# Study on Flotation of Sillimanite Using Plant-Based Collector

**N. Vasumathi, K. Chennakesavulu, I. Cassandra Austen, M. Sai Kumar,**
**T. V. Vijaya Kumar, and Ajita Kumari**

## 1 Introduction

In India, the heavy mineral beach sand carry minerals like ilmenite, garnet, rutile, monazite, sillimanite, and zircon. The west coast of Kerala, the east coast from Tamil Nadu to Odisha contains heavy mineral (ilmenite) rich beach sand deposits. These ilmenite samples of Indian origin has 50–60% of $TiO_2$ and is most suited for beneficiation by different processes. Also minerals such as monazite, sillimanite, and zircon are present in inland red Teri sands, apart from heavy mineral beach sands and has high potential for beneficiation. The conducting and magnetic minerals are separated first, leaving behind the non-conducting and non-magnetic sillimanite along with quartz in the processing of heavies in beach sand. The placer minerals of 348 Million tons (Mt) ilmenite, 107 Mt garnet, 21 Mt zircon, 18 Mt monazite, and 130 Mt Sillimanite are present in Indian resources. About 35% of world resources are contributed from India. The heavy mineral sands are basically sedimentary deposits of dense minerals which pile up with sand, silt, and in association with clay along the coastal line, leading to economic concentrations of these heavy minerals [1–5]. The conducting and magnetic minerals are separated first, leaving behind the non-conducting and non-magnetic sillimanite along with quartz in the processing of heavies in beach sand. Sillimanite, an important mineral for refractory application, is mainly recovered by flotation technique from its associated major gangue mineral, quartz by imparting selective surface hydrophobicity on sillimanite using a suitable collector. Sillimanite is a non-conducting and non-magnetic mineral and hence flotation technique was

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N. Vasumathi (✉) · M. S. Kumar · T. V. V. Kumar · A. Kumari
CSIR – National Metallurgical Laboratory, Madras Center, Chennai 600 113, India
e-mail: vasumatisamy@gmail.com

K. Chennakesavulu · I. C. Austen
Department of Chemistry, Sathyabama Institute of Science and Technology, Jepiaar Nagar, Chennai 600 119, Tamil Nadu, India

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adopted to separate it from other associated gangue minerals mainly quartz. Flotation is physico-chemical process and depends on surface hydrophobicity for separation of valuable minerals from its accompanying gangue minerals. Flotation process have been effectively used for fines and size of the sillimanite mineral present in the heavy mineral beach sand is most appropriate to be processed by flotation. In any separation process based on flotation, the flotation reagents added in order to modify/enhance the surface hydrophobic nature of the minerals intended to be separated and hence the appropriate selection of reagent plays a vital role in the efficiency of the flotation technique. Apart from the reagent selection, the dosage of the reagents added in the flotation circuits needs to be optimized for the required grade and recovery. Flotation studies on sillimanite by flotation column on Odisha sands were carried out using oleic acid as collector [6–14]. Recovery of sillimanite by flotation tree analysis method and conventional flotation technique from the non-magnetic product of red sediments were also studied. Also, some investigation on flotation of sillimanite at acidic pH were reported.

In this work, one such Indian beach placer sample has been attempted for beneficiation using flotation method. In preliminary flotation studies, pH and depressant dosage were varied to establish the optimized process criteria. Types of collectors used for flotation studies are oleic acid and plant-based collector SFA. Flotation of sillimanite sample was optimized by studying various process parameters. Sillimanite feed sample, collectors, and concentrate obtained from optimized set have been characterized using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy.

## 2 Material and Methods

### *2.1 Materials*

In this study, a placer sample after the removal of heavies from western coast of southern India containing 55.4% sillimanite along with 33.9% quartz, 1.7% magnetics, 1.4% rutile, 2.4% zircon, and 5.6% kynite was subjected to froth flotation for enriching the sillimanite content. A representative head sample was drawn, and the remaining material was used for flotation studies. A laboratory synthesized plant-based reagent, Collector SFA, and oleic acid were used as collector. Methyl isobutyl carbinol (MIBC) was used as frother. Sodium silicate was used as depressant and soda ash as pH regulator. The sillimanite used in this study was the feed to sillimanite flotation circuit of an operating heavy mineral beach sand beneficiation plant.

### 2.2 Methods

Bench scale flotation experiments were carried out in a standard Denver laboratory flotation machine. Representative feed and concentrate samples were subjected to X-ray diffraction (XRD) to identify the mineral phases. Fourier transform infrared (FTIR) was used to detect various functional groups present using Bruker Alpha II Compact FTIR Spectrometer-ATR module.

## 3 Results and Discussion

### 3.1 Characterization Studies

Fourier transform infrared (FTIR) spectroscopy analysis is used to identify organic, inorganic, and polymeric materials. Mineral phases present in the sample were identified qualitatively using a BRUKER ALPHA-II Compact FTIR Spectrometer—ATR module over the range of 4000–400 $cm^{-1}$ at room temperature with resolution of ± 4 $cm^{-1}$. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties.

The characterization of this natural source-based sillimanite collector is carried out and compared with that of the most commonly used oleic acid collector using FTIR to study the functional groups that enhances the selective sillimanite flotation. The peaks at 2700 to 3100 $cm^{-1}$ and 1708 $cm^{-1}$ confirm the presence of -COOH in the natural source-based collector (Fig. 1).

The adsorption of oleate and collector SFA on sillimanite surface were examined by FTIR spectroscopy. The FTIR spectrum of sillimanite does not show any peaks in 1400 to 4000 $cm^{-1}$ region. The FTIR of oleic acid coated sillimanite displayed few bands at 1462, 1372, and 722 $cm^{-1}$ indicating the oleic acid on sillimanite surface with calcium ions. The band at 1708 $cm^{-1}$ clearly suggests the presence of carbonyl group on sillimanite surface. The peaks at 2922 and 2853 $cm^{-1}$ corresponds to asymmetric and symmetrical stretching vibrations of -CH2 and CH3 group. The peak shifts in FTIR spectrum of oleic acid coated sillimanite indicates the chemisorption of oleate on sillimanite surface.

The FTIR of SFA reagent and SFA coated sillimanite samples showed that the SFA has chemical interaction with sillimanite hydroxyl group. The peaks at 1696 $cm^{-1}$ confirm the presence of free -COOH in then SFA collector. In order to distinguish the physical or chemical interaction between SFA and sillimanite surface, the SFA adsorbed sillimanite sample was washed with water, the samples was dried at room temperature and analyzed for FTIR. The peak at 1690 $cm^{-1}$ shifted to 1712 $cm^{-1}$ clearly indicates the chemical interaction between collector SFA and sillimanite (Fig. 2).

The sillimanite feed to flotation and the concentrate obtained from the flotation of feed is analyzed for its mineralogy using x-ray diffraction (XRD) studies. XRD study

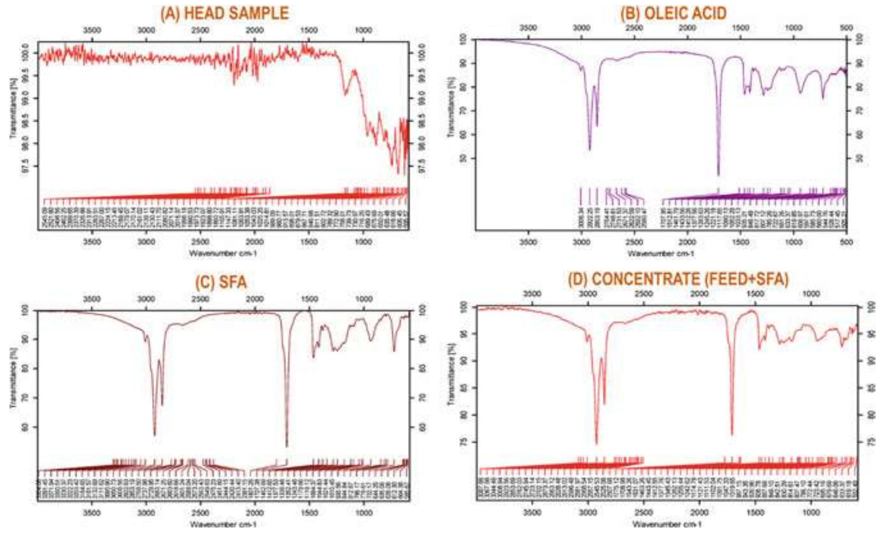


**Fig. 1** FTIR images of placer head sample (**a**), oleic acid (**b**), plant-based collector SFA (**c**), and concentrate obtained at optimized experimental set with SFA as collector (**d**)

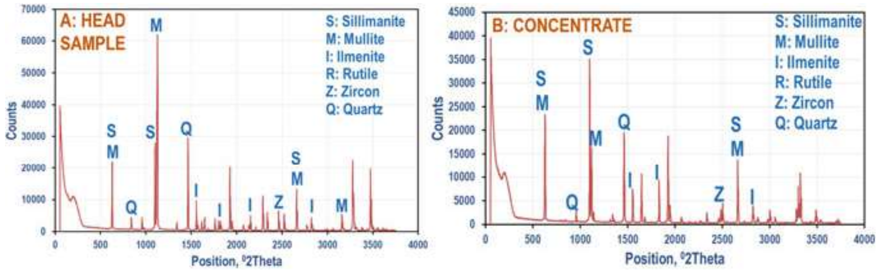


**Fig. 2** XRD spectra of **a** sillimanite head sample (feed) and **b** flotation concentrate obtained with SFA as collector

of the representative sample was carried out using X-Ray Diffractometer AXRD Benchtop, Canada. The anode material used was copper, and the generator settings were maintained at 30 mA and 40 kV. The X-ray patterns were acquired in the 2ϴ range of 10°–90° with a step size of 0.001°/s.

The XRD pattern indicates the presence of sillimanite, ilmenite, and rutile along with quartz as mineral phases. The ilmenite and rutile phases are present because of the contamination of wet circuit heavies product of the heavy mineral beach sands report to the sillimanite feed. The quartz mineral is the major phase and contributes as the major impurity mineral in the sillimanite flotation process. If the recovery process of ilmenite and rutile are effective, then these minerals would not report into the sillimanite circuit. It can be observed that from the x-ray diffractogram of sillimanite concentrate, the sillimanite phase appears to be prominent than the quartz gangue mineral phase indicating the better separation efficiency of the flotation process.

## 3.2 *Beneficiation Studies Using Froth Flotation*

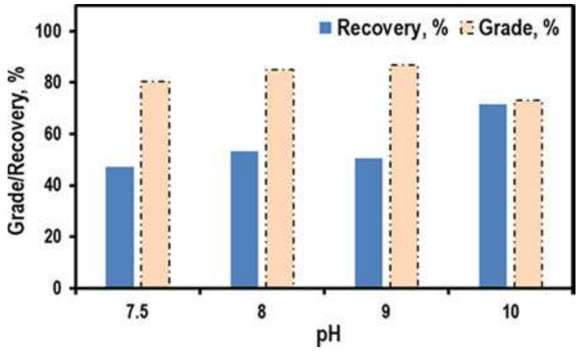
The flotation process optimization and the effect of variation of process parameters such as pH, depressant, and both the collectors were evaluated. Operational parameters maintained during flotation experiments are 33% solids by weight, 1250 rpm, 5 min conditioning time. Reagent dosages and pH have been varied in the successive series of experiments.

### 3.2.1 Effect of Variation in pH

Effect of variation in pH on sillimanite flotation was studied. Initial test was conducted at natural pH (~7), and then pH was varied to 8.0, 9.0, and 10.0 using soda ash while maintaining depressant dosage at 0.8 kg/t and collector (oleic acid) dosage at 0.65 kg/t.

As it can be seen from Fig. 3 that maximum recovery of 53.41% could be obtained at a concentrate grade of 85% sillimanite at pH 8.0. Hence it was considered as the optimum and maintained constant in the subsequent series of tests for optimizing the depressant dosage. The flotation of aluminosilicate minerals using alkyl guanidine as collector was done and results are effective at pH 4 to 12. The extensive study on adsorption of oleic acid on sillimanite also suggest that at pH 8.0, the adsorption density of oleate on sillimanite was maximum.

**Fig. 3** Grade and recovery of sillimanite obtained at varying pH



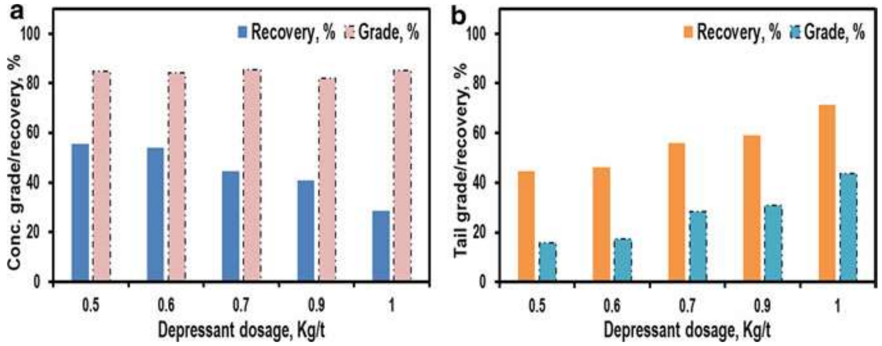


**Fig. 4** Grade and recovery of sillimanite concentrate **a** and tailings **b** obtained at various dosage of depressant, sodium silicate

### 3.2.2 Effect of Variation in Depressant Dosage

Effect of variation in depressant dosage on sillimanite flotation was observed. Flotation tests were conducted at varying dosage of depressant (sodium silicate) while maintaining constant collector (oleic acid) dosage of 0.65 kg/t at pH 8.0.

It can be seen from Fig. 4 that increase in depressant dosage from 0.5 to 1.0 kg/t resulted in increasing tailings loss of sillimanite from 15.8 to 31.0%. A lower dosage of 0.5 kg/t was found to be optimum. At this depressant dosage, a concentrate of 84.9% sillimanite with 55.54% weight recovery could be obtained. On gradual increase in dosage of sodium silicate, the recovery of the sillimanite concentrates decreases gradually, indicating that the depressant is effective as a depressant to quartz as the grade is not diluted even at lower dosage of sodium silicate. In case of tailings, the recovery is increasing as more gangue are being depressed on increasing the dosages of depressant. It is also proven that from various investigations that sodium silicate proves to be a better depressant in depressing quartz mineral.

### 3.2.3 Effect of Variation in Collector Dosage

Effect of variation in collector dosage on sillimanite flotation was observed. Flotation tests were conducted at varying dosage of collector (SFA and oleic acid) while maintaining constant depressant (sodium silicate) dosage of 0.5 kg/t at pH 8.0.

By using the plant based collector SFA, the increase in dosage of this collector showed a gradual improvement in recovery thereby indicating the better and steady collective property of this novel reagent developed. Apart from collection property, Collector also has better selectivity which is evident from the increase in grade along with recovery with increase in reagent dosages. This can be achieved when the reagent specifically adsorbs on the surface of the targeted mineral, here its sillimanite, and imparts hydrophobicity to the mineral surface and thereby enhancing the mineral's ability to float to the surface of the slurry. Because of the high selectivity nature of Collector SFA, the grade and recovery improvement is observed with increasing dosage of the collector. However, in case of collector oleic acid, the recovery decreases as the dosage is increased leading to the diluting the grade of the tailings due to loss of sillimanite in to the tailing. This is a clear indication of inferior collection property of the oleic acid as compared to that of the plant-based sillimanite collector SFA.

It can be observed from Fig. 5 that grade and recovery is higher in case of plant-based collector SFA than that of the conventional collector oleic acid. The study on flotation of kyanite and sillimanite with collector oleic acid also suggests that the sillimanite recovery is maximum at pH 8.0 and 1 mM oleate concentration. Concentrate weight recovery of 67.8% with 85.1% sillimanite was obtained using the plant-based collector SFA (1.5 kg/t dosage) while the concentrate weight recovery of 58.5% with 79.9% sillimanite was obtained using oleic acid from feed with 55.4% sillimanite (collector dosage: 0.55 kg/t). This shows that plant-based collector SFA has better collector properties in case of sillimanite flotation. The present study also confirms the plant-based SFA was selective towards sillimanite and hence maximum recovery could be observed at pH 8.0. The sillimanite collector SFA developed is also bio-degradable and environmental friendly and provides a safe and economically viable option for heavy mineral beach sand separation industries.

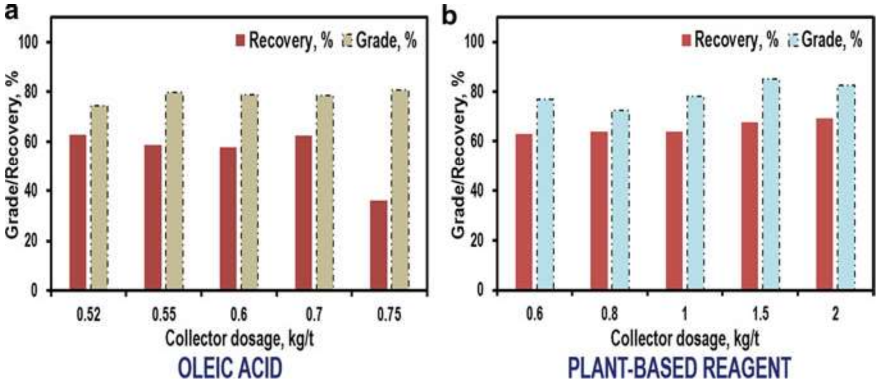


**Fig. 5** Grade and recovery of sillimanite obtained at various collector dosage of **a** oleic acid and **b** plant-based reagent SFA

## 4 Conclusion

Flotation process for sillimanite was optimized by varying process parameters such as pH, depressant dosage and two types of collectors. It was observed that flotation performance of the natural plant source based-collector SFA has better selectivity resulting in improved recovery as compared to that of oleic acid as sillimanite collector. An improved weight recovery of 67.8% with 85.1% sillimanite was obtained using the newly developed natural source-based collector SFA while a weight recovery of 58.5% with 79.9% sillimanite from feed with 55.4% sillimanite was obtained using oleic acid. The improved sillimanite recovery by above 9% using this new plant source-based collector SFA than that of the conventional oleic acid would be more economical in industrial scale sillimanite recovery in beach sand processing industries.

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