Natural and Roman cements of the 19th and early 20th centuries: an early industrial binder of world-wide use



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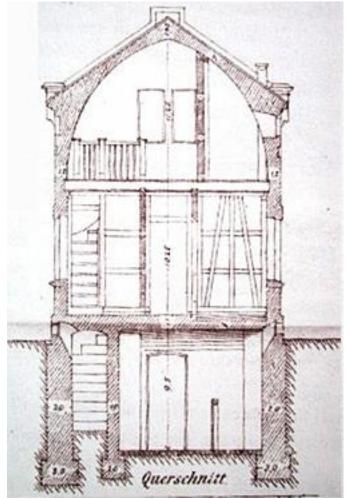
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tunnel and sewage construction



concrete construction







Cast stones for construction





bedding and pointing





stone repair and restoration

Exterior renders and stuccoes























UK (Harwich around 1850)

RC architecture shapes large aereas of central european cities

AT (Vienna 1870-1910)





CZ (Prague 1870-1910)





FR (Grenoble 1879)





SP (Barcelona 1882 - recent)

Unique features of "Natural Cements"

Calcined from **natural marlstone** (carbonate + clay in fine-grained intimate mixture; minor constituents: quartz, feldspar, pyrite, ...)

Variety of brands of differing composition and properties

Low temperature of calcination below sintering (ca. 900 °C)



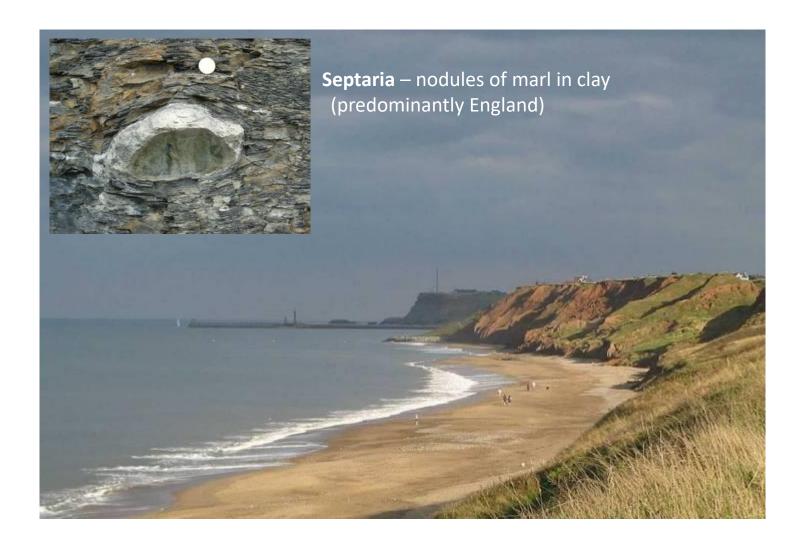
Formation of "clinker" with highly reactive and many unreactive phases Quick set and early strength, slow further strength development

(virtually) no free lime



Purely hydraulic, no slaking just grinding

Sources of raw material



Sources of raw material

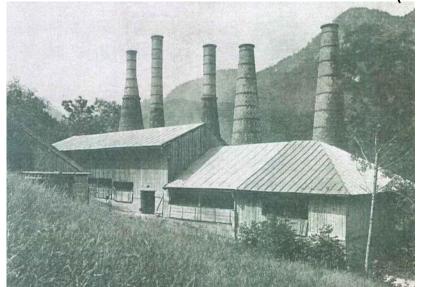
Historic (Austria)



Recent (Catalonia)

Shaft kilns





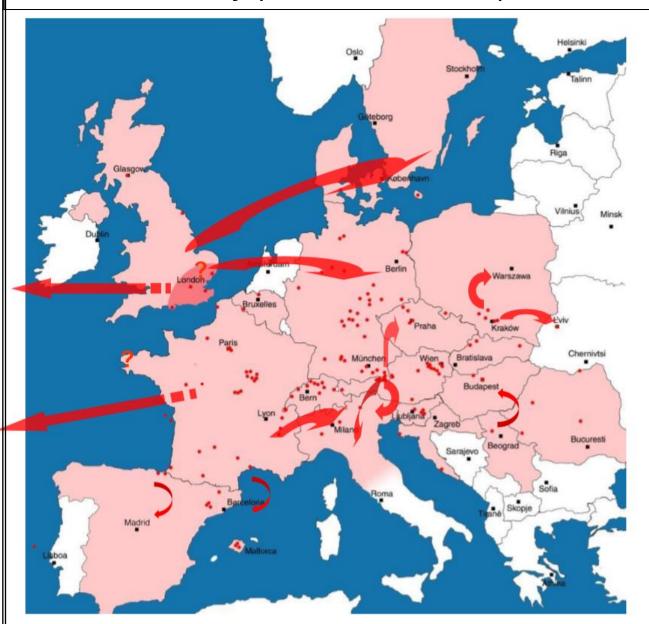






Recent (Catalonia)

Historic centers of production in Europe



Notes on history

1796: patented by James Parker (England) as "Parker's or Roman cement"

1st half of 19th century: eventually exported to continental Europe and the USA. Small centers of production in France and Southern Germany

2nd half of 19th century: boom of NC-production and use in most European countries

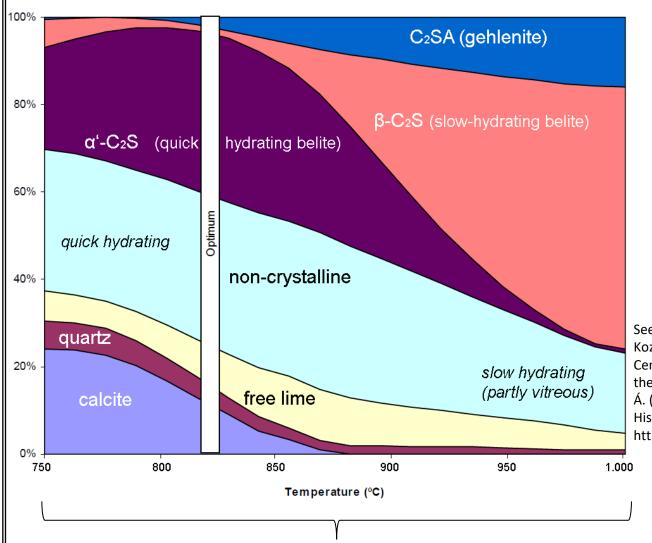
Around WWI: quick decline of NC in favour of PC-binders, only local centers especially in northern Spain (Catalonia)

Late 20th century until recent: only few producers and restricted size of market, but increasingly in the focus of architectural heritage sectors

Technical properties of NC versus PC and NHL

		Portland cement	Natural ("Roman") Cement	Natural Hydraulic Lime
Source of	modern	artificial mixture limestone + clay	natural mixture of carbonate + clay (marlstone)	
raw feed	historical	sometimes: sandy marlstone		
Type of raw feed		pellets or similar	fist-sized stones	?
Usual type of kiln	modern	rotary kiln	shaft kiln	
	historical	Shaft kiln -> rotary kiln		
Peak temperature		approx. 1.450 °C	approx. 900 °C (max. 1.200 °C)	
Melt formation		yes	no (only exceptionally small amounts)	
Cooling		quick	slow	
Products of calcination	reactive phases	C ₃ S, C ₂ S, C ₃ A, C ₄ AF	non-cryst. C/A/S, α'/β-C ₂ S	CaO, C ₂ S, non-cryst.?
	non-reactive phases	none	CS, C ₃ S ₂ , C ₂ AS, etc.	?
Factory processing	Additives	gypsum/anhydrite	none	
	slaking	-	-	+
	grinding	+	+	-/+
Products of hydration	early hydration	CSH (from C ₃ S)	AFm, AFt, C-S-H (from α' -C $_2$ S)	? -
	final hydration	CSH (from C ₂ S)	C-A-S-H (from β-C ₂ S)	Ca(OH) ₂ , C-A-S-H
Set		intermediate	rapid	slow
Early strength		dependant on PC-type	rel. high	low
Final strength	achieved at age	28 d	≥1 y	?
	MPa	40 100	15 50	3 10
Colour		grey (white)	ochre to reddish	light ochre
Capillarity		low	high	very high

Mineral composition of natural cement in dependence of temperature of calcination

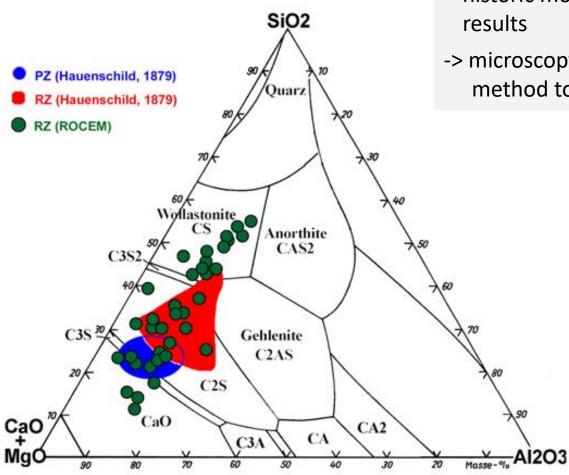


See also:

Kozłowski R., Hughes D., Weber J. (2010) Roman Cements: Key Materials of the Built Heritage of the 19th Century. In: Dan M.B., Přikryl R., Török Á. (eds) Materials, Technologies and Practice in Historic Heritage Structures. Springer, Dordrecht https://doi.org/10.1007/978-90-481-2684-2_14

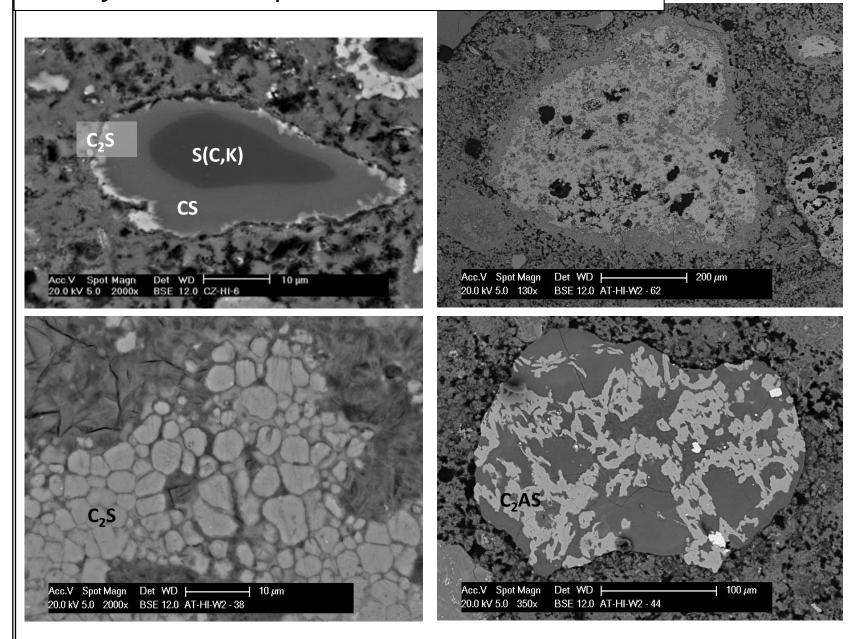
Range of temperatures in shaft kiln

Chemical composition

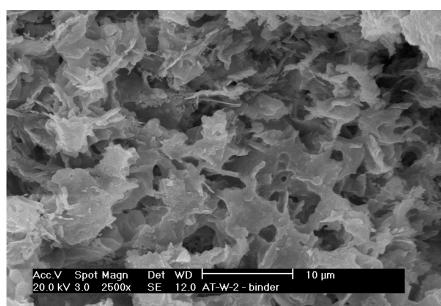


- Chemical composition is not indicative for natural cement
- Phase composition by XRD in historic mortars gives no clear results
- -> microscopy and SEM is the best method to identify NC

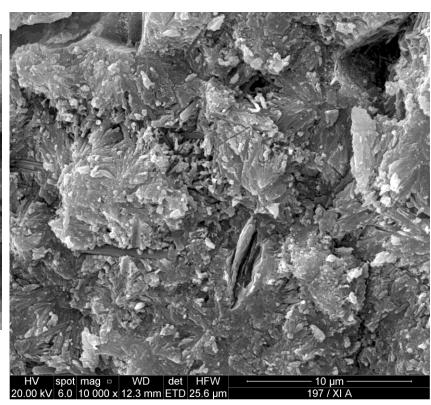
SEM of residual NC phases in historic mortar



Microstructure of cement matrix by SEM



(historic) Natural cement



(historic) Portland cement

Existing standards and products

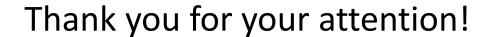
Current products and standards

No single approach to specifying each cement, national standards are not fully consistent

- NF P15-314:1993 Liants hydrauliques: Ciment prompt naturel. AFNOR, Paris
- UNE 80309:2006 Cementos naturales: Definiciones, classificacion y especificaciones de los cementosnaturales. AENOR, Madri
- D. Hughes et al., ROCARE Standard for the classification of Roman cements (draft based on EN 196-1 to adjust for the rapid set and the high water demand of typical Roman cements)

A small number of producers:

- Prompt (Vicat, France)
- Tigre Rapido (Cemento Natural Tigre, Spain)
- Marfil (Cementos Collet, Spain)
- Cemento Rapido Figueres (Ciments Figueres S.A., Spain)
- Cemento Mallorquin (Sa Cimentara, Spain)
- Folwark (Institute of Ceramics and Building Materials, Poland)



In case of questions, please contact me at johannes.weber@uni-ak.ac.at