CHAPTER 8

INDUSTRIAL USE

8.1. Introduction:

Carbonate rocks are raw materials indispensable to industrial development. The uses to which carbonate rocks and minerals can be put is a function of their physical and/or chemical properties. A myriad of uses exist for carbonate minerals and rocks or products derived from them. Indeed, industrial development of a region is often reflected in the number of tonnes of carbonate raw material produced and sold each year. The major consumer of limestone is the cement industry. The second largest consumers are iron and steel, ferro alloys, foundry plants and secondary steel manufactures where it is used as a fluxing agent. It also finds use as fluxing agent in the smelting of copper and lead. Other important consumers are calcium carbide and the glass industries. In the form of lime it is utilised and consumed in a number of industries. Lime is chiefly used in the refining of sugar, paper making, cooking of rags, bleaching of textiles and leather manufacture. Lime is an important constituent of mortar and white wash in the building industry. High grade lime (fat lime) is used for the manufacture of chemicals like bleaching powder, calcium carbide, soda ash, hydrated lime, calcium chloride and slaked lime. Since the beginning of 1964 limestone is being utilised in India for the manufacture of nitro-lime fertilizer.
8.2. Cement:

Limestone is the principal raw material for the manufacture of cement. The most common variety 'Portland cement' is a mixture of calcined calcareous and argillaceous material forming a complex composition consisting of tricalcium aluminate, tetra-calcium alumina ferrite, dicalcium silicate, and tetracalcium ortho-silicate. The proportion of the last two constituents in the Portland cement varies from 70-76 percent. The proportion of the first constituent, tricalcium aluminate is about 10 percent, the balance being the second constituent.

Portland cement of standard specification contains 60-70 percent CaO, 20-25 percent SiO₂, 5-12 percent Al₂O₃ + Fe₂O₃, and MgO always below 5 percent. There is no hard and fast specification for limestone for the manufacture of cement. The cement manufacturers generally prefer limestone containing about 45 percent CaO. The presence of impurities like SiO₂, Al₂O₃ and Fe₂O₃ are desired. The only stipulation is that MgO should not be more than 3 percent in the total calcareous and argillaceous mixture. A maximum of 5 percent is tolerated. These impurities help to a great extent in reducing the requirements of argillaceous clay. In the preparation of raw materials for cement manufacture, three important moduli are taken into consideration: (i) hydraulic modulus, (ii) silica modulus, and (iii) iron modulus. In addition, the limestone
saturation factor (LSF) is also regarded as an important consideration for the final product—cement. The values of these moduli are calculated as follows:

Hydraulic modulus:

\[
\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \text{ should be between 1.7 and 2.4}
\]

Silica modulus:

\[
\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \text{ should be between 1.2 and 4.0}
\]

Iron modulus:

\[
\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \text{ should not be less than 0.66}
\]

LSF:

\[
\frac{\text{CaO} - 0.7 \text{SO}_3}{2.8 \text{SiO}_2 + 1.2 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3} \text{ should be between 0.66 and 1.02}
\]

As a thumb rule, for the manufacture of cement, the raw materials should consist of three parts of limestone and one part of clay including laterite, bauxite and other additives. This proportion may vary depending upon the chemical composition of the raw material, but the composition of the mixture should be such that it should contain 75 CaCO$_3$; 20 percent Al$_2$O$_3$ +
$SiO_2 + Fe_2O_3$ and 5 percent other ingredient including MgO and alkalies. The proportion of $Al_2O_3 + Fe_2O_3 : SiO_2$ should be 1 : 2.5. A slight excess proportion of $SiO_2$ is allowed.

Any deficiency in the moduli is made up by the addition of suitable corrective material such as clay, iron ore, laterite, bauxite, shale etc. Sulphur, magnesia and phosphorus are regarded as most undesirable impurities in the cement raw material. Sulphur in the form of sulphide or sulphate in the mixture leads to formation of calcium sulpho-aluminate, which is highly expensive like periclase (MgO). The presence of phosphorus and $P_2O_5$ more than 1 percent considerably slows down the setting time of portland cement. It may take several days to set (Sinha, 1932).

In the manufacturing process of cement gypsum is added to clinker. Gypsum controls the setting time. It prevents rapid setting which avoids wrinkles and cracks.

Physical characteristics:

For use in certain industries, there are constraints on the physical characteristics in addition to the chemical constituents of limestone.

(i) For the cement industry the limestone should possess the following physical properties:

(a) It should possess a fair degree of uniformity and homogeneity. It should be soft and fine grained.
In general the limestone of the present area found to be soft and fine grained. In the investigated area the percentage of CaO varies from 41.12 to 50.32 and from 34.09 to 50.82 in the upper and lower bands of limestone respectively in block no. I.

In block no. II the CaO percentage varies from 44.11 to 46.65 in the upper band limestone and in the lower band limestone it varies from 41.79 to 51.35.

The percentage variation of CaO is from 30.52 to 46.98 in upper band limestone and from 41.26 to 47.75 in lower band limestone in block no. III.

The average percentage of CaO in the limestone is 45.23.

The hydraulic modulus (\(P_{\text{H}}\)) is found to be 3.69 and 4.64 in the upper and lower bands of limestone in block no. I. The average hydraulic modulus in the limestone of block no. I is 4.16.

The silica modulus (\(M_{\text{S}}\)) is 0.79 and 0.45 both in the upper and lower bands of limestone of block no. I. The average silica modulus is 0.62 in the limestone of block no. I. The iron modulus (\(M_{\text{I}}\)) for upper band limestone is 1.81 and for lower band limestone is 1.86 in block no. I. The average iron modulus is 1.83 in the limestone of block no. I.
The limestone saturation factor (LSF) is found to be 1.97 and 2.03 both in the upper and lower bands of limestone of block no. I. The average limestone saturation factor is 2.4 in the limestone of block no. I.

The hydraulic modulus ($M_H$) is 4.33 and 7.09 in the upper and lower bands of limestone of block no. II. The average hydraulic modulus in the limestone of block no. II is 5.71.

The silica modulus ($M_S$) is 0.88 and 0.93 in the upper and lower bands of limestone of block no. II. The average silica modulus in the limestone of block no. II is 0.91.

The iron modulus for upper band limestone is 0.80 and for lower band limestone is 0.65 in block no. II. The average iron modulus of the limestone of block no. II is 0.73.

The limestone saturation factor (LSF) for upper band limestone is 2.34 and for lower band limestone is 3.92 in block no. II. The average limestone saturation factor in the limestone of block no. II is 3.13 in the limestone of block no. II.

The hydraulic modulus ($M_H$) is found to be 3.99 and 5.93 in the upper and lower bands of limestone in block no. III. The average hydraulic modulus in the limestone of block no. III is 4.96.

The silica modulus for upper and lower band limestone of block no. III is found to be 0.93 and 0.77. The average silica modulus in the limestone of block III is 0.85.
The iron modulus \( (M_i) \) is 0.98 and 1.01 in the upper and lower bands of limestone of block no. III. The average iron modulus in the limestone of block no. III is 0.99.

The limestone saturation factor \( (LSF) \) is found to be 2.90 and 3.22 both in the upper and lower bands of limestone of block no. III. The average limestone saturation factor is 3.06 in the limestone of block no. III. The values of different moduli are given in a tabular form (Table 7).

The values of different moduli of the limestone of the studied area (Table 3) when compared with the stipulated values it is found that the values of hydraulic modulus and the limestone saturation factor are higher. The values of iron modulus are found to be within the stipulated range. The values of silica modulus is found to be slightly lower than the stipulated value. But the values of the different moduli may be corrected by adding suitable corrective material like clay, sand, laterite etc.

When compared the values of the different moduli of the limestone of the present area are found to more or less similar to the values of different moduli of the limestone used by cement industry in India. The analyses of some limestones used by cement industry in India are given in Table 8 for comparison.
Table 7 The value of different moduli in the limestone of the investigated area.

<table>
<thead>
<tr>
<th>Bands</th>
<th>Hydraulic modulus ($M_H$)</th>
<th>Silica modulus ($M_S$)</th>
<th>Iron modulus ($M_I$)</th>
<th>Limestone saturation factor (LSF)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Block no. I</td>
<td>Block no. II</td>
<td>Block no. III</td>
<td></td>
</tr>
<tr>
<td>Upper band limestone</td>
<td>3.69</td>
<td>4.33</td>
<td>3.99</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>0.88</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>1.81</td>
<td>0.80</td>
<td>0.98</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>1.97</td>
<td>2.34</td>
<td>2.90</td>
<td>3.22</td>
</tr>
<tr>
<td>Lower band limestone</td>
<td>4.64</td>
<td>7.09</td>
<td>5.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>0.93</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>0.65</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.83</td>
<td>3.92</td>
<td>5.22</td>
<td></td>
</tr>
</tbody>
</table>
Table 8. Analysis of some limestone used by cement industry in India (Sinha, 1982).

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Hydraulic modulus</th>
<th>Silica modulus</th>
<th>Iron modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.8</td>
<td>13.4</td>
<td>1.95</td>
<td>0.75</td>
<td>1.30</td>
<td>2.86</td>
<td>4.96</td>
<td>2.6</td>
</tr>
<tr>
<td>2</td>
<td>44-46</td>
<td>7-9</td>
<td>2-2.3</td>
<td>1-1.3</td>
<td>2-3.5</td>
<td>4.21</td>
<td>2.3-2.5</td>
<td>0.8-0.6</td>
</tr>
<tr>
<td>3</td>
<td>45.6</td>
<td>12</td>
<td>2</td>
<td>0.8</td>
<td>3.8</td>
<td>3.33</td>
<td>4.29</td>
<td>2.50</td>
</tr>
<tr>
<td>4</td>
<td>42-43</td>
<td>13-14</td>
<td>3-4</td>
<td>1.5-2</td>
<td>3-5</td>
<td>2.1-2.3</td>
<td>2.4-2.8</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>49-54</td>
<td>1-3</td>
<td>0.3-1.8</td>
<td>0.5-1</td>
<td>1-4</td>
<td>9.27</td>
<td>1-1.2</td>
<td>0.6-1.8</td>
</tr>
</tbody>
</table>
From the study of the results of chemical analyses and calculated moduli and the physical characteristics of the limestone of the studied area it is found that the limestone of investigated area is suitable for the manufacture of ordinary portland cement (OPC), the most common cement for normal construction purposes.

Permission for establishing a mini cement plant in the investigated area has already been given to a private party by the government of Meghalaya to this effect.

8.3. Chemical industry:

Lime to be used for the chemical purpose must be of high purity magnesia, alumina, silica, iron oxide, sulphur and phosphorus are objectionable impurities, as they adversely affect either the quality of the product or the smooth and economical operation of the furnace. The material should be in the form of lumps free from dirt and added impurities.

Indian Standard 3204-1965 specification for limestone for chemical industries.

Grades: The limestone shall be of the following four grades depending upon its suitability for various uses on the basis of its chemical properties.

Grade 1 - Suitable for making bleaching powder, bleach liquor, textiles, varnishes, pulp and paper.
Grade 2 - Suitable for the manufacture of soda ash by the solvay process and caustic soda by the lime-soda process.

Grade 3 - Suitable for the manufacture of calcium carbide.

Grade 4 - Suitable for sugar manufacture.

Requirement of limestone for use in chemical industries

(I.B.M.'s publication 1982).

<table>
<thead>
<tr>
<th>S1. No.</th>
<th>Characteristic</th>
<th>Requirements for grade 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on ignition percent by weight, max.</td>
<td>46.0</td>
<td>46.0</td>
<td>46.0</td>
<td>44.00</td>
<td></td>
</tr>
<tr>
<td>Silica (as SiO₂), percent by weight, max.</td>
<td>0.75</td>
<td>-</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Iron (as Fe₂O₃) percent by weight, max.</td>
<td>0.15</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Calcium (as CaO) percent by weight, min.</td>
<td>54.0</td>
<td>53.0</td>
<td>54.0</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>Magnesium (as MgO), percent by weight, max.</td>
<td>2.0</td>
<td>1.0</td>
<td>0.8</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Manganese (as MnO₃), percent by weight, max.</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide (as CO₂), percent by weight, min.</td>
<td>42.0</td>
<td>42.0</td>
<td>42.0</td>
<td>41.0</td>
<td></td>
</tr>
<tr>
<td>Sulphur, percent by weight, max.</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Phosphorus, percent by weight, max.</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Glass industry also requires limestone of high purity and inter alia it should have nonvolatile matter insoluble in HCl (max.) 2.0 percent and moisture (max,) 3.0 percent.

Specifications are as follows (as per CSIR)

CaCO$_3$ (min)- 94.5 percent
CaCO$_3$ + MgCO$_3$ - 97.5 percent
Fe$_2$O$_3$ (max) - 0.20 percent

Total non-volatile matter insoluble in HCl (max) 2.0 percent, moisture (max) 3.0 percent.

The percentages of silica, iron, alumina (Table 7) in the limestone of the investigated area are found to be higher than the stipulated values of different grades of limestone used in the chemical industries. The limestone of the present area is found to be unsuitable for any chemical industry.
The limestone of the present area is found to be not suitable for use in the glass industry as it contains higher percentages of iron (Fe₂O₃) and its CaCO₃ (87.3) and CaCO₃ + MgCO₃ (90.3) percentages are found to be much below the stipulated values.

8.5. Reserve:

The reserve of limestone in Darrang-Iranj (block no. I) area is estimated at 12 million tonnes while in Jadigithim Pathargithim area (block nos. II and III) it comes to 54.5 million tonnes. The total reserve of limestone in the investigated area is 66.5 million tonnes.