INTRODUCTION TO CEMENT

Classification – Manufacture – Properties and Hydration of Cement

Contents

Introduction

"A cement is a binder, a substance that sets and hardens and can bind other materials together. It principal constituents for constructional purpose are compounds of Ca(calcareous) and Al + Si (argillaceous)"

Chemical Composition of Cement	
Lime	63%
Silica	22%
Alumina	06%
Iron oxide	03%
Gypsum	01 to 04%

The cements have property of setting and hardening under water, by virtue of certain chemical reaction with it and are called '***hydraulic cements***'

Classification of Cements

- Cements
  - Natural Cement
  - Puzzolana Cement
  - Slag Cement
  - Portland Cement

It is the variety of artificial cement. It is called Portland cement because on hardening (setting) its color resembles to rocks near Portland in England.

Portland Cement

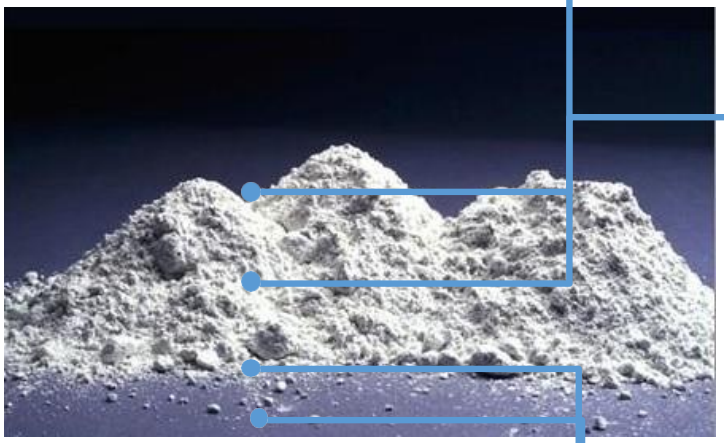
"An extremely finely ground product by calcinising together , at above 1500°C , an intimate and properly proportioned mixture of argillaceous (clay) and calcareous (lime) raw materials, without the addition of anything subsequent to calcination , excepting the retarder gypsum"

Pile of Portland cement

Clinker	CCN	Mass %
Tricalcium silicate $(CaO)_3 \cdot SiO_2$	C_3S	45–75%
Dicalcium silicate $(CaO)_2 \cdot SiO_2$	C_2S	7–32%
Tricalcium aluminate $(CaO)_3 \cdot Al_2O_3$	C_3A	0–13%
Tetracalcium aluminoferrite $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	0–18%
Gypsum $CaSO_4 \cdot 2\ H_2O$		2–10%
Calcium Oxide - CaO		2%
Magnesium Oxide - MgO		4%

Chemical Composition of Portland Cement

Raw materials of Portland Cement and it's use



Calcareous materials, CaO [eg. Limestone]

- Principal Constituent and its proportion can be regulated
- Excess of lime reduces the strength and makes the cement expand & disintegrate
- Lesser amount of lime also reduces the strength by quick setting

Argillaceous materials, Al_2O_3 and SiO_2 [eg. Clay]

- Imparts strength
- Makes quick setting
- Excess of alumina weakens the cement

Powdered Coal or fuel oil

- For burning

Gypsum ($CaSO_4$ $2H_2O$)

- Retards and enhances quick setting

Manufacturing Cement

1. Mixing and Crushing of raw materials
    a) Dry process

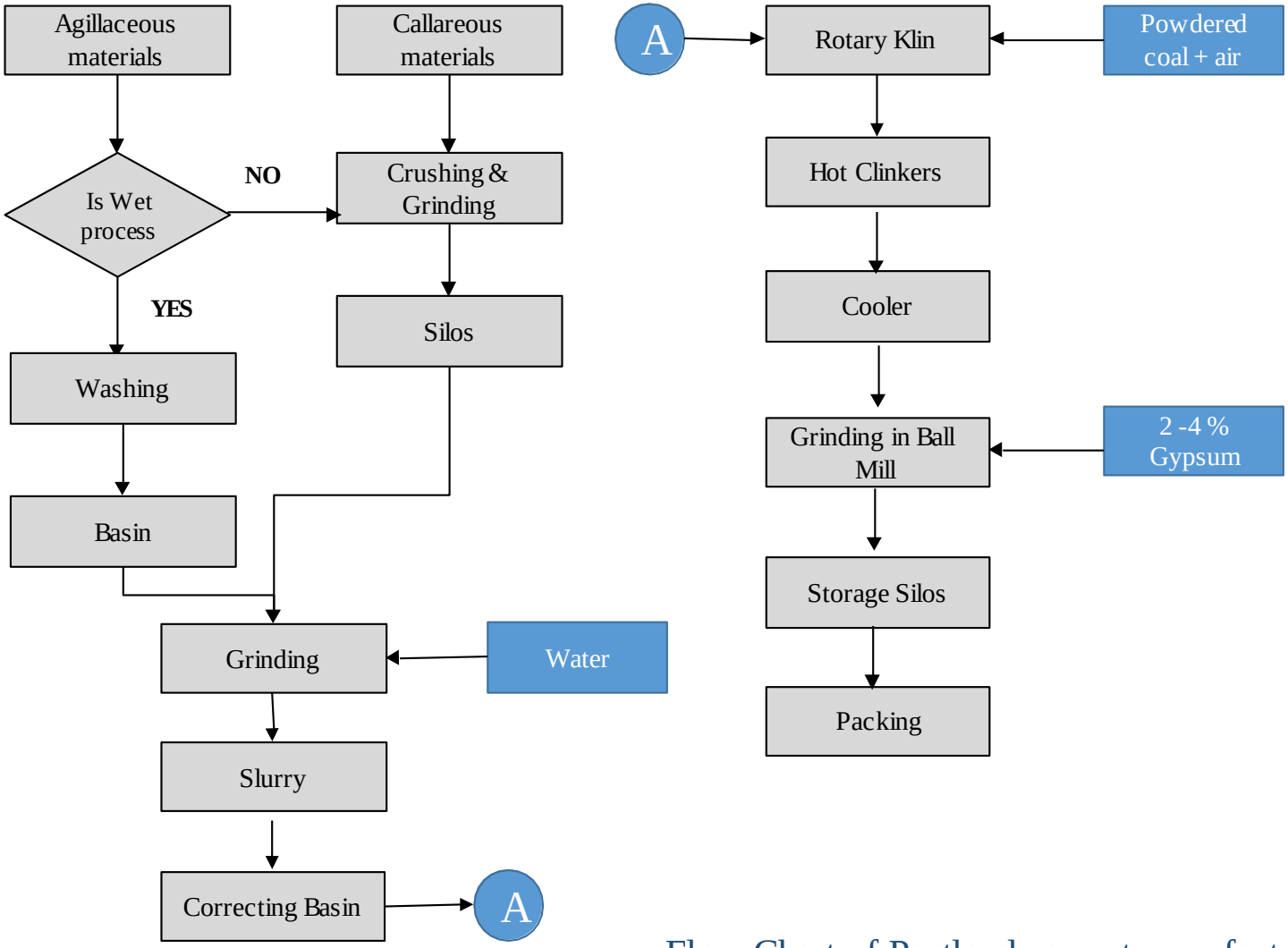
    a) Wet process

2. Burning

3. Grinding

4. Storage and Packing

Manufacturing of Portland cement



Flow Chart of Portland cement manufacturing process

Mixing and Crushing: a) Dry Process

Hot clinkers are cooled with atmospheric air and pulverized together with 2-3% of gypsum in ball mills

4. Storage & Packing

Mixing and Crushing: b) Wet Process

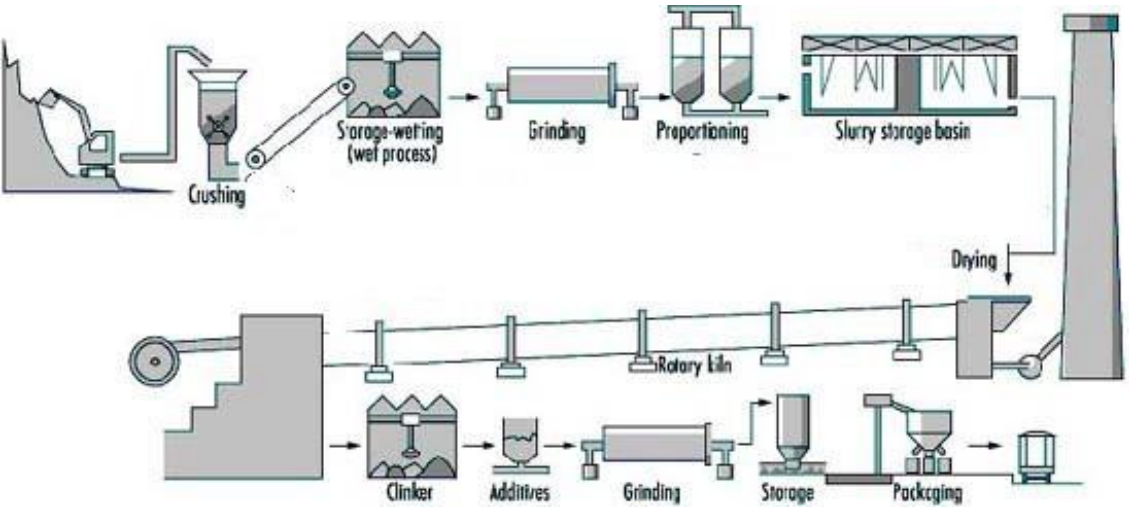
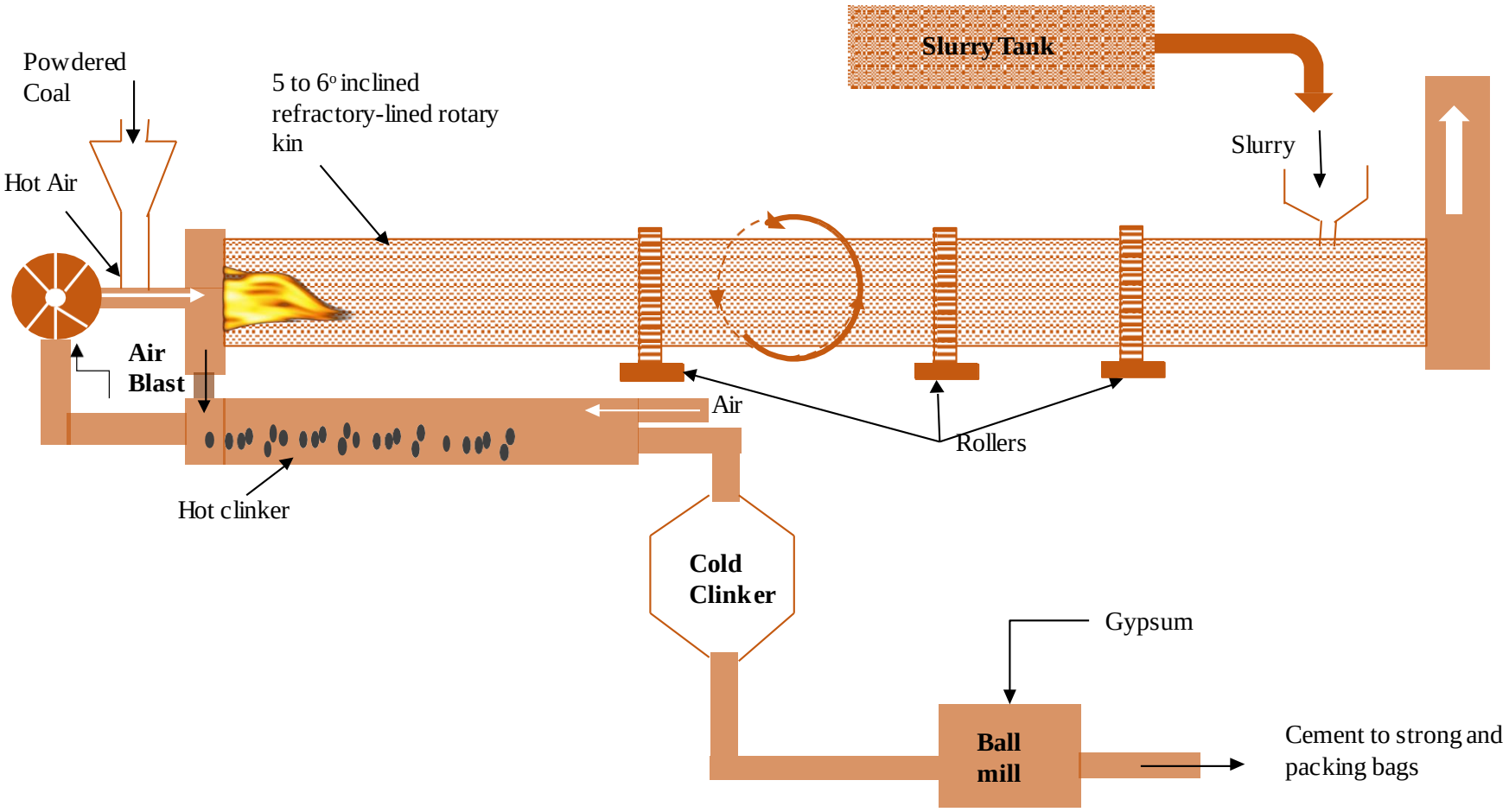


Figure showing manufacturing of cement using wet process

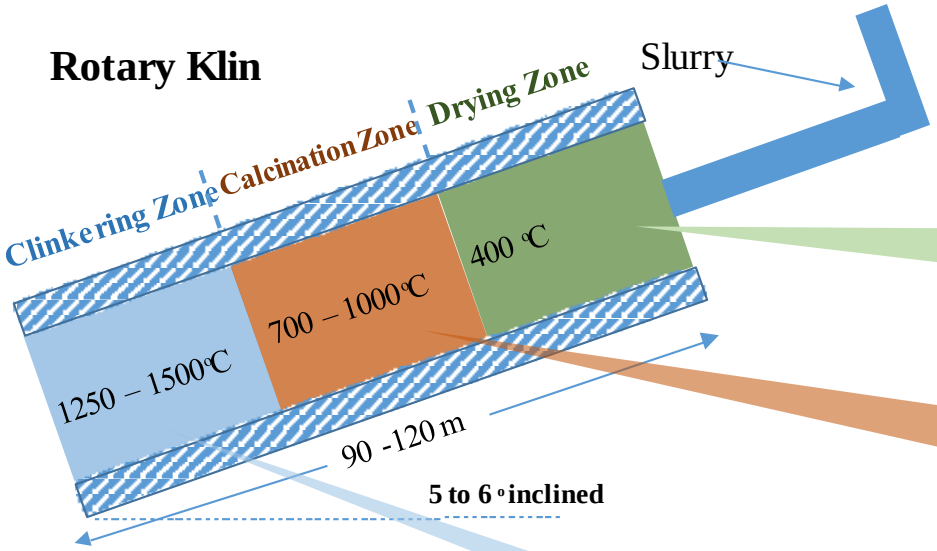
- Limestone is crushed, powdered and stored in silos
- Clay is washed with water to remove organic matter and stored in basin
- Both these materials are mixed in grinding mill to form slurry
- Slurry contains 38-40% water stored in correcting basin

Burning Process : View of complete setup

Fig. Rotary Cement Klin



Burning Process : Zones of Rotary Klin



- Upper part of the kiln
- About 400 ^{0}C
- Most of the water in the slurry gets evaporated

- Center part of the kiln
- About 700°C – 1000°C
- Lime gets decomposed into CaO and CO_2

- Lower part of the kiln
- About 1250°C - 1500°C
- Reacts with clay to form various bouge compounds

Burning Process : Chemical Reactions in Rotary Klin Zones

- Calcination Zone :

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

- Clinkering Zone :

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4 \text{ (Dicalcium silicate – } C_2S \text{)}$$

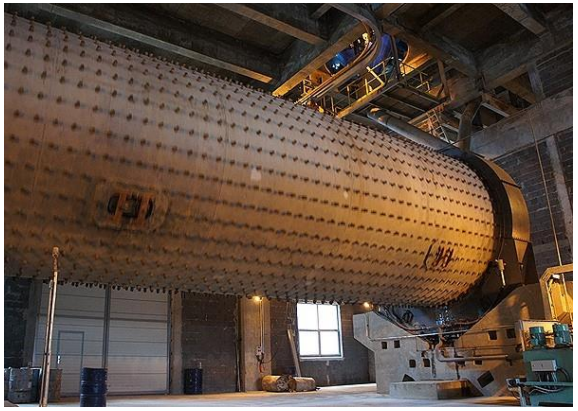
$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 \text{ (Tricalcium silicate – } C_3S \text{)}$$

$$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6 \text{ (Tricalcium aluminate – } C_3A \text{)}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$$

(Tricalcium aluminoferrite – C_4AF)

Grinding and Packaging



Grinding

- Cooled clinkers are ground to fine powder in ball mills
- At final stages of grounding about 2-3% of powdered gypsum is added.
  (This is to avoid setting of cement quickly when it comes in contact with water)

- Gypsum acts as a retarding agent for early setting of the cement

$$3CaO + Al_2O_3 + x\ CaSO_4 \,.\, 7H_2O \longrightarrow 3CaO \,.\, Al_2O_3 \,.\, xCaSO_4 \,.\, 7H_2O$$

After initial set — Gypsum — Tricalcium sulphoaluminate (Insoluble)

Packaging

- Ground cement is stored in silos
- From silos they are automatically packaged into bag which are about 50 Kg

Properties of cement : Setting and hardening

- When the cement is mixed with water, hydration and hydrolysis reactions of Bogue compounds of cement begin, resulting in formation of gel and crystalline products.

- These products have the ability to surround inert materials liks sand , bricks , crushed stones, etc.

" **Setting** is the stiffening of original plastic mass due to the formation of tobermonite gel". It can be divided into 2 stages a) Initial Set b)Final Set

¬Initial Set is when paste being to stiffen
¬Final Set is when the paste beginning to harden and able to sustain some loads

" **Hardening** is the development of strength due to formation of crystals"

Setting and hardening

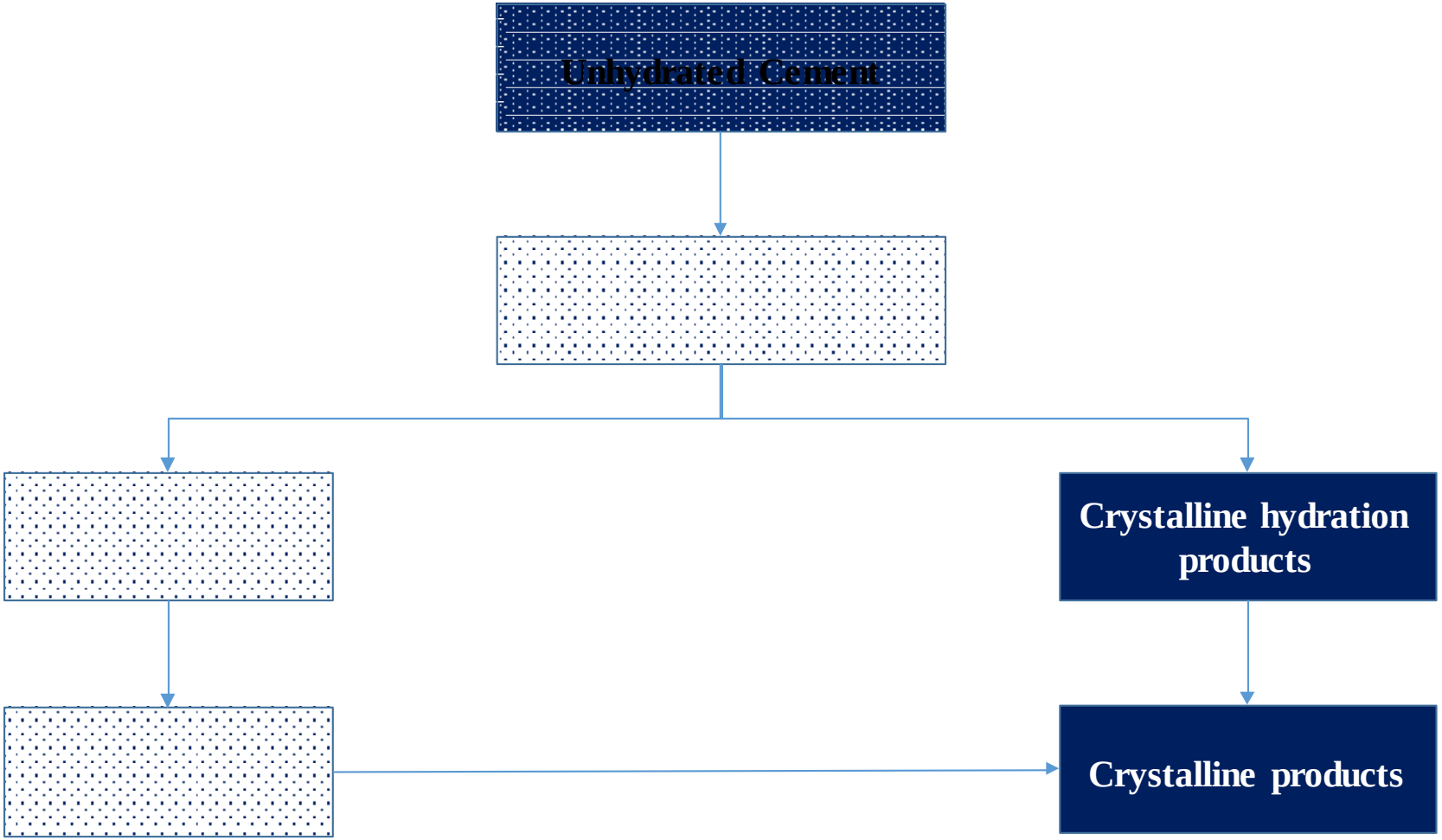
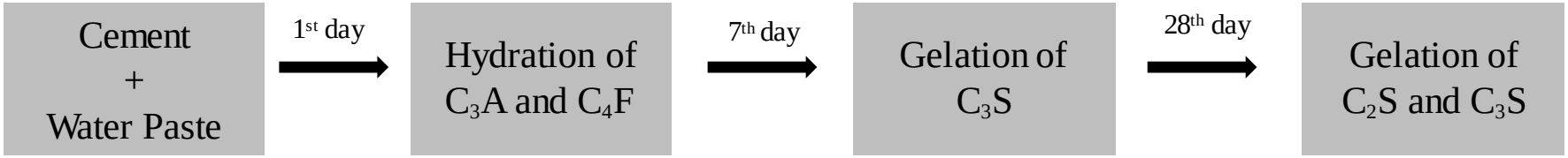


Figure showing setting and hardening of cement

Sequence of changes during setting and hardening



Setting and Hardening : Chemical Reactions

Day 1 :

- When cement is mixed with water, hydration of tricalcium aluminate (C_3A) takes place within a day
- The paste becomes rigid, which is known as Initial set or Flash set

$3CaO . Al_2O_3 + 6H_2O \rightarrow 3CaO . Al_2O_3 . 6H_2O + 880\ kJ/Kg$

Tricalciumaluminate — Hyderated tricalcium aluminate (Crystalline)

[OR]

$C_3A + 6H_2O \longrightarrow C_3A . 6H_2O + 880\ kJ/Kg$

- To avoid early setting of C_3A , gypsum is added which acts as retarding agent

$C_3A + 3CaSO_4 . 2H_2O \longrightarrow C_3A . 3CaSO_4 . 2H_2O$

Caclium sulpho aluminate

Setting and Hardening : Chemical Reactions contd…

Day – 2 to 7 :

- After hydration of C_3A, C_3S beings to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$, which is responsible for initial strength of the cement
- The hydration of C_3S gets completed within 7 days

$$2[3CaO.SiO_2] + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + 500\ kJ/Kg$$

Tricalcium silicate — Tobermonite gel — Crystalline

[OR]

$$2C_3S + 6H_2O \longrightarrow C_3S_2.3H_2O + 3Ca(OH)_2 + 500\ kJ/Kg$$

Tobermonite gel possesses a very high surface area and very high adhesive property

Setting and Hardening : Chemical Reactions contd…

Day – 7 to 28 :

- Dicalcium silicate (C_2S) reacts with water very slowly and gets completed in 7 to 28 days

$$2[2CaO \cdot SiO_2] + 4H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 + 250\ kJ/Kg$$

Dicalcium silicate — Tobermonite gel — Crystalline

[OR]

$$2C_2S + 4H_2O \longrightarrow C_3S_2 \cdot 3H_2O + Ca(OH)_2 + 250\ kJ/Kg$$

- Increase of strength is due to formation of tobermonite gel and crystalling $Ca(OH)_2$ of both C_2S and C_3S

Setting and Hardening : Chemical Reactions contd…

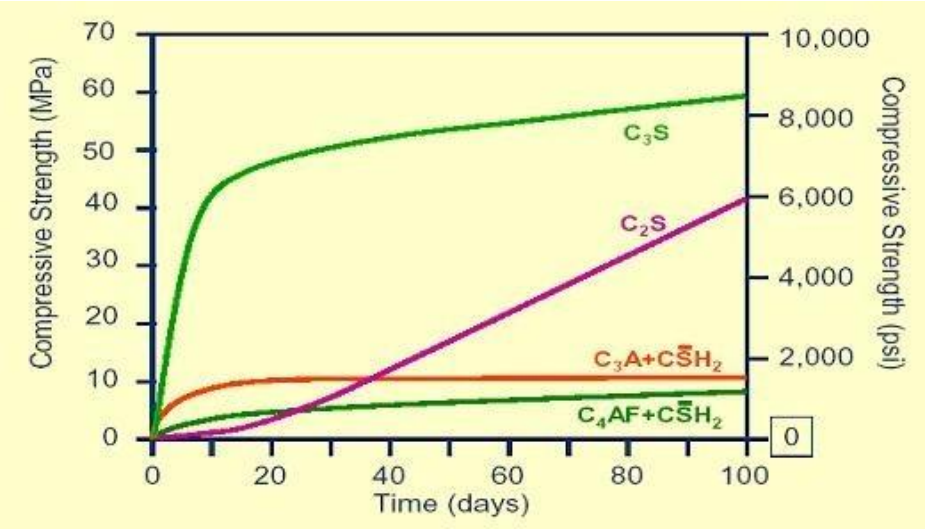
- After initial hyderation of tetracalcium alumino ferrite (C_4AF) , hardening takes place through crystallization , along with C_2S

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot Fe_2O_3 \cdot H_2O + 420\ kJ/Kg$$

Tetracalcium alumino ferrite — Crystalline — Gel

[OR]

$$C_4AF + 7H_2O \longrightarrow C_3A \cdot 6H_2O$$



Graphical representation of development of compressive strength

"Hydration and Hydrolysis of Bogue compounds causes cement to develop compressive strength"(Shown in the figure)

Function of Gypsum ($CaSO_4 \cdot 2H_2O$) in cement

- Tricalcium aluminate (C_3A) combines with water very rapidly with the evolution of large amount of heat

$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O + \text{Heat}$$

- After the initial set, the paste becomes stiff.
- Adding gypsum retards the dissolution of C_3A by forming *insoluble calcium sulpho-aluminate*

$$3CaO \,.\, Al_2O_3 \,.\, xCaSO_4 \,.\, 7H_2O$$

- The above reaction shows how gypsum retards the early initial set of cement

Heat of Hydration of Cement

- When cement is mixed with water, hydration , hydrolysis an gelation reaction starts and some heat is liberated
- On an average of 500 kJ/Kg of heat is evolved during complete hydration of cement

Bogue Compounds	Heat of hydration (kJ/kg)
C_3A	880
C_3S	500
C_4AF	420
C_2S	250

Heat of hydration of Bogue compounds

Special Cement : White Portland Cement (or) White cement

- Is white in color due to absence of iron compounds
- Obtained by calcining the raw materials of Portland cement which are free from iron oxide

Properties

- More expensive than ordinary Portland cement
- Acts as pore – blocking and water – repelling agent

- Repairing and joining marble pillars and blocks
- Manufacture of tiles and mosaic walls

Special Cement : Water proof Cement (or) Hydrophobic cement

- Is a cement obtained by adding water proofing substances like calcium stearate, aluminium stearate and gypsum with tannic acid to ordinary Portland cement

Properties

- More expensive than ordinary Portland cement
- Acts as pore – blocking and water – repelling agent

- Used to make concrete which is impervious to water under pressure
- Used in construction, where absorption of water need to be avoided
- Used in construction of bridges and under water constructions

THANK YOU