CHAPTER X

USES OF LIMESTONE

10.1 INTRODUCTION

The limestone and lime are prehistoric and among the oldest materials used by mankind. Limestone uses are an outgrowth of the Stone age in which primitive man utilized limestone and other forms of rock.

Limestone is a general term embracing carbonate rocks or fossils; it is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and alumina. In contrast, lime which is invariably derived from limestone is always a calcined or burned form of limestone popularly known as "quicklime" or "hydrated lime". The calcination process expels the carbon dioxide from the stone forming calcium oxide (quicklime) and when water is added—calcium hydroxide (hydrated or slaked lime) is created.

The carbonate rocks are raw materials indispensable to different industrial fields. The uses to which carbonate rocks and minerals can be put is a function of their physical and chemical properties. The limestones are directly and indirectly used in industrial fields. But it depends upon the quality of the limestone.

10.2 SPECIFICATIONS

There are so many highly individualized specifications even for
the same ostensible use. Some of the physical and chemical characteristics demanded in these exacting specifications are:

(i) Good white colour—high degree of reflectivity
(ii) Minute particle size—10 micron to submicron sizes
(iii) Special particle size gradations in micron sizes
(iv) Particle shape and high specific surface area
(v) Freedom from grit—namely material retained on a No. 325 sieve
(vi) Plasticity and rheological properties
(vii) High absorption of oil, ink, and color pigments
(viii) Low to zero chemical activity (alkalinity)
(ix) Freedom from impurities—strict tolerances on SiO₂, Al₂O₃, FeO, Fe₂O₃, CaSO₄, H₂O, heat and ignition loss and even copper and manganese are cited.
(x) Bulk density
(xi) Specific gravity

10.3 PHYSICAL USES

The physical uses of limestone categorized below (Boynton, 1966):

(i) Raw material
(ii) Refractory
(iii) Foundry
(iv) Filler
(v) Fertilizer/Agriculture
(vi) Non-ferrous metals
(vii) Filter aid
10.3.1 RAW MATERIAL

The limestone directly used as a raw material in the cement industry.

10.3.1(A) CEMENT INDUSTRY

The 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, tetracalcium alumina ferrite, dicalcium silicate and tetracalcium ortho-silicate. The proportion of the last two constituents in the ordinary portland cement varies from 70-76 percent. The proportion of the first constituent - tricalcium aluminate is about 10 percent and the balance being the second constituent.

Ordinary portland cement of standard specification contains 60-70 percent CaO, 20-25 percent SiO₂, 5-12 percent Al₂O₃ with Fe₂O₃ and MgO always below 5 percent. There is no hard and fast specification for limestone for the manufacture of cement. The cement manufacturers normally prefer limestone containing about 45 percent CaO. The impurities like SiO₂, Al₂O₃ and Fe₂O₃ are desired. The only stipulation is about 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 normal 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 of cement. The values of these moduli are calculated as follows:

(i) Hydraulic Modulus (MH):\[
\frac{CaO + MgO}{SiO_2 + Al_2O_3 + Fe_2O_3} \text{ should be between 1.7 and 2.4}
\]

(ii) Silica Modulus (MS):\[
\frac{SiO_2}{Al_2O_3 + Fe_2O_3} \text{ should be between 1.2 and 4.0}
\]

(iii) Iron Modulus (MI):\[
\frac{Al_2O_3}{Fe_2O_3} \text{ should not be less than 0.66}
\]

(iv) Lime Saturation Factor (LSF):\[
\frac{CaO - 0.7 SO_3}{2.8 SiO_2 + 1.2 Al_2O_3 + 0.65 Fe_2O_3} \text{ should be between 0.66 and 1.2}
\]
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 mixtures should be such that it should contain 75 percent CaCO\(_3\), 20 percent Al\(_2\)O\(_3\), SiO\(_2\) with Fe\(_2\)O\(_3\) and 5 percent other ingredients including MgO and alkalies. The proportion of Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) : 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 sulpha-alminate which is highly expensive like portlandite (MgO). The presence of phosphorus and P\(_2\)O\(_5\) more than 1 percent considerably slows down the setting time of portland cement. It may take several days to set (Sinha, 1982).

Gypsum is added to clinker in the manufacturing of cement. It controls the setting time of cement. It prevents rapid setting which avoids wrinkles and cracks. In cement industry—limestone should possess a fair degree of uniformity and homogeneity. It also should be soft and fine grained. The typical chemical composition of ordinary portland cement was proposed by American Society of Testing Materials (ASTM) in 1963 as shown in Table 22.
The lower horizon of limestone of the investigated area is found to be soft and fine grained. The CaO varies from 46.19 to 51.62, 28.31 to 50.61 and 47.91 to 51.23 percent in Garampani, Umrangchu and Newumrangchu area respectively. The CaO in borehole samples of Umrangchu and Newumrangchu area ranges from 38.21 to 49.55 and 30.16 to 51.40 percent respectively.

The average percentage of CaO in the present limestone is 45.98 in surface and 42.33 in borehole samples.

The hydraulic modulus (MH) is found to be 2.78 in Garampani, 2.23 in Umrangchu and 3.06 in Newumrangchu limestone.

The silica modulus (MS) is 1.56 in Garampani, 0.45 in Umrangchu and 1.01 in Newumrangchu limestone.

The iron modulus (MI) is 0.66, 0.34 and 1.07 in Garampani, Umrangchu and Newumrangchu limestone respectively.

The lime saturation factor (LSF) is found to be 2.50 in Garampani, 2.31 in Umrangchu and 3.78 in Newumrangchu area respectively.

The values of different moduli of limestone when compared with the stipulated values—it is observed that the values of hydraulic modulus and lime saturation factor are slightly higher (Table 23). The values of iron modulus and silica modulus are found to be within the stipulated range. Of course, the values of different moduli may be corrected by adding suitable corrective material like clay, sand, laterite, etc.
When compared the values of different moduli of the limestone of the investigated area are found to more or less similar to the values of different moduli of limestones used by cement industry in India as shown in Table 24.

From the study of chemical analyses and calculated moduli of limestones of the present area are found to be suitable for the manufacture of ordinary portland cement for normal construction.

Sinha (1982) suggested that raw materials are used for making portland cement by blending various combinations of materials as shown in Table 26.

10.3.1(B) OTHER INDUSTRIES

Limestone is used in the iron and steel industry as a fluxing agent. Besides the limestones are used in refractory, foundry, filler, fertilizer, non-ferrous metals industries. But the limestone of the investigated area could not be used due to presence of more impurities in these industries.

10.4 CHEMICAL USES

The limestone indirectly used in chemical process industries including metallurgical and portland cement plants. Limestone is employed directly in high temperature thermal processes - smelting, sintering, calcining, etc.- embracing numerous industries in which the limestone is converted or calcined into lime before the desired chemical
reaction can be effected. It is the most basic economical source of lime (calcium oxide). When limestone thermally converted to lime (1000 to 2000°C) the resulting calcium and magnesium oxides are highly reactive.

10.4.1 CHEMICAL PRODUCTS

Lime is used for the chemical products but it must be of high purity, magnesia, alumina, silica, iron, 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 impurities.

Indian Standard Institute (ISI) recommended 3204-1965 specification of limestone for the chemical industries.

The limestone classified into four grades for various uses depending upon its chemical properties (Boynton, 1966).

Grade I : Suitable for making bleaching powder, bleach liquor, textiles, varnishes, pulp and paper.

Grade II : Suitable for the manufacture of soda ash by the solvay process and caustic soda by the lime soda process.

Grade III : Suitable for the manufacture of calcium carbide.

Grade IV : Suitable for sugar manufacture

The general requirements of limestone for use in chemical industries (ISM, 1982) is shown in Table 23.
10.4.1(A) GLASS INDUSTRY

The limestone requires in glass industry of high purity and inter alia it should have non-volatile matter insoluble in HCl (max.) 2.0 percent and moisture (max.) 3.0 percent.

CSIR specifications are as follows:

CaCO₃ (min.) - 94.5 percent
CaCO₃ + MgCO₃ - 97.5 percent
Fe₂O₃ (max.) - 0.20 percent

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

The limestone of the investigated area is found to be not suitable for use in the glass industry as it contains higher amount of Fe₂O₃, CaCO₃ and CaCO₃ + MgCO₃.

The percentages of silica, iron, alumina in the limestones of the study area are found to be higher than the stipulated values of different grades of limestone used in the chemical process industries.

10.4.1(B) LIME INDUSTRY

This is the third largest chemical use of limestone. Theoretically only 1.65 to 1.90 tons of limestone depending upon its purity and type are necessary to make one ton of quicklime. The industry has standardized its calculation on a reasonable approximate factor of 2.
tonnes of stone for 1 ton of lime. Actually some plants depending upon the physical and chemical characteristics of the stone will be slightly above or below this average factor.

This limestone of the investigated area is not suitable for this industry. The high grade quality of limestone required for this industry.

10.5 SPECIFICATIONS OF LIME MATERIALS

The following are current ASTM lime materials specifications for specific uses (Boynton, 1966):

C 258-52 Quicklime for Calcium Carbide Manufacture
C 5-59 Quicklime for structural purposes
C 46-62 Quicklime and Limestone for Sulfite Pulp Manufacture
C 259-52 Hydrated Lime for Grease Manufacture
C 207-49 Hydrated Lime for Masonry Purposes
C 141-61 Hydraulic Hydrated Lime for Structural purposes
C 6-49 Normal Finishing Hydrated Lime
C 206-49 Special Finishing Hydrated Lime
C 433-63 Quicklime and Hydrated Lime for Hypochlorite Bleach Manufacture
C 415-63 Quicklime and Hydrated Lime for Sand-Lime Products
C 49-57 Quicklime and Hydrated Lime for Silica Brick Manufacture
C 53-63 Quicklime and Hydrated Lime for Water Treatment
C 379-561 Fly Ash for use as a pozzolanic Material with Lime
C 432-59T Pozzolans for Use with Lime
No ASTM specifications exist on some of the most important enduses, like steel fluxing, road stabilization, sulfate pulp manufacture, leather tanning, etc. largely because there is so much variance in individual requirements.

10.6 MISCELLANEOUS USES

The lime is used for alkali and allied chemicals, soda ash, caustic soda, paints, rubber, cosmetics, ceramic, pulp and paper industries. It is required for electric products, ingredient in oil well drilling muds, rayon, rice milling, silicones and water treatment. But the lime of the study area could not be used in these industries or chemicals.

10.7 RESERVE

The reserve of limestone in Garampani area is estimated at 20.6 million tones of cement grade and 10.1 million tones of high grade while in Umrangchu area— it comes to 6.6 million tones of cement and high grade limestone. The reserve is measured in Newumrangchu area at 275 million tones of cement grade and 4.56 million tones of high grade limestone.

10.8 DISCUSSION

From the above study, it can be inferred that the Sylhet limestone of the investigated area is suitable for manufacture of ordinary portland cement for normal construction.
Table 23. Characteristic requirements for grade of limestone

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on Ignition (LOI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>percent by weight max.</td>
<td>46.0</td>
<td>46.0</td>
<td>46.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Silica (SiO₂) percent by weight max.</td>
<td>0.75</td>
<td>-</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Iron (Fe₂O₃) percent by weight max.</td>
<td>0.15</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>Calcium (CaO) percent by weight min.</td>
<td>54.0</td>
<td>53.0</td>
<td>54.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Magnesium (MgO) percent by weight max.</td>
<td>2.0</td>
<td>1.0</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Manganese (Mn₂O₃) percent by weight max.</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂) percent weight min.</td>
<td>42.0</td>
<td>42.0</td>
<td>42.0</td>
<td>41.0</td>
</tr>
<tr>
<td>Sulphur percent by weight max.</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Phosphorus percent by weight max.</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Alumina (Al₂O₃) and Ferric Oxide (Fe₂O₃) together percent by weight max.</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Silica (SiO₂), Alumina (Al₂O₃) and Ferric Oxide (Fe₂O₃) together percent by weight max.</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 24. Typical chemical composition of ordinary Portland cement (ASTM, 1963)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxide composition</th>
<th>Stoichiometric composition</th>
<th>Approx. content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>(CaO)$_3$SiO$_2$</td>
<td>Ca$_3$SiO$_5$</td>
<td>45</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>(CaO)$_2$SiO$_2$</td>
<td>Ca$_2$SiO$_4$</td>
<td>27</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>(CaO)$_3$Al$_2$O$_3$</td>
<td>Ca$_3$Al$_2$O$_6$</td>
<td>11</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>(CaO)$_4$(Al$_2$O$_3$)</td>
<td>Ca$_4$Al$_2$Fe$<em>2$O$</em>{10}$</td>
<td>8</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO$_4$</td>
<td>CaSO$_4$</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Table 25. The value of different moduli in the limestones of the investigated area (Surface & Borehole samples)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Area</th>
<th>Hydraulic Modulus (MH)</th>
<th>Silica Modulus (MS)</th>
<th>Iron Modulus (MI)</th>
<th>Limestone saturation Factor (LSF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Garampani</td>
<td>2.78</td>
<td>1.56</td>
<td>0.66</td>
<td>2.50</td>
</tr>
<tr>
<td>2</td>
<td>Umrangchu</td>
<td>2.23</td>
<td>0.45</td>
<td>0.34</td>
<td>2.31</td>
</tr>
<tr>
<td>3</td>
<td>Newumrangchu</td>
<td>3.06</td>
<td>1.01</td>
<td>1.07</td>
<td>3.78</td>
</tr>
</tbody>
</table>
Table 26. Analyses of some limestones 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>4.9</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>0.5-0.6</td>
</tr>
<tr>
<td>3</td>
<td>45.6</td>
<td>12.0</td>
<td>2.0</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>3-4.0</td>
<td>1.5-2</td>
<td>3-5.0</td>
<td>2.1-2.3</td>
<td>2.4-2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>1-3.0</td>
<td>1-3.0</td>
<td>0.3-1.8</td>
<td>0.5-1</td>
<td>9.27</td>
<td>1-1.2</td>
<td>1-1.2</td>
<td>0.6-1.8</td>
</tr>
</tbody>
</table>
Table 27. Raw materials used in making portland cement by blending various combinations of materials (Sinha, 1982)

<table>
<thead>
<tr>
<th>Calcareous</th>
<th>Argillaceous</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Cement rock&quot;</td>
<td>Clay</td>
</tr>
<tr>
<td>Limestone</td>
<td>Aluminium ore refuse</td>
</tr>
<tr>
<td>Marl</td>
<td>Staurolite</td>
</tr>
<tr>
<td>Alkali waste</td>
<td>Diaspore clay</td>
</tr>
<tr>
<td>Blast-furnace and other slages</td>
<td>Granodiorite</td>
</tr>
<tr>
<td>Carbide sludge</td>
<td>Kaolin</td>
</tr>
<tr>
<td>Siliceous</td>
<td>Ferriferous</td>
</tr>
<tr>
<td>Sand</td>
<td>Iron ore</td>
</tr>
<tr>
<td>Traprock</td>
<td>Iron pyrite</td>
</tr>
<tr>
<td>Calcium silicate wastes</td>
<td>Iron calcine</td>
</tr>
<tr>
<td></td>
<td>Iron sinters</td>
</tr>
<tr>
<td></td>
<td>Iron dust</td>
</tr>
<tr>
<td></td>
<td>Iron oxide</td>
</tr>
<tr>
<td>Sulfurous</td>
<td>Blast-furnace flue dust</td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
</tr>
<tr>
<td>Iron pyrite</td>
<td></td>
</tr>
</tbody>
</table>

Iron calcine: This material is derived from iron ore and is used as a source of iron in the production of cement. It is a common component in the blends used to make portland cement, providing a significant source of iron oxide, which is essential for the strength and durability of the final product. The use of iron calcine helps to ensure the cement's resistance to chemical attack and degradation over time.