Recovery of calcite using eco-friendly bio-collector in the flotation of low-grade limestone

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Abstract

Limestone flotation is a vital process in mineral processing, aimed at selectively separating valuable minerals such as calcite, from its associated gangue in the limestone matrix. The flotation of a low-grade limestone analyzing 41.78% CaO, 5.74% MgO, and 9.87% SiO_2 by utilizing a new eco-friendly, plant seed oil processing industry waste-based fatty acid, as an anionic bio-collector for developing a sustainable process, was studied. A flotation concentrate of 59.94% weight recovery and analyzing 2.67% MgO, 49.92% CaO and 2.79% SiO_2 could be obtained at 2.4 kg/t bio-collector dosage.

The flotation results indicated the selective recovery and enrichment of CaO and reduction of MgO and SiO_2 content from the low-grade limestone thereby making it a suitable raw material for cement manufacturing. The study highlights the development and the effective utilization of industrial waste-derived, bio-based calcite collector that aligns with the growing emphasis on the broader industry trend toward more sustainable mineral processing practices.

Keywords: Low-grade limestone, Flotation, Eco-friendly bio-collector, Cement, Calcite recovery.

Introduction

Limestone deposits mostly contain magnesium carbonate either as dolomite $CaMg(CO_3)_2$ or magnesite ($MgCO_3$) mixed with calcite and these types of rocks are termed 'dolomitic' or 'magnesian' limestone[1]. The majority of limestone is utilized in the cement industry, followed by iron and steel industry, adhesives, as soil conditioner, leather, water purification, paper, plastic, textile, foundry, fertilizer, and tanning industries[10,11]. The required grade of limestone for lime preparation in kilns is considered to be above 45% CaO, SiO_2 around 12-15%, and MgO less than 3%[6]. Hence low-grade limestone invariably has to be beneficiated, and flotation is one such technique that can be opted for when liberation of valuables is at finer size ranges.

The limestone flotation process involves the separation of calcite minerals from their associated gangue using selective flotation collectors[5,7]. Generally, flotation process involves adding fatty acid collectors to the mineral slurry, creating conditions for selective attachment of the collector to the target mineral, calcite. Common collectors include fatty acids, particularly oleic acid, and various other surfactants. Fatty acids are amphiphilic molecules, meaning they have both hydrophobic and hydrophilic parts. This property allows them to selectively adsorb onto the surface of minerals, making them hydrophobic and amenable to flotation. The choice of collector depends on the specific characteristics of the limestone and the impurities associated. One of the most commonly employed collectors in limestone flotation is oleic acid, a fatty acid derived from animal or vegetable oils[3,8].

Oleic acid adsorbs onto mineral surfaces through the interaction between its hydrophobic hydrocarbon chain and the mineral surface and acts as an effective collector[4]. Sodium silicate is a common, versatile, and low-cost depressant used in flotation for non-sulphide minerals and used as a depressant in mineral beneficiation. Generally, direct flotation of limestone, utilizing sodium oleate as a collector and sodium silicate as a depressant, selectively floats CaO-bearing minerals while depressing SiO_2-bearing minerals[9].

Despite the effectiveness of oleic acid, researchers continue to explore alternative collectors to improve the efficiency and selectivity of the limestone flotation process. Various surfactants, such as alkyl amines, quaternary ammonium salts and carboxylates, have been investigated for their potential as collectors[2,3]. The choice of collector depends on factors such as the mineralogical composition of the limestone, the presence of impurities, and the desired product specifications. In this study, a plant seed oil processing industry waste-based fatty acid as a bio-collector in a low-grade limestone flotation was attempted and this may be a promising avenue for achieving better selectivity and recovery, contributing to the optimization of mineral processing operations, and moving towards sustainable and environmentally friendly practices.

Material and Methods

Low-grade limestone: The experimental studies were carried out on a low-grade limestone ore from Southern India. A run-of-mine (r.o.m) sample lumps were size reduced stage-wise to below 2mm. A representative sample was drawn for size distribution and size-wise chemical composition analysis. Further liberation and flotation studies were carried out by optimizing the mesh-of-grind.

Anionic collector: Calcite minerals are generally floated using fatty acids and the most commonly used collector is sodium oleate. In this study, a new eco-friendly, plant seed oil processing industry waste-based fatty acid-, bio-collector was used for the enrichment of calcite thereby reducing the magnesia and silica content in the low-grade limestone. Sodium silicate was used as a depressant for silica and silicate-bearing mineral phases. Sodium hydroxide (laboratory grade) was used as a pH regulator during flotation experiments.

Particle size distribution and chemical analysis: -2mm size material was subjected to wet sieve analysis and the chemical analysis of the corresponding size fractions was also carried out to evaluate the size-wise distribution of CaO, MgO, and SiO_2.

Flotation studies: The low-grade limestone flotation was performed in a laboratory mechanical Denver D12 flotation cell and agitator speed was maintained at 1250 rpm. Direct conventional flotation experiments for floating calcite using a natural waste source-based bio-collector were carried out while depressing silica-bearing minerals.

Results and Discussion

Size distribution and chemical analysis: The size analysis of the -2mm sized limestone sample and size-wise chemical analysis were carried out. The results are shown in figure 1. The chemical analysis of r.o.m. limestone shows the presence of 41.78% CaO, 5.74% MgO, and 9.87% SiO_2. The size analysis of size reduced -2mm limestone r.o.m reveals the presence of CaO, MgO, and SiO_2 across all size ranges indicating that the limestone is of low grade and needs further liberation by size reduction. The above analysis indicates that beneficiation is required to obtain a concentrate of less than 3% MgO and 44-52% CaO for its application as raw material for cement manufacturing.

Mineralogy of limestone: The identification of mineral phases in the r.o.m limestone was carried out by X-ray diffraction (XRD). The major mineral phases were found to be calcite, dolomite, and quartz as shown in figure 2. The presence of dolomite contributes to the MgO content in the limestone while the quartz phase contributes to the SiO_2 content in the limestone.

Optimization of mesh-of-grind: The optimum mesh-of-grind of a -2mm limestone sample was carried out at different grinds (wet grinding) using laboratory ball mill followed by flotation at constant reagent dosages and experimental conditions. The limestone sample was ground for obtaining different size ranges at 66% solids with 1.5 kg/t of sodium silicate as a depressant for silica/silicate-bearing minerals. The milled slurry was used as feed to flotation, and a representative sample was subjected to wet sieve analysis, and its d_{80} size was calculated. Tests were carried out at pH 10.0 (using NaOH solution), with 1.5 kg/t sodium silicate as a depressant and 2 kg/t eco-friendly calcite bio-collector.

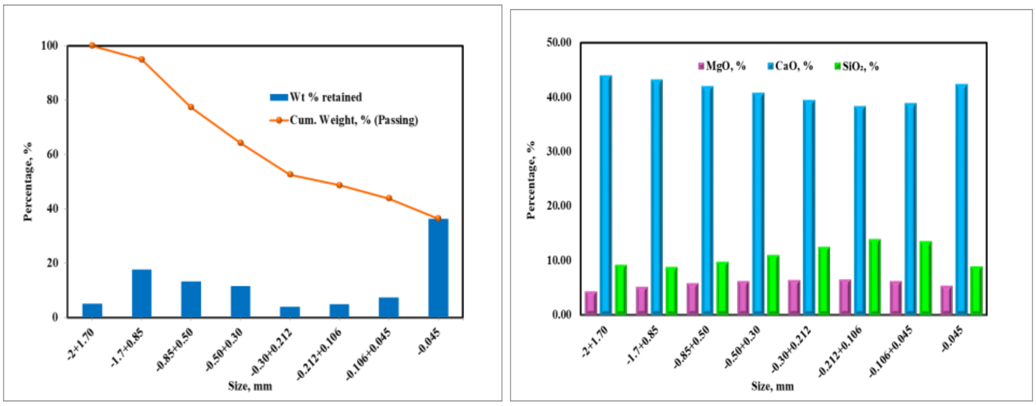

Fig. 1: Size distribution and size-wise chemical analysis of limestone feed sample

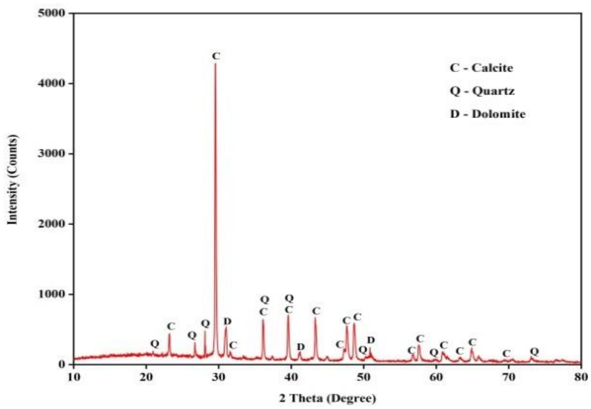

Fig. 2: XRD analysis of r.o.m limestone sample

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Figure 3 shows the concentrate weight recovery and corresponding assay analysis at d_{80} values of various grinds. The mesh-of-grind was optimized at d_{80}: 45µm as the concentrate contains relatively lower MgO of 2.87% and higher CaO of 49.09% with 52.3% weight recovery as compared to the concentrates generated at the other grinds.

Optimization of sodium silicate dosage as a depressant during grinding: The effect of variation in depressant dosage was studied by varying its dosage from 1.5 kg/t to 6.0 kg/t during grinding and the results are presented in figure 4. All the experiments were conducted at pH 10.0 and at the bio-collector dosage of 2 kg/t.

The sodium silicate dosage was varied from 1.5 kg/t to 6.0 kg/t during grinding. The concentrate weight recovery after flotation was in the range of 52.30% to 62.04% while MgO content varied from 2.87% to 3.27%. The maximum rejection of SiO_2 content (79.40%) into tailings took place at a sodium silicate dosage of 1.5 kg/t at which MgO content in concentrate was found to be a minimum of 2.87% in this series of experiments. Hence, the optimum sodium silicate dosage during grinding for subsequent studies was treated as 1.5 kg/t.

Optimization of slurry pH for calcite recovery: The grind size was optimized at 45µm (d_{80}) and the depressant dosage at 1.5 kg/t during grinding, the effect of slurry pH variation on CaO recovery and MgO reduction was studied at the fixed bio-collector dosage of 2 kg/t. The slurry pH was adjusted using NaOH solution and the flotation tests were conducted and the results are shown in figure 5.

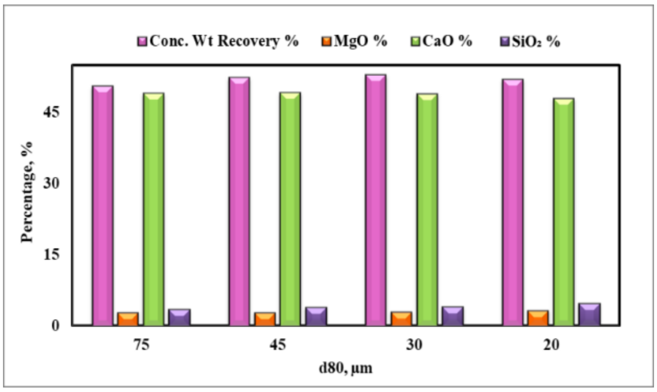

Fig. 3: Effect of grind variation of limestone on CaO recovery and MgO reduction in flotation concentrate

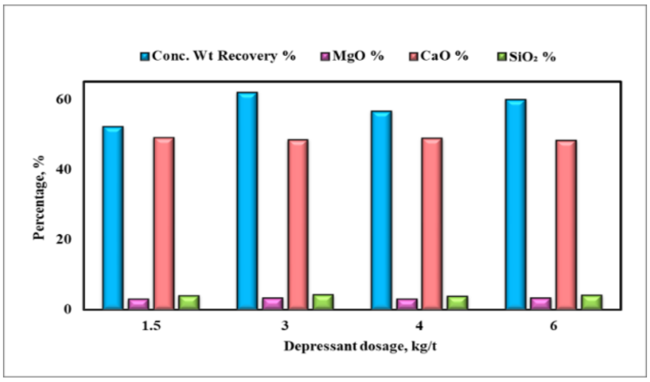

Fig. 4: Effect of grind depressant of limestone on CaO recovery and MgO reduction in flotation concentrate

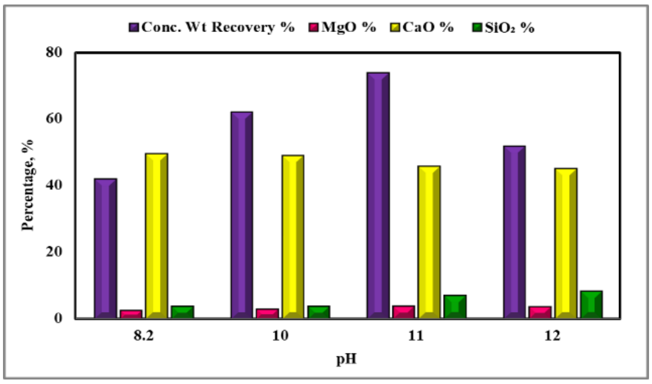

Fig. 5: Effect of variation of limestone slurry pH on CaO recovery and MgO reduction in flotation concentrate

The pH of the slurry for flotation was varied from 8.2 (natural) to 12.0 to study its effect on the flotation process. MgO in concentrate at natural pH was found to be minimum at 2.61% under the experimental conditions mentioned above. At relatively higher pH values of the slurry, selective separation of MgO-bearing mineral from the associated gangue was minimal. Therefore, subsequent flotation tests were carried out at a natural pH of 8.2.

The optimized flotation conditions using a bio-collector (2 kg/t) were grind size of 45µm (d_{80}), sodium silicate of 1.5 kg/t during grinding, natural pH (8.2) of the slurry during flotation, further addition of 1.5 kg/t sodium silicate during flotation followed by bio-collector dosage variation studies. At these optimized conditions, a concentrate (rougher flotation concentrate) of 42.10% weight recovery with 2.61% MgO, 49.61% CaO and 3.83% SiO_2 could be obtained from the feed analyzing 5.74% MgO, 41.78% CaO and 9.87% SiO_2.

Optimization of bio-collector dosage for calcite recovery: The mesh-of-grind was optimized at 45µm (d_{80}), depressant dosage at 1.5 kg/t during grinding, and natural pH was found to be the optimum slurry pH. By maintaining these optimized test conditions, further flotation tests were carried out using the bio-collector by direct flotation of low-grade limestone. The bio-collector dosage was varied to study its flotation performance efficacy in terms of recovery of CaO and reduction of MgO in the concentrate and the results are shown in figure 6.

As the dosage of bio-collector was increased from 1.6 to 2.4 kg/t, weight recovery of the concentrate also increased. At 2.4 kg/t of the bio-collector, a concentrate of 59.94% weight recovery analyzing 2.67% MgO, 49.92% CaO and 2.79% SiO_2 could be obtained from a feed of 5.74% MgO, 41.78% CaO and 9.87% SiO_2. The enriched flotation concentrate produced could be used as raw material for cement production.

Conceptual flowsheet on limestone flotation: The conceptual flowsheet was developed based on the laboratory-scale flotation studies carried out on a low-grade limestone sample for CaO recovery and reduction of MgO (Figure 7).

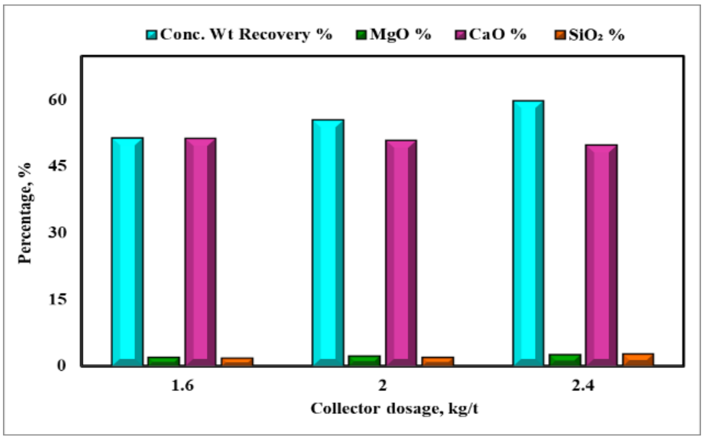

Fig. 6: Effect of variation of bio-collector on CaO recovery and MgO reduction in flotation concentrate

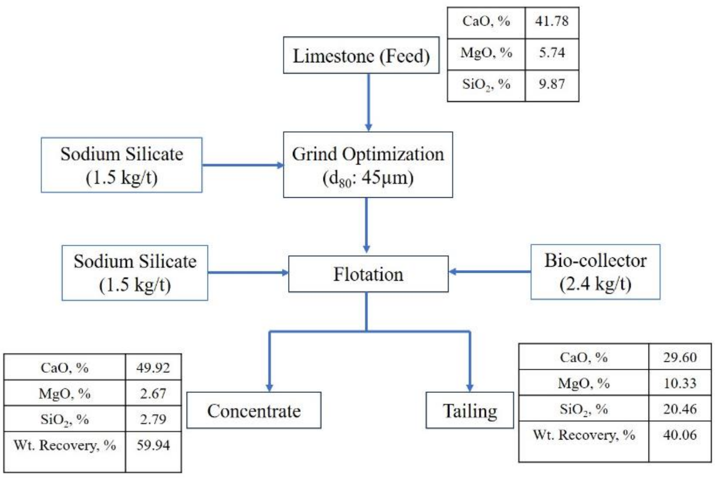

Fig. 7: Conceptual flowsheet of low-grade limestone flotation

Conclusion

The flotation of a low-grade limestone was studied utilizing an eco-friendly plant seed oil processing industry waste-based fatty acid, a bio-collector, for improving its grade by enriching CaO and reducing the MgO and SiO_2 content for its use in Portland cement manufacturing. The major mineral phases in limestone were found to be calcite, dolomite, and quartz. The chemical characterization revealed the presence of 5.74% MgO, 41.78% CaO, and 9.87% SiO_2.

The optimized flotation process conditions were a grind size of 45µm (d_{80}), sodium silicate of 1.5 kg/t during grinding, natural pH of the slurry (8.2), sodium silicate of 1.5 kg/t during flotation and bio-collector dosage of 2.4 kg/t and the concentrate with 59.94% weight recovery analyzing 2.67% MgO, 49.92% CaO and 2.79% SiO_2. Thus, the present research work highlights the development of eco-friendly fatty acids as alternative green collectors derived from industry waste/renewable resources for recovery of calcite in low-grade limestone.

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