CHAPTER III

L I M E S T O N E S - T H E I R U S E S

GENERAL:

Limestone finds wide utilization in various industries, (Fig.7) and in this chapter the various uses to which the rock is put have been briefly discussed.

The limestone consumption for various trades in India, and comparative figures for somewhat similar purposes in U.S.A., are given below:

TABLE NO.2

U.S.A.		INDIA	
	Percent		Percent
Building	20.7	Cement	24.4
Metallurgy	20.4	Iron & Steel	47.3
Refractory lime (Dead-burnt dolomite)	17.8	Ferro-Manganese	0.6

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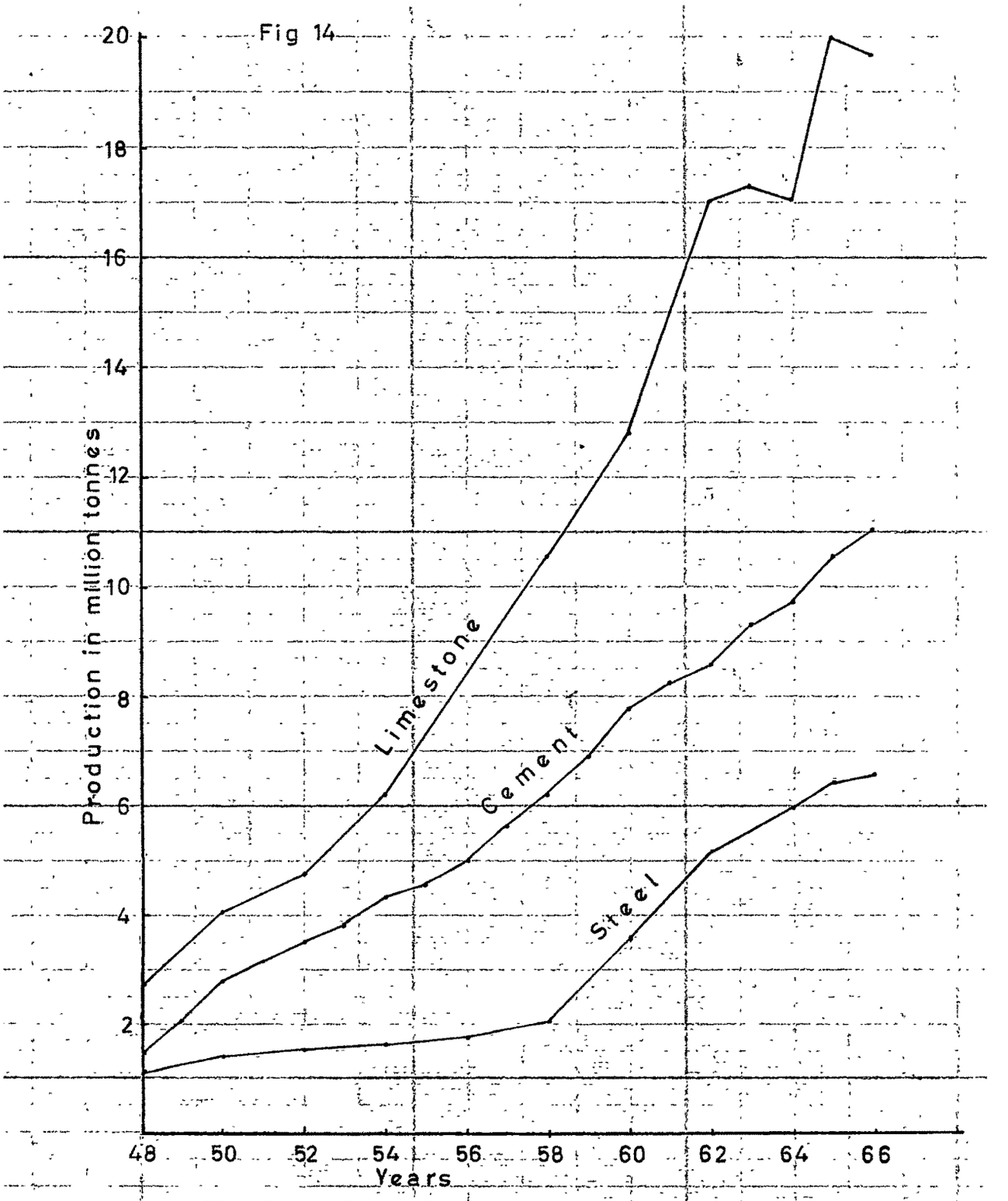
U.S.A.		INDIA	
	Percent		Percent
Paper mills	11.6	Paper	9.2
Agriculture	7.5	Fertilizer (Calcium ammonium nitrate)	3.4
Water purification	5.4	Bleaching powder.	0.2
Glass works	3.4	Calcium Carbide	1.0
Tanning	1.5	Caustic soda and soda ash	8.4
Sugar refining	0.4	Sugar	5.5
Others	11.3		
	100.00		100.00

From the above table, it will be seen that about 25 percent of limestone is utilized for the manufacture of cement, while about 50 percent goes for the metallurgical purposes. Fig.14.

The annual limestone production in India is about 20 m.tonnes; out of which Gujarat's contribution is only 8.60 percent. Its position among other States

Fig 14



GRAPH SHOWING THE PRODUCTION OF LIMESTONE, CEMENT AND STEEL IN INDIA DURING THE PERIOD 1948-1966.

in this respect can be seen from the following table:

TABLE NO.3.

	State/Union Territory	Percentage of all India Total
1.	Madhya Pradesh	18.84
2.	Madras ...	13.08
3.	Orissa ...	12.33
4.	Bihar ...	11.28
5.	Andhra Pradesh..	9.70
6.	Rajasthan ...	9.15
7.	Gujarat ...	8.60
8.	Mysore ...	7.89
9.	Uttar Pradesh..	5.38
10.	Punjab ...	2.70
11.	Maharashtra ...	0.64
12.	Assam ...	0.24
13.	West Bengal ...	0.13
14.	Himachal Pradesh	0.10
15.	Jammu & Kashmir	0.04
	Total ..	100.00

(Based on Monthly bulletins of Mineral Statistics - Indian Bureau of Mines)

SPECIFICATIONS:

The specifications of limestones for various industries and products are given in the following paragraphs.

(A) Metallurgical Industry:

For metallurgical purposes only high grade limestone is suitable. It is mainly used as flux in metallurgical furnaces, particularly those of ferrous and non-ferrous metals.

High grade magnesia limestones are suitable for some metallurgical purposes. In the manufacture of ferrosilicon and ferro-manganese, dolomitic limestone finds extensive use as flux, because it carries away very little silica or manganese into the slag. In addition to its utilisation as flux, dead burnt dolomite is extensively used as refractory material in metallurgical blast furnaces.

(B) Chemical Industry:

Limestone and dolomite are extensively used in the following chemical industries:

TABLE NO.4

(All figures are of percentage)

Use of limestone	Composition		Other conditions
Flux	$CaCO_3$	Not less than 90	(a) Fine grained, compact and non-fritting on burning, and should withstand crushing under load in furnace.
	$SiO_2 + Al_2O_3$ (Insolubles)	Not more than 6 (upto 11.5% tolerance permitted in blast furnace)	
	SiO_2	Not more than 5	(b) Slightly crystalline varieties tolerable provided calcite crystals are small and not easily crushable.
	MgO	Not more than 4	
	P & S	As low as possible.	(c) 2 to 4 inch in size.

TABLE NO.4 (Contd..)

LIMESTONE USED IN INDIAN STEEL PLANTS.

	TISCO	Rourkela		Bhilai		Durgapur		Mysore Iron.	
		S.M.S.	B.F.	S.M.S.	B.F.	S.M.S.	B.F.	S.M.S.	B.F.
CaO	48 (Min.)	46 (Min.)	46	46 (Min.)	45-50	52-55	47 (Min.)	47.5	44.5 (Min.)
MgO	3.5 (Max.)			3 (Max.)	4-5 (Max.)	1.5 (Max)	3 (Max.)	3.5	3.5
SiO_2	B.F. 6-7(Max) / O.H. 4	11.5 (Max.)		4 (Max.)		2.5 (Max.)	11.5 (Max.)	4.4	10.0
Al_2O_3						0.8 (Max.)			
Fe_2O_3						1.0 (Max)	1.0(Max)	1.0	1.0
Acid Insol		4.5 (Max.)		4 (Max.)	10(Max.)				
Size		+ 80 to 180 mm					125 to 150 mm		

Note: S.M.S. - Steel Melting Shop. B.F.- Blast Furnace. O.H. - Open Hearth

TISCO - Tata Iron and Steel Co.

Manufacture of calcium carbide, cyanamide, ammonia, potassium and sodium chemicals, calcium carbonate, baking powder, pigment and varnish constituents, silicon, bricks, insecticides, fungicides and disinfectants, magnesia, paints, gelatine, glue, grease, bleaching liquids and powders, soap and fat, rubber, and polishers and buffers. In addition, limestone is widely used in refining of salt, sugar, fuel gas and petroleum.

The specifications of limestones or lime required for important industrial uses are given in the table No.5.

TABLE NO.5

Specifications of limestones for industrial uses.

Use of limestone	Composition	Other conditions	Remarks
1	2	3	4
(i) Calcium carbide	CaO 54 ($CaCO_3$ 95) SiO_2 1 - 3 P 0.01 - 0.06 MgO 1 Objectionable impurities MgO, Al_2O_3, SiO_2, Fe_2O_3, S, P & alkalies.	Dense, non-fritting, fine grained, so will not crumble during manufacturing process.	1.6 tonnes of limestone is required for 1 tonne of calcium carbide.

Use of limestone	Composition	Other conditions	Remarks
1	2	3	4
(ii) Soda ash. Ammonia-Soda process	$CaCO_3$ 90-99(Leblanc process-96) R_2O_3+SiO_2 0.3 MgO Upto 6.0(some prefer $MgCO_3$ 0.6)	2 to 10 cm size.	1.6 tonnes of limestone is required for 1 tonne of soda ash.
(iii) Caustic soda	CaO 85 MgO Not more than 3	Lime free of clayey matter.	1.6 tonnes of limestone for 1 tonne of caustic soda.
(iv) Bleaching	$CaCO_3$ More than 96 MgO Less than 1.5 SiO_2 2 R_2O_3 1.1 (Fe_2O_3 upto 0.5%) Objectionable: Mn, Fe.	a) Fine powder on slaking. b) On slaking 3 times volume after 20-30 minutes. c) Porous texture of lime to permit penetration of gases.	0.9 tonne of limestone is required for 1 tonne of bleaching powder.

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Use of lime-stone	Composition	Other conditions	Remarks
1	2	3	4
(v) Quick lime for water treat-ment.	(ASTM) SiO_2 (Max) 2 R_2O_3 (Max) 1(Fe_2O_3 upto 0.5%) CaO (Min) 92 MgO (Max) 1.75 S (Max) 0.2 P (Max) 0.02 Loss Ign. 4		(a) Addition of lime precipitates $CaCO_3$ formed from bicarbonate. (b) Lime + soda ash removes permanent hardness by Mg and Ca sulphates.
(vi) Ceramics.	$CaCO_3$ + $MgCO_3$ Not less than 97 Fe_2O_3 Upto 0.3 SiO_2 2. SO_3 0.1 In grade 1 stone $MgCO_3$ upto 1 In grade 2 stone $MgCO_3$ upto 8		(a) In the form of limestone, marble, chalk or whiting. (b) Powder mixed with water should pass through 140 and 200 mesh with 1, and 2% residue respectively
(vii) Textile Industry.	CaO 94 MgO(Max) 3 R_2O_3 2 SiO_2 and Insol. matter(Max) 2 CO_2(Max)- at places of manufacture- 3 in hydrated lime, 5 in quick lime; at other places - 5 in hydrated lime 7 in quick lime	Lime with readily soluble iron and considerable amount of non-hydrated magnesia should not be used.	

Use of lime-stone	Composition	Other conditions	Remarks
1	2	3	4
(viii) Silica-Brick.	ASTM Specification 49-57 In quick lime or slaked lime -		(a) 99% lime to pass through No.30 (590 micron), and 95% through No.200 (74 micron) sieve.
	CaO Not less than 90		
	MgO 4.5	) Volatile basis (Max)	
	R_2O_3 1.5	)	
	SiO_2 +Insolubles 3		
	CO_2 -If sampled elsewhere 10		
	If sampled at the site of manufacture 5		(b) Quick slaking and fineness of the hydrated product are preferred.

(ix) Glass Industry.

(a) Glass	ASTM Specifications Class I		Class II		Class III	
	Max.	Min.	Max.	Min.	Max.	Min.
CaO + MgO	94	-	-	91	-	83
Fe_2O_3	0.2	-	1	-	1	-
Al_2O_3	33	-	5	-	5	-
$SO_3+P_2O_5$	1	-	1	-	1	-
SiO_2	4	-	9	-	17	-

20 to 25 tonnes of limestone is required for 100 tonnes of glass.

All products must pass through No. 16 sieve (aperture 1.10 mm) unless otherwise specified.

(b) Colourless glass	B.S.S.		
	CaO	55.2 ($CaCO_3$: 98.5)	
	Fe_2O_3	0.035	Acid solubles including silica.
	Organic matter	0.1	
	Mn, Pb, S, and P Oxides	0.1	
	Moisture upto 2%		
(c) Optical glass	CaO + MgO	99%	
	Fe_2O_3	In traces.	
	P & S	Upto 0.2	
(d) Bottle and Sheet glass	CaO + MgO(Min)	89	To be ground between 20 and 100 mesh.
	Fe_2O_3 upto ...	0.5	
	SiO_2+ Al_2O_3 upto	15	
	S & P "	1	
	Organic matter "	0.3	
(x) Bichromate.	$CaCO_3$	95	1 Tonne limestone for 1 tonne of bichromate.

(xi)	Sugar Industry.	Insol. in HCl	not exceeding	1	Lime used for precipitating impurities from juices, or for precipitating sugar from impurities as in Steffen process. Lime forms insoluble salts with sugar which are split by CO_2 made at factories by burning limestone.
		SiO_2	" "	1	
		R_2O_3	" "	1	
		SO_3	" "	0.1	
		Alkalies	" "	0.5	
		$CaCO_3$	not less than	95	

United States Bureau specifications

		Sugar soluble lime (Min.)	MgO (Max.)	Loss Ign. (Max.)
(a)	Limestone for Steffen processes	90	3	-
(b)	Limestone for other processes	85	3	-
(c)	Quick lime for Steffen processes	90	3	2
(d)	Quick lime for other processes	85	3	5
(e)	Lime powder	90	3	2
(f)	Hydrated lime	86	3	-

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(xii)	Fertilizer Calcium Ammonium nitrate.	It is produced by diluting ammonium nitrate with limestone, forming nitrolimestone granules. Limestone acts only as carrier.	
		CaO 42.14 ($CaCO_3$ 84) Min	
		SiO_2 5 (12.05 - in Hindustan Steel Ltd. Fertilizer Plant) Max.	
		MgO 4.92 Max.	
		Al_2O_3 3.13 Max.	
		Fe_2O_3 0.19 Max.	
(xiii)	Leather Tanning.	High calcium limestone. Except for Morocco leather, MgO is objectionable. Iron and metallic impurities should be low.	Lime acts as a dehairer, and retards putrefaction.
(xiv)	Paints, distempers, and allied materials.	Lime should be perfectly white with low density and very fine powder. For varnish - hydrated lime with high CaO and low MgO. Material should not darken varnish.	Precipitated chalk or $CaCO_3$ often used.
(xv)	Rubber, soap and allied industries.	Chalk, whiting or recovered $CaCO_3$	90% should pass through a 300 mesh sieve.

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(xvi)	Disinfectant.	Lime is a coagulating agent. Used in disinfectants, insecticides, fangicides, etc.
	Sewage treatment.	For sewage and trade waste purification - stone should withstand weathering and need be free from clay, pyrites, shale, chert and ochre.

(c) Cement and Lime:

(1) Cement:

Limestone is the principal raw material for the manufacture of Portland cement. The chemical composition of limestone governs its suitability for the manufacture of cement. Types of cement and specifications are discussed in detail in the chapter No. VI.

Large quantities of limestone are required to feed cement factories. 1.6 tonnes of limestone of suitable grade is required to produce one tonne of cement.

(2) Lime:

This is obtained by calcining limestones, kankar, shells, etc., and its use depends upon its purity; important uses are already mentioned above. Its use as a building material, is discussed in the chapter No. VII.

Hydraulic lime has a property of setting and hardening under water on account of the chemical combination of CaO, Al_2O_3, Fe_2O_3 and SiO_2 in the required proportion. Roughly one tonne of lime is produced from two tonnes of limestone allowing under and overburning and other losses. On adding water for quick or slaked lime, the weight increases by one-third.

(D) Building Stone:

Limestones are known to be very good building stones. On account of their softness, they are amenable to cutting and carvings.

Marbles are known world over for their beauty as ornamental stones. Those are used for the decorative purposes in buildings, sculptures and in carvings. Marbles of various varieties are used lavishly in the construction of temples and palaces etc.

(E) Agriculture:

Limestone powder, lime, marl, and oyster shells are used as soil - conditioners.

Lime helps in (i) correcting soil acidity, (ii) granulating heavy clayey soils, and (iii) providing

plant food. It also promotes digestion of other fertilizers, decay of vegetable matter to form nitrates, and counteracts some soil poisons.

(F) Paper Industry:

Limestone or lime is used in the liquor for cooking rags in wood pulp manufacture, and finely divided white lime is used as filler. The limestone for this purpose should not have less than 95% $CaCO_3$, and MgO should preferably be less than 3% as it is detrimental to sizing of the paper in its later stages. Agrillaceous limestones are not suited.

Roughly one tonne of lime is needed for every three and half tonnes of paper made.

(G) Mineral Wool:

Impure limestone with a wide range of chemical composition of mixes can be used for this purpose. The rock should be hard and massive and should possess sufficient strength to support the weight of the charge without packing and blocking the escape of gases released from the furnaces. This is used for insulation in place of asbestos.

(H) Lithographic Printing:

Fine grained and compact limestone of uniform texture is used in lithographic printing. The stone should be free from calcareous crystallisation, vermiculations, siliceous specks, and conspicuous veins. The fracture should have glassy surface free from grains, and should be generally conchoidal. SiO_2 + Al_2O_3 + Fe_2O_3 should not exceed 5 percent. Nitric acid should completely dissolve the stone leaving only an insignificant residue.

GRADING OF LIMESTONES:

As can be seen from specifications of limestones required for various industries, the sole basis for it is their chemical composition. Thus, the author has worked out the following classification of limestones into various grades, on the basis of their chemical composition, so that it becomes convenient to assign and recommend the different limestones for suitable utilisation.

TABLE NO.6

(Percent)

Grade	$CaCO_3$	CaO content	Uses
1	2	3	4
Grade-Super	Above 95	Above 53	Manufacture of calcium carbide, bleaching powder, ceramics, colourless and optical glass, paints. In paper, rubber, soap and allied industries.
Grade-I	95 to 90	53 to 51	Flux grade for soda ash, in silica bricks, glass Class I & II, leather tanning, paints, textile industry, etc.
Grade-II	90 to 95	51 to 48	For caustic soda, in sugar industry, glass industry-Class III, bottle and sheet glass, disinfectant, etc.
Grade-III	85 to 78	48 to 44	Portland cement, and other equivalent- cements, such as pozzolana cement, white cement, Portland blast-furnace slag cement, etc. Also manufacture of fat lime, and fertilizer-calcium ammonium-nitrate.
Grade-IV	78 to 60	44 to 35	Building limes - best quality (even for hydraulic structures) etc.

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Grade	$CaCO_3$	CaO content	Uses
1	2	3	4
Grade-V	60 to 50	35 to 30	Hydraulic limes of good quality for normal building works, rock and mineral wool.
Grade-VI	Below 50	40 to 30	Useful as good building material similar to other rocks, viz. building stones, crushed aggregates, road metal, boundary stones, etc.

Higher MgO or Fe_2O_3 is indicated in bracket when present, as Grade-I (Mg), or Grade-I (Fe), etc.; $MgCO_3$ is included for grading purpose, when MgO is present in more quantity.