FLOTATION OF LOW GRADE MUSSORIE PHOSPHATE ORE

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ABSTRACT

Separation of Mussorie rock phosphate (P₂O₅ = 20%) from Uttar Pradesh, India, containing pyrite, calcite and other carbonaceous impurities by flotation has been successfully attempted to upgrade the phosphate values. Based on Hallimond cell flotation results of single and synthetic mineral mixtures of calcite and apatite using oleic acid and potassium phosphate, conditions were obtained for the separation of calcite from apatite which is considered to be the most difficult step in the beneficiation of calcareous phosphates. Further studies using 250 gms of the mineral (-60 +150 and -150 mesh fractions, deslimed) in laboratory size Fagergren subaeration machine employed a stagewise flotation viz. carbonaceous materials using terpineol, pyrite using potassium-ethyl xanthate and calcite using oleic acid respectively. Separation was, however, found to be unsatisfactory in the absence of a depressant.

Among starch, hydrofluosilic acid and dipotassium hydrogen phosphate, which were tried as depressants for apatite in the final flotation stage, dipotassium hydrogen phosphate proved to be superior to others. However, the tests with the above fractions did not yield the required grade. This was possibly due to insufficient liberation of the phosphate mineral from the ore body and different experimental conditions due to scale up operations. Experiments conducted using -200 mesh deslimed fractions has yielded an acceptable grade of 27.6% P₂O₅ with a recovery of about 60%. The results have been explained in terms of the specific adsorption characteristics of phosphate ions on apatite and the liberation size of the mineral.

INTRODUCTION

Mussorie rock phosphate from Uttar Pradesh, India contains about 19-20% P₂O₅. It is necessary to upgrade its phosphate values to about 28-30% for economic use of this ore in the fertilizer industry. Siliceous phosphate ores are generally beneficiated on an industrial scale by a two-stage flotation technique using amines and fatty acids, respectively for silica based gangue and phosphates. On the other hand, Mussorie rock phosphate which is calcareous in nature (containing about 15% calcite) appears not to be amenable to such a flotation treatment. Mineralogical and chemical analysis of a typical sample of this ore (Mussorie rock phosphate) given in Table I clearly indicates its complex nature. Even though the separation of gangue materials such as pyrite and quartz could be easily achieved by flotation, removal of calcite from phosphate posed the major problem in this case. This is believed to be due to the similarities in the surface chemical and electrokinetic properties of calcite and phosphate as a result of which both minerals respond similarly to cationic and anionic collectors. This problem is further complicated by the fact that the attempts to separate phosphate

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from calcite even from their synthetic mixture often failed under conditions where good separation was predicted based upon single mineral tests (Somasundaran, 1975). This has been suggested to be due to the influence of dissolved mineral species on the flotation properties of each other (Somasundaran, 1975, Ananthapadmanabhan, et al, 1977).

Because of such problems in the beneficiation of the present phosphate, a systematic study to obtain solution conditions such as pH, collector concentration and depressant concentration was conducted in Hallimond tube using single minerals and their synthetic mixtures. Subsequent studies in Fagergren flotation machine using the crushed ore with additional steps to separate the carbonaceous and sulfite gangue yielded a product having an acceptable grade of 27.6% P2O5 with 60% recovery. Experiment with the single minerals, synthetic mixtures and the ore are discussed in the following sections with suggestions for further improving the grade and recovery.

EXPERIMENTAL

Materials

Calcite. Iceland spar calcite crystals purchased from Ward's Natural Science Establishment were crushed in a roll crusher to obtain -35 +48 mesh fraction for flotation studies.

Apatite. Canadian fluorapatite containing about 5% calcite was crushed and then leached with dil. HNO₃ (pH = 1.5) several times to remove the calcite from it. Complete removal of calcite was ensured by treating the mineral surface with Alizarin Red, which stains calcite preferentially. The mineral was then washed with triple distilled water several times till the pH of the supernatant reached a constant value of 6.9. -35 +48 fraction apatite was used for flotation experiments.

Phosphate ore. Mussorie rock phosphate obtained from Pyrite Phosphate and Chemicals, Ltd., India was crushed and deslimed to obtain -150 mesh (BSS) and -200 mesh (BSS) fractions for flotation feed.

Reagents. Oleic acid reagent grade (UCP specifications) purchased from Fisher Scientific Company was used to prepare potassium oleate solutions for simple mineral and synthetic mixture structures. The stock solution was stored in the refrigerator under nitrogen atmosphere in order to prevent its oxidation. Other chemicals such as KOH, KNO₃, K₂CO₃, K₃PO₄ were of ACS grade purchased from Fisher Scientific Company. Triple distilled water was used for preparing all the solutions and in the case of oleate solutions deaerated triple distilled water was used.

Methods

Single mineral and synthetic mixture flotation experiments were carried out using a modified Hallimond cell described elsewhere (Somasundaran and Moudgil, 1974). A special feature of this apparatus was the automatic control of gas flow and stirring time which yielded reproducible results. For flotation tests, about one gram of the mineral was deslimed and conditioned with the collector solutions in a 100 ml. volumetric flask by tumbling it at
a rate of 17 rpm. At the end of ten minutes, the mineral and the solution were transferred to the Hallimond tube for flotation. Purified nitrogen at a rate of 20 ml/min. was used for 10 seconds in all the experiments. pH of the mineral supernatant solution was measured before and after conditioning and the latter was reported as flotation pH. Froth product and the tailings were dried and weighed to obtain percent floated. In the case of synthetic mixtures, heavy liquid separation using bromoform was employed for the analysis for calculating the grade of the froth product and tailing.

Ore flotation tests were conducted with 250 g.s sample in laboratory size Fagergren subaeration machines.

RESULTS AND DISCUSSION

Flotation of calcite and apatite as a function of the concentration of potassium oleate under the same pH conditions is given in Figure 1. Appropriate concentrations for the study of pH dependence of flotation were chosen from these results so that under the concentration range selected flotation will be sensitive to addition of reagents. Thus, $10^{-4} \text{M}$ and $7.5 \times 10^{-5} \text{M}$ oleate concentrations were selected for calcite and apatite respectively. Dependence of flotation of apatite on pH is shown in Figure 2. Maximum flotation is observed around pH 6-7. It is to be noted that this is the range in which oleate-oleic acid soap complex, which is possibly more surface active compared to other forms of oleate, is expected in solution. This important aspect of oleate chemistry on flotation behavior of minerals is discussed elsewhere (Kulkarni and Somasundaran, 1975; Kulkarni, et al., 1977; Ananthapadmanabhan, et al., 1978). Addition of $K_3PO_4 (1 \text{ M})$ to the system, as can be noted from Figure 2, has completely suppressed the apatite flotation under all the pH conditions considered. It would be interesting to look at the effect of potassium phosphate on the flotation properties of calcite (see Figure 3). Significant decrease in calcite flotation due to phosphate addition is observed only in the alkaline range. This result combined with earlier observations on the phosphate effect on apatite flotation suggested a scheme for calcite-apatite separation which would involve oleate flotation of calcite in the presence of potassium phosphate as a depressant for apatite. However results obtained earlier for the effect of dissolved mineral species on the flotation properties of calcite and apatite (Ananthapadmanabhan and Somasundaran, 1977) had shown flotation of both calcite and apatite to be depressed by the dissolved species of both the minerals, but only in the alkaline range for calcite. Since the overall aim is to depress the flotation of apatite, the effect of dissolved species in the acidic range is to be considered beneficial for the present separation. Under such conditions, it should be possible to selectively float calcite and depress apatite in the acidic range. This has been confirmed during the studies with synthetic mixtures which were conducted with certain modifications. When the mineral mixture was treated with oleate solutions for ten minutes, as in the case of single mineral tests, only about 40% of the apatite was depressed, whereas reducing the conditioning time to one minute improved the recovery to 90% with all the calcite in the froth product (see Figure 4).

It would be interesting to investigate the reasons for the selective depression of apatite by phosphate in the acidic region. The depression of
apatite by phosphate \((\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-})\) could be due to the specific adsorption of phosphate ions on the Ca-sites of the apatite surface (Somasundaran and Agar, 1972) preventing the oleate adsorption. Similar mechanism can be expected to operate on the calcite surface also. On the other hand, the formation of microparticles of carbon dioxide on the calcite surface in the acidic region can possibly enhance the bubble-particle attachment for flotation.

After the chemical conditions were established for the selective flotation of calcite from apatite, studies were extended to the beneficiation of the ore. Initial tests were carried out using the deslimed -150 mesh fraction; these results are given in Figure 5. Even though the recovery obtained was about 70%, the \(\text{P}_2\text{O}_5\) content of the non-floated concentrate was less than 24%, far below the acceptable value. Even a three stage flotation using terpineol for carbonaceous materials, potassium ethylxanthate for pyrite and oleic acid for calcite with \(\text{K}_2\text{HPO}_4\) as the depressant for phosphate did not yield satisfactory results. Tests were also performed with hydrofluosilicic acid and starch instead of \(\text{K}_2\text{HPO}_4\) as depressants for phosphate, but the results were inferior to those obtained using \(\text{K}_2\text{HPO}_4\). At this stage, the feed size was reduced to -200 mesh (again deslimed) and a similar three stage flotation scheme using terpineol, potassium ethylxanthate, oleic acid and dipotassium hydrogen phosphate was employed. The results are given in Figures 5 and 6. Percent recovery and grade are given as a function of concentration of \(\text{K}_2\text{HPO}_4\) in the former and as a function of the concentration of oleic acid in the latter. Increase in the amount of \(\text{K}_2\text{HPO}_4\) above 3 kg/ton did not produce any improvement in the recovery. Increase in oleic acid concentration decreased the recovery but did improve the grade. Test results, under the conditions considered here, have yielded an acceptable grade of 27.6% \(\text{P}_2\text{O}_5\) with 60% recovery. The improvement in grade obtained by reducing the feed size to -200 mesh could be due to the better liberation achieved under these conditions.

It should be mentioned here that these results support the contention that Hallimond tube results are extremely valuable in understanding the chemistry of the system. Arguments often heard against the Hallimond tube that uses only a one gram mineral sample are unfounded.

Further improvements, in both grade and recovery are possible by adding cleaning and scavenging steps to the calcite flotation circuit.

Experiments were also conducted as a function of the conditioning time with \(\text{K}_2\text{HPO}_4\), as this was found to be an important parameter during the synthetic mineral studies. The results given in Figure 7 suggested five minutes to be the optimum conditioning time. Here again, at higher conditioning time, percent recovery was found to decrease, even though an improvement in grade was observed.

CONCLUSIONS

Selective flotation of calcite from apatite using oleic acid has been successfully attempted by depressing the phosphate with dipotassium hydrogen phosphate. Chemical conditions for selective flotation were evaluated first by conducting single mineral and synthetic mixture flotation tests. A three
Stage flotation scheme developed subsequently for the beneficiation of Mussorie rock phosphate (Uttar Pradesh, India) employing terpineol for carbonaceous material, potassium ethyl-xanthate for pyrite and oleic acid in combination with dipotassium hydrogen phosphate for calcite yielded a product containing 27.6% $P_2O_5$ with 60% recovery. Inclusion of cleaning and scavenging steps in calcite flotation circuit should further improve both the grade and recovery of phosphate.

ACKNOWLEDGMENTS

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REFERENCES


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Figure 1 - Effect of concentration of potassium oleate on the flotation of calcite and apatite.

- pH = 9.9 ± 0.1
- Flot. Time - 10 sec.
- Cond. Time - 10 MTS.
- K-Oleate
- Oleate Concentration, M

Calcite

Apatite
Figure 2 - Effect of $K_3PO_4$ on apatite flotation.
Figure 3 - Effect of $\text{K}_3\text{PO}_4$ on calcite flotation.
Figure 4 - Effect of conditioning time on the recovery of apatite from a calcite-apatite synthetic mixture.
Figure 5 - Recovery and grade of Mussorie phosphate as a function of $K_2HPO_4$ Concentration.
MUSSORIE PHOSPHATE
FEED - -200 MESH (BSS)
(P₂O₅ - 22.07%)
K₂HPO₄ - 3Kg/Ton
COND. TIME - K₂HPO₄ - 5MTS.
OLEIC ACID - 5MTS.

Figure 6 - Recovery and grade of Mussorie phosphate as a function of Oleic acid concentration.
MUSSORIE PHOSPHATE
FEED - -200 MESH (BSS)
(\(P_2O_5\) – 22.07%)

OLEIC ACID – 1 Kg/Ton
\(K_2HPO_4\) – 3 Kg/Ton
COND. TIME – OLEIC ACID – 5 MTS.
pH – 6.5

Figure 7 - Dependence of recovery and grade of Mussorie phosphate on conditioning time in \(K_2HPO_4\).