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ABSTRACT

Using K-oleate as a collector and alizarin red S (ARS) as a modifying agent, selective depression of dolomite from francolite was achieved in alkaline medium (pH > 9.0). Interestingly, ARS was also found to depress igneous apatite in alkaline medium in oleate flotation of apatite and calcite.

Adsorption of ARS alone on dolomite was found to be higher than that on francolite. Complimentary adsorption experiments of ARS and K-oleate showed that oleate adsorption was increased in the presence of ARS on francolite but not on dolomite. K-oleate adsorbs on both francolite and dolomite and causes precipitation of calcium and magnesium oleate. Such precipitates can be prevented when ARS is present. The results are explained in terms of competitive adsorption for the active sites on francolite and dolomite by oleate and ARS, and their interactions with dissolved mineral species in solution.

INTRODUCTION

Beneficiation of phosphate rock containing carbonaceous gangues such as calcite, magnesite and dolomite is complicated due to the similarities in the chemical composition and the semi-soluble nature of the constituent minerals (Hanna and Somasundaran, 1976). Poor selectivity is often obtained in many flotation schemes (Lawver et al., 1982; Moudgil and Somasundaran, 1986). Our previous work has shown that surface conversion and dissolved mineral species-surfactant interactions are major reasons for the poor selectivity in flotation separation of various salt-type mineral systems (Amankonah and Somasundaran, 1985; Somasundaran and Ananthapadmanabhan, 1986; Somasundaran, 1987; Xiao et al., 1987). It is. therefore, essential to understand the interactions between dissolved mineral species and structually modified surfactants (collectors and modifiers) in salt-type mineral systems. Towards this objective, simultaneous adsorption, dissolution and flotation experiments using potassium oleate and alizarin red S were conducted to monitor the interactions between dissolved mineral species and anionic surfactants in francolite/ dolomite flotation system.

MATERIALS AND METHODS

Materials

<u>Francolite</u>: High purity phosphate $[(Ca,X)_{10}(P, C)_{6}(0,F)_{26}]$ concentrate of sedimentary origin (P₂0₅>36.1%) was supplied by Florida Institute of Phosphate Research. The -48+65 mesh fraction was used for flotation and -100+150 mesh fraction was used for adsorption experiments. The surface area of both fractions were determined using Quantasorb (BET method) and found to be 8.3 and 18.3 m²/g, respectively, indicating that the sample is possibly porous. Scanning electron micrograph (Figure 1a) showed that this is indeed the case.

Dolomite: Sedimentary dolomite sample was received from International Mineral and Chemical Corporation (IMC). The as-received mineral was jaw-crushed and roll-crushed. The roll-crushed material was dry-ground in ball mill and sieved. The -48+65 mesh fraction was used for flotation and ~100+250 mesh for adsorption and electrokinetic studies. The surface area of the -100+150mesh was found to be $0.5 \text{ m}^2/\text{g}$. Dolomite sample, unlike francolite, is non-porous (Figure 1b).

Oleic Acid: Oleic acid (>99.07 pure) as purchased from Alfa Chemical Co.. Oleate solution was prepared in KOH solution ($_{pH=11}$). ¹⁴C label led oleic acid (>99.07 pure) was purchased from ICN Chemicals.

Alizarin red S: Certified grade of alizarin red S (ARS) was purchased from Fisher Scientific Co.. The molecular structure of ARS is shown in Figure 2.

Inorganic chemcials: KNC, , KOH and HNO3 were purchased from Fisher Scientific Co..

Methods

Quantative analysis of ¹⁴C labelled oleic acid: The concentration of ¹⁴C labelled oleic acid was determined using beta-scintillation counting technique (Beckman LS-100c liquid scintillation system).

Determination of alizarin red S concentration: The residual concentration of ARS was determined by UV spectroscopy (Beckman DU-8 spectrophotometer).

Dissolved mineral species analysis: The concentration of dissolved calcium and magnesium species in the supernatants of francolite and dolomite was analyzed using inductively-coupled plasma (ICP) spectroscopy (Perkin-Elmer Model ICP 6500). Ca and Mg standards were supplied by Environmental Resources Associates.

Adsorption: The mineral sample (3.0 g) was first conditioned in KNO3 solution at the required pH for three hours on a wrist action shaker. The required amount of surfactant solution was then added and the suspension (10 ml of total volume) was shaken for 24 hours, which was found to be sufficient for ARS and oleate adsorption on each mineral. The supernatant of each sample was pipetted out for the analyses of residual surfactants and dissolved species after centrifugation.

Flotation: The mineral sample (1.0 g) was added to a cylinder (100 ml) containing KNO3 solution, pH modifiers (acid/alkali) and surfactant solution. ARS was added one minute before K-oleate. The suspension was conditioned using a magnetic stirrer for 10 minutes. Flotation was carried out in a modified Hallimond tube for 15 seconds with purified N2. In the case of binary mixture of dolomite and francolite (1:1), the individual minerals were separated after flotation by gravity in bromoform. In all the cases an aliquot was taken just prior to flotation for pH measurements.

RESULTS AND DISCUSSION

Adsorption and dissolved mineral species in francolite/dolomite/K-oleate system

Adsorption isotherms of ¹⁴C labelled K-oleate on francolite and dolomite are shown in Figure 3. Both francolite and dolomite gave linear isotherms with a slope of about 1.0. This shows that oleate adsorption on both minerals could be predominantly due to electrostatic forces. The adsorption behavior of oleate on francolite and dolomite is different from that obtained by Somasundaran (1969) who found a sudden increase in adsorption beyond 3.0×10^{-5} M of oleate concentration for calcite / K-oleate system.

The onsets of the precipitation of CaOl,

and MgOl₂ are calculated from the solubility product of CaOl₂ and MgOl₂ [K_{CaOl₂} = 3.81×10^{-13} ; K_{MgOl₂} = 1.58×10^{-11} , Du Reitz, 1975] for dolomite /oleate and francolite/oleate systems (Figure 4). The adsorption isotherms did not show any change near the range of precipitation of CaOl2 (around 1.5x10-5M for francolite and 3.5x10-5M for dolomite) and MgOl₂ (around 2.5x10⁻⁴M for francolite and 1.0x10""M for dolomite). The analyses of dissolved Ca and Mg species present in the supernatants, however, showed that bulk precipitation of calcium and magnesium oleates occured when K-oleate concentration exceeded 1.0x10-5M for francolite (Figure 4a) and 3.0x10⁻⁵M for dolomite (Figure 4b). The onset of precipitation calculated from the solubility data of . CaOl2 and MgOl2 and that obtained from dissolved species analyses are in good agreement with each other.

Adsorption and dissolved species in francolite / dolomite /alizarin red S system

Alizarin red S was reported to be a specific staining agent for calcite (Friedman, 1959) and a depressant for igneous apatite (Fu and Somasundaran, 1936). Adsorption of ARS on igneous apatite, dolomite and francolite was determined as a function of ARS concentration, and the results obtained are given in Figure 5. All the three minerals gave linear adsorption isotherms. Adsorption of ARS on francolite was found to be one order of magnitude lower than that on dolomite [which has alternate sheets of CaCO₃ and MgCO3 layers (Lippman, 1973)]. Interestingly, adsorption of ARS on igneous apatite (Fu & Somasundaran, 1986) was found to be much higher than that on francolite (close to that on dolomite, Figure 5). Such differences in adsorption could alter the flotation behavior of apatite minerals significantly. Selective depression of igneous apatite in apatite /calcite system could be due to such preferential adsorption of ARS on igneous apatite over calcite. Similarly, in dolomite / francolite/ARS system, dolomite is expected to be depressed by ARS preferentially over francolite. This trend is quite opposite to what has been found by Fu and Somasundaran. It can be also seen that, when compared dissolved mineral species in the absence (Figure 4) and presence of ARS in dolomite / francolite system (Figure 6), the level of dissolved calcium and magnesium species in dolomite /ARS system has increased significantly whereas that in francolite / ARS system has remained constant. No precipitation of Ca and Mg species was found in both dolomite /ARS and francolite / ARS systems.

Adsorption and dissolved mineral species in the presence of alizarin red S (ARS) and K-oleate

Adsorption behavior of K-oleate on dolomite and francolite was also studied in the presence of ARS and the results obtained are given in Figure 7. It can be seen that oleate adsorption is increased in the presence of ARS on francolite but decreased on dolomite. One possible reason for the decreased oleate adsorption on dolomite could be due to increased adsorption of ARS on dolomite and, thus, a reduced number of active sites for oleate by competitive adsorption. Complimentary analyses of dissolved mineral species (Figure 8) showed that there is no precipitation of calcium and magnesium in dolomite / francolite / K-oleate system in the presence of ARS. This may be attributed to the interactons between dissolved Ca and Mg species and ARS to form more stable Ca and Mg complexes with ARS in solution than Ca and Mg oleates. The complexation reactions of ARS with Ca²⁺ and Mg²⁺ ions are shown as follows:



Such complexation reactions can affect the kinetics of dissolution of Ca and Mg species from dolomite surface. Unlike dolomite / francolite / K-oleate system, where we found significant precipitates of Ca and Mg oleates, precipitation of Ca and Mg oleates are not observed in dolomite / francolite / K-oleate / ARS system. This is very interesting because the loss of selectivity in oleate flotation without ARS is mainly due to the precipitation of Ca and Mg oleates in bulk as well as on mineral surfaces. In the presence of ARS, such precipitation of Ca and Mg oleates could be eliminated.

Flotation of dolomite and francolite using Koleate and alizarin red S

The flotation behavior of francolite and dolomite was studied as a function of oleate concentrations (Figure 9) and pH (Figure 10). It appears from Figure 9 that the flotability of both dolomite and francolite is quite similar and very sensitive to oleate concentration. It can be also observed from Figure 10 that selective flotation of francolite might be possible above pH 9.0 or dolomite below pH 5.0. When ARS was used as a modifying agent, it is found from Figure 11 that ARS can depress the flotation of dolomite (beyond pH 8 in Figure 11) but not that of francolite. Selective flotation of francolite from dolomite is possible at about 1.0 x 10^{-5} M of ARS (Figure 12). This observation is in agreement with our adsorption results (Figure 4), where we found that ARS adsorbs much more on dolomite than francolite and also enhances the adsorption of K-oleate on

Flotation of binary mixture of dolomite and francolite

Flotation of binary mixtue of dolomite and francolite (1:1) using K-oleate and ARS is shown in Table 1. Flotation of binary mixtures using 1.7×10^{-4} K-oleate alone showed that francolite could not be selectively floated from dolomite at these pH conditions. The loss of the selectivity of francolite flotation can be attributed to the alteration of the surface properties of both minerals by the dissolved mineral species. suggesting the need to use structurally modified collectors or modifiers to minimize or even prevent such surface alterations. By using ARS as a modifier, we are able to selectively depress dolomite in the binary mixture flocation with K-oleate (70.8% grade and 90.5% recovery of francolite). The grade can be further improved upon by mild acid washing and cleaning.

CONCLUSIONS

1. Potassium oleate adsorbs on both francolite and dolomite and causes bulk precipication of calcium and magnesium oleates.

2. Adsorption of alizarin red S alone on dolomite is highter than that on francolite. In dolomite / francolite / K-oleate / ARS system, ARS was found to increase oleate adsorption on francolite but not on dolomite. Precipitation of Ca and Mg oleates are prevented in the presence of ARS due to competing complexation reactions of ARS with Ca and Mg species.

3. Alizarin red S was found to be a promising depressant for dolomite in the selective flotation of dolomite and francolite using K-oleate. The loss of selectivity in oleate flotation of francolite and dolomite in absence of ARS is due to interactions between dissolved mineral species and surfactants leading to the formation of surface and bulk precipitates.

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REFERENCES

- Amankonah, J.O. and Somasundaran, P., 1985. Colloids and Surfaces, Vol. 13, 335-353. Du Reitz, C., 1975. Proceedings of XIth Int. Miner. Process. Congress, Cagliali, 29. Friedman, F. and Anger, V., 1959, J. Sediment Petrol., Vol 29, 29-43. Fu. E. and Somasundaran, P., 1986. Int. J. Miner Process., Vol. 18, 287-96 Hanna, H.S. and Somasundaran, P., 1976. Flotation - A.M. Gaudin Memorial Volume (M.C. Fuerstenau ed.), Vol. 1, ALME, N.Y., 197-272. Lawver, J.E., Wiegel, R.L., Snow, R.E. and Huang, C.L., 1982. Proceedings of XIVth Int. Miner. Process. Congress, Session IV-Flotation. Paper IV-20, Toronto Moudgil, B.M. and Somasundaran, P., 1986, Advances in Mineral Processing (P. Somasundaran ed.)
- , Surveille, Colorado, 426-441. Lippman, F., 1973. Sedimentary Carbonate

Minerals, Springer-Verlag, New York. Somasundaran, P., 1969. J. Colloid and Interface

- Sc1., Vol. 31, 55-65 Somasundaran, P. and Ananthapadwanabhan, K.P.,
- 1986. <u>Advances in Mineral Processing</u> (P. Somasundaran ed.), SME/AIME, Colorado, 137-53.
- Somasundaran, P., 1987. <u>Beneficiation of Dolomite</u> Phosphate. <u>Annual Report Submitted to FIPR</u> Columbia University, New York
- Xiao, L., Viswanathan, K.V. and Somasundaran, P., 1987. <u>Extractive Metallurgy and Material</u> <u>Science</u>, Proceeding of International Symposium organized by Central-South University of Technology and Technical University of Clausthal, Changsha, China, 110-120.





Scanning electron micrograph of francolite showing pores.



Dolomite CaMg(CO3)2

Figure 1 b: Scanning electron micrograph of magnified dolomite particle showing absence of pores.



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Figure 2. The molecular structure of alizarin red S (ARS)



Adsorption isotherm of ¹⁴C labelled oleic acid on francolite and dolomite



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Figure 4. Dissolved Ca and Mg levels from a)francolite b)dolomite as a function of K-oleate concentration

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Figure 5 Adsorption isotherms of alizarin red S on francolite, dolomite and igneous apatite.



Figure 6. Dissolved Ca and Mg analyses in the presence of ARS with a) dolomite and b) francolite.



Figure 7. Adsorption isotherms of ¹⁴C labelled oleic acid on francolite and dolomite in the presence of ARS





Figure 9. Flotation of francolite and dolomite as a function of Koleate concentration at pH 9.0.



Figure 10: Flotation of francolite and dolomite as a function of pH with 1.7×10^{-4} M K-oleate.



Figure 11: Flotation of francolite and dolomite as a function of pH in the presence of alizarin red S.



Figure 12. Flotation of francolite and dolomite as a function of alizarin red S concentration at pH 9.0.

CONDITIONS	GRADE Z	RECOVERY % (fran)
K-OLEATE 1.7X10 ⁻⁴ M pH = 5.2	58.0	85.0 (dol)
рН = 9.0	58.7	86.1
K-OLEATE 1.7X10 ⁻⁴ M ARS 1.0X10 ⁻⁵ M pH = 9.0	70.8	90.5
K-OLEATE 1.7X 10 -4 M A R S 1.0X10 -5 M		
pH = 9.0 ACID WASHING 3 MIN.	88.7	61.

TABLE 1. SEPARATION OF BINARY MIXTURE OF FRANCOLITE AND DOLOMITE