

# Studies on the Beneficiation of Barite

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## Abstract

Barite is extensively used as drilling mud in oil exploration operations. Beneficiation of barite by flotation was investigated using cationic and anionic collectors. Commercially available fatty amines such as Armoflote 17 and Liquid B50 were tried as collectors to float gangue minerals (reverse flotation) whereas oleic acid was used for direct flotation of barite. Effect of collector concentration on flotation was studied and the results were discussed. Barite concentrate assaying 96% BaSO<sub>4</sub> with less than 1% SiO<sub>2</sub> could be obtained by single stage flotation using cationic collectors. Zeta-potential measurements were conducted to study the interaction of cationic collectors on silica and anionic collector on barite. While cationic collectors were found to adsorb on silica by electrostatic interaction, oleic acid was found to adsorb on barite by chemisorption. Advantage of reverse flotation over direct flotation technique was discussed.

**Keywords:** Barite, Cationic collector, Oleic acid, Adsorption and Flotation

## Introduction

Barite deposit at Mangampet, Cuddapah district of Andhra Pradesh, is the world's largest deposit containing 61 million tonnes of recoverable barite. Because of these huge reserves, India has occupied second rank in barite production. Barite is an important and vital raw material to the petroleum industry. It is used as drilling mud because of its high specific gravity, inertness to acids and low solubility in water. While high-grade barite produced from the mines can be directly used for the manufacture of barium chemicals, pigments and paper coating applications, low-grade dumps require beneficiation for effective utilization. Beneficiation strategies mainly depend on the grade of the ore, nature of gangue and liberation size. Barite is generally beneficiated by using physical separation techniques like crushing, screening, log washing, jigging, heavy media separation, tabling and spiral concentration, magnetic separation and in some cases by flotation. Heavy media separation and jigging are normally employed on high grade and coarsely liberated ores while gravity concentration techniques are adopted to produce intermediate concentrates. Flotation is followed where the ore is finely disseminated.

Selective flotation of barite from quartz, fluorite and carbonates was investigated by earlier researchers using alkylsulfonates as collectors (Schubert and Schneider 1970). It was observed that small additions of barium chloride could activate and enhance the flotation of barite. Significance of

slurry pH for the effective separation of barite from different gangue minerals was discussed by various authors (Clement and Klossel 1963 and Martinez, Haagensen and Kudryk 1975). Better separation of barite was observed in alkaline pH (above 9.0) while using fatty acid collector. However, pH of below 9.0 was preferred if the ore contain carbonates and sulfides. Tall oil, tannic acid, quebracho and sodium silicate are reported as best modifiers to float barite from quartz-barite mixtures (Bahr, Clement and Surmatz 1968). Sodium silicate was found to play a vital role in the dispersion of particles and also in the removal of  $\text{Ca}^{2+}$  ions, which will otherwise activate various gangue minerals in fatty acid flotation of barite from siliceous barite (Tsailas, Catrakis and Frangioskis 1968). Separation of barite by flotation and the adsorption mechanism of fatty acids on various salt type minerals were discussed by earlier researchers (Hanna and Somasundaran 1976). Most of the earlier investigators have followed direct flotation using oleate as collector. Though high-grade concentrates could be obtained by using oleic acid or oleate, barite surface contaminated with oleic acid is not suitable for certain applications. M/s Indian Bureau of Mines, Nagpur has suggested heat treatment method to remove adsorbed oleate from barite surface. Complete elimination of adsorbed oleate molecules from the barite surface by heat treatment on an industrial scale is difficult and expensive. Hence reverse flotation technique wherein silica and silicate minerals were floated from barite ore using fatty amines as collector was attempted. Further, it is the most advantageous to separate silica, which constitute only 12% instead of barites that constitute about 80%. Since silica is negatively charged, cationic reagents are most suitable as collectors. Earlier investigations conducted at NML Madras Centre on reverse flotation were proved beneficial on variety of ores. The present study describes the beneficiation of barite both by cationic and anionic collectors.

## **Experimental Materials And Methods**

### **Sample**

Sieve and chemical analyses of barite sample obtained from the mines was shown in Table 1A & 1B. From the analysis it is apparent that the ore contain 80% barite with  $\text{SiO}_2$  and  $\text{CaCO}_3$  as major gangue minerals. Material was ground to below 45-micron size (80%) to liberate barite from other gangue minerals.

**Table.1A: Chemical analysis of Head Sample**

Radical	Assay (%)
BaSO <sub>4</sub>	80.72
SiO <sub>2</sub>	13.64
Al <sub>2</sub> O <sub>3</sub>	0.83
CaCO <sub>3</sub>	3.84
MgCO <sub>3</sub>	0.48
Fe	0.08

**Table.1B: Sieve analysis of Head Sample**

Sl.No	Aperture size ( μ )	Weight retained (%)
1	+100	0.7
2	-100 +75	1.2
3	-75 +63	3.8
4	-63 +53	9.6
5	-53 +45	2.7
6	-45	82.0

## Reagents

Armoflote-17 supplied by Akzo Nobel, Liquid B-50 from Ideal Specialty Chemicals private Ltd, Pune and oleic acid from BDH chemicals were used as collectors. While the collectors are of commercial grade, all the other reagents used in this study are of analytical grade.

## Flotation

Flotation experiments are conducted by using Denver laboratory model flotation cell. A known weight of barite sample at a desired solids percentage was transferred into the flotation cell. pH of the slurry was adjusted by using either HNO<sub>3</sub> or NaOH. After adjusting the pH, slurry was conditioned with reagents for a specific duration and finally air was released for flotation. Both float and sink products were collected separately and dried in an oven at 105<sup>0</sup>C. Pulp density was measured using Denver pulp density scale. Representative samples of float and sink were prepared from bulk sample for chemical analysis.

## Zeta potential (ζ) measurements

Zeta potential measurements were conducted using Zeta-meter 3.0 + model of Zeta-meter Inc. Each sample was equilibrated for half an hour. Equilibrated slurry was injected in to the micro electrophoresis cell using disposable syringes. Minimum of three readings with a standard deviation of less than 2% were taken and an average value was reported. Prior to each measurement, electrophoresis cell was thoroughly washed and rinsed with de-ionized water followed by rinse with sample to be measured.

## Chemical Analysis

Standard gravimetric procedures (Roland Young 1971) were adopted to estimate the BaSO<sub>4</sub> and SiO<sub>2</sub>.

## Results and Discussion

### Effect of collector type on flotation

Flotation tests were conducted using cationic and anionic collectors and the results are presented in Tables 2-4. In the presence of cationic collectors i.e Armoflote-17 and Liquid B-50, most of the silica and silicate minerals were floated in preference to barite (reverse flotation). However barite alone was found to float in the presence of oleic acid, an anionic collector (direct flotation). As the concentration of cationic collector is increased, the quality of the concentrate was found to increase with decrease in recovery of barite.

**Table 2: Effect of collector (Armoflote-17) dosage on grade and recovery of barite**

#### Conditions

Slurry pH : 8.70 (Natural)                      Pulp density : 1.23  
 Conditioning time : 240 Seconds                      Flotation time : 360 Seconds

Sl.No	Collector (kg/t)	Weight (g)		Concentrate assay (%)		BaSO <sub>4</sub> Rec. (%)
		Float	Sink	BaSO <sub>4</sub>	SiO <sub>2</sub>	
1	0.3	205	794	88.26	6.04	85.55
2	0.4	250	746	89.62	3.54	83.00
3	0.5	283	721	88.82	3.66	78.81
4	0.6	328	666	93.54	1.81	76.18
5	0.7	347	650	94.20	1.85	76.00
6	0.8	351	635	94.43	1.04	73.78
7	1.0	364	634	95.29	0.48	73.66

**Table.3: Effect of collector (Liquid B-50) dosage on grade and recovery of barite**

#### Conditions

pH : 8.50 (Natural)                      Pulp density : 1.23  
 Conditioning time : 180 s                      Flotation time : 360 s

Sl.No.	Reagent (kg/t)	Weight (g)		Concentrate assay (%)		BaSO <sub>4</sub> Rec. (%)
		Float	Sink	BaSO <sub>4</sub>	SiO <sub>2</sub>	
1	0.20	166	825	84.61	5.98	87.4
2	0.25	350	646	92.96	4.71	72.2
3	0.35	430	568	95.56	0.43	65.0



## Interaction of collector molecules at mineral/water interface

Zeta-potential measurements were conducted to understand the surface properties of barite and silica and also the interaction of collector molecules at the mineral/water interface. Zeta-potential of barite and silica at various pH values were measured and the results are shown in Figs.1-2.

From the results shown in Fig.1, the Iso Electric Point (IEP) of pure barite sample collected from the mines was observed around pH 8.5. In other words, barite is positively charged up to pH 8.5 and becomes negative beyond pH 10. However, in the presence of added  $\text{Na}_2\text{SO}_4^{2-}$  ( $7 \times 10^{-4}$  moles. $\text{L}^{-1}$ ), the IEP of barite was found to shift towards acidic range. This clearly reveals the adsorption of  $\text{SO}_4^{2-}$  ions on the barite surface. While Bokern et.al (2003) have reported the IEP of pure barite around pH 4.0, Ofor and Nwoko (1996) have observed it around pH 9.5 for Nigerian barite. Such vast difference was attributed to different degrees of crystallinity and relative ease of release of potential determining ions i.e  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$ .

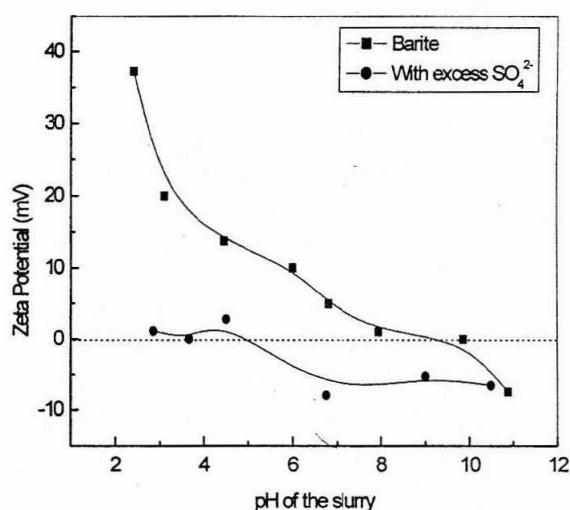


Fig.1. Zeta Potential of Barite

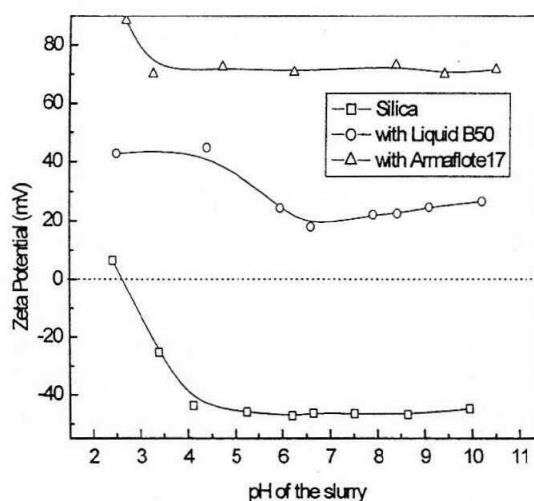
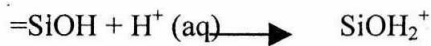


Fig.2. Zeta Potential of Silica

Buchanan and Heymann (1948) have observed positive zeta-potential even in basic pH and argued that  $\text{SO}_4^{2-}$  is less strongly bound to its surface positions in the crystal than  $\text{Ba}^{2+}$  ions. This relative ease of release of sulfate, giving rise to a positive potential, was found to increase with increasing imperfection of the surface structure. Similarly the negative zeta-potential of barite was attributed either to preferential release of  $\text{Ba}^{2+}$  or to preferential adsorption of  $\text{SO}_4^{2-}$ . The positive zeta potential observed in the present case may be attributed to deficient sulphate sites. The minimum floatability of barite with cationic collectors could be attributed to the positive surface charge on which the adsorption of cationic collector is minimum.

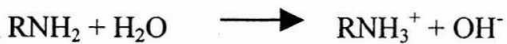
On the other hand, cationic reagent molecules, which are positively charged, are expected to adsorb on silica particles through electrostatic interaction. Thus silica and silicate minerals could be easily floated by using cationic collectors. Species distribution diagram of silica and amine are presented in Fig.3 for better understanding. When silica particles are equilibrated with aqueous solution, three different hydroxylated sites i.e.  $=\text{SiOH}_2^+$ ,  $=\text{SiOH}$  and  $\text{SiO}^-$  can be expected depending on the pH. In acidic conditions,  $\text{H}^+$  may interact with silica surface to form a hydronium ion according to the following equation.



The positive zeta-potential at low pH could be explained due to the presence of such hydronium species. The negative charge above the pH of isoelectric point is explained due to the presence of  $\text{SiO}^-$  species formed according to the following equation.



The reaction of amine in aqueous solution can be written as



From the species distribution diagram, it may be noted that amine will be in the form of  $\text{RNH}_3^+$  up to pH 10 where as the silica surface will be negative from pH 3.0 onwards. Thus there exists a favourable environment for the adsorption of  $\text{RNH}_3^+$  ions on a negatively charged  $\text{SiO}^-$  surface by electrostatic interaction. In the presence of amine collectors, silica particles have shown positive zeta-potential through out the pH range studied. This could be attributed to excess precipitation of  $\text{RNH}_3^+$  on silica surface. Detailed mechanism of adsorption of long chain alkylamines on silicates was reported by Chernyshova et.al (2000). From the above discussion, it could be concluded that the silica and silicate minerals can be selectively floated from barite using cationic collectors.

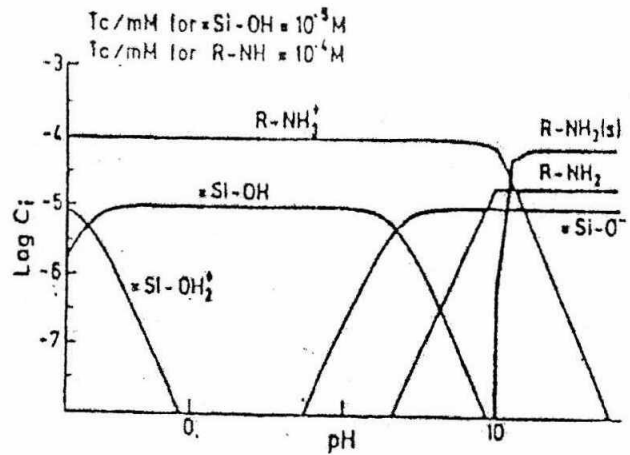


Fig.3. Species distribution diagram of Silica and Amine

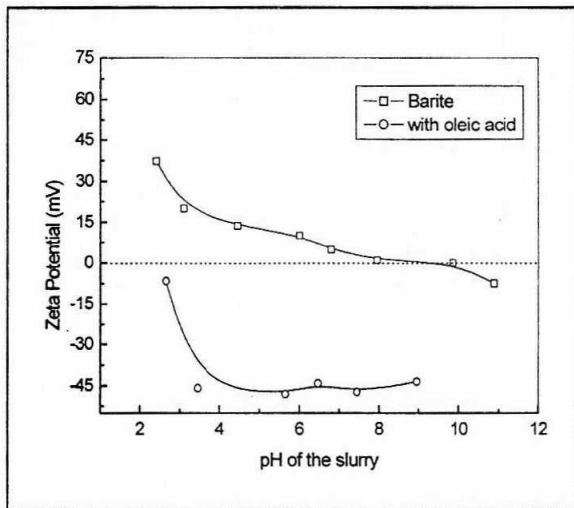


Fig.4. Zeta Potential of barite with oleic

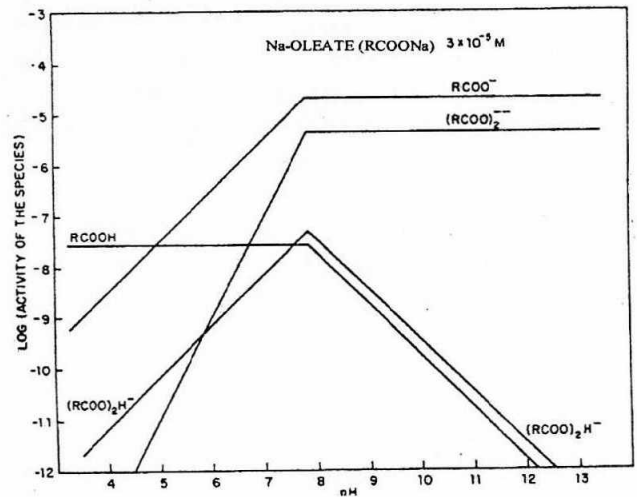


Fig.5. Species distribution diagram of Amine

Adsorption of oleic acid on barite could be explained by zeta-potential results shown in Fig.4 along with species distribution diagram of oleic acid shown in Fig.5. It is known that the oleic acid would exist in different species while in equilibrium with water. Negative zeta-potential of barite particles in the presence of oleic acid could be explained due to the adsorption of anionic species  $\text{RCOO}^-$ ,  $(\text{RCOO})_2^{2-}$  and  $(\text{RCOO})_2\text{H}^-$  on positively charged barite surface. In the presence of oleic acid, the IEP was found to shift from 8.5 to 3.0. The shift in IEP in the presence of oleic acid clearly suggests the chemisorption of oleate molecules on barite surface. Detailed adsorption studies conducted on barite sample (Buchanan and Heymann 1948) have revealed the chemisorption of oleate even on neutral barite surface.

## Conclusions

Beneficiation of barite was studied using both cationic and anionic collectors. Two types of cationic collectors viz Liquid B-50 and Armoflote-17 were tried to separate silica from barite. Though both the reagents are selective towards silica, consumption of Liquid B-50 was found to be less (0.35kg/t) compared to Armoflote-17 (1.0kg/t). High-grade barite concentrates with silica content of less than 0.5% could be obtained by using cationic collectors. Silica content in barite concentrate obtained by direct flotation was found to be relatively high (2.5%). Since the barite particles are coated with oleate molecules, the applicability of these concentrates will be limited. It was also observed that the tailings of direct flotation process are highly dispersed and as such required flocculation/coagulation before discharging. While cationic collectors were found to adsorb on silica by electrostatic interaction, oleic acid was found to adsorb on barite by chemisorption.



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## References

1. Schubert, H. and Schneider, W. 1970. The function of non-polar and non-ionizable polar-non-polar additives during flotation, Vol.1, 189-196. IX International Mineral Processing Congress, Prague.
2. Bahr, A., Clement, M and Surmatz, H. 1968. On the effect of inorganic and organic substances on the flotation of some non-sulfide minerals by using fatty acid type collectors, Paper S-11, 12 pp VIII International Mineral Processing Congress, Leningrad.
3. Tsailas, D.P., Catrakis, S.D and Frangioskis, A.Z. 1968. The role and the mechanism of the action of sodium silicate in the flotation of barite, Paper D-17, VIII International Mineral Processing Congress, Leningrad.
4. Clement, M and Klossel, E. 1963. Flotation and Cycloning of barite out of the tailings of Rammelberger sulfide flotation. *Zeit-schrift Erzbergbau Metall.* 16:387-395.
5. Martinez, E., Haagensen, R.B., and Kudryk, V. 1975. Application of new techniques in developing a barite flotation process. *Trans.SME/AIME* 258:27-30.
6. Hanna, H.S and Somasundaran, P. 1976. Flotation of salt type minerals. In *Flotation A.M. Gaudin Memorial Volume. Volume.1* p 197-272. New York; American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.
7. Roland S.Young. 1971. *Chemical Analysis in Extractive Metallurgy*, p 35-40 and 302-307. London:Charles Griffin & Company Ltd.
8. Bokern, D.G., Hunter, K.A and McGrath, K.M. 2003. Charged barite-Aqueous solution interface: Surface potential and atomically resolved visualization, *Langmuir* (to be published).
9. Ofor, O and Nwoko, C. 1996. Oleate flotation of a Nigerian barite: The relation between flotation recovery and adsorption density at varying oleate concentrations, pH and temperatures, *J. Colloid and Interface Science*, 186, 225-233.
10. Buchanan, A.S and Heymann, E. 1948. *Proc. R. Soc. London*, A195, 150-162.
11. Chernyshova, I.V., Hanumantha Rao, K. and Vidyadhar, A. 2000. Mechanism of adsorption of long chain alkylamines on silicates. A spectroscopic study. 1. Quartz, *Langmuir*, 16, 8071-8084.