Separation of sillimanite from beach sands contaminated with shell

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Abstract-- *Sillimanite is a very important raw material for the manufacture of refractory bricks used in iron and steel, cement and glass industries. In some coastal stretches of south India, the beach sand is contaminated with shell. After recovering heavy minerals like ilmenite, rutile, zircon and garnet by various physical separation techniques, the final sand containing sillimanite, quartz and shell is presently dumped as waste. Separation of sillimanite from these rejects was studied by flotation process using oleic acid and octylhydroxamate as collectors for selective flotation of sillimanite. Starch and tannin were tried as depressants for shell and sodium silicate as dispersant for quartz. Though the quartz could be depressed effectively, the shell was found to float along with sillimanite both in the presence of oleic acid and octylhydroxamate. When starch or tannin was added to suppress the shell flotation, the floatability of sillimanite and in turn its recovery was drastically affected. Alternatively shell was totally removed by treating with dilute hydrochloric acid and sillimanite was separated from quartz using oleic acid and sodium silicate. The concentrate analyzing 97% sillimanite free from shell were achieved from the initial sand assaying 48 % sillimanite, 46 % quartz and 3.3% shell.*

Keywords: Sillimanite, oleic acid, octylhydroxamate, starch, tannin, shell removal.

1. Introduction

The placer minerals such as sillimanite, ilmenite, garnet, rutile, zircon and monazite are present along the coastal stretch of India. Large deposits are located in south Kerala and adjacent region of TamilNadu, south Orissa and north Andhra Pradesh. Sillimanite is the main raw material for refractory industries because of its ability to form mullite phase at high temperatures. Major portion (97%) of sillimanite is consumed for refractory bricks that are extensively used in steel, glass, ceramics, cement kilns, furnaces and also in petrochemical industries.

The individual minerals from beach sands are separated based on their physical properties. Sillimanites being non-conducting and non magnetic mineral, the physical separation methods including gravity methods are ineffective to enrich sillimanite especially in the presence of quartz and zircon. Hence flotation is necessary to separate sillimanite from gangue minerals like quartz. It was reported that the concentrates assaying 58.6% Al_2O_3 with a recovery of 78% was achieved by using two stage flotation processes. The mica and quartz minerals were separated in the first stage using amine as collector and Kynite-sillimanite was separated in the second stage using lactic acid and sodium sulfonate [1]. In another study, sillimanite was floated using oleic acid as collector.

Citric acid was tried to suppress the activation of quartz by Al^{3+} and Fe^{3+} [2]. Beneficiation circuit consisting of crushing, grinding, magnetic separation and gravity separation was suggested to separate sillimanite and garnet from the pelitic and semi-pelitic schist [3]. At Manavalakurichi, after recovering heavy minerals by various physical separation techniques, the final sand containing sillimanite, quartz and shell is presently rejected. The sillimanite concentrate obtained by two-stage flotation was further subjected to electrostatic plate separator to reduce the shell content [4]. The efficacy of flotation column for the beneficiation of sillimanite was studied on a pilot scale and found to be highly beneficial in terms of economics of the process and separation efficiency [5]. The present study was undertaken to develop a process to separate shell from sillimanite.

2. Experimental Materials and Methods

All the flotation experiments were conducted using Denver Flotation cell supplied by Denver Equipment Company, USA. The slurry with 20% solids was uniformly maintained in all the experiments. Tachometer was provided to know the rotation speed (rpm) of the agitator and the aeration was controlled using a needle valve. The pH was adjusted using dilute NaOH solution. After the addition of each reagent, the slurry was conditioned for 3 minutes for equilibration. Immediately after the experiment, the float and non-float products were filtered, dried, weighed and analyzed.

2.1. Estimation of Shell

A known quantity of sample (W1) was taken in a beaker and dilute HCl (1:4) was slowly added till the effervescence was completely seized. After the complete dissolution of the shell, the resultant solution was filtered and the residue was thoroughly washed with distilled water. The residue was dried and the percent of shell was calculated from the dried weight of the residue (W2).

2.2. Estimation of quartz

Known quantity of the above acid treated residue (W1) was taken in a separating funnel and sufficient quantity of bromoform ($CHBr_3$) was added. The contents of separating funnel were thoroughly shaken and kept in a stand until the quartz and sillimanite are separated as float and sink products. The float and sink materials were collected separately and the weight of float (W2) was taken and computed to arrive at % of quartz.

2.3. Estimation of sillimanite

It is known that the material with a specific gravity of above 2.90 will sink in bromoform. Known weight (W1) of material reported to sink in bromoform was taken in a separating funnel and sufficient quantity of Di-iodomethane (CH_2I_2) was added. The contents of the separating funnel were thoroughly shaken and allowed to separate. Since the specific gravity of sillimanite is less than 3.22, the same will float and the other minerals heavier would sink in CH_2I_2. The float and sink materials were collected separately in filter papers. The weight of the float material (W2) was taken to arrive at % of sillimanite.

2.4. Particle size, surface area and contact angle

Particle size and contact angle were determined using CILAS-1180 particle size analyzer and Tensiometer, Model K100 respectively. Surface area was measured using BET surface area and porosity analyzer, Model ASAP 2020 supplied by Micromeritics.

2.5. Physical characterization

Sillimanite is brownish in color with specific gravity of 3.21. From the microscopic examination (Leica Stereo zoom microscope) shown in Fig 1a, it is apparent that the sillimanite grains are angular, euhedral, elongated, subhedral and subrounded. Scanning electron microscope (Hitachi S3000-H) was used to study the mineral alteration and micro morphology. The micrograph (Fig 1b) show that the sillimanite particles of irregular shapes with angular edges. It was also observed that some sillimanite grains are fractured due to the process of collision of particles under wave action in the tidal zone [6]. Channels at different angles over the grains were also observed.
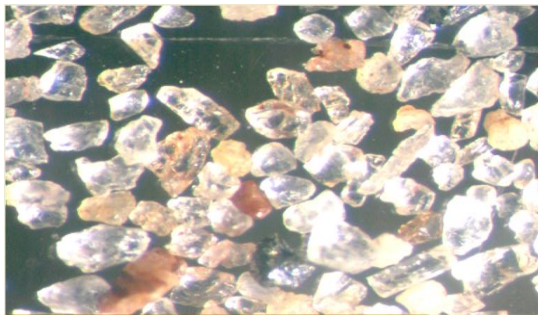

Fig 1a: Microscopic study of sillimanite (Angular, euhedral, elongated, subhedral and subrounded sillimanite grains)
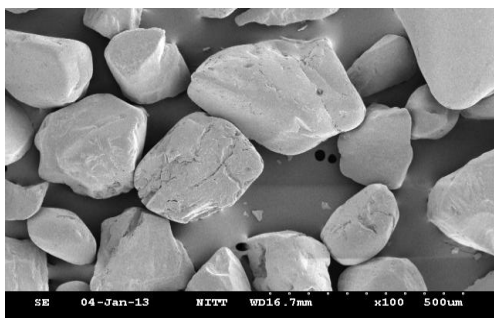

Fig 1b: Scanning Electron Micrograph of sillimanite showing surface alteration with fracture and channels

The particle size was measured using CILAS particle size analyzer and distribution of the sillimanite sample was shown in Fig 1c. It is evident that nearly 80 % of the particles are in the size range of 150-475 microns. The surface profile of sillimanite particle was studied using Atomic Force Microscope (NT-MDT, Russia) in semi-contact mode using silicon nitride cant lever. The 3D view shown in Fig 1d reveals that the sillimanite surface is highly uneven with sharp projections all over the surface. The average surface roughness was observed to be 8.9 nm.
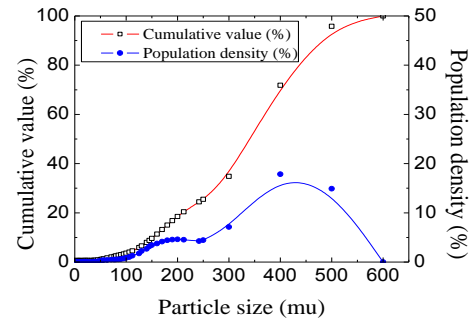

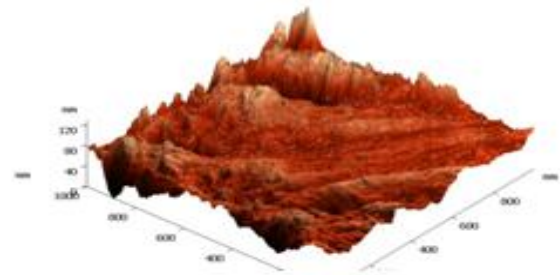Fig 1c: Particle size distribution of sillimanite sample

Fig 1d: Surface topography of sillimanite particle (Atomic force microscopic)

The sillimanite sample was characterized for mineralogical phase identification using X-ray powder diffractometer. The characteristic copper-Kα x-ray radiation with 1.54 Å wave-lengths was used in this diffraction study. The diffraction pattern of the sample was recorded for the scanning angle ranging from 10° to 70°. The so generated diffraction pattern was indexed for the mineralogical phases by comparing with the powder diffraction standard database maintained by International Center Diffraction Data (ICDD).
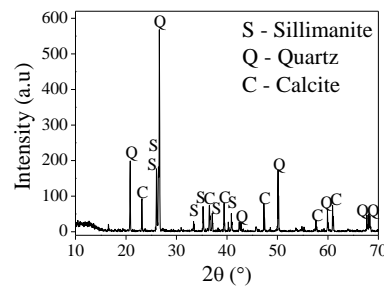

Fig 1e: X-Ray Diffractogram of sillimanite sample

The XRD reveals the presence of quartz, sillimanite and calcite as major minerals. The presence of calcite in the sample is attributed to the breakage of shell. The sillimanite sample contains 3.3% of shell, 46.4% of quartz, 48.3% of sillimanite and minor amounts of zircon, garnet and rutile.

3.   Results and Discussion

3.1 *Effect of oleic acid dosage*: Flotation tests were conducted at different concentrations of oleic acid and the results are presented in Fig 2. It is apparent that the recovery of sillimanite increases as the oleic acid dosage is increased.
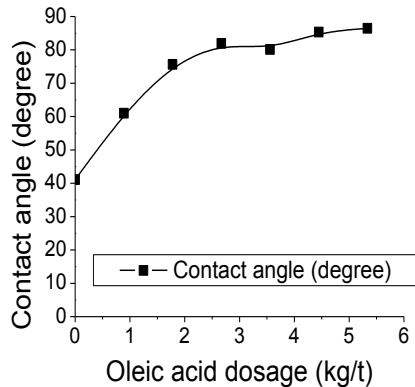

Fig 2: Effect of oleic acid dosage on sillimanite flotation

Around 90% of sillimanite was recovered at an oleic acid dosage of 3.56 kg/t. At low oleic acid concentration, the flotation rate of shell is higher compared to sillimanite. When the concentration of oleic acid is beyond 1.75 kg/t, both shell and sillimanite were found to float and as a result, the quality of sillimanite is affected. The hydrophobicity of floated sillimanite at different oleic acid dosages was measured using tensiometer (KRUSS, Model K100) and the results are shown in Fig.3.
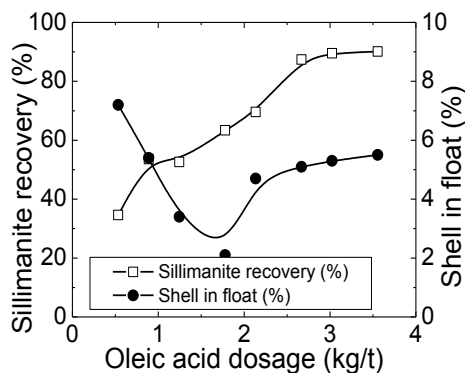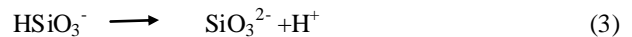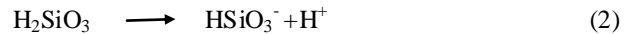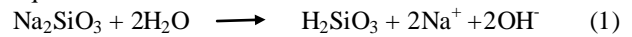

Fig 3: Effect of oleic acid on contact angle

Contact angle of above 80^0 was observed beyond the oleic acid dosage of 3.0 kg/t which is in good correlation with the maximum floatability of sillimanite. Thus high dosage of oleic acid is essential to float sillimanite. The high consumption of oleic acid may be due to incorporation of water molecules within the crystal structure. Inclusion of water molecules in

sillimanite and Al_2SiO_5 polymorphs was established by earlier researchers by means of polarized Infra Red spectroscopy [7-8]. Many mechanisms were proposed to explain the water within the Al_2SiO_5 polymorphs. The OH^- can be incorporated by substitution of SiO_4 groups by $(OH)_4$, the H_3O^+ ion, interstitial water, OH^- ions associated with dislocations and isolated substitution of OH^- ions [9]. Thus the hydrophilic character of sillimanite particles could be explained due to the adsorption of H_2O, OH^- and H_3O^+ molecules. High dosage of oleic acid is required to overcome the hydrophobic environment. It is reported that flotation of calcite needs high concentration of oleic acid compared to apatite and fluorite [10]. Thus selective separation of sillimanite from shell appears to be difficult due to floatability of shell.

3.2 *Effect of sodium silicate and carbonate*

In order to minimize the contamination of quartz in sillimanite, sodium silicate is generally used as depressant for quartz. The dissociation of sodium silicate in water produces OH^-, $H_2SiO_2^-$, $HSiO_3^-$, and SiO_3^{2-} according to the following equations

$$Na_2SiO_3 + 2H_2O \longrightarrow H_2SiO_3 + 2Na^+ + 2OH^- \qquad (1)$$

$$H_2SiO_3 \longrightarrow HSiO_3^- + H^+ \qquad (2)$$

$$HSiO_3^- \longrightarrow SiO_3^{2-} + H^+ \qquad (3)$$

The OH^- ions increases the pH of pulp whereas $HSiO_3^-$ and SiO_3^{2-} act as depressing/dispersing agents for quartz. The dosage of oleic acid (3.56 kg/t) and sodium carbonate (1.0 kg/t) was maintained constantly while varying the sodium silicate dosage. The results of the flotation tests are presented in Fig 4.
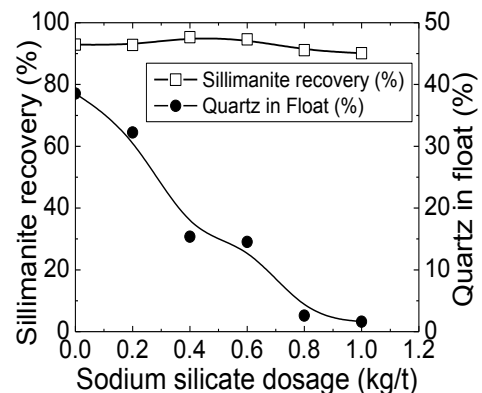

Fig 4: Effect of sodium silicate dosage on sillimanite flotation

It is apparent that the quartz content in float was drastically decreased to 1.6% by increasing the sodium silicate dosage to 1.0 kg/t. Consequently the grade of sillimanite was improved to 92%. The recovery of sillimanite was remained constant around 93%. The adsorption of heavily hydrated silicic acid on quartz renders the quartz surface highly hydrophilic. At very high dosage, hydroxyl ions released (equation 1) readily adsorb on sillimanite and facilitate the detachment of oleic acid by competitive adsorption [11]. The excess dosage of sodium silicate adversely affects the floatability of sillimanite. Thus optimum dosage of sodium silicate is very essential. The

presence of calcium and magnesium ions in aqueous phase may affect the adsorption of oleic acid on sillimanite. Therefore, sodium carbonate (Na_2CO_3) was used as a modifier cum pH regulator in the flotation. The Ca^{2+} and Mg^{2+} ions present in pulp are precipitated into corresponding carbonates so that the interaction of oleate with Ca^{2+} and Mg^{2+} is minimized and in turn the consumption of oleic acid. The flotation results depicting the effect of sodium carbonate on sillimanite recovery and grade were shown in Fig 5.
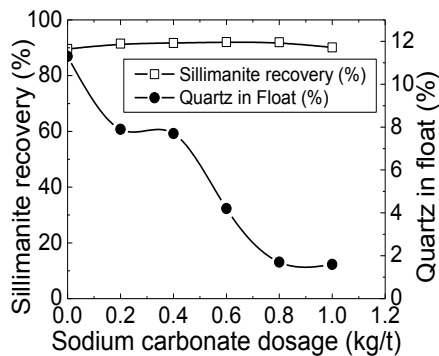

Fig 5: Effect of sodium carbonate dosage on sillimanite flotation

In the absence of Na_2CO_3, quartz was floated to the extent of 11%. This may be attributed to the adsorption of Ca^{2+} and Mg^{2+} on quartz which may facilitate the activation of quartz flotation. The flotation of quartz was effectively suppressed in the presence of sodium silicate and Na_2CO_3.

3.3 Effect of Starch

From the flotation results, it is apparent that both sillimanite and shell are floating in the presence of oleic acid. Hence an attempt was made to depress shell using starch. Floatation experiments were conducted by varying the starch dosage from 0.25-1.0 kg/t. The dosage of Na_2SiO_3 and Na_2CO_3 was maintained at 1.0 kg/t and oleic acid at 3.57 kg/t while varying the dosage of starch. From the results presented in Fig 6, it is evident that the flotation recovery of sillimanite is drastically reduced to 55% by increasing the starch dosage. The selective adsorption of starch on shell and thereby its depression during flotation was expected. However, it was observed that the sillimanite is also getting depressed.
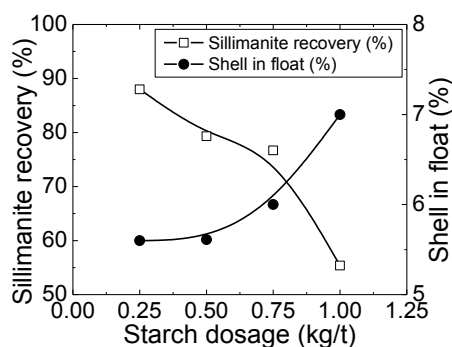

Fig 6: Effect of starch dosage on sillimanite flotation

The mechanism of depression/ dispersion of various minerals using starch were discussed by several authors [12-15]. It was demonstrated that metal hydroxy sites play a vital role in dextrin/starch adsorption. The maximum adsorption of dextrin was noticed around the pH where mineral surface is highly hydroxylated. The adsorption of starch and oleate on calcite was studied in aqueous solutions [16]. The co-adsorption of starch and oleate was interpreted in terms of a clathrate formation between starch in its helical form and oleate held inside the starch helix. The depressant nature of starch is attributed to hydroxyl groups which are hydrophilic. In the present study selective depression of shell by starch was found to be difficult and hence chelating collector was tried for selective flotation of shell prior to sillimanite flotation.

3.4 Octylhydroxamate as collector

Effective separation of fluorite, calcite, apatite, barite and bastnaesite by flotation using octylhydroxamate as collector was demonstrated by Pradip et al [17]. The relative affinity of a particular reagent molecule with different mineral surfaces was correlated using the knowledge of the crystal structure of the surfactant molecules as well as mineral surfaces. In the present study, octyl hydroxamate was tried as collector for the selective separation of shell from sillimanite. The results of the flotation tests presented in Table 1 indicates that at low collector dosage though the rate of shell flotation is slightly higher, selective removal of shell was found to be difficult. Also the quantity of floated material is hardly 5%. However, the floatability of minerals was found to increase drastically in the presence of pine oil and sodium oleate as co-collector. Quartz to the extent of 33% was reported in the float when combination of octyl hydroxamate and oleate was tried as collector.

Since the shell separation was found to be difficult by flotation, the same was dissolved in dilute hydrochloric acid which can be represented as

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O \qquad (4)$$
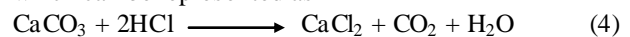
After the complete dissolution, the sample was filtered and thoroughly washed with fresh water. In the second stage, separation of sillimanite from quartz by flotation was tried using 1.0 kg/t of each sodium carbonate and sodium silicate by varying the dosage of oleic acid. Severe frothing with fine bubbles was noticed. The analysis of froth product indicated that sillimanite was severely contaminated with quartz (Table 1).

This may be due to the decreased mean bubble size and foamability of oleate solution under alkaline condition. At alkaline pH value, soluble oleate species are formed which strongly promote foaming. The dissolved surfactant and the salt effect of carbonate-bicarbonate buffer induce the emulsification of oil-water interface which leads to alkaline flooding [18]. However, rigorous foaming phenomenon was totally seized in the absence of sodium carbonate. Thus after eliminating shell by HCl treatment, sillimanite concentrate with a quartz content of less than 3% was achieved.

Table 1: Effect of octylhydroxamate, oleate and tannin on sillimanite flotation OHM: Octylhydroxamate

S. No	Reagents (kg/t)	Sodium oleate (kg/t)	Float (g)	Sink (g)	Float Assay (%)		Sillima nite recovery (%)
					sillima nite (%)	Shell (%)	
1	OHM:0.397	-	17	481	85.2	13.8	6.56
2	OHM:0.529	-	18	480	86.2	13.4	7.03
3	OHM:0.661	-	27	470	81.1	17.25	9.92
4	OHM:0.793	-	27	471	83.0	16.10	10.15
5	OHM:0.079	0.1	40	458	96.73	1.14	17.53
6	OHM:0.132	0.3	280	220	64.07	2.32	81.28
7	-	0.18	5	494	79.80	19.73	1.80
8	-	0.3	12	470	86.18	13.53	4.68
9	-	0.4	65	437	85.80	13.71	25.27
10	-	0.5	100	398	89.0	10.12	40.32
11	Tannin: 0.1	3.57	24	475	84.65	15.0	9.20
12	Tannin: 0.2	7.11	30	468	83.7	16.1	11.37
13	Na₂SiO₃:1.0	3.20	210	288	98.03	--	82.1
14	Na₂SiO₃:1.0	3.56	213	287	97.83	--	82.04
15	Na₂SiO₃:1.0 + Na₂CO₃:1.0	3.56	248	245	85.64	Quartz :14.36	83.61

4. Conclusions

Separation of sillimanite from beach sand containing sillimanite, quartz and shell was studied by flotation process using starch as depressants for shell and sodium silicate as dispersant for quartz. Oleic acid and octylhydroxamate were tried as collectors for selective flotation of sillimanite and shell. Though the quartz could be depressed effectively, the shell was found to float along with sillimanite. When the concentration of oleic acid is beyond 1.75 kg/t, both shell and sillimanite was seen floating. The contact angle and oleic acid dosage are in good correlation with the maximum floatability of sillimanite.

The effect of sodium silicate dosage on quartz depression was found to be significant. The quartz in float was drastically decreased to 1.6% by increasing the sodium silicate dosage to 1.0 kg/t. When starch and tannin was added to suppress the shell flotation, the floatability of sillimanite and in turn its recovery was drastically reduced to 55% from 90%. The selective removal of shell using octyl hydroxamate was found to be poor.

Alternatively shell was dissolved using dilute hydrochloric acid and sillimanite was successfully separated from quartz using oleic acid and sodium silicate. The concentrate analyzing 96% sillimanite and free from shell were achieved from the initial sand assaying 48.4% sillimanite, and 3.3% shell.

Acknowledgement

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