CONCRETE TECHNOLOGY MODULE

WEEK 2

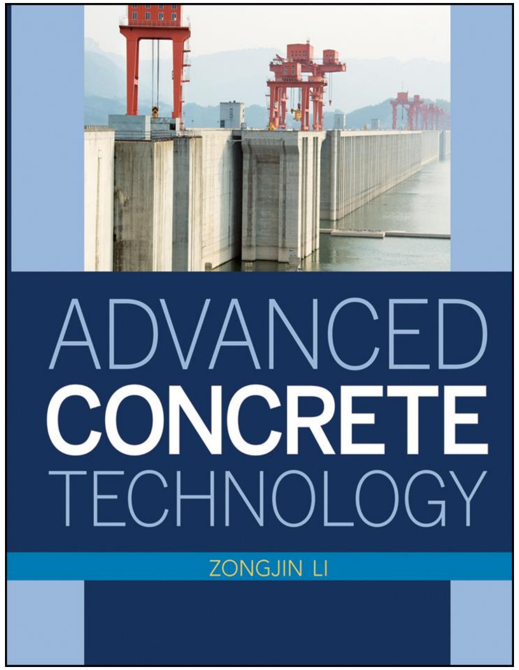
REFERENCES

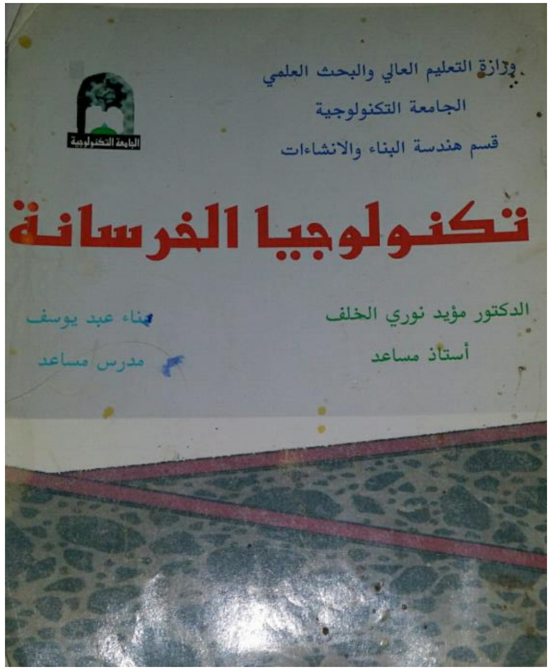
Main Reference

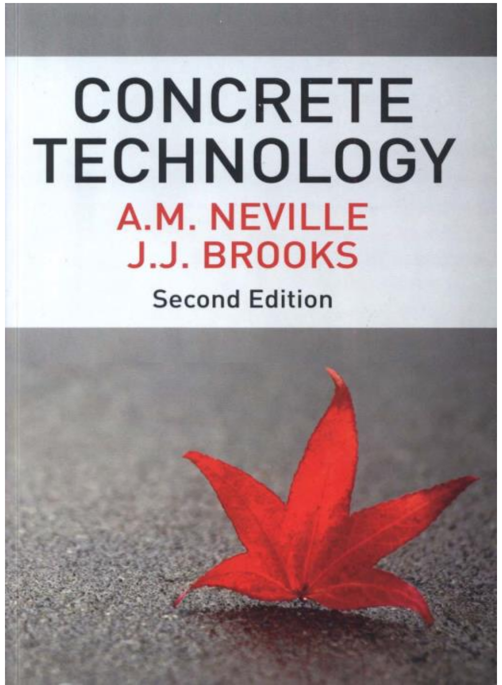
- Advanced concrete technology by Zongjin Li

Other references

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







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2.2.1 CLASSIFICATION OF BINDERS

1) **Organic Binder**

- An organic binder can be easily burned and thus cannot stand with fire.
- **Polymer and Asphalt** are two commonly used organic binders.

Polymer can be classified into:

- **Thermoplastics**
- the chains interact with one another through weak van der Waal forces
- The stiffness values of thermoplastics are very low, and range from 0.15 to 3.5 GPa at room temperature
- **Thermoset**
- The individual chains interact through van der Waal force as well as occasional cross-links.
- The cross-links are also hydrocarbon chains whose ends are bonded to the main polymer chains. Due to their presence, **the stiffness of thermosets is higher than that of thermoplastics.**

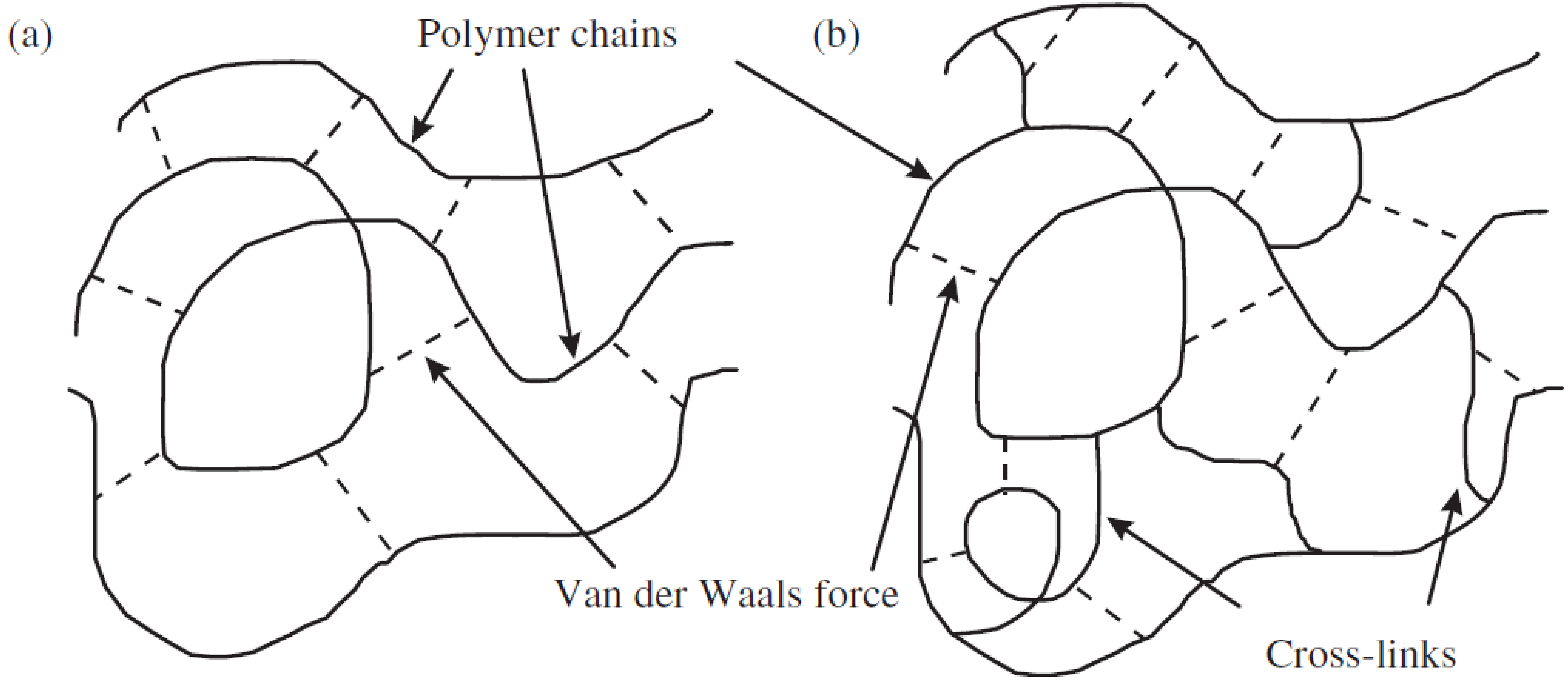


Figure 2-7 Difference between (a) thermoplastics and (b) thermosets

Elastomers or rubbers

- Are thermosets with a small number of cross-links. Also, they have very low glass transition temperatures, which means that the van der Waals force has disappeared at room temperature.
- Therefore, rubbers have very low stiffness values within the range of 0.002 to 0.1 GPa.
- In concrete technology, the most widely used polymers are **Epoxy and Latex.**
- **Epoxy** is composed of resin and hardener and can be used to bind aggregate together or to repair cracks
- **Latex** is mainly used to modify the concrete properties for repair.
- **Epoxy resins** are thermosetting polymers

Asphalt

- Asphalt cement is mainly obtained from the distillation of crude oil.
- asphalt is **generally hard and relatively solid** in its original form
- To use it in practice, asphalt needs to be **softened by heating.**
- **To reduce the need for heating,** asphalt can be modified by the addition of volatile components or emulsifying agents.

Depending on the added component, there are three different types of liquid asphalts:

1. **Rapid-curing (RC)** cutback, a mixture of asphalt and gasoline; it produce a harder material, which is appropriate for hot weather.
2. **Medium-curing (MC)**, a mixture of asphalt and kerosene (lamp oil); MC cutbacks give a softer material, which is less brittle under cold weather. and
3. **Slow-curing (SC)**, a mixture of asphalt and diesel. SC cutbacks, which would produce too soft a material, are used only for dust binding.

Curing here refers to the hardening of the asphalt due to evaporation of the volatile component.

Inorganic Binders

- are usually made of different natural minerals.
- The inorganic binder can be further classified into **nonhydaulic** cement and **hydaulic** cement.
- However, nonhydraulic here does not mean that it does not need water. In fact, all inorganic binders need water for mixing and reacting to form bonds. Nonhydraulic cement also needs water for mixing.
- Nonhydraulic means only that such cement cannot harden and thus gain strength in water.
- Typical examples of nonhydraulic cement are **gypsum and lime.**
- They have been used since 6000 BC, as mentioned in Chapter 1.

Gypsum is a soft mineral composed of calcium sulfate dihydrate, called two-water gypsum. Under a temperature of 130◦C, two-water gypsum can change to half-water gypsum and release some water:

$$2CaSO_4 \cdot 2H_2O \xrightarrow{(130^\circ C)} 2CaSO_4 \cdot \frac{1}{2}H_2O + 3H_2O$$

When half-water gypsum is mixed with water, **it can return to two water gypsum and form bonds.**

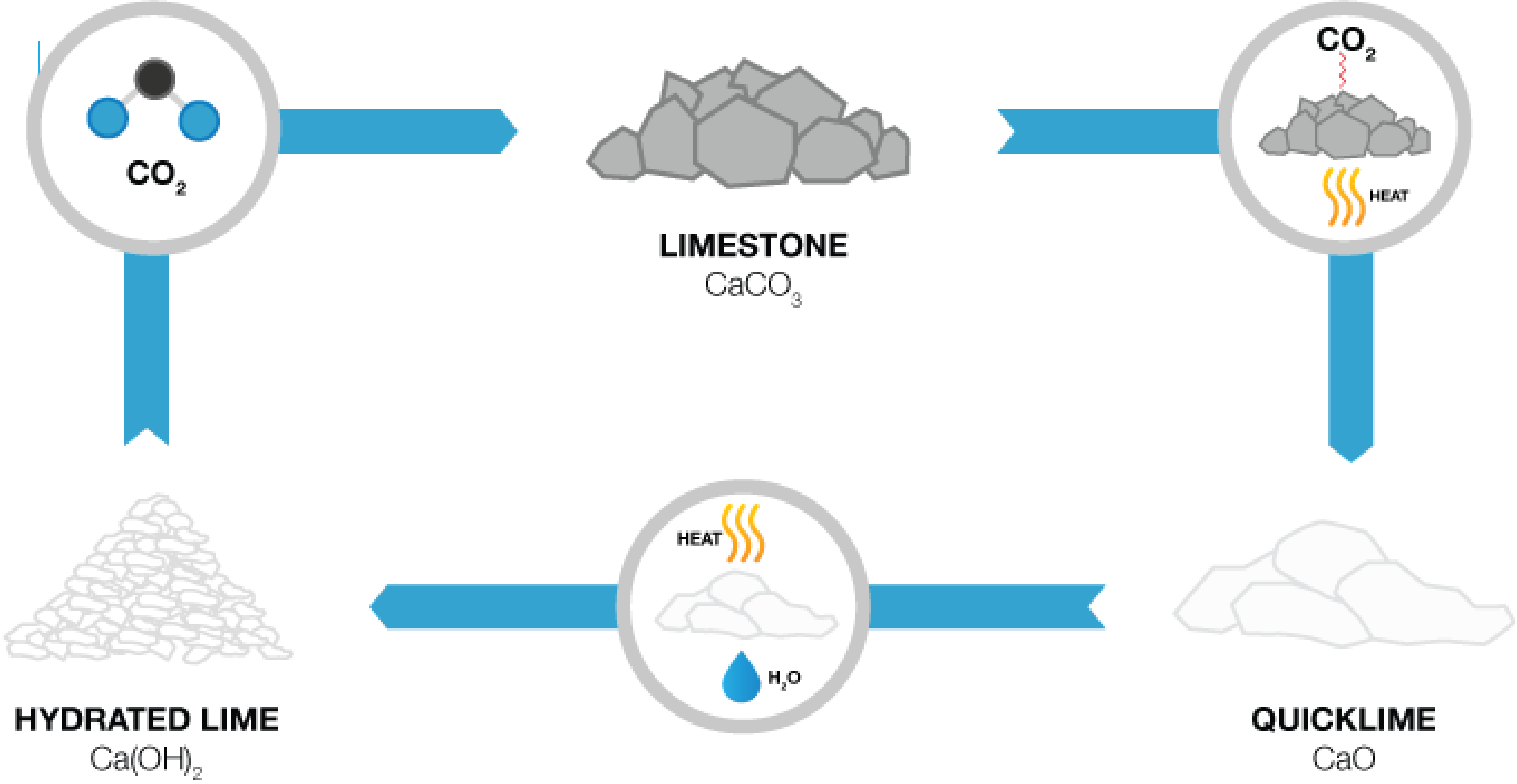
Lime is the product of calcination of limestone under 1000◦C, and consists of the oxides of calcium:

$$CaCO_3 \xrightarrow{(1000^\circ C)} CaO + CO_2$$

When CaO is mixed with water again, the following reactions occur:

$$CaO + CO_2 + H_2O \rightarrow Ca\,(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

- **It can be seen that lime returns to limestone and forms bonds.**



CO2
LIMESTONE
CaCO3
CO2
HEAT
HEAT
H2O
HYDRATED LIME
Ca(OH)2
QUICKLIME
CaO

Hydraulic cement can harden and gain strength in water.

The main difference in composition between two types of inorganic cements is that the hydraulic cement contains some amounts of clayey impurities (silicate composition).

Examples of hydraulic cement include **hydraulic lime, pozzolan cement, and Portland cement.**

Hydraulic lime is composed of lime and clayey impurities.

The pozzolan cement contains lime and volcanic rock powders.

Portland cement (PC) concrete is the most popular and widely used building material, due to the availability of the basic raw materials all over the world, and its ease of use in preparing and fabricating all sorts of shapes.

The applications of concrete in the realms of infrastructure, habitation, and transportation have greatly promoted the development of civilization, economic progress, stability, and quality of life.

Yet, there are **two major drawbacks** with respect to sustainability:

(1) **About 1.5 tons of raw materials** is needed in the production of **every ton of PC,** while, at the same time, about **1 ton of carbon dioxide (CO2)** is released into the environment during the production. The world's cement production has increased from **1.4 billion tons in 1995** to almost **3 billion tons by the year 2009**. Therefore, the production of PC is an extremely resource- and energy-intensive process.

(2) **Concrete made of PC deteriorates** when exposed to harsh environments, under either normal or severe conditions. Cracking and corrosion have significant influence on service behaviour, design life, and safety.

To overcome these problems, other different cementitious materials have been developed recently. Two of them to be discussed in this chapter are **geopolymer and magnesium phosphate cement (MPC).** Compared with Portland cement, the properties of these two cements have some advantages to the sustainable development of modern society.

2.2.2 Portland cement

Development of Portland cement can be summarized as follows:

1796	James Parker	England	Patent on a natural hydraulic cement
1813	Vicat	France	Artificial hydraulic lime
1824	Joseph Aspdin	England	Portland cement

Portland cement was developed by Joseph Aspdin in 1824, so named because its color and quality are similar to a kind of limestone, Portland stone (Portland, England).

2.2.2.1 Manufacture of Portland cement (PC)

- Portland cement is made by blending an appropriate mixture of limestone and clay or shale together, and by heating them to 1450◦C in a rotary kiln.
- Currently, the capability of a rotary kiln can reach 10,000 metric tons daily.
- The preliminary steps in the production process of PC are **a variety of blending and crushing operations.**
- The raw feed must have a **uniform composition and be of fine enough size that reactions among the components can be completed in the kiln.**
- Subsequently, the **burned clinker is ground with gypsum** to form the familiar grey powder known as Portland cement.
- The basic raw materials used for manufacturing Portland cement **are limestone, clay, and iron ore.**

The primary reactions during the calcination process are listed as below:

(a) Clay is mainly providing silicates (SiO2) together with small amount of Al2O3 and Fe2O3.

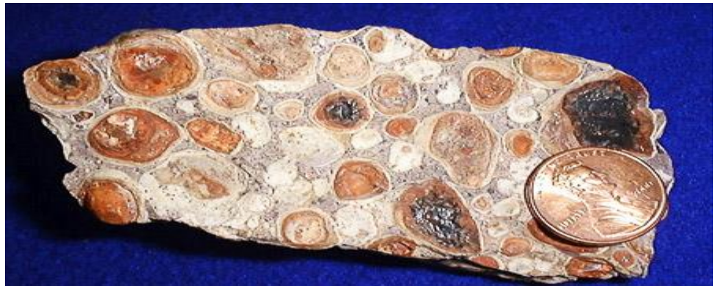
- The decomposition of clay happens at a temperature around 600◦C:

$$\text{Clay} \xrightarrow{(600^\circ\text{C})} SiO_2 + Al_2O_3 + Fe_2O_3 + H_2O$$

(b) Limestone (CaCO3) is mainly providing calcium (CaO) and is decomposed at 1000◦C:

$$CaCO_3 \xrightarrow{(1000^\circ\text{C})} CaO + CO_2$$

(c) Iron ore and bauxite (source of aluminium) provide additional aluminium and iron oxide (Fe2O3), **which help the formation of calcium silicates at low temperature.** They are incorporated into row mix.



(d) There are different temperature zones in a rotary kiln. At various temperatures between 1000 and 1450◦C, different chemical compounds are formed. The initial formation of **C2S occurs at a temperature of around 1200◦C. C3S is formed around 1400◦C.**

$$\left.\begin{array}{l}\text{Limestone}\\ \text{Clay}\\ \text{Iron ore, bauxite}\end{array}\right\} \xrightarrow[\text{High temperature}]{(1450^{\circ}C)} \left\{\begin{array}{l}3CaO\cdot SiO_2\\ 2CaO\cdot SiO_2\\ 3CaO\cdot Al_2O_3\\ 4CaO\cdot Al_2O_3\cdot Fe_2O_3\end{array}\right.$$

(e) The final product from the rotary kiln is called clinker. **Pulverizing the clinker into small sizes (<75 µm) with addition of 3–5% gypsum or calcium sulf produces the Portland cement.**

- **Gypsum added is to control fast setting caused by 3CaO · Al2O3.**

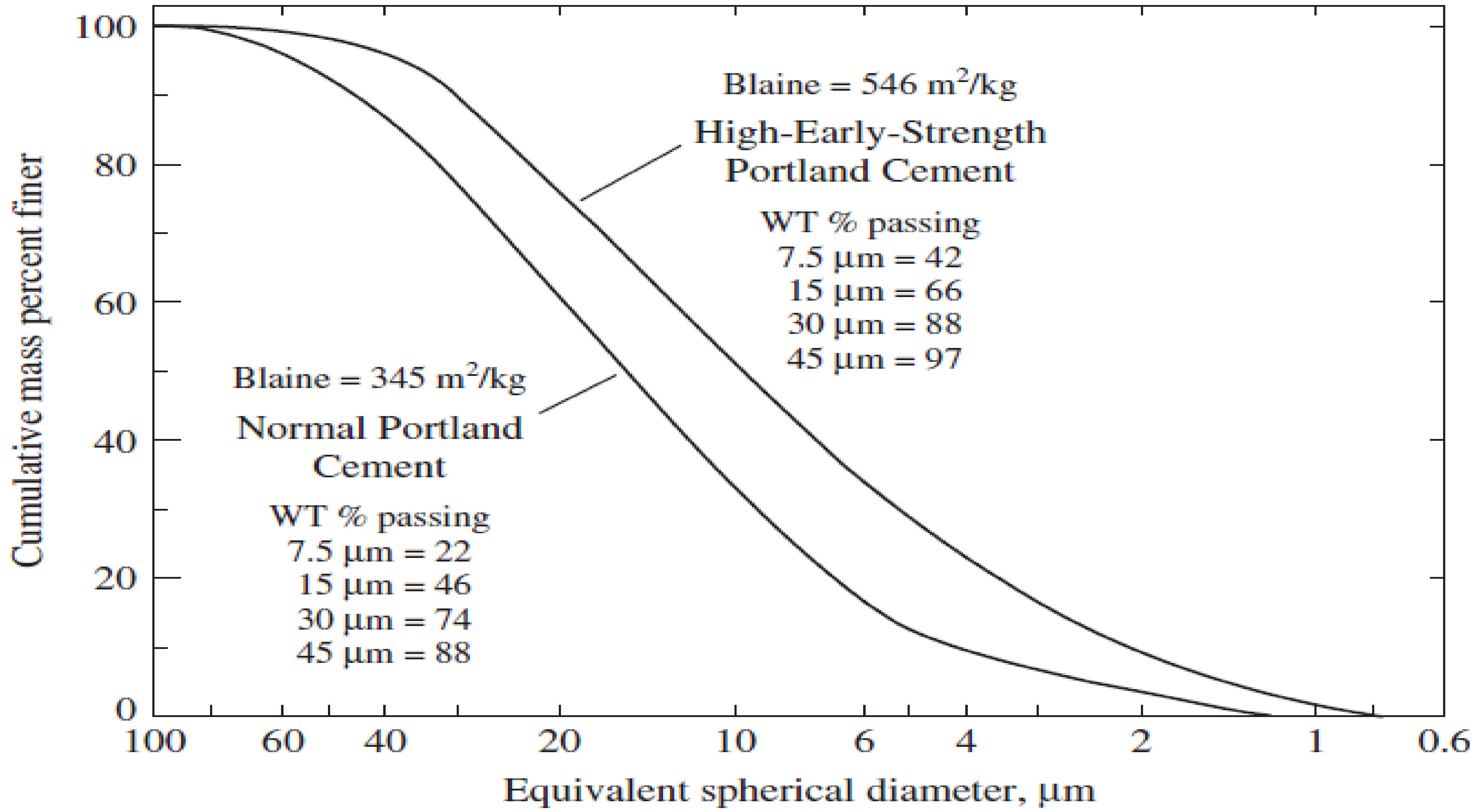


Figure 2-10 Typical particle size distributions of Portland cement

2.2.2.2 Chemical composition

(a) ***Abbreviations***: In cement chemistry, the following abbreviations are adopted. Please note that they are not consistent with other types of chemistry, although these notations are also frequently used in ceramic chemistry.

$$CaO = C \qquad SiO_2 = S \qquad Al_2O_3 = A \qquad Fe_2O_3 = F$$
$$H_2O = H \qquad SO_3 = \overline{S} \qquad MgO = M$$

Thus, we can write $Ca(OH)_2 = CH$, $3CaO = C_3$, and $2CaO \cdot SiO_2 = C_2S$.

(b) ***Major compounds***: The major compounds of ordinary Portland cement are listed in Table 2-4.

They are C3S, C2S, C3A, and C4AF.

- C3S is called tricalcium silicate;
- C2S, dicalcium silicate;
- C3A, tricalcium aluminate; and
- C4AF, tetracalcium aluminoferrite.

In addition, C3S the nickname **alite**; C2S, **belite**; and C4AF, **ferrite**.

Table 2-4 Major compounds of ordinary Portland cement

Compound	Oxide Composition	Color	Common Name	Weight Percentage
Tricalcium silicate	C_3S	White	Alite	50
Dicalcium silicate	C_2S	White	Belite	25
Tricalcium aluminate	C_3A	white/grey	n/a	12
Tetracalcium aluminoferrite	C_4AF	Black	Ferrite	8

It should be indicated that **C3S and C2S occupy 68 to 75%** of Portland cement.

Since the primary constituents of Portland cement are **calcium silicates**, we can define **Portland cement** ***as a material that combines CaO and SiO2 in such a proportion that the resulting calcium silicate will react with water at room temperature and normal pressure.***

The typical oxide composition of a general-purpose Portland cement can be found in Table 2-5.

Table 2-5 Typical oxide composition of a general-purpose Portland cement

Oxide	Shorthand Notation	Common Name	Weight Percent
CaO	C	lime	64.67
SiO_2	S	silica	21.03
Al_2O_3	A	alumina	6.16
Fe_2O_3	F	ferric oxide	2.58
MgO	M	magnesia	2.62
K_2O	K	alkalis	0.61
Na_2O	N	alkalis	0.34
SO_3	$\overline{S}$	sulfur trioxide	2.03
CO_2	$\overline{C}$	carbon dioxide	—
H_2O	H	water	—

From the weight percentage of these oxides, the weight percentage of **C3S, C2S, C3A, and C4AF** in Portland cement can be calculated using an equation initially **developed by Bogue and adopted by ASTM C150** as follows:

$$C3S(\%) = 4.071C - 7.600S - 6.718A - 1.450F - 2.852S$$

$$C2S(\%) = 2.867S - 0.754C3S$$

$$C3A(\%) = 2.650A - 1.692F$$

$$C4AF(\%) = 3.043F$$

where C, S, A, F, and S are weight percentage of corresponding oxide in a Portland cement such as what listed in Table 2-5.

- **It should be noted that the above equations are valid only when A/F ≥ 0.64. Fortunately, most Portland cements satisfy the condition.**

(c) *Minor components of Portland cement*: The most important minor components of cement are gypsum, MgO, and alkali sulfates.

Gypsum ($2CaSO_4 \cdot 2H_2O$) is added in the last procedure of grinding the clinker to produce Portland cement.

The reason for adding gypsum cement is to avoid the flash setting caused by fast reaction of C_3A,

because Gypsum can react with C_3A and form a hydration product called **ettringite** on the surface of C_3A to prevent further reaction of C_3A as a barrier.

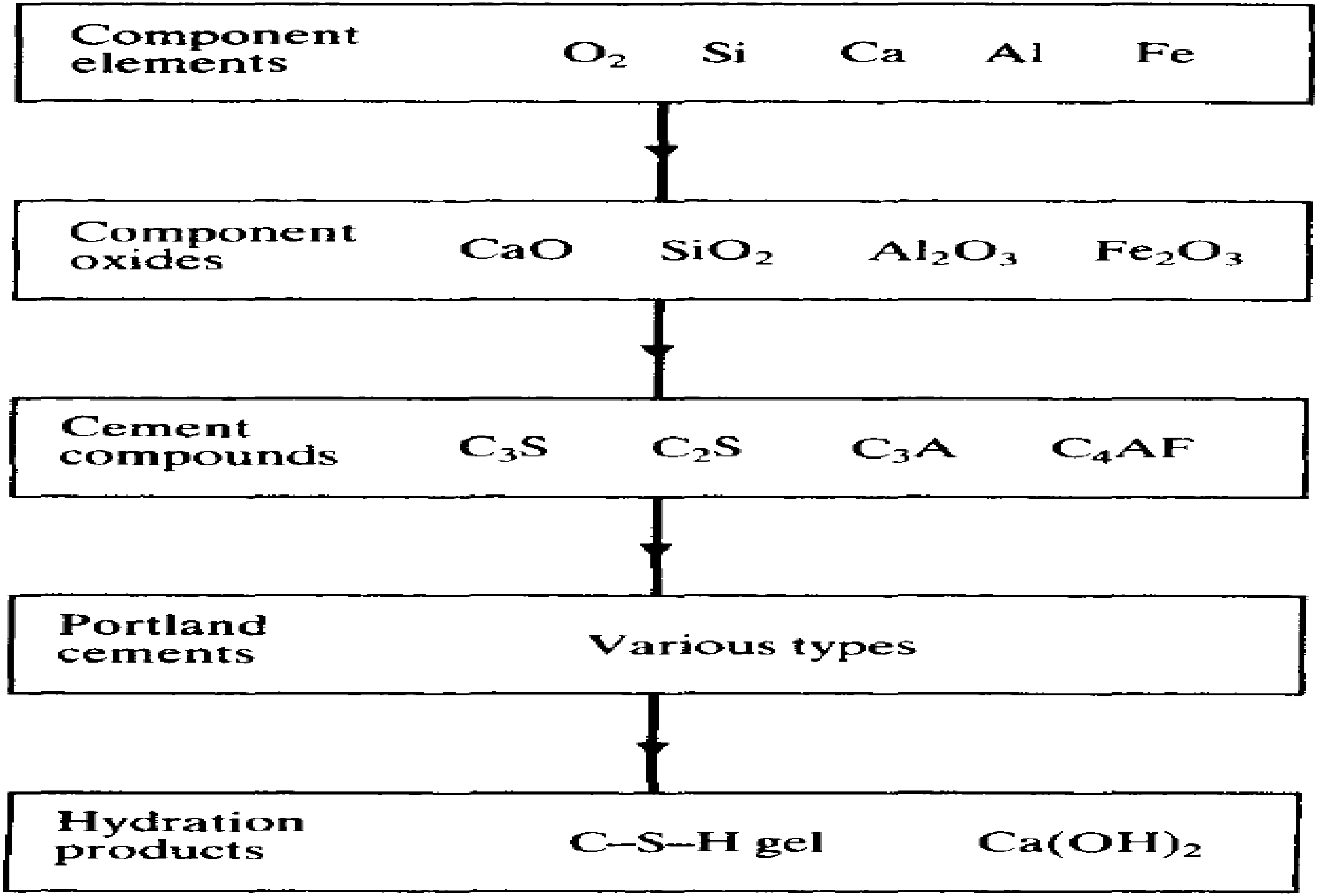
The normal percentage of gypsum added to cement is about **4–5%.**

Only when gypsum is more than 3% in a Portland cement, can the formation of ettringite be guaranteed.

When the percentage of gypsum is between 1 and 3%, both ettringite and monosulfoaluminate will be formed.

When the percentage of gypsum is less than 1%, only monosulfoaluminate will be formed.

- Alkalies (MgO, Na2O, and K2O) can increase the pH value of concrete up to 13.5, which is good for reinforcing steel protection.
- However, a high alkaline environment can also cause some durability problems, such as alkali aggregate reaction and leaching.


Component elements
O2 Si Ca Al Fe
Component oxides
CaO SiO2 Al2O3 Fe2O3
Cement compounds
C3S C2S C3A C4AF
Portland cements
Various types
Hydration products
C–S–H gel Ca(OH)2

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:

$$\mathbf{2C3S + 11H \rightarrow C3S2H8 + 3CH}$$

$$\mathbf{2C2S + 9H \rightarrow C3S2H8 + CH}$$

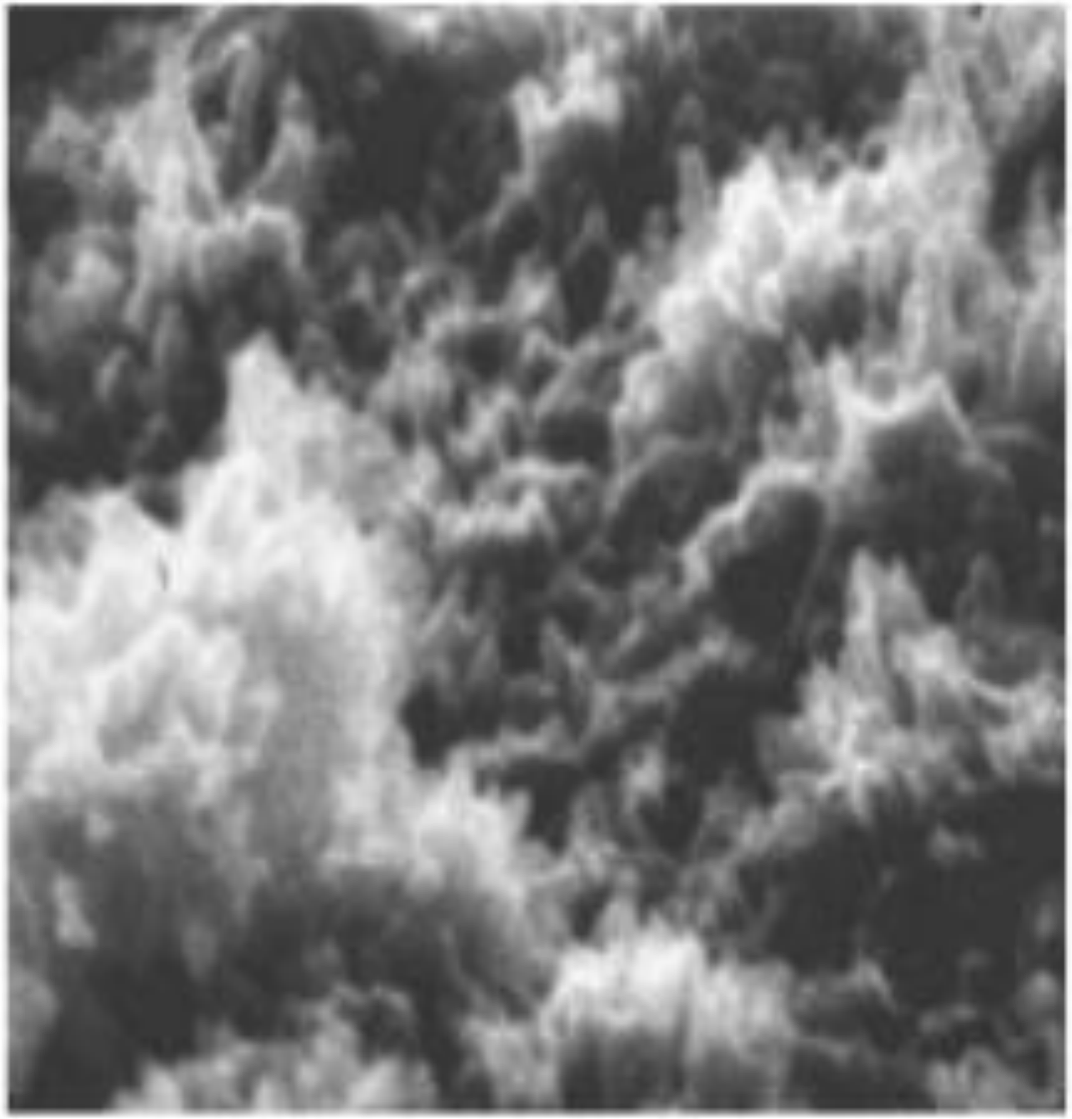
- The principal hydration product is C3S2H8, calcium silicate hydrate, or C–S–H.
- **C–S–H occupies about 50% of the** structural component in a cement paste and **forms directly on the surface of cement particles.**
- In addition, the size of C–S–H is quite small. It is believed that **C–S–H is the 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.

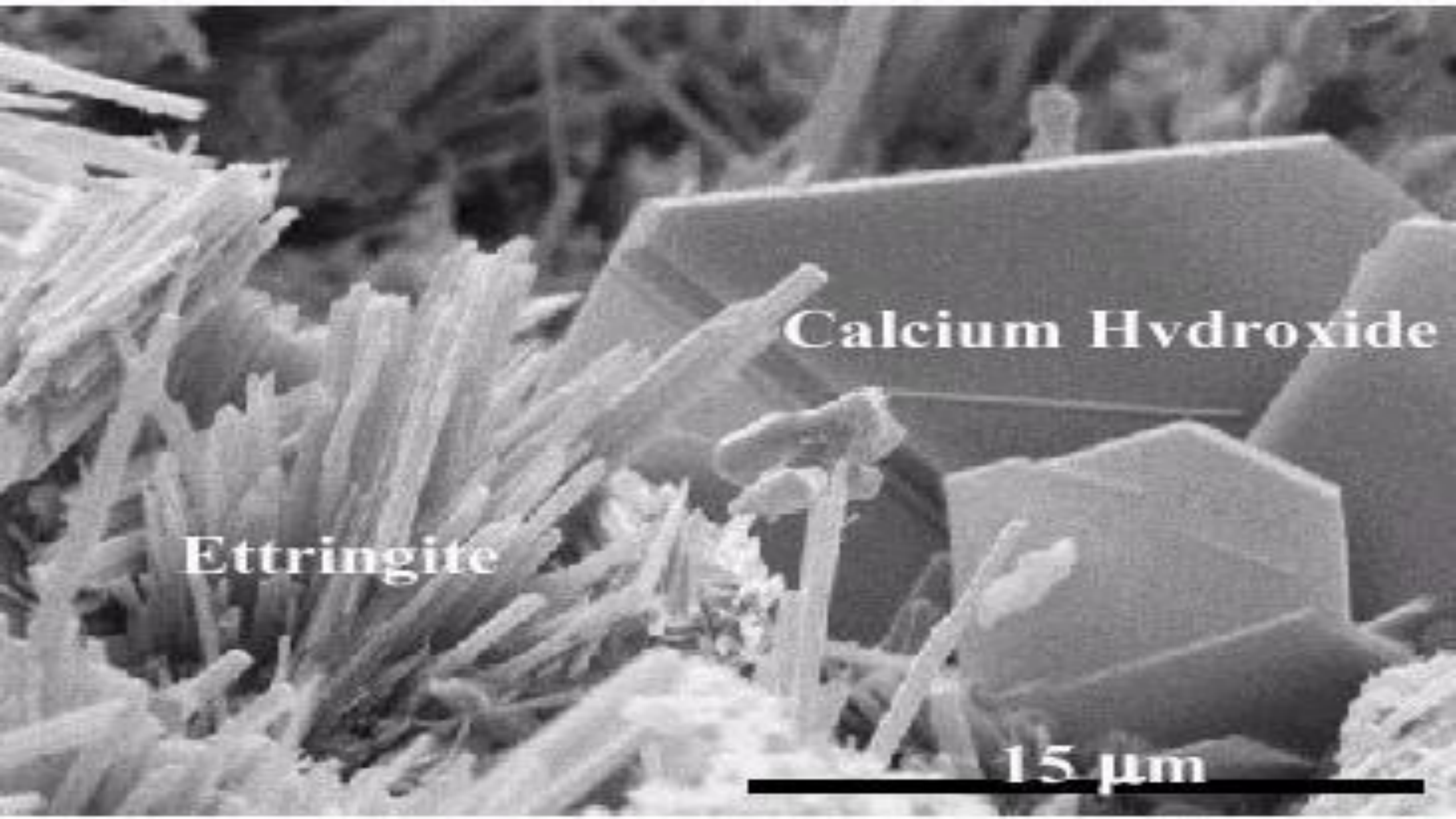
(1) C-S-H



(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 → **C6AS3H32 (*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 ettingite 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 Hvdroxide
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 (SO_4)** 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**:

$2C_3A + C_6A_3H_{32} + 4H \rightarrow 3C_4ASH_{12}$ (monosulfoaluminate)

Monosulfoaluminate is also called tetracalcium aluminate monosulfate-12-hydrate. Its nickname is **AFm.**

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

$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32}$

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

$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$ (not stable nor solid state)

The hydrates can be further converted to

$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$ (stable and solid)

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:

C4AF + 3CSH2 + 21H → C6(A, F)S3H32 + (F, A)H3

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 + C6(A, F)S3H32 + 7H → 3C4(A, F)SH12 + (F, A)H3

- 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 C4AFbecomes 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.**


Thank you for your attention!