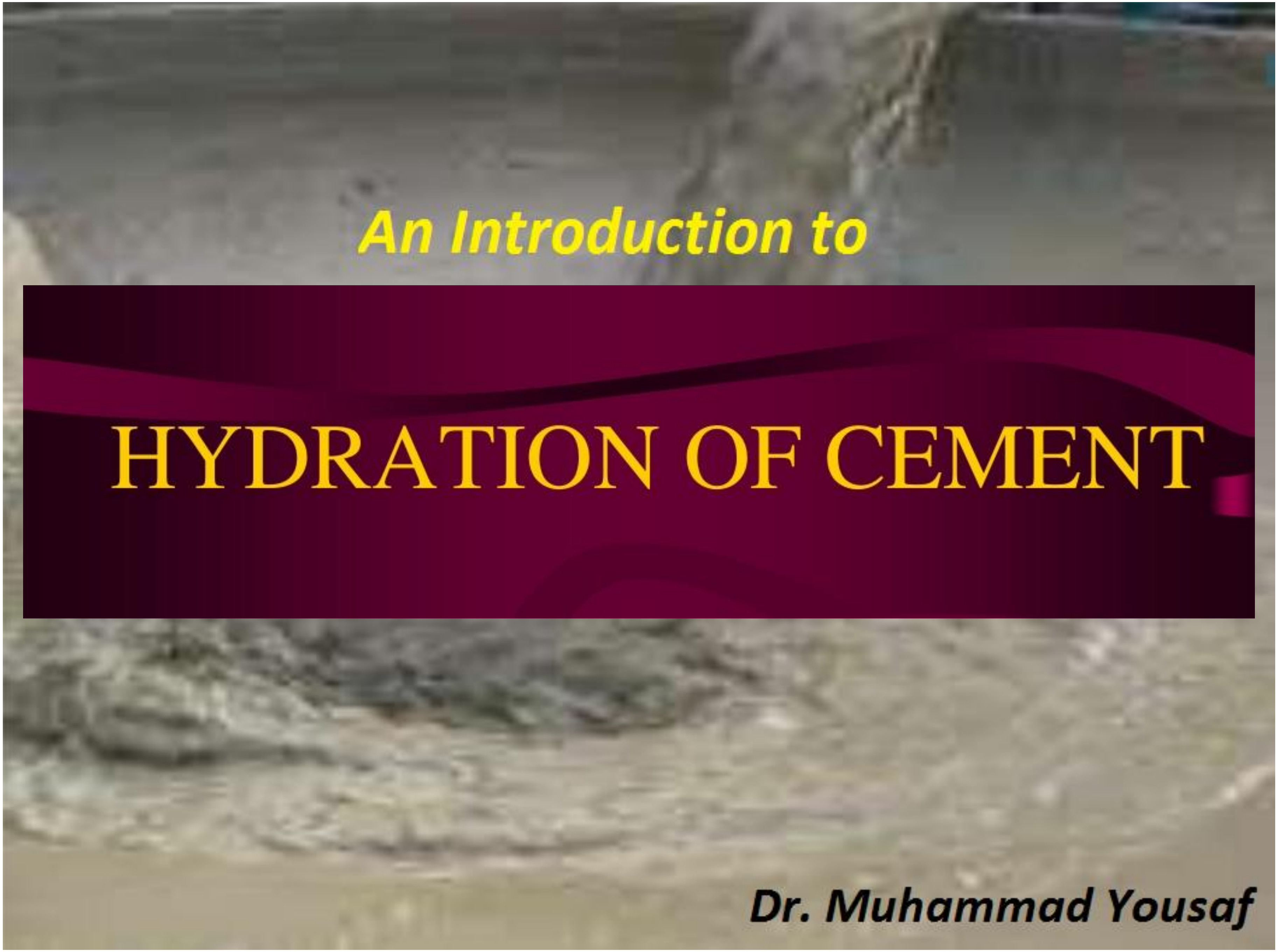


An Introduction to

HYDRATION OF CEMENT

Dr. Muhammad Yousaf

CONTENTS

The discussion is divided in to the following sections:

Structure Investigation level

- The type, amount, size, shape, and distribution of phases present in a solid constitute its **structure**.
- The gross elements of the structure of a material can readily be seen, whereas the finer elements are usually resolved with the help of a microscope.
- The term **macrostructure** is generally used for the gross structure, visible to the human eye.
- The limit of resolution of the unaided human eye is approximately one-fifth of a millimiter (200 µm).
- The term **microstructure** is used for the microscopically magnified portion of a macrostructure.

SIGNIFICANCE

- Progress in the field of materials has resulted primarily from recognition of the principle that the properties of a material originate from its internal structure.
- The properties can be modified by making suitable changes in the structure of a material.

COMPLEXITIES

- From examination of a cross section of concrete, the two phases that can easily be distinguished are aggregate particles of varying size and shape and the binding medium, composed of an incoherent mass of the hydrated cement paste (henceforth abbreviated HCP).

Background, Cement composition

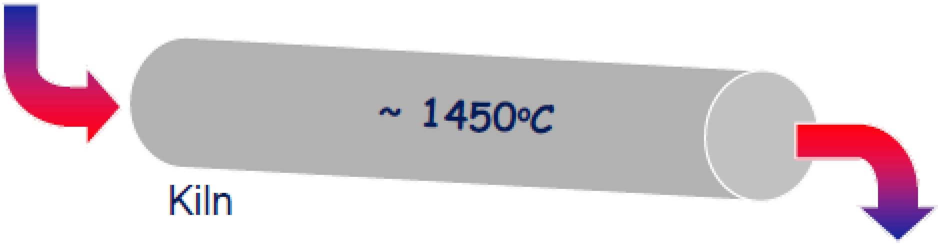
Cement Composition

$CaCO_3$ (limestone)

$2SiO_2 \cdot Al_2O_3$ (clay, shale)

Fe_2O_3 (iron oxide)

SiO_2 (silica sand)



$3CaO \cdot SiO_2$

$2CaO \cdot SiO_2$

$3CaO \cdot Al_2O_3$

$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

$CaO \cdot SO_3 \cdot 2H_2O$

Gypsum + Clinker

interground

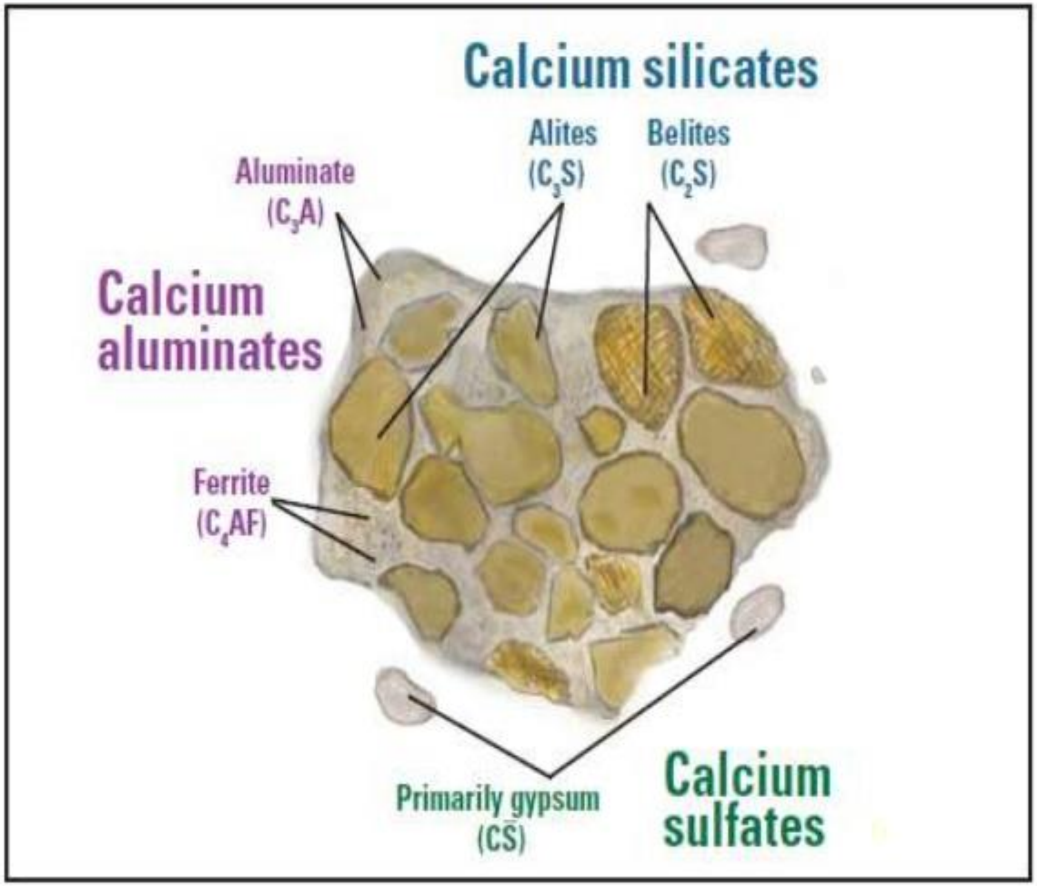
Finished cement

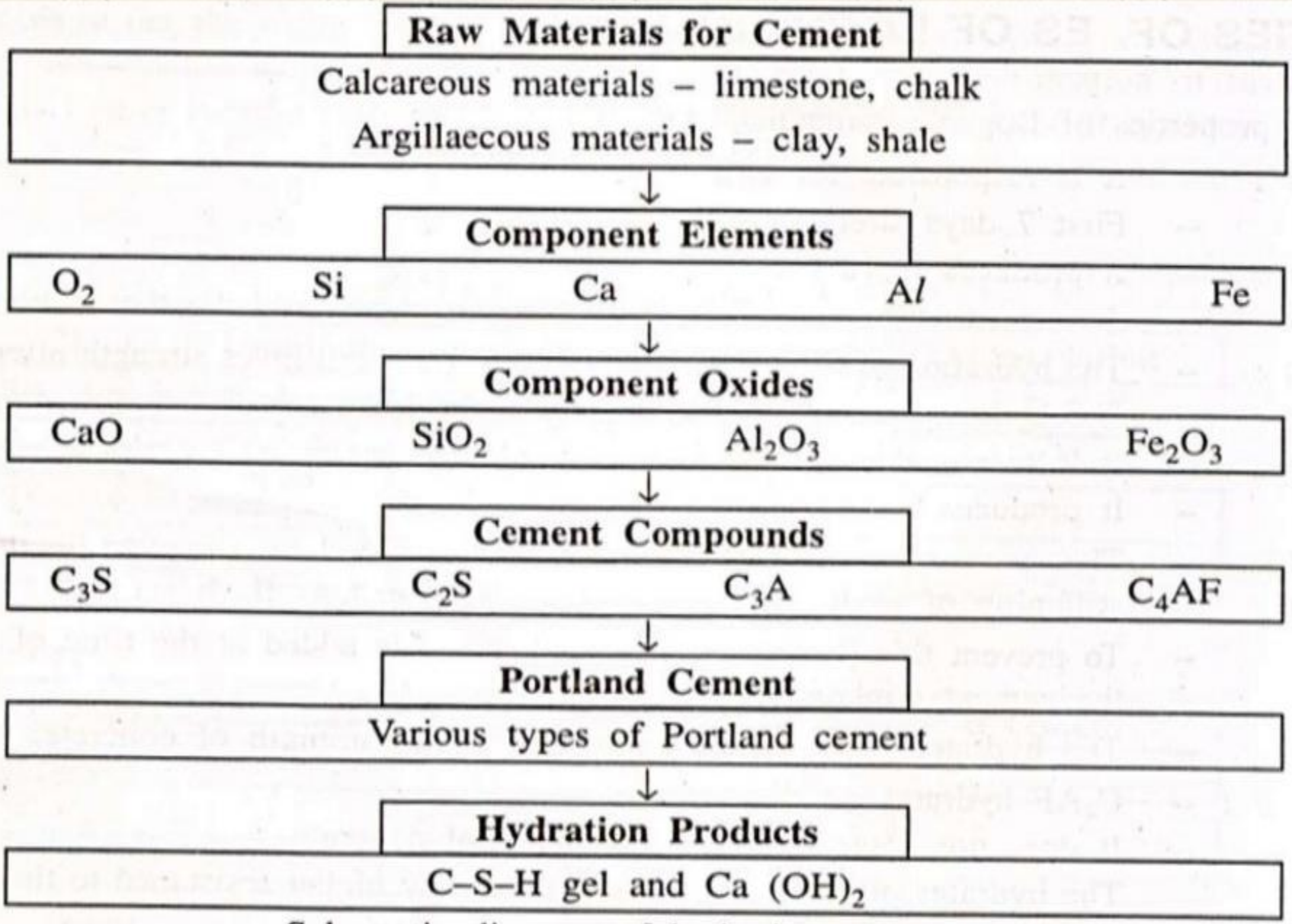
Composition of Cement Clinker

Consists primarily of calcium aluminates and calcium silicates

- Calcium aluminates
  - Tricalcium aluminate (C_3A)
  - Ferrite (C_4AF)
- Calcium silicates:
  - Alite (C_3S)
  - Belite (C_2S)

➢ Gypsum is added to avoid the uncontrolled setting resulting from C_3A reaction with water.





Raw Materials for Cement

Calcareous materials – limestone, chalk
Argillaecous materials – clay, shale

↓

Component Elements

O_2 Si Ca Al Fe

↓

Component Oxides

CaO SiO_2 Al_2O_3 Fe_2O_3

↓

Cement Compounds

C_3S C_2S C_3A C_4AF

↓

Portland Cement

Various types of Portland cement

↓

Hydration Products

C–S–H gel and Ca $(OH)_2$

Schematic diagram of hydration of cement

Hydration; Introduction: (ASTM C-186)

- Portland cement is a hydraulic cement, hence it derives its strength from chemical reactions between the cement and water. The water causes the hardening of cement or concrete through a series of irreversible and exothermic process called hydration.

- Major compounds in **cement** form chemical bonds with water molecules, becoming hydrates producing **hydration products.** This is not a momentary action but a process that continues for long. The rate of hydration is fast to start with, but continues longer at a decreasing rate.

Hydration; Introduction: (ASTM C-186)

- Cement-water paste sets and hardens “gluing” the aggregates together in a solid mass.

Formation of hydration products over time leads to:

- Stiffening of cement paste (Loss of workability)
- Setting (Solidification)
- Hardening (Strength gain)

Why is it important to know about it?

Understanding the basics of hydration is important to;

- Ensure the strength and durability of concrete
- Recognize and mitigate the stresses to prevent cracking (plastic shrinkage cracks / thermal cracks etc.)
- Appreciate the importance of good curing and construction practices at site
- May not proceed to 100% completion
- Hydration of cement is responsible for and affects the
    - time to stiffening
    - setting time &
    - hardening rate of concrete

Why is it important to know about it?

When portland cement is mixed with water, heat is liberated. This heat is called the heat of hydration, the result of the exothermic chemical reaction between cement and water. The heat generated by the cement’s hydration raises the temperature of concrete.

- During normal concrete construction, the heat is dissipated into the soil or the air and resulting temperature-changes within the structure are not significant.
- In massive structures, such as dams, mat foundations, or any element more than about a meter or yard thick, the heat can not be readily released. The mass concrete may then attain high internal temperatures, especially during hot weather construction, or if high cement contents are used.

Why is it important to know about it?

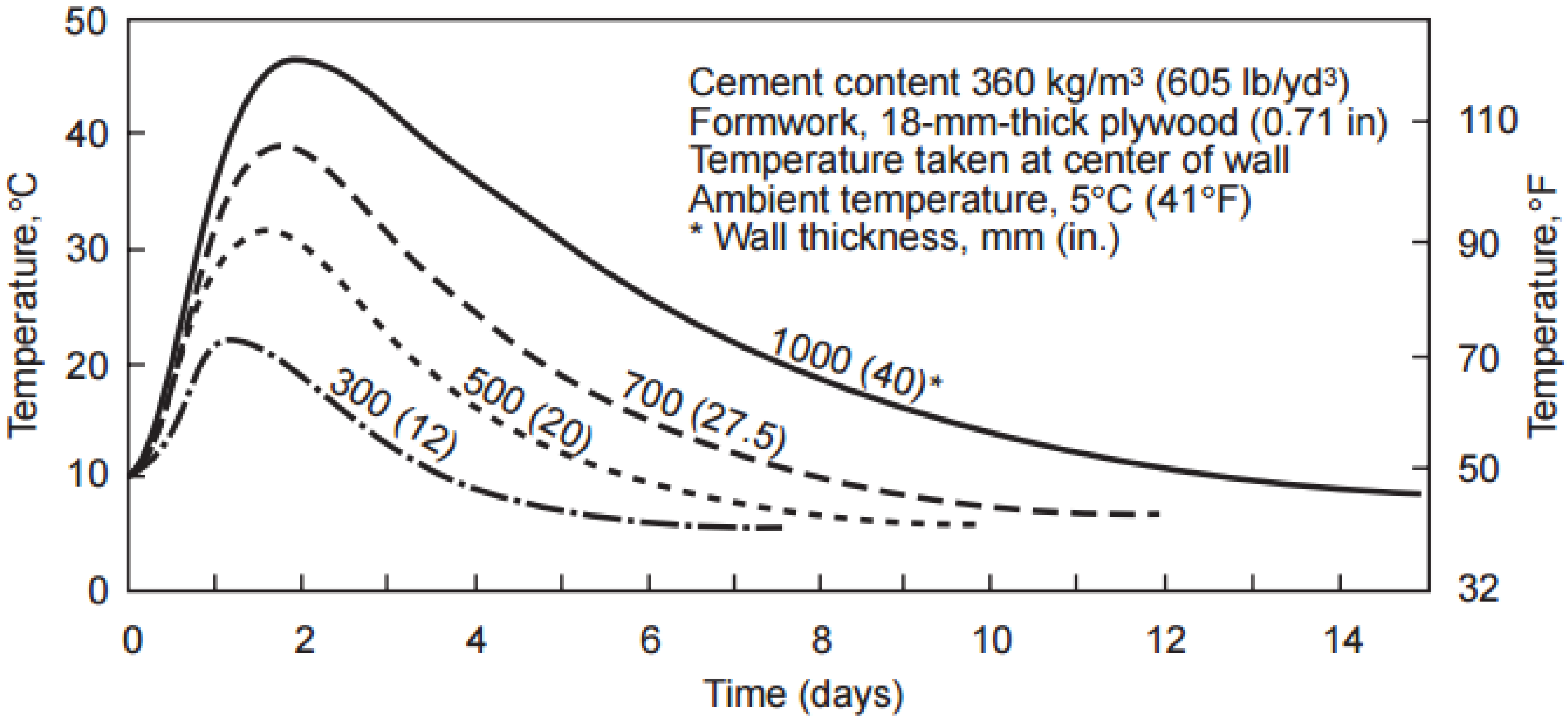


Fig. 1. Effect of member thickness on temperature of concrete.

Overview of the Hydration Process

Broadly speaking, it is a Two-step process:

- **Dissolution:** Cement dissolves, releasing ions into the mix water. The mix water is thus no longer pure H_2O, but an aqueous solution, containing a variety of ionic species, called the *pore solution*. The gypsum and the cement minerals C_3S and C_3A are all highly soluble, meaning that they dissolve quickly. Therefore the concentrations of ionic species in the pore solution increase rapidly as soon as the cement and water are combined.
- Eventually the concentrations increase to the point that the pore solution is *supersaturated*, meaning that it is energetically favorable for some of the ions to combine into new solid phases rather than remain dissolved. This second step of the hydration process is called **precipitation**.

Overview of the Hydration Process

- A key point, of course, is that these new *precipitated solid phases*, called *hydration products*, are different from the starting cement minerals. Precipitation relieves the super saturation of the pore solution and allows dissolution of the cement minerals to continue.

- Thus cement hydration is a *continuous process* by which the cement minerals are replaced by new hydration products, with the pore solution acting as a necessary *transition zone* between the two solid states.

The reactions between portland cement and water have been studied for more than a hundred years, and the fact that hydration proceeds by a “dissolution-precipitation process” was first elaborated by the famous chemist Le Chatelier.

Overview of the Morphology of the Main Hydration Products

(study of the forms of things, in particular)

Morphology (Shape of the hydration products):

- ➡ Defines shape, form, or structure at the microscopic scale, i-e nanometers and microns.
- ➡ Has greater impact on its macroscopic properties than its chemical composition; as for cement paste and concrete.
- The combined morphology of cement paste is one of the major components of its microstructure.

The morphology of a particular solid phase will depend on many factors, including the crystal structure, the mechanism of formation, the temperature, and the space available for the phase to form. In addition, the morphology of a solid phase can change over time in response to changes in its surrounding environment.

It becomes more significant when we need to produce any special concrete like Self compacting concrete.

Overview of the Morphology of the Main Hydration Products

One of the major reasons, that the science of cement and concrete is so complex is that the ***morphology of the hydration products are both complex and highly variable***. The standard approach for studying a complex material or process is *to* ***break it down into individual phases*** *or steps and to study each of these in isolation*. This is also problematic to do with cement, because the morphology of the phases depends strongly on the complex local conditions that exist during the hydration process. This is particularly true of the C-S-H gel phase, which is by far the most important hydration product.

Investigation at micro-level

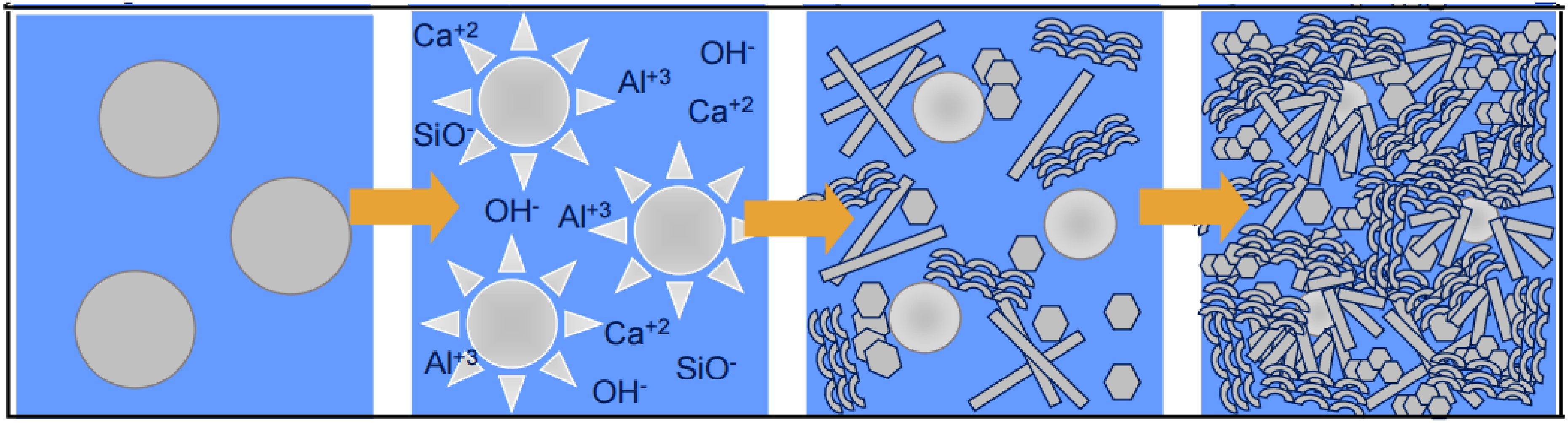
- Following different helping tools are employed for analysis of cement paste and concrete at micro and nano level investigation

  - Scanning electron microscope (SEM)
  - Transmission electron microscope (TEM)
  - Energy-dispersive x-ray (EDX)
  - X-ray powder diffraction (XRD)

Hydration Process ; an overview

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



Hydration Process ; an overview

Cement compounds have the following properties:

- Tricalcium silicate, C_3S,
  - hydrates and hardens rapidly
  - largely responsible for initial set and early strength.
  - early strength of portland cement concrete is higher with increased percentages of C_3S.
- Dicalcium silicate, C_2S,
  - hydrates and hardens slowly
  - contributes largely to strength increase at ages beyond one week.
- Tricalcium aluminate, C_3A,
  - becomes active on water mixing and liberates heat
  - liberates a large amount of heat during first few days
  - contributes to early strength development.

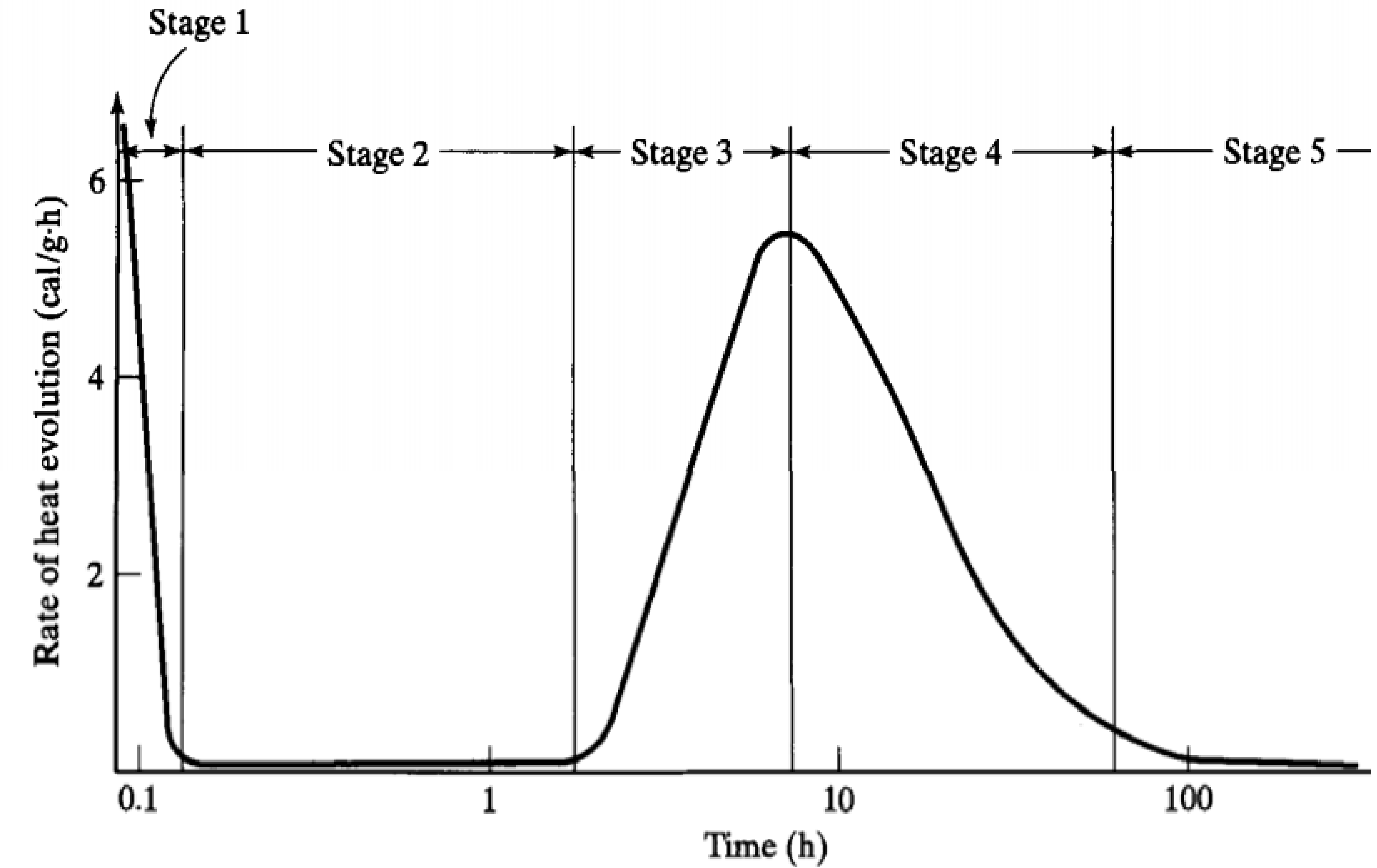
Hydration Process ; an overview

- Tetracalcium aluminoferrite, C_4AF,
  - reduces the clinkering temperature, thereby assisting in the manufacture of cement.
  - It hydrates relatively slowly and contributes very little to strength.
  - Most color effects are due to C_4AF and its hydrates.

Characteristics of hydration cement compound

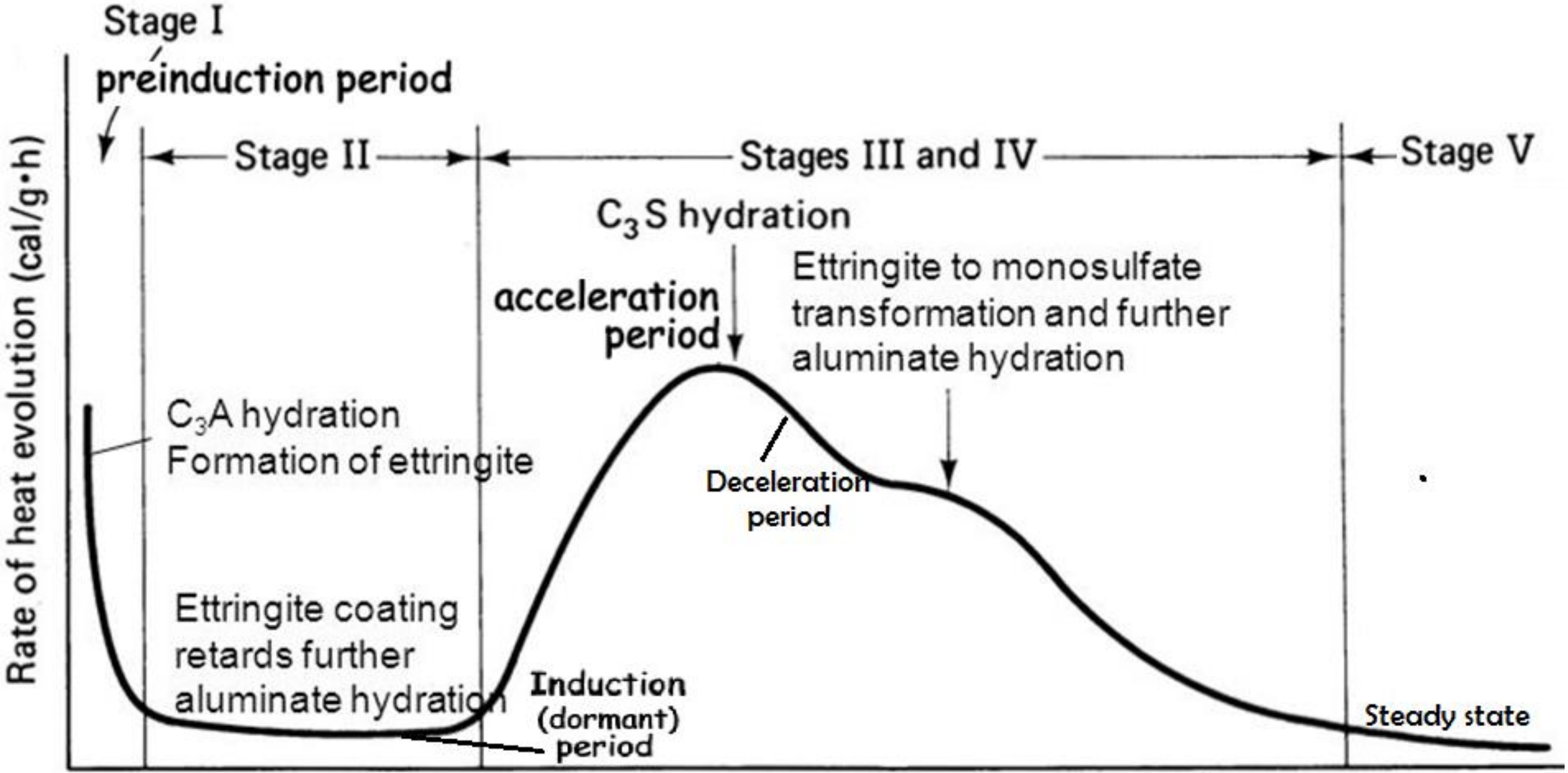
Compounds	Reaction rate	Amount of Heat Liberated	Contribution to Cement Heat Liberation
C_3S	Moderate	Moderate	High
C_2S	Slow	Low	Low
$C_3A + C\bar{S}H_2$	Fast	Very High	Very High
$C_4AF + C\bar{S}H_2$	Moderate	Moderate	Moderate

Stages of hydration of cement compounds:



Calorimetric curve (i.e. time versus rate of heat evolution curve)

Hydration reactions



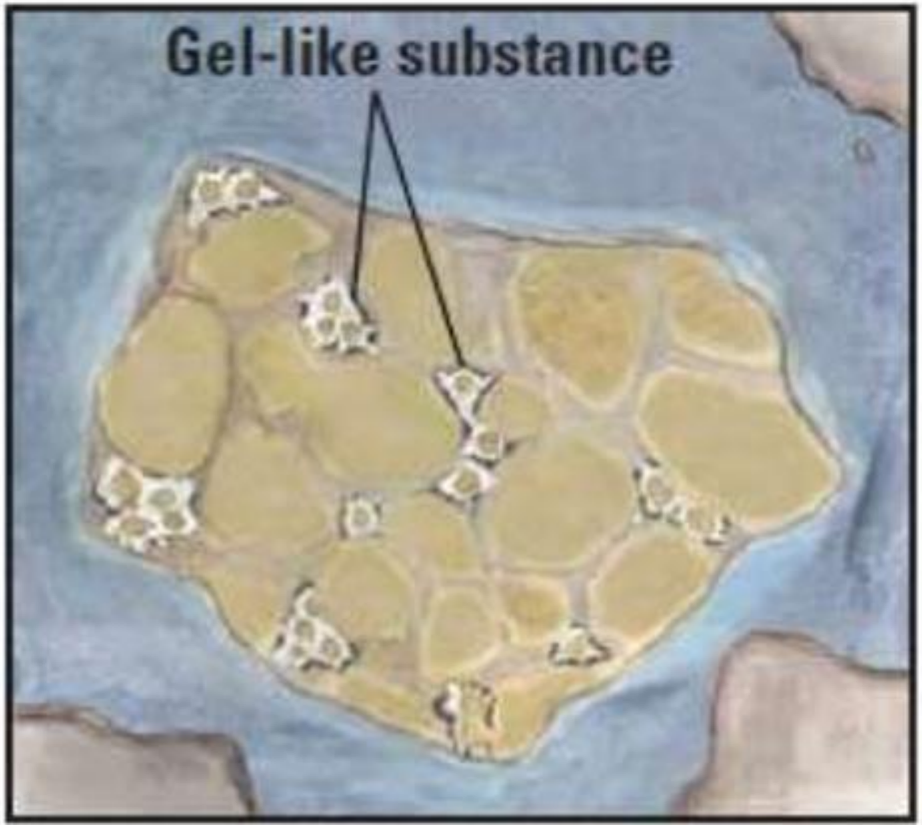
Relationship between reactions and heat evolution

Stage 1: Mixing/ Dissolution Stage (< 15 minutes)

Sulfate reacts with aluminate and water to form C-S-A-H, a precursor to Ettringite.
The gel limits water's access to aluminate

Reactions slow. Heat drops

Too little sulfate: flash set
Too much sulfate: false set

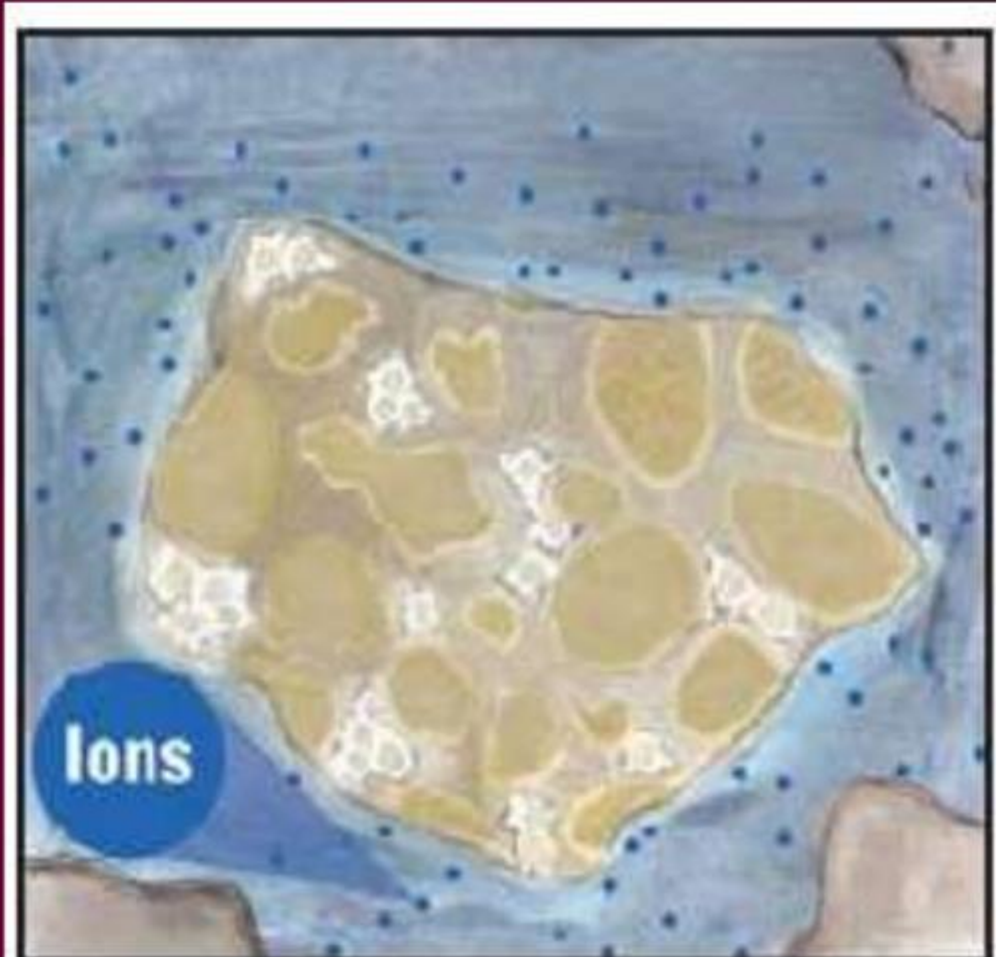


Stage 2: Dormant/ Induction Period

Hydration is almost at halt. This is the reason why the concrete remains in plastic state for several hours.

During this dormant period, the silicates (alite and belite) slowly dissolve, releasing calcium ions in solution

During dormancy; before initial set; the mix can be transported, placed, finished, and textured.



HYDRATION OF CEMENT: Hydration of C_3A

In Portland cement the hydration of C_3A involves *reactions mostly with sulfate ions* which are supplied by the dissolution of gypsum added during the manufacturing of cement

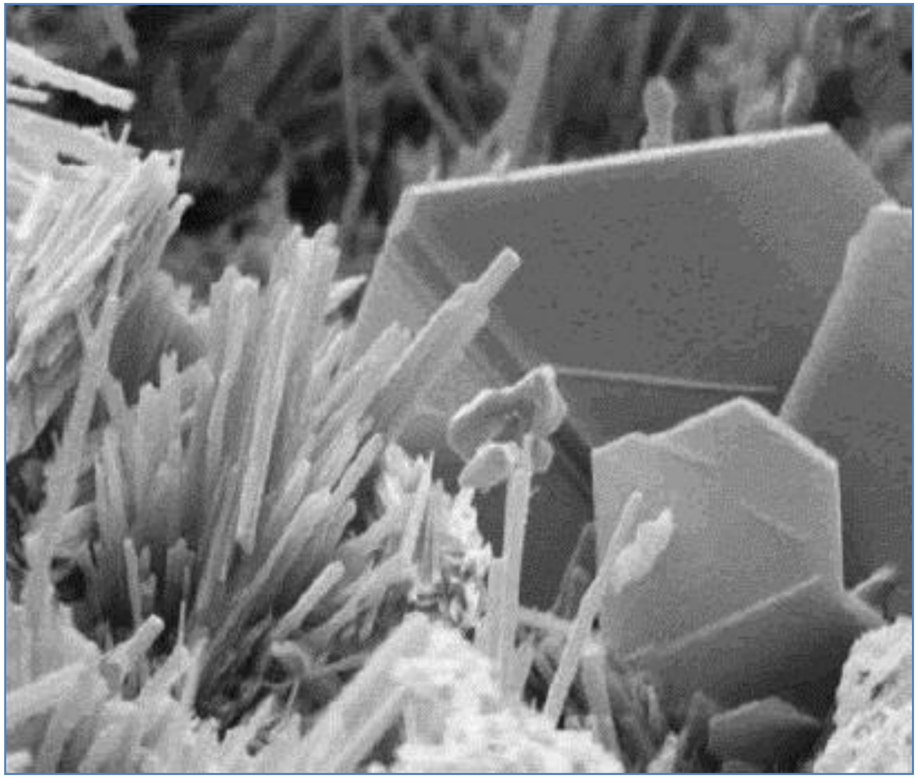
Reactions involved in the hydration of C_3A:

1. The primary initial reaction of C_3A, when ample amount of gypsum is present, is as follows:

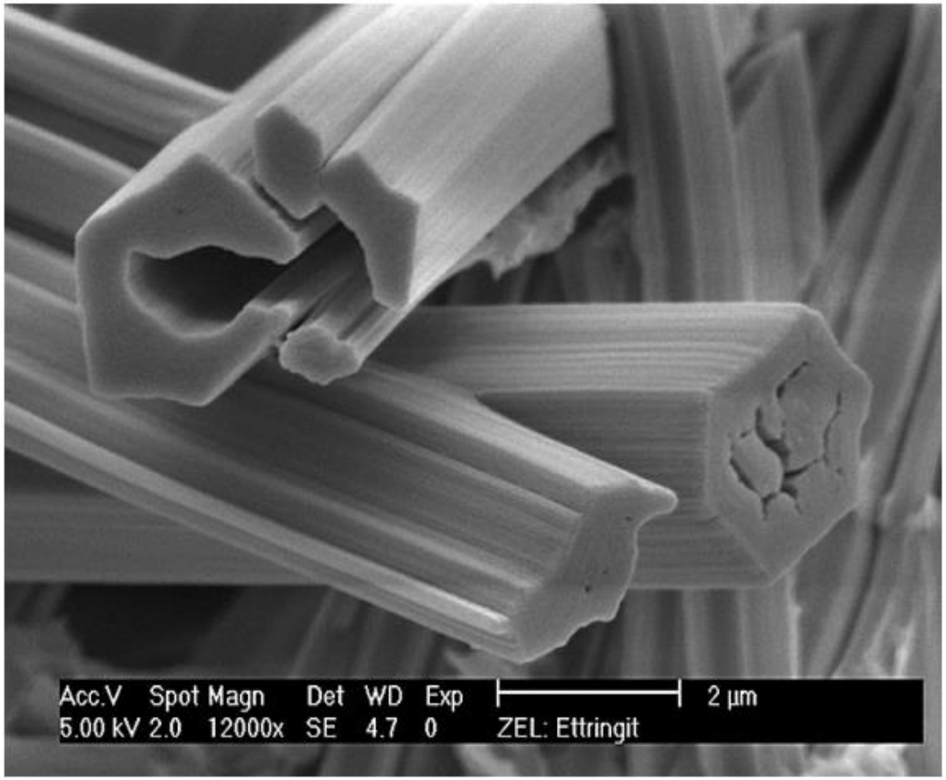
$$\underset{\text{tri-calcium aluminate}}{C_3A} + \underset{\text{gypsum}}{3C\bar{S}H_2} + \underset{\text{water}}{26H} \rightarrow \underset{\text{ettringite}}{C_6A\bar{S}_3H_{32}}$$

- The above reaction is exothermic
- Ettringite (i.e. "calcium sulfoaluminate hydrate") is the name given to a naturally occurring mineral of the same composition
- Ettringite is a stable hydration product *only while* there is an ample supply of sulfate available
- The formation of ettringite slows down the hydration of C_3A by creating a diffusion barrier around unhydrated C_3A particles, analogous to the behavior of C-S-H during the hydration of silicates

Ettringite is formed in hydrated Portland cement system as a result of the reaction of calcium aluminate with calcium sulfate, both present in Portland cement



SEM image of fractured hardened cement paste, showing plates of calcium hydroxide and needles of ettringite (micron scale)

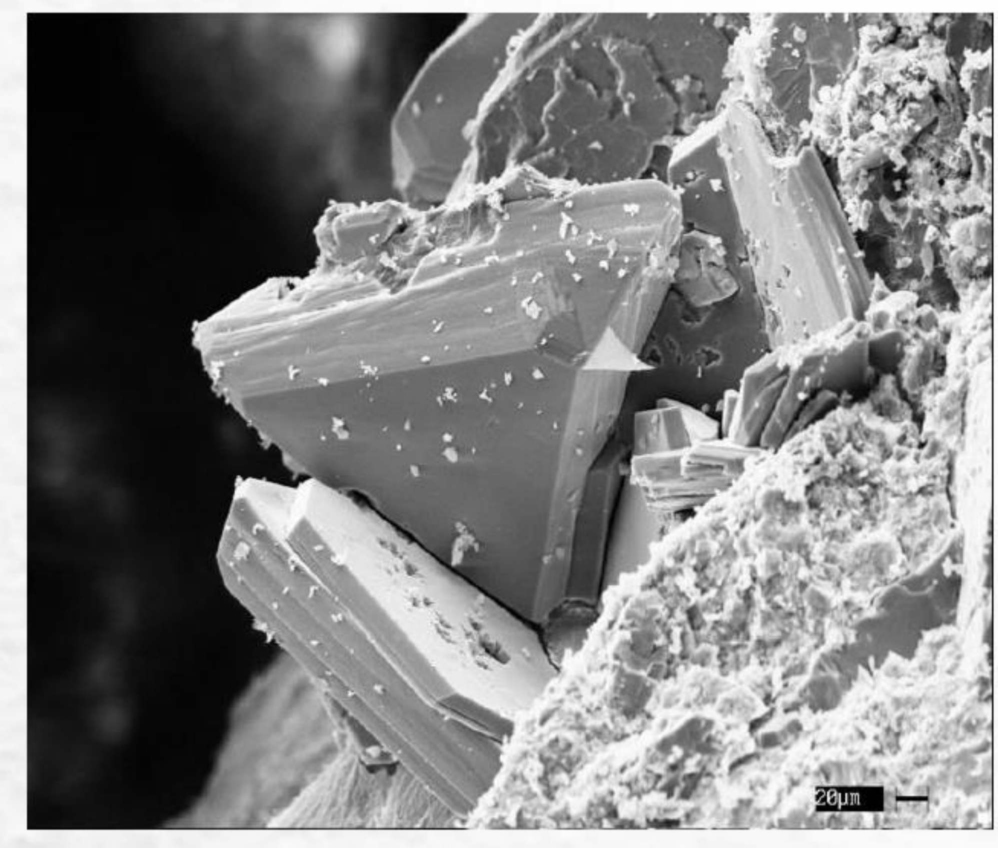


Very slender ettringite crystals forming needle-shaped formations with hexagonal cross-section and a thickness of about 2 µm

Microstructure of Hydrated Cement Paste

Calcium Hydroxide or portlandite

- **Large hexagonal crystals can be formed**
- **Low surface area (0.5 m^2/g)**
- **Low Van der Waals forces**
- **Volume – 20-25%**



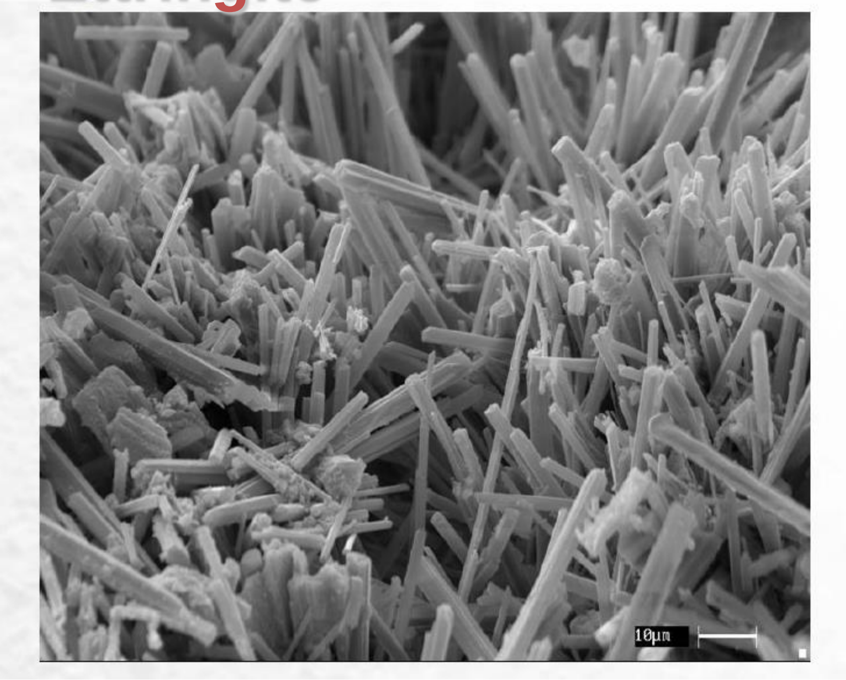
Mehta and Monteiro

Microstructure of Hydrated Cement Paste

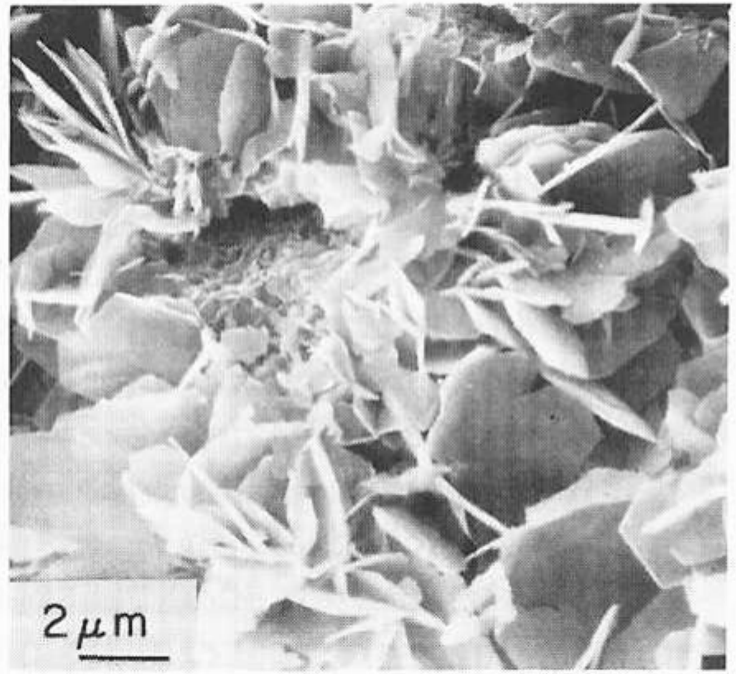
Calcium Sulfoaluminates

- **Ettringite (first): Prismatic needles**
- **Monosulfate (later): Plane hexagonal crystals (low surface area: 2 m^2/g)**
- **Volume – 15-20%**

Ettringite



Monosulfoaluminate



Mehta and Monteiro; Mindess and Young

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

1. If all the sulfate is consumed before the C_3A has completely hydrated, then ettringite becomes unstable and transforms to another calcium sulfoaluminate hydreate containing less sulfate through following reaction:

$$2C_3A \quad + \quad C_6A\bar{S}_3H_{32} \quad + \quad 4H \quad \rightarrow \quad 3C_4A\bar{S}H_{12}$$

- The second product $3C_4A\bar{S}H_{12}$ is simply called as "monosulfoaluminate"
- Monosulfoaluminate may sometimes form before ettringite if C_3A reacts more rapidly with the sulfate ions than they can be supplied by the gypsum to the mix water
- The diffusion barrier, created by the formation of ettringite, is broken down during the conversion of ettringite into monosulfoaluminate and C_3A is allowed to react rapidly again

*The work of Lerch serves as the foundation for our understanding of the role of sulfates in cement [Lerch, 1946].

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

3. **When monosulfoaluminate is brought into contact with a new source of sulfate ions (e.g. external source of sulfate ions), then ettringite can be reformed, as fllows:**

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32}$$

This potential for reforming ettringite is the *basis for sulfate attack* of Portland cements when exposed to an external supply of sulfate ions.

4. **If gypsum is not added in the cement, the hydration of C_3A can lead to flash set due to the rapid formation of calcium aluminate hydrates (C-A-H):**

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

These hydrates (C_4AH_{13} + C_2AH_8) are not stable and later convert to C_3AH_6 (hydrogarnet)

$$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

5. When quite a small amounts of gypsum are present, there may still be unhydrated C_3A present when all of the ettringite has been converted to monosulfoaluminate.

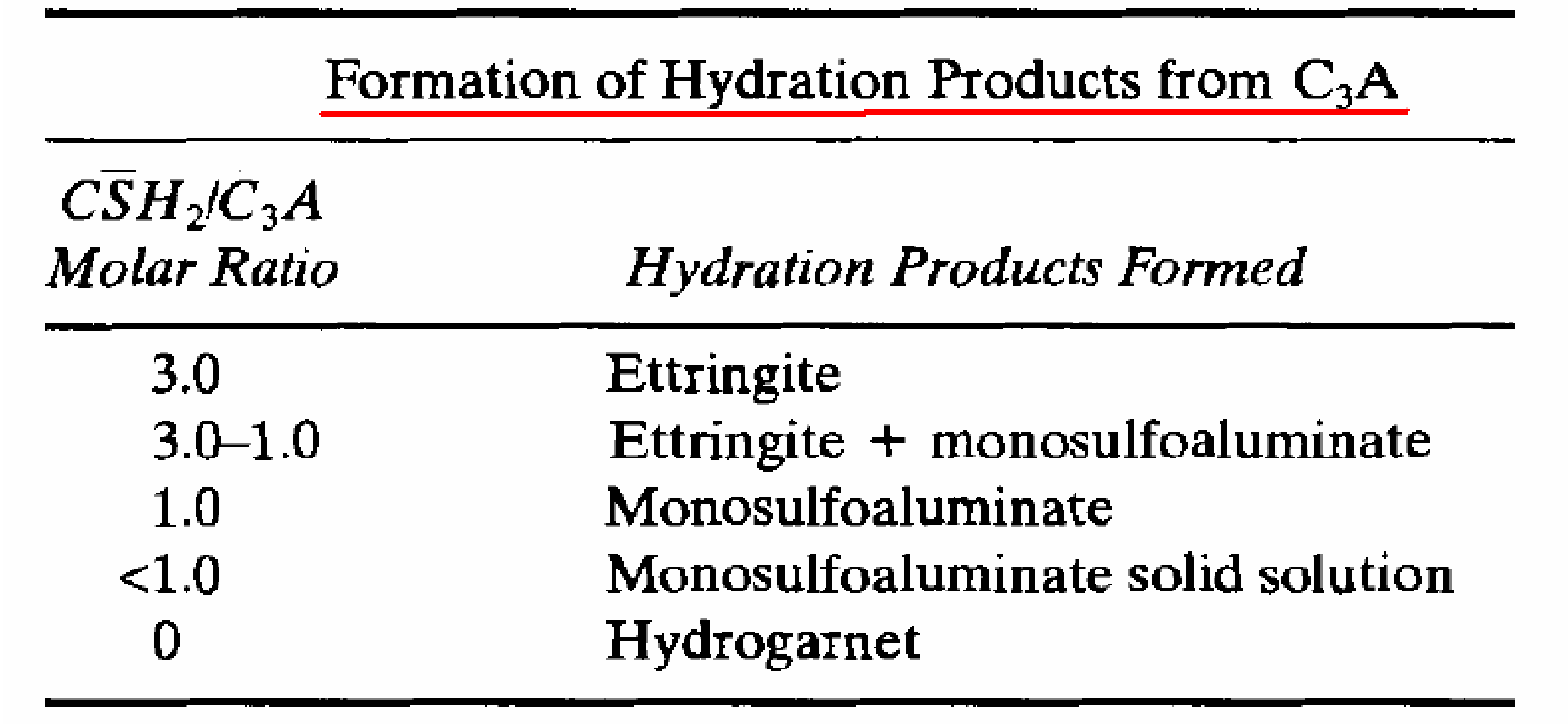
   In such cases, the monosulfoaluminate reacts with the unhydrated C_3A forming the monosulfoaluminate solid solution $[C_3A(C\overline{S}CH)H_{12}]$

$$C_4A\overline{S}H_{12} + C_3A + CH + 12H \rightarrow C_3A(C\overline{S}CH)H_{12}$$

HYDRATION OF CEMENT: Hydration of C_3A

Formation of hydration products from C_3A:

Formation of the hydration products from C_3A, depending upon the sulfate/C_3A molar ratio, is presented in the following table:



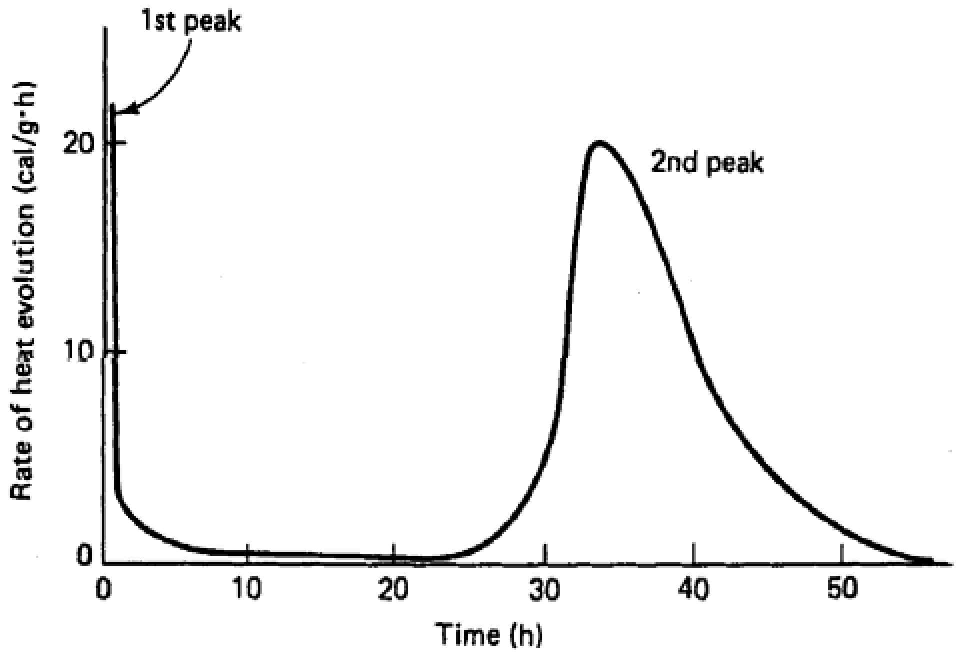
Formation of Hydration Products from C_3A

$C\bar{S}H_2/C_3A$ *Molar Ratio*	*Hydration Products Formed*
3.0	Ettringite
3.0–1.0	Ettringite + monosulfoaluminate
1.0	Monosulfoaluminate
<1.0	Monosulfoaluminate solid solution
0	Hydrogarnet

HYDRATION OF CEMENT: Hydration of C_3A

Hydration curve for C_3A:

The calorimetric for hydrating C_3A, which looks qualitatively much like the curve for C_3S, is shown below:

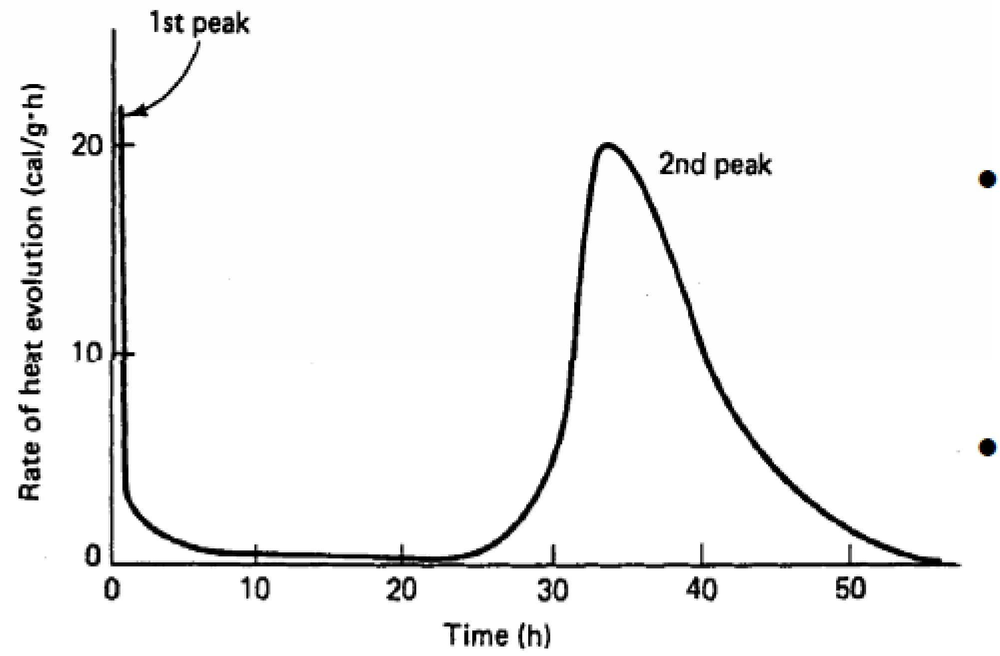


Rate of heat evolution during hydration of tricalcium aluminate with gypsum.

- **The first heat peak is completed in 10 to 15 min and then the rate of heat evolution has been reduced to a very lower value due to the formation of the ettringite barrier**
- **The heat of hydration remains at low value till the ettringite barrier is broken by transformation of ettringite to mono-sulfo-aluminate after all the gypsum has been used to form the ettringite**

HYDRATION OF CEMENT: Hydration of C_3A

Hydration curve for C_3A:



Rate of heat evolution during hydration of tricalcium aluminate with gypsum.

- The more gypsum there is in cement, the longer the ettringite will remain stable
- In most cements ettringite remains in stable condition for a period of 12 to 36 hours.
- The rate of heat evolution starts increasing with start of ettringite conversion to mono-sulfo-aluminate and reaches to the second heat peak and then again starts decreasing approaching to a steady-state condition

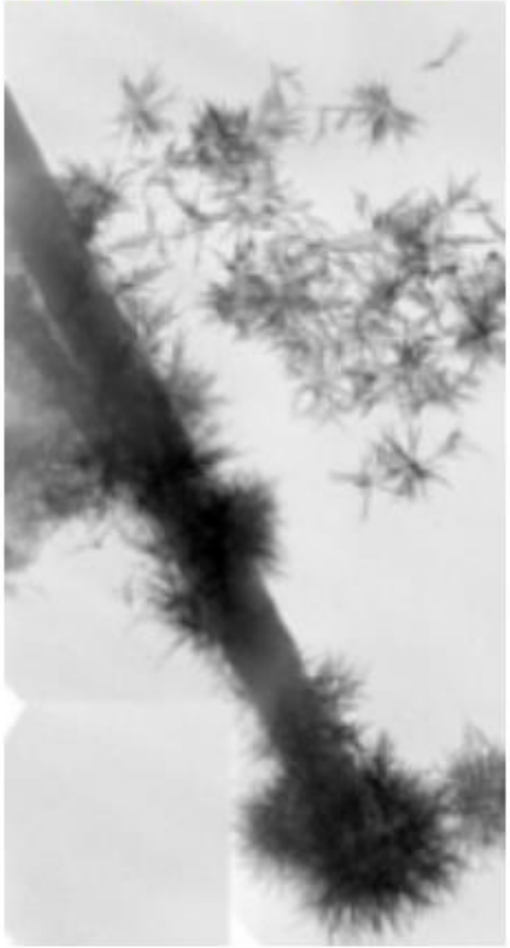
Role of Sulfates in Hydration Reactions / What Is Ettringite? (Stage 1 & 2)

- The use of gypsum or other forms of calcium sulfate to control rapid stiffening in cement was discovered over a century ago [Hansen et al., 1988].
- Calcium sulfate sources, such as gypsum, are intentionally added to portland cement to regulate early hydration reactions to:
  - prevent *flash setting*,
  - improve strength development, and
  - reduce drying shrinkage.
- Sulfate and aluminate are also present in supplementary cementitious materials (SCMs) and admixtures. Gypsum and other sulfate compounds react with calcium aluminate in the cement to form ***ettringite*** within the first few hours after mixing with water.
- i-e C_3A , gypsum and water combine to form $3CaO \bullet AI_2\ O_3 \bullet 3CaSO_4 \bullet 32H_2\ O$: (Calcium tri-sulfoaluminate hydrate- ettringite).

Hydration of the Calcium Aluminates

$C_6A\check{S}_3H_{32}$ (Ettringite, A_{ft})

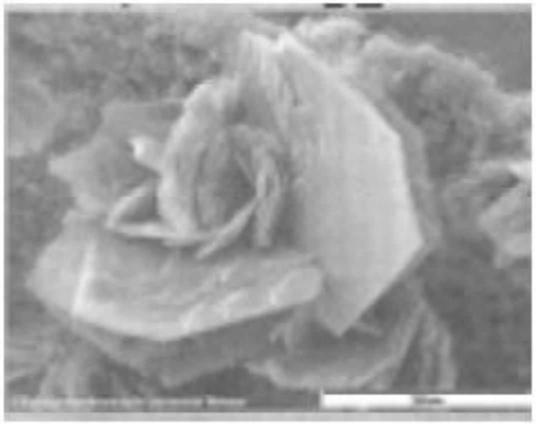
- Needle-like morphology
- Needles interlock, take up much water
- contributes to stiffening of mixture
- some early strength



Hydration of the Calcium Aluminates

$C_4A\check{S}H_{12}$ (monosulfate, A_{fm})

- hexagonal plate morphology arranged in "rosettes" during early hydration
- become more "platey" with continued hydration
- can contain impurities
- vulnerable to sulfate attack



Brief Overview of the Role of Sulfates in Hydration Reactions:

- Other forms of calcium sulfate are associated with dehydrated forms of gypsum. These forms occur naturally or as gypsum is heated to higher temperatures: Gypsum ($CaSO_4 \cdot 2H_2O$) , one form is

  - Hemihydrate ($CaSO_4 \cdot 1/2H_2O$) at ~ 180 °C (350 °F)

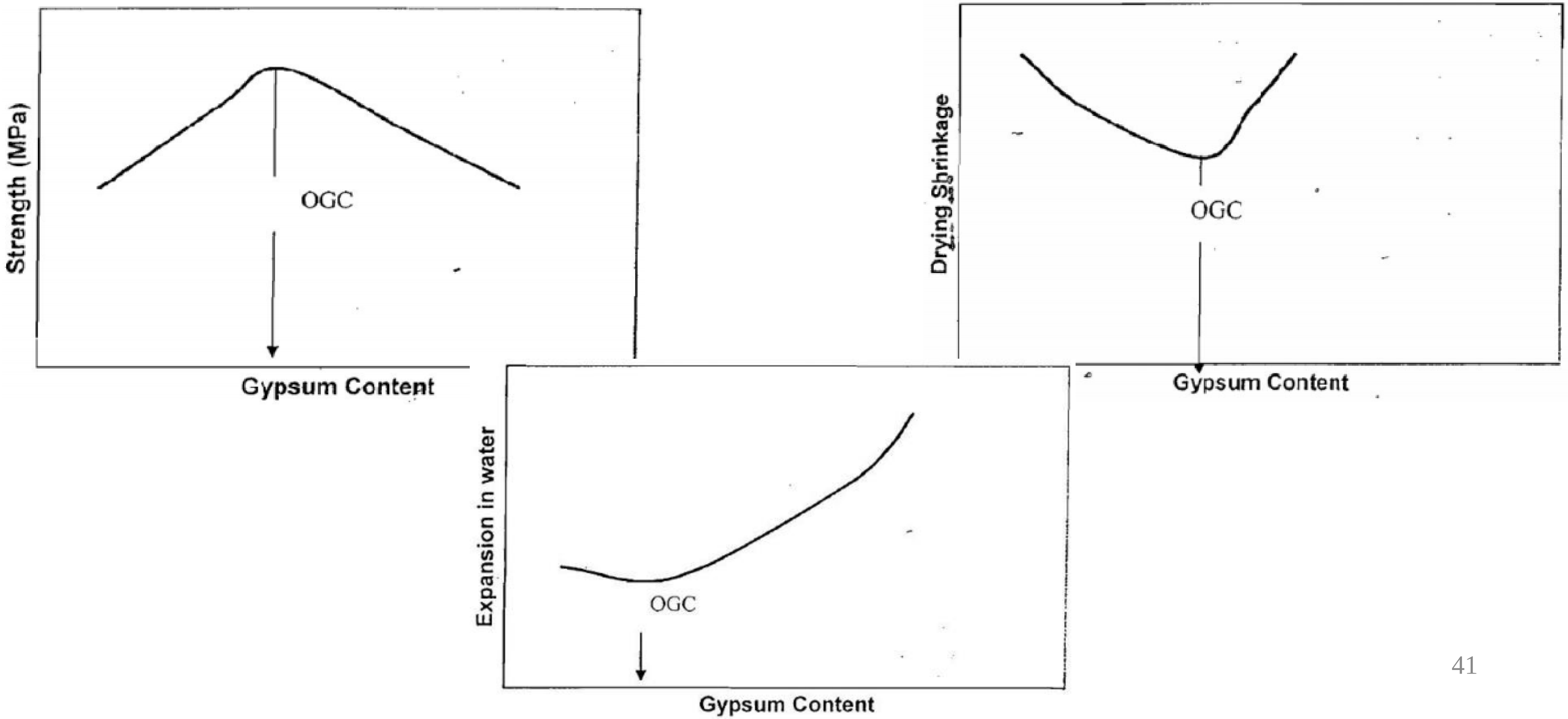
The hemihydrate form is commonly called **Plaster of Paris**.

Other forms of gypsum are

  - Soluble anhydrite ($CaSO_4$) at ~ 260 °C (500 °F)
  - Anhydrite ($CaSO_4$) at ~ 650 °C (1200 °F)

Brief Overview of the Role of Sulfates in Hydration Reactions:

- ***Optimum Gypsum Content (O.G.C)***: Optimum Gypsum Content is a percentage of gypsum that give higher compressive strength, low drying shrinkage and no excessive expansion in concrete volume when immersed in water, as shown in Figures.



Brief Overview of the Role of Sulfates in Hydration Reactions:

Factors affecting on O.G.C;

1. *C_3A content*: Increase C_3A content need to increase O.G.C because higher percentage will react in short time.
2. *Cement fineness*: Increase in cement fineness promote to increase O.G.C.
3. *Alkali content*: Increase in alkali content means increase reaction of gypsum that leads to increase O.G.C.
4. *Curing temperature*: Increase in temperature of curing cause increase the reacrion of C_3A with gypsum that means increase in O.G.C.

*Generally O.G.C ranges between 2–8%, but typically 5% is used in clinker

Hydration Process

(a) Cement grains in water

(b) Growth of colloidal coating of calcium silicate hydrate (CSH) gel

(c) Local disruption and secondary growth of CSH gel. Some crystallization of calcium hydroxide

(d) Further growth of CSH gel and infilling by CSH gel

Stage 3: Hardening/ Acceleration Stage

Corresponds to acceleration period starting at the end of dormant period and lasting till the rate of heat evolution reaches a maximum value.

C-S-H, fiber-like particles & CH forms and give concrete its strength
Heat is generated causing thermal expansion

Initial and Final Set occur

The gel-like C-A-S-H transforms into a needle-like solid (ettringite) that contributes somewhat to early strength.

Curing necessary right after finishing

- By this time final set has been passed and early hardening has begun.

Stage 4: Cooling/ Deceleration Stage (several hours)

After final set, the buildup of C-S-H and CH begins to limit access of water to undisclosed cement

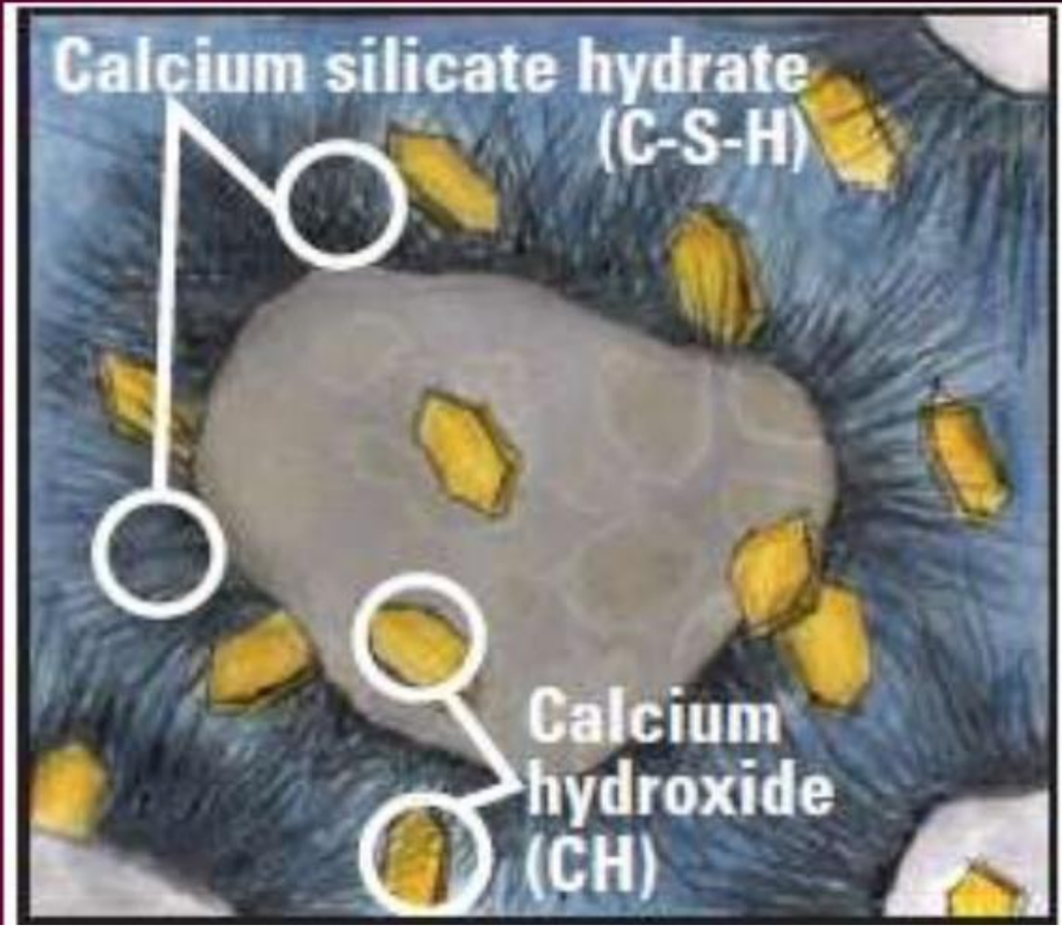
Silicate reactions slow.

Heat peaks and begins to drop

Concrete cools and contracts

Cracking can occur

During which the rate of heat evolution reduces from its maximum value to a very low steady state rate



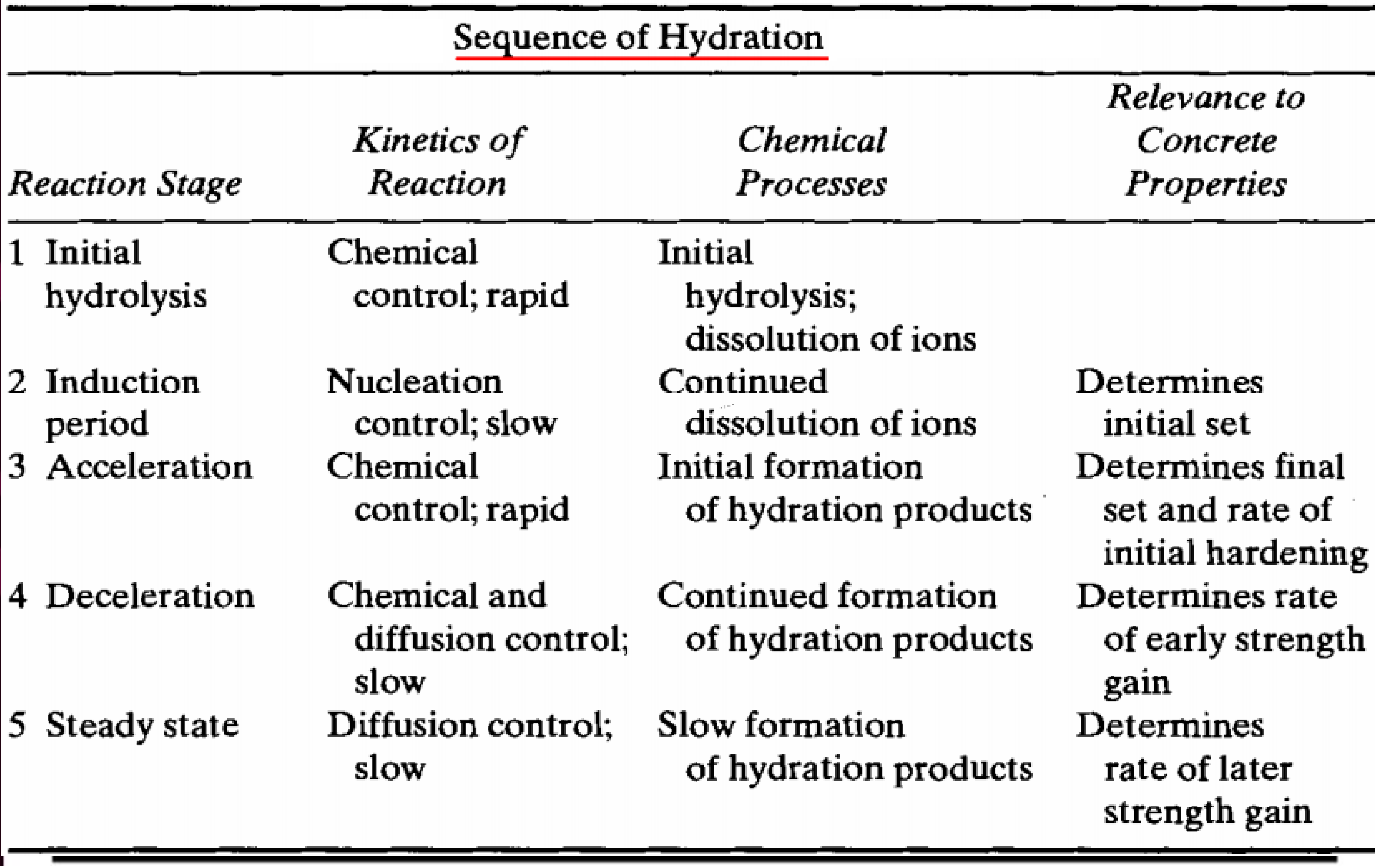
Stage 5: Densification/ Steady Stage (can continue for years)

Start of belite reactions and they can continue for years
Belite reactions also produce C-S-H and CH, forming a solid mass

Longer length of this stage gives:
- Greater concrete's strength
- Lower permeability
- Greater durability

To promote continued hydration, moisture must be retained as long as possible

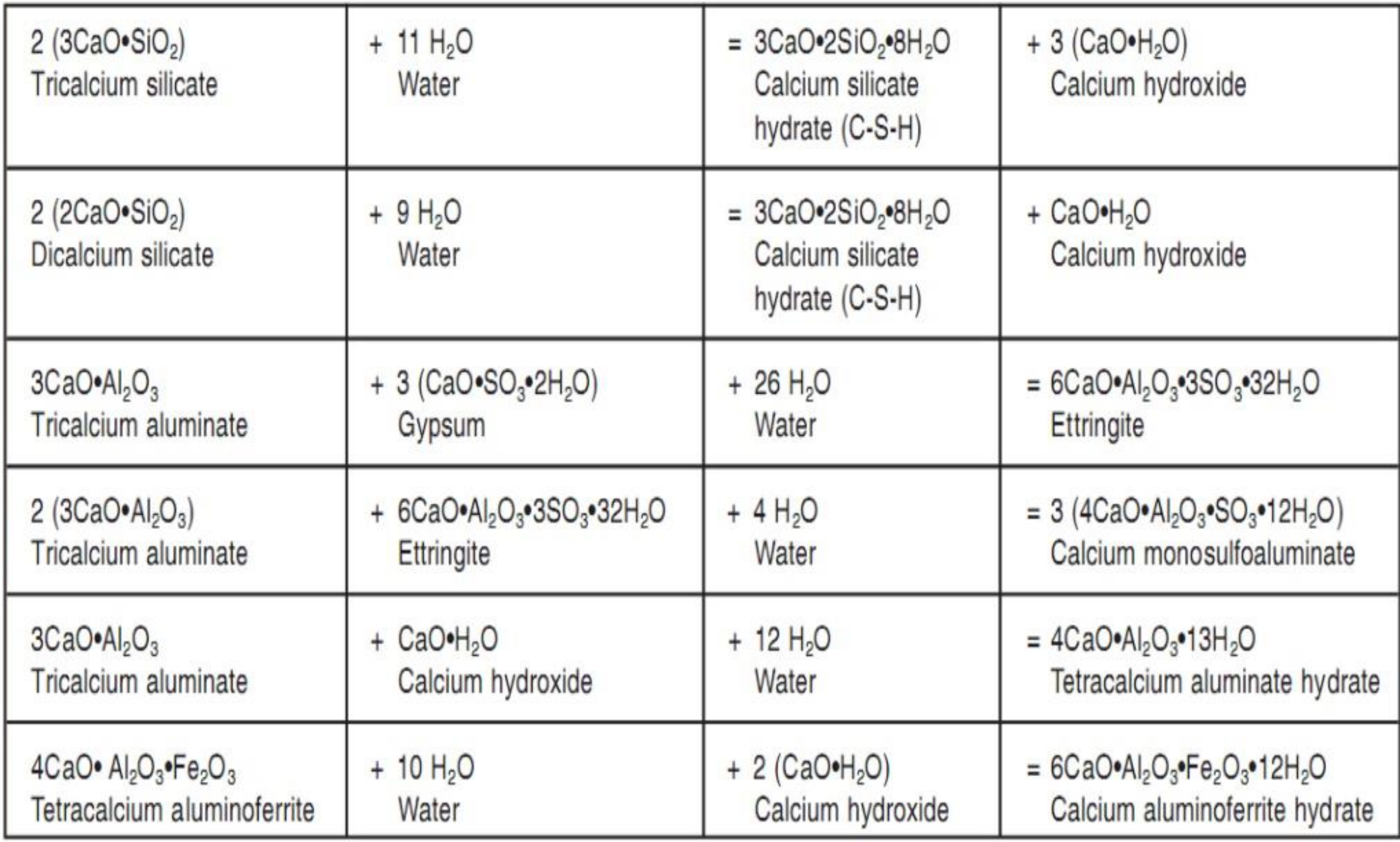
5 Stages of Hydration



Sequence of Hydration

Reaction Stage	*Kinetics of Reaction*	*Chemical Processes*	*Relevance to Concrete Properties*
1 Initial hydrolysis	Chemical control; rapid	Initial hydrolysis; dissolution of ions	
2 Induction period	Nucleation control; slow	Continued dissolution of ions	Determines initial set
3 Acceleration	Chemical control; rapid	Initial formation of hydration products	Determines final set and rate of initial hardening
4 Deceleration	Chemical and diffusion control; slow	Continued formation of hydration products	Determines rate of early strength gain
5 Steady state	Diffusion control; slow	Slow formation of hydration products	Determines rate of later strength gain

Hydration Reactions



$2\,(3CaO{\bullet}SiO_2)$ Tricalcium silicate	$+\ 11\,H_2O$ Water	$=\ 3CaO{\bullet}2SiO_2{\bullet}8H_2O$ Calcium silicate hydrate (C-S-H)	$+\ 3\,(CaO{\bullet}H_2O)$ Calcium hydroxide
$2\,(2CaO{\bullet}SiO_2)$ Dicalcium silicate	$+\ 9\,H_2O$ Water	$=\ 3CaO{\bullet}2SiO_2{\bullet}8H_2O$ Calcium silicate hydrate (C-S-H)	$+\ CaO{\bullet}H_2O$ Calcium hydroxide
$3CaO{\bullet}Al_2O_3$ Tricalcium aluminate	$+\ 3\,(CaO{\bullet}SO_3{\bullet}2H_2O)$ Gypsum	$+\ 26\,H_2O$ Water	$=\ 6CaO{\bullet}Al_2O_3{\bullet}3SO_3{\bullet}32H_2O$ Ettringite
$2\,(3CaO{\bullet}Al_2O_3)$ Tricalcium aluminate	$+\ 6CaO{\bullet}Al_2O_3{\bullet}3SO_3{\bullet}32H_2O$ Ettringite	$+\ 4\,H_2O$ Water	$=\ 3\,(4CaO{\bullet}Al_2O_3{\bullet}SO_3{\bullet}12H_2O)$ Calcium monosulfoaluminate
$3CaO{\bullet}Al_2O_3$ Tricalcium aluminate	$+\ CaO{\bullet}H_2O$ Calcium hydroxide	$+\ 12\,H_2O$ Water	$=\ 4CaO{\bullet}Al_2O_3{\bullet}13H_2O$ Tetracalcium aluminate hydrate
$4CaO{\bullet}\,Al_2O_3{\bullet}Fe_2O_3$ Tetracalcium aluminoferrite	$+\ 10\,H_2O$ Water	$+\ 2\,(CaO{\bullet}H_2O)$ Calcium hydroxide	$=\ 6CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3{\bullet}12H_2O$ Calcium aluminoferrite hydrate

HYDRATION OF CEMENT: Hydration of C_3S

The following chemical reaction takes place when C_3S comes in contact with water:

$$\underset{\text{tri-calcium silicate}}{2C_3S} + \underset{\text{water}}{6H} \rightarrow \underset{\text{C-S-H}}{C_3S_2H_3} + \underset{\text{calcium hydroxide}}{3CH}$$

- **C-S-H (calcium-silicate-hydrate) is the principal hydration product**
- **The formula $C_3S_2H_3$ for C-S-H is only approximate because the composition of C-S-H is actually variable over a quite a wide range**
- **C-S-H is poorly crystalline material which forms extremely small particles in the size range of colloidal matter (< 1 μm)**
- **CH (calcium hydroxide) is the secondary hydration product**
- **Unlike the C-S-H, CH is a crystalline material with a fixed composition**

HYDRATION OF CEMENT: Hydration of C_3S

Chemical and Physical Processes Controlling C_3S Hydration

Chemical control:

- The *hydrolysis* of the C_3S (i.e., *the chemical reaction between* C_3S *and water*) which results into release of calcium ions and hydroxide ions from the surface of the C_3S grains, forming C-S-H and CH through crystallization of ions and increasing the pH to over 12 within a few minutes, is called as chemical control.

- The chemical control (i.e. the hydrolysis of C_3S) slows down quickly but continues throughout the dormant period.

- During the dormant period, the increase in Ca^{++} and OH^{-} concentrations continues slowly.

HYDRATION OF CEMENT: Hydration of C_3S

Chemical and Physical Processes Controlling C_3S Hydration

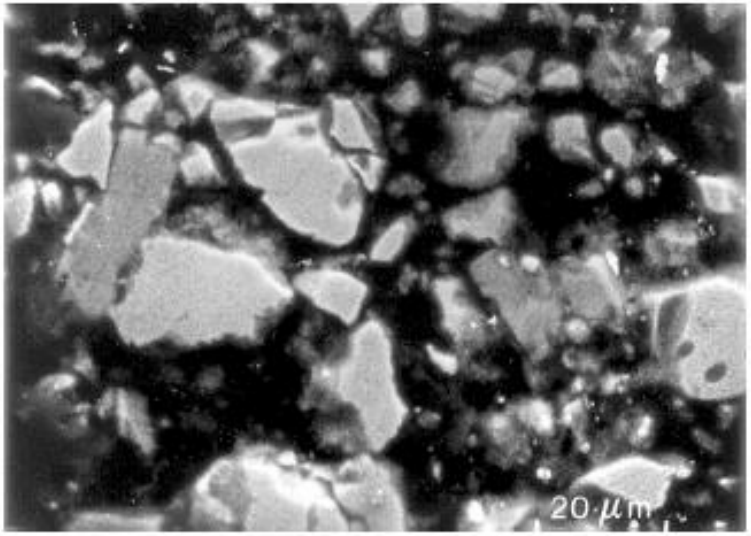
Nucleation control:

- When the Ca^{++} and OH^- concentrations reach a critical value, the hydration products (C-S-H and CH) start to crystallize from solution and the hydrolysis of C_3S again proceeds rapidly.
- This whole process of attenuation of critical concentrations of Ca^{++} and OH^- corresponding to which the nuclei of the C-S-H and CH crystals starts forming giving way to the further hydrolysis of C_3S is termed as nucleation control.

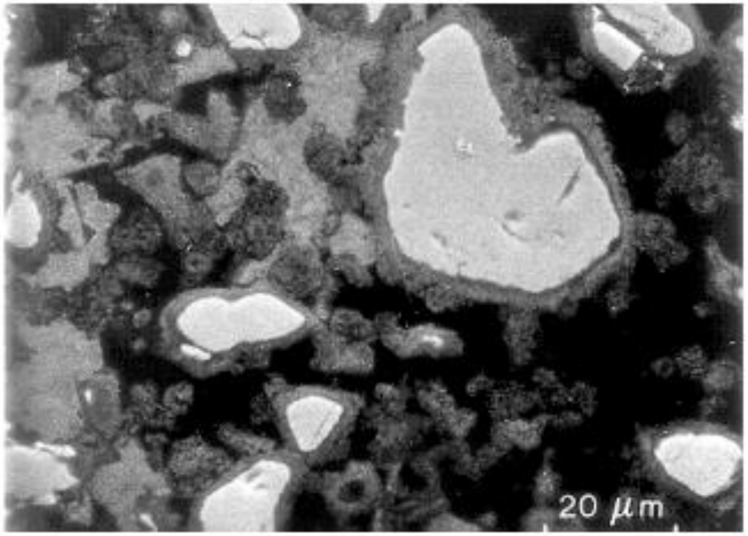
Diffusion control:

- The hydration process is said to be under diffusion control when the coating over the C_3S grains, formed by layers of C-S-H, put a barrier through which water must flow to reach the un-hydrated C_3S for its hydrolysis and through which ions must diffuse to reach the growing crystals.

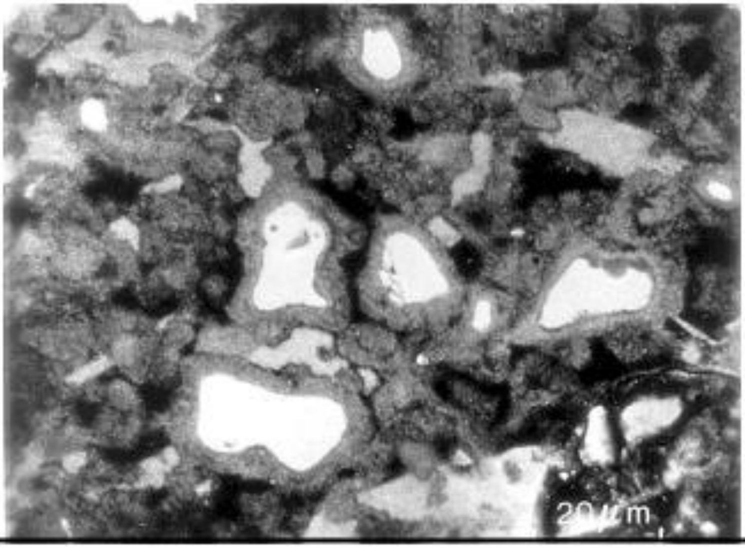
C_3S Hydration



1 Day



3 Days



28 Days

HYDRATION OF CEMENT: Hydration of C_2S

- C_2S hydrates in a similar manner as that of C_3S:

$$2C_2S \quad + \quad 4H \quad \rightarrow \quad C_3S_2H_3 + \quad CH$$

$2C_2S$	$4H$	$C_3S_2H_3$	CH
dicalcium silicate	water	C-S-H	calcium hydroxide

- But the hydration of C_2S is much slower than C_3S because it is a less reactive compound than C_3S. This is the reason why C_2S does not contribute to initial strength.

- Due to very low amount of heat liberated on the hydration of C_2S, it is not easy to measure the low heat experimentally and therefore calorimetric curve for C_2S hydration is hardly plotted

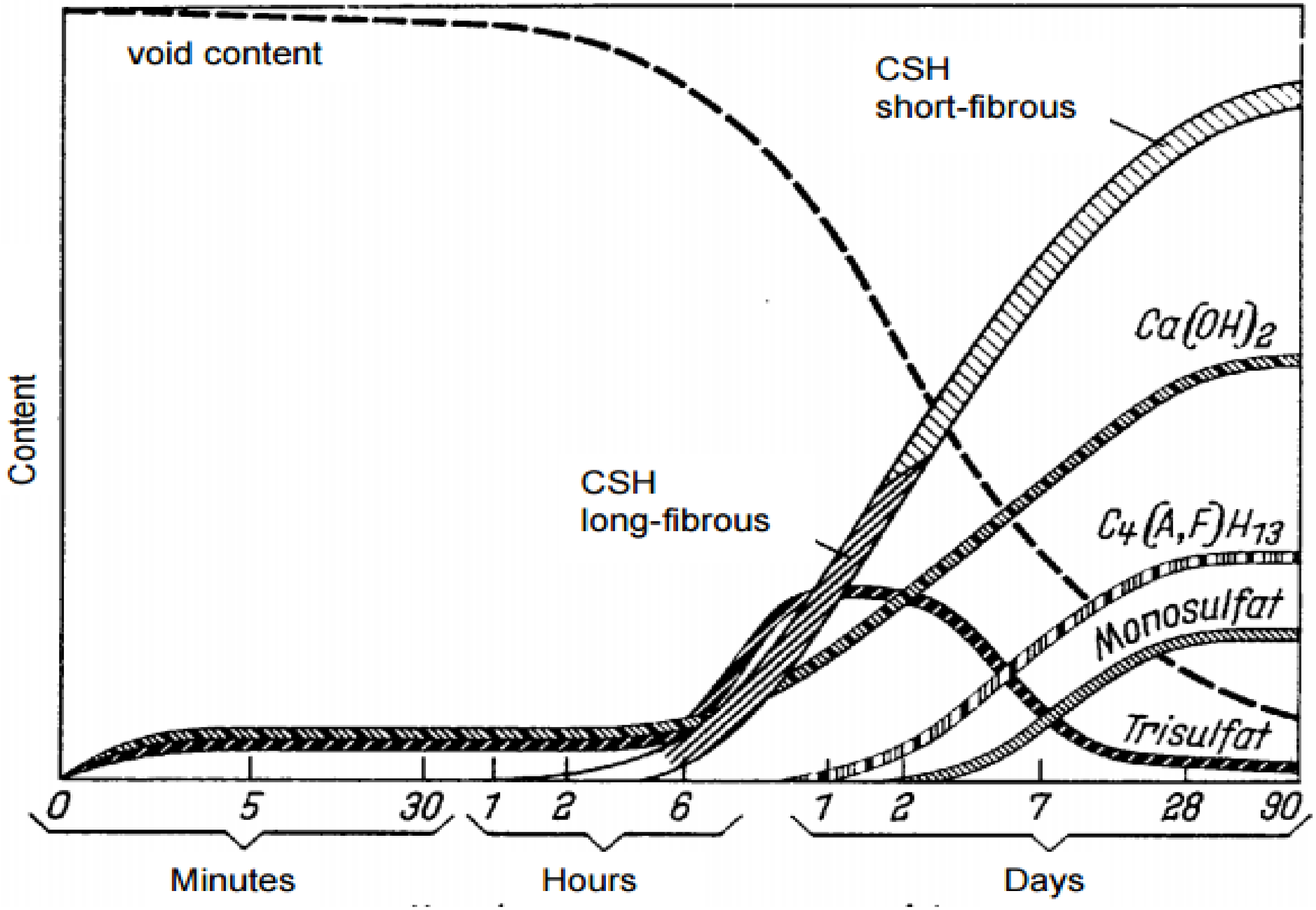
HYDRATION OF CEMENT: Hydration of C_4AF

- C_4AF forms the same sequence of hydration products as does C_3A, with or without gypsum

$$C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A, F)\bar{S}_3H_{32} + (A, F)H_3$$
$$C_4AF + C_6(A, F)\bar{S}_3H_{32} + 7H \rightarrow 3C_4(A, F)\bar{S}H_{12} + (A, F)H_3$$

- The reactions are slower and involve less heat
- C_4AF never hydrates rapidly enough to cause flash set, and gypsum retards C_4AF hydration even more drastically than it does C_3A
- With increase in iron content in C_4AF, hydration of C_4AF becomes slower
- Practical experience has shown that cements low in C_3A and high in C_4AF are resistant to sulfate attack
- This means that the formation of ettringite from mono-sulfo-aluminate does not occur in case of C_4AF due to presence of iron in it.

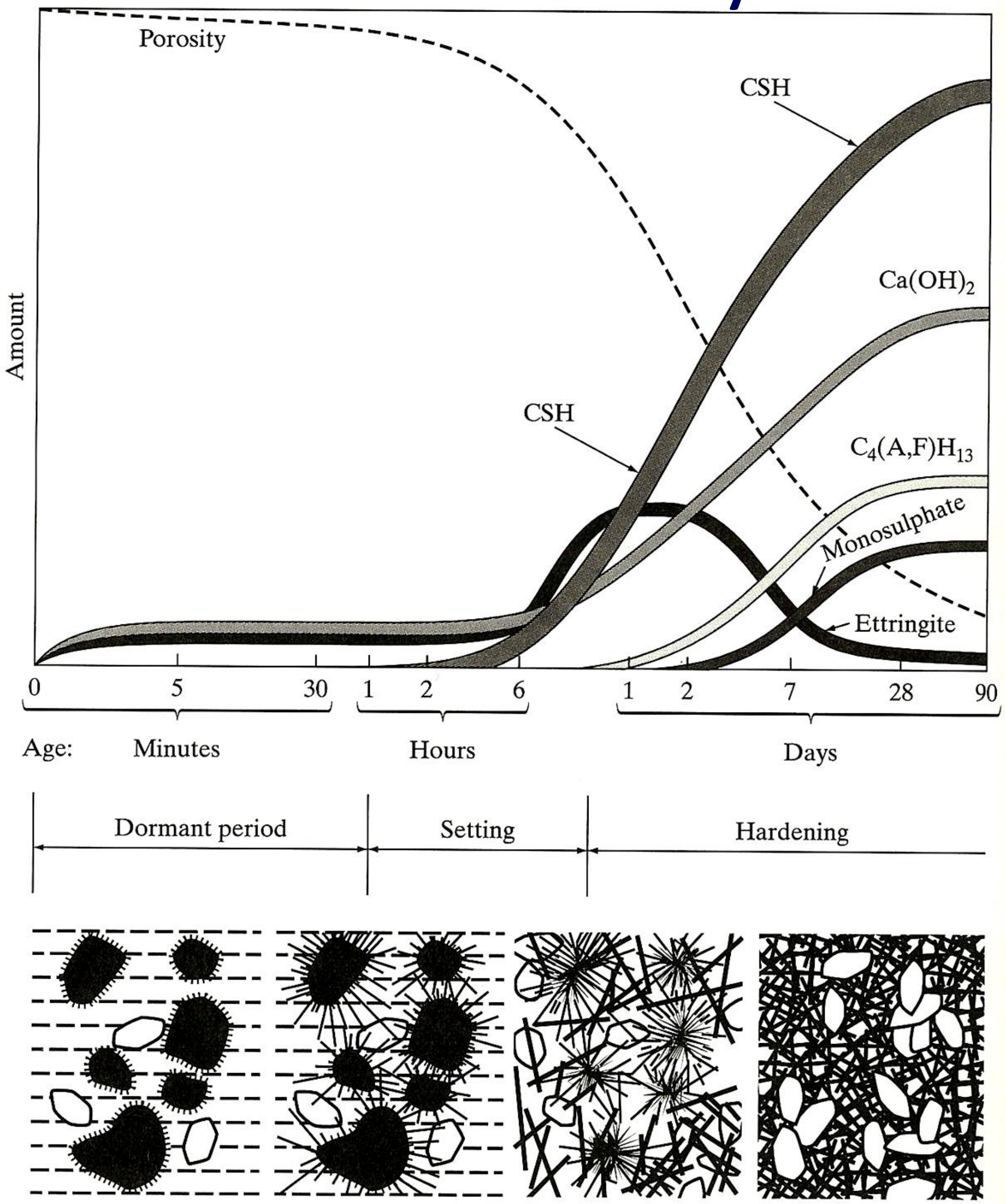
Formation of Hydration products with time



C-S-H = calcium silicate hydrate

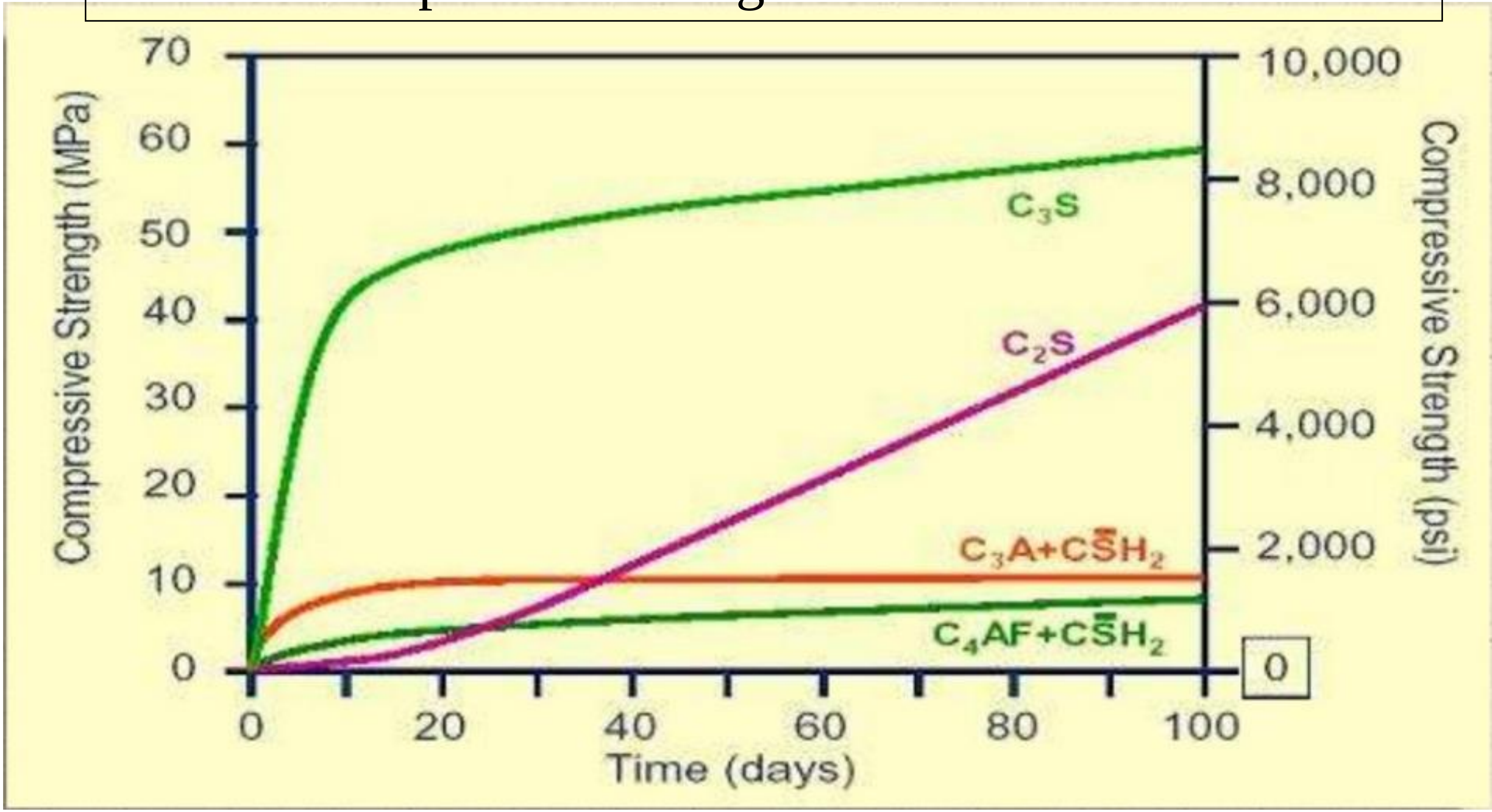
$C_4(A,F)H_{13}$ = iron-oxide-containing tetra-calcium aluminate hydrate

Evolution of Hydration



Young et

Relation between Hydration products with time and effect on compressive strength



Heat of Hydration

- Cement hydration is exothermic
- Concrete is an insulator

Heat of hydration can be:

- detrimental (thermal gradients --> cracking)

- helpful (heat provides activation energy when concreting in cold weather; higher early strength)

Heat of Hydration

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

(1) Initial dissolution of solids (increasing ionic concentration)

(2) Induction period

(3) Acceleration

(4) Deceleration

(5) Steady state

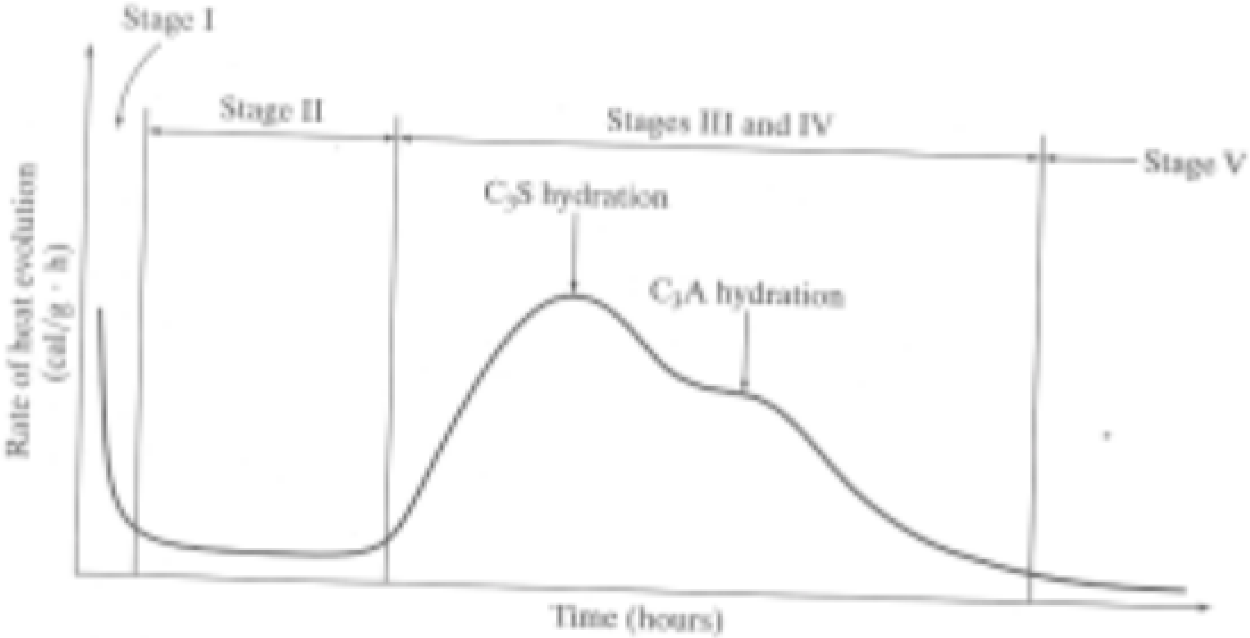


Figure 11.4
Rate of heat evolution during the hydration of portland cement (after S. Mindess and J. F. Young, *Concrete*, Prentice Hall, 1981, Fig. 4.4, p. 85).

Kinetics of cement hydration:

- At *much lower temperatures* present during cement hydration, the cement minerals are actually quite unstable, meaning that there are many other solid phases that will form preferentially in their place once they dissolve.
- In fact, the whole point after the *high-temperature cement manufacturing process is to create solid phases that will readily dissolve in water*, allowing new phases to form. When one phase is converted into another phase with a lower free energy, there is usually a release of excess energy in the form of heat. Such a reaction is termed exothermic, and the exothermic heat associated with cement hydration as defined earlier is termed as "***heat of hydration***"**.**

Kinetics of cement hydration:

- Information about the rate of a reaction is called kinetics.

The progress of cement hydration depends on:

- Rate of dissolution (mechanism of breakdown in to ions) of the involved materaial /phases (in the initial stages), and at later stages,
- Rate of nucleation (assemblage of products) and crystal growth of hydrates
- Rate of diffusion of water and dissolved ions through the hydrated materials already formed

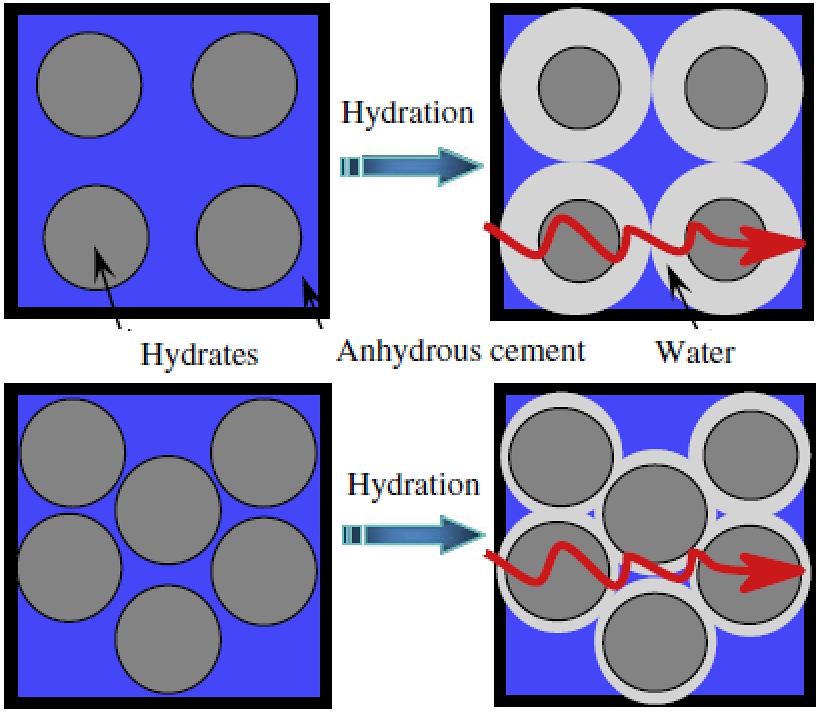


Fig.Schematic representations of hydration and mechanical percolation.

Approaches to control heat of hydration

- **Control of Cement Amount**
- **Use of low-heat Cement**
- **Use of Pozzolans**
- **pre-cooling** **(of the materials)**
- **post-cooling**

Factors affecting Kinetics of cement hydration:

- The factors affecting the kinetics of hydration are:

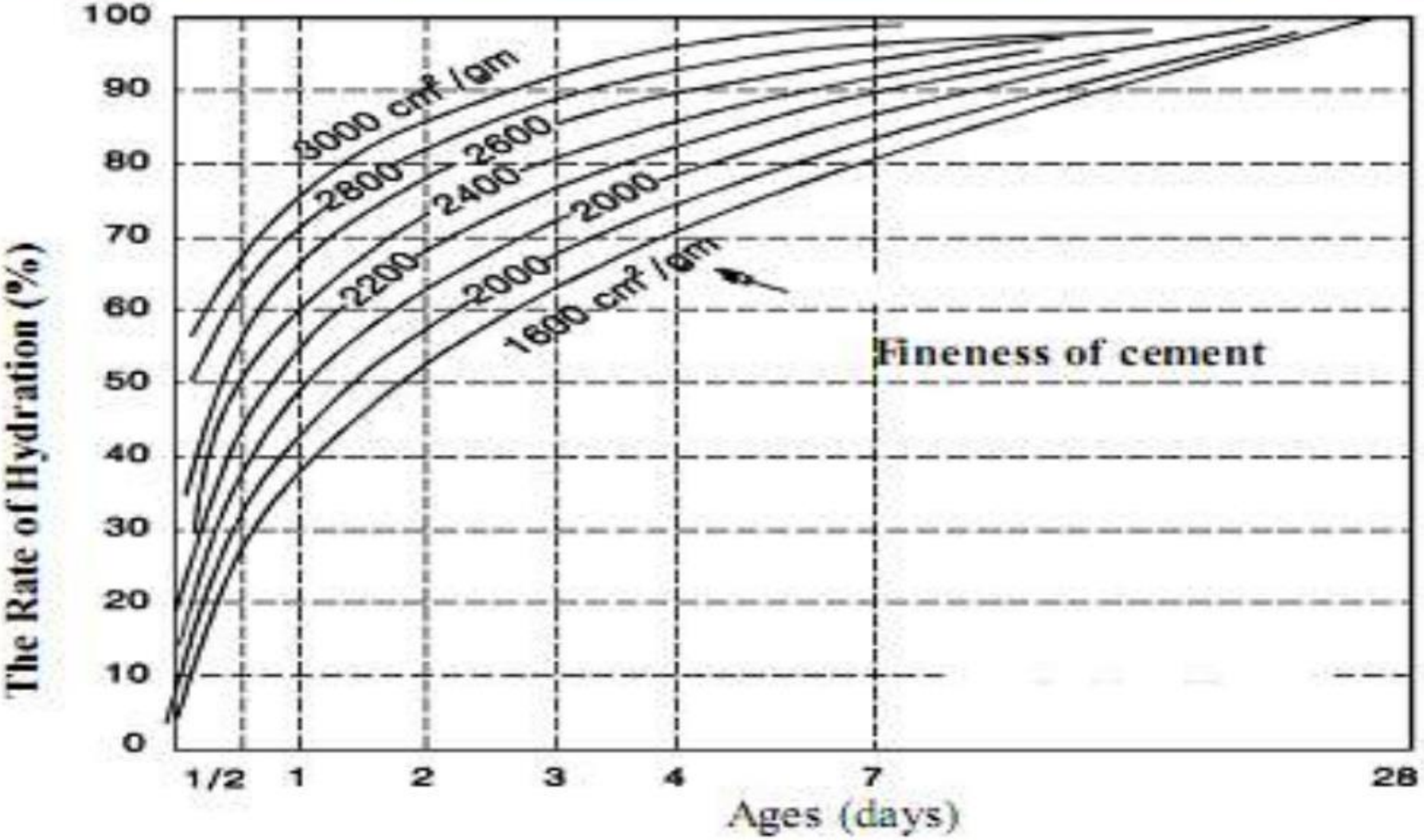
- The *composition* of cement
- The amount and form of *gypsum* in the cement: Whether gypsum is present in the dihydrate, hemihydrate, or the anhydrite form.

- $CaSO_4$ (anhydrite): anhydrous state.
- $CaSO_4 \cdot 2\,H_2O$ (gypsum): dihydrate.
- $CaSO_4 \cdot 0.5\,H_2O$ (bassanite): hemihydrate, also known as plaster of Paris. It takes very short setting time as compared to anhydrous gypsum.

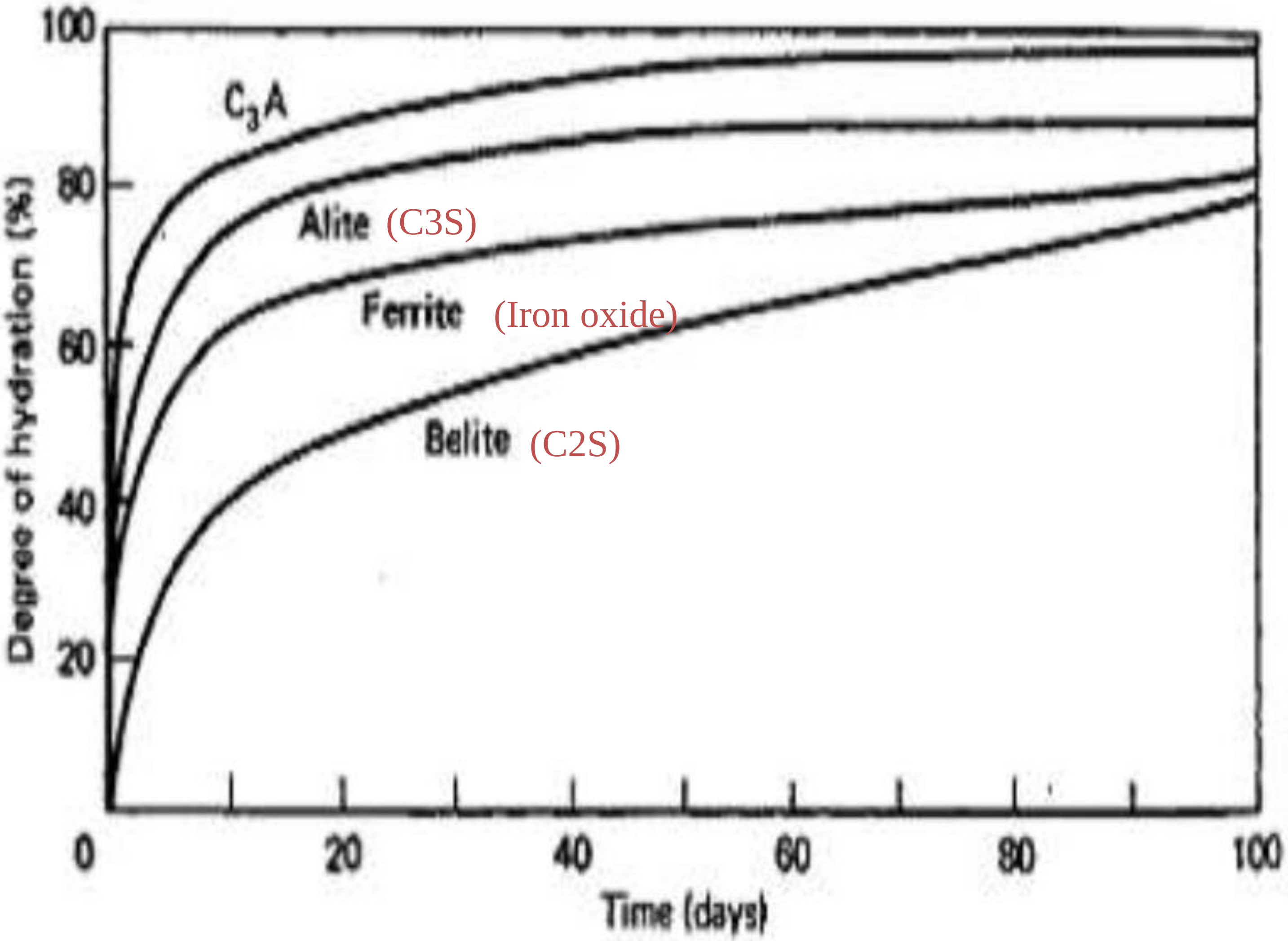
Factors affecting Kinetics of cement hydration:

- *Fineness of cement*: Higher the fineness, higher the rate of reaction due to availability of a larger surface area.
- *w/c of mix*: At high w/c, hydration may progress till all of the cement is consumed, while at low w/c the reaction may stop altogether due to lack of water.
- *Curing conditions*: The relative humidity can have major effects on the progress of hydration.
- *Hydration temperature*: Increase in temperature of the ingredients generally causes an increase in the rate of the reaction, although the hydrated structure can be different at different temperatures.
- *Presence of chemical admixtures*: Plasticizers also affect the kinetics of cement hydration.

Fineness of Cement



Chemical Composition of Cement

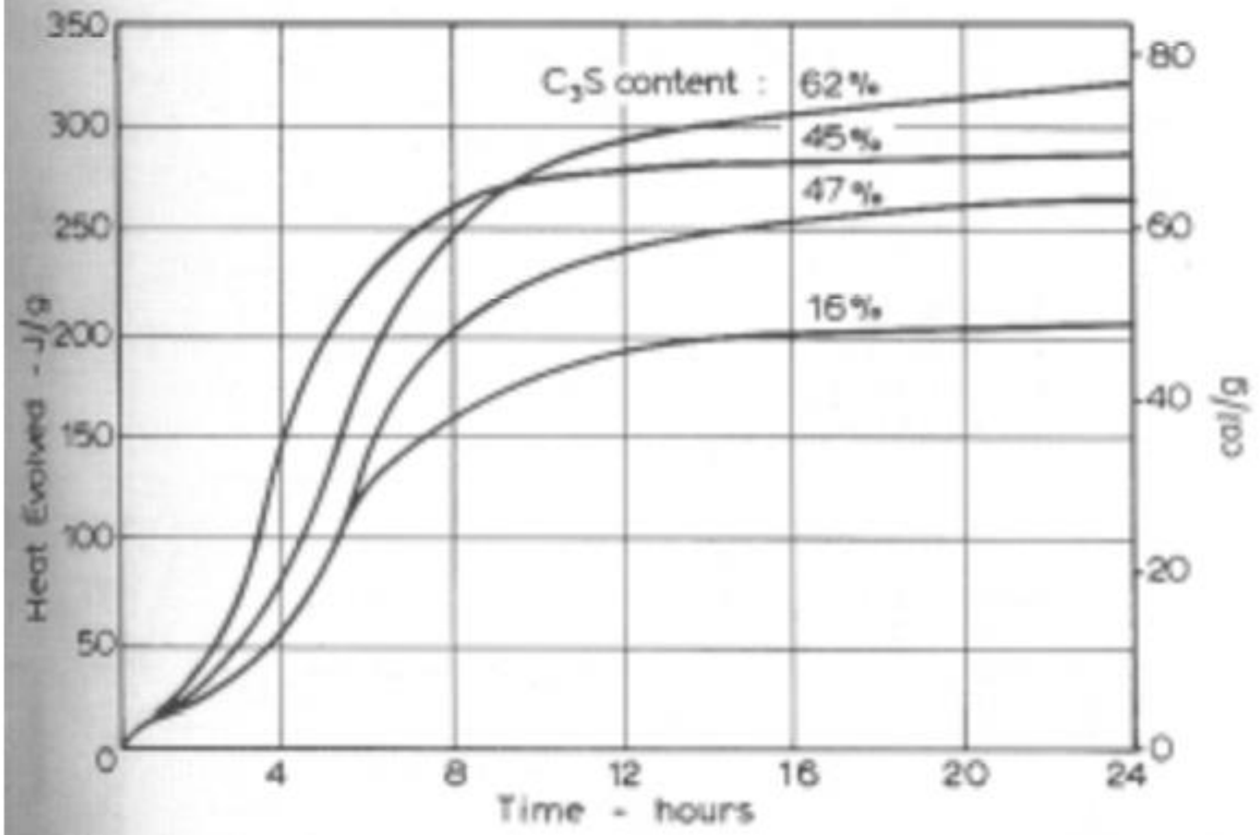


(C3S)

(Iron oxide)

(C2S)

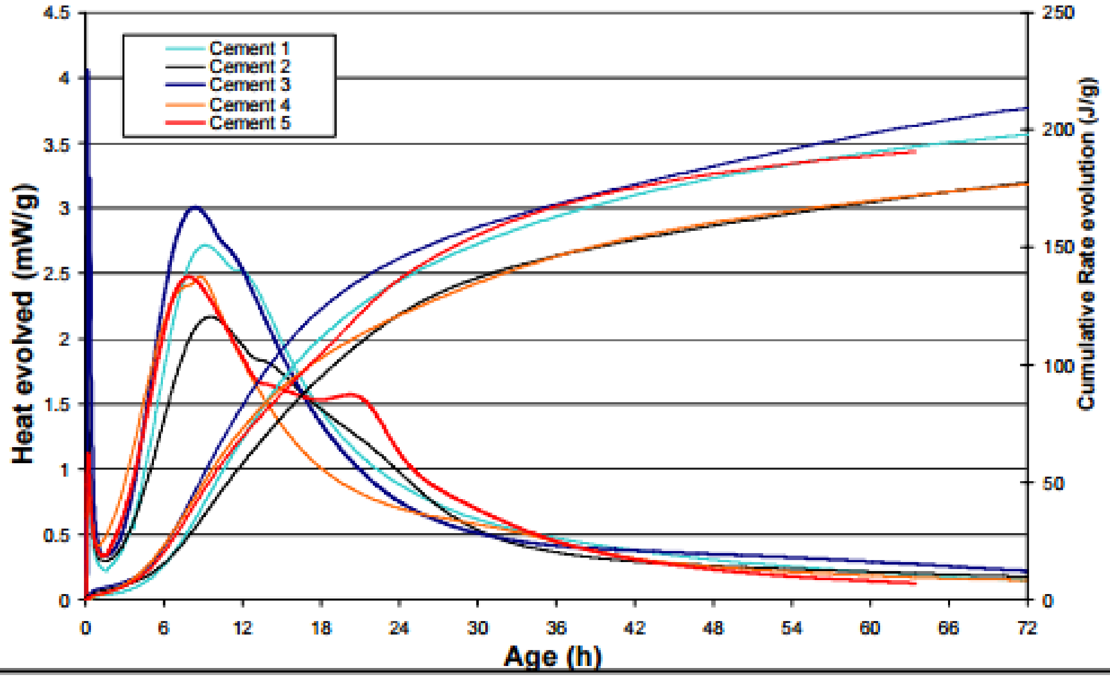
Heat of Hydration: Influence of Cement Composition



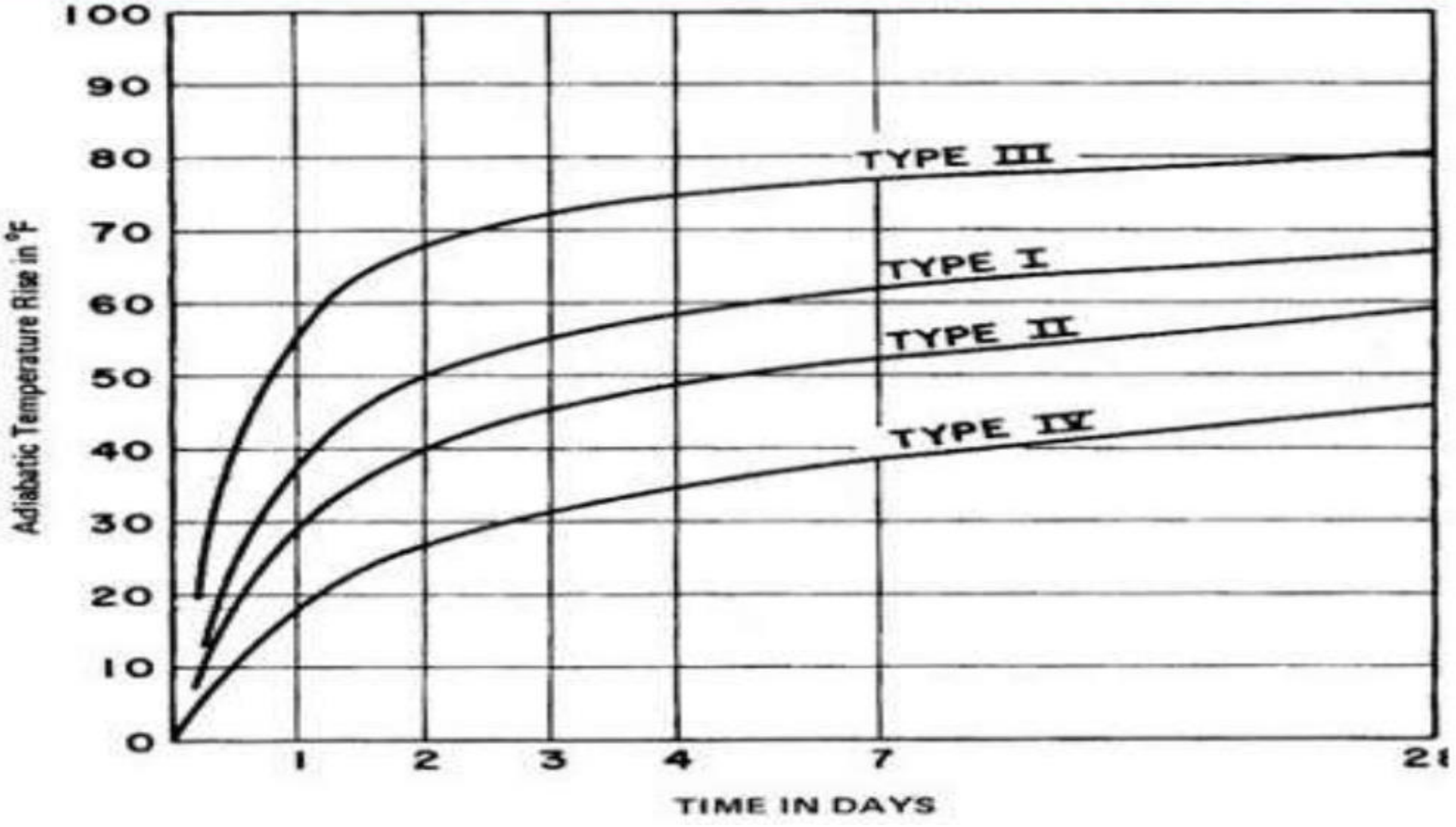
1.16 Influence of C_3S content on heat evolution[1.32] (C_3A content approximately constant)

Heat of Hydration: Influence of Cement Composition

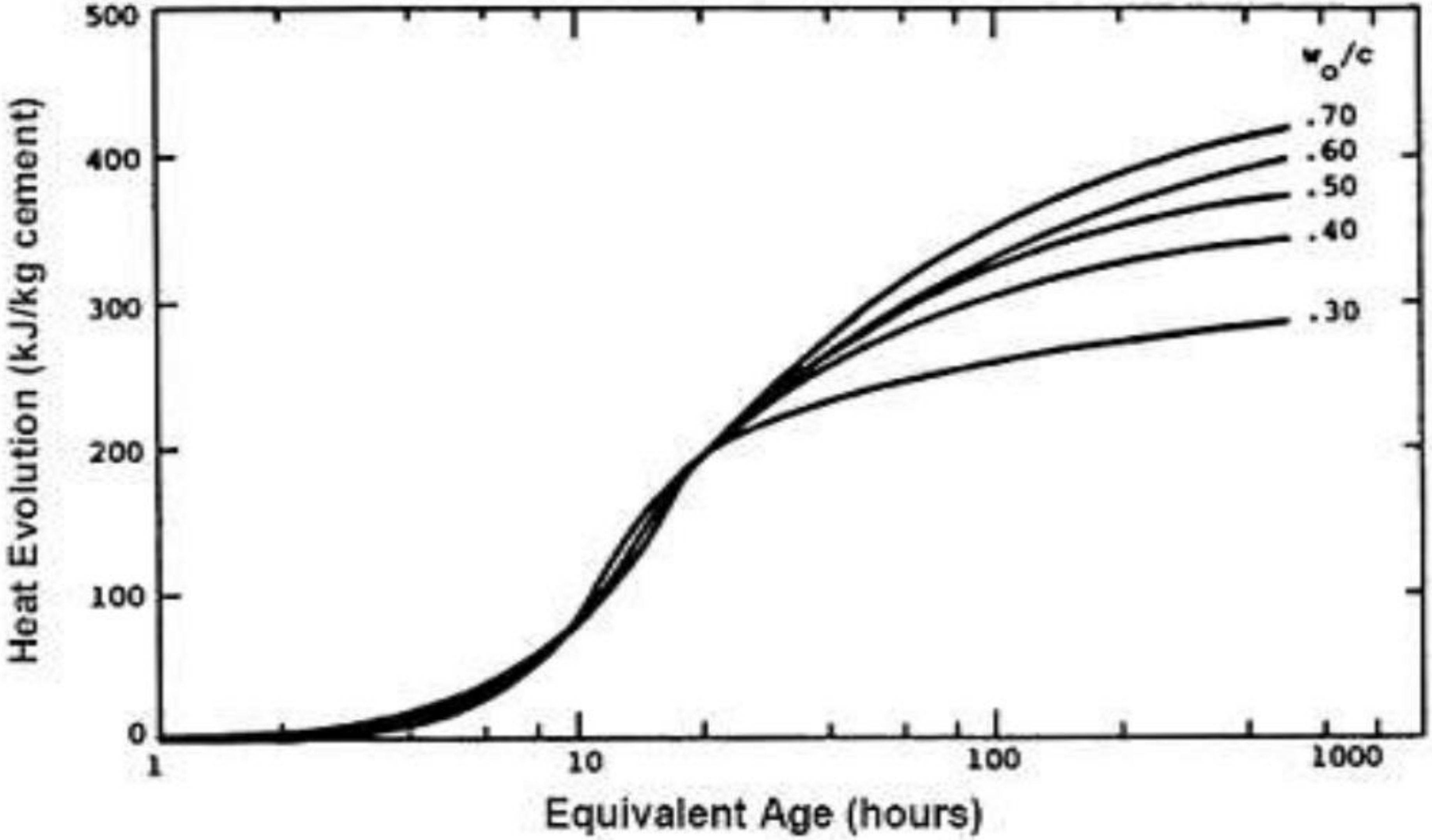
	Cement 1	Cement 2	Cement 3	Cement 4	Cement 5
C3S	59	55.9	62.9	50.4	42
C2S	16	19	7.9	20.6	26
C3A	4	7.5	10.1	7.1	9
C4AF	11	9.1	8.6	12.2	10

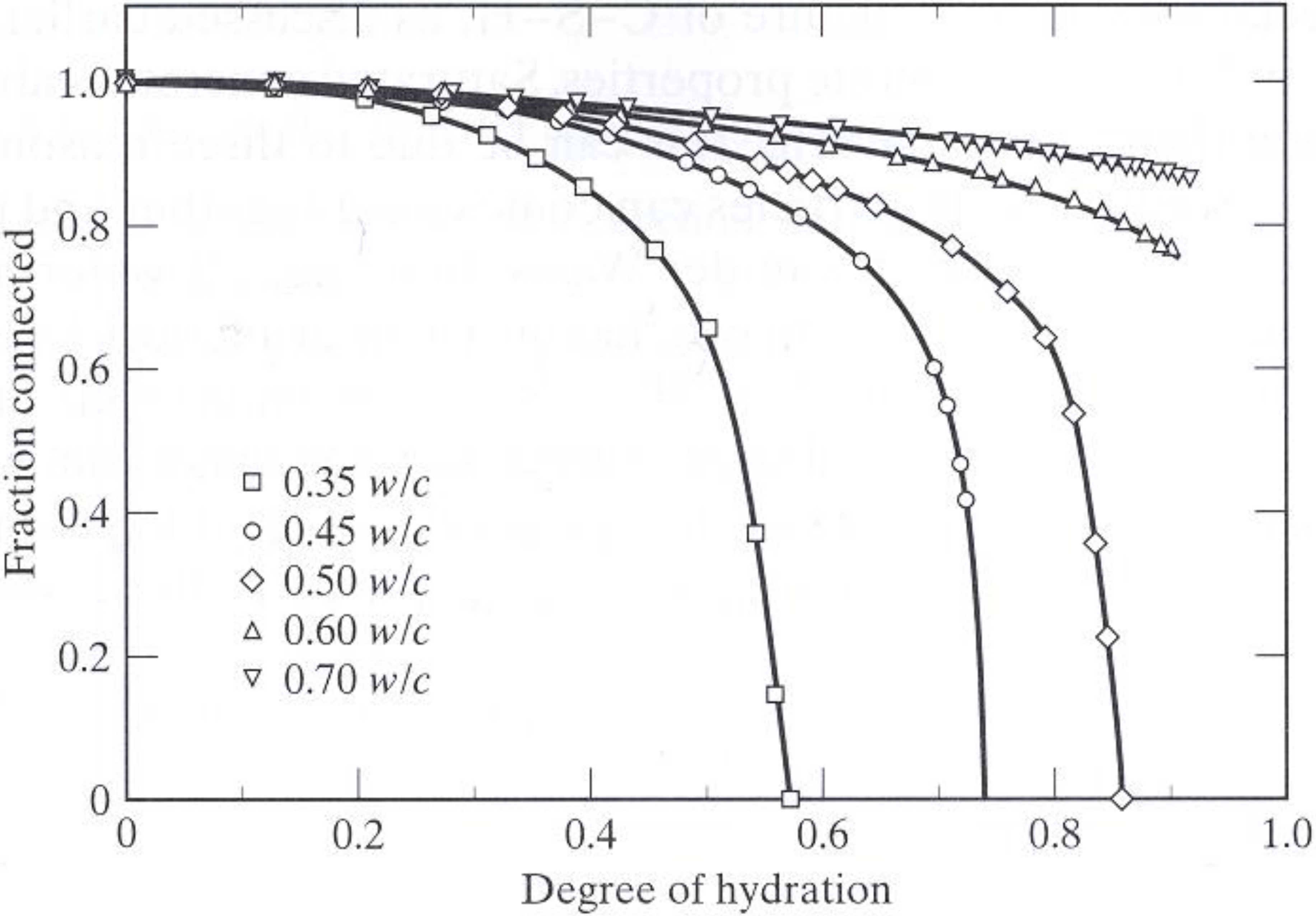


Cement Type


100
90
80
70
60
50
40
30
20
10
0
Adiabatic Temperature Rise in °F
1
2
3
4
7
2
TIME IN DAYS
TYPE III
TYPE I
TYPE II
TYPE IV

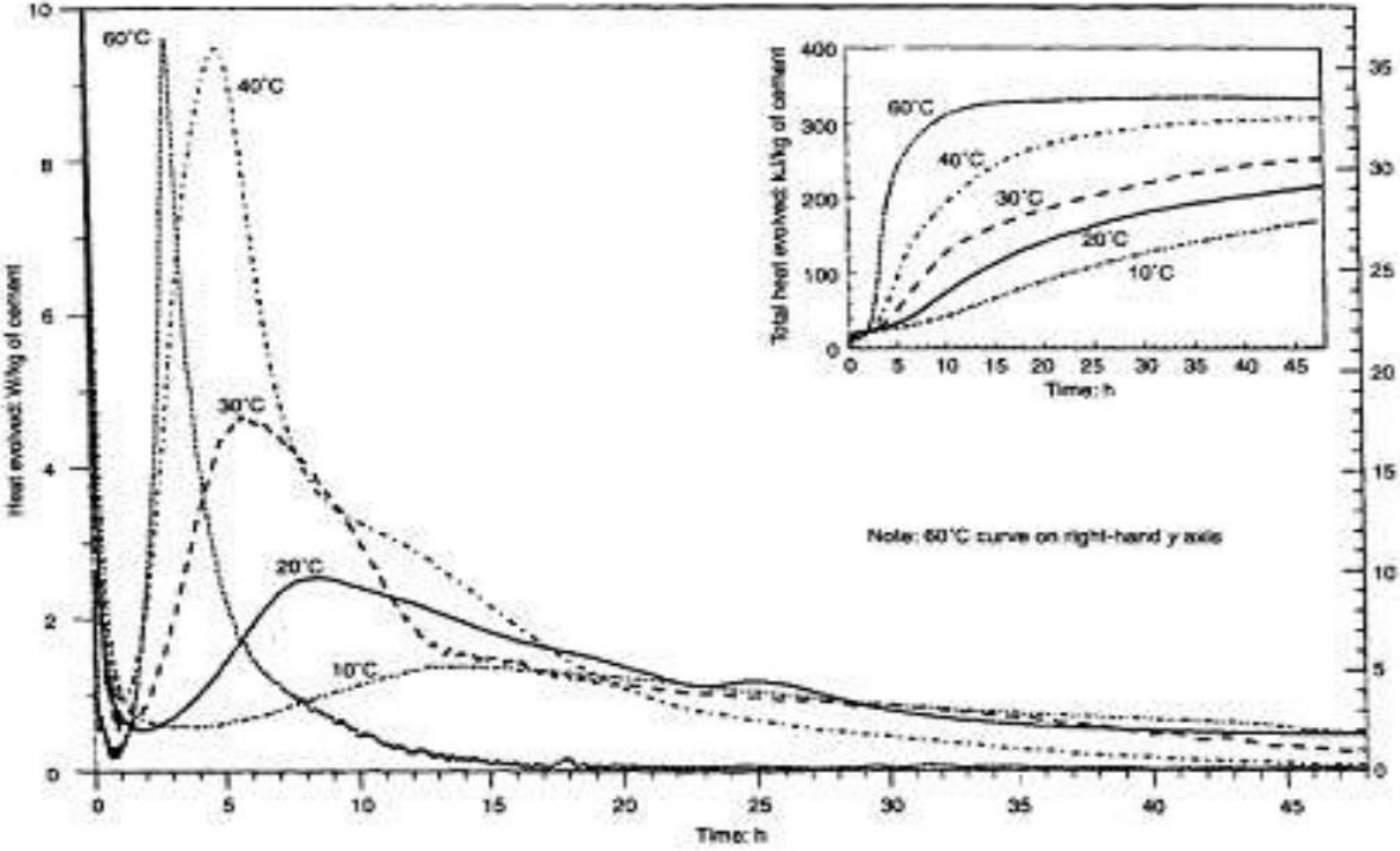
Water/Cement Ratio





Fraction connected
Degree of hydration
0
0.2
0.4
0.6
0.8
1.0
0
0.2
0.4
0.6
0.8
1.0
□ 0.35 *w/c*
○ 0.45 *w/c*
◇ 0.50 *w/c*
△ 0.60 *w/c*
▽ 0.70 *w/c*

Curing Temperature



Supplementary Cementitious Materials

(Usage effect)

How they work

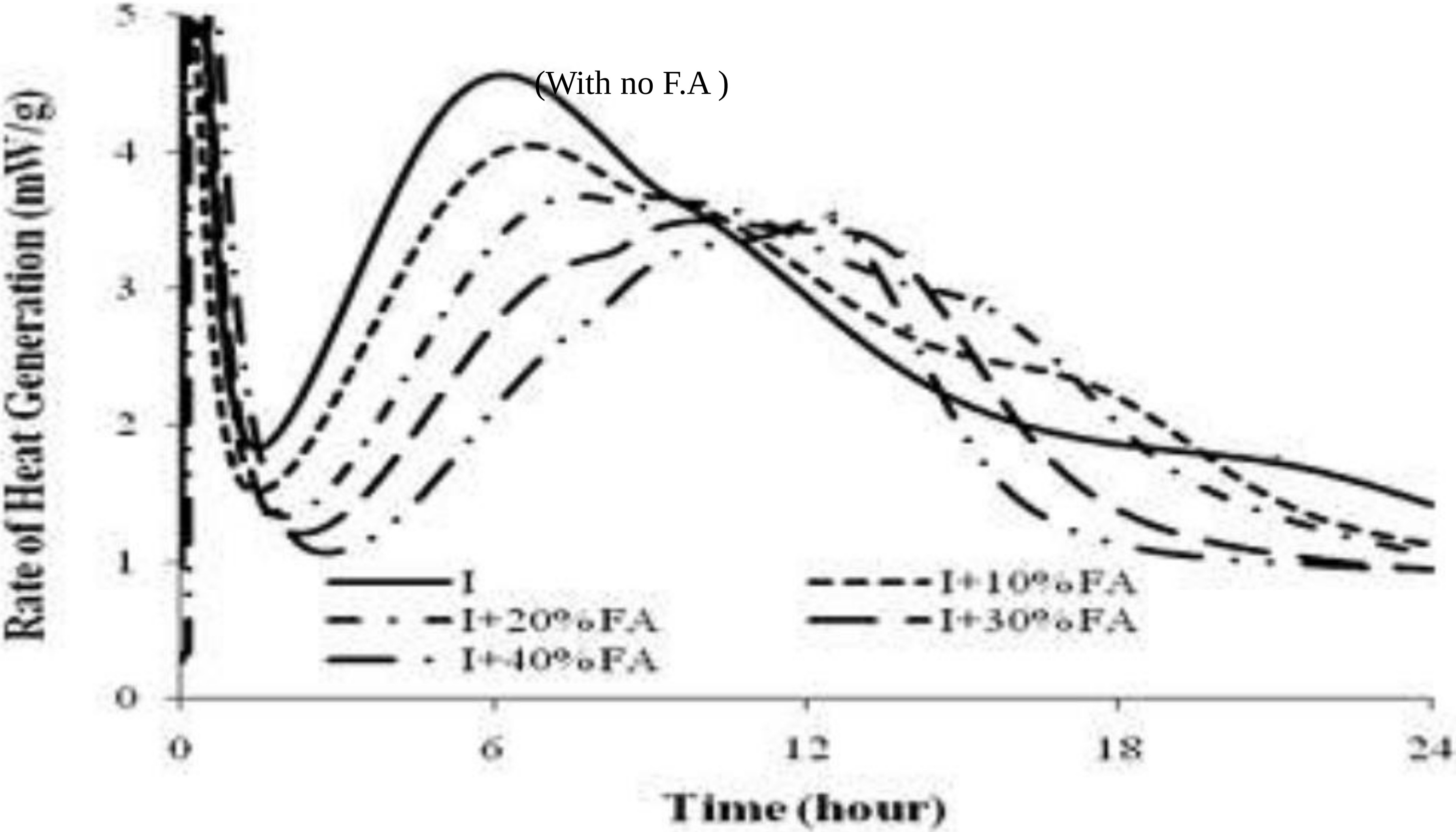
- SCMs convert CH (a somewhat less desirable product of hydration) into C-S-H (which gives concrete its strength).

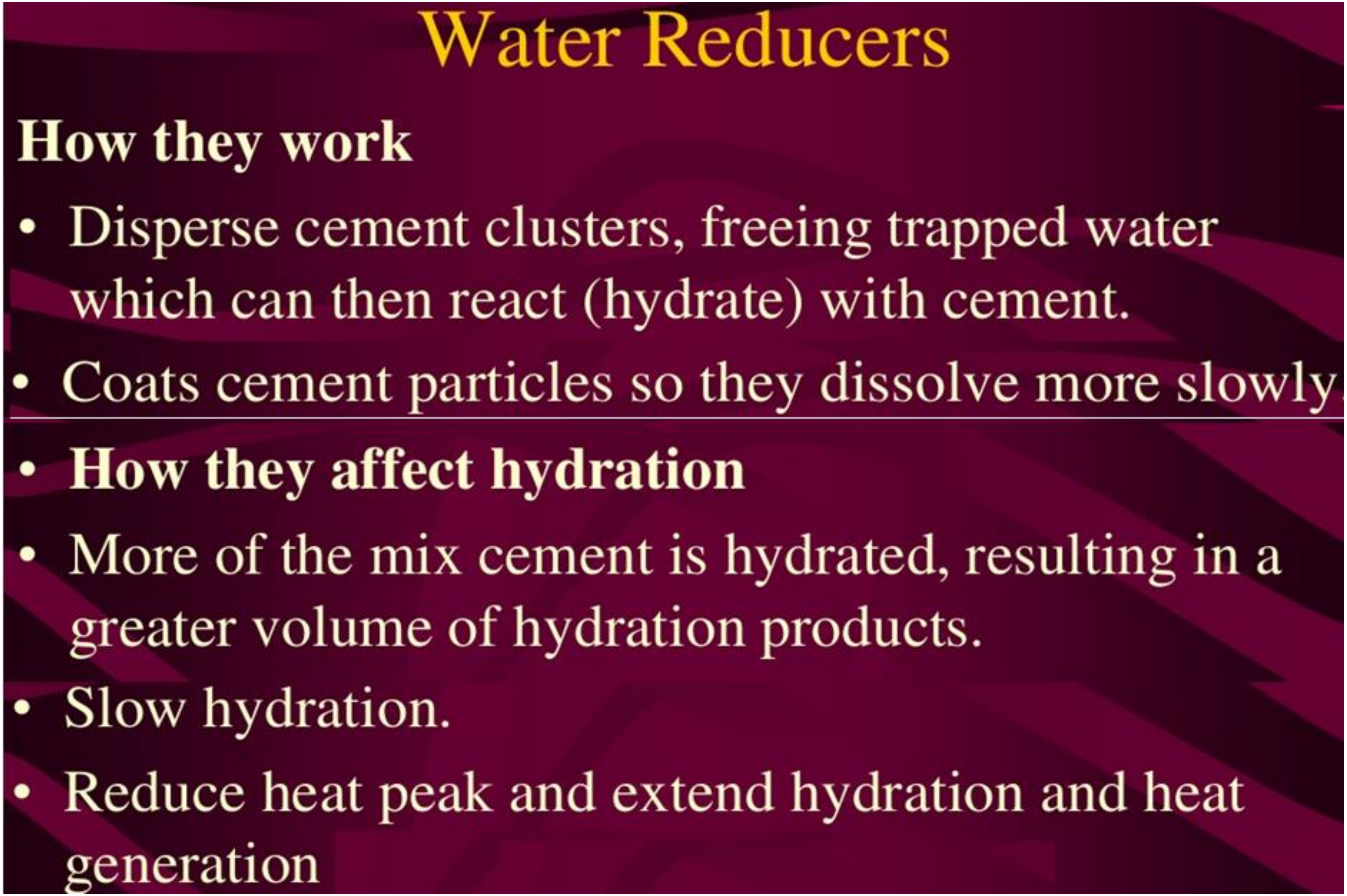
$$SiO_2/\ Al_2O_3 + Ca(OH)_2 \rightarrow \text{C-S-H gel}$$

How SCMs may affect hydration

- Often slow hydration, extending working time and delaying set, strength gain.
- Reduce heat peak.
- Extend heat generation.

Fly Ash Replacement Effect


(With no F.A)



Water Reducers

How they work

- Disperse cement clusters, freeing trapped water which can then react (hydrate) with cement.
- Coats cement particles so they dissolve more slowly

- **How they affect hydration**
- More of the mix cement is hydrated, resulting in a greater volume of hydration products.
- Slow hydration.
- Reduce heat peak and extend hydration and heat generation

Set Accelerators

How they work

- Reduce time required for super saturation of calcium ions.

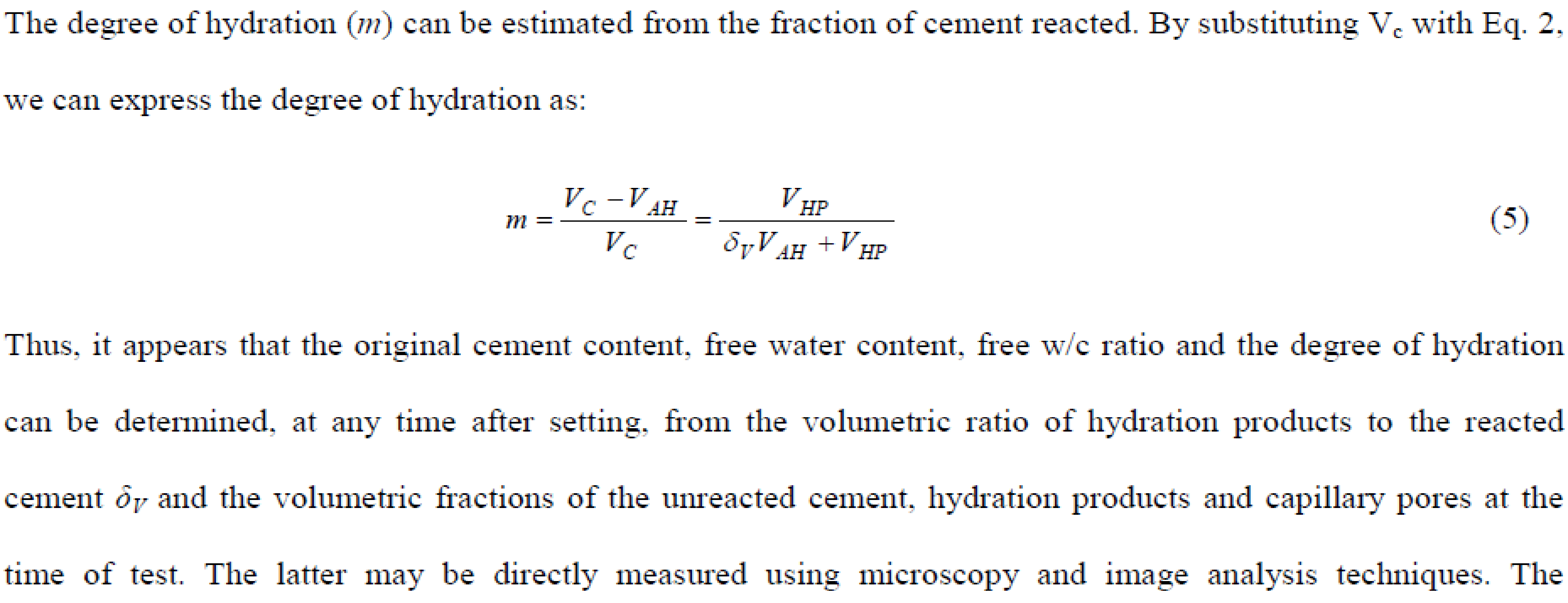
How they affect hydration

- Earlier initial and final sets.
- Increased heat generation; higher maximum peak on the hydration curve.

Degree of hydration

- The overall progress of the hydration reactions is described by the degree of hydration, which simply reflects *the fraction of the cement that has reacted*.
- Complete hydration of all the cement is referred to 1.
- The degree of hydration is expected to be directly proportional to the chemically bound water. So, it is assumed that a certain quantity of cement binds exactly the same amount of water, may it be at the beginning of the hydration process or at the end of this.
- All chemically bound water is assumed to be lost at igniting the sample to 1000° C, (no chemically bound water is assumed to be lost at heating to 105° C).
- The degree of hydration can be measured by weighing the sample after drying to 105° C and after ignition to 1000° C. The weight difference corresponds to chemically bound water

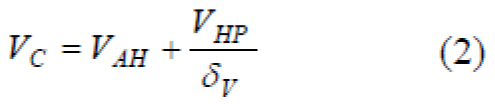
Degree of hydration



The degree of hydration (m) can be estimated from the fraction of cement reacted. By substituting V_c with Eq. 2, we can express the degree of hydration as:

$$m = \frac{V_C - V_{AH}}{V_C} = \frac{V_{HP}}{\delta_V V_{AH} + V_{HP}} \qquad (5)$$

Thus, it appears that the original cement content, free water content, free w/c ratio and the degree of hydration can be determined, at any time after setting, from the volumetric ratio of hydration products to the reacted cement δ_V and the volumetric fractions of the unreacted cement, hydration products and capillary pores at the time of test. The latter may be directly measured using microscopy and image analysis techniques. The



$$V_C = V_{AH} + \frac{V_{HP}}{\delta_V} \qquad (2)$$

Where V_C , V_{AH} , V_{HP} and V_{CP} represent the absolute volumes of the original cement, unreacted (anhydrous) cement, hydration products and capillary pores. δV *is the* volumetric ratio of hydration products to the reacted cement. It is well known that for any room temperature cement cured at any w/c ratio and age, the cement hydration products occupy approximately twice the volume of reacted cement, i.e. $\delta V \sim 2$. The actual value of δV is slightly dependent on the cement composition , however the typical values of between 2.1 and 2.2 have been reported in the literature

Degree of hydration

- Here, the original cement content, free water content, free w/c ratio and the degree of hydration can be determined, at any time after setting, from the volumetric ratio of hydration products to the reacted cement δ_V and the volumetric fractions of the unreacted cement, hydration products and capillary pores at the time of test.
- The latter may be directly measured using microscopy and image analysis techniques. The application of the method is not affected by curing age; hence it may be suitable for testing field samples.

Degree of hydration

- Another parameter that can be used to monitor the progress of hydration is the *compressive strength*. This is not a precise measure, since the strength depends on many factors other than the progress of the chemical reactions, but it is very practical since the development of strength is the primary reason for using cement and concrete in the first place. This is because the strength of cement paste depends primarily on the amount of capillary porosity, and the amount of capillary porosity decreases in proportion to the amount of hydration that has taken place.

Degree of hydration

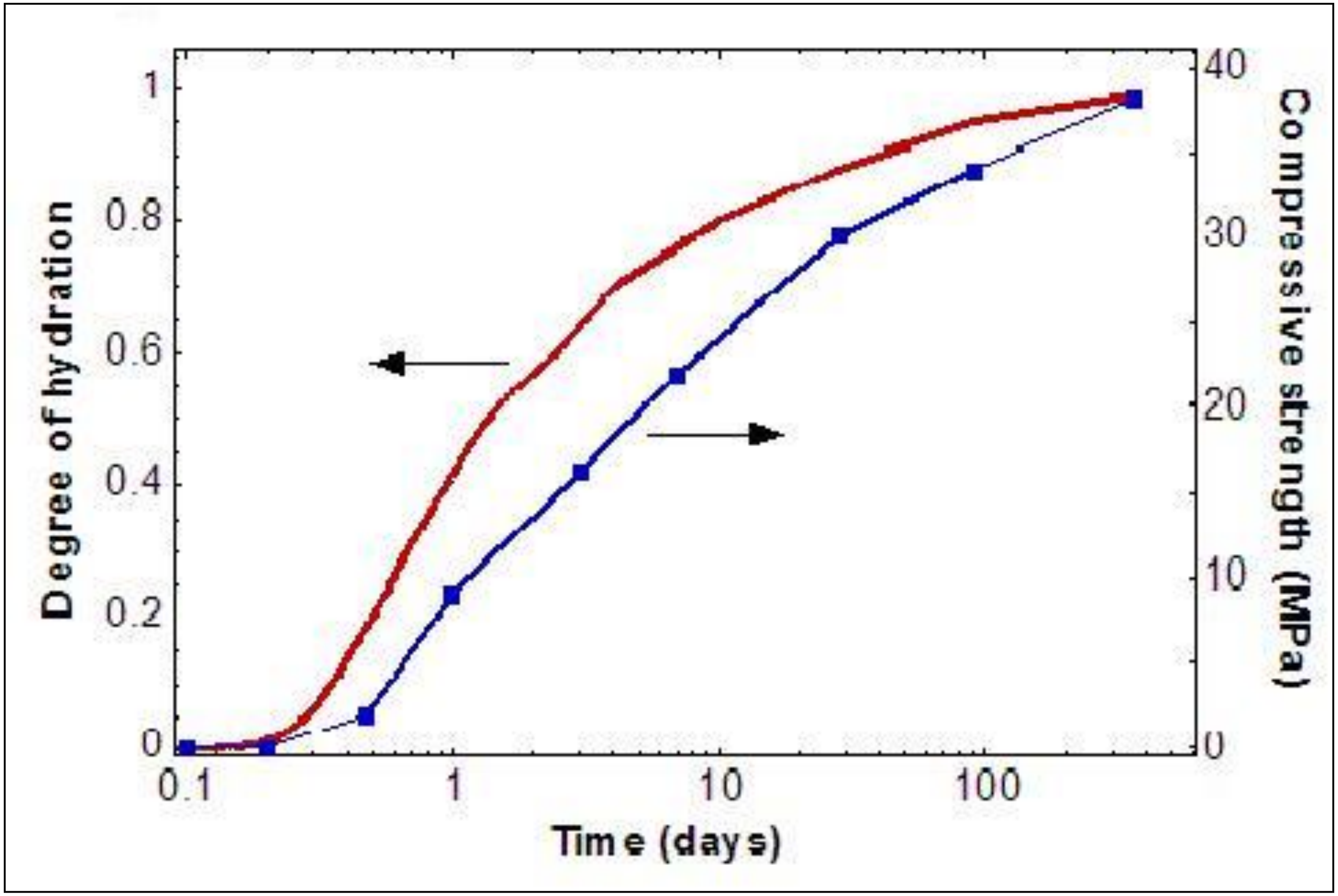


Figure: Degree of hydration and the strength track together, particularly at later times.

Degree of hydration

The final degree of hydration will depend on the w/c of the paste, the cement particle size, and the curing conditions. Hydration will continue at a slow rate during Stage 4 until one of the three following criteria is met:

1) All of the cement reacts.

This indicates that the paste has a moderate or high w/c and was cured correctly. While it is the best possible outcome from the given mix design, it does not guarantee high quality concrete as the w/c may have been too high. If the cement contains some large particles, full hydration of these particles may not occur for years. However this is generally not the case with modern cements.

Degree of hydration

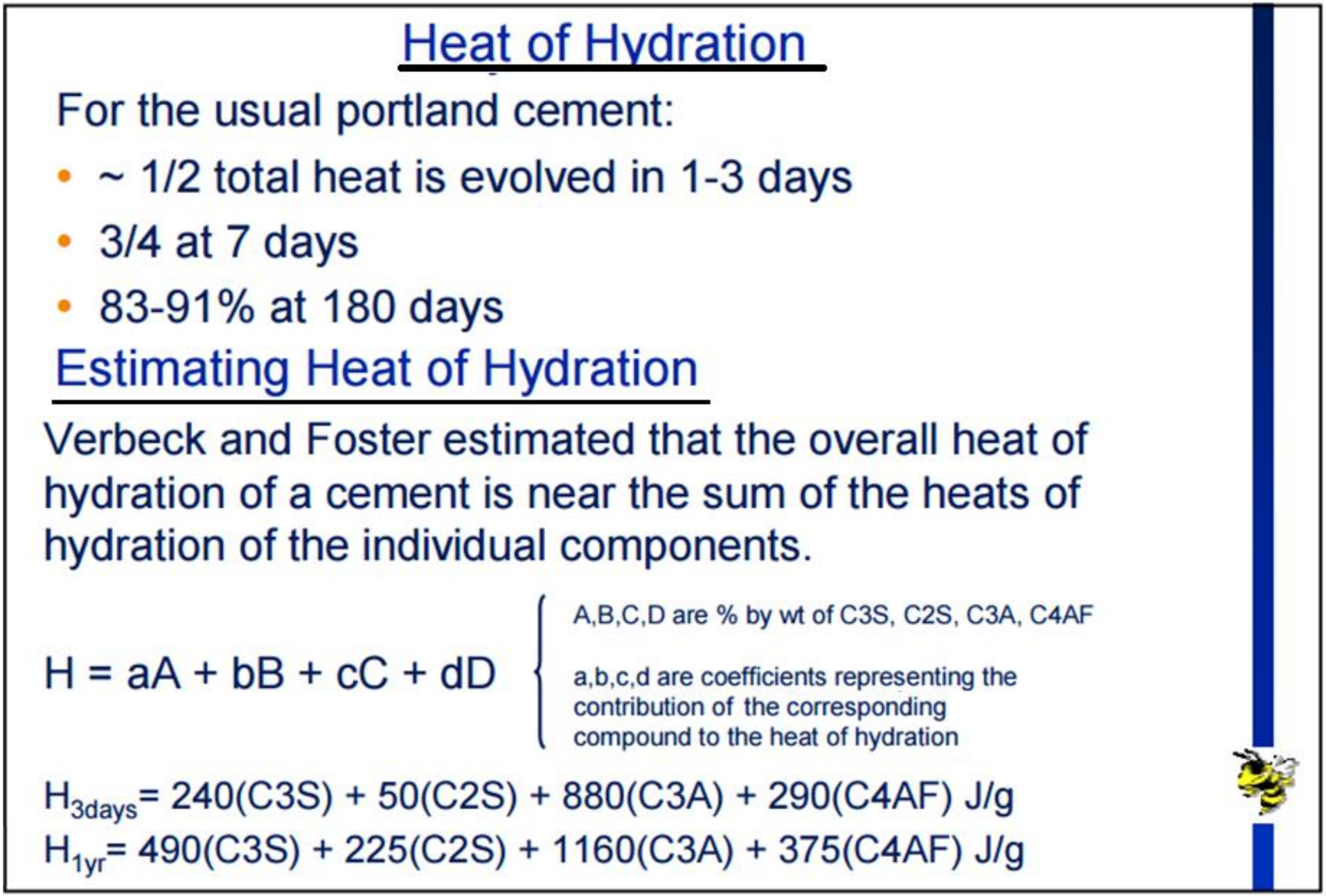
2) There is no more liquid water available for hydration.

If the cement has a w/c less than about 0.4, there will not be enough original mix water to fully hydrate the cement. If additional water is supplied by moist curing or from rainfall, hydration may be able to continue. However, it is difficult to supply additional water to the interior of large concrete sections. If the cement is improperly cured so that it dries out, hydration will terminate prematurely regardless of the w/c. This is the worst-case scenario, as the strength will be lower (perhaps significantly) than the value anticipated from the mix design.

Degree of hydration

3) There is no more space available for new reaction product to form.

When the capillary porosity is reduced to a certain minimal level, hydration will stop even if there is unreacted cement and a source of water. This is the best possible outcome, and it is only possible if the w/c is less than about 0.4. Not only cement paste or concrete will have high strength, but it will also have a low permeability and thus be a durable concrete.



Heat of Hydration

For the usual portland cement:

- ~ 1/2 total heat is evolved in 1-3 days
- 3/4 at 7 days
- 83-91% at 180 days

Estimating Heat of Hydration

Verbeck and Foster estimated that the overall heat of hydration of a cement is near the sum of the heats of hydration of the individual components.

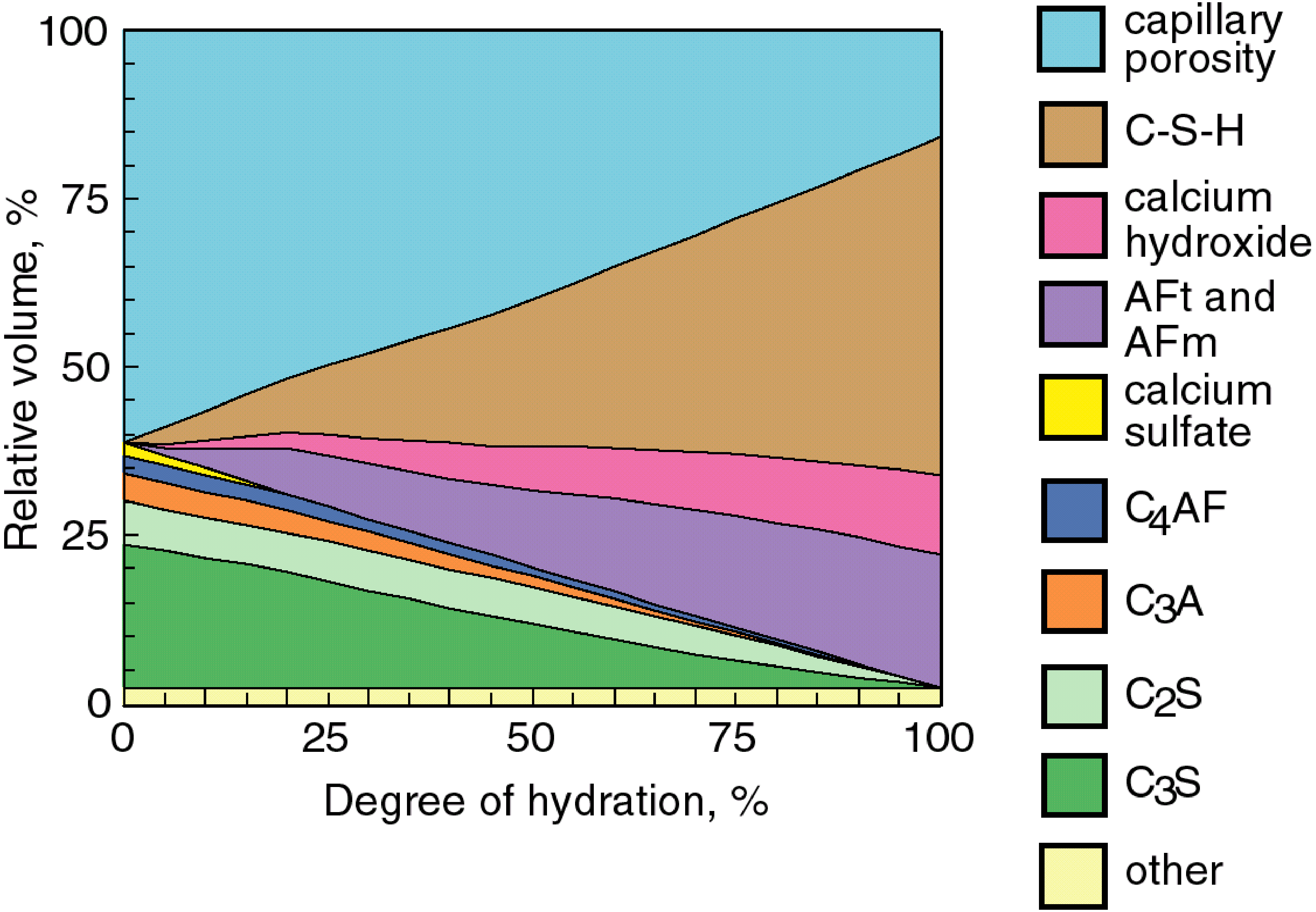
$$H = aA + bB + cC + dD$$

A,B,C,D are % by wt of C3S, C2S, C3A, C4AF

a,b,c,d are coefficients representing the contribution of the corresponding compound to the heat of hydration

$$H_{3days} = 240(C3S) + 50(C2S) + 880(C3A) + 290(C4AF)\ J/g$$
$$H_{1yr} = 490(C3S) + 225(C2S) + 1160(C3A) + 375(C4AF)\ J/g$$

Cement Hydration



Heat of Hydration

Type of cement	Name	Heat of hydration (kj/kg)
I	Normal	100%(349)
II	Moderate	80-85% (263)
III	High early strength	up to 150% (370)
IV	Low heat of hydration	40-60% (233)
V	Sulfate resistant	60-75% (310)

C-S-H Models, Importance

- Cement hydration-products phase accounts for about 70%, the Nano scale microstructure of C-S-H gel plays a decisive role on the properties of the Cement Based Materials (CBMs) especially the shrinkage and cracking.
- The C-S-H nano scale structure is an important theoretical basis of the Cement-Materials-Science which has been considered through different models based on morphology of the hydration products like Feldman-Sereda model, T.C.Powers model, Hough Sharansky model,, Powers-Brunauer model, etc.
- These models describe the adsorption and desorption of C-S-H and adsorption medium, and explain the swelling and shrinkage mechanism of CBMs.

Adsorption is a surface process; describing the accumulation of gas or liquid on a liquid or solid

Desorption is the release of one substance from another, either from the surface or through the surface -

C-S-H Models, Importance

- It is generally recognised that nanotechnology and molecular modelling have, facilitated the shift from *descriptive* to *predictive models*, saving the time and resources by extrapolating results of very lengthy experiments, e.g. by mathematically manipulating the C–S–H components to derive different structures and assemblages, that would have been difficult or impossible in practice.
- The atomic structure of C–S–H is still not fully determined and the nanostructure of the C–S–H continues to be explored and is still being debated . Taylor has published a review with the models on the nanostructure of C–S–H presented until 1993 and Scrivener and Kirkpatrick have thrown more light on a number of more recent models .
- Two main obstacles to the atomic resolution of C–S–H have been identified; (i) the fact that the hydrated phases are difficult to separate and (ii) the low diffraction of C–S–H . New experimental techniques (for example nuclear magnetic resonance and neutron scattering) have been devised and the older ones (for example electron, atomic force or field emission microscopy enhanced with X-ray energy dispersive spectroscopy) and analytical techniques (for example molecular modelling or quantum simulations) have been further developed.

C-S-H Models, Importance

- There is still controversy and dispute as to whether C–S–H is made of
- ➢ globules (a small round particle of a substance; a drop),
- ➢ platelets (a small colourless disc-shaped cell without a nucleus, found in large numbers) or disks 5 nm thick or
- ➢ a morphology derived from a foil-like growth mechanism.
- ➢ a branched structure of less than 6 nm dimensions , or
- ➢ a clay-like structure of layers 1–5 nm thick, stacking up to form compounds.

Consequently, the following questions are pertaining; is the structure of the C–S–H colloidal or continuous, amorphous and up to what scale, “very poorly crystalline” or nanocrystalline and how has it emerged?

C-S-H

- Calcium silicate hydrate
- C/S varies between 1.1-2; ~1.5 is typical
- H is even more variable
- Structure ranges from poorly crystalline to amorphous - highly variable and poorly understood
- Occupies 50-60% of the solid volume of the hydrated cement paste (hcp)
- Huge surface area (100-700 m^2/g)
- Strength due to covalent/ionic bonding (~65%) and Van der Waals bonding (~35%) within the complex structure
- Primary strength-giving phase in portland cement concrete

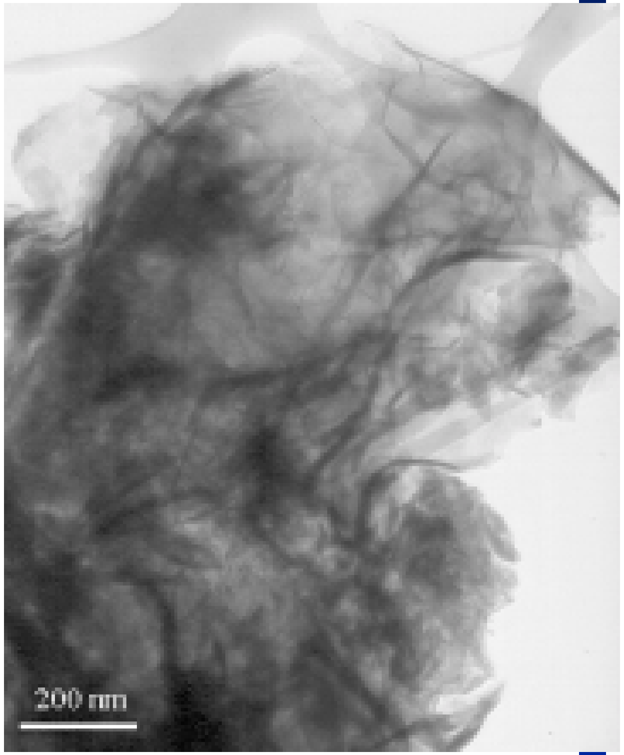
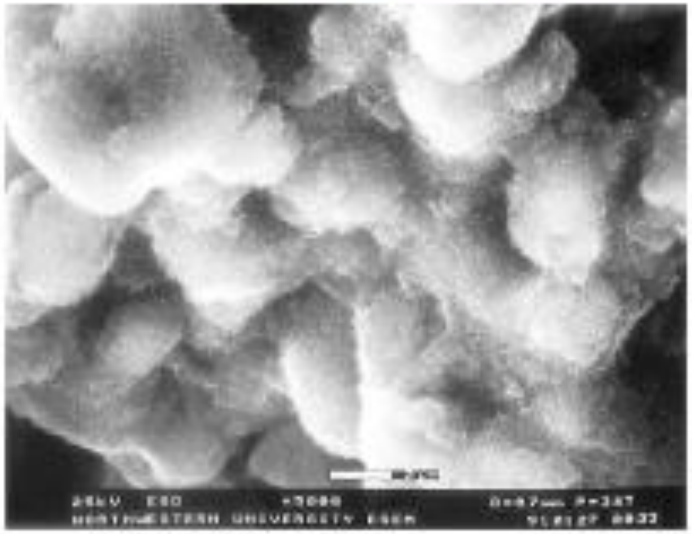


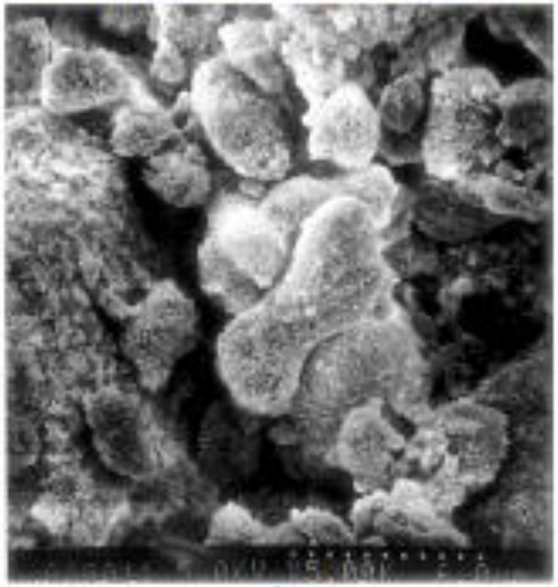
image credit: Dr. Eric Lachowski, S.Y. Hong, and F.P. Glasser via Concrete Microscopy Library at UIUC

C-S-H

The structure of C-S-H is poorly understood.



wet

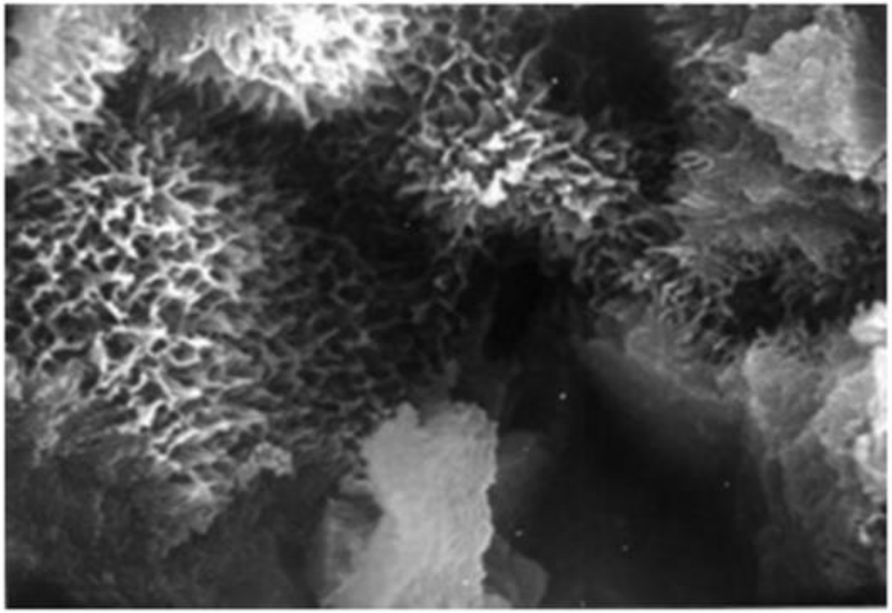


dry

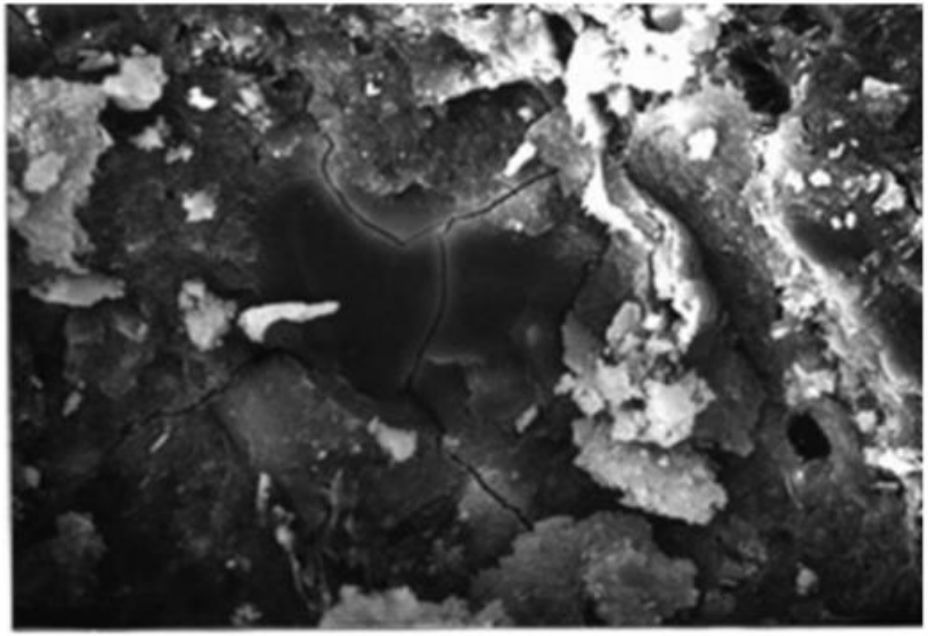
16 hr. C_3S paste

Variations in surface area, depending on technique used

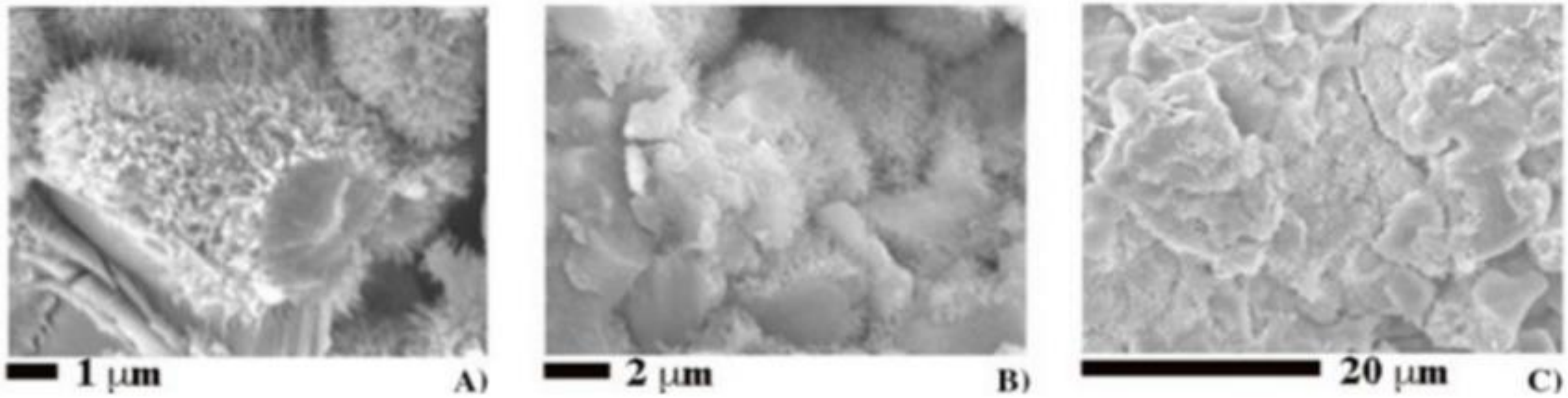
$$\begin{cases} S_{H_2O} = 200\ \mathrm{m^2/g} \\ S_{N_2} = 5\text{-}50\ \mathrm{m^2/g} \\ S_{neutrons} = 50\ \mathrm{m^2/g} \end{cases}$$



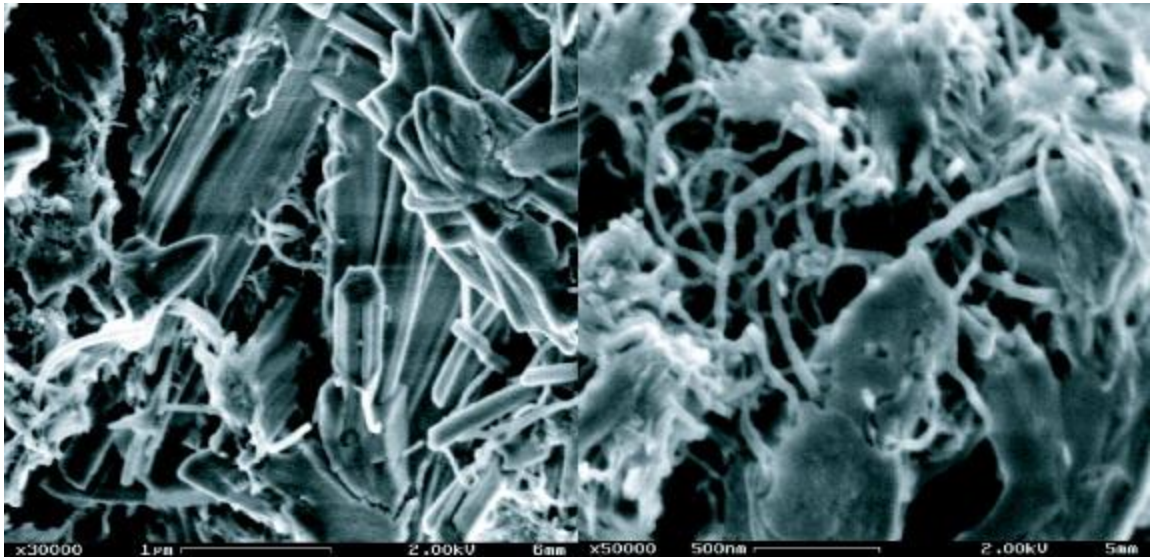
Early Porous C-S-H gel (Eternite shingle, 2100x)



Late dense C-S-H gel (Eternite shingle, 800x)

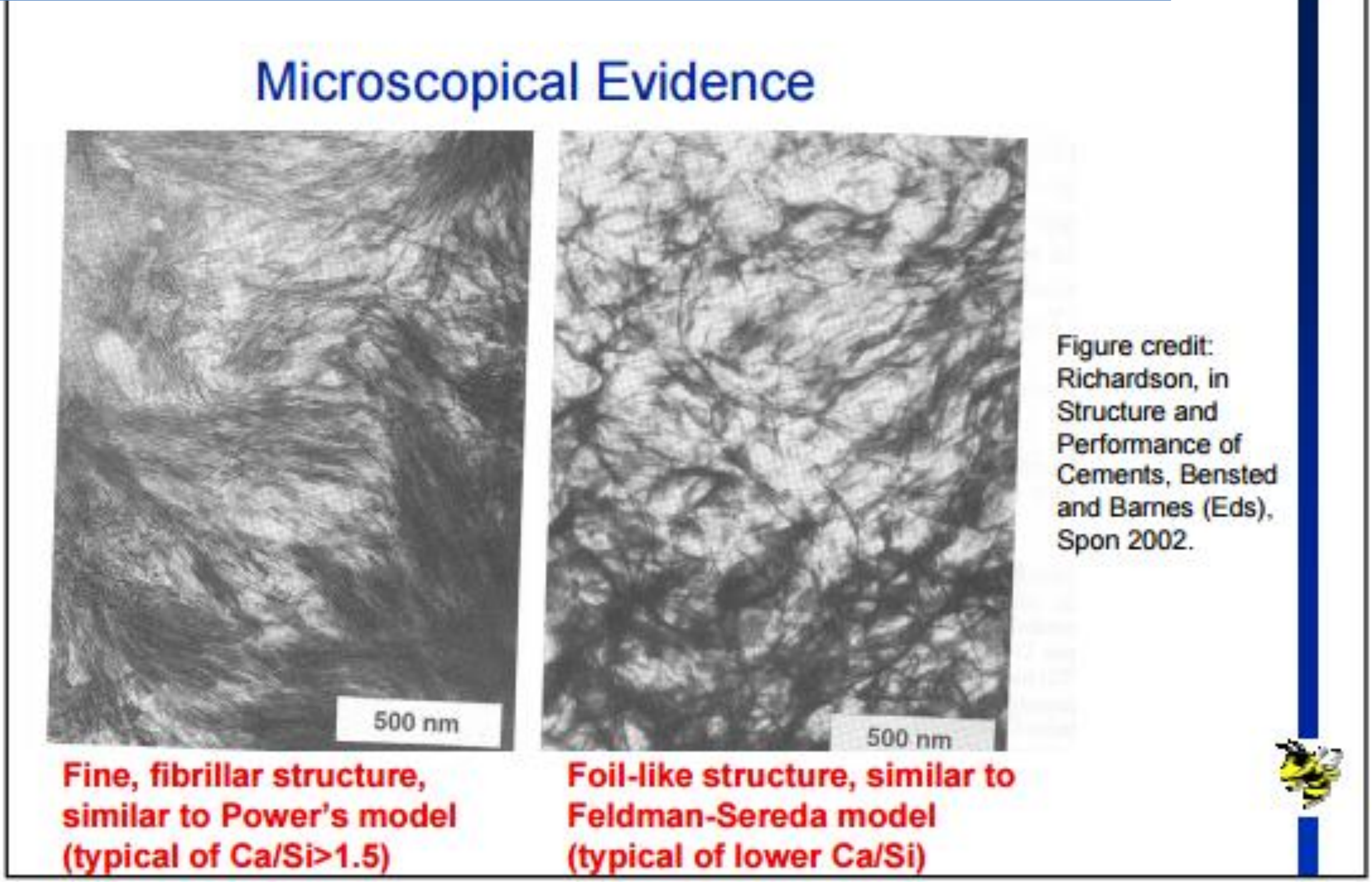


SEM micrographs of fractured C_3S pastes (w/c = 0.4) in pure water at (A) 7 days, (B) 13 days, (C) 1 month of hydration



SEM images of the hardened cement paste (curing in water for 28 days) after the mechanical test. Images revealing the connection formed after the cement hydration process.

C-S-H Models on the basis of morphology



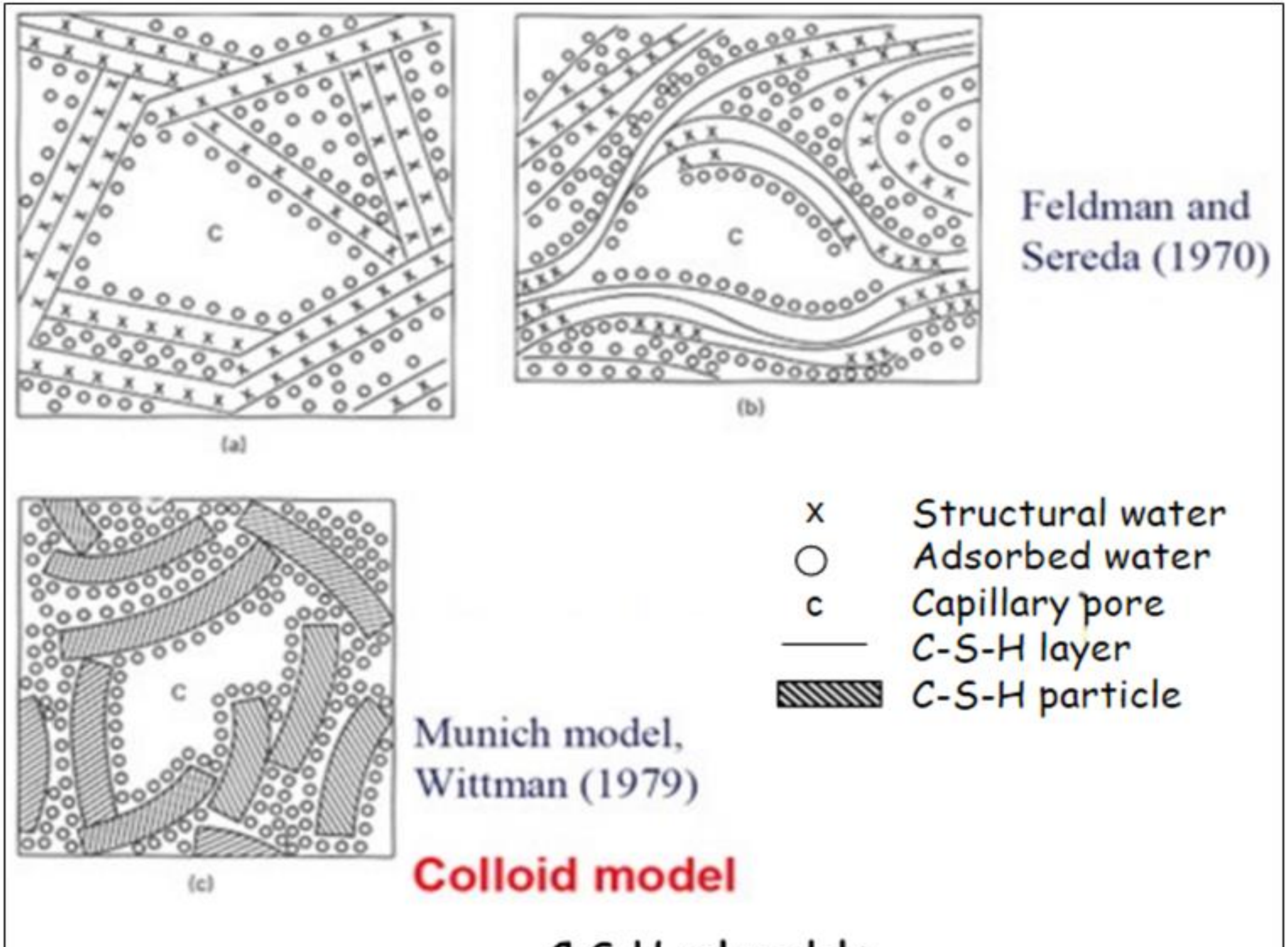
Microscopical Evidence

Fine, fibrillar structure, similar to Power's model (typical of Ca/Si>1.5)

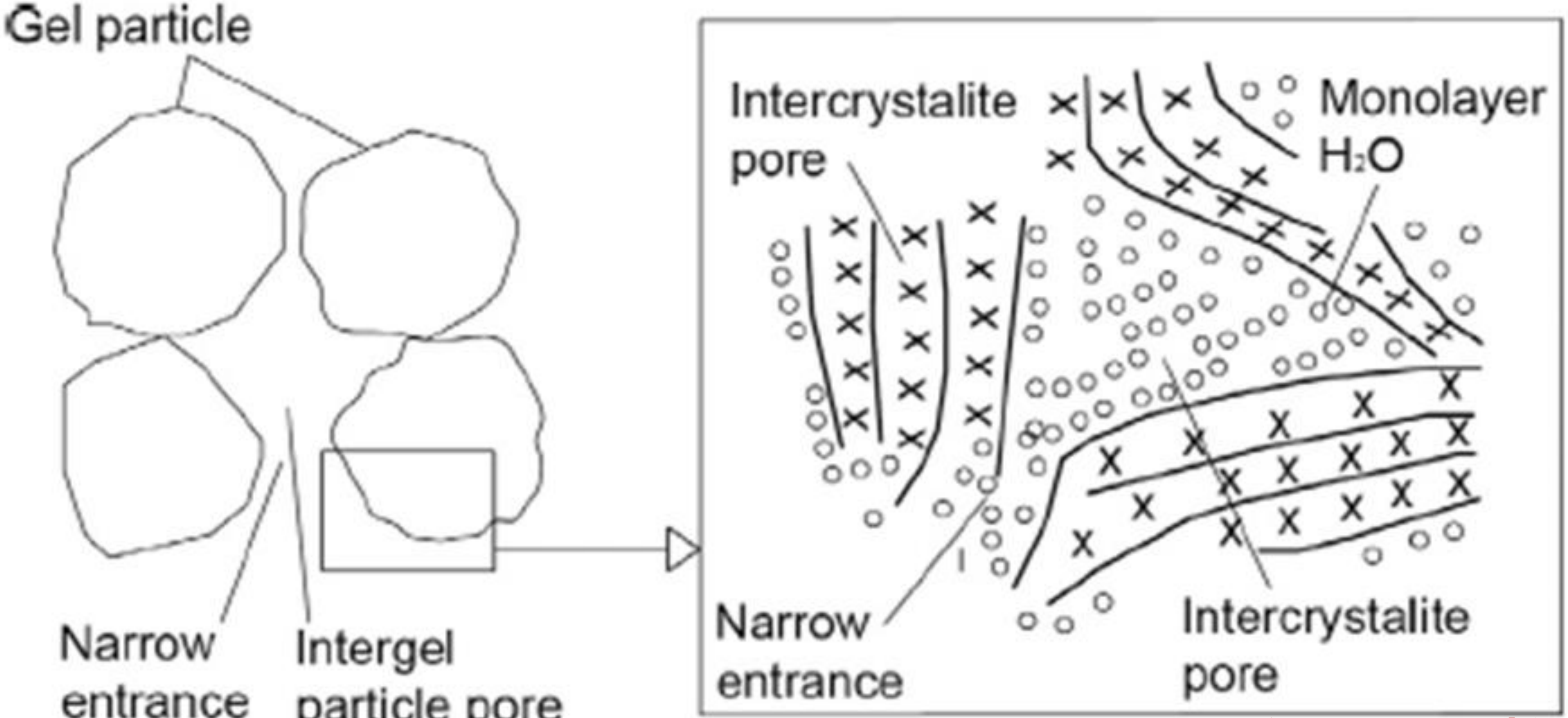
Foil-like structure, similar to Feldman-Sereda model (typical of lower Ca/Si)

Figure credit:
Richardson, in
Structure and
Performance of
Cements, Bensted
and Barnes (Eds),
Spon 2002.

C-S-H Models on the basis of morphology



C-S-H gel models



(Between crystals)

Fig. Pore model of the C–S–H gel

(Daimon M.et al., 1977)

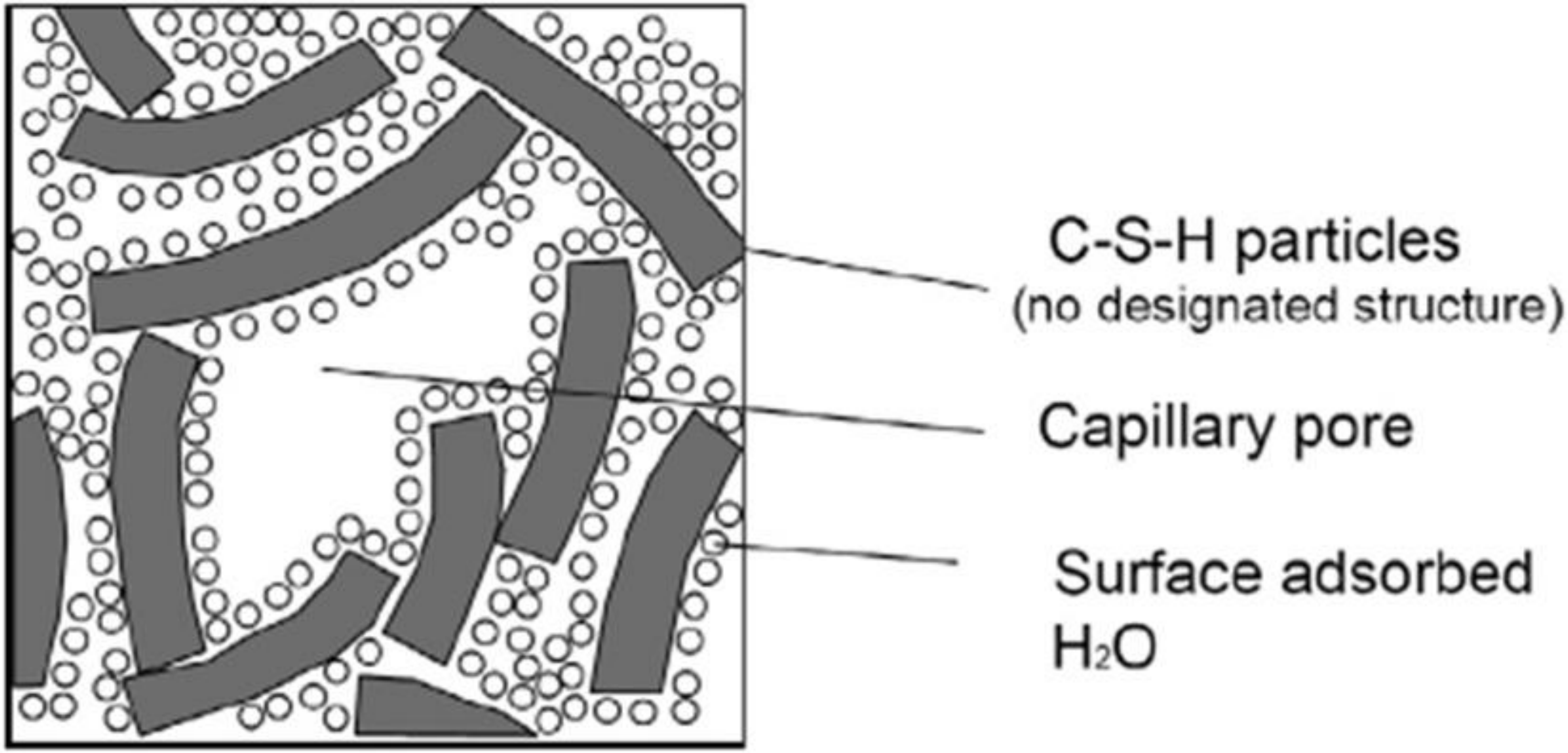
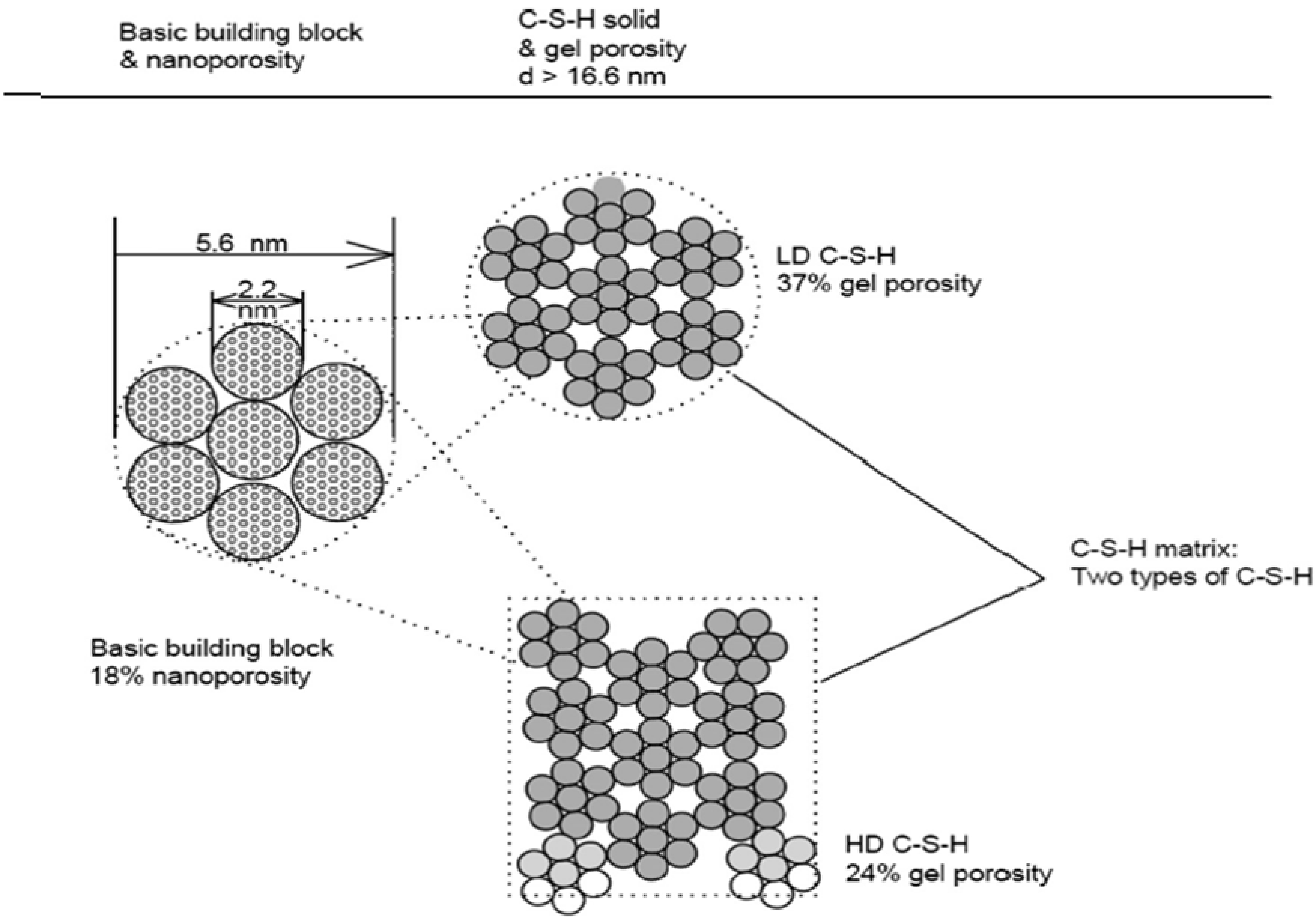


Fig. Colloidal C–S–H model: Munich model

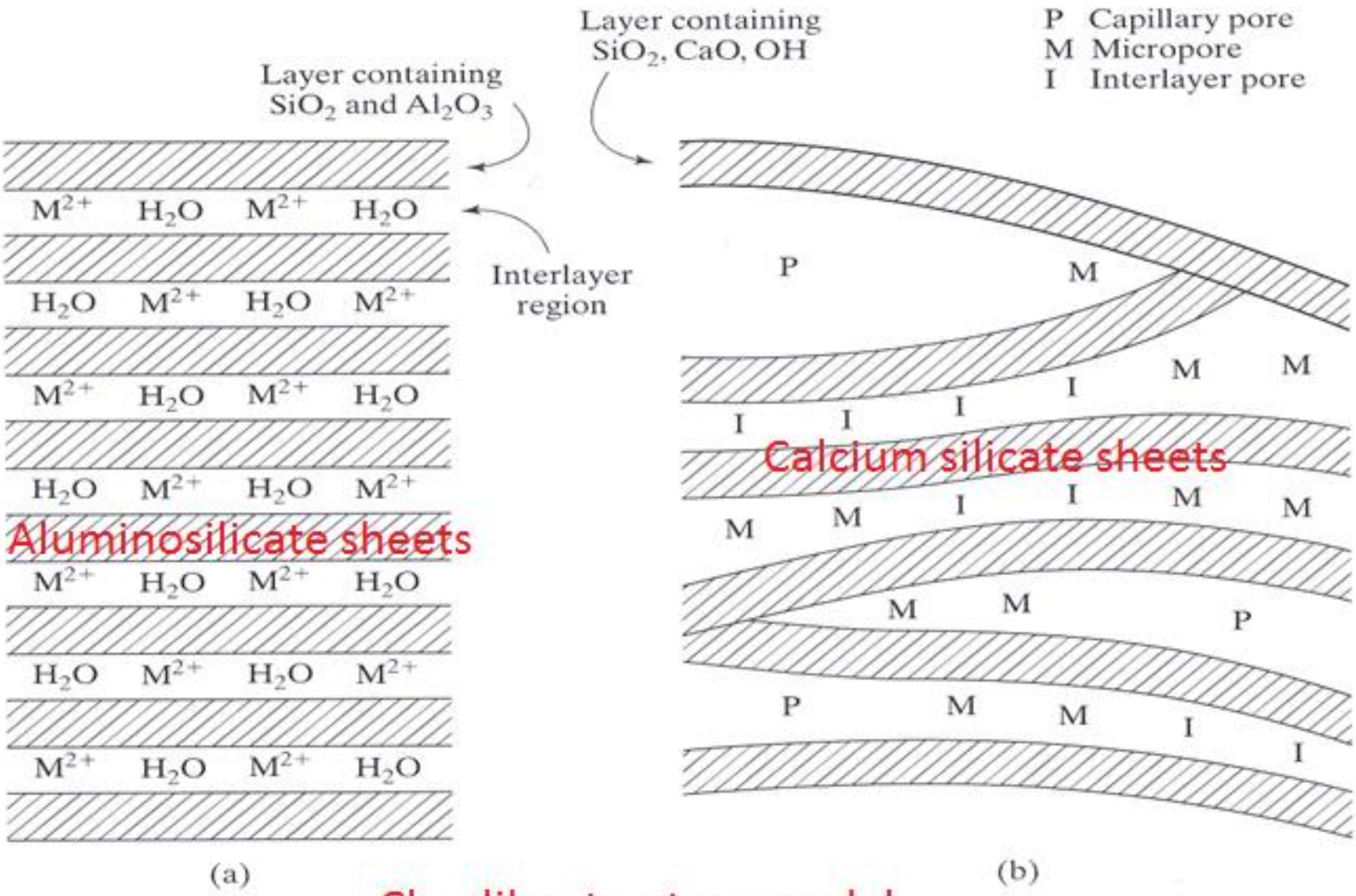
(After Wittmann, 1976)



- Colloidal structure of the C–S–H

(Jinning H.M, 2000)

C-S-H Models on the basis of morphology



Clay-like structure model

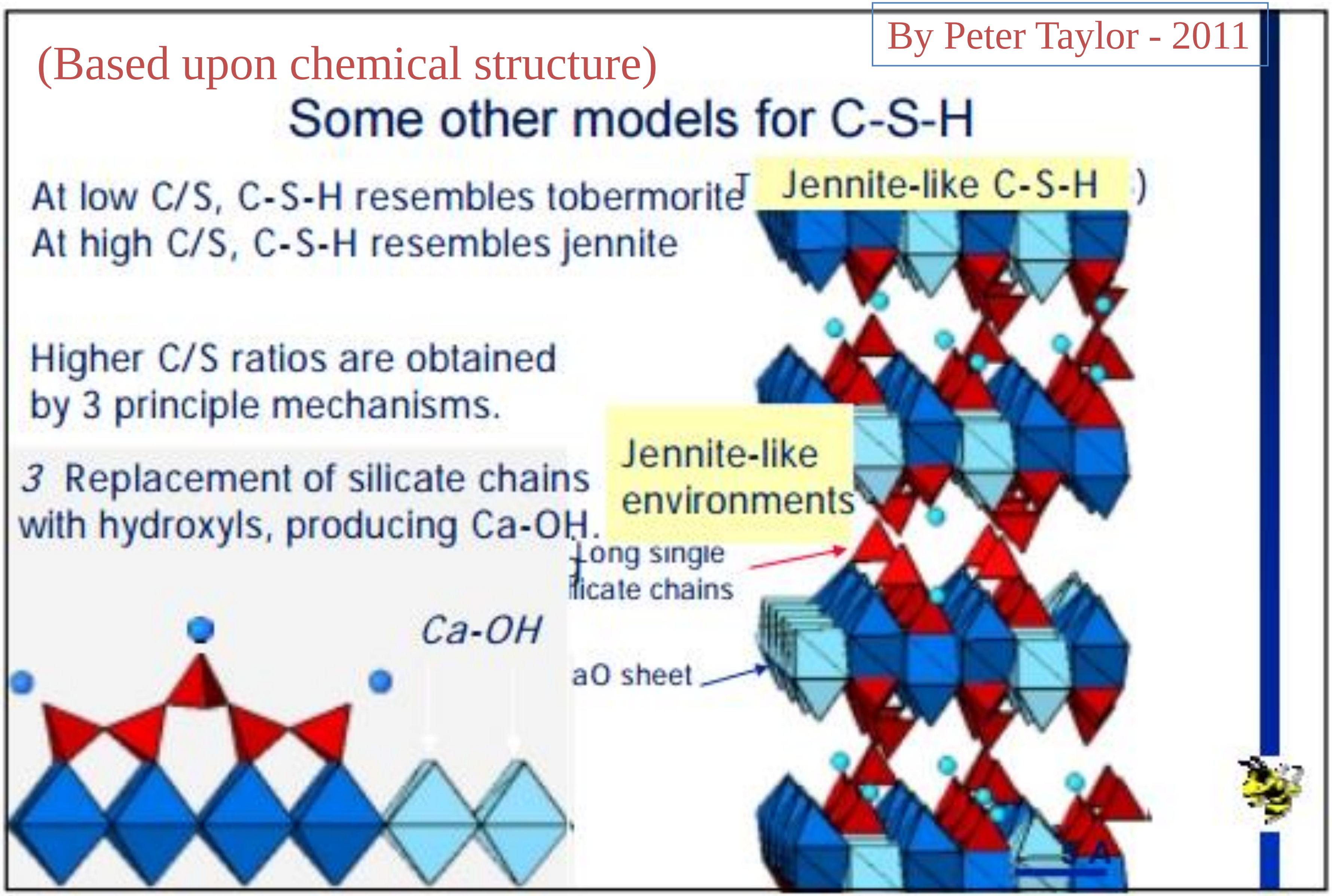
FIGURE 4.5

Schematic model of C–S–H in cement paste: (a) well-crystallized clay mineral; (b) poorly crystallized C–S–H.

(Source: Mindess, Young, and Darwin, 2004)

By Peter Taylor - 2011

(Based upon chemical structure)



Some other models for C-S-H

At low C/S, C-S-H resembles tobermorite

At high C/S, C-S-H resembles jennite

Higher C/S ratios are obtained by 3 principle mechanisms.

3 Replacement of silicate chains with hydroxyls, producing Ca-OH.

Tobermorite: A crystalline mineral having the formula 5CaO•6SiO2•5H2O.

Jennite: Crystalline structure with chain length containing several-tetrahedra.

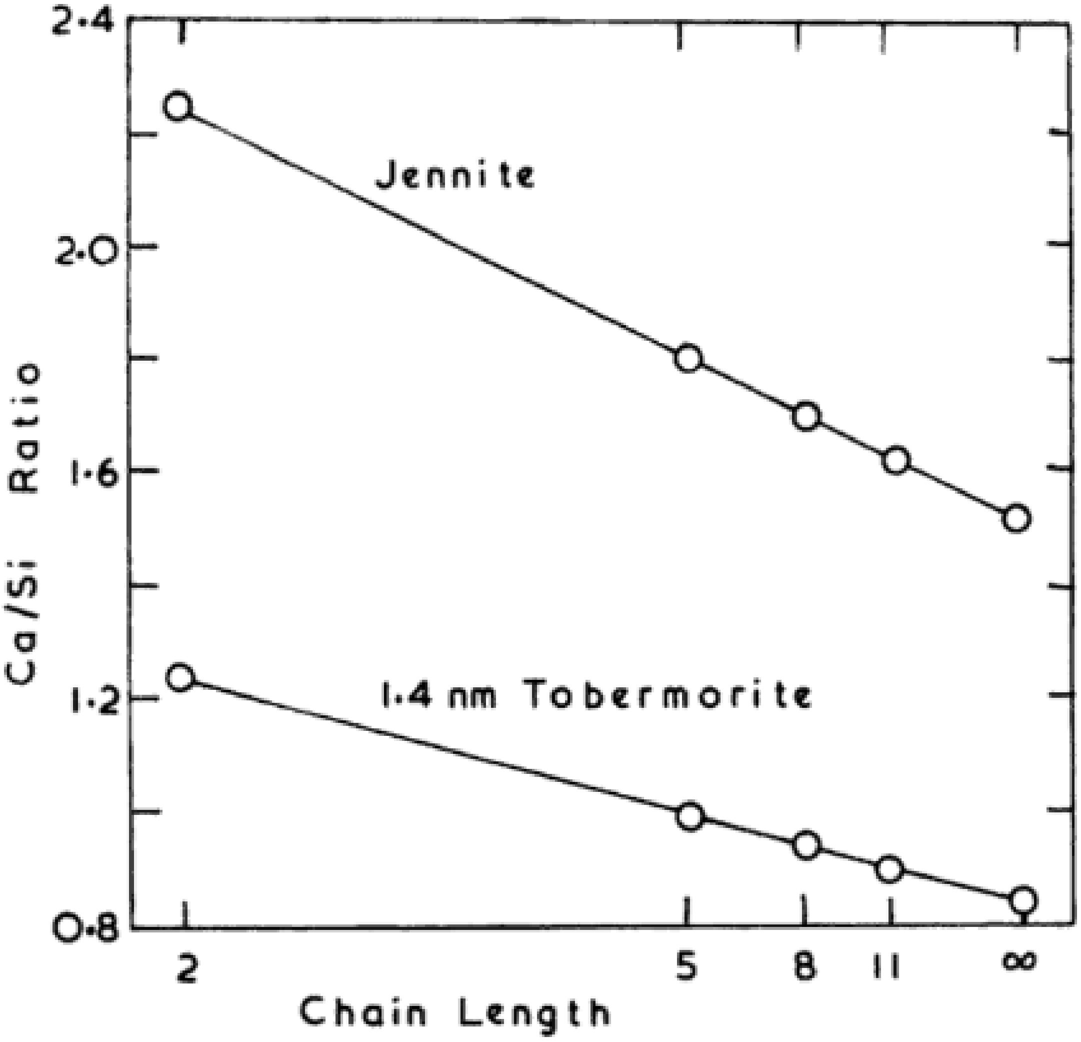
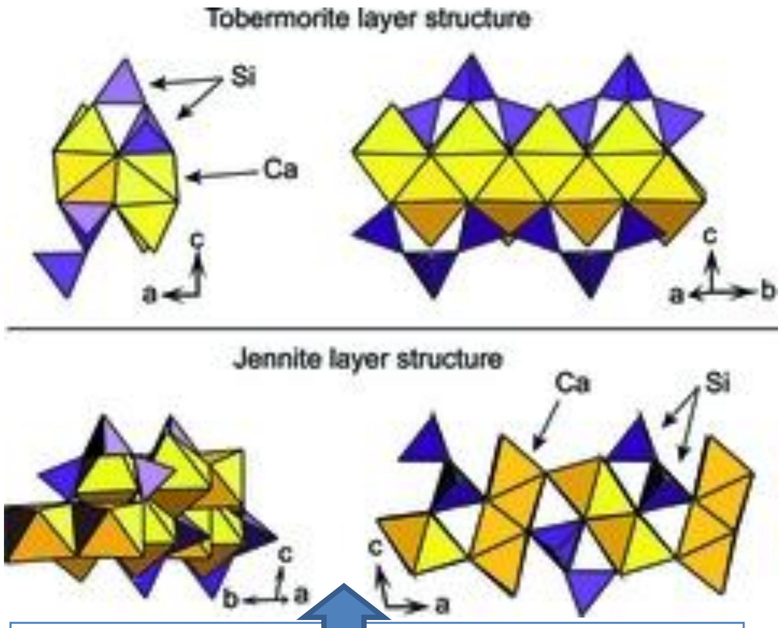


Fig. 5.9 *Calculated Ca/Si ratio plotted against a function of chain length for jennite and 1·4 nm tobermorite modified by omission of bridging tetrahedra. From T21.*



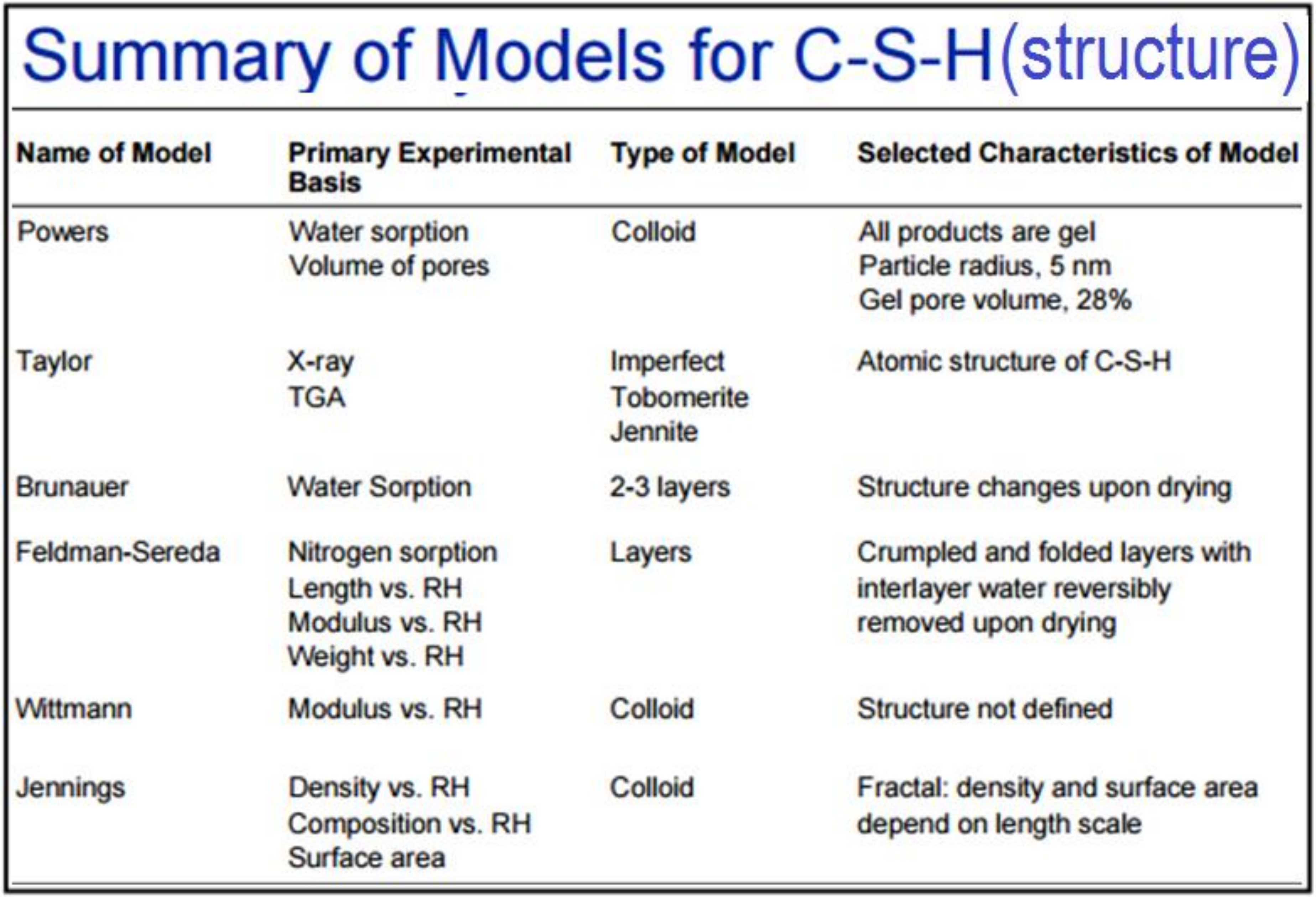
- **Sketch** of the layer structure from tobermorite (top) and jennite (bottom).
- **Two model minerals commonly used to describe C-S-H crystal chemistry**. Yellow polygons and purple tetrahedra respectively symbolize calcium and silicon coordination spheres.

Table 1

Key descriptive experiment based models on the structure of C–S–H.

Researchers	Year	Model	Main characteristics of model	Type of model	Experimental basis
Powers and Brownyard [18]	1946–7	P–B	Porosity capillary/nonevaporable water, gel/absorbed/evaporable water & total retained water (nonevaporable + gel)	Colloidal	Various drying methods, pycnometer, chemical shrinkage & Freeze/thaw, Water sorption
Bernal et al. [19]	1952		First dreierkette based model-evidences of similarity to 1.1 nm tobermorite	Dreierkette	Crystallographic tests
Brunauer et al. [20]	1967		Tobermorite and jennite Structure changes with drying	Layers	Water sorption & porosimetry
Feldman and Sereda [21–25]	1966–1972, 1980	F–S	Tangled layers with pores and interlayer water between them. Interlayer water can be reversibly removed with drying	Layers	N_2, helium, methanol & lime solution, length change isotherms & modulus/weight measurements against relative humidity
Wittmann [26]	1976	Munich	Creep and drying shrinkage not addressed	Colloidal	Modulus & relative humidity
Daimon et al. [27]	1977		Pores were divided in two categories: a "wider intergel-particle pore" and a "smaller pore within the gel particle"	Layers	N_2& water isotherms, pore structure investigation
Taylor [28]	1986		Atomic structure following $3n - 1$ rule	Imperfect/defect tobermorite and jennite	XRD & TGA
Allen et al. [29]	1987		5 nm globules conglomerating in structures of 40 nm length	Colloidal conglomerate & fractal structure	SANS
Viehland & Xu [30,31]	1996		Mesostructure amorphous with nanocrystalline regions (<5 nm) of high homogeneity	Nanocrystals	TEM
Cong and Kirkpatrick [32–34]	1996–1997		Confirmed that the presence of CaOH and Si–OH in the C–S–H is affected by the *C/S* ratio	1.4 nm Defect tobermorite	MAS & Magic angle NMR
Jennings [35]	2000	CM-I	CM-I (Colloidal Model I): Basic units form globules, which pack to into two different arrangements: LD & HD. Size, density and packing efficiency are determined	Colloidal & possibly fractal	SANS, SAXS & NMR

Tennis and Jennings [10]	2000	On CM-I	Density, the nitrogen accessible gel porosity, and associated surface area of C–S–H are quantified	Colloidal	N_2 sorption
Chen et al. [36]	2004		Methods of increasing the *C*/*S* ratio 1.4 nm Defect tobermorite, jennite or a combination of both	Defect tobermorite/jennite	Magic angle NMR & solubility studies
Bonaccorsi et al. [37]	2004		Resolution of the crystal structure of jennite	Jennite	XRD
Plassard et al. [11]	2004		Structural properties: $Ca(OH)_2$ concentration and evolution of the C–S–H elastic modulus-crystal nanoparticles 60x30x5 nm	Defect tobermorite nanocrystals	AFM (nanoindentation)
Nonat [11,38]	2004		Three different C–S–H phases according to Ca/S ratio lamellae $60 \times 30\ nm^2$ and 5 nm thick	Tobermorite but not necessarily defect – nanocrystalline	NMR, XRD & AFM
Jennings [39]	2004	On CM-I	Rearrangement of the globules under stress or drying and aging with creep and shrinkage	Colloidal	N_2 sorption, DMT
Constantinides and Ulm [40]	2004	On CM-I	Elastic property, packing density and hardness of LD and HD	Colloidal	AFM (nanoindentation)
Bonaccorsi et al. [41]	2005		Resolution of the crystal structure of Tobermorite 14 Å (Plombierite)	Tobermorite	NMR, IR & XRD
Thomas and Jennings [9]	2006	On CM-I	Validation of CM-I linking chemical aging with creep, drying shrinkage and permeability	Colloidal	N_2 sorption, DMT & *silicon* i-NMR
Jennings et al. [7]	2007	On CM-I	Nanoporosity investigation: Change in the CM-I: basic unit: globule diameter >5 nm	Colloidal & Fractal	AFM (nanoindentation), SANS
Allen et al. [8]	2007		Formula determination: $(CaO)1.7(SiO_2)(H_2O)$ 1.80 and density 2.604 Mg m^{-3}		SANS & SAXS
Plassard et al. [42]	2007		Elastic properties of C–S–H: the elastic modulus of C–S–H drastically increases with the Ca/Si ratio	Constantinides and Ulm [40] model	AFM (nanoindentation) & XRD
Jennings [6]	2008	CM-II	CM-II (Colloidal Model II): Investigation of LD C–S–H – globule packing s and characteristics of water within the small pores amongst globules	Granular: Combination of F-S model, with colloidal model	Water sorption



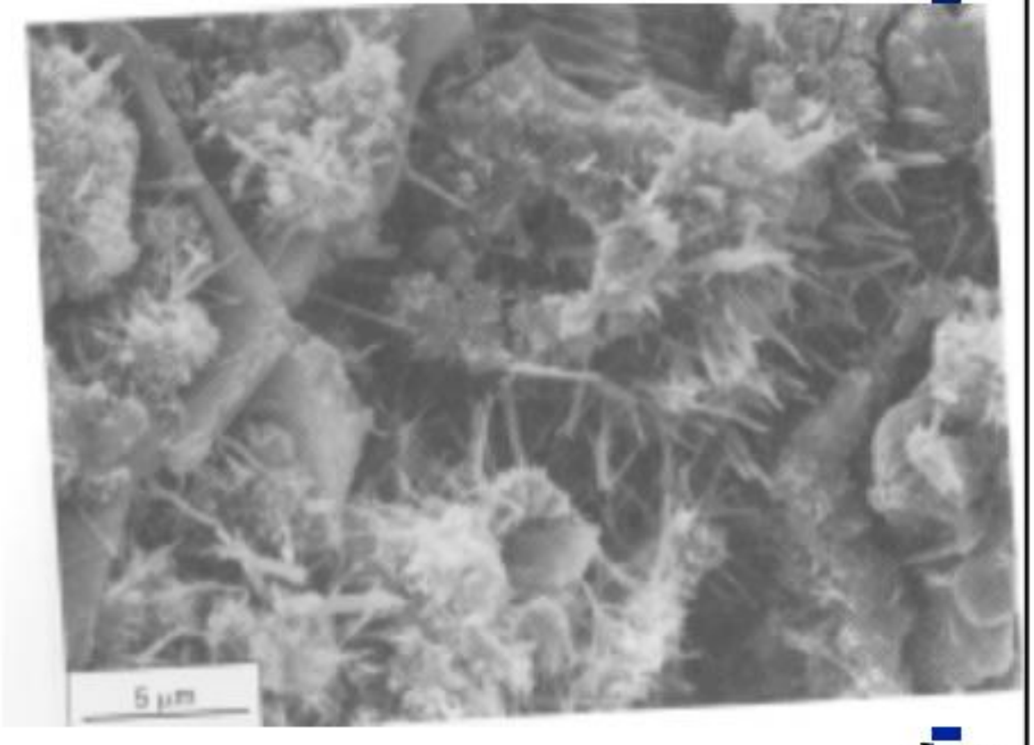
Summary of Models for C-S-H (structure)

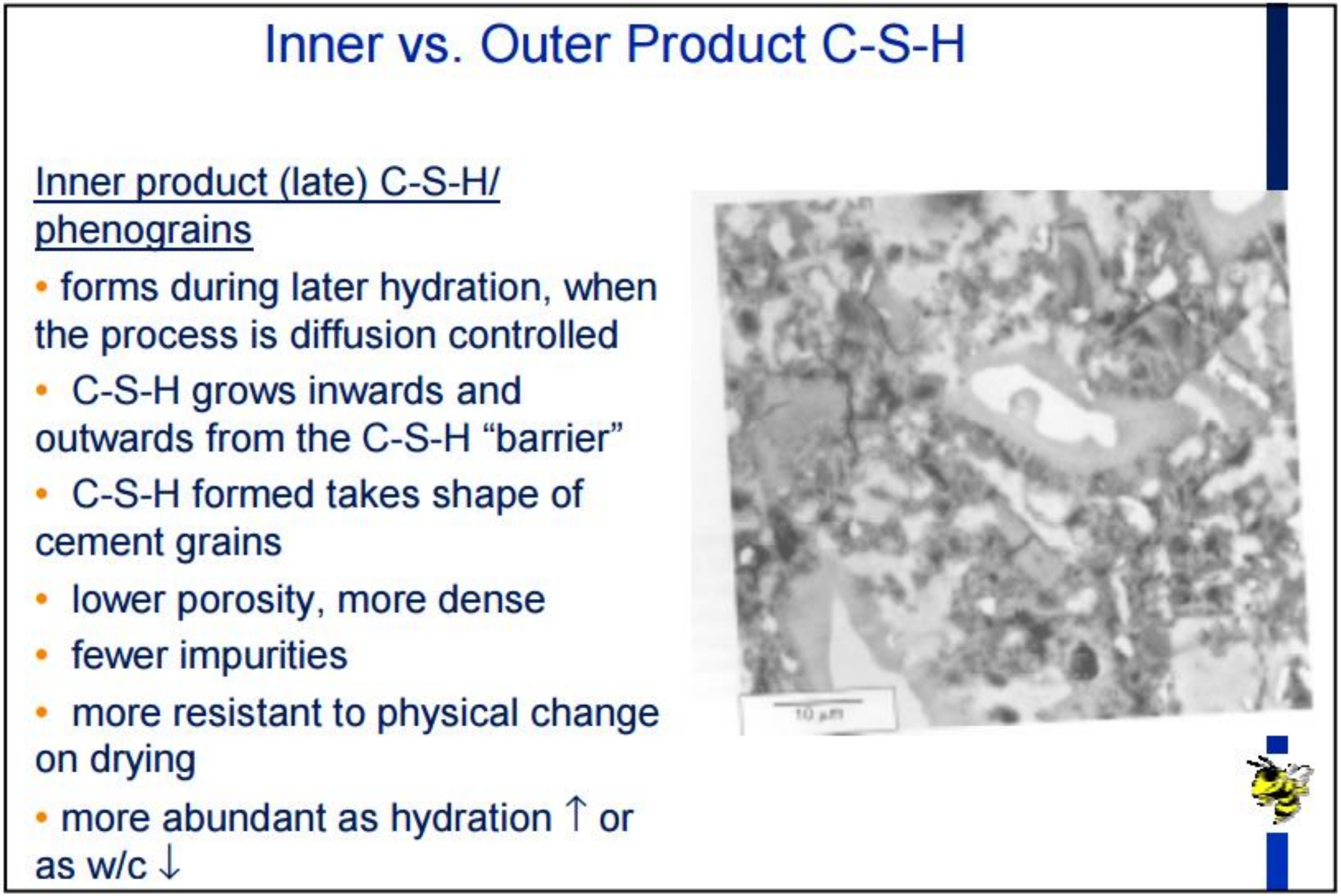
Name of Model	Primary Experimental Basis	Type of Model	Selected Characteristics of Model
Powers	Water sorption Volume of pores	Colloid	All products are gel Particle radius, 5 nm Gel pore volume, 28%
Taylor	X-ray TGA	Imperfect Tobomerite Jennite	Atomic structure of C-S-H
Brunauer	Water Sorption	2-3 layers	Structure changes upon drying
Feldman-Sereda	Nitrogen sorption Length vs. RH Modulus vs. RH Weight vs. RH	Layers	Crumpled and folded layers with interlayer water reversibly removed upon drying
Wittmann	Modulus vs. RH	Colloid	Structure not defined
Jennings	Density vs. RH Composition vs. RH Surface area	Colloid	Fractal: density and surface area depend on length scale

Inner vs. Outer Product C-S-H

<u>Outer product (early) C-S-H/ groundmass</u>

- forms during early hydration
- C-S-H forms away from the cement particle surface, filling water-filled space
- higher porosity
- contains high levels of impurities
- probably admixed with nano-scale $C_4A\check{S}H_{12}$





Inner vs. Outer Product C-S-H

Inner product (late) C-S-H/ phenograins

- forms during later hydration, when the process is diffusion controlled
- C-S-H grows inwards and outwards from the C-S-H “barrier”
- C-S-H formed takes shape of cement grains
- lower porosity, more dense
- fewer impurities
- more resistant to physical change on drying
- more abundant as hydration ↑ or as w/c ↓

Water Requirement for Hydration

- It has been estimated that for C_3S and C_2S compounds, on an average 23 % of water by weight of cement is required for chemical reaction. Thus 23 % of water chemically combines with cement and, therefore it is called bound water. A Certain Quantity of water is inadequate to fill up the gel pores, the formation of gel itself will stop and gel pores will not form. Gel water of about 15 % by weight of cement is required. Therefore, a total 23 + 15= 38 % of water by weight of cement is required for complete hydration. If less than 38 % of water is used then complete hydration is not possible as the volume available is insufficient to accommodate all the product of hydration. Hence, Strength of Concrete will be reduced.
- If more than 38 % of water is used, then the excess of water will cause undesirable capillary cavities and concrete becomes porous.

Water requirement for cement hydration:

- Generally the water cement ratio's necessary for hydration of cement range is from 0.19 to 0.26 which is the additional water added to cement, sand and rock, beyond that needed for hydration of the cement is water added for convenience.
- This means we need a certain amount of extra water in the mix to get the workability needed for placement and finishing. This extra water in the mix that is not used in hydration remains throughout the cement paste to evaporate at some later time.
- Higher water-Cement ratios cause the cement paste to become more porous. The more porous the cement paste, the weaker and less durable the concrete will be.

Nature of Water in HCP

(Hydrated Cement Paste)

- Chemically combined water
  - non-evaporable water
  - water in CSH Layers
- Water in pores
  - Capillary pores
  - gel pores
  - adsorbed water interspace of the CSH particles

Powers' Model (Cement Gel Structure)

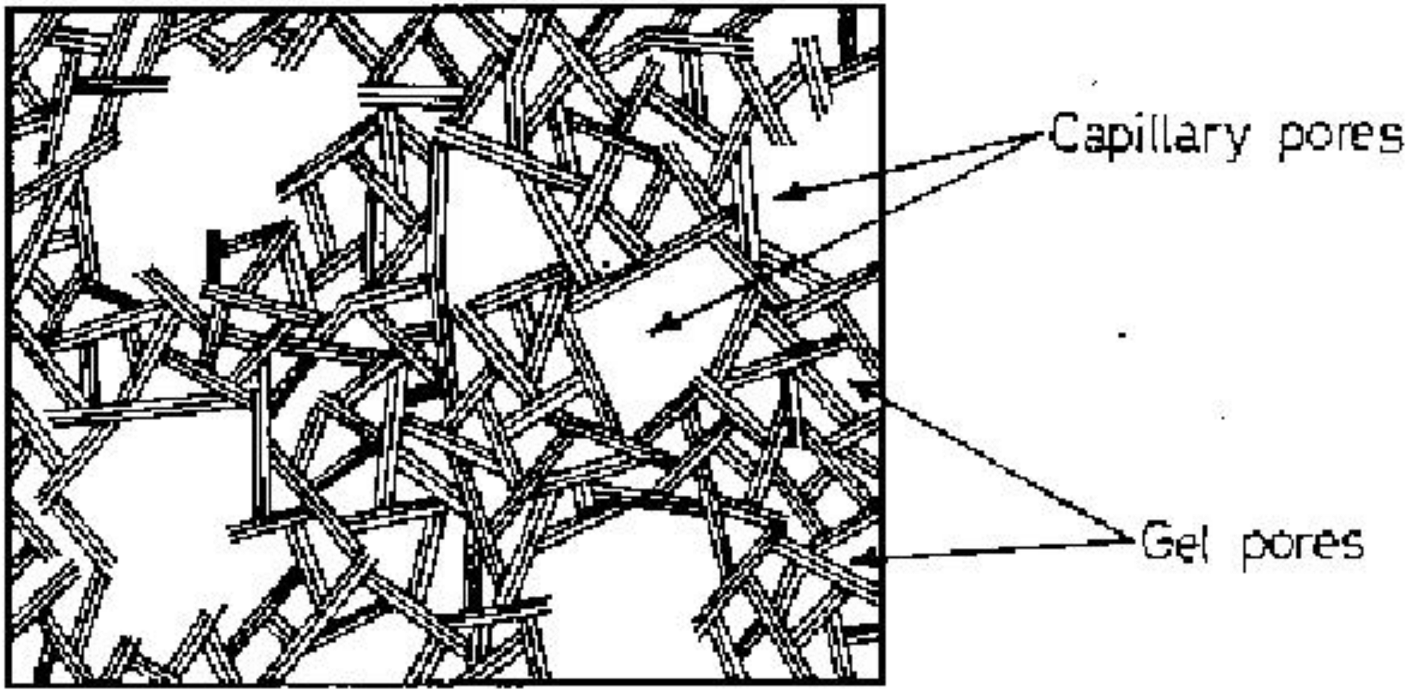


Figure 3.3 *Schematic description of the structure of the cement gel (after Powers*[5]*)*

Voids in Hydrated Cement paste

a) Interlayer hydration space
  - *space between atomic layers*
  - *shrinkage if humidity <11%*

b) Capillary voids
  - *w/c ratio too high*
  - *decrease strength and increase permeability*

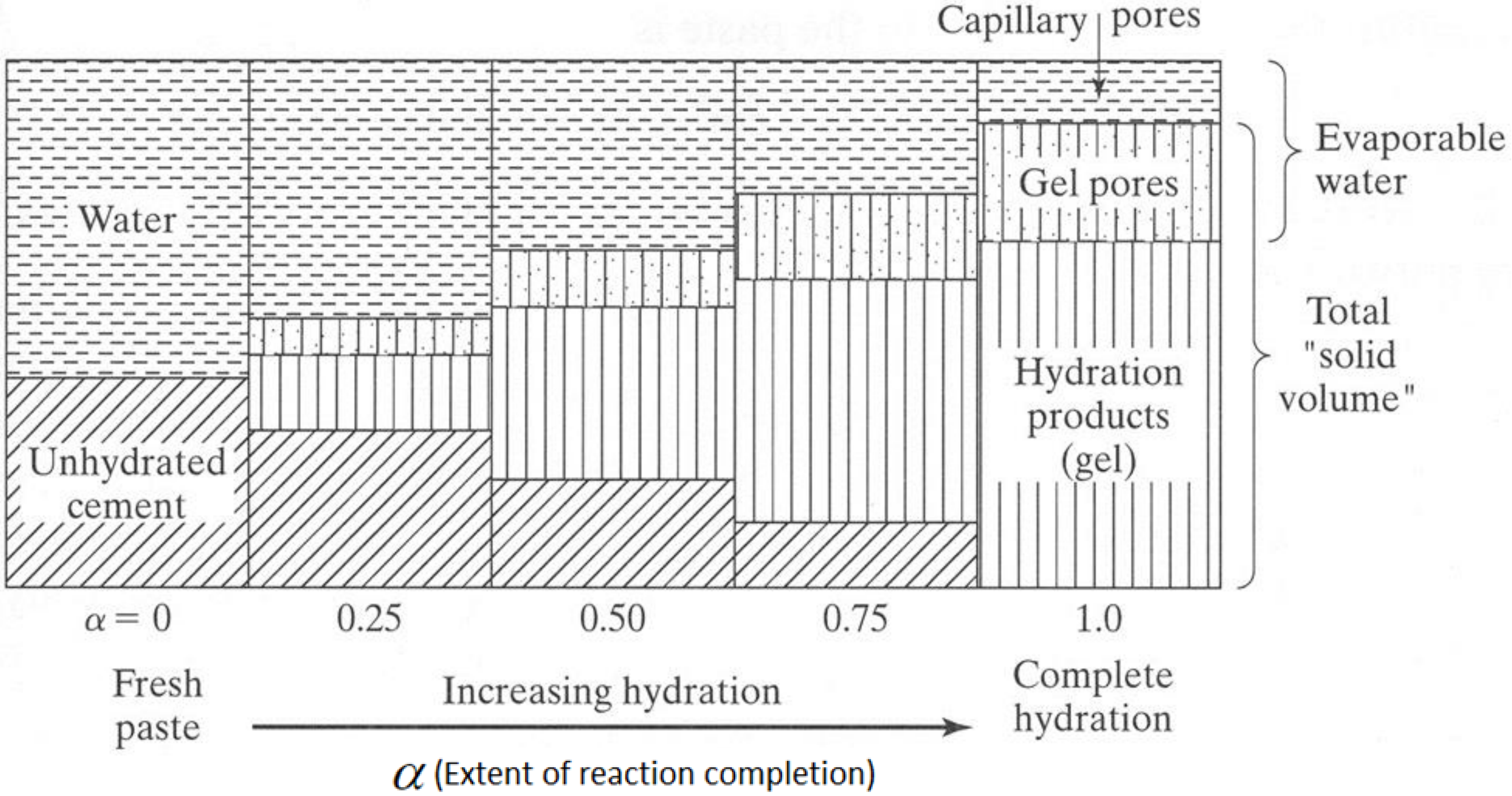
c) Trapped voids
  - *large pockets caused by handling*
  - *decrease strength and increase permeability*

d) Entrained air
  - *microscopic bubbles caused by admixtures*
  - *increases durability*

Voids in Hydrated Cement

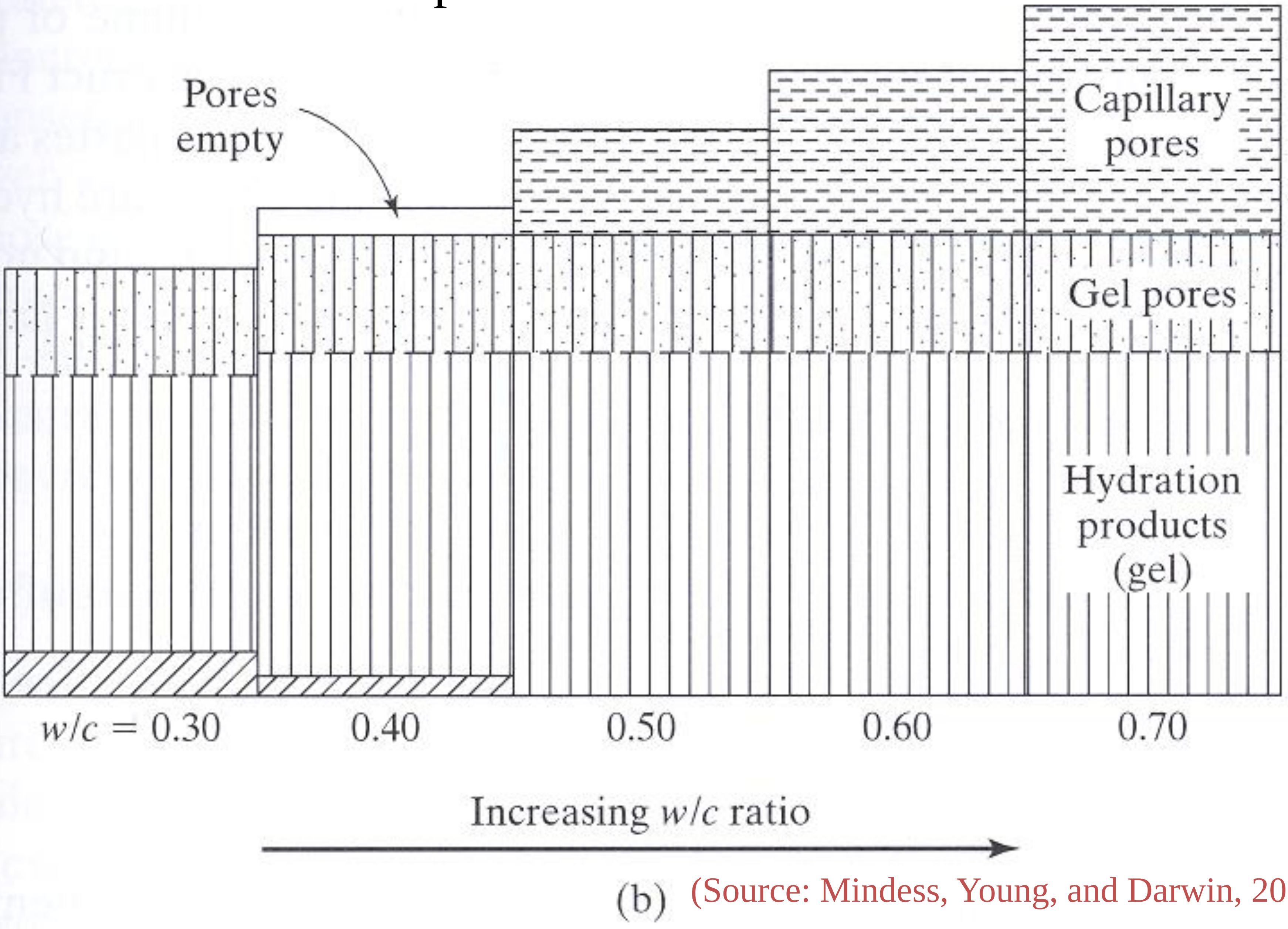
- Concrete strength, durability, and volume stability is greatly influenced by voids in the hydrated cement paste
- Two types of voids are formed in hydrated cement paste
    - interlayer hydration space (gel pores)
    - capillary voids
- Concrete also commonly contains entrained air and entrapped air
- Interlayer Hydration Space
    - Space between layers in C-S-H with thickness between 0.5 and 2.5 nm
    - Can contribute 28% of paste porosity
    - Little impact on strength, permeability, or shrinkage
- Capillary Voids
    - Depend on initial separation of cement particles, which is controlled by the ratio of water to cement (*w/c*)
    - On the order of 10 to 50 nm, although larger for higher *w/c*
    - Larger voids effect strength and permeability, whereas smaller voids impact shrinkage

Volume relationship:



(Source: Mindess, Young, and Darwin, 2004)

Volume relationship:



(Source: Mindess, Young, and Darwin, 2004)

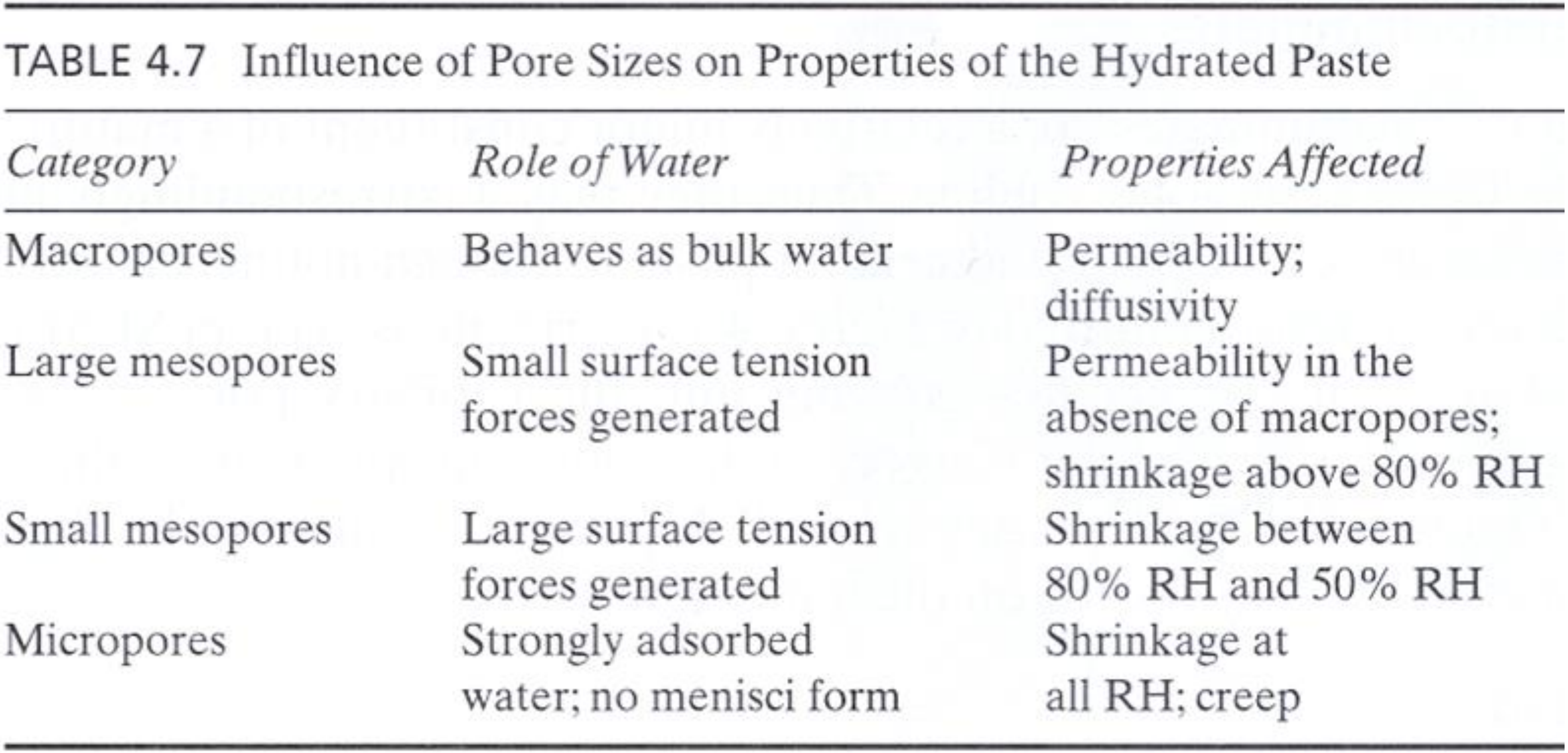


TABLE 4.7 Influence of Pore Sizes on Properties of the Hydrated Paste

Category	*Role of Water*	*Properties Affected*
Macropores	Behaves as bulk water	Permeability; diffusivity
Large mesopores	Small surface tension forces generated	Permeability in the absence of macropores; shrinkage above 80% RH
Small mesopores	Large surface tension forces generated	Shrinkage between 80% RH and 50% RH
Micropores	Strongly adsorbed water; no menisci form	Shrinkage at all RH; creep

(Source: Mindess, Young, and Darwin, 2004)

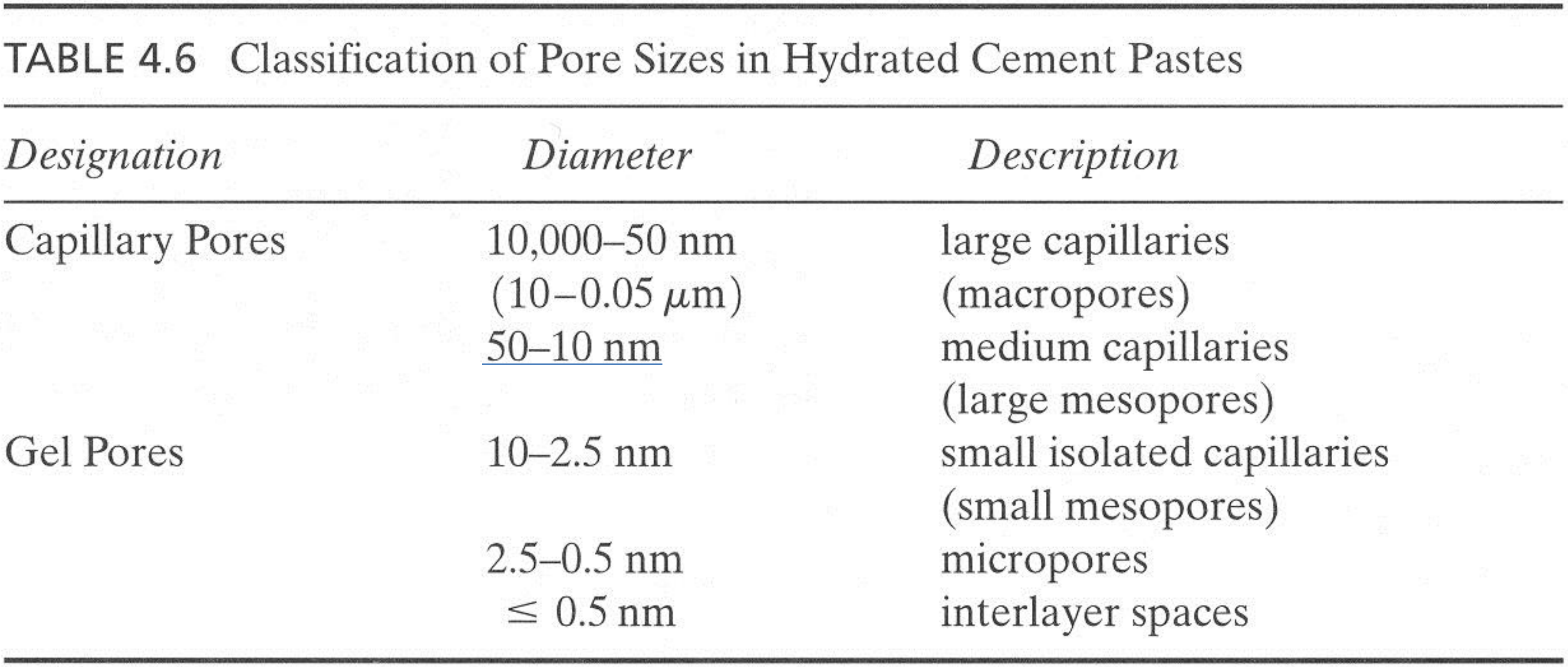
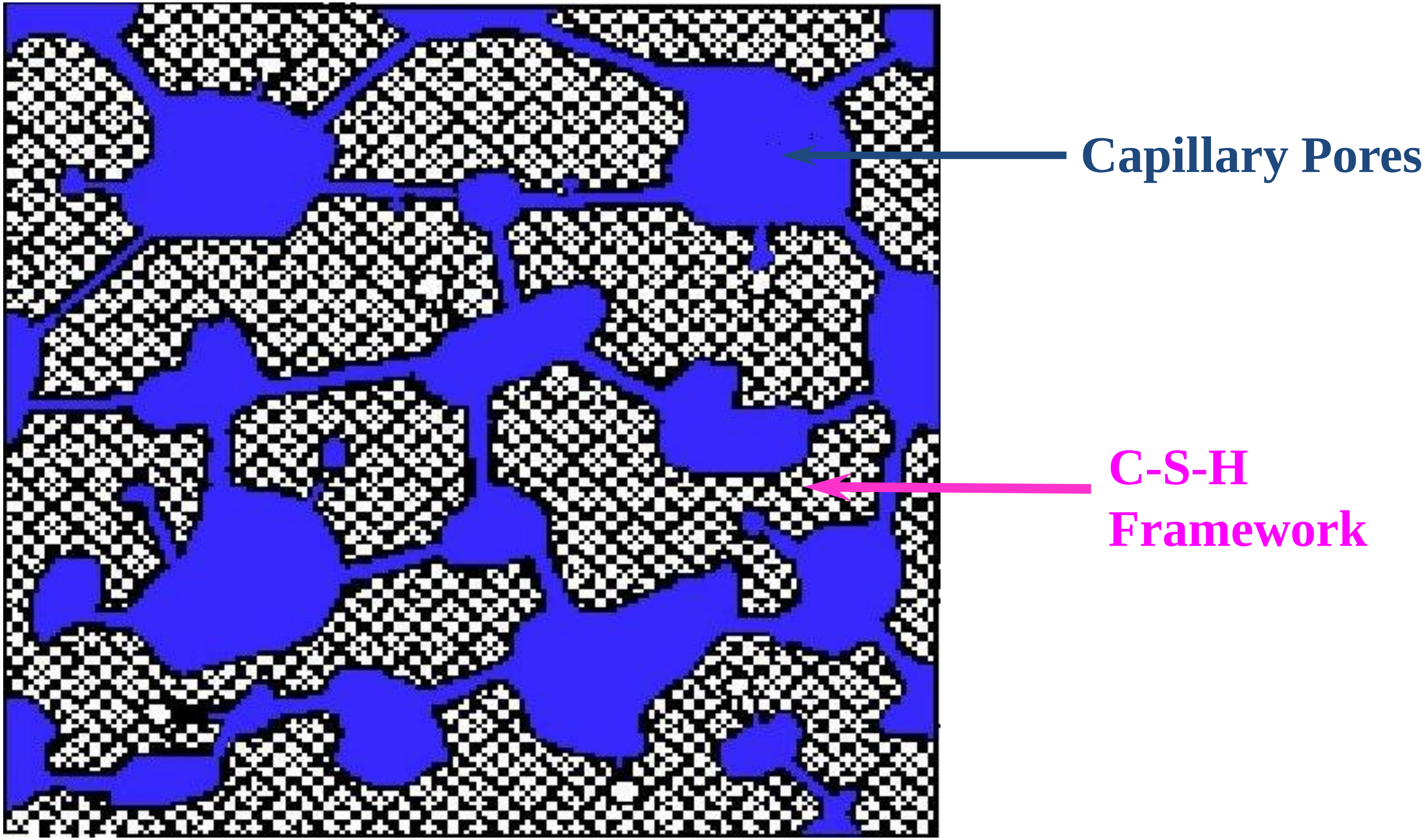


TABLE 4.6 Classification of Pore Sizes in Hydrated Cement Pastes

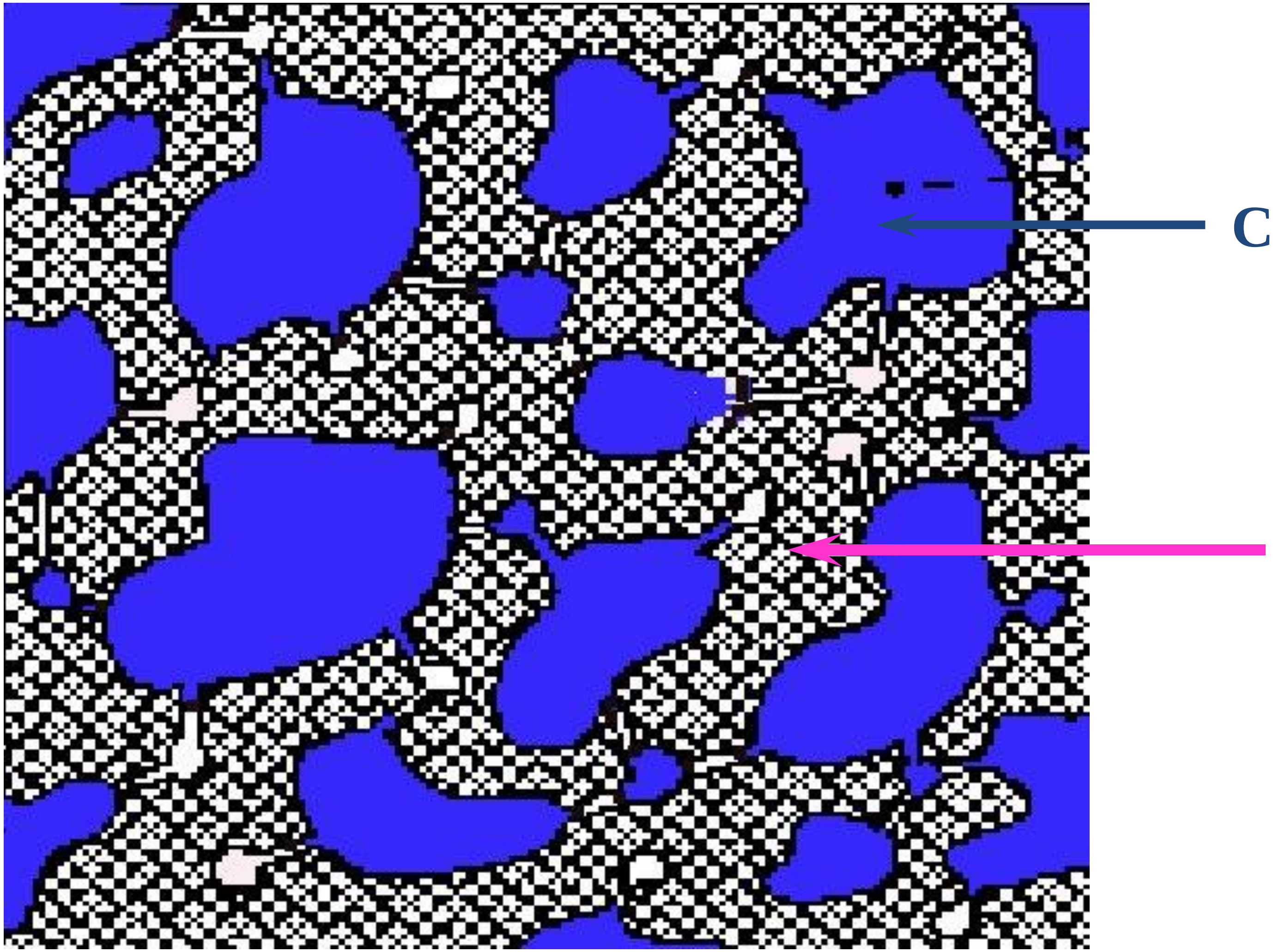
Designation	*Diameter*	*Description*
Capillary Pores	10,000–50 nm (10–0.05 μm)	large capillaries (macropores)
	50–10 nm	medium capillaries (large mesopores)
Gel Pores	10–2.5 nm	small isolated capillaries (small mesopores)
	2.5–0.5 nm	micropores
	≤ 0.5 nm	interlayer spaces

(Source: Mindess, Young, and Darwin, 2004)

High Permeability
(Capillary Pores Interconnected)



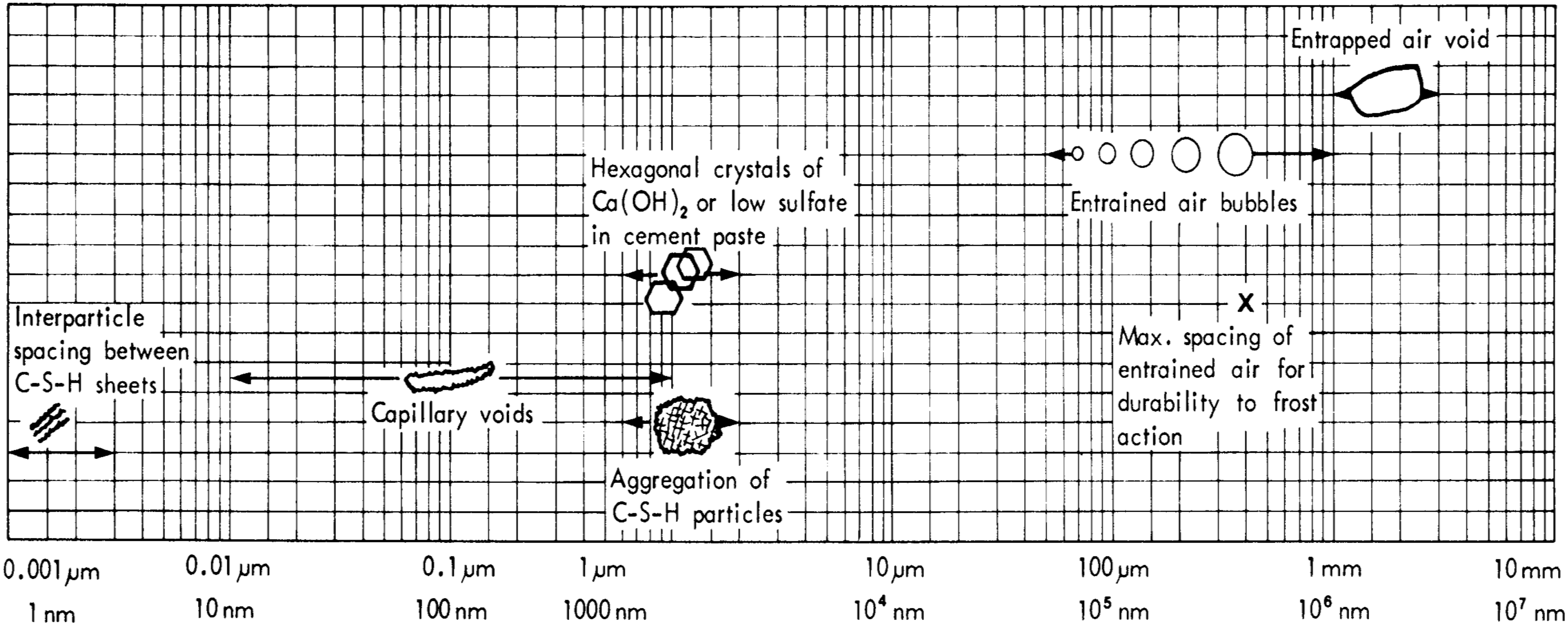
Low-Permeability Capillary Pores Segmented and Only Partially Connected



Capillary Pores

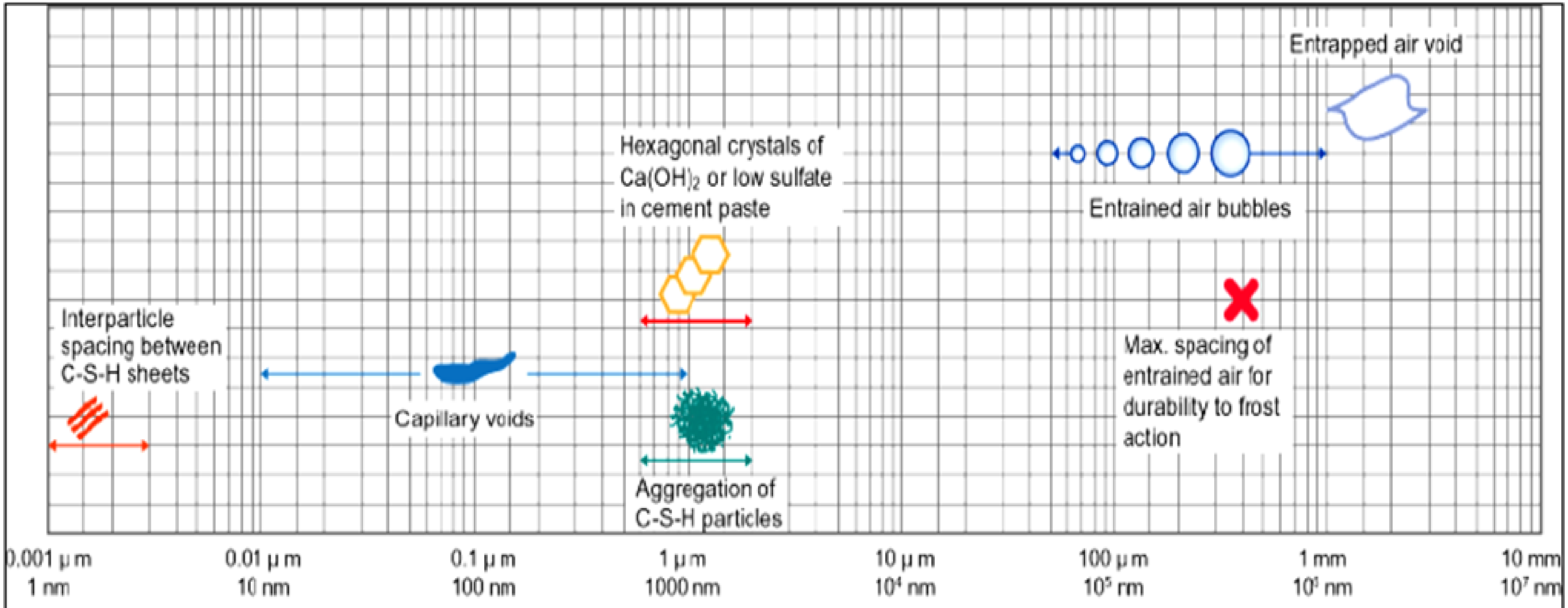
C-S-H Framework

Dimensional Range of Solids and Voids in Hydrated Cement Paste



Source: Mehta and Monteiro, 1993

Microstructure of Hydrated Cement Paste



Dimensional range of solid and pores in a hydrated cement paste.

Mehta and Monteir

False and Flash setting

- **Flash setting** : this is due to a lack (or absence) of calcium sulfate (gypsum/anhydrite) addition to clinker.
- This addition is useful to 'divert' the natural hydration route of aluminates towards ettringite. Hydroaluminates induce flash setting: a rapid and exothermic hardening in a matter of minutes. Ettringite and counterparts induce a much softer hydration route, easier to manage in terms of workability.
- **False setting**: this is usually due to the *nature* of calcium sulfates added, specifically too much calcium sulfate hemihydrate (more commonly plaster).
- Calcium sulfates come in various degrees of hydration: dihydrate (gypsum), hemihydrate (bassanite), anhydrous (anhydrite). When too high an amount of hemihydrate is present, it simply follows its own hydration route towards gypsum precipitation, leading to an early setting of cement.

Setting and Hardening of Cement

Setting of Cement	Hardening of Cement
Setting is the term used to describe the stiffening of the cement Paste	Hardening refers to the gain of strength of a set of cement paste
It refers to a change from a fluid to a rigid state	It refers to formation of solid mass possessing good compressive strength.
The setting of Cement Starts after 30 minutes from the instant when water is added to cement and compacted within 10 hours	The process of hardening of cement continues for a period more than 1 year.
To know the setting of cement, initial setting time test and final setting time test are conducted	To know the hardening of cement, compressive strength test is conducted.

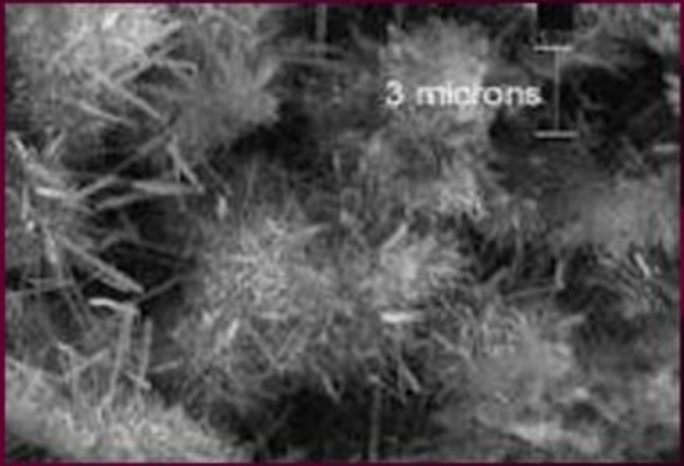
Process of Setting and Hardening

Initial period	Initial dissolving and hydration; mobile and plastic lasting for 5-10min
Incubation period	The performance of gel layer surrounding cement is excellent; particle growth; lasts for 1h
Setting period	The cement particle expands , bonds and hydrates after the cracking gel layer; Lasts for 6h; Porous spatial net-coagulation structure;Losing plasticity
Hardening period	Fillings of gel to capillaries; lasting for 6h~several years.

Measurement of Heat of Hydration

- ✓Standards:

  ASTM C 186



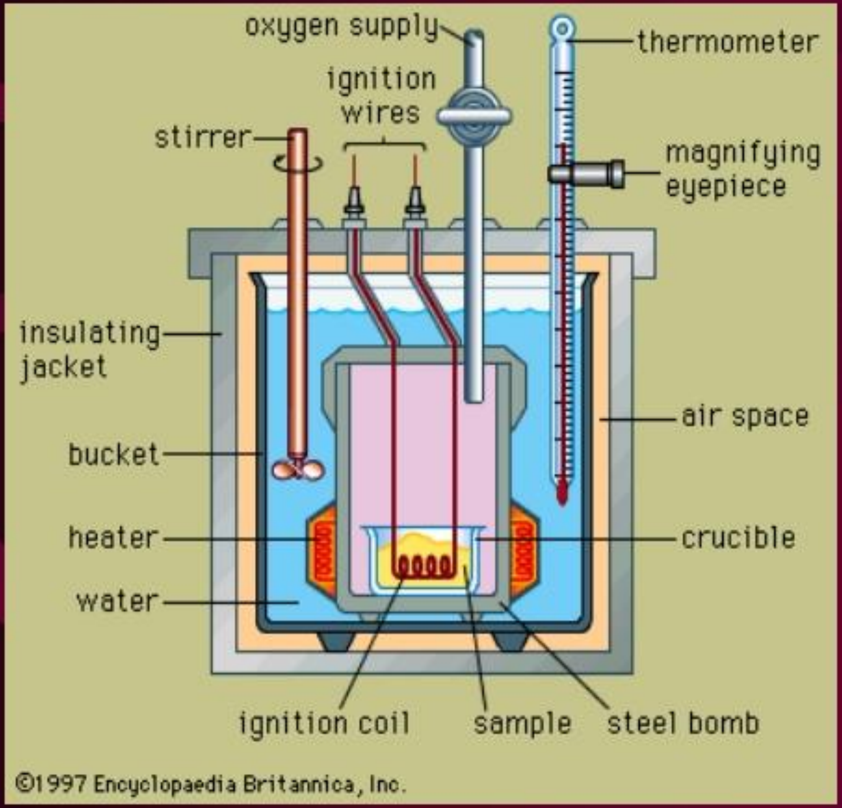
- Dry cement.
- Partially hydrated cement.

Use & Significance

- Cement specification.
- For research purposes at any age.
- Helpful for calculating temperature rise in mass concrete

Apparatus

- Calorimetric apparatus.



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Cont..

- Mixer
- Storage
- Mortar
- Drying oven
- Weighing bottles
- Stop watch
- Sieves
- weights

Cont…

Plastic vials

Muffle furnace

Cont…

crucibles

Analytical balance

Reagents &Materials

- HF (Hydrogen Floride)
- HNO_3
- WAX
- ZnO

Determination of heat capacity of apparatus

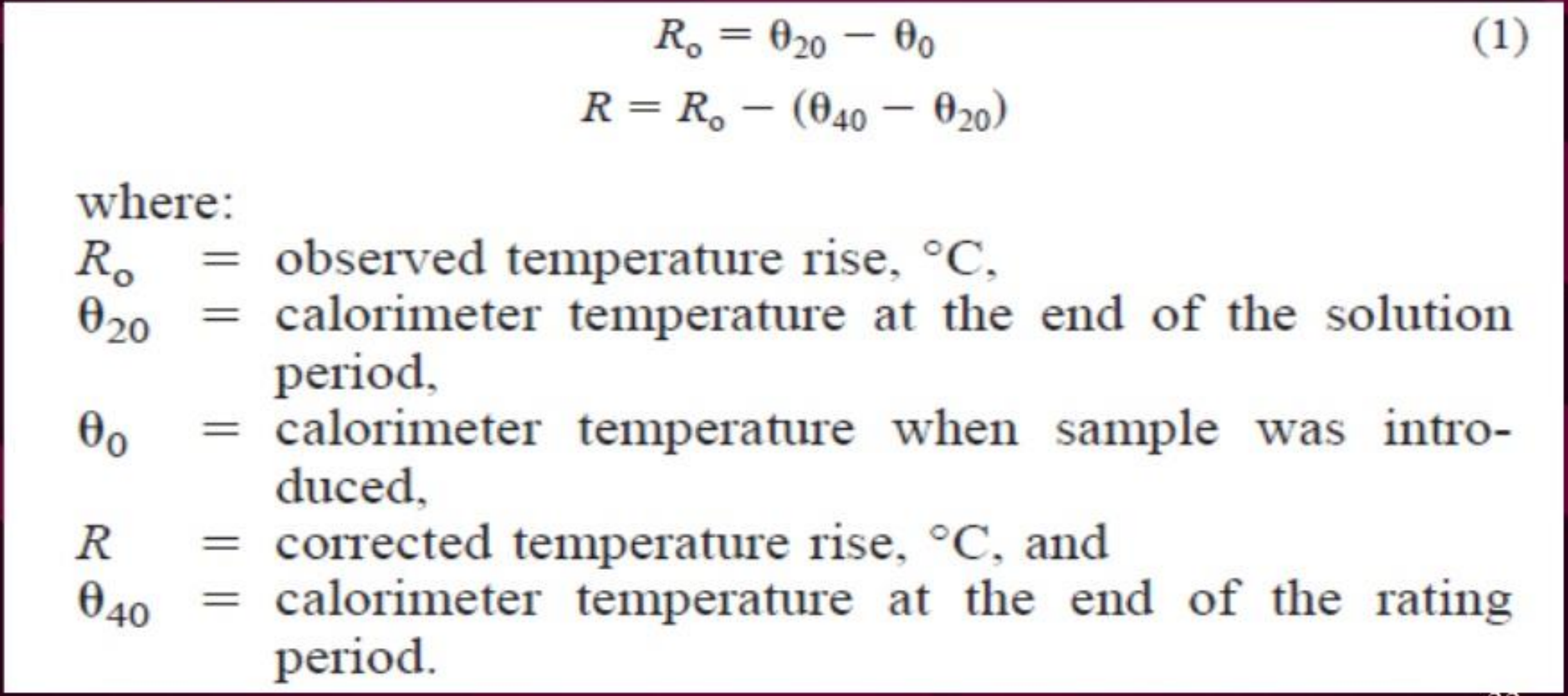
- Take total weight of the solution to 425g
- Assemble calorimeter
- Start stirring motor (20 mint)
- Allow system to become uniform
- Introduce ZnO
- Read the temperature OF;

✓ solution period

✓ rating period

Cont..

- **Calculate the corrected temperature rise as follows:**



$$R_o = \theta_{20} - \theta_0 \tag{1}$$

$$R = R_o - (\theta_{40} - \theta_{20})$$

where:

R_o = observed temperature rise, °C,
θ_{20} = calorimeter temperature at the end of the solution period,
θ_0 = calorimeter temperature when sample was introduced,
R = corrected temperature rise, °C, and
θ_{40} = calorimeter temperature at the end of the rating period.

Cont..

- Calculate the heat capacity of the calorimeter and contents as follows:

$$C = \frac{W[1072 + 0.4(30 - t) + 0.5(T - t)]}{R} \qquad (2)$$

Sampling & Test Specimens

- **Preparation of Cement Paste**
- **Preparation of Partially Hydrated Sample for Heat of Solution Test**

Procedure:

- ***Calorimetric Procedure***

✓ Determine the heat of solution of the dry cement sample.

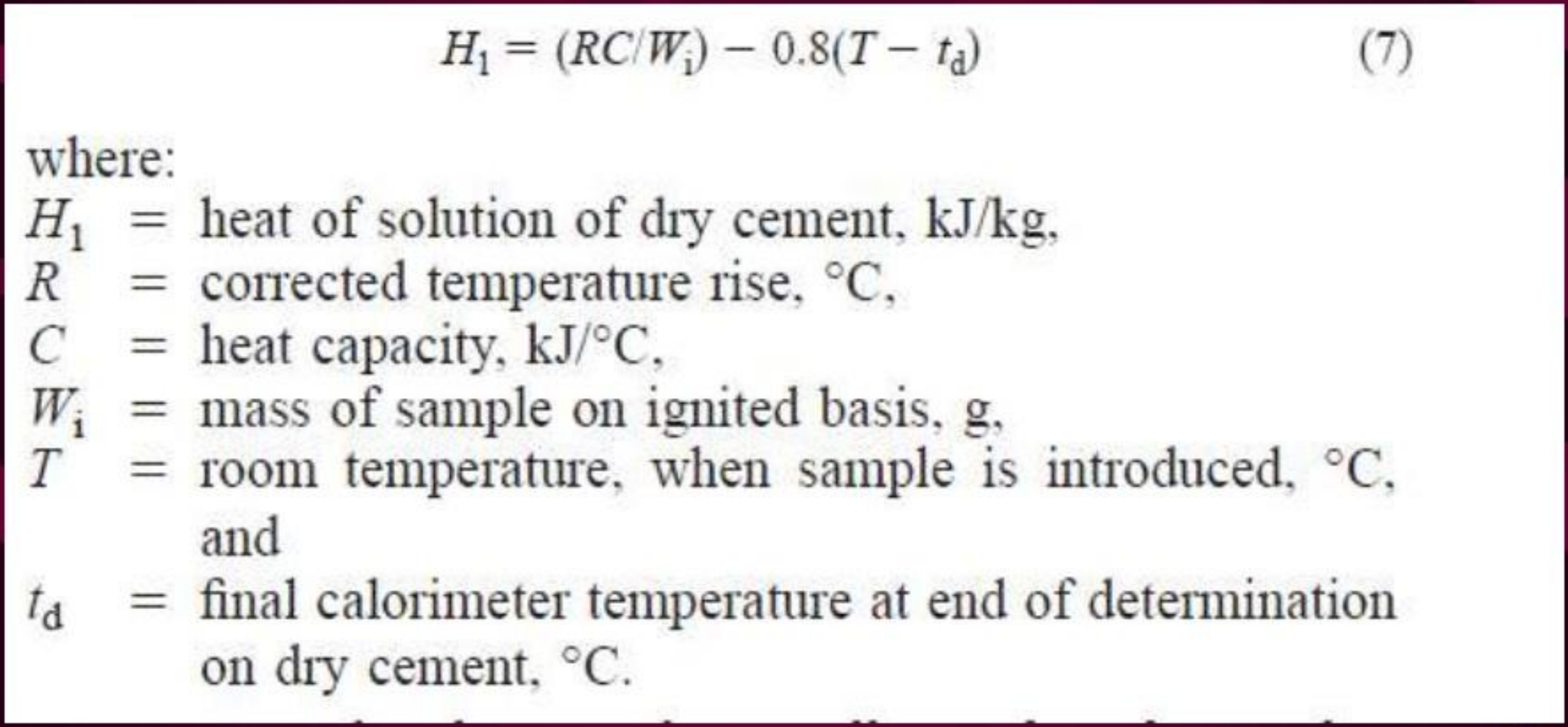
✓ Determine the heat of partially hydrated sample.

- Determine loss on Ignition

-

Calculations.

- **Heat of Solution of Dry Cement**



$$H_1 = (RC/W_i) - 0.8(T - t_d) \qquad (7)$$

where:

H_1 = heat of solution of dry cement, kJ/kg,

R = corrected temperature rise, °C,

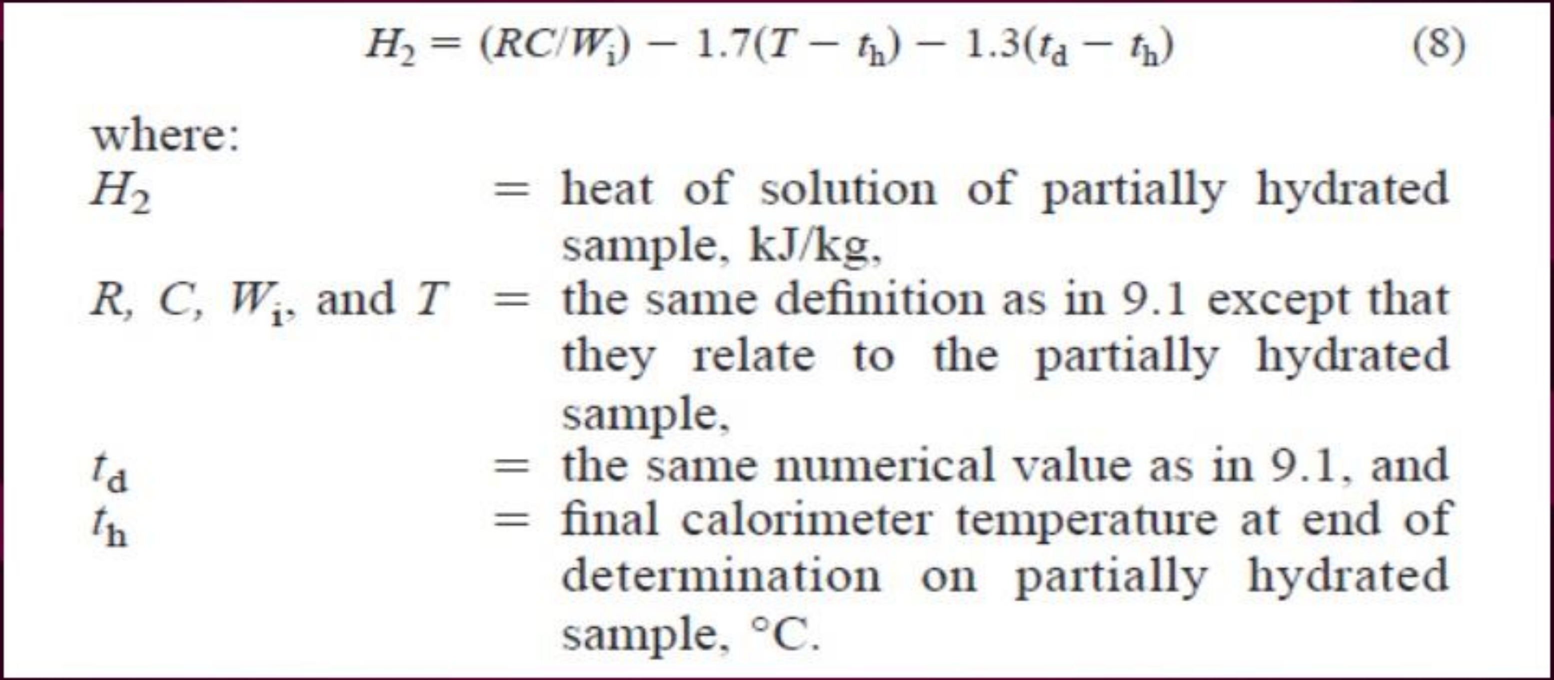
C = heat capacity, kJ/°C,

W_i = mass of sample on ignited basis, g,

T = room temperature, when sample is introduced, °C, and

t_d = final calorimeter temperature at end of determination on dry cement, °C.

- **Heat of Solution of Partially Hydrated Sample**



$$H_2 = (RC/W_i) - 1.7(T - t_h) - 1.3(t_d - t_h) \quad (8)$$

where:

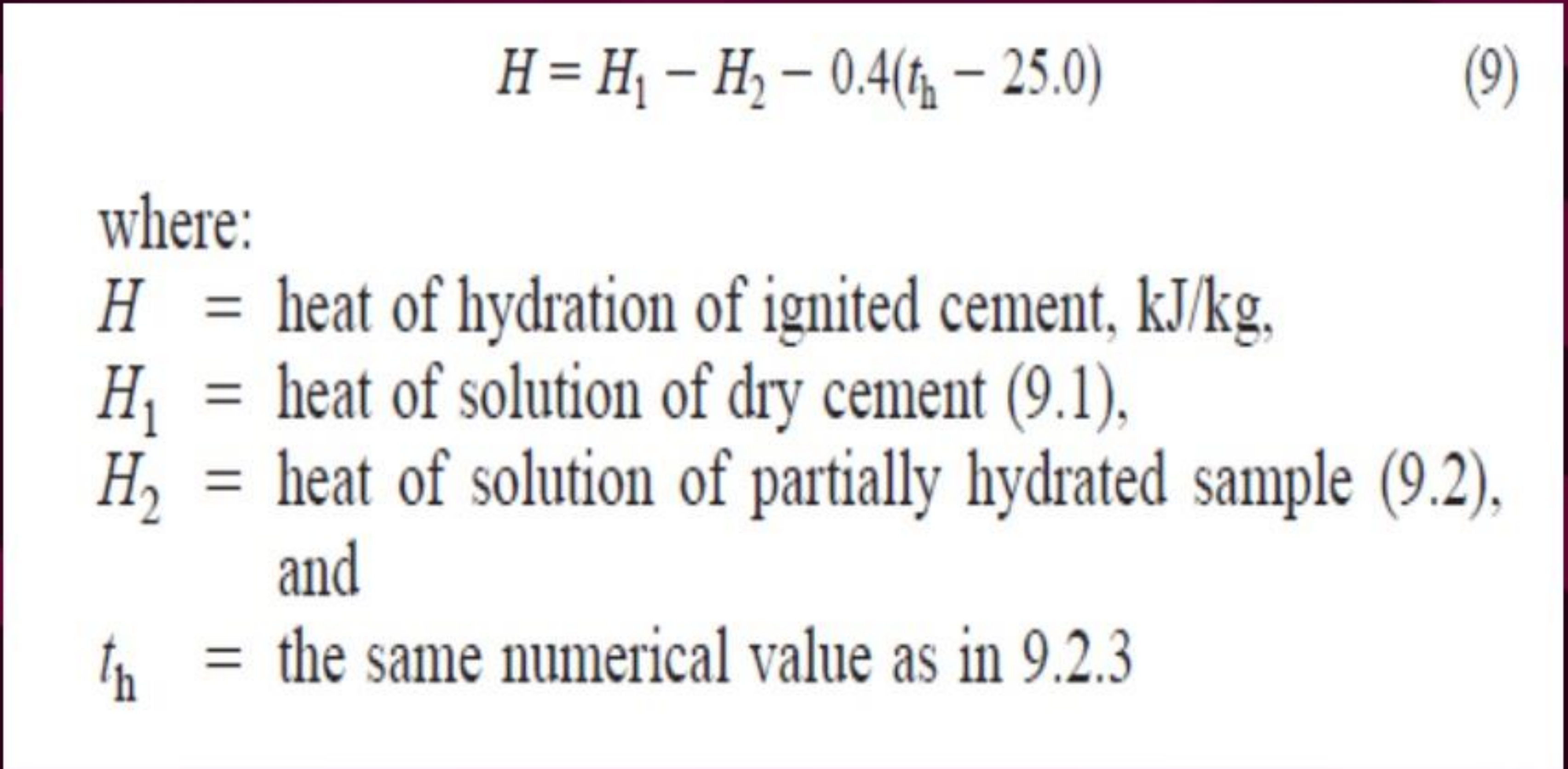
H_2 = heat of solution of partially hydrated sample, kJ/kg,

R, C, W_i, and T = the same definition as in 9.1 except that they relate to the partially hydrated sample,

t_d = the same numerical value as in 9.1, and

t_h = final calorimeter temperature at end of determination on partially hydrated sample, °C.

- **Heat of Hydration**



$$H = H_1 - H_2 - 0.4(t_h - 25.0) \qquad (9)$$

where:

H = heat of hydration of ignited cement, kJ/kg,
H_1 = heat of solution of dry cement (9.1),
H_2 = heat of solution of partially hydrated sample (9.2), and
t_h = the same numerical value as in 9.2.3

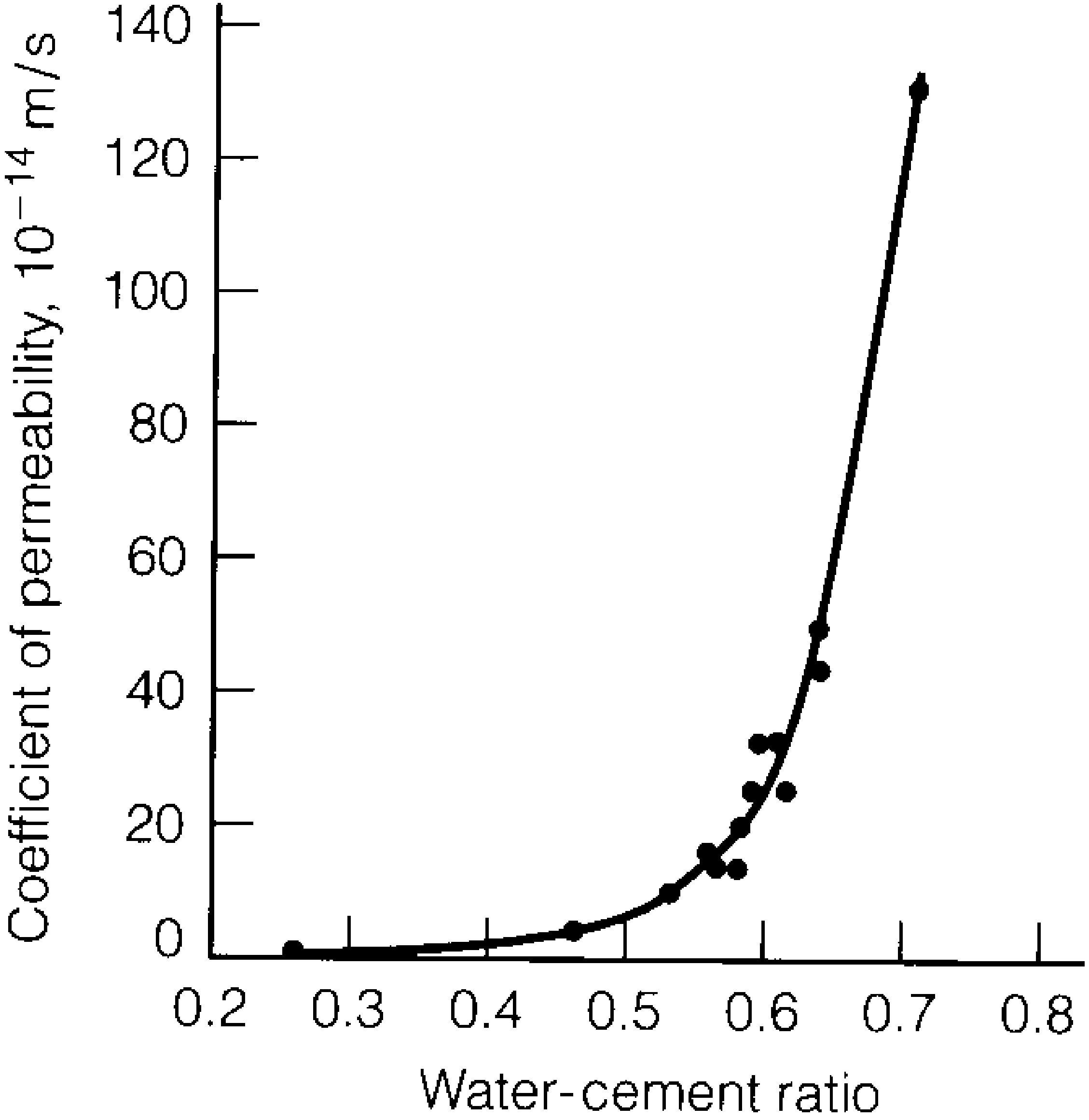
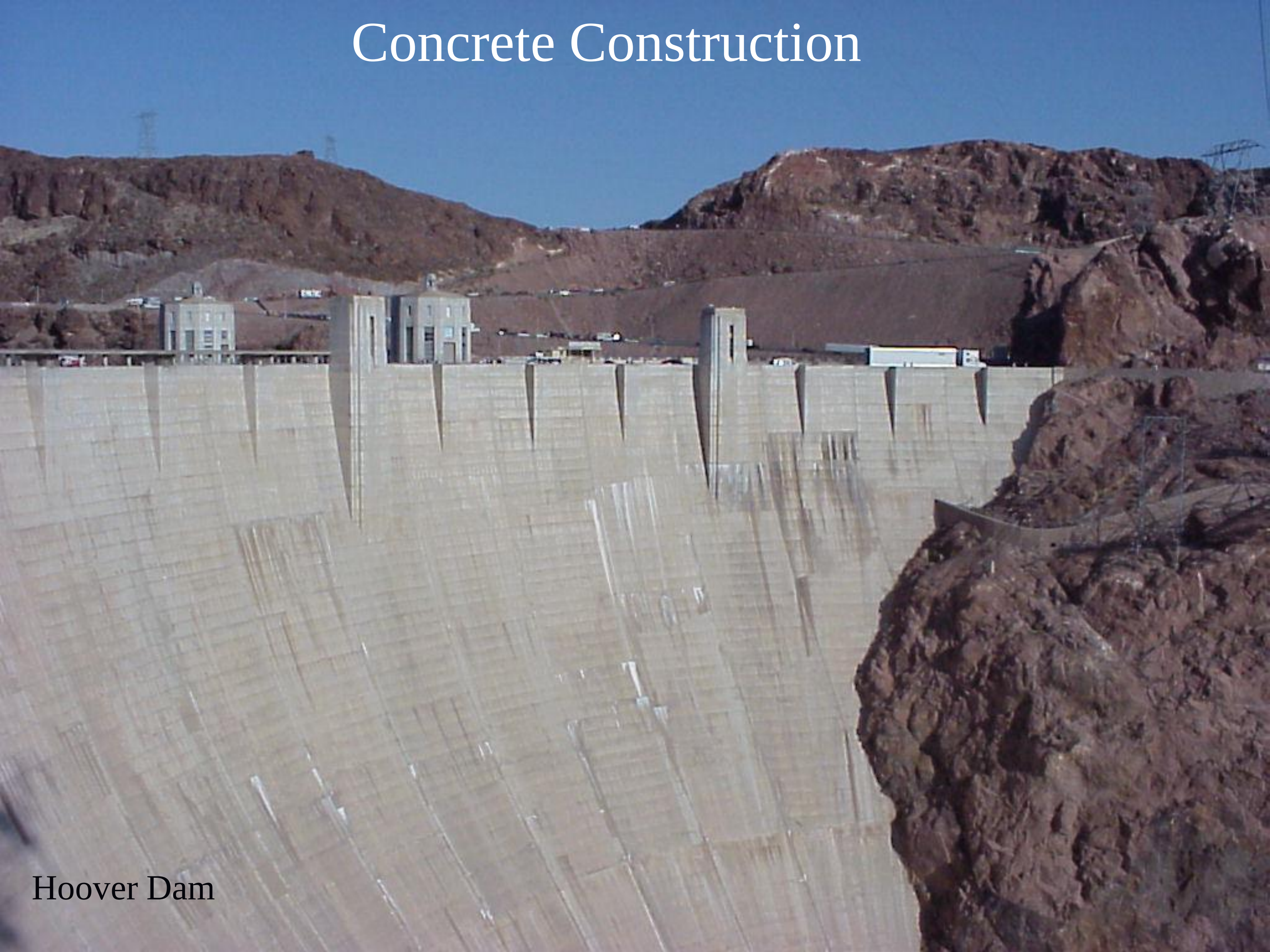


FIGURE 7.9 Relation between water-cement ratio and permeability of mature cement paste.

Questions and Assignment

- Discuss various types of Cement available in Pakistan and its Characteristics. (*Note*: *Put colour pictures of aggregates*)
- Different tests on Cement
- Report and Power point Presentation
- Need to submit in Group
- Due date: next week

Concrete Construction



Hoover Dam