A method of separation of lime from high or low calcium oxide containing limestone

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A method of separation of lime (CaO) from limestone either by treating with water or by treating with concentrated hydrochloric acid at pH 9-10. This method will help to enrich the concentration of various other elements associated with limestone and pure CaO may be used for industrial purpose.

The interest in limestone is due to its accelerated and diverse uses. It is the one mineral for which over 2000 uses are known. In nature limestone is widely scattered either as simple mineral calcite or associated with other minerals. There are several books which cover the details of commercial grading, exploitation and industrial utilisation of limestone. Literature survey revealed that in chemical industry, limestone is mostly used in the form of lime (CaO), a major intermediary product of calcined limestone.

Reported chemical analysis of limestone and dolomitised limestone shows that limestone is generally associated with SiO₂, MgO, Al₂O₃, MnO₂, TiO₂, Fe₂O₃, Na₂O, K₂O, etc. as impurities and often display considerable variability. Uses of limestone/lime depend upon its purity. But comparatively little work has been reported on the separation of lime in pure form from limestone. Some of earlier reports describe the preparation of calcium compound from limestone viz. (i) CaO prepared by calcining limestone. (ii) CaCl₂ is prepared by the reaction of hydrochloric acid and limestone, where FeCl₃ obtained as impurity which is removed by chemical treatment. (iii) From dolomite, calcium is removed by ion-exchange after calcination. (iv) Mg(OH)₂ precipitated from MgCl₂ or seawater by milk of lime. In most of the cases high calcium oxide containing limestone is used because of its availability. So the demand for low calcium oxide containing limestone is comparatively less at present, but may be very feasible and attractive resource. The present work describes a method of separation of lime from the associated oxide containing limestone.

Experimental Procedure

Limestone samples (seven numbers) were selected having different chemical composition. The sample is used in powder form and dried in an air-oven at 105°C. The percentage of various oxides present in limestone, burned limestone and oxides remain after separation of CaO from burned limestone was analysed by standard methods. A solution was made by taking a known weight (5g) of sample, digested with hydrochloric acid (1:1) and few drops of concentrated nitric acid, baked (120°C), dissolved in dilute hydrochloric acid and filter. Silica was determined by hydrofluorization of the insoluble left and percentage of silica was calculated as,

\[
\text{SiO}_2 \% = \{w_2 - w_3\} \times 100 / w_1
\]

where \(w_2\) = weight (g) of platinum crucible before hydrofluorization.

\(w_3\) = weight (g) of platinum crucible after hydrofluorization with the residue.

\(w_1\) = weight (g) of the sample.

The residue was fused after hydrofluorization with fusion mixture and extracted with hydrochloric acid (1:1). Extract was added to the filtrate obtained before and made up to the known volume (100 mL). From an aliquot (25 mL) of the main solution, mixed oxide (R₂O₃) was precipitated by ammonia solution in the presence of ammonium chloride, filtered, ignited and weight as R₂O₃ is calculated as follows.

\[
\text{R}_2\text{O}_3 \% = \{w_2 - w_3\} \times 100 / w_1
\]

where \(w_2\) = weight (g) of the silica crucible with R₂O₃ after ignition.
After removing mixed oxides from an aliquot (10 mL) of the main solution as mentioned earlier and titrated against standard ethylenediaminetetra-acetic acid disodium salt for percentage of total (CaO + MgO) in the presence of buffer solution and percentage of MgO was calculated as

$$\text{MgO} \% = \frac{(\text{total} \%- \text{CaO} \%)/1.4}{\text{A}}$$

Analytical and experimental data are presented as Tables 1 and 2. An electric muffle furnace (-1200°C max) and electronic balance, Shimadzu, AEU220 were used for carrying out the experiment. pH were measured by Whatman pH paper. pH range was 1-14. All other chemicals were of analytical grade.

**Calcination of limestone**

(i) Dry powder limestone sample (-10g) was taken in platinum dish and burnt in electric muffle furnace at 925°C for 2h. The platinum dish and content was cooled in a desiccator and weighed. The operation was repeated till attained constant weight and percentage of various oxides were calculated.

(ii) The burnt limestone thus obtained in operation A is quantitatively transferred in 2000 mL glass beaker and 1000mL distilled water is added. The solution is allowed to stand for an hour and the pH (-14) of the solution is measured by pH paper. The whole mixture is stirred and kept overnight. The pH of the mother liquor is measured and filtered by Whatman filter paper No. 40. The residue is washed three times by distilled water, dried in air and then transferred to platinum crucible which is burned in electric muffle furnace at 925°C for 2h. The platinum crucible is cooled and weighed. The operation is repeated till constant weight is obtained.
SARKER: SEPARATION OF LIME FROM CALCIUM OXIDE CONTAINING LIMESTONE

Table 2—Experimental data

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<tr>
<th></th>
<th>CaO remaining</th>
<th>CaO obtained</th>
<th>pH</th>
<th>CaO separated</th>
<th>Purity of CaO</th>
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<td>1</td>
<td>b 66.95</td>
<td>44.90</td>
<td>10-12</td>
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<td></td>
<td>c 42.12(22.37)*</td>
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<td>2</td>
<td>b 49.70</td>
<td>35.60</td>
<td>10-12</td>
<td>71.75</td>
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<tr>
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<td>c 23.07(13.99)*</td>
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<tr>
<td>3</td>
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<td>74.51</td>
<td>10-12</td>
<td>84.53</td>
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<tr>
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<td>c 59.98(14.45)*</td>
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<td>4</td>
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<td>88.14</td>
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<td>10-12</td>
<td>71.15</td>
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</tr>
<tr>
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<td>d 21.76(13.79)*</td>
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<tr>
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<td>89.40</td>
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<td>97.60</td>
<td>99.90</td>
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<td>d 31.54(2.60)*</td>
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CaO remaining:— Percentage of CaO remaining in residual oxide of experimental procedure (A), (B), (D), represented by the data b, c & d. of Table 1.

(*)*:— equivalent amount of CaO present in b = CaO % in c or d X SiO₂ in b/SiO₂ % of c or d, value of CaO % in c or d & SiO₂ % in b, c or d are taken from Table 1.

CaO obtained:— percentage of CaO obtained from the filtrate of experimental procedure (C) & (E), by oxalate method data in parentheses is required = CaO % in b-equivalent CaO in b.

The residue thus remaining in platinum crucible is transferred to 2000 mL beaker and whole operation was repeated as above till the pH of the solution reaches 10-12. The percentage of various oxides remaining in the residue is calculated after final operation.

(iii) The filtrate and washing of every operation B is collected after neutralisation by HCl and concentrated (~200 mL) on a hot plate. After concentration CaO is precipitated from the concentrated solution by standard oxalate method⁹. The oxalate thus obtained is then burned in platinum crucible at 925°C for 2 h in electric muffle furnace. The crucible is cooled and weighed. The operation is repeated till the weight becomes constant and the percentage of calcium oxide is calculated.

(iv) Burned limestone obtained in operation A is quantitatively transferred in 400 mL beaker and 200mL distilled water added. The solution is allowed to stand for an hour and the pH (~14) is measured by pH paper. The whole mixture is stirred by glass rod and concentrated HCl is added drop-wise with stirring till the pH reaches 9-10. The solution is kept overnight, the pH of the solution is measured and then filtered by filter paper No. 40. The residue is washed by cold distilled water, dried in air and transferred in
platinum crucible which is burned in electric muffle furnace at 925°C for 2 h and then cooled and weighed. The operation is repeated till constant weight is obtained. The percentage of various oxides remaining in residue are calculated.

(v) CaO, is obtained from the filtrate and washing obtained in operation D by procedure similar to operation C. CaO can be obtained from the filtrate by treating it first with supersaturated aqueous solution of Na₂CO₃ and then ignited at 925°C for 2 h in electric muffle furnace.

Results and Discussion
The percentage of various oxides present in the limestone have been assigned by chemical analysis of limestone, burned limestone and the oxides remaining after separation of CaO from burned limestone and are presented in the Tables 1 and 2 respectively. For the present experiment, seven limestone samples having CaO ranging from 53.7% to 29.58% and MgO from 0.69 to 15.71% were chosen.

Lime was produced by burning limestone at well defined temperature ranging between 900 and 1100°C. In the present experiment limestone was burned at 925°C for 2 h in electric muffle furnace, when along with major intermediatory product CaO, a host of other product viz. SiO₂, R₂O₃, (Fe₂O₃ + Al₂O₃ etc), MgO were obtained. When limestone is heated at particular temperature, they decomposed evolving CO₂ and leaving behind the corresponding oxides. In case of dolomitic limestone, magnesium carbonate decompose first, followed by calcium carbonate e.g.

$$\text{CaCO}_3 \cdot \text{MgCO}_3 \xrightarrow{600-800^\circ\text{C}} \text{MgO} + \text{CaCO}_3 + \text{CO}_2$$

$$\text{MgO} + \text{CaCO}_3 \xrightarrow{850^\circ\text{C}} \text{MgO} + \text{CaO} + \text{CO}_2$$

Burned limestone thus obtained when treated with water lime is hydrolysed with the evolution of heat and the hydroxide was dissolved sparingly. (1.29g of CaO/L at 15°C or 0.67 g at 80°C). Lime is not attacked by CO₂ at ordinary temperature but it reacts with Ca(OH)₂. The burned MgO is relatively inert, it slowly combines with water and forms hydroxide, which is insoluble in water (1x10⁻⁴g/L at 20°C). Other oxides are insoluble or sparingly soluble in water. Solubility product of Ca(OH)₂, Mg(OH)₂, Fe(OH)₃, and Al(OH)₃ are 4x10⁻⁶, 1x10⁻¹¹, 4x10⁻⁵⁰, 1x10⁻³³ respectively at 25°C. More solubility of Ca(OH)₂ than that of Mg(OH)₂ favoured the separation of lime from burned limestone by treating with water. When burned lime is treated with water, the pH of the solution reaches 14. This may be due to the presence of Ca(OH)₂, which is a strong base, sparingly soluble in water resulting in the increased number of (OH)⁻ in the solution compared to Mg(OH)₂, a weak base. These may further reduce the solubility of Mg(OH)₂ in the solution resulting in separation of above 99% pure CaO, as shown in Table 2. Literature survey further reveal that Mg(OH)₂ can be precipitated from a solution of MgCl₂ or sea water by adding milk of lime. The reduction of CaO%, increase the other components in burned limestone. The change in pH from 14 to 10-12 may be due to step wise separation of CaO in the form of Ca(OH)₂ by repeated operation of the same sample. In the present experiment 4 to 6 operations were carried out to reach the pH 10-12, depending upon the percentage of CaO in burned limestone. By this process 67 to 95% CaO separated from burned limestone. Less yield also may be due to the fact that Ca(OH)₂ solution on exposure to air becomes covered with a crust of calcium carbonate which on breaking settle at the bottom with other components and another layer of crust reappears at the surface. The yield can be increased from 85 to 95% by using concentrated hydrochloric acid. In this experiment burned limestone is treated with water and then the pH of the mixture is brought down to 9-10 by dropwise addition of concentrated hydrochloric acid, which react with soluble hydroxide resulting in more and more CaO passing into the solution as Ca(OH)₂ and due to the continuous neutralisation by hydrochloric acid, pH of the solution comes down thereby increasing the yield of CaO%. CaO is separated from filtrate by standard oxalate method or by carbonate method and there after by burning the oxalate or carbonate.

This observation is drawn from chemical analysis results shown in Tables 1 and 2. By lowering the pH below 9-10 impurities like MgO, Fe₂O₃, Al₂O₃, etc may come along with the product thereby lowering the purity of the yield.

This method may be used to enrich the concentration of various other elements associated with burned limestone as shown in Table 1. The enrichment thus obtained may help to a great extent in analytical work on one hand and may be used as an attractive source of some elements on the other. The pure CaO/Cal₂O₃ may be utilised for industrial purposes.

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References