Building Materials

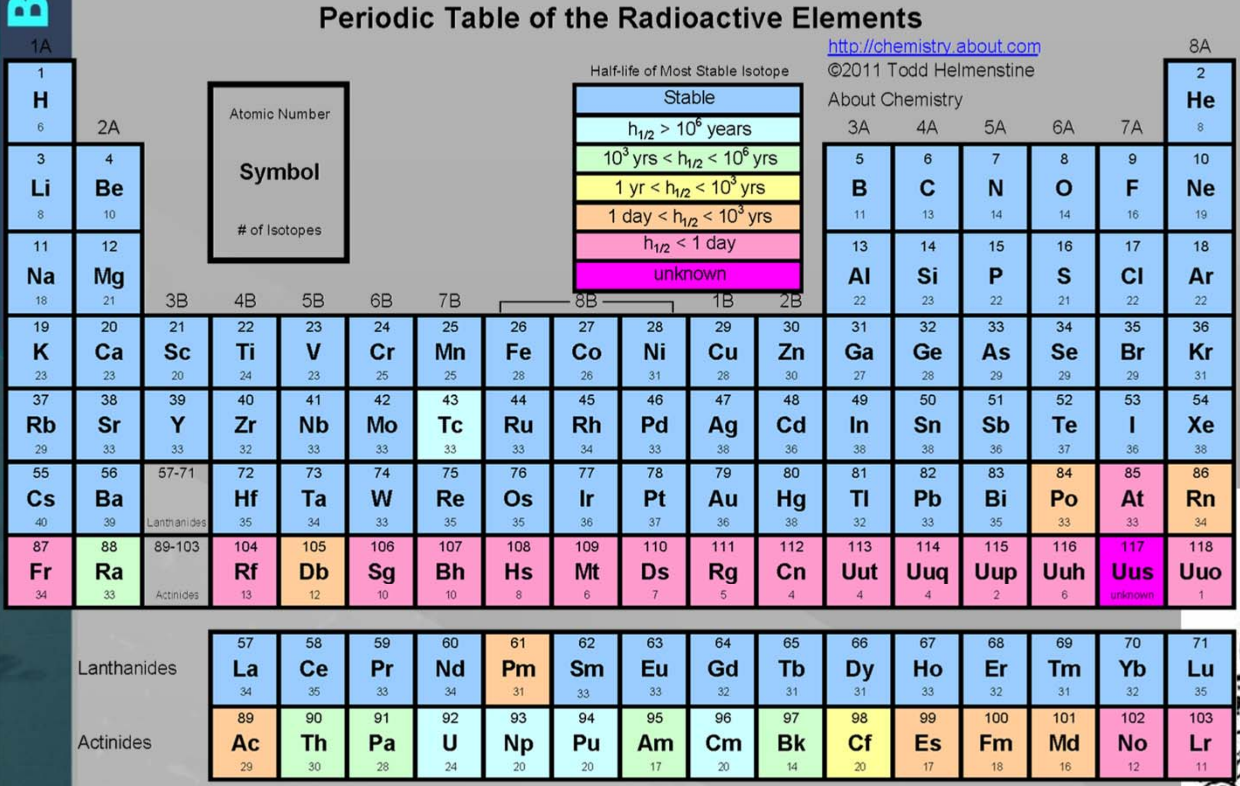
Lecture 6

Department of Materials Engineering
and Chemistry
Faculty of Civil Engineering

Other properties

Radioactivity

- natural radioactivity of materials



Periodic Table of the Radioactive Elements

http://chemistry.about.com
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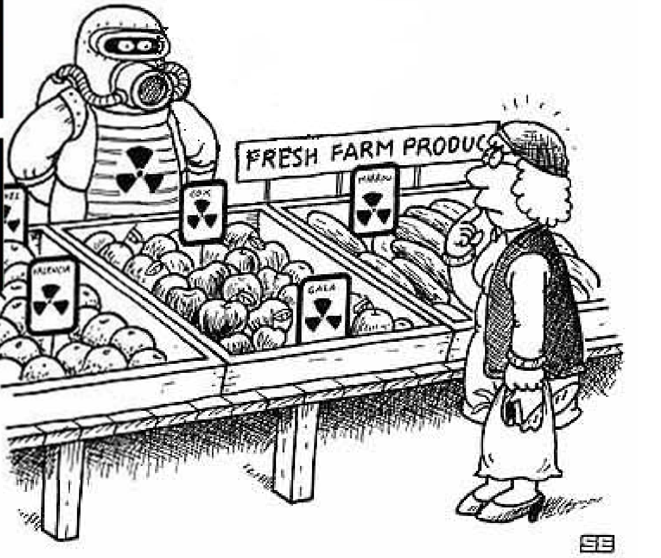
About Chemistry

Atomic Number
Symbol
# of Isotopes

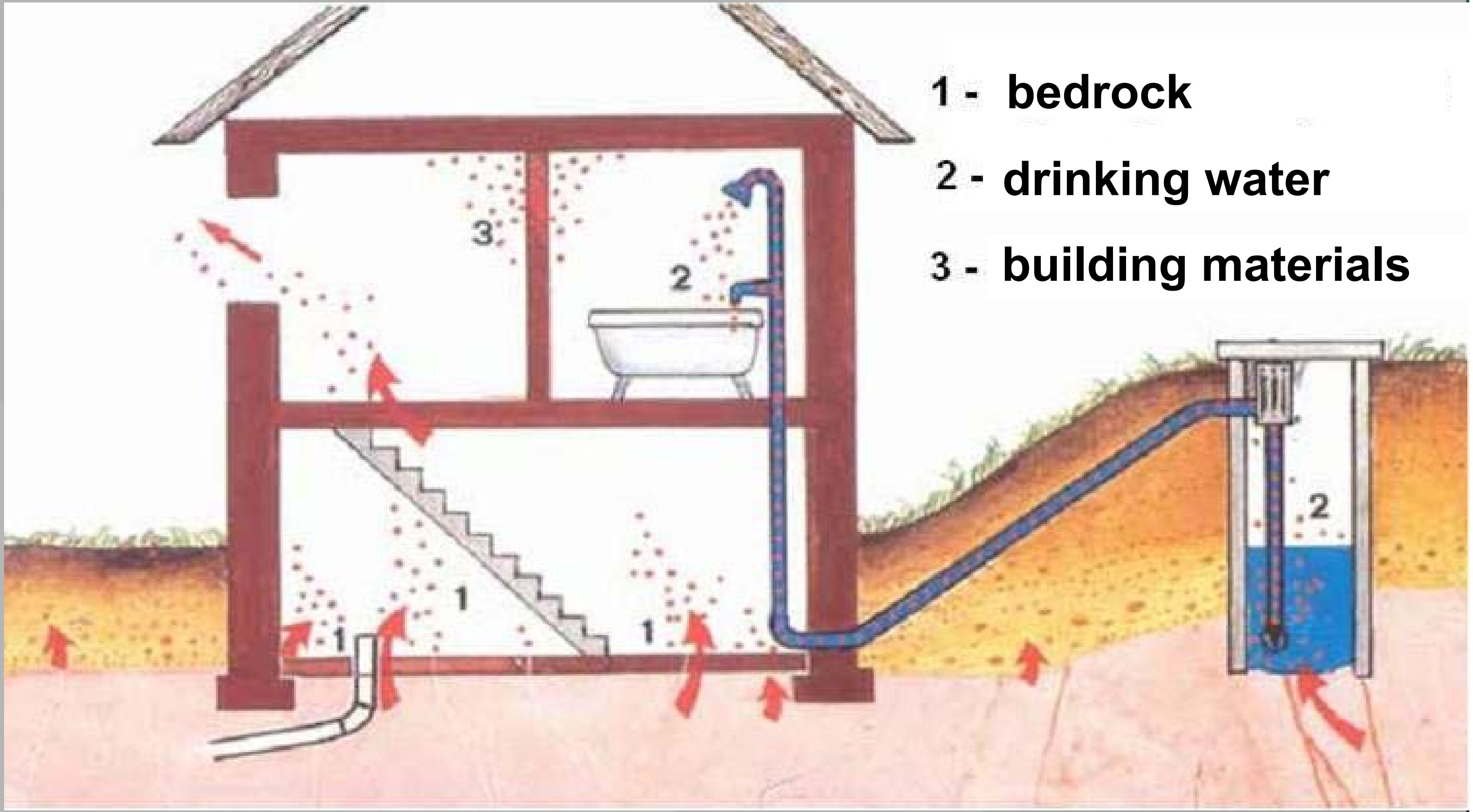
Half-life of Most Stable Isotope
Stable
$h_{1/2} > 10^6$ years
10^3 yrs $< h_{1/2} < 10^6$ yrs
1 yr $< h_{1/2} < 10^3$ yrs
1 day $< h_{1/2} < 10^3$ yrs
$h_{1/2} <$ 1 day
unknown

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 **H** 6																	2 **He** 8
3 **Li** 8	4 **Be** 10											5 **B** 11	6 **C** 13	7 **N** 14	8 **O** 14	9 **F** 16	10 **Ne** 19
11 **Na** 18	12 **Mg** 21											13 **Al** 22	14 **Si** 23	15 **P** 22	16 **S** 21	17 **Cl** 22	18 **Ar** 22
19 **K** 23	20 **Ca** 23	21 **Sc** 20	22 **Ti** 24	23 **V** 23	24 **Cr** 25	25 **Mn** 25	26 **Fe** 28	27 **Co** 26	28 **Ni** 31	29 **Cu** 28	30 **Zn** 30	31 **Ga** 27	32 **Ge** 28	33 **As** 29	34 **Se** 29	35 **Br** 29	36 **Kr** 31
37 **Rb** 29	38 **Sr** 33	39 **Y** 33	40 **Zr** 32	41 **Nb** 33	42 **Mo** 33	43 **Tc** 33	44 **Ru** 33	45 **Rh** 34	46 **Pd** 33	47 **Ag** 38	48 **Cd** 36	49 **In** 38	50 **Sn** 38	51 **Sb** 36	52 **Te** 37	53 **I** 36	54 **Xe** 38
55 **Cs** 40	56 **Ba** 39	57-71 Lanthanides	72 **Hf** 35	73 **Ta** 34	74 **W** 33	75 **Re** 35	76 **Os** 35	77 **Ir** 36	78 **Pt** 37	79 **Au** 36	80 **Hg** 38	81 **Tl** 32	82 **Pb** 33	83 **Bi** 35	84 **Po** 33	85 **At** 33	86 **Rn** 34
87 **Fr** 34	88 **Ra** 33	89-103 Actinides	104 **Rf** 13	105 **Db** 12	106 **Sg** 10	107 **Bh** 10	108 **Hs** 8	109 **Mt** 6	110 **Ds** 7	111 **Rg** 5	112 **Cn** 4	113 **Uut** 4	114 **Uuq** 4	115 **Uup** 2	116 **Uuh** 6	117 **Uus** unknown	118 **Uuo** 1
	Lanthanides		57 **La** 34	58 **Ce** 35	59 **Pr** 33	60 **Nd** 34	61 **Pm** 31	62 **Sm** 33	63 **Eu** 33	64 **Gd** 32	65 **Tb** 31	66 **Dy** 31	67 **Ho** 33	68 **Er** 32	69 **Tm** 31	70 **Yb** 32	71 **Lu** 35
	Actinides		89 **Ac** 29	90 **Th** 30	91 **Pa** 28	92 **U** 24	93 **Np** 20	94 **Pu** 20	95 **Am** 17	96 **Cm** 20	97 **Bk** 14	98 **Cf** 20	99 **Es** 17	100 **Fm** 18	101 **Md** 16	102 **No** 12	103 **Lr** 11



- ^{40}K, ^{226}Ra, ^{228}Th

Sources of radioactivity in the building



1 - bedrock

2 - drinking water

3 - building materials

Radioactive materials

Radioactive could be (but not necessary!) e.g.:

- **aggregate from uranium ores**
- **blast–furnace slag**
- **cinder**
- **coal fly ash**
- **phosphogypsum**

Asbestos is not radioactive !

Radioactivity of building materials

- ^{226}**Ra mass activity concentration** [Bq.kg^{-1}]
- **activity concentration index I** [unitless]

$$I = \frac{a_K}{3000} + \frac{a_{Ra}}{300} + \frac{a_{Th}}{200}$$

where a_K, a_{Ra} , a_{Th} are radium, thorium and potassium activity concentrations in material

Activity concentration

Activity concentration range (Bq/kg) of common building materials.

Building material	**^{226}Ra [Bq/kg]**	**^{232}Th [Bq/kg]**	**^{40}K [Bq/kg]**
Concrete	18 - 67	3 - 43	16 - 1100
Light weight concrete	10 - 60	6 - 66	51 - 870
Bricks	7 - 140	8 - 127	227 - 1140
Gypsum	1 - 67	0.5 - 190	22 - 804
Cement	13 - 107	7 - 62	48 - 564

Activity concentration range (Bq/kg) of selected covering building materials.

Building material	**^{226}Ra [Bq/kg]**	**^{232}Th [Bq/kg]**	**^{40}K [Bq/kg]**
Ceramics	25 - 193	29 - 66	320 - 1049
Granite	ND - 160	ND - 354	24 - 2355
Tiles	33 - 61	45 - 66	476 - 788
Marble	1 - 63	0.4 - 142	9 - 986

Radioactivity of building materials

- most countries with reference levels for radioactive elements in building materials apply activity indices or maximum permissible/recommended concentrations
- some countries - one reference level for Ra^{226}
- other countries – level for each Ra^{226}, Th^{232} and K^{40}
- in most of the countries the levels are enforced, only in Norway are the reference levels advisory

Reference Levels for Radioactive Elements in Building Materials

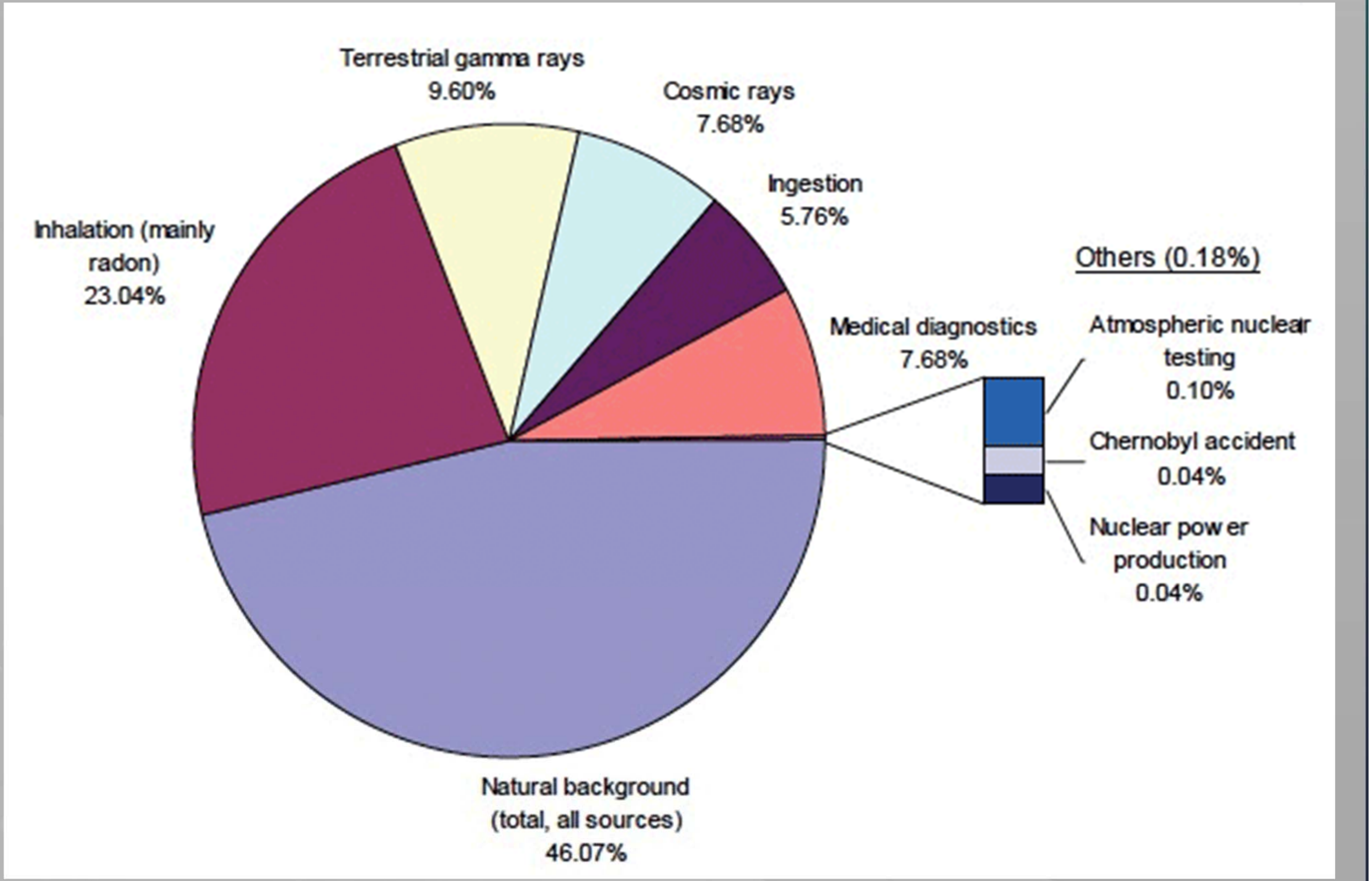
Czech Republic:

- **enforced level**: **150-200 Bq/kg** - materials in buildings where people could stay more than 1000 h/year (depending on the type of material); 1000 Bq/kg for materials in other buildings.
- **advisory level**: **80-120 Bq/kg** in buildings where people normally stay more than 1000 h/year; 300-500 Bq/kg for materials in other buildings

Reference Levels for Radioactive Elements in Building Materials

I	Type of building material	Example
0,5	materials used in bulk amount	bricks, cement, concrete, gypsum
1	raw materials	aggregates, stones, clay
2	materials used in „small“ amount	ceramic tiles

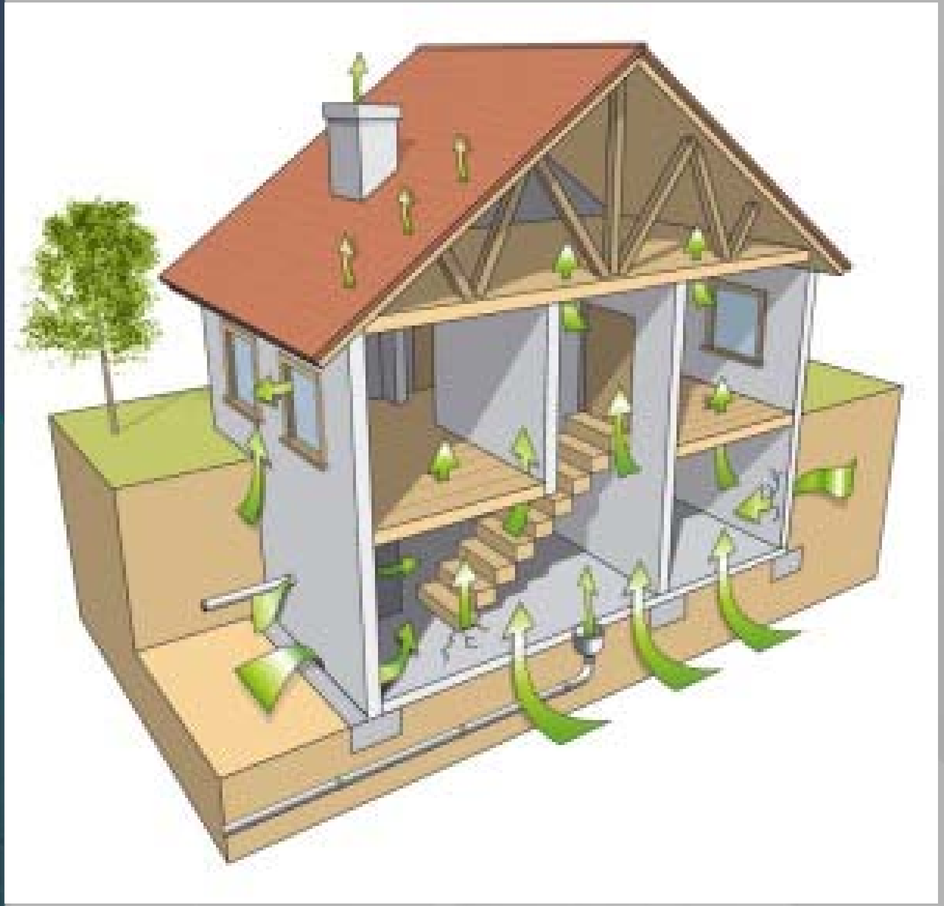
Doses from radiation sources



Radon

- colorless, odorless, tasteless gas
- radioactive product of decay uranium or thorium
- half-life 3,8 days → **radon daughters** (solids Po, Pb, Bi) stick to surfaces such as dust particles in the air
- if contaminated dust is inhaled, these particles can stick to the airways of the lung and increase the risk of developing lung cancer

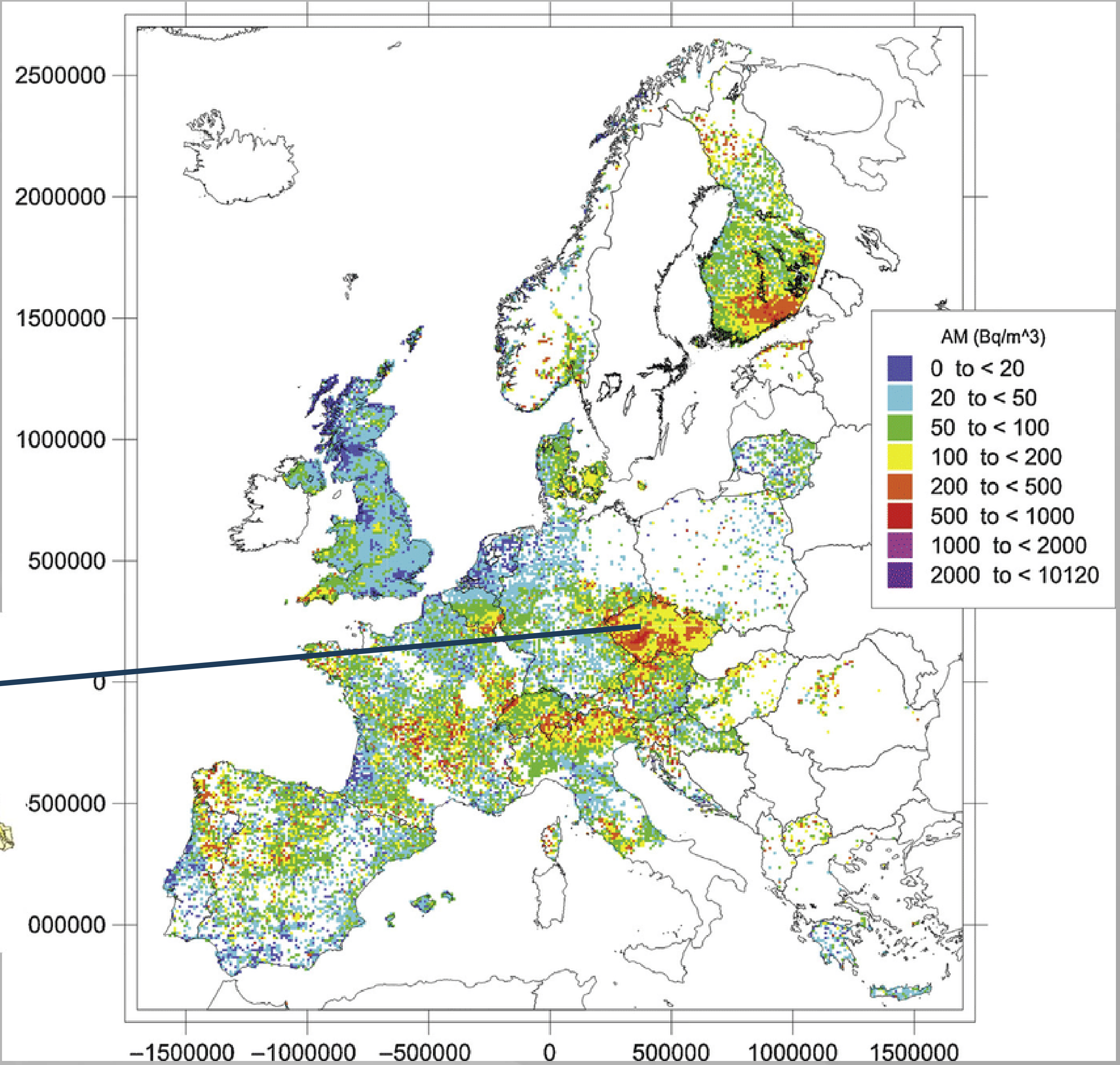
Radon in houses

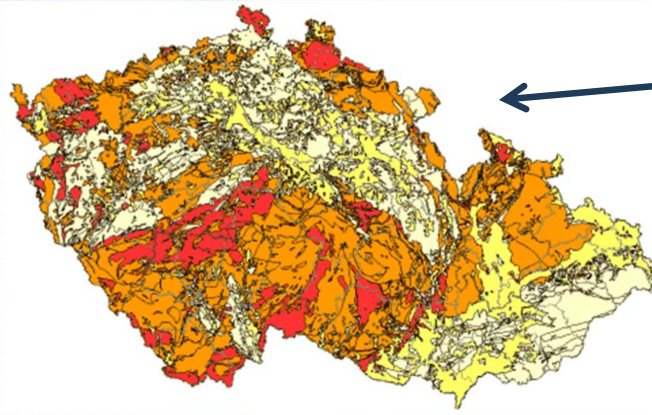


- Cracks in solid floors
- Construction joints
- Cracks in walls
- Gaps in suspended floors
- Gaps around service pipes
- Cavities inside walls
- The water supply

Radon map

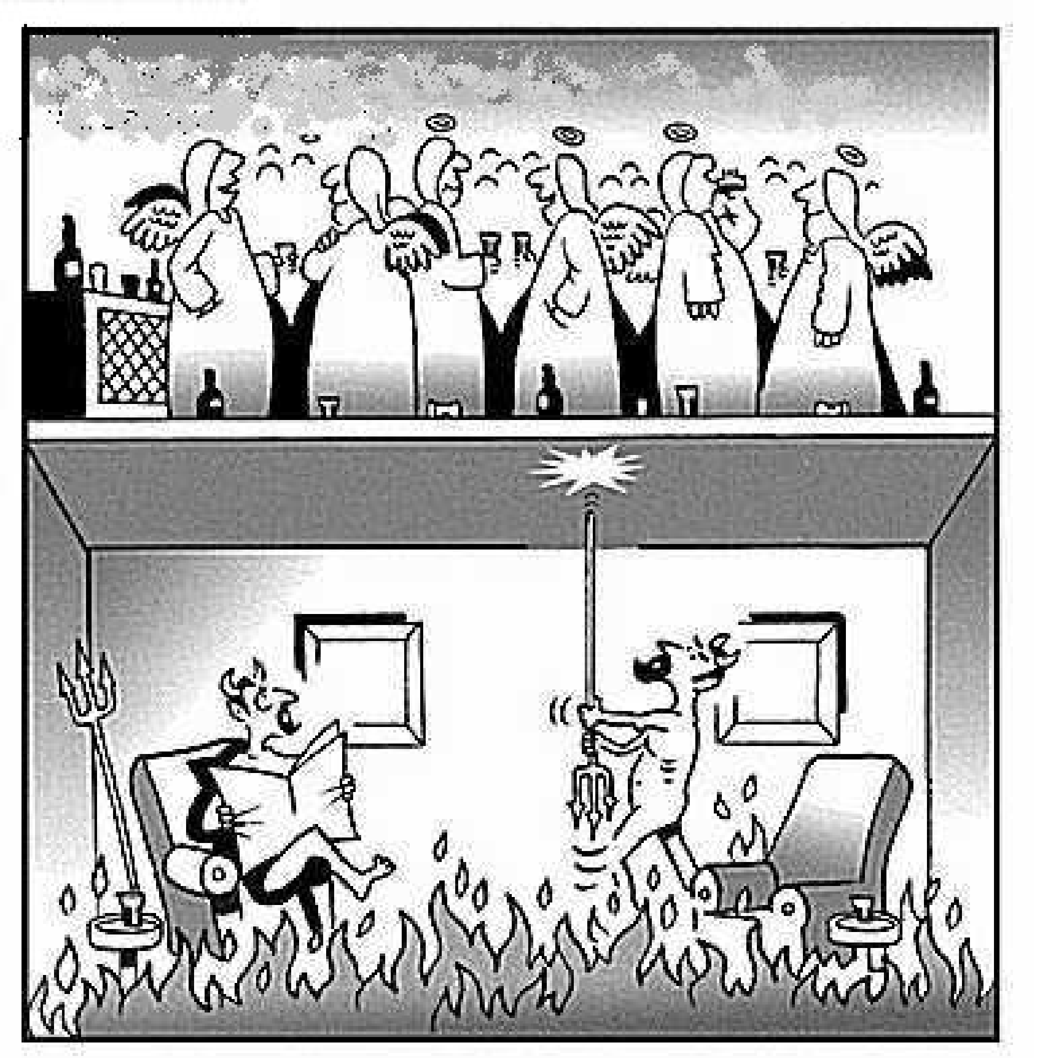
Europe





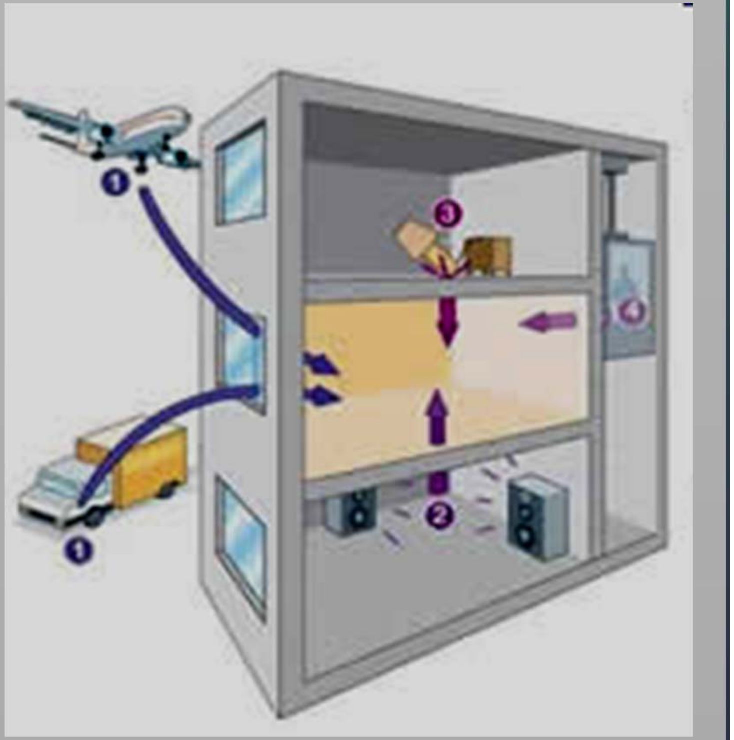
Czechia

Acoustic properties

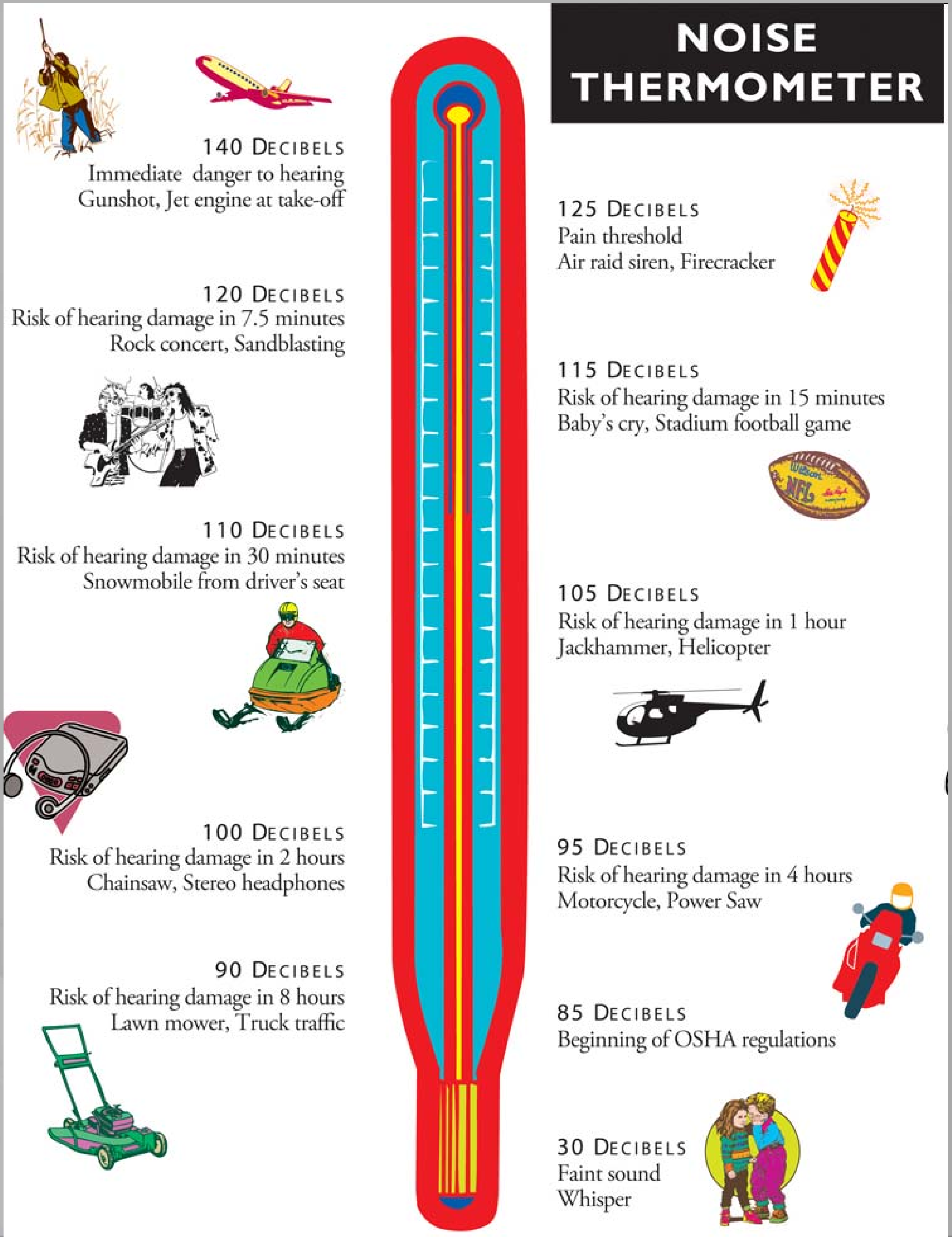


Noise sources

- **Outside air-borne noises**: road, rail or air traffic
- **Inside air-borne noises**: conversations, hi-fi, TV...
- **Impact**: movement of people or furniture, falling objects...
- **Equipment noises**: lift, taps, mechanical ventilation, heating or air conditioning installation.



Noise level



NOISE THERMOMETER

140 DECIBELS
Immediate danger to hearing
Gunshot, Jet engine at take-off

120 DECIBELS
Risk of hearing damage in 7.5 minutes
Rock concert, Sandblasting

110 DECIBELS
Risk of hearing damage in 30 minutes
Snowmobile from driver's seat

100 DECIBELS
Risk of hearing damage in 2 hours
Chainsaw, Stereo headphones

90 DECIBELS
Risk of hearing damage in 8 hours
Lawn mower, Truck traffic

125 DECIBELS
Pain threshold
Air raid siren, Firecracker

115 DECIBELS
Risk of hearing damage in 15 minutes
Baby's cry, Stadium football game

105 DECIBELS
Risk of hearing damage in 1 hour
Jackhammer, Helicopter

95 DECIBELS
Risk of hearing damage in 4 hours
Motorcycle, Power Saw

85 DECIBELS
Beginning of OSHA regulations

30 DECIBELS
Faint sound
Whisper

Noise maps

Prague

Potential quiet areas in Europe, based upon Quietness Suitability Index (QSI)

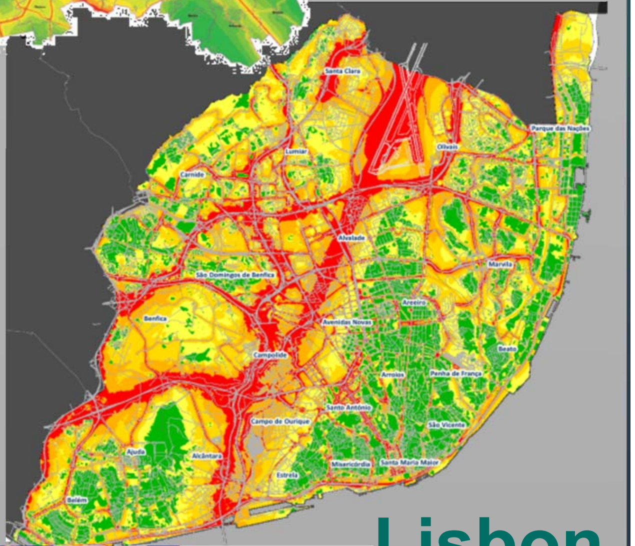
Value

High: 1

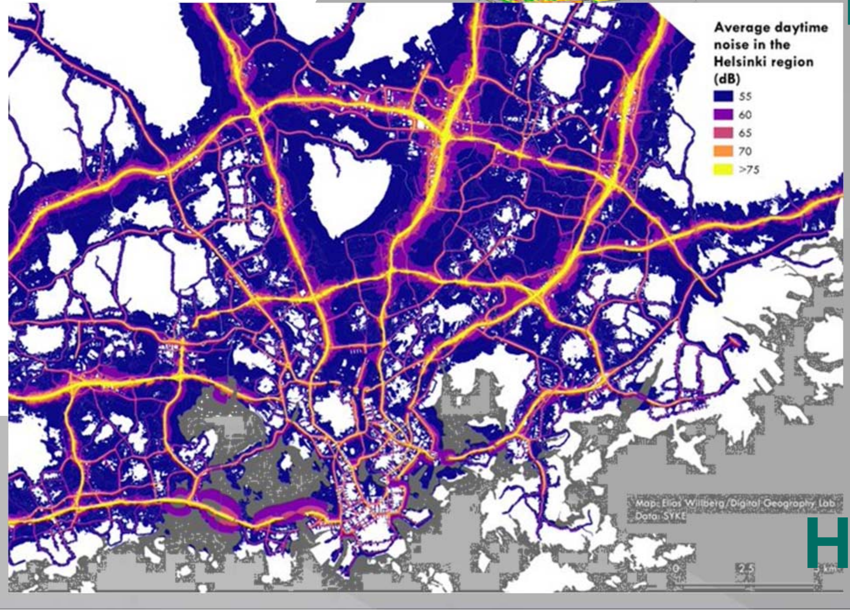
Low: 0

☐ No data

▨ Outside coverage



Lisbon

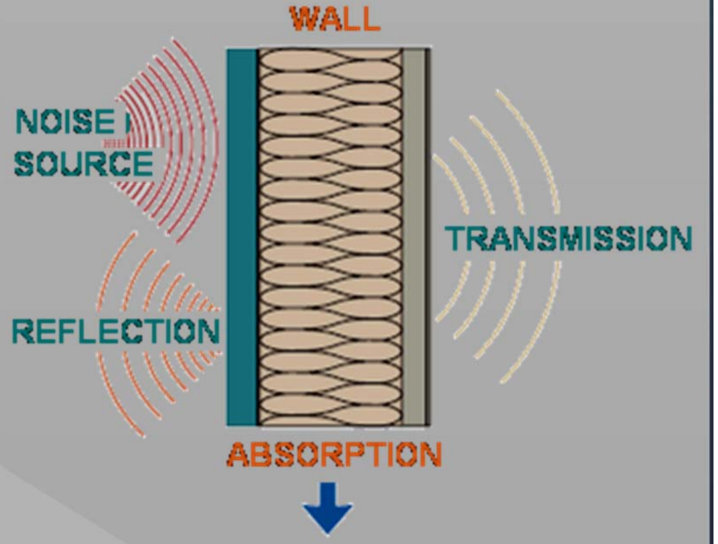


Helsinki

Basic acoustic parameters

Acoustic absorptivity

- **sound energy is reduced when sound waves pass through a medium or strike a surface** - the incident sound that strikes a material is not reflected back



Reverberation

- **the collection of reflected sounds from the surfaces**

Sound absorption coefficient

- how much of the sound is absorbed in the material

$$\alpha = \frac{I_a}{I_i}$$

I_a ….. sound intensity absorbed [W/m^2]

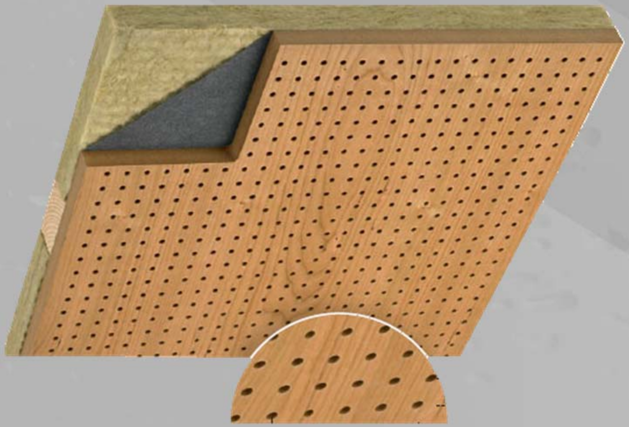
I_i …. incident sound intensity [W/m^2]

Material	α
Plaster walls	0.01 - 0.03
Unpainted brickwork	0.02 - 0.05
Painted brickwork	0.01 - 0.02
3 mm plywood panel	0.01 - 0.02
6 mm cork sheet	0.1 - 0.2
Hardwood	0.3
100 mm mineral wool	0.65
Persons, each	2.0 - 5.0

Acoustic constructions

- against sound reflection – **materials with good sound absorptivity**
  - soft, pliable, porous materials
- against sound transmission – **sound insulating materials**

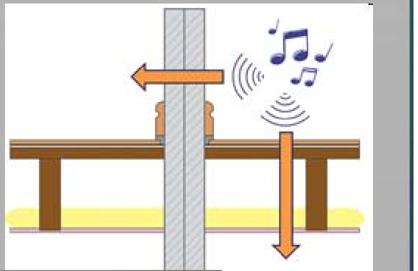
  \- materials with high surface density



Noise insulation

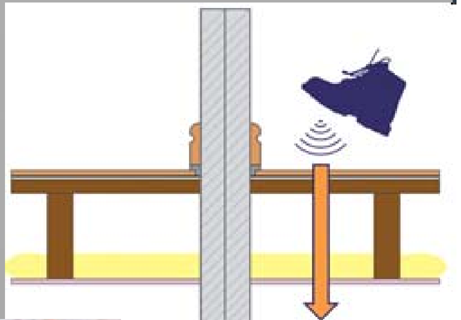
Airborne noise (voices, music)

- materials with high surface density (mass per unit area) - min 350 $kg.m^{-2}$




Impact noise (feet, moving furniture, dropped items)

- padding or cushioning - soft, sound absorbing materials (carpets, mineral wool)




Soundproofing

= sound blocking

- reducing the sound pressure
- to stop sound from entering or leaving a space

Sound absorption

= acoustic enhancement

- to enhance the properties of sound by improving speech clarity and sound quality

Acoustic comfort

- **good sound environment**
  - lower sound level
    - an acoustic ceiling with high absorption factor
  - reduced sound propagation
  - increased speech intelligibility
    - combination absorbers which enhance early reflections and minimize late reflections
  - appropriate reverberance
    - the room volume, the amount of absorbing material and the position of absorbers and reflectors

Chemical properties

- **Chemical reactions in materials:**
  - **processing** (setting and hardening , foaming…)
  - **materials (in)compatibility**
  - **ageing**
  - **corrosion** (degradation) (inorganic materials, metals, biocorrosion…)

Materials incompatibility

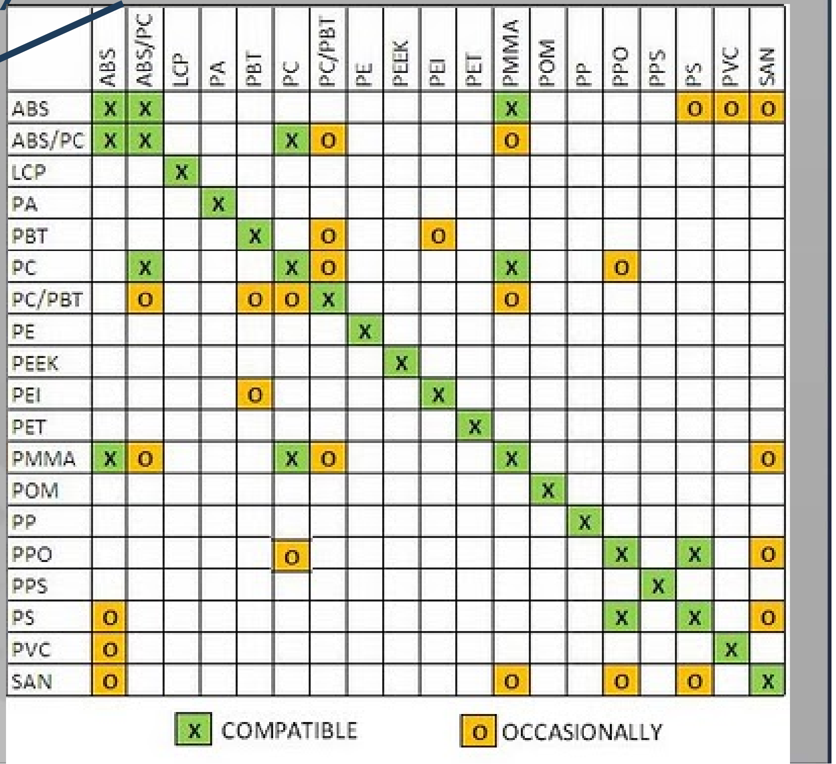
Metals:

- **galvanic corrosion** (dissimilar metal corrosion)
  - contact of two metals with different electrical potentials
- **aluminum + alkali** environment
- **copper + low pH** water, + **aggressive** soils
- **steel + gypsum**

Materials incompatibility

Plastics:

- **EPS + solvents** (in the paints)
- **PVC + formaldehydes**
- **phenolic foam** (acid pH) + steel



	ABS	ABS/PC	LCP	PA	PBT	PC	PC/PBT	PE	PEEK	PEI	PET	PMMA	POM	PP	PPO	PPS	PS	PVC	SAN
ABS	X	X										X					O	O	O
ABS/PC	X	X				X	O					O							
LCP			X																
PA				X															
PBT					X		O			O									
PC		X				X	O					X			O				
PC/PBT		O			O	O	X					O							
PE								X											
PEEK									X										
PEI					O					X									
PET											X								
PMMA	X	O				X	O					X							O
POM													X						
PP														X					
PPO						O									X		X		O
PPS																X			
PS	O														X		X		O
PVC	O																	X	
SAN	O											O			O		O		X

X COMPATIBLE O OCCASIONALLY

Materials incompatibility

Cement, concrete:

- **cement + wood**
  - – sugar content in the wood
- **concrete + glass fibers**
- **cement + some type of aggregates**
  - – ASR - alkali-silica reaction

Corrosion

- the deterioration of a material due to interaction with its environment
- the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings
- **metals** – atmospheric corrosion
- **non-metal materials** -
  - ceramic
  - plastics
  - concrete
  - glass
  - biodegradation

Corrosion of non-metal materials (degradation)

Ceramic

- refractory materials + wood combustion gases
- bricks + flue gases

Concrete

- decalcification (water without minerals)
- leaching
- sulphates
- bacteria

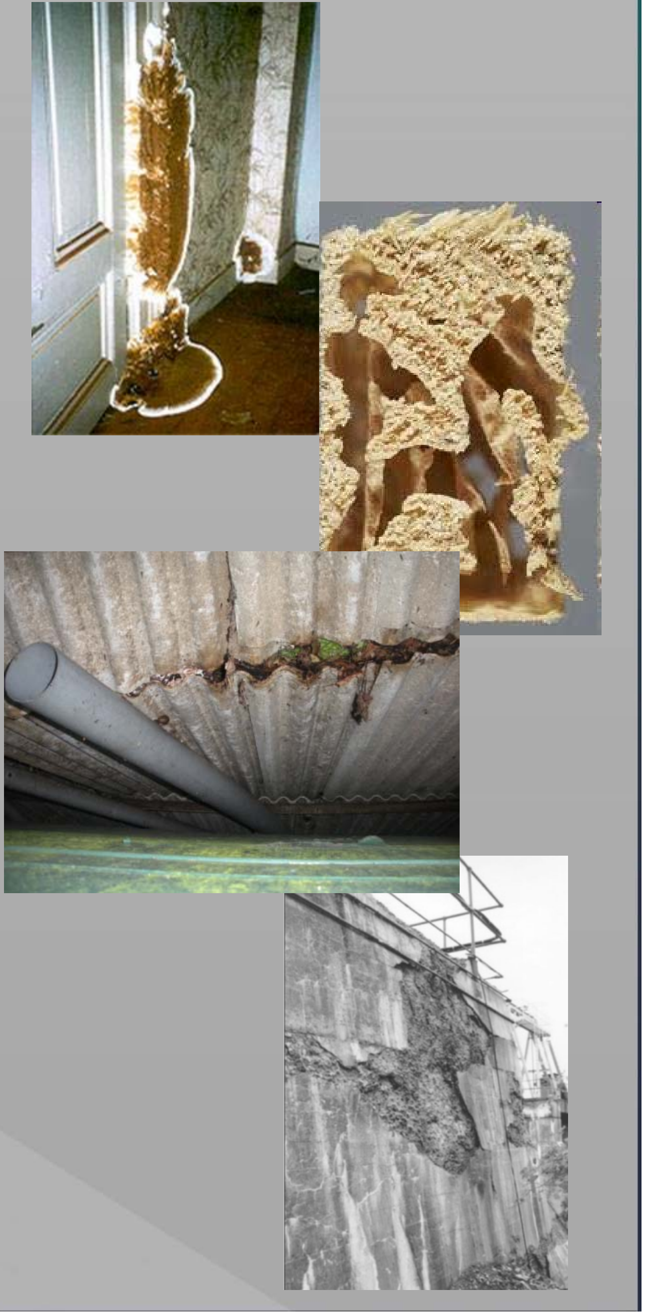
Biodegradation

Caused by:

- microorganism
- fungi
- insects
- birds
- plants
- rodents

Biodegradation is natural process!

Biodegradation - examples



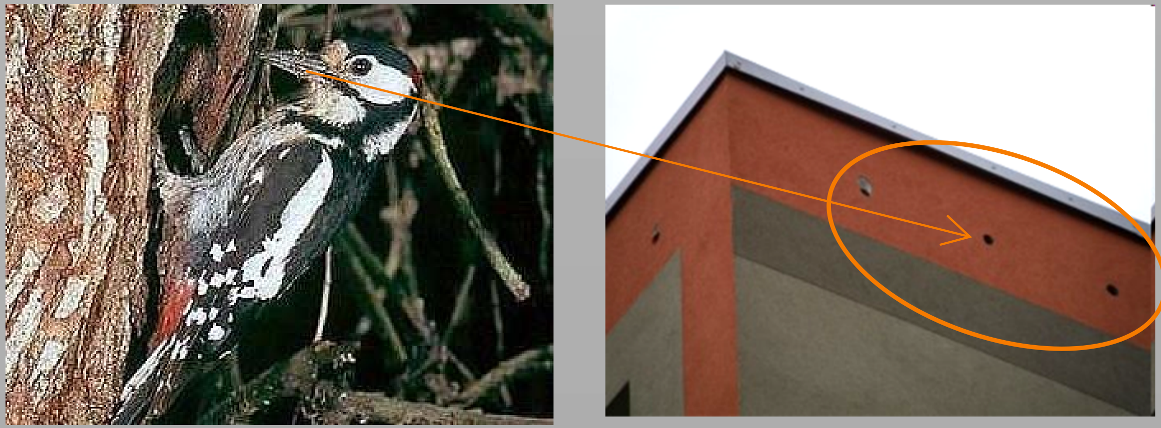
- **wood + fungi** (dry rot - Merulius Lacrymans)
- **wood + insects** (old house borer - Hylotrupes Bajulus)
- **nitrifying bacteria** on the **asbestos-cement** roofs
- **sulphur oxidizing bacteria** on **concrete**

Biodegradation - examples

- stone + lichen
- building + plants
- termites + thermal insulation

Biodegradation - examples

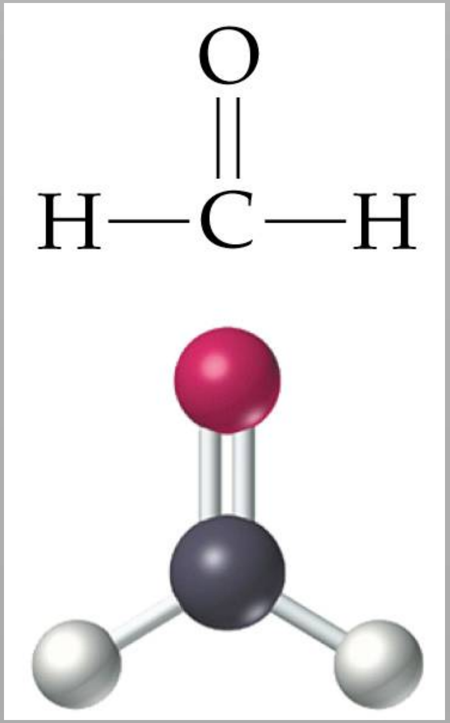
- insulated facade + woodpeckers



- rodents

Hygienic properties

- pollutants in air (styrene, formaldehyde, plasticizers in PVC)
- contact with the skin (biocides, paints)
- respirable fibers (asbestos, glass)



The higher amount of pollutants can be caused by more accurate measuring methods, not in reality !

Environmental safety

- low energy consumption at production
- the renewable resources
- recycling possibility
- low liquidation costs

- PVC – bad recyclability, toxicity at incineration

Durability of materials

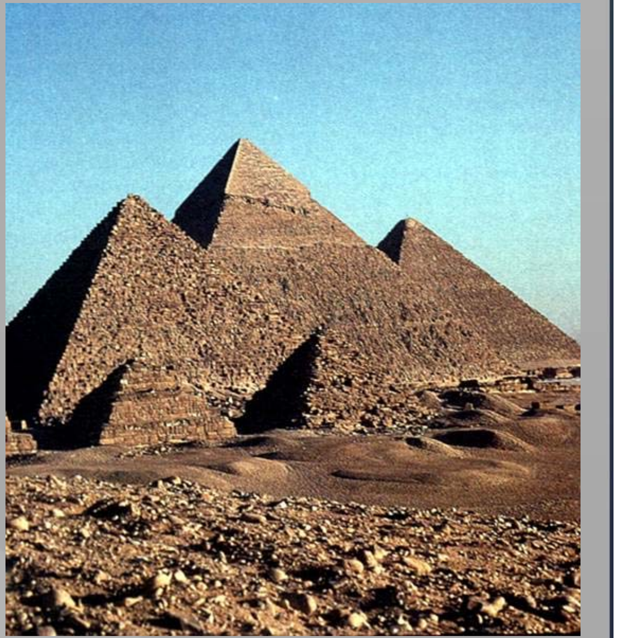
- ability to be used over a desired period

Factors affecting durability:

  - **age**
  - **maintenance**
  - **high temperature**
  - **UV radiation**
  - **load**
  - **chemical attacks**
  - **weathering actions** (frost)

Life span of buildings

- **40 – 100** years – industrial buildings
- **50 – 100** y. - residential buildings
- **70 – 500** y. – bridges and monuments
- special causes: **2 – 5 millennia** – nuclear waste disposals



Durability of buildings and materials

Life span of building		Expected durability of building materials		
	Yrs.	Easily replaceable	Replaceable with some effort	Unreplace-able
short	**10**	**10**	**10**	**10**
middle	**25**	**10**	**25**	**25**
normal	**50**	**10**	**25**	**50**
long	**100**	**10**	**25**	**100**

Durability of some materials

Roofing

Ceramic tiles	100 years
Concrete tiles	100 years
Steel sheets	50 years
Asphalt shingle	less than 50 years

Waterproof insulation

asphalt felts	15 years
modified bitumen membranes	100 years (exp.)
rubber membrane	70 years
PVC membrane	25 years

Binders

Binders

- materials, that binds other materials together

0 **processing** 1 **setting** 2 **hardening**

0 ..... activation (mixing water and binder)

1 ..... initial setting time

2 ..... final setting time

Binders - terminology

Processing

- mixing, transport, placing

Setting

- change from liquid to solid phase

Initial setting time

- material begins to stiffen to such a degree that, although still soft, it becomes unworkable

Final setting time

- material may be regarded as a rigid solid

Hardening

- increase of strength

Binders

- in the building industry mostly inorganic

Non-hydraulic

(air binders)

- **need air to set**

Hydraulic

- **can set and harden in water**
- **water resistant**

Hydraulic binders

- binders which set and harden as a result of chemical reactions with water and continue to harden even if subsequently placed under water
- for this the presence of **hydraulites** is necessary: SiO_2, Al_2O_3, Fe_2O_3

Non-hydraulic binders:

- gypsum
- lime
- magnesia binder
- water glass

Hydraulic binders:

- hydraulic lime
- cement
- geopolymers

Hydraulic modulus

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

• air (non-hydraulic) lime	**HM > 6**
• hydraulic lime	**HM < 6**
• portland cement	**HM < 2,5**
• high alumina cement	**HM < 1,5**

Hydraulic binders

Hydraulic binders

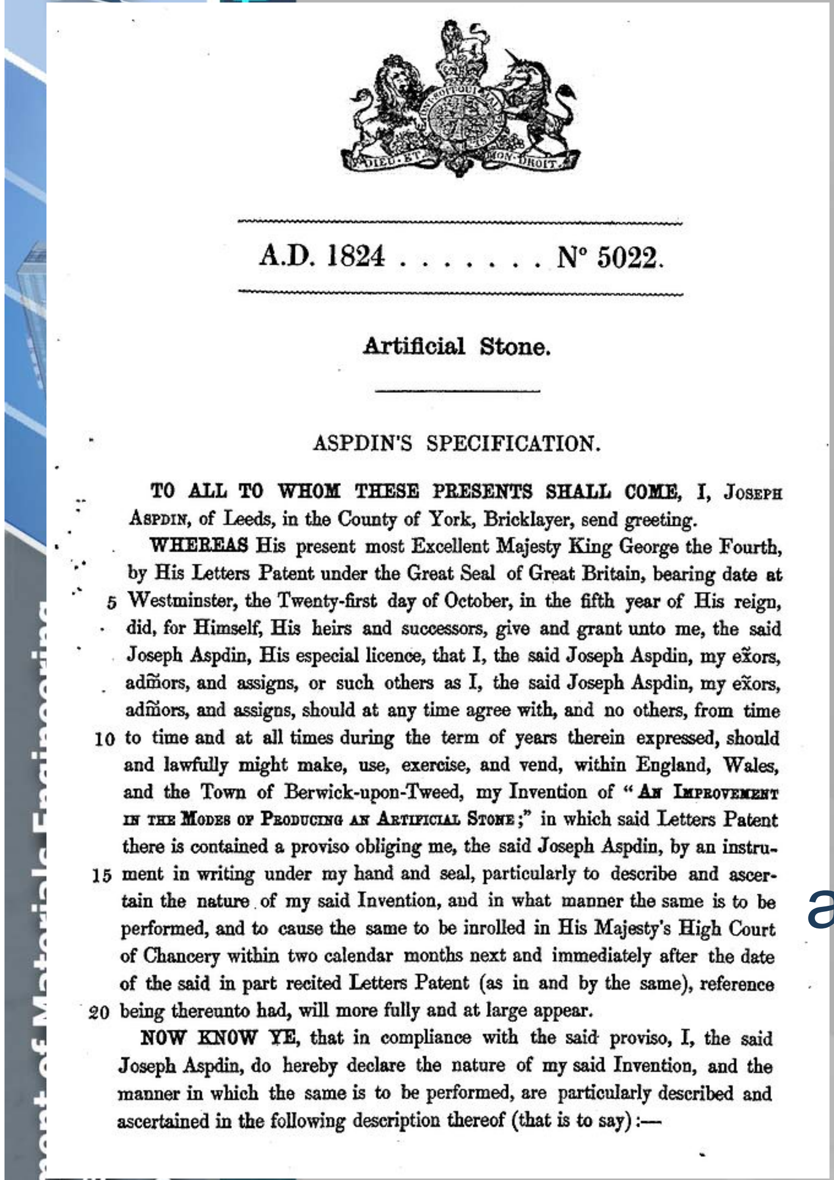
- **opus caementicium**

  "There is also a kind of powder from which natural causes produces astonishing results. This substance, when mixed with lime and rubble, not only lends strength to buildings of other kinds, but even when piers are constructed of it in the sea, they set hard under water."

Marcus Vitruvius Pollio, 13 B.C.

Cement

Cement



A.D. 1824 . . . . N° 5022.

Artificial Stone.

ASPDIN'S SPECIFICATION.

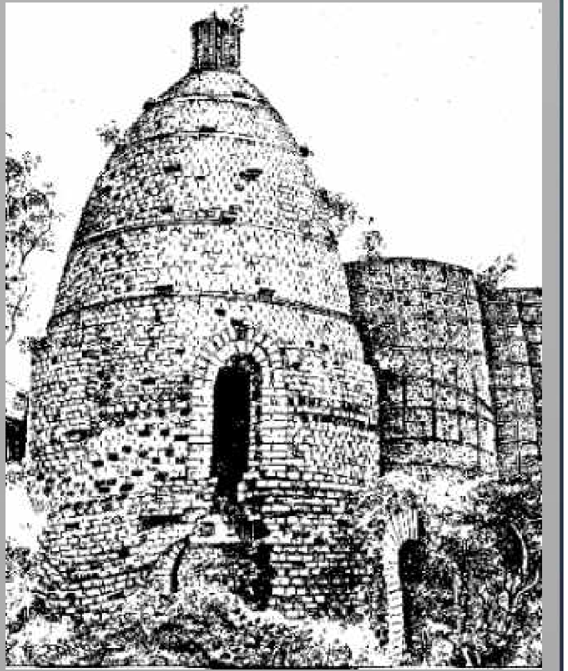
TO ALL TO WHOM THESE PRESENTS SHALL COME, I, Joseph Aspdin, of Leeds, in the County of York, Bricklayer, send greeting.

WHEREAS His present most Excellent Majesty King George the Fourth, by His Letters Patent under the Great Seal of Great Britain, bearing date at Westminster, the Twenty-first day of October, in the fifth year of His reign, did, for Himself, His heirs and successors, give and grant unto me, the said Joseph Aspdin, His especial licence, that I, the said Joseph Aspdin, my ex̃ors, adm̃ors, and assigns, or such others as I, the said Joseph Aspdin, my ex̃ors, adm̃ors, and assigns, should at any time agree with, and no others, from time to time and at all times during the term of years therein expressed, should and lawfully might make, use, exercise, and vend, within England, Wales, and the Town of Berwick-upon-Tweed, my Invention of "An Improvement in the Modes of Producing an Artificial Stone;" in which said Letters Patent there is contained a proviso obliging me, the said Joseph Aspdin, by an instrument in writing under my hand and seal, particularly to describe and ascertain the nature of my said Invention, and in what manner the same is to be performed, and to cause the same to be inrolled in His Majesty's High Court of Chancery within two calendar months next and immediately after the date of the said in part recited Letters Patent (as in and by the same), reference being thereunto had, will more fully and at large appear.

NOW KNOW YE, that in compliance with the said proviso, I, the said Joseph Aspdin, do hereby declare the nature of my said Invention, and the manner in which the same is to be performed, are particularly described and ascertained in the following description thereof (that is to say):—

Joseph Aspdin

author of the patent for „Portland cement“ (1824)



First cement kiln „Beehive“

More information – cement history:
https://www.dartfordarchive.org.uk/technology/cement.shtml

Cement manufacture

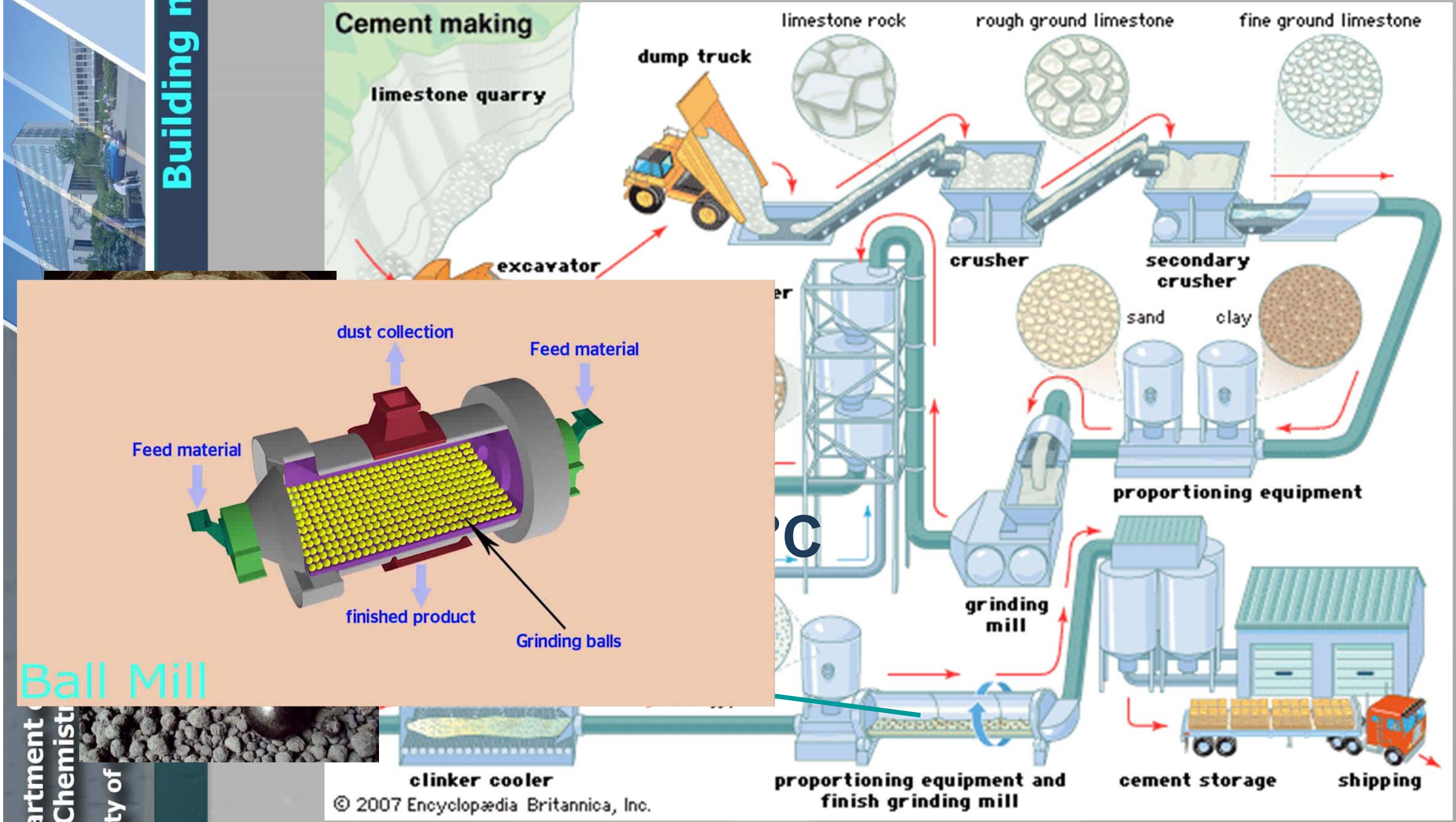
Raw material:

- **minerals containing $CaCO_3$ + SiO_2** (+ other hydraulic oxides)
  - impure limestone, marl, chalk
- **secondary raw materials** (as source of hydraulic oxides)
  - clay, shale, fly ash, slag
- **calcium sulphate** (as setting retarder)
  - gypsum, anhydrite

Limestone quarry „America“, Czech Rep.

Cement manufacture

Cement manufacture



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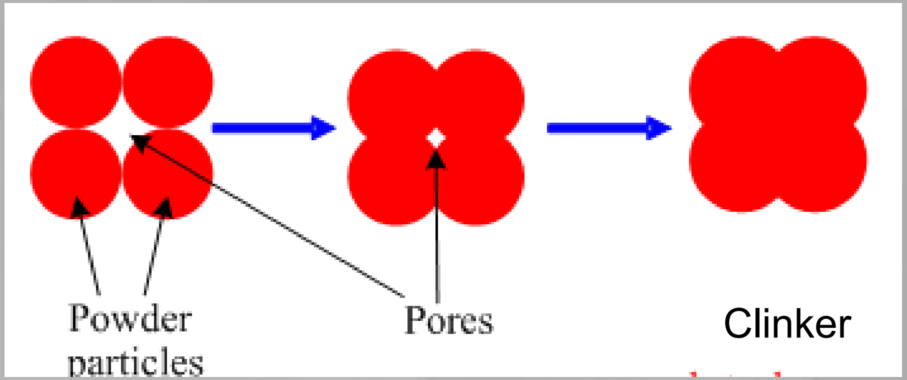
Sintering

- consolidation of powder particles by heating at 1300 - 1400°C → **clinker**
  - the separate particles diffuse to the neighboring powder particles



  - chemical reactions → formation of **cement compounds – clinker minerals** (calcium silicates)

Rotary kiln

about 1480 °C

Building materials

Department of Materials Engineering and Chemistry

Faculty of Civil Engineering

Chemical composition of cement

- expressed as amount of oxides in mass %
- determined by chemical analysis (EN 196-2)

Ca	46,4 %
Si	9,8 %
Al	3,2 %
Fe	2,1 %
Mg	1,2 %
S	1,0 %
O	35,3 %
Σ	99,0 %

CaO	65 %
SiO_2	21 %
Al_2O_3	6 %
Fe_2O_3	3 %
MgO	2 %
SO_3	2 %
Σ	99,0 %

Main clinker minerals

- cement oxides are (mostly) not free, but form **clinker minerals**

Tricalcium silicate	Alite	$3CaO \cdot SiO_2$
Dicalcium silicate	Belite	$2CaO \cdot SiO_2$
Tricalcium aluminate	-	$3CaO \cdot Al_2O_3$
Tetracalcium aluminoferrite	Ferrite (brown-millerite)	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Cement chemist notation
(CCN)

- an abbreviated record of the cement compounds

Compound	Name	CCN	Formula
Calcium oxide	lime	**C**	CaO
Silicon dioxide	silica	**S**	SiO_2
Aluminum oxide	alumina	**A**	Al_2O_3
Iron oxide	rust	**F**	Fe_2O_3
	water	**H**	H_2O

Clinker minerals in cement notation

Mineral	Abbreviation	Formula
Tricalcium silicate	**C_3S**	$3CaO \cdot SiO_2$
Dicalcium silicate	**C_2S**	$2CaO \cdot SiO_2$
Tricalcium aluminate	**C_3A**	$3CaO \cdot Al_2O_3$
Tetracalcium aluminoferrite	**C_4AF**	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Cement minerals properties

C_3S

- hydrates and hardens rapidly
- responsible for initial set and early strength

C_2S

- hydrates and hardens slowly
- responsible for later strength increase
- low hydration heat

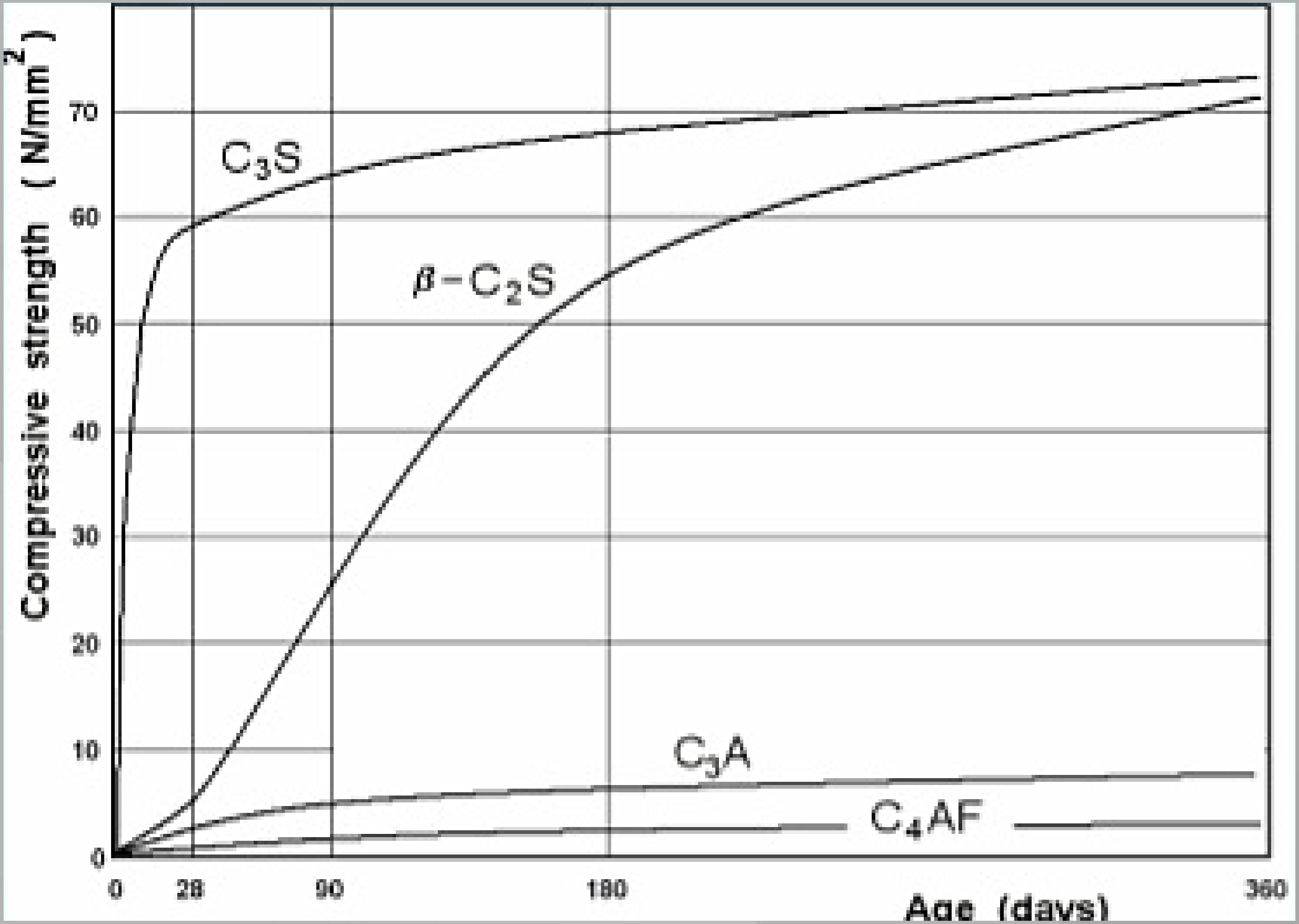
C_3A

- hydrates and hardens the quickest
- a large amount of heat
- important in sulphate corrosion of concrete

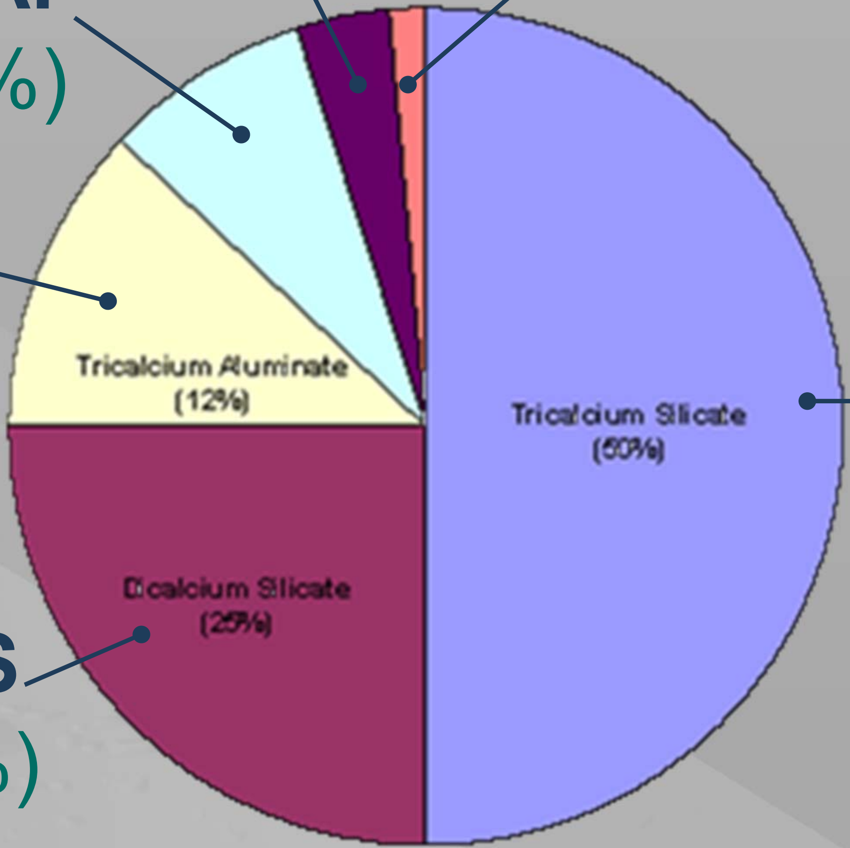
C_4AF

- contributes little to strength
- color effects

Contribution of cement minerals to strength



Composition of Portland cement



gypsum
(3,5 %)

other
(1,5 %)

C_4AF
(8%)

C_3A
(~12%)

C_3S
(~50 %)

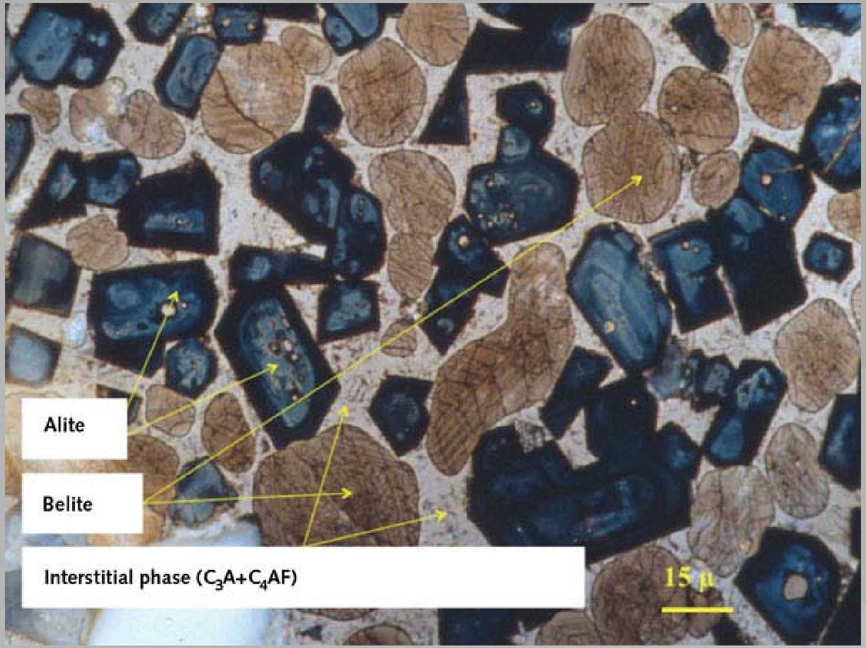
C_2S
(~25%)

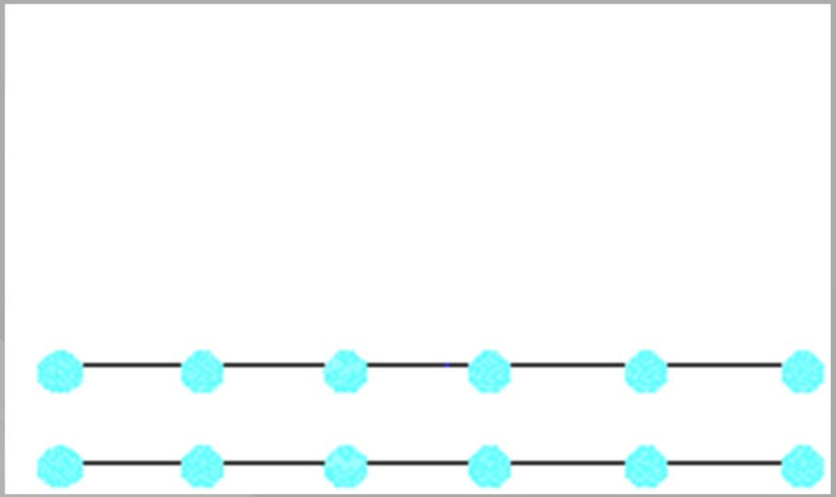
Composition of different cements

Comp. / Cement type	C_3S	C_2S	C_3A	C_4AF
Portland cement	**65**	**15**	**8**	**9**
C. with low heat of hydration	**25**	**55**	**3**	**14**
Sulphate resistant c.	**73**	**9**	**2**	**13**
White cement	**73**	**14**	**11**	**0**

Cement compound composition determination

- microscope
- roentgen diffraction
- Bogue calculation





Bogue calculation

- determines the approximate proportions of the four main minerals in Portland cement clinker
- the calculation assumes that the four main clinker minerals are pure minerals
- there is necessary to know chemical composition of cement (% amount of oxides)

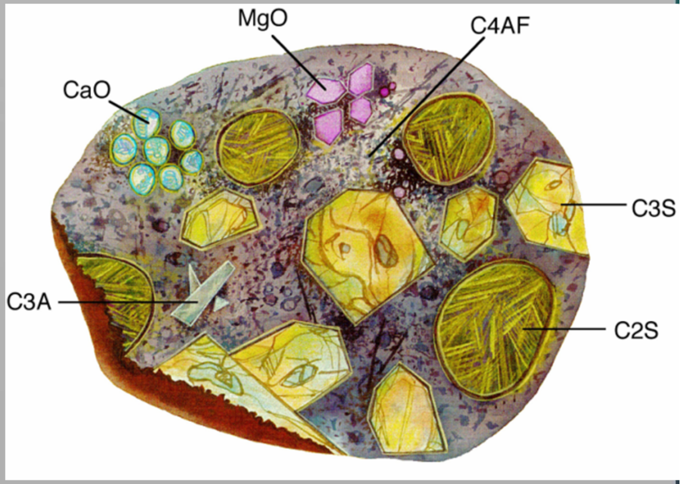
- refers to cement clinker, but it can be adjusted for use with cement

Bogue calculation principles

1. Ferrite is the only mineral to contain iron. Assume that all the Fe_2O_3 is in C_4AF.
2. The aluminate content is fixed by the total alumina content minus the alumina in the ferrite. This can now be calculated, since the amount of ferrite has been calculated.
3. Deduct from the CaO content the amounts attributable to C_4AF, C_3A and free lime, and solve two simultaneous equations to obtain the contents of C_3S and C_2S.

C_3A	$3CaO\boxed{\cdot Al_2O_3}$
C_4AF	$4CaO\boxed{\cdot Al_2O_3}\boxed{\cdot Fe_2O_3}$

Bogue calculation



$[C_4AF] = 3.04*[F]$

$[C_3A] = 2.65*[A] - 1.69*[F]$

$[C_3S] = 4.07*[C] - 1.43*[F] - 6.72*[A] - 7.60*[S]$

$[C_2S] = 8.6*[S] - 3.07*[C] + 1.08*[F] + 5.1*[A]$

- where the [F], [C], [A], [S] are the weight percentages of the oxides F_2O_3, CaO, Al_2O_3, SiO_2 in the clinker

Cement hydration

- series of irreversible chemical reactions between cement and water
- during hydration the cement sets and hardens, “gluing” the aggregate together in a solid mass

Hydration depends on:

- cement type (chemical composition)
- fineness
- amount of water added
- presence of other admixtures

Cement hydration

- when water is added - mostly exothermic reactions occur
- evolution of heat (monitored by conduction calorimetry) → **5 stages**:

1. **Pre-induction**
2. **Dormancy** (induction period)
3. **Setting and hardening**
4. **Cooling**
5. **Densification**

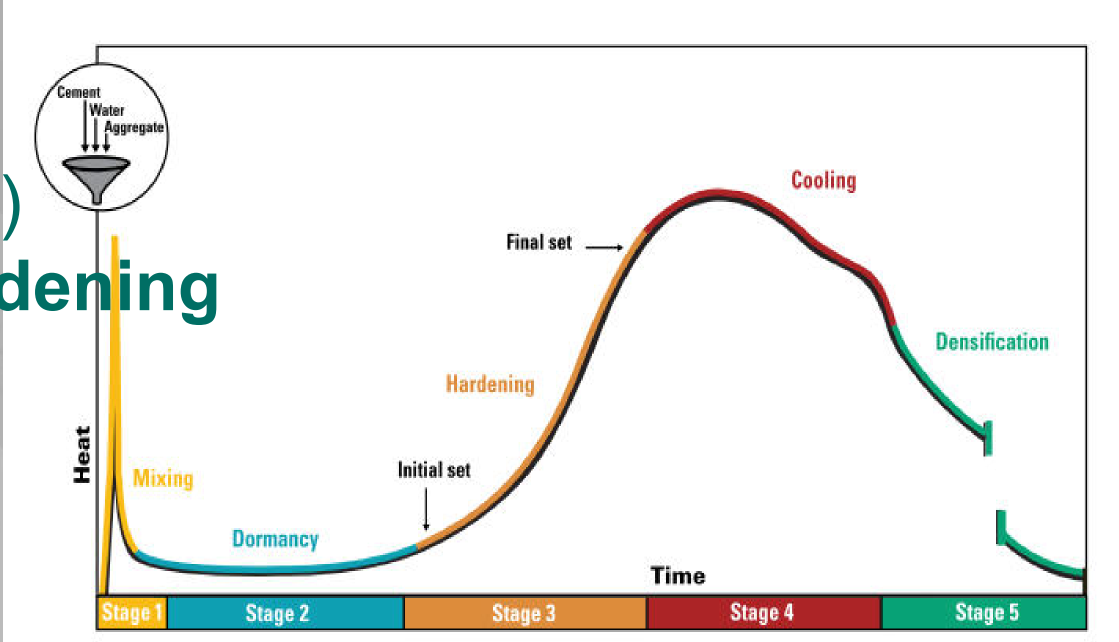


Figure 4-2. General hydration curve delineating the five stages

Cement hydration stages

Stage 1

- immediately on adding water some of the clinker sulphates and gypsum dissolve producing an alkaline, sulfate-rich, solution
- the **C_3A reacts with the water** to form an aluminate-rich gel (CAH gel)
- the CAH gel reacts with sulfate in solution to form small rod-like crystals of ettringite
- C_3A reaction is strongly exothermic and does not last long, typically only a few minutes

Stage 2 (dormant or induction period)

- the period of a few hours of relatively low heat evolution

Cement hydration stages

Stage 3

- the alite (C_2S) and belite (C_3S) start to react → calcium silicate hydrate (CSH gel) and calcium hydroxide are formed
- cement strengths increases
- the individual grains react from the surface inwards, and the anhydrous particles become smaller
- C_3A hydration also continues, as fresh crystals become accessible to water
- period of maximum heat evolution occurs typically between about 10 and 20 hours

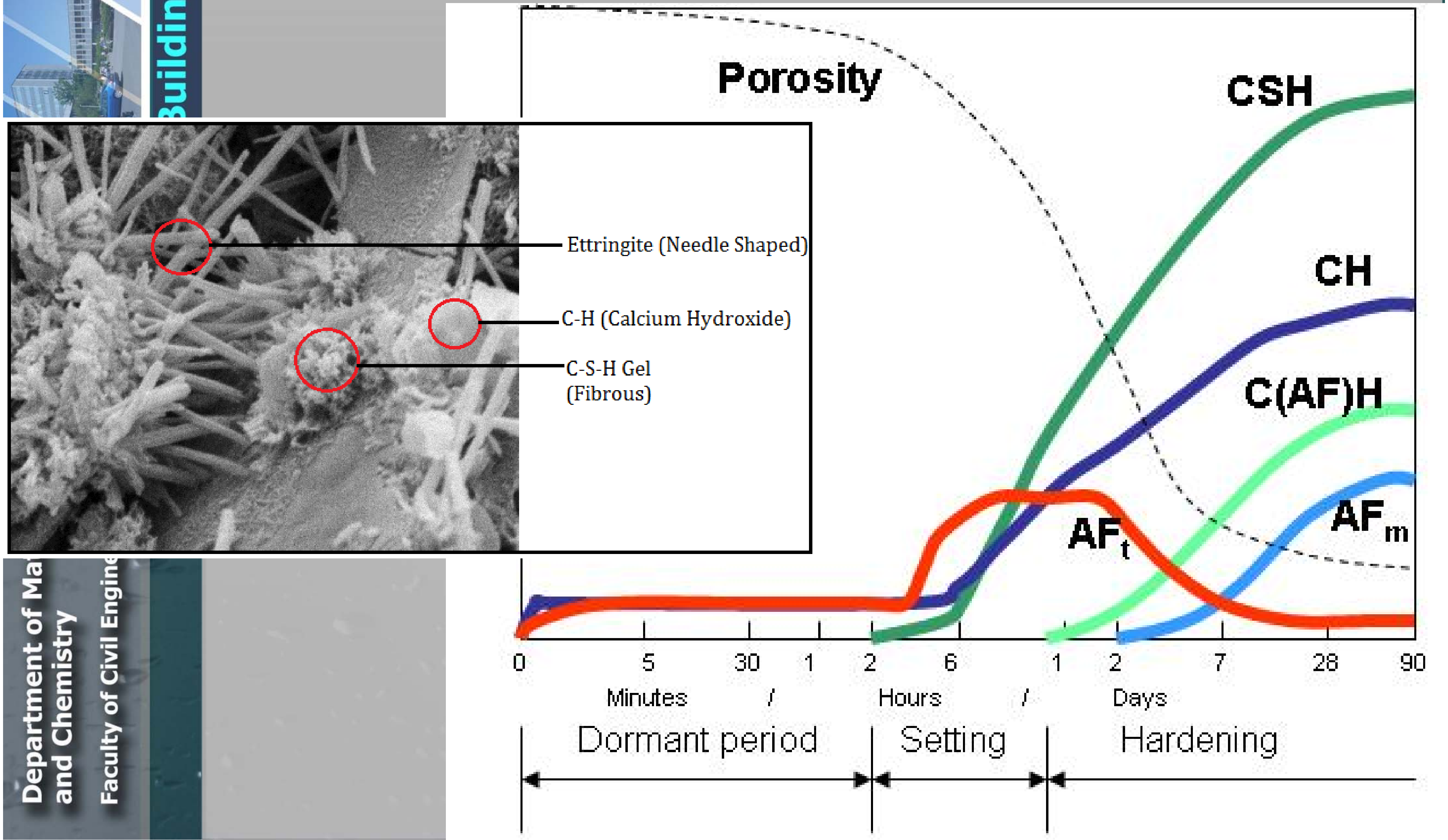
Stage 4

- gradual decrease of heat evolution

Products of cement hydration

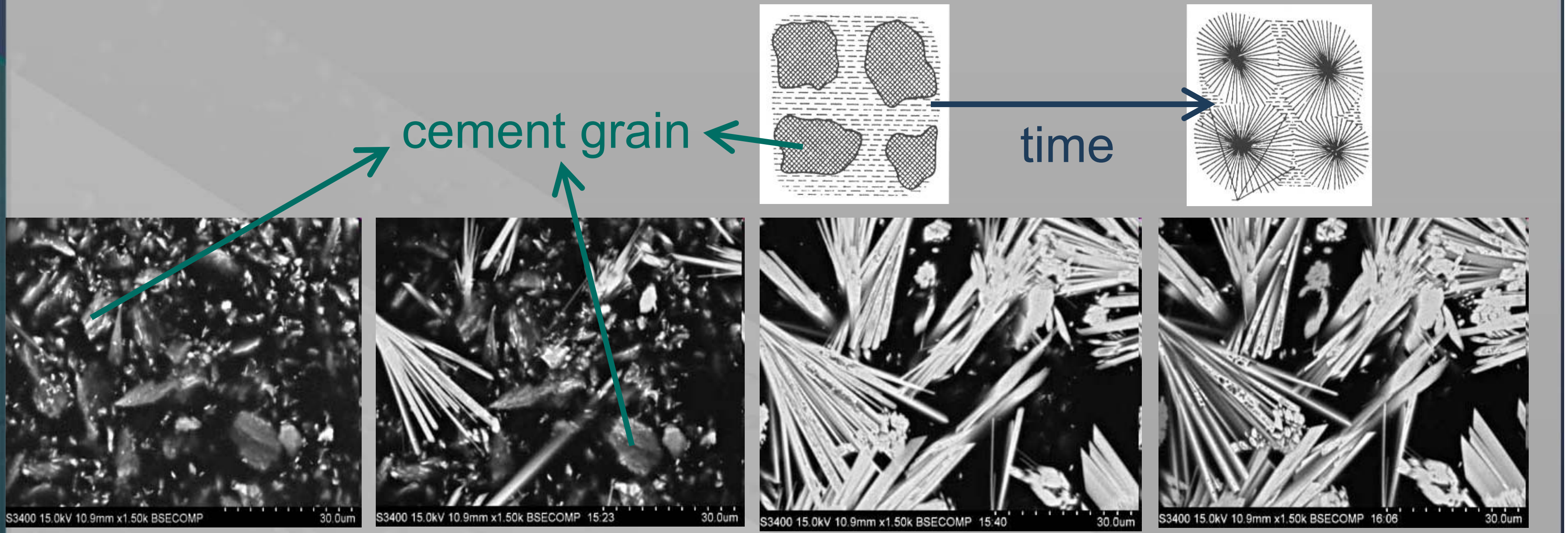
- **Calcium silicate hydrate (**abbrev. C-S-H)**:**
  - main reaction product
  - main source of concrete strength.
- **Calcium hydroxide** $Ca(OH)_2$ = portlandite (abbrev. CH)
  - formed mainly from alite
- **AFm and AFt phases:**
  - most common AFm - monosulfate ($C_3A.CaSO_4.12H_2O$)
  - most common AFt - ettringite ($C_3A.3CaSO_4.32H_2O$)
- **Monocarbonate:**
  - produced in the presence of fine limestone as some of the limestone reacts with the cement pore fluid ($C_3A.CaCO_3.11H_2O$)

Products of cement hydration



Cement setting and hardening

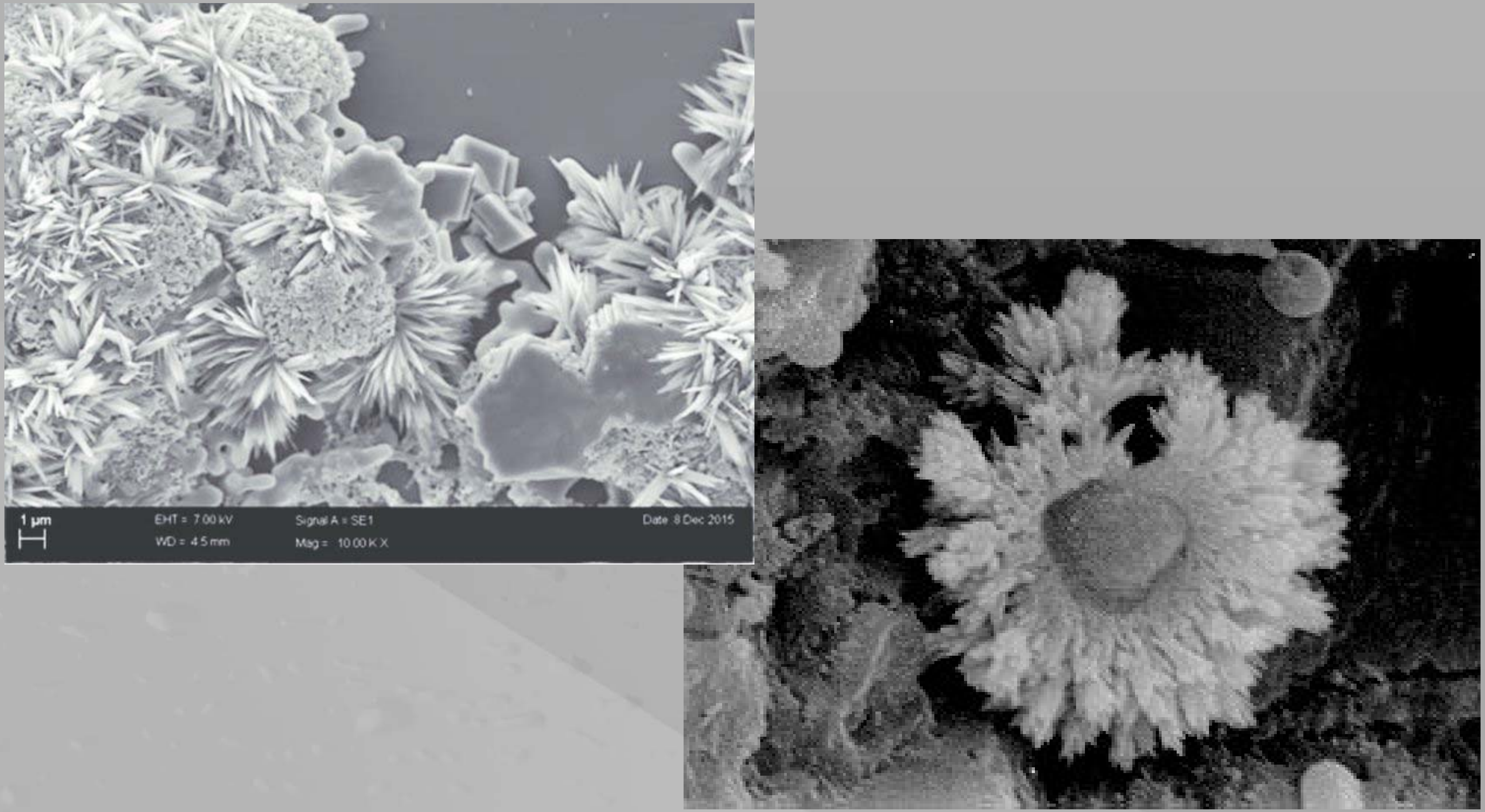
- **Setting**:
  - stiffening of the original plastic mass due to initial gel formation.
- **Hardening**
  - development of strength, due to crystallization
  - crystals form and interlock with each other



0 min **15 min** **30 min** **55 min**

Cement hydration

- **SEM** (scanning electron microscope) **images of hydrated cement grains**



Cement types (EU)

EN 197-1: 5 main types - 27 common cements

- **CEM I - Portland cement**
  - min 95% of clinker
- **CEM II - Portland composite cement**
  - up to 35% of siliceous fly ash
- **CEM III - Blastfurnace cement**
  - up to 95% blastfurnace slag
- **CEM IV- Pozzolanic cement**
  - up to 55% of pozzolana
- **CEM V - Composite cement**
  - up to 80% of blastfurnace slag or fly ash and pozzolana

27 Products in the family of Common Cement / Cement Types

EN 197-1

Main Types	Notation of the 27 products (types of common cement)		Composition [proportion by mass$^{1)}$]										
			Main constituents										Minor Additional constituents
						Pozzolana		Fly ash			Limestone*		
			Clinker K	Blastfurnace slag S	Silica fume D$^{2)}$	natural P	natural calcined Q	siliceous V	calcareous W	Burnt shale T	L	LL	
CEM I	Portland cement	CEM I	95-100	--	--	--	--	--	--	--	--	--	0-5
CEM II	Portland-slag Cement	CEM II/A-S	80-94	6-20	--	--	--	--	--	--	--	--	0-5
		CEM II/B-S	65-79	21-35	--	--	--	--	--	--	--	--	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	--	6-10	--	--	--	--	--	--	--	0-5
	Portland-Pozzolana cement	CEM II/A-P	80-94	--	--	6-20	--	--	--	--	--	--	0-5
		CEM II/B-P	65-79	--	--	21-35	--	--	--	--	--	--	0-5
		CEM II/A-Q	80-94	--	--	--	6-20	--	--	--	--	--	0-5
		CEM II/B-Q	65-79	--	--	--	21-35	--	--	--	--	--	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	--	--	--	--	6-20	--	--	--	--	0-5
		CEM II/B-V	65-79	--	--	--	--	21-35	--	--	--	--	0-5
		CEM II/A-W	80-94	--	--	--	--	--	6-20	--	--	--	0-5
		CEM II/B-W	65-79	--	--	--	--	--	21-35	--	--	--	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	--	--	--	--	--	--	6-20	--	--	0-5
		CEM II/B-T	65-79	--	--	--	--	--	--	21-35	--	--	0-5
	Portland-limestone cement	CEM II/A-L	80-94	--	--	--	--	--	--	--	6-20	--	0-5
		CEM II/B-L	65-79	--	--	--	--	--	--	--	21-35	--	0-5
		CEM II/A-LL	80-94	--	--	--	--	--	--	--	--	6-20	0-5
		CEM II/B-LL	65-79	--	--	--	--	--	--	--	--	21-35	0-5
	Portland-composite cement$^{3)}$	CEM II/A-M	80-94	← 6-20 →									0-5
		CEM II/B-M	65-79	← 21-35 →									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	--	--	--	--	--	--	--	--	0-5
		CEM III/B	20-34	66-80	--	--	--	--	--	--	--	--	0-5
		CEM III/C	5-19	81-95	--	--	--	--	--	--	--	--	0-5
CEM IV	Pozzolanic cement$^{3)}$	CEM IV/A	65-89	--	← 11-35 →					--	--	--	0-5
		CEM IV/B	45-64	--	← 36-55 →					--	--	--	0-5
CEM V	Composite cement$^{3)}$	CEM V/A	40-64	18-30	--	← 18-30 →			--	--	--	--	0-5
		CEM V/B	20-38	31-50	--	← 31-50 →			--	--	--	--	0-5

1) The values in the table refer the sum of the main and minor additional constituents.

2) The proportion of silica fume is limited to 10%.

3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.

* L: total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

Cement constituents

- **Portland cement clinker (K)**
  - made by sintering a mixture of raw materials
- **Granulated blastfurnace slag (S)**
  - made by rapid cooling of a slag, as obtained by smelting iron ore in a blastfurnace
  - possesses hydraulic properties when suitably activated

Cement constituents

Pozzolanic materials

- natural substances of siliceous or silico-aluminous composition
- when finely ground and in the presence of water, they react with dissolved calcium hydroxide $Ca(OH)_2$

- **Natural pozzolana** (volcanic origin) **(P)**
- **Natural calcined pozzolana (Q)**
  - activated by thermal treatment

Pozzolanic materials

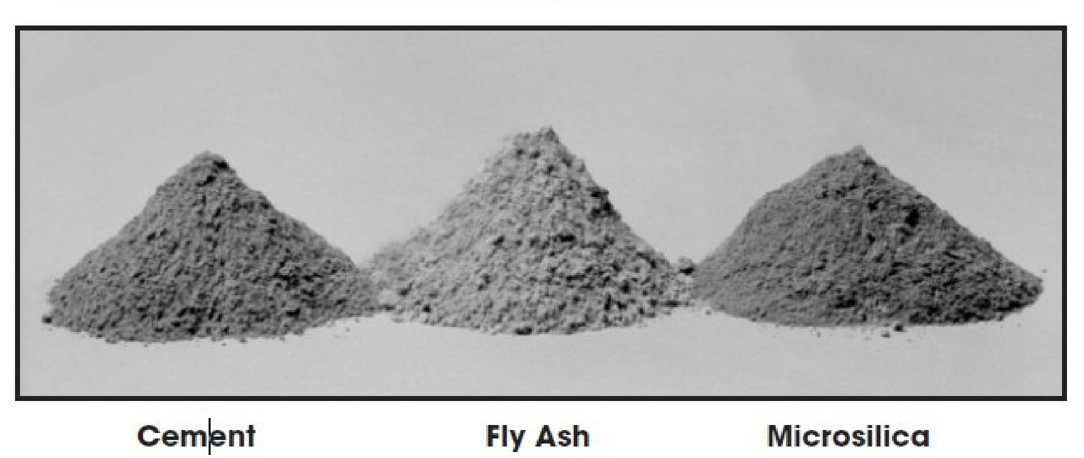
- contain active silica (SiO_2)
- not cementitious in itself but will, in a finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form cementitious compounds
- silica must be glassy and amorphous

Cement constituents

Fly ashes

- – obtained by electrostatic or mechanical precipitation of dust-like particles from flue gases from furnaces fired with pulverised coal

- **Siliceous fly ash (V)**
- **Calcareous fly ash (W)**



Cement constituents

- **Burnt shale (T)**
  - specifically burnt oil shale at approximately 800 °C
- **Limestone (L, LL)**
  - $CaCO_3$ content ≥ 75 % by mass
- **Silica fume (D)** (microsilica)
  - originates from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon and ferrosilicon alloys (very fine spherical particles)

Cement classification

(EN 197-1)

CEM I 42,5 R

I → **type**

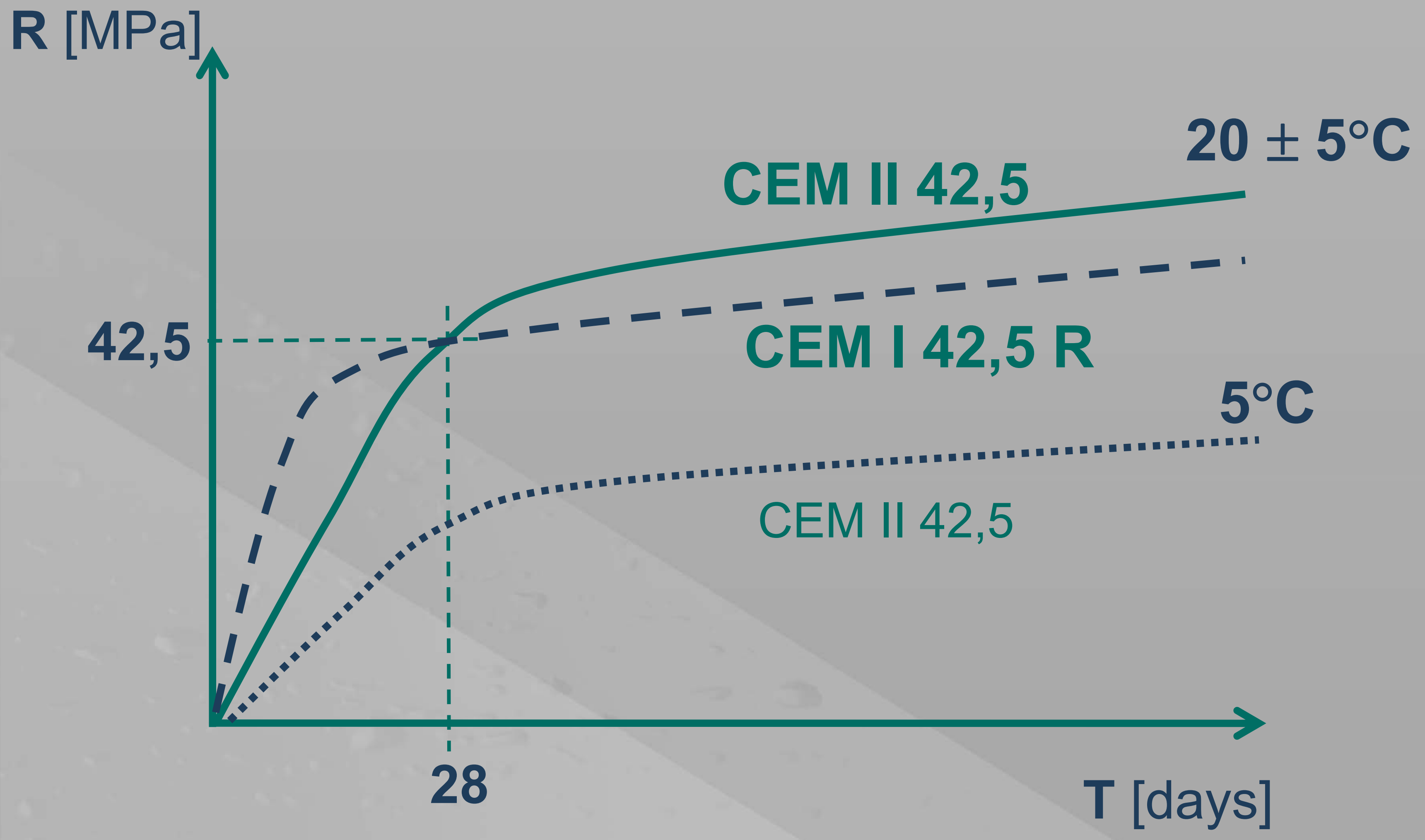
42,5 → **strength class**

R → **high early strength**

Strength classes of cement

- the **standard strength** of a cement is the compressive strength in MPa determined in accordance with EN 196-1 at 28 days
- three classes of standard strength:
  - **32,5**
  - **42,5**
  - **52,5**

Strength increase



Properties of cement types

- **Portland cement**
  - high strength
  - fast increase of strength
  - big amount of hydration heat
- **Portland slag blastfurnace cement**
  - high sulphate resistance
  - low hydration heat
- **silica-fume cement**
  - low porosity of concrete
  - exceptionally high strength
- **fly-ash cement**
  - good workability,
  - lower concrete water content

Use of Portland cement

- concretes with high strength
- reinforced and prestressed concrete
- demanding precast products
- constructions exposed to frost and deicing admixtures (air-entrained concretes)
- sprayed concrete (shotcrete)

Use of Portland composite cement

- common concretes, esp. ready-mixed
- common reinforced concrete construction
- massive concrete constructions (supporting walls, waterworks)
- not suitable in chemically aggressive environment and for frost-resisting constructions

Use of other cements

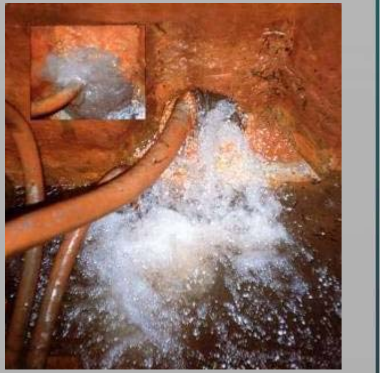
Blastfurnace cements:

- water-resisting constructions
- massive constructions

Composite cements:

- massive construction, fundaments eg.
- less demanding precast products

Special cements



- **expansive cement**
  - against drying shrinkage
- **fast repair cement**
- **sulphate resistant** - $C_3A < 3,5\%$
- **white** - Fe < 1%
- **colored** - 5-10 % of pigments
- **strontium and barium cements**
  - Ba or Sr instead of Ca
  - high resistance to attack by sea water,
  - resistance to high temperatures
  - radiation shields

Masonry cement (MC)

EN 413-1

- for use in mortars for masonry construction
- lower strength

  MC5, MC 12,5, MC 22,5
- **can contain besides the portland cement lime, clay**

Calcium aluminate cement

(High-alumina cement)

- consisting predominantly of hydraulic calcium aluminates
- over 35 % of Al_2O_3
- ultra - rapid strength development
- high chemical resistance
- refractory material (to 1750°C)

But !

- loss of strength due to „conversion“
- several failures in the 1970s

→ forbidden for the use in the bearing constructions !

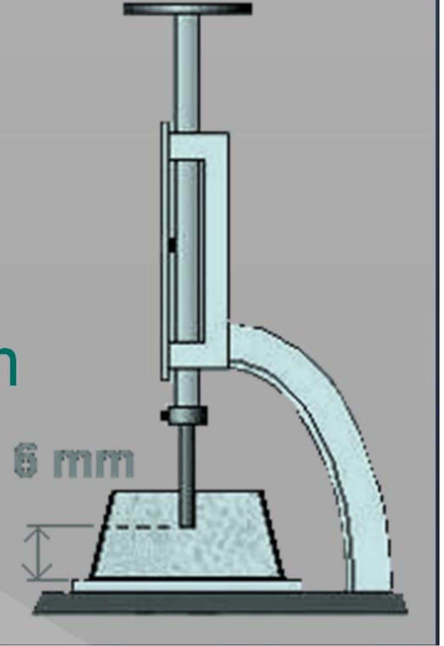
Cement testing

EN 196 – Methods of testing cement

- 1 Determination of strength
- 2 Chemical analysis of cement
- 3 Determination of setting time and soundness
- 4 Quantitative determination of constituents
- 5 Pozzolanicity test for pozzolanic cement
- 6 Determination of fineness
- 7 Methods of taking and preparing samples of cement
- 10 Determination of the water soluble chromium (VI) content of cement
- 21 Determination of the chloride, carbon dioxide and alkali content of cement

Testing of cements - terms

- **cement paste**
  - cement + water
- **cement mortar**
  - cement + water + **fine aggregates**
- **concrete**
  - cement + water + fine + **coarse aggregates**
- **water/cement ratio w/c**
  - mass of water/mass of cement
- **standard** (normal) **consistency**
  - the Vicat plunger penetrates 5 – 7 mm from the bottom of the mould



Determination of strength

(EN196-1)

compressive

flexural

(bending)

$$R_t = \frac{F_{max}}{A}$$

$$R_y = \frac{M_{max}}{W}$$

Expression of test results of compressive strength

- **test set - 3 prism → 6 halves**
- arithmetic mean of the 6 individual result
- if one result within the 6 individual results varies by more than ± 10 % from the mean, discard this result and calculate the arithmetic mean of the 5 remaining results
- if one result within the 5 remaining results varies by more than ± 10 % from their mean, discard the set of results and repeat the determination

Chemical analysis of cement
(EN196-2)

- loss on ignition
- residue insoluble
- determination of sulfate
- determination of major elements
  - silica
  - oxides Fe, Al, Ca, Mg
  - chloride
  - carbon dioxide
  - alkali

Setting time (EN196-3)

- **initial seting time**
- **final setting time**

Vicat apparatus

Louis **Vicat**
(1786 -1861)

Soundness (EN196-3)

- the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion caused by CaO or MgO

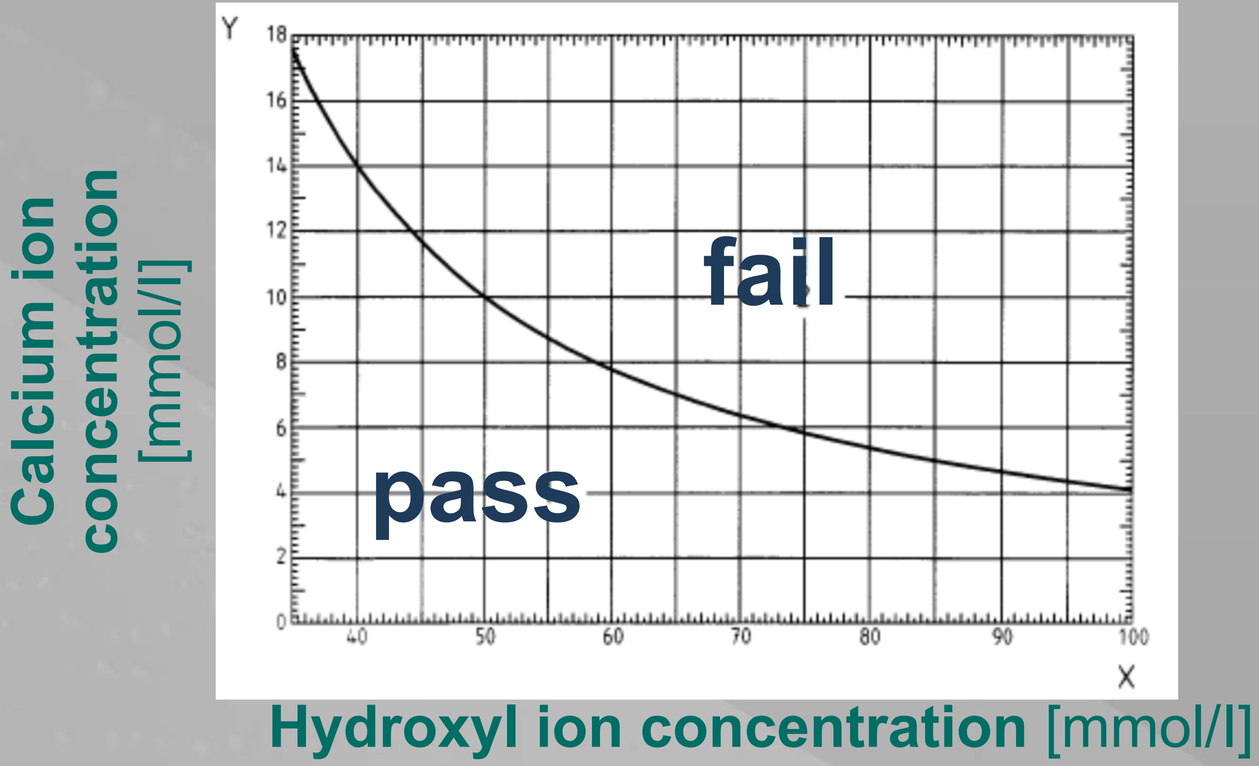
Henry Louis
Le Chatelier
(1850 - 1936)

Quantitative determination of constituents (EN196-4)

- Portland cement clinker
- blastfurnace slag
- siliceous fly ash
- natural pozzolans
- limestone
- silica fume
- set regulators

Pozzolanicity (EN196-5)

- comparing the concentration of calcium ion, expressed as CaO, present in the aqueous solution in contact with the hydrated cement, after a fixed period of time, with the quantity of calcium ion capable of saturating a solution of the same alkalinity



Finneness (EN196-6)

- **Blaine apparatus** (see Lecture 2)

$$S = \frac{K}{\rho} \times \frac{\sqrt{e^3}}{(1-e)} \times \frac{\sqrt{t}}{\sqrt{0,1\eta}}$$

Taking and preparing samples (EN196-7)

- from bags, containers, bulk, silos, filling machines
- quartering, sampling tube, screw sampler

Water soluble chromium (VI) content (EN196-10)

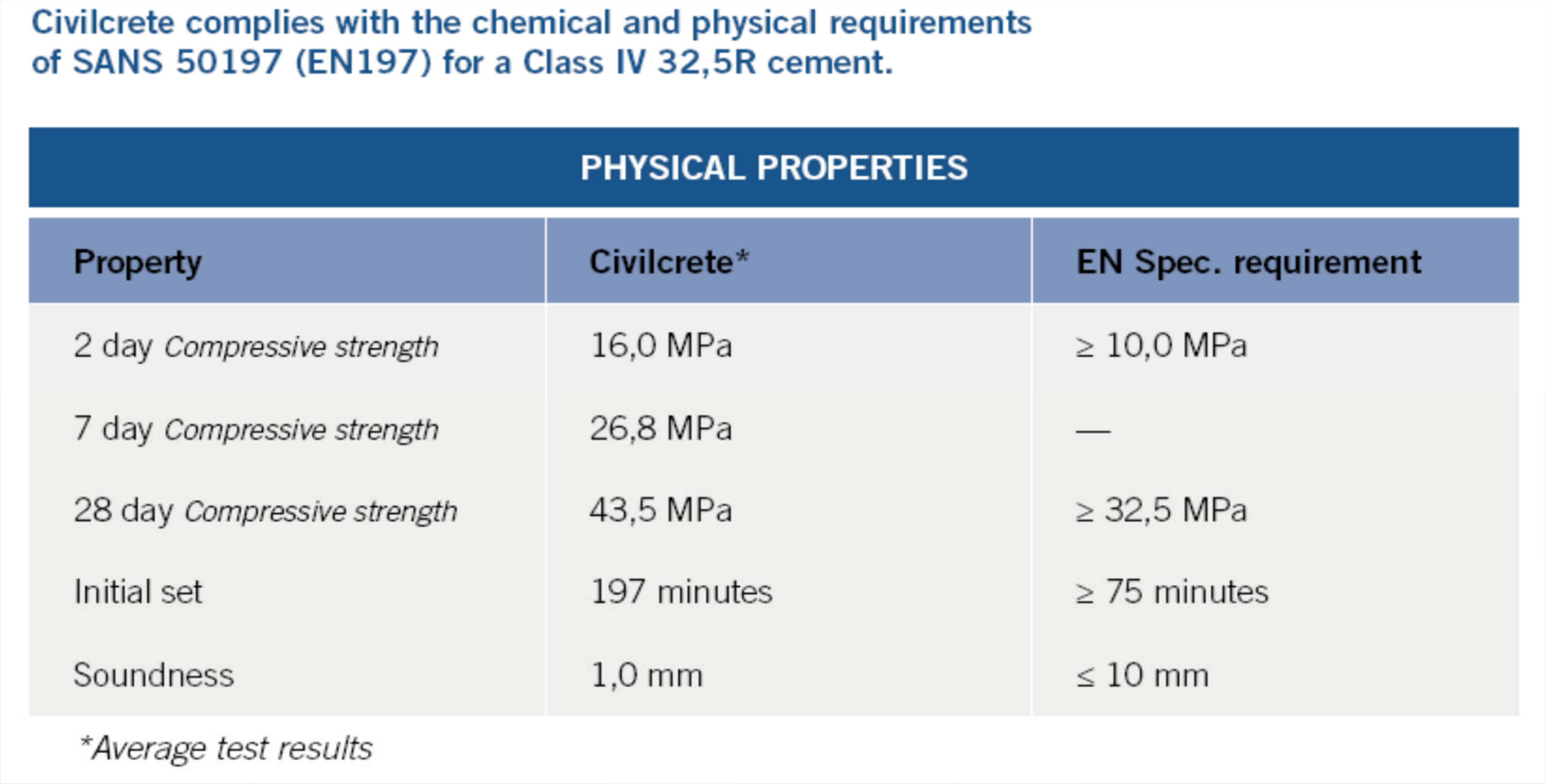
- hygienic and ecological properties

Mechanical and physical requirements (EN197-1)

Strength class	Compressive strength MPa				Initial setting time	Soundness (expansion)
	Early strength		Standard strength			
	2 days	7 days	28 days		minut	mm
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5	≥ 75	≤ 10
32,5 R	≥ 10,0	-				
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5	≥ 60	
42,5 R	≥ 20,0	-				
52,5 N	≥ 20,0	-	≥ 52,5	-	≥ 45	
52,5 R	≥ 30,0	-				

Civilcrete

general purpose cement



Civilcrete complies with the chemical and physical requirements of SANS 50197 (EN197) for a Class IV 32,5R cement.

PHYSICAL PROPERTIES

Property	Civilcrete*	EN Spec. requirement
2 day *Compressive strength*	16,0 MPa	≥ 10,0 MPa
7 day *Compressive strength*	26,8 MPa	—
28 day *Compressive strength*	43,5 MPa	≥ 32,5 MPa
Initial set	197 minutes	≥ 75 minutes
Soundness	1,0 mm	≤ 10 mm

**Average test results*

Building materials

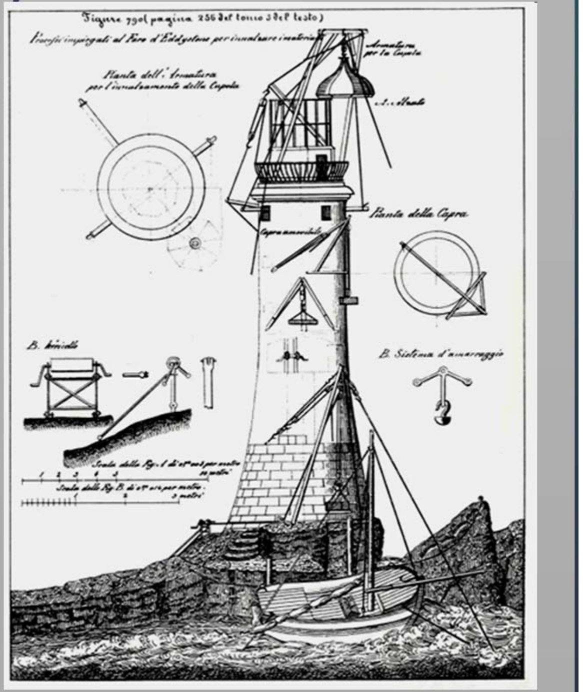
Department of Materials Engineering and Chemistry

Faculty of Civil Engineering

Hydraulic lime

- used by the Romans (100 B.C.)
  - (Plinus, Vitruvius)

    „Opus caementicium“
- forgotten in the middle age
- discovered again in the 18th century by burning **limestone containing clays**
  - 1756 – John Smeaton
  - 1796 - „roman cement“ (James Parker)
  - Louis Joseph Vicat



Eddystone Lighthouse

Hydraulic lime

Raw material:

- **argillaceaous** (= containing clays) **limestones** → **natural hydraulic lime** (NHL)
- **quick lime** (burned limestone) + **pozzolanic** materials → **hydraulic lime** (HL)

Pozzolanic materials (pozzolans):

- consist mainly from reactive silica (SiO_2) and alumina (Al_2O_3)
- when finely ground and in the presence of water, they react with dissolved $Ca(OH)_2$
- volcanic ash, fly ash, silica fume, high-reactivity metakaolin, ground granulated blast furnace slag

Hydraulic lime manufacture

Natural hydraulic lime (NHL):

- burning of raw materials at the temperature **under 1250 °C**
- slaking (only when HM > 3)

Hydraulic lime (HL):

- grinding of quicklime together with pozollans

Hydraulic lime

- **in contrast to portland cement has higher amount of the free CaO and no alite (C_3S)** → lower strength than cement

According the degree of hydraulicity (hydraulic modulus):

- **feebly hydraulic lime** (HM 6 - 9) - need slaking
- **moderately hydraulic lime** (HM 3 - 6) – need slaking
- **eminently hydraulic lime** (HM 1,7 - 3) – does not need slaking

Natural hydraulic lime - EN 459

Type	SO_3 (mass %)	Free lime (mass %)	Strength after 28 days [MPa]
NHL 1	≤ 2	≥ 50	≥ 0,5 - ≤ 3
NHL 2	≤ 2	≥ 40	≥ 2 - ≤ 7
NHL 3,5	≤ 2	≥ 25	≥ 3,5 - ≤ 10
NHL 5	≤ 2	≥ 15	≥ 5 - ≤ 15

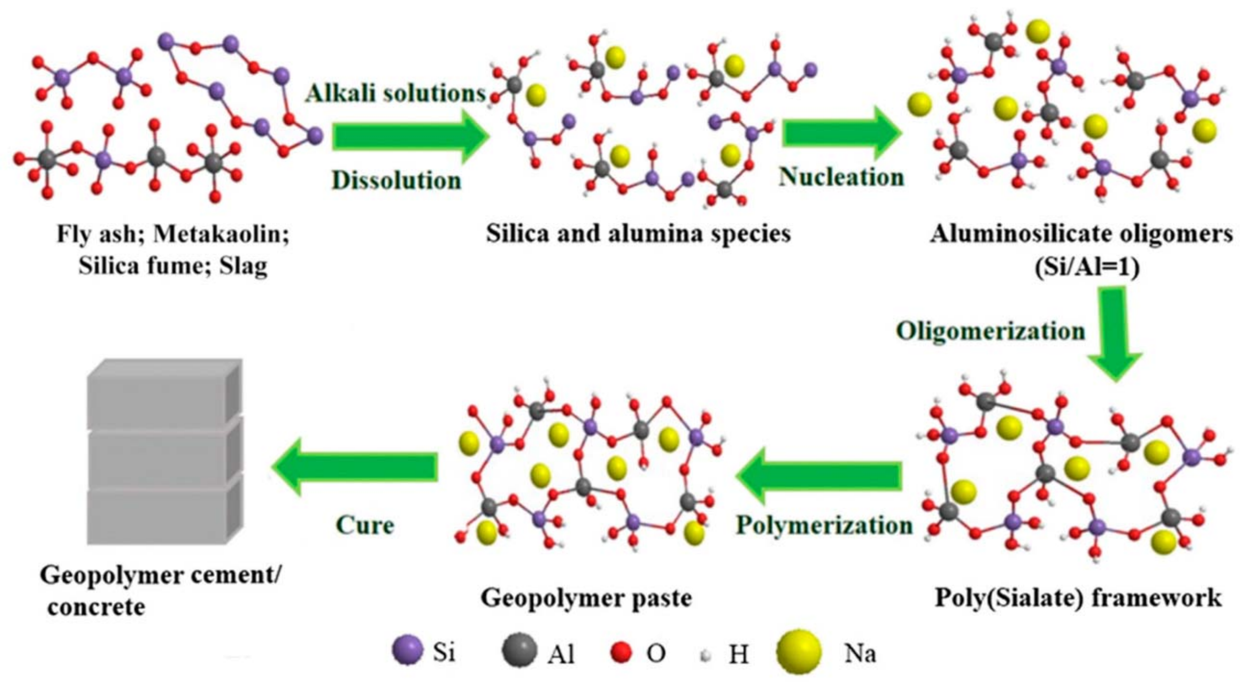
Hydraulic lime use

- **monuments renovations**
  - better breathing of walls
  - moisture can evaporate
  - mortars and renders do not set too hard
  - expansion joints can often be avoided
  - reduced condensation
  - no salt staining

Using of cement with old bricks

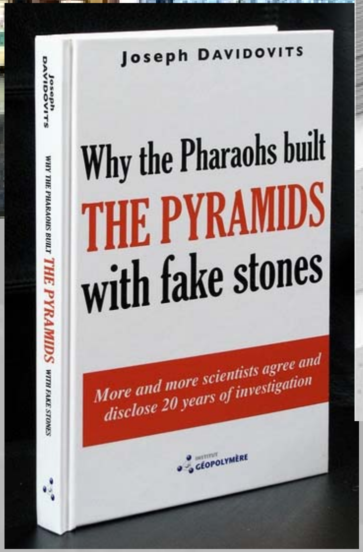
Geopolymers

- synthetic aluminosilicate polymers formed in alkaline environment at normal temperature
- raw material – pozzolans, e.g. thermaly activated clays (metakaolin), fly ash + strong alkali activator



Geopolymers

- Prof. Joseph Davidovits

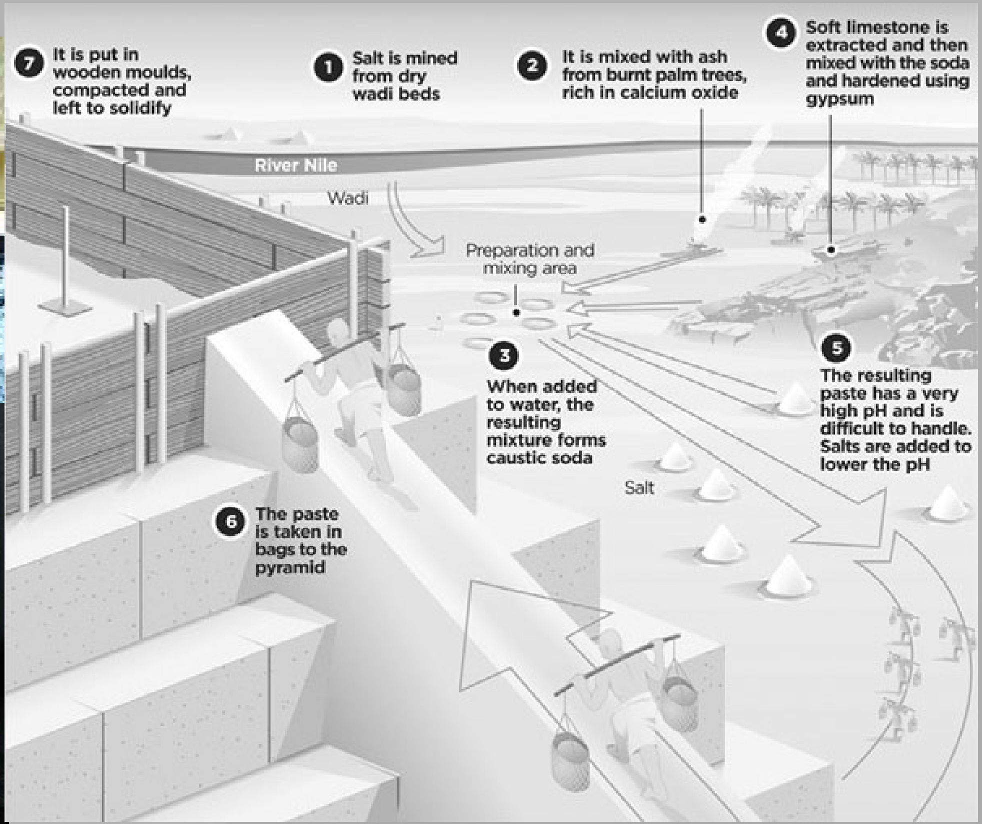


Joseph DAVIDOVITS

Why the Pharaohs built
THE PYRAMIDS
with fake stones

More and more scientists agree and disclose 20 years of investigation

GÉOPOLYMÈRE



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Video: *https://www.geopolymer.org/archaeology/pyramids/pyramids-4-videos-download-chapter-1/*

Geopolymer concretes

- \+ high strength
- \+ fire resistant
- \+ lower energy consumption
- \+ chemically resistant
- \+ durability
- \+ utilization of wastes

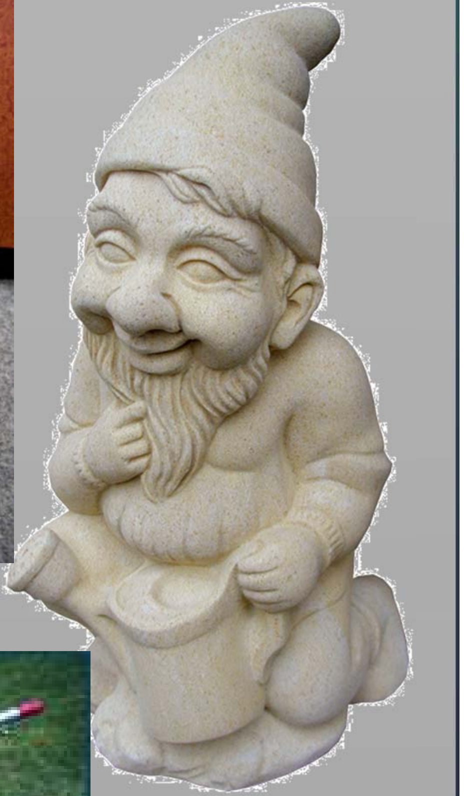
- \- price
- \- efflorescence
- \- difficult preparation (some alcali activators are harmfull)
- \- worse workability

Geopolymers - use

- repair of damaged concrete
- fire protection systems
- building chemistry (sealants, heat systems)
- fixation of heavy metals and radioactive waste
- restoration
- imitation of natural materials

Non-hydraulic binders

- **gypsum binder**
- **anhydrite binder**
- (non-hydraulic) **lime**
- **water glass**
- **magnesium binder**



Calcium sulphate binders

- contain calcium sulphate ($CaSO_4$)
  - a) **gypsum binder** (= plaster of Paris)
  - b) **anhydrite binder**

Raw materials:

a) calcium sulphate dihydrate

- **$CaSO_4 \cdot 2H_2O$**

b) calcium sulphate anhydrite

- **$CaSO_4$**

Giant gypsum rock crystals, Naica mine, Mexiko

Gypsum binder - raw materials

- natural rock (selenite, alabaster, satin spar…)
- **FGD gypsum**
  - synthetic product from **F**lue **G**as **D**esulfurization systems at coal power stations

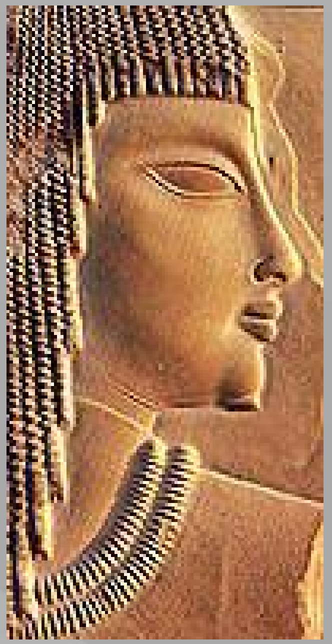
- phosphogypsum
  - by-product of processing phosphate ore into fertilizer with sulfuric acid
- citrogypsum
- titanogypsum

Gypsum binder

- calcium sulphate hemihydrate

$CaSO_4 \cdot 0,5H_2O$

- one of the oldest binders
  - Anatolia and Syria – 5000 b.C.
  - Egyptians
  - Greeks
  - Romans

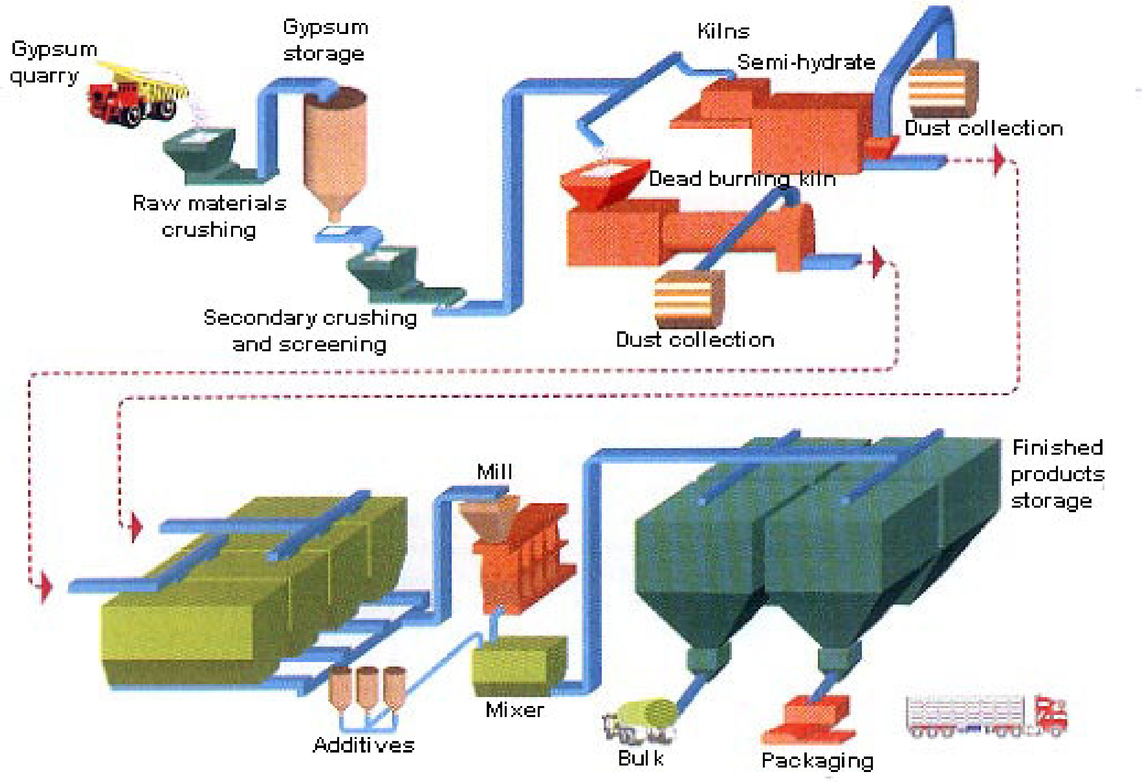


Department of Materials Engineering and Chemistry
Faculty of Civil Engineering

Gypsum binder manufacture

- **calcination** (150 – 180 °C)

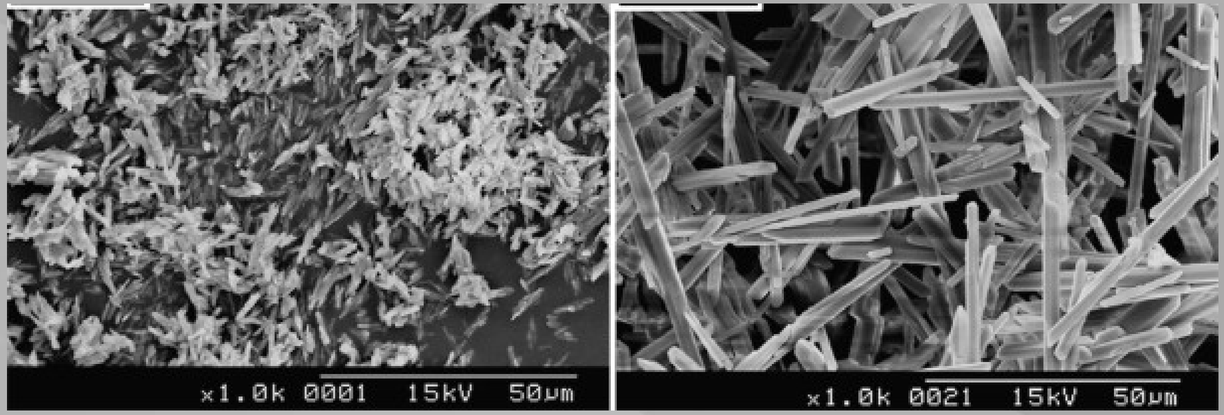
$$CaSO_4 \cdot 2H_2O \xrightarrow{heat} CaSO_4 \cdot 0{,}5H_2O + 1{,}5H_2O$$



Gypsum binder types

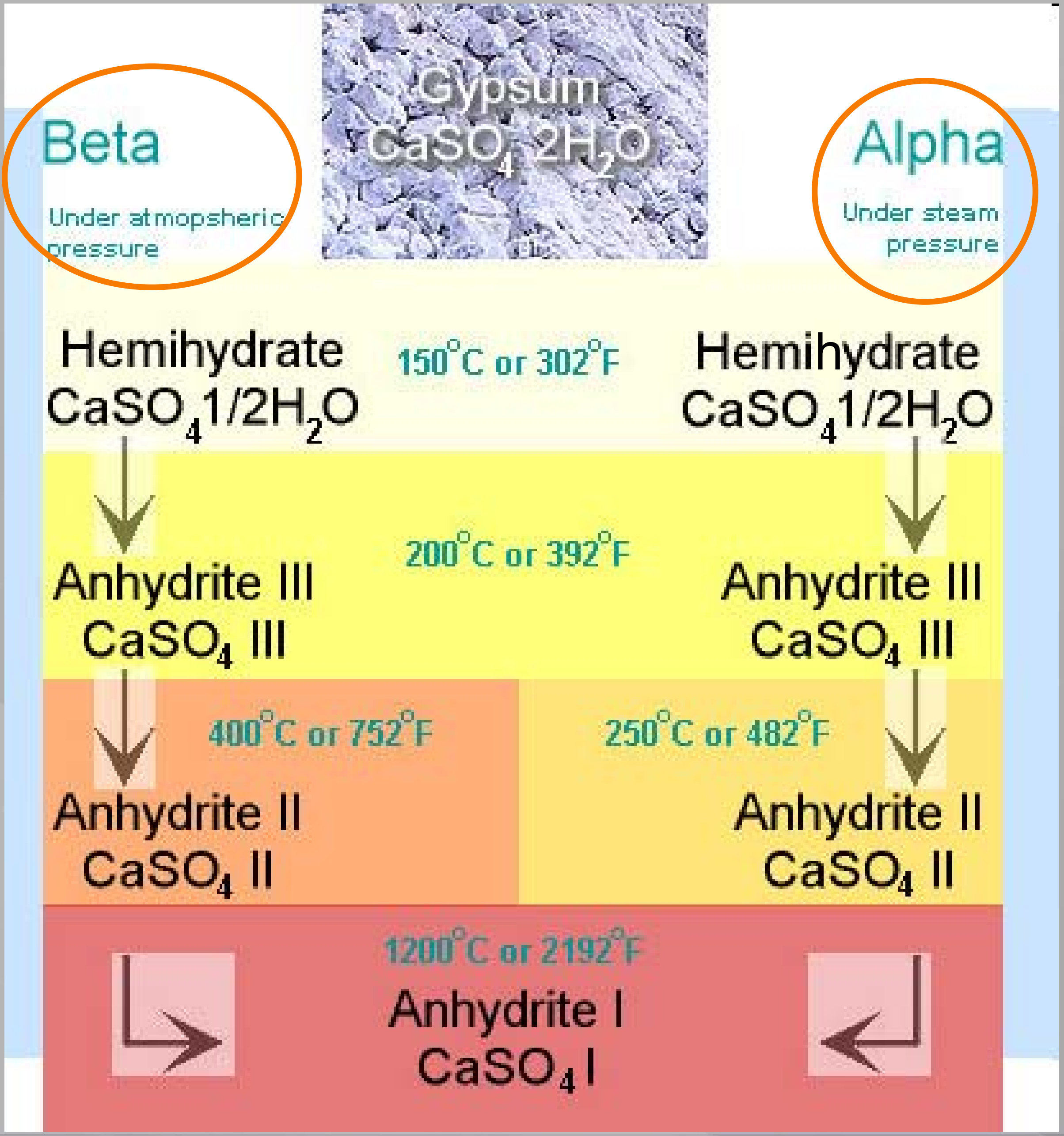
According production process:

- **β - gypsum**
  - production at high temperature in normall air pressure
- **α- gypsum**
  - production at high temperature and high steam pressure in autoclave



Gypsum crystals: β **- gypsum** α **- gypsum**

Gypsum dehydration



Gypsum
$CaSO_4\ 2H_2O$

Beta
Under atmopspheric pressure

Alpha
Under steam pressure

150°C or 302°F

Hemihydrate $CaSO_4 1/2H_2O$ → Anhydrite III $CaSO_4$ III (beta)

Hemihydrate $CaSO_4 1/2H_2O$ → Anhydrite III $CaSO_4$ III (alpha)

200°C or 392°F

400°C or 752°F

Anhydrite II $CaSO_4$ II

250°C or 482°F

Anhydrite II $CaSO_4$ II

1200°C or 2192°F

Anhydrite I
$CaSO_4$ I

Difference between α a β gypsum

- chemically identical ($CaSO_4 \cdot 0{,}5H_2O$), but different properties

	β - gypsum	**α- gypsum**
Particle size	1 – 5 μm	10 – 20 μm
Particle porosity	high	low
Specific surface	big	small
Strength increase	fast	slower
Final strength	lower	higher

Gypsum setting and hardening

$$CaSO_4 \cdot 0{,}5H_2O + 1{,}5H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Initial setting:

- due to a colloidal mechanism or action of capillary forces causing a packing together of hemi-hydrate particles

Hardening and final setting

- a crystallization process

EN 13 279 - Gypsum binders and gypsum plasters. Definitions and requirements

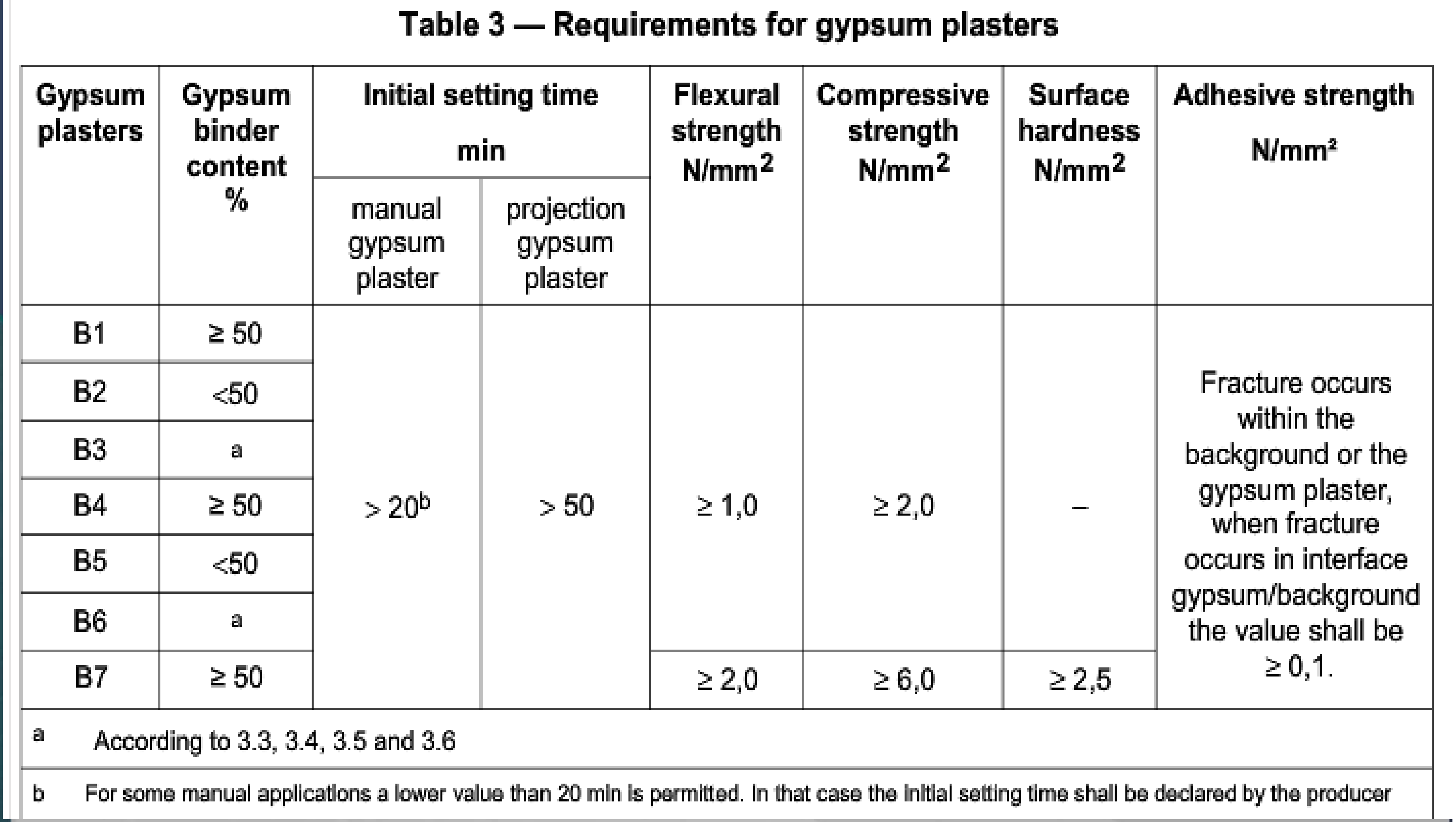


Table 3 — Requirements for gypsum plasters

Gypsum plasters	Gypsum binder content %	Initial setting time min		Flexural strength N/mm^2	Compressive strength N/mm^2	Surface hardness N/mm^2	Adhesive strength N/mm²
		manual gypsum plaster	projection gypsum plaster				
B1	≥ 50	> 20[b]	> 50	≥ 1,0	≥ 2,0	–	Fracture occurs within the background or the gypsum plaster, when fracture occurs in interface gypsum/background the value shall be ≥ 0,1.
B2	<50						
B3	a						
B4	≥ 50						
B5	<50						
B6	a						
B7	≥ 50			≥ 2,0	≥ 6,0	≥ 2,5	

[a] According to 3.3, 3.4, 3.5 and 3.6

[b] For some manual applications a lower value than 20 min is permitted. In that case the initial setting time shall be declared by the producer

Modification of gypsum properties

- setting retarders (citric acid, molasses, blood, saliva, agar)
- setting accelerators (hardened gypsum = calcium dihydrate)
- fungicides
- hydrophobic additives
- pigments
- plasticizers (Althaea officinalis - Marshmallow root)
- reinforcement (glass fibers, animal hairs)

Althaea officinalis

Strength of gypsum

Depends on:

- **moisture content**
  - with increasing moisture the strength decreases
- **water/gypsum ratio**
  - with increasing w/g the strength decreases

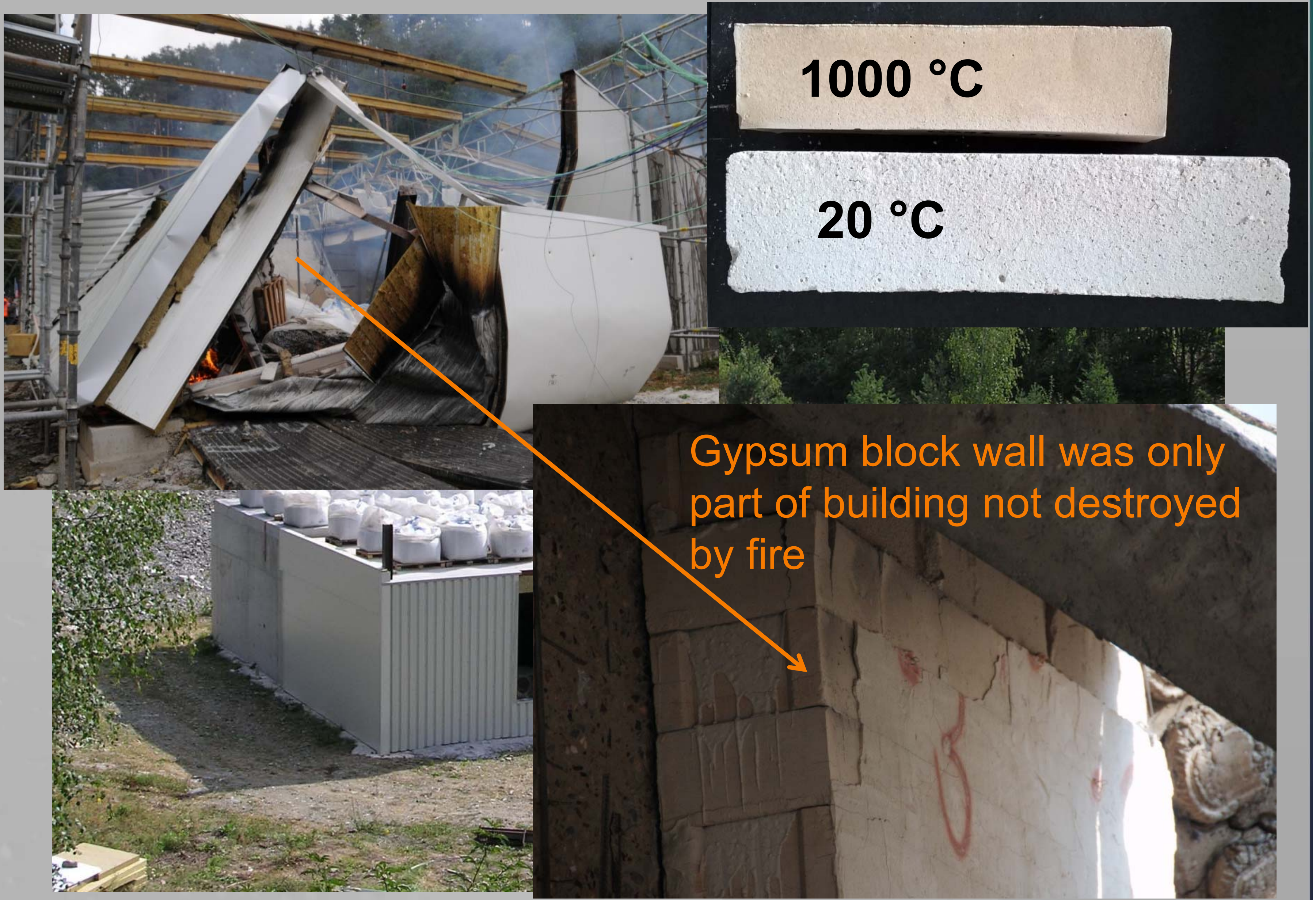
Conditioning	Moisture in gypsum	Compressive strength	
	%	MPa	%
Dried at 35 - 40 °C	0	13,8	100
In air with 65 % RH	0,04	13,6	98,5
In air with 90 % RH	0,15	12,9	93,5
Immersed in water	17,50	6,4	46,5

w/g	Bulk density	Compressive strength
	kg.m^{-3}	MPa
0,50	1410	14,6
0,55	1300	13,0
0,60	1230	11,4
0,65	1170	10,8
0,75	1040	9,5

Gypsum fire resistance

- **non – flammable** (class A1)
- contains water of crystallization (17 % of its weight)
- exposed to the fire, the chemically combined water is released in the form of water vapor → the dehydration (calcination) of gypsum occurs
- calcined gypsum adheres to the uncalcined material and retards the further calcination process
- until all the water of crystallization has been liberated, the temperature on the unexposed side will not exceed 100°C
- **gypsum can serve as a fire retardant** with ability to delay the spread of fire up to 4 hours → protection of wood and steel elements against fire

Gypsum after fire test

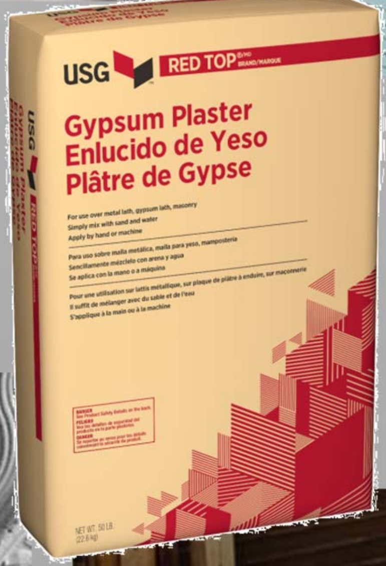


Gypsum block wall was only part of building not destroyed by fire

Gypsum uses

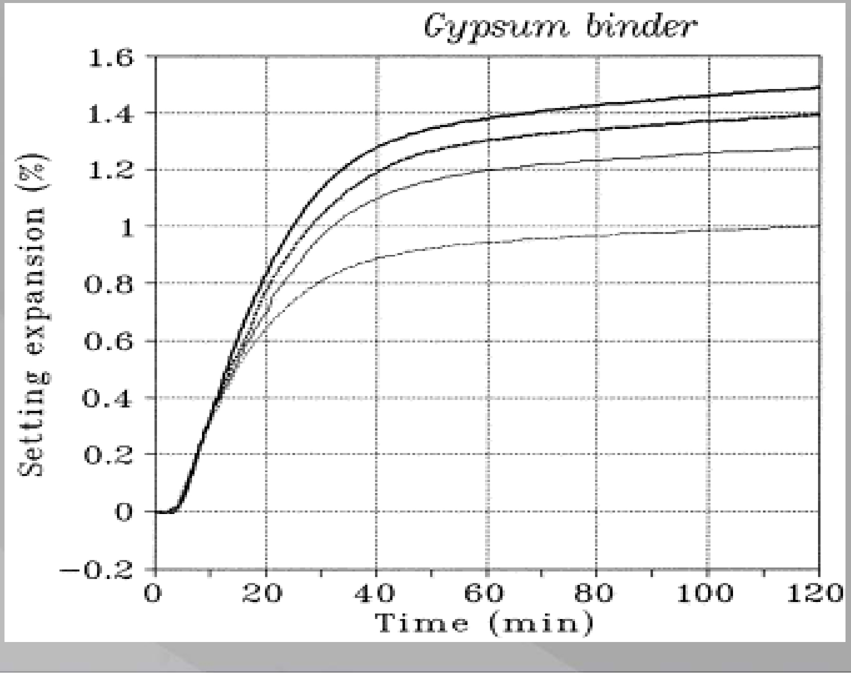
Interior only

- plasters
- blocks
- floor screeds
- gypsum boards (drywall)
- gypsum fiberboards



Lime - gypsum plaster

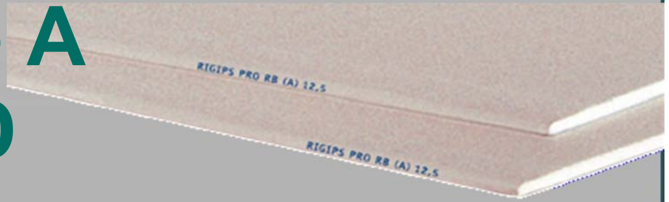
- gypsum sets quickly, lime is slow to set → combination of lime and gypsum plasters sets at a medium speed
- while setting, gypsum plaster expands slightly and lime contracts slightly → the plaster does not crack
- better workability



Gypsum board (drywall)

- panel made of a paper liner wrapped around an inner core made from gypsum with fibers (cellulose and/or fiberglass)

Gypsum board types



- **Gypsum plasterboard** - type **A**
- G. p. with **control density** - **D**
- Gypsum sheathing board - **E**
  - in external walls. reduced water absorption rate with a minimum water vapor permeability

- G. p. with **improved core adhesion at high temperatures** - **F**
  - mineral fibers and / or other additives in the gypsum core

- G. p. with **reduced water absorption rate** - **H1 – H3**
- G. p. with **enhanced surface hardness** - **I**
- G. **baseboard** - **P**
- G. p. with **enhanced strength** - **R**

Special gypsum boards

- **fire proof (F)**
  - – glass fibre and other additives in the core
- **acoustic** (D)
  - – high density core
  - – special dimensional configuration
- **thermal insulating**
  - – bonded to an expanded polystyrene

Gypsum board use

- standard boards – to 65%RH
- impregnated boards –
  permanently to 75 %RH
  for a short term to 100 %

?

~~Basement, showers~~

Gypsum fiberboards

- gypsum (80%) + cellulose fibers (20 %)
  - no paper on surface
  - higher bulk density
  - higher strength
  - better fire resistance
  - in the higher humidity

Anhydrite

- **anhydrous $CaSO_4$**
  - – needs activator to set
- activators: lime, cement, sulphates
- slow setting even with activator
- used for „self-leveling“ screeds

Self-leveling screeds

- contains gypsum or anhydrite + plasticizer + sand (1:1 – 1:2)
- very good for under-floor heating
- used in interiors only