

Selective flocculation of fines

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Abstract: A number of factors that affect selective flocculation of fines have been identified and the effect of some of parameters on process behavior has been explained with the help of a few case studies. Experiments with francolite-montmorillonite and francolite-palygorskite mixtures indicated that francolite recovery depends on pH and the type of dispersant. The results showed that removal of multivalent ionic species on clay mineral surfaces seems to enhance flocculation, and separation efficiency increases as Ca^{2+} ions are removed from the surface. When chalcopyrite and quartz are present together, it is however necessary to clean the flocs obtained to remove entrapped quartz.

Key words: flocculation; clay minerals; phosphate minerals; dispersant

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1 INTRODUCTION

As the earth's resources are being consumed steadily and as demand for mineral products continues to increase, the need to utilize low-grade ores more efficiently has become more severe. This indeed results in the generation of a large quantity of fine particles during mining and processing of such ores. Large amounts of fine mineral values are discarded currently as techniques to recover ultra-fine minerals are not adequate. Conventional processing techniques such as flotation are not efficient to process fines due to the intimate mixing of values and gangue materials. This is especially true in the case of fines in the sub-micron range. Also, these fines cannot be disposed off easily as it results in environmental hazards and in some cases, waste of useful land.

Thus, there is a great need to develop processes to utilize the fine ores and selective flocculation has shown some promise and potential in this regard. The objective of the present communication is to elucidate the basic principles and mechanisms of selective flocculation, identify the critical process parameters, present results obtained for materials of industrial importance and suggest directions for future research.

2 SELECTIVE FLOCCULATION

This process involves selectively flocculating the desirable/undesirable mineral from a mixture of minerals. Though this appears simple, it is quite complex in nature. Selective flocculation has to always deal with a binary or even a multicomponent mixture of materials. Also, long chain polymers are normally used as flocculants. So, it is necessary to understand not only the interactions between particles, polymers and the solvent but also the interactions between different particles in the pulp. The surface chemistry of different materials in the presence of each other becomes an important factor in this situation.

2.1 Basic principles and mechanisms of separation

The basic principles of selective flocculation are actually similar to those of the conventional selective flotation process. First, the individual mineral particles need to be liberated and dispersed, then a reagent is required that can selectively adsorb onto one or several of the mineral surfaces. So, the two main criteria for selective flocculation are dispersion of the fines and selective polymer/reagent adsorption.

When particles are in suspension, they collide either due to the Brownian motion or due to external forces induced by agitation, magnetic field etc. The probability of aggregation during such collisions is determined by the nature of interactions between the particles. Attractive interactions arise due to London-Van der Waals type of forces whereas repulsive interactions arise generally due to the electrostatic forces. There is always a net total energy of interaction and it is necessary that the following conditions are met so that selective aggregation can take place:

1) All types of particles should carry the same charge so that there will be no heterocoagulation between them. Repulsive energy should be larger than the energy of attraction between different particles.

2) Charge on the particles to be aggregated should be such that repulsive energy between them should be less than that of the attractive energy.

Floc formation takes place by either of the following three mechanisms:

1) Reduction of electrostatic repulsion between particles;

2) Formation of polymer bridges between particles;

3) ion-exchange reactions between polymers and particle surfaces.

Selectivity in flocculation can be achieved by any one or combination of the following treatments:

1) Altering the surface potential of different minerals;

2) Incorporating specific functional groups into

the polymer chain;

- 3) Controlling flocculation/polymer-particle interaction time;
- 4) Selective polymer adsorption;
- 5) Coating impurities or specific ions on solid surfaces.

2.2 Important process parameters

Some of the important factors that affect selective flocculation are

- 1) size distribution of colloidal particles;
- 2) shape and surface heterogeneity of particles;
- 3) concentration, molecular weight distribution and charge density of the polymer;
- 4) functional groups present on the polymer chain;
- 5) suspension pH, temperature, density and viscosity;
- 6) dissolved ionic species in solution;
- 7) speed of agitation and type of impeller.

3 CASE STUDIES

We now present a few examples of selective flocculation in which the effect of some of the factors mentioned above is discussed in detail.

3.1 Selective flocculation of sulfides

As indicated earlier, selective flocculation of a mixture of minerals is significantly different from that of a single mineral. One of the reasons for this is the dissolution, precipitation/readsorption of mineral species from one mineral onto another. When mineral fines are suspended in solution, species such as Cu^{2+} , Ni^{2+} , Fe^{2+} and S^{2-} present on the surface of a mineral can dissolve and then precipitate/readsorb on another mineral surface. It has been reported that specifically adsorbing ions can change and/or even reverse the zeta potential of a mineral and thereby cause heterocoagulation as well as enhanced polymer flocculation^[1-3]. Acar and Somasundaran^[4] studied separation of chalcopyrite and pentlandite from a mixture of these minerals using polymers such as polyacrylamide (PAM) and polyethylene oxide (PEO). Flocculation was observed both in the presence and absence of the polymer. Though the presence of PEO enhanced the efficiency of overall flocculation, the separation efficiency was not significant.

Electron spectroscopy for chemical analysis (ESCA) and electrophoretic mobility measurements showed that nickel ions present on the chalcopyrite surface and copper ions present on the pentlandite surface cause nonselective adsorption of polymer. The amount of dissolved species was significant especially under the acidic pH conditions. In order to overcome this problem diphenylguanidine (DPG) was introduced into the system so that it can form complexes

with the dissolved species.

Experimental results obtained from the studies on selective flocculation of synthetic mixtures of chalcopyrite and pentlandite using PEO and DPG are presented in Fig. 1. It can be observed from Fig. 1 that flocculation of the mixture is enhanced by the presence of DPG and PEO together, particularly under acidic pH conditions.

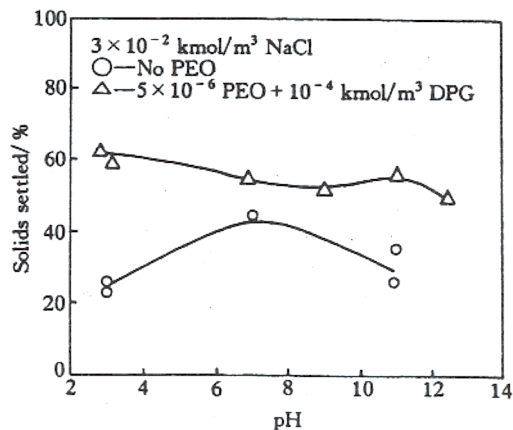


Fig. 1 Flocculation of chalcopyrite and pentlandite mixture

3.2 Separation of phosphate minerals from clay minerals

Florida phosphatic clay is disposed off in enormous quantities though it is rich in phosphate minerals and causes serious environmental hazards. The waste is in the form of fine slimes and because of this the clay minerals such as montmorillonite and palygorskite are intricately mixed with the phosphate mineral, francolite. Traditional separation processes such as flotation are extremely inefficient because the slimes are in the micron and sub-micron size range. Another problem is the presence of organic matter and cementing materials such as oxides and hydroxides of Al and Fe. Andersen and Somasundaran^[5] studied this separation problem by preparing synthetic mixtures of clay and phosphate minerals and using the naturally occurring slimes. After initial screening experiments, polyacrylic acid with an average molecular mass of 3 million was found to be best suited for polymer flocculation. Sodium silicate and sodium tripolyphosphate were used as dispersants. Electrokinetic measurements indicated that all the pure minerals as well as the natural slimes are negatively charged in the entire pH range (4~11) studied.

Experiments with francolite-montmorillonite (Fig. 2) and francolite-palygorskite (Fig. 3) mixtures indicated that francolite recovery depends on pH and the type of dispersant. For both the mixtures, recovery decreased at high pH, where it is likely that electrostatic repulsion is inhibiting polymer adsorption and flocculation. The behavior of the two systems with respect to francolite recovery at lower pH values

was quite different. In the case of montmorillonite, gel formation was observed after polymer addition, resulting in a decrease in the recovery. In the case of palygorskite, recovery increased with decreasing pH. The floc grade in both systems is hardly affected by pH. The difference between the two systems can be explained by examining the differences in the crystal structure of the two clay minerals. Due to the edge face charge characteristics, the plate-shaped montmorillonite particles can form a card-house structure in suspension. This prevents the clay particles as well as the francolite particles from settling which results in low recovery of francolite. The needle-shaped palygorskite crystals cannot form such an expanded structure in the suspension. So these particles flocculate and settle together with francolite. For both the systems, maximum separation occurred in the pH range of 9~9.5 with sodium silicate as the dispersant.

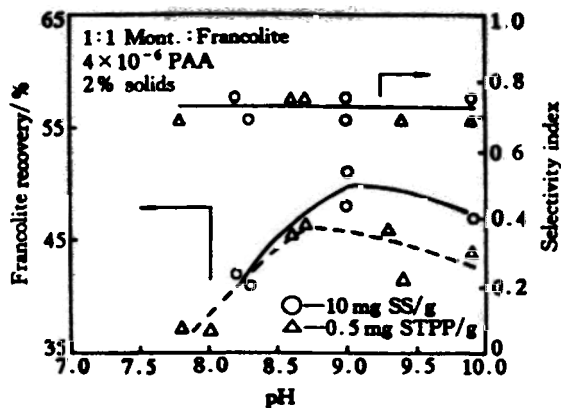


Fig. 2 Separation results for francolite-montmorillonite mixtures using polyacrylic acid

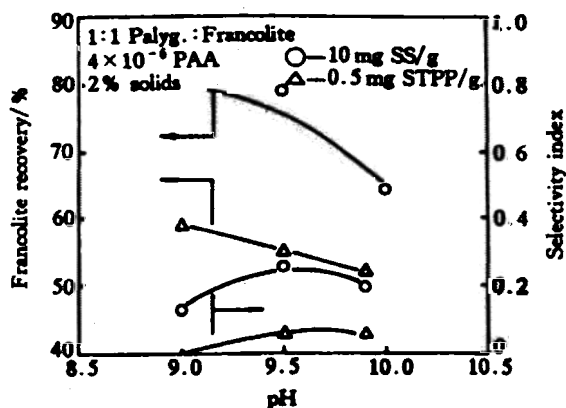


Fig. 3 Separation results for francolite-palygorskite mixtures using polyacrylic acid

The separation achieved in the above experiments was far from the maximum that can be achieved theoretically. Pure francolite contains 32% P_2O_5 . The feed had 16% P_2O_5 while the best that could be achieved was 28% in the presence of mont-

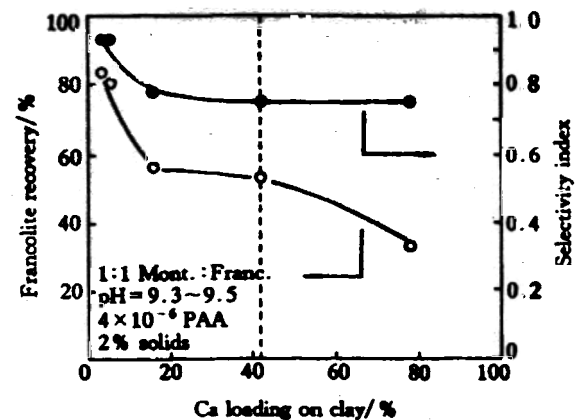


Fig. 4 Effect of the presence of exchangeable calcium and sodium on separation of francolite-montmorillonite mixtures by polyacrylic acid

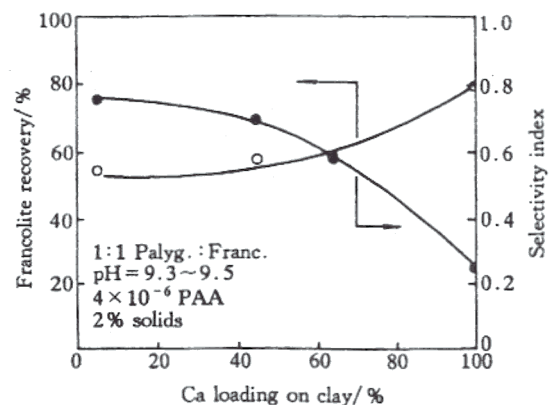


Fig. 5 Effect of the presence of exchangeable calcium and sodium on separation of francolite-palygorskite mixtures by polyacrylic acid

Selective flocculation of natural phosphatic slimes was attempted next. Sedimentation experiments indicated that the as-received natural slimes flocculated and settled at pH 7 within one-half hour. But, selective flocculation experiments, under the optimum conditions obtained for synthetic mixtures, did not result in any specific separation of francolite. The

main reason for this appeared to be the presence of cementing materials such as organic matter and inorganic (mainly Al and Fe) hydroxide precipitates which inhibit dispersion of particles. Al and Fe were found to be 10 times more abundant in natural slimes than in pure clay minerals. The organic and inorganic matter causes aggregation of particles. In addition, the Al and Fe compounds might be causing non-selective polymer adsorption also.

3.3 Beneficiation of mineral slimes

The type of functional group on a polymer chain can also modify the behavior of flocculation. Sresty and Somasundaran^[6] studied selective flocculation of chalcopyrite-quartz system in the presence of hydroxypropylcellulose xanthate. Hydroxypropylcellulose was modified to incorporate the xanthate functional group, as it is known that xanthates adsorb selectively on heavy minerals such as chalcopyrite, galena and sphalerite. Fig. 6 shows the variation of percent solids settled as a function of xanthate concentration. It can be observed that chalcopyrite flocculates and settles very well whereas quartz stays suspended in solution. When the two minerals were present together, it was however necessary to clean the flocs obtained to remove entrapped quartz.

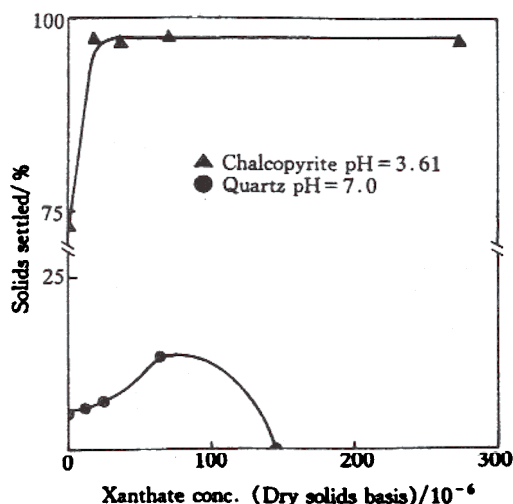


Fig. 6 Percentage of chalcopyrite fines and quartz fines settled as a function of concentration of hydroxypropylcellulose xanthate (Reagentizing time, 30 s; settling time, 45 s)

4 CONCLUSIONS

Selective flocculation has been found to be a feasible technique for the separation of sulfides, oxides and phosphatic minerals. However, dissolution of mineral species has a significant impact on the selectivity of polymer adsorption. This problem however,

can be overcome by introducing a complexing agent into the system.

A number of factors that affect selective flocculation of fines have been identified and the effect of some of these parameters on process behavior has been explained in this paper with the help of a few case studies.

It has been found^[7] that polymer conformation at the solid-liquid interface has a significant impact on flocculation. It is necessary to understand how the conformation changes depending on the mineral surface heterogeneity and take advantage of that for selective adsorption. Also, there is a need to develop new processing techniques to remove undesirable ions (for example, Ca^{2+} ions in the case of Florida phosphatic slimes) present on the mineral surfaces in multicomponent mixtures of minerals.

Hydrodynamics will play a major role in the case of large scale industrial separation operations. However, very little research has been done in this direction. It needs to be seen as to how existing knowledge on mixing of fluids can be extended for particulate suspensions.

Even though a number of mathematical models have been proposed in the literature, very few take polymer adsorption into account. It is important to incorporate knowledge on all aspects of flocculation in order to arrive at meaningful conclusions.

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