고성능 콘크리트 공학
High Performance Concrete Engineering

〈Cement Chemistry〉

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Progress

HPCE_0_Intro

HPCE_1_Cement Chemistry

HPCE_2_Admixture, Aggregate, Water

HPCE_3_Fresh and Hardened Properties

HPCE_4_Durability

HPCE_5_UHPC

HPCE_6_Time Dependent Behavior

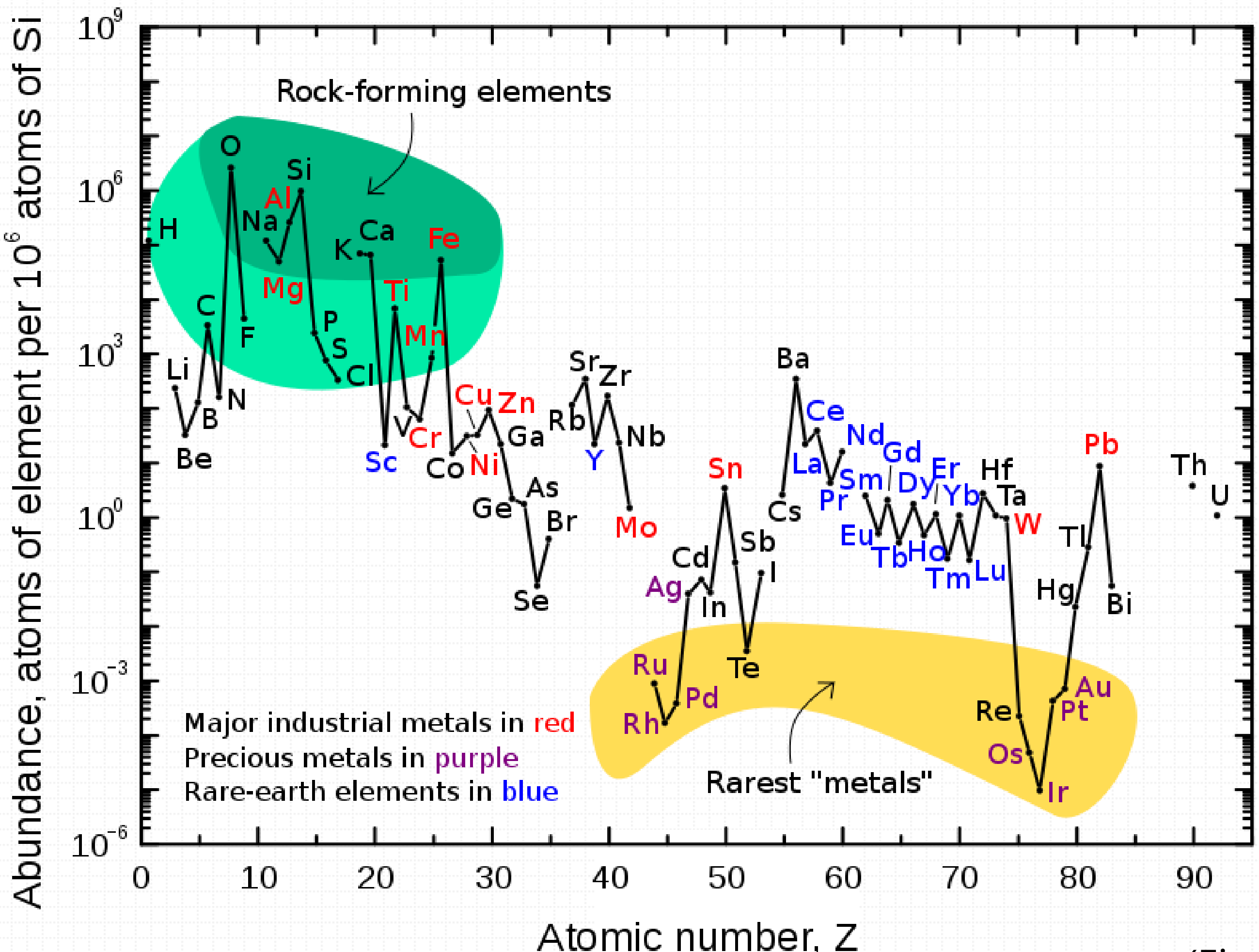
Cement definition:

A cement is a binder, a substance used for construction that sets, hardens, and adheres to other materials to bind together.

Cement is seldom used on its own, bur rather to bind sand and gravel (aggregate) together. Cement mixed with find aggregate produces mortar for masonry, or with sand and gravel, produces concrete.

(from Wikipedia)

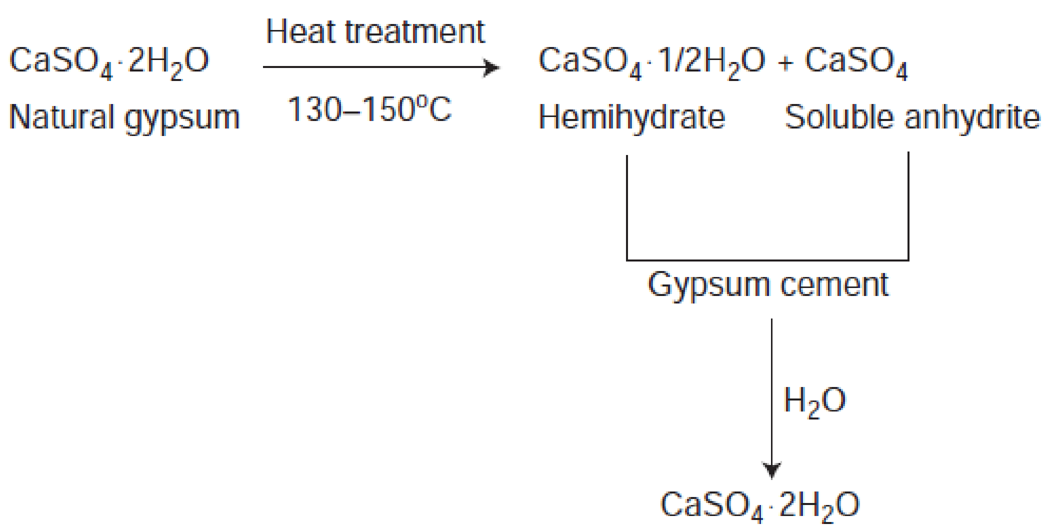
Potential raw material sources for cement



(Figure from Wikipedia)

Ancient cements: Egyptian cement

- The simplest form is that found in the brick walls of ancient Egyptian buildings using burnt gypsum.
- The bricks are dried in the sun without baking, and each course is covered with a moist layer of the loam (Nile mud) used for making the bricks, with or without the addition of chopped straw.



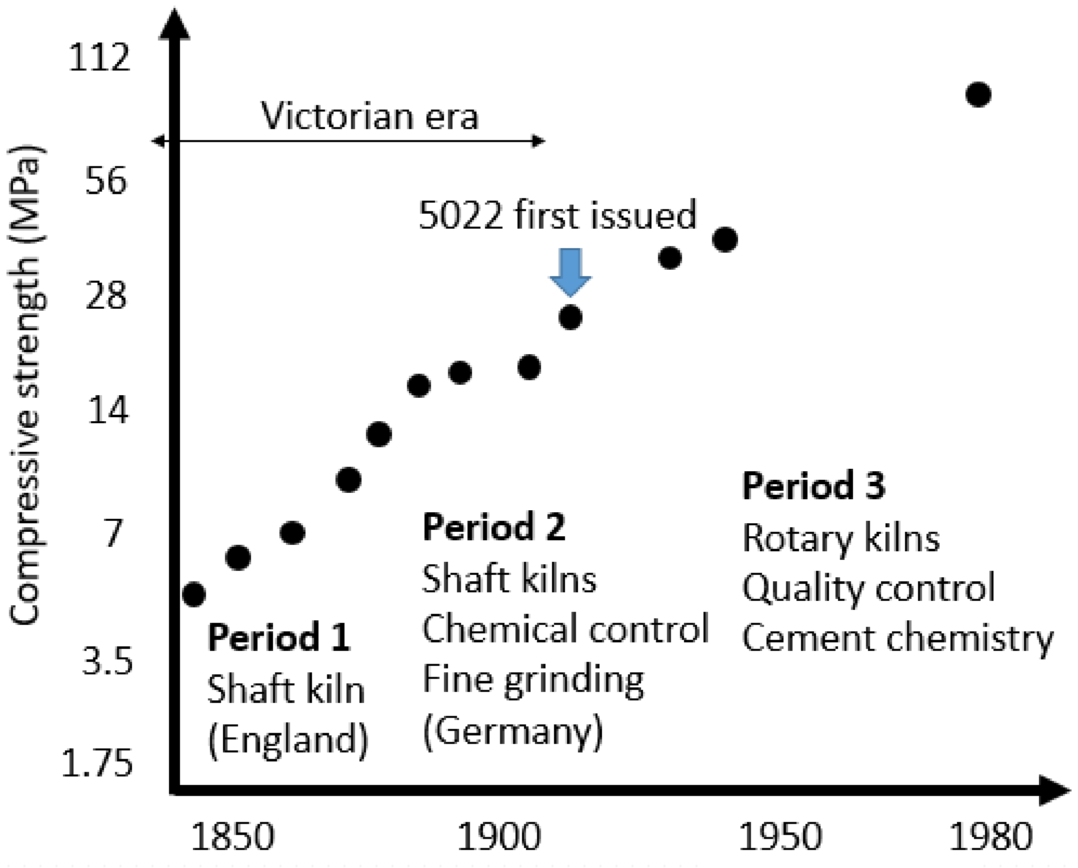
(Figure from Wikipedia)

Ancient cements: Roman cement

- Roman builders used the red volcanic tuff found at different points near the Bay of Naples.
- At the best variety of this clay was obtained from the neighborhood of Pozzoli (Latin Puteoli), the material acquired the name of Pozzolana and this designation has been extended to the whole class of mineral matters of which it is a type.

(Figure from Wikipedia)

Technical development of ordinary Portland cement (OPC)



(Image from Wikipedia)

Modern cement formulation

- The manufacture of one ton of Portland-cement clinker releases one ton of CO2 into atmosphere.

$$\text{Limestone} \rightarrow CaO + CO_2$$

$$\text{Clay} \rightarrow SiO_2 + Al_2O_3 + Fe_2O_3$$

$$\text{Clay} + \text{Limestone} \rightarrow \left\{ \begin{array}{c} 3CaO \cdot SiO_2 \\ 2CaO \cdot SiO_2 \\ 3CaO \cdot Al_2O_3 \\ 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \end{array} \right. + CO_2 \uparrow$$

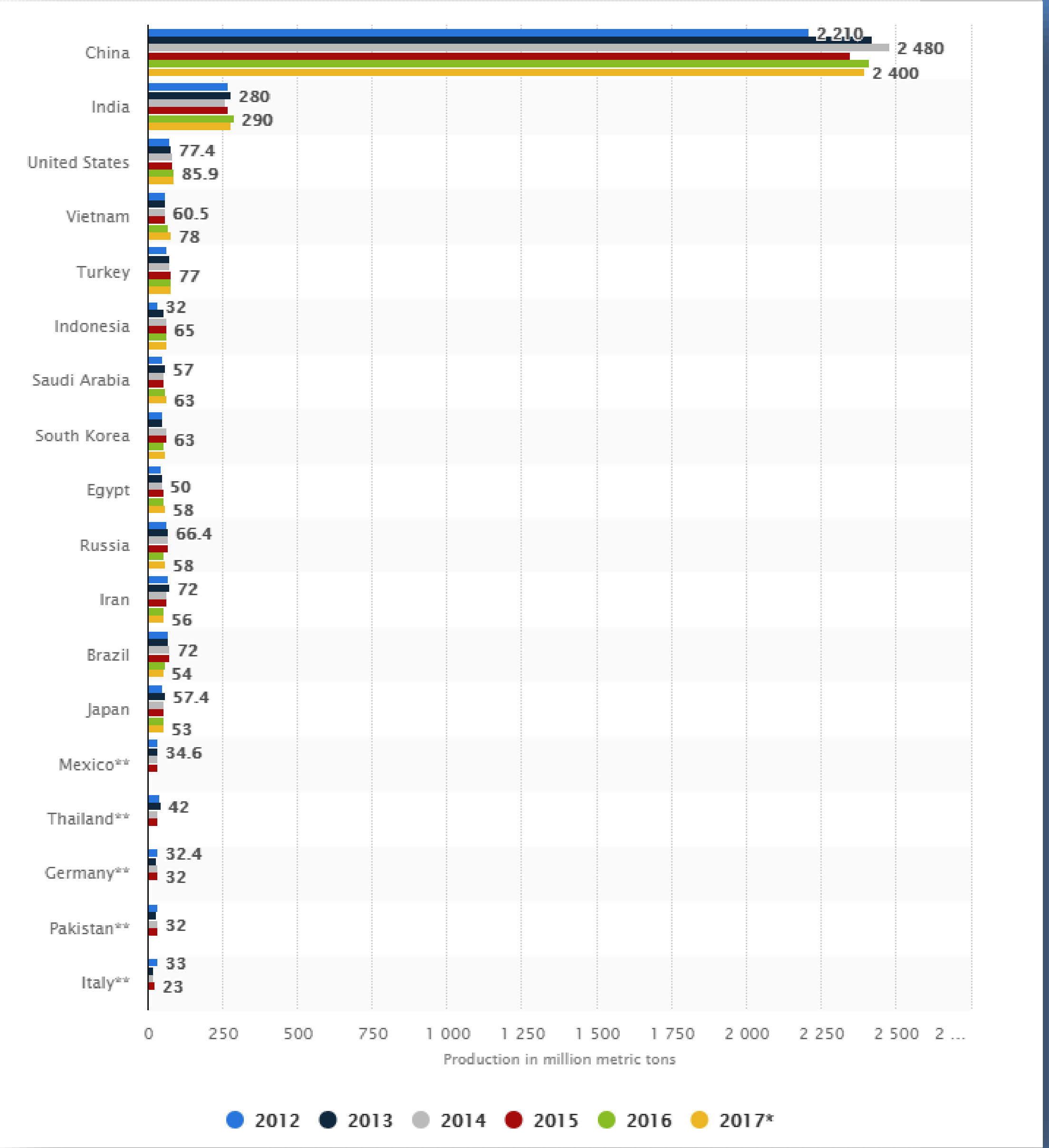
Heating at 1850°C
Energy Input

- Every person consumes 0.7 ton of cement annually.
- Currently, cement production is responsible for 5~8% of global CO2 emission

(Image from Wikipedia)

World cement production

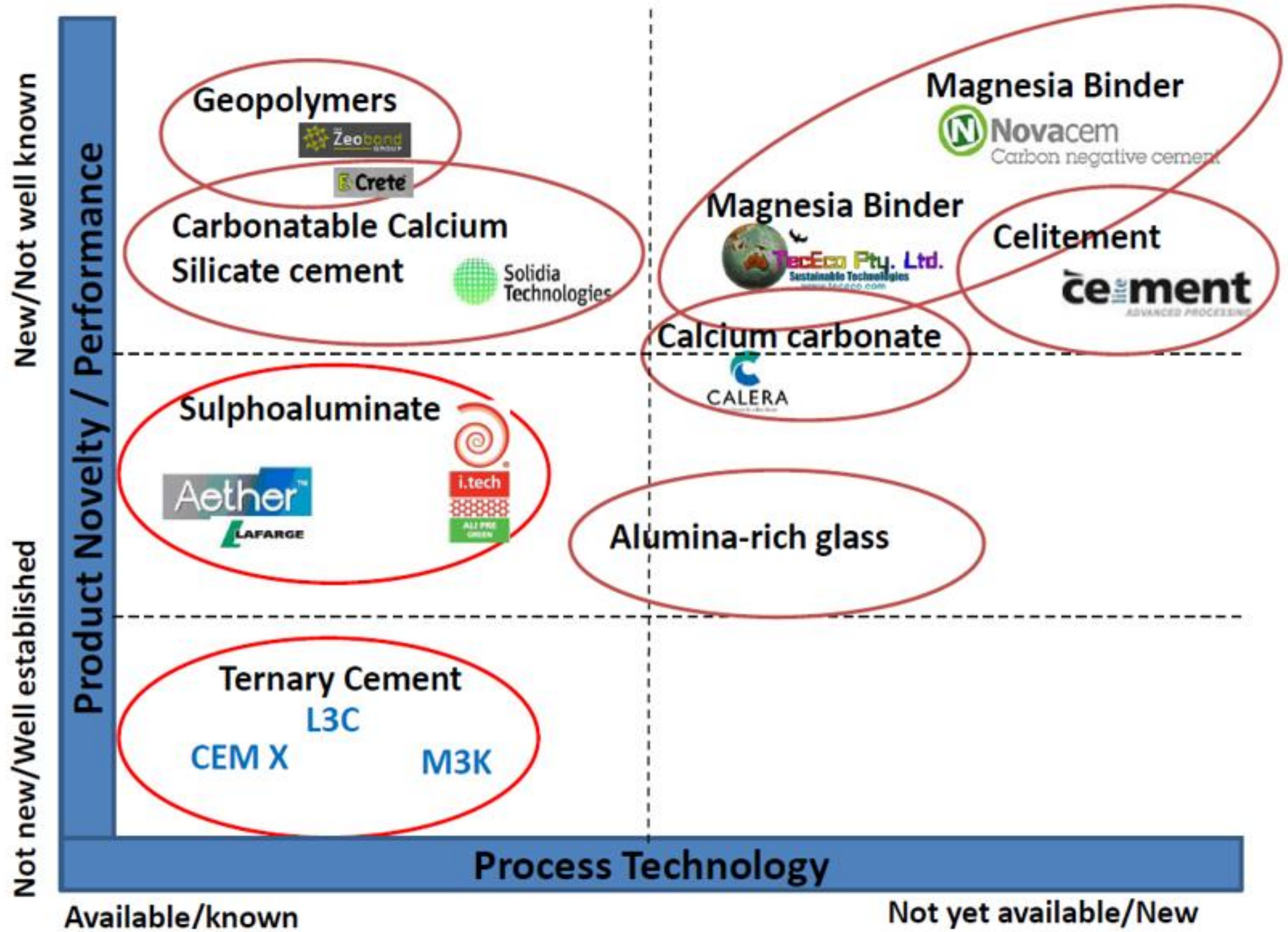
- The world demand of concrete is expected to grow to 18 billion tons a year by 2050.
- Annual cement production in Korea is 50 million tons
- 1.2 ton of CO_2 releases by a Korean person annually.



(U.S. Geological Survey, 2017)

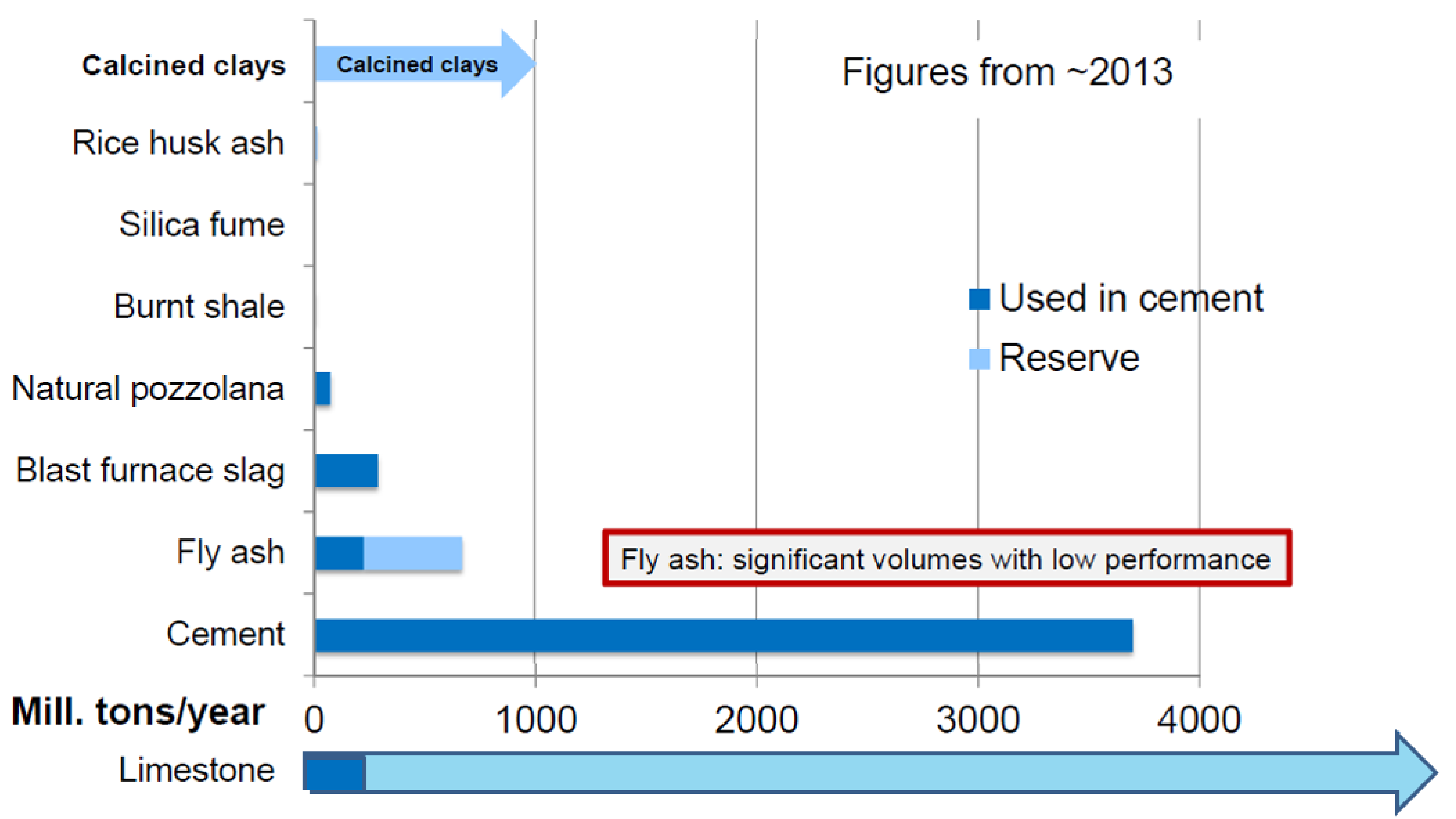
Global competition for green cement

(Slide from Prof. Scrivener)



Supplementary Cementitious Materials (SCM)

(Slide from Prof. Scrivener)



Typical oxide composition of a general-purpose Portland cement

Cement Chemistry Notation

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_3	N		0.34
SO_3	$\bar{S}$	sulfur trioxide	2.03
CO_2	$\bar{C}$	carbon dioxide	-
H_2O	H	water	-

Composition of Portland Cement

- **Raw materials**
  - **Limestone/chalk/marl (CaO)**
  - **Clay/shale (SiO_2, Al_2O_3)**

Typical composition of Ordinary Portland Cement

Chemical Name	*Chemical Formula*	*Shorthand Notation*	*Weight Percent*
Tricalcium silicate	$3CaO.SiO_2$	C_3S	55
Decalcium silicate	$2CaO.SiO_2$	C_2S	18
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	10
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	8
Calcium sulfate dihydrate (gypsum)	$CaSO_4.2H_2O$	$C\bar{S}H_2$ or $C\$H_2$	6

Hydration of Cement Compounds

- Hydration = reaction with water
- **Calcium silicates**

$$2C_3S + 7H \rightarrow C_3S_2H_8 + 3CH \qquad \Delta H = -500\,J/g$$

$$2C_2S + 5H \rightarrow C_3S_2H_8 + CH \qquad \Delta H = -250\,J/g$$

- The C-S-H is the main contributor to the concrete strength

Hydration of Cement Compounds

- **Tricalcium aluminate**
  - C3A reacts with water, results in rapid formation of calcium aluminate hydrates which lead to flash set

$$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

  - These hydrates are not stable, later convert to C3AH6
  - In Portland cement, hydration of C3A involves reaction wich sulphate ions that are supplied by gypsum.

- **Calcium sulfate (Gypsum)**
  - Calcium sulfate is important to avoid flash set: but if it is too much, affect setting and hardening, also affect long-term volume stability.
  - The required amount increases with C3A content.

Hydration of Cement Compounds

- **Tricalcium aluminate**
  - Primary initial reaction

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\overline{S_3}H_{32} \qquad \Delta H = -1350\,J/g$$

$$C_3A \cdot 3C\bar{S} \cdot H_{32}$$

  - Ettringite is stable hydration product only whyile there is an ample supply of sulphate
  - If the sulphate is consumed before C3A has completely hydrated

$$2C_3A + C_6A\overline{S_3}H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$$

$$C_3A \cdot C\bar{S} \cdot H_{32}$$

Hydration of Cement Compounds

- **Ferrite Phase**
  - Forms similar hydration products to C3A, but less reactive

$$3C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A,F)\overline{S_3}H_{32} + (F,A)H_3$$

$$C_4AF + C_6(A,F)\overline{S_3}H_{32} + 7H \rightarrow 3C_4(A,F)\bar{S}H_{12} + (F,A)H_3$$

  - Reactions are slower and involves less heat

Hydration of Portland Cement

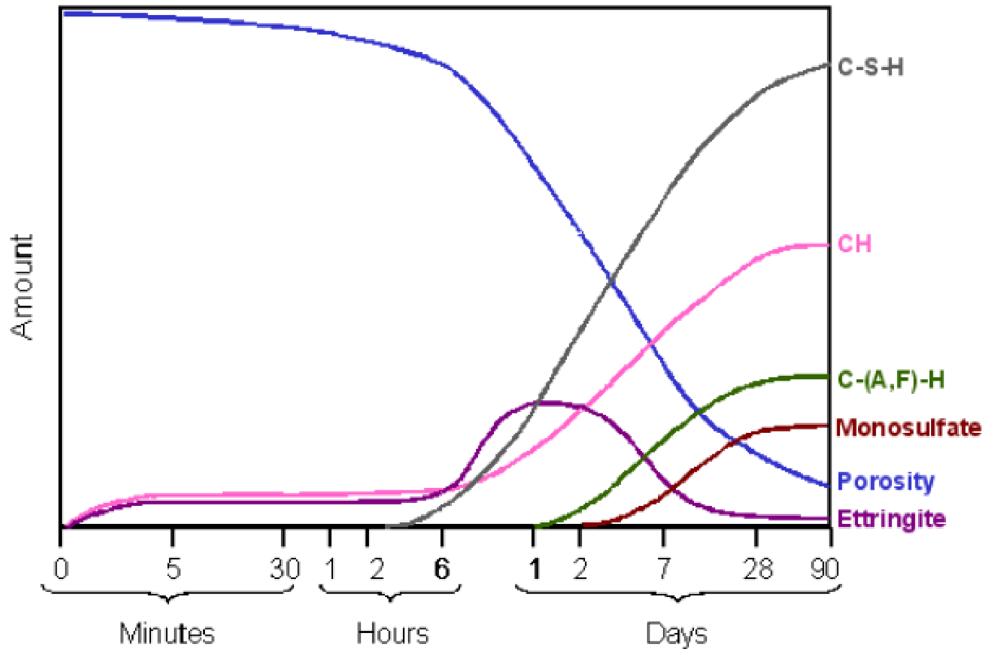
- Assumption: the cement compounds hydrate independently

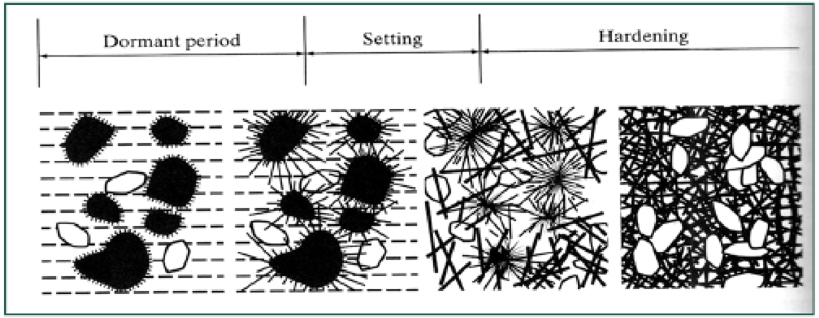
- Kinetics
    - The rate of hydration during the first few days

$$C_3A > C_3S > C_4AF > C_2S$$

- Hydration is exothermic, generates heat
    - Overall rate of heat evolution depends on
        - Heat of hydration of each compound
        - Rate of hydration of each compound
        - Relative percentage of each compounds in cement

Hydration Products

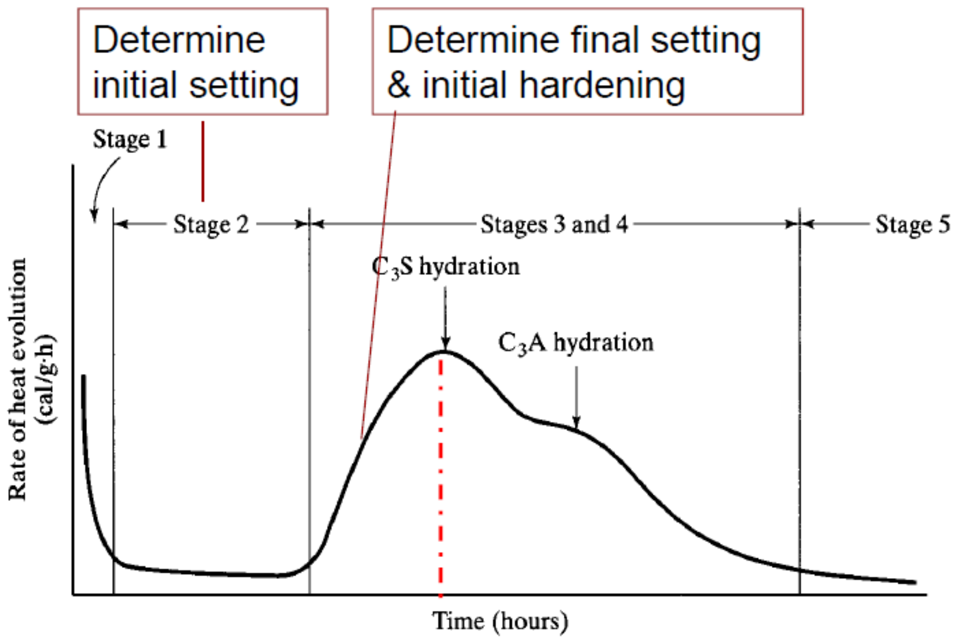




(Locher & Richartz 1976)

- Precipitation of CH and ettringite at early time
- After ~2 hrs, C-S-H formed
- 6 hrs – 1 day, rapid increase of CH, CSH, and ettringite
- After ~2 days, ettringite decomposes to monosulfate

Rate of heat evolution



Stage 1 – dissolution

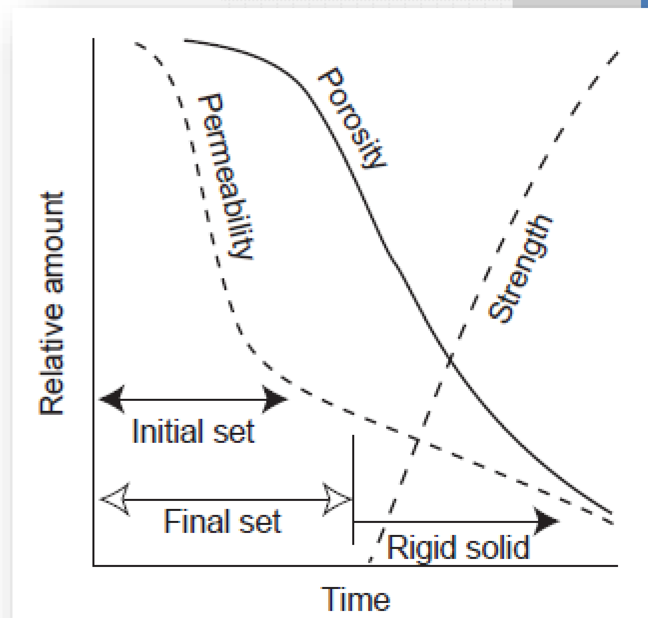
Stage 2 – induction (dormant)

Stage 3 – Acceleration

Stage 4 – Deceleration

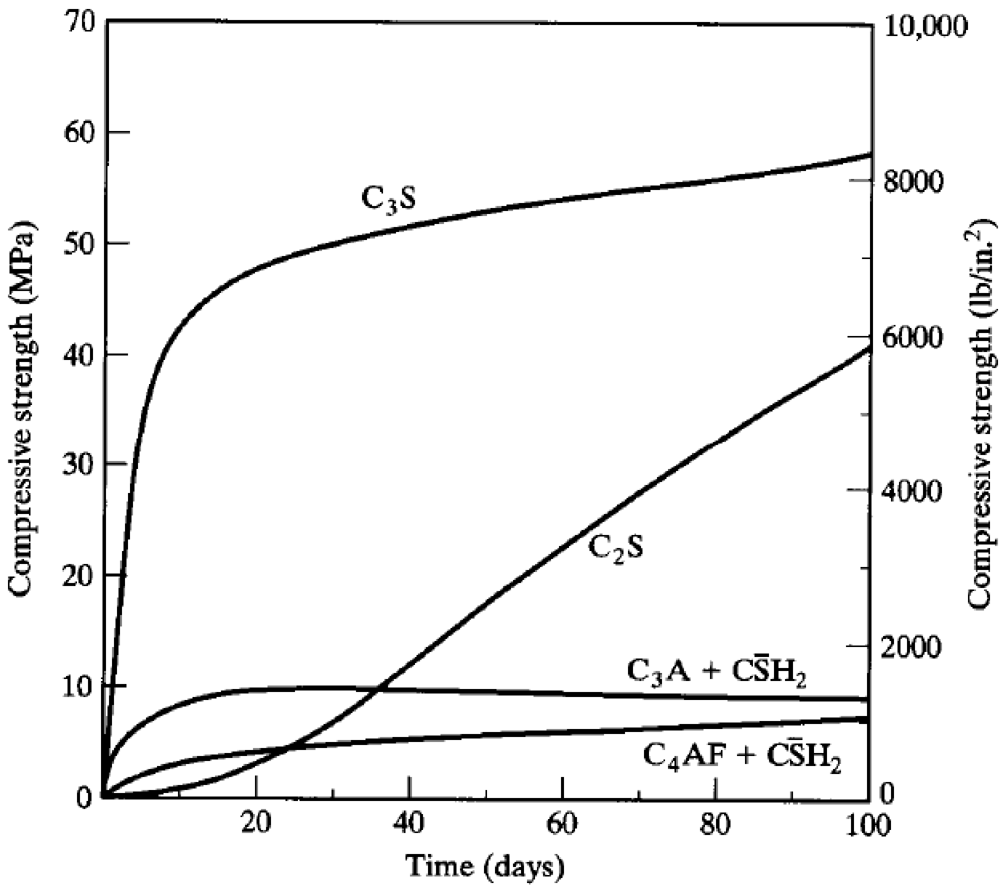
Stage 5 - Steady

(Mindess et al. 2003)



(Metha and Monteiro 2006)

Compressive strength development



(Mindess et al 2003)

- C3S provides most of the early strength (in the first 3-4 weeks)
- Both C3S and C2S contributes to ultimate strength

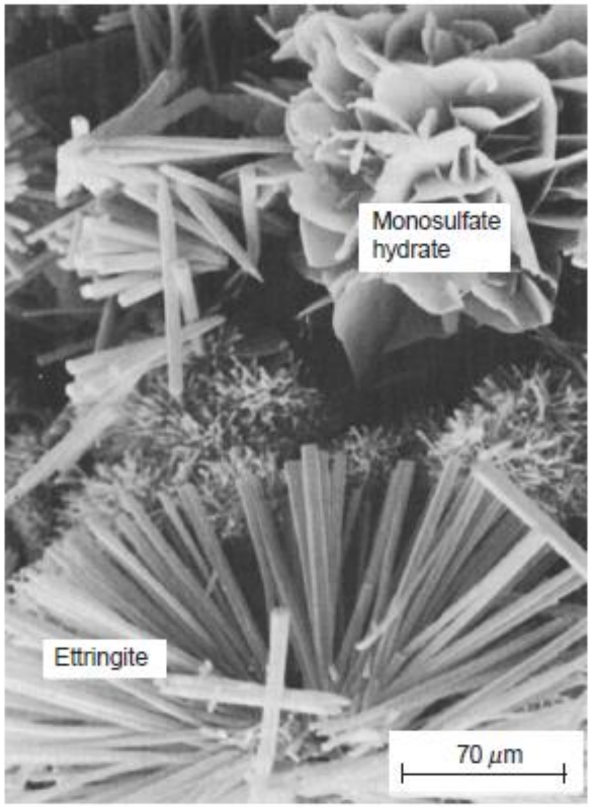
Characteristics of the hydration products

- **C-S-H (calcium silicate hydrates)**
  - Occupy > 50% volume of hydrated phase
  - Amorphous, extremely small irregular particles

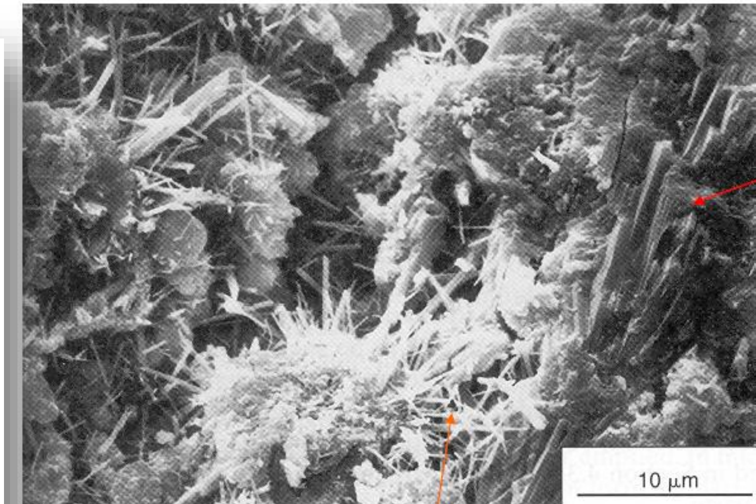
- **Calcium Hydroxide (CH)**
  - Occupy ~20-25% of the paste's solid volume

- **Calcium sulphoaluminates**
  - Occupy only ~10-15% by solid volume
    - Ettringite
      - Hexagonal crystals in the form of needles, often found in voids or cracks in mature concrete
    - Monosulphoaluminate (monosulfate)
      - Clusters or "rosettes" of irregular plates when first formed, grow into well-developed, but very thin, hexagonal plates

Actual crystal shapes



(Metha and Monteiro 2006)



(Mindess 2003)

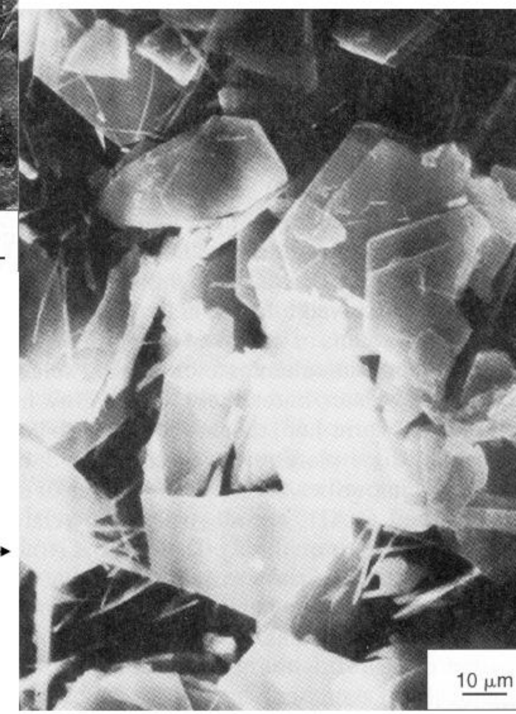
CH (striated)

Ettringite

(Hexagonal crystals in the form of needles, often found in voids or cracks in concrete)

Monosulphoaluminate →

Irregular plates when first formed, grow into very thin, hexagonal plates



Ettringite crystal structure

Ettringite: $C_3A \cdot 3C\bar{S} \cdot H_{32}$

Monosulfate: $C_3A \cdot C\bar{S} \cdot H_{32}$

(Metha and Monteiro 2006)

Calcium-silicate-hydrates

Let's search in google scholar

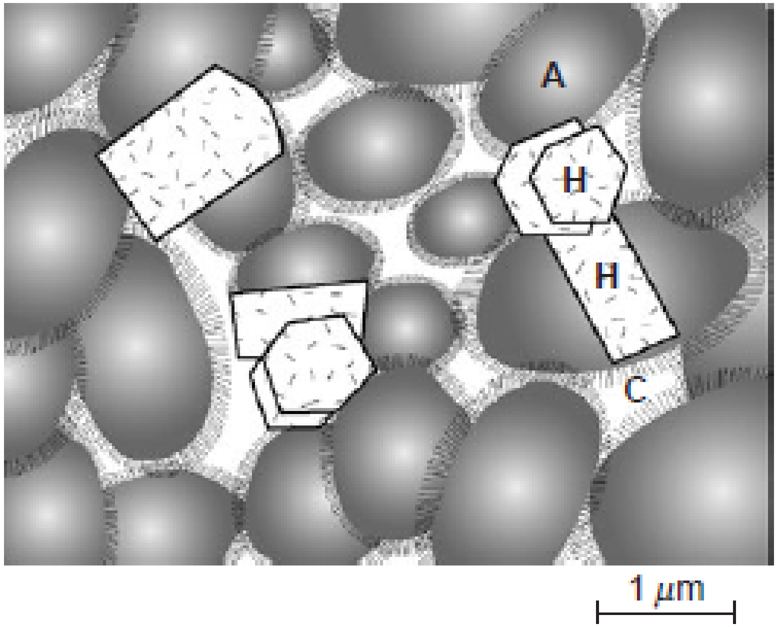


Figure 2-6 Model of a well-hydrated portland cement paste. "A" represents aggregation of poorly crystalline C-S-H particles which have at least one colloidal dimension (1 to 100 nm). Inter-particle spacing within an aggregation is 0.5 to 3.0 nm (avg. 1.5 nm). H represents hexagonal crystalline products such as $CH=C_4AH_{19}=C_4A\bar{S}H_{18}$. They form large crystals, typically 1 μm wide. C represents capillary cavities or voids which exist when the spaces originally occupied with water do not get completely filed with the hydration products of cement. The size of capillary voids ranges from 10 nm to 1 μm, but in well-hydrated pastes with low water/cement, they are less than 100 nm.