Optimization studies on limestone beneficiation

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Received 20 September 1996; accepted 6 February 1997

Limestone rejects from Bagalkot mines have been beneficiated by froth flotation with a view to reducing the magnesia content. In order to ascertain the effect of the main parameters such as sodium oleate concentration, sodium silicate concentration and pH on the MgO content, statistically designed experiments have been performed. The results indicate that under the optimum conditions arrived at limestone rejects could be beneficiated to produce a concentrate with magnesia content meeting the specifications for cement manufacture.

Limestone is an important mineral in the manufacture of cement. Out of the total production of limestone, about 84% is used by the cement industry, about 7% is of iron and steel grade, about 3% is of chemical grade and the rest 6% accounts for other grades. The major reserves of limestone are found in Karnataka, Madhya Pradesh, Andhra Pradesh, Gujarat and Rajasthan. For the manufacture of cement, magnesia, sulphur and phosphorus are regarded as undesirable impurities. Limestone should have a maximum limit of 5% MgO. The presence of phosphorus and P2O5 in excess of 1% considerably slows down the setting time of portland cement. The limit placed on the amount of MgO is due to the fact that its slow hydration can cause disruptive expansions in the hardened phase.

Extensive work has been carried out on the flotation of calcite bearing minerals using various collectors and depressants. Morozov et al. have highlighted that for selective separation of fluorite and calcite, the ionic composition of the aqueous phase has to be carefully controlled. In a study on the selective flotation of apatite from calcite, the recovery of calcite was found to increase with increase in pH, but calcite could be depressed using dilute sodium silicate solution at pH 10-11 due to the adsorption of polymeric silica on calcite surfaces. Somasundaran and coworkers have found that in calcite-apatite separation, the flotation of both minerals is affected markedly due to the dissolution of other mineral. The surface-chemical alterations in the supernatants of calcite and apatite have also been examined. A new reagent regime using N-acylamino carboxylic acids has proved to be effective collectors for fluorite-calcite separation, as reported by Baldauf et al. The surface-chemical mechanism of colemanite-calcite separation by flotation using sodium dodecyl benzene sulphonate as a selective collector for colemanite has been delineated by Yarar. A novel technique of pressure type flotation has been successfully used to separate ultrafine particles of calcite and quartz using a polymeric flocculant. Higher separation efficiency has been achieved in the flotation separation of calcite from wolframite using a chelating collector with neutral oil compared to sodium oleate by Dianzuo and Yuehua. The dependence of calcite: scheelite ratio on the selectivity of separation has been stressed by Beyzavi. Adsorption studies on calcium carbonate by Ivanova and Shehukin using single and mixed surfactants have indicated that while individual cationic surfactants can be adsorbed on the negatively charged surface of calcium carbonate, no significant adsorption from mixed binary solutions could be detected. Oleoyl sarcosine has been found to enhance the flotation efficiency of scheelite, but had no effect on calcite flotation.

The efficiency of experimental investigations can be improved significantly by the use of experimental design and data analysis based on statistical principles. The common approach used in experimental research is to study a property of a system as a function of “one-variable-at-a-time”. Several authors have pointed out the inadequacy and deceptiveness of this method. Experimental programs using statistical designs offer an effective method to solve this problem. The program involves use of factorial design to study the effect of varying two or more factors simultaneously according to an ordered plan. The factorial experiments can determine the significance of each factor and interaction between various fac-

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tors. Statistical design of experiments as originated by Fisher and developed further by Box and Wilson have been found very helpful in industrial research. Optimization strategies adopted in flotation plants have been critically reviewed by Mular. The principles and techniques for the design and analysis of flotation experiments have been well brought out by Griffith.

In this investigation, a sample of limestone rejects from Bagalkot Cement Company has been subjected to flotation to reduce the magnesia content in order to obtain cement grade limestone concentrate. The optimum values for the important variables namely sodium oleate concentration, sodium silicate concentration and pH have been arrived at using statistically designed experiments.

The strategy adopted in this paper is based on well-established procedures followed by several workers.

**Experimental Procedure**

**Materials**

- **Limestone**—Limestone rejects having high magnesia content were obtained from Bagalkot mines. About 20 kg of the bulk sample of rejects was ground in a ball mill to 70% passing 200 mesh (75 μm) and stored in a polythene container.

- **Sodium oleate**—Technical grade sodium oleate from BDH was used as the collector in all the experiments.

- **Sodium silicate**—Sodium silicate with Na2O : SiO2 ratio of 1:3.5 from Riedel de Haenag was used as the depressant.

- **Reagents used for pH control**—KOH, HCl and for other analytical estimations were of Analar grade. All the reagent solutions were prepared using laboratory distilled water.

**Methods**

- **Flotation Tests**—Sodium oleate (collector) and sodium silicate (depressant) solutions of desired concentrations were freshly prepared and used in the flotation tests. In each experiment, 2 g of the sample was initially conditioned with the required quantity of the depressant for 10 min followed by addition of the collector and further conditioning for 10 min in a beaker after adjusting the pH to the desired value. The total volume of the slurry was fixed at 200 mL. The pulp was conditioned using a teflon coated magnetic stirrer and then transferred to a modified Hallimond tube flotation cell. Nitrogen gas of commercial purity was passed at a flow rate of 50 mL/min and the flotation was carried out for 2 min. The float and the sink fractions were separately collected, filtered, dried and weighed. The magnesium and calcium contents in the concentrate have been analysed and the % MgO and % CaO values have been arrived at.

**Chemical analyses**—The Mg and Ca contents in the float fraction of the limestone rejects were analysed using the Thermo-Jarrel Ash atomic absorption spectrophotometer (Video 11E) and the Jobin-Yvon (JY-24) ICP atomic emission spectrometer (Table 1). The calibration was carried out using spectroscopic pure Mg and Ca adopting standard procedures. The MgO and CaO values were calculated stoichiometrically.

**Results and Discussion**

Preliminary screening experiments were performed to establish a satisfactory test procedure and to obtain approximate magnitudes of the factor levels to be used in the initial factorial tests. The effects and mean squares were calculated using the Yates Algorithm method. The main factors and interactions which are significant based on F-test were ascertained. The limiting values of the three independent variables were thus calculated. In order to investigate the effects of various parameters such as pH, collector and depressant concentrations which were found to significantly affect the flotation process, a 3-factor orthogonal composite design based on the procedure described by Davies was used to optimize the process. The composite design and product data are given in Table 2.

A Doolittle solution was performed to generate regression equations (mathematical models) relating the various responses to different parameters affecting them. Analysis of variance for the composite design was then performed and the developed regression equation is given below.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Assay, %</th>
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<tr>
<td>CaO</td>
<td>30.4</td>
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<tr>
<td>MgO</td>
<td>6.5</td>
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<tr>
<td>SiO₂</td>
<td>22.1</td>
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<tr>
<td>Acid Insolubles</td>
<td>33.1</td>
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The variables were coded between +1.215 and -1.215 as indicated in Table 2. This equation was tested by comparing the lack of fit variance with the experimental error variance estimated by the duplicate tests. It was found that the model was statistically acceptable as attested to by the F-test and by the magnitude of the multiple correlation coefficient. The next step towards optimization is to generate response surface contours with respect to a two dimensional representation keeping the third variable at constant levels for the response studied, viz., %MgO in the concentrate. Values near the optimum levels could readily

Table 2—Composite design and product data

<table>
<thead>
<tr>
<th>Design Levels</th>
<th>Factor Levels</th>
<th>Responses</th>
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Factors
$X_1$ = Sodium silicate (mg/g), $X_2$ = Sodium oleate (M), $X_3$ = pH
Responses
$Y_1$ = %MgO in the concentrate, $Y_2$ = %CaO in the concentrate
Code $X_1$ = (Amount of sodium silicate-15)/10
$X_2$ = (Amount of sodium oleate-2.55 x $10^{-4}$)/2.45 x $10^{-4}$
$X_3$ = (pH-8.75)/2.75

Fig. 1—Response contours for sodium silicate concentration as a function of pH (sodium oleate: $2.55 \times 10^{-4}$M)
Fig. 2—Response contours for sodium silicate concentration as a function of pH (sodium oleate: $3.8 \times 10^{-4}$M)
be obtained from these figures. Since it is very difficult to solve the regression equation manually, a computer programme was developed for this purpose23. The response contours generated are plotted in Figs 1-6.

The response contours for sodium silicate concentration as a function of pH at a constant value of sodium oleate concentration \((2.55 \times 10^{-4} \text{ M})\) are shown in Fig. 1. The response contours are concave with respect to the pH axis up to a sodium silicate concentration of about 10 mg/g and at high concentrations of sodium silicate, viz., around 22 mg/g, the contours become convex to the pH axis. Under these conditions, the % MgO in the concentrate decreases from about 8 to approximately 6 and beyond 25 mg/g sodium silicate concentration there is further increase in the % MgO content. A careful scrutiny of Fig. 1 indicates that the regimes for lower MgO content lie in two distinct ranges, i.e., below pH 6 and above pH 11 and in the sodium silicate concentration range of about 12-22 mg/g. It is noteworthy that the % MgO content in the limestone concentrate could be reduced below 5% in actual experiments (Table 2) as per the model predictions. However, pH values below 5 were not studied due to problems associated with dissolution of the limestone and hence the alkaline range was preferred.

The response contours obtained using a constant sodium oleate concentration of \(\approx 3.8 \times 10^{-4} \text{ M}\) for sodium silicate as a function of pH are depicted in Fig. 2. By and large, the trends obtained in Fig. 1 are observed in this case also, i.e., the % MgO content in the limestone concentrate are lowered beyond pH 11 and in the range of pH

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**Fig. 3—Response contours for sodium oleate concentration as a function of pH (sodium silicate: 10 mg/g)**

**Fig. 4—Response contours for sodium oleate concentration as a function of pH (sodium silicate: 22 mg/g)**

**Fig. 5—Response contours for sodium silicate concentration as a function of sodium oleate concentration (pH: 11.5)**

**Fig. 6—Response contours for sodium silicate concentration as a function of sodium oleate concentration (pH: 12.3)**
5-6 using a sodium silicate concentration between 10 to 25 mg/g as the case may be.

A comparison of Figs 1 and 2 indicates that with increase in sodium oleate concentration, further reduction in the % MgO content could be achieved in the alkaline pH range (> pH 11). It was found that increase in the sodium oleate concentration beyond $5.0 \times 10^{-4}$ M did not decrease the % MgO content in the concentrate (Table 2).

The surface contours for the pH versus sodium oleate at constant sodium silicate concentration of 10 mg/g are portrayed in Fig. 3. At a lower concentration of sodium oleate, namely $0.1 \times 10^{-4}$ M, as the pH is increased from about 6 to 11, there is a tendency for the MgO content in the concentrate to increase from about 5 to 7%. On the other hand, at higher sodium oleate concentration, i.e., beyond $3.78 \times 10^{-4}$ M, in the pH range of 6-11, the MgO content decreases from about 5.5% to below 4%. The useful regimes are apparently closer to pH 11 and higher sodium oleate concentrations, i.e., $> 3.78 \times 10^{-4}$ M with sodium silicate concentration of 10 mg/g.

The contours generated using sodium silicate concentration of 22 mg/g for pH as a function of sodium silicate are depicted in Fig. 4. These contours are akin to those reported in Fig. 3 and it is evident that at pH values > 11 and higher sodium oleate concentration ($\approx 4 \times 10^{-4}$ M) the MgO content in the concentrate could be reduced below 4.5%.

Fig. 5 shows the response contours for sodium oleate as a function of sodium silicate at a constant pH of 11.5. It is apparent that with increase in sodium silicate concentration, the % MgO content can be reduced for a given concentration of sodium oleate. It is evident that the optimum regime for lower MgO content lies at a sodium silicate concentration of about 20-25 mg/g and sodium oleate concentration of about $4.0-5.0 \times 10^{-4}$ M.

Response contours at pH 12.3 for sodium oleate as a function of sodium silicate are shown in Fig. 6. The shape of the contours are similar to those obtained in Fig. 5. However, at this pH value (12.3) the MgO content could be reduced to below 3% at a sodium silicate concentration of about 20-25 mg/g and a sodium oleate concentration of about $4.5 - 5.0 \times 10^{-4}$ M. It is thus advantageous to carry out the flotation at alkaline pH values and higher sodium silicate and sodium oleate concentrations.

From the results highlighted in Figs 1-6 and Table 2, the optimum values for the parameters studied in order to obtain limestone concentrate with low MgO content can be summarized as follows:

- sodium silicate concentration: 20-25 mg/g
- sodium oleate concentration: $4.5-5.0 \times 10^{-4}$ M
- pH: 11.5-12.5

**Conclusion**

The significant parameters that affect the MgO content in the concentrate are (a) the amount of sodium silicate, (b) the amount of sodium oleate and (c) pH. It was found that the optimum sodium silicate concentration for lower MgO content in the concentrate was 20-25 mg/g whereas the optimum sodium oleate concentration for an acceptable MgO content in the concentrate was $4.5 - 5.0 \times 10^{-4}$ M. The optimum pH was found to be 11.5-12.5 for achieving lower MgO content in the concentrate.

Limestone rejects could be beneficiated to produce the concentrate with acceptable MgO content to meet the specifications for cement manufacture.

**Acknowledgement**

The authors are grateful to the Indian Bureau of Mines, (IBM), Bangalore for supplying the sample of limestone rejects. Stimulating discussions with Mr K T Louis and Mr A B K Prasad of IBM, are gratefully acknowledged. Mr T Seshacharyulu, Department of Metallurgy, Indian Institute of Science is thanked for the computational assistance rendered.

**References**