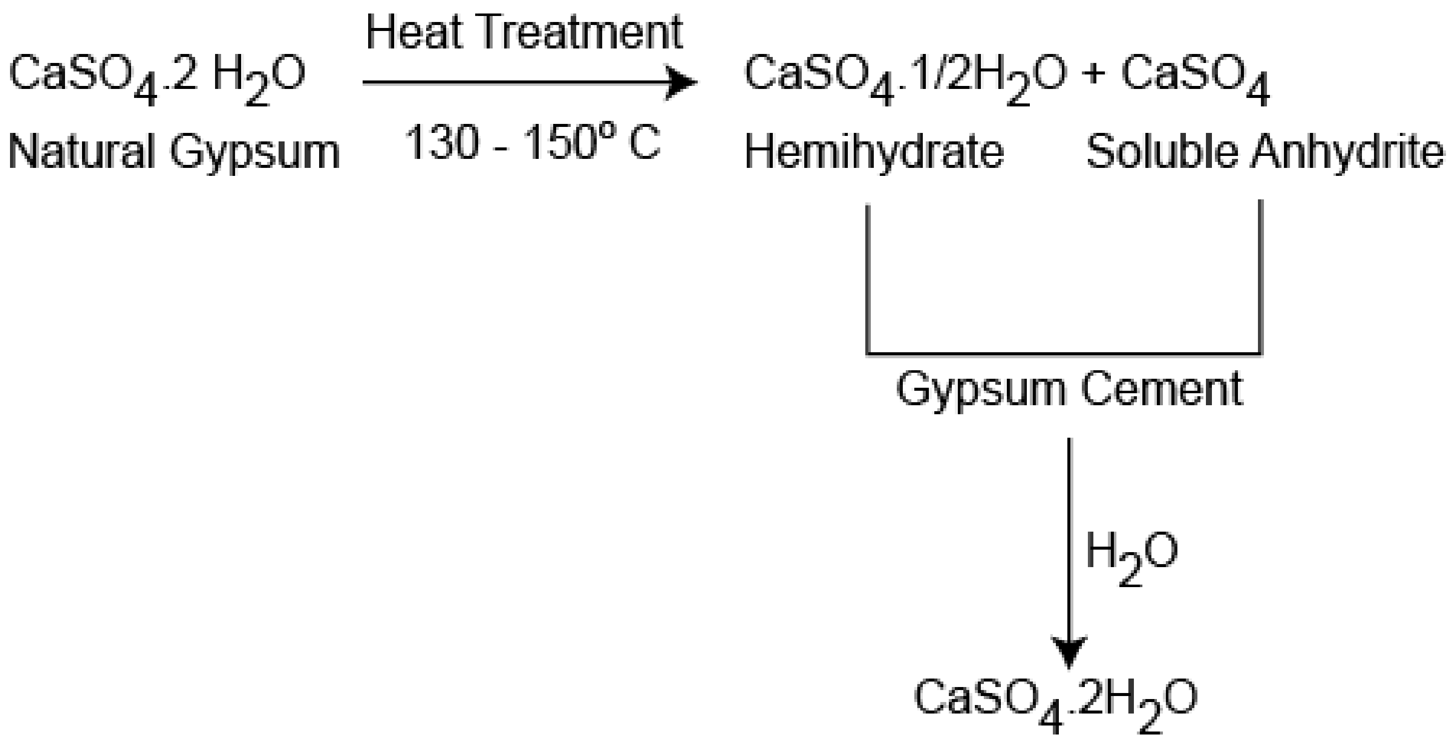
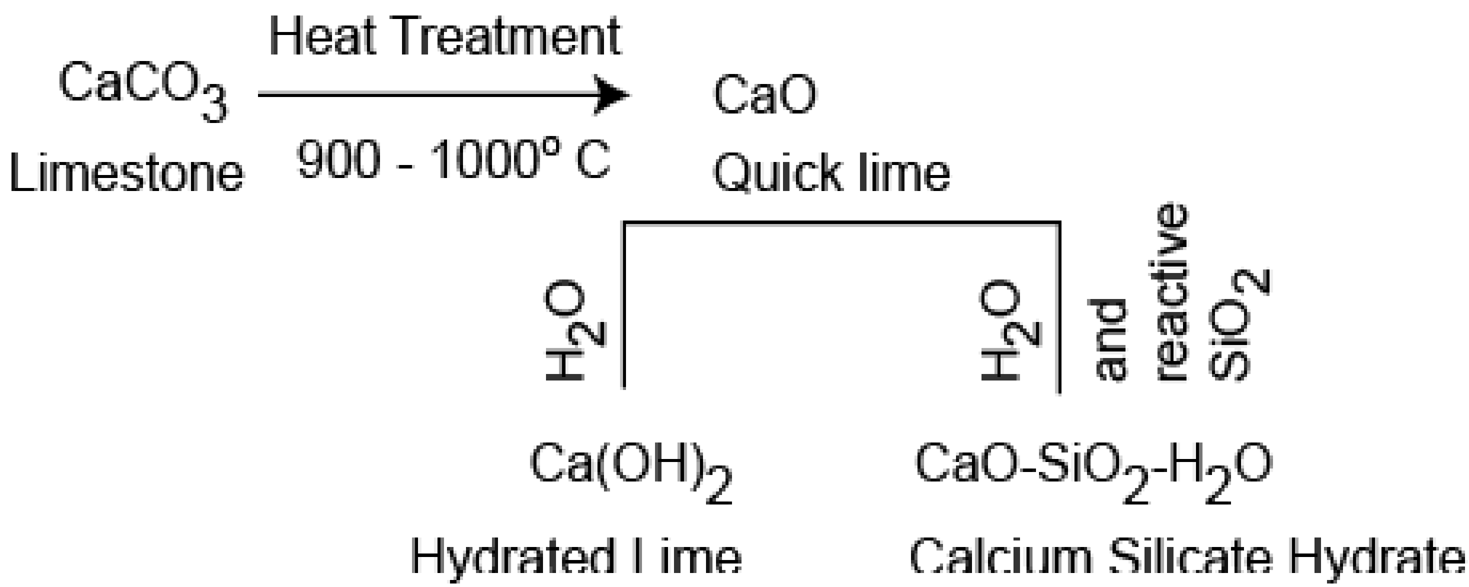
HYDRAULIC CEMENTS

Read Chapter 6

Gypsum Cement



Lime Cement



Heat Treatment
CaCO3
Limestone
900 - 1000° C
CaO
Quick lime
H2O
H2O
and reactive SiO2
Ca(OH)2
Hydrated Lime
CaO-SiO2-H2O
Calcium Silicate Hydrate

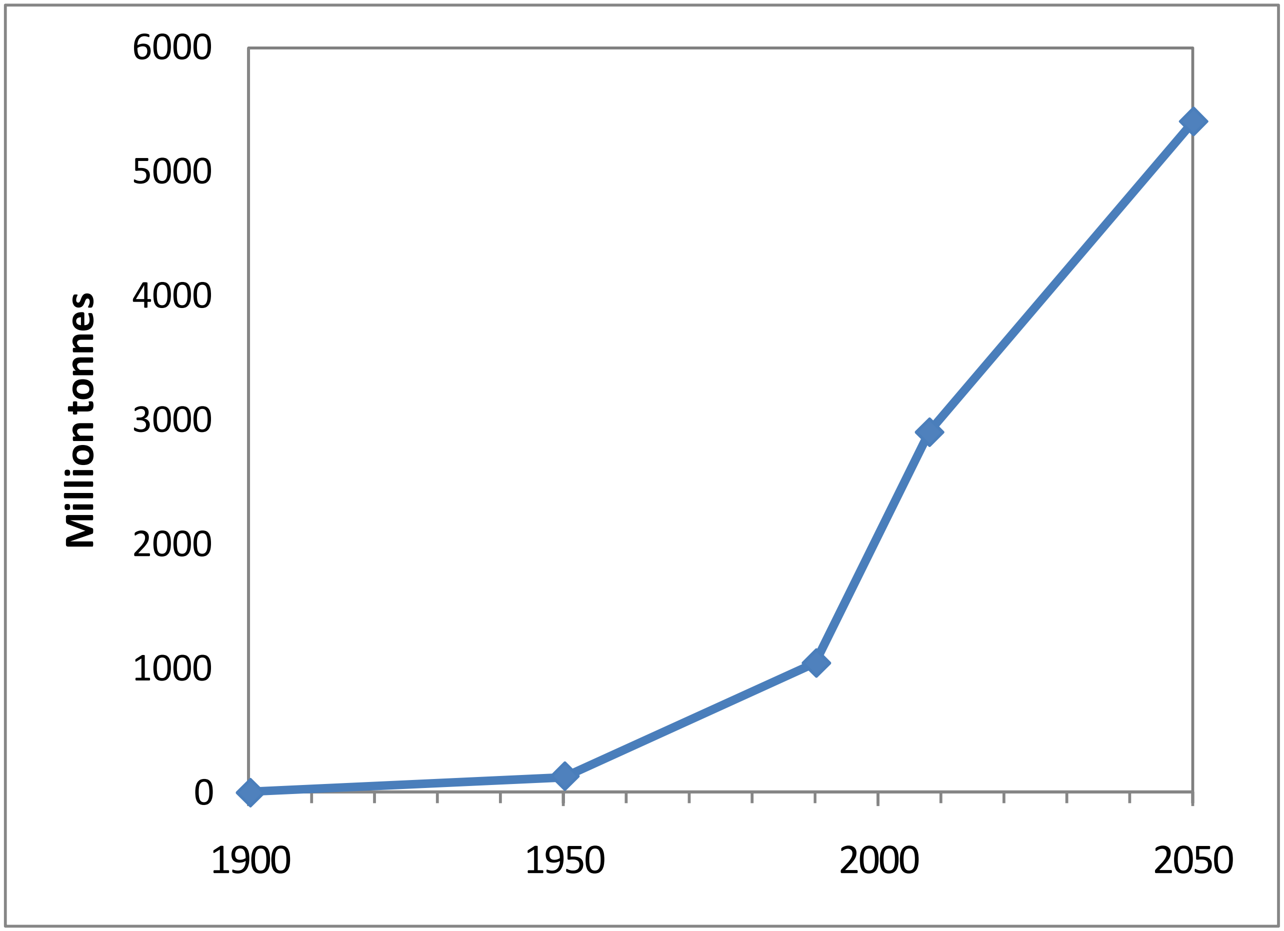
Portland Cement

A hydraulic cement capable of setting, hardening and remaining stable under water.

It consists essentially of hydraulic **calcium silicates**, usually containing calcium sulfate.

Portland Cement

Global production of Portland Cement



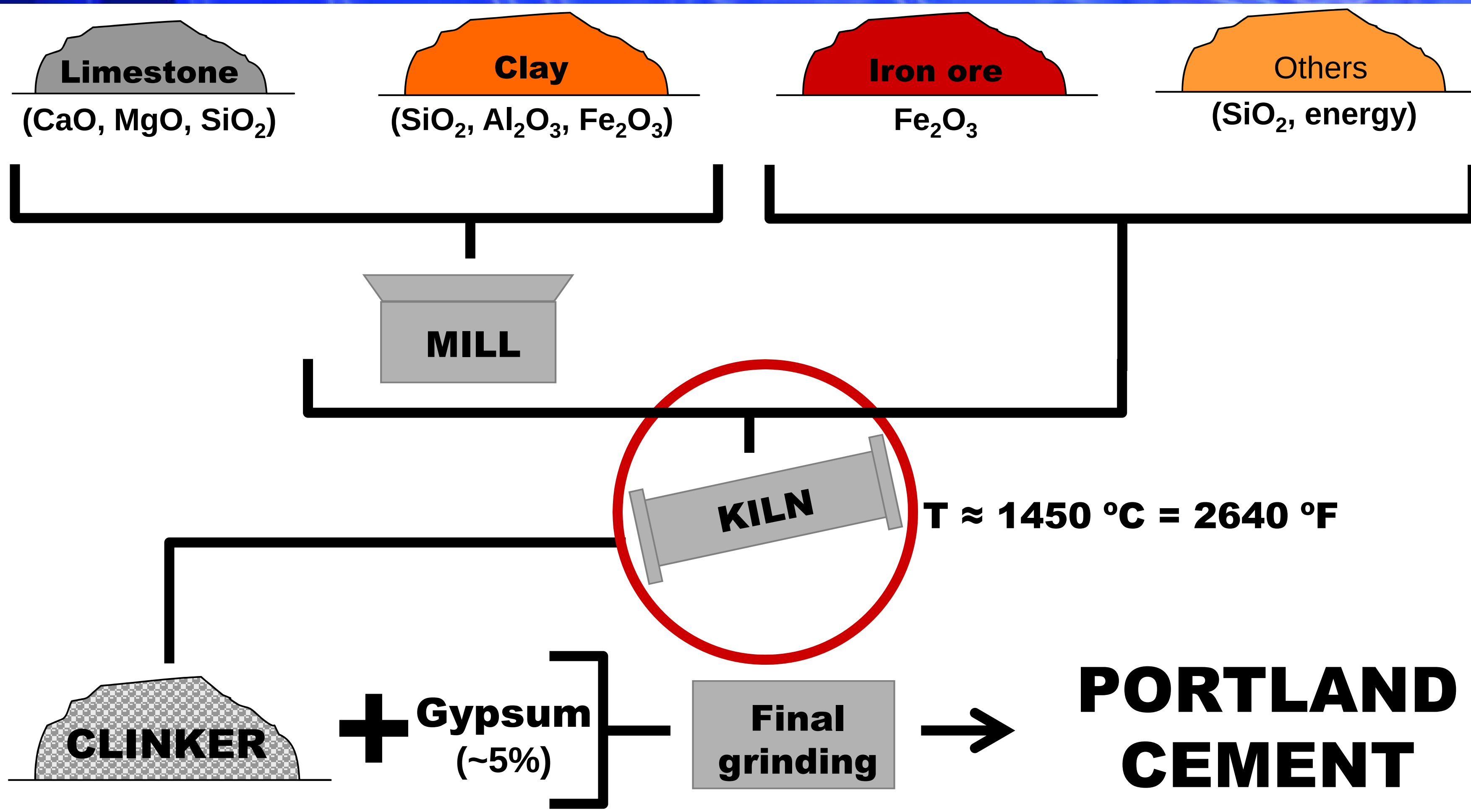
PC manufacture

Raw Materials:

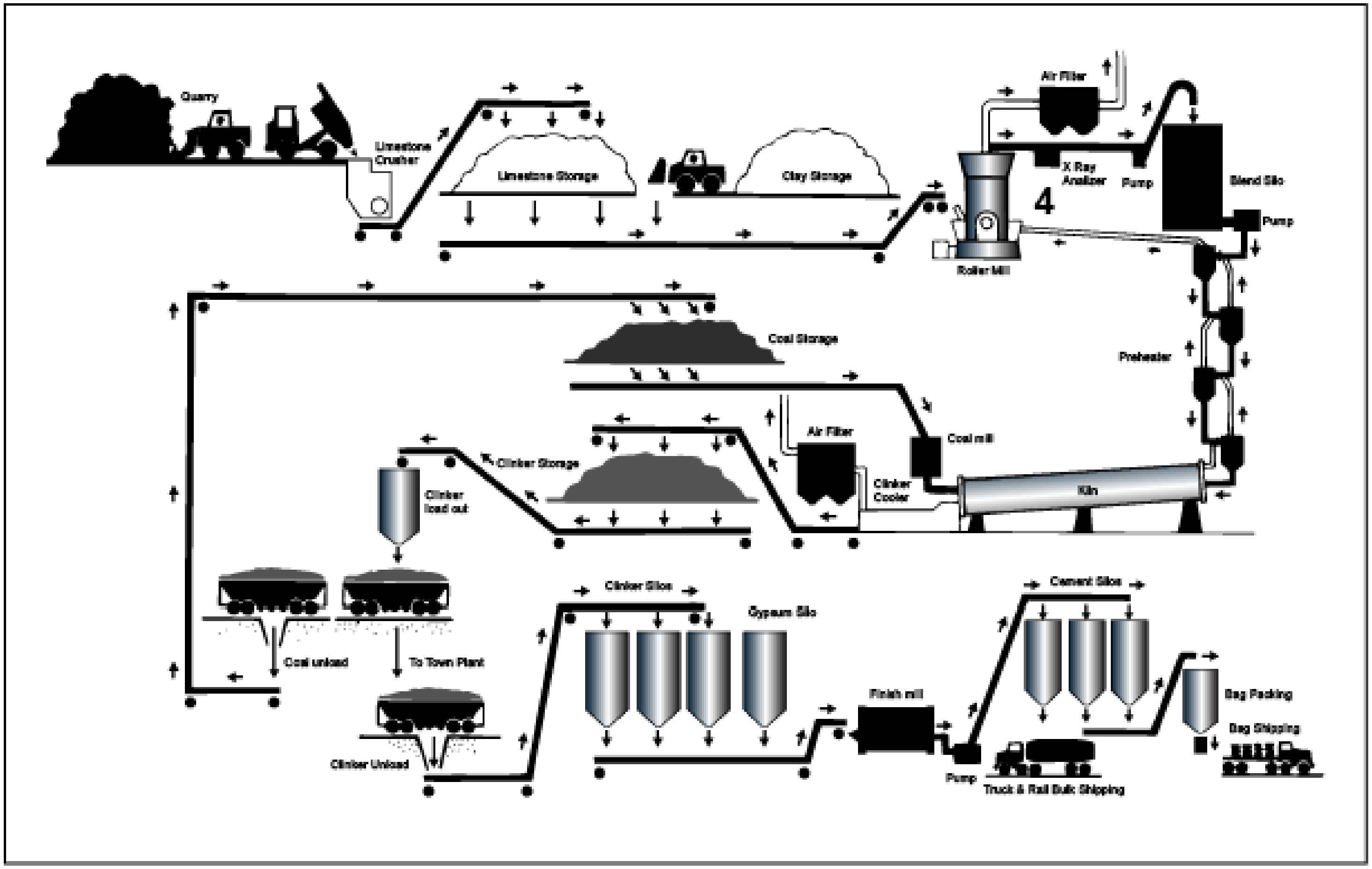
2/3 calcareous materials (lime bearing) - limestone

1/3 argillaceous materials (silica, alumina, iron) - clay

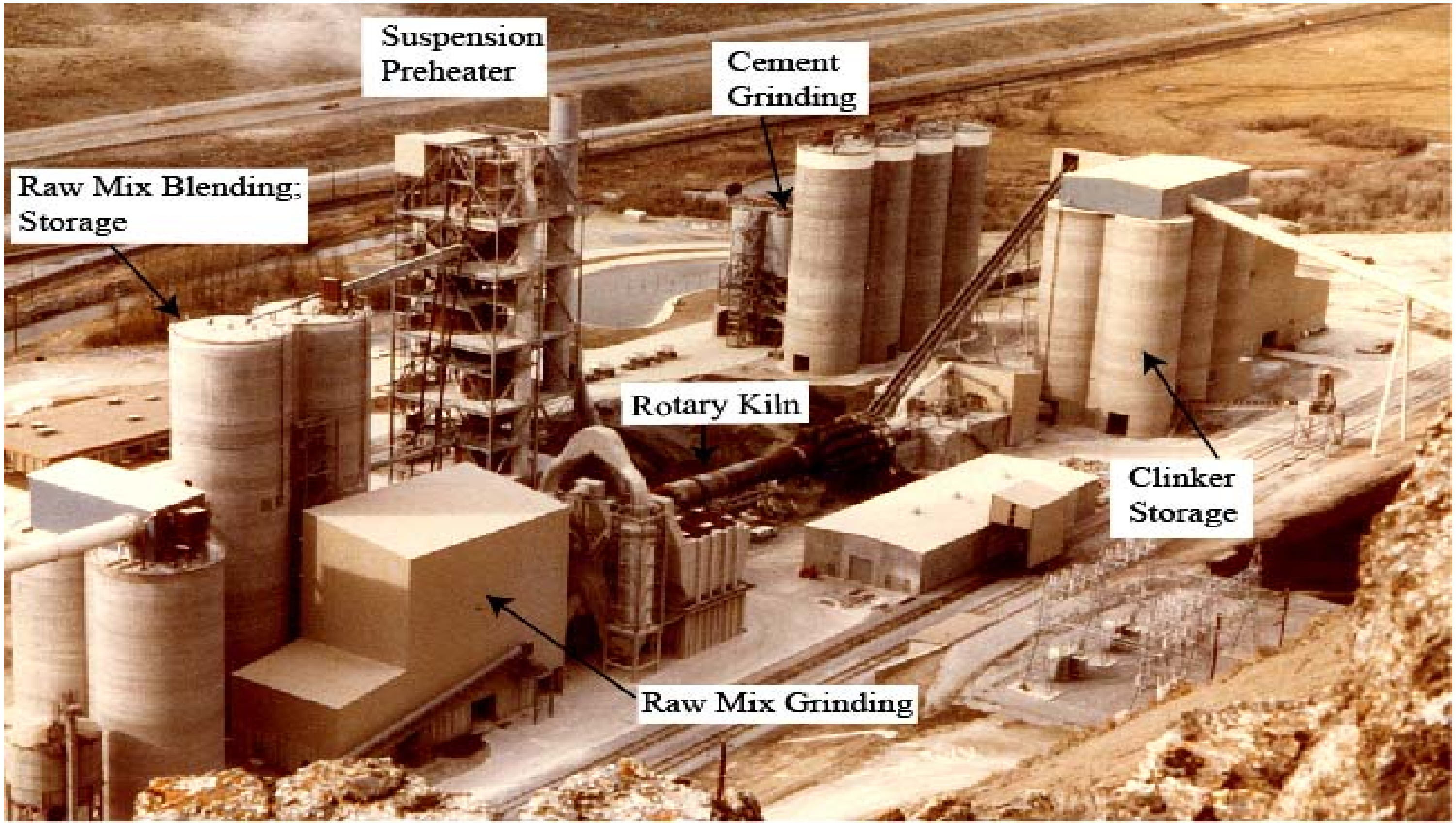
Cement manufacturing



Manufacturing Process

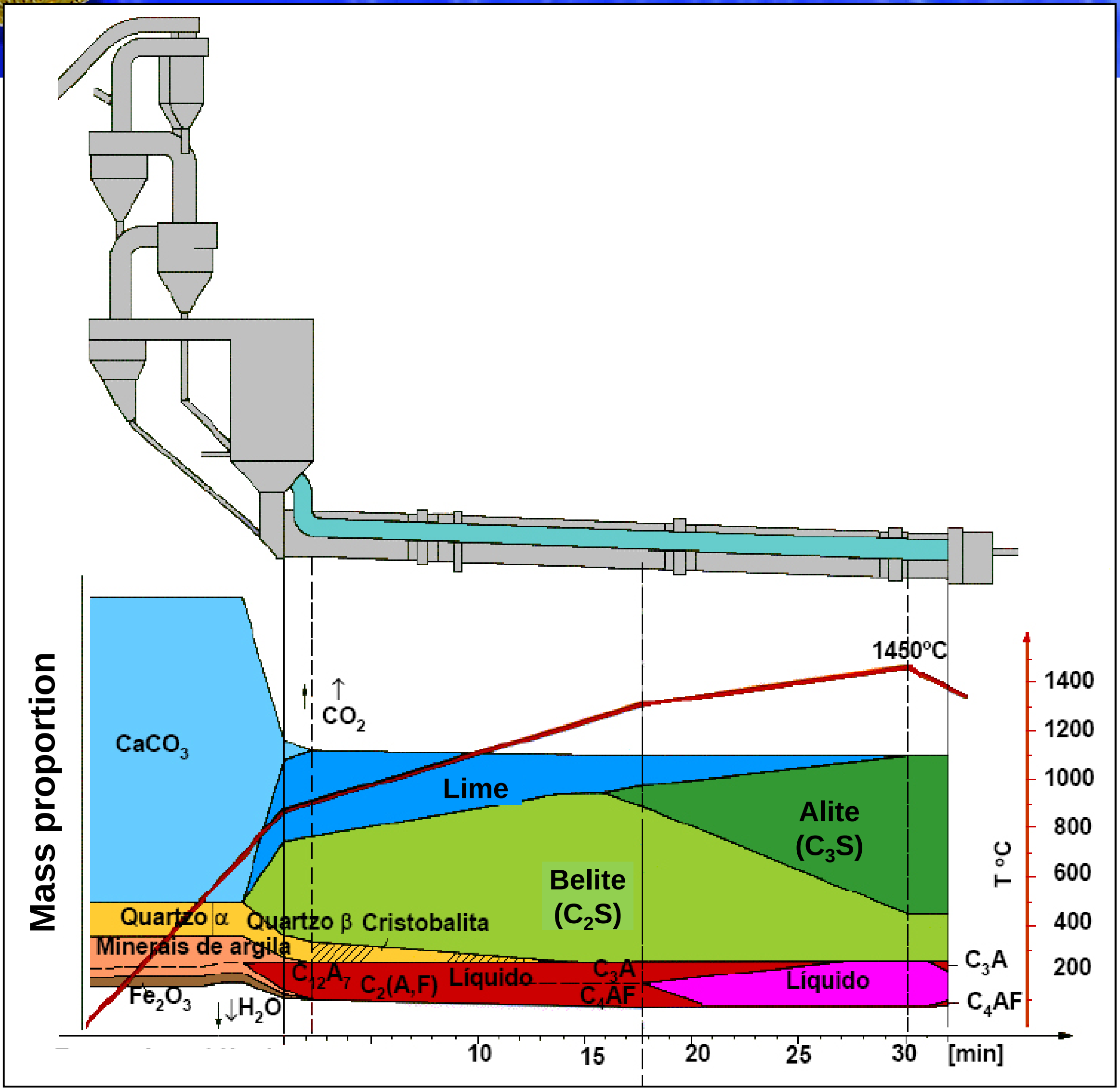


Cement Factory



Cement Factory

Clinker production



Typical rotary cement kiln equipped with preheater and precalciner.

Clinker composition

Raw materials

Limestone
($CaO + SiO_2 + Fe_2O_3 + CO_2$)

Clay
($SiO_2 + Al_2O_3 + Fe_2O_3 + H_2O$)

Other
(e.g. Rice husk: SiO_2)

• • •

Compounds	Abbreviation
$3CaO.SiO_2$ →	C_3S
$2CaO.SiO_2$ →	C_2S
$3CaO.Al_2O_3$ →	C_3A
$4CaO.Al_2O_3.Fe_2O_3$ →	C_4AF

Production Process

Production of cement is responsible for **~8% CO_2 emissions** in the World

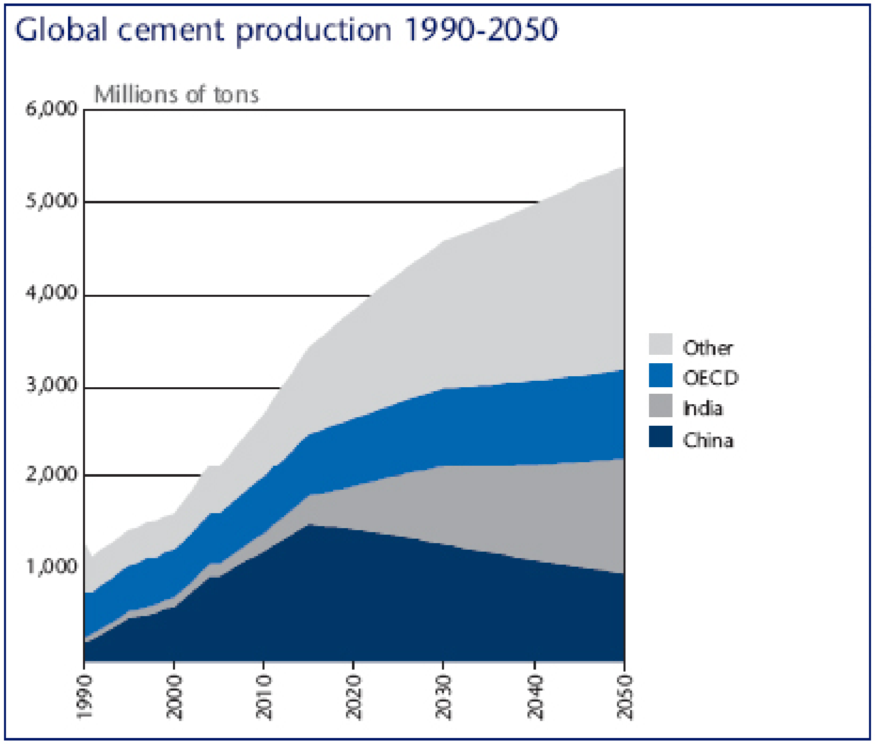
Clinker production: CO_2 emissions

- **Calcination reaction**

$$CaCO_3 \rightarrow CaO + CO_2$$
$$1kg \rightarrow 0,56kg + 0.44kg$$

- **For 1000kg of $CaCO_3$:**
  - **440 kg CO_2 (due to the chemical reaction only)**
  - **560kg CaO**
    - **Energy consumed by the reaction= 3,16 GJ per ton. CaO**
    - **Coal → ~93kg CO_2/GJ**
    - **560kg CaO → 1,77 GJ → ~ 165kg CO_2**
  - **Total = ~605 kg CO_2 (per ton. $CaCO_3$ calcined)**
- **About <u>815kg CO_2</u> are generated for every <u>1000kg of clinker</u> produced**
  - **Calcination (chemical reaction) = ~52%, Energy use = ~48%**

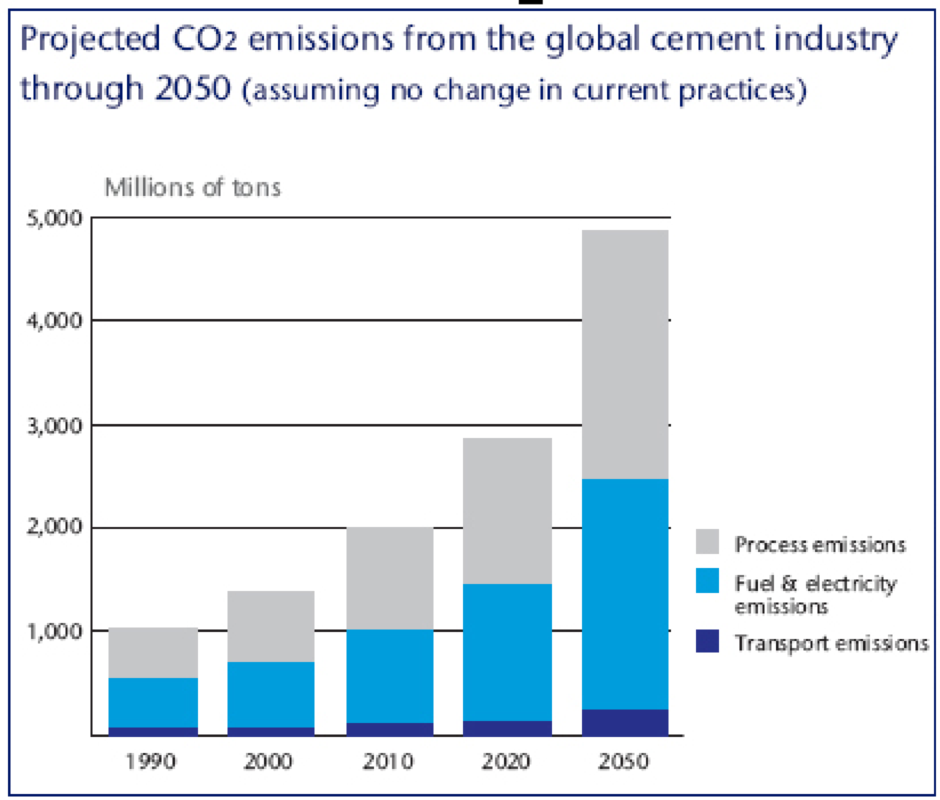
Cement production: CO_2 emissions



Source: International Energy Agency

Cement production

CO_2 emissions



Source: Battelle Memorial Institute (in *Agenda for Action*, p. 21)

Cement notation:

C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
H	H_2O

Cement Composites

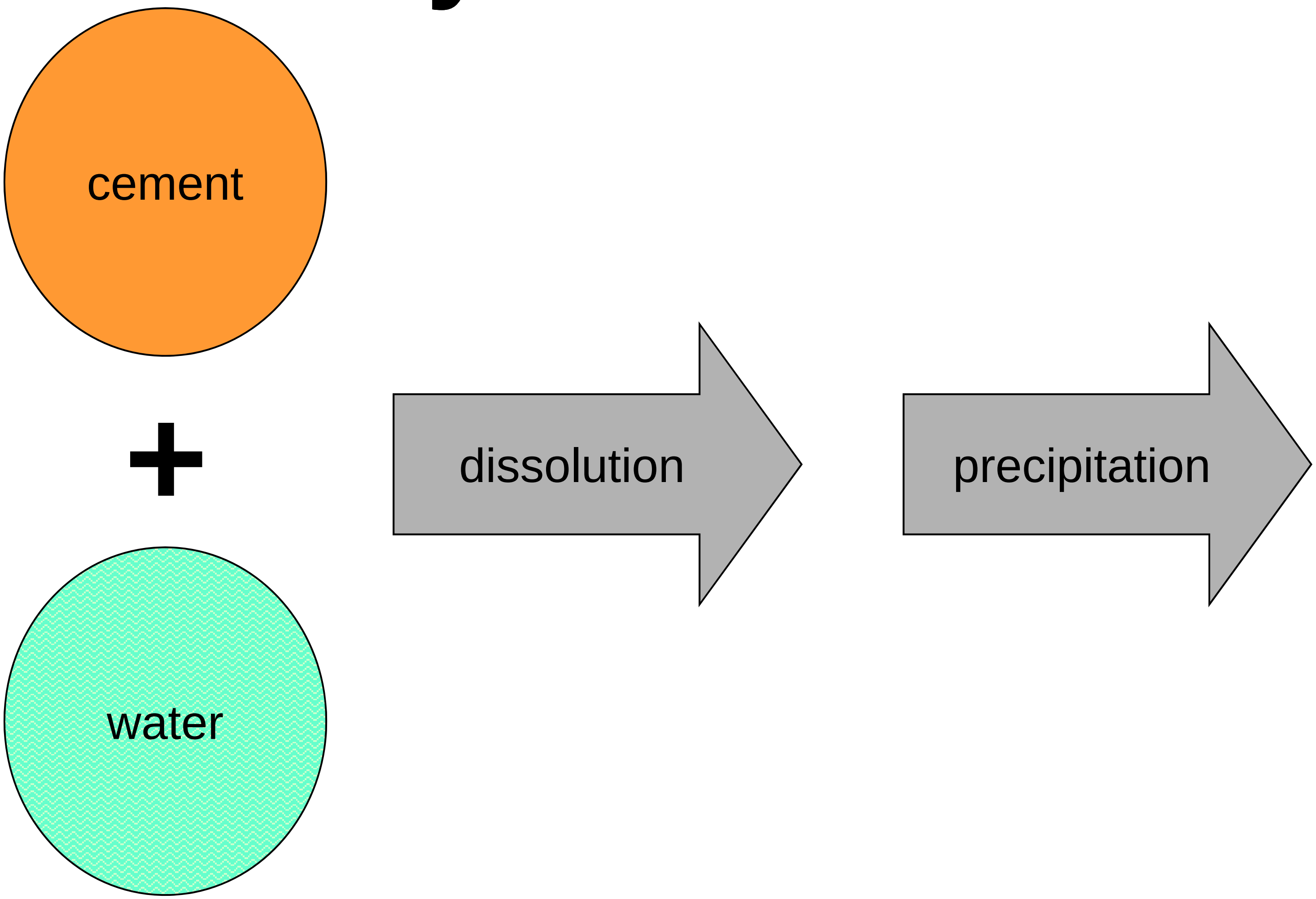
$$C_3S = 3CaO.SiO2$$

$$C_2S = 2CaO.SiO2$$

$$C_3A = 3CaO.Al2O3$$

$$C_4AF = 4CaO.Al2O3.Fe2O3$$

Hydration



Courtesy: Prof. Karen Scivener, EPFL

CHEMICAL REACTIONS

Important!!!

2C3S + 6H --> C3S2H3 + 3CH + 120 cal / g

2C2S + 4H --> C3S2H3 + CH + 62 cal / g

C3A + CSH2 --> Ettringite + 300 cal / g

Main Components of Portland Cement

Main Components of PC

	amount	notes
C3S	50%	very reactive compound, high heat of hydration, high early strength
C2S	25%	low heat of hydration, slow reaction
C3A	10%	problems with sulfate attack, high heat of hydration
C4AF	10%	
gypsum	5%	used to control the set of cement

SOLIDS IN CEMENT PASTE

Calcium Silicate Hydrate

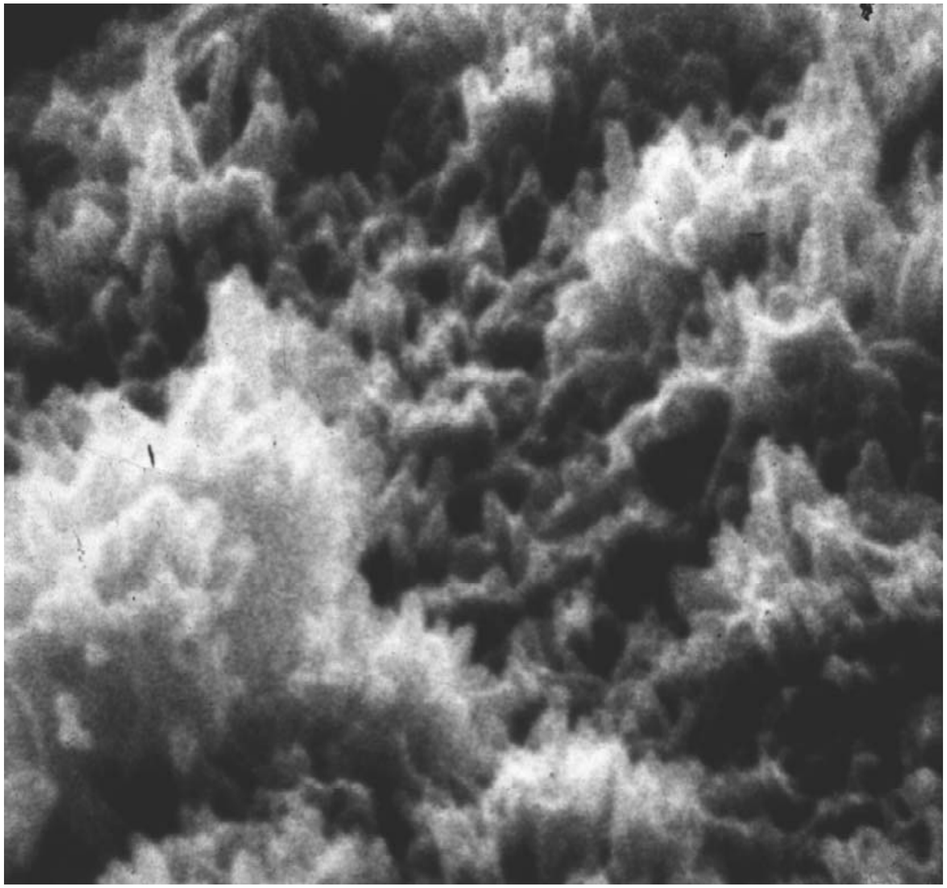
Notation: C-S-H
C/S Ratio: 1.5 to 2.0

Main Characteristics:

High Surface (100 to 700 m2/ g) ----> High Van der Walls Force -----> Strength.

Volume: 50% to 60%

C-S-H



SOLIDS IN CEMENT PASTE

Calcium Hydroxide (portlandite)

$Ca(OH)_2$
Volume: 20% to 25%
Low Van der Walls force,
problems with durability and strength

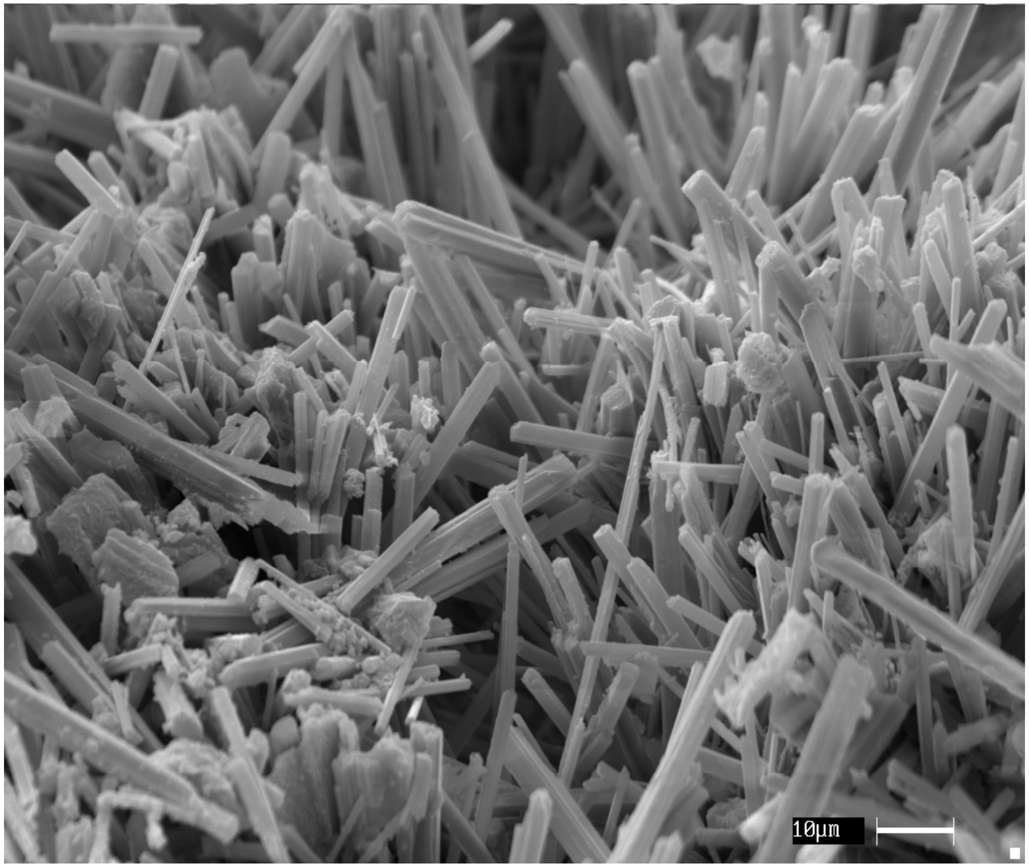
Calcium Hydroxide

SOLIDS IN CEMENT PASTE

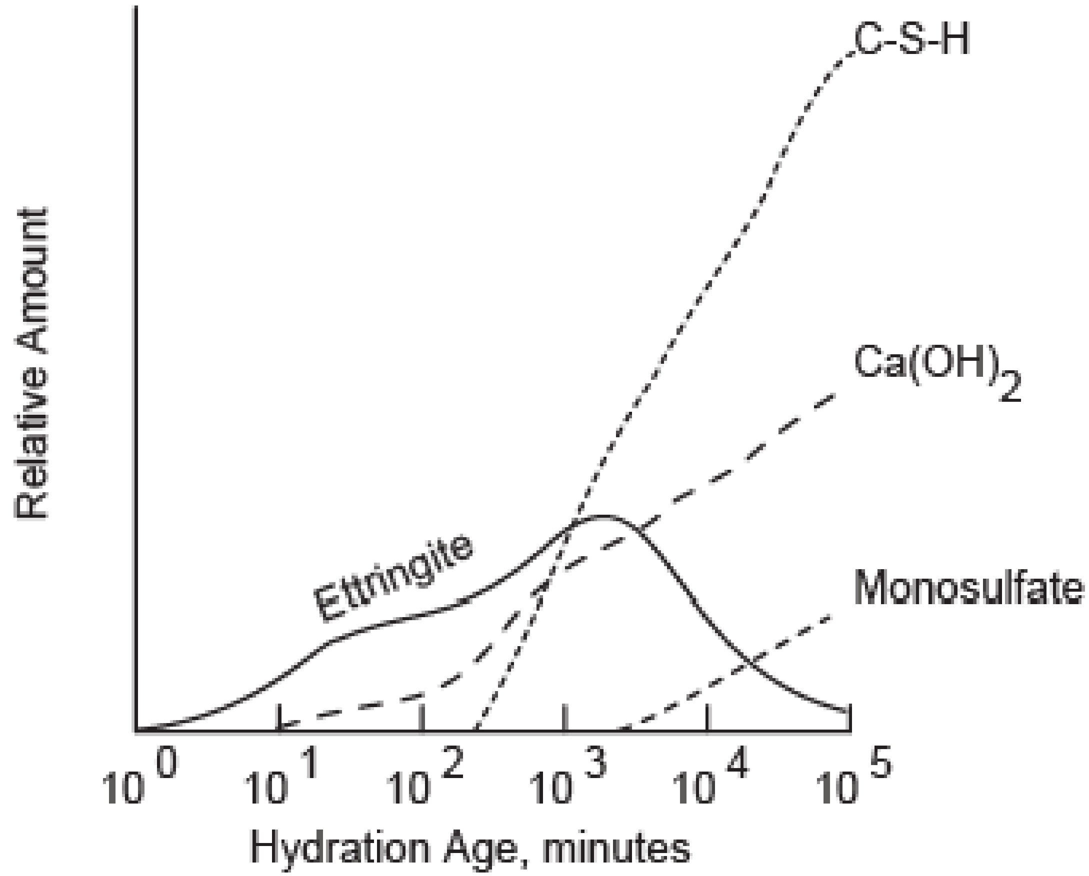
Calcium Sulfoaluminate Hydrates

Volume: 15% to 20%
first: ettringite
after: monosulfate hydrated

Ettringite



Hydration Evolution



Main Components of PC

Make a note

Main Components of PC

	amount	notes
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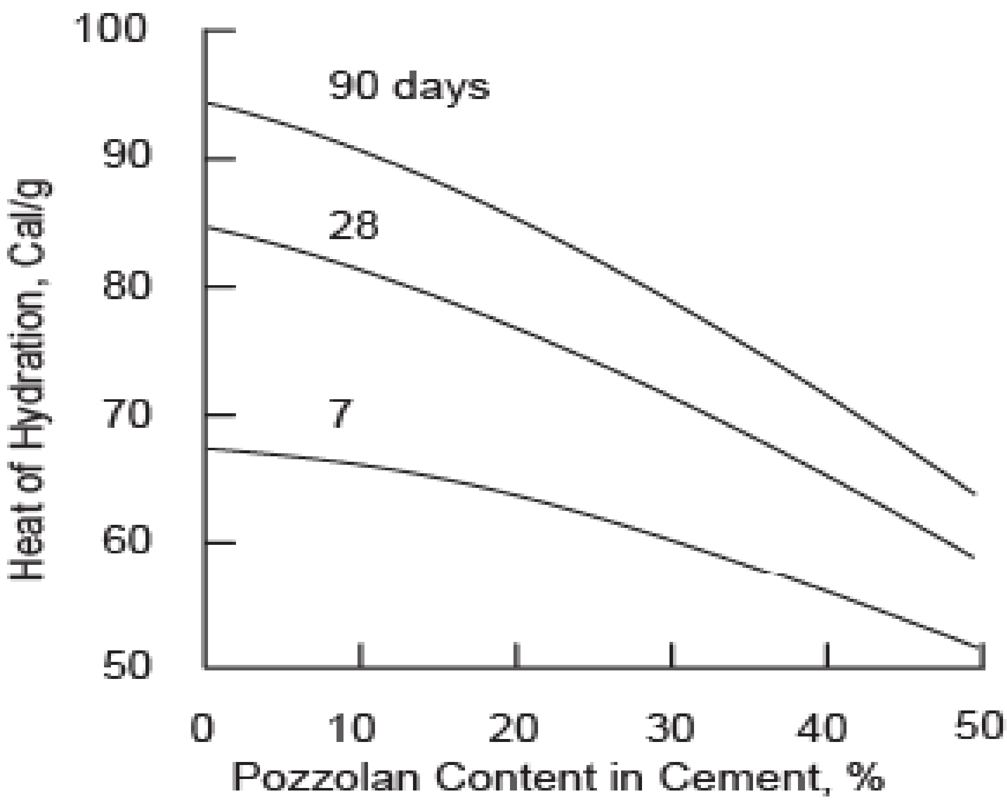
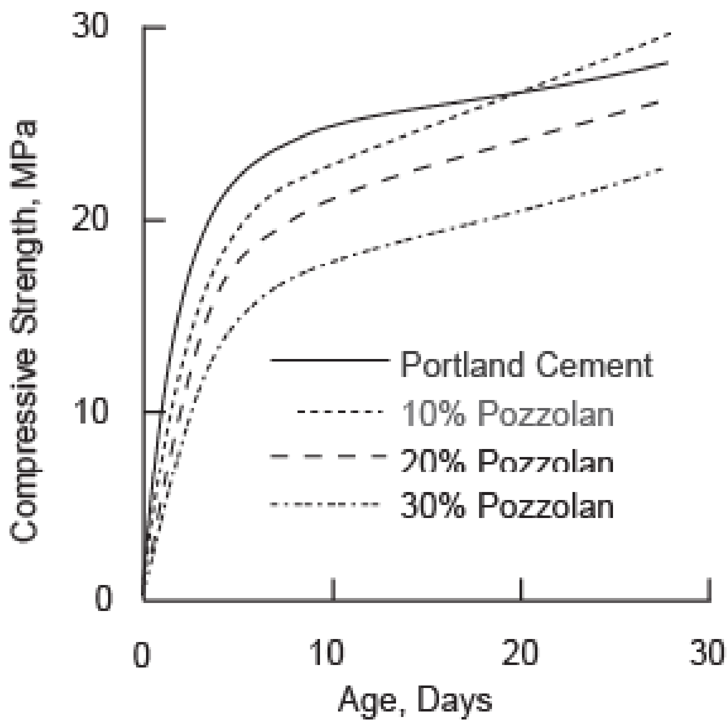
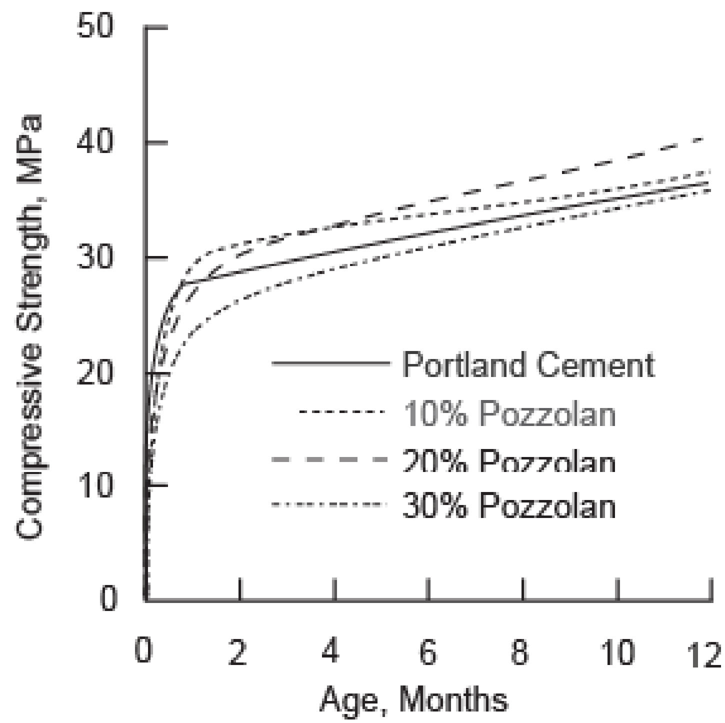
Effect of Pozzolan on Heat of Hydration



Compressive Strength





Setting and Hardening

Stiffening: **loss of consistency by the plastic cement paste and it is associated with the slump loss phenomena in concrete.**

Setting: **Solidification of the plastic cement paste**

Initial Set: **Beginning of solidification (point in time when the paste has become unworkable) (>45 min.)**

Final Set: **Final solidification (< 375 min.)**

Ordinary P.C (England) = Normal P.C. (USA) = Type I ASTM (general purpose PC).

TYPICAL COMPOUND COMPOSITION OF VARIOUS TYPES OF PORTLAND CEMENT

AVAILABLE IN THE UNITED STATES

ASTM type	General description	Compound composition range (%)			
		C_3S	C2S	C_3A	C4AF
I	General purpose	45-55	20-3O	8-12	6-1O
II	General purpose with moderate sulfate resistance and moderate heat of hydration	40-50	25-35	5-7	6-10
III	High early strength	50-65	15-25	8-14	6-10
V	Sulfate resistant	40-50	25-35	0-4	10-20

ASTM also has Types I-A, II-A, III-A -- cements with air entrainment

ASTM Portland Cements

Type I General Purpose

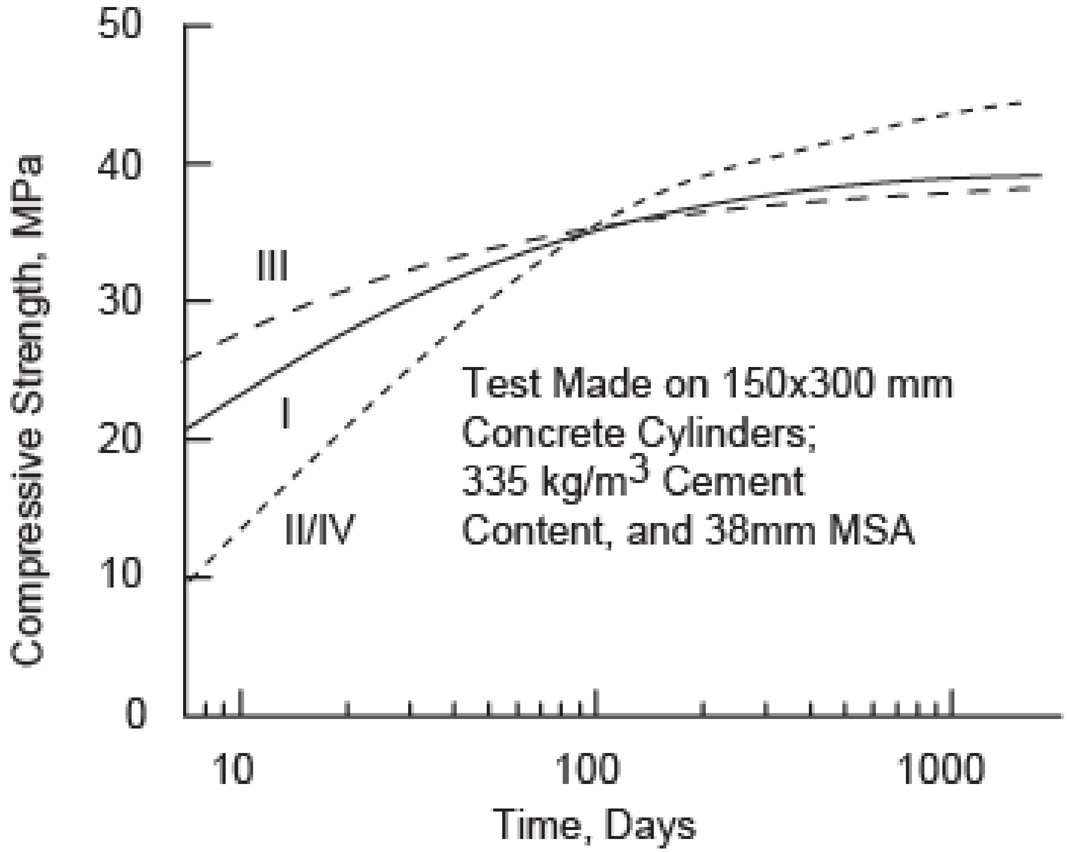
Type II moderate heat of hydration and sulfate resistance (**C3A < 8%**): general construction, sea water, mass concrete

Type III high early strength (C3A < 15%) : emergency repairs, precast, winter construction.

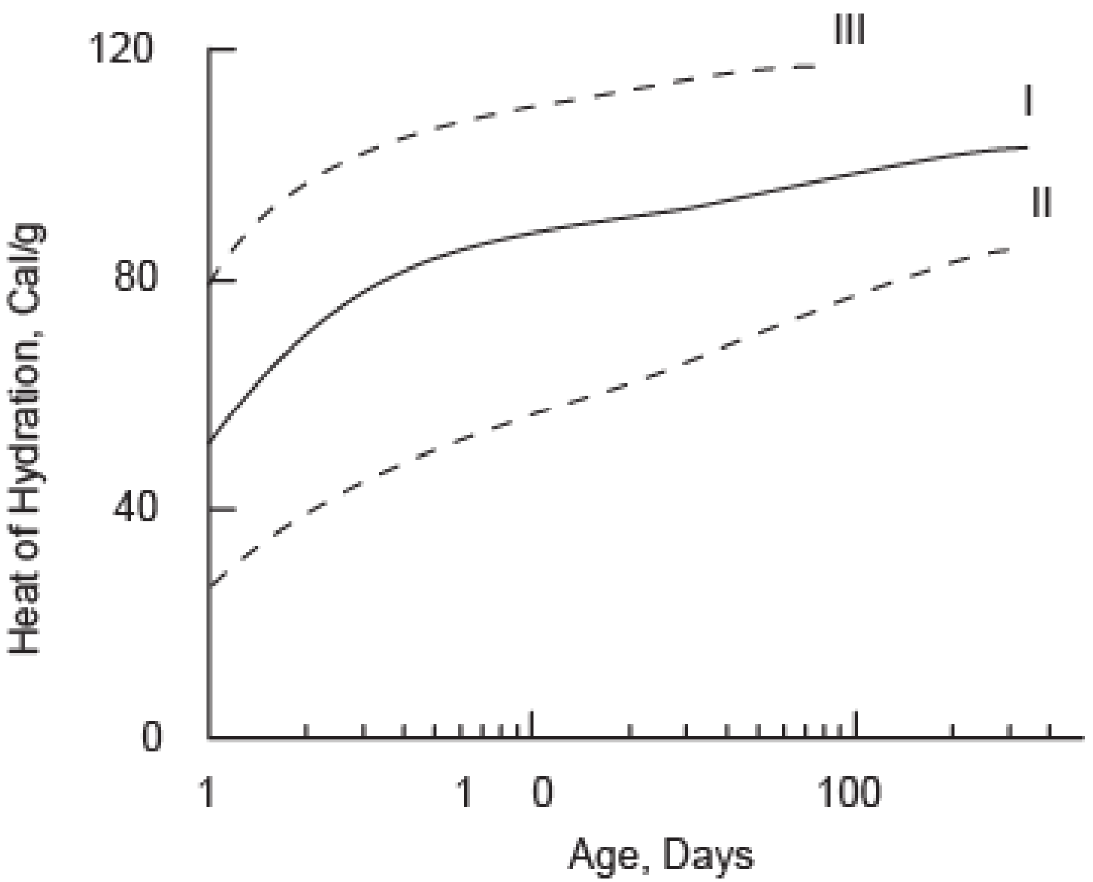
Type IV low heat (C3S < 35%, C3A < 7%, C2S > 40%) : mass concrete

Type V sulfate resistant (**C3A < 5%**): sulfate in soil, sewers.

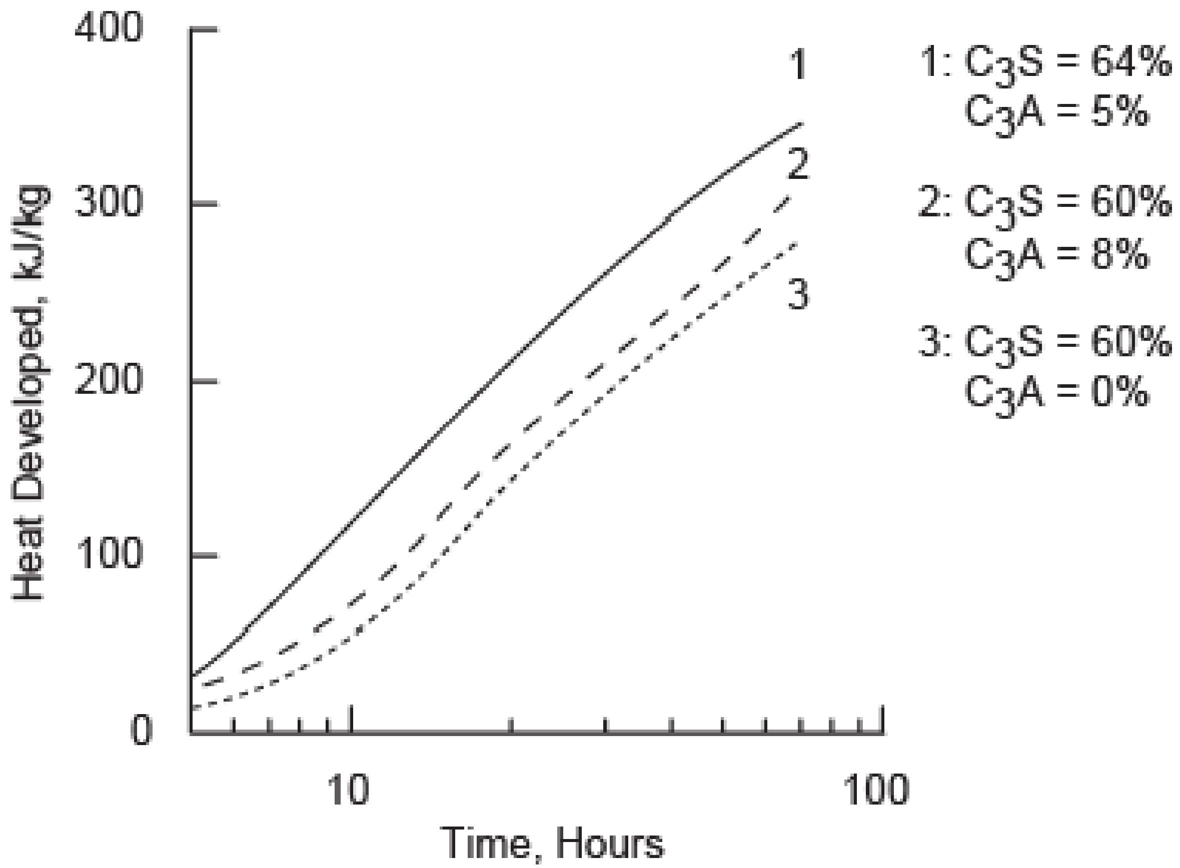
Strength Evolution



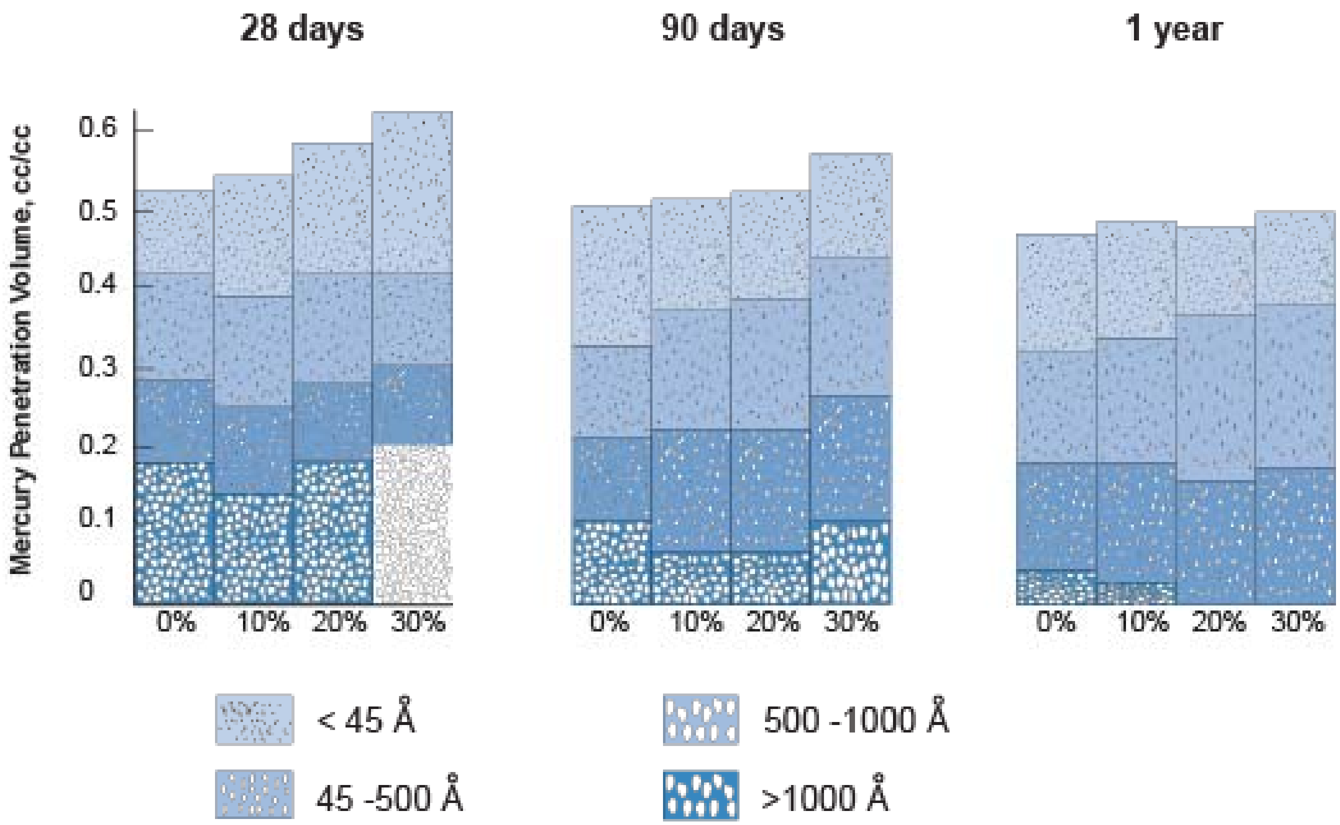
Heat Evolution



Effect of cement composition



Porosity evolution



Cement Requirements

Requirement specified by ASTM C 150	Type I	Type II	Type III	Type V
Fineness: minimum (m^2Ikg)	280	280	None	280
Soundness: maximum, autoclave expansion (%)	0.8	0.8	0.8	0.8
Time of setting				
Initial set minimum (min)	45	45	45	45
Final set maximum (min)	375	375	375	375
Compressive strength:				
minimum [MPa]				
1 day in moist air	None	None	12.4	None
1 day moist air + 2 days water	12.4	10.3	24.1	8.3
1 day moist air + 6 days water	19.3	17.2a	None	15.2

Other hydraulic cements

a) Blended P.C

b) Modified P.C.

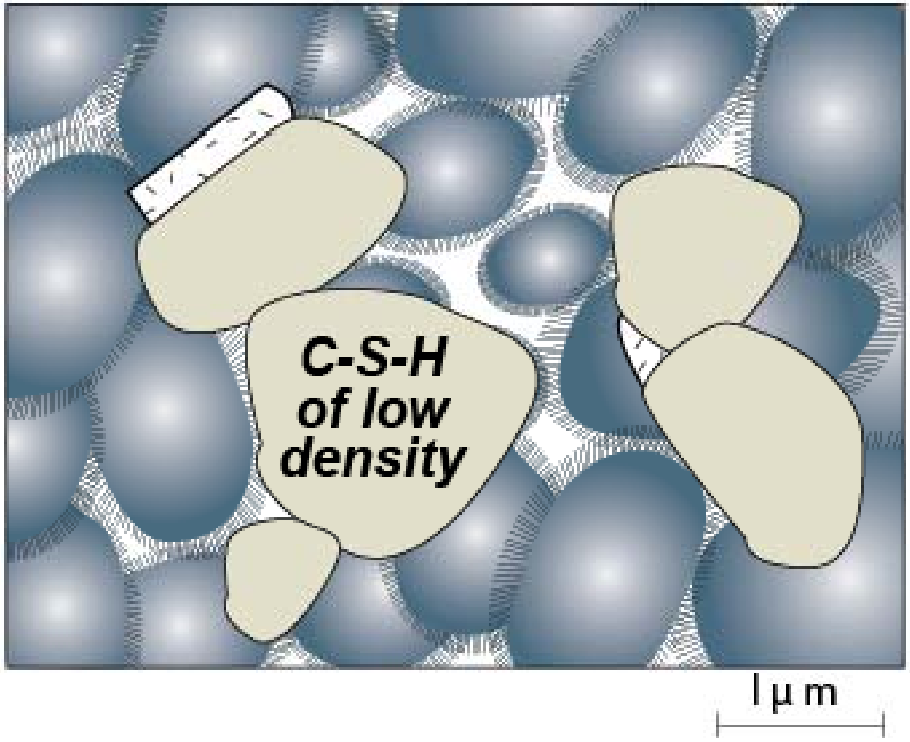
c) Non-calcium silicate cements

Blended PC

Type I-P P stands for pozzolan. It contains 25 to 30% of fly ash. It has low heat of hydration, develops strength over time.

Type I-S S stands for slag. It contains 50 to 60% of Blast-Furnace Slag.

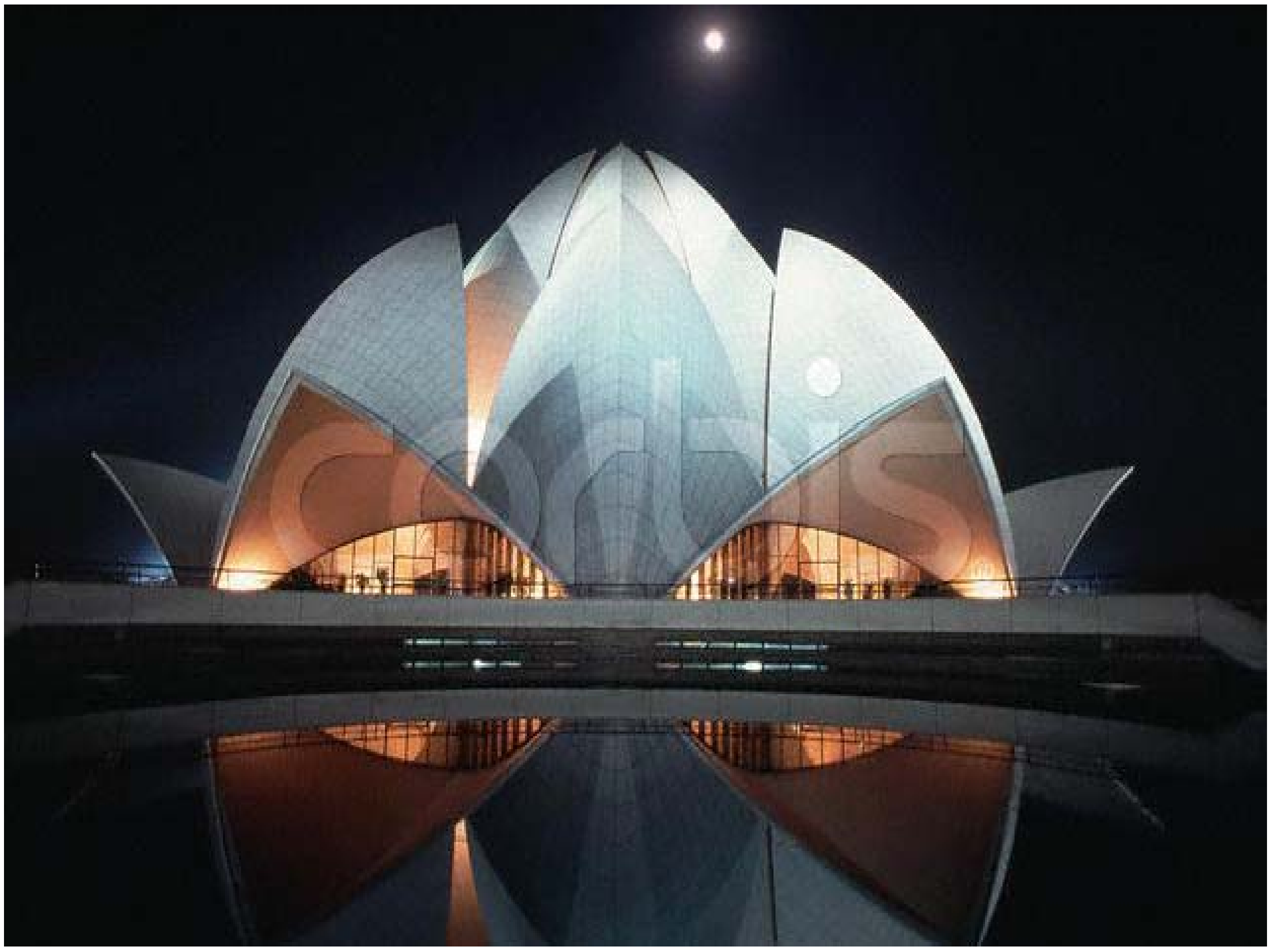
Blended Cement



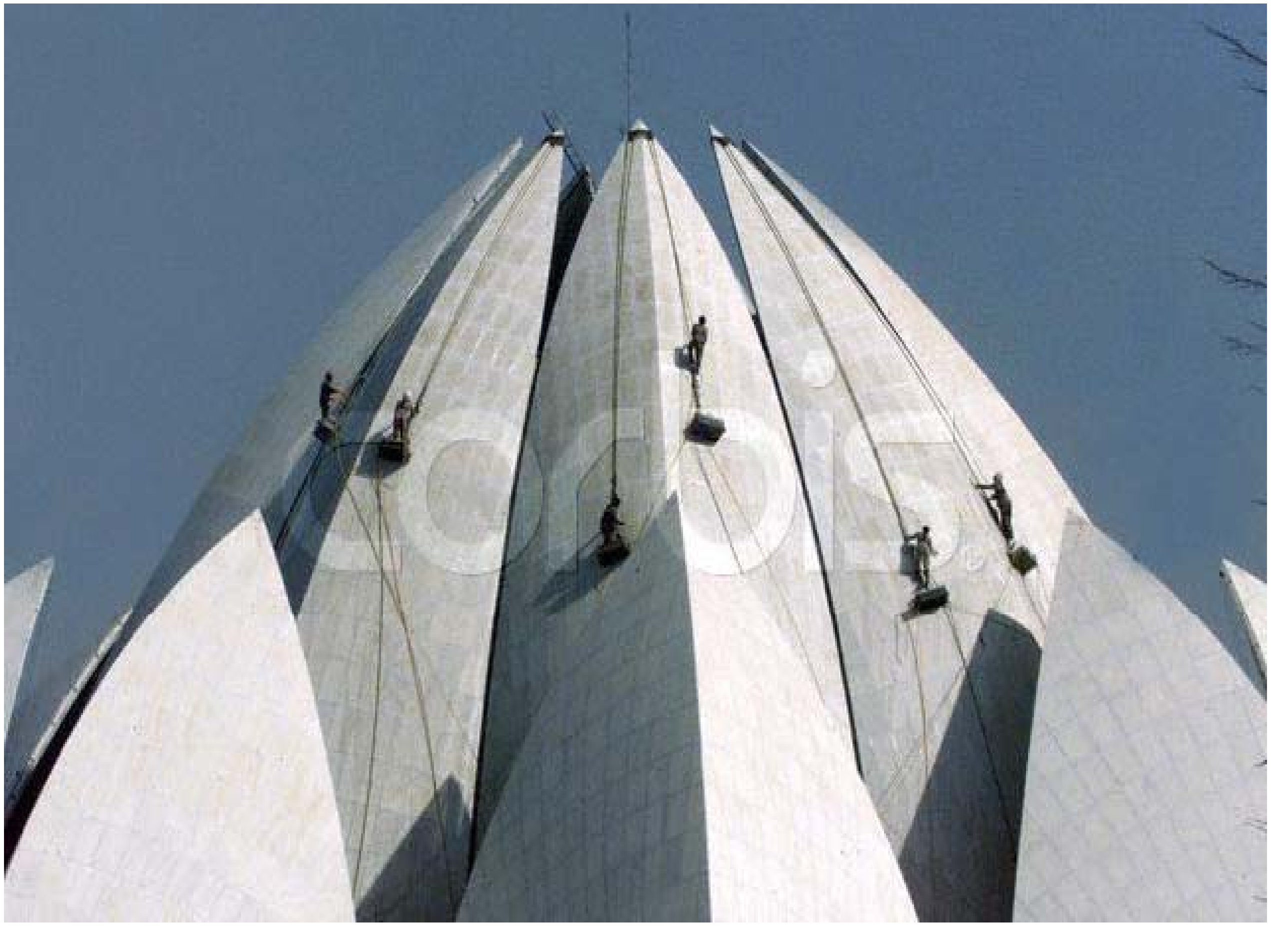
Modified PC

- Type K: shrinkage compensating cement
- Jet Set Cement: Fast Setting (3-5 min)
- Oil Well Cement
- White Cement

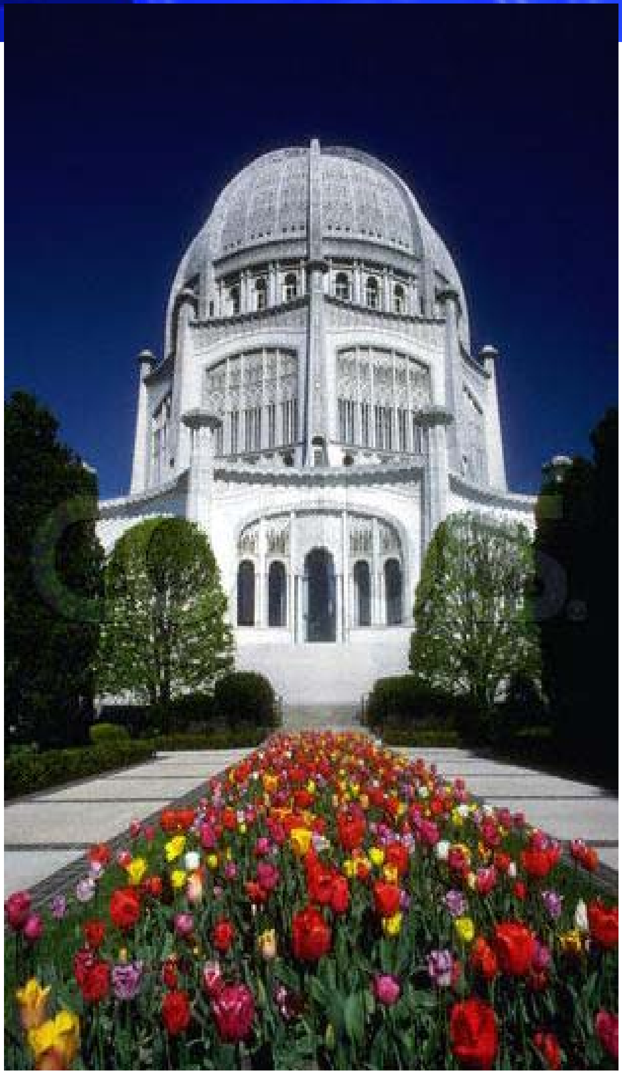
White Cement



White cement



Illinois



kitchens

Non Calcium Silicate Cement

Calcium Aluminate Cement

- high early strength
- hardening even at low temperatures
- superior durability to sulfate attack
- fast hydration

Drawback:

CA + 10 H → CAH10

↓ Conversion

C3AH6 + 2AH3 + 18H

CASE 1

Hot Cement

We are dealing with a cement shortage in our region, and during summer we must use cement which is quite hot. The cement comes directly from a cement plant located only 10 miles away from our concrete plant, and in the summer it is often so hot that it hurts to hold it in hand. This causes us many problems with our resistances. The compression resistances of our concretes are correct, though very erratic. Sometimes, for example, the resistance after 7 days is as high as it should have been after 28 days. What can we do about this?