Selective flocculation of celestite from celestite-calcite fines

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In this study, selective hydrophobic flocculation of celestite with sodium dodecyl sulphate (SDS) from the mixtures of celestite and calcite was investigated using sodium silicate as inorganic dispersant. Prior to the selective flocculation process, the critical surface tension of wetting (χ_c) values of these minerals were determined as a function of SDS concentration. A significant difference between the χ_c values of celestite and calcite was found at concentrations around 20 mg/dm^3, indicating that celestite particles can be selectively flocculated from the mixtures at these concentrations. Then, the effects of pH, dispersant concentration, flocculation and settling times on the selective flocculation of celestite mineral were studied. Experiments carried out with sodium silicate at optimum conditions yielded a concentrate, which is flocculated material, assaying 85% SrSO$_4$ with a recovery 90% and separation index of 0.90 from a mixture containing 50% SrSO$_4$.

Keywords: Celestite, Calcite, Selective flocculation, Sodium dodecyl sulphate, Sodium silicate

Celestite (SrSO$_4$), the most common strontium mineral, generally occurs with gangue minerals such as calcite, gypsum, anhydrite, quartz and clay minerals[1]. The celestite ores are generally beneficiated by gravity separation and flotation methods to remove the gangue minerals. Calcite (CaCO$_3$) is always present in celestite deposits and industrial use of celestite necessiates its separation from calcite[2]. Celestite and calcite are salt-type minerals in regard to their physicochemical properties[3] and therefore their separation by flotation is relatively difficult. Moreover, the recovery of the mineral particles by froth flotation decreases for particle size of slime[4]. Hence, size enlargements processes may be beneficial for mineral processing operations. One way to recover fine valuable minerals from slimes is to increase their size by selective flocculation and then to float the flocs. Secondly, one of the selective polymeric flocculation, selective hydrophobic flocculation or selective oil agglomeration methods is used to separate valuable minerals from fine particle mixtures, with the aggregation of the desired mineral[5,6].

Hydrophobic flocculation is the aggregation of fine particles at a convenient stirring regime after hydrophobization by the adsorption of surfactants[5]. Long-chain surfactants are more effective for obtaining a good flocculation, because the hydrocarbon chain association depends on the carbon number of adsorbed surfactant chain[7]. However, selectivity in separation of minerals by flocculation process is decreased in the presence of long-chain surfactants. On the other hand, dispersants are used in the selective flocculation applications to prevent aggregation of particles of unwanted mineral in the suspension. Thus, selectivity in the separation of minerals by selective flocculation process is improved[8]. The aim of this study is to investigate the possibility of selective flocculation of celestite with sodium dodecyl sulphate from celestite-calcite fines in the presence of sodium silicate as dispersant.

Experimental Procedure

Materials

High purity celestite and calcite mineral samples were used in this study. The results of the chemical analysis of the samples are given in Table 1. The samples were dry ground in a ceramic ball mill and sieved to −38 µm size fraction. The particle size distributions of the prepared samples were determined using an Andreasen pipette and the obtained results are shown in Fig. 1. As can be seen, the celestite and calcite samples have a similar particle size distribution. The mean sizes of celestite and calcite samples were calculated to be 15.4 and 15.3 µm, respectively. Also, the densities of celestite and calcite samples were determined as 3.94 and 2.69 g/cm^3, respectively, by a pycnometer. Sodium dodecyl sulphate (C$_{12}$H$_{25}$SO$_4$Na) was purchased from Merck. Sodium hydroxide (Merck) was prepared as 1

Table 1—The chemical compositions of the mineral samples (values in %).

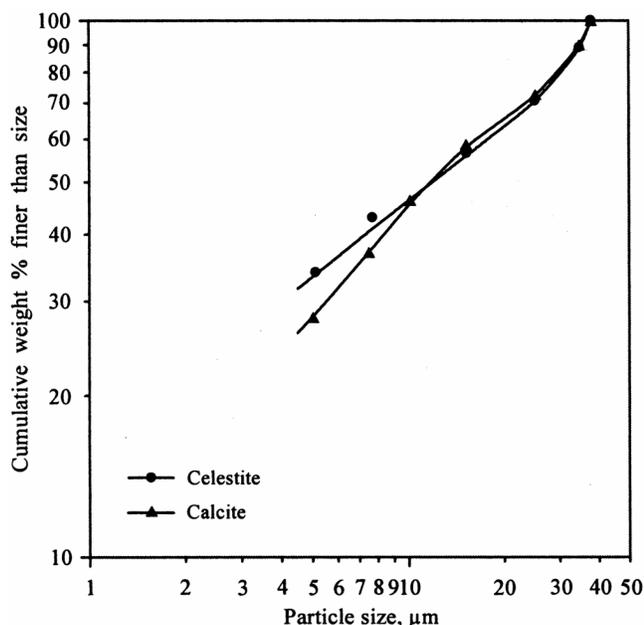| Celestite	SrSO$_4$	CaSO$_4$	Others
	99.06	0.58	0.36
Calcite	CaCO$_3$	SiO$_2$	Others
	99.14	0.30	0.56

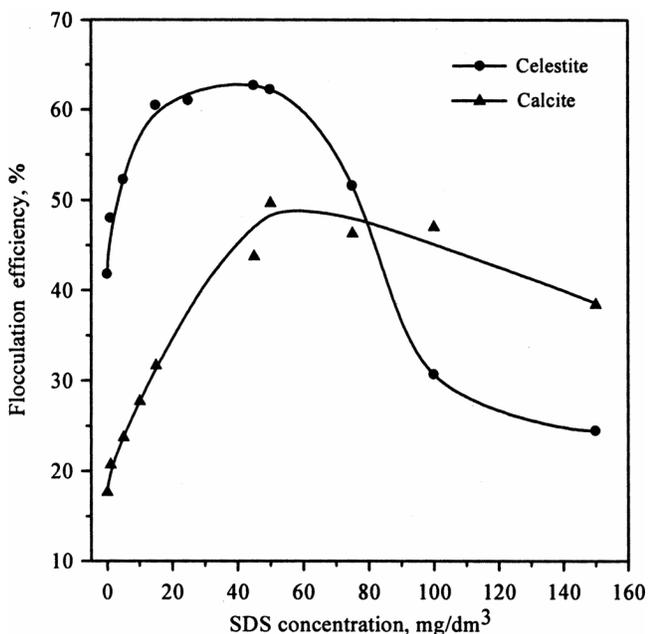Fig. 1—Particle size distributions of the samples used in the experiments.

Fig. 2—Flocculation of celestite and calcite as a function of SDS concentration.

and 5% solutions for modification of pH values. The pH of the suspension was measured by a digital pH meter. Sodium silicate, a dispersant was purchased from Merck. All of these chemicals were of analytical grade. Distilled water was used through out the experimental work.

Flocculation experiments

The flocculation experiments were carried out in a 400 mL cylindrical cell with four baffles using 0.5 g celestite+calcite mixture (1:1) and 300 mL water. The mixture was pre-conditioned for 1 min in order to obtain a well-dispersed suspension. The dispersed suspension, adjusted to the desired pH, was first conditioned at 500 rpm for 3 min and the dispersant was added to the suspension. After 2 min, the suspension was also conditioned (flocculation time) with surfactant for 3 min. Thereafter, the stirring speed was reduced to 160 rpm for 2 min to allow floc growth. After a settling time of 2 min, the supernatant was siphoned off, at a fixed distance of 4.5 cm below the air-liquid interface, by a special system. The settled fractions were filtered, dried, weighed and analyzed by GBC Atomic Absorption Spectrophotometer (AAS) for their SrSO$_4$ content. The flocculation experiments were carried out at 20±1°C. The effectiveness of the selective flocculation experiments was also assessed by calculating separation index (SI) proposed by Sresty and Somasundaran[9]: SI = [(percentage of celestite recovered in the settled portion) + (percentage of calcite rejected in the dispersed portion) − 100]/100.

The flocculation approach to determine the critical surface tension of wetting (γ_c) of minerals was devised recently by Ozkan[10]. This method is based on the decrease of the flocculation of the mineral suspension, with decreasing of the surface tension of the liquids used. The solution surface tension value at which effective flocculation does not occur can be defined as the critical surface tension of wetting (γ_c) value of the mineral. That is, while the effective flocculation of mineral suspension occurs at $\gamma_c < \gamma_{LV}$ (solution surface tension), no effective flocculation takes place at $\gamma_c \geq \gamma_{LV}$.

Results and Discussion

The flocculation of celestite and calcite minerals as a function of sodium dodecyl sulphate (SDS) concentration has been investigated previously[11,12]. As seen in Fig. 2, SDS strongly flocculated the celestite suspension with respect to the calcite suspension and

hydrophobic flocculation of celestite and calcite suspensions increased rapidly with increasing SDS concentration depending on the improved surface hydrophobicity. The adsorption of sodium dodecyl sulphate and sodium dodecyl sulphonate as anionic surfactants onto celestite and calcite surfaces was attributed to chemical adsorption mechanism[13–15]. The studies indicate that marginal adsorption occurs to a certain surfactant concentration and precipitation of the salt (strontium dodecyl sulphate/dodecyl sulphonate, calcium dodecyl sulphonate/dodecyl sulphonate) takes place on the mineral surface beyond such a concentration. On the other hand, it is well known that the hydrophobic flocculation needs hydrophobization of the particles in the suspension and it increases with increasing hydrophobicity or decreasing wettability[10,16–18].

Wettability characteristics of mineral surfaces can be defined in terms of their values of critical surface tension of wetting (γ_c), which is an essential property to achieve selectivity in surface chemistry-based processes such as froth flotation, flocculation, oil agglomeration, solid-liquid separation, and dust abatement[19,20]. Therefore, the critical surface tension of wetting (γ_c) values for the studied minerals were determined for each SDS concentration in relation to flocculation using the flocculation approach[10]. The variations of the γ_c values of celestite and calcite minerals with SDS concentration are shown in Fig. 3. Celestite and calcite have a hydrophilic character whose $\gamma_c > 72$ mN/m, therefore the water spreads completely on the mineral surfaces when no chemical treatment is applied to the mineral surfaces. As seen in Fig. 3, the γ_c values of these minerals decreased sharply when SDS was present in the suspension. At concentrations around 20 mg/dm^3, the γ_c value of celestite mineral was significantly lower than that of calcite mineral. This means that the celestite particles can be flocculated better compared to the calcite particles at these concentrations of the surfactant. This can be of significance when selective flocculation of celestite from celestite-calcite mixtures is practiced because the hydrophobic flocculation technique utilizes differences in wettability of minerals and the γ_c value determines the behaviour of minerals during the wettability−based processes. On the other hand, the flocculation efficiency values did not increase at SDS concentrations than 15 mg/dm^3 for celestite and 50 mg/dm^3 for calcite as seen in Fig. 2. Therefore, the selective flocculation experiments of celestite from

celestite-calcite mixtures were performed at SDS concentration of 15 mg/dm^3, because this concentration has proved to be the most appropriate for celestite[21].

Figure 4 shows the effect of pH on the selective flocculation of celestite from celestite-calcite fines in the presence of 1 g/dm^3 sodium silicate. As seen in Fig. 4, the grade of the flocculated material and separation index increased towards to the pH value of 10.5 and then decreased, whereas the recovery values increased with increasing pH. The effect of pH on the
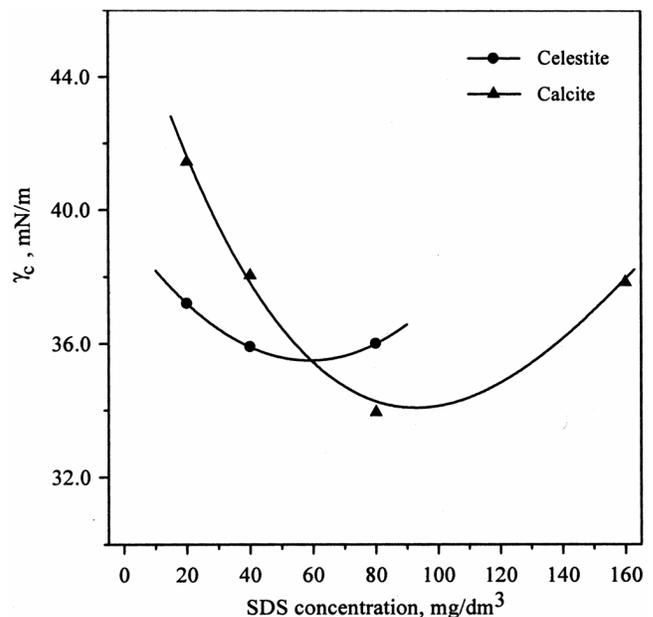

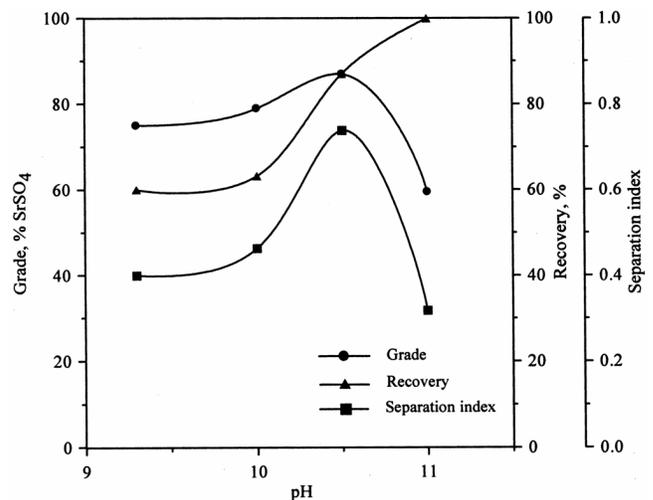Fig. 3—Variations of the γ_c values of celestite and calcite minerals with SDS concentration.

Fig. 4—Effect of pH on the selective flocculation of celestite in the presence of 1 g/dm^3 sodium silicate.

selective flocculation of celestite was also investigated at 0.5 and 2 g/dm³ concentrations of sodium silicate and the similar tendency for the grade, recovery and separation index curves were observed. As a result, the optimum results were obtained at a pH of 10.5, where the grade, separation index and recovery were 85% $SrSO_4$, 0.75 and 85%, respectively. The silicate species [$Si(OH)_{4(aq)}$ and $SiO(OH)_3^-$] are adsorbed on calcite surfaces as a function of pH rendering its surface more hydrophilic[14], therefore flocculation of calcite particles in the suspension is decreased and the celestite grade in the settled fraction is increased, particularly at a pH of 10.5. However, the selectivity in the separation of celestite from calcite particles decreased sharply above the pH value of 10.5. This was probably due to a decrease in the concentration of these silicate species depending on increasing pH.

The variation of the selective flocculation of celestite with sodium silicate concentration is shown in Fig. 5. At low concentrations of sodium silicate, almost all of the celestite particles in the suspension could be flocculated, where the recovery of celestite mineral was higher than 93%. Consequently, sodium silicate exerted a more marked effect on calcite than on celestite at low concentrations as indicated in the literature[2,14]. However, the grade and separation index values were low due to insufficient dispersion of the calcite particles at these dispersant concentrations, but as the concentration of sodium silicate was increased, the grades of the settled fractions and separation index values improved. Thereafter, the grade and separation index curves reached a plateau at concentration higher than 1 g/dm³, i.e., high concentration of sodium silicate did not provide an increase in the grade of the flocculated material. Moreover, the recovery values showed a decreasing trend with increasing dispersant concentration, i.e. sodium silicate also dispersed the celestite particles in the suspension.

Figure 6 shows that effect of flocculation time on the selective flocculation of celestite fines in the presence of 1 g/dm³ sodium silicate. As shown in Fig. 6, the grade of the flocculated material did not change largely after 3 min of flocculation time. Also, the recovery and separation index had high values at the flocculation time beyond 3 min. Consequently, the aggregation was still selective at long times of flocculation, i.e. celestite particles are flocculated whereas most of calcite particles remain dispersed. The grade, separation index and recovery for 5 min of
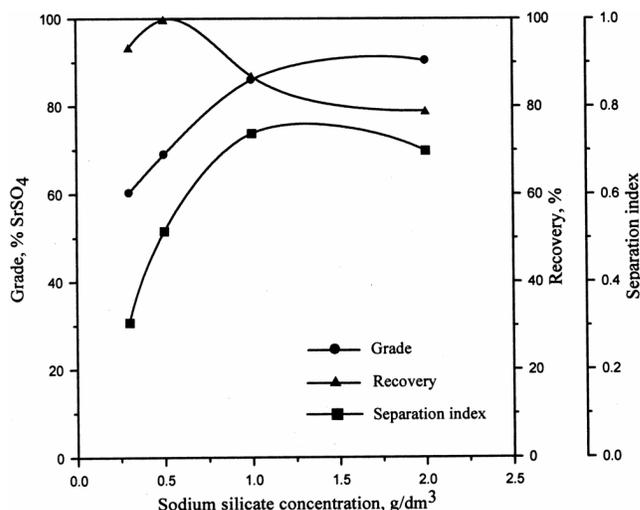

Fig. 5—Effect of sodium silicate concentration on the selective flocculation of celestite at pH of 10.5.
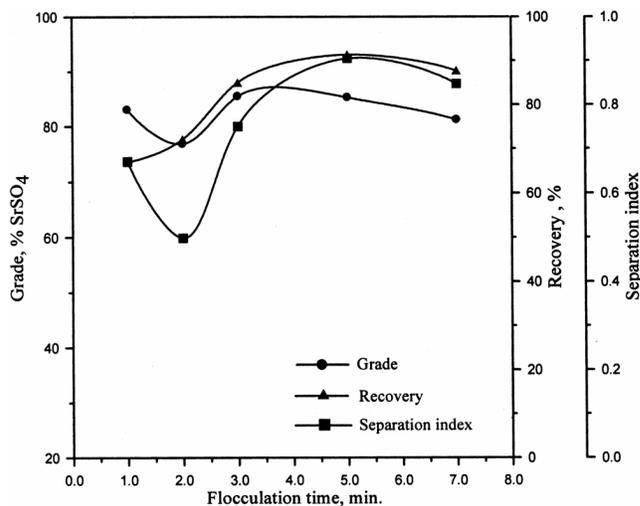

Fig. 6—Effect of flocculation time on the selective flocculation of celestite in the presence of 1 g/dm³ sodium silicate at pH of 10.5.

flocculation time were 85% $SrSO_4$, 0.90 and 90%, respectively. Figure 7 shows the variation of selective flocculation of celestite with settling time at pH 10.5. As can be seen, the grade, separation index and recovery values reached the optimum values at 2 min of settling time. Longer settling times reduced the selectivity by settling calcite along with celestite.

Conclusion

A significant difference between the critical surface tension of wetting (χ_c) values of celestite and calcite minerals at low concentrations of sodium dodecyl sulphate (SDS) has been observed which indicates that celestite can be selectively separated from calcite by hydrophobic flocculation technique.
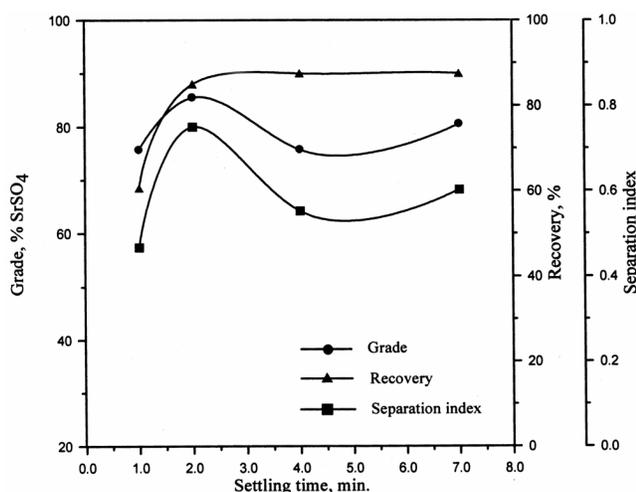
Fig. 7—Effect of settling time on the selective flocculation of celestite in the presence of 1 g/dm^3 sodium silicate at pH of 10.5.

The selective hydrophobic flocculation of celestite from celestite-calcite fines is possible in sodium dodecyl sulphate solutions. The use of sodium silicate as inorganic dispersant significantly improves the selectivity between celestite and calcite minerals.

A concentrate of 85% SrSO$_4$ was obtained with a recovery of 90% and separation index of 0.9 from a mixture containing 50% SrSO$_4$ at optimum conditions, which were as: pH 10.5; SDS concentration, 15 mg/dm^3; sodium silicate concentration, 1 g/dm^3; flocculation time, 5 min; settling time, 2 min. The concentrations higher than the optimum value of sodium silicate did not provide an increase in the grade of the settled material. On the other hand, while the aggregation was selective at long times of flocculation, long settling times caused a low selectivity in the separation of these minerals.

Acknowledgement

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