

Chapter 2: Portland Cement



2.1 Definition

A cement is any substance which binds together other materials by a combination of chemical processes known collectively as **setting**. Cements are dry powders and should not be confused with concretes or mortars, but they are an important constituent of both of these materials.

Cement act as the '**glue**' that gives strength to structures. Mortar is a mixture of cement and sand whereas concrete also includes rough aggregates.

Cement is a powdered material with water forms a paste that hardens slowly. It has an important property that when mixed with water a chemical reaction (**hydration**) takes place.

2.2 History of Cement

1. 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.
2. Lime mortars and concretes continued to be used in the middle Ages.
3. 1824, Joseph Aspdin from Leeds city - England, produced a powder made from the calcined mixture of limestone and clay.
4. He called it "Portland Cement", because when it hardened it produced a material similar to stones from the quarries near Portland Island in UK.

2.3 Raw Materials of Portland Cement

2.3.1 Raw Materials

1. Calcareous rocks such as limestone, marl, chalk.
2. Argillaceous rocks (silica and alumina) such as in clay and shale.

Portland cement production must contain, in proper form and proportions of **lime, silica and alumina**.

2.3.2 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:

The oxide composition of ordinary PC

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

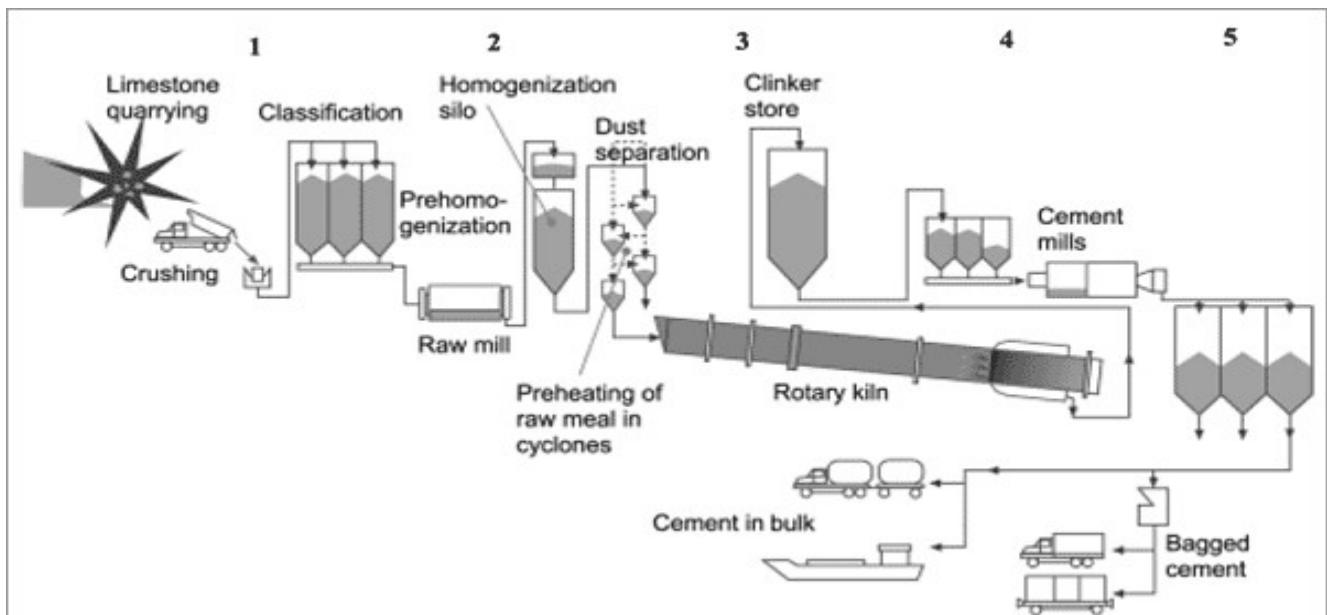
A Typical Chemical Composition of Ordinary Portland Cement (OPC)

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

2.4 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.

- 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 800oC. At this temperature, the calcium carbonate dissociated into calcium oxide (free lime), and carbon dioxide 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 1400oC. 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 60-150oC 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

- 1- Crushing, screwing, and stockpiling the raw materials.
- 2- Calculating the proportions of raw materials.
- 3- Preparing the raw mix by blending.
- 4- Feeding the raw mix into rotary kiln.
- 5- 100°C: Free water is evaporated.
- 6- 150-300°C: Loosly bound water is evaporated.
- 7- 500°C: More firmly bound water is evaporated.
- 8- 600°C: $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
- 9- 900°C: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- 10- Reaction between lime and clay starts.

- 11- 1300°C: Major compound formation starts.
- 12- 1400-1600°C: Output temperature.
- 13- (Around 1600°C clinker forms C3A, C2S, C3S, C4AF)
- 14- Clinker cooled and stored.
- 15- Clinker is ground with gypsum.
- 16- Storing and marketing.

2.5 Main Chemical Compounds of Portland Cement

(a) Major Compounds

Portland cements are composed of four basic chemical compounds shown with their names, chemical formulas, and abbreviations:

Tricalcium silicate = $3\text{CaO} \cdot \text{SiO}_2 = \text{C3S}$ (Alite) (White)
 Dicalcium silicate = $2\text{CaO} \cdot \text{SiO}_2 = \text{C2S}$ (Belite) (White)
 Tricalcium aluminate = $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = \text{C3A}$ (White/grey)
 Tetracalcium aluminoferrite = $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 = \text{C4AF}$ (Ferrite) (Dark)

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

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 which contains moderate to high sulfate concentrations. Cements made with low C3A contents usually generate less heat, develop higher strengths, and show greater resistance to sulfate attacks.

Tetracalcium aluminoferrite:

C4AF contributes very little to strength of concrete even though it hydrates very rapidly.

C3S and C2S are the most stable compounds of cement. They are together form from 70 to 80 percent of the constituents in the cement. When cement comes into contact with water, **C3S** begins to hydrate rapidly, generating a considerable amount of heat and making a significant contribution to the development of the early strength particularly in the first 14 days.

In contrast **C2S** which hydrates slowly and is mainly responsible for the development in strength after about 7 days. The cement rich in C2S result in a greater resistance to chemical attack and a smaller drying shrinkage than the other Portland cements.

The hydration of **C3A** is extremely exothermic and takes place very quickly. It contributes to high early strength but produces little strength after about 24 hours. C3A is the least stable and cements containing more than 10 percent of this compound produces concretes, which are susceptible to sulphate attack.

(b) Minor components

The most important minor components are **gypsum**, MgO, and **alkali sulphates**.

Gypsum ($2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is an important component added to avoid **flash set**.

Alkalies (MgO, Na₂O, K₂O) can increase pH value up to 13.5 which is good for reinforcing steel protection. However, for some aggregates, such a high alkaline environment can cause **alkali aggregate reaction problem**.

2.6 Physical Properties of Cement

2.6.1 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. It will of course cost more for grinding the clinker more finely.

Fine cement in general improve the **cohesiveness** of fresh concrete and can be effective in reducing the risk of **bleeding** but they increase the risk of being air-set before use and they increase the tendency of shrinkage cracking.

The measurement of fineness is defined as specific surface and is expressed as surface area of the grains in a sample per mass of that sample. In practice, the fineness is usually in the range 350-380 m²/kg.

2.6.2 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 calories per gram. The rate of hydration

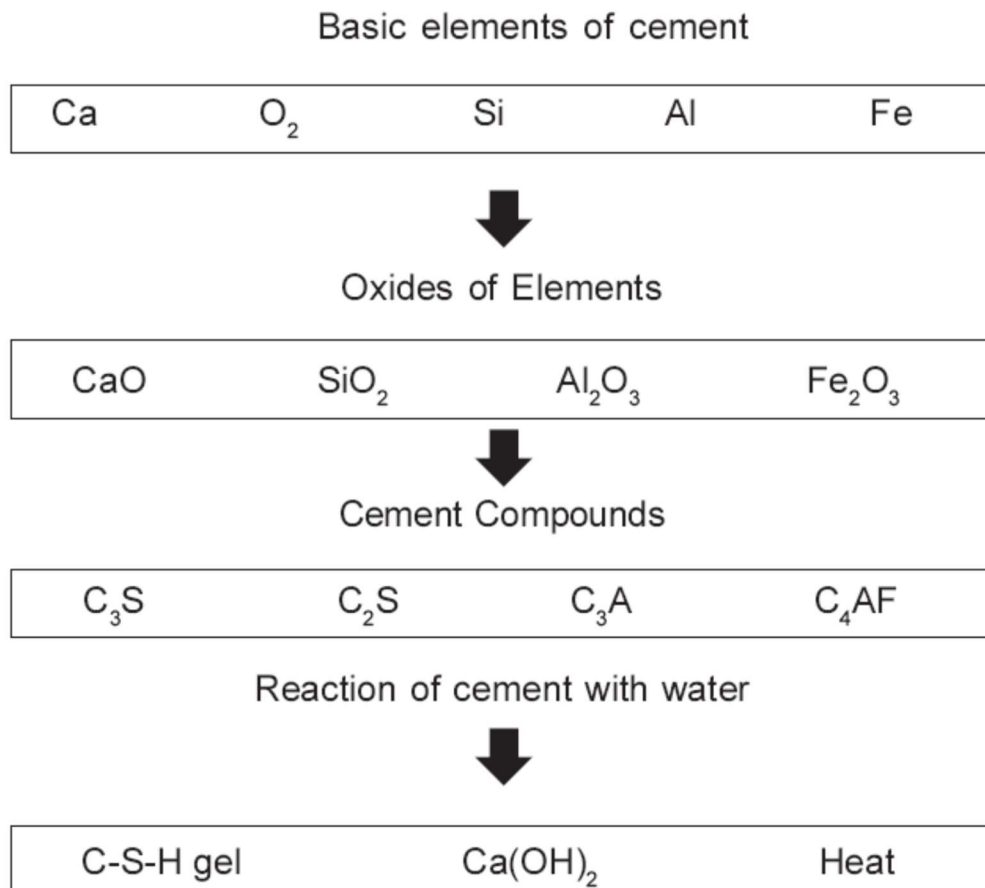
depends on the relative properties of silicates and aluminate compounds, the fineness of the cement, and the ambient temperature.

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

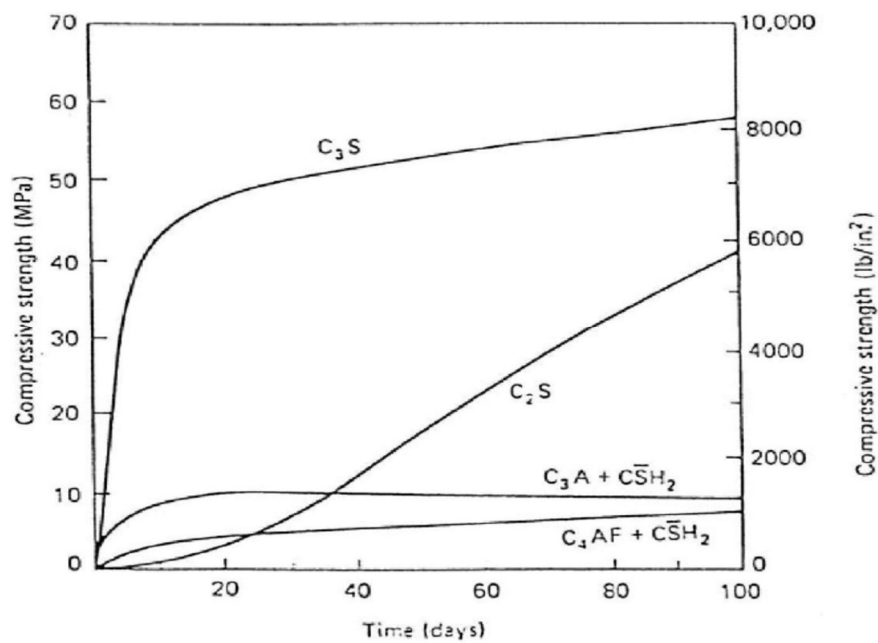
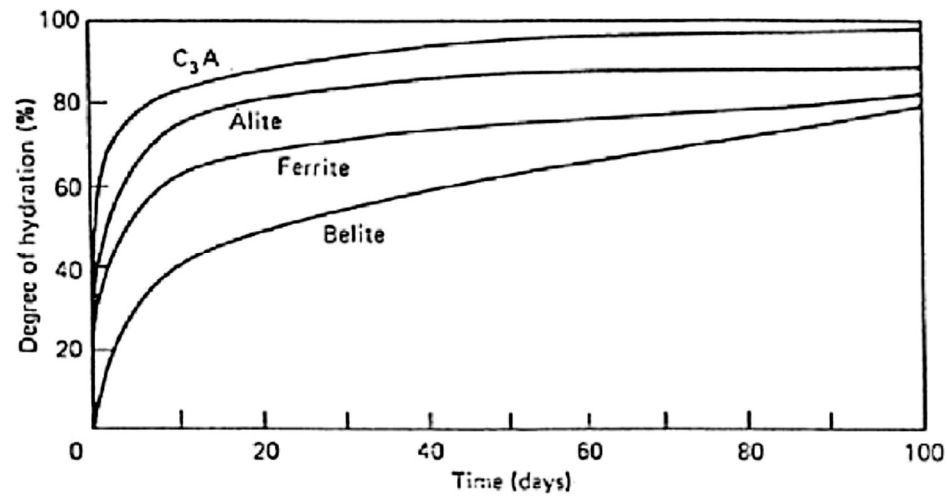
Chemical compounds	Time to achieve 80% hydration (days)	Heat of hydration (J/g)
C_3S	10	502
C_2S	100	251
C_3A	6	873
C_4AF	50	419

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.

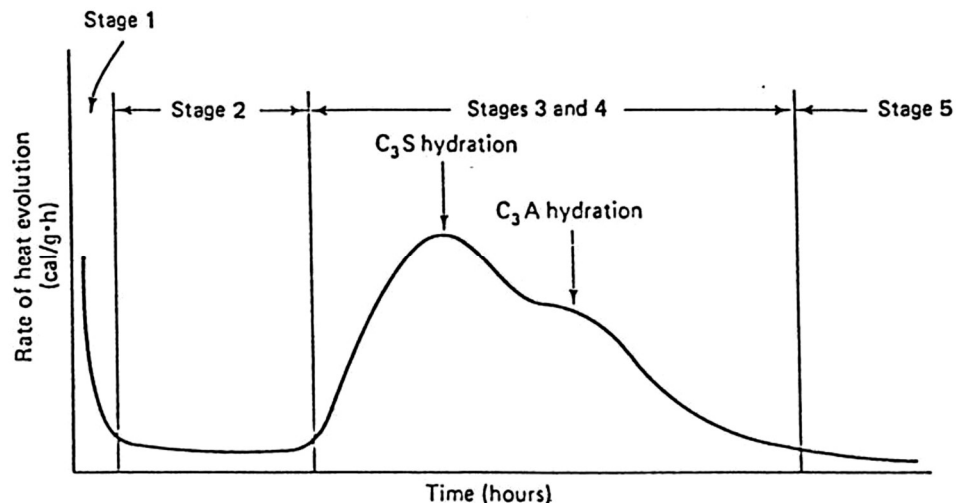
The principal hydration product is $C_3S_2H_4$, **calcium silicate hydrate**, or **C-S-H** and is called **glue gel binder**. C-S-H is believed to be the material governing concrete strength. Another product is CH [$Ca(OH)_2$], calcium hydroxide. CH can bring the pH value to over 12 and it is good for corrosion protection of steel.



The rate of hydration during the first few days is in the order of $C_3A > C_3S > C_4AF > C_2S$.



A typical calorimetric curve of Portland cement is shown in the following figure.



2.6.3 Setting and Hardening:

Setting and hardening of the cement paste are the main physical characteristics associated with hydration of cement.

The setting times: The time from the addition of the water to the initial and final set are known as the setting times.

The initial set: The beginning of noticeable stiffening in the cement paste is known as the initial set.

The final set: The final hardening process which is responsible for its strength known as the final set.

Setting time is affected by **cement composition, cement fineness, rate of hydration, and the ambient temperature.**

2.6.4 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.

2.6.5 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 Ca(OH)_2 and Mg(OH)_2 occupy larger volume, expansion takes place.

The unsoundness may be reduced by;

- 1- limiting MgO content to less than 5%,
- 2- fine grinding,
- 3- thorough mixing,
- 4- Allow cement to aerate for several days (lime may have hydrated or carbonated in cement).

Tests to measure soundness are (Self Study);

- Le Chatelier test (due to free lime only).
- Autoclave test (sensitive to free CaO and MgO).

2.7 Types of cements

The same type of cement may not be suitable for different locations and climatic conditions. Therefore, various types of cement have been developed as per the actual requirements. The necessary changes have been achieved by different methods such as:

- 1- Changing the oxide composition
- 2- Changing fineness of cement.
- 3- Using different additives or mineral mixtures like slag, fly-ash or silica fumes etc.

2.7.1 Types of Cement based on ASTM

ASTM (American Society for Testing and Materials) Types:

Type I: Normal (ordinary) Portland Cement.

Type I-A: Air-entrained type-I Cement.

Type II: Modified Portland Cement.

Type II-A: Air-entrained type-II Cement.

Type III: High Early strength Portland Cement.

Type III-A: Air-entrained type-III Cement.

Type IV: Low heat Portland Cement.

Type V: Sulfate Resistant Portland Cement.

	I	II	III	IV	V
C_3S	50	45	60	25	40
C_2S	25	30	15	50	40
C_3A	12	7	10	5	4
C_4AF	8	12	8	12	10
$\bar{C}SH_2$	5	5	5	4	4
Fineness (Blaine, m^2/kg)	350	350	450	300	350
Compressive strength at 1 day, MPa (psi)	7 (1,000)	6 (900)	14 (2,000)	3 (450)	6 (900)
Heat of hydration (7 days, J/g)	330	250	500	210	250

Other Types

White Portland Cement.

High Alumina Cement.

Portland Pozzolan Cement.

Portland Blast Furnace Slag Cement.

Masonry Cement.

Natural Cement.

Expansive Cement.

Type I (Ordinary Portland cement):

It is used for general construction work when the special properties of the other types are not required and 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.

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. It also 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)

It is used where high early strengths are required at early periods, usually a week or less. It is particularly useful 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.

2.7.2 Types of Cements based on European Standards (EN 197-1)

EN 197-1 Ordinary Portland Cements (27 products)

	Clinker	Main Additives	Minor Additives
CEM I Portland Cement:	95 - 100	-	0 - 5%
CEM II Compound Portland Cement:	A: 80 - 94	6 - 20	0 - 5%
	B: 65 - 79	21 - 35	
CEM III Blastfurnace Cement:	A: 35 - 64	36 - 65	0 - 5%
	B: 20 - 34	66 - 80	
	C: 5 - 19	91 - 95	
CEM IV Pozzolanic Cement:	A: 65 - 89	A: 11 - 35	0 - 5%
	B: 45 - 64	B: 36 - 55	
CEM V Composite Cement:	A: 40 - 64	A: 34 - 60	0 - 5%
	B: 20 - 38	B: 61 - 80	

الرمز	نوع الإضافات الأساسية	
S	خبث الأفران	Granulated blast furnace slag
P	البوزولانا الطبيعية	Natural Pozzolanic
Q	بوزولانا الكلس الطبيعية	Natural Calcined Pozzolanic
V	الرماد المتطاير السيليكوني	Siliceous fly ash
W	الرماد المتطاير الجيري	Calcareous fly ash (W)
T	مسحوق صخور الطين المحرقة	Burnt shale (T)
LL ، L	مسحوق الصخر الجيري	Limestone (L, LL)
D	غبار السيليكا	Silica fume
M	اثنين أو أكثر من الإضافات المذكورة أعلاه	Two or more of the above

مستوى المقاومة القياسية MPa	مستوى المقاومة المبكرة	
32.5	N (Normal)	عادية
	R (Rapid)	عالية
42.5	N	عادية
	R	عالية
52.5	N	عادية
	R	عالية

CEMII / A – M (S-V-L) 42.5 N

CEM II / B – LL 42.5 N

European Standards ENV 197-1 classification of common cement types by strength

Cement class	Characteristic compressive strength (MPa)		Absolute minima (MPa)	Characteristic 28-day compressive strength (MPa)		Absolute minima (MPa)
	2 days	7 days		minimum	maximum	
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 1 — The 27 products in the family of common cements

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass ^a)											Minor additional constituents
			Main constituents											
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone			
			K	S	D ^b	natural P	natural calcined Q	siliceous V	calca-reous W	T	L	LL		
CEM I	Portland cement	CEM I	95-100	—	—	—	—	—	—	—	—	—	0-5	
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	—	—	—	—	—	—	—	—	0-5	
		CEM II/B-S	65-79	21-35	—	—	—	—	—	—	—	—	0-5	
	Portland-silica fume cement	CEM II/A-D	90-94	—	6-10	—	—	—	—	—	—	—	0-5	
	Portland-pozzolana cement	CEM II/A-P	80-94	—	—	6-20	—	—	—	—	—	—	0-5	
		CEM II/B-P	65-79	—	—	21-35	—	—	—	—	—	—	0-5	
		CEM II/A-Q	80-94	—	—	—	6-20	—	—	—	—	—	0-5	
		CEM II/B-Q	65-79	—	—	—	21-35	—	—	—	—	—	0-5	
	Portland-fly ash cement	CEM II/A-V	80-94	—	—	—	—	6-20	—	—	—	—	0-5	
		CEM II/B-V	65-79	—	—	—	—	21-35	—	—	—	—	0-5	
		CEM II/A-W	80-94	—	—	—	—	—	6-20	—	—	—	0-5	
		CEM II/B-W	65-79	—	—	—	—	—	21-35	—	—	—	0-5	
	Portland-burnt shale cement	CEM II/A-T	80-94	—	—	—	—	—	—	—	6-20	—	0-5	
		CEM II/B-T	65-79	—	—	—	—	—	—	—	21-35	—	0-5	
	Portland-limestone cement	CEM II/A-L	80-94	—	—	—	—	—	—	—	—	6-20	0-5	
		CEM II/B-L	65-79	—	—	—	—	—	—	—	—	21-35	0-5	
		CEM II/A-LL	80-94	—	—	—	—	—	—	—	—	—	6-20	0-5
		CEM II/B-LL	65-79	—	—	—	—	—	—	—	—	—	21-35	0-5
	Portland-composite cement ^c	CEM II/A-M	80-94	<----- 6-20 ----->										0-5
		CEM II/B-M	65-79	<----- 21-35 ----->										0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	—	—	—	—	—	—	—	—	0-5	
		CEM III/B	20-34	66-80	—	—	—	—	—	—	—	—	0-5	
		CEM III/C	5-19	81-95	—	—	—	—	—	—	—	—	0-5	
CEM IV	Pozzolanic cement ^c	CEM IV/A	65-89	—	<----- 11-35 ----->					—	—	—	0-5	
		CEM IV/B	45-64	—	<----- 36-55 ----->					—	—	—	0-5	
CEM V	Composite cement ^c	CEM V/A	40-64	18-30	—	<----- 18-30 ----->			—	—	—	—	0-5	
		CEM V/B	20-38	31-50	—	<----- 31-50 ----->			—	—	—	—	0-5	

a The values in the table refer to the sum of the main and minor additional constituents.

b The proportion of silica fume is limited to 10 %.

c In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).