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Efficacy Of Oleic Acid As Collector For Selective Separation Of Finely Disseminated Low-Grade Iron Ores

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ABSTRACT

The efficacy of conventional oleic acid collector for the separation of iron values from low grade ores containing quartz and alumina as gangue minerals was investigated. Adsorption of oleic acid on hematite, quartz and alumina was studied and found to be pH dependent. The adsorption maximum was observed where the surface charge is neutral and/or hydroxylated. The nature of oleic acid interaction at mineral/water interface was established by contact angle, zetapotential and FT-IR studies. The flotation tests have revealed that the hematite is floatable at low oleate dosage whereas quartz requires very high dosage. Flotation experiments on artificial mixtures of hematite and quartz have shown that selective separation of hematite is possible when the quartz content in the mixture is less than 15%. The selective flotation of hematite is severely affected by increasing the ratio of quartz content in the mixture. The efficacy of oleic acid on selective flotation of iron minerals was studied on two different low grade iron ores. The results clearly demonstrated that oleic acid lacks selectivity to separate hematite from banded hematite quartzite sample. The need for the development of effective collector for finely disseminated low-grade iron ores was emphasized.

1. INTRODUCTION

The depletion of high grade reserves over the years has necessitated the utilization of low grade finely disseminated iron ores available in large quantities. For example, the oolitic ores in France and Columbia, siderite ores in Bulgaria, Austria and Turkey, low-grade complex ores in China, low and moderate-grade taconite in the USA and similar low to moderate banded ores in Ukraine and India are considered valuable iron ore resources. The oolitic ores are made up of silicate, oxide and carbonate minerals in solid solution phase. Siderite, limonite and goethite are important sources of iron but relatively low in Fe content. In certain cases, hematite and magnetite may occur in banded formations in massive waste rock. The presence of sulfides, titanium, Manganese and vanadium in iron oxides may present special challenges. In addition, elemental substitutions in magnetite and hematite crystal lattice may lower the economic value of the final product. The utilization of such complex ores is a challenging task and needs collective efforts in designing process flow sheets within the frame work of sustainability. The conventional process flow-sheets involving washing, jigging, spiral concentration and magnetic separation are ineffective to achieve the required grade. Flotation technique is more opt to recover iron values from such complex ores. Depending on the liberation characteristics of the gangue minerals and their volume fraction, three different routes namely direct flotation, reverse flotation and selective dispersion and flocculation were devised. In direct flotation, iron bearing minerals are floated using oleic acid/oleate as collector. In the reverse floatation, quartz and silicate minerals are floated using cationic/anionic collector. Various cationic collectors like fatty mono amine, fatty di-amine, ether mono amine ether di-amine are available in the market with different trade names. In most of the cases, mono amine and di-amine are blended in certain proportion for thorough separation of silica from iron ore.

Better grade and recovery can be obtained by using flotation column compared to conventional flotation cells [1-3]. Mixed anionic and cationic collector scheme was suggested to enhance the hydrophobic character and in turn the floatability [4]. The effect of carbonate alkalinity on flotation behavior of quartz was studied and found that the floatability of quartz was decreased as the alkalinity of the process water is increased [5]. Process flow sheet containing selective flocculation, desliming and cationic flotation of coarse silica was suggested to beneficiate finely disseminated oxidized teconites containing predominantly hematite and goethite. Beneficiation of alumina rich Indian iron ore slimes by flotation [6] and removal of specific impurities like alumina, phosphorous and recent developments in flotation equipment were reviewed and reported [7].

The reverse cationic flotation route developed by Bureau of Mines, United States of America was widely utilized in USA and in other western countries. Initially, fatty amines were used as collector which was subsequently replaced by the more efficient ether amines. The effectiveness of various ether amines in iron ore beneficiation was reviewed and suggested that partial substitution of amine with non polar oils is most attractive route [8]. It was reported that iron ore concentrates with less than 1% silica could be obtained from iron ore tailings/rejects with iron recoveries of around 60% [9]. The effect of amine type and pH on quartz flotation was studied and found that ether di-amine was more effective to float medium and coarse quartz, while ether monoamine performs better in the case of fine quartz. It was also observed that the flotation of coarse particles is enhanced by the presence of fine particles in the system [10]. Twelve different amine collectors were evaluated on three different samples of magnetite taking coco primary amine acetate as standard for comparison. The oleyl and tallow di-amines were found to display better selectivity compared to other fatty amines. The trimethyl alkylammonium chloride was found to be more selective but less efficient than primary and di-amines [11-12].

Direct flotation of iron oxides using anionic collectors such as oleic acid, linoleic acid, combination of fatty acids, petroleum sulfonate was developed and implemented in plant scale [8,13-15]. The process of direct flotation is very attractive in the case of low grade minerals where Fe content is 25-30%. The effective separation of lean ores such as banded hematite quartzite (BHQ), banded hematite jesper (BHJ) and banded magnetite quartzite (BMQ) was found to be difficult and invariably results in low recoveries [16]. The sensitivity of the process appears to be seriously affected in the presence of hydrolysable cations like Ca^{2+} and Mg^{2+}. Further, the conditioning of collector solution with mineral slurry was reported to be crucial for the direct flotation process. In spite of extensive research on hematite-oleate system, perfect separation of hematite from quartz could not be established. The reason for complex behavior was explained in terms of solubility of oleic acid and ionomolecular complexes [17]. Flotation of quartz from iron ore was successfully practiced using sodium oleate as collector, starch as depressant for iron minerals and CaO as an activator for quartz flotation (reverse anionic flotation). After flotation, iron concentrate assaying 65% Fe and recovery of 70% were achieved. However, both grade and recoveries were affected in the presence of siderite ($FeCO_3$). To overcome the problems, two stage flotation was suggested [18] wherein siderate was floated using sodium oleate as collector at neutral pH in the first stage. After siderite separation, the silica was activated and separated using $CaCl_2$ as activator, sodium oleate as collector and starch as depressant. The mechanisms relevant to above process studied by means of adsorption and zeta-potential measurements [19].

The option of direct or reverse flotation is dictated by the volume of the mineral to be floated, cost of the collector and the kinetics of flotation. Generally, flotation of the mineral whose quantity is less is economical compared to the flotation of the mineral present in huge quantity. Thus flotation of iron minerals using oleic acid collector is beneficial in the case of low grade ores assaying 25-30% Fe. However, direct flotation of iron minerals from such low grade ores like BHQ, BMQ and BJQ was not reported. Above all, oleic acid is environmentally benign compared to fatty amine collector generally used in reverse flotation. Hence the efficacy of oleic acid for the selective separation of iron minerals from low grade ores was attempted in the present study. Ideal conditions for the floatability of pure hematite and quartz were established and the results were extended to separate hematite from to artificial mixture and natural iron ore samples.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials:

Pure mineral samples of hematite, quartz and alumina collected from the mine site were used in the present study. Oleic acid, hydroxamate and other chemicals used are of analytical grade. All the solutions were prepared in double distilled water.

2.2 Particle size analysis:

The CILAS laser particle size analyzer, model 1180 which works on the principle of laser diffraction was used to determine the size distribution.

1.3 Chemical analysis:

The chemical composition of various fractions of flotation was carried out by conventional wet chemical analysis. The following standard procedures [20] were followed for the determination of silica, iron and alumina.

The sample was dissolved in hydrochloric acid and baked for dehydration of silica. It was subsequently filtered and silica was determined by volatilization with hydrofluoric acid. The insoluble residue was fused with sodium carbonate, extracted with hydrochloric acid and added to the main filtrate obtained during first filtration. The solution was made up to a definite volume and reserved for the analysis of Fe and Al_2O_3. From this solution, an aliquot of sample was taken and diluted. The diluted solution of iron is reduced to ferrous state by stannous chloride and titrated with standard potassium dichromate solution using barium diphenylamine sulphonate as indicator. For the determination of alumina, an aliquot of the solution was acidified with hydrochloric acid and 25 ml of EDTA was also added. The pH was adjusted to 5.5 with ammonium hydroxide and hydrochloric acid and the solution was allowed to boil for 15 minutes. After the solution was cooled, 25ml acetic acid -ammonium acetate buffer solution was added followed by few drops of xylenol orange indicator. Standard zinc acetate was used to titrate the solution. The colour change from lemon yellow to purple indicates the end point. From the difference of titration value, the Al_2O_3 % was determined

2.4 BET Surface area:

The specific surface area and porosity was determined by BET analyzer (Brunauer, Emmett and Teller) Model ASAP 2020 supplied by Micro meritics, USA.

2.5 Contact angle measurement:

Contact angle of the mineral powders was determined by sorption measurement using Kruss Tensiometer, model- K 100. The Washburn equation was used to measure the contact angle on powder samples. When a column of powder bed is in contact with liquid, the pores between the particles act like small capillaries and the rise of liquid is measurable. The capillary constant in the Washburn equation was determined using n-hexane. Mineral sample was placed into a glass sample tube and was carefully and equally packed each time. Each measurement was repeated at least 3 times and an average value was reported.

2.6 Zeta potential Measurements:

The zeta potentials were measured using a Zeta Meter 3.0+, Zeta Meter Inc, USA. A suspension of 0.01g/L of mineral (ground to -10µm) was prepared in $1x10^{-3}$ M KCl electrolyte solutions.

After adjusting the pH to the desired value, the suspension was conditioned for half an hour at 25 ° C. The conditioned slurry was transferred in to the electrophoresis cell for measurements. The average value of the zeta potential of the five readings with standard deviation of less than 1 unit was reported as the final result.

2.6 Adsorption Studies:

The adsorbed amount of oleate was determined from the difference in initial and final concentrations [21]. Required quantity of the mineral sample was taken in Erlenmeyer flask and known quantity of oleate solution (pH adjusted) was added and thoroughly equilibrated at 25 ° C. After equilibration time of 30 half an hour, the concentration of un- adsorbed oleic acid was determined. The amount of oleic acid was arrived by subtracting from initial oleate concentration.

2.7 FT-IR Spectroscopy:

The FT-IR spectra of the samples were recorded using Perkin-Elmer spectrophotometer. 10 mg of the dried sample was dispersed in 200 mg of spectroscopic grade KBr and 40 scans were collected for each spectrum at a resolution of +/- 4 cm^{-1}.

2.8 Surface characterization:

Scanning probe microscope, model 5500 series, Agilent Technologies, USA was used for surface characterization. Measurements were made in contact mode using NSC 15 Cantilever and Picoview 1.12.2 software. Handpicked mineral samples were cut to the size of the sample holder and were mirror polished. The polished samples were immersed in the aqueous solutions and subjected to ultrasonication treatment for 30 minutes to remove the adhered slimes. The fresh sample was equilibrated with oleate solution for 30 minutes and dried in vacuum desiccators. The dried samples were examined by scanning probe microscope.

2.9 Flotation tests:

Batch scale flotation tests were conducted in D-12 Denver flotation machine. The flotation tests were conducted at 25% solids at an impeller speed of 1200 rpm. The pH was adjusted prior to the addition of depressant, activator and collector. The conditioning time of 3 minutes was maintained for each reagent addition. The floated fraction and residue was collected separately and analyzed.

2. RESULTS AND DISCUSSION

3.1 Adsorption studies:

The nature of collector adsorption at mineral/water interface is paramount to make the mineral particles hydrophobic. Adsorption of oleic acid on hematite, quartz and alumina was studied at different pH conditions at a constant oleic acid concentration of 10 ppm and the results are presented in Fig.1.

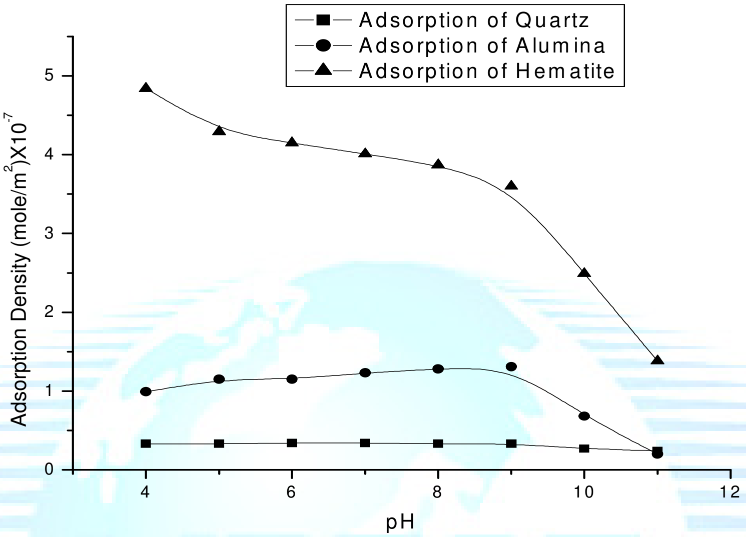

Fig 1: Effect of pH on the adsorption of oleate on hematite, alumina and quartz

From the results it is evident that the adsorption density remains same in the pH range 4.0 to 8.5 and decreases drastically beyond pH 8.5. It is also apparent that around $12x10^{-5}$ g/m^2 and $3.5x10^{-5}$ g/m^2 was adsorbed on hematite and alumina respectively. However the adsorption of oleic acid on quartz and the role of pH on adsorption were found to be negligible. The reason for high adsorption oleic acid on hematite in acidic pH was reported earlier [6]. Further, the adsorption of oleate on hematite was reported to depend on solution pH, ionic strength, oleate concentration and temperature. The maximum adsorption and flotation of iron oxide minerals at neutral pH was attributed to the preferential adsorption of oleic acid on neutral surface site. The constant adsorption density in the pH range 4.0-8.0 on all the minerals could be explained by considering the speciation of hematite and oleic acid at different pH conditions. From the previous research work, it is evident that the isoelectric point of most of the iron minerals falls between pH 5.0-8.5. In other words, all the iron minerals exhibit neutral charge in the pH range 5-9. The species such as FeOH, $FeOH_2^+$, AlOH and $AlOH_2^+$ are predominant in the acidic and neutral pH. Similarly the un-dissociated oleic acid (RCOOH) is a dominant species up to pH 8.0. The RCOOH molecules are expected to interact with neutral -FeOH and -AlOH by condensation mechanism. In the vicinity of a highly hydroxylated surface, the protons of oleic acid can polarize easily toward hydroxyl groups. Consequently, the protons from oleic acid, neutralizes the surface -OH groups, thus forming water molecules. Thus the surface -OH groups facilitate de-protonation of oleic acid and its subsequent adsorption. This type of interaction (condensation mechanism) is very common in organic reactions. The interaction of oleic acid with neutral sites of -FeOH and -AlOH can be represented as

$$\equiv FeOH + RCOOH \longrightarrow \equiv FeOOCR + H_2O \qquad (1)$$

$$\equiv AlOH + RCOOH \longrightarrow \equiv AlOOCR + H_2O \qquad (2)$$

The above mechanism was suggested for the adsorption of dextrin on hydroxylated mineral surfaces and metal hydroxides [22-23]. The contact angle measurements were carried out on the mineral samples equilibrated with 50 ppm of oleate at different pH conditions (Fig 2). From the results it is evident that the contact angle of hematite is much higher (75-80 degrees) compared to quartz which is below 40 degrees. Further, contact angles of hematite and quartz are slightly higher in the pH range of 7-9. This was explained due to the adsorption of ionomolecular complex $R(COO)_2H^-$ in the mid pH region. Though this species contributes only 0.2% of the total concentration of collector, the surface activity of this complex has been reported to be

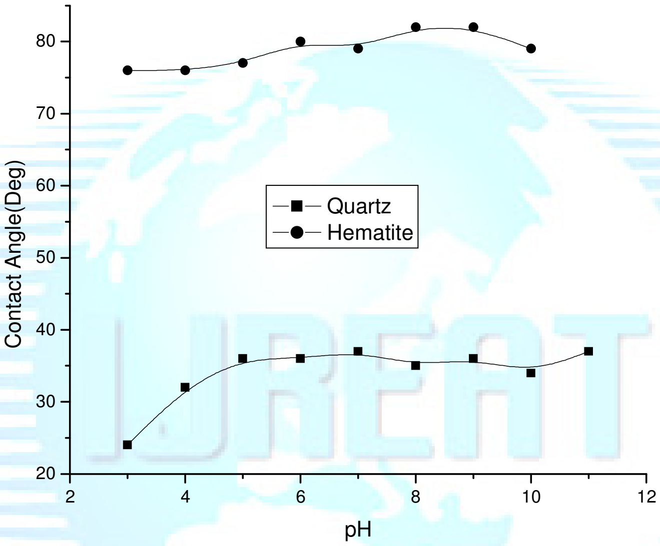

Fig 2: Contact angles of hematite and quartz at different pH (Oleate concentration 20 ppm)

several orders of magnitude higher than that of the neutral oleic acid [17]. From the above results, it is evident that the interaction of oleic acid molecules with surface hydroxyl sites proceeds by neutralization of surface hydroxyls by protons of oleic acid.

Adsorption of oleate on hematite, alumina and quartz was studied at 25^{o}C at a constant pH of 8.0 by varying the concentrations of sodium oleate and the data was plotted in Fig 3. Maximum adsorption density of 4 µmoles was observed on hematite, 1.2 µmoles on alumina and hardly 0.15 µmoles on quartz. These adsorption densities are well below the monolayer coverage of oleic acid. It is evident that the adsorption of oleate on all the minerals was found to be linear below monolayer coverage. Considering the effective parking area of oleate molecule as 33Å^2, number of moles required for monolayer coverage was calculated to be 5 μmol/m^2. It is known that the ionic surfactants containing more than eight methylene groups in the alkyl chains condense two dimensionally on mineral surfaces because of the strong lateral bonds.

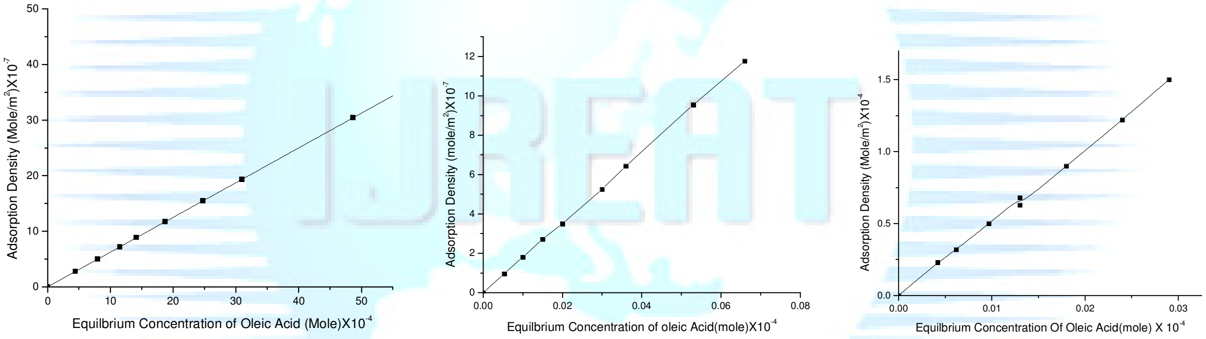

Fig 3: Adsorption Isotherm of Hematite-oleate (extreme left), Alumina-oleate (middle) and Quartz-oleate (extreme right)

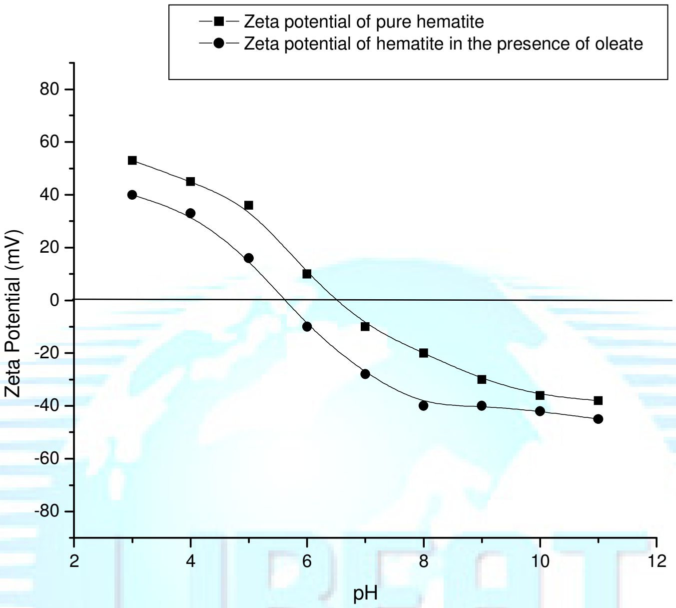

Fig 4a: Zeta potential of hematite in the presence and absence of sodium oleate

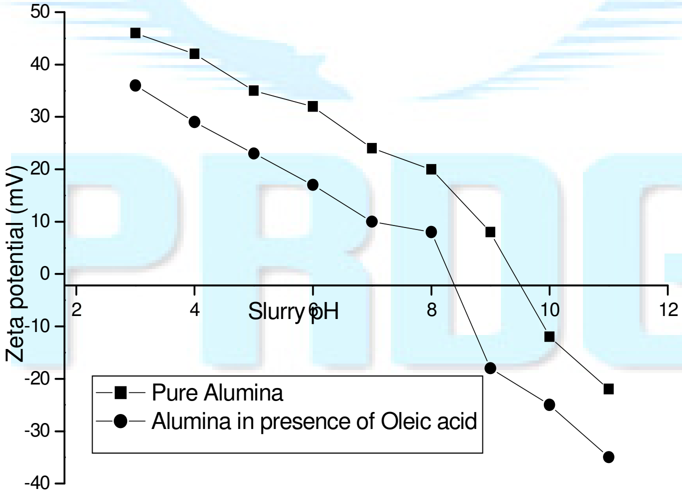

Fig 4b: Zeta potential of alumina in the presence and absence of sodium oleate

The nature of interaction of oleate molecules at mineral/water interface was examined by zeta-potential measurements and the results were presented in Fig 4. The iso electric point (iep) for hematite was observed at pH 6.5. This is in agreement with the iep values of hematite (pH 5.3-8.6) reported by earlier investigators [24-25]. The iep was shifted to pH 5.6 in the presence of 1 x 10^{-4} M sodium oleate. The shift in iep towards lower pH can be interpreted due to chemisorption of oleate molecules on hematite [26]. Since the difference in pH of iep before and after oleate adsorption is marginal, the chemisorption is expected to be very weak. The adsorption behavior of oleate on alumina surface was found to be similar to that of iron ore. The iep of pure alumina observed at pH 9.3 was found to shift to lower pH of 8.5 in the presence of $1x10^{-4}$M sodium oleate. The iep of alumina is in agreement with the reported value of 8.6 [27]. The zetapotential data suggest that oleate binds to hematite and alumina surfaces either as bidentate or monodentate. Study on oleate adsorption on magnetite revealed that the oleate molecules are bonded to iron atoms by bidentate mononuclear complex and form essentially a single layer with a distance between oleate molecules of ~36 $Å^2$ [28]. From the above it is apparent that the forces responsible for oleate adsorption are highly pH dependent. In the neutral and basic pH range, iron oleate is expected whereas physical adsorption between positively charged iron surface and oppositely charged oleate-oleic acid droplets is expected below pH 8.0. Further, acid soap precipitation would occur at neutral pH if the oleate concentration exceeds 10^{-4} M. It may be noted that among the various forms of oleate species, acid soap complex (R_2H^-) is highly surface active and capable to adsorb on neutral hematite surface.

The adsorption of oleic acid on the surface of hematite was also studied by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of oleic acid, hematite and equilibrated samples of iron hydroxide and hematite with oleic acid are shown in Fig.5. In the spectrum of oleic acid, a sharp peak at 2921 cm^{-1} could be attributed to the asymmetric $-CH_2$ stretching vibration. The intense peak at 1707 cm^{-1} and the band at 1285cm^{-1} is ascribed to C=O stretching and C-O stretching vibration respectively. The peaks with moderate intensity at 1019 cm^{-1}, 921 cm^{-1} and 804 cm^{-1} are interpreted due to C-C stretching vibration. The FTIR spectrum of hematite exhibited strong and intense bands at 540 cm^{-1} and 467 cm^{-1}. These bands are interpreted due to Fe-O stretching vibrations which are characteristic of hematite. The sharp bands in the region of 3600-3700 cm^{-1} shows the presence of surface –OH groups. An absorption band around 1730 cm^{-1} ascribed to C=O stretching was observed in the FT-IR spectra of hematite and iron hydroxide equilibrated with oleic acid. This clearly suggests the presence of oleic acid both on hematite and iron hydroxide precipitate. In addition to the peak at 1730, peak around 1445 cm^{-1} could be seen on the spectra of hematite and iron hydroxide treated with oleic acid. This peak is usually attributed to C=O stretching vibrations of carbonyl group or due to symmetric vibrations

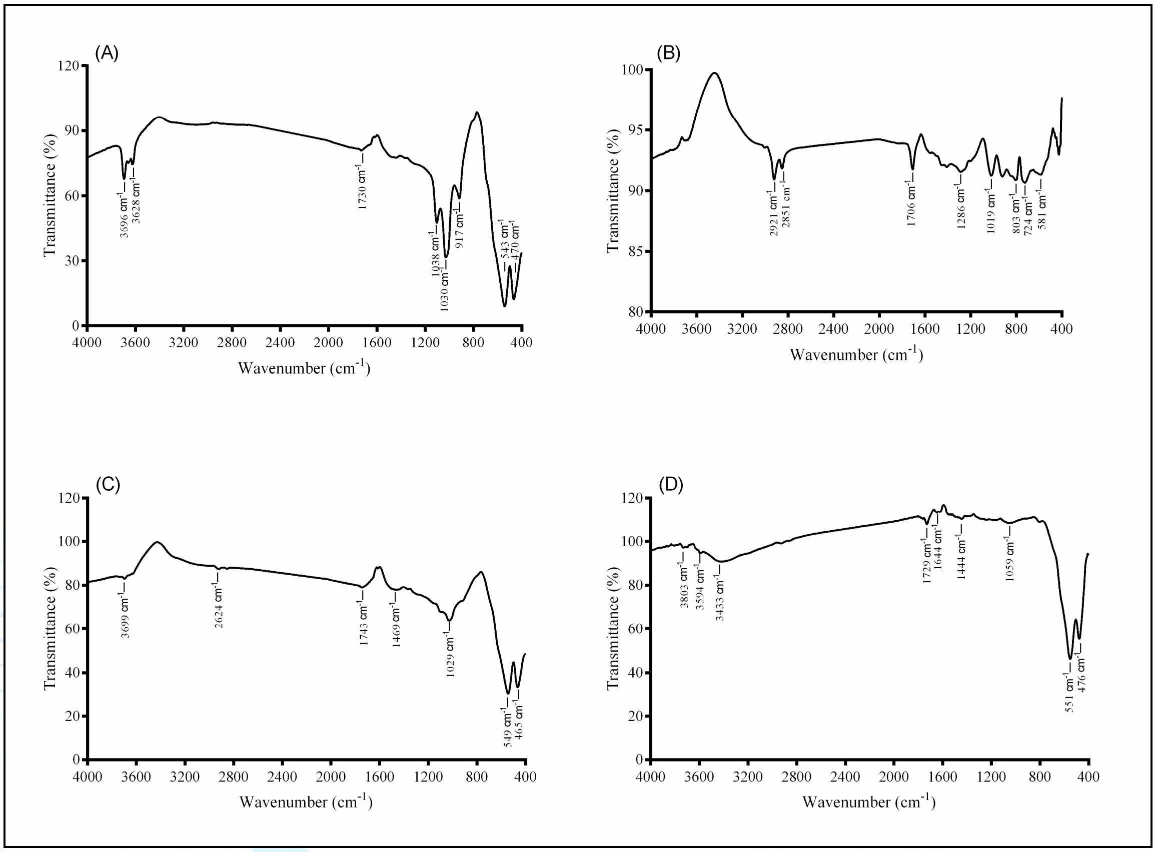

Fig.5. FT-IR spectra of (A) Iron Oxide, (B) Oleic acid, (C) Hematite equilibrated with oleic acid, (D) Iron hydroxide treated with oleic acid

of metal carboxylates. Thus it is evident that oleic acid is adsorbed on hematite and iron hydroxide. If the interaction between oleic acid and Fe of hematite or iron hydroxide is of chelating type (chelating bidentate) the peak around 1445 cm^{-1} related to C=O stretching should be absent. The symmetric stretching vibrations of C=O is possible only when the oleic acid form uni-dentate complex with Fe ions. Further, sharp peaks around 3600-3700 cm $^{-1}$ present in hematite generally attributed to surface hydroxyl groups are absent in the FT-IR spectrum of hematite treated with oleic acid. The disappearance of sharp peaks in the range 3600-3700 cm $^{-1}$ and appearance of broad band around 3500-3400 cm^{-1} attributed to hydrogen bonded water molecules in its place supports the formation of uni-dentate complex between oleic acid and Fe-OH as represented in equation 1. Thus the FT-IR data clearly suggest condensation type of interaction between oleic acid and iron oxide resulting uni-dentate complex. Some researchers have used the position and separation of symmetric and asymmetric modes of -COO$^-$ bands to deduce the carboxylate coordination mode [29-30].

The three dimensional (3D) micro-topography of the hematite surface and the height profile shown in Figs.6a and 6b reveals that the surface is uniform with a maximum height of roughness profile as 19.2 nm. The micro topography and height profile of hematite specimen after equilibrating with 1x10^{-3}M oleate solution is also shown in Figs 6d and 6e respectively. The roughness profile indicates highly uneven surface with a roughness of 712 nm. The roughness value has drastically increased several folds after equilibrating with oleate solution. From the data, it is evident that the oleic acid is adsorbed as patches. The multilayers of oleate adsorption on hematite could be interpreted due to the adsorption of iron oleate and oleate micelle over mono and bi-layered structures of oleate.

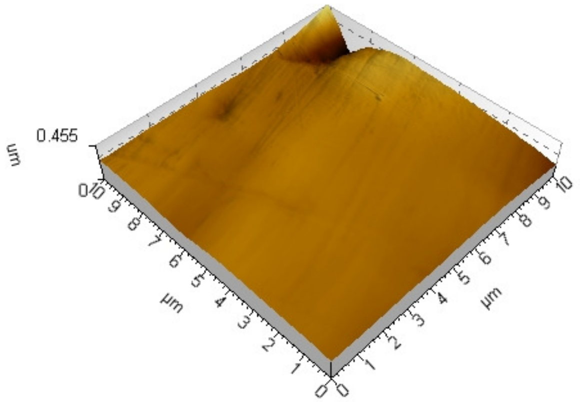

Fig.6a: 3D micro-topography of hematite surface

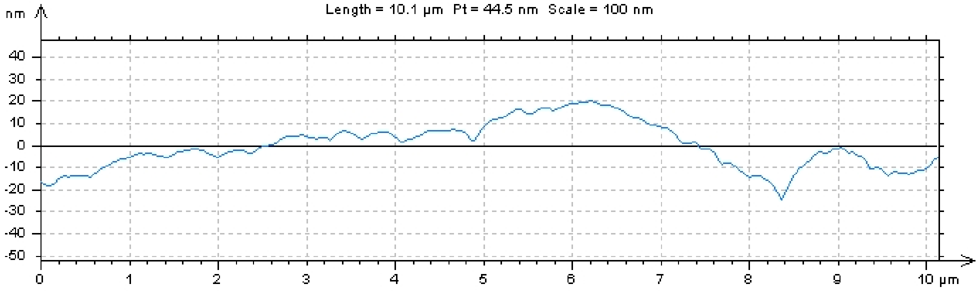

Fig. 6b: Height profile of hematite surface

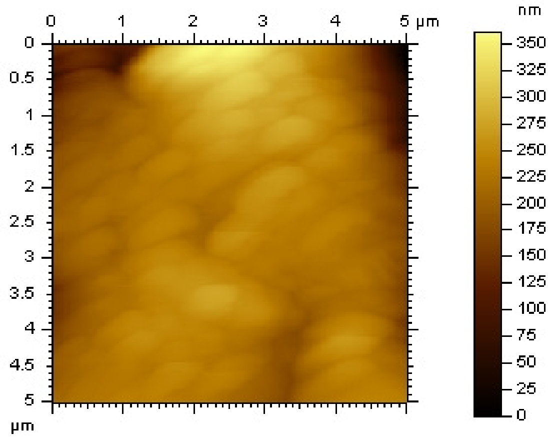

Fig.6c: Two dimensional topography of hematite surface

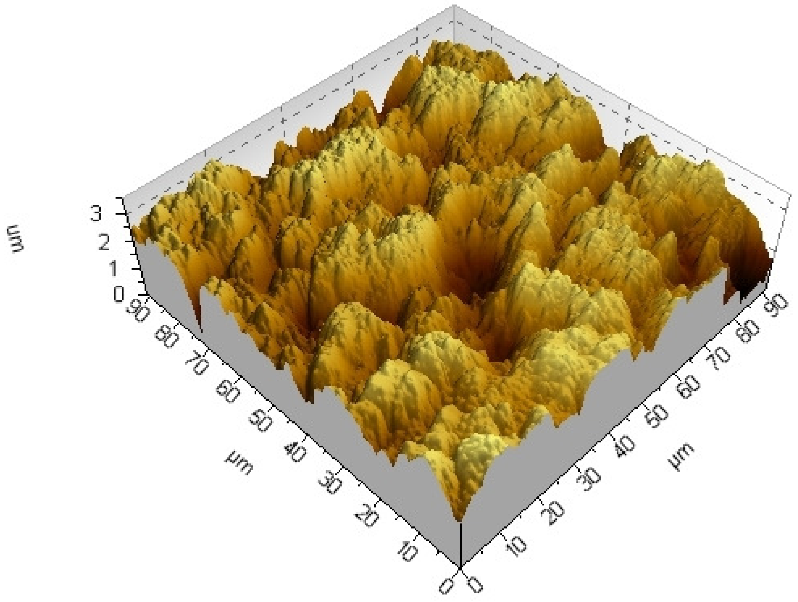

Fig. 6d: Three dimensional micro-topography of hematite (covered with oleate) equilibrated with $1x10^{-3}M$ oleate solution

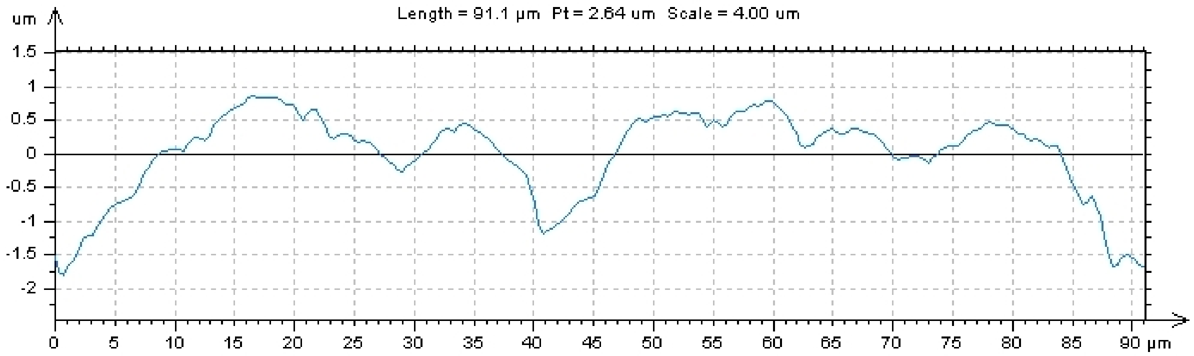

Fig. 6e: Height profile of hematite surface covered with oleate

3.2 Flotation studies on pure hematite and quartz/silica:

Pure mineral samples of hematite and quartz ground to below 45 microns were subjected to flotation at various concentrations of sodium oleate. Sodium silicate (1 kg/t) was added to depress quartz flotation and the results obtained are presented in Fig 7.

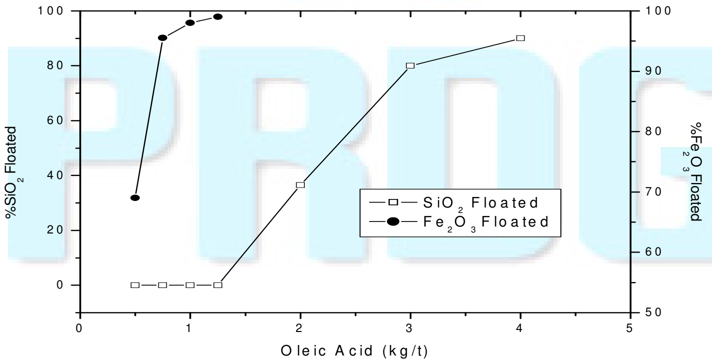

Fig.7: Effect of oleic acid dosage on the floatation response of hematite and quartz

From the results it is evident that 85% of hematite is floated around the oleic acid dosage of 1 kg/t whereas quartz particles did not respond to flotation at this dosage. While floating quartz alone, the froth remained very fragile even at 1.5 kg/t of oleic acid. Quartz particles started floating above 1.5 kg/t and 80% of quartz was floated around 3 kg/t. Thus it is apparent that hematite can be selectively floated from quartz at low oleic acid dosage.

3.3 Flotation of artificial mixture of hematite and quartz:

Flotation experiments were conducted on artificial mixtures of hematite and quartz. Hematite and quartz are mixed in different proportions and hematite was floated using oleic acid as collector around pH 8.0. Sodium silicate was used to depress quartz and the results were tabulated in Table 1.

Table.1: Flotation of synthetic mixture of Quartz and Hematite (Sodium oleate: 1 kg/t : Sodium silicate: 1.0 kg/t, pH: 8)

Sl no	Composition	Float (%) Weight	Float Assay	
			Fe_2O_3 (%)	SiO_2 (%)
1	100% Fe_2O_3	97.0	100	0.0
2	100 % SiO_2	4.8	0.0	100
3	95% Fe_2O_3 + 5% SiO_2	91.5	69.65	0.40
4	90% Fe_2O_3 +10 % SiO_2	91.0	67.50	3.50
5	85 % Fe_2O_3 +15% SiO_2	85.0	67.45	3.55
6	75% Fe_2O_3 + 25% SiO_2	49.0	62.05	8.20
7	50 % Fe_2O_3+ 50% SiO_2	40.5	51.75	24.8
8	25% Fe_2O_3+ 75% SiO_2	40.0	34.40	50.91

From the results it is evident that separation of hematite from quartz can be achieved if the quartz content in the mixture is below 15%. When the sample contain more than 15% quartz, the quality of the hematite concentrate was drastically affected. As the quartz content in the artificial mixture is increased from 15% to 75%, quartz in the floated material was increased from 3.55% to 50%. The contamination of froth product with quartz may be explained due to un-intentional activation of quartz with dissolved metal ions. It may also be attributed to entrainment of fine size quartz particles in the froth. Thus the selective separation of hematite using oleate drastically affected if the quartz/silica content is high. In other words, direct flotation of hematite using oleate is not suitable to achieve perfect separation of low grade iron ores.

3.4 Separation of iron minerals from natural iron ore deposits:

Two different low grade iron ores one with finely disseminated in nature and the other banded hematite quartzite (BHQ) were taken to separate iron ore from siliceous gangue by flotation. Flotation tests were conducted on banded hematite and quartzite assaying 36% of iron and 39% of quartz at different pH conditions and the results were compiled in tables 2 and 3.

Table 2: Effect of slurry pH on grade and recovery of BHQ ore

Head assay: Fe: 36.56, SiO_2: 39.18, Al_2O_3: 3.18, LOI: 4.35

Sodium silicate: 1 kg/t, Sodium oleate: 1.0 kg/t

pH	Product	Weight (%)	Assay %					% Recovery
			Fe	Fe_2O_3	SiO_2	Al_2O_3	LOI	
6	Float	33	43.50	62.21	30.92	2.70	3.53	39.27
	Sink	67	33.13	47.38	43.25	3.85	4.75	
7	Float	30.8	43.65	62.42	31.25	2.42	3.45	36.77
	Sink	69.2	33.40	47.76	42.70	3.95	4.75	
8	Float	34.4	44.10	63.06	29.95	2.57	3.66	41.49
	Sink	65.6	32.60	46.62	44.01	3.95	4.71	
9	Float	31.6	44.50	63.64	30.20	1.97	3.50	38.46
	Sink	68.4	32.90	47.05	43.35	4.20	4.75	
10	Float	32.4	43.85	62.71	31.50	2.25	2.98	38.86
	Sink	67.6	33.06	47.28	42.83	4.06	5.01	

Table 3: Effect of slurry pH on grade and recovery of finely disseminated ore

Head Assay: Fe: 45.44, SiO_2: 35.33, Al_2O_3: 1.05

Sodium silicate: 1 kg/t, Sodium oleate=1.0kg/t

pH	Product	Weight (%)	Assay %					% Recovery
			Fe	Fe_2O_3	SiO_2	Al_2O_3	LOI	
6.08	Float	40.2	51.42	73.53	22.6	0.72	2.72	45.51
	Sink	59.8	41.39	59.19	35.0	1.28	3.90	
7.27	Float	46.4	49.40	70.64	24.6	0.98	3.32	48.55
	Sink	53.6	42.15	60.28	34.3	1.12	3.50	
8.32	Float	42.0	49.75	71.14	24.6	0.48	3.25	46.02
	Sink	58.0	42.25	60.42	33.9	1.46	3.55	
9.12	Float	44.2	49.90	71.36	23.8	1.60	2.48	
	Sink	55.8	41.80	59.78	34.8	0.62	4.15	48.60
10.03	Float	47.6	47.55	67.00	26.9	1.13	3.42	49.85
	Sink	52.4	43.45	62.13	32.8	0.98	3.43	
11.0	Float	62.4	42.60	60.92	32.5	1.35	4.52	58.53
	Sink	37.6	**50.09**	71.63	25.9	0.55	1.60	

In the case of BHQ ore, the concentrates assaying around 44% of iron can be produced in a single stage flotation. The silica content was reduced from 39% to 30%. The recoveries also are found to be poor. In the case of finely disseminated ore, iron value in the froth product was improved to 50% from 45%. Better flotation observed under neutral conditions was attributed to the adsorption of ionomolecular complex $R(COO)_2H^-$ whose surface activity is several fold higher than neutral oleic acid.

Calcium chloride was tried as an activator to improve the flotation performance of iron ore. The $CaCl_2$ dosage of 0.5 kg/t which was found to be optimum in a separate study was uniformly maintained in all the tests and the flotation results are shown in table 4.

Table 4: Effect of $CaCl_2$ on grade and recovery of BHQ ore

Conditions: Calcium Chloride: 0.5 Kg/t, Sodium Oleate:1.0 Kg/t

pH	Product	Weight (%)	Assay (%)					(%) Recovery
			Fe	Fe_2O_3	SiO_2	Al_2O_3	LOI	
7	Float	55.0	42.02	60.09	31.58	3.55	3.92	63.2
	Sink	45.0	29.90	42.76	48.50	3.45	4.85	
8	Float	48.0	44.06	63.01	31.20	1.82	3.52	57.83
	Sink	52.0	29.65	42.40	46.55	5.05	5.12	
9	Float	45.6	44.92	64.24	30.21	1.98	3.25	56.04
	Sink	54.4	29.54	42.24	46.75	4.80	5.25	
10	Float	49.0	43.58	62.32	31.50	2.12	3.57	58.38
	Sink	51.0	29.85	42.69	46.55	4.80	5.12	
10.5	Float	55.0	38.85	55.56	36.55	3.13	4.25	58.45
	Sink	45.0	33.75	48.26	42.45	4.10	4.52	
11.5	Float	80.2	33.63	48.09	43.55	3.37	4.25	26.22
	Sink	19.8	48.50	69.34	21.27	4.02	4.75	

Though the overall recovery of iron was improved to 57% the quality of the concentrate remained same around 44% between pH 7.0-10.5. The trend of flotation was totally changed at pH 11.5. Instead of iron ore, quartz/silica was reported in the froth phase (reverse flotation). Thus iron content was increased in sink product with reduced recovery. This phenomenon of reverse flotation and activation of silica by calcium ions at high pH was well established by earlier studies. In recent years, reverse anionic flotation was successfully tried in china. In 2003, 6.77 million tonnes of iron ore with a feed grade of 30% Fe were processed to obtain the concentrates assaying 67.5% Fe. The recovery of iron from low grade (31.6% Fe) was reported using reverse anionic flotation of quartz. The calcium ion concentration of 50-100 ppm was found to be optimum [31]. Better activation and flotation of quartz was reported in the absence of carbonate ion and at pH 12.0 [17]. This process was found to exhibit better tolerance towards slimes that cause havoc in flotation circuit. However, operating the flotation circuit at highly basic environment of pH 12 has practical implications like corrosion and other environmental issues. Earlier studies have revealed that the hematite-oleate system needs prolonged conditioning time especially under pH levels below 8.0 where oleate adsorption at liquid/air interface as well as at hematite surface is slow. Under high pH conditions, i.e above pH 10, the low flotation recovery can be explained due to decreased oleate adsorption as well as unfavorable particle bubble interaction, owing to identical electrical charge on particles and bubbles. In general, the decrease in flotation at lower pH may be connected with the decreased hydrophobicity due to multilayer adsorption of oleate species and adsorption of oleic acid emulsion. It is known that oleic acid emulsion does not make the mineral surface fully hydrophobic. The decrease in flotation at higher pH is attributed to the increase of negative surface sites and hydroxyl ions. The high negative surface charge and the high concentration of hydroxyl ion are unfavorable for oleate adsorption. Thus the hematite oleate system is highly complex and requires more attention. Some researchers have adopted pre concentration of iron ore by magnetic circuit followed by oleic acid flotation to achieve the required grade [16]. This appears to be more appropriate solution for the separation of low grade iron ores. Perfect separation of iron minerals could not be achieved with oleic even after de-sliming.

Flotation tests were conducted using octylhydroxamate as collector at pH 9.0-10 and the results are compiled in Table 5.

Table 5: Efficacy of Octyl Hydroxamate on the flotation of hematite at pH10

Collector (kg/t)	Product	Weight (%)	Assay (%)					(%) Recovery
			Fe	Fe_2O_3	SiO_2	Al_2O_3	LOI	
0.4	Float	29.6	50.75	72.57	20.75	2.22	3.98	41.08
	Sink	70.6	30.6	43.76	46.90	4.01	4.50	
0.5	Float	33	50.45	72.15	20.8	2.21	4.01	45.51
	Sink	67	29.75	42.54	48.22	4.50	4.05	
0.6	Float	36.8	48.25	69.00	23.12	2.55	4.55	48.57
	Sink	63.2	29.75	42.54	48.5	4.02	4.22	
0.8	Float	40.4	43.2	61.78	29.02	4.02	4.45	47.74

	Sink	59.6	32.05	45.83	46.03	3.12	4.25	
1.0	Float	51.8	40.9	58.49	32.55	4.05	3.95	57.27
	Sink	49.2	31.75	45.40	45.75	3.05	4.75	

The octylhydroxamate being chelating type of collector, better selectivity can be expected compared to conventional oleic acid. It was tested for flotation of iron oxide during 1967 and found that iron ore concentrates assaying 58% to 68% can be achieved [32] from the pre concentrated iron ore by spirals. In the present study, the results clearly demonstrate that the octylhydroxamate is slightly better compared to oleate. However the results clearly show poor selectivity that was expected from a chelating hydroxamate. This may be attributed due to slime generation during processing.

From the economic point of view, direct anionic flotation of iron minerals is attractive to process finely disseminated low grade ores and to recover iron values from tailing ponds. Direct flotation is certainly advantageous where the volume of iron minerals compared to quartz and silicates is low. The present investigation clearly reveals the inadequacy of oleic acid/ oleate collector in achieving desirable iron ore concentrates. Most of the laboratory investigations indicated that the flotation of iron oxides either with anionic (fatty acids) or amphoteric collectors (sarcosinates and sulphosuccinamates) yield concentrates with high silica content. The effectiveness of sodium silicate as depressant for quartz and silicates is poor mainly due to slime coating in iron oxide-oleate system. The potential of hydroximate and other chelating agents as collector has not been explored due to their high cost. The viability of reverse flotation using cationic collector to float comparatively high volume of quartz / silica need to be studied. Thus pre concentration of iron ore before flotation with oleic acid is essential to obtain desired concentrates.

SUMMARY AND CONCLUSIONS

The effectiveness of oleic acid collector for the selective separation of hematite from artificial mixtures of hematite and quartz was investigated by adsorption, contact angle, zetapotential measurements and flotation studies.

The adsorption of oleate on hematite and alumina is found to be pH dependent and maximum adsorption was observed where the surface charge of the mineral particles is neutral. The zeta potential measurements have revealed that the oleate adsorption on hematite and alumina is of chemisorption. However the adsorption density of oleate and hydrophobicity (contact angles) of hematite, alumina and quartz particles was found to be different. The hematite particles have exhibited better hydrophobicity with a contact angle of 85 degrees whereas quartz particles have shown contact angle of only 45 degrees.

The flotation tests conducted on pure hematite and quartz have revealed that the hematite is floatable at low oleate dosage of 1 kg/t whereas quartz requires high dosage of 3.5 kg/t. Flotation experiments on artificial mixtures of hematite and quartz have shown that selective separation of hematite is possible when the quartz content in the mixture is less than 15%. The selectivity is severely affected by increasing the ratio of quartz in the mixture.

The selectivity of oleic acid was studied on two different low grade iron ores one with finely disseminated in nature and the other one is banded hematite quartzite (BHQ) containing more quartz. The selective separation of hematite was observed to be very marginal in both the cases. Based on the study, the inadequacy of oleic acid as collector for selective separation of hematite from low grade ores was established.

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