Upgradation of Chalcopyrite Ore by Flotation

S. MUSTAFA*, A. HAMID, A. NAEEM AND S. MURTAZA
National Centre of Excellence for Physical Chemistry
University of Peshawar, Peshawar, Pakistan

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Summary: The effect of important parameters e.g. conditioning time, collector concentration, pulp density, temperature, pH, particle size, water quality, collector chain length and cyanidation were studied thoroughly on the adsorption of xanthate ions and the subsequent flotation of chalcopyrite. Stepwise enhancement in upgradation and recovery was achieved by employing these parameters. After fully optimizing the parameters, the copper content was upgraded from 0.8% to 18.75%, achieving a recovery of 85.25%.

Introduction

A significant current problem in mining, metallurgy, and materials processing is to develop economic methods for extracting metals from ores. Conventional separation techniques being rarely economic for large volumes of ore, a relatively new approach involves complexing of the ions with relatively high molecular weight organic complexing agents known as collectors, to generate hydrophobic species, which can then be removed from the bulk solution by flotation. The process of flotation as explained by different authors [1-5] is based on manipulating the surface properties of minerals with reagents so that the mineral of interest acquires a hydrophobic surface (i.e., lacks affinity for water), while the minerals to be rejected are made to have, a hydrophilic surface (i.e. having a strong affinity for water). When air bubbles are introduced, the hydrophobic minerals attach themselves to the bubbles and are carried to the surface and skimmed away.

The mineral's behavior during froth flotation is controlled by its surface properties and these are a function of its chemistry, structure and the surface species formed by reactions during processing. A crucial part of the process is interaction of the reagents used to float minerals. These interactions are different for different minerals and collectors.

An extensive literature has been reported on the upgradation of sulphide ores [6-11]. Although the basic technique remains the same but the reagents used varies from one another [12-15].

The present study deals with the upgradation of chalcopyrite ore from Shinkai (North Waziristan Agency), Pakistan as a function of conditioning time, collector dosage, pulp density, temperature, pH, particle size, water quality, collector chain length and cyanidation.

Results and Discussion

Kinetic study

Percent recovery of copper versus conditioning time is plotted in Fig. 1(a). It shows that maximum flotation (% recovery, % upgradation) is observed at 10 minutes time interval. Afterwards both the recovery and upgradation decreases gradually with time. It may be attributed to the fact that maximum adsorption of xanthate gets completed within 10 minutes period as shown in Fig. 2. The process of xanthate ion desorption from mineral surface after 10 minutes results in a decrease in flotation.

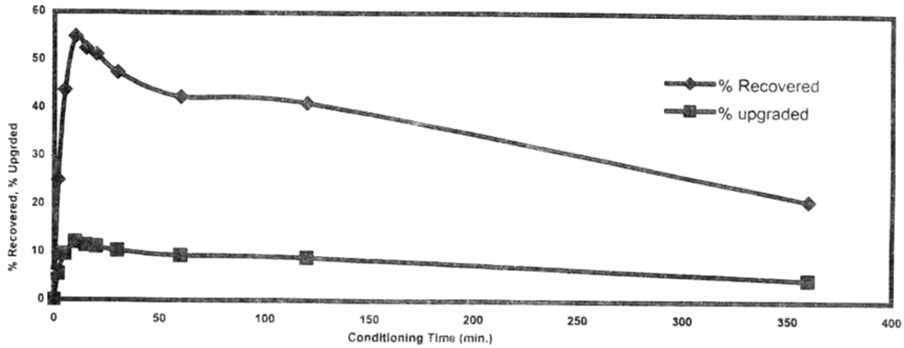
Collector dosage

The effect of collector dosage is studied in the range of 5×10^{-5} - 1×10^{-3} M is shown in Fig. 1(b). It shows that both the % recovery and % grade increase with increase in concentration [16] upto 4×10^{-4} M, after which the % recovery and % up gradation almost remains constant. It may be due to the formation of a complete monolayer of xanthate ion on copper ore surface.

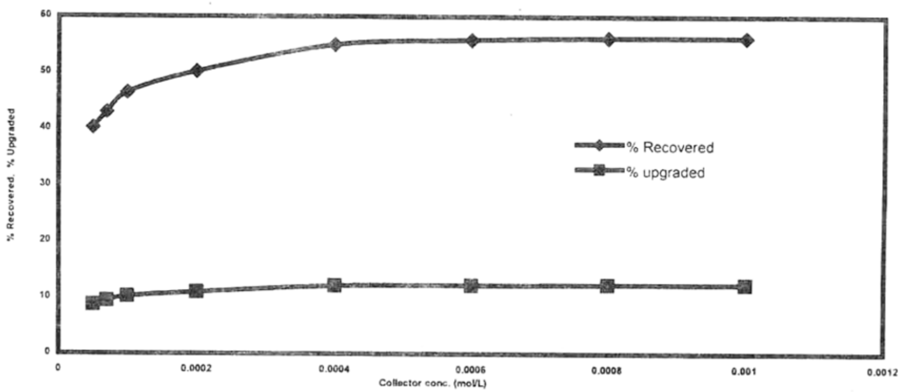
Pulp density

The pulp density effect on the % recovery of copper is presented in Fig. 1(c). The plot shows good recovery from 2 to 20% reaching a maximum value around 25% pulp density. After that the recovery and

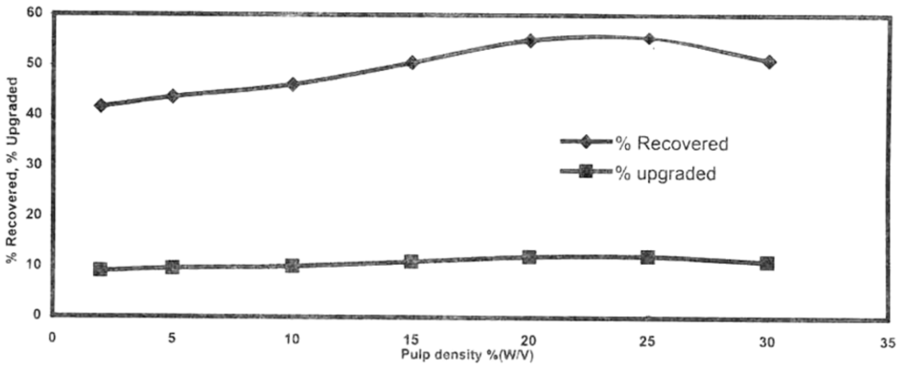
*To whom all correspondence should be addressed.



(a). pH 7.2, Temp. 293 K, Pulp density 20 % W/V, Potassium ethyl xanthate conc. 4E-4 M, mesh size -200 , Water singly distilled water



(b). pH 7.2, Temp. 293 K, Pulp density 20 % W/V, conditioning time 10 min., mesh size -200 , Water singly distilled water



(c). pH 7.2, Temp. 293 K, Potassium ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200 , Water singly distilled water

Fig. 1: Effect of (a) time, (b) collector concentration and (c) pulp density on the % recovery and % upgradation of copper.

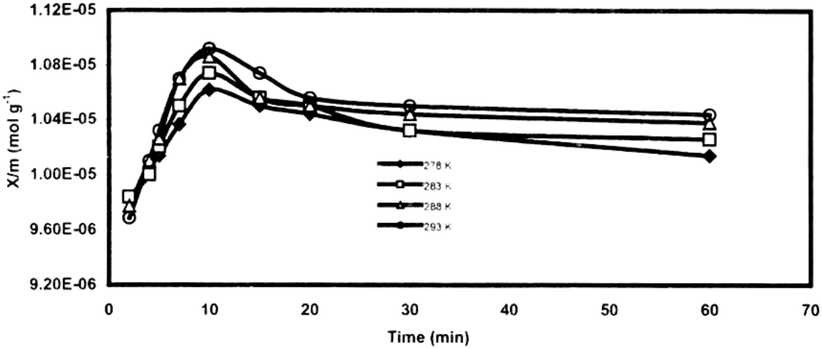


Fig. 2: Temperature effect on the kinetics of 2×10^{-4} M Potassium Ethyl Xanthate(KEX) adsorption at pH 7.

upgradation start decreasing. This may be due to the deposition of fine particles on large particles preventing them from further xanthate sorption.

Temperature effect

The effect of temperature in the range (278 – 293 K) is studied on the flotation of copper ore. The results are plotted in Fig. 3 (a). It shows positive effect on % recovery and % upgradation. The recovery increases from about 45.25 % to 55.25 % by increasing the temperature from 278 to 293 K. Similarly the grade is enhanced from 8.5 % to 10.5 %, which may be due to an increase in the adsorption of xanthate by the solid, as given in Fig. 4. The increase in flotation with temperature may also be due to the increase in solubility of xanthate in solution [17].

pH effect

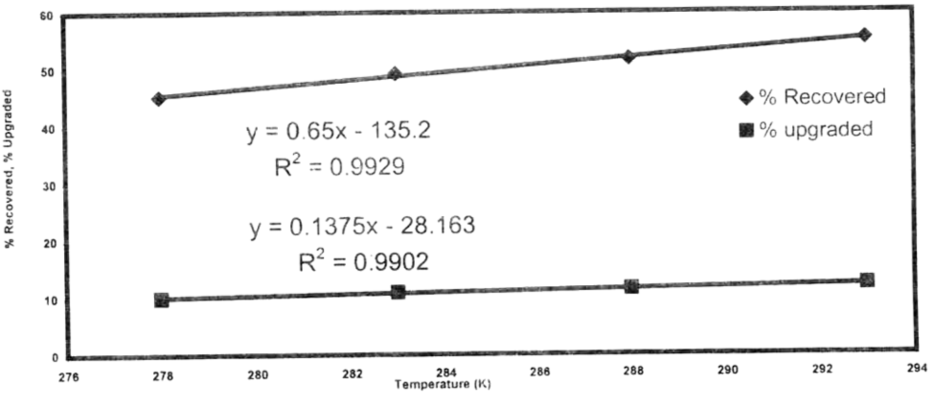
The effect of pH in the range (7-12) on % recovery and % upgradation is plotted in Fig. 3 (b). The result shows increase in recovery with rise in pH from 7 to 10 which is in good agreement with the observation of Buckley and Woods [18] that chalcopyrite is always floatable in alkaline medium only. It may be due to the increase in adsorption of xanthate ion with rise in pH as shown in Fig. 5. Maximum recovery observed at pH 10 is also in accordance with the findings of Markovic and Milosavljevic [19]. The % recovery and % upgradation then decreases sharply, which may be due to the destruction /dissolution of mineral surface at such high pH values. The increase in % recovery with rise in pH upto pH 10 is due to the stability of xanthates in alkaline medium. Selective flotation of chalcopyrite at pH 8 and above was also found by Southerland and Wark [4].

Particle size effect

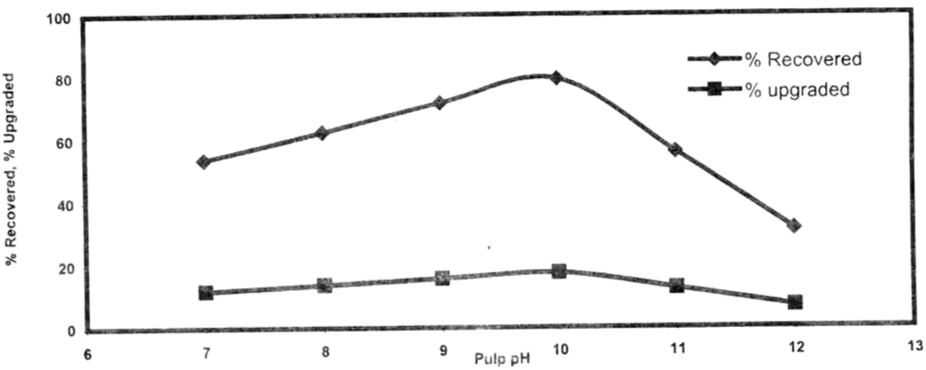
The effect of particle size on % recovery and % upgradation is presented in Fig. 3 (c). The observed plot indicates an increase in the recovery with reduction in particle size. Maximum recovery is observed on –200 mesh sample. It may be attributed to the increase in the surface area of solid, which leads to an enhanced adsorption of xanthate ions. Secondly, the increase in the size of particle reduces the adhesion between the particle and bubble, resulting in drop of mineral particle from froth [20]. The small difference in recovery between (-140+200) and (-200) mesh sizes is probably the result of an increase in number of small particle, which may deposit on the surface of large particle surface covering it completely and preventing further adsorption of collector on the solid. The % upgradation on (-200) mesh shows a decrease in grade, as excess grinding produces large number of powdered particle, which float with ore particle due to its small size and weight (density), hence lowering the grade of the floated ore.

Water quality effect

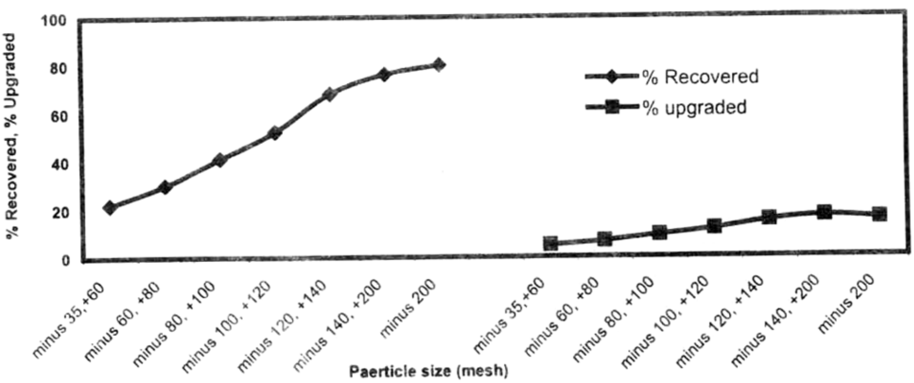
The effect of water quality (Tape water, singly distilled water, doubly distilled water) on the % recovery and % upgradation is presented in Fig. 6 (a). As can be seen good recovery and upgradation is observed in the order: doubly distilled water > singly distilled water > tape water. Similar order is also observed in adsorption study as given in Table 1.



(a). pH 7.2, Pulp density 20 % W/V, Potassium ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200 , Water singly distilled water



(b). Temp 293 K, Pulp density 20 % W/V, Potassium ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200 , Water singly distilled water



(c). Temp 293 K, Pulp density 20 % W/V, Potassium ethyl xanthate conc. 4E-4 M, conditioning time 10 min., pH 10 , Water singly distilled water

Fig. 3 Effect of (a) temperature, (b) pH and (c) particle size on the % recovery and % upgradation of copper.

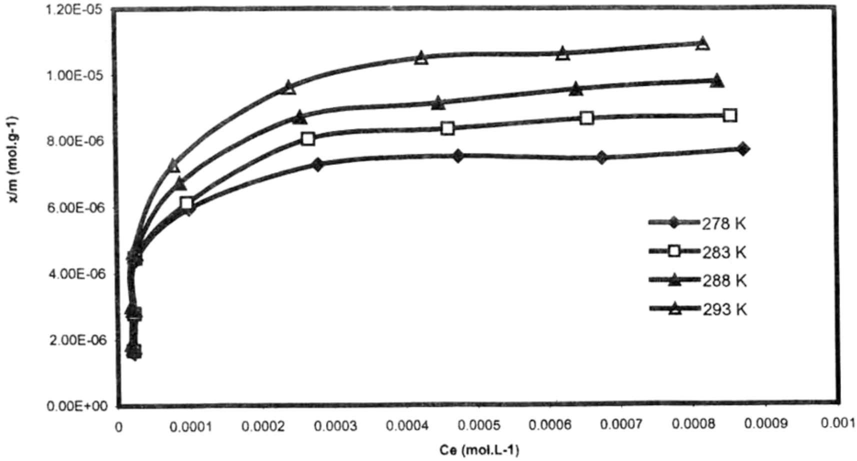


Fig. 4: Temperature effect on the adsorption isotherm at pH 10

Table-1: Water quality effect on xanthate adsorption at 293 K and pH 9.

Initial xanthate conc. mol.L^{-1}	Tape water mol.g^{-1}	Singly distilled water mol.g^{-1}	Doubly distilled water mol.g^{-1}
7×10^{-5}	2.65×10^{-6}	2.63×10^{-6}	2.69×10^{-6}
1×10^{-4}	4.40×10^{-6}	4.09×10^{-6}	4.31×10^{-6}
2×10^{-4}	5.09×10^{-6}	6.04×10^{-6}	7.38×10^{-6}
4×10^{-4}	5.09×10^{-6}	7.30×10^{-6}	9.12×10^{-6}
8×10^{-4}	3.33×10^{-6}	5.73×10^{-6}	7.72×10^{-6}
1×10^{-3}	3.34×10^{-6}	4.93×10^{-6}	9.78×10^{-6}

The analyses of different types of water used for flotation are presented in Table 2. These analyses, as evident from the table show a change in the total hardness, concentration of lime, $MgCO_3$, alkali,

Table-2: Effect of distillation on water quality

Elements	Tape water mg.L^{-1}	Singly distilled water mg.L^{-1}	Doubly distilled water mg.L^{-1}
Total hardness	318	60	BDL(Below detection limit)
Calcium as $CaCO_3$	172	8	BDL
Mg as $MgCO_3$	146	5.6	BDL
M.alkali	320	110	Traces
Potash alkali	Nil	Nil	Nil
NitriteNO^-_2	Nil	Nil	Nil
Nitrate NO^-_3	Nil	Nil	Nil
Chlorides Cl^-	31.5	10.6	BDL
Sulphate SO^{2-}_4	180	BDL	BDL
Dissolved oxygen	8.6	6	0.25
Sodium Na^+	25	2.2	0.4
Potassium K^+	3.0	0.6	0.1
pH	7.6	7.4	6.8

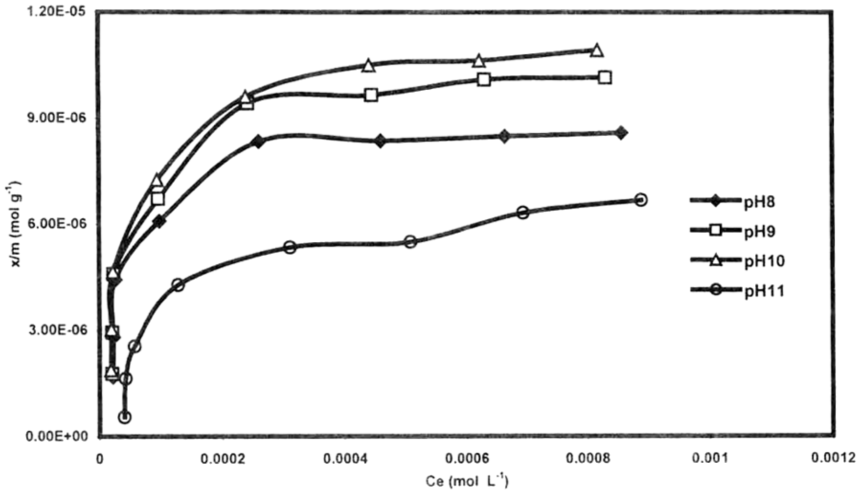
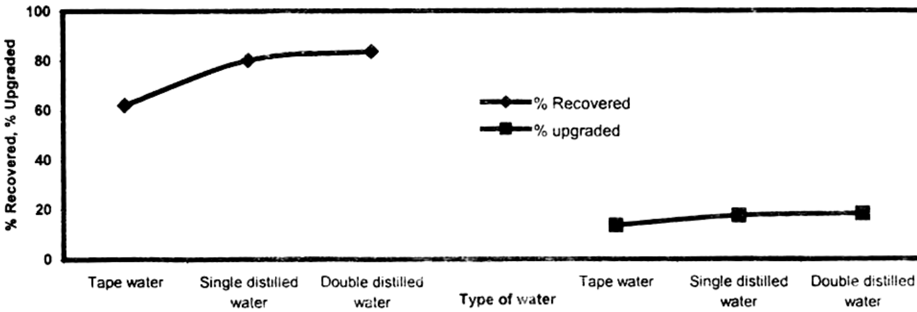
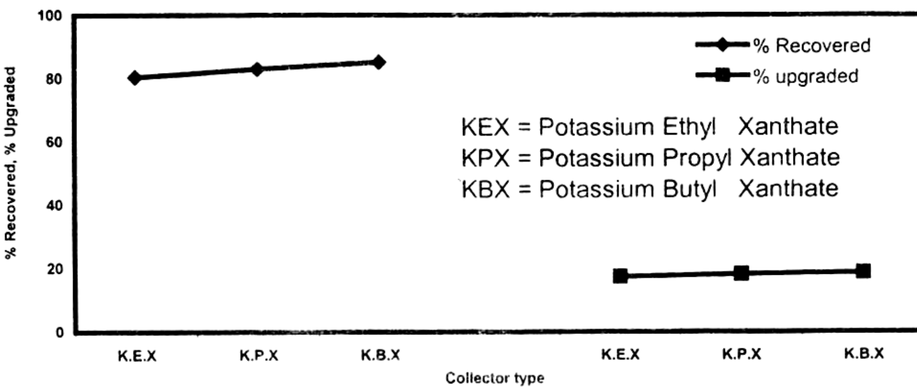


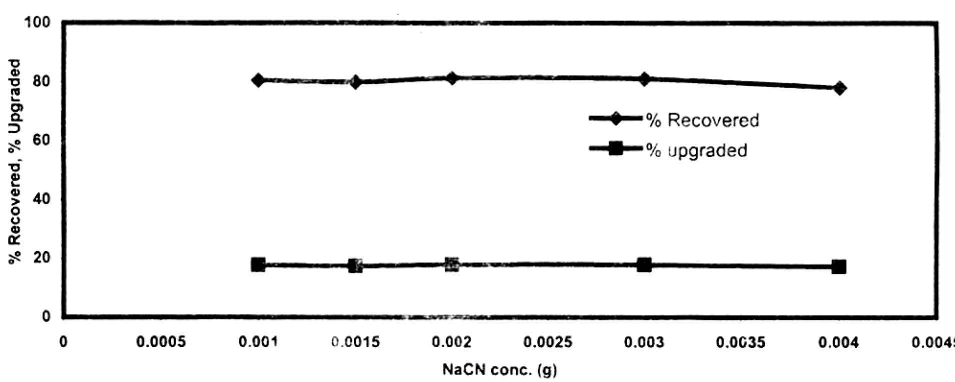
Fig. 5 pH effect on the adsorption isotherm at 293 K.



(a). pH 10, Temp 293 K, Pulp density 20 % W/V, Potassium ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200



(b). pH 10, Temp 293 K, Pulp density 20 % W/V, Ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200 , Water singly distilled water



(c). pH 10, Temp 293 K, Pulp density 20 % W/V, Ethyl xanthate conc. 4E-4 M, conditioning time 10 min., mesh size -200 , Water singly distilled water

Fig. 6 Effect of (a) water quality, (b) collector chain length and (c) sulphadizer on the % recovery and % upgradation of copper.

chlorides, Na, K, dissolved oxygen and pH with distillation. The decrease in recovery may be attributed to the presence of suspended solids, organics carbon and inorganics like, lime, sulphates of Ca, Fe (III), Al, Mg, silicon etc. which may be present in the precipitated form due to high pH values of the system. The formation of colloidal hydroxides, carbonates, sulphates etc. under these experimental conditions may lead to their adsorption on the sulphide surface as hydrophilic layers, preventing, thus, the adsorption of the collector and reducing the floatability of ore [21, 22]. Similarly loss in grade may be attributed to the hydrophobic coating of microbiological material in water on non-value (un-wanted) minerals causing also their flotation [21].

Chain length effect

Chain length effect (C_2 - C_4) of the collector on the copper ore is also studied and the results are plotted in Fig. 6 (b). It shows that as the number of carbon atom increases, the % recovery and % upgradation also increases, which may not only be due to the increased amount of xanthate ion but also due to a decrease in the polarity of xanthate molecule adsorbed on the surface [8,20].

Cyanidation effect

The effect of different amount of NaCN added to the pulp are shown in Fig. 6 (c). As can be seen no visible effect of cyanidation is observed on the % recovery and % upgradation when the amount of NaCN in solution is low. It may be due to the excess of NaCN as compared to the low contents of Pb and Zn in the sample and also due to the fact that pyrite remains in the pulp as the working pH range is 7-12. These findings are similar to those of Kakovskii [23] who found that, greater the solubility of the metal xanthate in cyanide, less stable is the attachment of the collector to the metal. However, decrease in % recovery and % upgradation by the addition of 0.004 g of NaCN may be due to the formation of soluble complexes of excess cyanide with slightly less soluble copper xanthates resulting in the depression of chalcopyrite [23].

Experimental

Sample preparation

Fresh ore sample from Shinkai, North Waziristan Agency, Pakistan were collected, crushed and grounded to different mesh sizes. The ore analyses showed that it consisted mainly of, 0.8 % Cu, 8.7 % Fe, 11.94 % Al, 7.5 % Mg, 19.68 % Si, 3.25 % S and Ni, Co, Zn and Ag is less than 0.0001%.

Reagents

All the reagents used in this study were of the analytical grade and were used without further purification. All the solutions and mixtures were prepared in double distilled water.

Potassium ethyl xanthate preparation (KEX)

Potassium ethyl xanthate was synthesized and then purified by recrystallization from acetone by the usual method given by Rao [13], Fuerstenau and Mishra [15]. The purity of the product obtained was tested spectrophotometrically. The xanthate thus synthesized was kept in a refrigerator below 293 K.

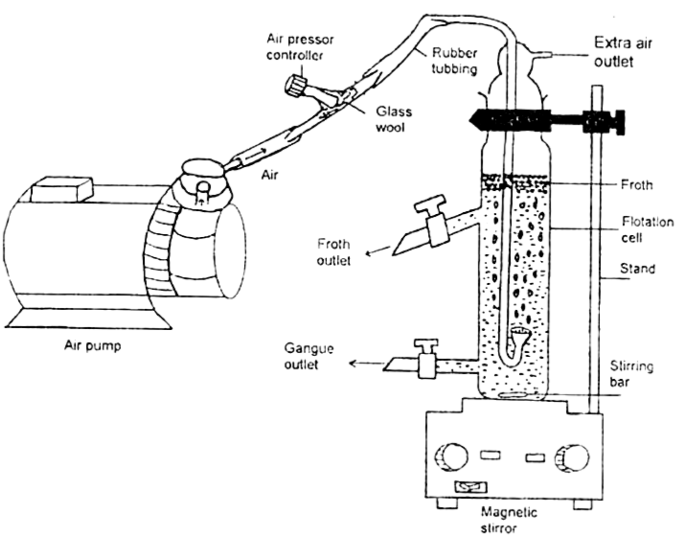


Fig. 7: Schematic diagram of flotation apparatus.

Flotation apparatus

A glass column of 150 mL or 250 mL capacities was used for the flotation as shown in Fig. 7. A tube fitted with gas sparger was immersed from the top so that it reaches 1 inch above the bottom. The gas sparger (pore size 25-50 μm) was commercially available gas dispersion funnel like shaped. A lipped side arm near the middle of the column served as foam out let. Another arm at the bottom was provided to drain the column. The compressed air was generated from an air pump. The rate of airflow was adjusted with a pressure-controlled valve between 20-80 ml/min. The air was purified and dried by passage through glass wool.

Flotation procedure

Twenty grams of feed material was placed in a flotation cell with 80-100 mls of distilled water. The pulp pH was adjusted between 9-10 with the help of dilute HNO_3 and KOH solution. The mixture was stirred continuously for 10 minutes. In case of any decrease or increase in pH, the pulp pH was readjusted between 9-10. After pH setting known volume of concentrated solution of potassium ethyl xanthate (KEX) was added, so that the concentration of potassium ethyl xanthate in the flotation cell becomes 4×10^{-4} M. The pulp was stirred for 10 minutes. Finally one mL of pine oil was added to the cell and agitated for 2-3 minutes. Then airflow valve was released and the compressed air was bubbled through the stirred solution. Stirring was stopped as soon as foams were formed on the surface of the solution. The flow of the compressed air was controlled so that the bubble just broke the surface. Most of the mineral was thus floated and the solution became clear within a few minutes. The floatable solids were transferred to the filter paper. Air was bubbled through the solution again with stirring to ensure complete recovery. The floated solid was washed with distilled water, dried with filter paper and then transfer into a polyethylene vial for mineral content analysis by atomic absorption spectrophotometer.

Conclusions

From the above discussion, it can be concluded that maximum flotation (% recovery and % upgradation) is observed within 10 minutes time interval. It was also observed that both the % recovery and % grade increase with increase in concentration upto 4×10^{-4} M potassium ethyl xanthate (KEX), after which the % recovery and % upgradation almost remains constant. The decrease in the recovery and upgradation after 20-25 % pulp density may be due to the deposition of fine particles on large particles preventing it from further xanthate sorption. The increase in flotation with temperature may also be assigned to the increase in solubility of xanthate in solution. Similarly, the increase in % recovery with rise in pH up to 10 is probably due to the stability of xanthate in alkaline medium. The increase in % recovery and % upgradation with the increase in the number of carbon atoms may be attributed to a decrease in the polarity of xanthate molecule adsorbed on the surface. Interestingly no visible effect of cyanidation on the % recovery and % upgradation is seen. Finally, it may be concluded that the increase in the number of distillation, reduces the availability of soluble salts in water, resulting an increase in the upgradation of copper.

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