



CONCRETE TECHNOLOGY MODULE

SEMESTER 1 – LECTURE 4

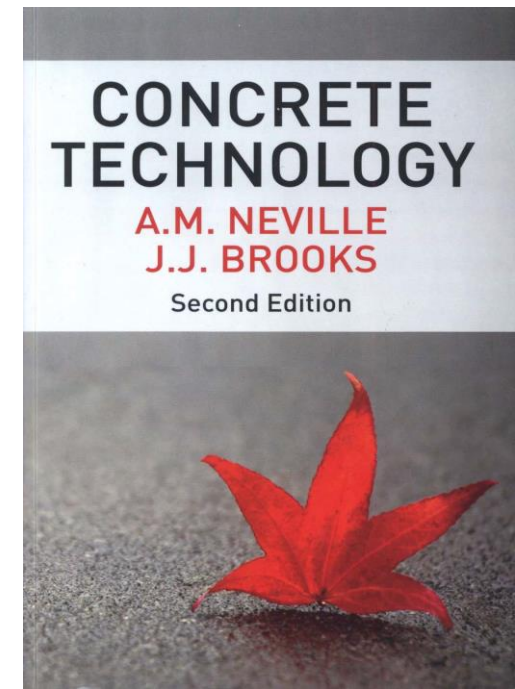
Dr. Khaldoon Shehab

SEMESTER 1 OUTLINE

Item	Subject	Item	
1	Introduction: Cement and Aggregate		
2	Manufacturing of concrete <ul style="list-style-type: none">- Mixing- Transportation- Placing and compaction- Curing- Finishing	4	Strength of Concrete <ul style="list-style-type: none">- Compressive strength- Tensile strength- Modulus of rupture- Bond strength with steel reinforcement- Factors affecting concrete strength- Factor affecting concrete test
3	Properties of Fresh Concrete <ul style="list-style-type: none">- Workability and Consistency- Segregation and Bleeding- Pressure on form work- Stripping of form	5	Deformation of Concrete <ul style="list-style-type: none">- Creep- Shrinkage- Modulus of elasticity and Poisson's ratio

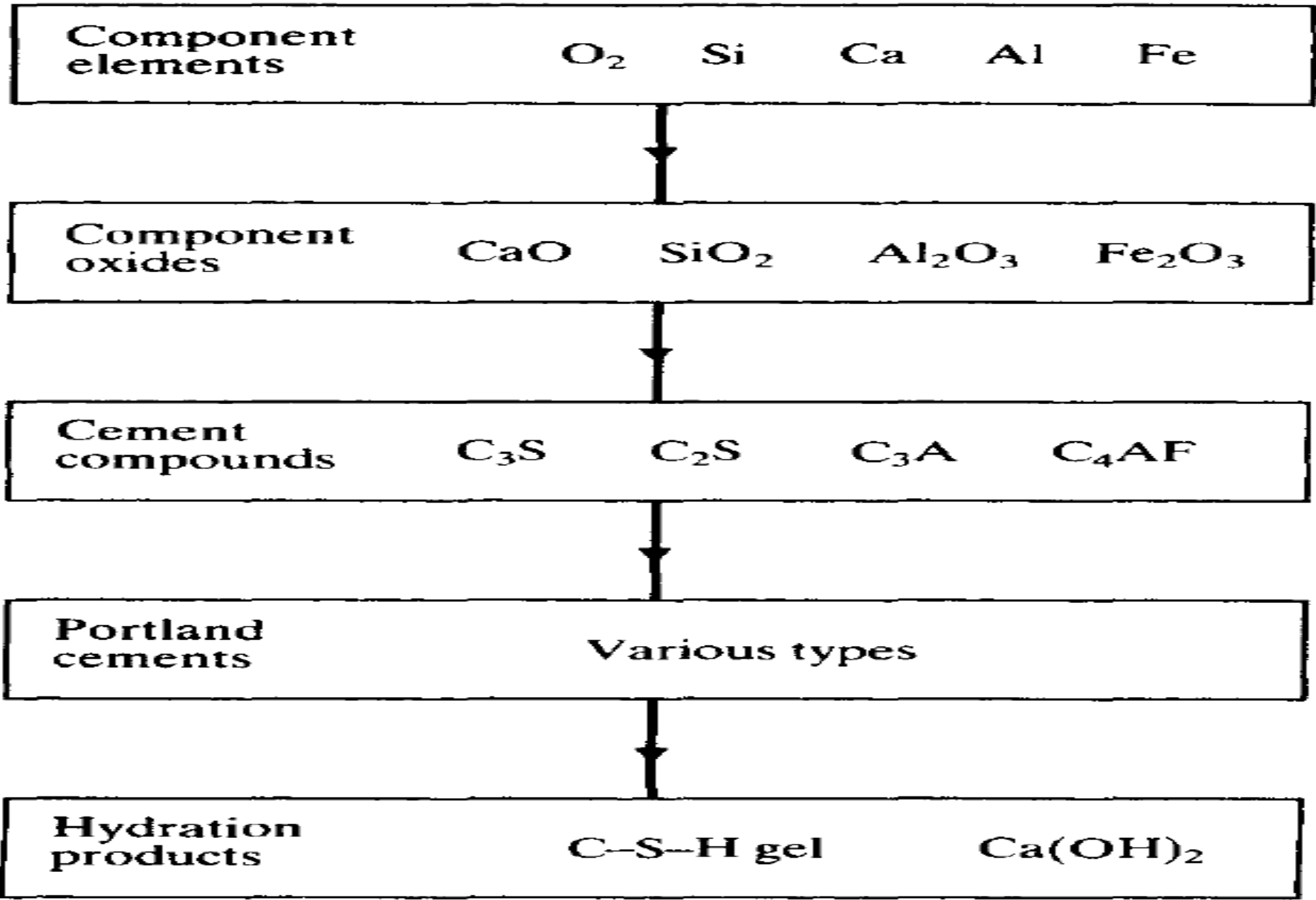
REFERENCES

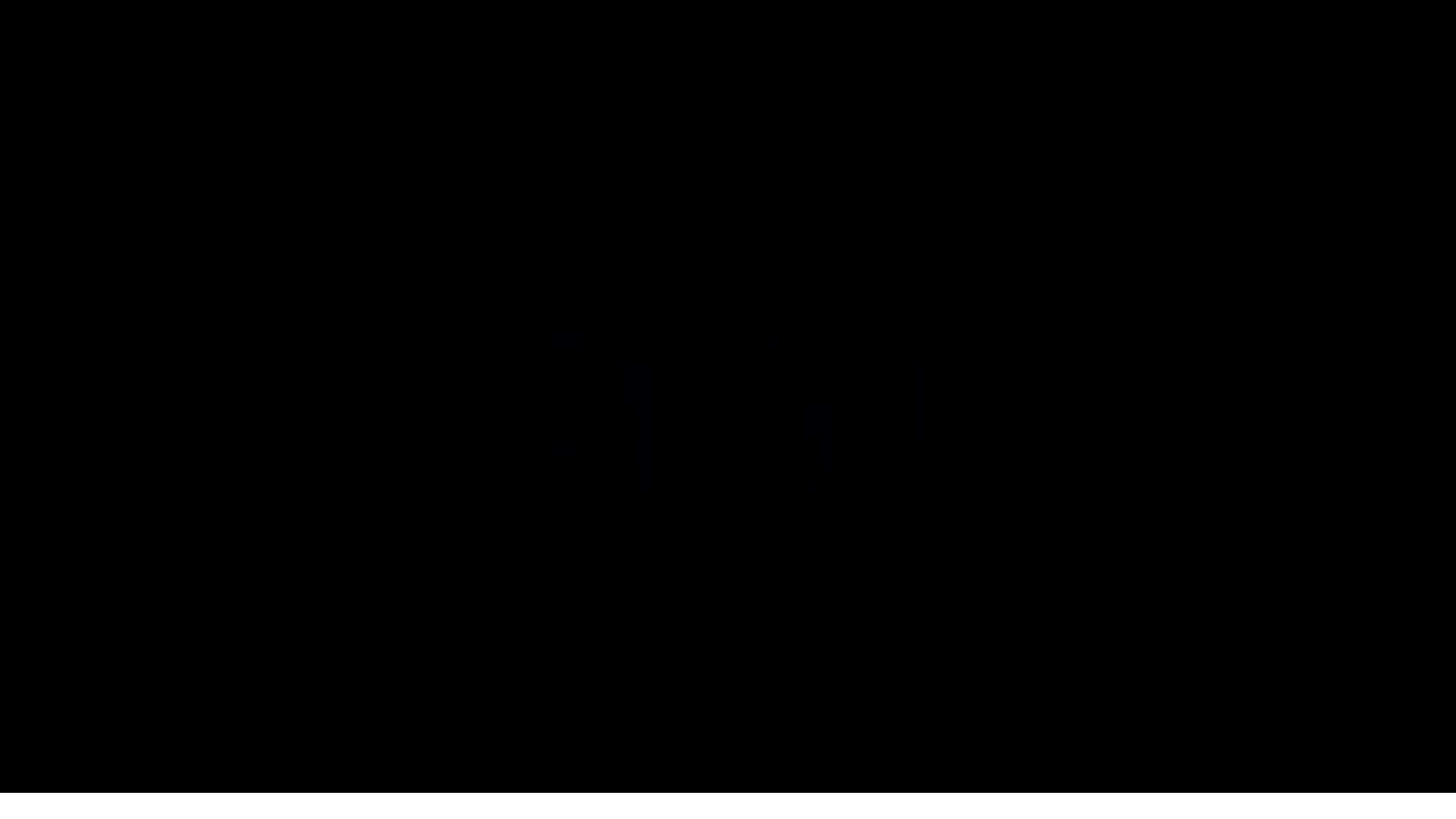
- Concrete technology by Dr. Moaid Nory
- Advanced concrete technology by Zongjin Li
- Concrete Technology -2dn Ed by A.M. NEVILLE



LECTURE CONTENTS

- 1. Cementitious Binders**
 - i. 2.2.2.3 Hydration



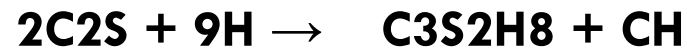
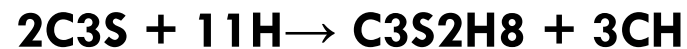


2.2.2.3 Hydration

(a) *Hydrations of pure cement compounds*

This assumes that the hydration of each compound takes place independently and no interaction occurs. Although this assumption is not valid completely, it helps to understand the chemistry of hydration.

(b) Calcium silicates: The hydrations of two calcium silicates are stoichiometrically similar, differing only in the amount of calcium hydroxide formed, the heat released, and the reaction rate:



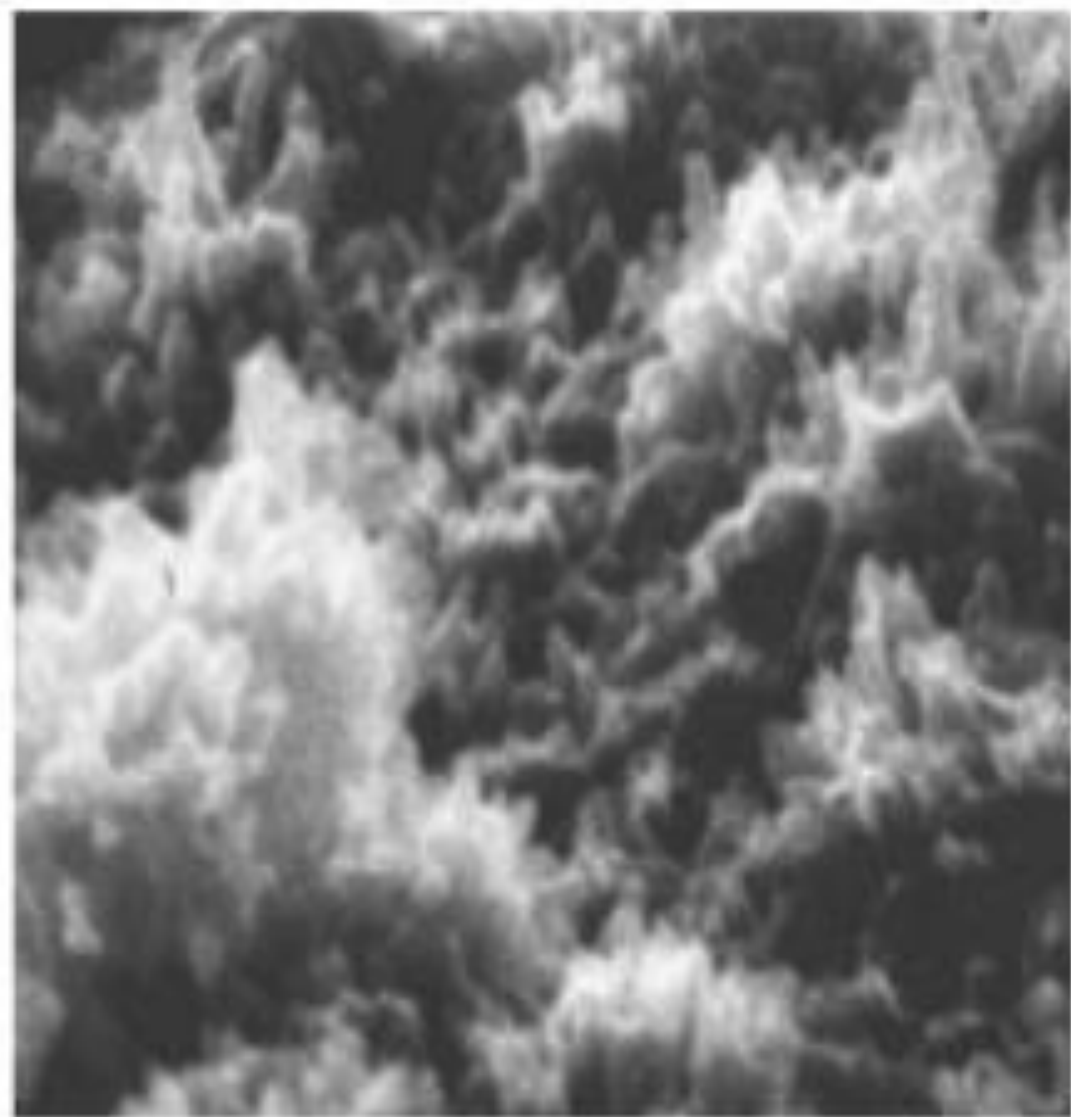
- The principal hydration product is C3S2H8, calcium silicate hydrate, or C–S–H.
- **C–S–H occupies about 50% of the structural component in a cement paste and forms directly on the surface of cement particles.**
- In addition, the size of C–S–H is quite small. It is believed that **C–S–H is the major strength provider for Portland cement concrete due to its amount and small size.**
- The structure of C–S–H is in the nanometer scale and is not a well-defined compound.

C–S–H does not show sharp peaks and has been considered as an amorphous structure.

C–S–H is usually called a glue gel binder.

- **Another product is CH, calcium hydroxide.**
- This product is a good crystalline with a plate shape in most cases.
- CH is formed in solution by crystallization and occupies about 25% of the structural component of cement paste.
- CH can bring the pH value to over 12 and it is good for corrosion protection of steel.
- From a durability of concrete point of view, CH may lead to leaching due to its solubility, carbonation due its reaction with carbon dioxide, **alkali aggregate reaction due to its high pH value**, or **sulfate attack due to its reaction with sulfate**.
- Hence, in contemporary concrete technology, there has been a trend to reduce amount of CH in concrete as much as possible.
- However, a minimum amount of CH is needed to keep the high alkali environment in concrete.

(1) C-S-H

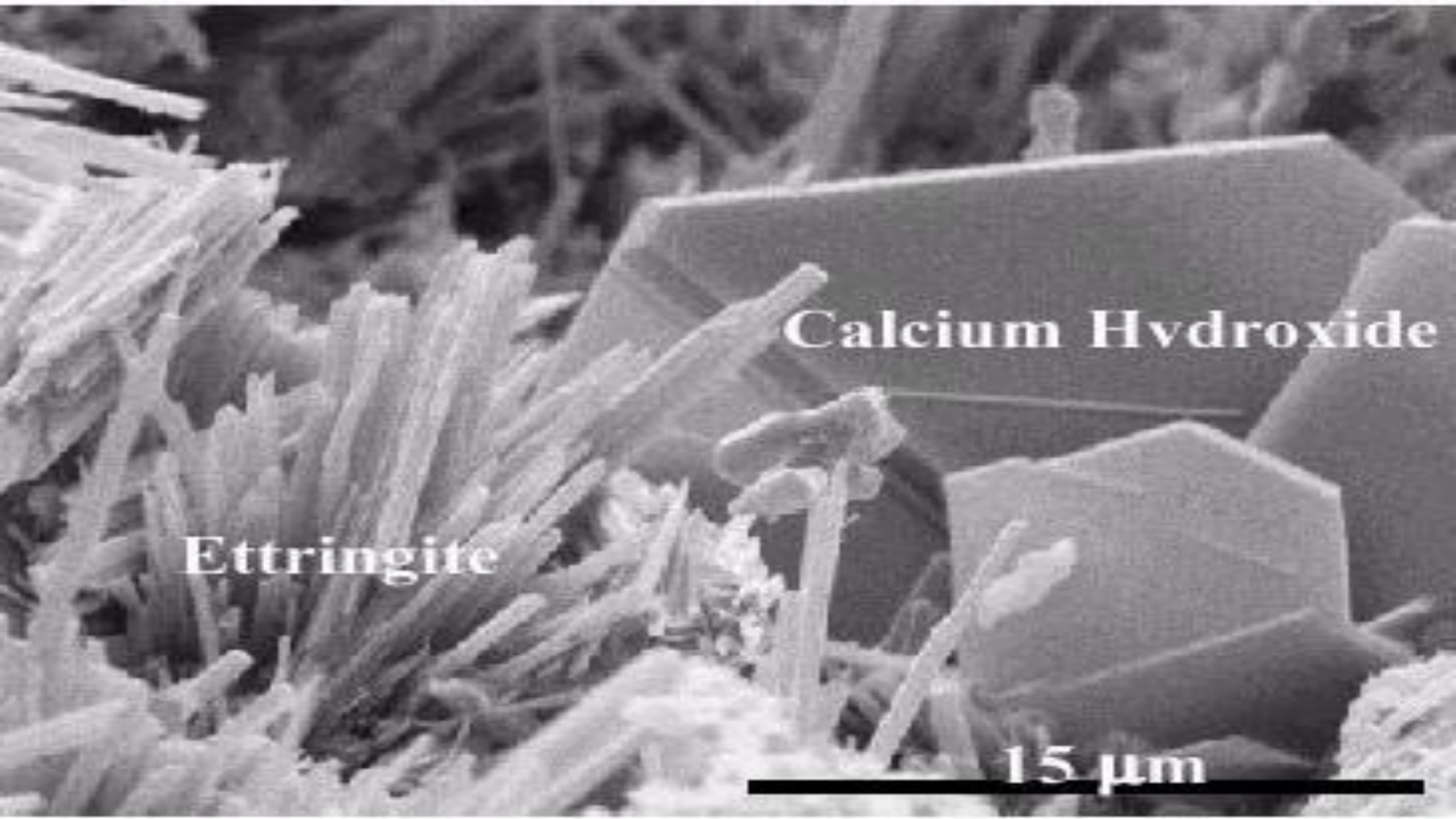


(2) C-H



(c) Tricalcium aluminate and ferrite phase:

- The primary initial reaction of C3A with water in the presence of a plentiful supply of gypsum is:
- $C3A + 3CSH2 + 26H \rightarrow C6A3H32$ (**ettringite miss spelled as C6A3H32**)
- The 6-calcium aluminate trisulfate-32-hydrate, is usually **called calcium sulfoaluminate hydrate** and more commonly **ettringite**, which is the name of a naturally occurring mineral of the same composition.
- **The nickname of ettringite is AFt.**
- **The formation of ettringite is right on the surface of the particles of C3A. It can slow down the hydration of C3A because it acts as a diffusion barrier around C3A, analogous to the behavior of C-S-H during the hydration of the calcium silicates.**
- Thus, it can avoid a C3A flash setting
- **Ettringite is a needle-shaped crystal with a large volume expansion.**



Calcium Hydroxide

Ettringite

15 μm

Moreover, ettringite is very aggressive and will make space to grow if there is no free space left.

The effect of ettringite on concrete strength can be evaluated in two cases.

In case 1, ettringite is formed before the paste has hardened and gained strength due to hydration of C3S. It will contribute to the early strength development of concrete since the needle-shaped crystals can work as reinforcement for the surrounding C-S-H, and the expansion is not so significant.

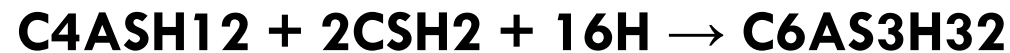
In case 2, if ettringite is formed after the concrete has hardened and free space has been occupied by other hydration products, it will make its space to grow by breaking the hardened hydration products **and hence create cracks and volume instability.**

- The ettringite is stable only when there is an ample supply of **sulfate (SO₄)** available and at a temperature lower than 60°C.
- If all the sulfate is consumed before the C₃A has completely hydrated or the temperature rises to above 60°C, it can be broken down during the hydration of the conversion to **monosulfoaluminate**:



Monosulfoaluminate is also called tetracalcium aluminate monosulfate-1 2-hydrate. Its nickname is **AFm**.

When monosulfoaluminate is brought into contact with a **new source of sulfate ions**, ettringite (**AFt**) can be formed again:



If there is no gypsum, C₃A will react with water very quickly:

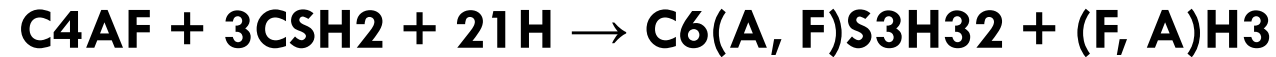


The hydrates can be further converted to



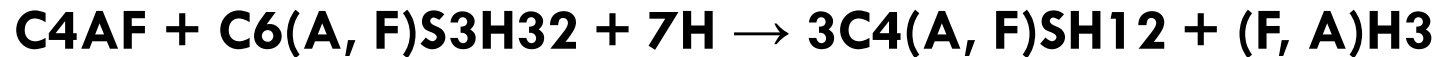
The hydration products of C4AF are similar to those of C3A. However, the reaction rate of C4AF is slower than that of C3A.

When reacting with gypsum, the following equation applies:



In the equation, the expression C6(A, F)S3 H32 indicates that iron oxide and alumina occur interchangeably in the compound. The order of symbols in the brackets implies the order of richness of the corresponding element in the compound.

C6(A, F)S3H32 can further react with C4AF and water:



- C4AF never hydrates rapidly enough to cause flash set, and gypsum retards C4AF hydration even more drastically than it does C3A
- With increase in iron content in C4AF, hydration of C4AF becomes slower
- practical experience has shown that cements low in C3A and high in C4AF are resistant to sulfate attack
- **This means that the formation of ettringite from mono-sulfo-aluminate does not occur in case of C4AF due to presence of iron in it.**

(d) **Kinetics and reactivities:** The rate of hydration during the first few days is in the order of **C3A > C3S > C4AF > C2S**.

The rate of hydration can be observed in Figure 2-11.

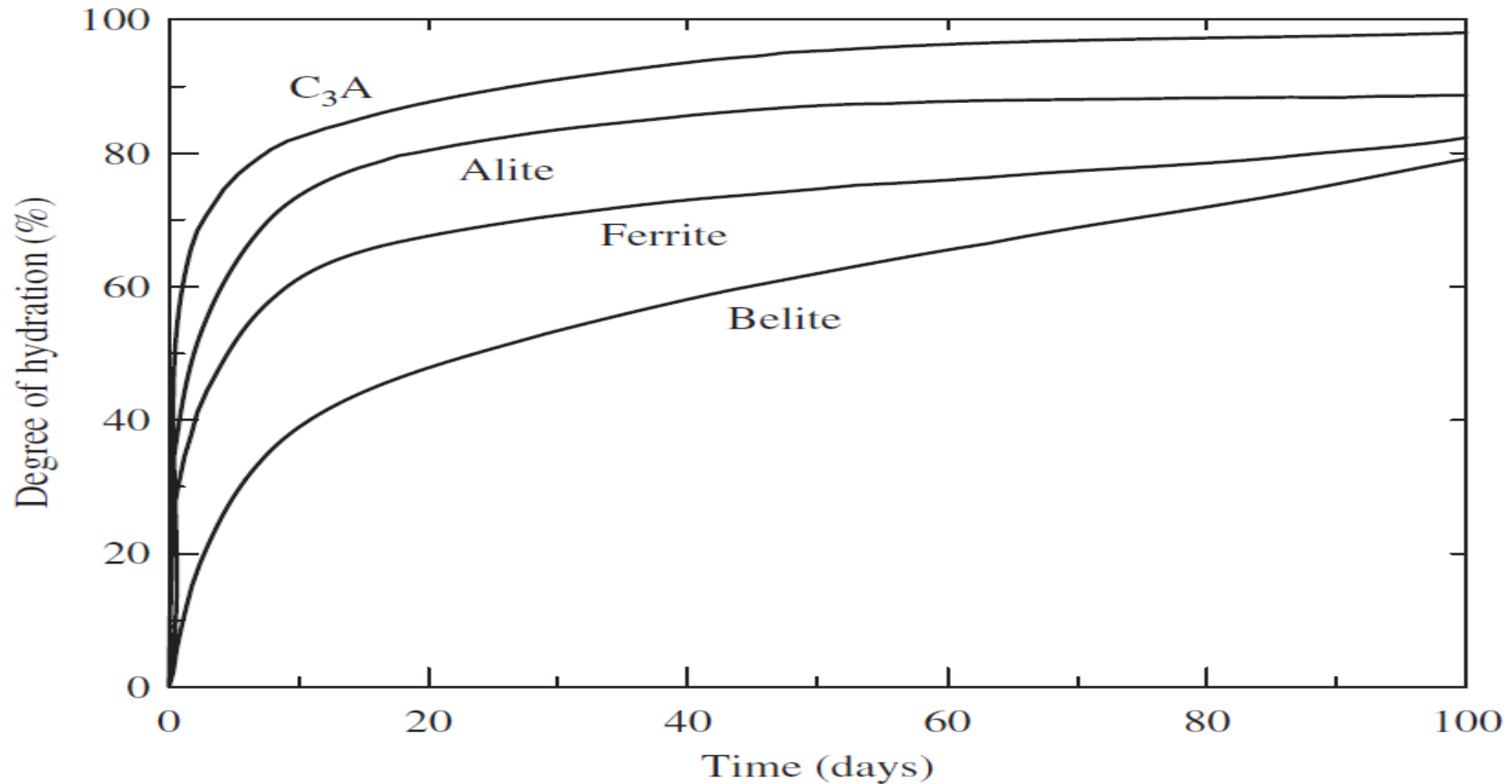


Figure 2-11 Hydration process of primary constituents of Portland cement

- **Figure 2-12 shows the strength development of different minerals.**
- **It can be seen that C3S has a high early strength and C2S develops its strength slowly in the early age but very fast later on.** It can be deduced that C3S contributes the most to early strength and C2S to long-term strength of Portland cement. On the other hand, the contribution to the strength of Portland cement from C3A and C4AF is not significant. Moreover, the strength development and kinetics of different minerals is somehow but not very closely related.

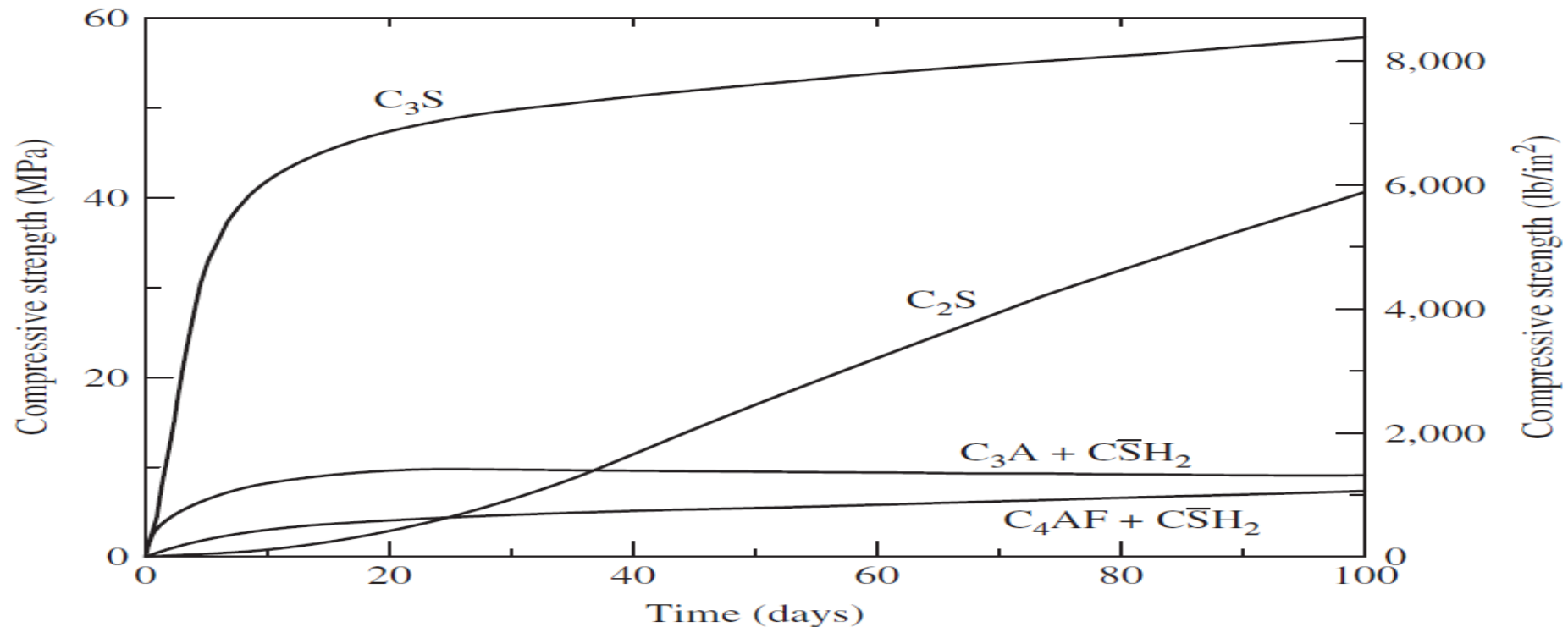


Figure 2-12 Strength development of primary constituents of Portland cement

- To study the dynamics of hydration of Portland cement, heat release rate measurement is frequently adopted because the process is exothermic. A typical calorimetric curve of Portland cement is shown in Figure 2-13.

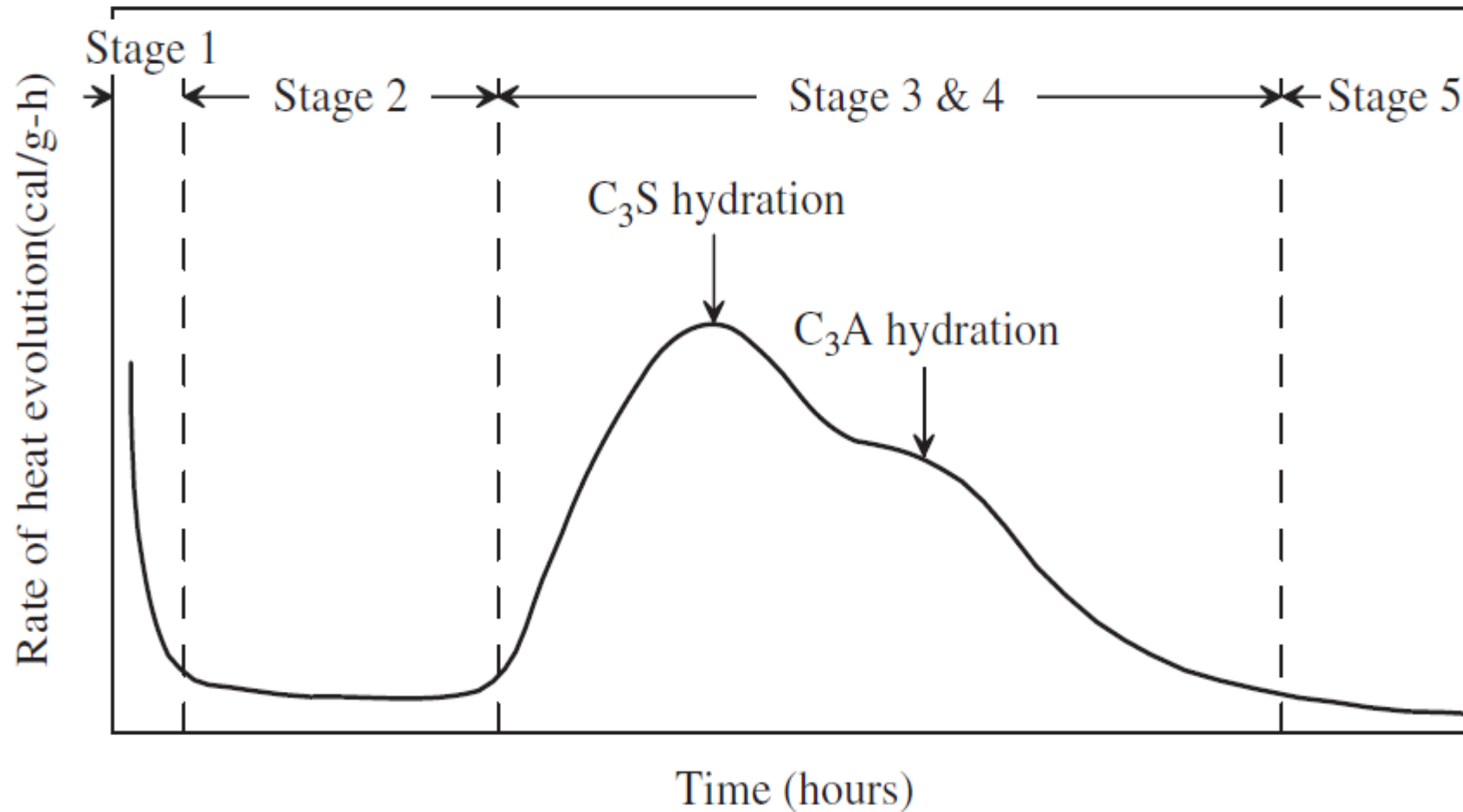


Figure 2-13 A typical calorimetric curve of Portland cement

Several characteristic points can be observed in the figure. The curve decreases initially and then keeps flat for a while after reaching the lowest value of heat evolution rate. Then it goes up in a very steep manner. After the first crest is reached, the curve goes down and rises up again to form the second peak. After that the curve decreases gradually.

The two peaks in the curve represent the dominant effect of C3S or C3A **correspondingly and their order of occurrence can be reversed.**

Based on the characteristic points on the curve, the hydration process of Portland cement can be easily distinguished in five stages; **dissolution, dormant, acceleration, deceleration, and steady state.**

It should be pointed out that the curve of heat evolution of Portland cement is very similar to that of C3S as that C3S has a dominant effect in cement.

Thus, the five stages traditionally defined in cement chemistry can be explained by using the reaction process of C3S, as detailed in Table 2-6.

Table 2-6 Kinetics of reaction, chemical processes, and relevance to concrete of the different reaction stages of cement

Reaction Stage	Kinetics of Reaction	Chemical Processes	Relevance to Concrete
1. Initial hydrolysis	Chemical control; rapid	Initial hydrolysis; dissolution of ions	n/a
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

On first contact with water, calcium ions and hydroxide ions are rapidly released from the surface of each C3S grain; the pH values rises to over 12 within a few minutes.

This hydrolysis slows down quickly but continues throughout the induction period.

The induction (dormant) period is caused by the need to achieve a certain concentration of ions in solution, before crystal nuclei form, from which the hydration products grow. At the end of the dormant period, CH starts to crystallize from the solution with the concomitant formation of C-S-H, and the reaction of C3S again proceeds rapidly (the third stage, acceleration, begins).

CH crystallizes from the solution, while C-S-H develops on the surface of C3S and forms a coating covering the grain. When the first peak of the rate of heat evolution is reached, the deceleration stage is started.

As hydration continues, the thickness of the hydrate layer increases and forms a barrier through which water must flow to reach the unhydrated C3S and through which ions must diffuse to reach the growing crystals.

Eventually, movement through the C-S-H layer determines the rate of reaction, and hydration becomes diffusion controlled and moves into the 5th stage, the steady-state stage.

(f) *Setting and hydration:* Traditionally, it is believed that the initial set of cement corresponds closely to the end of the induction period, 2–4 h after mixing.

The initial set indicates the beginning of gel formation. It is controlled primarily by the rate of hydration of C3S. The final set occurs 5–10 h after mixing, which indicates that sufficient hydration products are formed and the cement paste is ready to carry some external load.

It should be noted that the initial and the final set have a physical importance. However, there is no fundamental change in the hydration process for these two different sets. The hydration process of fresh cement paste is schematically illustrated in Figure 2-14.

The rate of early hardening, which means a gain in strength, is primarily determined by the hydration of C3S, and the strength gain is roughly proportional to the area under the heat peak in the calorimetric curves of Portland cement.

The strength development is mainly derived from the hydration of silicates.

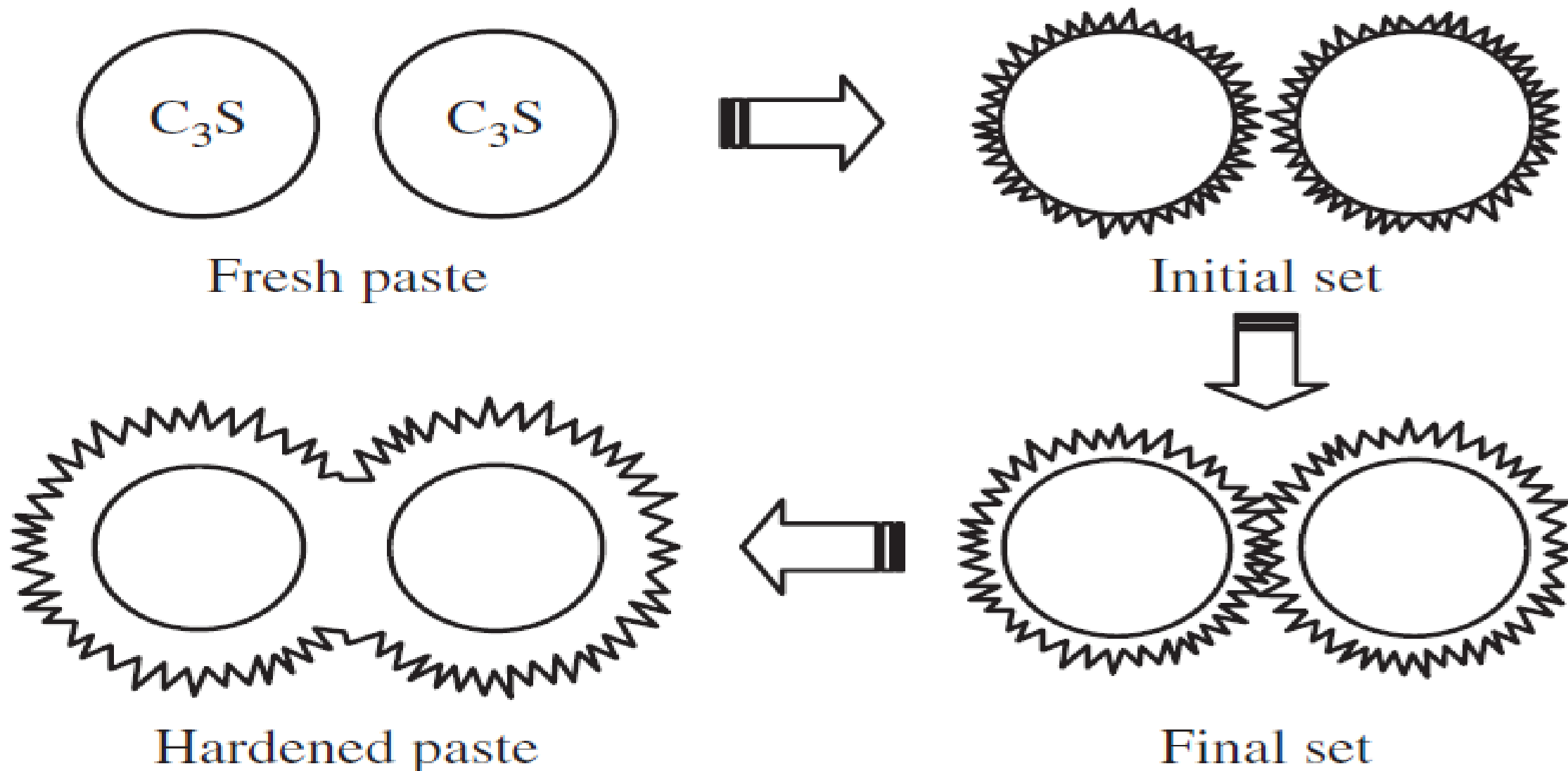


Figure 2-14 Setting of fresh cement paste

*Thank you for
your
attention!*