

Chemical Composition of Cement

The raw materials used for the manufacture of cement consist mainly of lime, silica, alumina and iron oxide. These oxides interact with one another in the kiln at high temperature to form more complex compounds. The relative proportions of these oxide compositions are responsible for influencing the various properties of cement; in addition to rate of cooling and fineness of grinding. Table 1.4 shows the approximate oxide composition limits of ordinary Portland cement.

Table 1.4. Approximate Oxide Composition Limits of Ordinary Portland Cement

<i>Oxide</i>	<i>Per cent content</i>
CaO	60–67
SiO ₂	17–25
Al ₂ O ₃	3.0–8.0
Fe ₂ O ₃	0.5–6.0
MgO	0.1–4.0
Alkalies (K ₂ O, Na ₂ O)	0.4–1.3
SO ₃	1.3–3.0

The identification of the major compounds of cement is largely based on Bogue’s equations and hence it is called “Bogue’s Compounds”. The four compounds usually regarded as major compounds are listed in table 1.5.

Table 1.5. Major compounds of cement

<i>Name of Compound</i>	<i>Formula</i>	<i>Abbreviated Formula</i>
Tricalcium silicate	3 CaO.SiO ₂	C ₃ S
Dicalcium silicate	2 CaO.SiO ₂	C ₂ S
Tricalcium aluminate	3 CaO.Al ₂ O ₃	C ₃ A
Tetracalcium aluminoferrite	4 CaO.Al ₂ O ₃ .Fe ₂ O ₃	C ₄ AF

It is to be noted that for simplicity’s sake abbreviated notations are used. C stands for CaO, S stands for SiO₂, A for Al₂O₃, F for Fe₂O₃ and H for H₂O. The equations suggested by Bogue for calculating the percentages of major compounds are given below.

$$C_3S = 4.07 (\text{CaO}) - 7.60 (\text{SiO}_2) - 6.72 (\text{Al}_2\text{O}_3) - 1.43 (\text{Fe}_2\text{O}_3) - 2.85 (\text{SO}_3)$$

$$C_2S = 2.87 (\text{SiO}_2) - 0.754 (3\text{CaO.SiO}_2)$$

$$C_3A = 2.65 (\text{Al}_2\text{O}_3) - 1.69 (\text{Fe}_2\text{O}_3)$$

$C_4AF = 3.04 (Fe_2O_3)$

In addition to the four major compounds, there are many minor compounds formed in the kiln. Two of the minor oxides namely K_2O and Na_2O referred to as alkalis in cement are of some importance and Expressed in terms of Na_2O . These alkalis basically react with active silica in aggregate and produce what is called alkali-silica gel of unlimited swelling type under favourable conditions of moisture and temperature in voids and cracks and further it causes disruption and pattern cracking.

Tricalcium silicate and dicalcium silicate are the most important compounds responsible for strength. Together they constitute 70 to 80 per cent of cement. The average C_3S content in modern cement is about 45 per cent and that of C_2S is about 25 per cent.

The calculated quantity of the compounds in cement varies greatly even for a relatively small change in the oxide composition of the raw materials. To manufacture a cement of stipulated compound composition, it becomes absolutely necessary to closely control the oxide composition of the raw materials.

SO_3 also appear in cement analysis which comes from adding gypsum (4-6) % during clinker gridding. The Iraqi and British specification for normal high rapid Portland cement pointed that SO_3 content must be between (3-2.5)% according to type of cement and C_3A content.

The percentage of MgO in cement which is come from Magnesia compounds in raw material. is about (4-1)% and 5% as maximum range to control expansion from hydration of this oxide in hard concrete.

An increase in lime CaO content beyond a certain value makes it difficult to combine with other compounds and free lime will exist in the clinker which causes unsoundness in cement.

Insoluble residue is that part of the Cement non-soluble in hydrochloric acid HCl and arise mainly from non active silica to form cement compounds dissolved in this acid therefore it express the completeness of the chemical reactions inside the rotary kiln.

Loss on Ignition

Loss on ignition is calculated by heating up a cement sample to $900 - 1000^\circ C$ until a constant weight is obtained. The weight loss of the sample due to heating is then determined. A high loss on ignition can indicate prehydration and carbonation, which may be caused by improper and prolonged storage. Iraqi specification limits is 4% as maximum for normal and rapid hardening Portland cement.

Setting and Hardening of Cement

Setting Process: The process of losing plasticity with time and becoming dense, which is formed by mixing the cement and water. It happened in two stage initial setting and final setting.

Hardening Process: The process of forming hardening cement paste, which loses plasticity and its strength increases with time.

Factors such as fineness and types of cement, blend of gypsum, age, water content, temperature and humidity which influence setting and hardening of Portland cement.

Setting is important in concrete work to keep fresh concrete plastic for enough time which helps the processes of transporting, casting, and compaction.

There are four stage occurs during setting of cement, First : when mixing cement with water, a rapid heat evolution, lasting a few minutes, This heat evolution is probably due to the reaction of cement compounds then, heat evolution ceases quickly. Second: this stage called “dormant period” and last (1-4) hours. Also cement particles start to form initial layer of hydration product. Bleeding and sedimentation appear in this stage. Third: Next heat evolution is on account of dissolution of weak gel which formed first on surfaces of C_3S crystals so water will reach these surfaces and starts to form new gel. This stage last about 6 hours. Forth: in this stage cement begin to harden and gain strength.

False and flash Setting

False setting is the rapid development of rigidity in freshly mixed Portland cement paste, mortar, or concrete occurs after few minutes of mixing cement with water without the generation of much heat. It can be controlled by re-mixing without additional water or strength loss. Causes of false setting are:

1. Drying of gypsum: when gypsum ($CaSO_4 \cdot 2H_2O$) gridding with hot clinker it loss 75% of its water and formed ($CaSO_4 \cdot 1/2 H_2O$) and if temperature of clinker increase gypsum loss all water in its composition and formed $CaSO_4$. When water add to cement $CaSO_4$ react causes rapid setting.
2. Bad storage: alkalis in cement react with carbon dioxide forming Alkali carbonate which reacts with calcium hydroxide forming $CaCO_3$ causing setting of cement paste.
3. Activate effective C_3A exposed to humidity: during bad storage water adhere on cement particles surface and during mixing these active surface combined rapidly with water within minutes.

Flash setting is a rapid development of rigidity in freshly mixed Portland – cement paste, mortar, or concrete. Further mixing can't dispel this rigidity, and a large amount of heat is produced in the process. It happened Due to rapid reaction of aluminates – when insufficient sulfate present so to prevent It A small amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) gridding with the cement clinker retards the hydration reaction of tricalcium aluminate so that the calcium silicates can set firstly.

Soundness of Cement

It refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion. This destructive expansion is caused by excessive amounts of free lime (CaO), (SO_3) or magnesia (MgO).

The hydrating speed of the over burnt CaO or MgO is slow, CaO or MgO begins to hydrate after cement hardening and causes the hardened cement to expand and crack.

When added too much, gypsum continues to react with calcium aluminate hydrate to form calcium sulfoaluminate hydrate, whose volume increase 1.5 times as big as gypsum and causes the hardened cement paste to crack. At this time, sulfoaluminate hydrate is called cement bacillus.