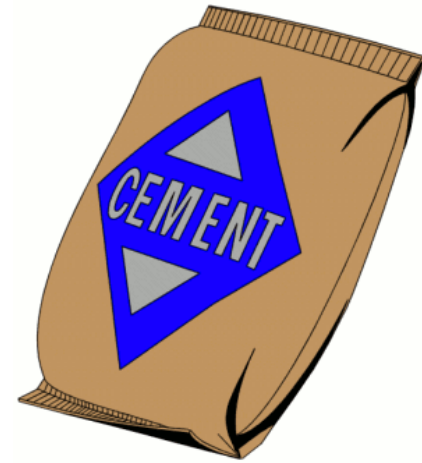


# CHAPTER 3 CEMENTS



# 3. CEMENTS



## Introduction

- Finely ground powders and all have the important property that when mixed with water a chemical reaction (**hydration**) takes place.
- Hydration produces a very hard and strong binding medium for the aggregate particles.
- The cement to be used in a particular concrete or mortar will be selected on the basis of the particular properties required.

# History of Cement

- The cementitious properties of lime in mortars and concrete have been known since early historic times. The Romans used lime concretes and developed pozzolanic cements of lime and certain volcanic earths.
- Lime mortars and concretes continued to be used in the middle Ages.
- 1824, Joseph Aspdin from Leeds city - England, produced a powder made from the calcined mixture of limestone and clay.
- He called it "Portland Cement", because when it hardened it produced a material similar to stones from the quarries near Portland Island in UK.

# History of Cement

- Although the method of making cement has been improved, the basic process has remained same.
- Cement production in Turkey was first started in Darıca Cement Factory in 1913 with a production capacity of 20,000 ton/year.
- Today the annual cement production in Turkey is more than 25 million tons from more than 50 cement factories all over the country.
- In North Cyprus, there is 1 cement factory (BEM--Boğaz Endüstri Madencilik Ltd.). Rest of cement comes from other countries (i.e. Turkey, Lebanon, Egypt, Syria).

# Raw Materials of Portland Cement

- Raw Materials:

1- ***Calcareous rocks*** ( $\text{CaCO}_3 > 75\%$  such as limestone, marl, chalk),

2- ***Argillaceous rocks*** ( $\text{CaCO}_3 < 40\%$  such as clay and shale),

3- ***Argillocalcareous rocks*** (40-75%  $\text{CaCO}_3$  such as clayey limestone, clayey marl).

- Materials from any two of these groups may be used for Portland cement production providing that they must contain, in proper form and proportions of lime, silica and alumina.

# Chemical Composition of Portland Cements

The raw materials used in the manufacture of Portland cement consist mainly of lime, silica, alumina and iron oxide.

The oxides account for over 90% of the cement. The oxide composition of (ordinary) Portland cement may be expressed as follows:

**Table 3.1 The oxide composition of ordinary PC**

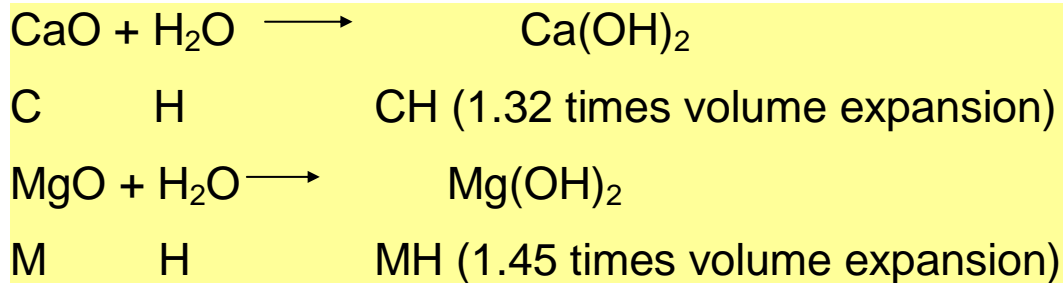
Common name	Oxide	Abbreviation	Approximate composition limits (%)
Lime	CaO	C	60-66
Silica	SiO <sub>2</sub>	S	19-25
Alumina	Al <sub>2</sub> O <sub>3</sub>	A	3-8
Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	F	1-5
Magnesia	MgO	M	0-5
Alkalies:			
-soda	Na <sub>2</sub> O	N	0.5-1
-potassa	K <sub>2</sub> O	K	0.5-1
Sulfur trioxide	SO <sub>3</sub>	<u>S</u>	1-3

**Table 3.2 A typical chemical analysis of ordinary  
PC**

Item	Percentage (%)
CaO	63.6
SiO <sub>2</sub>	20.7
Al <sub>2</sub> O <sub>3</sub>	6.0
Fe <sub>2</sub> O <sub>3</sub>	2.4
SO <sub>3</sub>	1.4
MgO	2.4
Na <sub>2</sub> O	0.1
K <sub>2</sub> O	0.7
Loss on ignition	1.2
Insoluble residue	0.3
Free CaO	1.1
Total	100



- ***SO<sub>3</sub> (sulfur trioxide)***: Comes from gypsum. The amount of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) can be approximated by multiplying the amount of SO<sub>3</sub> by 2.15.
- ***MgO (magnesia)***: To control the detrimental expansion, MgO is limited to 5% (expansion due to the hydration of free MgO in hardened concrete).
- ***Free CaO***: Same as free MgO, free CaO is undesirable. Because these oxides hydrate much later than other compounds of cement. Besides, they show a large volume expansion after hydration resulting in disintegration of hardened concrete.



- ***Na<sub>2</sub>O & K<sub>2</sub>O (alkali oxides):***

A limiting value of alkali oxides is often specified for cements which are used with reactive aggregates to prevent alkali-aggregate reaction which results in disruptive expansion.

- ***L.O.I. (loss on ignition):***

Indicates "prehydration or carbonation" due to prolonged or improper storage. LOI is the loss of the weight of a cement sample when heated at 1000°C.

i.e.  $LOI \leq 3\%$  (ASTM)

- ***I.R. (insoluble residue):***

Fraction of cement which is insoluble in HCl acid. It comes mainly from the silica which has not reacted to form silicate compounds in the rotary kiln. It is a measure of the completeness of reactions in the kiln.

$IR \leq 0.75\%$  (ASTM)

## Main Chemical Compounds of Portland Cement

- Oxides interact with each other and form more complex compounds. The measurement of the amount of these major compounds by conventional chemical methods is not possible.
- Portland cements are composed of four basic chemical compounds shown with their names, chemical formulas, and abbreviations:

Tricalcium silicate =  $3\text{CaO} \cdot \text{SiO}_2 = \text{C}_3\text{S}$

Dicalcium silicate =  $2\text{CaO} \cdot \text{SiO}_2 = \text{C}_2\text{S}$

Tricalcium aluminate =  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = \text{C}_3\text{A}$

Tetracalcium aluminoferrite =  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 = \text{C}_4\text{AF}$

### *Tricalcium silicate:*

Hardens rapidly. Responsible for initial set and early strength.

### *Dicalcium silicate:*

Hardens slowly and its effect on strength increases occurs at ages beyond one week.

### *Tricalcium aluminate:*

Contributes to strength development in the first few days. It is the first compound to hydrate. The least desirable component because of its high heat generation and its reactivity with soils and water containing moderate to high sulfate concentrations.

### *Tetracalcium aluminoferrite:*

Lowers clinkering temperature.  $C_4AF$  contributes very little to strength of concrete even though it hydrates very rapidly.

**Table 3.3 Main chemical compounds of PC**

<b>Name of Compounds</b>	<b>Chemical Composition</b>	<b>Usual Abbr.</b>	<b>Percentage %</b>
Tricalcium Silicate	$3\text{CaO} \cdot \text{SiO}_2$	$\text{C}_3\text{S}$	51
Dicalcium Silicate	$2\text{CaO} \cdot \text{SiO}_2$	$\text{C}_2\text{S}$	23
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$	8
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$	9

# Manufacturing of Portland Cement

The details of the cement making process vary widely. However, the fundamental stages in cement production are all the same and as follow. A schematic diagram of the cement manufacturing is shown in [Fig.3.1](#).

- 1. The raw materials are reduced to fine particle size.
- 2. Raw materials are blended and mixed to produce uniform chemical composition containing calcium carbonate, silica, alumina, iron oxide etc.

- 3. The blended raw mix is heated to the point where all the moisture is driven off as steam or water vapor.
- 4. The dried mix is heated to 800°C. At this temperature, the calcium carbonate dissociated into calcium oxide (free lime), and carbondioxide which driven off as gas.
- 5. As the temperature rises, principal active compounds of Portland cement form. This process is completed at a temperature of around 1400°C. Resulting product is Portland **cement clinker** (1.8 tons of raw material produces 1 ton of clinker).

- 6. Clinker is cooled to a temperature of about 60-150°C and stockpiled.
- 7. Clinker is ground to the specified fineness with the addition of a small proportion of gypsum to control the setting time of the finished cement.
- 8. The finished cement is stored in silos for a relatively short time before being sent to the customer in bags or in bulks.

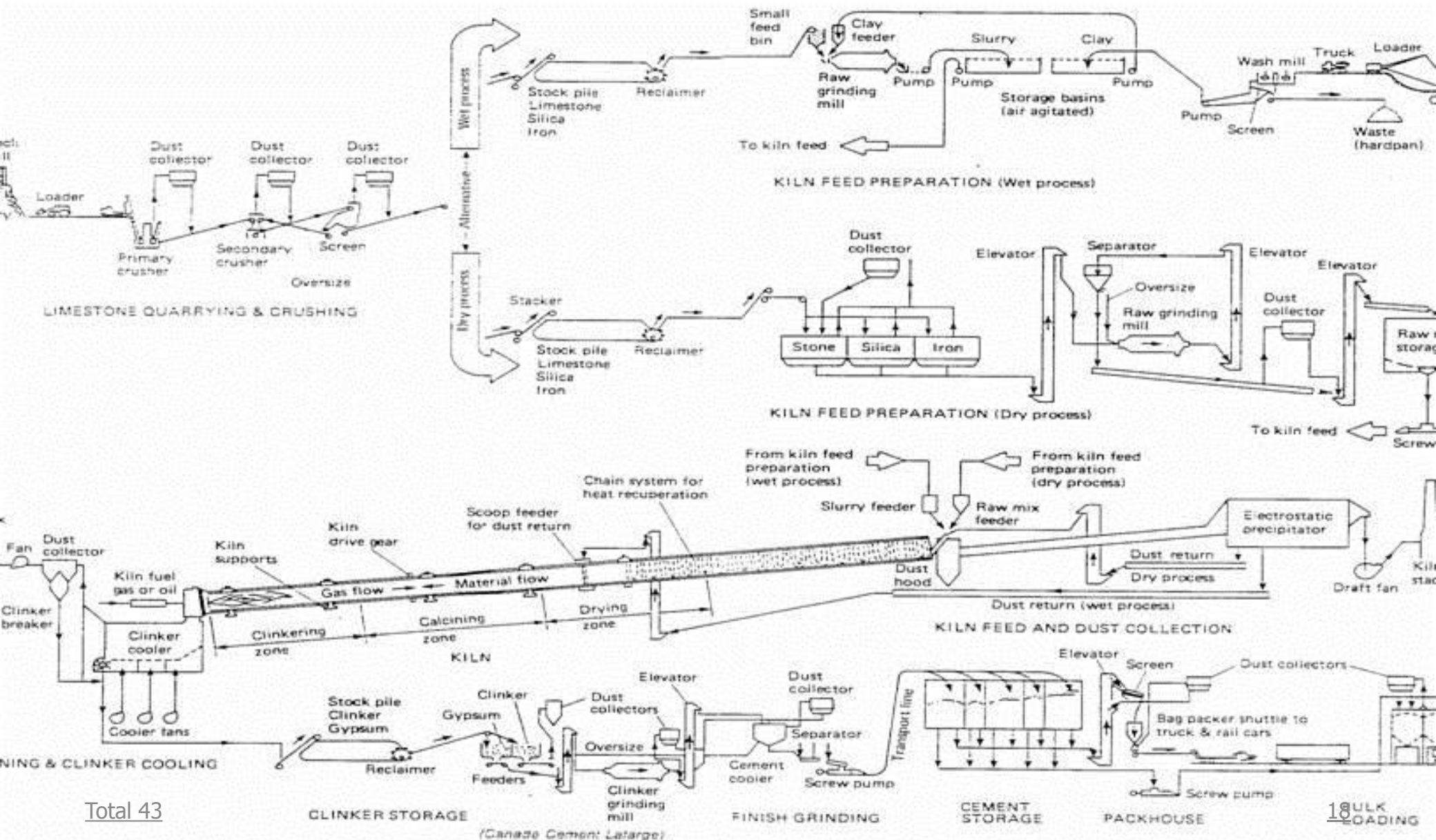


# Production Steps of Portland Cement

- Crushing, screwing, and stockpiling the raw materials
- Calculating the proportions of raw materials
- Preparing the raw mix by blending
- Feeding the raw mix into rotary kiln
- 100°C: Free water is evaporated.
- 150-300°C: Loosly bound water is evaporated.
- 500°C: More firmly bound water is evaporated.
- 600°C:  $\text{MgCO}_3 \longrightarrow \text{MgO} + \text{CO}_2$
- 900°C:  $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
- Reaction between lime and clay starts.
- 1300°C: Major compound formation starts.
- 1400-1600°C: Output temperature.
- (Around 1600°C clinker forms  $\text{C}_3\text{A}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{S}$ ,  $\text{C}_4\text{AF}$ )
- Clinker cooled and stored.
- Clinker is ground with gypsum.
- Storing and marketing.



Figure 3.1 Production of Portland cement (utube-Pr1KTVSXo)



# Physical Properties of Cement

## Fineness:

- The reaction between the water and cement starts on the surface of the cement particles. So the greater the surface area of a given volume of cement the greater the hydration. A fine cement will develop strength and generate heat more quickly than a coarse cement.
- The measurement of fineness:

Defined as specific surface and is expressed as surface area of the grains in a sample per mass of that sample. Usually it is in the range 350-380 m<sup>2</sup>/kg.

### Hydration:

- The chemical combination of cement and water known as hydration produces a very hard and strong binding medium for the aggregate particles in the concrete.
- At the end of hydration normally a heat is liberated which is expressed as cal/gr.

**Table 3.4 Time taken to achieve 80% hydration and heat of hydration of the main chemical compounds of Portland cement**

<b>Chemical compounds</b>	<b>Time to achieve 80% hydration (days)</b>	<b>Heat of hydration (J/g)</b>
$C_3S$	10	502
$C_2S$	100	251
$C_3A$	6	873
$C_4AF$	50	419

## HYDRATION

- In normal construction where the sizes of the structural members are not so large, the dissipation of this heat creates no problems.
- On cold weather concreting, this heat is advantageous.
- But in hot weather and in mass concrete construction, this generated heat may cause thermal cracks, and should be avoided.

The process of hydration in the cement can be determined by the measurement of;

- the amount of  $\text{Ca(OH)}_2$  in the paste,
- the heat evolved by hydration,
- the specific gravity of the unhydrated cement paste,
- the amount of chemically combined water,
- the amount of unhydrated cement paste.

## Measuring Heat of hydration of cement.



# Setting of cement

- The beginning of noticeable stiffening in the cement paste is known as the initial set.
- The final hardening process which is responsible for its strength known as the final set.
- The time from the addition of the water to the initial and final set are known as the setting times.
- Setting time is affected by: cement composition, cement fineness, rate of hydration, and the ambient temperature.



# Measurement of Setting Time of Cement

Vicat Apparatus



Gillmore apparatus



## Strength:

- The strength of hardened cement is its most important property.
- The rate of hardening of cement depends on the chemical and physical properties of the cement, the curing conditions and the water/cement ratio.

## Soundness:

- Soundness is a physical property of cement paste, which determines the ability of the cement paste to retain its volume after setting is completed.
- The unsoundness is due to the presence of free CaO (lime) and free MgO (magnesia) in cement.
- These constituents hydrate very slowly after setting of cement. Since  $\text{Ca(OH)}_2$  and  $\text{Mg(OH)}_2$  occupy larger volume, expansion takes place.

# Cement Types

## 1. ASTM (American Society for Testing and Materials) Types:

### **Type I (Ordinary Portland cement):**

- Used for general construction work when the special properties of the other types are not required.
- Normally used for reinforced concrete buildings, bridges, pavements and sidewalks when the soil conditions are normal, for concrete masonry units, and for all uses where the concrete is not subjected to special sulfate hazard, heat of hydration is not objectionable, where freezing-thawing is not expected.

## Type I-A (Air-Entrained Type-I):

- It is used where air entrainment is necessary.



### *Air-entrainment:*

- Air intentionally incorporated by means of a suitable agent.
- Magnitude of these air bubbles are in the order of 0.05 mm in size.
- Entrained air produces separate cavities in the cement paste so that no channels for the passage of water are formed and the permeability of the concrete is not increased.
- The voids never become filled with the products of hydration of cement as gel can form only in water.

## Type II (Modified Portland Cement):

- It has better resistance to the action of sulfates than normal (ordinary) Portland cement and used where sulfate concentrations in groundwater are higher than normal but not very severe.
- Generates heat at a slower rate than OPC and is used in certain concrete mass work like retaining walls.
- Reduced temperature rise is beneficial for hot weather concrete, too.

## Type II-A (Air-Entrained Type II Cement)

## Type III: (High Early Strength Cement)

- Used where high early strengths are required at early periods, usually a week or less.
- It is particularly usefull where it is required to remove forms as soon as possible or when the structure must be brought into service quickly.
- High-early strength makes it possible to reduce the period of protection for concrete during *cold* weather.

## **Type III-A (Air Entrained Type III)**

## **Type IV (Low Heat Portland Cement):**

It is used where the amount and rate of heat generation must be minimized.

Strength is also developed at a slower rate. It is intended for use in massive concrete structures such as dams.

## **Type V (Sulfate Resistant Portland Cement):**

- It is used in structures subject to sulfate attack, chemical plants, etc. It is also resistant to the action of sea water.

# OTHER CEMENTS

## White Portland Cement (WPC):

- It is made from raw materials containing very little iron oxide and manganese oxide. China clay (Kaolin) is generally used together with chalk or limestone free from specified impurities (iron oxide, manganese oxide).
- To avoid contamination by coal ash, oil is used as fuel in the kiln.
- The cost of grinding is higher and this completed with the more expensive raw materials makes White Cement rather expensive (about 2 times).
- Specific gravity and strength of White Portland Cement are less than those of OPC.
- WPC is used for architectural purposes. It is not liable to cause staining, since it has a low content of soluble alkalies.

## High Alumina Cement (HAC):

- The raw materials of HAC are limestone or chalk and bauxite (a residual deposit formed by weathering under tropical conditions of rock containing  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{TiO}_2$ ) which are interground and calcined at  $1600^\circ\text{C}$  in the kiln. The solidified material is fragmented and ground to a fineness of  $2500\text{-}3000\text{ cm}^2/\text{gr}$ . Its color is dark grey.

### Properties;

- High resistance to the action of sulfate waters (due to absence of  $\text{Ca}(\text{OH})_2$ ).
- Extremely high early strength (suitable for emergency repairs). 80% of the ultimate strength is achieved in 24 hours or even at 6-8 hours.
- Initial set = 4 hrs.
- Final set = 5 hrs.
- Rapid hardening is not accompanied by rapid setting.
- With special aggregates such as firebrick, it can be used to make refractory concrete that can stand high furnace temperature ( $T > 1300^\circ\text{C}$ ).
- It is expensive.
- Never use HAC in mass concrete.
- Never use with an admixture.
- Never mix HAC with PC (flash set and low strength).



## **Portland Pozzolan Cement:**

- *Pozzolan*: Volcanic dust found at Pozzuoli, Italy and used since Roman times as hydraulic cement when mixed with lime. All pozzolans contain silica and siliceous or aluminous minerals.
- Fly ash, slag (blast-furnace), silica fume are artificial pozzolans. Volcanic ash is natural pozzolan.
- Portland Pozzolan Cement produces less heat of hydration and offers greater resistance to the sulfate attack than OPC (useful for marine and hydraulic construction and mass concrete).
- Most pozzolans do not contribute to the strength at early ages, so strength gain of these cements is slow.
- Therefore they require larger curing period, but the ultimate strength is the same as OPC.

## Portland Blast-Furnace Slag Cement:



- PBFSC = OPC clinker + 25-60% granulated blast-furnace slag.
- Granulated blast-furnace slag is a waste product of the manufacture of iron. The amount of iron and slag being obtained is in the same order. A proper slag is a mixture of;
  - Lime = 40%
  - Silica = 30%
  - Alumina = 20%
  - Magnesia = 5%
  - Alkali Oxides = 1%
- This cement is less reactive than OPC and gains strength at a slower rate during first 28 days, so adequate curing is essential.

### Properties;

- suitable for mass concrete
- unsuitable for cold weather
- has high sulfate resistance (suitable for use in sea-water construction).

## Masonry Cement

- Is used in mortar for brickwork.
- Made by intergrinding very finely ground PC, limestone and air-entraining agent, or alternatively PC and hydrated lime, granulated slag or inert filler and an air-entraining agent.

### Properties;

- More plastic than OPC
- Higher water retaining power which leads lower shrinkage
- Due to low strength it can not be used for structural concrete.



## Natural Cement

- Raw material is cement rock (which is a clayey limestone containing up to 25% argillaceous material).
- The resulting cement is intermediate between PC and hydraulic lime.
- Contains no C3S and is therefore slow hardening.

## Expansive Cements

- These are cements which upon hydration give product capable of expansion.
- Expansive cements are used in special applications such as the prevention of water leakage.
- It has high resistance to sulfate attack.



## Nomenclature for Cements

- Cement is described in terms of cement type, strength class and rate of early strength development.

For example;

PC52.5R

PC: Portland Cement (Type of Cement)

52.5: 52.5 MPa (Standard Strength at 28 days)

R: Rapid (Sub-class: Indicated the rate of early strength development; i.e. R: rapid, N: Normal, L: Low)

# *Nomenclature for Cements*

- The recent standard for cement in European Norms is ENV 197-1.
- States two additional classification, -the proportion of cement clinker and the second main constituent.
- CEM II/A-S42.5N  
CEMII: Type of cement  
A: Proportion of cement clinker (A: high, B: medium, C: low)  
S: Sub-type indicates the second main constituent (silica fume, GGBS, PFA)  
42.5: 42.5 MPa (Standard strength at 28 days)  
N: Sub-class indicates the rate of early strength development (R: rapid, N: normal, L: low)

**Table 3.5 American (ASTM) standards<sup>6, 7</sup> (Lea`s book)**

Cement type	Clinker and calcium sulfate (%)	Slag (%)	Pozzolan (%)	Processing additions
Portland I, IA, IIA, III, IIIA, IV, V	100	0	0	Permitted
Slag-modified Portland I (SM)	>75	<25	0	Permitted
Pozzolan-modified Portland I (PM)	>85	0	<15	Permitted
Portland blastfurnace slag IS	30-75	25-70	0	Permitted
Portland-Pozzolan IP, P	60-85	0	15-40	Permitted
Slag S	Permitted	≥70	0	Permitted

<sup>6</sup> American Society for Testing and Materials. Standard Specification for Portland cement. ASTM, 1995; C 150-95

**Table 3.6 European Prestandard ENV 197-1-classification of common cement types by strength**

	Characteristic compressive strength (MPa)		Absolute minima (MPa)	Characteristic 28-day compressive strength (MPa)		Absolute minima (MPa)
Cement class	2 days	7 days	2/7 days	minimum	maximum	28 days
32.5	-	≥16	≥14	32.5	52.5	≥30.0
32.5 R	≥10	-	≥8	32.5	52.5	≥30.0
42.5	≥10	-	≥8	42.5	62.5	≥40.0
42.5 R	≥20	-	≥18	42.5	62.5	≥40.0
52.5	≥20	-	≥18	52.5	-	≥50.0
52.5 R	≥30	-	≥28	52.5	-	≥50.0



**Table 3.7 Production of the various types of cement in Europe in 1990 (mega tonnes)\***

Type	I	II-S	II-P/Q	II-V/W	II-L	II-T	II-D	II-M	III	IV	V	Total
Secondary material		GBF slag	Pozzo-lana	Fly ashes	Lime-stone	Burnt shale	Silica fume	Compo-site	GBF slag	Pozzo-lanic	Compo-site	
Secondary material (%)	0-5	6-35	6-35	6-35	6-35	6-35	6-10	6-35	36-95	11-55	18-50	
Austria	0.3	3.7		0.8					0.1			4.9
Belgium	1.8			1.2					2.0			5.0
Denmark	0.9			0.3	0.1							1.3
UK	13.3			0.4					0.1			13.8
Finland	1.2							0.4				1.6
France	9.0	1.4	0.1	0.6	6.5			5.2	1.2		0.3	24.3
Germany	18.4	1.2		0.1	0.9	0.5		0.4	3.8	0.1		25.4
Greece	1.8							5.8				7.6
Republic of Ireland	1.3											1.3
Italy	22.9								2.3	14.8		40.0

**Table 3.8 ENV 197-1<sup>4</sup> common cement types and composition: proportion by mass<sup>a</sup>**  
(Lea's Chemistry of Cement and Concrete, 4th Ed., Edited by Peter C Hewlett, 1998.)

Cement type	Designation	Notation	Clinker K	Granulated	Silica fume	Pozzolana		Fly ashes		Burnt	Limestone	Minor
				Blastfurnace Slag S	D <sup>c</sup>	Natural P	Industrial Q <sup>d</sup>	Siliceous V	Calcareous V	Shale T	Limestone L	Additional constituents <sup>b</sup>
I	Portland cement	I	95-100									0·5
	Portland slag cement	II/A-S	80-94	6-20								0·5
		II/B-S	65-79	20-35								0·5
	Portland silica fume cement	II-A-D	90-94		6-10							0·5
	Portland pozzolana cement	II/A-P	80-94			6-20						0·5
		II/B-P	65-79			21-35						0·5
		II/A-Q	80-94				6-20					0·5
		II/B-Q	65-79				21-35					0·5
II	Portland fly ash cement	II/A-V	80-94					6-20				0·5
		II/B-V	65-79					21-35				0·5
		II/A-W	80-94						6-20			0·5
		II/B-W	65-79						21-35			0·5
	Portland burnt shale cement	II/A-T	80-94						6-20			0·5
		II/B-T	65-79						21-35			0·5
	Portland limestone cement	II/A-L	80-94							6-20		0·5
		II/B-L	65-79								21-35	0·5
	Portland composite cement	II/A-M	80-94					6-20 <sup>e</sup>				
	II/B-M	65-79					21-35 <sup>e</sup>					

III	Blastfurnace cement	III/A	35-64	36-65						0-5
		III/B	20-34	66-80						0-5
		III/C	5-19	81-95						0-5
IV	Pozzolanitic cement	IV/A	65-89	-		11-35	-	-	-	0-5
		IV/B	45-64	-		36-55	-	-	-	0-5
V	Composite cement	V/A	40-64	18-30	-	18-30	-	-	-	0-5
		V/B	20-39	31-50	-	31-50	-	-	-	0-5

<sup>a</sup>The values in the table refer to the cement nucleus, excluding calcium sulfate and any additives.

<sup>b</sup>Minor additional constituents may be filler or may be one or more of the main constituents unless these are included as main constituents in the cement.

<sup>c</sup>The proportion of silica fume is limited to 10%.

<sup>d</sup>The proportion of non-ferrous slag is limited to 15%.

<sup>e</sup>The proportion of filler is limited to 5%.