Chemical Composition of Cement

Chemistry of cement

the raw materials used in the manufacture of Portland cement consist mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln and a state of chemical equilibrium is reached.

the rate of cooling will affect the degree of
crystallization and the amount of amorphous material present in the cooled clinker.

The major four compounds of cement are listed in the following table together with their abbreviated symbols, used by cement chemists, describes each oxide by one letter, CaO = C; Si02 = S; Al2O3 = A; and Fe203 = F. Likewise, H20 in hydrated cement is denoted by H.

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalciumalumino ferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

The percentage of the four compounds of Portland cement is calculated by using **Bogue's equations as** given below.

C3S = 4.07(CaO) - 7.60(SiO2) - 6.72(Al2O3) - 1.43(Fe2O3) - 2.85(SO3)

C2S = 2.87(SiO2) - O.754 (3CaO.SiO2)

C3A = 2.65 (Al2O3) - 1.69 (Fe2O3)

C4AF = 3.04(Fe2O3)

Where, the terms in brackets represent the percentage of the given oxide in the total mass of cement. Recently, these compositions are determined by x-ray diffraction.

Worked example of a Bogue calculation:

Clinker Analysis										
SiO_2	***Al_2O_3***	***Fe_2O_3***	***CaO***	***MgO***	***K_2O***	***Na_2O***	***SO_3***	***LOI***	***IR***	***Total***
21.5	***5.2***	***2.8***	***66.6***	***1.0***	***0.6***	***0.2***	***1.0***	***1.5***	***0.5***	***98.9***
Free lime = 1.0% CaO										

Using the above analysis, the calculation is as follows:

Combined CaO = (66.6% - 1.0% free lime) = 65.6%

This is the figure we use for CaO in the calculation.

From the analysis, we have:

CaO= 65.6%; SiO_2=21.5%; Al_2O_3=5.2% and Fe_2O_3=2.8%

The Bogue calculation is therefore:

$C_3S = 4.0710CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 - 6.7187Al_2O_3$

$C_2S = 8.6024SiO_2 + 1.1Fe_2O_3 + 5.0683Al_2O_3 - 3.0710CaO$

$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$

$C_4AF = 3.0432Fe_2O_3$

Therefore:

$C_3S = (4.0710 \text{ x } 65.6)-(7.6024 \text{ x } 21.5)-(1.4297 \text{ x } 2.8)-(6.718 \text{ x } 5.2)$

$C_2S = (8.6024 \text{ x } 21.5)+(1.0785 \text{ x } 2.8)+(5.0683 \text{ x } 5.2)-(3.0710 \text{ x } 65.6)$

$C_3A = (2.6504 \text{ x } 5.2)-(1.6920 \text{ x } 2.8)$

$C_4AF = 3.0432 \text{ x } 2.8$

So:

C_3S = 64.67%

C_2S = 13.17%

C_3A = 9.04%

C_4AF = 8.52%

The silicates, C3S and C2S, are the most important compounds, which are responsible for the strength of hydrated cement paste. In reality, the silicates in cement are not pure compounds, but contain minor oxides in solid solution.

These oxides have significant effects on the atomic arrangements, crystal form, and hydraulic properties of the silicates.

The presence of C_3A in cement is undesirable: it contributes little or nothing to the strength of cement except at early ages, and when hardened cement paste is attacked by sulfates, the formation of calcium sulfoaluminate (ettringite) may cause disruption. However, C_3A is beneficial in the manufacture of cement in that it facilitates the combination of lime and silica.

C_4AF is also present in cement in small quantities, and, compared with the other three compounds, it does not affect the behavior significantly; however, it reacts with gypsum to form calcium sulfoferrite and its presence may accelerate the hydration of the silicates.

The amount of gypsum added to the clinker is crucial, and depends upon the C_3A content and the alkali content of cement.

Increasing the fineness of cement has the effect of increasing the quantity of C_3A, and this raises the gypsum requirement. An excess of gypsum leads to expansion and disruption of the set cement paste.

The optimum gypsum content is determined on the basis of the generation of the heat of hydration, so that a desirable rate of early reaction occurs, which ensures that there is little C_3A available for reaction after all the gypsum has combined.

In addition to the main compounds there exist minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O, and Na_2O; and usually the amount is not more than a few percent of the mass of cement.

Two of the minor compounds are of interest: the oxides of sodium and potassium, Na2O and K2O, known as ***the alkalis*** (although other alkalis also exist in cement). They have been found to react with some aggregates, the products of the *alkali-aggregate* reaction causing disintegration of the concrete, and have also been observed to affect the rate of the gain of strength of cement.

According to I.Q.S. No. 5 As shown in the table below the oxide composition limits of Portland cements.

Oxide	**Content%**
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis	0.2-1.3
SO_3	1-3

The ***insoluble residue*** **(IR)**, it is that part of cement sample that is insoluble in HCl. It comes from the impurities in gypsum. The maximum insoluble residue permitted by Iraqi specification no. 5 is 1.5% by weight.

The ***loss on ignition*** **(L.O.I)** it is the loss of the cement sample weight when it exposes to the red temperature (at 1000° C). It shows the extent of carbonation and hydration of free lime and free magnesia due to the exposure of cement to the atmosphere. Also, part of the loss in weight comes from losing water from the gypsum composition. The maximum loss on ignition permitted by Iraqi specification no. 5 is 4% by weight.