

# Unit IV- Industrial application of Chemistry

**M.SC Semester II**  
**Core Course V**  
**Advances in Chemistry**

**Department of Chemistry**  
**L.S COLLEGE MUZAFFARPUR**  
**B. R. A. BIHAR UNIVERSITY**

**TOPIC:- Cement**

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# Introduction

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

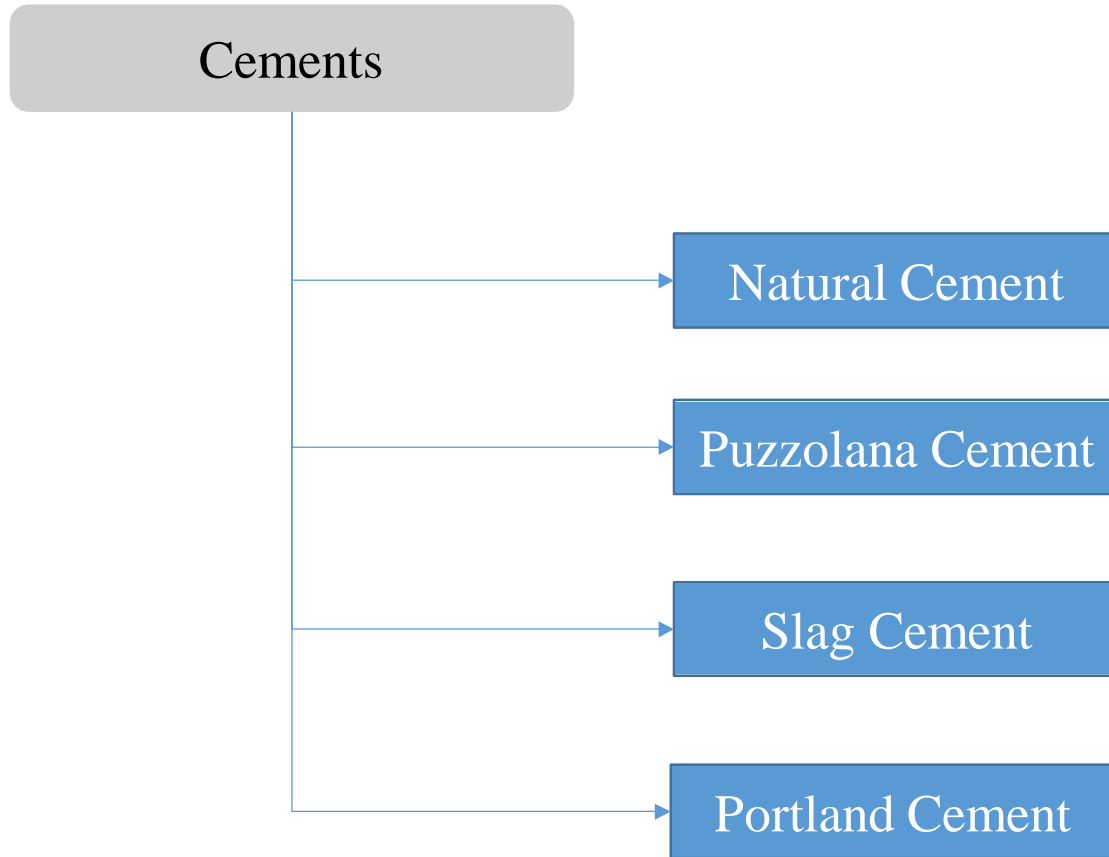
## Chemical Composition of Cement

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



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 $(\text{CaO})_3 \cdot \text{SiO}_2$	$\text{C}_3\text{S}$	45–75%
Dicalcium silicate $(\text{CaO})_2 \cdot \text{SiO}_2$	$\text{C}_2\text{S}$	7–32%
Tricalcium aluminate $(\text{CaO})_3 \cdot \text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$	0–13%
Tetracalcium aluminoferrite $(\text{CaO})_4 \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$	0–18%
Gypsum $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$		2–10%
Calcium Oxide - $\text{CaO}$		2%
Magnesium Oxide - $\text{MgO}$		4%

Chemical Composition of Portland Cement

# Raw materials of Portland Cement and it's use



Calcareous materials,  $\text{CaO}$  [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,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  [eg. Clay ]

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

Powdered Coal or fuel oil

- For burning

Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

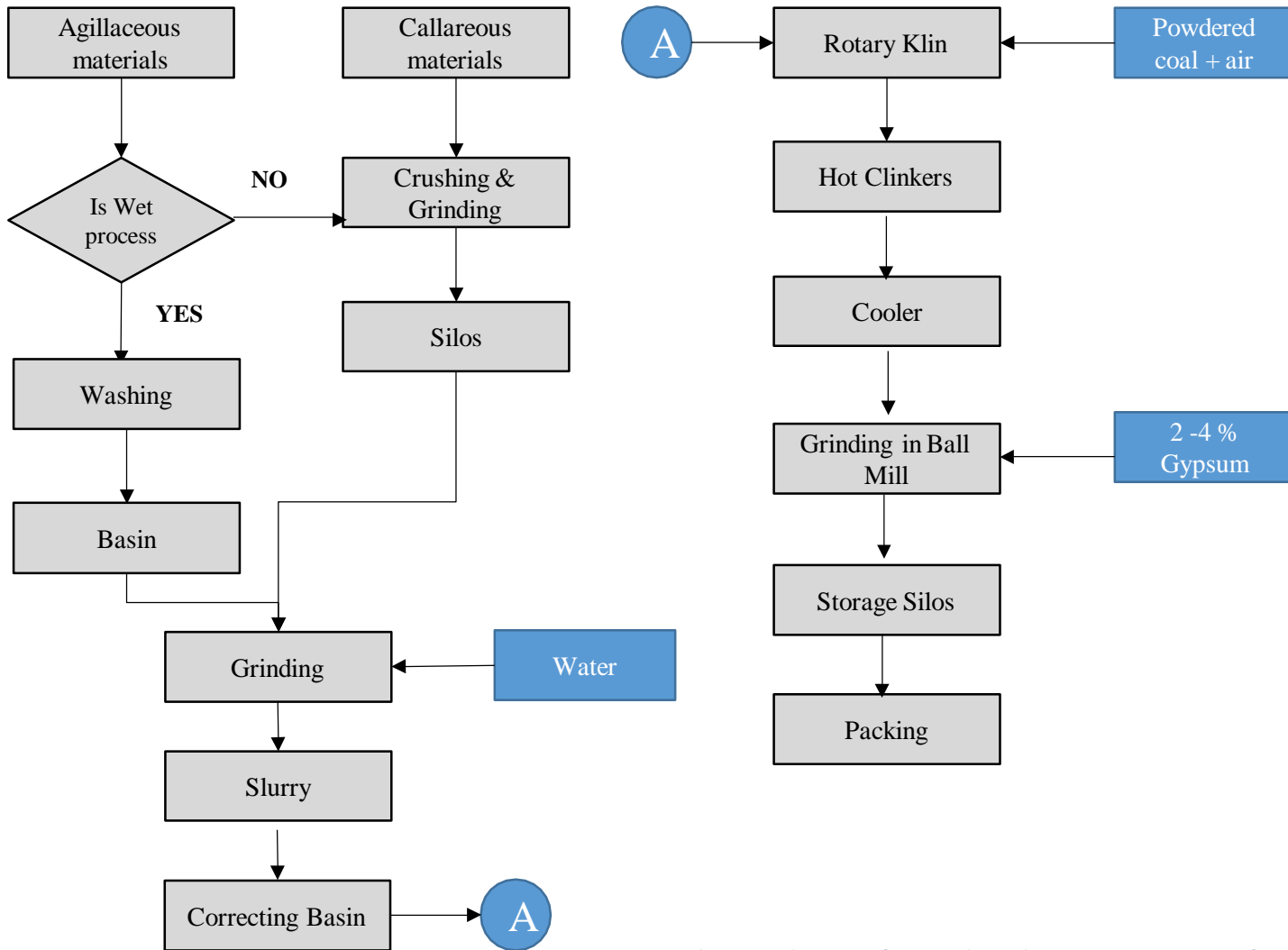
- Retards and enhances quick setting

# Manufacturing Cement

1. Mixing and Crushing of raw materials
  - a) Dry process
  - a) Wet process
2. Burning
3. Grinding
4. Storage and Packing



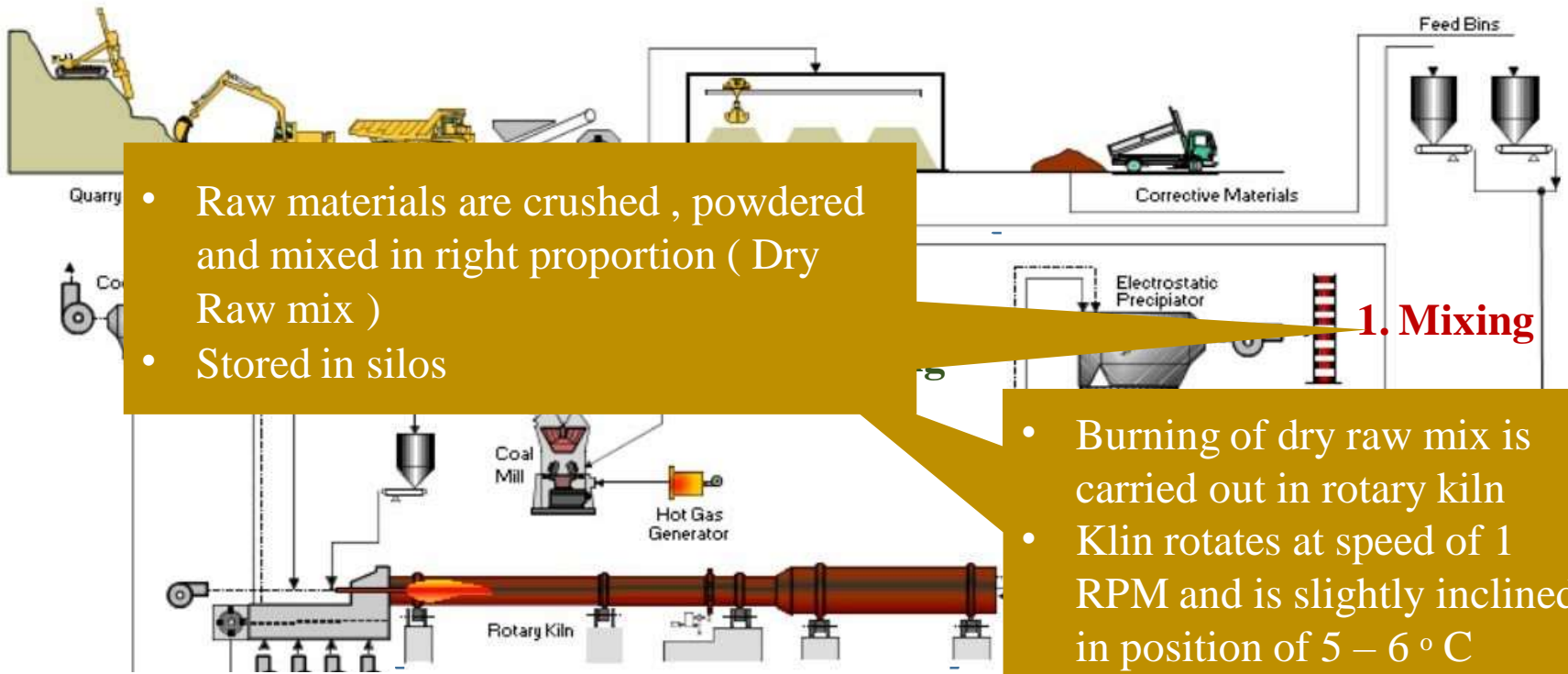
# Manufacturing of Portland cement



Flow Chart of Portland cement manufacturing process



# Mixing and Crushing: a) Dry Process



- Raw materials are crushed, powdered and mixed in right proportion ( Dry Raw mix )
- Stored in silos

**1. Mixing**

- Burning of dry raw mix is carried out in rotary kiln
- Klin rotates at speed of 1 RPM and is slightly inclined in position of  $5 - 6^\circ \text{C}$

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

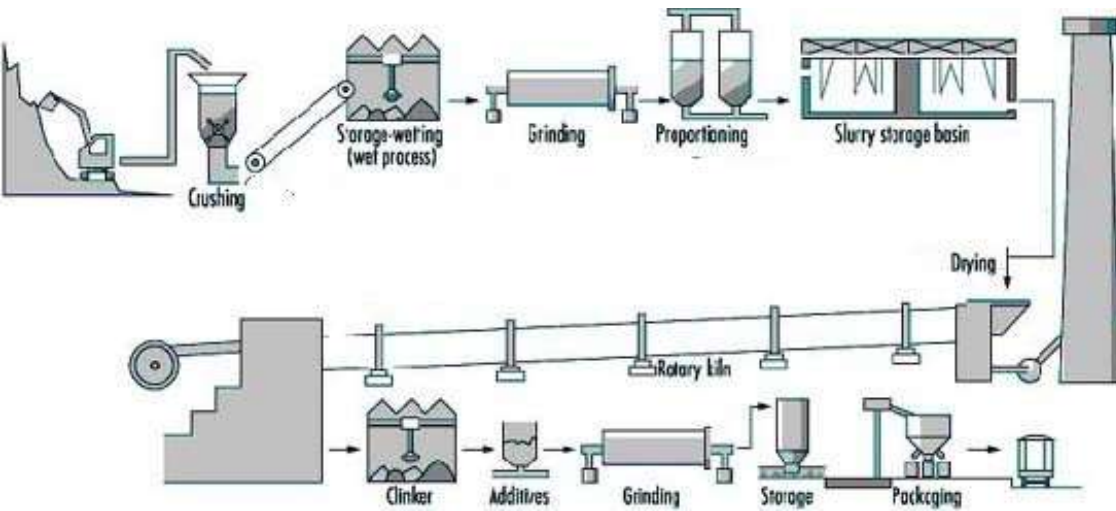
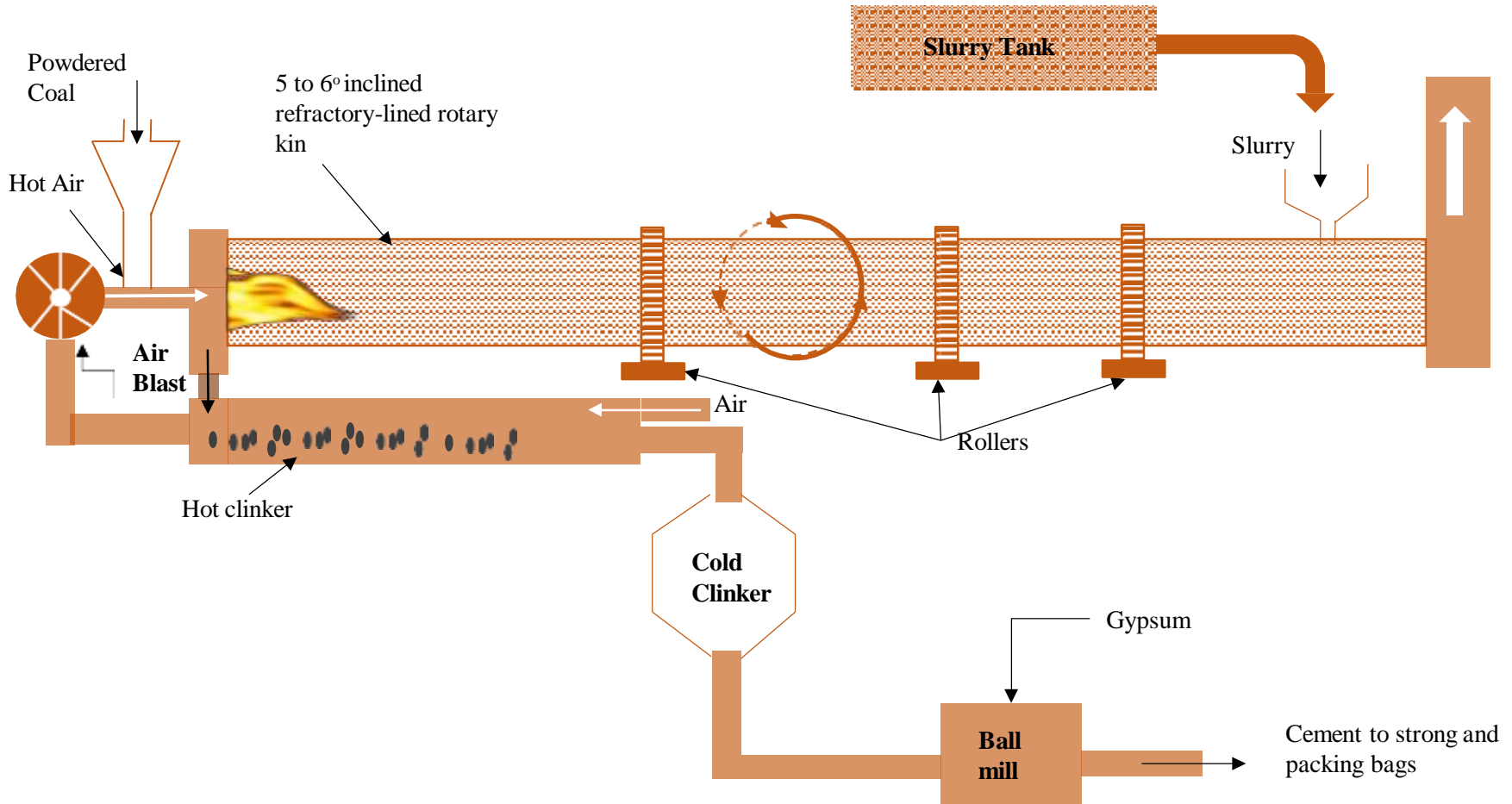


Figure showing manufacturing of cement using wet process

- 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

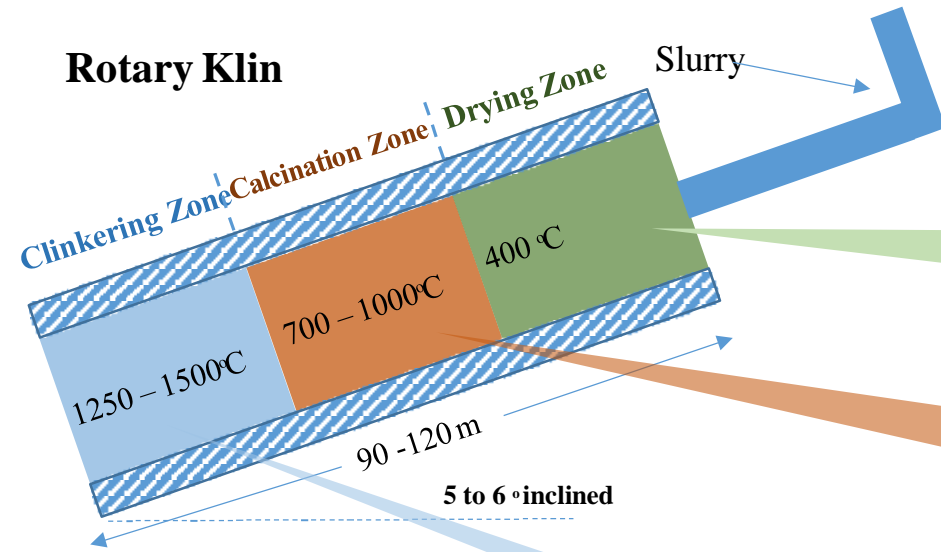
# Burning Process : View of complete setup

Fig. Rotary Cement Klin



# Burning Process : Zones of Rotary Klin

## Rotary Klin



- Upper part of the kiln
- About 400 °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<sub>2</sub>

- 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

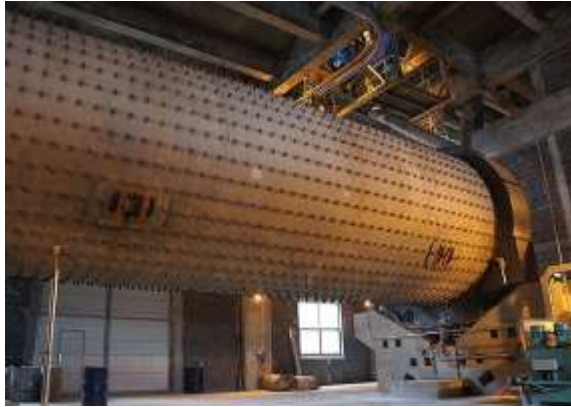
- Calcination Zone :



- Clinkering Zone :



# Grinding and Packaging



## Grinding

- Cooled clinkers are ground to fine powder in ball mills
- At final stages of grinding 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



## 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 like 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 begins to stiffen

– Final Set is when the paste begins to harden and able to sustain some loads

“ **Hardening** is the development of strength due to formation of crystals”

# Setting and hardening

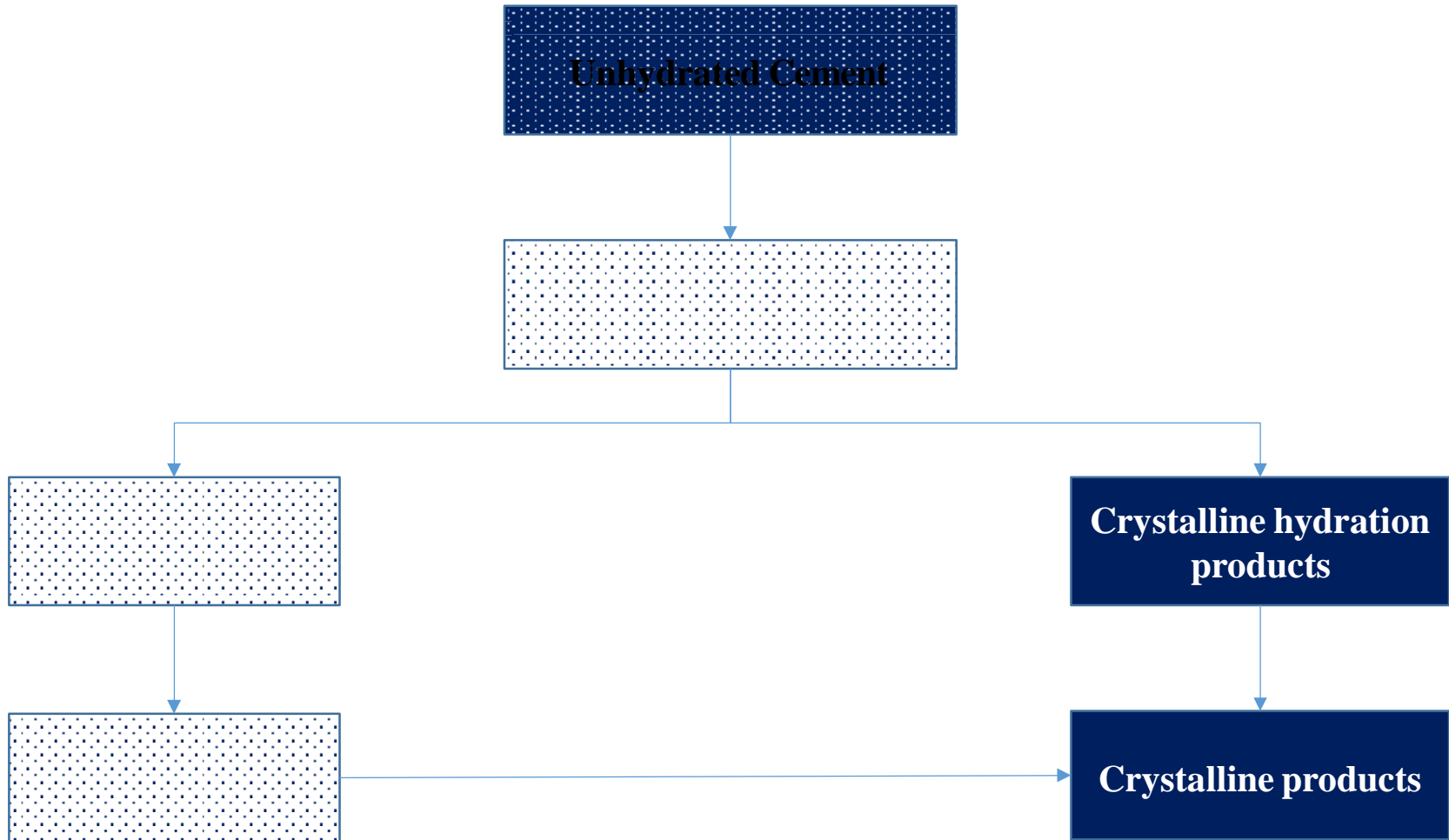
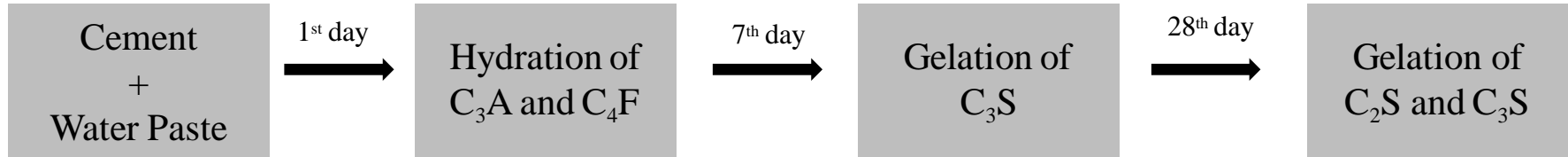


Figure showing setting and hardening of cement



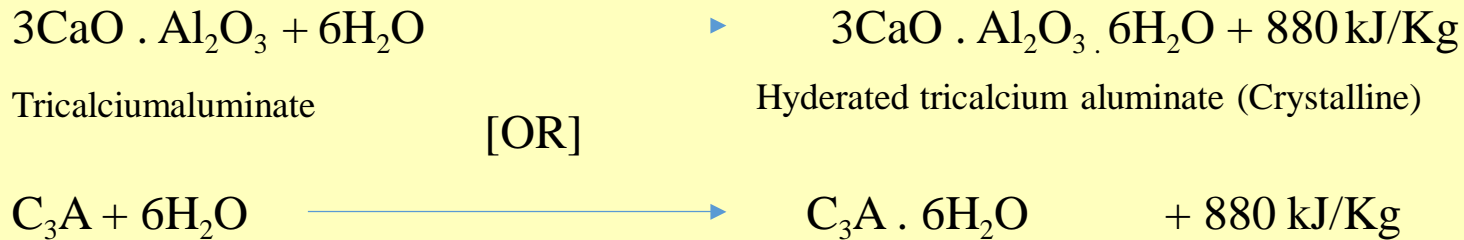
# Sequence of changes during setting and hardening



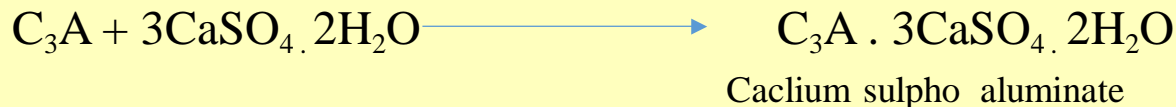
# Setting and Hardening : Chemical Reactions

## 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

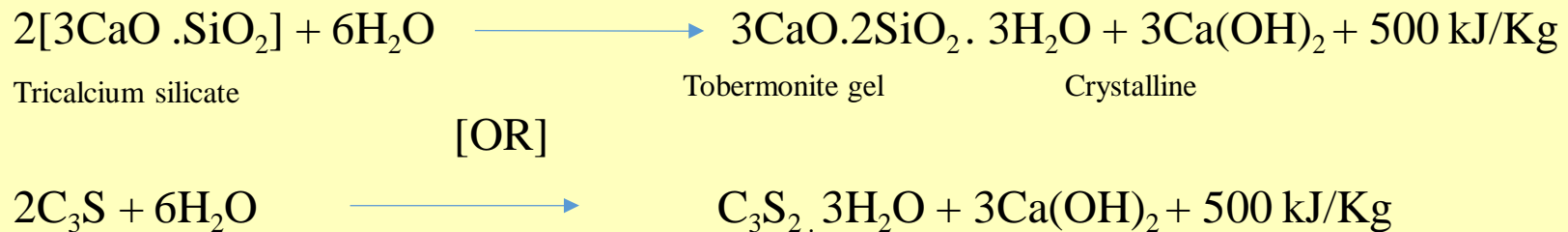


- To avoid early setting of  $C_3A$ , gypsum is added which acts as retarding agent



**Day – 2 to 7 :**

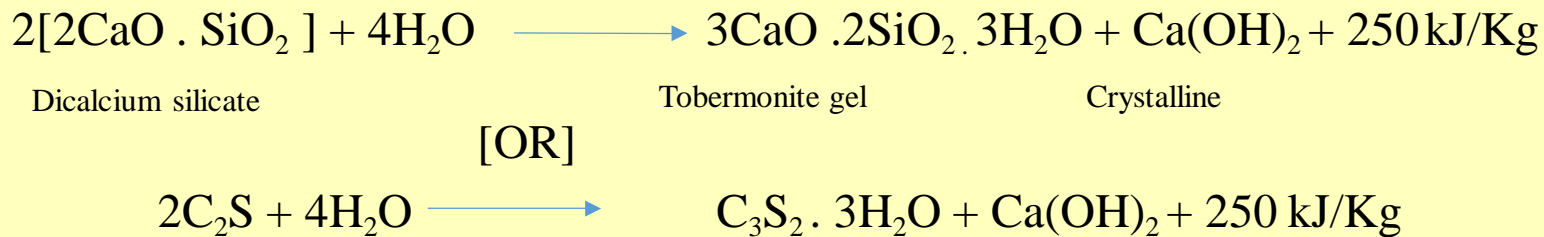
- After hydration of  $C_3A$ ,  $C_3S$  begins to hydrate to give tobermonite gel and crystalline  $Ca(OH)_2$ , which is responsible for initial strength of the cement
- The hydration of  $C_3S$  gets completed within 7 days



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

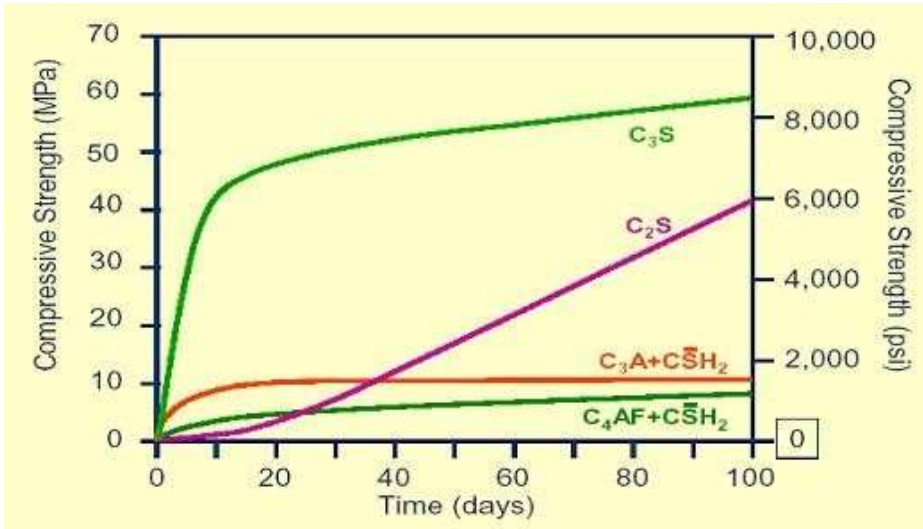
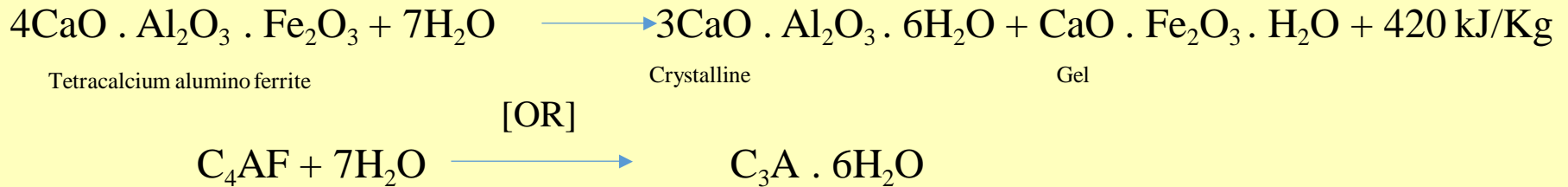
**Day – 7 to 28 :**

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



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

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



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

Graphical representation of development of compressive strength

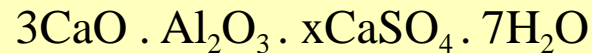
# Function of Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in cement



- Tricalcium aluminate ( $\text{C}_3\text{A}$ ) combines with water very rapidly with the evolution of large amount of heat



- After the initial set, the paste becomes stiff.
- Adding gypsum retards the dissolution of  $\text{C}_3\text{A}$  by forming *insoluble calcium sulpho-aluminate*



- 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 and 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