Beneficiation of a Low Grade Limestone by Flotation Column

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Abstract

Beneficiation of a low-grade limestone sample from Salem, Tamilnadu was carried out by pilot scale flotation column. Mineralogical studies have reveалled that quartz, freldspar, pyroxene & biotitic as gangue minerals while pyrite, in trace quantities, appear as opaque along with dominating calcite. Reverse flotation was tried using two different commercial amines viz. Chem750F and Flotamine-D. The studies clearly suggest that it is possible to produce a limestone concentrate assying around 96-97% of $CaCO_3$ with less than 1% SiO_2.

1. Introduction

The role of minerals and metals in economic development, especially in the developing countries has received much attention in recent years. Small-scale mines represent a growing and important component of mineral sector in the developing world in terms of value of output, contribution to the economy and rural employment. It has been established that small mines contribute about one sixth of the value of world's output. In India, around 3000 small mines account for about 50% of non-fuel mineral production.

The limestone deposits in Tamilnadu occur either in the form of crystalline or amorphous varieties. The bulk of the limestone deposits are found south of Moyar – Bhavani – Attur lineament. These crystalline limestone deposits of Salem, Thirucharapalli, Madurai and Thirunelveli form the limestone province of Tamilnadu. The total provan reserves of crystalline limestone are around 200 million tons out of which 50 million tones account for Salem and Namakkal districts [1]. Almost all these mines are owned by private small mine owners. Until recently all these small mine owners were supplying their limestone to the cement industry. Due to the recent suspension of production at many neighbouring cement factories, the limestone mining companies have opted to reach alternate market for their limestone. Production of high quality product, with special applications, such as poultry feed, paper and rubber industries is the most suitable option to sustain in the market.

The main objective of the present work is to study the beneficiation of limestone on a pilot scale, 0.50 metre dia semi-commercial automated flotation column. The experimental studies include the optimization of process parameters and generation of data required for scale-up. The main goal is to reduce silica content to less than 1% in limestone concentrate.

Minerals like calcite, apatite, barite, etc are generally beneficiated by using anionic collectors like carboxylic acid [2]. When the proportion of gangue minerals is relatively less and comprise mainly of quartz and other silicates, these minerals can be beneficiated by using cationic reagents as flotation collectors. This process is called reverse flotation. Silicate particles possess high negative charge due to the presence of oxygen in their molecular structure [3]. It has been established that mineralogically pure quartz cannot be floated with anionic collectors where as it can be easily floated using cationic collectors. Cationic collectors are generally the derivatives of amines and ammonium salts. The most common type of cationic collectors used in flotation are the fatty amines having a chain length of 12-18 carbon atoms. The flotation response of cationic collectors increases in proportion to the length of their hydrocarbon chain. Pentavalent nitrogen is characteristic of both amines and quaternary ammonium salts. In general, amines readily dissociate into ionic forms in aqueous medium according to the equation.

$$RNH_2 + H^+ \rightleftharpoons RNH_3^+$$

The cation thus formed is easily adsorbed on anionic sites of silica/silicate surface by way of electrostatic interaction [4]. The cationic flotation (reverse flotation) is attractive because the cationic collectors are insensitive towards hard water salts, low consumption, less induction time and high contact angles.

2. Materials and Methods

The beneficiation study of limestone was carried out for low-grade limestone from a small Mine, near Sankagiri, Salem district. The various rock types encountered within this limestone deposit are pegmatites, quartz veins, biotite gneisses and pyroxene gneisses. A few run of mine samples were collected for petrological characterization. These limestone samples vary in colour from white to pink/rose, are hard, compact and crystalline in nature. Occasionally banded limestone varieties were also observed. The banded type consisted of broad/thin deep grey coloured bands, which are bands of pyroxene, separated by white bands consisting chiefly of calcite.

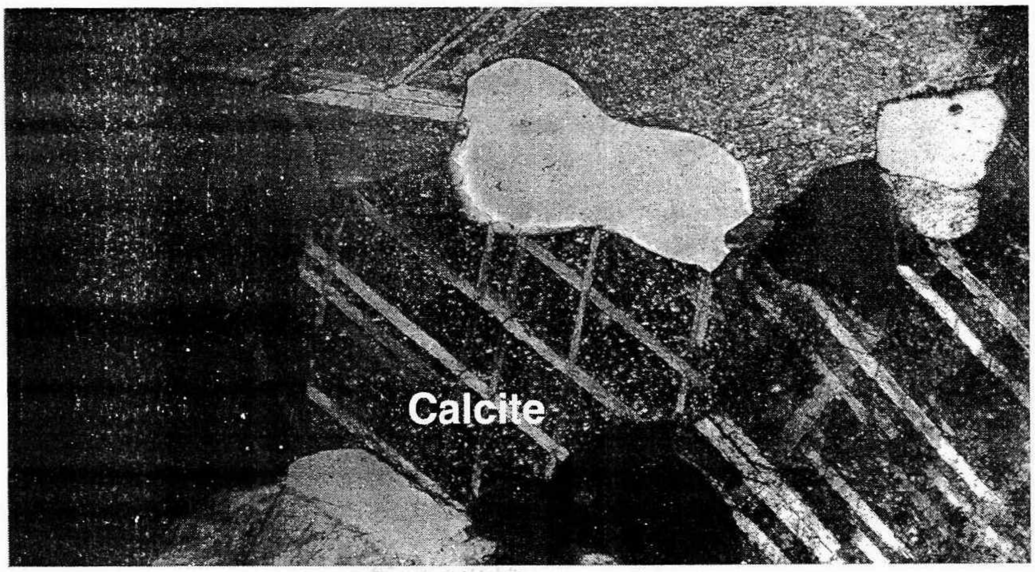


Fig.1: A calcite grain enclosed by silicates (quartz and feldspar), Crossed nicols, x100.

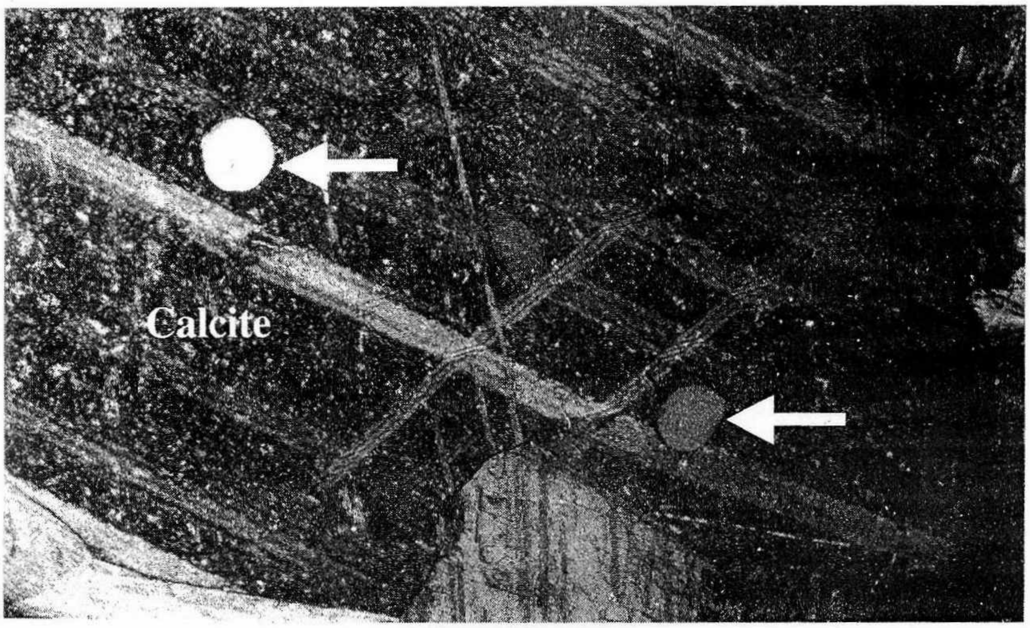


Fig.2: Few silicate grains (shown by arrow) enclosed within the calcite grains. Crossed nicols, x100.

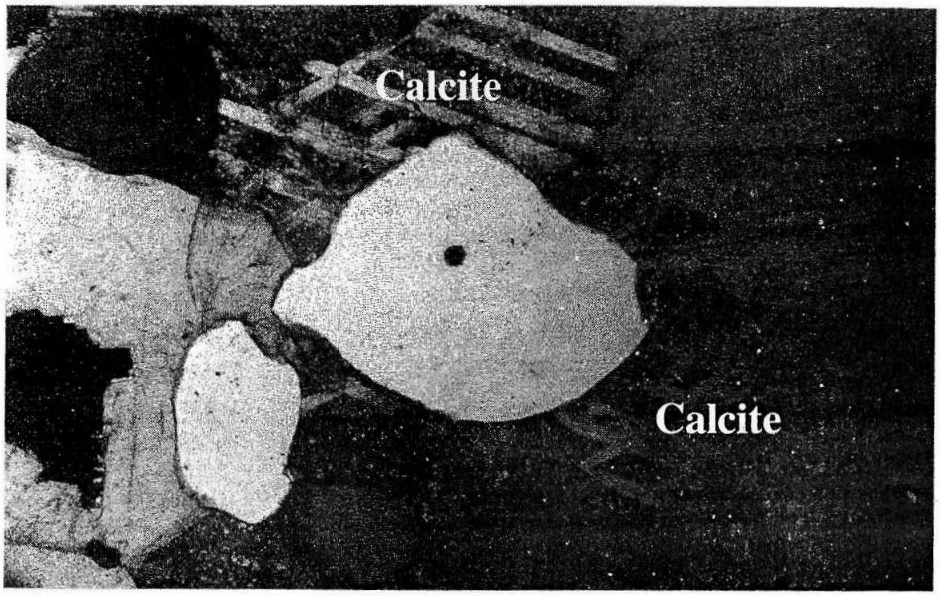


Fig.3: Calcite grains enclosed with silicates (quartz, feldspar), Crossed nicols, x 100.

On examining different thin sections under transmitted light microscope calcite was found to be the most predominant mineral. The associated silicate gangue minerals in order of abundance were quartz, pyroxene, feldspar, biotite (Figs. 1-3), while pyrite (in traces) as an opaque (Fig.4). The limestone sample sometimes shows equi-granular texture. Sometimes calcite shows twinning. The content of these silicates vary with respect to the colour of the limestone (Table XII); generally high content of silicates are encountered in the banded varieties. Grain size of these silicates varies from 5 microns to around 80 microns (Figs.1-3). Sometimes quartz and feldspar (of 5-15 microns sizes) are found as inclusions within calcite grains (Fig.2) giving rise to the problem of complete liberation. feldspar and pyroxene are partly weathered giving clay content to the sample. Rarely biotitic contains fine calcite grains along their cleavage planes giving a high content of calcite in the tailings.

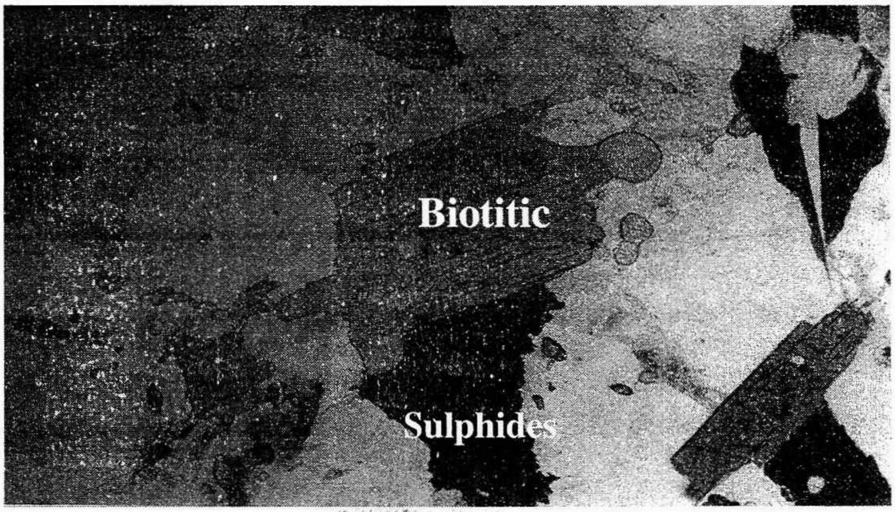


Fig.4: Biotitic, pyroxene and some opaques (sulphides like pyrite) surrounding the calcite grains Parallel light, x100.

The basic principle in column flotation is the use of counter current flow of air bubbles and solid particles. This is achieved by injecting air at the base of the column and allowing bubbles to rise through the downward flowing slurry. Counter current flow is accentuated in most columns by the addition of wash water at the top of the column. This flow pattern is in direct contrast to that found in conventional cells, where air, water and solids are driven in the same direction. Due to counter current flow, the column exhibits improved hydrodynamic conditions for flotation and thus produces a cleaner product at higher recoveries and lower consumption.

2.1 Salient features of NML pilot column:

- *Column:* The semi-commercial column was fabricated with MS consisting several flanged sections of various lengths. Overall column design permits the variation of parameters such as column height, feed injection point and froth depth.

- *Sparger:* Internal type spargers were used in semi-commercial size flotation column. Ceramic tubes made of silicon carbide were used as spargers. Provision was made to insert or take out these spargers without disrupting the continuous column operation.

- *Feed Pump:* The slurry pump with capacity up to $10m^3/h$ was used. The discharge capacity of the pump can be adjusted by changing the frequency through an AC frequency drive.

- *Level controller:* A Differential Pressure Transmitter (DPT) was used to maintain the interface between the slurry and froth. The output signal generated by DPT is looped to the control valve via microprocessor-based controller, so that discharge rate could be changed automatically to maintain the interface level at a fixed froth depth. The interface can be visualized on the LCD screen of the controller. During steady state, the interface level can be maintained at a constant value of +/- 10 mm. In the semi-commercial column, out-put signal of DPT was fed to an electro-pneumatic control valve.

- *Flow measurement:* Magnetic flow meter with digital display of flow-rate and totalizer was incorporated to measure and control the slurry feed flow, airflow and wash water flow rates. However, purge rota-meter was also used to measure the airflow rate.

- *Wash water distribution:* Specially designed rotating type wash water distributor with froth scrapping was provided for the uniform distribution of water and removal of froth covering the entire cross section of the column. For easy monitoring of the column parameters, all the controls were mounted in a centralized panel.

The schematic diagram of NML semi-commercial column flotation system used in the present investigation is shown in Fig.5.Two proprietary reagents basically amines with long carbon chains were used as collectors for the separation of silica and silicates from limestone. The entire test programme was carried out at natural pH.

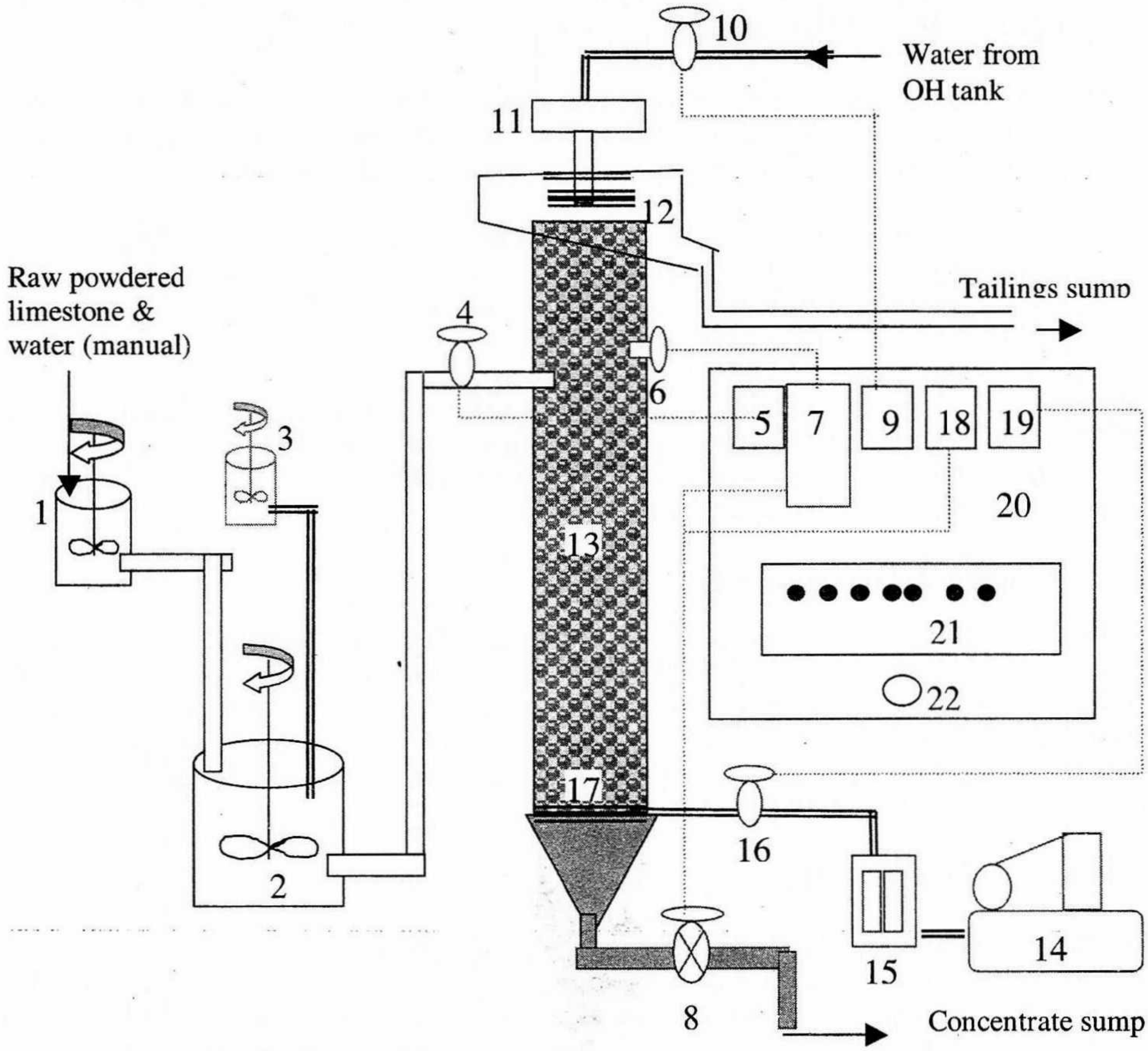
2.2 Installation & commissioning:

NML 0.5m dia flotation column equipment and accessories were transported to mine site near Salem and installed keeping the total height of the column as 10 m from the bottom of the column. The DPT and feed inlet were fixed at exactly 2.0m and 3.0m below from top of the column respectively. The underflow (concentrate) and the froth (tailings) are collected in the separate sumps. The layout of the column and other accessories installed are shown in the following (photographs), Figs. 6-8.

2.3 Experimental procedure:

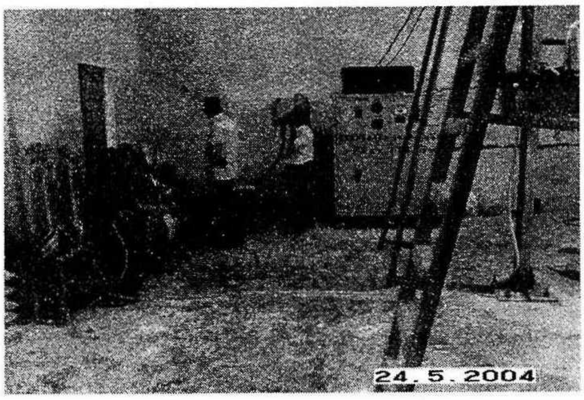
2.3.1 Slurry preparation: As there is no operating plant at the site near Salem, feed to the column has to be prepared from raw pulverized limestone powder manually. The limestone powder was added to the Conditioner I at the desired rate and the required water was pumped to obtain desired slurry density. This slurry flows to the Conditioner II by gravity. All the reagents were added in conditioner II, from which the slurry was fed to the column.

2.3.2 Column test procedure: Initially, column was filled with water at desired airflow, wash water rate, feed-rate and froth depth. After stabilization with water, slurry conditioned with desired dosage of reagent was fed to the column through the feed pump. The column was allowed to run steadily for at least three nominal residence times before sample collection. In order to check the steady state, column discharge samples were collected at different time intervals and pulp densities of the same were measured. Once the pulp density of the column discharge is constant, samples of feed, concentrate and tailings were collected manually. Simultaneously, air, feed and wash water flow rates were checked and recorded. The collected samples were dewatered, dried and analyzed for total $CaCO_3$ and SiO_2.



1. Conditioner I
2. Conditioner II
3. Reagent Tank
4. Feed flow sensor
5. Feed flow indicator
6. Interface level sensor
7. Process controller
8. Discharge valve
9. Wash water flow indicator
10. Wash water flow sensor
11. Wash water distribution & froth scrapping system
12. Froth launder
13. Column
14. Compressor
15. Dehumidifier
16. Air flow sensor
17. Spargers
18. Air flow indicator
19. Discharge valve position indicator
20. Control panel
21. Starters & Switches for equipment
22. AC power indicator

Fig: 5. Schematic diagram of NML Semi-commercial flotation column installed at site near Salem



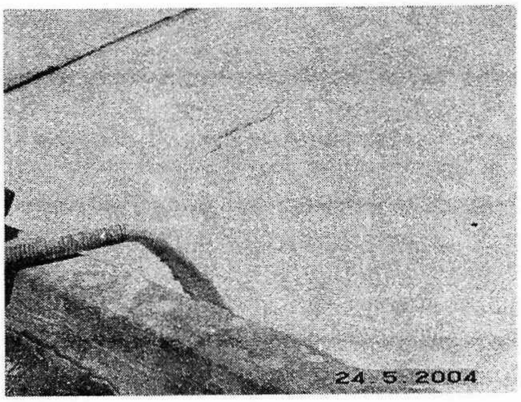


Fig.6 Layout of column and its accessories in the main shed

Fig.7 Concentrate sump

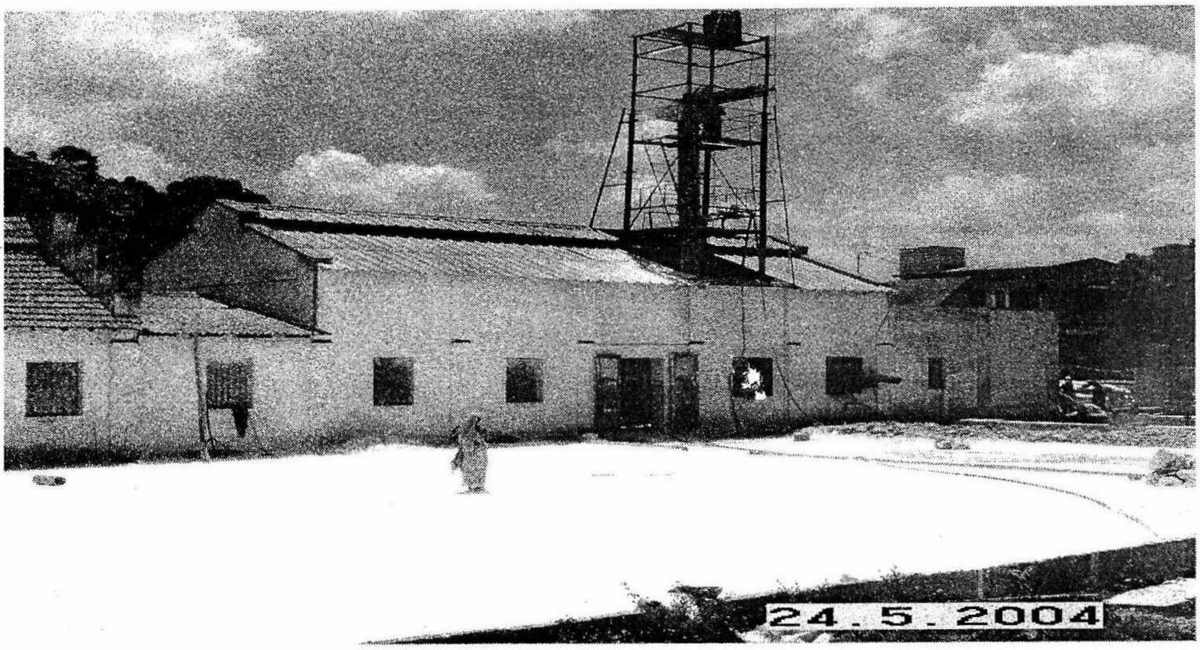


Fig.8 Column top view &Concentrate drying yard

3. Results and Discussion

3.1 Size distribution of head sample: Initially the head sample was subjected to particle size analysis to examine the size distribution. The results of the same are given in Fig.9. The results indicate that the mean diameter of the particles is 37.13 microns and the d_{80} is 63.22 microns.

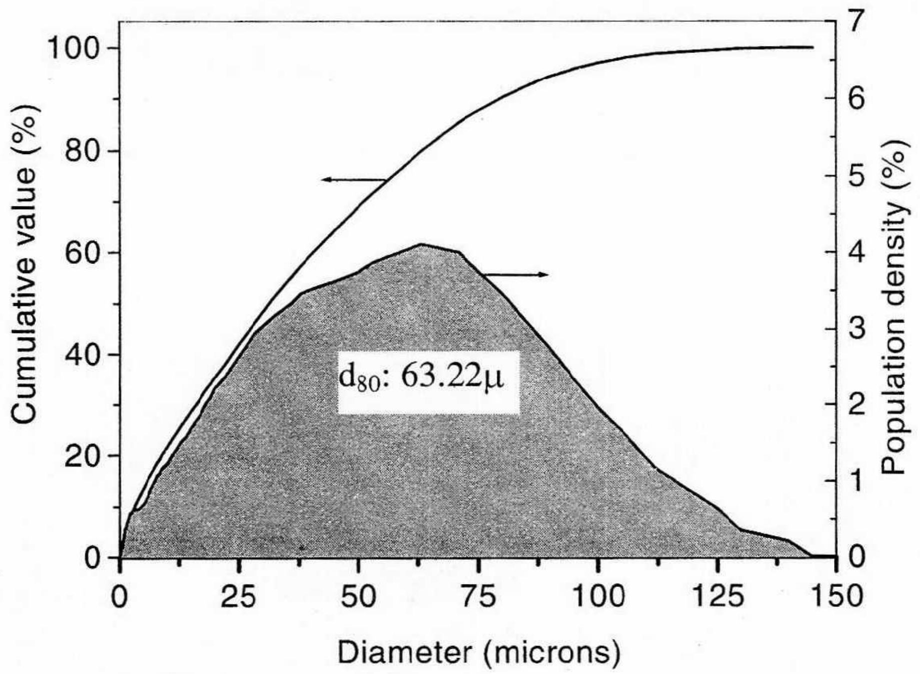


Fig.9. Particle size distribution of limestone sample

3.2 Effect of reagent dosage: Two types of cationic collectors namely Chem. 750 F and floatamine - D were tested for their efficiency in separation of silica from limestone at fixed conditions and it was observed that the results with flotamine – D are superior and consistent both in terms of grade and recovery over CHEM 750F. Also, during the test work, it was observed that the volume of froth generated with Chem750F is very high and stable. A de-frothing agent was found to be essential during dewatering operation. So, industrial application of such reagents poses many practical problems. Hence, all subsequent experiments were carried out with the reagent floatamine – D. Fig.10 shows the effect of floatamine D dosage on the limestone quality and recovery. The results clearly indicate that a reagent dosage of 0.35 – 0.45 kg/t are optimum to produce high grade lime stone concentrate with less than 1% silica.

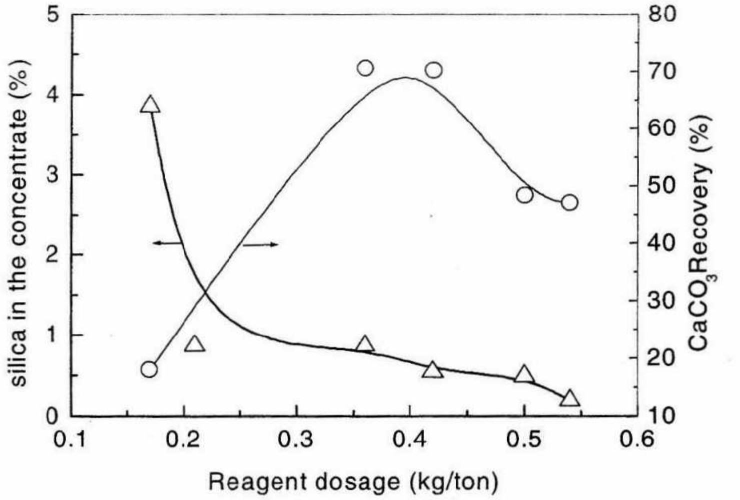


Fig.10. Effect of floatamine D dosage on the limestone concentrate quality and recovery.
[Head assay: $CaCO_3$: 82.94%, SiO_2: 15.70%, Slurry feed velocity :0. 78cm/sec, Solids feed rate: 1.0t/h, Airflow velocity: 1.19cm/sec, Froth depth: 45cm]

3.3 Effect of airflow rate: Generally airflow rate should be as high as possible to ensure a high throughput. At the same time, if the airflow rate is too high, the flow pattern will be disturbed and there is every possibility to lose bubbly swarm. It is to be noted that column should operate in a bubbly flow regime, where gas hold up varies linearly with air rate. Tests were conducted at different airflow rates and the results are presented in Table-1. From the results it could be seen that the quality of the concentrate increases with the airflow rate, but at the same time $CaCO_3$ recovery was found decreased. This may be due to the increase in bubble size at high air rates. As the bubble size increases its rising velocity also increases rapidly, displacing small bubbles down ward and the concentration of feed water in the froth increases, resulting in less recovery. It was also observed that the air flow rate of 100 lpm was found to be optimum to obtain acceptable grade with moderate recovery. Since amines are good frothing agents, the feed water entrainment will be very high and consequently, the system may switch over to negative bias at high airflow rates.

Table. 1 Effect of air rate

S. No.	Air flow rate (lpm)	Concentrate Assay (%)		Tailings Assay (%)		$CaCO_3$ recovery (%)
		$CaCO_3$	SiO_2	$CaCO_3$	SiO_2	
1	80	90.45	6.24	54.47	42.24	86.3
2	100	94.2	2.19	60.17	36.48	76.0
3	120	95.70	0.87	67.38	13.99	63.4
4	140	94.95	1.71	63.13	19.49	71.3

Conditions: Reagent dosage :0. 21kg/t Slurry velocity :0. 78 cm/sec
Solids feed rate: 1.0t/h Froth depth: 45cm
Head assay $CaCO_3$: 82.94%, SiO_2: 15.70%,

3.4 Effect of feed flow rate: Generally change in feed rate causes a change in the residence time of the pulp in the column and thereby affect grade and recovery. In the case of reverse flotation, the increase in slurry feed flow rate, residence time of the slurry will be reduced and thereby the grade. Hence, enough residence time has to be maintained to collect entire gangue from the slurry. In the present investigation, feed flow rates were varied from $3.3m^3$ /h to $7.5\ m^3$ /h by adjusting the feed pump capacity through frequency drive and the results are shown in Fig.11.

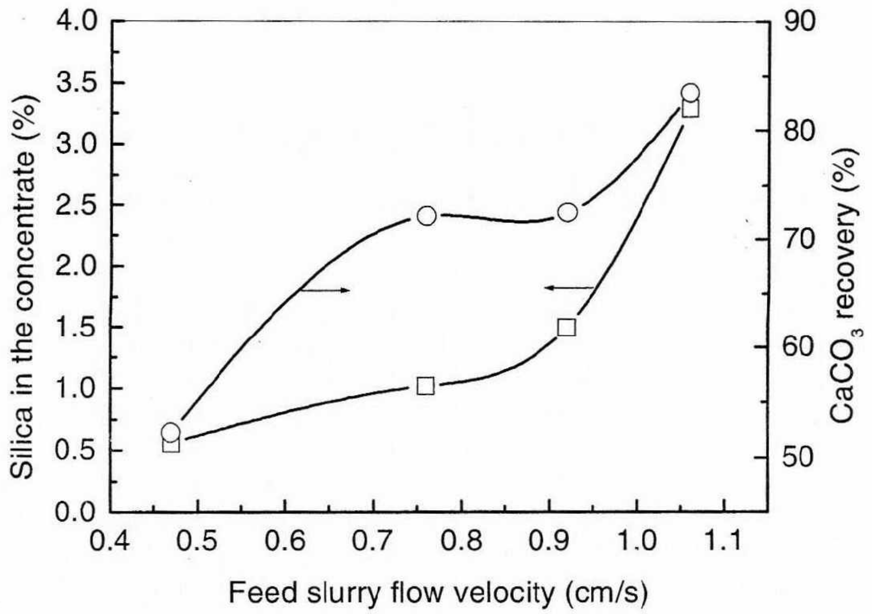


Fig.11 Effect of slurry velocity on limestone concentrate quality and recovery
[Head assay $CaCO_3$: 83.20%; SiO_2: 10.82%, Reagent dosage :0. 30kg/t, Air flow velocity :0. 85cm/sec, Solids: ~20%, Froth depth: 45cm]

The results clearly indicate that a feed flow rate of $5\text{-}6m^3$ per hour is optimum for acceptable grade with about 70% $CaCO_3$ recovery. It is also known that the increase in feed rate, results in decrease of bubble rising velocity. Due to this phenomenon, it is seen from the results that the froth weight is decreasing with an increase in feed flow rate resulting in bad quality of concentrate. From the data the residence time of slurry and particle the flotation rate constant was calculated using established equations and the same was found to be $0.69min^{-1}$.

3.5 Effect of pulp density: Column throughput can be increased by increasing the solids in the feed up to a point where sufficient bubbles are available to lift the particles. However, it is known that the increase in mineral solids in suspension results in increase in slurry density and slurry viscosity, which have opposing effects on bubble rising velocity. Thus, the gas holdup in the column will increase. Tests were conducted at three different pulp densities and the results are presented in Table.2.

Table.2 : Effect of pulp density

S.No.	Pulp density	Concentrate Assay (%)		Tailings Assay (%)		% Recovery
		$CaCO_3$	SiO_2	$CaCO_3$	SiO_2	$CaCO_3$
1	1.1	95.94	0.54	62.96	24.72	64.7
2	1.2	98.19	0.41	71.45	28.61	43.1
3	1.28	97.44	0.80	75.45	16.11	30.2

Conditions: Reagent dosage: 0.42kg/t Air flow velocity: 1.19cm/sec
Froth depth: 45cm Feed flow velocity: 0.78cm/sec
Head sample assay $CaCO_3$: 80.96%; SiO_2: 15.70%

From the results it is observed that pulp densities are better to produce high quality concentrate. Where as at high pulp density, though the quality of the concentrate is acceptable but the recoveries are very low. Increase of solids in the slurry beyond certain limit leads to froth overloading and burping action, which may affect the concentrate grade and recovery.

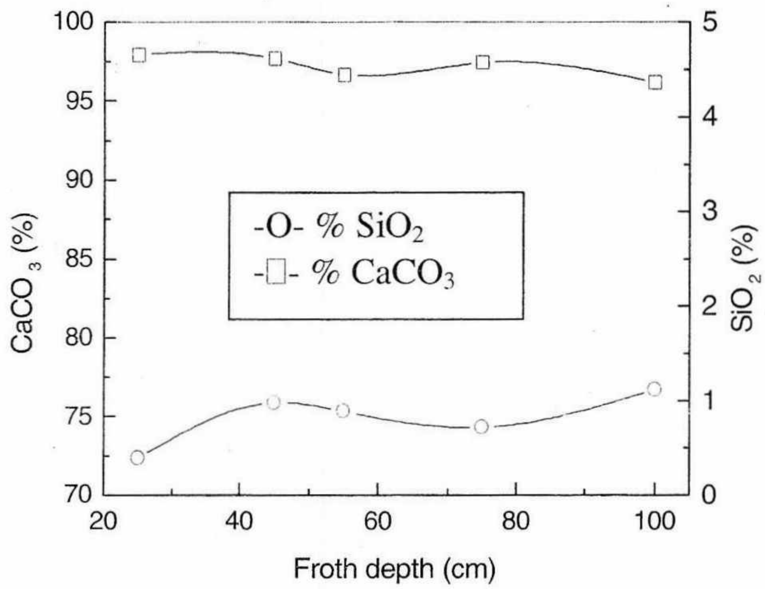


Fig. 12 Effect of froth depth on limestone grade and recovery
Head assay=$CaCO_3$: 79.70%, SiO_2: 13.7%, Reagent dosage: 0.30kg/t,
Air flow velocitv: 0.85cm/sec. Solids: ~20%. Feed flow velocitv: 0.71cm/s

3.6 Effect of froth depth: Column flotation offers the advantage of controlling froth depth during operation from a few millimeters to several centimeters and is only limited by the particular mineral system being processed. This provides an additional vehicle, which may be used to control the flotation separation process. It was hypothesized that froth depth variations may affect product grade and mineral recovery. Therefore, a series of tests was conducted on limestone mineral and the results are shown in the Fig. 12. Froth depth was adjusted to the required value using process controller. Experiments were carried out at different froth depths ranging from 25cm to 100cm. The rejection of entrained particles, in this case limestone, depends on the froth depth as observed from the results. At less froth depths the valuable limestone particles will be carried along with gangue affecting the recovery of limestone. At the same time deep froth bed may not produce cleaner concentrate because of froth overloading and froth drop back. In the froth zone, particles are subjected to repeated detachment/reattachment process. In the present case though there is no significant variation in grade and recovery of limestone, a froth depth in the range of 45cm to 75cm appears to be optimum.

3.7 Effect of wash water: Tests were performed to determine the effect of wash water on the limestone recovery and the results of the same are shown in the Table 3. Wash water was introduced through a system specially designed and located at the top of the column.

Table. 3 Effect of wash water

S.No.	Wash water rate (lpm)	Concentrate Assay (%)		Tailings Assay (%)		% Recovery
		$CaCO_3$	SiO_2	$CaCO_3$	SiO_2	$CaCO_3$
1	0.0	97.94	0.35	68.96	18.55	55.3
2	0.03	97.44	0.64	57.96	25.10	73.3

Conditions: Reagent dosage: 0.22kg/t; Air flow velocity: 1.02cm/sec
Feed flow velocity: 0.71cm/sec; Froth depth: 45cm
Pulp density: 1.15
Head sample assay $CaCO_3$: 82.46%, SiO_2: 13.53%

The principal reason for using wash water in column flotation technique is to increase the grade of the concentrate, but in the present case it is the recovery of limestone, as the process is reverse flotation. The recovery of limestone concentrate increases due to the displacement of entrained hydrophilic calcite particles that report to the froth. Tests with more wash water flow rates could not be conducted due to the limitations prevailing at the site.

3.8 Experiments at near optimum conditions: From the results, the optimum conditions of process and system parameters of flotation column to produce quality product with reasonable recovery are presented below.

Particle size:	37microns (mean size)
Reagent:	Floatamine D
Reagent dosage:	0.25 – 0.50 kg/t depending on the gangue volume in the feed.
Slurry pH:	Natural
Pulp density:	1.1-1.2
Total column height:	8.75 m
Air velocity:	~1.02 cm/sec
Feed velocity:	~0.76 cm/sec
Froth depth:	50 – 70 cm
Wash water rate:	~0.03 l/m

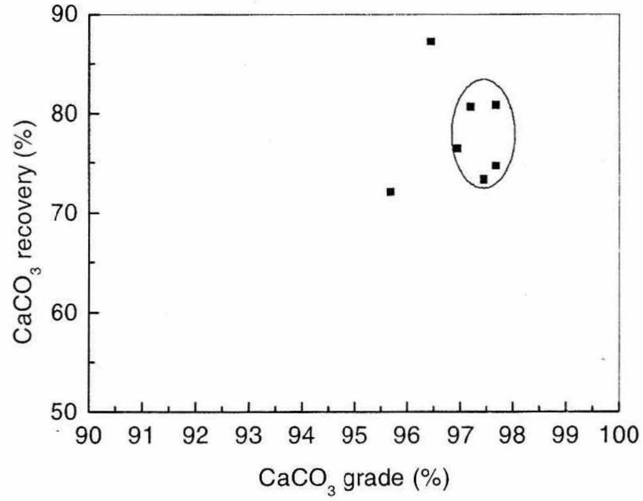


Fig.13 Limestone concentrate grade Vs recovery

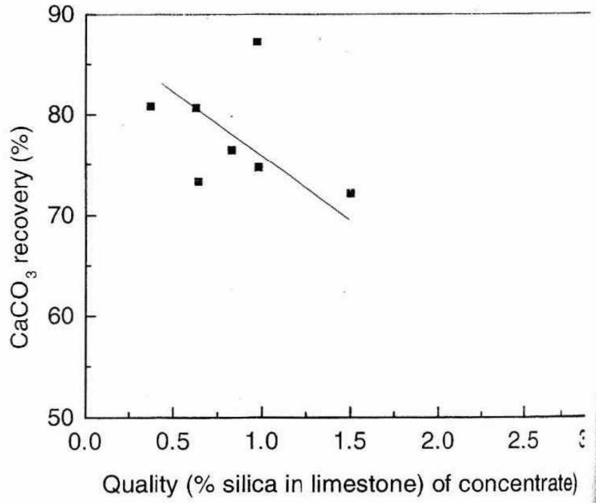


Fig.14 Limestone concentrate quality Vs Reco

Figs.13 and 14 gives the profiles of limestone grade vs. recovery and quality vs. recovery respectively. It is apparent that an average limestone ($CaCO_3$) grade of >96% could be achieved with recoveries between 65 – 75% keeping the silica content <1%.

4. Conclusions

Pilot scale flotation column was installed at Salem to test the application of column flotation technology for limestone beneficiation. Reverse flotation process, i.e., flotation of silica and other gangue minerals were adopted for the production of high-grade limestone concentrate with minimum silica.

Particle size analysis of the feed material indicated the average particle size as 37 microns and d_{80} as 63 microns. Petrological examination of the samples, has revealed the presence of quartz, feldspar, pyroxene and mica as the major silicate gangue minerals. Though majority of these silicates are liberated at the feed size, some amount of silicates in the size range of 5-15 microns are still locked with in the calcite grains as inclusions, which reports in concentrate.

Based on the results of preliminary pilot plant trials with two types of amines, viz. CHEM 750 F and Floatamine – D, It was observed that Floatamine-D was found to be excellent in terms of solubility, selectivity, consumption, froth stability and consistency.

The tests clearly suggest the amenability of flotation column for the beneficiation of limestone and the concentrates assaying around 96-97% of $CaCO_3$ and less than 1% of SiO_2 with a recovery of 65 to 75% could be produced. Concentrates with higher recovery could be achieved by the addition of wash water into the flotation column.

5. Acknowledgements

The authors are grateful to Prof. S.P. Mehrotra, Director, National Metallurgical Laboratory, Jamshedpur for his constant encouragement and permission to present/publish the results.

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