

RECYCLING AND REUSE OF RAW MATERIALS

1. CEMENT

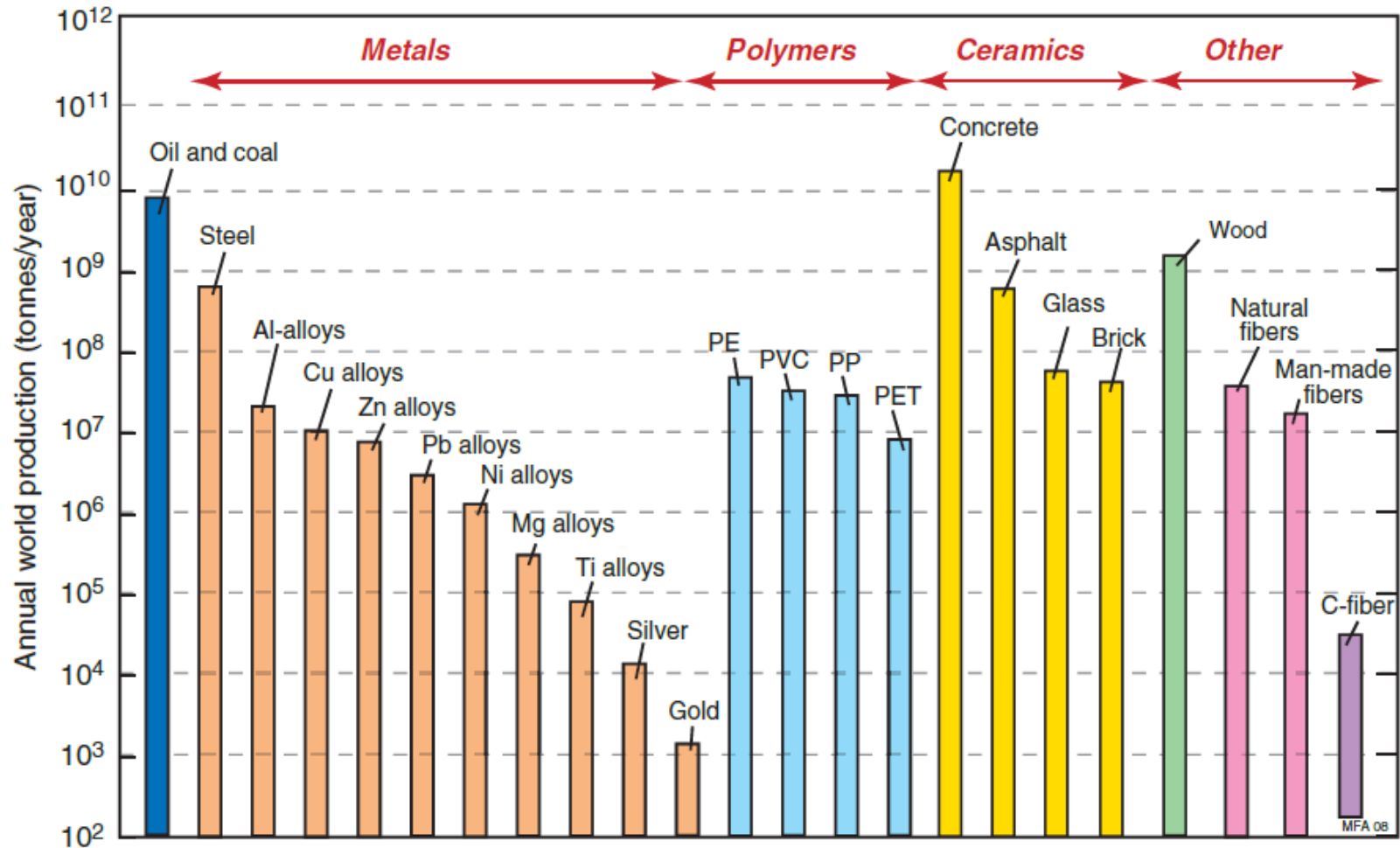
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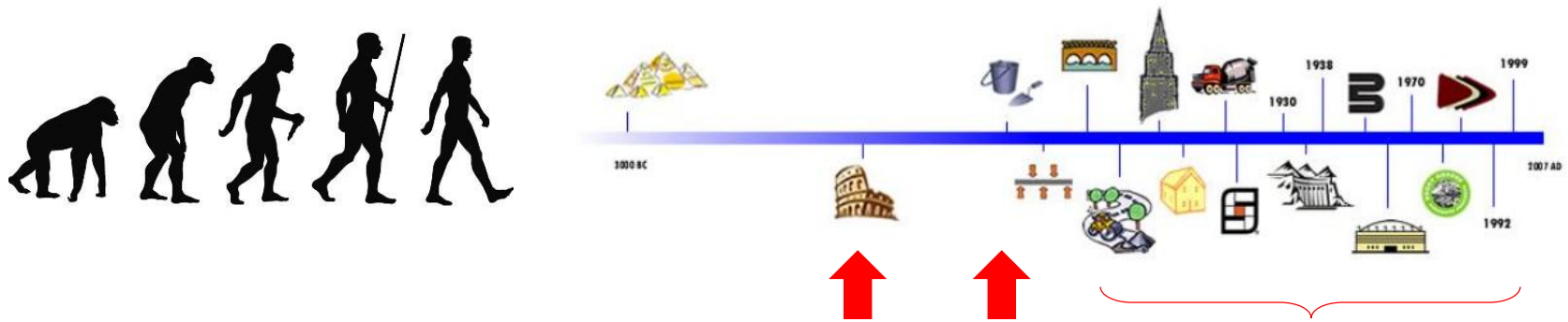


CERAMICS



CEMENT

Cement has a long history: from Romans.... until nowadays, with a rapid evolution



1. First cement produced by Romans mixing volcanic ashes with slaked lime: hydraulic cement.
2. This material was not used anymore during Middles Ages.
3. 1824: patent of the Portland cement, by Joseph Aspdin: obtained through the mix of calcareous and argilleous materials, i.e. silica-, alumina-, and iron-oxides. This mix was then burned at clinkering temperature, and after grinding, clinker results.
4. Modern cements.

CEMENT

Portland cement is a fine powder, gray or white in color, that consists of a mixture of hydraulic cement materials comprising primarily **calcium silicates, aluminates and aluminoferrites**.

Gray Portland cement is used for structural applications and is the more common type of cement produced. **White Portland cement** has lower iron and manganese contents than gray Portland cement and is used primarily for decorative purposes.

Step 1 – Quarrying → Limestone, shale, clay

Step 2 – Raw material preparation → composition, grinding

Step 3 – Clinkering → Raw materials are dried, heated and fed into a rotating kiln. Materials react at high temperature (until 1400-1500°C) to form $3\text{CaO}\cdot\text{SiO}_2$ (tricalcium silicate), $2\text{CaO}\cdot\text{SiO}_2$ (dicalcium silicate), $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (tricalcium aluminate) and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (tetracalcium aluminoferrate)

Step 4 - Cement milling → clinker is produced (particles with 3 cm diameter). Particles are grinded into a fine powder.

<https://www.cement.org/cement-concrete/how-cement-is-made>

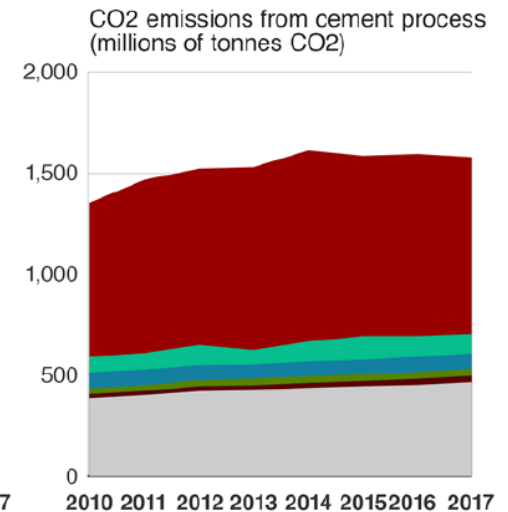
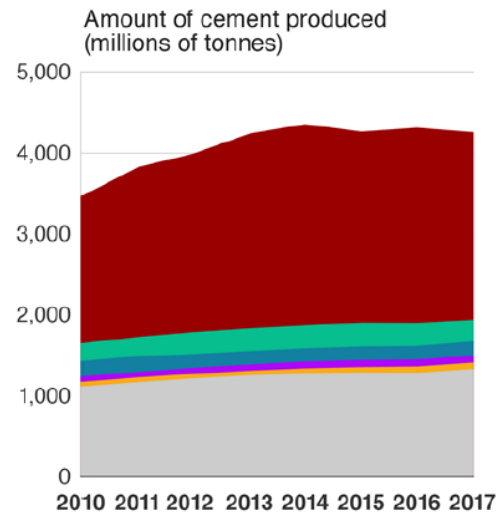
CEMENT

Environmental aspects: about 1 ton of CO₂ is generated per each ton of clinker produced.

The **production of cement** is:

- In the **world**: more than **4,000 million of tons** each year, representing around 8% of global CO₂ emissions.
- in **EU**: **170 millions of tons**.
- In **Spain**: **13 millions of tons**.
- In **Italy**: **18 millions of tons**.
- **China** is the higher producer of Cement, with **2,400 millions of tones**.

China produces most cement and therefore most cement-related CO₂ emissions



CEMENT

Raw materials react inside the kiln to form a series of complex compounds, and a part of small quantity of uncombined lime, a state of chemical equilibrium is reached. Such equilibrium is NOT maintained during the further operations of cooling, which affects its degree of crystallization and the amount of amorphous phase.

Name of compou	Both beneficial and negative effects	Responsible for hydrated cement strength	Abbreviation
Tricalcium silicate		$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium silicate		$2\text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium aluminate		$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium	Less influent	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF

Starting from the knowledge of the oxides composition of the cement, it is possible to know the amount of the main compounds present, through the **Bogue composition** of cement.

CEMENT

$$C_3S = 4.07(CaO) - 7.60(SiO_2) - 6.72(Al_2O_3) - 1.43(Fe_2O_3) - 2.85(SO_3)$$

$$C_2S = 2.87(SiO_2) - 0.754(3CaO \cdot SiO_2)$$

$$C_3A = 2.65(Al_2O_3) - 1.69(Fe_2O_3)$$

$$C_4AF = 3.04(Fe_2O_3)$$

Approx. Bogue composition (referred to Portland cement clinker, but can be adjusted for cement)

Compound	Abbreviation	Chemical formula	Typical concentration/%
Tricalcium silicate	C ₃ S	3CaO•SiO ₂	60-70
Dicalcium silicate	C ₂ S	2CaO•SiO ₂	10-20%
Tricalcium aluminate	C ₃ A	3CaO•Al ₂ O ₃	5-10%
Tetracalcium alumino-ferrate	C ₄ AF	4CaO•Al ₂ O ₃ •Fe ₂ O ₃	3-8%

CEMENT

Typical addition to the clinker: **gypsum**. Its amount is crucial, and it depends on the C3A and alkali content.

The higher is the cement fineness, the higher is the availability of C3A at early age, and this raises the gypsum requirement. An excess of gypsum content leads to expansion and consequent disruption of the set cement paste. Optimum gypsum content is determined on the basis of the heat of hydration.

Minor compounds present (overall between 1 and 5%): MgO, TiO, Mn₂O₃, K₂O, Na₂O.

CEMENT

Exercise (to be done during class)

Calculate the Bogue composition of a cement with the following composition:

Clinker analysis										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	IR	Total
21.5	5.2	2.8	66.6	1.0	0.6	0.2	1.0	1.5	0.5	98.9
Free lime = 1.0% CaO										

Recall that free CaO can be subtracted from the overall CaO to obtain the combined CaO, used in the calculation.

CEMENT

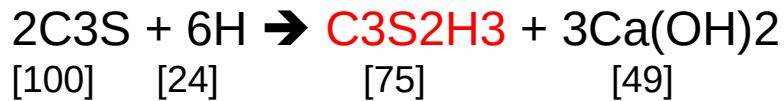
It should be stressed that the Bogue calculation does not give the 'true' amounts of the four main clinker phases present, although this is sometimes forgotten. The results of the Bogue calculation differ from the 'true' amounts (often called the phase proportions) principally because the actual mineral compositions differ - often only slightly, but occasionally more so and particularly in the case of the ferrite phase, from the pure phase compositions assumed in the calculation.

To **adjust the calculation** for use with **Portland cement**, it is necessary to consider first what other materials may be present in the cement. If the cement is a **mixture of clinker and gypsum only**, the calcium bound with the gypsum can be allowed for approximately by **deducting $(0.7 \times \text{SO}_3)$ from the total CaO**. Note that this does not allow for any clinker sulfate present as potassium or sodium sulfate and a small error will therefore be introduced.

A similar adjustment can be carried out **for limestone**; the limestone content can be estimated by **determining the CO₂ content of the cement** and calculating the corresponding CaO. If either **slag or fly ash is present**, in principle the formula could be adjusted to take it into account, but the slag or ash composition would need to be known accurately and in practice this is not an adjustment normally made.

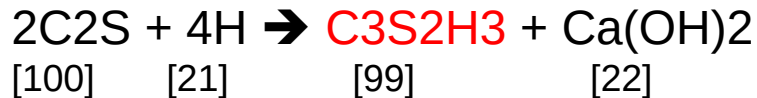
CEMENT

For C3S:



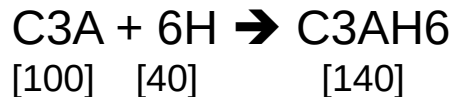
C-S-H gel, known also as
tobermolite gel + formation of
lime

For C2S:



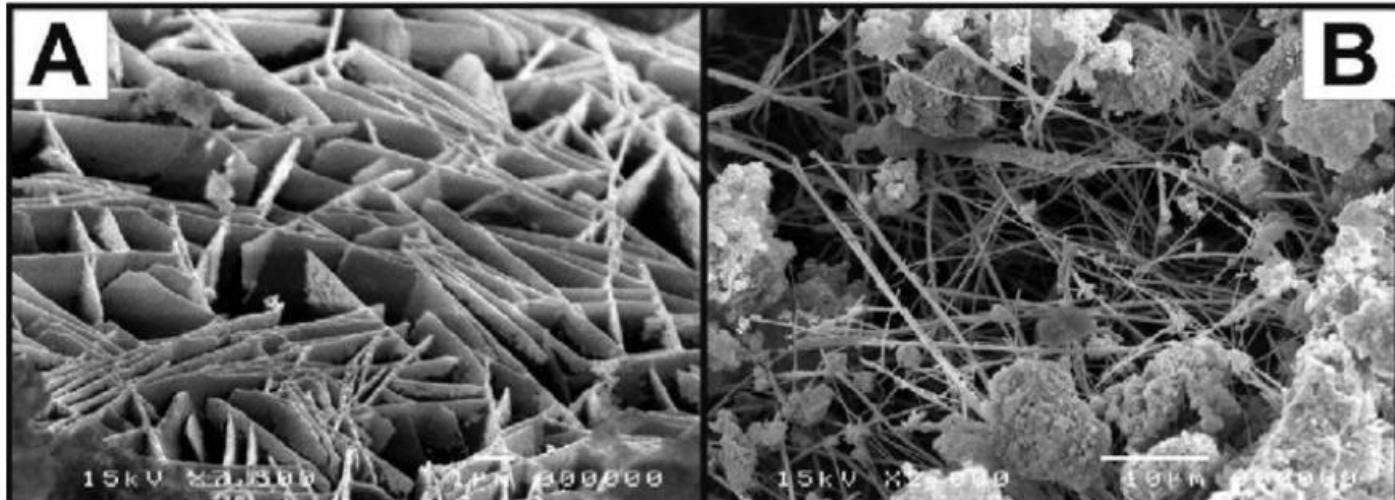
C3S hydrates much quicker
than C2S

For CA3



This reaction is very fast and it
produces the so-called flash
set. It is prevented by adding
gypsum.

CEMENT



Tobermorite. A: SEM image of platy crystals (POM 4); B: SEM image of acicular crystals.

CEMENT

The substances produced during the hydration deposit on the outer periphery of the nucleus of hydrated cement grains. Hydration is a slow reaction that occurs for 2 to 5 hours. The initial period of the hydration process is the Induction or Dormant period. The hydration process stops after the reaction between the entire cement particle.

The tobermorite gel occupies 50 to 60 % of the volume of hydrated cement.

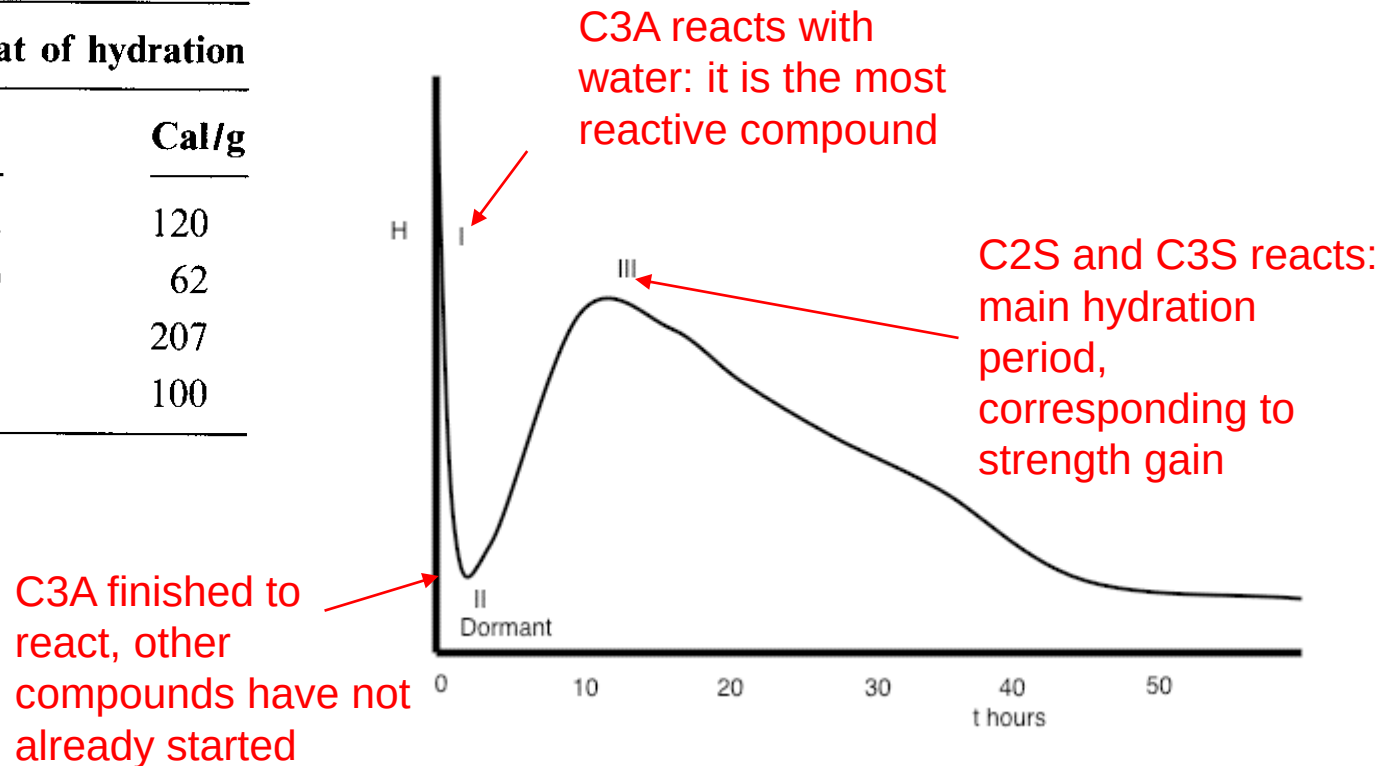
As many other chemical reaction, cement hydration is an exothermic reaction. The temperature at which hydration occurs **affects also the rate of heat development.**

CEMENT

For low heat cement, the heat of hydration for 7 days should not be greater than 66 cal/g and for 28 days should not be greater than 75 cal/g.

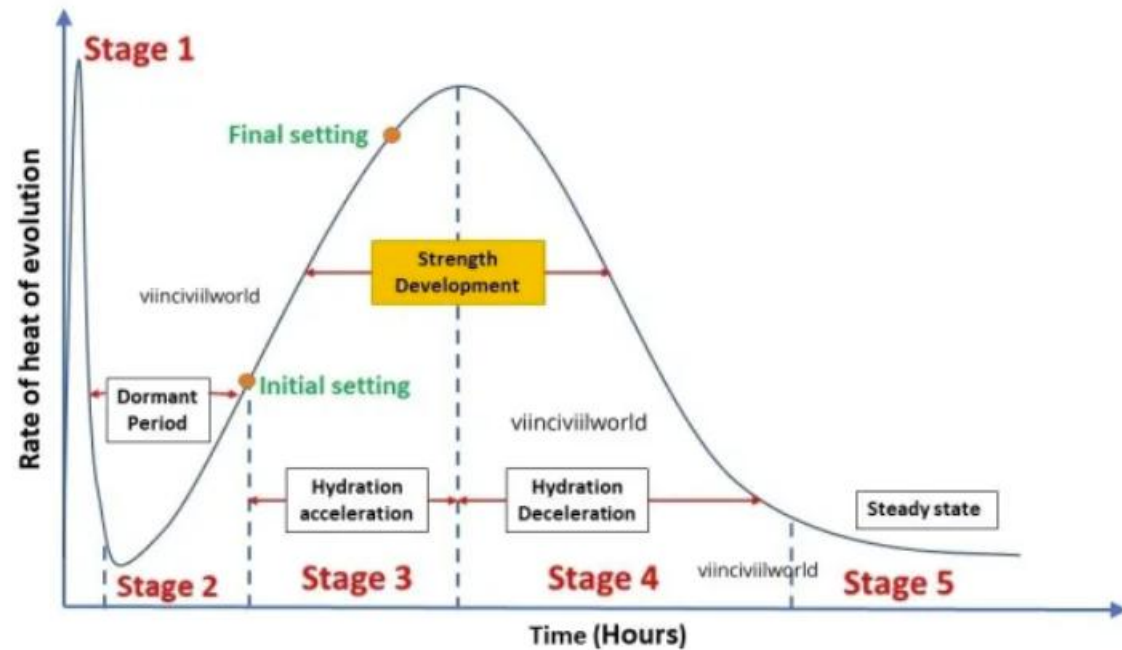
➔ The heat of hydration is measured with a specific apparatus named calorimeter

Compound	Heat of hydration	
	J/g	Cal/g
C ₃ S	502	120
C ₂ S	260	62
C ₃ A	867	207
C ₄ AF	419	100



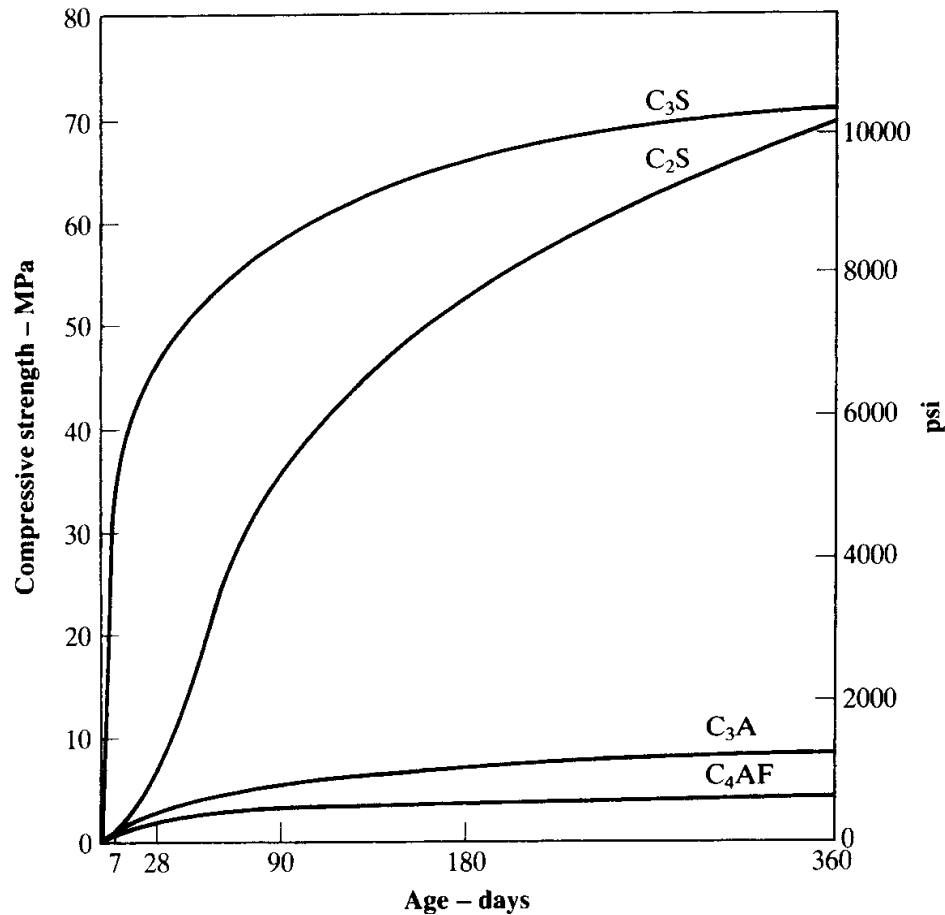
CEMENT

As many other chemical reaction, cement hydration is an exothermic reaction. The temperature at which hydration occurs affects also the rate of heat development → **and then it affects setting and strength development**



CEMENT

It is not possible to predict strength of cement pastes on the basis of their composition.



CEMENT

Classification depends on the Codes and Standards, e.g. ASTM classification

	Classification	Characteristics	Applications
Type I	General purpose	Fairly high C_3S content for good early strength development	General construction (most buildings, bridges, pavements, precast units, etc)
Type II	Moderate sulfate resistance	Low C_3A content (<8%)	Structures exposed to soil or water containing sulfate ions
Type III	High early strength	Ground more finely, may have slightly more C_3S	Rapid construction, cold weather concreting
Type IV	Low heat of hydration (slow reacting)	Low content of C_3S (<50%) and C_3A	Massive structures such as dams. Now rare.
Type V	High sulfate resistance	Very low C_3A content (<5%)	Structures exposed to high levels of sulfate ions
White	White color	No C_4AF , low MgO	Decorative (otherwise has properties similar to Type I)

Cement type	Compound composition, per cent							
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Free CaO	MgO	Loss on ignition
I	59	15	12	8	2.9	0.8	2.4	1.2
II	46	29	6	12	2.8	0.6	3.0	1.0
III	60	12	12	8	3.9	1.3	2.6	1.9
IV	30	46	5	13	2.9	0.3	2.7	1.0
V	43	36	4	12	2.7	0.4	1.6	1.0

* Neville AM, Brooks JJ (1987) Concrete Technology, Longman Group.

CEMENT

Classification depends on the Codes and Standards, e.g. EN 197-1

Cement Type	Designation	Notation	Clinker K	G.G.B.S. S	Silica fume D	Pozzolana		Fly ashes		Burnt Shale T	Limestone		Minor Additional constit.
						Natural P	Industrial Q	Silic. V	Calcar W		L	LL	
I	Portland Cement	I	95-100	-	-	-	-	-	-	-	-	-	0-5
	Portland Slag Cement	II / A-S II / B-S	80-94 65-79	6-20 21-35	-	-	-	-	-	-	-	-	0-5 0-5
II	Portland Silica Fume Cement	II / A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland Pozzolana Cement	II / A-P	80-94	-	-	6-20 21-35	-	-	-	-	-	-	0-5
		II / B-P	65-79	-	-	-	-	-	-	-	-	-	0-5
		II / A-Q	80-94	-	-	-	6-20 21-35	-	-	-	-	-	0-5
	Portland Fly Ash Cement	II / B-Q	65-79	-	-	-	-	-	-	-	-	-	0-5
		II / A-V	80-94	-	-	-	-	6-20 21-35	-	-	-	-	0-5
		II / B-V	65-79	-	-	-	-	-	-	-	-	-	0-5
		II / A-W II / B-W	80-94 65-79	- -	- -	- -	- -	- 6-20 21-35	- -	- -	- -	- -	0-5 0-5
	Portland Burnt Shale Cement	II / A-T	80-94	-	-	-	-	-	-	6-20 21-35	-	-	0-5
		II / B-T	65-79	-	-	-	-	-	-	-	-	-	0-5
	Portland Limestone Cement	II / A-L	80-94	-	-	-	-	-	-	-	6-20 21-35	-	0-5
		II / B-L II / A-LL II / B-LL	65-79 80-94 65-79	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - 6-20 21-35	-	0-5 0-5
	Portland Composite Cement	II / A-M	80-94	6-20									
		II / B-M	65-79	21-35									
III	Blastfurnace Cement	III / A	35-64	35-65	-	-	-	-	-	-	-	-	0-5
		III / B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		III / C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
IV	Pozzolanic Cement	IV / A	65-89	-	11-35					-	-	-	0-5
		IV / B	45-64	-	36-55					-	-	-	0-5
V	Composite Cement	V / A	40-64	18-30	18-30					-	-	-	0-5
		V / B	20-39	31-50	31-50					-	-	-	0-5

Relates Clinker content

type and % of addition

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CEMENT

Conversion table: note the presence of alternative binders in place of ordinary cement.



This will affect the strength gain during time

Traditional classification		European classification [BS 8500-1: 2006]	
British	American		
Ordinary Portland [BS 12]	Type I [ASTM C 150]	Type (CEM) I	Portland
Rapid-hardening Portland [BS 12]	Type III [ASTM C 150]	Type IIA	Portland with 6 to 20% fly ash, ggbs, limestone or 6 to 10% silica fume
Low-heat Portland [BS 1370]	Type IV [ASTM C 150]		
Modified cement	Type II [ASTM C 150]	Type IIB-S	Portland with 21 to 35% ggbs
Sulfate resisting Portland (SRPC) [BS 4027]	Type V [ASTM C 150]		
Portland blast-furnace (Slag cement) [BS 146]	Type IS Type S Type I(SM) [ASTM C 595]	Type IIB-V	Portland with 21 to 35% fly ash
High slag blast-furnace [BS 4246]	–	Type IIB+SR	Portland with 25 to 35% fly ash with enhanced sulfate resistance
White Portland [BS 12]	–	Type IIIA	Portland with 36 to 65% ggbs
Portland-pozzolan [BS 6588; BS 3892]	Type IP Type P Type I(PM) [ASTM C 595]	Type IIIA+SR	Portland with 36 to 65% ggbs with enhanced sulfate resistance
		Type IIIB	Portland with 66 to 80% ggbs
		Type IIIB+SR	Portland with 66 to 80% ggbs with enhanced sulfate resistance
		Type IIIC	Portland with 81 to 95% ggbs
		Type IVB-V	Portland with 36 to 55% fly ash

CEMENT

Cement types (EN197-1): strength classes

32.5 N – $f_{c,7d} > 16\text{MPa}$; $f_{c,28d} = 32.5 - 52.5\text{ MPa}$

32.5 R – $f_{c,2d} > 10\text{MPa}$; $f_{c,28d} = 32.5 - 52.5\text{ MPa}$

42.5 N – $f_{c,2d} > 10\text{MPa}$; $f_{c,28d} = 42.5 - 62.5\text{ MPa}$

42.5 R – $f_{c,2d} > 20\text{MPa}$; $f_{c,28d} = 42.5 - 62.5\text{ MPa}$

52.5 N – $f_{c,7d} > 20\text{MPa}$; $f_{c,28d} > 52.5\text{ MPa}$

52.5 R – $f_{c,7d} > 30\text{MPa}$; $f_{c,28d} > 52.5\text{ MPa}$

It is measured with standardized mortar mixes on prisms
(4x4x16 cm):

w/c = 0.5

Sand : cement = 3 : 1

Setting times:

32.5: $t \geq 75\text{ min}$

42.5 $t \geq 60\text{ min}$

52.5: $t \geq 45\text{ min}$

Cement strength depends on
grains fineness, calcium -
silicates compounds
percentage





QUESTIONS?