CONCRETE TECHNOLOGY MODULE

WEEK 3

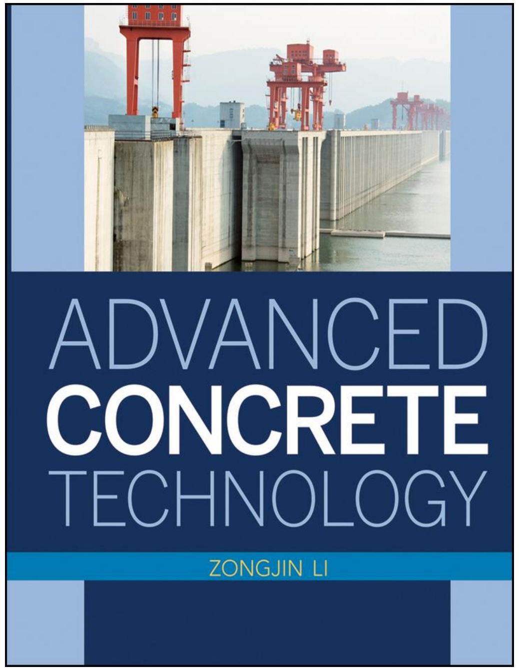
REFERENCES

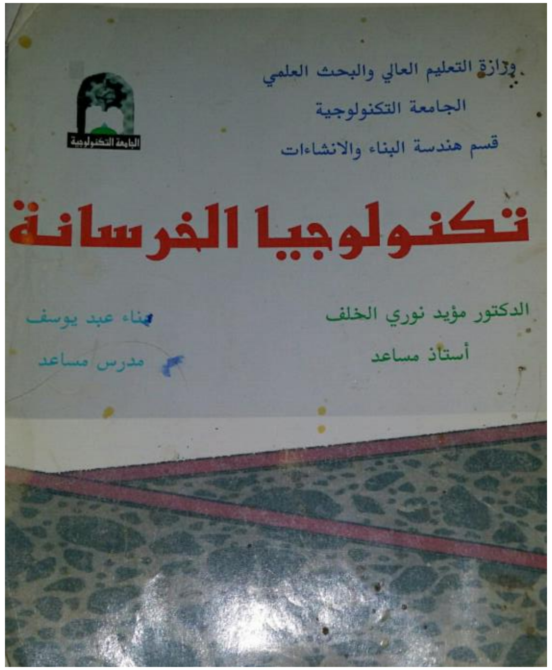
Main Reference

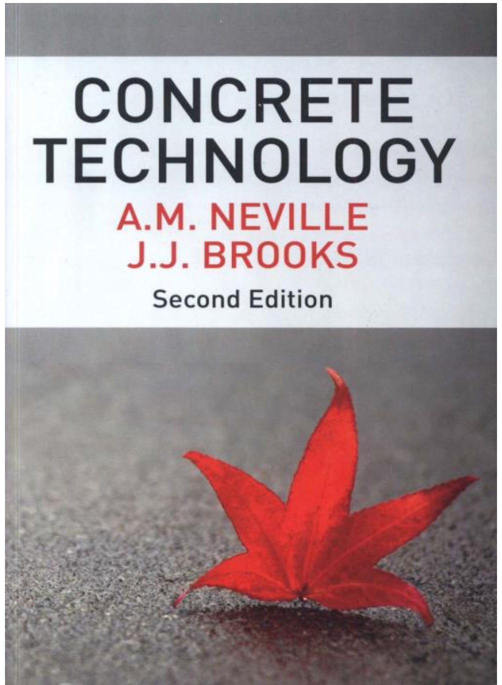
- Advanced concrete technology by Zongjin Li

Other references

- Concrete technology by Dr. Moaid Nory
- Concrete Technology -2dn Ed by A.M. NEVILLE







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(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.

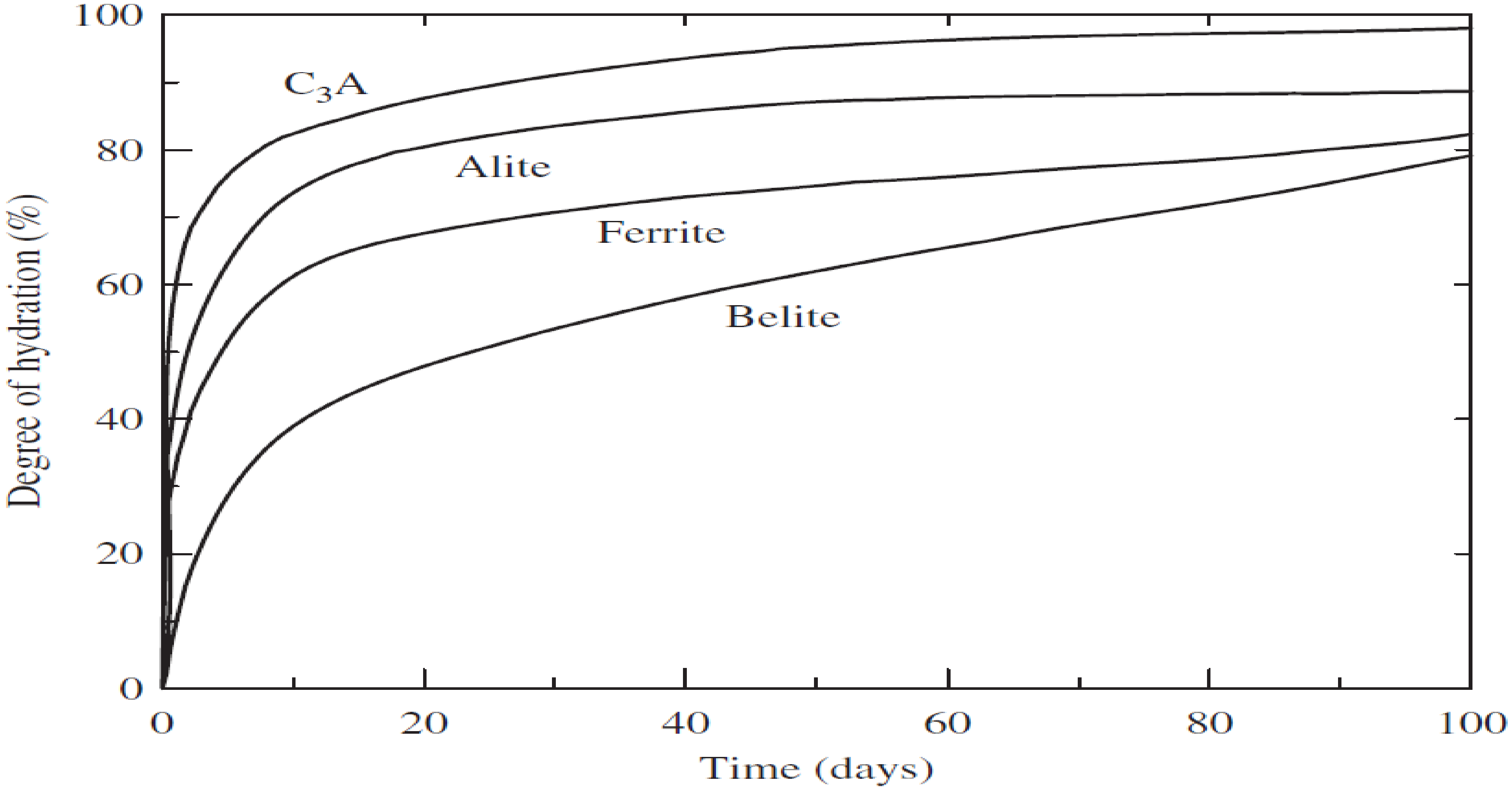


Figure 2-11 Hydration process of primary constituents of Portland cement

- **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.

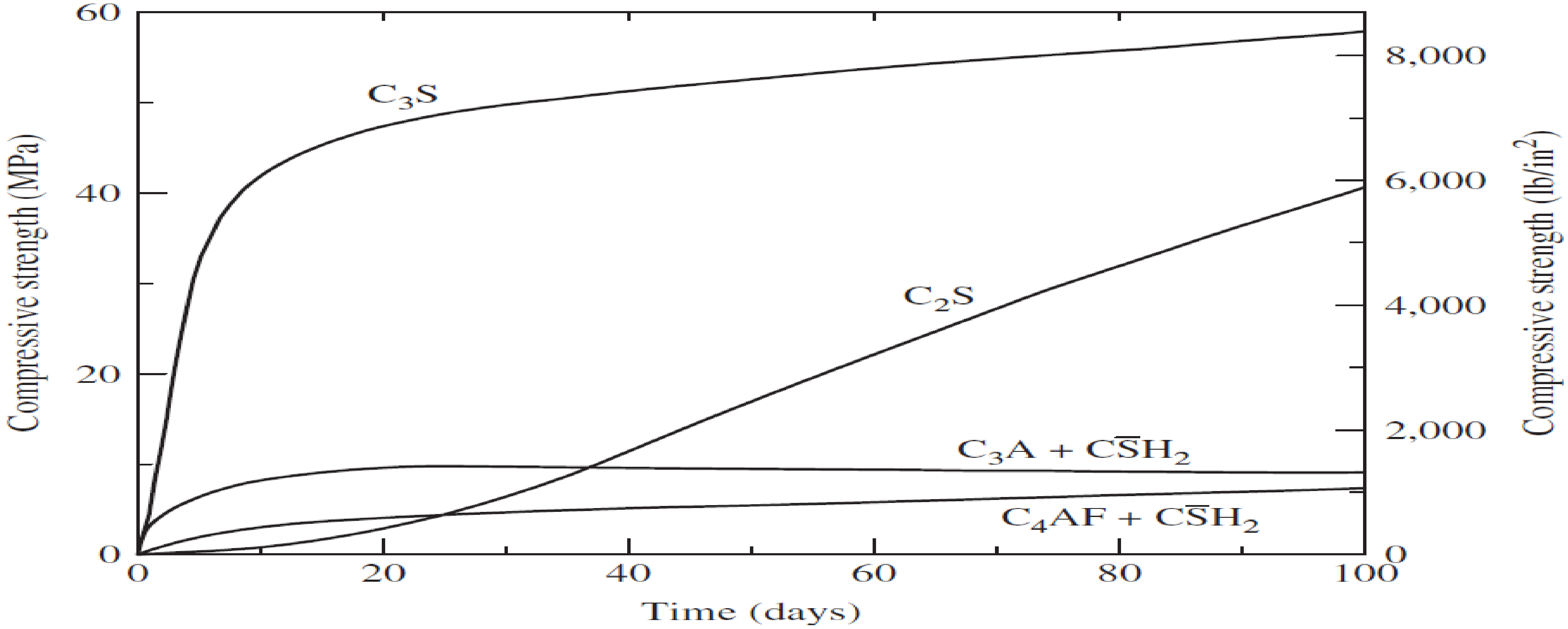


Figure 2-12 Strength development of primary constituents of Portland cement

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

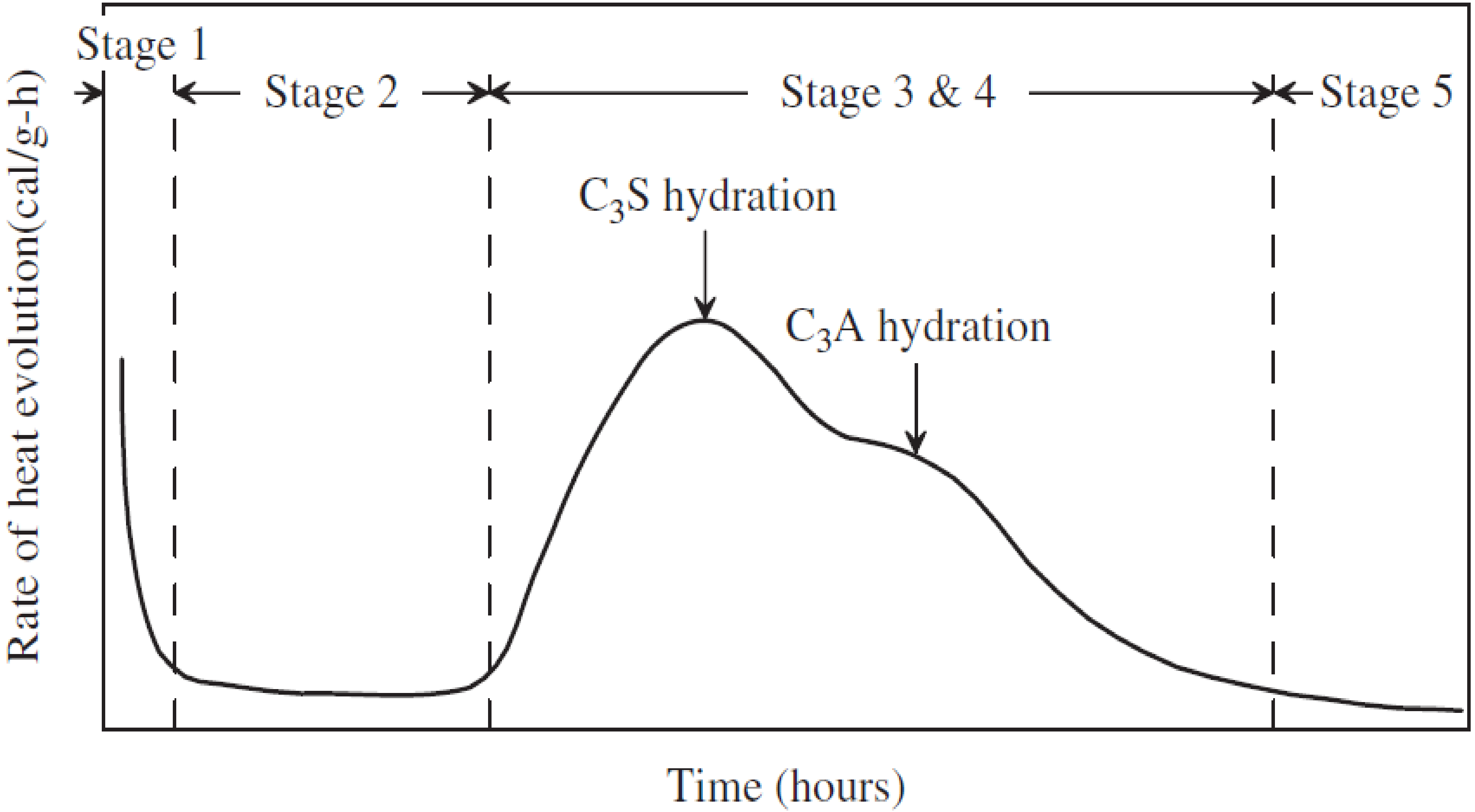


Figure 2-13 A typical calorimetric curve of Portland cement

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.

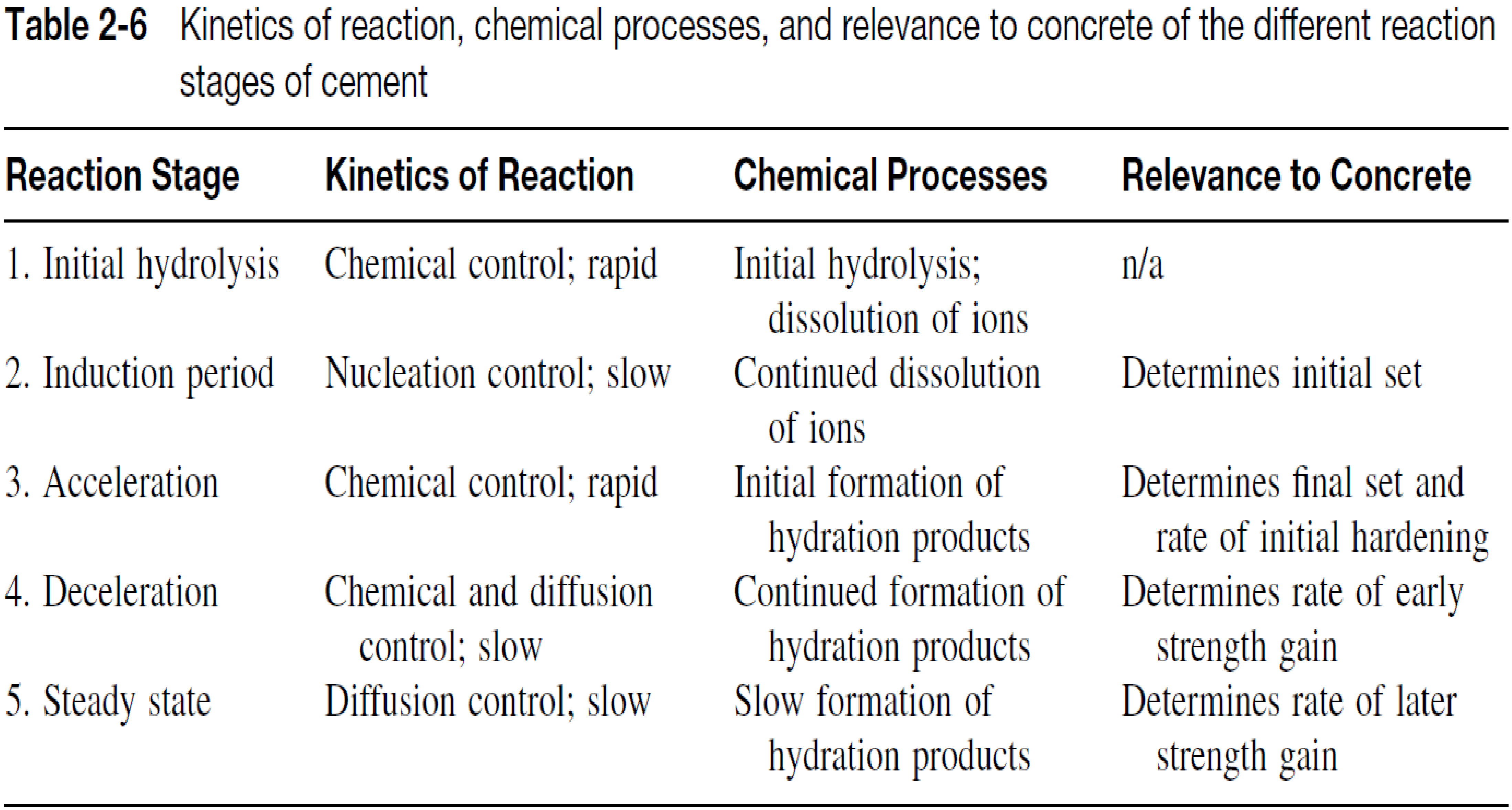


Table 2-6 Kinetics of reaction, chemical processes, and relevance to concrete of the different reaction stages of cement

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.

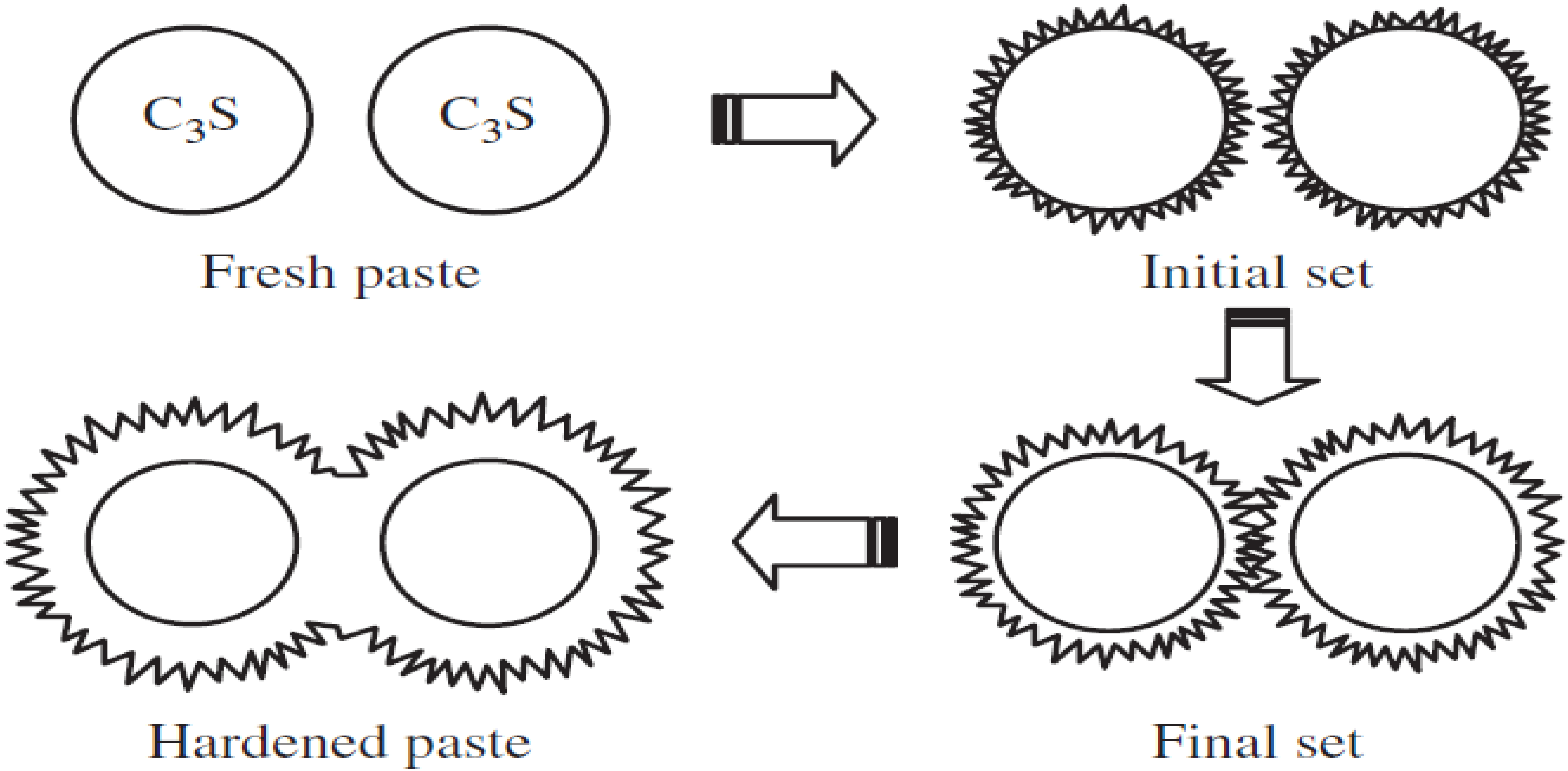


Figure 2-14 Setting of fresh cement paste

2.2.2.5 Types of Portland cements

According to the ASTM standard, there are five basic types of Portland cement:

- Type I regular cement, general use.
- Type II moderate sulfate resistance, moderate heat of hydration
- Type III increase C3S, high early strength
- Type IV low heat
- Type V high sulfate resistance

In BSI, four basic Portland cements are standardized:

- Ordinary Portland cement (OPC),
- Rapid hardening Portland cement (RHPC),
- Low-heat Portland cement (LHPC), and
- Sulfate-resistant Portland cement (SRPC).

OPC is equivalent to type I in ASTM, and RHPC, type III; LHPC, type IV; and SRPC, type V. There is no Portland cement similar to type II in BSI.

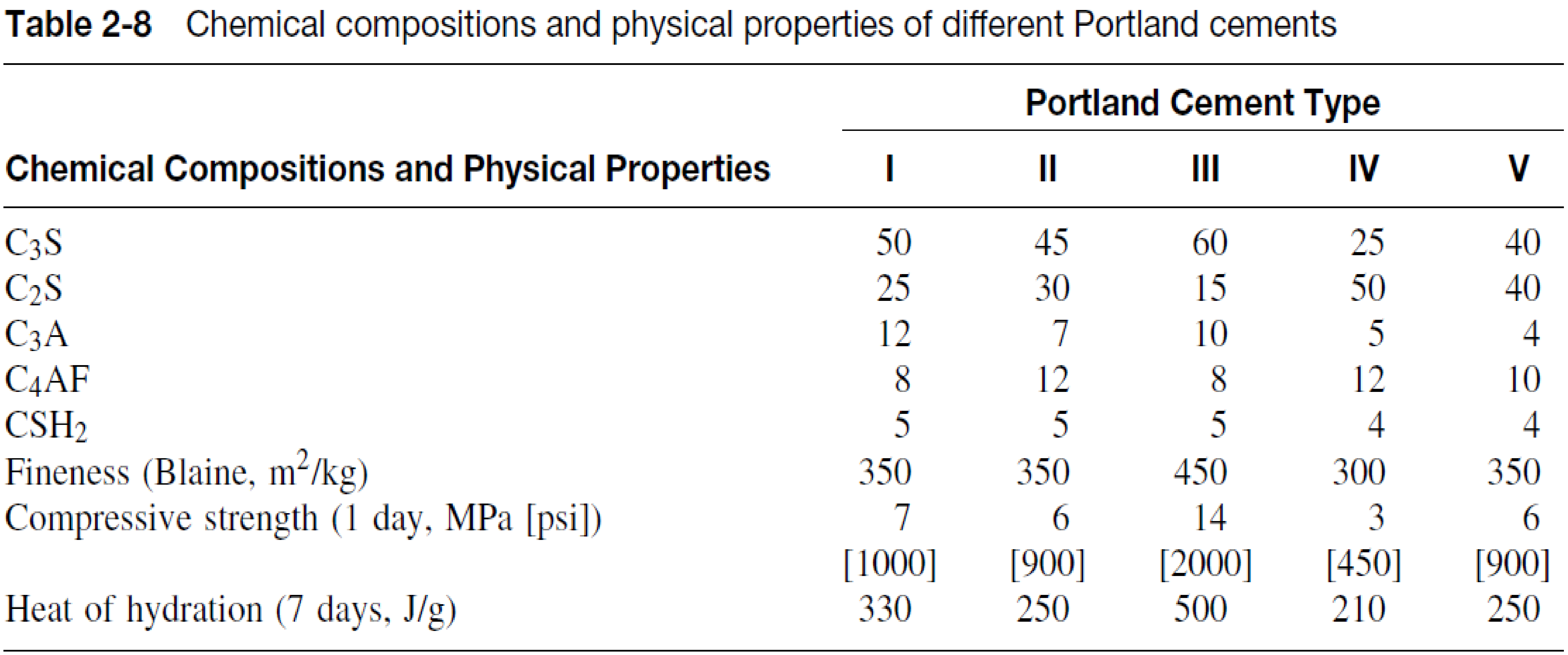


Table 2-8 Chemical compositions and physical properties of different Portland cements

	Portland Cement Type				
Chemical Compositions and Physical Properties	**I**	**II**	**III**	**IV**	**V**
C_3S	50	45	60	25	40
C_2S	25	30	15	50	40
C_3A	12	7	10	5	4
C_4AF	8	12	8	12	10
CSH_2	5	5	5	4	4
Fineness (Blaine, m^2/kg)	350	350	450	300	350
Compressive strength (1 day, MPa [psi])	7 [1000]	6 [900]	14 [2000]	3 [450]	6 [900]
Heat of hydration (7 days, J/g)	330	250	500	210	250

- The typical chemical compositions of five types of Portland cement in ASTM are given in Table 2-8.
- Type I is usually used as a reference, which contains 50% C3S, 25% C2S, 12% C3A, 8% C4AF, and 5% gypsum.
- Compared to type I, type III has more C3S (60%) and less C2S (15%). Moreover, type III has a larger fineness number than type I.
- As a result, the early strength of type III at 1 day is doubled as compared to that of type I.
- Meanwhile, the heat released by type III increases to 500 J/g (type I is 330 J/g).
- On the other hand, type IV has less C3S (25%) and more C2S (50%). Hence, the early strength of type IV at 1 day is only half of that of type I. However, the heat released by type IV greatly decreases to 210 J/g, and thus is called-low heat Portland cement.
- As for type V, its sum of C3A and C4AF is only 14% and much less than the 20% of type I. Since these two compounds readily react with sulfate, the lower content gives it less opportunity to be attacked by sulfate ions.

In addition, Figures 2-20 and 2-21 show the strength and temperature rise for the different types of cement, which are consistent with the information in Table 2-8.

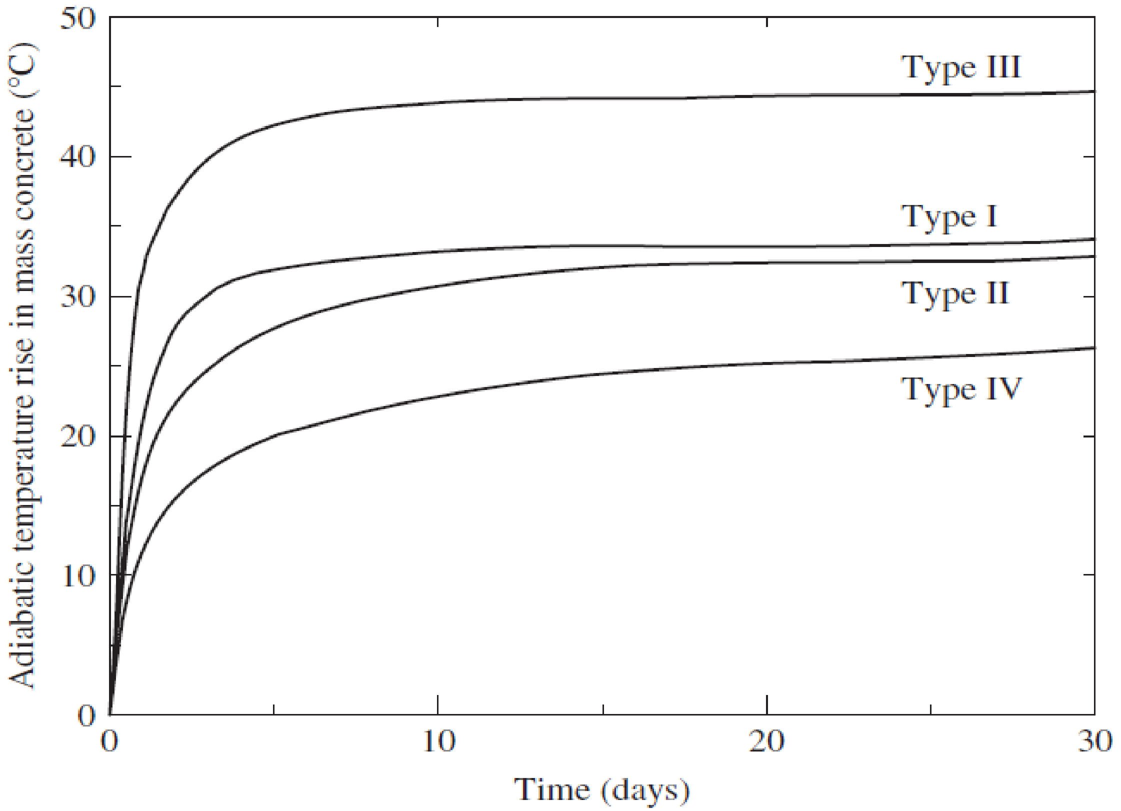


Figure 2-20 Adiabatic temperature rise in mass concretes with different types of cement

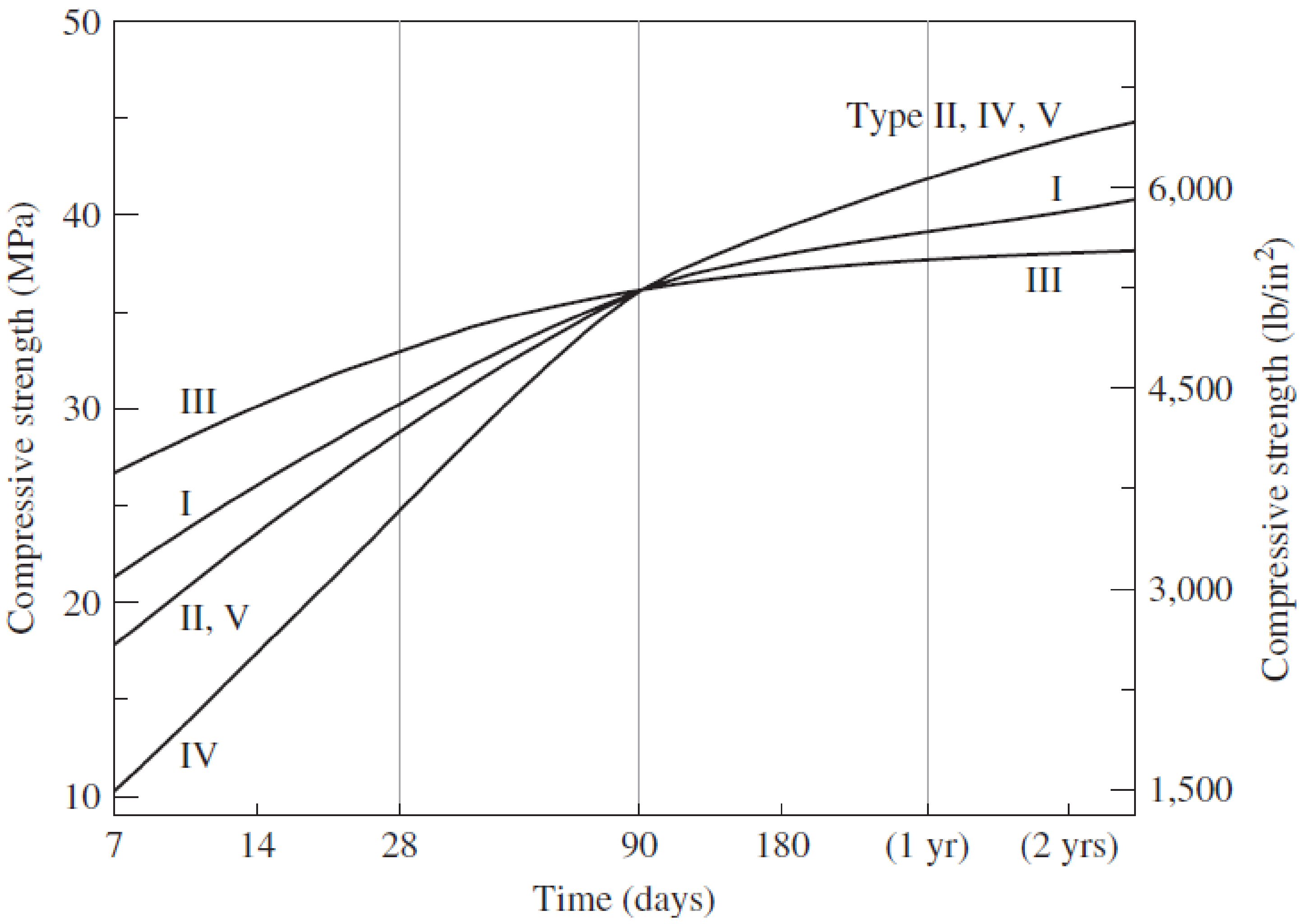


Figure 2-21 Strength development of cement pastes with different types of cement

- From the information provided in Table 2-8, we can evaluate the behaviour of each type of cement.
- The various behaviours provide the basic justification in selecting cement for engineering practice.
- For instance, for massive concrete structures, hydration heat is a big consideration because too much heat will cause a larger temperature gradient, thermal stress, and cracking. **Hence, type IV cement should be the first candidate** and type III should not be used.
- For a marine structure, high sulfate resistance and lower ettringite are needed; thus, **type V** should be selected.
- If high early strength is needed, **type III** will be the best choice.
- Generally, **type I** is the most popular cement used in civil engineering

2.2.2.6 The role of water

Of course, water is necessary for the hydration of cement. However, the water added in the mix is usually much higher than what the chemical reaction needs due to the fluidity requirement of concrete for placing.

Thus, we can distinguish the three kinds of water in cement paste according to their roles:

- **Chemically reacted water**

The chemically reacted water or chemically bonded water is the water that reacts with C, S, A, F, and S to form a hydration products such as C–S–H, CH, and AFt. This type of water is difficult to remove from cement paste and a complete decomposition happens at a temperature about 900◦C.

- **Absorbed water, and**

Absorbed water is the water molecules inside the layers of C–S–H gel. The loss of absorbed water causes shrinkage, and the movement or migration of absorbed water under a constant load affects the creep.

- **Free water.**

Free water is the water outside the C–S–H gel. It behaves as bulk water and creates capillary pores when evaporated, and can influence the strength and permeability of concrete.

Porosity is a major component of the microstructure that is mainly caused by loss of water.

The size of the capillary pores formed due to the loss of free water is in the range of 10 nm to 10 µm. The size of the gel pores involved in absorbed water is in the range of 0.5 to 10 nm.

A knowledge of porosity is very useful since porosity has such a strong influence on strength and durability. According to experiments, the gel porosity for all normally hydrated cements is a constant, with a value of 0.26. The total volume of the hydration products (cement gel) is given by

$\boldsymbol{V_g = 0.68\alpha}$ **cm3/g** of original cement

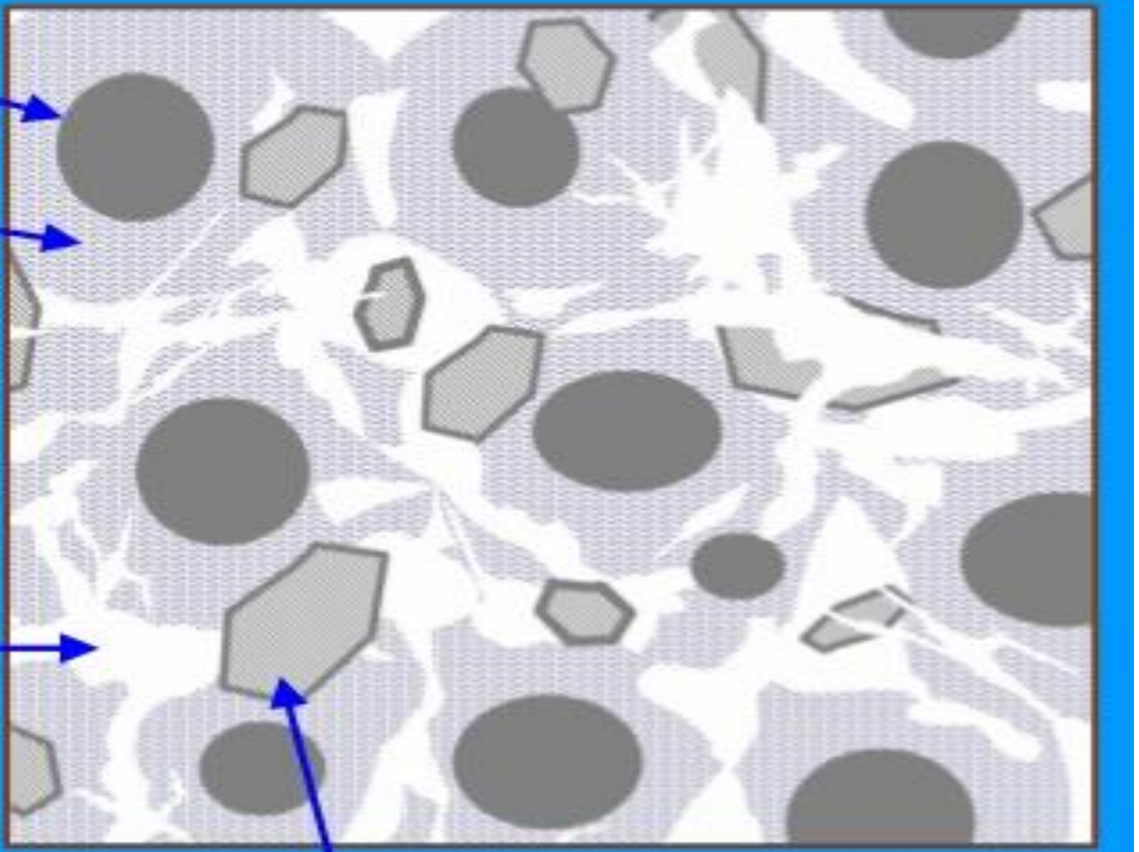
where $\boldsymbol{\alpha}$ represents the degree of hydration.

The capillary porosity can then be calculated by

$\boldsymbol{P_c = W/C - 0.36\alpha}$ **cm3/g** of original cement

Where $\boldsymbol{w}$ is the original weight of water, **c** is the weight of cement, and $\boldsymbol{w/c}$ is the water to cement ratio. It can be seen that with an increase of $\boldsymbol{w/c}$, the capillary pores increase.

Simplified scheme of hydrated cement paste microstructure



1. Unhydrated cement

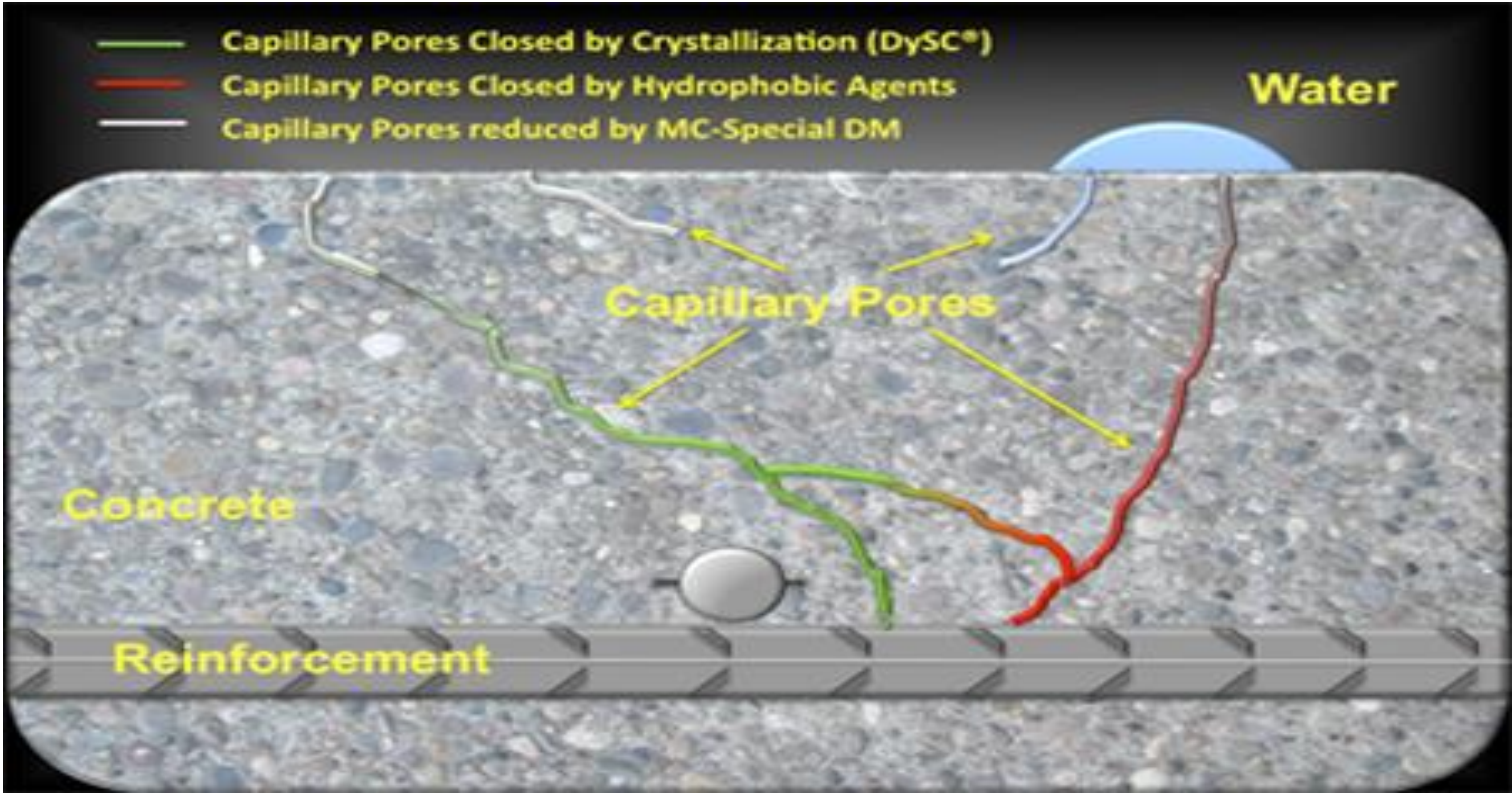
2. C-S-H gel containing gel pores (interlayer water)

Gel (or interlayer) pores have size of 0.5-2.5 nm and occupy about 28 vol. % of C-S-H gel

3. Capillary pores (capillary water)

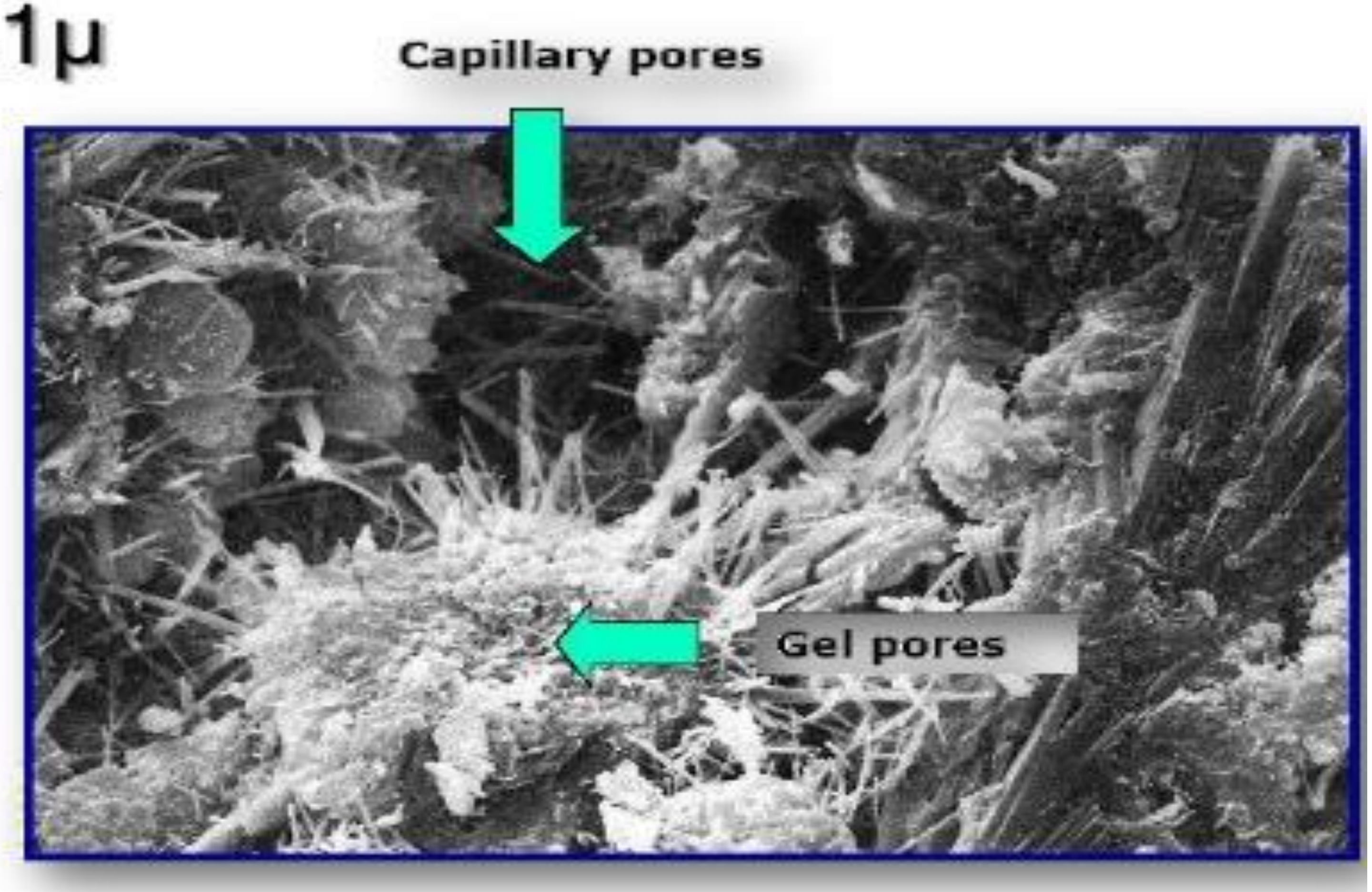
Capillary pores can have sizes from 10 to 1000 nm (1 μm) and even up to 5 μm. Volume and size depends on water/cement ratio and degree of hydration

4. Hexagonal crystals of calcium hydroxide (portlandite)


Capillary Pores Closed by Crystallization (DySC®)
Capillary Pores Closed by Hydrophobic Agents
Capillary Pores reduced by MC-Special DM
Water
Capillary Pores
Concrete
Reinforcement

Concrete Porosity

- Capillary Pores 0.1µ
- Gel Pores <0.01µ



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Capillary Segmentation

- **Capillary porosity**

capillary pores larger in size compared to that of gel pores, will allow water and hence aggressive chemicals into the concrete, which adversely affects the durability of concrete in long term

- **C-S-H gel porosity**

Less impact on concrete strength and durability

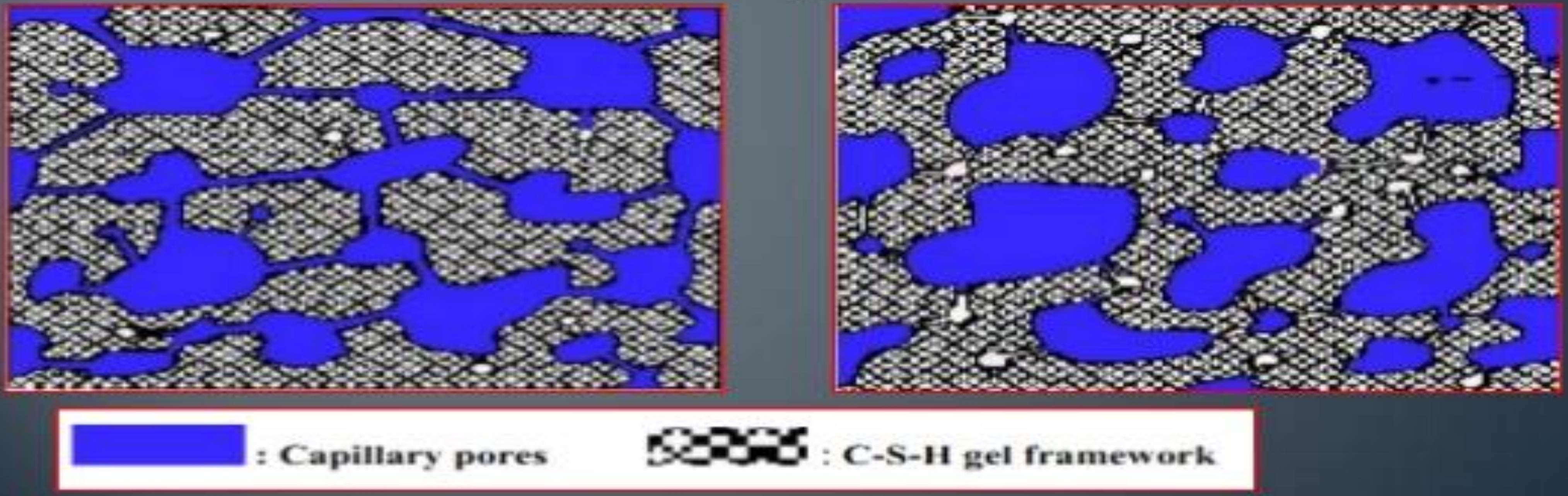

Fig: a)Capillary pores interconnected b) Partially connected capillary pores

The **gel/space** ratio (*X*) is defined as:

$$X = \frac{\text{volume of gel (including gel pores)}}{\text{volume of gel} + \text{volume of capillary pores}} = \frac{0.68\alpha}{0.32\alpha + w/c}$$

- The **gel/space** ratio reflects the percentage of solid materials in a cement paste. The higher the ratio, the more solid the materials and hence the higher the compressive strength.
- It can be seen from Equation that the **gel/space** ratio is inversely proportional to the ***w/c***.
- It can be deduced that a higher ***w/c*** leads to a low compressive strength of cement paste or concrete.
- The minimum ***w/c*** ratio for complete hydration is usually assumed to be **0.36 to 0.42.**
- It should be noted that complete hydration never happens and that residual anhydrate cement is beneficial for attaining a high ultimate strength.
- The space requirements for the cement gel are less than the requirements of water plus cement particles so that when the available water is used up, the cement paste will self-desiccate.

(d) *Soundness*: Unsoundness in cement paste results from excessive volume change after setting. Unsoundness in cement is caused by the slow hydration of MgO or free lime. The reactions are

$MgO + H_2O \rightarrow Mg(OH)_2$

and $CaO + H_2O \rightarrow Ca(OH)_2$

Another factor that can cause unsoundness is the later formation of ettringite.

Since these reactions are very slow processes, taking several months and even years to finish, and their hydration products are very aggressive, their crystal growth pressure will crack and damage the already hardened cement paste and concrete.

The soundness of the cement must be tested by an accelerated method due to the slow process.

One test is called the Le Chatelier test (BS 4550), and is used to measure the potential for the volumetric change of the cement paste.

The Le Chatelier test is used mainly for free lime detection.

The main procedures are as follows:

- Fill the cylinder-shaped container with cement paste of normal consistency as shown in the figure
- Cover the container with glass plates.
- Immerse in water (20◦C) and measure the distance of the indicator at the top of the apparatus.
- Boil the specimen for 1 h and measure the distance again after cooling.
- Expansion should be less than 10mm for acceptable cement quality.

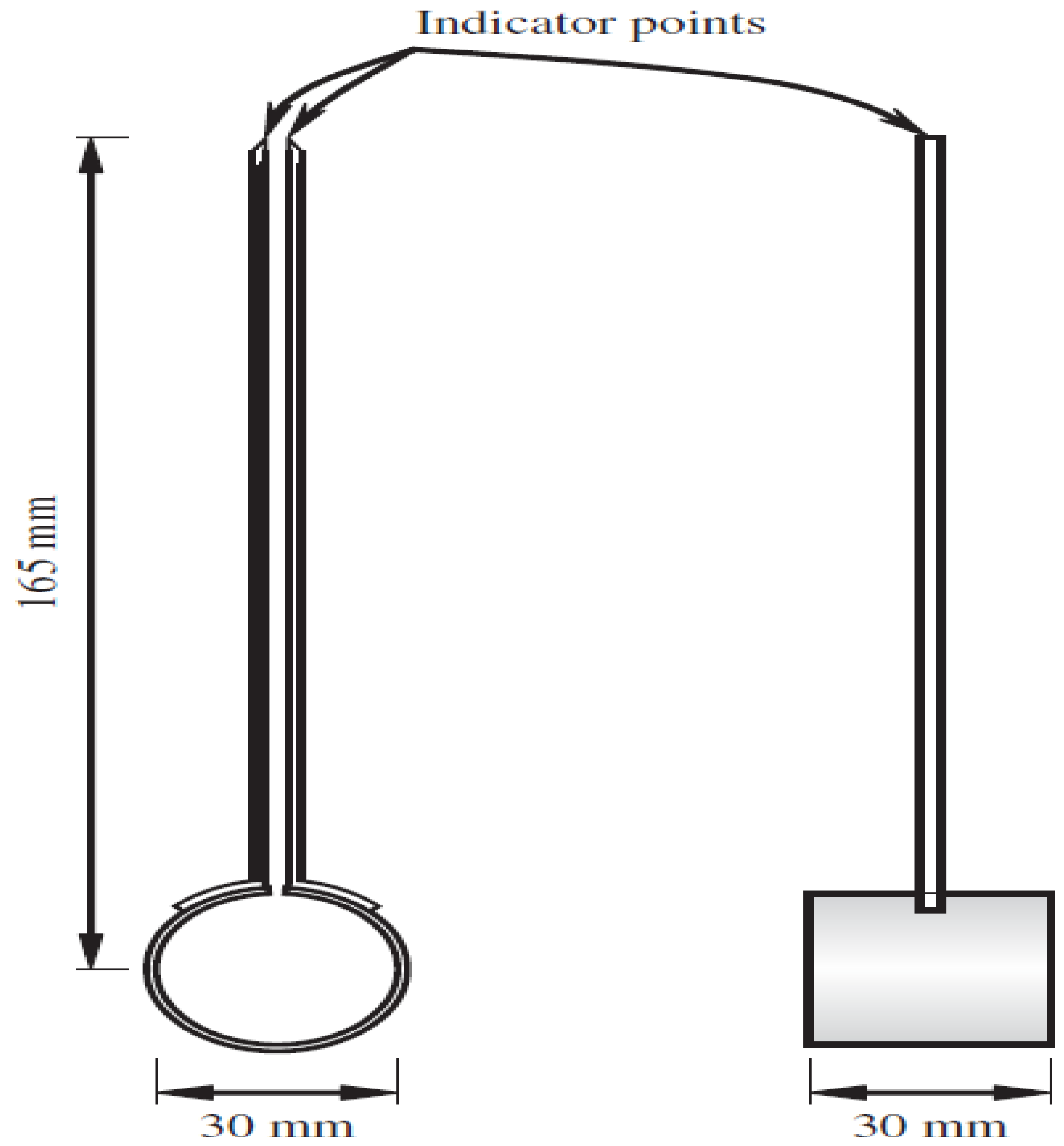

Figure 2-24 Le Chatelier test apparatus

- Another method is the autoclave expansion test (ASTM C151), which uses an autoclave to increase the temperature to accelerate the process. The procedures are as follows:
- Mold a cement paste with normal consistency into a container and cure normally for 14 h.
- Then remove from the mold, measure the size of the specimen, and place the specimen into autoclave.
- Raise the temperature in the autoclave so that the stem pressure inside can reach 2MPa in 45 to 75 min. And Maintain the pressure of 2MPa for 3 h.
- Cool the autoclave down so that the pressure is released in 1.5 h.
- Cool the specimen in water to 23°C in 15 min. After another 15 min, measure the size of the specimen again;
- The expansion must be less than 0.80% to be acceptable.
- Autoclave testing can test both excess free lime and excess MgO.

2.2.3 Geopolymers

2.2.3.1 Advantages and applications of geopolymers

Compared with ordinary Portland cement, newly developed inorganic binder geopolymers possess the following characteristics:

- ***Abundant raw material resources***

Any pozzolanic compound or source of silicates or aluminosilcates that is readily dissolved in alkaline solution will suffice as a source for the production of a geopolymer.

- ***Energy saving and environment protection***

about 60% less energy is required, and 80–90% less CO2 is generated for the production of geopolymers than for Portland cement

- ***Good volume stability***

Geopolymers have 80% lower shrinkage than Portland cement. *Reasonable strength gain in a short time*: **Geopolymers can obtain 70% of the final compressive strength in the first 4 hrs of setting.**

- ***High fire resistance and low thermal conductivity***

Geopolymer cement possesses excellent high temperature resistance up to 1200◦C and can endure 50-kW/m2 fire exposure without sudden property degradation. In addition, no smoke is released after the extended heat flux.

The heat conductivity of geopolymers varies from 0.24 to 0.3 w/m-k, and compares well with that of lightweight refractory bricks (0.3 to 0.438 w/m-k).

Geopolymers are an abundant raw resource, and have low CO2 emission, less energy consumption, low production cost, high early strength, and fast setting.

These properties make geopolymers suitable for applications in many fields of industry, such as **civil engineering**, **automotive and aerospace industries**, nonferrous foundries and metallurgical industries, plastics industries, **waste management**, art and decoration, and retrofitting of buildings.

2.2.4 Magnesium phosphoric cement (MPC)

2.2.4.1 Advantages and applications of MPC

MPC concrete is a type of artificial stone made from an acid–base reaction of magnesia and phosphates. They possess some properties that Portland cements do not possess according to the previous studies. Therefore, they can be utilized in fields in which Portland cements are not suitable.

The applications of MPCs include the following:

(a) Due to its rapid setting and high early strength, MPC has been utilized in rapid repair of concrete structures, such as highways, airport runways, and bridge decks, for many years.

(b) MPC can be incorporated with nontoxic industrial waste, such as class F fly ash (FA) and be converted into useful construction materials.

(d) MPC can be used in the management and stabilization of toxic and radioactive wastes, including solids and liquids.

(e) **MPCs are very suitable for repairing deteriorated concrete pavements in cold regions.**

(f) The raw material of MPC is hard burnt magnesia, and is, in fact, a refractory material. Therefore, **MPC can be designed to be fireproof and/or as a cold setting refractory, according to practical need.**

2.2.5 Magnesium oxychloride cement

Magnesium oxychloride cement (MOC), also known as Sorel cement (Sorel, 1867), is a type of nonhydraulic cement. It is formed by mixing powdered magnesium oxide (MgO) with a concentrated solution of magnesium chloride ($MgCl2$).

Magnesium oxychloride cement has many superior properties as compared to ordinary Portland cement: these include:

- **It has high fire resistance,**
- **low thermal conductivity,**
- **good resistance to abrasion,**
- **Is unaffected by oil, grease, and paint.**
- **It also has high early strength**
- **is suitable for use with all kinds of aggregates in large quantities,** including gravel, sand, marble flour, asbestos, wood particles, and expanded clays.
- **Has a lower alkalinity of magnesium oxychloride (pH of 10–11),** which makes it suitable for use with glass fiber.

Thank you for your attention!