Materials Properties, Use and Conservation: Construction Materials and Binders

Hydraulic binders

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CIBA Centro per i Beni Culturali
Diagnostica . Rilievo . Tecnologie

Binders classification

Table 3.6. Main classes of binding compounds produced by pyrotechnology.

Starting reactive material	***Production process***	***Material-water mixture***	***Final product***	***Mineral phases in the hardened aged material***
Lime-plaster (quicklime)	Calcinations of limestone	Slaked lime (lime putty)	Lime plaster	Calcite
		Slaked lime + fine aggregate	Lime mortar	Calcite + aggregate
		Slaked lime + fine aggregate + pozzolan	Hydraulic mortar (Roman opus caementitium)	Calcite, zeolites, C-S-H + aggregate
	Calcination of dolomite	Slaked magnesia-lime	Dolomitic or magnesian plaster	Calcite, brucite, periclase
Gypsum-plaster (plaster of Paris)	Calcination of gypsum	Bassanite (± anhydrite)	Gypsum plaster	Gypsum
		Bassanite + fine aggregate	Gypsum mortar	Gypsum + aggregate
Portland-clinker	Calcinations of limestones+clay	Portland cement paste	Portland cement	Portlandite, C-S-H, calcite
		Portland cement paste + fine aggregate	Portland cement mortar	Portlandite, C-S-H, calcite + aggregate
		Portland cement paste + fine and coarse aggregate	Concrete	Portlandite, C-S-H, calcite + aggregate
		Cement paste + fine aggregate + pozzolan	Pozzolanic Portland cement mortar	Portlandite, C-S-H, calcite, Ca-aluminosilicates

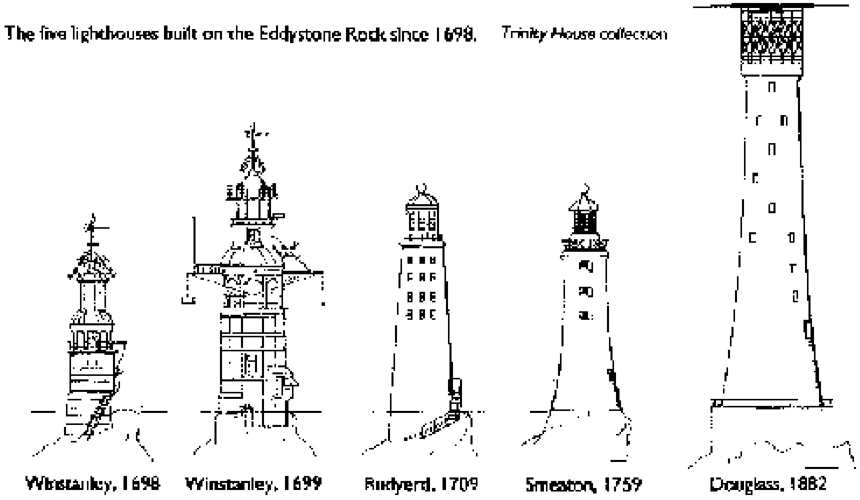
Hydraulic binders

- The art of producing and using excellent binders was slowly lost after the fall of the Roman Empire.

- Lime-based binders continued to be used through the Middle Ages, though in many cases they are of rather low quality, made of partially burned lime, and unaged and poorly slaked putty. The careless preparation would make them mostly porous and degradable. Many of the Saxon, Norman, or Longobardic materials are of this kind.

- The **standardized production** of the Roman Empire left place to very **local productions**, mostly having very low technological content, and only in specific and prestigious construction sites high quality binders were produced, such as in the case of the Bizantine mosaics of Ravenna, or the Leaning Tower of Pisa (Franzini et al. 2000).

Hydraulic binders



Hydraulic binders

- A significant change from traditional lime binders was made by **John Smeaton** in England in 1756, when he was involved in the reconstruction of the **Eddystone lighthouse** (Blezard 1998). He was driven by the need to develop a masonry construction that would be durable in a marine environment and composed by a binding agent that would not dissolve in seawater. Among several attempts, he departed from the Vitruvian recommendations of using pure white limestone, and by using **clay-rich carbonates of marly composition** he obtained better hydraulic properties than lime. This class of materials may be defined as hydraulic limes and can be considered intermediate between slaked lime and modern Portland cement. Eventually the material that Smeaton selected for the lighthouse was a binder prepared with equal proportions of local argillaceous limestones (blue Liassic limestones) and Italian pozzolana from Civitavecchia. The hydraulic properties of the binder are derived from the aluminosilicates formed during the firing. Slightly improved mixtures of this kind were in use until the introduction of Portland cement.

Hydraulic binders

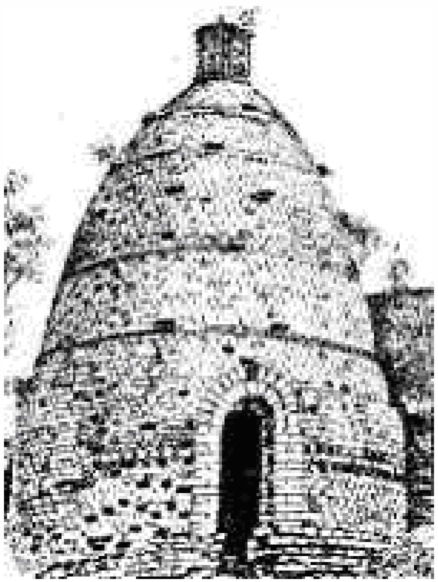
- In the first half of the 19th century the search for optimal hydraulic binders was actively pursued in several countries (Blezard 1998, Bentur 2002).

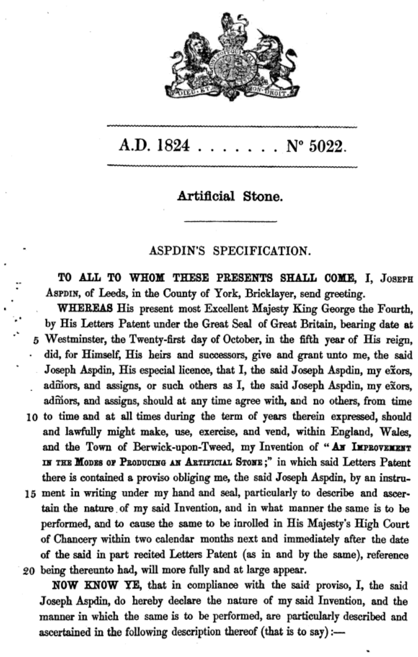
- In Britain, **John Smeaton** attempted alternative formulations of hydraulic binders and **James Parker** introduced and patented a so-called "Roman cement" (Patent by James Parker, of Northfleet, Kent, No. 2120 (1796) *Cement or tarras to be used in acquatic and other buildings and stucco work*), which was made by calcinations of nodules of argillaceous limestones (known as *septariae*) and produced a quickly setting cement.

- In France, **Louis Vicat** experimentations lead to the preparation of hydraulic lime by calcination of a mixture of high-grade quicklime (produced by the chalk of the Upper Cretaceous carbonatic formation of the Paris Basin) and clay (L.J. Vicat, *Mortier et ciment calcaires*, Paris, 1828). His formulation, called the "twice-kilned" process, met with considerable success and lead his son Joseph Vicat to establish the well known Vicat Cement company. This is considered by many the predecessor of **Portland cement**.

Hydraulic binders

- A large number of patents were issued around the same time to establishing plants in Southern Britain, including the London area. The most famous one is the one related to the three-stages process of **Joseph Aspdin** (1824), who described his product as **Portland cement**, because at that time Portland limestone had a reputation for quality and durability among builders, and he wanted to capture the similitude between his cement and Britain's favoured quarried stone. Portland cement was marketed as an improvement of the modes of **producing artificial stone**.





A.D. 1824 . . . . N° 5022.

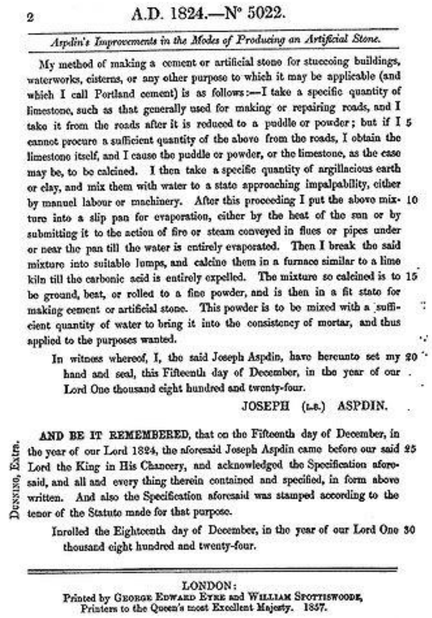
Artificial Stone.

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 exors, admors, and assigns, or such others as I, the said Joseph Aspdin, my exors, admors, 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):—



2 A.D. 1824.—N° 5022.

Aspdin's Improvements in the Modes of Producing an Artificial Stone.

My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call Portland cement) is as follows:—I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillacious earth or clay, and mix them with water to a state approaching impalpability, either by manuel labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan till the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar, and thus applied to the purposes wanted.

In witness whereof, I, the said Joseph Aspdin, have hereunto set my hand and seal, this Fifteenth day of December, in the year of our Lord One thousand eight hundred and twenty-four.

JOSEPH (L.S.) ASPDIN.

AND BE IT REMEMBERED, that on the Fifteenth day of December, in the year of our Lord 1824, the aforesaid Joseph Aspdin came before our said Lord the King in His Chancery, and acknowledged the Specification aforesaid, and all and every thing therein contained and specified, in form above written. And also the Specification aforesaid was stamped according to the tenor of the Statute made for that purpose.

DUNNING, Extra.

Inrolled the Eighteenth day of December, in the year of our Lord One thousand eight hundred and twenty-four.

LONDON:
Printed by GEORGE EDWARD EYRE and WILLIAM SPOTTISWOODE, Printers to the Queen's most Excellent Majesty. 1857.

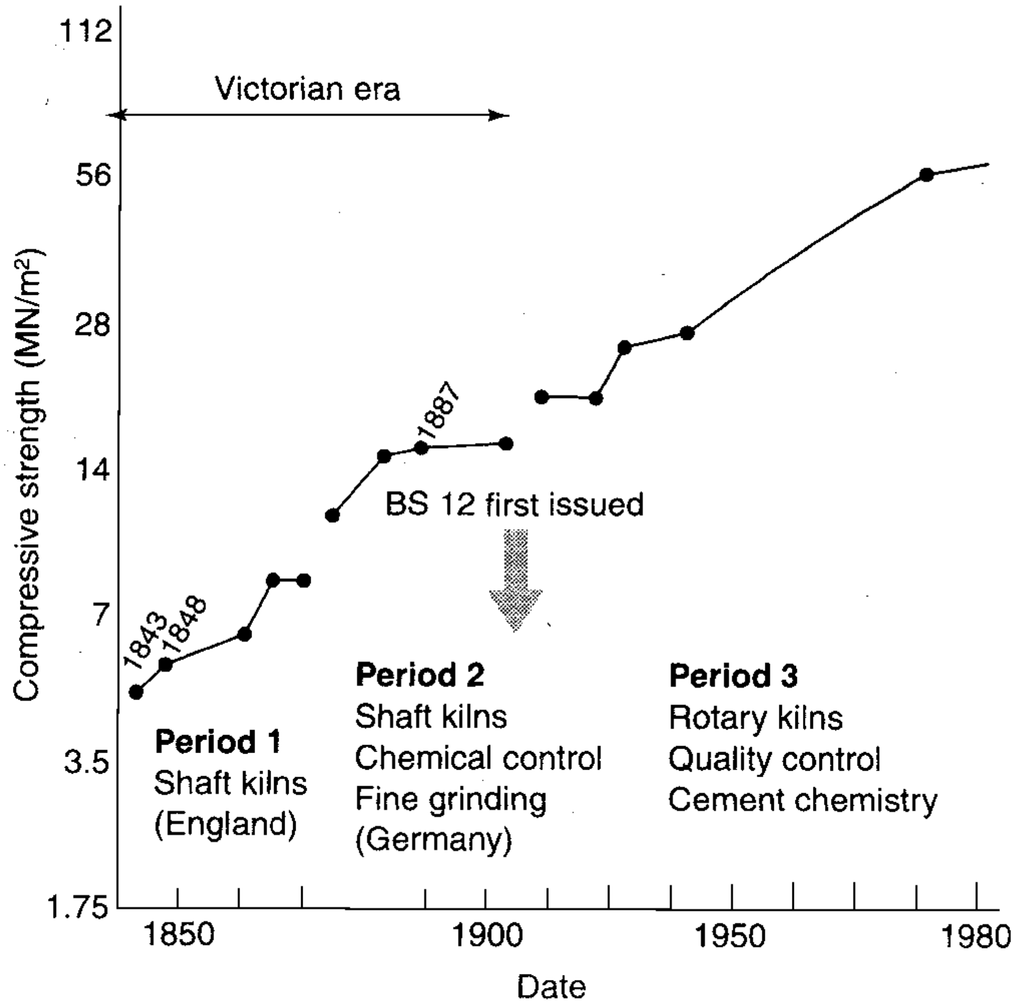
Hydraulic binders

- In one of the several plants established by **Joseph Aspdin and his son William**, the temperatures were running high enough to produce partial or complete vitrification and crystallize **alite**, as shown by the retrospective analysis of the type clinker material from Aspdin's kiln (Blezard 1981).

The Patent Portland Cement Works of Ed. Fewer at Lagerdorf in Holstein. This factory was founded in 1862 by English expatriates Edward Fewer and William Aspdin

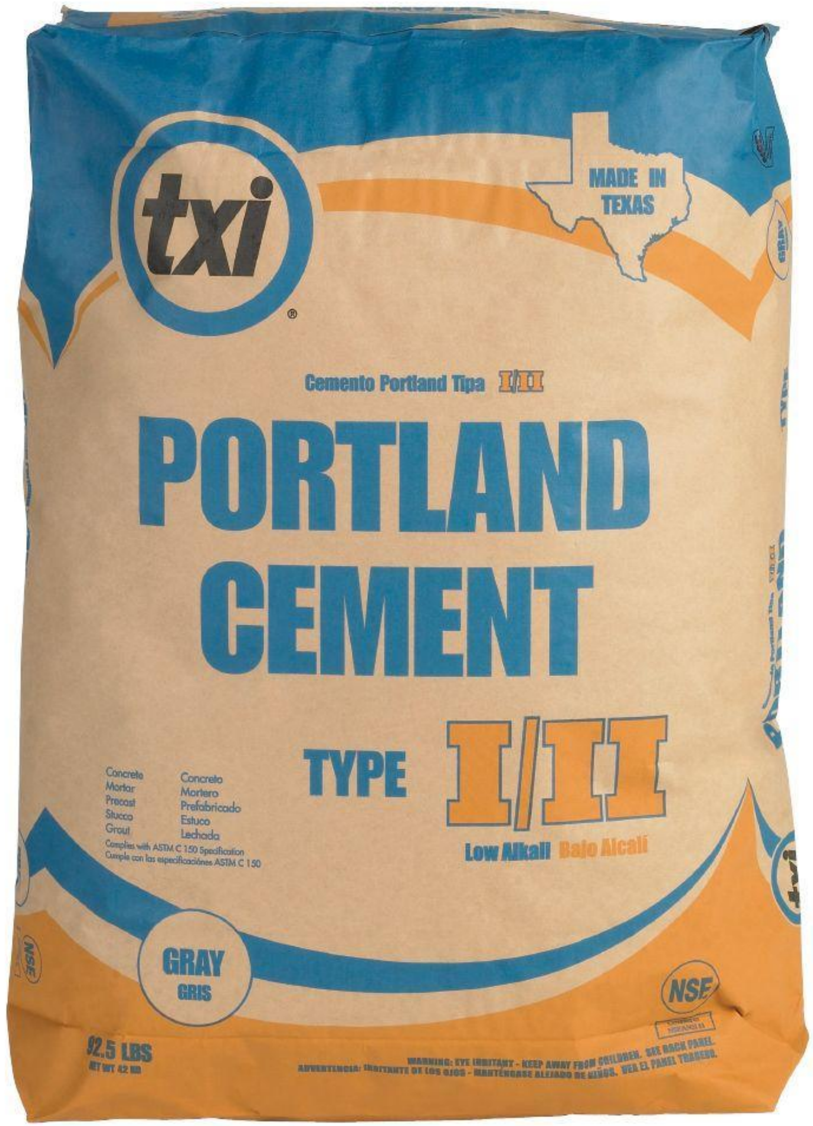
Hydraulic binders

Hydraulic binders



Compressive strength of OPC at 28 days

Hydraulic binders



Hydraulic binders

- Hydraulic binder constituted by a poliphasic mixture (clinker) of calcium silicates (C_3S, C_2S), calcium aluminate (C_3A) and calcium-aluminoferrite (C_4AF) + calcium sulphates (to prevent flash set).
- Clinker is obtained after firing a mixture of limestone and clays at temperatures around 1450°C. The obtained compound is finely ground after the firing process.

MATERIALI GREZZI (raw materials) —forno, 1500℃→ CLINKER (+ solfati →cemento) —H_2O, 25℃→ MANUFATTO (set cement)

Calcite, caolinite, quarzo, pirofillite
.....
CaO, Al_2O_3, SiO_2, Fe_2O_3, ...

Ca_3SiO_5	C3S
$Ca_3Al_2O_6$	C3A
$Ca_4(Al,Fe)_2O_{10}$	C4AF
β-Ca_2SiO_4	C2S
.....	

Silicati di Ca idrati

Hydraulic binders

Hydraulic binders

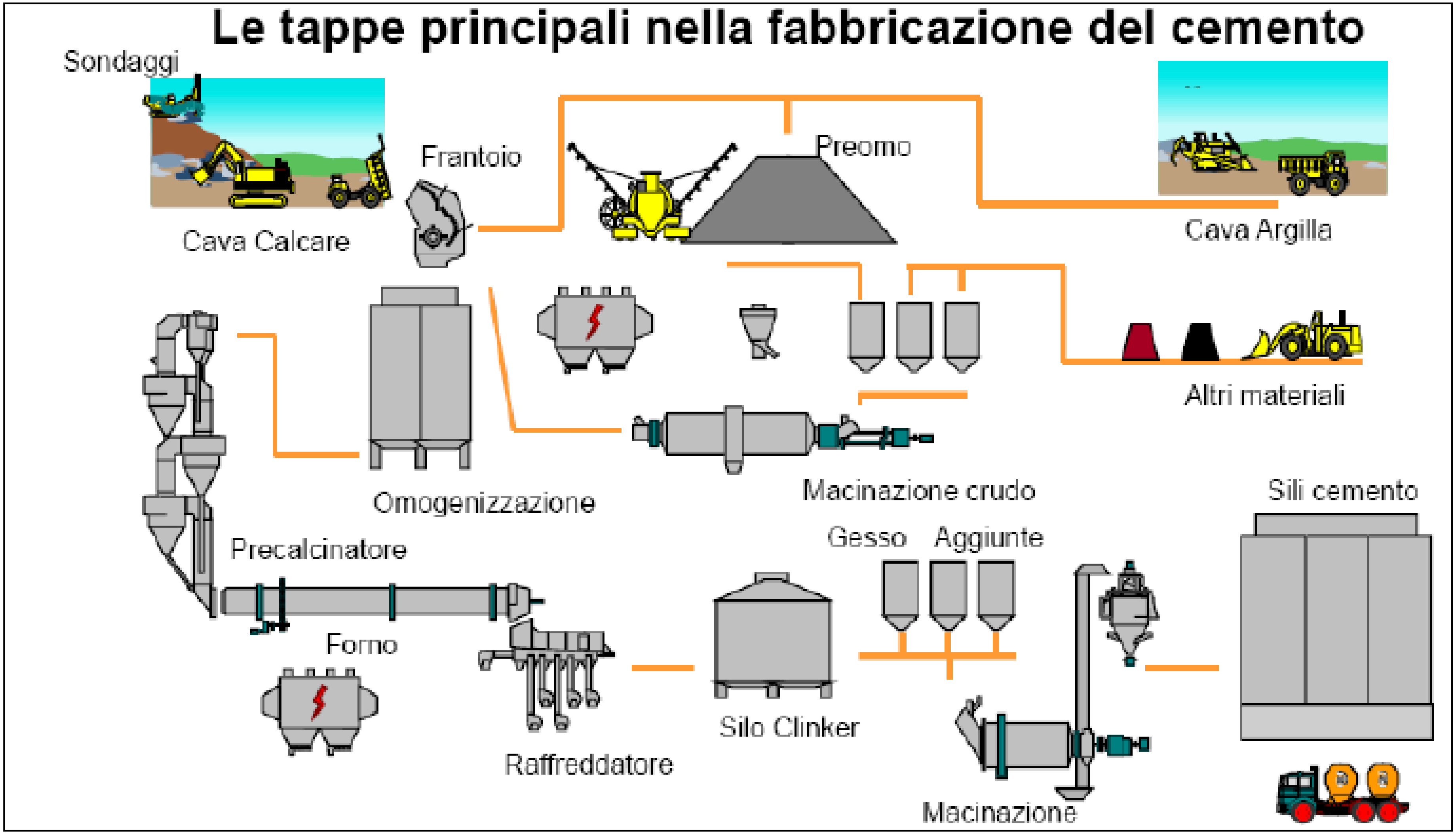
Hydraulic binders

Cement composition

Ossidi peso %		Fasi peso %	
CaO	60 – 69	C3S	50 - 70
SiO_2	16 -26	β-C2S	10 - 30
Al_2O_3	4 – 8	C3A	5 - 12
Fe_2O_3	4 – 8	C4AF	5 - 12
SO_3	2	Periclasio (MgO) Calce libera (CaO) Portlandite ($Ca(OH)_2$) Solfati alcalini: Arcanite (K_2SO_4) Aphtitalite $(K,Na)SO_4$	0 – 3%
MgO	2		
K_2O, Na_2O	1		
Altri	3		

Hydraulic binders

Cement production process

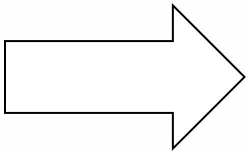


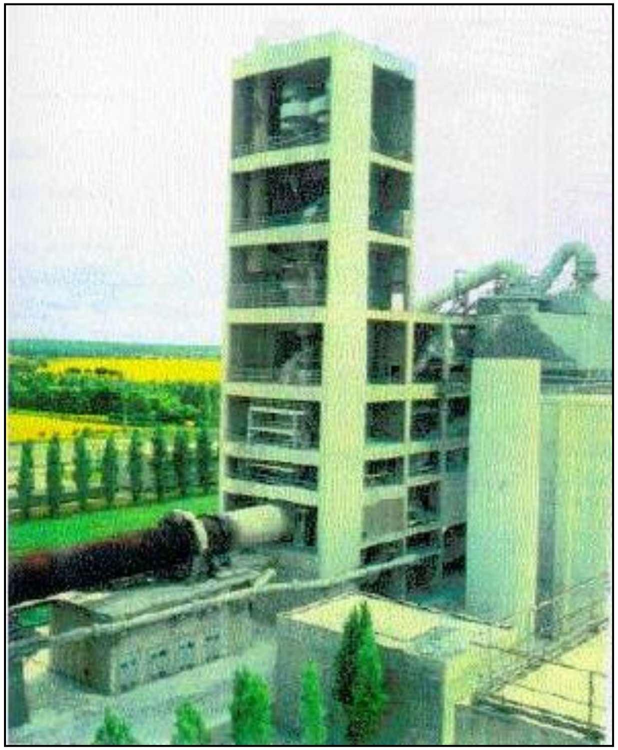
Hydraulic binders

Hydraulic binders

Cement production process: grinding and pre-heating

- Fine grinding of the raw materials (Ø < 160 μm) and drying of the obtained flour.
- Progressive heating (100°C → 900°C) within a series of cyclone stages (4 – 5).
- Elicoidal movement of the flour in the cyclone stages, against a flow of hot gases.

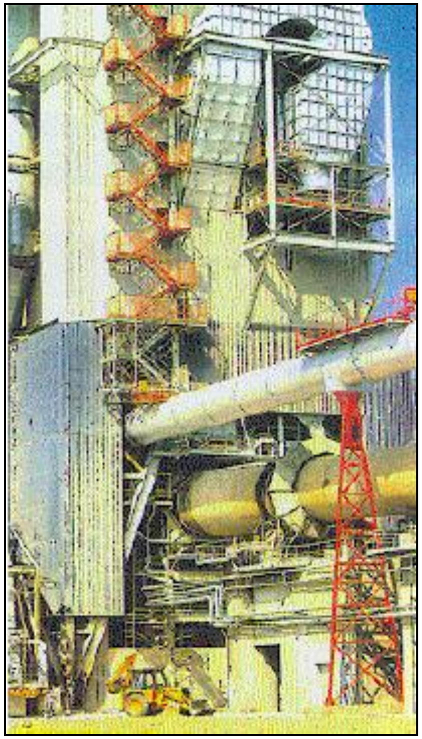


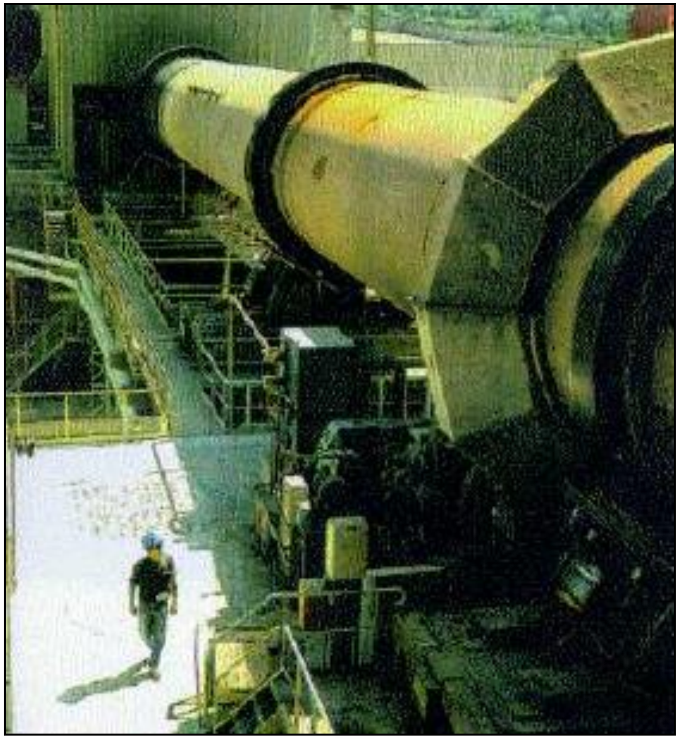


Hydraulic binders

Cement production process: pre-calcination and firing

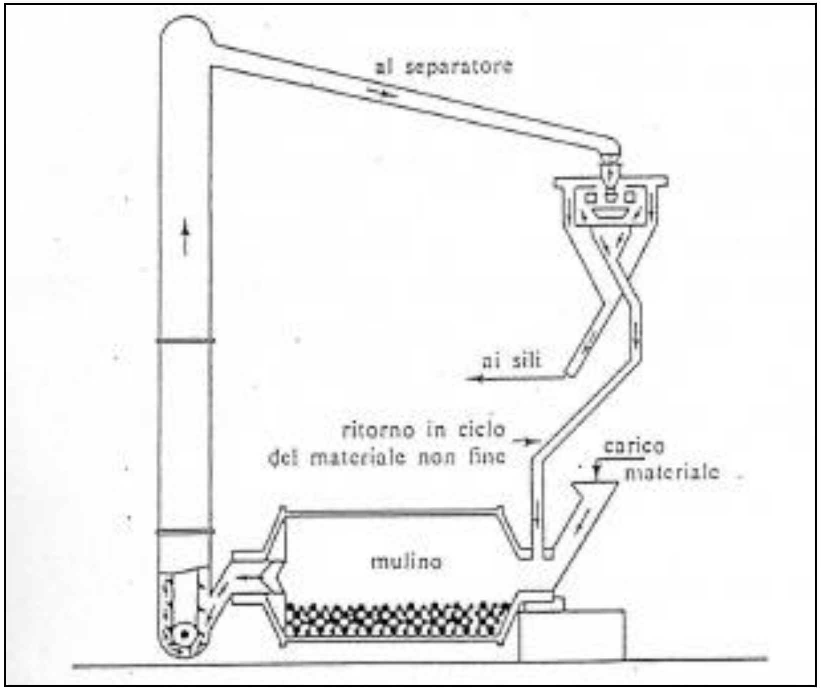
- Pre-calcination stage (completion of limestone decarbonation around 900°C). Relevant fuel consumption (endothermic process).
- Firing in horizontal rotary kiln. Slow movement of the flour within the kiln and agglomeration of the mixture around 1300°C after partial fusion. Permanence at the higher temperature (~ 1450°C) to favour the clinkering processes.





Cement production process: cooling and grinding

- Two cooling systems: 1) satellite cooler → cooling pipes parallel to the kiln; 2) grid cooler (better temper of the clinker) → cold air flux toward horizontal grids over which the clinker flows through oscillatory movement.
- Grinding in ball mills → transfer of the clinker material and mineral additions within chambers loaded with grinding elements of variable diameters.

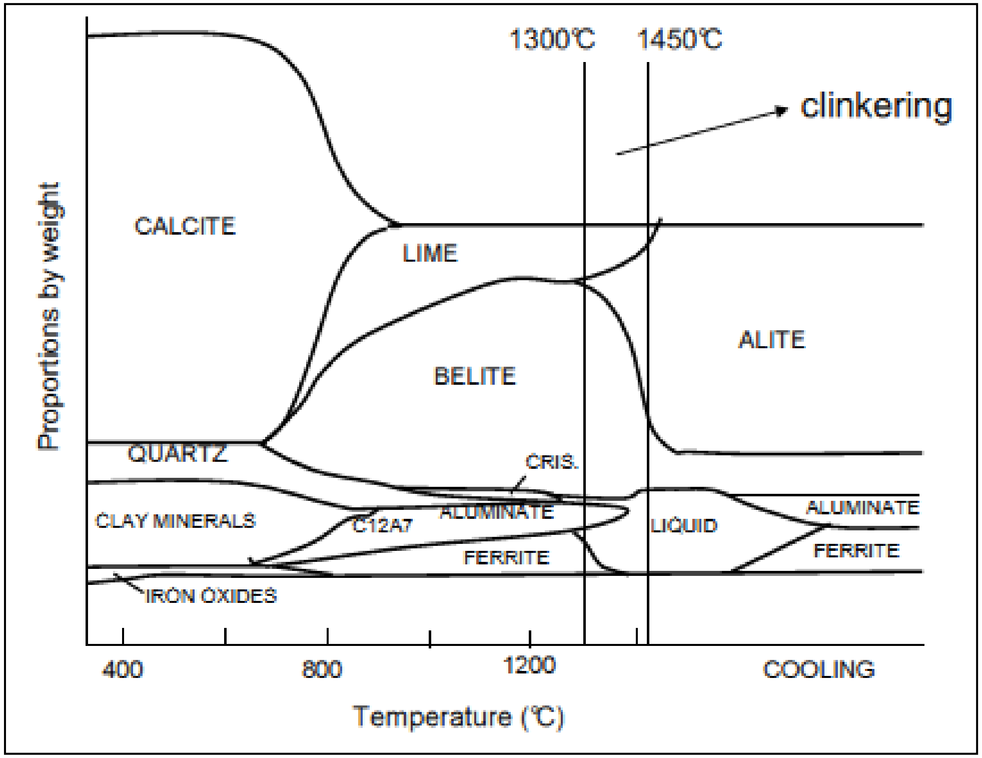


Hydraulic binders

Chemical-physical transformations during the firing process

Main reactions subdivided in three groups:

- Reactions under 1300°C: a) calcite decomposition, b) clay minerals decomposition, c) CaO reaction with silica and clays decomposition products to form belite, aluminates and ferrite. The liquid phase is present in low amounts;



- Reactions between 1300°C and 1450°C (clinkering): formation of a molten mass mainly derived from aluminates and ferrite (liquid fraction: 20-30% of the total mixture), reaction of belite with CaO to form alite;
- Reactions during rapid cooling: crystallization of the liquid phase to form aluminates and ferrite, polymorphic transformation of alite and belite.

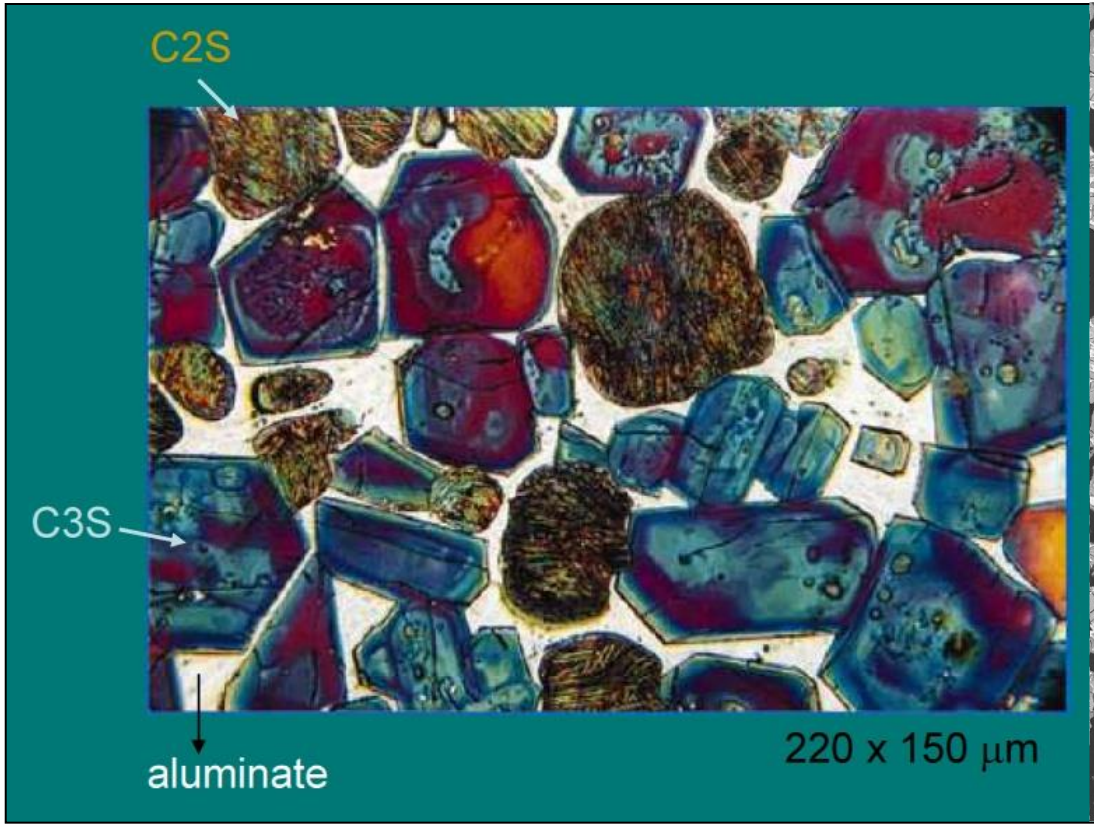
Hydraulic binders

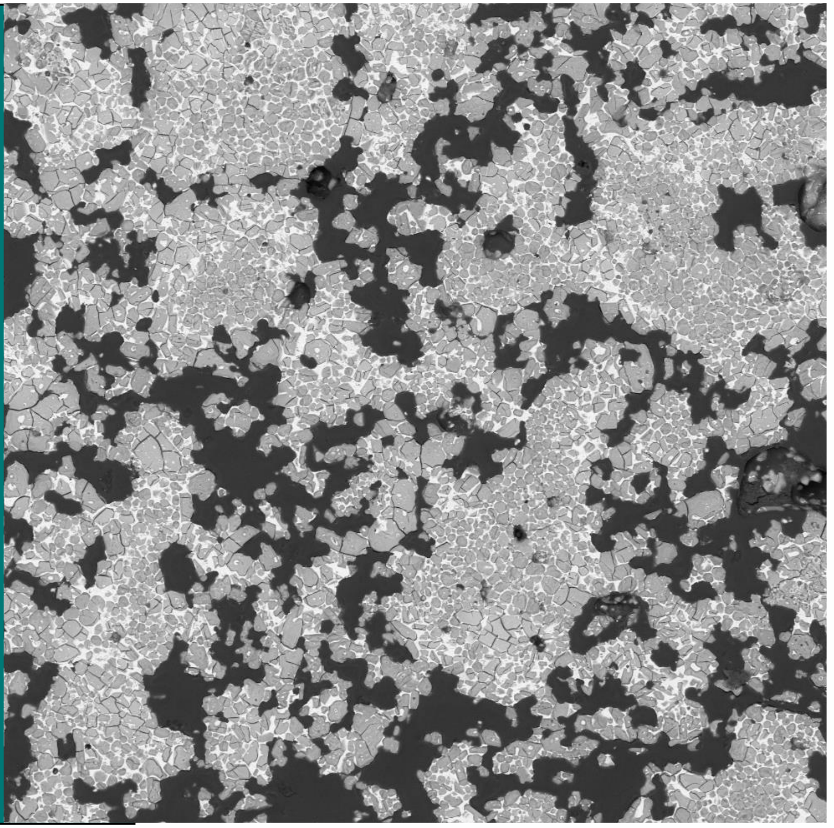
Chemical-physical transformations during the firing process

T℃ cottura	Componenti iniziali	Prodotto di reazione	Tipo di reazione
100℃			Evaporazione acqua
450 - 500℃	$2SiO_2 \cdot Al_2O_3 \cdot H_2O$	$2SiO_2 + Al_2O_3 + H_2O$	Parziale decomposizione argille
800 - 900℃	$CaCO_3$	$CaO + CO_2$	Dissociazione carbonato di calcio
800 - 900℃	$2CaO + SiO_2$	$2CaO \cdot SiO_2$ (C2S)	Reazione tra CaO e componenti argille
1000 - 1100℃	$3CaO + Al_2O_3$	$3CaO \cdot Al_2O_3$ (C3A)	Reazione tra CaO e componenti argille
1000 - 1200℃	$3CaO \cdot Al_2O_3$ + $CaO \cdot Fe_2O_3$	$3CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C4AF)	Inizio formazione fase liquida
1300 - 1450℃	$2CaO \cdot SiO_2$ (C2S) + CaO	$3CaO \cdot SiO_2$ (C3S)	Continua formazione fase liquida e C3S

Hydraulic binders

Cement microstructure

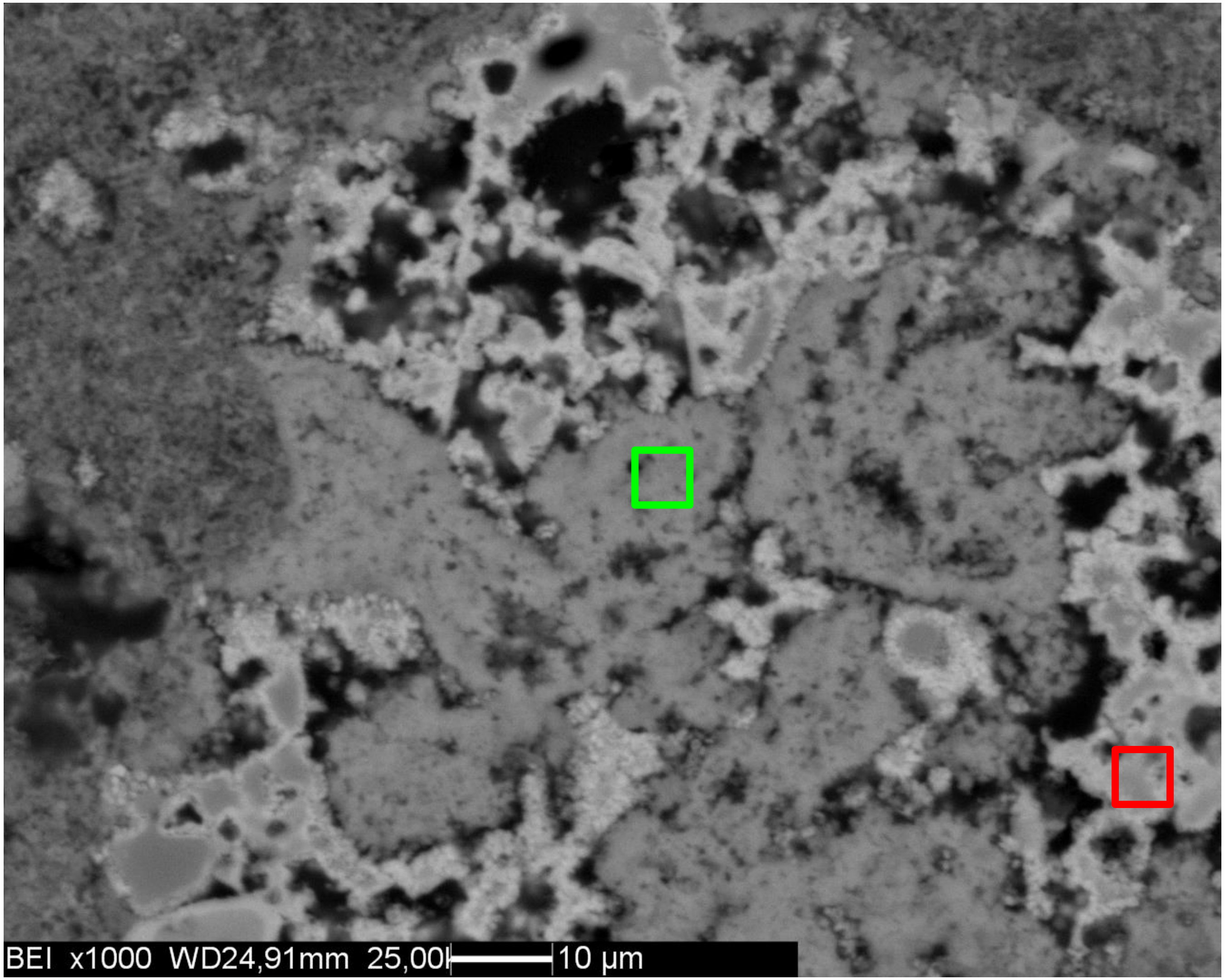


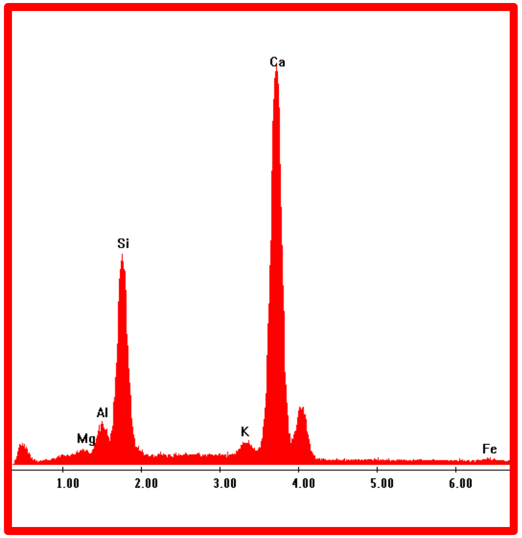


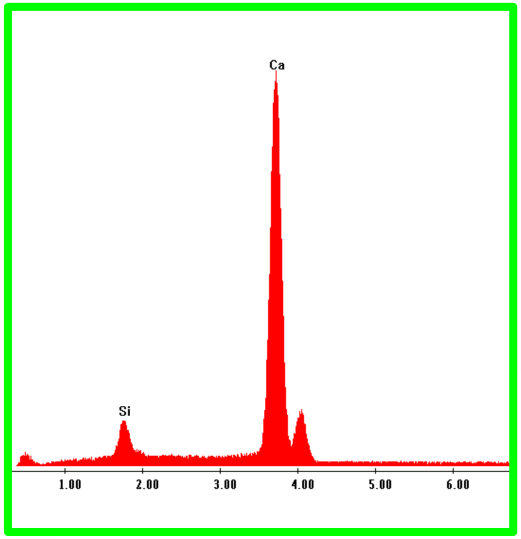
The reactions during the firing process influence the clinker texture (dimensions, shape and distribution of the phases). C_2S, C_3S: euhedral crystals formed at high temperature in presence of liquid phase. Cystallization of the liquid phase during cooling without relevant crystal growth, formation of a fine interstitial matrix of C_3A and C_4AF

Hydraulic binders

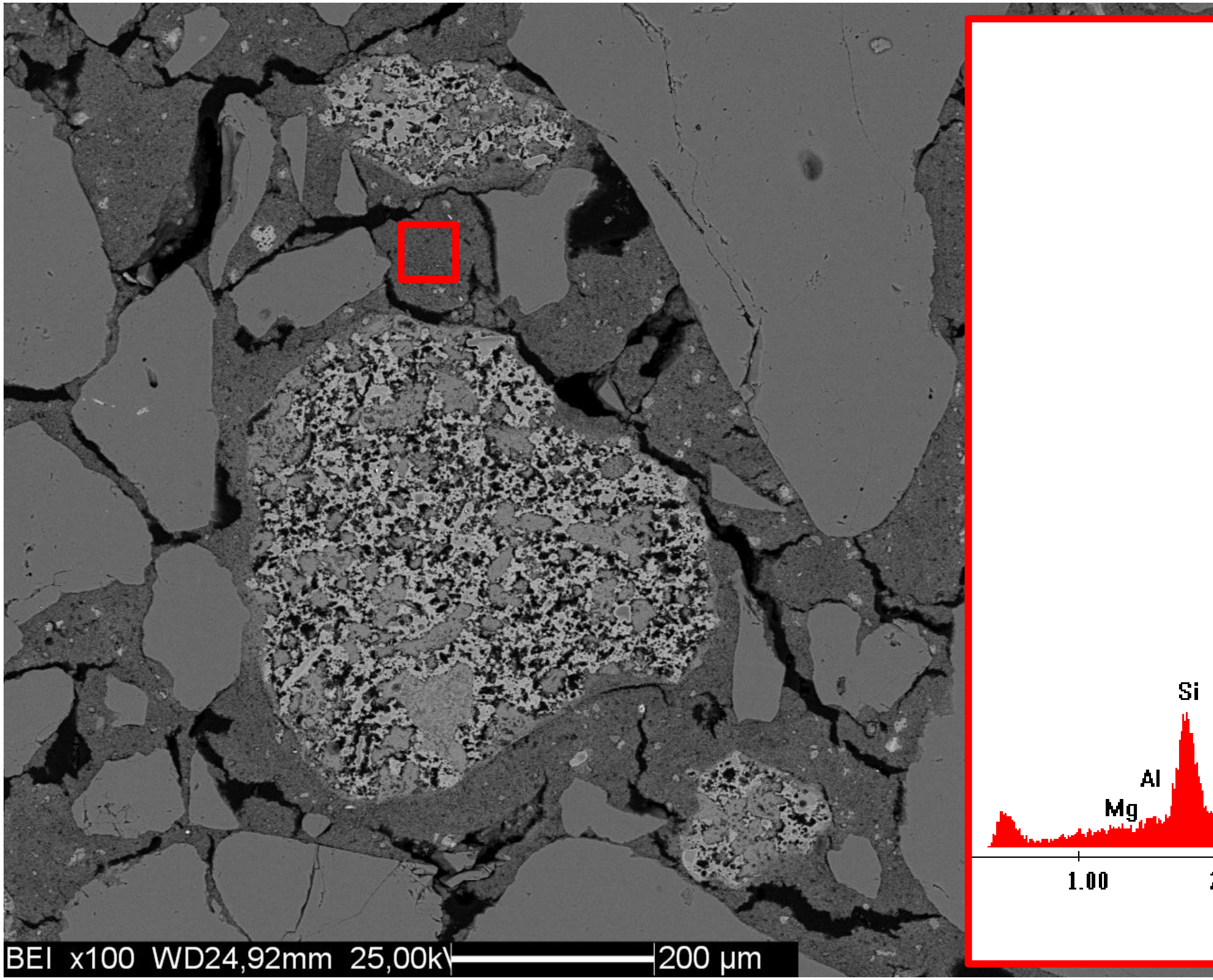
Hydraulic lime microstructure

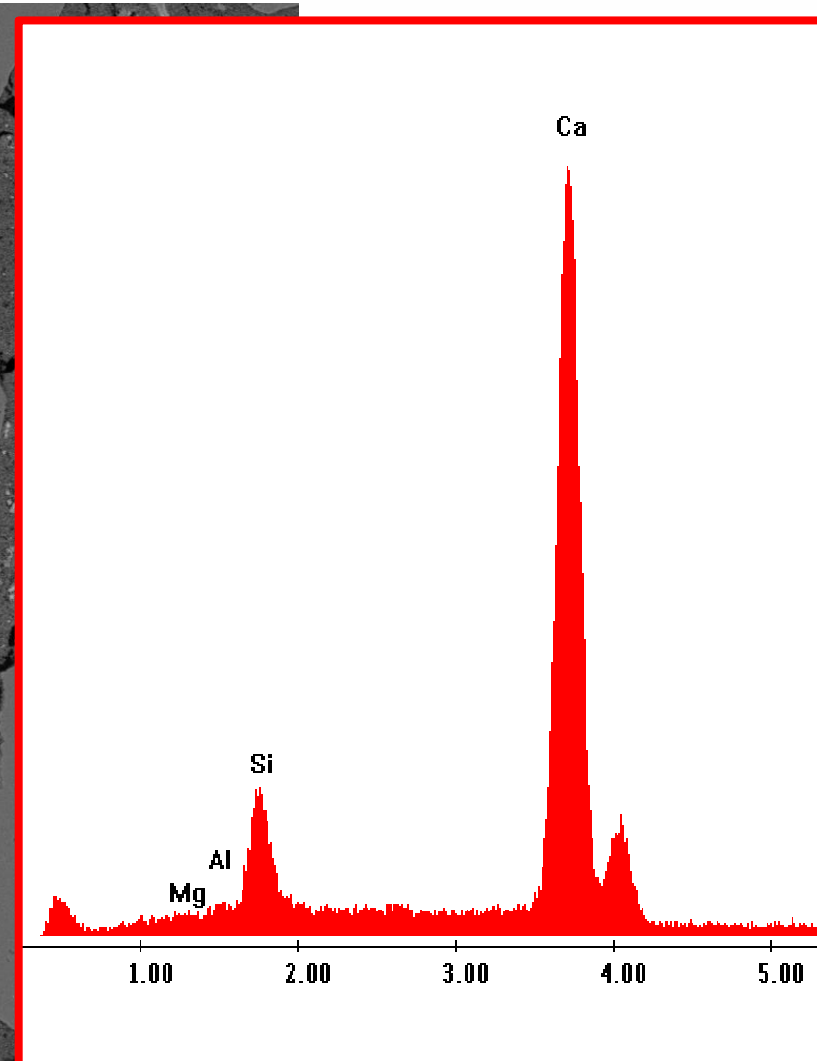






Hydraulic lime microstructure





Alite – C_3S

- Stable between 2070°C and 1250°C. Decomposition under 1250°C to form C_2S + CaO.
- Slow tranformation process → Room T permanence due to the rapid cooling.
- 7 polymorphs, 3 spatial groups (industrial products: M1, M3).

$$T_1 \xleftrightarrow{620\,°C} T_2 \xleftrightarrow{920\,°C} T_3 \xleftrightarrow{980\,°C} M_1 \xleftrightarrow{990\,°C} M_2 \xleftrightarrow{1060\,°C} M_3 \xleftrightarrow{1070\,°C} R$$

(T: triclino; M: monoclino; R: trigonale)

SG: P –1
a = 11.67; b= 14.24, c= 13.72
α = 105.5, β=94.3 γ=90.0
Z=18
Ref: Golovastikov et al (1975)

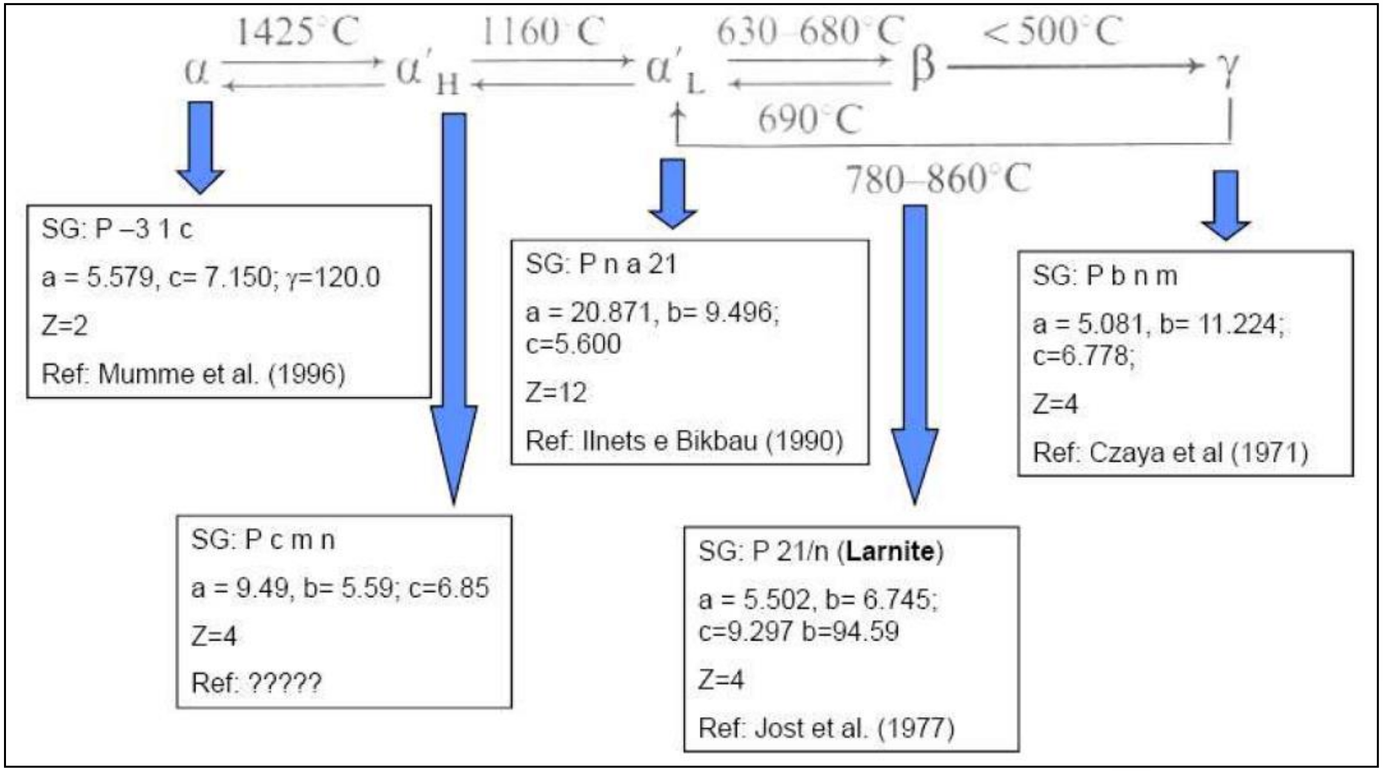
SG: C m
a = 33.083; b= 7.027, c= 18.499; β=94.12
Z=36
Ref: Nishi et al (1985)
Ref. De La Torre et al. (…)
Ref. Mumme (1995)

SG: R 3 m
a = 7.0; c= 25.0
Z=9
Ref: Ilinets et al (1985)

Hydraulic binders

Belite – C_2S

- 5 polymorphs.
- β polymorph is the only reactive.
- β polymorph formed during the cooling process. If it is not formed the α polymorphs are transformed into the γ one (volume increase, detrimental after hardening).



Calcium aluminate – C_3A

- Pure: No polymorphism.
- Na^+ incorporation within the crystal structure → polymorphic solid solutions.

% Na_2O	Compositional Range (x)	Type	Space group	Designation
0 - 1.0	0 – 0.04	Cubic	*Pa*3	C_I
1.0 - 2.4	0.04 - 0.10	Cubic	$P2_13$	C_{II}
2.4 - 3.7	0.10 - 0.16	-	-	C_{II} + O
3.7 - 4.6	0.16 - 0.20	Orthorhombic	*Pbca*	O
4.6 - 5.7	0.20 - 0.25	Monoclinic	$P2_1/a$	M

Ferrite – C_4AF

- Solid solution: $Ca_2(Al_xFe_{1-x})_2O_5$ (0<x<0.7) → 5 polymorphs, 2 two spatial groups.

x	a (Å)	b (Å)	c (Å)	Space group
0	5.5980	14.7687	5.4253	*Pcmn*
0.285	5.588	14.61	5.380	*Ibm2*
0.36	5.583	14.58	5.374	*Ibm2*
0.5	5.5672	14.521	5.349	*Ibm2*
1	5.41	14.45	5.23	*Ibm2*

Substitutions

Table 1.2 *Typical compositions of phases in Portland cement clinkers (mass per cent)*

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
Alite*	0·1	1·1	1·0	25·2	0·1	0·1	0·1	71·6	0·0	0·0	0·7
Belite*	0·1	0·5	2·1	31·5	0·1	0·2	0·9	63·5	0·2	0·0	0·9
Aluminate (cubic)*	1·0	1·4	31·3	3·7	0·0	0·0	0·7	56·6	0·2	0·0	5·1
Ferrite*	0·1	3·0	21·9	3·6	0·0	0·0	0·2	47·5	1·6	0·7	21·4
Aluminate (orthorhombic)†	0·6	1·2	28·9	4·3	0·0	0·0	4·0	53·9	0·5	0·0	6·6
Aluminate (low Fe)‡	0·4	1·0	33·8	4·6	0·0	0·0	0·5	58·1	0·6	0·0	1·0
Ferrite (low Al)§	0·4	3·7	16·2	5·0	0·0	0·3	0·2	47·8	0·6	1·0	25·4

*Typical values for an ordinary Portland cement clinker with 1·65% MgO, 3·1% Fe_2O_3 and molar $SO_3/(K_2O+Na_2O) < 1{\cdot}0$. For clinkers not approximating to these conditions, the compositions of the phases may differ significantly from those given in the table, as explained in the text.
† Orthorhombic or pseudotetragonal forms, present in some clinkers high in alkalis. Na/K ratio varies with that of the clinker.
‡ Tentative composition for aluminate phase in white cement clinkers.
§ Values for the ferrite phase in a typical sulfate-resisting clinker (MgO, 2·1%; Al_2O_3, 3·8%; Fe_2O_3, 4·7%)(G5)· Compositions of other such clinkers may vary considerably (see text).

Hydraulic binders

Secondary phases

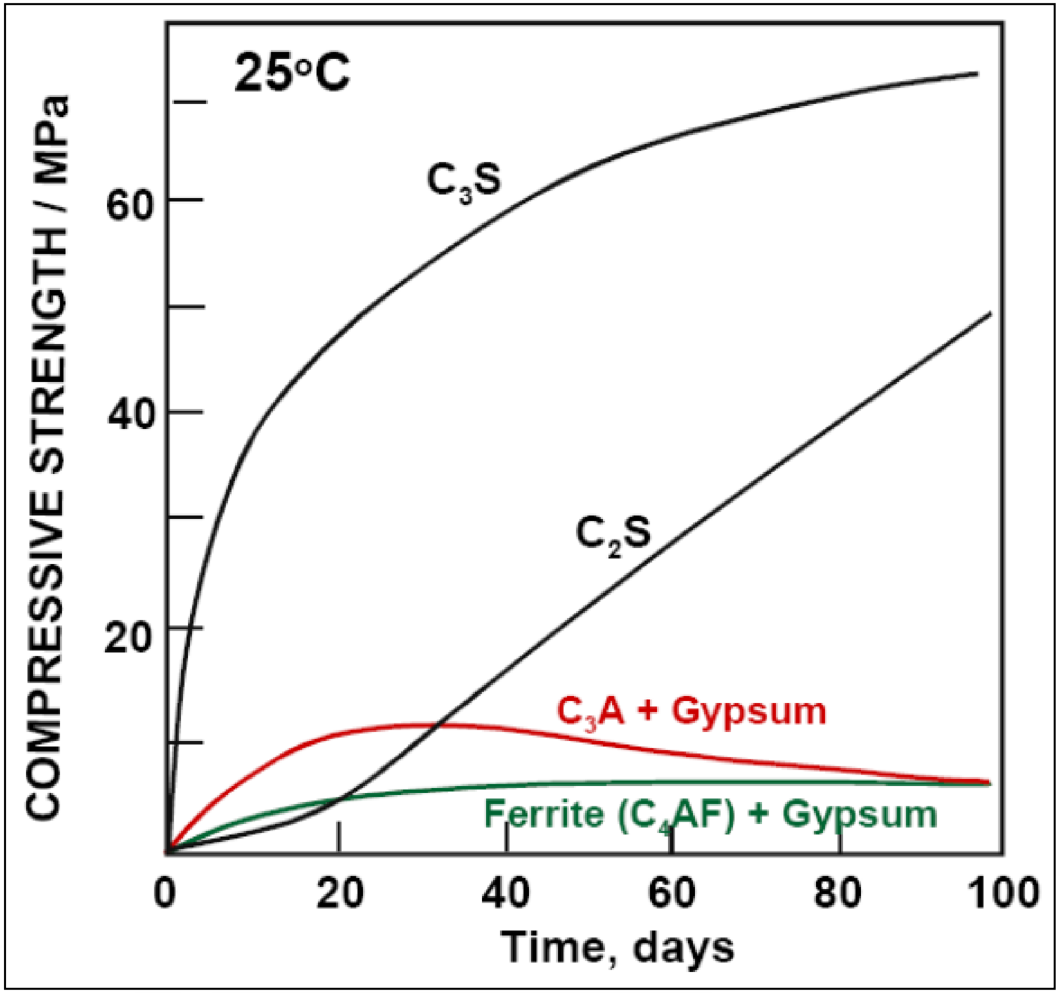
Periclasio (MgO)
Calce libera (CaO)
Portlandite ($Ca(OH)_2$)
Solfati alcalini:
Arcanite (K_2SO_4)
Aphtitalite $(K,Na)SO_4$

→ 0-3%

↓ Limite di rilevabilità

Hydration of hydraulic binders

- Mix with water → dissolution of the reactive anhydrous phases, hydraulic reaction with H_2O, formation of low solubility phases, mainly hydrated microcrystalline compounds.
- Setting: reaction stage implying loss of workability of the binder-water mixture.
- Hardening: slow process producing a progressive gain of mechanical properties. It ends when all the reactions between water and binder are completed.
- Differentiated contribution of the hydraulic phases to the hydration speed and strength gain.



Hydration of hydraulic binders: silicates

- Main process related to the setting and hardening of the cement paste.
- C_3S – C_2S in contact with water → dissolution and release in solution of Ca^{2+}, silicates and OH^- in solution, pH increase (> 12), formation of amorphous calcium silicate hydrates (CSH) and calcium hydroxide portlandite (CH).
- Ca/Si ratio of CSH: between 0.8 and 2.3, variable amount of structural water.

$$C3S + H_2O \xrightarrow{V1} C\text{-}S\text{-}H + CH$$

$$C2S + H_2O \xrightarrow{V2} C\text{-}S\text{-}H + CH$$

v1 > v2

$$Ca_3SiO_{5(s)} + 3H_2O \rightarrow 3Ca^{2+}_{(aq)} + 4OH^-_{(aq)} + H_2SiO_4^{2-}{}_{(aq)}$$

$$H_2SiO_4^{2-}{}_{(aq)} + xCa^{2+}_{(aq)} + (2x-2)OH^-_{(aq)} + (y-x)H_2O_{(l)} \rightarrow (CaO)_x(SiO_2)\cdot(H_2O)_y$$

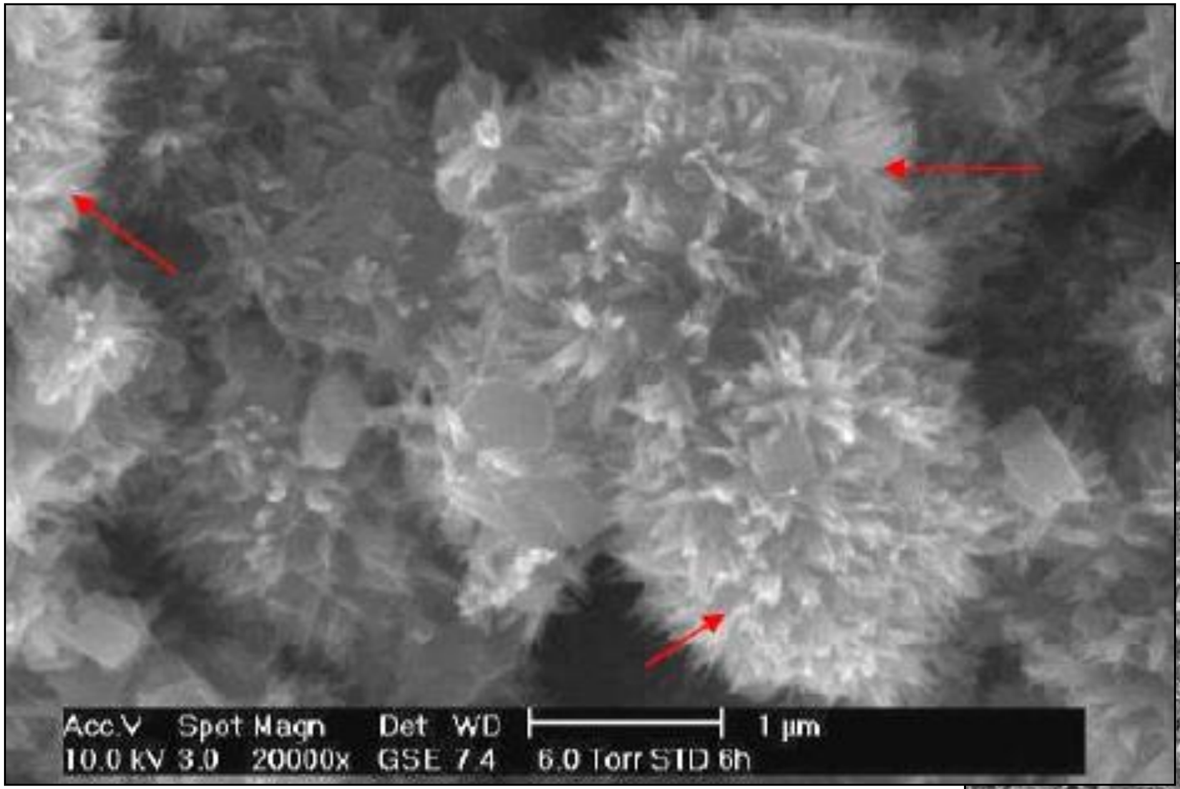
$$Ca_3SiO_5 + (3 + y - x)H_2O \rightarrow (CaO)_x(SiO_2)\cdot(H_2O)_y + (3 - x)Ca(OH)_2$$

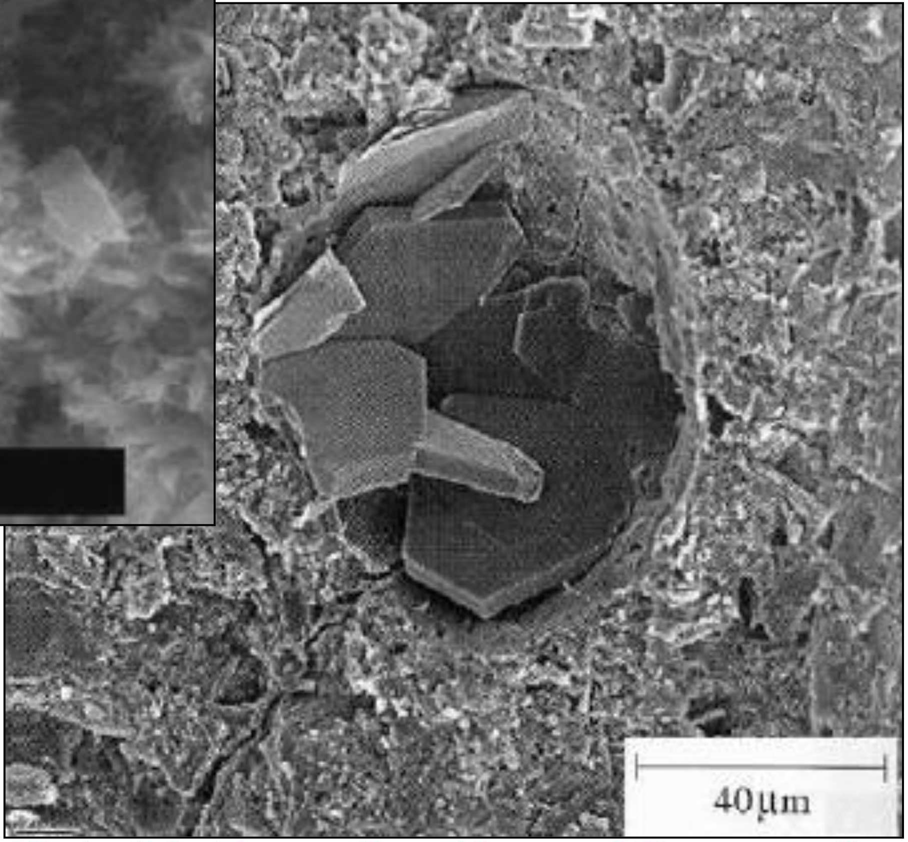
x controlla il rapporto C/S

y il contenuto di acqua in struttura

x ed y variano durante la reazione

Hydration of hydraulic binders: silicates





Hydration of hydraulic binders: aluminates

$$C3A + H_2O \xrightarrow{v1} \text{alluminati idrati}$$

$$C4AF + H_2O \xrightarrow[v2]{} \text{alluminati ferriti idrati}$$

$$v1 > v2$$

- C_3A hydration during the first minutes of reaction → flash set.
- Poorly crystalline phases, metastable and varying in composition → amorphous gel progressively crystallizing to form exagonal phases, named AFm phases (A: Al, F: Fe, m: mono).
- Conversion of AFm to the stable cubic hydrogarnet phase.

$$2C3A + 21H_2O \rightarrow C_4AH_{13} + C_2AH_8 \quad (C_4AH_{19}, CAH_{10}, \ldots)$$

⇩

$$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

Hydration of hydraulic binders: aluminates

- Presence of gypsum and other soluble sulphates → C_3A reaction to form AFt phase ettringite.
- Ettringite forms a barrier around C_3A granules hindering water and ions diffusion, preventing the formation of AFm phases and the consequent flash set.
- Ettringite is stable when sulphate ions are available in solution. Total SO_4^{2-} consumption → conversion to monosulphate (AFm) , dissolution of the passivating layer and restart of C_3A hydration.

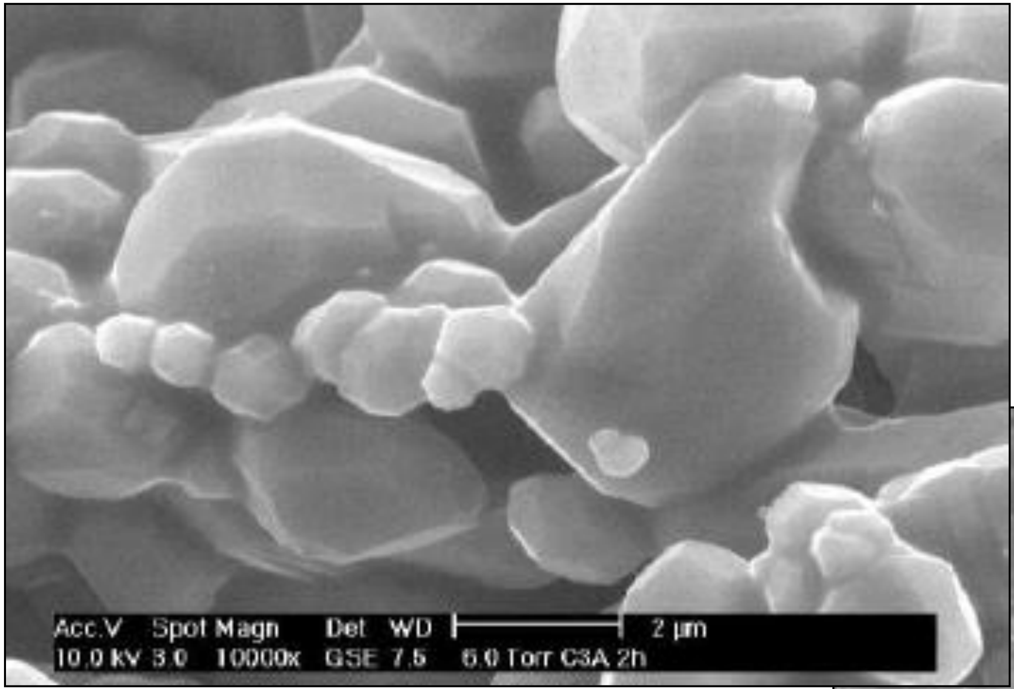
$$C3A + 3C\check{S}H2 + 26H \rightarrow C_6A\check{S}_3H_{32} \quad \text{ETTRINGITE}$$

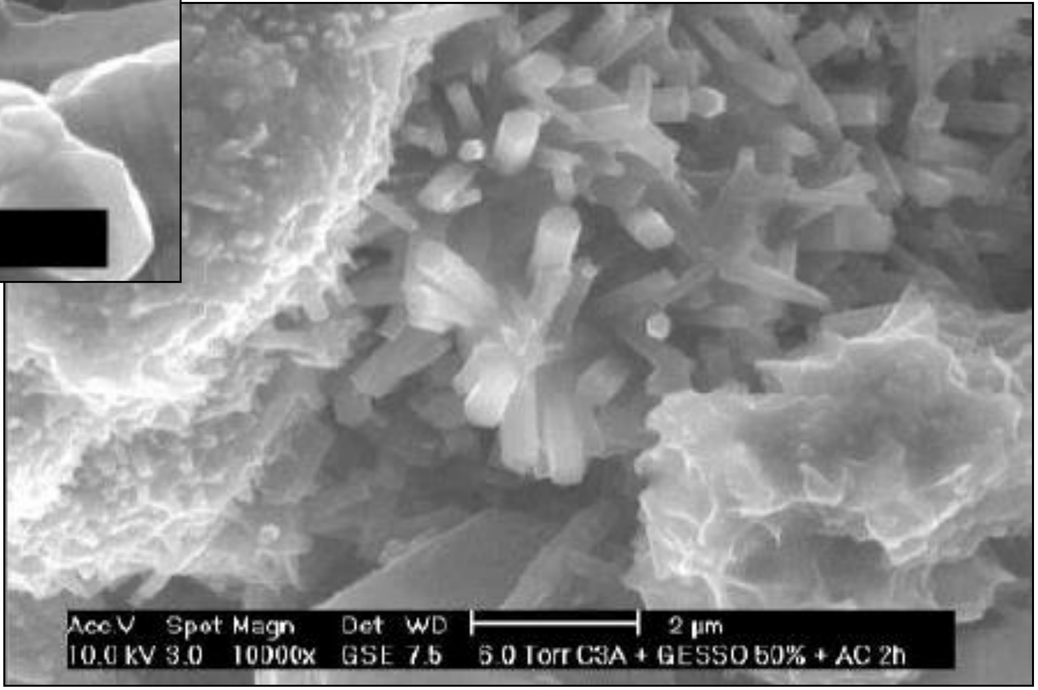
⇩

$$2C3A + C_6\check{S}_3H_{32} + 4H \rightarrow 3C_4A\check{S}H_{12} \quad \text{MONOSOLFATO}$$

Hydraulic binders

Hydration of hydraulic binders: aluminates





Hydraulic binders

Cements classification: EN 197-1

Tipi di cemento	Denominazione	Sigla	Clinker	Loppa d'altoforno	Fumi di silice	Pozzolana naturale	Pozzolana industriale	Cenere Volante silicica	Cenere Volante calcica	Scisto calcinato	Calcare	Calcare	Costituenti secondari
			K	S	D	P	Q	V	W	T	L	LL	
CEM I	Cemento Portland	I	95-100										0-5
CEM II	Cemento Portland alla loppa	II / A-S	80-94	6-20									0-5
		II / B-S	65-79	21-35									0-5
	Cemento Portland ai fumi di silice	II / A-D	90-94		6-10								0-5
	Cemento Portland alla pozzolana	II / A-P	80-94			6-20							0-5
		II / B-P	65-79			21-35							0-5
		II / A-Q	80-94				6-20						0-5
		II / B-Q	65-79				21-35						0-5
	Cemento Portland alla cenere volante	II / A-V	80-94					6-20					0-5
		II / B-V	65-79					21-35					0-5
		II / A-W	80-94						6-20				0-5
		II / B-W	65-79						21-35				0-5
	Cemento Portland allo scisto calcinato	II / A-T	80-94							6-20			0-5
		II / B-T	65-79							21-35			0-5
	Cemento Portland al calcare	II / A-L	80-94								6-20		0-5
		II / B-L	65-79								21-35		0-5
		II / A-LL	80-94									6-20	0-5
		II / B-LL	65-79									21-35	0-5
	Cemento Portland composito	II / A-M	80-94	<-- 6-20 -->									0-5
		II / B-M	65-79	<-- 21-35 -->									0-5
CEM III	Cemento d'altoforno	III / A	35-64	36-65									0-5
		III / B	20-34	66-80									0-5
		III / C	5-19	81-95									0-5
CEM IV	Cemento pozzolanico	IV / A	65-89		<-- 11-35 -->								0-5
		IV / B	45-64		<-- 36-55 -->								0-5
CEM V	Cemento composito	V / A	40-64	18-30		<-- 18-30 -->							0-5
		V / B	20-39	31-50		<-- 31-50 -->							0-5

Hydraulic binders

Supplementary cementitious materials: pozzolans

- Natural pozzolans: pyroclastics powders mainly composed of silicate matrices of low crystalline order.
- Industrial pozzolans: clays that underwent a thermal process transforming them into a silicate glass.
- Pozzolanic reaction: dissolution in alkaline solution of glasses and silicate minerals due to the rupture of Si-O chemical bonds, release in solution of silicate ions, reaction with Ca ions released by portlandite dissolution → formation of calcium silicate hydrates (C-S-H).

$$\text{Pozzolan} + Ca(OH)_2 + H_2O \rightarrow \text{C-S-H}$$

SiO_2	50 – 70 %
Al_2O_3	16 – 22 %
Fe_2O_3 + FeO	3 – 10 %
CaO	2 – 10 %
Alcali	4 – 8 %
MgO	0,5 – 4 %

Hydraulic binders

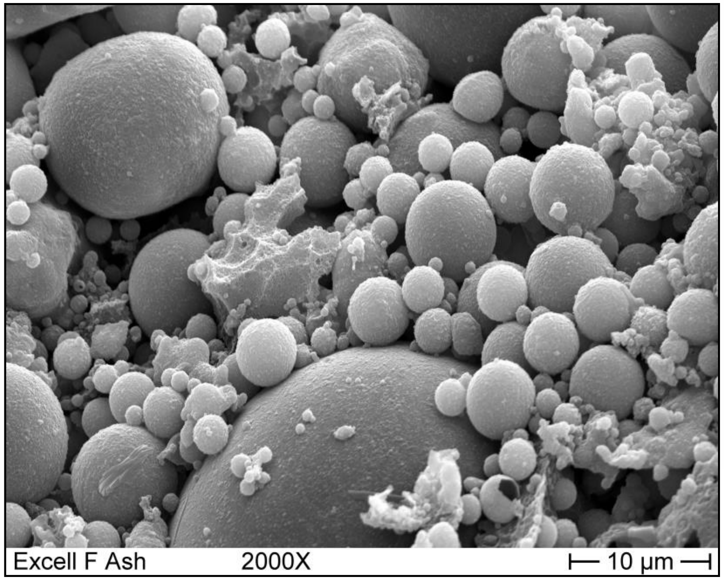
Supplementary cementitious materials: blastfurnace slags

- Foundry slags related to the production process of metallic iron.
- Variable composition, generally high in SiO_2, CaO and Al_2O_3.
- Formation of a highly reactive silicic-calcic glass due to rapid cooling.
- Latent hydraulic reaction → CSH formation not related to pozzolanic reaction processes, but after dissolution of slag in alkaline solution and subsequent reaction between calcium and silicate ions released in solution by the slag itself.

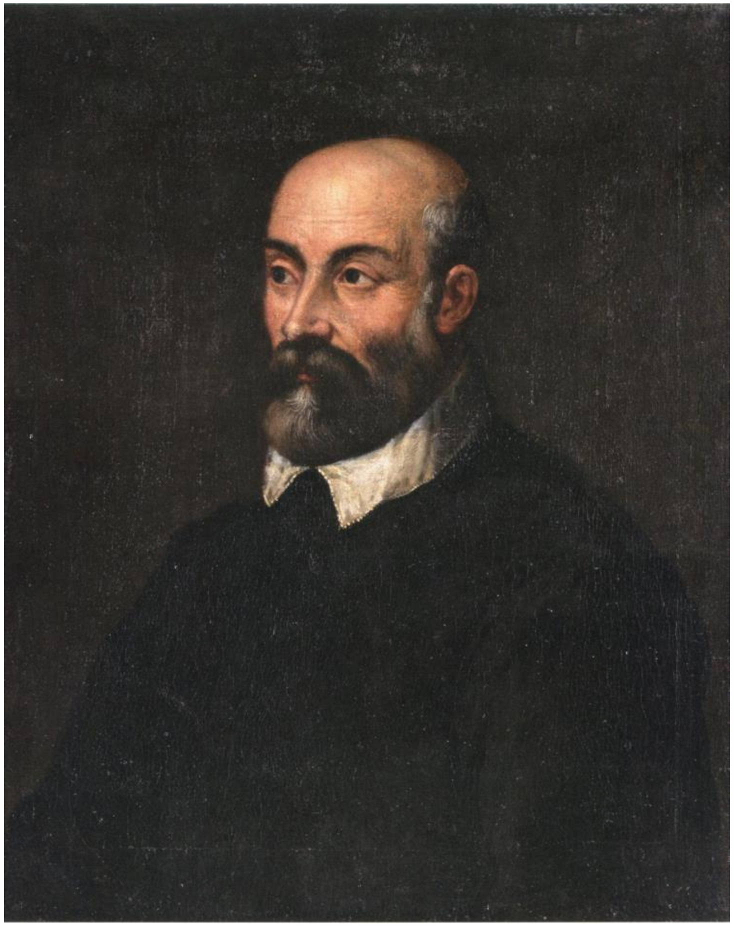
Hydraulic binders

Supplementary cementitious materials: fly ashes and silica fumes

- Fly ashes: glassy microspheres (Ø 5 – 90 µm) obtained as byproducts of the coal power plants; composition strictly related to the one of the original coal and to the combustion processes (high in SiO_2, Al_2O_3, variable in CaO).
- Silica fumes: glassy micro-nanospheres (mean Ø 0.1 µm) obtained as byproducts of the metallic Si and Si-Fe alloys productive process; composed of 95 - 99.5% amorphous silica.
- Pozzolanic reaction with portlandite and fillering effect (silica fumes).



Andrea Palladio (1508-1580)



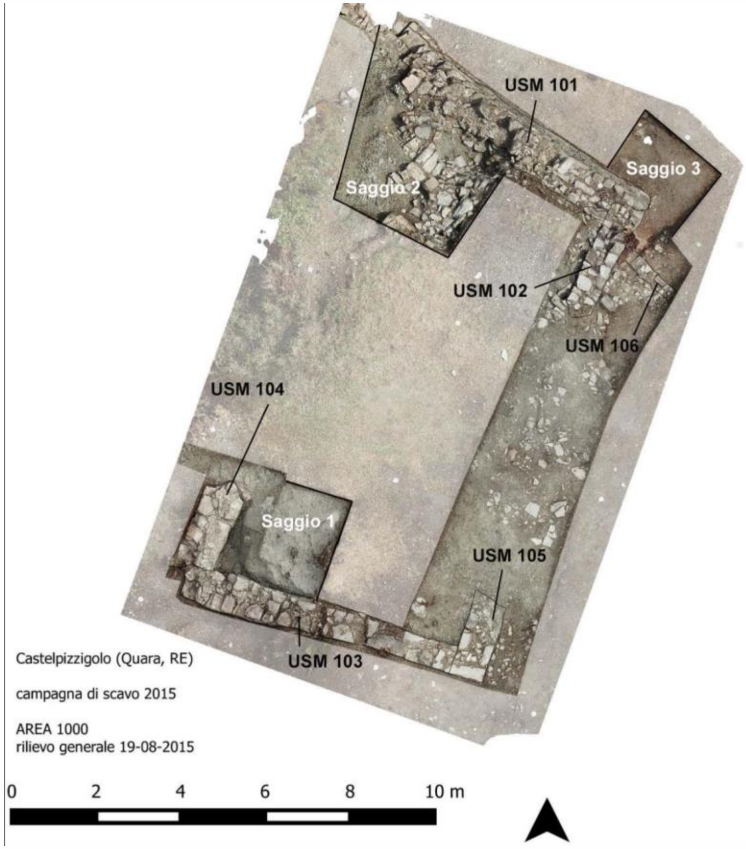
Hydraulic binders

«Calce Nigra Padoana»

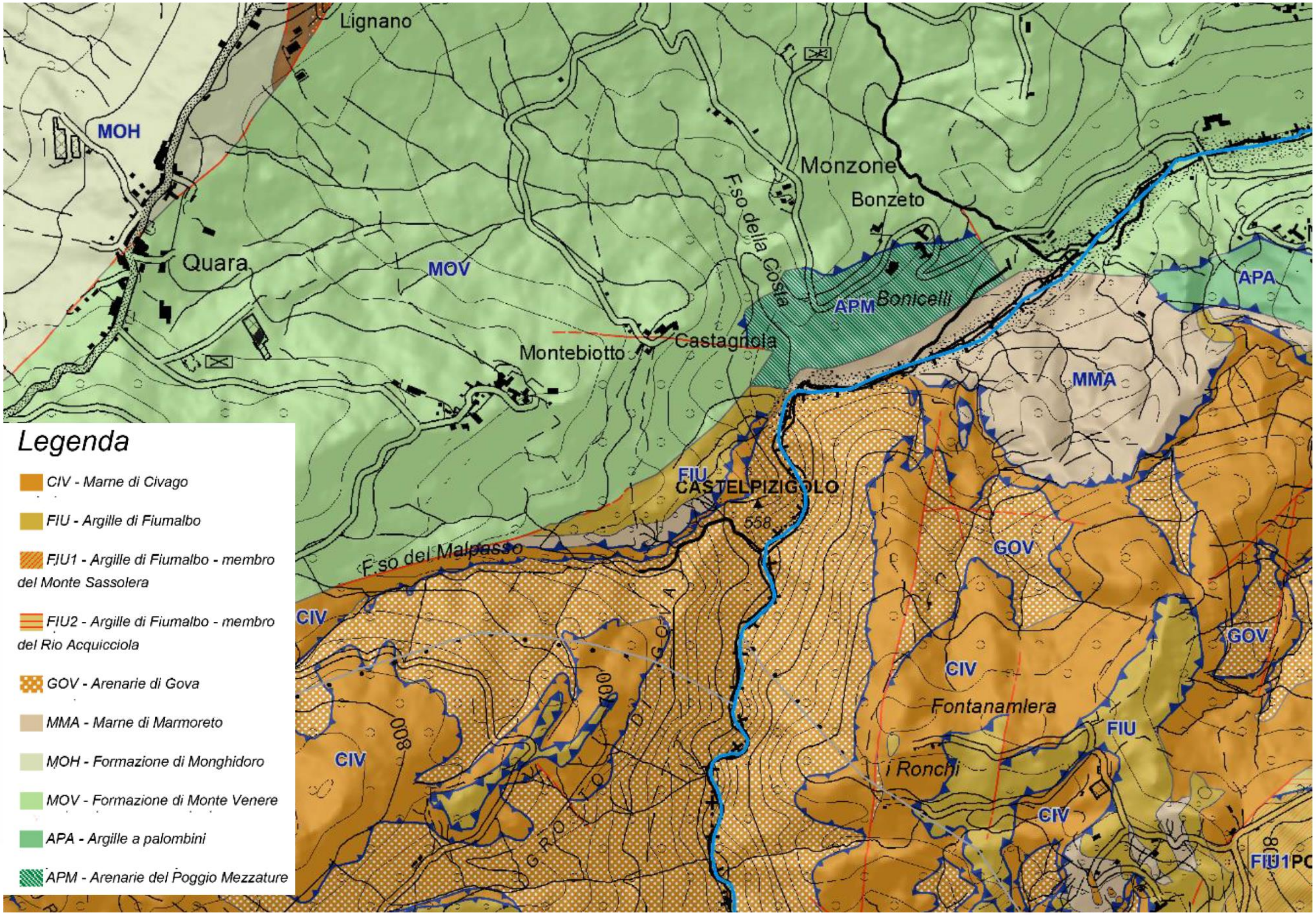
Hydraulic binders

Hydraulic binders

Castel Pizigolo (Toano, Reggio Emilia, XI-XII century AD)

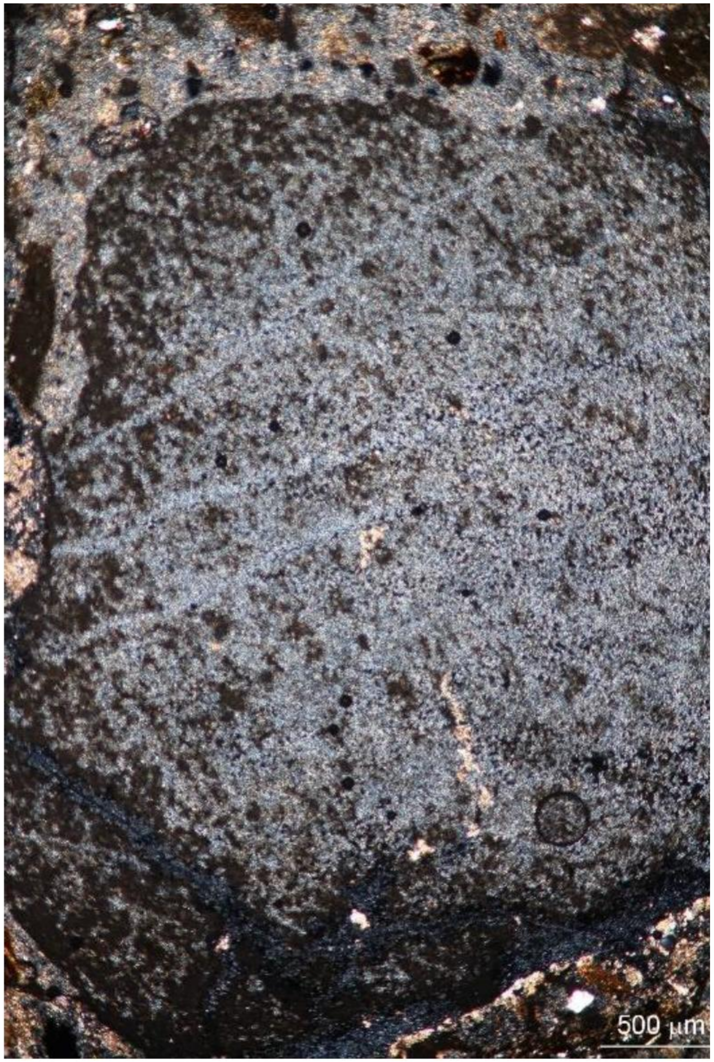


Castel Pizigolo (Toano, Reggio Emilia, XI-XII century AD)



Hydraulic binders

Castel Pizigolo (Toano, Reggio Emilia, XI-XII century AD)



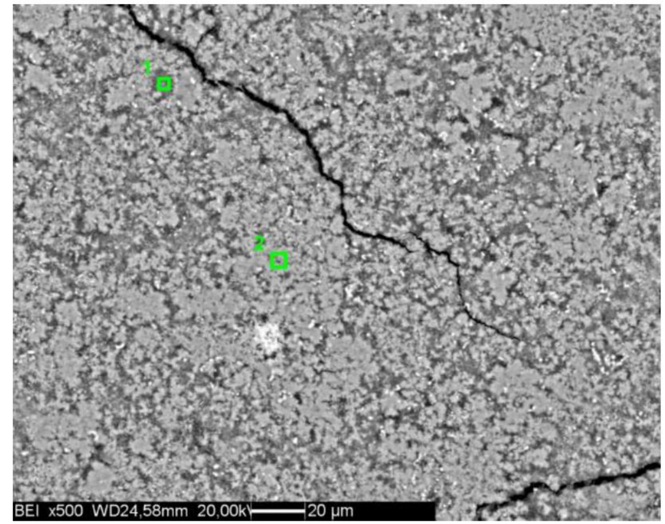


Fig. 55 Campione CPIZ-4, immagine BEI, 500x. Ingrandimento di un grumo di incotto parzialmente reagito, in cui si nota che la componente silicea [1] è concentrata in piccole aree più scure, mentre le zone chiare [2] individuano una preponderanza di carbonati di calcio. (Foto C. BANDIERI).

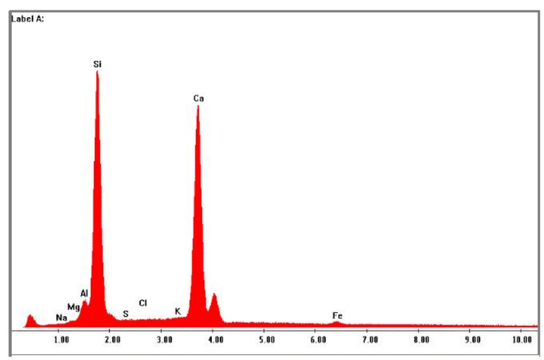


Fig. 56 Campione CPIZ-4, analisi EDS del punto [1]. La concentrazione di silicio è maggiore rispetto al calcio.

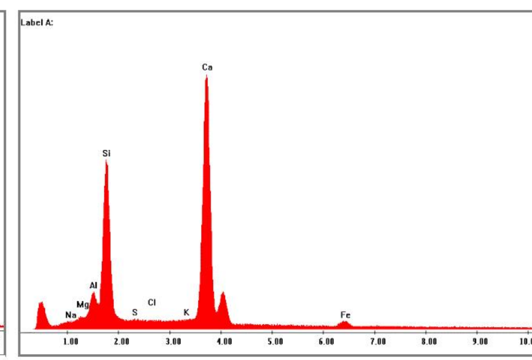


Fig. 57 Campione CPIZ-4, analisi EDS del punto [2]. Maggiore concentrazione calcica nelle aree più chiare.

THANK YOU FOR YOUR ATTENTION!