°, kerosene 12 mg/ℓ, B_0=0.93 T.

It can be seen in Fig. 5 that the volume mean diameters d_{w50} of the original particles, of the magnetic and hydrophobic flocs, and of the SHMF flocs of fine siderite are 6.6 μm, 17.8 μm, 41 μm and 49 μm, respectively. Conclusions obtained in Fig. 4 were further proved by experimental results with fine siderite particles shown in Fig. 5.

The effects of the magnetic field strength and of the contact angle of the particle surfaces on the aggregation behaviour of fine rhodochrosite particles rendered hydrophobic by adsorption of sodium oleate are illustrated in Fig. 6. The experimental results shown in Fig. 6 agree very well with theoretical calculation of



(a)



(b)

Fig. 6 The effect of the magnetic field strength B and contact angle θ on the aggregation behaviour of SHMF of fine rhodochrosite particles rendered hydrophobic by adsorption of sodium oleate with 15 mgℓ kerosene addition. (a) contact angle was kept constant, (b) field strength was kept constant.

the potential energy shown in Figs. 2 and 3. As the magnetic field strength increases, the aggregation efficiency of suspension slowly rises which is followed by a sharp rise after a critical value of the field strength is reached. At B = 0.85 T the aggregation efficiency increased by about 30% compared to the hydrophobic flocculation alone. With the increase of the contact angle of the particle surfaces, the aggregation efficiency dramatically rises, similar to our observations [5] in hydrophobic flocculation.

APPLICATION IN MINERAL PROCESSING

Separation of Fine Rhodochrosite and Quartz

An artificial mixture of fine rhodochrosite (the mean diameter 1.7 μm) and quartz (the mean diameter 5.5 μm) was separated with the SHMF process in our laboratory. A slurry of the mineral mixture was strongly stirred in an external magnetic field, with addition of sodium hexametaphosphate, sodium oleate and kerosene. After the fine rhodochrosite particles were selectively aggregated, the slurry was moved to a vessel for desliming to separate the flocs from dispersed particles. The results of separation are shown in Table 2.

Table 2 The separation results of fine rhodochrosite and quartz with the SHMF process

Separation Process	Parameter	Feed	Concentrate	Tailings
SHMF-Desliming	% mass	100	51.78	48.22
	$MnCO_3$ grade, %	50	82.89	14.67
	$MnCO_3$ recovery, %	100	85.85	14.15
Hydrophobic flocculation	% mass	100	52.98	47.02
	$MnCO_3$ grade, %	50	75.02	21.8
	$MnCO_3$ recovery, %	100	79.5	20.5

Test conditions: pH=8.8, sodium hexametaphosphate 6 mg/l, NaOl 10 mg/l, kerosene 20 mg/l, magnetic field strength in SHMF 0.92 T.

It can be seen from this Table that SHMF provided much better separation than simple hydrophobic flocculation. The concentrate grade and recovery increased by 7.8% and 6.3% respectively.

Beneficiation of Daye Siderite Ore

The Daye siderite ore located in the Hubei Province in China is a refractory ore. The liberated size of siderite is in the range –18 μm + 2 μm. It is very difficult to be beneficiated with conventional separation techniques. Simultaneous hydrophobic and magnetic flocculation process was used to treat this ore [27].

The feed ore was ground to 61.6% – 10 μm. Then, a slurry was strongly mixed in an external magnetic field with addition of proper dispersant, collector, non–polar oil and fine magnetite. After that, the slurry with siderite flocs thus formed was fed into a magnetic separator, and the siderite concentrate was collected. Table 3 summarised the results of beneficiation.

Table 3 Results of beneficiation of Daye siderite ore by SHMF process

Separation process	Parameter	Feed	Concentrate	Tailings
SHMF-Magnetic separation with 2% fine magnetite addition	% mass	100	52.83	47.17
	Fe grade, %	26.87	39.04	13.24
	Fe recovery, %	100	76.76	23.24
Hydrophobic flocculation-Magnetic separation with the same reagent conditions	% mass	100	47.98	52.02
	Fe grade, %	26.58	39.28	14.86
	Fe recovery, %	100	70.91	29.09

Test conditions: pH 9.0, slurry concentration 20% by mass, dosages of dispersant D6, collector s8 and non-polar oil N10 were 1.5 kg/t, 2.0 kg/t and 4.0 kg/t, respectively. Magnetic field strength in SHMF 0.16 T, fine magnetite particles used contained 68.4% Fe, and 100% -10 μm, magnetic field strength of the magnetic separator was 1.25 T.

Note: the results shown above were obtained after subtracting the effect of the magnetite added.

It is apparent that good results of beneficiation of the the Daye siderite ore were achieved. The concentrate was close to the theoretical iron content of Daye siderite (32.22% to 40.33%), while the recovery reached about 77%. Comparing the upper data with lower data in Table 3, it is obvious that SHMF is more efficient way of treating fine particles than hydrophobic separation alone.

CONCLUSIONS

1. Fine rhodochrosite and siderite particles, rendered hydrophobic by adsorption of sodium oleate in aqueous suspension, and exposed to an external magnetic field, tend to strongly aggregate The volume mean diameter of compact flocs is 55.5 μm for rhodochrosite at $\theta = 33^0$, kerosene 15 mg/ℓ and $B_0 = 0.85$ T. Such flocs consist of more than 14 000 original particles.

2. Simultaneous hydrophobic and magnetic flocculation possesses much stronger and more rapid aggregation than either hydrophobic flocculation or magnetic flocculation.

3. Hydrophobicity of the particle surfaces and the magnetic field strength are the main parameters affecting simultaneous hydrophobic and magnetic flocculation of fine weakly magnetic particles in aqueous suspension. The bigger the contact angle of the particle surfaces and bigger the field strength, the stronger is the aggregation behaviour of SHMF.

4. With SHMF–desliming process, an artificial mixture of fine rhodochrosite and quartz was well separated. The grade and recovery of the concentrate were higher by 7.8% and 6.3%, respectively,, than hydrophobic flocculation alone.

5. The Daye siderite ore which is difficult to beneficiate, was processed with SHMF–magnetic process. The SHMF process achieved recovery of about 77% which is the best beneficiation result, and is higher by 7% than hydrophobic flocculation.

6. Theory of suspension stability in the case of simultaneous hydrophobic and magnetic flocculation has been established through an extension of the classical DLVO theory. When there is no satisfactory theoretical model for qualitative evaluation of the hydrophobic interaction, empirical exponential function given by eq. (10) is an appropriate expression.

7. Calculation of the potential energies in the case of SHMF demonstrated that hydrophobicity of the particle surfaces and the magnetic field strength played very important roles. The action of the magnetic field in SHMF is mainly to flatten the potential energy barrier, and even to make it disappear. The role of strong hydrophobicity is mainly to generate a deep potential energy valley which can prevent the flocs from breaking up, and keeps the flocs growing.

REFERENCES

[1] Y.A. Attia: *Sep. Sci. Technol.* **17** (1982), 485

[2] L.J. Warren: *Chem. Technol.* **11** (1981), 180

[3] S. Lu and S. Song: *Colloids and Surfaces* **57** (1991), 49

[4] M.R. Parker,R.P.A.R. van Kleef, H.W. Myron and P. Wyder: *IEEE Trans. Magn.* **18** (1982), 1647

[5] S. Song and S.Lu: *J. Coll. Interface Sci.* **166** (1994), 35

[6] P.T.L. Koh: *Int. J. Min. Proc.* **17** (1986),45

[7] L.J. Warren: *Colloid Chemistry in Mineral Processing*, Chapter 10, Elsevier, 1992, p. 309

[8] C.E. Capes and R.J. Germain: *Physical Cleaning of Coal.* Marcel Dekker Inc., 1982, p. 311

[9] J.H.P. Watson: *Proc. 6th Int. Cryog. Eng. Conf.*, London (1976), 222

[10] V. Hencl and J. Svoboda: *In: Proc. 13th Int. Conf. Miner. Process. Congress*, Warsaw, Poland (1979), 209

[11] J. Svoboda: *Int. J. Min. Proc.* **8** (1981), 377

[12] R.P.A.R. van Kleef, H.W. Myron, P. Wyder and M.R. Parker: *Proc. Conf. Powder Technol.83: Particle Technology*, EFCE (1983), p. 83

[13] R.P.A.R. van Kleef, et al: *IEEE Trans. Magn.* **20** (1984), 1168

[14] M.R. Parker, R.P.A.R. van Kleef, H.W. Myron and P. Wyder: *J. Magn. Magn. Meter.* **27** (1982), 250

[15] S. Song and S. Lu: *Nonferrous Metals* **40** (1988), 28 (in Chinese)

[16] S. Song, S. Lu and L. Zhu: *J. Wuhan Iron and Steel Univ.* **11** (1988), 11 (in Chinese)

[17] J.N. Israelachvili and R.M. Pashley: *Nature* **300** (1982), 341

[18] K. Eriksson, S. Ljunggren and P.M. Claesson: *J. Chem.Soc. Farad. Trans.* **85** (1989), 163

[19] P. Attard: *J. Phys. Chem.* **93** (1989), 6441

[20] E. Ruchenenstein and N. Churaev: *J. Coll.Interface Sci.* **147** (1991), 535

[21] J.N. Israelachvili and R.M. Pashley: *J. Cool. Interface Sci.* **98** (1984), 500

[22] R.M. Pashley: *Science* **229** (1985), 1088

[23] P.M. Claesson: *J. Coll. Interface Sci.* **114** (1986), 234

[24] H.K. Christenson: *J. Phys. Chem.* **93** (1989), 1472

[25] K. Kurihara: *Chem. Lett.* **9** (1990), 1555

[26] Y.I. Rabinovich and B.V. Derjaguin: *Colloids and Surfaces* **30** (1988), 243

[27] S. Song and S. Lu: *In: Proc. Innovation in Mineral Processing,* Sudbury, Canada, 1994, p. 303

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