March 14

Lecture 6 – Hydration of Portland Cement

CE 344
Materials of Construction

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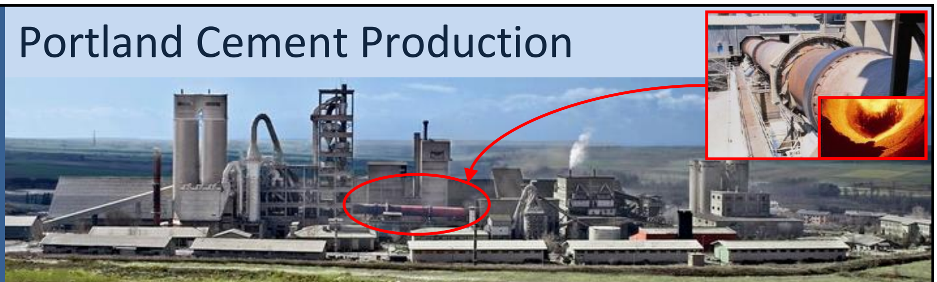
Department of Civil Engineering,
METU - Ankara

Cement

Portland Cement Production



Limestone + Clay
(2 parts) (1 part)

↓

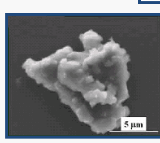
Crushing
Proportioning
Blending

↓

Preheating → Kiln (~1450°C) → Clinker → Cooling → Grinding (with ~4% Gypsum) → Portland Cement

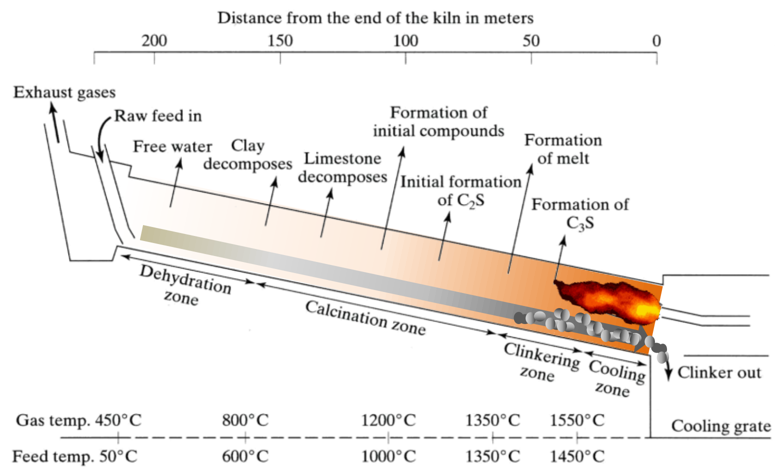
Calcination
$CaCO_3 \rightarrow CaO + CO_2 \uparrow$

1 ton Cement
↓
0.5 ton CO_2



Conditions and reactions in a dry-process rotary kiln

When suspension preheaters are used, dehydration and initial calcination takes place outside the kiln in the preheater tower.



*Adapted from Figure 3.2 from Mindess, Young, and Darwin, 2004

CE 344 – Tentative Outline

Week	Dates		Topic
1	16-Feb	20-Feb	**1 – INTRODUCTION to MATERIALS of CONSTRUCTION ✓ -- Q1**
2	23-Feb	27-Feb	**2 – GYPSUM ✓** **3 – LIME ✓**
3	2-Mar	6-Mar	**4 –** PORTLAND CEMENT – **manufacture**, hydration, tests, types
4	9-Mar	13-Mar	**(1st Lab)**
5	16-Mar	20-Mar	
6	23-Mar	27-Mar	**5 –** POZZOLANS
	Specific date TBA		**1st MIDTERM**
7	30-Mar	3-Apr	
8	6-Apr	10-Apr	**6 –** AGGREGATES
9	13-Apr	17-Apr	**(2nd Lab)**
10	20-Apr	24-Apr	**7 –** CONCRETE
11	27-Apr	1-May	**(3rd Lab)**
12	4-May	8-May	
	Specific date TBA		**2nd MIDTERM**
13	11-May	15-May	**8 –** POLYMERS
14	18-May	22-May	**9 –** FERROUS METALS, ALLOYS, AND CONCRETE REINFORCEMENT **10 –** CLAY BRICKS

(*) The detailed course schedule is available at the course web page.

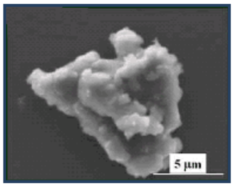
HYDRATION OF PORTLAND CEMENT

Overview

- Hydration
- Solids in hydrated cement matrix
- Rate/ heat of hydration
- Voids in hydrated cement matrix
- Water in hydrated cement matrix
- Fineness of cement
- Soundness of cement
- Setting
- Strength

Cement

Major compounds in portland cement



Cement

Calcium Silicates
$3(CaO).SiO_2$
$2(CaO).SiO_2$

Calcium Aluminates
$3(CaO).Al_2O_3$

Calcium Aluminoferrites
$4(CaO).Al_2O_3.Fe_2O_3$

- Portland cement is composed of four major oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3 ≥90%) & some minor oxides.
- CaO (C), SiO_2 (S), Al_2O_3 (A) & Fe_2O_3 (F) are the major oxides that interact in the kiln & form the major compounds.
  - C_2S - Belite
  - C_3S - Alite
  - C_3A
  - C_4AF

Cement

Ordinary portland cement (OPC)

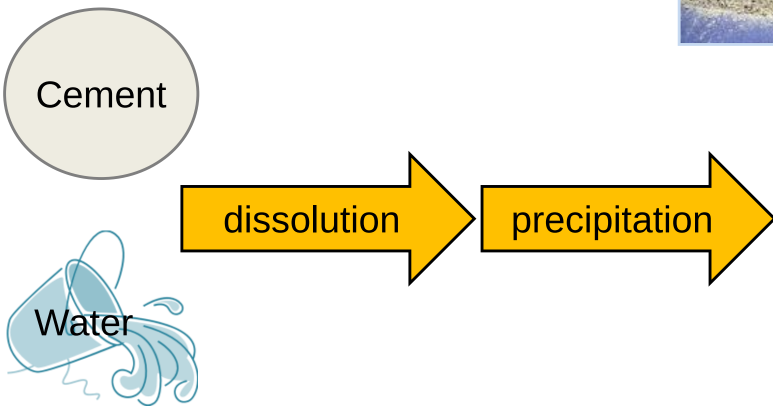
- Typical mineralogical composition of OPC:

Abbreviation	Compound	Formula	Wt% in OPC
C_3S	Tricalcium Silicate (Alite)	$3(CaO).SiO_2$	50-55
C_2S	Dicalcium Silicate (Belite)	$2(CaO).SiO_2$	19-24
C_3A	Tricalcium Aluminate	$3(CaO).Al_2O_3$	6-10
C_4AF	Tetracalcium aluminoferrite	$4(CaO).Al_2O_3.Fe_2O_3$	7-11
$C\bar{S}H_2$	Gypsum	$CaSO_4.2H_2O$	3-7

(C_3S) Clinker mineral; imparts early strength and set.
(C_2S) Clinker mineral; imparts long-term strength.
(C_3A) Clinker mineral; contributes to early strength and set
(C_4AF) Clinker mineral; acts as a flux to lower clinkering temp; imparts gray color.
($C\bar{S}H_2$) Interground with clinker to make portland cement. Controls early set.

Cement

Portland Cement Hydration

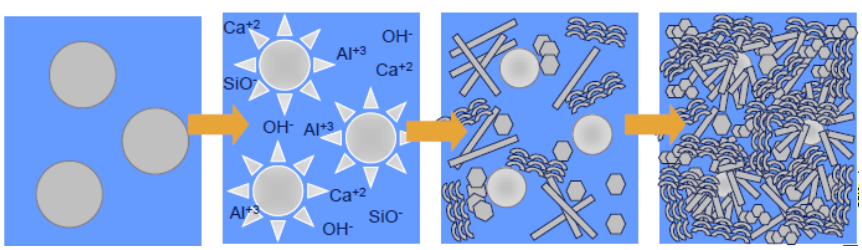


- Is the chemical combination of cement and water to form hydration products
- Takes time
- May not proceed to 100% completion

Cement

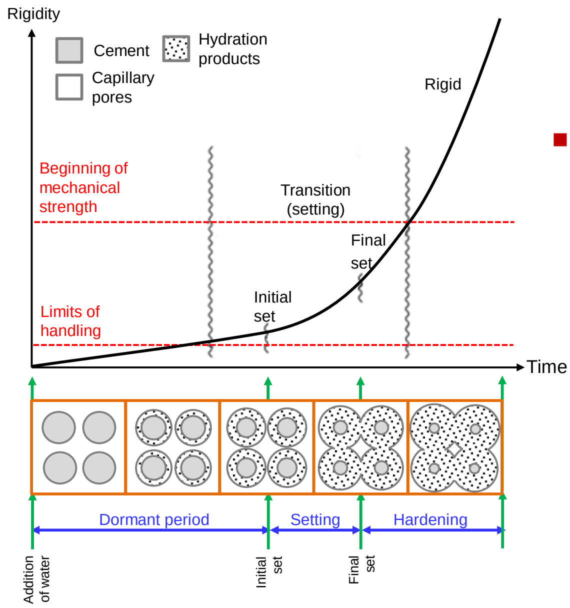
Portland Cement Hydration

- When water is added to cement, what happens?
  - Dissolution of cement grains
  - Growing ionic concentration in “water” (now a solution)
  - Formation of compounds in solution
  - After reaching a saturation concentration, compounds precipitate out as solids (“hydration products”)
  - In later stages, products form on or very near the surface of the anhydrous cement



Cement

Hydration



- Formation of hydration products over time leads to:
  - Stiffening
    - loss of workability
  - Setting
    - solidification
  - Hardening
    - strength gain

Cement

Portland Cement Hydration

Hydrated Cement Paste

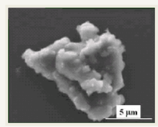
Cement + Water

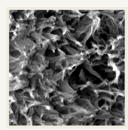
Calcium Silicates
$3(CaO).SiO_2$
$2(CaO).SiO_2$

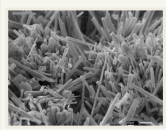
Calcium Aluminates
$3(CaO).Al_2O_3$

Calcium Aluminoferrites
$4(CaO).Al_2O_3.Fe_2O_3$

Unhydrated Cement Particle
+
Calcium Silicate Hydrates
+
Calcium Hydroxide
+
Calcium Sulfoaluminate Hydrates







Hydrated Cement Paste

- Solids
  - C-S-H
  - CH
  - Ettringite
  - Monosulfate hydrate
  - Residual unhydrated cement
- Voids
  - Entrapped air (>1mm)
  - Entrained air (75-500um)
  - Capillary pores (macro → meso)
  - Interlayer space (micropores)
- Water
  - Capillary water
  - Adsorbed water
  - Interlayer water
  - Chemically combined water

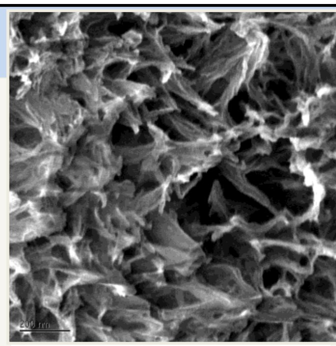
Calcium Silicate Hydrates

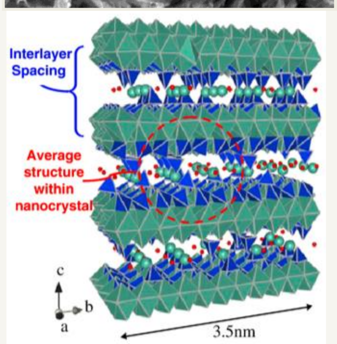
Cement

- Notation: C-S-H
  - C/S varies between 1.5-2
  - H is even more variable
- Structure from poorly crystalline to amorphous
- Layered structure with very high surface area (100-700 m^2/g)
  - High Van der Walls forces

    ↓

  - Highest contribution to strength
- 50-60% of solids in hydrated cement paste



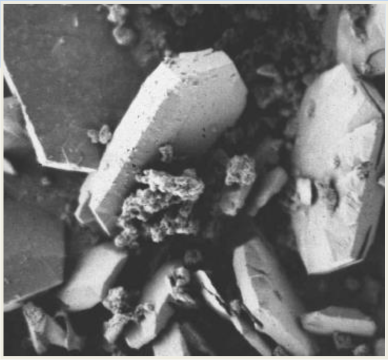


* Meral et al., Cement and Concrete Research 41 (2011)

Calcium Hydroxide

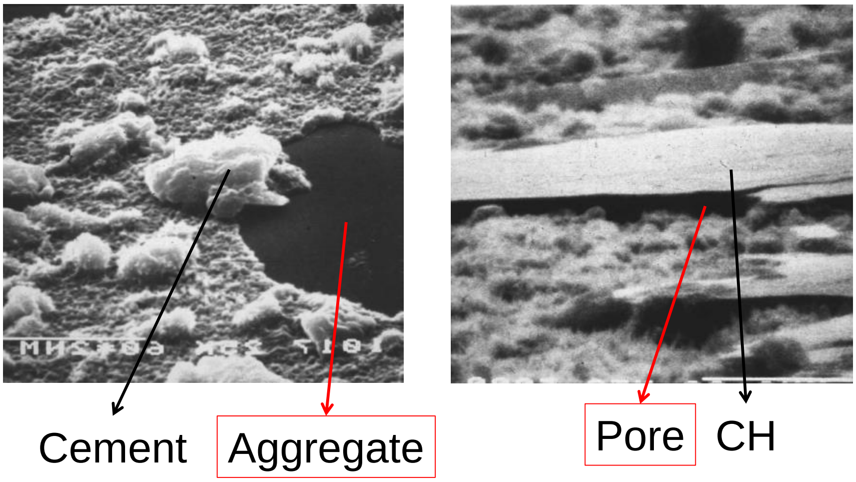
Cement

- Notation: CH
- Definite stoichiometry
- Large, weak crystals with hexagonal – prism morphology
  - Lower Van der Walls forces
    ↓
  - Lower strength contribution
- Size of the crystals depends on the amount of available space
- 20-25% of solids in hydrated cement paste
- Keeps the pore solution alkaline (pH 12.4-13.5)



* Image courtesy of P.J.M. Monteiro

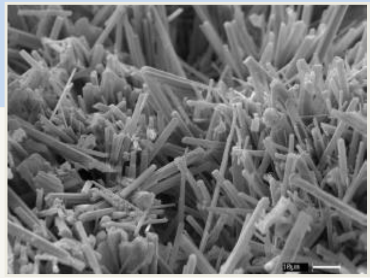
Transition Zone



Calcium Sulfoaluminate Hydrates

Cement

- 15-20% of solids in Hydrated Cement Paste
- Ettringite $C_6A\bar{S}_3H_{32}$
  - Trisulfate hydrate
  - Needle shaped prismatic crystals
  - Contributes to stiffening
  - Some early strength
- Monosulfate Hydrate $C_4A\bar{S}H_{12}$
  - Hexagonal crystals
  - Vulnerable to sulfate attack



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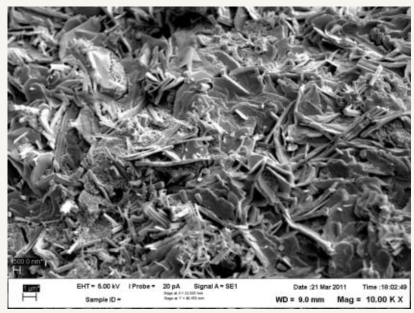


Hydration of Calcium Silicates

$$2C_3S + 6H \rightarrow C\text{-}S\text{-}H + 3CH + 120\ cal/g$$

$$2C_2S + 4H \rightarrow C\text{-}S\text{-}H + CH + 62\ cal/g$$

- Both produce C-S-H and CH as reaction products
- C_2S produces less CH
  - Important for durability in sulfate rich environments
- More heat is evolved during C_3S hydration
- C_3S hydration is more rapid
  - Higher contribution to early age strength (2-3 hrs to 14 days)
- C_2S hydration occurs more slowly
  - Contributes to strength after 14 days

Hydration of Calcium Aluminates

- C_3A
  - Reaction of C_3A with water occurs very quickly and liberates high heat → Flash Set
  - Gypsum $C\bar{S}H_2$ is added to the clinker to control the hydration of C_3A:

    $C_3A + 26\,H + 3\,C\bar{S}H_2 \rightarrow C_6A\bar{S}_3H_{32}$ (Ettringite) + 207 cal/g
  - When more C_3A remains:

    $2\,C_3A + 4\,H + C_6A\bar{S}_3H_{32} \rightarrow 3\,C_4A\bar{S}H_{12}$ (Monosulfate)

Hydration of Calcium Alumino Ferrites

- C_4AF
  - Reaction of C_4AF (ferrite) phase is slower and evolves less heat than C_3A:

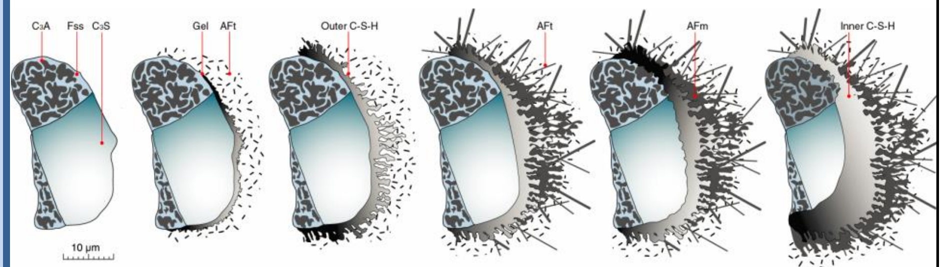
    $C_4AF + 14\,H + 2\,CH \rightarrow C_4(A,F)H_{13} + (A,F)H_3$ + Heat
  - Also heavily retarded by gypsum ($C\bar{S}H_2$):

    $C_4AF + 21\,H + 3\,C\bar{S}H_2 \rightarrow C_6(A,F)\bar{S}_3H_{32} + (F,A)H_3$ + Heat

    $C_4AF + C_6(A,F)\bar{S}_3H_{32} \rightarrow 3\,C_4A(A,F)\bar{S}H_{12} + (F,A)H_3$ + Heat
  - Products of C_4AF are more resistant to sulfate attack than those of C_3A hydration

Hydration in detail: Chemical reactions with water

- As water comes into contact with cement particles, hydration reactions immediately starts at the surface of the particles.
- Although simple hydrates such as C-H are formed, process of hydration is complex and results in reorganization of the constituents of original compounds to form new hydrated compounds



a) Unhydrated section of polymineralic grain (scale of interstitial phase exaggerated).

b) ~10 min Some C_3A (or Fss) react with calcium sulphate in solution. Amorphous aluminate-rich gel forms on the surface and short AFt rods nucleate at edge of gel and in solution.

c) ~10 h Reaction of C_3S to produce "outer" product C-S-H on AFt rod network leaving ~ 1 μm between grain surface and hydrated shell.

d) ~18 h Secondary hydration of C3A (or Fss) producing long rods of AFt. C-S-H "inner"product starts to form on inside of shell from continuing hydration of C_3S.

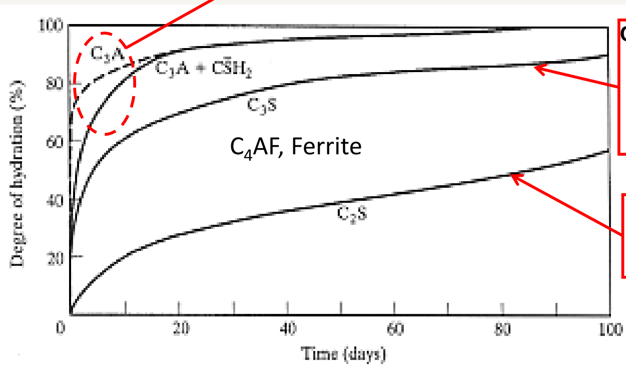
e) 1-3 days C_3A reacts with any AFt inside shell forming hexagonal plates of AFm. Continuing formation of "inner" product reduces separation of anhydrous grain and hydrated shell.

f) ~14 days Sufficient "inner" C-S-H has formed to fill in the space between grain and shell. The "outer" C-S-H has become more fibrous.

Rates of hydration

- The hydration rates of the 4 key phases vary considerably, therefore some properties will vary with cement composition such as:
  - time to stiffening
  - setting time
  - hardening rate

C_3A: Liberates a large amount of heat during first few days → add gypsum,, cements with low %ages are more resistant to sulfates



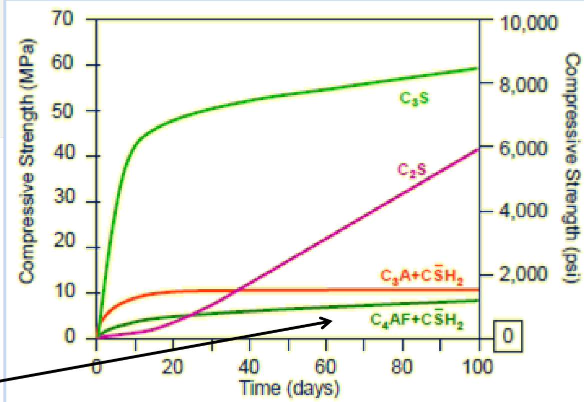
C_3S: Very reactive, high heat of hydration, hydrates & hardens rapidly, responsible for initial set and early strength

C_2S: Hydrates & hardens slowly, contributes to later age strength (beyond 7 days)

Strength development over time

- The hydration rates of the 4 key phases vary considerably, therefore some properties will vary with cement composition such as:
  - time to stiffening
  - setting time
  - hardening rate

C_4AF: Reduces clinkering temperature, hydrates rapidly but contributes little to strength ,color of hydrated cement (gray) due to ferrite hydrates



Compressive Strength development in pastes of pure cement compounds (*Mindess et al, 2003*)

Heat of Hydration of Pure Compounds

- The amount of heat liberated is affected by the fractions of the compounds of the cement.

- Heat of hydration(cal/g):
  - $120\times(\%C_3S) + 62\times(\%C_2S) + 207\times(\%C_3A) + 100\times(C_4AF)$

	Heat of Hydration (cal/g)
C_3S	120
C_2S	62
C_3A	207
C_4AF	100

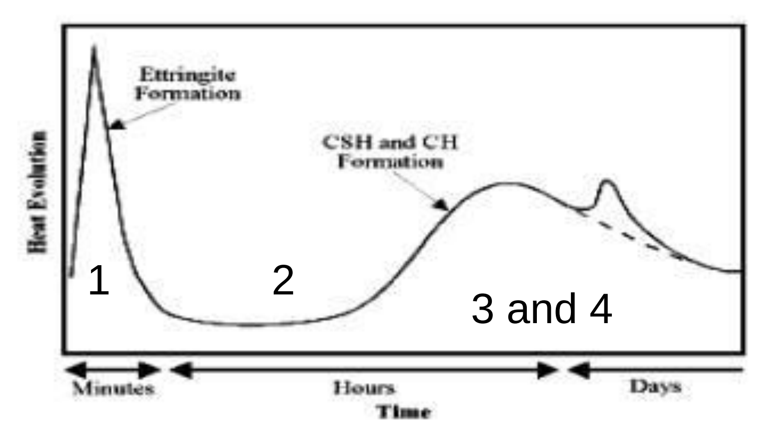
Heat of Hydration

- Hydration process of cement is accompanied by heat generation (exothermic).
  - Concrete is a fair insulator:
    - generated heat in mass concrete may result in expansion & cracking → This could be overcome by using suitable cement type.
  - It could also be advantages for cold wheather concreting.
  - Heat of hydration of typical PC ≈ 85-100 cal/g.
  - About 50% of this heat is liberated within 1-3 days & 75% within 7 days.
  - By limiting C_3S & C_3A content heat of hydration can be reduced.

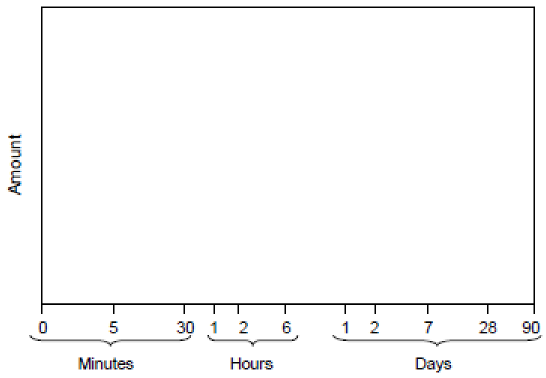
Heat evolution

- Heat evolution can be used to map the progress of hydration:

1. Dissolution of ions
2. Induction period
3. Acceleration
4. Deceleration
5. Steady State



Formation of hydration products over time



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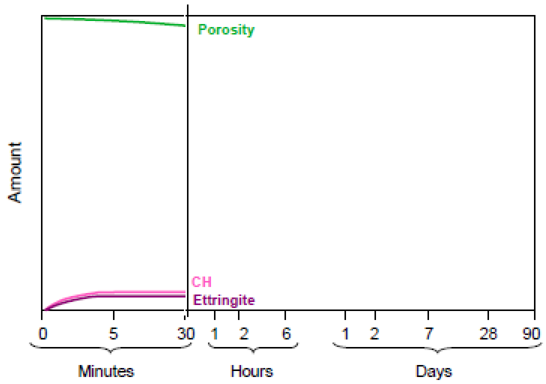

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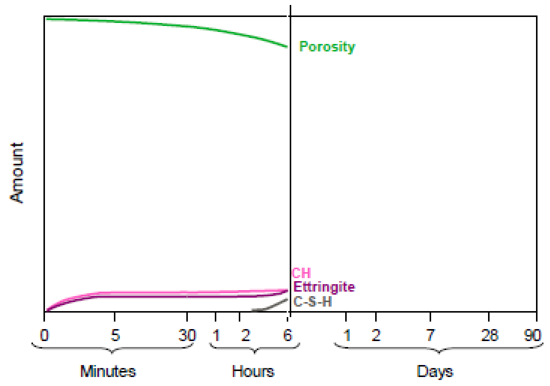

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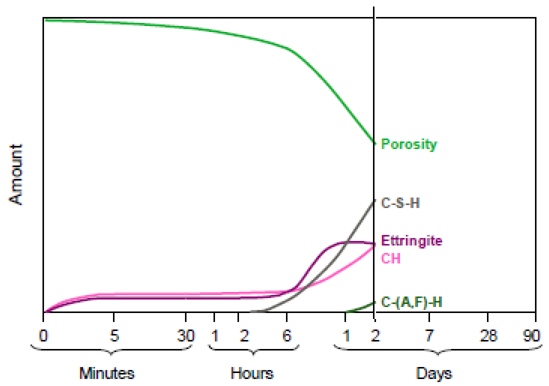

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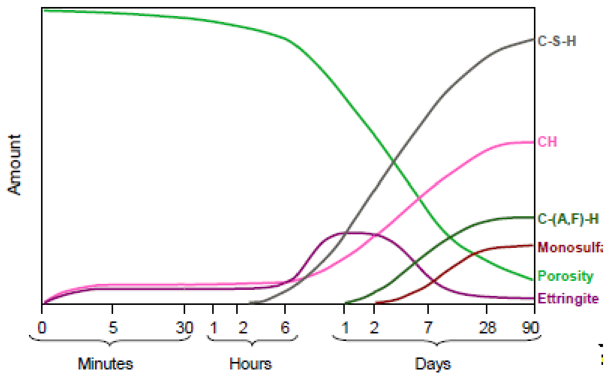
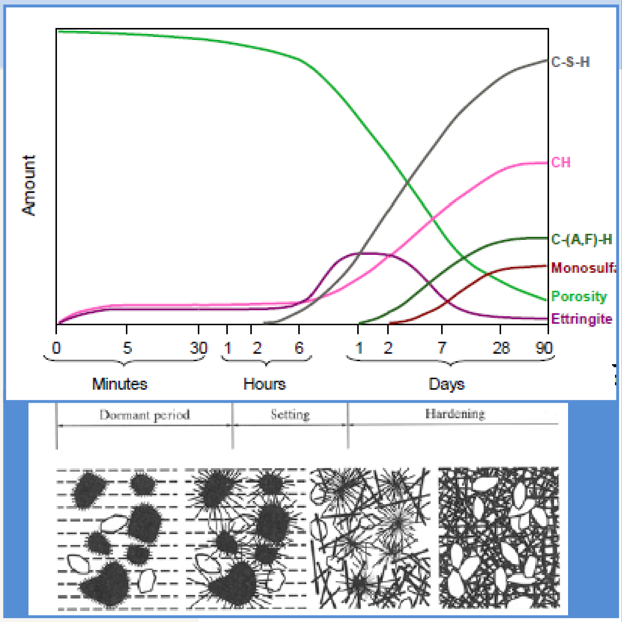
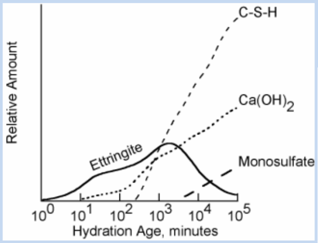


Over time

- Formation of hydration products over time leads to:
  - Stiffening
    - Loss of workability
  - Setting
    - Solidification
  - Hardening
    - Strength gain



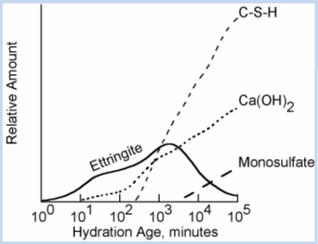
Portland Cement Hydration



- Main hydration reactions:
  - (C=CaO, S=SiO$_2$, A=Al$_2$O$_3$, $\bar{S}$ = SO$_3$)
  - $2C_3S + 6H \rightarrow$ C-S-H + 3CH + 120 cal/g
  - $2C_2S + 4H \rightarrow$ C-S-H + CH + 62 cal/g
  - $C_3A + C\bar{S}H_2 \rightarrow$ Ettringite + ~207 cal/g
- Influence of Compound Composition

	C_3S	C_2S	C_3A	C_4AF
Rate of Reaction	Moderate	Slow	Fast	Moderate
Heat Liberation	High	Low	Very High	Moderate
Early Cementitious Value	Good	Poor	Good	Poor
Ultimate Cementitious Value	Good	Good	Poor	Poor

Portland Cement Hydration



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- Influence of Compound Composition

Compound	Amount	
C_3S	50%	very reactive compound, high heat of hydration, high early strength
C_2S	25%	low heat of hydration, slow reaction
C_3A	10%	problems with sulfate attack, high heat of hydration
C_4AF	10%	
gypsum	5%	used to control the set of cement

Stiffening and setting of Portland Cement

Q

- Which compound is primarily responsible for rapid stiffening and setting of Portland cement?

Massive dam construction

Q

- At METU Cement, we produce two cements with the following compound compositions. Both cements do not incorporate any mineral admixtures, and each contains 3% gypsum.

Compound (%)	Cement A	Cement B
C_3S	55	30
C_2S	16	46
C_3A	12	5
C_4AF	8	13

Compressive Strength (MPa)	Cement A	Cement B
2 days	26	13
28 days	50	40

- They want to use one of our cements at a massive dam construction. Which cement would you prefer to use in that construction, why?

Hydrated Cement Paste

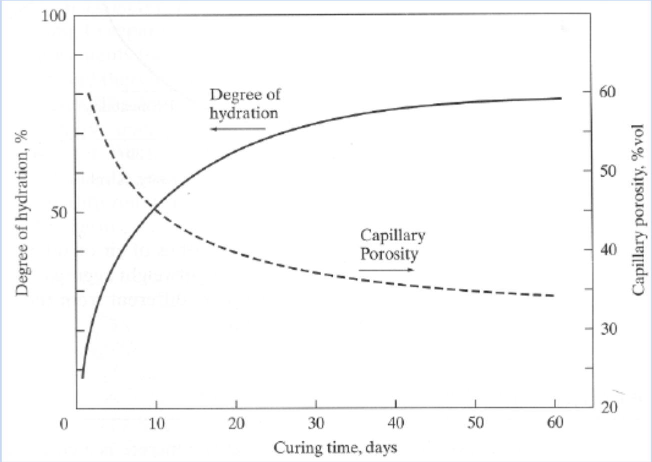
- Solids
  - C-S-H
  - CH
  - Ettringite
  - Monosulfate hydrate
  - Residual unhydrated cement
- Voids
  - Entrapped air (>1mm)
  - Entrained air (75-500um)
  - Capillary pores (macro → meso)
  - Interlayer space (micropores)
- Water
  - Capillary water
  - Adsorbed water
  - Interlayer water
  - Chemically combined water

Voids in hydrated cement paste

- Voids in the Hydrated Cement
  - Interlayer space in CSH Paste
    - size = 5 to 25 Å
    - no adverse effect on strength and permeability
    - some effect on drying shrinkage and creep
  - Capillary Voids
    - Irregular in shape
    - > 50 nm : detrimental to strength and impermeability
    - < 50 nm: important to drying shrinkage and creep.
  - Air Voids
    - entrapped air: ~ 3 mm → irregular in shape
    - entrained air: 50 to 200 µm → spherical; added for freeze/thaw resistance

Voids in hydrated cement paste

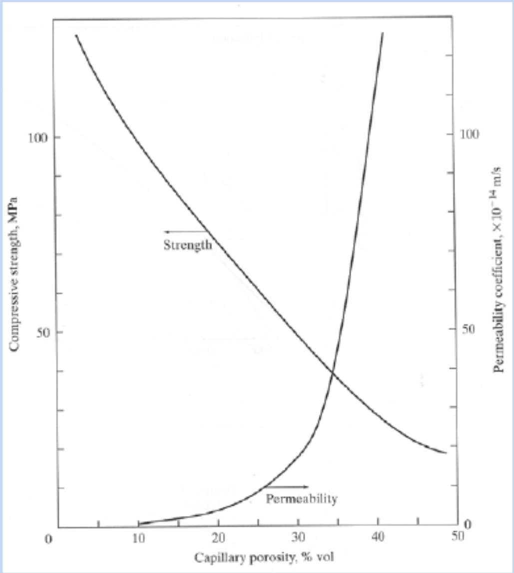
- The presence of voids affects:
  - Strength
  - Stress distribution
  - Permeability
  - Freeze/thaw resistance



Voids in hydrated cement paste

- Inverse relationship between strength (f_c) and porosity (p) where k=strength of voidless mortar (~34,000 psi):

  $f_c = k\,(1-p)^3$



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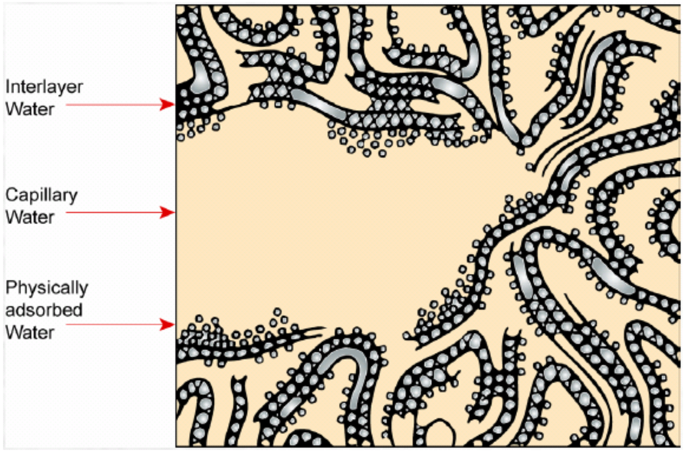
  - Chemically combined water

Water inside the pores

- Water is
  - Introduced to concrete during mixing
  - Permeates the concrete during service
  - Because the water in concrete contains ions, it is usually called "pore solution" and has a high pH
- Ratio of mass of water to mass of cement in a mixture is the "water-to-cement ratio" or w/c
- When supplementary cementitious materials are used, this is "water-to-cementitious ratio" or w/cm
- w/c or w/cm may range between 0.2-0.8; but 0.4-0.6 is typical range

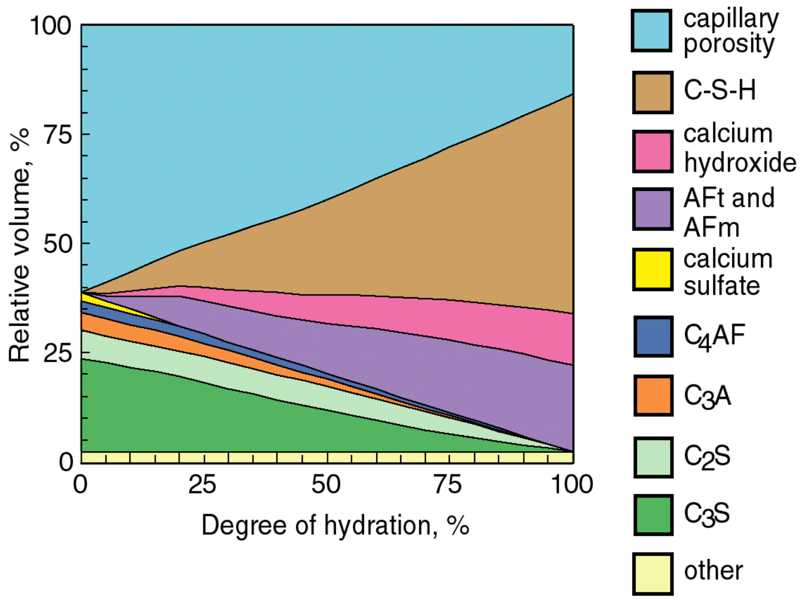
Water inside the pores



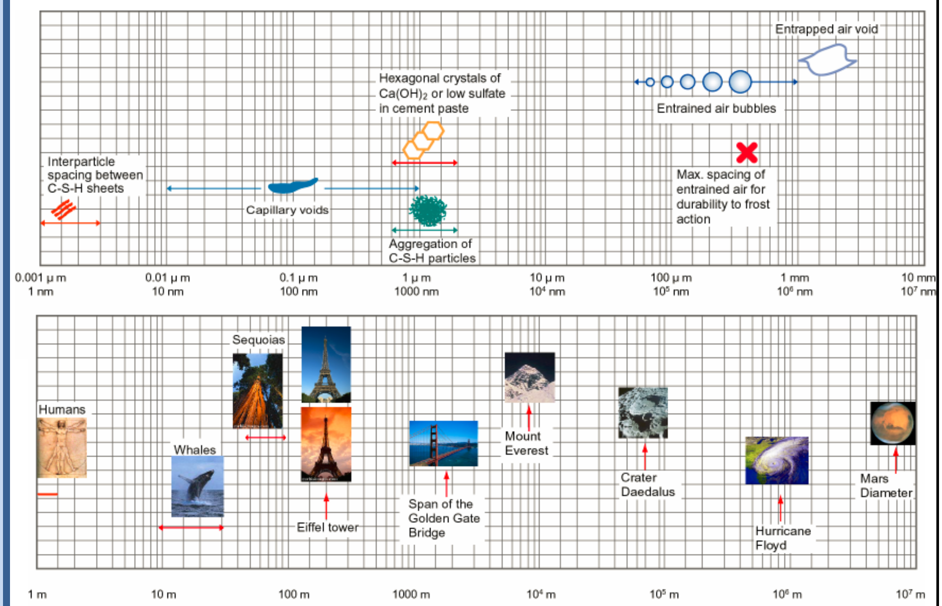
Water in hydrated cement paste

- Water in the Hydrated Cement
  - Interlayer space in CSH Paste
    - Water associated with the C-S-H structure
    - Can be removed only on strong drying to RH~11%, resulting shrinkage
  - Capillary Water
    - > 50 nm : free water because its removal does not cause volume change
    - < 50 nm: removal of water results in shrinkage because new bonds can form between C-S surfaces
  - Adsorbed water
    - Water physically adsorbed to the solid surface in C-S-H
    - Can be removed on drying to RH ~30%, resulting in shrinkage
  - Chemically combined water
    - Water that is an integral part of various hydration products
    - Lost only on decomposition during heating

Degree of hydration vs hydration products



Orders of magnitude



Next lecture

- Pozzolans