# CLASSIFICATION OF CONSTRUCTION MATERIALS

Traditional building materials can be divided into six main groups:

- i) Rocklike materials
  - Natural rocks (magmatic rocks, sedimentary rocks, and metamorphic rocks)
  - Calcium-based binders (cement, lime, gypsum)
  - Baked soil materials-clay products (brick, tile, porcelain)
  - Glass
  - Concrete (aggregate, cement, chemical admixtures, mineral additives)
- ii) Metals
  - Ferrous metals (pig iron, cast iron, wrought iron, steel)
  - Nonferrous metals (aluminum, copper, lead, brass)
- iii) Wood material
- iv) Plastics (thermoplastics, thermosetting polymers, synthetics, natural resins)
- v) Bituminous materials (asphalt, tar)
- vi) Dyes, varnishes, and glues

# CALCIUM-BASED BINDERS

Substances that are used to hold granular or particulate materials together as a whole are called *binders*. Substances containing large amounts of calcium in its composition are known as "calcium-based binders". This material group, which has a special importance in terms of civil engineering, consists of gypsum, lime and cement.

The types of calcium-based binders that harden after reacting with water and do not soften under the influence of water after hardening are called *hydraulic binders*. Based on this definition, gypsum and air lime are not hydraulic binders. Both produce a chemical reaction when mixed with water, but the hardening of air lime is not due to this reaction. The hardening of the gypsum is due to this reaction. However, if the hardened gypsum comes into contact with water again, it softens. Among the calcium-based binders, only water lime and cement are hydraulic binders.

# GYPSUM

Gypsum is a building material obtained by heating rocks which are in the composition of  $CaSO_4 \times 2H_2O$ , known as gypsum in nature, and evaporating some or all of its water and then grinding it. If the heating is done above 190°C, all the water in the gypsum rock evaporates. The gypsum obtained in this way is known as *anhydrous gypsum*. The reactions associated with the dehydration of the gypsum rock can be given as follows:

 $100^{\circ}\text{C}-190^{\circ}\text{C}$ CaSO<sub>4</sub> × 2H<sub>2</sub>O  $\rightarrow$  CaSO<sub>4</sub> ×  $\frac{1}{2}$ H<sub>2</sub>O +  $\frac{3}{2}$ H<sub>2</sub>O  $\nearrow$ Gypsum rock Gypsum above 190°C CaSO<sub>4</sub> × 2H<sub>2</sub>O  $\rightarrow$  CaSO<sub>4</sub> + 2H<sub>2</sub>O Anhydrous gypsum The gypsum is white in color and is supplied to the market in powder form. Approximately 75% of the gypsum available in the market is the gypsum obtained by heating the gypsum and evaporating 75% of its water. Gypsum can be produced pure or some additives can be added in small amounts to improve its properties. Pure gypsum is mostly used for plaster works and plasterboard (ceiling decorations) works. These gypsums, known as ordinary gypsum, are gypsums with a solidification time of not less than 10 minutes. Gypsum contained additives is used in fine gypsum plaster, plasterboard, mold making, wired plaster (rabiç) works. It is gypsum with a solidification time of not less than 20 minutes. Additives can be added during or after production.

The manufacturing of gypsum involves three stages:

- Crushing of the gypsum rock into small pieces,
- Calcination (heating) of the crushed gypsum rock, and
- Pulverization of the final product.

Gypsum is a low-density stone found since the existence of the world. The mixture of gypsum and water (gypsum paste) is too sticky to be troweled. The addition of sand to the gypsum paste both eliminates the stickiness of the gypsum paste and reduces its shrinkage. Due to its porous structure, its strength is quite low. In addition to water to gypsum ratio, the amount of sand added to the gypsum paste is of great importance in relation with the ultimate strength. Set retarders, set accelerator, plasticizer additives and natural or synthetic fibers can be used to increase the cohesion and tensile strength of gypsum paste and mortar and to improve some of its properties.

# Properties of Gypsum

- Although gypsum sticks well to brick and stone, it does not stick to wood.
- Gypsum may cause corrosion of reinforcement and metal parts due to the sulfate in its composition.
- Hardened gypsum softens when it comes into contact with water. Therefore, it is not used in the outer parts of the buildings. If it is used indoors, it must be protected against the effect of water.
- As the fresh gypsum paste solidifies, there is an increase in its volume. Because of this feature, it is used in the process of removing molds in sculpture.

#### Uses of Gypsum

Gypsum plaster is used in plastering of ceiling and interior panel walls. Gypsum is cast into building blocks for the partition walls of roofing and it finds use in model extraction, mold making and medical application. Gypsum is also used in the ceramic industry due to its porous structure. The porous mold absorbs water from the plastic clay and makes the clay more rigid with less danger of distortion upon removal of the mold.

Gypsum plasters are generally used for plaster works in masonry. Plaster consists of approximately 70-75% sand, 15-25% gypsum and some additives added to control solidification and workmanship quality. Sometimes light aggregates such as perlite or vermiculite can be used instead of sand to provide sound insulation and reduce the building load.

#### LIME

Lime can be divided into two classes as follows:

i) Air lime

White lime	CaO ↗ MgO ↘
<ul> <li>Dolomite lime</li> </ul>	CaO ↘ MgO ↗

ii) Water lime or hydraulic lime

Air lime is a building material obtained by firing calcium carbonate stones (limestone, chalk) at a temperature below the sintering temperature and crushing or grinding them by quenching with water or steam. Limestone contains 56% CaO and 44% CO<sub>2</sub> by weight. It is rarely found in pure form in nature. It usually contains an appreciable amount of magnesium carbonate together with some small amounts of impurities such as silica, alumina, iron oxide, and alkalis. The total amount of impurities in its composition is around 1% to 6%.

Limestone containing calcium carbonate and magnesium carbonate is known as dolomite. When dolomite is heated up to 900-1000°C, the  $CO_2$  in calcium carbonate and magnesium carbonate is removed. The quicklime obtained in this way is rich in CaO and contains a small amount of MgO in its composition.

Lime is obtained from calcium carbonate (limestone,  $CaCO_3$ ) by heating limestone in the furnace. When  $CaCO_3$  is heated between 900°C and 1000°C,  $CO_2$  (and water, if any) is removed from the body, leaving anhydrous calcium oxide, known as quicklime, remains behind, as indicated below:

 $\begin{array}{cccc} 900^{\circ}\text{C}\text{-}1000^{\circ}\text{C} \\ \text{CaCO}_{3} & \rightarrow & \text{CaO} & + & \text{CO}_{2} \nearrow & \text{(Burning process)} \\ \text{Limestone} & & \text{Quicklime} \end{array}$ 

When quick lime is used, it must be quenched with water. When the quicklime is soaked with water, it is slaked as Ca(OH)<sub>2</sub> as follows.

 $CaO + H_2O \rightarrow Ca(OH)_2 + Heat$  (Slaking process) Slaked lime

Since quicklime is not pure, 24.3% water by weight of  $Ca(OH)_2$  is required in the quenching process. During the quenching, an appreciable amount of heat is released, and the volume expands about 2.5 to 3 times. The quench reaction rate and the amount of heat released depend mainly on the factors such as the physical properties and the chemical composition of the quicklime, and the burning temperature. The increase in volume causes the lime to explode and crumble. For this reason, as will be seen later, it is not desired to have high free lime (CaO) in the composition of cements.

Lime used in buildings is slaked lime. Therefore, quenching process is done in plants by using optimum amount of water and mixing it carefully. The quicklime to be slaked is initially crumbled and mixed thoroughly with the optimum amount of water to convert it to  $Ca(OH)_2$ . After quenching process is completed, the resulting product is usually dried and marketed in powder form.

Lime is the main component of lime mortars. When slaked lime is mixed with water, it becomes plastic (malleable). This mixture solidifies and hardens over time. Air lime, as the name suggests, only harden in air. Solidification and hardening occur by taking  $CO_2$  from the atmosphere and depending on the diffusion rate of  $CO_2$ , it may even take months and years. The hardened lime (CaCO<sub>3</sub>) structure is quite porous. Although such a structure negatively affects the strength, it gives it flexibility. As it gets wet and dries, no significant changes occur in its volume.

 $\begin{array}{rcl} \text{Ca(OH)}_2 &+ & \text{CO}_2 & \rightarrow & \text{CaCO}_3 &+ & \text{H}_2\text{O} & & (\text{Hardening process}) \\ \text{Slaked lime} & & \text{Limestone} \end{array}$ 

Water lime or hydraulic lime is quite different from air lime. Water lime is produced by burning and grinding clay-based limestones that contain  $SiO_2$ ,  $Al_2O_3$ , and  $Fe_2O_3$ . When it comes into contact with water, it reacts and hardens, so the water lime is not quenched. Materials which show this effect are called pozzolanic additives. Therefore, water lime is a hydraulic binder.

When quicklime is exposed to atmosphere, it absorbs moisture from the atmosphere and becomes slaked lime. Slaked lime is immediately attacked by the  $CO_2$  present in the atmosphere. This phenomenon is known as *carbonation* and the product formed is CaCO<sub>3</sub>. Thus, quicklime on the surface loses its binding properties. However, it creates a film that protects the interior of the material.

Hydraulic limes can be used for the same purposes as air lime. However, due to their too slow hardening, these materials are not usually preferred for use in construction. Although hydraulic limes possess a certain ability to solidify and harden under water, they are not very suitable for subaqueous construction.

Lime is one of the main components of lime mortars. The strength of lime mortar depends mainly on the factors such as chemical composition of the lime, the amount and the properties of the sand used in the mortar, along with the amount of water used in producing the mortar, and the conditions under which the mortar hardens.

The difference between water lime and air lime is due to the less (CaO+MgO) amount contained in water lime. While CaO is greater than 80% in air lime, in water lime CaO+MgO is greater than 45-65%.

#### Uses of Lime

Air lime is mostly used in buildings. It is used as mortar material in whitewash, plastering and masonry works. Since air lime hardens by taking  $CO_2$  from the air, it is applied in thin layers to facilitate diffusion and accelerate hardening, and the second is not applied before one layer hardens. Another usage area of lime is sand-lime brick and gas-concrete or aerated concrete. Sand-lime brick is obtained by mixing sand rich in silica and lime in certain proportions and pouring it into the mold and compacting, it in the mold and cooking it under pressurized steam. This material looks like a white solid brick. It is used like brick in buildings.

Gas-concrete or aerated concrete is known as Ytong in our country. It is obtained by cooking a mixture of water, sand, lime and some aluminum powder under pressurized steam. Aluminum powder creates pores in the mortar as small air bubbles. Due to its porous structure, its thermal conductivity coefficient is quite low.

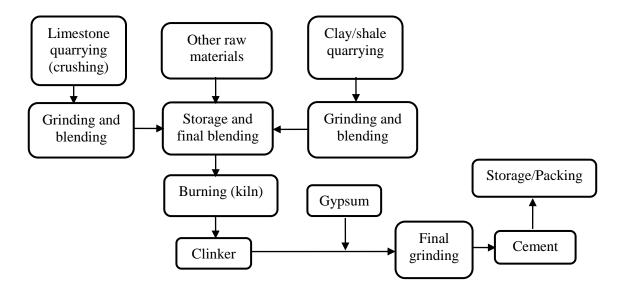
#### PORTLAND CEMENT

Portland cement is one of the most widely used building materials and is made by firing a mixture of limestone and clay and grinding it finely with some gypsum. Portland cement is a hydraulic binder. That is, it hardens as a result of its reaction with water and does not soften in case of contact with water after it hardens. It can be used in all kinds of structural concrete such as in walls, floors, bridges, tunnels, etc. When Portland cement is mixed with coarse aggregate, fine aggregate (sand) and with enough water to ensure a good consistency, concrete is obtained. Variety types of cements are produced today; among those, Portland cement is the most commonly used and it constitutes approximately 75% of the cement production of the world.

Portland cement was discovered by a brick mason Joseph Aspdin in England in 1824. Joseph Aspdin made this product by baking finely ground limestone and clay in an oven. Although there have been great changes in the production technology of Portland cement since then, its composition has remained almost the same. In recent years, many natural and artificial pozzolanic materials are added to clinker in different proportions, and cements with different characteristics compared to Portland cement are produced.

#### MANUFACTURE OF PORTLAND CEMENT

Portland cement is obtained by mixing the calcareous and clayey materials in appropriate proportions and by grinding the clinker obtained by firing at approximately 1400 to 1500°C with a small amount (3-6%) of gypsum. The reason for adding gypsum to the clinker is to slow down the reaction of the cement with water and to control the setting process and thus prevent sudden setting. At high temperature, limestone decomposes into calcium oxide; clay decomposes into silicon dioxide, aluminum oxide and iron oxide. In some cases, the silicon dioxide and iron oxide content in the clinker may be insufficient. In this case, quartz sand or pyrite is added to the mixture. In addition, small amounts of chemicals can be added to reduce the melting temperature of the clinker. The final product is in powder form and gray in color. The gray color is due to iron oxide. Cements that do not contain iron oxide will be white in color. The production process of Portland cement can be summarized as follows.



Schematic illustration of Portland cement manufacturing process

#### COMPOSITION OF PORTLAND CEMENT

The primitive components of the cement are limestone and clay. At high temperature, these two substances chemically react with each other in the rotary kiln to form solid melts with different chemical compositions. The most important stage in cement production is the decomposition of raw materials in the rotary kiln and the formation of active products with different chemical properties after they become semi-melted. In order to obtain quality cement, maximum care must be taken during the production phase.

Limestone and clay decompose at 1400 to  $1500^{\circ}$ C in a rotary kiln. Upon decomposition, the limestone turns into lime (CaO), while the clay turns into silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and a small amount of magnesia (MgO). Cement also contains iron oxide (Fe<sub>2</sub>O<sub>3</sub>) from clay and added soil, as well as sometimes alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and relatively large amounts of sulfur anhydride (SO<sub>3</sub>). Acid and basic elements combine with each other in the rotary kiln to form silicates and aluminates, which form the basis of cement and give the cement its binding property. The potential efficiency of cement varies depending on the proportion of these combined oxides in the cement composition.

In some cases, the amount of silicon dioxide and iron oxide required for the clinker may not be enough, and in this case, for example, quartz sand and/or pyrite are added to the mixture. However, the chemical composition of the mixture forming the raw material must be controlled precisely, considering the composition of the clinker. The table below indicates the range of oxide composition usually found in Portland cement.

Components	Chemical composition	Range, %
Lime	CaO	60-66
Silica	SiO <sub>2</sub>	17-25
Alumina	Al <sub>2</sub> O <sub>3</sub>	3-8
Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	1-5
Sulfite	SO <sub>3</sub>	1-3
Magnesia	MgO	1-4
Alkalis	Na <sub>2</sub> O+K <sub>2</sub> O	0.2-1.3
Free lime	CaO	0-2
Insoluble residue		~2.5
Loss on ignition		~2.5

Typical oxide composition of Portland cement

As can be seen from the table, most of the cement consists of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. These are the main components and are responsible for the performance of the cement. Minor components such as magnesia, sulfite, alkalis, free lime and insoluble residue in the cement composition make up a few percent of the cement by weight.

<u>Sulfite (SO<sub>3</sub>):</u> It can enter the cement composition from gypsum rock or from the fuel used in the burning process. If too much gypsum is added to the clinker, the expansion caused by SO<sub>3</sub> can reach the level of damage to the concrete and therefore standards allow a maximum of 3% SO<sub>3</sub> to be added to Portland cement.

<u>Alkalis (Na<sub>2</sub>O, K<sub>2</sub>O)</u>: Na<sub>2</sub>O and K<sub>2</sub>O make up only a few percent of cement by weight. It has been found that these react with reactive silica in the aggregate and cause the formation of *alkali-silica gel* that creates volume increase in the concrete. This reaction may take months

or years to develop, and expansion in hardened concrete causes disintegration and cracking. The total alkali content in Portland cement should not exceed approximately 0.6% of the cement weight if it is to be used with reactive aggregates in concrete.

<u>Magnesia (MgO) and Free Lime (CaO)</u>: Not all lime in the cement composition may turn into major compounds during burning. The uncombined lime is called *free lime*. Free lime reacts with water, causing an increase in volume. High contents of MgO and free CaO cause expansion upon slaking. As a result of the reaction of free lime and magnesia with water, Ca(OH)<sub>2</sub> (Portlandite) and Mg(OH)<sub>2</sub> (Brucite) are formed, respectively. Their reaction with water is very slow and the reaction is usually completed after the cement has set and hardened, and they often cause cracking of the concrete. Therefore, the relevant standards limit the maximum free CaO and MgO values.

<u>Insoluble Residue</u>: The siliceous substances in the cement composition contain some minerals that are insoluble in hydrochloric acid. Most of them melt during burning, combine with other substances and become acid soluble. The insoluble residue in the composition increases if the burning is not done very well. These substances are collectively known as *insoluble residue*. The amount of insoluble residue should not exceed 5%, according to relevant standards.

<u>Loss on Ignition</u>: Organic compounds lost as a result of burning the cement at about  $1000^{\circ}$ C are substances such as water and CO<sub>2</sub>. High loss of ignition indicates that the cement is stale. Therefore, a decrease in the strength of such cement is expected. The relevant standards allow a maximum of 5% loss on ignition in Portland cement.

# POTENTIAL COMPOUNDS OF PORTLAND CEMENT

The oxides of lime, silica, alumina, and iron oxide melt during the burning process in the kiln and then interact with one another and combined to form about 20 complex solid compounds. Four of these are known as the basic compounds of cement. Approximately 90% of cement consists of these four mixed oxides. These mixed oxides also have an important function on the behavior of the cement. The names, compositions and short names of these four basic compounds are tabulated below.

Name of compound	Oxide composition	Abbreviation	Content, %
Tricalcium silicate	$3$ CaO $\times$ SiO <sub>2</sub>	C <sub>3</sub> S	45-55
Dicalcium silicate	2CaO×SiO <sub>2</sub>	$C_2S$	15-30
Tricalcium aluminate	$3\text{CaO} \times \text{Al}_2\text{O}_3$	C <sub>3</sub> A	8-12
Tetracalcium aluminoferrite	4CaO × Al <sub>2</sub> O <sub>3</sub> × Fe <sub>2</sub> O <sub>3</sub>	$C_4AF$	6-10

Apart from these solid compounds, there is some gypsum rock ( $CaSO_4 \times 2H_2O$ ), free lime (CaO), insoluble residue and loss on ignition in the cement composition. The amount of the main compounds cannot be determined by direct analysis but can be calculated using Bogue formulas (1955) using oxide amounts as follows. To do this, it is necessary to know the oxide composition of the cement or the clinker as determined by their chemical analyses. The terms in the brackets indicate the percentage of the oxides in the mass of cement.

While calculating the main compounds for clinker, the last term, 2.85 (SO<sub>3</sub>), in the expression used in calculating the amount of  $C_3S$ , is ignored.

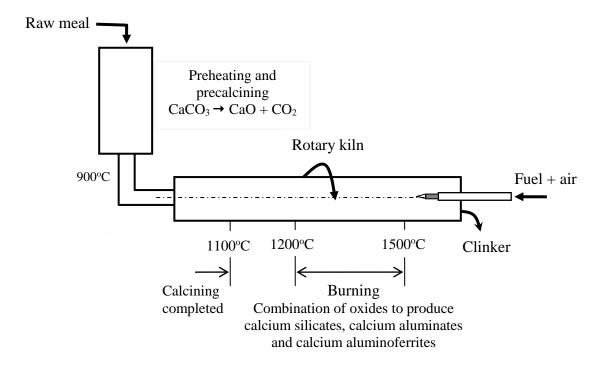
$$C_{3}S = 4.07 \times (CaO) - 7.60 \times (SiO_{2}) - 6.72 \times (Al_{2}O_{3}) - 1.43 \times (Fe_{2}O_{3}) - 2.85 \times (SO_{3})$$
  

$$C_{2}S = 2.87 \times (SiO_{2}) - 0.754 \times (C_{3}S)$$
  

$$C_{3}A = 2.65 \times (Al_{2}O_{3}) - 1.69 \times (Fe_{2}O_{3})$$
  

$$C_{4}AF = 3.04 \times (Fe_{2}O_{3})$$

These compounds start to form at somewhat different temperatures as the clinker heats up when passing down the kiln.  $C_2S$  (often known as belite) starts to form at about 700°C and  $C_3S$  (known as alite) starts to form at about 1300°C. As the temperature rises to about 1450°C most of the belite formed at lower temperatures is transformed into alite.  $C_3A$  and  $C_4AF$  both start to form at about 900°C. The manufacturing process of Portland cement can be simplified as follows:



The main process in the heating of raw meal to produce Portland cement clinker

Silicates ( $C_2S$  and  $C_3S$ ) are the main compounds responsible for the strength development of cement. The efficacy of  $C_3S$  emerges in early ages and  $C_2S$  efficacy occurs in later ages. The contribution of aluminates ( $C_3A$  and  $C_4AF$ ) to the strength development of cement is insignificant compared to silicates. Therefore,  $C_3A$  is not desired to be present in high amounts in the composition of cement, as it contributes very little to strength development.

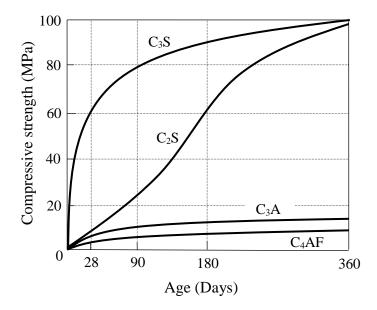
If gypsum is not added, as a result of the rapid reaction of  $C_3A$  with water, the cement makes a flash set. Cements with low  $C_3A$  content have high resistance in sulfate bearing environments.  $C_4AF$  also behaves similarly to  $C_3A$ . It does not contribute to the strength and binding properties of cement. Neither of them directly contributes to the strength and binding properties of cement. They act like a catalyst to speed up the chemical reaction of silicates.

The amount of gypsum added to the clinker is very important and depends on the  $C_3A$  and alkali content of the cement. Excessive amounts of gypsum can cause expansion and consequently damage to the concrete. Therefore, gypsum added to the clinker should be in optimum amount. This amount is usually 3% to 6% of the clinker.

Compound	Amount of heat	Rate of	Strength		Resistance to
Compound	liberated	hydration	Early	Ultimate	chemical attack
C <sub>3</sub> S	Medium	Medium	High	High	Good
$C_2S$	Low	Slow	Low	High	Good
C <sub>3</sub> A	High	Fast	Low	Low	Poor
C <sub>4</sub> AF	Low	Slow	Low	Low	Medium

Some of the properties of the four main compounds are tabulated below.

The composition of any cement depends on the composition, quality and proportions of the raw materials and can therefore vary from one cement plant to another or even in a single factory over time.



Graphical representation of the effect of basic compounds on the strength development of cement

As can be seen from the graph, while  $C_3S$  is the compound responsible for cement paste and thus concrete gaining strength at an early age,  $C_2S$  shows its effect at later ages. At the end of about a year, the contributions of both compounds to the strength development of cement are equalized. It can be said that cements rich in  $C_3S$  gain strength in a short time, whereas cements rich in  $C_2S$  are more resistant to chemical effects and have less volume change. It is more suitable to use cements with low  $C_3S$  and  $C_3A$  content in mass concretes and high  $C_3S$  and  $C_3A$  content in concrete pouring in winter.

Different types of Portland cements can be produced by regulating the proportions of the raw materials to produce the desired compound compositions. The typical values for compound composition of Portland cement may range between 45-55% for  $C_3S$ , 15-30% for  $C_2S$ , 8-12% for  $C_3A$ , and 6-10% for  $C_4AF$ .

#### HYDRATION OF PORTLAND CEMENT

When cement is mixed with water, a series of chemical reactions occur that cause the cement to solidify and harden. These reactions that occur between cement and water are called *hydration*. As a result of hydration, the cement paste loses its plasticity and hardens. This phenomenon is called *setting*. As the hydration progresses, the cement paste hardens and gains strength.

Hydration is a very complex process. During the development of this process, new products that are structurally different from each other, known as *hydration products*, are formed. Hydration starts as soon as cement and water are mixed. Water reacts with each component that makes up the cement, and in this way, different hydration products are formed. The reaction of cement components with water takes place at different speeds and the resulting hydration heat is also different. The amount of heat released mainly depends on the chemical composition of the cement, the fineness of the cement and the curing temperature. The reactions and hydration products for the four main compounds are given below.

 $2C_{3}S + 6H_{2}O \rightarrow 3CaO \times 2SiO_{2} \times 3H_{2}O + 3Ca(OH)_{2}$ Tobermorite gel Portlandite

 $\begin{array}{ccc} 2C_2S + 4H_2O \rightarrow 3CaO \times 2SiO_2 \times 3H_2O + Ca(OH)_2 \\ Tobermorite \ gel \end{array} Portlandite$ 

 $C_2S$  and  $C_3S$  are the main compounds of cement and  $C_3S$  hydrates much faster. As a result of their hydration, *tobermorite* and *portlandite* are formed. Tobermorite gel is the only product with binding property and its abbreviated name is C-S-H. Ca(OH)<sub>2</sub>, known as Portlandite, has no binding property. Both silicates require the same amount of water for hydration, but  $C_3S$  produces three times as much Ca(OH)<sub>2</sub> than  $C_2S$ .

 $C_3A$  reacts very quickly with water and causes the water in the cement paste to be consumed in a short time and thus the paste to solidify rapidly. Because of this,  $C_3A$  hydrates rather quickly than silicates. This is known as *quick set* or *flash set*. If the flash setting is not controlled, the cement paste hardens completely, and silicates are prevented from forming. This is the reason for adding some gypsum rock to the clinker. However, the addition of gypsum rock in excess is undesirable, as it causes the cement paste to expand as a result of hydration. When  $C_3A$  and gypsum react together in an aquatic environment, one or both of the following products are produced.

$$C_{3}A + CaSO_{4} \times 2H_{2}O + 10H_{2}O \rightarrow 3CaO \times Al_{2}O_{3} \times CaSO_{4} \times 12H_{2}O$$
  
Gypsum Calcium sulfoaluminate hydrate

 $\begin{array}{c} \mathrm{C_3A} + 3\mathrm{CaSO_4} \times 2\mathrm{H_2O} + 26\mathrm{H_2O} \rightarrow 3\mathrm{CaO} \times \mathrm{Al_2O_3} \times 3\mathrm{CaSO_4} \times 32\mathrm{H_2O} \\ \mathrm{Gypsum} & \mathrm{Ettringite} \end{array}$ 

The calcium sulfoaluminate hydrate formed at the end of the first reaction does not have a stable structure and it creates expansion since it contains 12 moles of water. When there is excess gypsum in the environment, calcium trisulfoaluminate hydrate, known as *ettringite*, is formed.

$$3\text{CaO} \times \text{Al}_2\text{O}_3 \times \text{CaSO}_4 \times 12\text{H}_2\text{O} + 2\text{CaSO}_4 \times 2\text{H}_2\text{O} + 16\text{H}_2\text{O} \rightarrow \text{Ettringite}$$

The structure of ettringite is stable and it contains 32 moles of water. When there is enough gypsum in the environment, the amount of ettringite increases; cement paste expands and the concrete cracks. When used in concretes exposed to sulphate bearing environments, the  $C_3A$  content of cement is not required to be more than 5%.

When  $C_4AF$  reacts with gypsum and water, products similar to the hydration products formed as a result of the hydration of  $C_3A$  are produced. These products may cause a small amount of heat to be released and expansion, but the heat released is not enough to cause flash setting. These products may cause a small amount of heat to be released and consequently expansion, but the heat released is not enough to cause flash setting.

# HYDRATION HEAT AND STRENGTH DEVELOPMENT

Thermodynamically, the basic compounds in cement have high entropy due to the high heat they take in the kiln. When they react with water, this energy absorbed is released and their hydration takes place exothermically. Since the reactions are exothermic, there may be some technological drawbacks such as cracking of concrete. The heat released as a result of the reaction of cement with water is known as the heat of hydration and the amount of heat released mostly depends on the chemical composition of the cement. The amount of heat released is approximately equal to the sum of the hydration heats of the main compounds determined by their weight in the cement. The typical hydration heat values of the individual pure compounds are given below in tabular form.

<u>Compound</u>	Heat of	hydration	
	J/g	cal/g	
$C_3S$	502	120	
$C_2S$	260	62	The hydration heat of Portland cement is
C <sub>3</sub> A	867	207	approximately 85-100 cal/g.
C <sub>4</sub> AF	419	100	

During the setting and hardening of the cement, the temperature inside the concrete constantly rises and this increase in temperature causes an increase in the heat inside the concrete. The temperature occurring inside the concrete is related to how quickly the heat is released and how quickly it leaves the concrete. The amount of heat released mostly depends on the composition and fineness of the cement and the curing temperature. The amount of heat and the rate of release are important in mass concrete. If the heat that is released does not leave the building quickly, the temperature of the concrete can increase significantly. This is not desirable as it may cause thermal expansion. If the hardened concrete does not cool uniformly, undesirable stresses may arise within the structure and consequently significant cracks may occur in the concrete. On the other hand, the amount of heat released can provide some advantages, especially in winter concrete casting.

In concretes where Portland cement is used, approximately half of the total hydration heat is released within 1 to 3 days, approximately 75% within 7 days and 90% within 6 months. By reducing the  $C_3S$  and  $C_3A$  ratios, the hydration heat of the cement and the rate of heat release can be reduced. While  $C_3S$  is responsible for the strength of cement and therefore concrete for the first 4 weeks (28 days), the effect of  $C_2S$  on the strength occurs at advanced ages. At the end of about one year, the two compounds, contribute approximately equally to the strength of concrete.

#### MORPHOLOGY OF HYDRATED CEMENT PASTE

In the first few minutes of the hydration process, ettringite (calcium sulfoaluminate hydrate) begins to form in the form of needle-shaped crystals. A few hours later, portlandite as large prismatic crystals and tobermorite gel (calcium silicate hydrate) are formed in the form of very fine wiry crystals. After a few days, depending on the alumina/sulfate ratio of the cement, the stable structure of ettringite disrupts and turns into hexagonal plate monosulfate hydrate. Hexagonal-plate morphology is also the characteristic of calcium aluminate hydrates.

Calcium silicate hydrate (C-S-H) is the basic product that constitutes 50-60% of cement paste in volume and gives cement binding property. Portlandite,  $Ca(OH)_2$ , has a prismatic hexagonal crystal structure and constitutes 20-25% of the hydrated cement paste. Due to its small surface area, portlandite does not contribute much to the strength development of cement paste compared to tobermorite. Due to its high solubility in water, the presence of  $Ca(OH)_2$  in cement paste adversely affects the chemical resistance of concrete exposed to acidic environments. Ettringite (calcium sulfoaluminate hydrate) constitutes 15-20% of the cement paste in volume. If ettringite turns into monosulphate hydrate, the durability of concrete in sulphate-containing environments is adversely affected. Compared to C<sub>4</sub>AF, cements with low C<sub>3</sub>A content are more suitable for concrete production exposed to sulphatebearing environments.

At any stage of the hydration process, the cement paste consists of hydration products in the form of a gel, cement grains that have not yet become hydrated, and capillary spaces filled with gel or water. Gel spaces and capillary spaces are different in size. The gel spaces are part of the cement paste and are of the order of 5 to 25 Å in diameter and 28% of the solid gel consists of these spaces. Due to their small dimensions, gel spaces do not have adverse effects on the strength and permeability of the cement paste. On the other hand, the hydrated cement paste has relatively large capillary voids. The size of the capillary voids depends on the water to cement ratio and the degree of hydration of the cement paste. Capillary voids range from 10 to 50 nm in cement paste with a low water to cement ratio that is well hydrated, whereas in pastes with a high water to cement ratio and in the early phase of the hydration process, it varies between 3 and 5  $\mu$ m. The effects of capillary gaps larger than 50 nm on strength and impermeability are negative. The permeability of the hydrated cement paste is mostly related to whether the capillary voids are bridged with each other.

Cement paste contains air voids as well as gel and capillary voids. Although the capillary voids do not have a certain shape, the air voids are generally spherical. While the entrapped air gaps are in the order of 3 mm, the gaps formed by the addition of chemical admixture are around 50-200  $\mu$ m. Both types of air gaps are considerably larger than capillary voids. In this respect, they have negative effects on strength and impermeability.

The cement paste initially consists of cement grains and water-filled voids between these grains. When 1 cm<sup>3</sup> of cement is fully hydrated, a volume of 2 cm<sup>3</sup> is required for the products formed to fit. As the hydration progresses, the resulting gel fills the capillary gaps, reducing both the capillary gaps and the bridging between them. At the end of the first day, the capillary gaps are largely filled with tobermorite gel. At the end of 28 days, the gel structure becomes denser and the physical structure of the paste varies depending on the water to cement ratio. As this ratio increases, a porous structure occurs because the tobermorite gel formed cannot fill all the capillary spaces. This adversely affects the stability of the cement paste.

Due to the tobermorite gel formed on the surface of the cement grains, the hydration of the inner parts of the grains becomes difficult. Hydration of the entire cement may take a long time. Theoretically, hydration is expected to continue as long as the following conditions are present.

- If there is cement whose hydration has not yet been completed,
- Enough water for reactions,
- Suitable ambient temperature.

Hydration is an event that progresses over time and can last for years (10-15 years). For this reason, the strength of the materials produced with cement increases with time.

# WATER IN HYDRATED CEMENT PASTE

Cement paste has a high water holding capacity depending on the ambient humidity and porosity of the paste. Water can be found in several forms in the hydrated cement paste. However, there is no clear line between the different states of water as the water in the paste is constantly decreasing due to the decrease in relative humidity. However, in order to understand the properties of hydrated cement paste, it may be useful to make a classification for the state of water in the paste. In addition to the water vapor in empty or partially water-filled cavities in the cured cement paste, water can be present in the cement paste in the following forms:

i) <u>Chemically bound water</u>: It is water chemically bound within the solid crystal grains forming the gel. Like water in Tobermorite gel  $(3CaO \times 2SiO_2 \times 3H_2O)$ . Chemically bound water cannot be evaporated. This water can be removed by heating and/or superheating the cement paste to 1000°C and above. In this case, the crystal structure of the gel is disrupted.

ii) <u>Adsorbed water</u>: It is the water physically held water by the surface of the solid crystal grains forming the gel. If this water evaporates, the surface tension of the gel particles and the balance of pressure existing between these particles and in the cavities changes. As a result, the gel grains converge. This phenomenon, which occurs as a result of the loss of water of cement paste, is known as *shrinkage*.

iii) <u>Free water</u>: It is water or water vapor in the gel cavities larger than 50 Å, but not held by the gel crystals. The evaporation of free water does not cause any volume change in the cement paste.

# PROPERTIES OF CEMENT

Since the quality of cement is of vital to produce good concrete, the manufacture of cement requires a stringent control. Various tests are carried out to ensure that the cement is of the desired quality and produced in accordance with the relevant standards. These tests are mainly aimed at determining the chemical, physical and mechanical properties of cements. Chemical properties are rather the chemical composition of cements, oxide analysis, amounts of compound composition and similar information. Since these features are determined by the factory at certain intervals and presented to the consumer, not all of them will be discussed here. Only the concepts of lime saturation factor and alumina ratio will be explained.

<u>Lime Saturation Factor (LSF)</u>: The lime saturation factor is calculated by the formula below. The calculated value should not be less than 0.66 and greater than 1.02.

$$LSF = \frac{CaO-0.7 \times (SO_3)}{2.8 \times (SiO_2) + 1.2 \times (Al_2O_3) + 0.65 \times (Fe_2O_3)}$$

The terms in parenthesis refers to the percentage by weight of total cement. A lime saturation factor within the limits indicates that the proportion of raw materials is satisfactory and that there is no excess of lime beyond that which can combine with silica and alumina. An increase in silica at the expense of lime reduces the rate of strength development, whereas more lime than can combine with silica and alumina adversely affects the volume stability of the hardened cement paste.

<u>Alumina Ratio (AR)</u>: The ratio of alumina (aluminum oxide) to iron oxide,  $AR = \frac{Al_2O_3}{Fe_2O_3}$ ,

should not be less than 0.66. The decrease in the ratio may result from an increase in ferric oxide content, which reduces the proportion of  $C_3A$  and increases that of  $C_4AF$  in the cement.

#### Physical Properties

The common physical properties of Portland cement are fineness, specific gravity, normal consistency of cement, setting times, and soundness.

<u>Fineness</u>: It is an indicator that expresses the average size of cement grains. As the cement becomes finer, when mixed with water, the cement surface that will react with water will be more, so the hydration rate will increase, and the cement will gain strength faster. As time elapses, the chemical reaction of the tobermorite gel slows down, so the effect of fineness on strength is not much in the long term. The fineness of the cement is increased by grinding the clinker longer. The effect of cement fineness on hydration rate is significant. The finer the cement, the faster the rate of gaining strength since the amount of heat released at an early age will be higher. For this reason, the fineness is increased in order to produce high strength cement, which gains strength in a short time. Very fine grinding does not affect the total heat released, only the rate at which this heat is released. Moreover, extremely fine grinding does not increase the final strength of the cement. As the fineness of the cement increases, the following properties are acquired:

- Powdered cement is affected more quickly by ambient humidity and deteriorates.
- Setting times shorten.
- Strength increases at an early age.
- Alkali-silica reaction accelerates.
- Shrinkage accelerates and thus cracking increases.
- Bleeding decreases.
- Water demand of cement increases.

Cement grains are approximately 1-100  $\mu$ m in diameter. The fineness of cement can be determined by the sieving method or by measuring the specific surface. While Blaine apparatus is used to determine the specific surface, two sieves with a mesh size of 90  $\mu$ m (0.09 mm) and 200  $\mu$ m (0.2 mm) are used in the sieving method. In the sieving method, it is determined what percentage by weight of the sieved cement remains on the sieve. Specific

surface is the sum of the surface areas of the grains that make up one gram of cement. For Portland cement, the specific surface determined by the Blaine apparatus should be at least  $2800 \text{ cm}^2/\text{g}$  (or  $280 \text{ m}^2/\text{kg}$ ).

<u>Specific gravity</u>: The specific gravity of the cement is measured using a graduated glass flask known as the Le Chatelier balloon. When a certain amount of cement is poured into this graduated glass flask filled with gasoline up to the zero line, the gasoline level increases in proportion to the volume of cement. This value, which is read directly, is the volume of cement. The specific gravity is calculated by dividing the weight of cement by this volume. While the specific gravity of Portland cement is generally around 3.15 g/cm<sup>3</sup>, the specific gravity of cements containing pozzolanic materials is around 2.90 g/cm<sup>3</sup>.

<u>Normal consistency</u>: The cement paste is prepared in a consistency called *normal consistency* in order to ensure that the tests are carried out under standard conditions in determining the setting time. For cements, the normal consistency is determined with the Vicat apparatus. With this apparatus, exactly how much water is required for the cement paste to have a normal consistency is determined. This amount varies depending on the cement composition, type and fineness. Accordingly, the amount of water required for normal consistency is approximately 25% to 33% of the cement weight. Vicat probe with a diameter of 10 mm is inserted under its own weight into the cement paste prepared in this way. If the probe weighing 300 g enters 5 to 7 mm from the bottom, the cement paste is considered to have normal consistency.

<u>Setting time</u>: Setting is the term used to describe the *stiffening* of the cement paste. Broadly speaking, setting refers to the transition from plastic to solid state. The length of time starting from the mixing of the cement and water until the cement paste sets is called the *setting time*. In practice, the terms *initial set* and *final set* are used to describe arbitrarily chosen stages of setting. The setting process is accompanied by temperature changes in the cement paste. Initial set corresponds to a rapid rise in temperature, and final set to the peak temperature.

Setting times are determined on the cement paste prepared in standard consistency. Vicat apparatus is used in the setting time determination test. This time, however, a  $1 \text{ mm}^2$  cross-section needle is used as a probe. When the needle penetration into the fresh cement paste reaches 3 to 5 mm from the bottom, the setting is considered to have started. The time elapsed from the mixing of cement with water until this moment is taken as *the initial set time*. If the needle penetrates at most 1 mm from the top, it indicates that the setting has ended. The time elapsed since the cement is mixed with water until this moment is known as *the final set time*.

The setting time of the cement paste is important because the cement paste can only be shaped during this time. Some cement types set quickly within a few minutes, while others may take relatively longer to harden. For this reason, it is not desired that the setting time is too short or too long. Because it takes a while for the concrete to be prepared, transported, placed in the mold and compacted. It is desirable that the concrete does not solidify during this time. On the other hand, it is desirable for the concrete placed in the mold to solidify and gain strength before a long time passes. For this reason, it is desired that the cement starts to solidify in a normal time and complete its solidification in a normal time.

In order to prevent the cement paste from solidifying in a very short time, gypsum is added to the clinker and grinded. Cement paste can solidify in a very short time in two different ways. One of them is called *flash setting*; the other is called *false setting*. Flash setting takes place when the amount of gypsum is not enough. In the flash setting, the cement paste solidifies as a

result of the release of a significant amount of hydration heat. Because, as a result of the rapid reaction of  $C_3A$  with water, a significant amount of heat is released, the cement paste that solidifies in this way cannot be turned into plastic again.

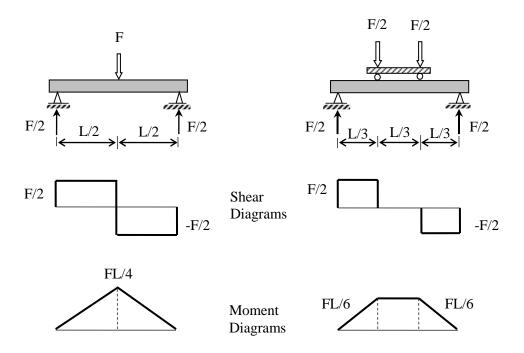
False setting occurs as the gypsum added during the grinding of the clinker loses some of its water due to the high temperature effect in the kiln, and when the cement is mixed with water, it reacts with water and solidifies as a result of taking the lost water into its body. False set is solidification that takes place without any heat being released. The cement paste solidified in this way can be made plastic by mixing only. The difference of a false setting from a flash setting is that solidification takes place without the release of heat.

<u>Soundness</u>: Soundness or volume stability is determined by the Le Chatelier ring in the form of a metal cylinder with a slit on one side. The ring is 30 mm in diameter and 30 mm high. The standard consistency cement paste filled into this ring is kept in water at 20°C for 24 hours, then kept in boiling water for 4 hours and the opening amount of the ring is measured. Two 15 cm long metal rods are attached to both sides of the slit to easily measure the opening amount. The amount of opening is measured as the distance between these metal rods. This test is carried out to determine whether there are harmful amounts of CaO (free lime) and MgO (magnesia) in the cement.

It is essential that the cement paste, once it has set, does not undergo a large change in volume. One restriction is that there must be no appreciable expansion that could cause the hardened cement paste to disrupt under restraint conditions. Such expansion may occur due to reactions of free lime, magnesia, and calcium sulfate. Cements that make this type of expansion are considered to be unsound cements.

# **Mechanical Properties**

Mechanical properties are values related to the standard bending and compressive strength of cements. Standard sand is used to determine the flexural and compressive strength of cements, as in the method adopted by RILEM Cembureau. Standard sand is sand that is very rich in silica (SiO<sub>2</sub>> 88%) and has a granulometry with a grain size ranging from 0.60 to 1.39 mm. The mortar used for the standard bending and compression test is prepared as follows. Accordingly, the mortar is prepared as 1 part of cement (450 g) + 3 parts of standard sand (1350 g) +  $\frac{1}{2}$  part of water (225 g) by weight. The prepared mortar is filled in a 4x4x16 cm triple mold in a standard manner and compacted. The prisms, which are kept in their molds for 1 day, are cured in standard conditions (usually  $20 \pm 2^{\circ}$ C water bath) until the testing day (usually 2, 7 or 28 days) after they are removed from the mold. The prisms removed from the curing room on the day of the test are first subjected to the bending test and divided into two parts, and then a compression test is applied on both parts. The experimental implementation is shown schematically below.



Shear and moment diagrams of a prism in cases of mid-point and two-point loading

Prisms are first subjected to bending test and then compression test. The bending test is performed by loading the prisms either from the midpoint or from the  $\frac{1}{3}$  point. Depending on the loading state, the flexural strength is calculated using the following equations.

$$\sigma_{f} = \frac{3}{2} \times \frac{F \times L}{b \times d^{2}} \qquad \text{(Mid-point loading state)}$$
$$\sigma_{f} = \frac{F \times L}{b \times d^{2}} \qquad (\frac{1}{3} \text{ point loading state})$$

Where F is the breaking load, L is the distance between the supports, b is the width of the prism, and d is the height of the prism.

Compressive strength is calculated as  $\sigma_c = \frac{F}{A}$ . Here, F is the breaking load and A is the crosssectional area of the specimen. In this case, the cross sectional area of the sample is  $A = 4 \times 4 = 16$  cm<sup>2</sup>. Thus, the flexural strength is determined as the average of three measurements and the compressive strength as the average of 6 measurements.

#### CEMENT TYPES

Many of the cements have been developed to make the concrete more durable under a variety of environmental conditions. However, it may not be possible to find a complete answer to the durability problem of concrete considering only the composition of the cement. The basic mechanical and physical properties of hardened concrete such as strength, permeability, resistance to environmental conditions, shrinkage and creep are also affected by factors other than cement composition, although this largely determines the rate of strength gain. Significant differences in the important physical properties of the different types of cements are only observed in the early stages of hydration, in well-hydrated cement paste the differences are minor. There may sometimes be wide differences between cements of normally the same type. However, there are often no sharp discontinuities in the properties of different types of cements, and some of the cements can be considered as more than one type.

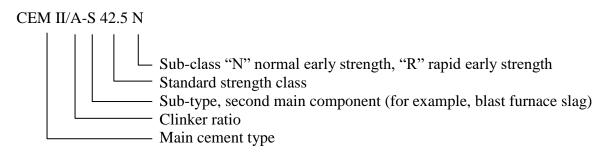
Within the scope of TS EN 197-1, cements are given in 27 different types under 5 groups. The short names, compositions and component proportions of the cements are given in Table 1.

- CEM I Portland cement
- CEM II Portland-Composite Cement
- CEM III Blast-Furnace Slag Cement
- CEM IV Pozzolanic Cement
- CEM V Composite Cement

Table 1. Cements types produced

Main Types	General Cement Types	Composition (%, by mass)			
CEM I	Portland Cement	CEM I 95-100 Clinker			
	Portland-Slag	CEM II/A-S	80-94 Clinker; 6-20 S		
	Cement	CEM II/B-S	65-79 Clinker; 21-35 S		
	Portland-Silica Fume Cement	CEM II/A-D	90-94 Clinker; 6-10 D		
		CEM II/A-P	80-94 Clinker; 6-20 P		
	Portland-Pozzolan	CEM II/B-P	65-79 Clinker; 21-35 P		
	Cement	CEM II/A-Q	80-94 Clinker; 6-20 Q		
		CEM II/B-Q	65-79 Clinker; 21-35 Q		
		CEM II/A-V	80-94 Clinker; 6-20 V		
CEM II	Portland-Fly Ash	CEM II/B-V	65-79 Clinker; 21-35 V		
	Cement	CEM II/A-W	80-94 Clinker; 6-20 W		
		CEM II/B-W	65-79 Clinker; 21-35 W		
	Portland-Baked	CEM II/A-T	80-94 Clinker; 6-20 T		
	Schist Cement	CEM II/B-T	65-79 Clinker; 21-35 T		
		CEM II/A-L	80-94 Clinker; 6-20 L (TOC $\leq$ 0.50)		
	Portland-Lime	CEM II/B-L	65-79 Clinker; 21-35 L (TOC $\leq$ 0.50)		
	Cement	CEM II/A-LL	80-94 Clinker; 6-20 LL (TOC $\leq$ 0.20)		
		CEM II/B-LL	65-79 Clinker; 21-35 LL (TOC $\leq$ 0.20)		
	Portland-Composite	CEM II/A-M	80-94 Clinker; 6-20 (S+D+P+V+W+L+LL)		
	Cement	CEM II/B-M	65-79 Clinker; 21-35 (S+D+P+V+T+L+LL)		
	Blast-Furnace	CEM III/A	35-64 Clinker; 36-65 S		
CEM III	Slag Cement	CEM III/B	20-34 Clinker; 66-80 S		
	Slag Cement	CEM III/C	5-19 Clinker; 81-95 S		
CEM IV	Pozzolanic Cement	CEM IV/A	65-89 Clinker; 11-35 (D+P+Q+V+W)		
	rozzolallic Cellielit	CEM IV/B	45-64 Clinker; 36-55 (D+P+Q+V+W)		
CEM V	Composite Cement	CEM V/A	40-64 Clinker; 18-30 S; 18-30 (P+Q+V)		
CEM V Composite Cement CEM V/B 20-38 Clinker; 31-40 S			20-38 Clinker; 31-40 S; 31-40 (P+Q+V)		
The proportions given in the table are the sum of the major and minor ingredients.					
S: Blast-furnace slag; D: Silica fume; P: Natural pozzolan; Q: Natural calcined pozzolan;					
V: Siliceous fly ash; W: Calcareous fly ash; T: Baked schist; L: Lime (TOC $\leq 0.50$ by mass);					
LL: Lime (TOC $\leq$ 0.20 by mass); TOC: Total organic carbon content.					

In the TS EN 197-1 standard, the definition of cements is made by considering the main cement type, clinker ratio, second main component, standard strength class (28 days) and early strength gain rate. Below is an example of showing the cement type.



The strength classification of cements is given in three classes as 32.5, 42.5 and 52.5 MPa in the relevant standards.

# USAGE AREAS OF CEMENTS

All cements produced in accordance with the standards can be used in the production of all kinds of concrete. However, for concrete with special conditions, the selection of a suitable cement type is indispensable for the performance and service life of the concrete.

<u>Usage areas of CEM I type cements</u>: This type of cement can be used in all types of concrete production. In applications requiring high strength, those with strength of 42.5 MPa or 52.5 MPa are preferred. In cases where high early strength is desired, in cold weather concrete casting, in early molding and repair works, R marked ones should be used. N marked ones should be used in concrete casting under normal conditions.

<u>Usage areas of CEM II type cements</u>: These cements are produced in two types, A and B. There is 6-20% additive in type A and 21-35% in type B. If the additive type has pozzolanic properties such as trass, fly ash or blast furnace slag, especially those with B marked can be used in applications where high strength is not required, especially in places where low hydration temperature is required. Since the ratio of additives in the composition of A marked cements is low, these types of cements have the structure of Portland cement with additives and can be used instead of Portland cement. B marked ones are preferred in structures exposed to water and in applications in contact with aggressive underground waters due to their effects reducing the permeability of concrete.

Cements containing silica fume are suitable for use with super plasticizers in the production of high strength concrete and in concretes where harmful chemical effects are dominant. Since those containing burnt shale show little hydraulic properties, they can be used instead of Portland cement in water structures.

<u>Usage areas of CEM III type cements</u>: These cements are of three types in terms of the blast furnace slag they contain. Types A and B are ideal for concretes with low heat of hydration and resistant to chemical effects. Since these cements have low hydration heat, they are particularly suitable for mass concrete applications. Type C contains 81-95% blast furnace slag. For this reason, it is very resistant to sulfate effect.

<u>Usage areas of CEM IV type cements</u>: These types of cements are pozzolanic and their hydration heat is low. Due to the effect of reducing the permeability of concrete, they are preferred to be used in environments with chemical effects. For example, marine structures and mass concrete are the applications where they are commonly used.

<u>Usage areas of CEM V type cements</u>: These cements contain blast furnace slag, trass and fly ash. Therefore, these cements have high pozzolanic effects. These types of cements are widely used in harmful environments, in marine structures, in the casting of mass concretes.

		Compressive Strength (N/mm <sup>2</sup> )				
Property	Cement Type	Early Strength		Standard Strength		
		2 Days	7 Days	28 I	28 Days	
	CEM 32.5 N		≥16.0	> 22.5	≤ 52.5	
	CEM 32.5 R	≥10.0		≥ 32.5		
Strength	CEM 42.5 N	$\geq 10.0$		> 12.5	≤ 62.5	
(N/mm <sup>2</sup> )	CEM 42.5 R	≥20.0		≥ 42.5		
	CEM 52.5 N	$\geq$ 20.0		> 52.5		
	CEM 52.5 R	≥ 30.0		≥ 52.5		
Initial Setting	CEM 32.5			75 min		
Time	CEM 42.5	$\geq$ 60 min				
Time	CEM 52.5		$\geq 1$	45 min		
Volume	CEM 32.5	≤ 10 mm				
Stability	CEM 42.5					
Subility	CEM 52.5					
	CEM 32.5 N					
	CEM 32.5 R	≤%3.5				
	CEM 42.5 N	(CEM I, O	CEM II, CEM	I IV and CEM V	/)	
Sulfite Content						
(SO <sub>3</sub> ), (%)	CEM 42.5 R					
	CEM 52.5 N	≤ %4.0				
	CEM 52.5 R					
	CEM III	(All CEM III type cements)				
Loss on	CEM 32.5					
Ignition	CEM 42.5	$\leq$ %5.0				
-8	CEM 52.5	(for only CEM I and CEM III)				
Insoluble	CEM 32.5					
Residue	CEM 42.5	$\leq$ %5.0				
rebrade	CEM 52.5	(for only CEM I and CEM III)				
	CEM 32.5					
Chloride	CEM 42.5	$\leq$ %0.10				
	CEM 52.5					
	res determining th		s correspond	to the 28-day st	andard	
	ength of the cemen					
	sign in the cement			cement is norma	l strength	
	sign (R) is early str	•			_	
Note 3. There is	no limit on the fin	eness of ceme	nte in FN eta	ndards. The mai	nufacturare	

 Table 2. Some characteristics properties of cements

Note 3: There is no limit on the fineness of cements in EN standards. The manufacturers could adjust the degree of grinding to obtain the required strength value.

#### BLENDED PORTLAND CEMENTS

As earlier stated, Portland cement is manufactured by intergrinding clinker with a small amount of gypsum rock. The term "blended Portland cement" is confined to blends of Portland cements with either rapidly cooled blast furnace slag or pozzolans or pozzolanic materials such as fly ash and silica fume. These materials do not possess binding properties in themselves; however, when they are in a finely divided form and combined with calcium hydroxide in the presence of moisture, they possess hydraulic binding properties. Blended cements are produced by intergrinding a mixture of Portland cement clinker with each of these materials together with 3-6% gypsum rock. Volcanic tuff and volcanic ash are the commonly used natural pozzolans for manufacturing blended cements. Due to its pozzolanic behavior, granulated blast furnace slag is used in manufacturing slag cements.

In the production of blended cements, some of the clinker is replaced by pozzolanic materials and they are interground together. The amount of pozzolanic material replacing clinker varies between 6 and 94%. When blended cement is mixed with water, the  $C_3S$  compound in Portland cement starts to produce C-S-H gel and calcium hydroxide. The calcium hydroxide thus produced and the pozzolanic material react together to produce new C-S-H gel.

Cost saving is probably the main reason for the development of blended Portland cements, as they contain less clinker. In certain aspects, the blended cements perform better than Portland cements. The strength development of pozzolan starts after the formation of calcium hydroxide. Therefore, the heat of hydration, and strength development of the blended cements are low in the early days. However, the ultimate strength of the blended cement reaches that of Portland cement.

# COMPARISON OF CEMENTS

Cements other than Portland cements are produced by adding gypsum and some pozzolanic materials to Portland cement clinker during grinding. Therefore, in terms of production, cements are divided into two as Portland cements and blended cements. Portland cements are general purpose cements. They can be used in all kinds of concrete production. Usage areas of blended cements are similar to Portland cements. Blended cements have some advantages and some disadvantages compared to Portland cements.

#### Advantages:

- As the pozzolanic materials used as additives in production bind the free lime in the cement, the chemical resistance increases.
- The hydration temperature and the release rate of this heat are low. In this respect, it is especially suitable for mass concrete production and concrete casting in hot weather.
- The concrete they are used has less permeability due to their high fineness.
- Their frost resistance is higher.
- Even though the sales prices are very close, their production is cheaper than Portland cement. This is beneficial for the country's economy.
- The use of artificial pozzolanic materials as additives is ecologically beneficial.

#### Disadvantages:

- They gain strength more slowly than Portland cement.
- Since their hydration heat is low, they are not suitable for concreting in cold weather.
- Due to the slow strength gain, it may be necessary to keep the concrete in the mold for a longer time and to maintain suitable humidity conditions for a longer time.
- They should be ground finer than Portland cement.
- More water is needed for the same consistency compared to Portland cement since they are grinded finer. This increases the shrinkage. For this reason, it is not very suitable for use in narrow section building elements and high dosage concrete production.
- Because they are finer, they are more likely to degrade by air humidity.

# STORAGE OF CEMENT

Cements can deteriorate by hydration as a result of being affected by moisture. That is, their binding properties and therefore their strength may be reduced. Cement affected by moisture becomes lumpy. If the lumps in the cement do not disperse when crushed by hand, this cement should not be used in reinforced concrete construction. Especially cements with higher fineness are more prone to degradation in this way. Therefore, attention should be paid to the storage conditions of blended cements. They should be stored at the construction site in paper bags, on wooden flooring, in a closed place or outdoors, but covered. The bags are stacked not exceeding two meters or 12 bags on top of each other. If the cement is stored in a silo at the construction site, the probability of deterioration is considerably reduced.

The strength of bag cement stored for more than three months decreases. The amount of reduction is around 5% per month in proportion to the age of the cement. Especially high strength cements with pozzolan additives should not be kept for more than one month and others for more than two months. When the quality of stored cement is doubtful, standard strength tests and/or loss on ignition tests should be performed.

# SPECIAL CEMENTS

These cements are not general purpose but defined as "special cements". The important ones are white Portland cement, mortar cement, sulfate resistant cement, aluminous cement.

White Portland Cement (WPC 32.5 and WPC 42.5): It is a Portland cement whose raw materials are white clay, limestone and marble powder. Due to the low amount of iron oxide, this white cement is used in applications where aesthetic appearance is important. These cements, which are widely used in floor tiles, urban furniture production, artificial stone, plaster, mosaic and flooring works, are more expensive than Portland cement due to their different raw materials and different production methods.

<u>Mortar Cement (HÇ 16)</u>: It is cement with a pozzolanic substance up to 60% in its composition. It is used for filling, plaster and mortar works that do not require high strength. Mortars produced with mortar cement have more plastic properties and less shrinkage than those produced with Portland cement.

<u>Sulfate Resistant Cement (SRC 32.5 and SRC 42.5)</u>: The most unstable compound of cement against sulfate attack is  $C_3A$ . Since the amount of  $C_3A$  in Portland cement is 8 to 11%, it is

not reasonable to use this type of cement in reinforced concrete structures exposed to sulfate effect. Sulfate resistant cements are produced with a maximum of 5%  $C_3A$ . These types of cements are most suitable for sea water and sulfate water containing grounds and other sulfate bearing environments.

<u>Aluminous Cement</u>: These cements are produced by burning bauxite and limestone at 1700°C. The amount of alumina they contain is more than 30%. Its main composite compounds are calcium aluminate (CA) and C<sub>2</sub>S. Its chemical reactions are different from Portland cement and the hydration process is very fast. Since it is acidic, it is not damaged by acids. Since  $Ca(OH)_2$  is not formed among the hydration products, it is very resistant to chemical effects. It is a cement resistant to high temperatures. These cements are mixed with Portland cements and used to prevent water leakage in dams and tunnels, and at the same time, because they are resistant to high temperatures, they are used in places such as furnaces and chimneys.