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SHEAR FLOCCULATION OF COARSE FLUORITE AND EFFECT OF DIVALENT IONS

In this study, possible recovery of coarse fluorite by shear flocculation, and the effect of divalent ions on the fluorite flocculation were investigated. The degree of flocculation was determined by measuring the amount of settled particles and the turbidity of the pulp. The effects of pH, collector concentration, flocculation time, and stirrer speed on flocculation were examined. It was found that Mg^{2+} increased the aggregation while Ba^{2+} decreased, and Ca^{2+} did not show any influence.

INTRODUCTION

Shear flocculation is the aggregation of fine particles by stirring after hydrophobization with a suitable reagent addition. This method has advantages for flotation systems since the aggregates are hydrophobic and thus suitable for direct recovery by froth flotation (Warren 1981). It is well known that the factors affecting the degree of shear flocculation are zeta potential, hydrophobicity, collector concentration, stirrer speed, and stirring time (Warren 1975 and 1982; Yarui and Daxin 1986; Sivamohan 1988; Lu et al. 1988; Sivamohan and Cases 1990; Subrahmanyam et al. 1990; Raju et al. 1991; Bilgen and Wills 1992). Since the reagents used in flotation are also used in shear flocculation both methods show some similarities. However, kinetics and dynamics of these two systems can differ at the same time. Detailed studies about the shear flocculation of fine sizes ($-10\ \mu m$) and effect of divalent ions on flotation exist in literature but application of shear flocculation to coarser particles and the effect of divalent ions on shear flocculation have not been taken into consideration yet.

The present work deals with the shear flocculation of fluorite at relatively coarse size ($-37\ \mu m$) and the effect of Ca^{2+} , Mg^{2+} , Ba^{2+} ions on shear flocculation.

MATERIAL AND METHODS

A fluorite ore taken from Beylikahir district of Sivrihisar, Turkey was concentrated to 92.9% CaF_2 content by shaking table, and magnetic separation. The close control size reduction was done by Retsch centrifugal ball mill to $-37\ \mu m$.

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Shear Flocculation Experiments

The experiments were carried out in an 800 ml cell using 1.20 g fluorite sample with distilled water. The cell had 4 baffles which provided intensive agitation. The suspension was stirred by a stainless steel single bladed paddle stirrer with variable speed.

The degree of flocculation was determined by measuring the amount of settled particles and turbidity of the pulp. La Motte Model 2008 Turbidimeter was used for this purpose. The initial turbidity (T_i) of the suspension was measured after adjusting the pH of the pulp while the final turbidity (T_f) was determined at the end of the experiment as explained below. Finally, the turbidity ratio T_f/T_i was calculated.

At the end of the flocculation experiment the suspension was transferred into a graduated cylinder, the height of the pulp being 34.5 cm, and agitated by inverting the cylinder 6 times. The particles were allowed to settle for 1 minute and the supernatant was siphoned off at 7 cm from the bottom of the cylinder. The turbidity of this unsettled material was measured to find T_f . The amount of settled material was calculated as follows;

$$\text{Settled material (\%)} = W_s/W_i \times 100$$

where W_i and W_s are the weights of the feed and settled material, respectively.

A lower turbidity ratio and higher percentage of settled material values indicate a successful aggregation.

Electrokinetic Potential Measurements

The zeta potentials were measured by using a Rank-Brothers Micro-Electrophoresis Apparatus Mark II with flat cell and palladium electrodes. A stock solution of fluorite particles of $-10 \mu\text{m}$ were prepared with double distilled water for the electrokinetic measurements. The solutions prepared were kept in an ultrasonic bath before the measurements for 1 minute to ensure the particle dispersion.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on shear flocculation of fluorite was investigated in the pH range from 3.4 to 11.0. NaOH or HCl were used to adjust the pH of pulp. The results are shown in Fig. 1. The comparison of these results with the results of zeta potential vs. pH (Fig. 2) shows that maximum settling, i.e., the highest shear flocculation, and minimum turbidity ratio were at around isoelectric point of fluorite.

Effect of Collector Concentration

Adsorption of negative oleate ion on fluorite surface made an i.e.p. at pH 3.5–4.5 depending on collector concentration. Figure 3 shows the effect of Na-oleate concentra-

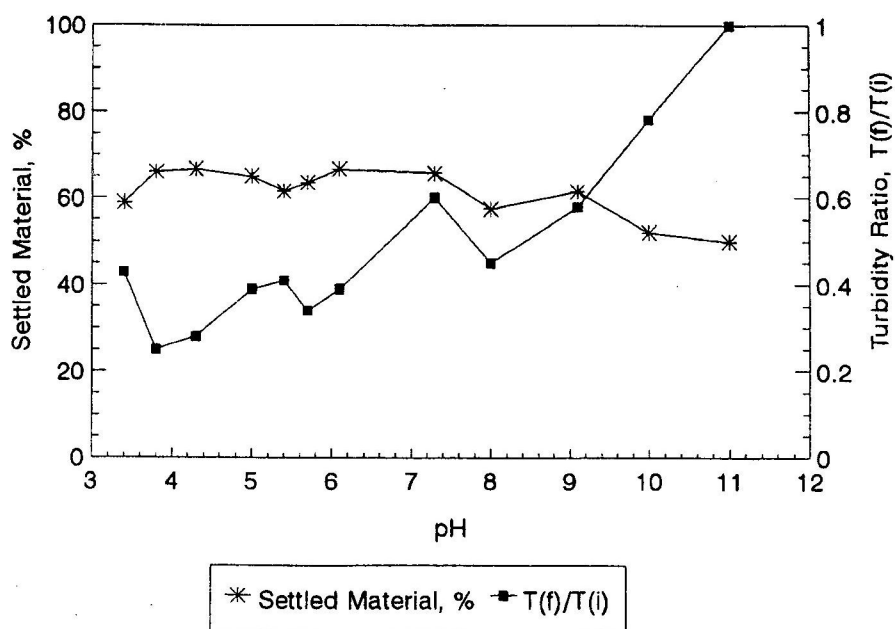


Fig. 1. The effect of pH on the shear flocculation of fluorite

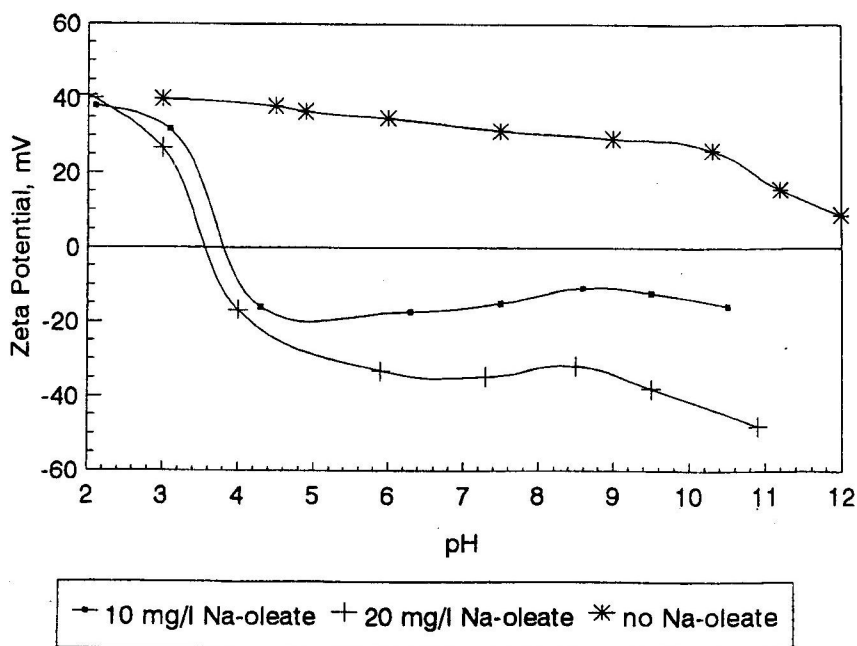


Fig. 2. The effect of different concentrations of Na-oleate on the zeta potential of fluorite

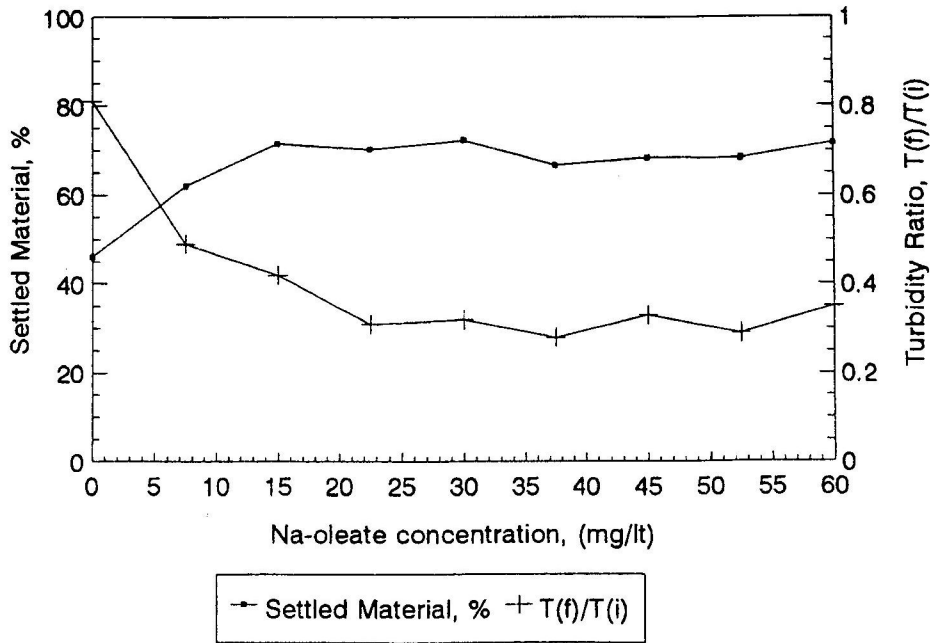


Fig. 3. The effect of Na-oleate concentration on the shear flocculation of fluorite

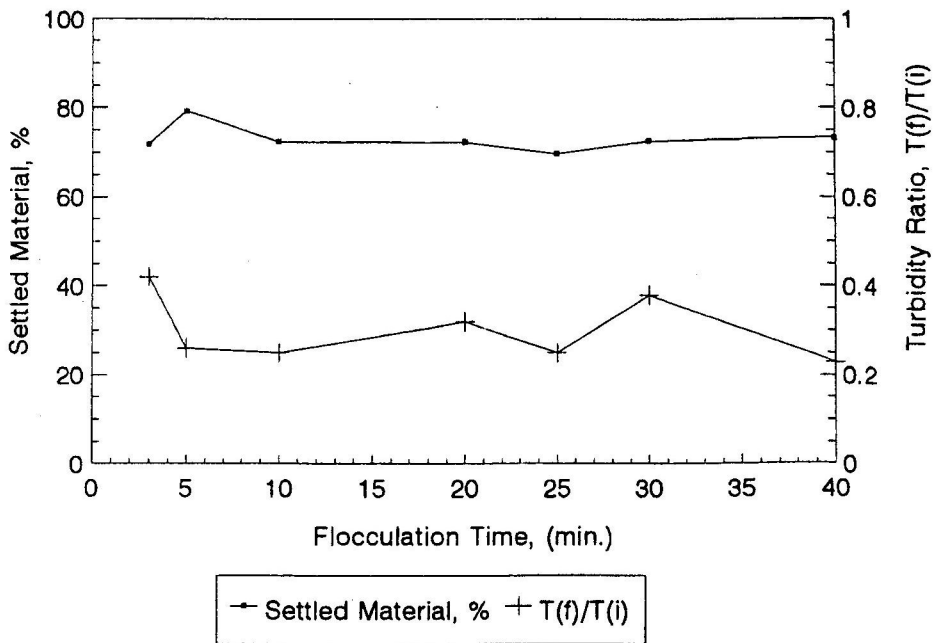


Fig. 4. The effect of flocculation time on the shear flocculation of fluorite

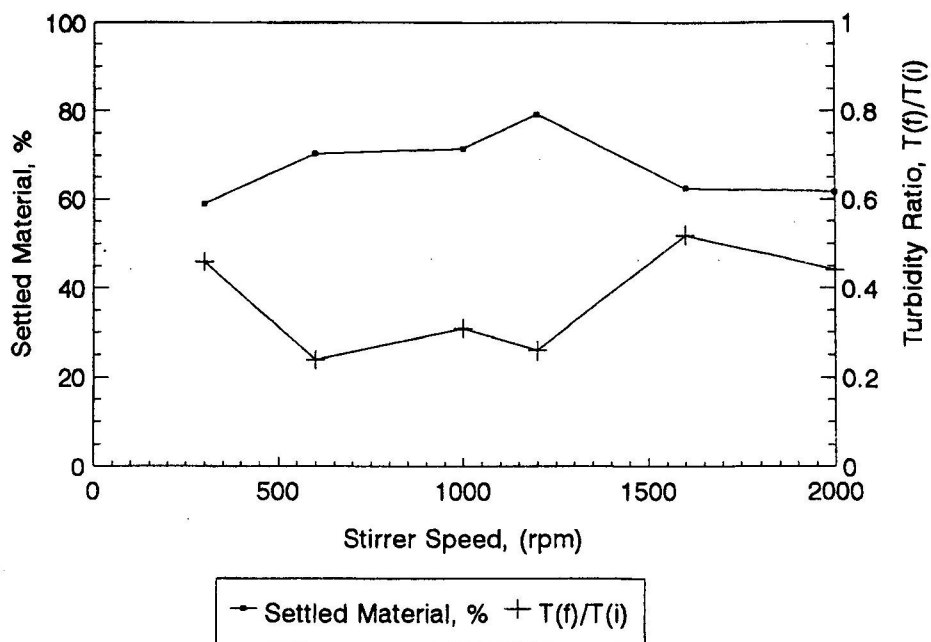


Fig. 5. The effect of stirrer speed on the shear flocculation of fluorite

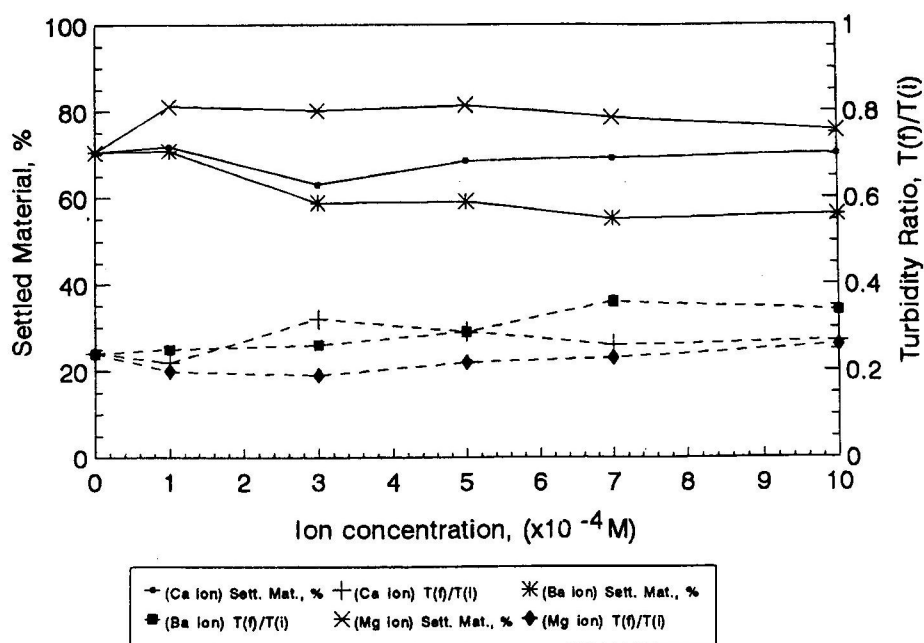


Fig. 6. The effect of divalent ions on the shear flocculation of fluorite

tion on shear flocculation of fluorite. The use of Na-oleate increased the amount of settled material more than 25%. These results show the importance and necessity of collector even for shear flocculation of coarse sized particles. The flocculation increases with collector concentration up to a certain level and then remains almost constant, showing similarities with the results of Raju et al. (1991).

Effect of Flocculation Time

The shear flocculation of fluorite was also investigated as a function of flocculation time. The results show that (Fig. 4) flocculation is a rapid process, starting immediately and reaching equilibrium within 5 minutes. Although longer flocculation time causes breaking of some flocs, the amount of flocculated material indicates the strength of flocs. This is consistent with the work of Sivamohan (1988) where 80–90% of shear flocculation was completed within 5 minutes.

Effect of Stirrer Speed

In another set of experiments the effect of stirrer speed on the the settling rate and turbidity was examined (Fig. 5). As seen from Fig. 5, shear flocculation is increasing with stirrer speed up to 1200 rpm above which it is decreased since energy of impact exceeds the energy of hydrophobic association, leading to particle redispersion.

Effect of Divalent Ions

The effect of foreign ions on flotation is known to be important. To investigate the effect of ions on the shear flocculation behaviour of fluorite, experiments were carried out in the presence of Ca^{2+} , Mg^{2+} , and Ba^{2+} ions.

Ca^{2+} ion which is the potential determining ion for fluorite, affected neither the flocculation (Fig. 6) nor the electrokinetic behaviour of fluorite (Fig. 7) significantly. Studies have shown that Ca^{2+} has a depressive effect on flotation of fluorite (Ghaemi 1995; Raatz 1992; Hanna and Gruner 1972) due to the formation of insoluble salts that decrease the available oleate ion (Gallios and Matis 1992). However, Iskra et al. (1973) have found that the addition of 10^{-4} M CaCl_2 had practically no influence on the oleate adsorption on fluorite. All of these together with our results support the suggestion of Iskra et al. (1973).

Although a significant change in zeta potential of fluorite was not observed with Mg^{2+} ion (Fig. 7), the presence of Mg^{2+} in the solution positively affected the flocculation. The amount of settled material was increased by 10% (Fig. 6). Hanna and Gruner (1972) observed that the flotation recovery increased by ca. 10% with MgCl_2 addition at pH 6.5. Ca^{2+} ion exchange by Mg^{2+} (Raatz 1992) may also create a surface whose affinity to oleate is higher, resulting in better collector adsorption and shear flocculation.

The effect of Ba^{2+} ions on shear flocculation and zeta potential of fluorite is shown in Fig. 6 and 7, respectively. The increase in zeta potential of fluorite with BaCl_2 concentration indicates the specific adsorption of Ba^{2+} on fluorite. About 10% decrease in

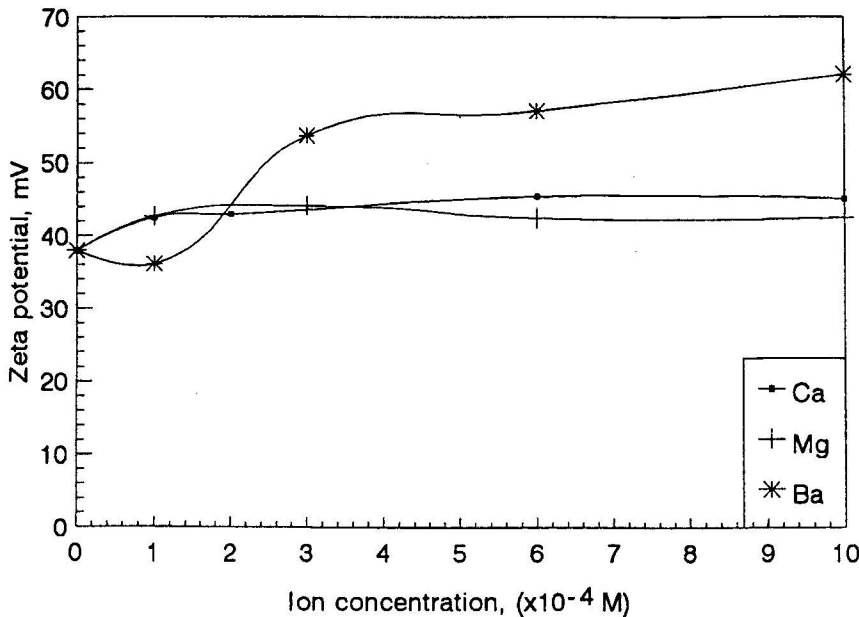


Fig. 7. The effect of divalent ions on the zeta potential of fluorite

the flocculation must, then, be due to high repulsive forces between the fluorite particles rather than the formation of insoluble salts with barium.

CONCLUSIONS

1. Shear flocculation of fluorite at relatively coarse size ($\sim 37 \mu\text{m}$) is possible in aqueous solutions of sodium oleate.
2. Zeta potential is one of the most important parameters influencing the shear flocculation. Best results were obtained when zeta potential was minimum.
3. For an effective shear flocculation even at coarse size ($\sim 37 \mu\text{m}$), a reasonable amount of collector is necessary.
4. Shear flocculation is a rapid process, 80% of flocculation completed within 5 minutes.
5. Shear flocculation of fluorite is possible at a stirrer speed range of 600 rpm to 1200 rpm with a maximum flocculation of 80% at 1200 rpm.
6. Divalent ions affected the shear flocculation of fluorite. Mg^{2+} increased the aggregation while Ba^{2+} decreased. Ca^{2+} did not show any influence on the aggregation.

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Przedstawiono wyniki badań agregacji grubych ziarn fluorytu wskutek intensywnego mieszania. Określono stopień flokulacji przez pomiar ilości sedymentujących ziarn i mętności pulpy. Badano również wpływ pH, stężenie kolektora oraz czasu i szybkości mieszania na flokulację. Stwierdzono, że jony Mg^{2+} zwiększają flokulację, jony Ba^{2+} ją zmniejszają, jony Ca^{2+} natomiast nie wpływają na badany proces.