Lecture 2

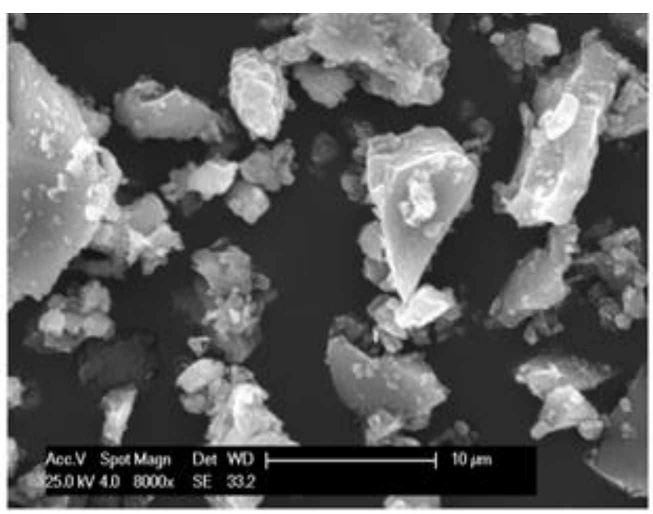
Cement, definition, manufacturing and basic chemistry

Cement is invented by Joseph Aspdin in 1824. The name of Portland cement came from the similarity between the concrete made by this cement and a widely-used building stone in England (Portland stone). However, cementitious and binding materials are used firstly by ancient Egyptians and Romans. They used gypsum and calcite after burning them with water and sand to form binding materials for construction.

Cement

Anhydrous Portland cement is a grey powder composed of angular particles typically in the size range from 1 to 50 μm. It is produced by pulverizing a clinker then supplementing the resulting powder with a small amount of calcium sulfate, the clinker being a heterogeneous mixture of several compounds produced by high-temperature reactions between calcium oxide and silica, alumina, and iron oxide.

Cement grains at macro level



Cement grains at micro level

Manufacturing of cement:

The main steps of cement manufacturing can be summarised into five main steps:

1- Quarrying (collection of raw materials: $CaCO_3$ and Clay)

2- Mixing and grinding (raw material with or without water)

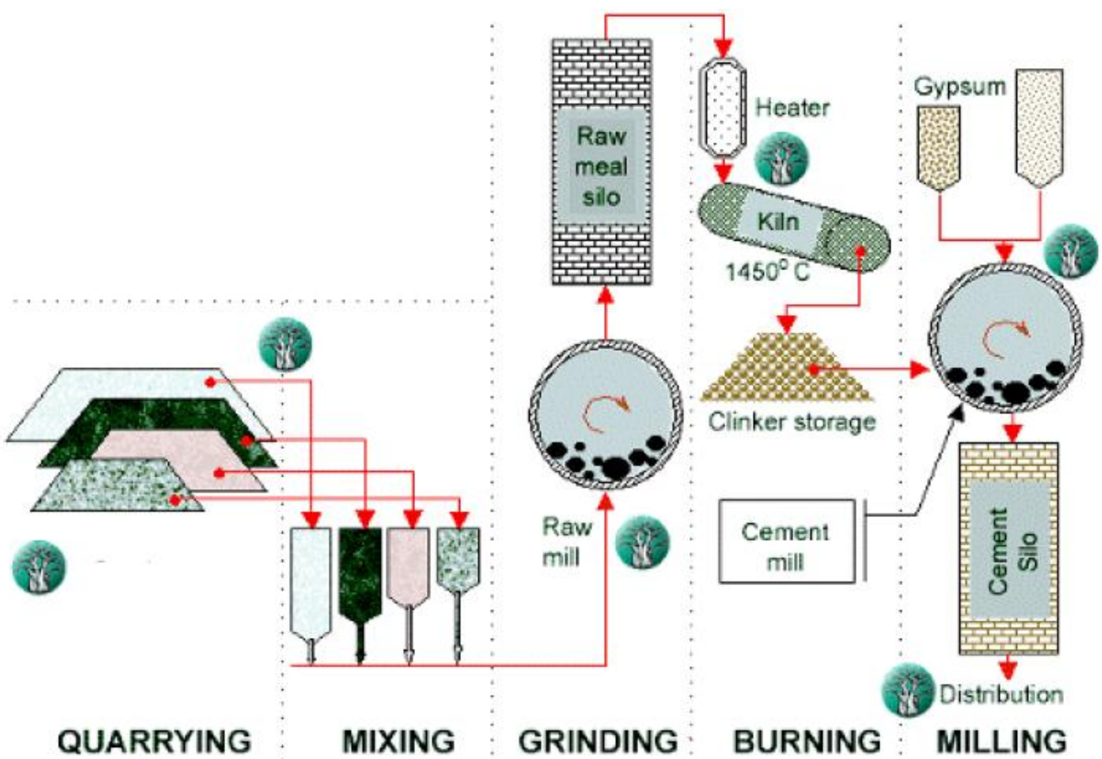
- Dry method
- Wet method

What are the differences between them?

3- Burning (Rotary kiln to about 1450 C: D: about 2.7 and L: 23-60m with a decline angle why?)

4- Milling (What is the benefit of adding Gypsum in this stage?)

5- Marketing



A diagram showing the main steps of cement manufacturing

The main chemical changes in the rotary kiln are:

- Heating of $CaCO_3$ and emission of CO_2 (de-carbonation). Now, what is the main disadvantage of cement manufacturing and how to reduce it? Give your suggestions!
- Complex chemical reactions between CaO and clay minerals (SiO_2 and Al_2O_3) to create the main compounds of cement.(See next section)
- 20-30 % of the material will milt and re-agglomerate again to form the clinker at clinkering temperature (1400-1500 ºC).
- Formation of cement clinker with a diameter of (10-25) mm.

<u>Basic chemistry of cement:</u>

Main compounds of cement are shown in below Table:

Name of the Compound	Formula	Abbreviated Formula	Typical Compound Composition Percent
Tricalcium Silicate	$3\ CaO\ SiO_2$	C3S	54.1
Dicalcium Silicate	$2\ CaO\ SiO_2$	C2S	16.6
Tricalcium Aluminate	$3\ CaO\ Al_2O_3$	C3A	10.8
Tetracalcium Aluminoferrite	$4\ CaO\ Al_2O_3\ Fe_2O_3$	C4AF	9.1

<u>Abbreviations in cement chemistry</u>

CaO = C

SiO_2 = S

Al_2O_3 = A; and

Fe_2O_3 = F.

Likewise, H_2O in hydrated cement is denoted by H, and SO_3 by $\bar{S}$.

Bogue equations to compute the main compounds of cement from knowing the main oxides:

C3S = 4.07(CaO) – 7.6 (SiO_2) – 6.72 (Al_2O_3) – 1.43 (Fe_2O_3) – 2.85(SO_3)

C2S = 2.87(SiO_2) – 0.754(C3S)

C3A = 2.65(Al_2O_3) – 1.69(Fe_2O_3)

C4AF = 3.04(Fe_2O_3)

Main and minor oxides in typical cement are shown in Table below:

Oxide	**Percent**
CaO	63
SiO_2	20
Al_2O_3	6
Fe_2O_3	3
MgO*	1.5
SO_3**	2
K_2O, Na_2O (Alkalis)***	1
Others: Mn2O3، TiO2	1
Loss on Ignition (LOI)	2
Insoluble Residue (IR)	0.5

* Minor oxide: Should not exceed 5% why?

** Minor oxide: Comes from Gypsum – important to determine the setting time.

*** Minor oxide: Should not exceed 1% why?

<u>Loss on ignition (LOI)</u> is the weight loss due to heat of a cement sample to 1000°C. A high loss on ignition indicates a pre-hydration and carbonation. This may be due improper and prolonged storage. Iraqi specification IQS and British Standards BS limit is 4% as maximum.

<u>Insoluble residue (IR)</u> is a part of the cement that cannot be dissolved using hydrochloric acid HCl. It is a measure of impurities in cement. British Standards and American Standards ASTM limit are 1.5% and 0.75% as maximum.

IQS, BS,ASTM?

<u>Properties of main compounds in cement:</u>

A- Cement Silicates (C2S and C3S)

<u>C3S</u>

- C3S+C2S represent about 75% by weight of cement and they are responsible for strength gain.
- Greater percent than C2S.
- Hydrates faster than C2S (take about 1 year for complete hydration).
- Small - no color equally dimensions grains.
- Needs 24% of water by weight of cement for complete hydration.
- Reacts with water to form Tobermorite (CSH) and Portlandite (CH):

$$2\,C_3S \quad + \quad 6\,H \rightarrow \quad \underset{61\%}{C_3S_2H_3} \quad + \quad \underset{39\%}{3\,CH}$$

- Responsible for early strength gain.
- Cement contains high percentages of C3S has less resistance to aggressive environment compared with high C2S content.

C2S

- Three forms: **A-** α C2S at degree greater than 1450 ºC, **B-** βC2S at degree = 1450 ºC and **C-** γC2S at degree 675 ºC.
- Twin-rounded grains.
- Hydrates slower than C2S (take about 4 year for complete hydration).
- Needs 21% of water by weight of cement for complete hydration.
- Reacts with water to form Tobermorite (CSH) and Portlandite (CH):

$$2\,C_2S \quad + \; 4\,H \rightarrow \quad C_3S_2H_3 \quad + \quad CH$$

82% 18%

B- Cement Aluminates (C3A and C4AF)

C3A

- Less percentage in cement
- It is mainly responsible for cement setting with C4AF.
- Prismatic dark grains
- Reacts with water to form Ettringite (AFt/ AFm) + Δ

$$C_3A \quad + \; SO_3 + 6\,H \rightarrow C_3A\overline{S}\,H_6$$

- Can react with sulfates salts and cause expansion.

C4AF

- The smallest percentage in cement
- Can react with Gypsum to form calcium sulfa ferrite.
- Responsible for the grey color of cement sue to the presence of Fe_2O_3

After knowing the cement chemistry, what are the ideas and suggestions to develop cement manufacturing and cement quality?