

# Concrete Technology

## Lecture 2

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# Introduction

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- ▶ Cement is a finely ground inorganic powder that sets, hardens and adheres to other materials, binding them together
- ▶ The most important types of cement are used in the production of mortar in masonry, and of concrete, which is a combination of cement and an aggregate to form a strong building material.
- ▶ Cements used in construction are usually inorganic, often lime or calcium silicate based, and can be characterized as being either **hydraulic** or **non-hydraulic**, depending upon the ability of the cement to set in the presence of water
- ▶ **Hydraulic cements** (e.g., Portland cement) harden because of hydration, a chemical reaction between the anhydrous cement powder and water.



# Introduction (Cont'd)

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- ▶ **Non-hydraulic** cements do not harden underwater; for example, slaked limes harden by reaction with atmospheric carbon dioxide (Carbonation)
- ▶ First calcium oxide (lime) is produced from calcium carbonate (limestone or chalk) by calcination at temperatures above 825 °C (1,517 °F) for about 10 hours at atmospheric pressure:  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- ▶ The calcium oxide is then *spent* (slaked) mixing it with water to make slaked lime (calcium hydroxide):  $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
- ▶ Once the excess water is completely evaporated (this process is technically called *setting*), the carbonation starts:  $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
- ▶ This reaction takes a significant amount of time because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires the dry cement to be exposed to air, and for this reason the slaked lime is a non-hydraulic cement and cannot be used under water. This whole process is called the *lime cycle*



# Raw Materials for Manufacturing of Portland Cement

## □ Basic Chemical Components of Portland Cement

- Calcium (60-67%)
- Silica (17-25%)
- Alumina (3-8%)
- Iron (0.5-6%)

## □ The common Raw materials

- Limestone
- Sand
- Shale, Clay
- Iron ore
- Gypsum

*Table 1: Examples of raw materials for Portland Cement manufacture*

Calcium	Silicon	Aluminum	Iron
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Fly ash	Mill scale
Gypsum	Shale	Aluminum ore refuse	Shale
Marly limestone	Fly ash	Phyllite	Blast furnace dust
Sea Shells	Rice hull ash	slate	slag
Cement kiln dust	Silica		
Chalk	Sand		

# Manufacturing of Portland Cement

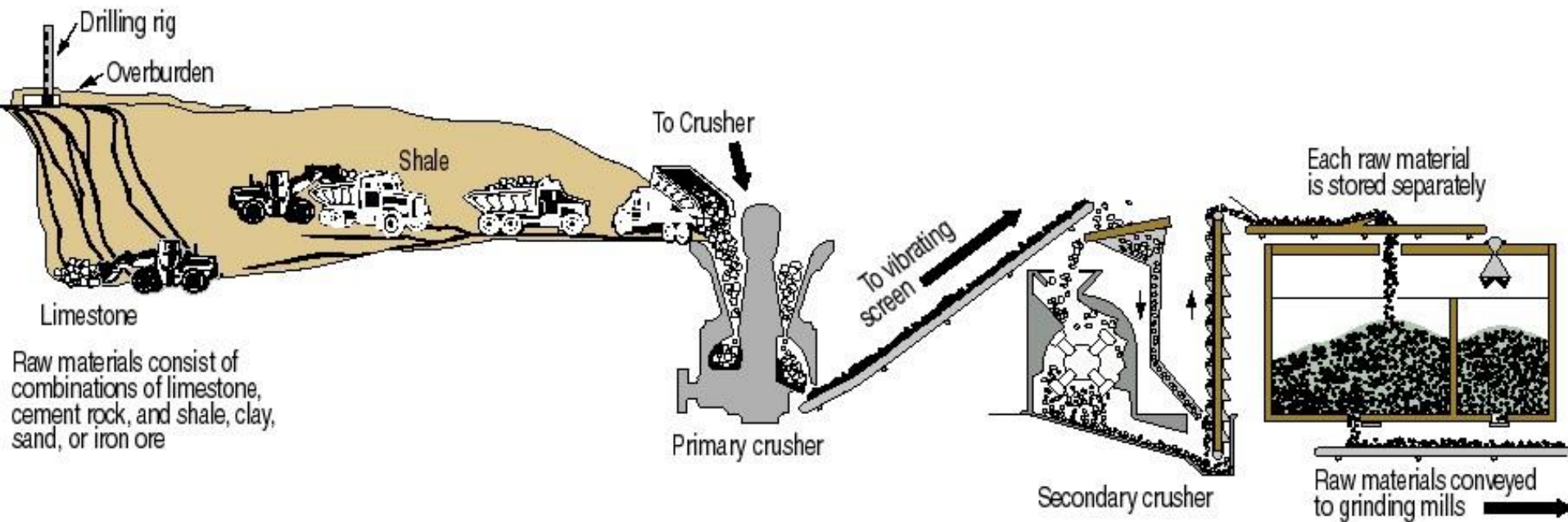
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- ▶ The process of manufacture of cement consists of grinding of raw materials, mixing them intimately at certain proportions and burning them in a kiln at about 1300 to 1500°C temperature, at which the material partially fuses to form nodular shaped clinker. The clinker is cooled and ground to fine powder with addition of 3 to 5% gypsum. The product formed by using this procedure is called Portland cement.



# Manufacturing of Portland Cement

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**1. Stone is first reduced to 125 mm (5 in.) size, then to 20 mm (3/4 in.), and stored.**

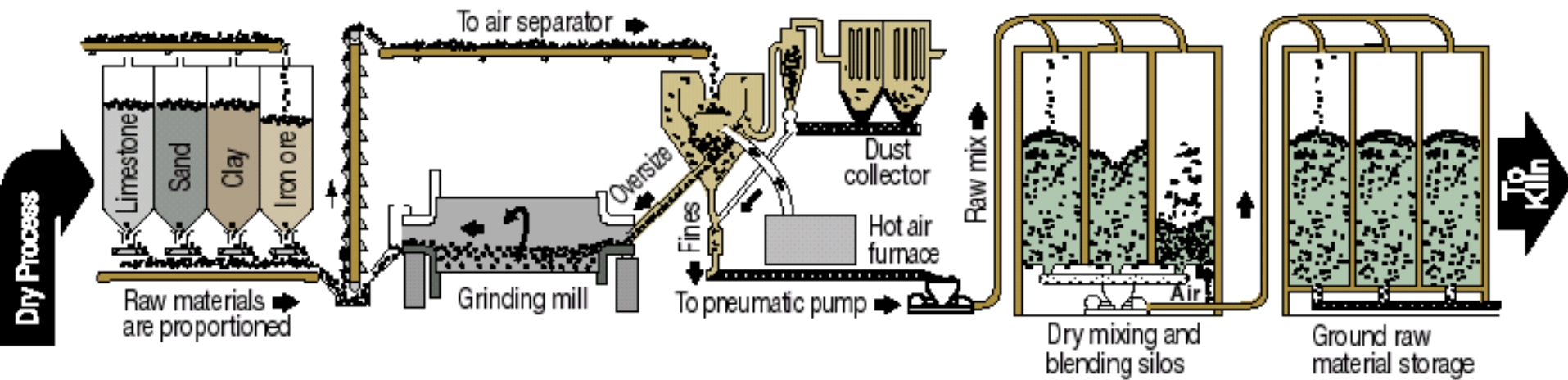
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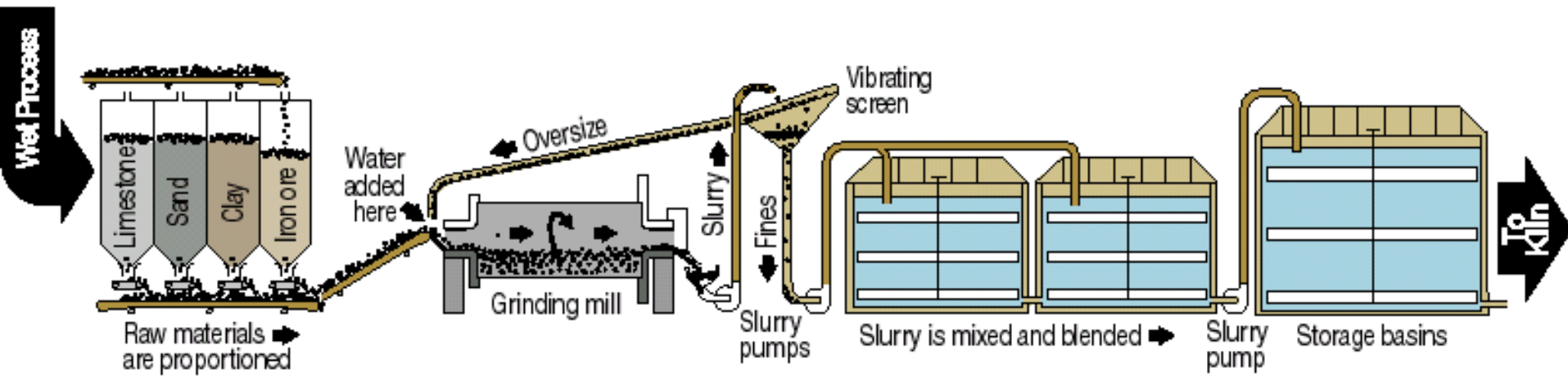


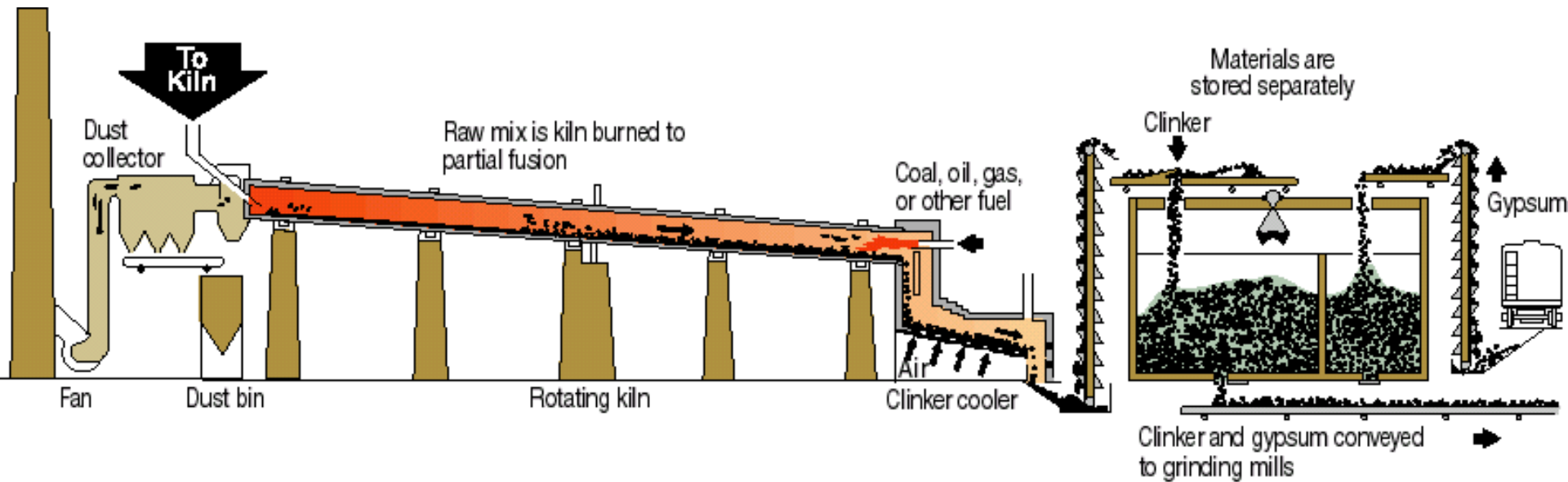
## 2. Raw materials are ground to powder and blended. (Dry process)



or

## 2. Raw materials are ground, mixed with water to form slurry, and blended. (Wet Process)





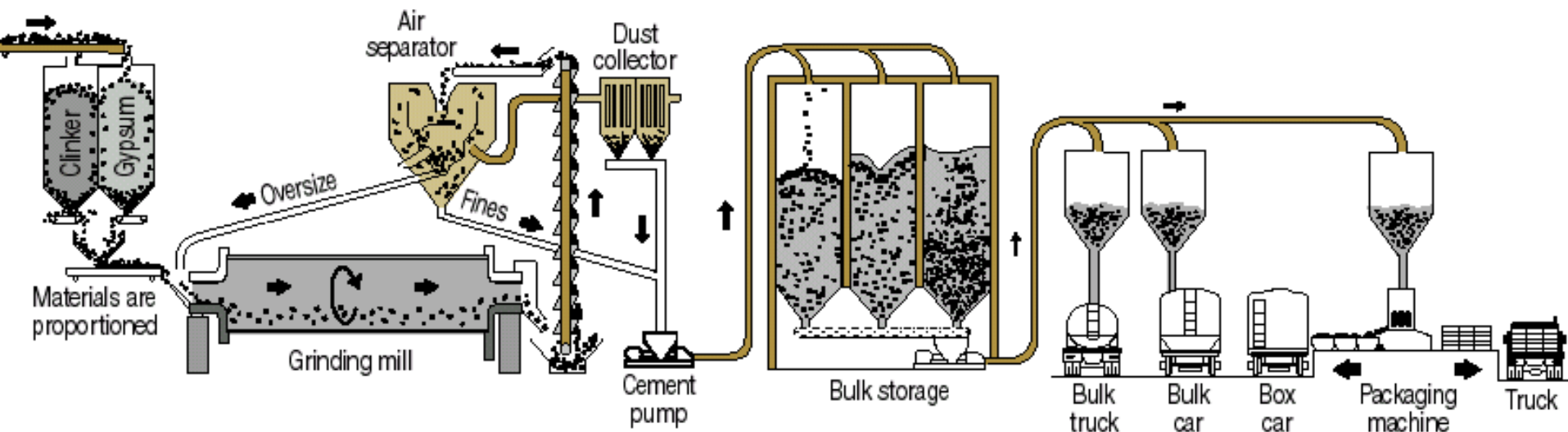
### 3. Burning changes raw mix chemically into cement clinker.











**4. Clinker is ground with gypsum into portland cement and shipped.**





# Clinker

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Portland cement clinker is formed by burning calcium and siliceous raw materials in a kiln. This particular clinker is about 3mm to 20 mm (3¼ in.) in diameter

# Gypsum



Gypsum, a source of sulfate, is inter-ground with Portland clinker to form Portland cement. It helps control setting, drying shrinkage properties, and strength development

# Chemical Composition of Cement

Name	Formula	Shorthand	Weight %
Tricalcium silicate (Alite)	$3 \text{ CaO} \cdot \text{SiO}_2$	$\text{C}_3\text{S}$	~55-60
Dicalcium silicate (Belite)	$2 \text{ CaO} \cdot \text{SiO}_2$	$\text{C}_2\text{S}$	~15-20
Tricalcium aluminate	$3 \text{ CaO} \cdot \text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$	~5-10
Tetracalcium aluminoferrite	$4 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$	~5-8
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\overline{\text{C}}\text{SH}_2$	~2-6

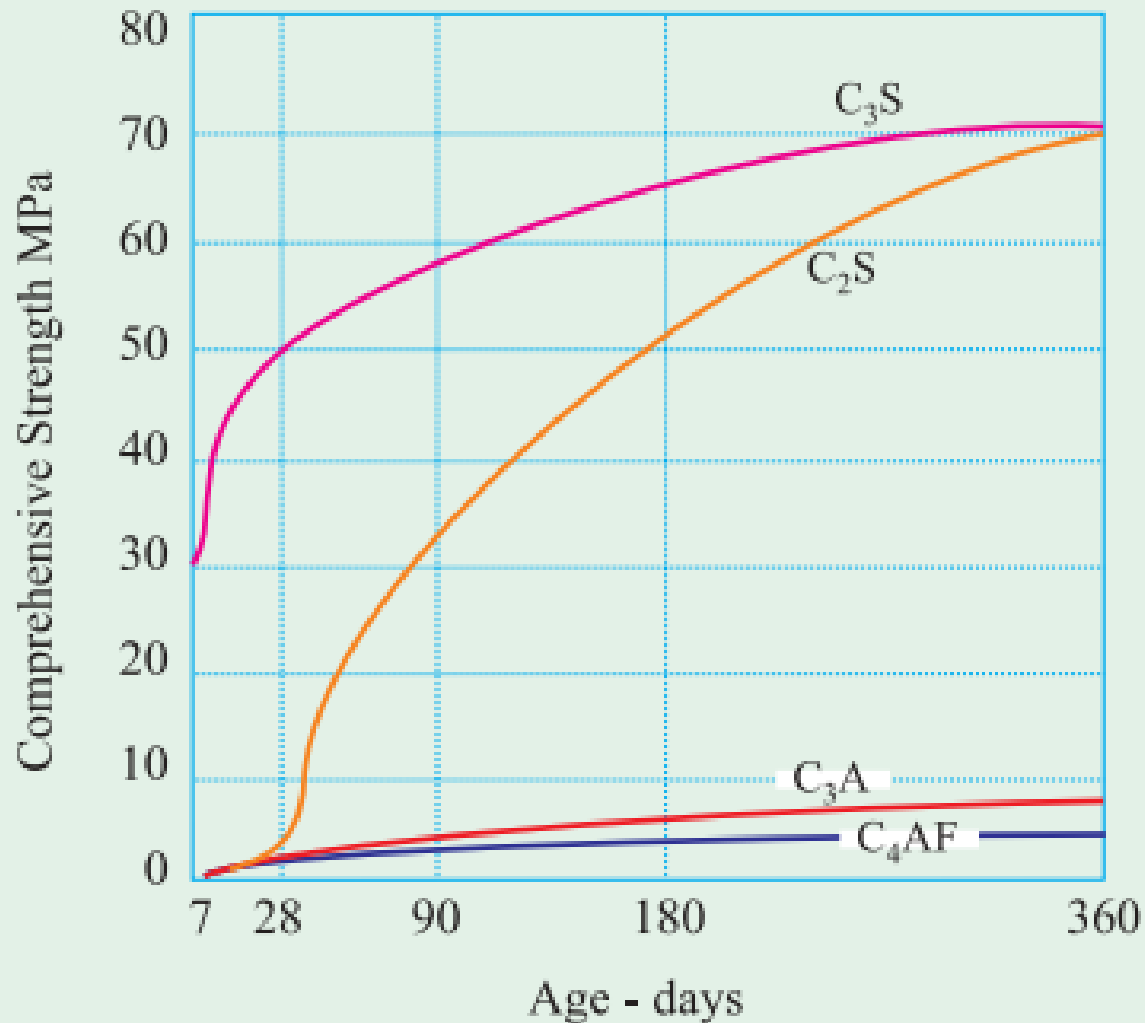
# Properties of main chemical compounds

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- ❑ **Tri-calcium silicate:** is responsible for early strength. Cement with high content of  $C_3S$  is favored in regions of cold climate.
- ❑ **Di-calcium silicate:** Contributes to later age strength (after one week). High percentage of  $C_2S$  is recommended in hydraulic structures.
- ❑ **Tri-calcium Aluminate:** Reacts immediately with water and defines set. In the absence of gypsum, it causes *flash set*. Generates high heat and is more reactive with soils and water containing moderate to high Sulphate concentrations and is thus the least desirable compound.
- ❑ **Tetra-calcium Alumino-ferrite:** Lowers clinkering temperature and contributes very little to strength of concrete even though it hydrates very rapidly.



# Development of Strength of Pure Compounds



# Hydration

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- ▶ Cement acquires binding properties when mixed with water
- ▶ The chemical reaction that takes place between water and cement is referred to as hydration of cement
- ▶ The reaction of cement with water is exothermic. This liberation of heat is called heat of hydration.
- ▶ Although simple hydrates such as C-H are formed, process of hydration is a complex one and results in reorganization of the constituents of original compounds to form new hydrated compounds






# 5 Stages of Hydration

Reaction Stage	Kinetics of Reaction	Chemical Processes
1 Initial hydrolysis	Chemical control; rapid	Dissolution of ions
2 Induction period	Nucleation control; slow	Continued dissolution of ions
3 Acceleration	Chemical control; rapid	Initial formation of hydration products
4 Deceleration	Chemical and diffusion control; slow	Continued formation of hydration products
5 Steady state	Diffusion control; slow	Slow formation of hydration products



# Hydration Reactions

$2 (3\text{CaO}\cdot\text{SiO}_2)$ Tricalcium silicate	$+ 11 \text{H}_2\text{O}$ Water	$= 3\text{CaO}\cdot 2\text{SiO}_2\cdot 8\text{H}_2\text{O}$ Calcium silicate hydrate (C-S-H)	$+ 3 (\text{CaO}\cdot\text{H}_2\text{O})$ Calcium hydroxide
$2 (2\text{CaO}\cdot\text{SiO}_2)$ Dicalcium silicate	$+ 9 \text{H}_2\text{O}$ Water	$= 3\text{CaO}\cdot 2\text{SiO}_2\cdot 8\text{H}_2\text{O}$ Calcium silicate hydrate (C-S-H)	$+ \text{CaO}\cdot\text{H}_2\text{O}$ Calcium hydroxide
$3\text{CaO}\cdot\text{Al}_2\text{O}_3$ Tricalcium aluminate	$+ 3 (\text{CaO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O})$ Gypsum	$+ 26 \text{H}_2\text{O}$ Water	$= 6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ Ettringite
$2 (3\text{CaO}\cdot\text{Al}_2\text{O}_3)$ Tricalcium aluminate	$+ 6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ Ettringite	$+ 4 \text{H}_2\text{O}$ Water	$= 3 (4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{SO}_3\cdot 12\text{H}_2\text{O})$ Calcium monosulfoaluminate
$3\text{CaO}\cdot\text{Al}_2\text{O}_3$ Tricalcium aluminate	$+ \text{CaO}\cdot\text{H}_2\text{O}$ Calcium hydroxide	$+ 12 \text{H}_2\text{O}$ Water	$= 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ Tetracalcium aluminate hydrate
$4\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{Fe}_2\text{O}_3$ Tetracalcium aluminoferrite	$+ 10 \text{H}_2\text{O}$ Water	$+ 2 (\text{CaO}\cdot\text{H}_2\text{O})$ Calcium hydroxide	$= 6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{Fe}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ Calcium aluminoferrite hydrate


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# Characteristics of Hydration cement compound

Compounds	Reaction rate	Amount of Heat Liberated	Contribution to Cement Heat Liberation
$C_3S$	Moderate	Moderate	High
$C_2S$	Slow	Low	Low
$C_3A + C\bar{S}H_2$	Fast	Very High	Very High
$C_4AF + C\bar{S}H_2$	Moderate	Moderate	Moderate



# Heat of Hydration

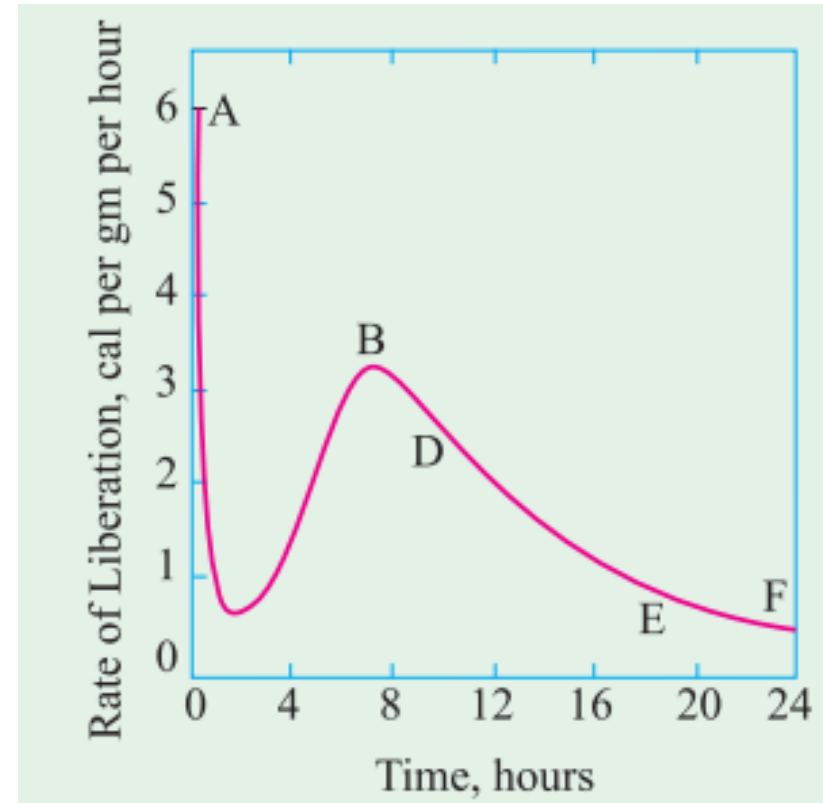
Compound	Heat of hydration at given age (cal/g)		
	3 days	90 days	13 years
CS	58	104	122
C <sub>2</sub> S	12	42	59
C <sub>3</sub> A	212	311	324
C <sub>4</sub> AF	69	98	102

Normal cement produces 89-89cal/g in 7 days and 90-100cal/g in 28 days.



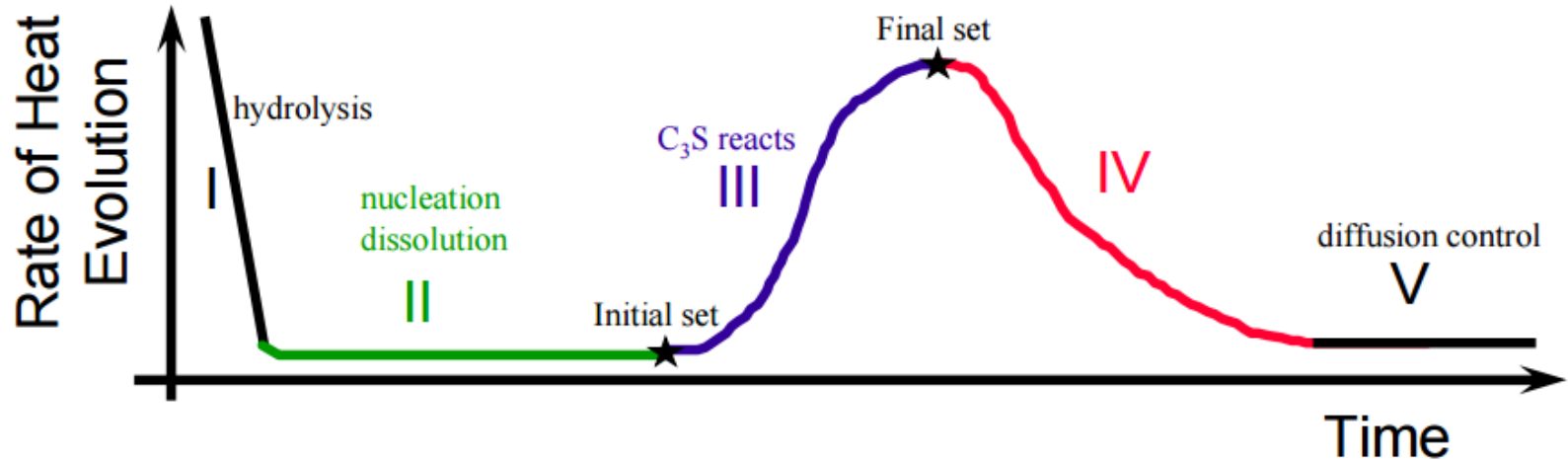
# Heat of Hydration

- ▶ The reaction of cement with water is exothermic
- ▶ The reaction results in the release of considerable amount of heat known as **heat of hydration**
- ▶ **Minimum water requirement for complete hydration is 38% by weight.**





# Heat of Hydration (Cont'd)



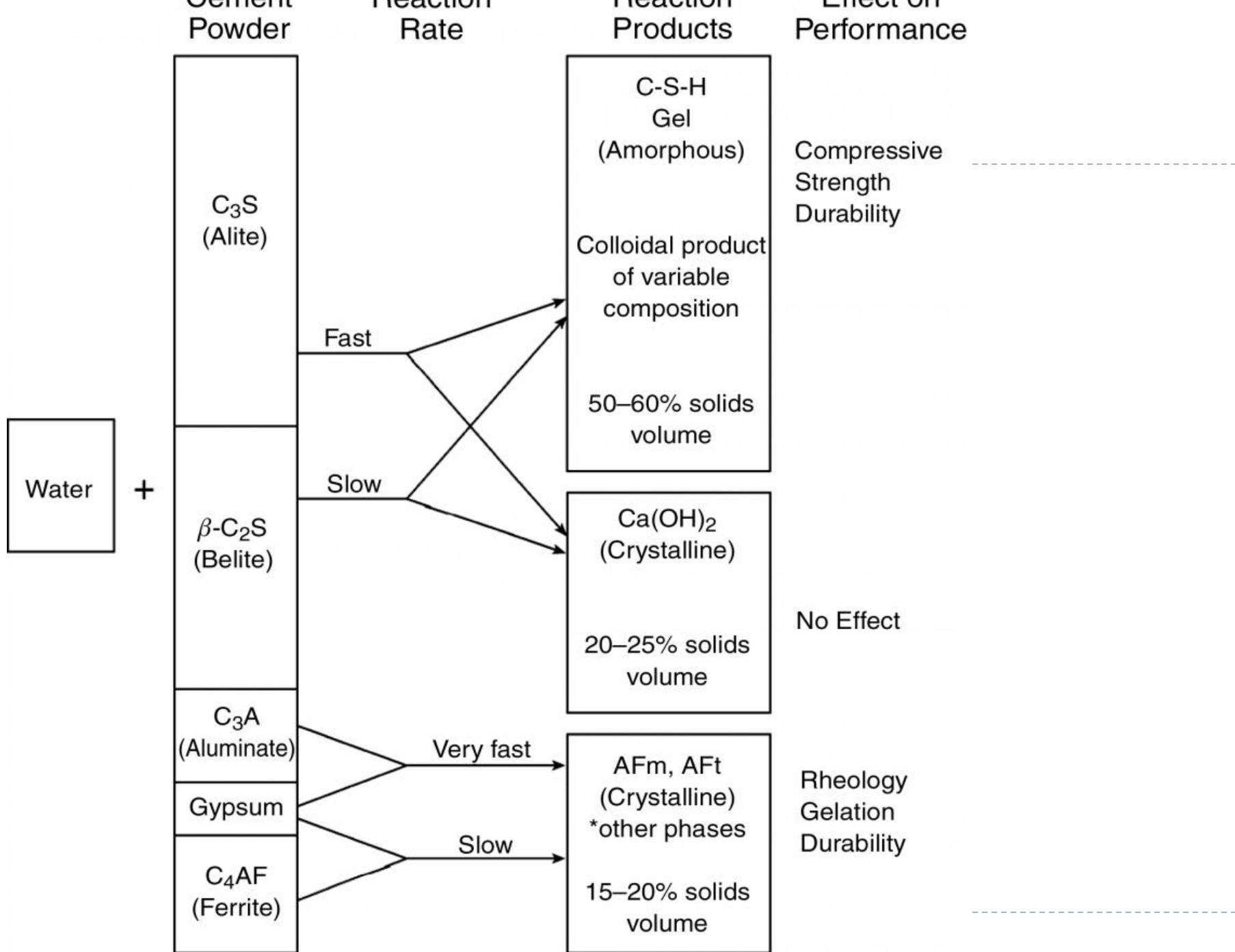
Stage I	Rapid Heat Evolution		(<15 mins)
Stage II	Dormant Period	Important for transportation	(2-4 hrs)
Stage III	Accelerating Stage	Begins with initial set	(4-8 hrs)
Stage IV	Deceleration Stage	No longer workable	(12-24 hrs)
Stage V	Steady State		

# Structure of Hydrated Cement

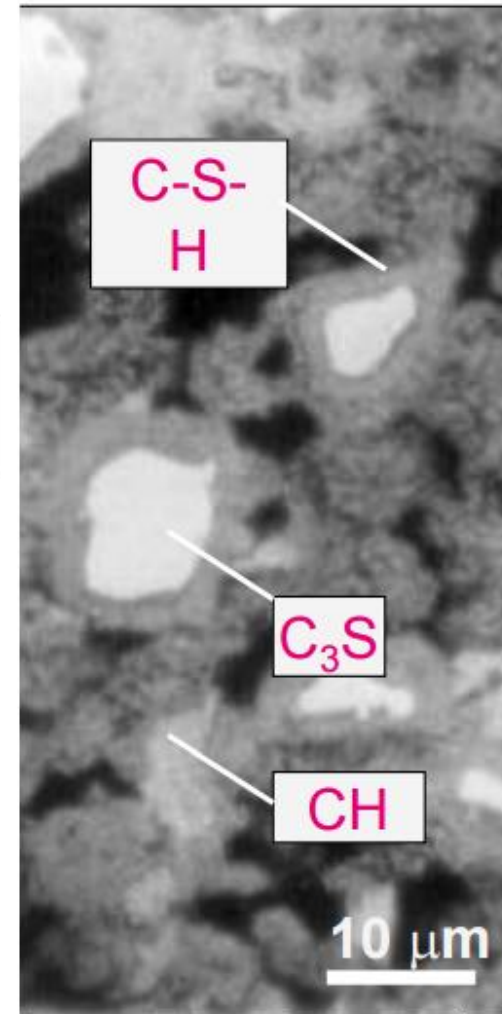
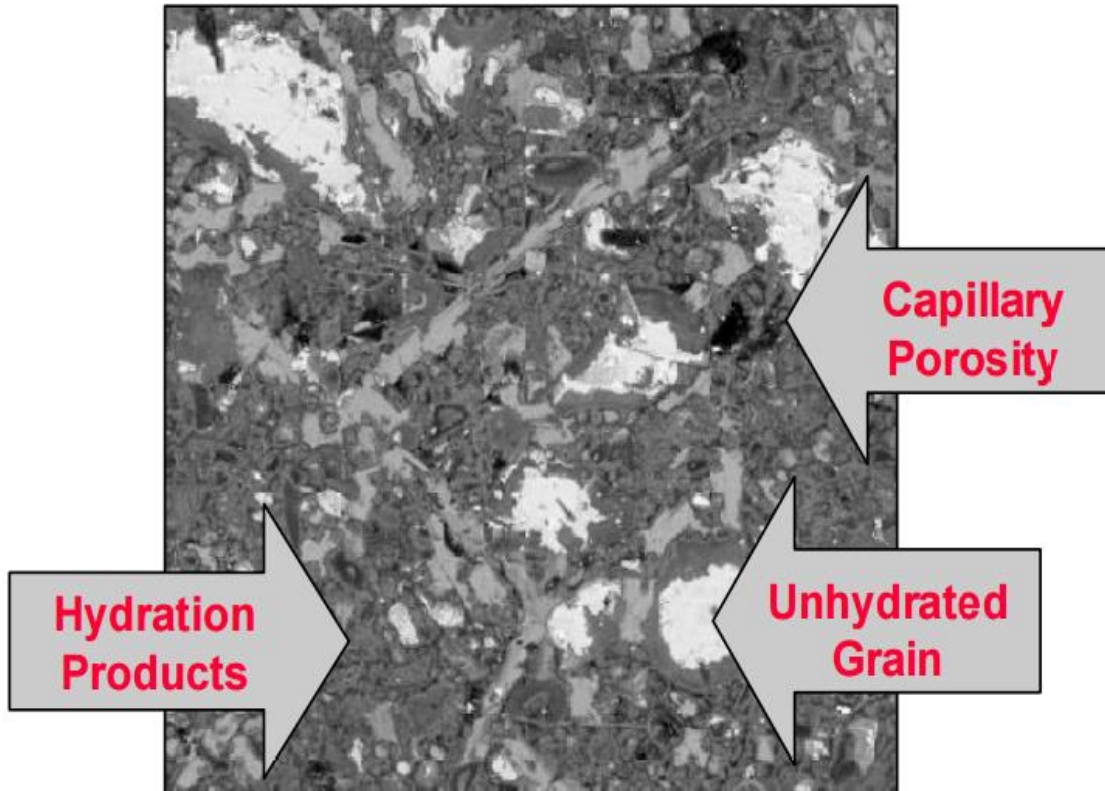
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- ❑ Hydrated cement paste consists of
  - Hydration Products
  - Un-hydrated Clinker Grain
  - Water
  - Air
- ❑ Hydration Products are
  - Calcium Silicate Hydrate (C-S-H)
  - Calcium Hydroxide (C-H)
  - Calcium Sulfo-aluminates (ettringite)





# Structure of Hydrated Cement ( Cont'd)

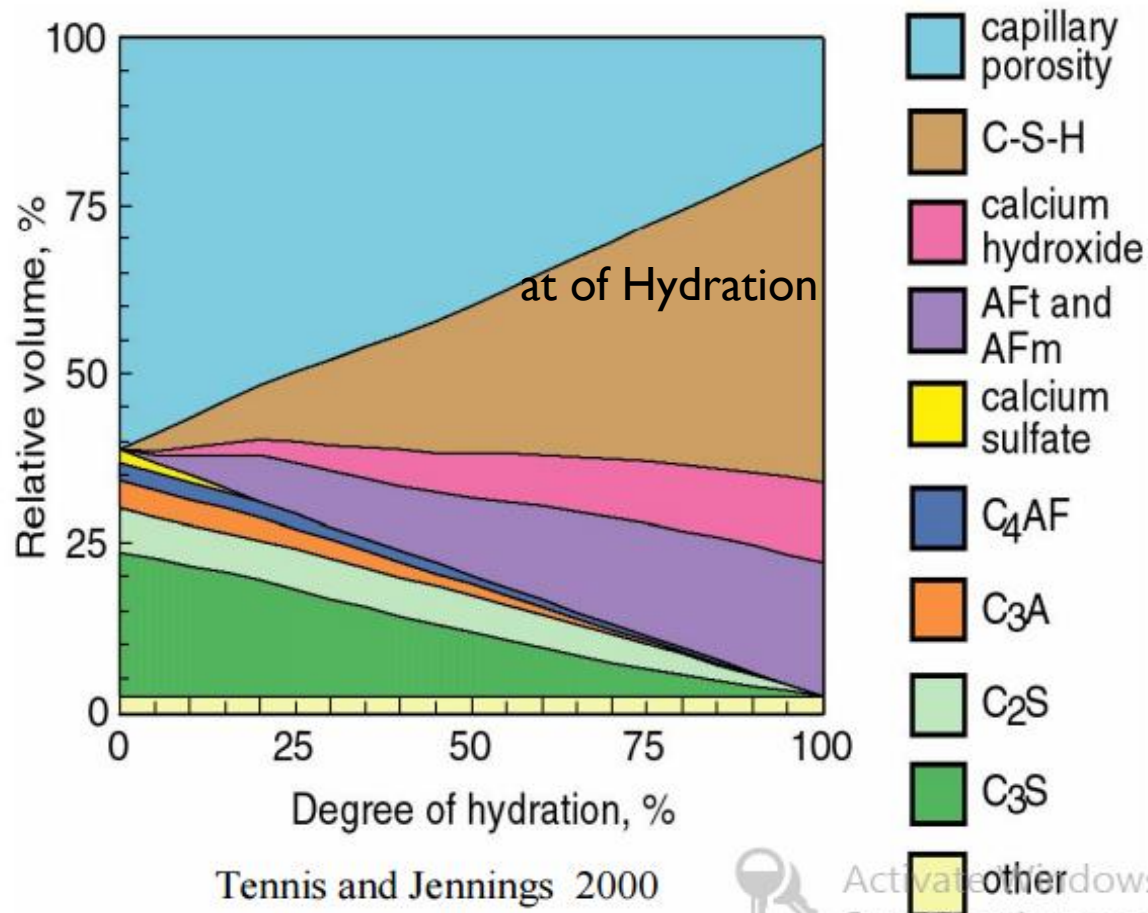


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# Relative volume of major compounds in hydrated pastes

## Function of Degree of Hydration



Tennis and Jennings 2000



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# References

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- ▶ Concrete Technology by A.M Neville, J.J Brooks.
- ▶ Concrete Technology by M.S Shetty.



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**THE END**

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