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## HYDROPHOBIC AGGREGATION OF CASSITERITE BY STIRRING

Fine cassiterite particles ( $\sim 10\ \mu\text{m}$ ) were aggregated by stirring when the particle surfaces were made hydrophobic with sulphosuccinamate surfactant. Optimum collector concentration was different at different pH values. Floc formation started immediately but floc growth required 30–45 min. agitation. The adsorption mechanism of sulphosuccinamate on cassiterite is mainly through electrostatic attraction with involvement of a chemisorption component. Floccs had an open structure which decreases the possibility of entrainment of gangue particles in the floccs.

### 1. INTRODUCTION

Flotation recovery of many minerals decreases as the particle size decreases and fine particles are often removed prior to flotation. In particular, flotation is very inefficient in recovering cassiterite from the  $-6\ \mu\text{m}$  fraction. This fraction is generally removed as slime before flotation (Bulled 1982; Lepetic 1986). About 50% of the tin distribution of the cassiterite flotation feed at Wheal Jane Mine, Cornwall, England was either in the  $-6\ \mu\text{m}$  fraction or specific gravity less than 4.0 fraction which shows considerable locking to silicates (Hobba 1984).

By increasing the apparent particle size it is possible to recover fines by flotation. Hydrophobic aggregation, which requires hydrophobic particle surface (Bilgen and Wills 1991), is the aggregation of particles under high shear conditions.

This paper presents the study on hydrophobic aggregation of fine cassiterite. Adsorption mechanism of sulphosuccinamate, the effect of stirring time and particle size on the flocculation were discussed.

### 2. MATERIAL AND METHODS

#### Flocculation

A cassiterite sample taken from the high grade gravity tin concentrate produced at Wheal Jane, England was used in the experiments. It was ground in a tab mill and mortar and the particles finer than  $10\ \mu\text{m}$  were separated by beaker decantation.

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The experiments were carried out in a 1-litre beaker. A frame with four PVC baffles was inserted in the beaker to provide turbulence in the suspension and to prevent vortex formation and air entrainment when the suspension was stirred at high speeds. A stainless steel single-bladed paddle stirrer was inserted and located about 10 mm above the base of the beaker.

The size distribution was determined by Andreasen pipette.

One litre of double distilled water was added to 1 g of the mineral powder in the beaker and the suspension was stirred for 20 min. at 1500 rpm for wetting and dispersion. The pH was then adjusted to the required pH, the speed decreased to the predetermined speed and the collector was introduced. HCl and NaOH were used as pH regulators and sulphosuccinamate (Allied Colloids surfactant CA 540) as collector. At the end of the test the suspension was syphoned off into the Andreasen pipette while stirring continued.

### Electrokinetic Measurements

Pure stannic oxide produced by Fisons was used without further treatment for electrokinetic measurements.

To prepare the solutions, sufficient amount of the sample and double distilled water were put in a beaker and the pH was adjusted with HCl or NaOH. To ensure particle dispersion, solutions were kept in an ultrasonic bath for 1 min.

A Rank Brothers Micro-Electrophoresis Apparatus Mark II, connected to a TV monitor through a camera was used to measure the electrophoretic mobilities at 25 C in a flat cell. At least 5 particles were timed in each direction at both stationary levels. The mobilities were averaged and the zeta potentials calculated using the Smoluchowski equation (Smith 1973).

## 3. RESULTS

The experiments were carried out by stirring the suspensions for 5, 15, 30, 45 and 60 min. at four different pH values (3.0, 4.0, 5.0 and 6.0) by using five different collector concentrations (0.0, 0.2, 1.0, 3.0 and 5.0 mg/l). Since the stirrer speeds of 250 and 400 rpm were found to be the optimum speeds at pH 3.0 and the other pHs (Bilgen and Wills 1992), respectively, these speeds were kept constant at related pHs.

The results of the experiments carried out at pH 3.0 are given in Fig. 1. The 0.0 and 0.2 mg/l series were not included in the figure because the particle size distributions gave  $d_{57}$ ,  $d_{60}$  rather than  $d_{50}$  (equivalent Stokes' diameter corresponding to 50% by weight undersize). At least 1.0 mg/l CA 540 was required for the flocculation and aggregation started immediately when sufficient amount of collector was present in the pulp. However, it took 30–45 min. to reach equilibrium. Although the  $d_{50}$  decreased when the suspension was stirred longer than 30–45 min. it was still coarser than the  $d_{50}$  of 5 min. for each collector concentration.

At pH 4.0, while the particles were dispersed with stirring in the absence of collector they were aggregated when the collector was introduced (Fig. 2). Maximum

$d_{50}$  was obtained by stirring the suspension 45 min. at 1.0 mg/l CA 540 concentration. The collector concentrations of 3.0 and 5.0 mg/l did not produce a significant increase

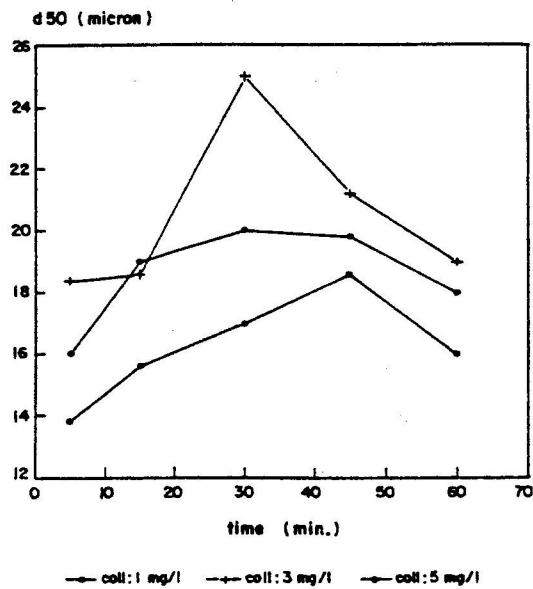


Fig. 1. Variation of degree of aggregation with stirring time at pH 3.0; stirring speed: 250 rpm

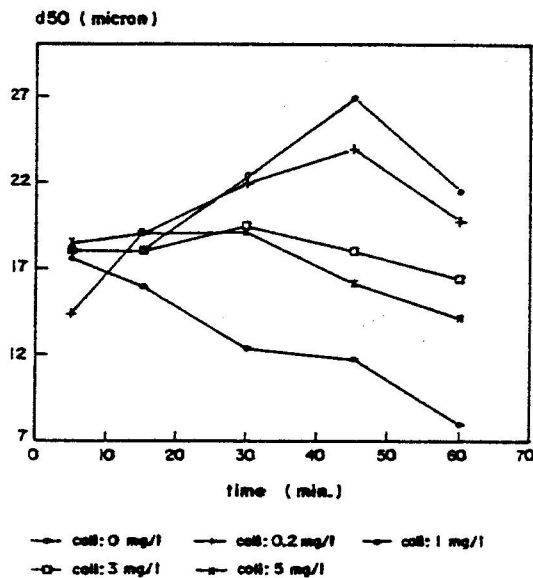


Fig. 2. Variation of degree of aggregation with stirring time at pH 4.0; stirring speed: 400 rpm

in  $d_{50}$  but they kept it relatively same throughout the studied time range. After stirring 60 min.  $d_{50}$  values were 16.4 and 14.2  $\mu\text{m}$  at 3.0 and 5.0 mg/l concentration, respectively, where it was 8.0  $\mu\text{m}$  without collector. The aggregation had taken place immediately, with a sufficient amount of collector at pH 3.0 but it did not happen at pH 4.0. Except for 0.2 mg/l, the  $d_{50}$  showed no change during first 15 min. On the other hand, Fig. 3 shows that the amount of fine particles ( $<4.5 \mu\text{m}$ ) decreased when the amount of CA 540 was more than 0.2 mg/l, indicating the aggregation of these fines.

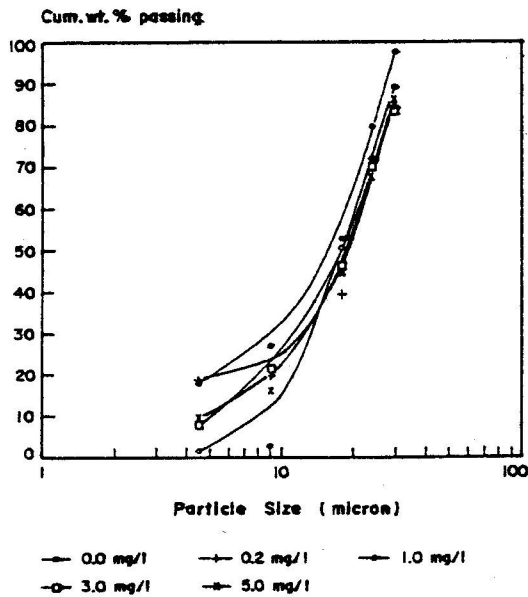


Fig. 3. Particle size distribution at pH 4.0; stirring speed: 400 rpm, time: 15 min.

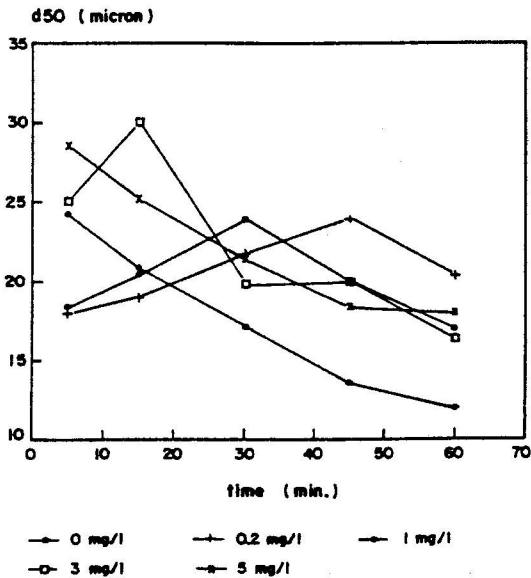


Fig. 4. Variation of degree of aggregation with stirring time at pH 5.0; stirring speed: 400 rpm

However, the absence of a significant shift in  $d_{50}$  indicates that the aggregates were not coarse enough to shift  $d_{50}$ .

The suspension was heavily aggregated without collector within 5 min. by stirring at pH 5.0, the  $d_{50}$  being almost 25.0  $\mu\text{m}$  (Fig. 4). This is not unexpected because pH 5.0 was the pH where maximum coagulation took place (Bilgen 1992). The aggregates were broken up with increased stirring time, resulting in a sharp decrease in  $d_{50}$  values. While 15 min. stirring gave maximum  $d_{50}$  at 3.0 mg/l concentration it was 30 and 45 min. for 1.0 and 0.2 mg/l CA 540, respectively, showing that the stirring times corresponding to maximum  $d_{50}$ s of each concentration level decreased with increased collector concentration.

The particles were more dispersed in first 15 min. at 0.2 and 1.0 mg/l CA 540 than the particles of collectorless suspension. It was only 5.0 mg which produced a  $d_{50}$  greater than the  $d_{50}$  of original suspension after stirring 5 min. The  $d_{50}$  increased with CA 540 above 1.0 mg/l by stirring 5 min. but maximum  $d_{50}$  was still smaller than that of 3.0 mg – 15 min. series which was maximum of this group.

The  $d_{50}$  dropped sharply to 20.0  $\mu\text{m}$  from 30.0 at 3.0 mg/l when the stirring time was increased from 15 to 30 min. Figure 5 shows the size distributions of 0.0 mg – 15 min., 3.0 mg – 15 min. and 3.0 mg – 30 min. series. Fine particle contents of the

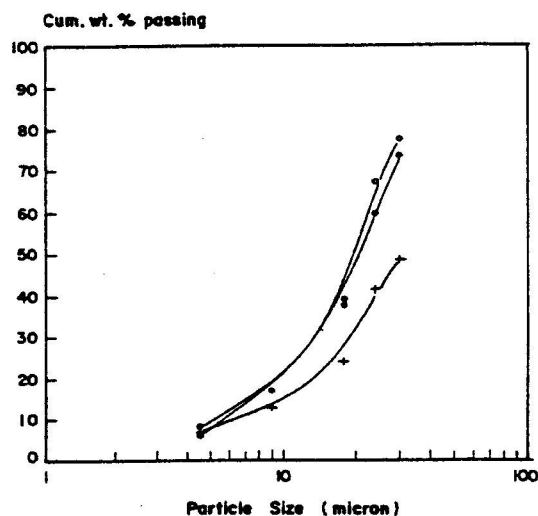


Fig. 5. Particle size distribution at pH 5.0; stirring speed: 400 rpm

—•— 0.0 mg/l, 15 min      —○— 3.0 mg/l, 15 min  
—×— 3.0 mg/l, 30 min

suspensions being the same in three cases indicate that they were aggregated just by stirring so it was the collector's effect for the aggregation of coarser ones. After stirring 15 min. 50% of the aggregates were coarser than 30.0  $\mu\text{m}$ . When the stirring time was increased to 30 min. these coarse aggregates started to disperse. This shows that the energy of impact exceeds the energy of hydrophobic association when the flocs reach a certain size and breaks up the flocs. It may be concluded that during the early stages of flocculation the degree of hydrophobicity is dominant but in the later stages the impact

due to the collision of flocs comes into effect and finally the energy of hydrophobic association and the energy of impact balance each other, so equilibrium is reached.

#### 4. DISCUSSION

Stirred suspensions of cassiterite aggregated more when the particle surfaces were made hydrophobic by sulphosuccinamate collector. The collector concentrations corresponding to maximum aggregations were different at each pH and higher degree of hydrophobic aggregation was obtained with increased acidity. This is apparently related to the degree of hydrophobicity and consequently with the adsorption of sulphosuccinamate on cassiterite surface.

##### Sulphosuccinamate adsorption

Sulphosuccinamate is an anionic collector. The surface chemistry of the adsorption of sulphosuccinamate surfactant on cassiterite has been studied by a variety of experimental techniques. While found to be chemical in nature, sulphosuccinamate adsorption has been shown to be strongly influenced by collector/mineral electrostatic attraction. Maximum adsorption and flotation recovery occurring when the mineral surface is positively charged and hence of opposite sign of the collector (Berger et al. 1980; Salas et al. 1977; Goschin and Solari 1983).

The variation of zeta potential of stannic oxide with pH for different collector concentrations is given in Fig. 6. Zeta potential decreased with increasing collector concentration up to pH 6.0. Furthermore, the decreasing degree of zeta potential of the

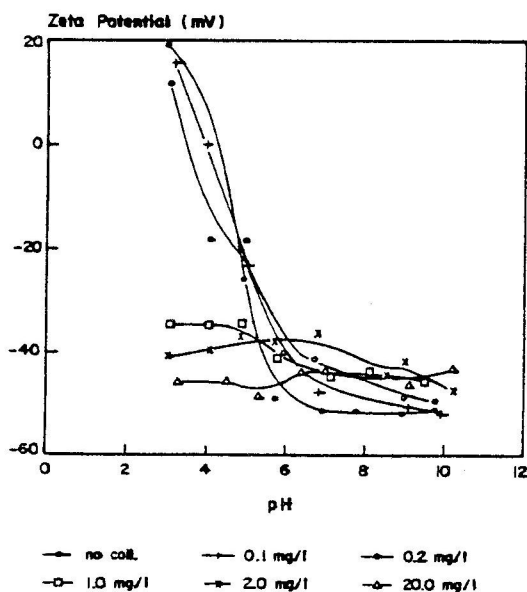


Fig. 6. Effect of collector concentration on zeta potential of stannic oxide

mineral is higher at pH values below the isoelectric point (iep). In this respect sulphosuccinamate physically adsorbed on cassiterite surface.

On the other hand, again up to pH 6.0 at and above 1.0 mg/l collector concentration zeta potential remained same at each concentration. In other words the degree of acidity of the environment did not play a significant role. Moreover, decrease in zeta potential continued at and above the iep; so, it can be said that chemical adsorption also took place.

The charge develops on cassiterite surface because of the adsorption-dissociation of  $H^+$  from the surface hydroxyls (Jaycock et al. 1964), and below the iep the number of  $SnOH_2^+$  sites increases with increased acidity. Therefore, there will be more  $SnOH_2^+$  sites available for the adsorption of collector at pH 3.0 and the number of the sites will decrease with increased pH. This explains higher degree of aggregation at pH 3.0 and also gives evidence for the dominance of physical adsorption. At pH 5.0 and 6.0, the effect of physical adsorption is expected to be less and chemisorption component of the adsorption mechanism will be relatively more effective. Requirement of higher collector concentration at these pHs (e.g. 5.0 mg/l at pH 6.0) together with the electrokinetic measurements may indicate that more amount of the collector should be available in the pulp for a sufficient chemical adsorption.

Electrokinetic behaviour and hydrophobic aggregation of the cassiterite lead to a conclusion that the adsorption mechanism of sulphosuccinamate is a combination of physical and chemical adsorption. Although the lack of quantitative data makes it difficult to say which one is dominant, overall electrokinetic behaviour shows apparent dominance of physical adsorption.

### Stirring time

Hydrophobic aggregation has been reported to be a relatively slow process, requiring long conditioning times (Warren 1975). Our experiments have shown that aggregation started immediately but longer stirring was necessary to reach equilibrium. The  $d_{50}$  shifted to 18.4  $\mu m$  from 4.5 after 5 min. stirring with CA 540 concentration of 3.0 mg/l at pH 3.0. However, the system reached equilibrium after 30 min. stirring, where the  $d_{50}$  was 25.0  $\mu m$  (Fig. 1). Although larger flocs were broken up with longer stirring because they possess higher kinetic energy than the smaller ones and the energy of impact during collision exceeds the energy of hydrophobic association the aggregation was still better than that at 5 min. At pH 4.0, increase in the  $d_{50}$  was observed within 15 min. but as seen from Fig. 3 the aggregation had already started. These results support the suggestion that to commence or accelerate the aggregation of fine particles with high surface charge it is probably necessary to form seed flocs initially (Bilgen and Wills 1992).

Stirring time varied from 5 to 45 min., depending on pH. Warren (1982), found the optimum stirring time for cassiterite of  $\sim 6 \mu m$  as 30–60 min. Our sample was slightly coarser ( $\sim 10 \mu m$ ) than the sample Warren used. Very narrowly sized ultrafine scheelite was found to require stirring as long as 90 min. (Warren 1975), but 5 min. agitation was sufficient for scheelite sample which was not narrowly fractioned (Sivamohan 1988). Slime coating of ultrafine scheelite particles to coarser ones took place within

shorter time (Warren 1975a). Quartz particles of  $-5\ \mu\text{m}$  aggregated with the coarse size fraction of  $-38+20\ \mu\text{m}$  within 15 min. (Raju et al. 1991). Samygin et al. (1968) found that the adhesion rate of fines to coarse particles to be  $10^3$ – $10^4$  as high as the rate of cohesion between the fines. Evidently, particle size distribution affects the agitation time in hydrophobic aggregation.

### Floc structure

From the observation of the samples under binocular microscope before and after the agitation it was seen that the particles were aggregated after stirring but they were not closely packed. The flocs had an open structure. When compared to the collectors with shorter hydrocarbon chains such as steyene phosphonic acid which has a hydrocarbon chain of  $\text{C}_6\text{H}_5$  (Jarret and Warren 1977), sulphosuccinamate with a chain of  $\text{C}_{18}\text{H}_{37}$ , is expected to produce more open floc structure.

Entrainment of gangue particles in the flocs is not desired but inevitable. However, the possibility of entrainment should be more for closely packed flocs. Then, loose floc structure becomes an advantage rather than a disadvantage.

Hydrophobic aggregation is the first step of recovering fine particles. The aggregates produced should be tough enough to withstand the turbulence in the following mineral processing operations. Therefore, floc strength is more important than the floc structure. Conditioning hydrophobic particles under high shear conditions has been reported to increase flotation recovery (Senior and Poling 1986; Subrahmanyam et al. 1990; Song and Lu 1990; Bulatovic and Salter 1989), indicating that the flocs were strong enough to resist the turbulence in flotation. Our observation, where shear flocculated material was stirred as long as 45 min. in a Denver laboratory flotation machine at 1500–2000 rpm, supports these reports. Besides this, column flotation following shear flocculation can be a suitable alternative method if the turbulence in conventional flotation becomes a handicap for the shear flocs.

## 5. CONCLUSIONS

Fine cassiterite particles hydrophobised with sulphosuccinamate were aggregated by stirring. Hydrophobic aggregation is a relatively slow process. Aggregation starts immediately but longer stirring is necessary for floc growth.

The adsorption mechanism of sulphosuccinamate on cassiterite surface is a combination of physical and chemical adsorption.

Hydrophobic aggregation has potential for the recovery of fine cassiterite particles which otherwise report to tailings.

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Drobne klasy ziarnowe ( $\sim 10 \mu\text{m}$ ) kasytetytu były agregowane podczas mieszania. Ziarna materiału były wcześniej zhydrofobizowane przy użyciu surfaktanta sulfonowo-bursztynianowego. Optymalne stężenie kolektora było różne dla różnych wartości pH. Tworzenie się flokuł rozpoczynało się natychmiast po rozpoczęciu procesu jednak wzrost flokuł wymagał czasu 30–45 min agitacji. Stwierdzona, że mechanizm adsorpcji sulfonobursztynianu na kasyterycie ma przede wszystkim charakter przyciągania elektrostatycznego zawierającego w sobie składową chemisorpcji. Otrzymane flokuły miały luźną strukturę dzięki czemu charakteryzowały się zmniejszoną tendencją przechwytywania do swego wnętrza cząstek skały płonnej.