

Selective flotation of scheelite and calcite

* D. P. Patil and * U. B. Nayak

INTRODUCTION :

The gold tailings from Kolar Gold Fields containing low scheelite values has a complex mineralogy with hornblende, quartz, arsenopyrite and calcite as major gangue minerals. The most difficult problem in scheelite flotation is not the removal of the siliceous or sulphide gangue, but the separation of scheelite and calcite minerals which have similar surface properties. This is greatly influenced by many factors⁽¹⁾ such as (1) the extent of adsorption of the collectors (2) the dissolution of the minerals and the interference by the released species and (3) the interaction of adsorbed ions with the mineral surface. Direct flotation tests to recover scheelite from tailings failed due to the dilution of the concentrate by calcite. Hence to adopt the flotation process successfully, it is necessary to depress the calcite selectively which is not achieved easily⁽²⁾ due to the presence of small amounts of Ca, Mg and Fe salts and the lean grade of the ores to be treated. Slime coating⁽³⁾ is also another factor adversely affecting the flotation of scheelite. The present study is an attempt to improve the selectivity of separation of scheelite, based on the flotation of pure calcite-scheelite system using sodium oleate as collector.

EXPERIMENTAL :

Materials :

1. Calcite :

Iceland spar calcite crystals used for the flotation experiments was supplied by V.I.S.L., Bhadravati. The mineral samples were prepared by roll crushing and wet sizing using B.S.S. sieves. The size fraction -300+350 mesh selected for flotation experiments, was washed three times with alcohol and then with double distilled water several times till all alcohol was removed from the calcite. The calcite was

tested for non-floatability and non-contamination of the surface by vacuumatic cylinder flotation using terpineol as frother. The cleaned calcite analysed 97.3% CaCO_3 .

2. Scheelite :

Scheelite concentrate was supplied by BGML, at K.G.F. and analysed 65.3% WO_3 . The concentrate was further purified by the method described by Arnold and Warren⁽⁴⁾. The -300+350 mesh fraction was cleaned and tested in a similar way as that of calcite. The cleaned scheelite analysed 76.4% WO_3 .

3. Sodium oleate :

Reagent grade sodium oleate from Fisher Scientific, U.S.A. was used for the flotation studies without further purification.

The other analytical reagents such as sodium tri-polyphosphate, sodium hexametaphosphate, ferrous sulphate, sodium silicate were certified ACS grade purchased from Fisher Scientific Company and used as 1% solution in double distilled water.

4. pH regulators :

A. R. grade HCl and NaOH in different normalities in double distilled water were used as pH regulators.

5. Glassware :

All the glassware used was cleaned with freshly prepared chromic acid and then with alcoholic potassium hydroxide. This was followed by washing with distilled water ten times and then by rinsing with double distilled water.

6. Hydrosol :

The metal silicate mixture or hydrosol was prepared by adding, with continuous stirring equal

* Department of Metallurgy, Indian Institute of Science, Bangalore - 560 012.

volumes of 1% solution of ferrous sulphate to 5% solution of sodium silicate. This was done to avoid formation of zones of lower pH values which would result in coagulation of silica.

Apparatus :

The flotation cell is a modified Hallimond tube⁽⁵⁾ sufficient to hold 100 c.c. with a glass frit bottom for gas entrance. Controlled agitation was obtained using a magnetic stirrer with a teflon coated stirring bar. Nitrogen at 20ml/mt was passed through ascarite and its rate was controlled with a regulating valve, mercury manometer, a constant head reservoir and a gas flow-meter. A schematic diagram of the micro-flotation apparatus is shown in Fig. 1. All the experiments were conducted at room temperature.

Flotation :

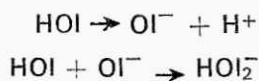
A known amount of deslimed mineral was placed in the microflotation cell and calculated amount of reagent under test was added and made upto the required volume in double distilled water. Mineral and solution were agitated with a magnetic stirrer for five minutes. After conditioning, collector solution was added, pH of the solution adjusted and agitated for 10 minutes. After this conditioning time, nitrogen gas was introduced into the cell. At the end of 20 seconds (flotation time) the gas flow was stopped, stirring terminated and the system allowed to remain undisturbed until all movements due to the mineral particles and the gas had ceased. The concentrate and the tailings were filtered separately, dried overnight in an oven at 90°C, weighed and the recovery was calculated.

The minerals were tested in the solutions of supernants which were prepared as follows. The mineral whose supernant required was conditioned with double distilled water for 15 minutes (which was the same as the flotation conditioning time) and the supernant was centrifuged. The decanted solution thus obtained after separation from mineral particles containing all the species released from the mineral was used for flotation tests.

Results and discussion :

The flotation behaviour of scheelite as a function of pH is shown in Fig. 2. Scheelite floats in a wide pH range and the flotation is almost 100% in the pH region 4—11, at collector concentration of 24—125mg/lit of sodium oleate and showing a minimum at pH 12.5. Collector adsorption on salt type minerals can be due to either electrostatic adsorption, exchange adsorption with lattice or gegen ions, chemisorption or surface precipitation. The effective species of the collector, its solubility as well as the presence of other extraneous species in the aqueous phase are other factors to be considered apart from surface properties of the mineral including charge characteristics at the mineral solution interface and chemical composition of the mineral.

Oleic acid being the collector used in this investigation has a pK value⁽⁶⁾ of 4.7 at which pH its ionic as well as molecular concentrations are identical. Above pH 4.7, one can expect the ionic composition to predominate and below pH 4.7 the molecular composition can be expected to predominate. It has a solubility⁽⁷⁾ of 3.0×10^{-7} M/litre (.08mg/lit) of water. Also it forms an acid soap⁽⁸⁾ complex in the pH range of 7—8 and this complex is more surface active than the acid or the soap alone.



The variation in the composition of the effective species of collector at different pH values has been summarized by Sutherland and Wark⁽⁹⁾.

Scheelite is negatively charged in distilled water⁽¹⁰⁾ throughout the pH range from 3 to 12 and even in 1M CaCl₂ concentration in the pH range 4 to 12.5 the negativity of the charge is maintained without any signs of charge reversal. The negativity is also maintained even in the presence of sodium tungstate at pH 9.5. Also, scheelite is not soluble in distilled water. In contrast, calcite dissolves in water and under-

goes various reactions⁽¹¹⁾ giving rise to a number of chemical species including H_2CO_3 , HCO_3^- , CO_3^{2-} , Ca^{2+} , CaHCO_3^+ , CaOH^+ and $\text{Ca}(\text{OH})_2$. These -ve and +ve chemical species give rise to a surface charge at the solid-solution interface of the calcite resulting in a negative charge at high pH value and +ve charge at low pH value. According to Somasundaran⁽¹²⁾, calcite has a point of zero charge at pH 9.5, so that above this pH it is -vely charged and below this pH it is +vely charged. However, other values for point of zero charge are also known in literature⁽¹³⁾.

Excellent flotation of scheelite in the pH range 4 to 11 when it is negatively charged throughout the pH range rules out the possibility of physical adsorption of oleic ion or oleate acid. The pK value of oleic acid being 4.7, one can expect a preponderance of oleate ions in the entire flotability range of scheelite. Chemisorption of the oleate ion in exchange for tungstate ion on the crystal lattice is a clear possibility in the flotation of scheelite. Such chemisorption of fatty acids or their soaps on salt type minerals resulting in the formation of alkaline-earth soaps has been suggested by a number of other investigators^(14,15). Also in the alkaline solution, the formation of acid soap of different composition is ruled out due to the insolubility of scheelite and the nonavailability of calcium ions. Non-flotation of scheelite at high pH values above 12 is due to high ionic strength of OH ions which compete with the oleate ions for the scheelite surface and thus decrease its flotability which falls from 100% to 45%.

Flotation of calcite as a function of pH is shown in Fig.3. Flotation of calcite has not been studied in the acid range as it is possible for the calcite to react with the acid with the formation of micro bubbles of CO_2 on the surface of the mineral and make it float. Floatability of calcite shows a minimum at pH 9.5 and increases with increase in pH. Below pH 9.5, calcite is positively charged and pK value of the collector being 4.7, the ionic species of the collector can be expected to be predominant in the pH range 7 to 12. As such, upto pH 9.5 the oleate ions can be

expected to adsorb on calcite electrostatically. Between pH 9--10, the clear solution appears turbid due to the precipitation of the acid soap thus locking up the oleate ions available for adsorption resulting in the decrease in the flotation of calcite which reaches a minimum at pH 9.5. Above pH 9.5, calcite is negatively charged and hence oleate ions cannot be expected to be electrostatically adsorbed on the calcite. However, as the flotation of calcite increases with pH above 9.5, suggests a different mechanism for the flotation. It is possible for the oleate to be chemisorbed on the calcite surface in exchange for CO_3^{2-} and HCO_3^- with the formation of calcium oleate. Also, the acid formed, which according to Kulkarni and Somasundaran⁽⁸⁾ is more surface active, can also be expected to be reactive on the mineral surface facilitating an increased flotation above pH 9.5. This dual mechanism of electrostatic adsorption and chemisorption of oleate ions has also been advocated by Peck and Wadsworth⁽¹⁶⁾ during the flotation of fluorite and by Somasundaran⁽¹²⁾ on the flotation of calcite.

The flotation behaviour of calcite and scheelite at a constant collector concentration as a function of pH in Fig. 4 indicates the possibility of separation at high pH assuming the minerals behave independently of each other. However, experiments for separation from artificial mixtures showed poor selectivity thereby establishing the need for the use of selective depressants in the separation of scheelite and calcite.

Calcite in water gives rise to different chemical species which may have a bearing on the flotation of scheelite. The effect of these ions as well as $\text{Ca}(\text{NO}_3)_2$ and Na_2CO_3 on the flotation of scheelite is shown in Figs. 5 and 6. From Fig. 5, it is evident that the calcite supernatant containing different dissolved chemical species has no effect on the flotation of scheelite. A similar effect is obtained by the use of $\text{Ca}(\text{NO}_3)_2$ which shows excellent flotability of scheelite in a wide pH range. In contrast to calcite, scheelite flotation is affected in the

presence of high concentration of Na_2CO_3 at pH 10.

The results are in agreement with that of Arnold and Warren's⁽¹⁰⁾ data on zeta potential of scheelite in the presence of Na_2CO_3 which showed increased negativity with concentration suggesting thereby the specific adsorption of CO_3^{2-} and HCO_3^- ions to depress the mineral. Calcite dissolves in water⁽¹⁷⁾ to the extent of 14 mg/lit and as such the concentration of CO_3^{2-} and HCO_3^- ions can be expected to be very low without in any way affecting the flotability of scheelite. Hence separation of scheelite and calcite using a calcite supernant is impossible as proved theoretically and observed experimentally on a 1:1 synthetic mixture which showed 100 % flotability of the minerals. This is contrary to the results obtained by Ananthapadmanabhan and Somasundaran⁽¹⁷⁾ on the possibility of separation of apatite from calcite using a supernant.

Thus the need of a specific depressant in the separation of scheelite from calcite is evident and Fig. 7 shows the flotability of scheelite as a function of pH at various concentrations of sodium silicate. At low concentrations of 80 mg/lit of sodium silicate, scheelite flotation is not affected in the alkaline range and is almost 100% throughout the pH range 7 to 12. However with increased concentrations of sodium silicate, flotability decreases with increased pH reaching a minimum of 20 % at pH 12. The results are similar to the effect of sodium carbonate on the flotation of scheelite and in agreement with Arnold and Warren⁽¹⁰⁾ showing increased negativity of the mineral with concentration of sodium silicate suggesting thereby the specific adsorption of silicate ions to depress the mineral. The results on calcite as indicated in Fig. 8 are contrary to that obtained on scheelite and shows a marked increase in flotability with increase in pH in the range 8 to 12 for a given sodium silicate concentration. Since calcite is negatively charged above pH 9.5, the effect of negative silicate ions as a depressant can be expected to be less on

the flotation of calcite due to electrostatic repulsion. However, oleate ions can be chemisorbed on the calcite surface with the formation of calcium oleate. Decrease in flotability with increase in sodium silicate at constant pH is attributed to the competition between Ca^{++} and Na^+ ions resulting in lower concentration of calcium ions and lesser flotability of the mineral. Comparison of Figs. 7 and 8 show that scheelite flotation is better than calcite in the presence of sodium silicate.

Fig. 9 shows the effect of sodium tripolyphosphate (STPP) and sodium hexametaphosphate (SHMP) as modifiers on the flotation of scheelite and calcite at pH 10. SHMP decreases the flotation of calcite drastically with increase in concentration with the recoveries falling from 90% to 20%. In comparison, scheelite floats very well in the presence of SHMP even at high concentrations. For scheelite, STPP is a better depressant than SHMP and the reverse is true for calcite. However, selectivity of separation can be expected to be better in the presence of SHMP. Fig. 10 indicates the effect of pH on the flotation of calcite and scheelite at a constant sodium oleate and SHMP concentration. For calcite, flotation decreases continuously from pH 8 to 12, as the mineral acquires more and more negative charge above pH 9.5, the point of zero charge for calcite. From pH 8—9.5, the decrease in positive charge decreases the electrostatic adsorption of collector resulting in decreased flotation. Above pH 9.5, chemisorption of the collector is hindered by the presence of phosphate ions which again decreases the hydrophobicity of the mineral and the flotation recovery. Scheelite being negatively charged throughout the pH range rules out the possibility of electrostatic adsorption. Chemisorption of the oleate ion for the tungstate ion on the mineral lattice floats the scheelite which reaches a maximum at pH 10 and then decreases the flotability due to competition of the OH^- ions with the collector ions for the mineral surface. Separation of scheelite from calcite should be possible at pH 10.

The presence of polyvalent cations increased the depressing action of sodium silicate on salt type calcium minerals according to Belash and Pugina⁽¹⁸⁾. In the presence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and sodium silicate 95.5% of scheelite floated in comparison with 18.3% flotation of calcite. The effect of order of addition of these reagents on the flotation of scheelite and calcite is indicated in Figs. 11 and 12. For scheelite the recovery depends upon the order of addition of reagents and simultaneous additions gave higher recoveries than separate individual additions. In comparison, calcite recoveries are poorer than scheelite. Fig. 13 shows the effect of concentration of sodium silicate and ferrous sulphate added in the form of hydrosol on the flotation of scheelite and calcite at pH 10. Increased concentration of hydrosol decreased the flotation of scheelite as well as calcite and scheelite flotation was higher than calcite at all concentrations of the hydrosol. The effect of hydrosol as a function of pH on the flotation of

scheelite and calcite is indicated in Fig. 14. Calcite flotation was poorer than scheelite in pH range 7 to 11 and scheelite flotation after reaching a maximum around pH 9, decreased with further increase in pH falling from 95% to 20% at pH 12. Calcite flotation tending towards a minimum at pH 9, good separation of the minerals should be possible in the pH range 9–10.

Figs. 15 and 16 indicate an attempt on the separation of scheelite and calcite from synthetic mixtures (1 : 1) using sodium silicate, SHMP and the hydrosol of sodium silicate and ferrous sulphate. It is seen that SHMP gave better selectivity of separation and recovery than sodium silicate at 4.25 and 70%. This is further enhanced to 4.90 and 75% by the combination of sodium silicate along with it. The use of hydrosol increased the selectivity of separation at 5.4 with a recovery of 67%.

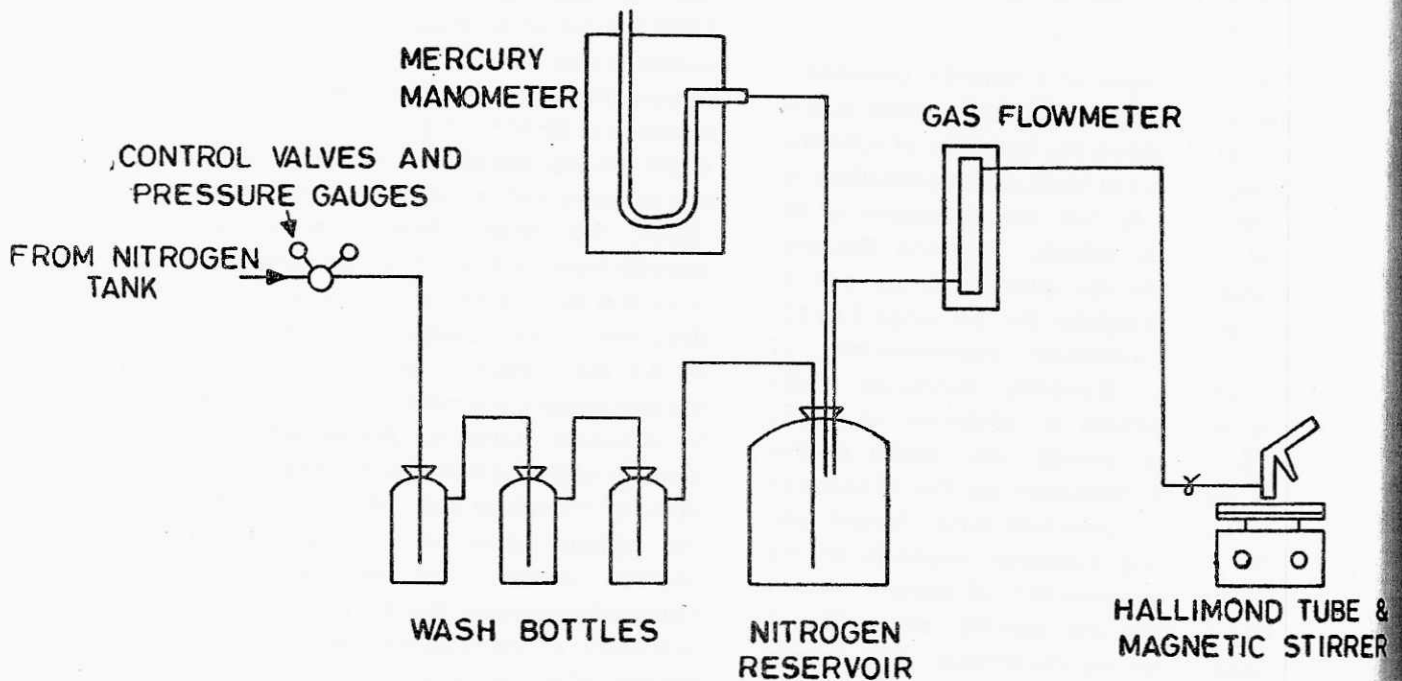


FIG. 1 SCHEMATIC DIAGRAM OF THE MICRO-FLOTATION APPARATUS

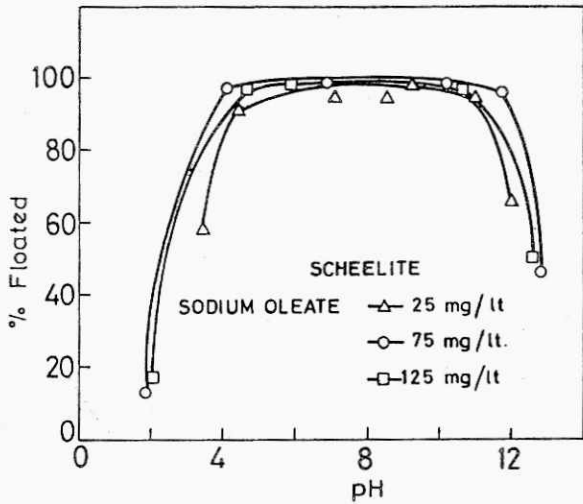


FIG 2 SCHEELITE FLOTATION AS A FUNCTION OF pH AT DIFFERENT COLLECTOR CONCENTRATION.

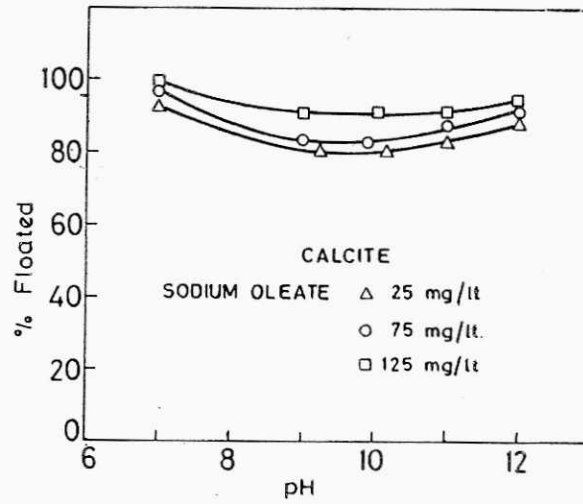


FIG 3 CALCITE FLOTATION AS A FUNCTION OF pH AT DIFFERENT COLLECTOR CONCENTRATION

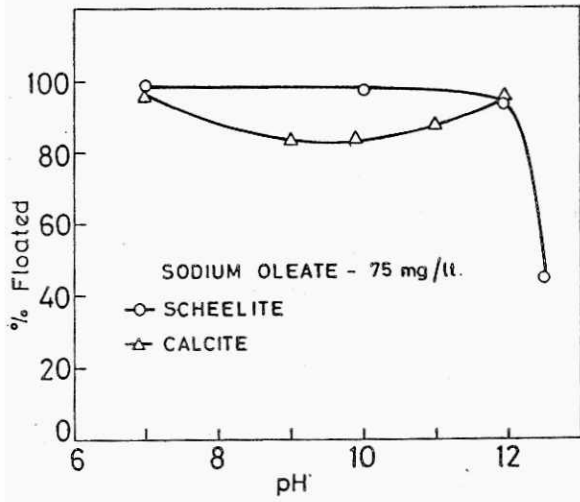


FIG. 4. FLOTATION OF SCHEELITE AND CALCITE AT CONSTANT COLLECTOR CONCENTRATION.

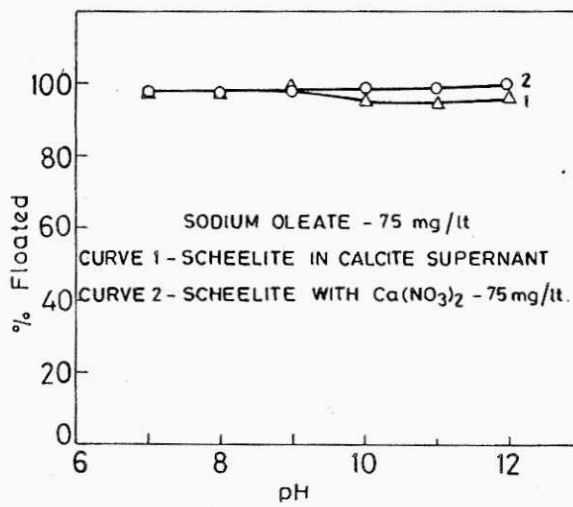


FIG. 5 SCHEELITE FLOTATION IN CALCITE SUPERNANT AND IN Ca(NO₃)₂

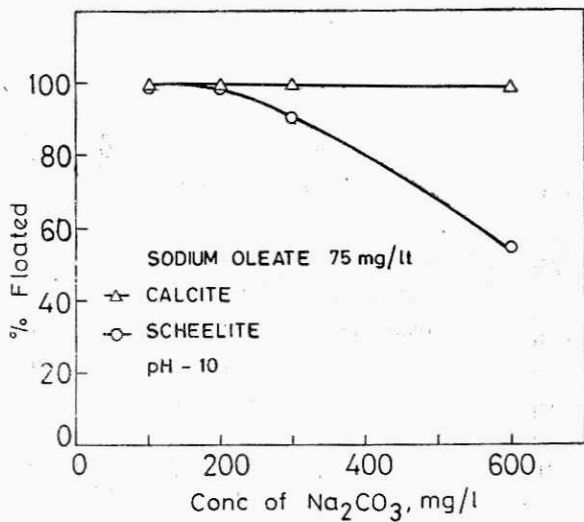


FIG. 6 EFFECT OF Na₂CO₃ ON FLOTATION OF SCHEELITE AND CALCITE

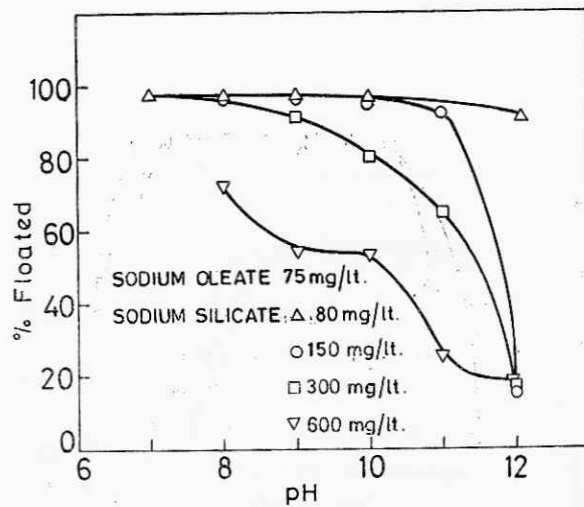


FIG. 7 EFFECT OF SODIUM SILICATE ON SCHEELITE FLOTATION.

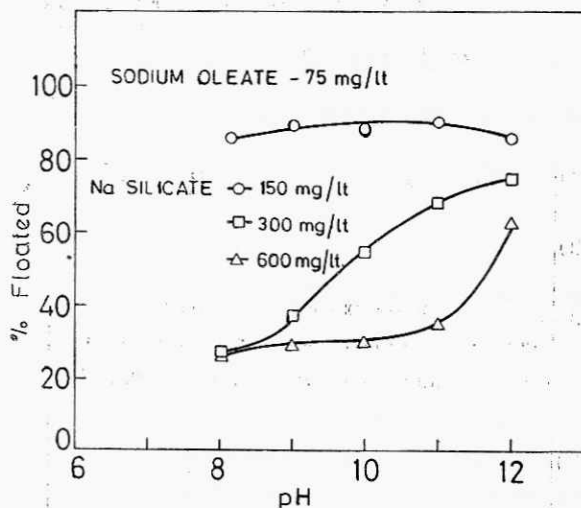


FIG. 8. EFFECT OF SODIUM SILICATE ON CALCITE FLOTATION.

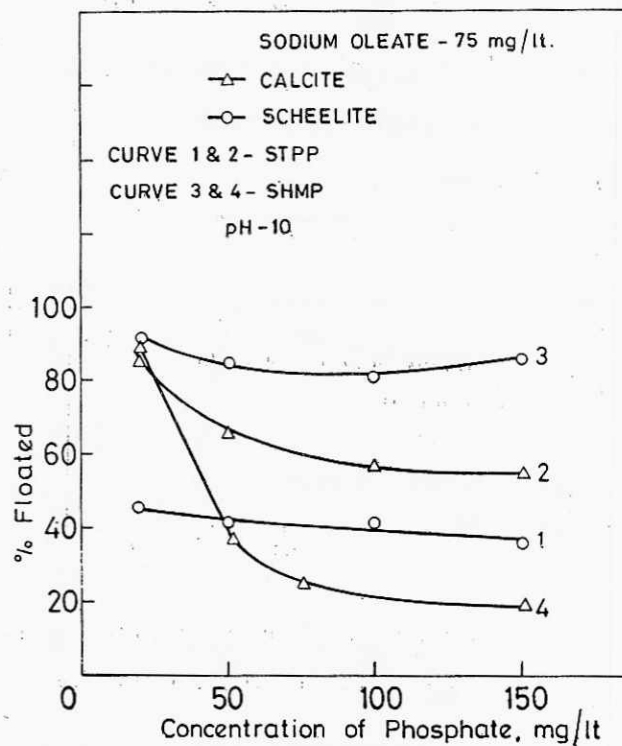


FIG. 9. EFFECT OF STPP AND SHMP ON SCHEELITE AND CALCITE FLOTATION.

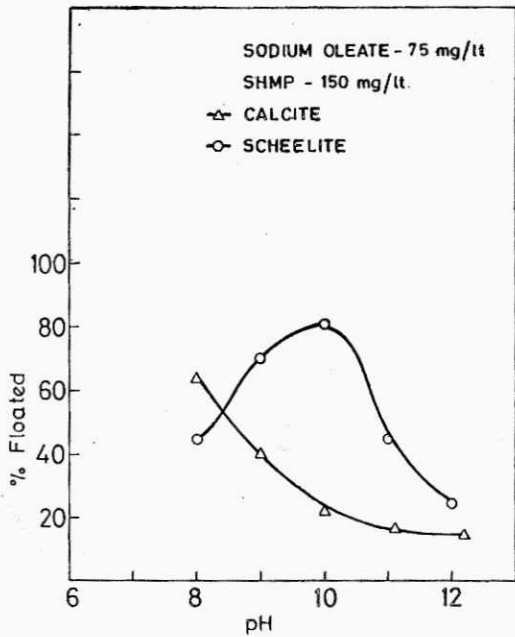


FIG 10 EFFECT OF SHMP ON SCHEELITE & CALCITE FLOTATION AS A FUNCTION OF pH

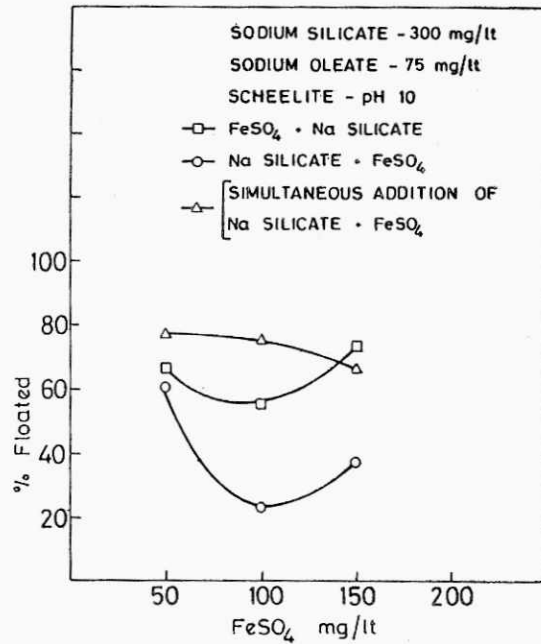


FIG 11 EFFECT OF Na SILICATE AND FeSO₄ ON SCHEELITE FLOTATION

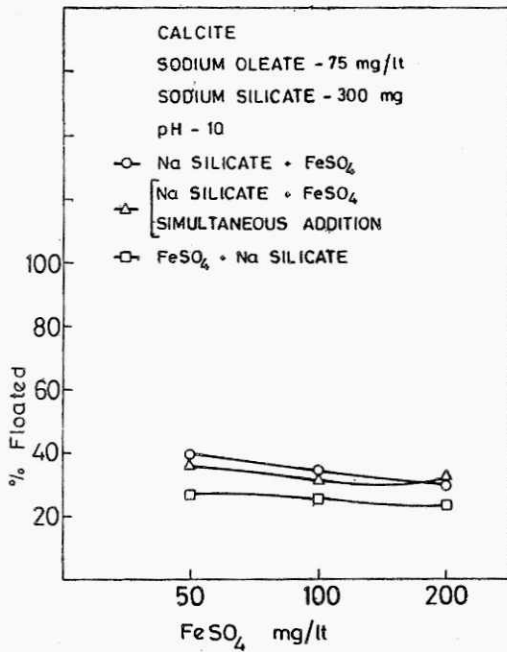


FIG 12 EFFECT OF Na SILICATE AND FeSO₄ ON CALCITE FLOTATION

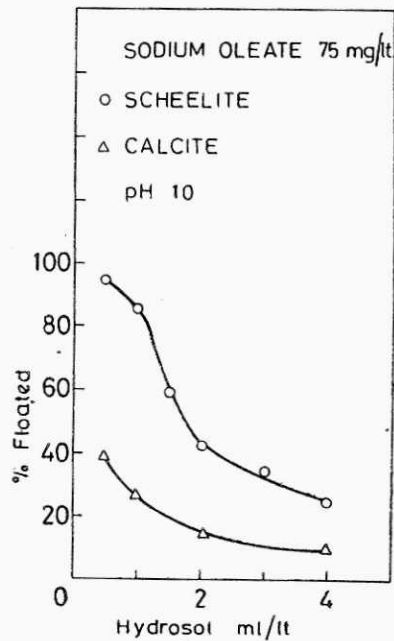


FIG 13 EFFECT OF Na SILICATE AND FeSO₄ ON CALCITE & SCHEELITE FLOTATION WHEN ADDED AS HYDROSOL

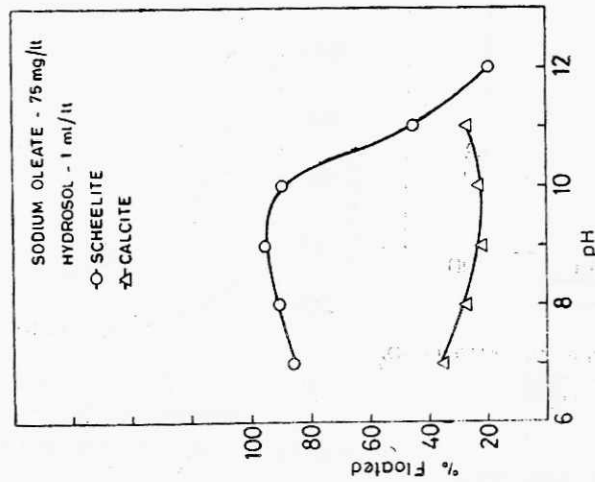


FIG. 14 EFFECT OF HYDROSOL ON THE FLOTATION OF CALCITE AND SCHEELITE AS A FUNCTION OF pH

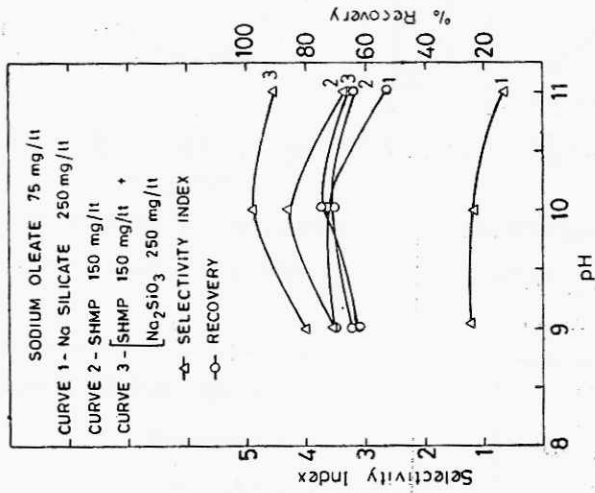


FIG. 15 EFFECT OF SODIUM SILICATE AND SHMP ON THE FLOTATION OF CALCITE-SCHEELITE MIXTURE (1:1)

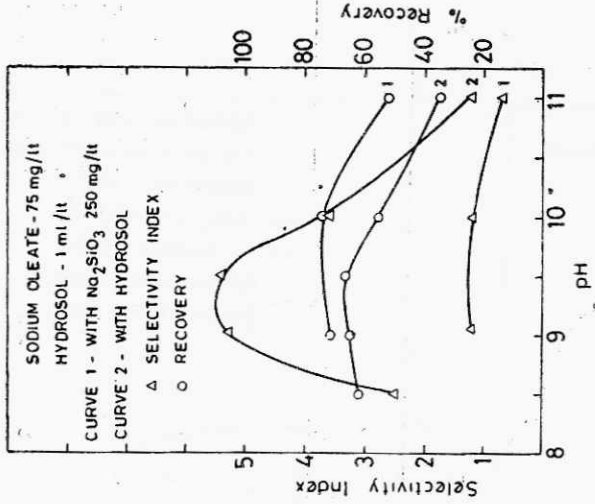


FIG. 16 EFFECT OF HYDROSOL ON THE FLOTATION OF CALCITE SCHEELITE MIXTURE (1:1)

Summary and conclusions :

- 1) Flotation of scheelite and calcite has been studied with sodium oleate as a collector as a function of pH using a Hallimond tube flotation assembly.
- 2) Collector adsorption on scheelite has been explained on the basis of chemisorption and on calcite on the basis of dual mechanism of electrostatic adsorption below the point of zero charge and chemisorption above the point of zero charge.
- 3) Inorganic modifiers like $\text{Ca}(\text{NO}_3)_2$, Na_2CO_3 sodium silicate, sodium tripoly-phosphate, sodium hexametaphosphate, hydrosol of sodium silicate and ferrous sulphate have been studied on the soap flotation of scheelite and calcite.

- 4) Theoretical conditions of separation of scheelite from calcite have been predicted using sodium silicate, sodium hexametaphosphate and hydrosol of sodium silicate and ferrous sulphate.
- 5) Translation of results on artificial mixtures of scheelite and calcite (1 : 1) has indicated a good separation of scheelite at a S.I. of 5.4 and recovery of 67% at pH 9.5 using the hydrosol of sodium silicate and ferrous sulphate.
- 6) Further work on the tailings from KGF has to be carried out to optimize the laboratory results and establish the feasibility of beneficiation of the KGF tailings for higher recoveries and better grades of the scheelite concentrate.

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