CHAPTER VI

LIMESTONE FOR CEMENT

One of the principal uses of limestone is in the manufacture of Portland Cement. With the rapid industrial and irrigation development in Gujarat region, the demand for cement is going up every day. Neither the existing cement factories in Gujarat nor those in the neighbouring States, can meet the requirement of the State, and there is a good scope for establishing new cement factories in the Gujarat State.

The existing position of the cement industry in the Gujarat State is given in the table No.53 below:

TABLE NO.53

Sr. No.	Company	Location	Capacity tonnes/year (in lakhs)	Type of cement produced.
1.	Associated Cement Companies Ltd.	Sevalia	2.30	Portland cement.
2.	"	Porbandar	0.43	White cement.
3.	"	"	2.30	Portland cement.
4.	"	Dwarka	2.24	Portland cement.
5.	Saurashtra Cement and Chemicals Ltd.	Ranavav (Porbandar)	4.60	Portland cement. Pozzolana cement.
6.	Digvijaya Cement Co.Ltd.	Sikka	8.20	Portland cement.

PORTLAND CEMENT:

Portland cement is an active combination of silicates, aluminates, and ferroaluminates of lime, obtained by preliminary grinding and mixing of the requisite quantities of lime (usually in the form of carbonate), silica, iron oxide, and alumina, burning the mixture to incipient vitrifaction, and grinding the resulting clinker to a fine powder together with a small percentage of gypsum to adjust the setting time. It is popularly known that Joseph Aspidin of Leeds, the inventor of the cement chose this name in 1824 from the similarity of the set cement to the colour of the Portland stone.

Portland cement was introduced in our country by British in the beginning of the century and a cement factory was started in 1904 at Madras. Since then, there is a rapid progress in the cement industry, and at present there are 55 cement factories spread all over India.

Types of cement:

American Society of Testing Material recognize following five major types of Portland cement:

TABLE NO.54.

Type	Designated as	Remarks
I	Standard Portland Cement	Used for the general purpose.
II	Modified Cement, or Moderately sulphate-resisting, or Moderately low heat.	Used for highway pavement construction, Dams, etc.
III	High early strength (H.E.S.) or quick-hardening cement.	Ground considerably finer.
IV	Low-Heat cement	Used in mass concrete construction (e.g. Boulder Dam).
V	Extreme-sulphate resistant cement	Used in works of ports and harbours.

The range in chemical analysis and compound compositions of present day Portland cements are given in the table No.55.

TABLE NO.55

Range in chemical composition of present day

Portland Cements

Percent

Constituents	Type I Standard		Type II Moderate Heat		Type III H.E.S.		Type IV Low Heat		Type V Sulphate Res.
	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Ave.
CaO	66-62	64	65-62	63	67-63	65	65-68	60.5	64
SiO_2	23-19	21	24-20	22	22-18	20	26-22	24	26
Al_2O_3	8-5	6.5	6-4	5	7-4	5.5	6-3	5	2.5
Fe_2O_3	4-2	2.5	6-3	4	4-2	3	6-2	4.5	1.5
MgO	4-1	2.5	4-2	3	4-0	2.3	4-1	3	2.5
SO_3	2.5-1	2.1	2-1	1.5	3-2	2.5	2-1	1.7	2
Loss-Ignition	2-0.6	1.3	2-1	1.1	2-0.8	1.5	2-1	1.1	1.3
Insoluble residue	0.08-0.01	0.02	0.05-0.01	0.02	0.07-0.01	0.02	0.03-0.01	0.02	0.02
Compound Composition									
C_3S (Tricalcium Silicate)		48		43		57		20	39
C_2S (Dicalcium Silicate)		27		30		20		52	33
C_3A (Tricalcium aluminate)		12		7.5		11		6	4.5
C_4AF (Tetracalcium aluminoferrite)		8		12		7		14	16

Tricalcium silicate has all the essential properties of Portland cement. It undergoes an initial and final setting within few hours after gauging. Dicalcium silicate exhibits no definite setting time and the gauged mass sets only slowly over a period of some days, and dicalcium silicate neither sets nor hardens when mixed with water.

TABLE NO.56

- Portland Cement specifications -
Chemical requirements (ASTM-C-150)

Percent

	Type I	Type II	Type III	Type IV	Type V
Si_2O, Min.	-	21.0	-	-	-
Al_2O_3, Max.	-	6.0	-	-	6.0
Fe_2O_3	-	6.0	-	6.5	6.0
MgO, Max	5.0	5.0	5.0	5.0	4.0
SO_3, Max	2.0	2.0	2.0	2.0	2.0
Loss Ign. Max	3.0	3.0	3.0	3.0	3.0
3 $CaO.SiO_2$ Max.	-	50	-	35	50
2 $CaO.SiO_2$ Min	-	-	-	40	-
3 $CaO.Al_2O_3$ Max.	-	8	15	7	5

The low alkali cement is specified in localities where highly reactive siliceous aggregates occur. Indian cements are normally low alkali cements. The use of air-entraining agent is also encouraged for the great improvement in workability, durability, and salt resistance of concrete; it is used in works of Bhakra, Koyna, Hirakud, and other dams in India. Other cements are described later.

Raw Materials:

The limestone forms the principal raw material for making Portland cement. The range in analysis of raw mix for various types of cements is as follows:

TABLE NO.57

Percent

Constituents	Type I Standard		Type II Moderate Heat		Type III H.E.S.		Type IV Low Heat		Type V Sulphate Res.
	Range	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Ave.
SiO_2	15-12	14.1	15.5-13	14.7	14-11.5	13.7	17-14	16.3	12.4
Al_2O_3	5-3	4.2	4-2.5	3.2	5-3	3.6	4-2	3.3	1.6
Fe_2O_3	2.5-1.3	1.6	4-2	2.6	2.5-1.3	2	4-1.3	3	1.0
$CaCO_3$	77-73	75.8	76-73	74.7	78-74	77.3	76-68	72.5	76.0
$MgCO_3$	5.5-3	3.5	5.5-2.8	4.2	5.5-1	3	5.5-3	4.2	3.5
Alkalies	0.5-1	0.9	0.5-1	0.6	0.5-1	0.4	0.5-1	0.7	0.5

In most of the cases the raw mix of the desired composition is attained by mixing calcareous and argillaceous material in required proportions. It is essential that the variation in the chemical composition of the mixture be confined within narrow limits, as small variations in the ratios of the principal components of the mixture may be sufficient to alter the properties of the cement. A variation of only 0.5 percent in $CaCO_3$ content also affects the tensile strength of the cement. Other things being equal, high lime content increases the strength and low lime content reduces it.

<u>Process of cement manufacture</u>:

There are two types of processes of manufacturing cement, viz. (a) wet process, and (b) dry process. The choice of process depends mainly on the characteristics of the limestones available.

(a) <u>Wet process</u>: This is a more common process and it is applicable mainly, to soft materials, generally containing high percentage of moisture. The water content of the slurries of limestone and shale increases as much as 35 to 40 percent while in those of limestone and clay will be about 55 percent. The blending of material with high moisture is more easily accomplished by wet process. Wet process assures thorough blending, uniformity of kiln feed and better quality of clinker. A unique feature of the wet process is its suitability for the application of floatation to remove undesirable or unwanted constituents in the raw materials, thus making possible utilisation of raw material sources which otherwise would be useless.

(b) Dry Process: If limestones are suited to adopt dry process, this is economical as the consumption of fuel, which is otherwise required to drive out water from the slurry, is much low. Also in this process shorter kilns are required, which are less costly.

The water added in the raw mix is very little, and powders of materials are blended in dry state. This process is adopted in Gujarat by Saurashtra Cement & Chemical Ltd., Ranavav, and Associated Cement Companies Ltd. at Porbandar (new plant); Digvijay Cement Co.,Sikka are also examining the possibilities of its adoption.

Beneficiation of limestones:

Sometimes it is necessary to remove undesirable constituents in limestones by beneficiation. This is generally accomplished by floatation methods. This method is adopted on a limited scale by the Associated Cement Companies Ltd. in their Sevalia Cement Factory, as the limestones that they use have high silica content. Floatation have raises $CaCO_3$ content in limestones from 70 percent to as high as 85 percent. The process involves a combination of grinding, classification, floatation and thickening.

The typical frothers - mixtures of monohydrolic alcohols, dilute resinates, and cresylic acid - are satisfactory, and are introduced at various points in the circuit to maintain the desired froth balance. A total of 0.0416 of alcohol frother per ton of rock, suspended in about 4 tons of water, is sufficient for the entire circuit. The major portion of the water of the pulp is returned to the floatation circuit.

The usual collecting reagents or promoters for oxide ore minerals are oleic acid, fish oil, fatty acids and their emulsions and soaps, and refined talloel.

Dispersers (calcium lignin sulphonate with additions of sodium silicate, or soda ash) are used to reduce flocculation and colloidal filming and thereby improve both floatation and classification.

Depressors are used to decrease floatability of an undesired material; e.g. calcium lignin sulphonate for carbon.

Quality of cement:

The quality of cement depends on -

(a) chemical composition of clinker,

(b) fineness of the cement,

(c) gypsum content, and

(d) absence of deleterious substances.

The chemical analysis of a cement is not the only criterion of quality. The chief strength giving crystalline compound is 'alite' which is probably a solid solution of tri-calcium aluminate and tri-calcium silicate.

Different ratios given as under are used to check the raw mix and cement:

... contd..

(a) Silica ratio (silica modulus):

$$\frac{SiO_2}{Al_2O_3 + Fe_2O_3} \text{ or } \frac{SiO_2}{R_2O_3} = 1.7 \text{ to } 3.0$$

subject to $\frac{Al_2O_3}{Fe_2O_3}$ = 1. Ideal : 2.5 or reasonable one.

(b) $\frac{Al_2O_3}{Fe_2O_3}$ (Iron ratio) = 1.6 to 3.5 (It is preferable to use a lower ratio in this range than a higher one).

As per B.S.S.No.12 - 1940, a minimum permissible limit is 0.67 to this ratio, or $\frac{Fe_2O_3}{Al_2O_3}$ = 1.6

If both the above ratios are low, there is likelihood of encountering difficulty in burning due to excessive formation of molten glass.

(c) Hydraulic modulus:

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 2.2 \text{ or higher}$$ - High grade cement

(quantities in percent)

Less than 1.8 - not permitted.

(d) Hydraulic index: $\frac{(Si_2O + Al_2O_3)}{CaO + MgO} \times 100$

Commercial cement: 44 to 48.

OTHER CEMENTS

(1) Pozzolanic cements:

Pozzolans are siliceous and aluminous mineral substances which, though having no cementitious qualities themselves, react with lime in the presence of water at atmospheric temperatures to form cementitious compounds. These pozzolanic materials, natural or artificial, such as volcanic tuffs or ashes, surkhi (ground calcined clay), are mixed with Portland cement. This mixed variety of cement has following advantages:

1. Improved workability.
2. Lower heat of hydration and thermal shrinkage.
3. Increased water-tightness.
4. Improved resistance to attack by sulphate soils and waters, and sea water, particularly with type I cement.
5. Improved extensibility or resistance to cracking.
6. Improved plastic or stress adjusting characteristics.
7. Reduced alkali - aggregate reaction.
8. Lower susceptibility to dissolution and leaching.
9. Lower costs.

It is now a common practice to use pozzolans in the construction of major structures for hydropower, irrigation, etc.

Pozzolanic cements are either manufactured in the cement plants by grinding clinker and pozzolans, or by blending of the two materials at the site of construction in concrete mixers.

(2) Natural cement:

This is made by calcining finely pulverised argillaceous limestones at temperature high enough to drive off the carbonic acid.gas. It has properties of toughness, resistance to sulphate attack, and low heat of hydration. In addition to being used in masonry, it is used in blending with Portland cement. An idea of its composition will be had from the following:

TABLE NO.58

Percent

	Unburnt cement rock		Finished natural cement		
SiO_2	19.0	15.8	SiO_2	26.5	21.5
R_2O_3	6.0	4.4	Al_2O_3	3.2	4.2
$CaCO_3$	41.0	60.1	Fe_2O_3	5.4	1.7
$MgCO_3$	33.5	19.7	CaO	33.9	48.4
			MgO	21.4	12.5
			Loss Ign.	6.4	7.0

If hydrated during the manufacturing process or during the mortar mixing period, MgO formed serves to add to the plasticity and workability of the concrete or mortar mixture.

(3) Aluminous cement

(Calcium aluminate or high alumina cement):

The raw materials for this cement are low-grade bauxite and limestone. It needs to be burnt at high temperature like 1427°C (2600°F). It is sulphate resistant and attains high strength rapidly. The chemical analysis of this cement is as follows:

TABLE NO.59

Percent

	SiO_2	FeO	Fe_2O_3	Al_2O_3 + TiO_2	CaO	MgO	SO_3
Typical	9.6	5.6	4.9	41.1	36.8	0.97	0.18
Range	3-10	2-11	1-15	37-46	36-42	0.1-1.5	0-1.25

The 15-hour strength of aluminous cement is about the same as 24-hour strength of high early strength Portland cement.

This cement is used in the preparation of (1) refractory concrete, (2) heat-resistant concrete, (3) corrosion-resistant concrete, (4) Overnight concrete, and for (5) sealing of rock or concrete against internal water flow.

(4) Slag cement:

Slag cement is a mixture of blast furnace slag and lime ground together. It is known as Portland blast furnace slag cement when the slag is intimately interground with Portland cement clinker, and gypsum.

This type of cement is now being manufactured at Chaibasa in Bihar.

Granulated slag by itself is only feebly hydraulic when mixed with water. Hydrated lime is one of the best activators for the slag, and in the cement, it is derived from the hydration of the Portland cement constituent. The typical chemical analysis of these is as follows:

TABLE NO.60

Percent

	Portland cement Type I	Granulated slag	Portland Blast furnace - slag - cement
SiO_2	20.8	33.0	26.2
Al_2O_3	6.8	15.5	9.2
Fe_2O_3	4.0	0.5	3.4
CaO	64.8	47.0	56.4
MgO	2.0	2.0	2.4
S	-	1.8	0.7
SO_3	1.7	-	1.7

(5) Masonry cement:

In practice the name 'Masonry or mortar cement' is applied to undefined cement which can be used with fine mason's sand and water to produce a smooth, plastic, cohesive mortar for cementing together masonry units. However, in recent years, the name is restricted to specially formulated and interground mixtures of Portland cement clinker, limestone, gypsum and air-entraining agent.

(6) Oil well cement:

Special types of cements are needed for the cementation purpose at depths in oil fields. On account of high temperature, the setting time has to be controlled. The oil well cements are of two types:

(a) Regular or unretarded cements, and

(b) Slow-setting or retarded cements.

For retarding, in addition to or in place of gypsum, special retarders are interground or blended with Portland cement during manufacture.

Oil cement is used as a thin cement paste or slurry and pumped into place. Chemical analysis of this cement is as follows:

TABLE NO.61

Percent

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Insol.	Loss Ign.
1	20.78	4.38	7.98	63.83	0.80	1.37	0.50	0.36
2	24.50	3.80	6.00	62.00	0.80	1.50	1.00	0.40

	C_3S	C_2S	C_3A	C_4AF	C_2F	$CaSO_4$
1	55.5	17.8	0	21.0	1.9	2.5
2	27.8	49.3	0	18.2	0.1	2.5

The oil well cements are useful in

(1) Preventing water from infiltrating the oil-bearing sand, (2) preventing blow outs from high pressure oil and gas in the drilled formations, (3) protecting the oil well casing from disintegration by corrosive waters, and (4) helping support the oil well casing and thus minimize tension in the steel pipe.

(7) White Portland cement:

It is characterised by low iron and manganese oxide content. The manufacture of white cement limits Fe_2O_3 content to 0.5 percent maximum. The chemical analysis of typical white cement is as follows:

TABLE NO.62

Percent

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Mn_2O_3	SO_3	Loss Ign
24.2	4.2	0.39	65.8	1.1	0.02	1.5	2.4

C_3S	C_2S	C_2A	C_4AF
50.8	31.5	10.3	1.2

It is a quick setting cement.

GUJARAT'S POTENTIALITIES.

In our country, as mentioned earlier the iron and steel industry consumes nearly 50 percent of the total production of limestones, while roughly 25 percent is consumed by the cement industry. Other industries in the order of limestone consumption are paper, caustic soda and soda ash, sugar, fertilizer, etc.

The review indicates that the limestone wealth of Gujarat is sufficiently large enough to support more and more industries without any difficulty.

The Portland cement industry requires Grade-III limestone. About 16 tonnes of limestone are required to produce 10 tonnes of cement (1 m^3 limestone weighs roughly 2.5 tonnes, or 14 cft. weigh 1 tonne). Thus one sq.mile area in one foot thickness gives roughly 2 m.tonnes of limestone, or one km^2 in one metre thickness gives roughly 2.6 m.tonnes.

The minimum life of a cement factory of a capacity of 0.2 m.tonnes (smallest workable unit) should be 30 years from the economic point of view, thus the net quantity of limestone required for such a unit is 10 m. tonnes for 30 years, and estimated gross reserves should be 15 m.tonnes to cover uncertain factors.

Taking all these factors in view, the author recommends the following areas as prospective for establishing cement factories.

Mainland Gujarat

Banaskantha & Sabarkantha districts:

The band of Delhi limestone extending from Posina to Sandoshi is of Grade-III having 47 percent CaO.

This is a suitable limestone for the manufacture of Portland cement and reserves are over 71 m.tonnes upto 15 m. depth. A cement plant of 4 m.tonne-capacity can be established conveniently in this area. The limestone being hard, it is difficult to employ dry process. However, feasability of dry process could be examined in detail to avoid the large requirement of water. The proposed storage project on the Sabarmati river at Dharoi (Mehsana district) would solve the water problem.

The small deposit at Bhetali (near Idar) of magnesia limestone has a reserve of 1 m.tonne, and can be utilised for making natural cement on a small scale for the local use.

Kaira district:

Though the area holds about 800 m.tonnes of limestones (Lametas), the larger bulk is of Grade-IV to VI; a very small part say 10 to 20 m.tonnes are of Grade-II & III. There is only one cement factory at Sevalia, belonging to Associated Cement Companies Ltd., utilising these limestones from Balasinor. At present Grade IV limestones are beneficiated on a small scale by floatation to supplement the deficit of the cement grade limestone. Also Grade-I limestone from Ganguwada (Banaskantha district) from a lead of over 300 km is brought for blending.

The Grade-III limestone from Parbia, 35 km from the Sevalia factory can be utilised. This deposit itself is not large enough-having 5m.tonnes reserves - to support an independent plant.

Baroda and Broach districts:

Gora - Limdi and adjoining areas of Broach district have large deposits of Bagh limestones with a reserve of over 85 m.tonnes, and in quality those are of Grade -IV.

By blending the limestone with the chalk available as a byproduct of Gujarat State Fertilizer Corporation near Baroda, Portland cement can be manufactured.

The site suitable for the factory is in the same area where adequate water-supply can be had from Narmada, and power is also available. The communication can be developed by converting the existing narrow gauge rail line to broad gauge with some additional length. Gora is 90 km from Baroda by road.

The cement plant here should necessarily have a wet process.

Saurashtra

Bhavnagar district:

This district has Miliolite limestones of Grades-II and III, to the extent of 525 m.tonnes, which are quite suitable for Portland cement.

A cement plant of 0.4 m.tonnes can very well be established on the lines of Digvijaya cement Co., i.e. the clinkar may be prepared here and be ground wherever the cement is required, Digvijaya Co.'s clinkar is transported by sea and is ground at Bombay.

The reserves of limestones are so large that even after setting aside the needs of a larger size cement plant viz. 30 m.tonnes for 0.4 m.tonne capacity, there shall be quite a huge surplus for utilization in other industries. Vast calcareous sand-dunes also are of great use for blending purpose.

The dry process for cement manufacture is better suited in view of the suitability of limestone to this type of process and shortage of water supply in the area.

Amreli district:

Jafrabad area has 169 m.tonnes of Miliolite limestone of Grades-I, II and III. There is good scope for setting up a cement factory around Jafrabad in addition to other industries based on limestones.

Kodinar area too holds a very large limestone deposits of Grade-I out of which about 50 m.tonnes are exploitable for chemical as well as cement industries.

Here too, these limestones are more suited for the dry process of cement manufacture.

Junagadh district:

Miliolite limestones occupying Prachi, Veraval, Chorwar, Mangrol, Porbandar, and Junagad areas in this district are easily over 100 m.tonnes available for use. Almost half of those are of Grade-Super and rest of Grade-I. These are already being utilised for chemical and cement industries; there are 3 cement factories and two major chemical works in this area.

Even after setting aside the needs of the present industries, there is a large surplus of limestones available for further development and new cement plants.

Jamnagar district:

The limestones in this district are of Grade-III. The area holds over 100 m.tonnes of limestones.

The present cement factory at Sikka near Jamnagar has the largest capacity of 0.82 m.tonnes a year in the State, and this is still being increased. Limestone and sea sand (containing 90 percent $CaCO_3$) obtained from Narara and Kotia islands are used.

Another cement factory at Dwarka utilises limestone of Grade-I. The present capacity of this factory can be increased from 0.23 to 0.46 m.tonnes a year conveniently.

Kutch

This region holds very large limestone deposits of Grades-I and II to the tune of 7765 m.tonnes. These limestones are mainly Nummulitic; Miliolites are in subordinate quantities. Those all limestones are still left untouched, and there is a large scope of developing industries based on limestones, say chemical as well as cement. The drawback of this area is the lack of fresh water supply and of communication facilities. If these two things are provided, the limestone can easily be utilised for cement industry.

There are several water storage schemes envisaged in this area. These schemes will encourage people to utilise these limestones for industrial purpose and cement manufacture.

For the cement plant here, the dry process suits well, and the clinkar can be transported out by sea at a cheap cost, and can be ground wherever required.

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