From marlstone to rotary kilns – the early development of Portland cements in Central Europe

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Abstract

Based on the optical and electron microscopic investigations of Portland cement structures from nine Central European historic objects built between the 1860s and 1908, the present paper discusses the phase composition, microstructural properties of unhydrated residues and hydrated cement phases as well as fingerprints of the main milestones of the development of early Portland cement production. The early cements of the 1860s were characterized by their coarse grain size and very heterogeneous composition containing, besides C_3S, C_2S, C_3A and ferrite, a wide range of under and over burned components. Although the Portland cements produced in the following decades were less heterogeneous, cement phases suggest the absence of accurate control of the raw mix and the use of different types of shaft kilns and ring kilns. Finally, Portland cements produced in the early 1900s show features characteristic of clinker burned in early rotary kilns. Despite the slight increase in cement fineness, analyses suggest that the evolution of milling technique could not keep up with the calcination technologies. The compositional differences of hydration products between the samples produced in different periods were mostly due to the addition of calcium sulfate which presumably started in the last decades of the 19th century.

Introduction

The history of modern hydraulic binders started with the invention of natural hydraulic lime, NHL (1756) which was followed by James Parker´s Roman cement (RC) in 1796 [1]. Realizing the advantages of cementitious binders, the early 19th century was characterized by intensive experiments, especially in England and France, to achieve hydraulic binders with enhanced properties. In 1824 the product name Portland cement (PC) was introduced by Joseph Aspdin. Nevertheless, this so-called "proto PC" showed more similarities with Smeaton´s NHL than those of PCs produced in the second half of the 19th century [1]. Two decades later, in 1844 William Aspdin and Isaac Johnson succeeded in burning cement

clinker above the sintering temperature (i.e. >1300°C) for the first time [1]. Nevertheless, the PCs of the second half of the 19th century were characterized by very inhomogeneous mineral compositions. Despite the technological progress the cement heterogeneity was a consequence of a simple shaft kiln technology and the lack of exact adjustment of the raw materials. Especially in the Alpine regions (i.e. South Germany, Austria and Switzerland), but also in Hungary a few cement plants used the local natural rocks (i.e. marlstone, clayey limestone) to produce, similarly to RC, so-called natural PC [2], [3], [4], [5]. Consequently, the PCs of the "early years" (i.e. 1850 to 1900) frequently had variable qualities and achieved lower strengths compared to their 20th century followers [1]. The establishment and evolution of European cement plants strongly depended on the economical development of the countries. In the early years (i.e. 1850s) English PC was exported to the western part of the Continent, but shortly after (1855) the first German PC plants started also supplying their products [6]. One year later Austria (i.e. the Austro-Hungarian Empire) also launched its first PC plant in Kirchbichl, Tyrol [7]. In the following decades Germany and Austria were the two biggest PC producers in Central Europe. These countries not only dominated the market, but also hindered the development of the cement industry in the surrounding territories, particularly in Switzerland (establishment of the first PC plant in 1871, [8] and Hungary (establishment of the first PC plant in 1878 [4]). The 1880-90s were characterized by the abrupt growth of cement plants and technological investments especially in the Austro-Hungarian Empire and Germany. In this period three main type of kilns existed; discontinuous and continuous shaft kilns [7] and ring kilns (in Germany since 1864 [9]). The most important technological development of PC production took place around the turn of the 20th century with the adoption of rotary kilns [1] followed by the development of clinker coolers. Germany was among the first countries that started operating rotary kilns (1899 [10]). Some years later also Switzerland (1904), Hungary (1904) and Austria (1906) [4], [7], [8] introduced the rotary kiln technology. However, it has to be mentioned that the dissemination of rotary kilns took slowly place and even in the first decade of the 20th century the lion's share of the Central European PCs was produced in continuous and automatic shaft kilns as well as in ring kilns [4], [10], [11].

Although ball mills were already in operation in the second half of the 19th century, the milling technology was mainly restricted to the use of edge mills. The wider dissemination of ball mills can be dated back to the early 20th century. Table 1 summarizes the most significant development in PC production in the countries of this study.

Presently, there is an increasing interest and importance in investigating historical PC-based construction materials due to their use in a large number of heritage buildings. The insight into the material characteristics of PC-based historic objects supports the understanding of early cement production techniques and the often good to excellent performance of these materials after more than a century. Consequently, the information obtained may contribute to gain more data for conservation, preservation and maintenance of PC-based historic structures. The present study attempts to outline the main characteristics of early PCs based

on the investigation of concretes, artificial stones and mortars originated from the former Austro-Hungarian Empire, Germany and Switzerland between the 1860s and 1908.

Table 1. Milestones in the development of PC production in Austria, Hungary, Germany and Switzerland between the late 1850s and early 1900s

Age	Austria	Hungary	Germany/ S-Germany	Switzerland
1850-60	1856: start of (natural) PC production in Kirchbichl, Tyrol	-	1855: start of (artificial) PC production in Stettin (today in PL)	-
	Kiln technology: shaft kilns			
1860-80	Establishment of approx. 25 cement plants all-over Austria	1878: start of (artificial) PC production in Lábatlan	*1864-1883: production of natural PC in Blautal (S-Germany)* 1864: introduction of ring kilns 1878: first German standard to test PC	1871: start of (artificial) PC production in Luterbach/ Soleure; until 1880 four cement plants in CH
	Kiln technology: shaft kilns, continuous shaft kilns and ring kilns Milling technology: edge mills and double pendulum rapid mills with built-in sieves, ancillary ball mills			
1880-1900	1888: Austrian standard to test PC 1894: Association of Austrian Cement Producers		1899: first commercial use of a rotary kiln in Niedersachsen	1880: creation of the Federal Laboratory of Materials Testing (EMPA)
	1890s: beginning of the use of calcium sulfate as a retarding agent?			
1900->	1906: first rotary Kiln (Mannersdorf)	1903: auto-matic shaft kiln (Beocsin) 1904: first rotary Kiln (Lábatlan) 1912: introduction of ball mill technology	*1929: introduction of first rotary kilns in Blautal, S-Germany*	1904: start of (artificial) PC production; first rotary kiln
	Spread and development of rotary kilns, clinker coolers and ball mills			

Sampling and analytical methods

A total of 20 samples from 9 objects (Table 2) constructed in Austria, Hungary, Germany and Switzerland between the 1860s and 1908 were taken and analyzed by optical and electron microscopy. To assure the originality of the materials historical sources have been

thoroughly investigated prior to sampling. Samples were embedded in epoxy resin and thin sections of standard 30 μm thickness as well as polished sections were prepared. Thin sections were analyzed in the optical microscope (Zeiss AXIOScope A1) using transmitted plain (PPL) and cross-polarized (XPL) in order to determine the mineral composition of the unhydrated cement residues and secondary phases in the binders. Prior to analysis polished sections were etched with Nital (1.5 ml of HNO_3 in 100 ml of isopropyl alcohol for 6 to 8 seconds), and the residue of the etchant was removed by ethanol [12] in order to highlight unhydrated cement grains and their microstructure by reflected light (RL) in the optical microscope. The distribution of the average and maximal grain sizes of residual cement was estimated in the optical microscope by the counting and measuring of 50 to 80 single grains in each sample. The etched surface was then re-polished and coated with carbon to be analyzed by scanning electron microscope (Zeiss EVO15, acceleration voltage 15kV) coupled with an energy dispersive X-ray spectrometer (Oxford DryCool). A large number of analysis points and atomic ratio plots were used to characterize unhydrated residual cement grains and hydration products. Cement chemistry notation is used throughout this document with the following abbreviations: $A=Al_2O_3$, $C=CaO$, $F=Fe_2O_3$, $H=H_2O$ $S=SiO_2$ and $\$=SO_3$.

Table 2. Samples of the study

Sample	Object	Year	Sample	Analyses
G-1860s	Cathedral of Freiburg, Germany	1860s(?)	joint mortar	cement residues
A-1869	Collegiate church Admont, Austria	1869-70	mortar, artifical stone	cement residues, hydration products
G-1879	Federal Fortress Ulm, Germany	1879	joint mortar	cement residues, hydration products
A-1893	Collegiate church, Weißenbach/Triesting, Austria	1891-93	artifical stone	cement residues, hydration products
A-1899	House Anderhalden, Bregenz, Austria	1899	cement mortar	cement residues
CH-1900	Aventicum (archaeological site), Switzerland	1897-1900	cement restoriartion mortar	cement residues, hydration products
A-1903	Former slaughterhouse, Vienna 11th distr., Austria	1903	artificial stone, mortar	cement residues
A-1907	Depot, Vienna 20th distr., Austria	1907	artificial stone	cement residues
H-1908	Budapest University of Technology and Economics, Budapest, Hungary	1906-08	concrete, cement mortar	cement residues, hydration products

Results

Composition and evolution of cement clinker

Historical PCs are characterized by large amounts of coarse residual cement grains [12], [13]. Their evaluation (Figure 1) indicates a slight decrease of the average grain sizes, however in the cements of the early 20th century oversize particles of up to 1 mm were also detected. Further characteristic of early PCs, which can be attributed to the development of kiln technology, is that the cements became more homogenous in their mineralogical composition. The following section discusses the above properties in detail.
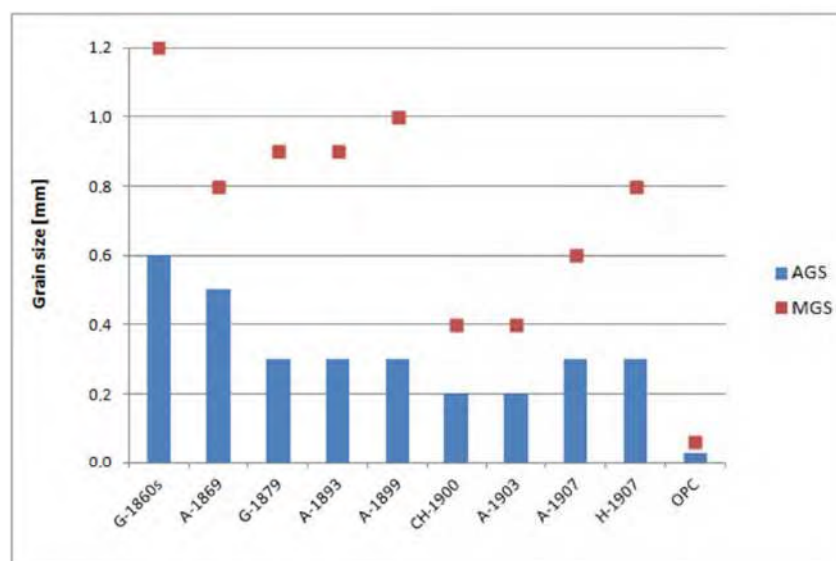

Figure 1. Distribution of average (AGS) and maximum (MGS) grain sizes of residual cement grains in the samples compared to that of modern Ordinary Portland cement (OPC)

Samples from the 1860s to the early 1870s

The cements of "early ages" (samples G-1860s and A-1869) are characterized by very coarse (Figure 1) and mineralogical very heterogeneous materials. Although all four PC clinker minerals (i.e. C_3S, C_2S, C_3A and ferrite) are present, C_2S dominates over C_3S and their crystal sizes, shape and inner structure indicate not only inhomogeneous firing (i.e. presumable temperature differences of up to 700°C within one batch and existence of hot spots >1400°C) and slow cooling conditions, but also heterogeneous raw materials in terms of composition and grain size distribution [5]. The combination of these factors resulted not only in the above described properties of the PC clinker minerals, but also in the formation of mineral phases atypical for modern PCs [13], [14], [15], on the other hand frequently reported in historical RCs [16]. Glassy residues containing tabular gehlenite laths (C_2AS), wollastonite (CS), Ca-pyroxene and silica residues with rims of calcium diffusion and formation of calcium silicates, such as CS, C_3S_2 etc, are the most frequently detected phases formed in the low temperature regimes of the kiln [16].
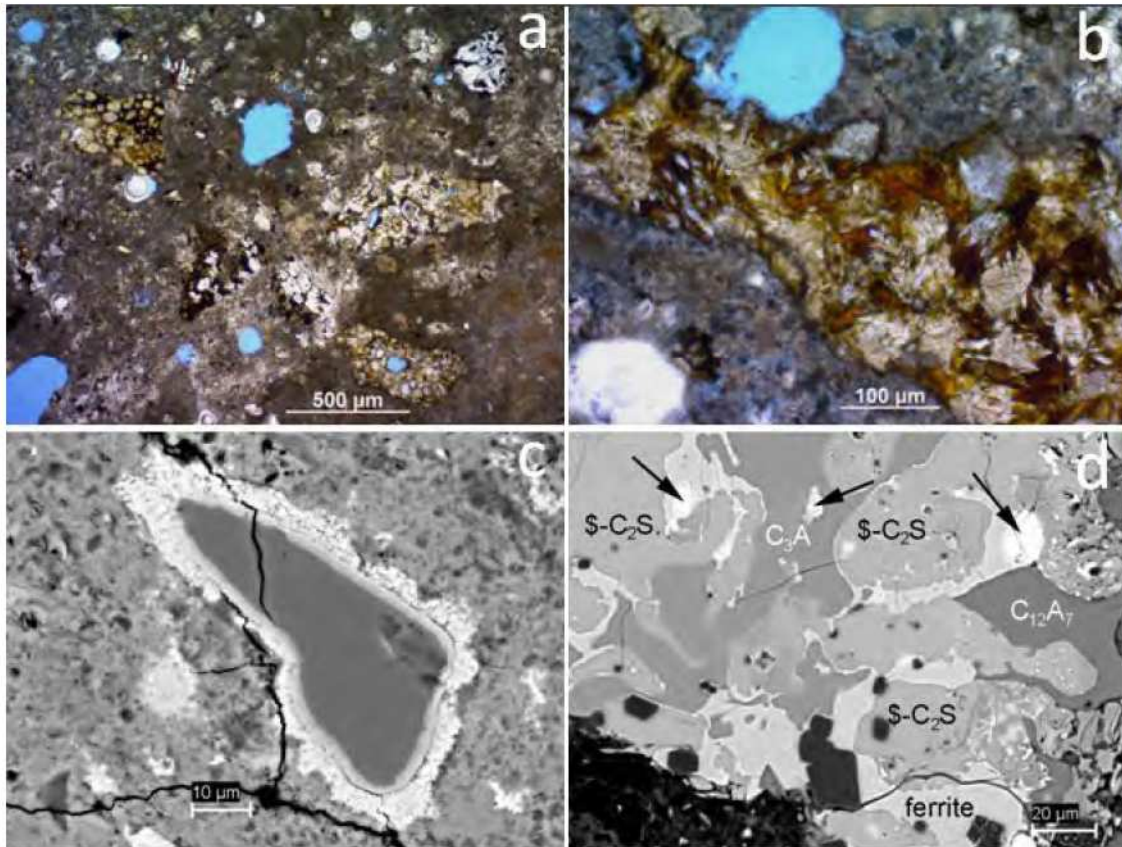
Figure 2 Typical residues in the samples from the 1860s; a: large unhydrous cement grains in a completely carbonated binder (G-1860s, PPL), b: large residue containing C_2S with finger-like extensions into brown ferrite (G-1860s, PPL), c: silica residue with traces of calcium diffusion (outer rim of C_2S; A-1869, SEM-BSD), d: heterogeneous residue containing different type of sulfur-bearing cement phases (CaS is indicated by arrows). Coarse crystal sizes indicate slow cooling rates (A-1869, SEM-BSD).

Flux phases typically form large crystals which are indicative for very slow cooling rates and besides C_3A also $C_{12}A_7$ can be found suggesting high amounts of alumina-rich phases (i.e. clay minerals and feldspars) in the raw material [5], [14]. The samples from Admont (A-1869) represent a specific type of PC produced from a natural marlstone source rock [5]. In this cement under burned particles similar to the characteristic cement lumps of RC [17] are indicative for the original source rock. The sulfate content of solid fuel (e.g. brown coal) or the raw material (i.e. pyrite in the marlstone) used for cement burning could also contribute to the formation of sulfur-bearing cement clinker phases [5]. Although they occur only in minor amounts, $-C_2S$ (sulfo-belite), C_5S_2, C_4A_3 and calcium sulfide in the samples A-1869 could have also a slight influence on the formation of hydration products (see below). Figure 2 shows some typical examples of cement clinker phases observed in the mortars from the 1860s.

Samples from 1879 to 1900

Despite a few inventions in the field of cement kiln technology (e.g. introduction of continuous shaft kiln, etc.) the examples from the second half and the late 19th century (G-1879, A-1893, A-1899, CH-1900) show many similarities (Figure 3) with that of early PCs of

the 1860s. The cements are ground coarsely; structures contain lots of unhydrated cement grains and components formed at lower temperature are still present along with the PC clinker phases. Furthermore, the features of C_2S and aluminate phases clearly indicate long residence time of burning, slow cooling rates and the presumable existence of hot spots in the shaft kilns. Nevertheless, some features, such as the slightly increased ratio of C_3S to C_2S, the decrease of the amount of low temperature phases and the slight decrease of cement grain sizes can be interpreted as fingerprints of the technological improvements of the late 19th century [13], [18], [19].
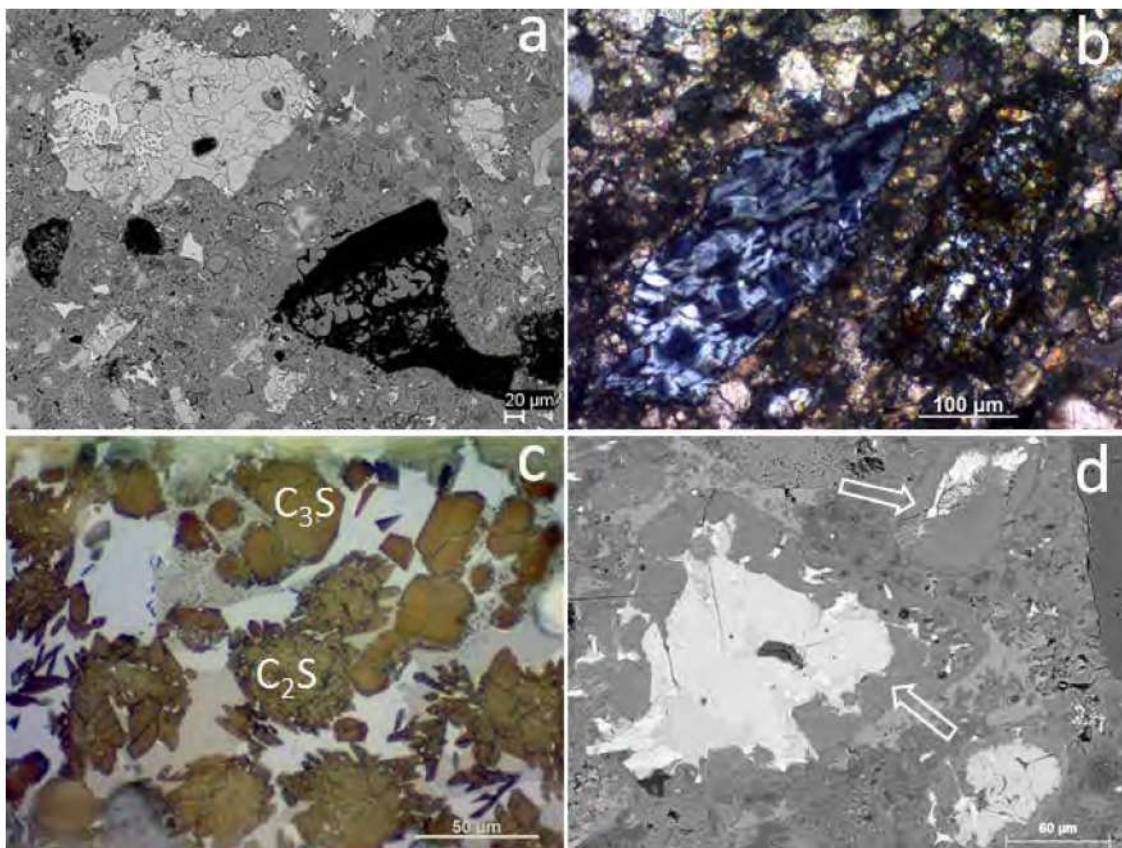

Figure 3 Typical residues in the samples between 1879 and 1900; a: unhydrous cement grains (top left) and brow coal residue from the fuel (black, G-1879, SEM-BSD), b: large residue containing tabular C_2AS in a glassy matrix (left) and anhydrous cement (right; A-1893, XPL), c: cement residue with coarse aluminate (grey) and ferrite (white), C_3S (brown angular grains) and dismembered C_2S indicating slow cooling (A-1899, RL, Nital etch), d: cement grains exhibiting thick hydration rims (arrows, CH-1900, SEM-BSD).

Samples from 1900 to 1908

The above described trends can also be followed in the samples of the early 20th century (A-1903, A-1907 and H-1907, Figure 4); C_3S dominates over C_2S, under burned, low temperature components are rare or, in some cases, completely missing. Nevertheless, due to the co-existence of different kiln technologies, differences can also be found between PC-based

structures of this period. This is well-visible when comparing the cement mortars of two Viennese objects constructed in 1903 (A-1903) and 1907 (A-1907).
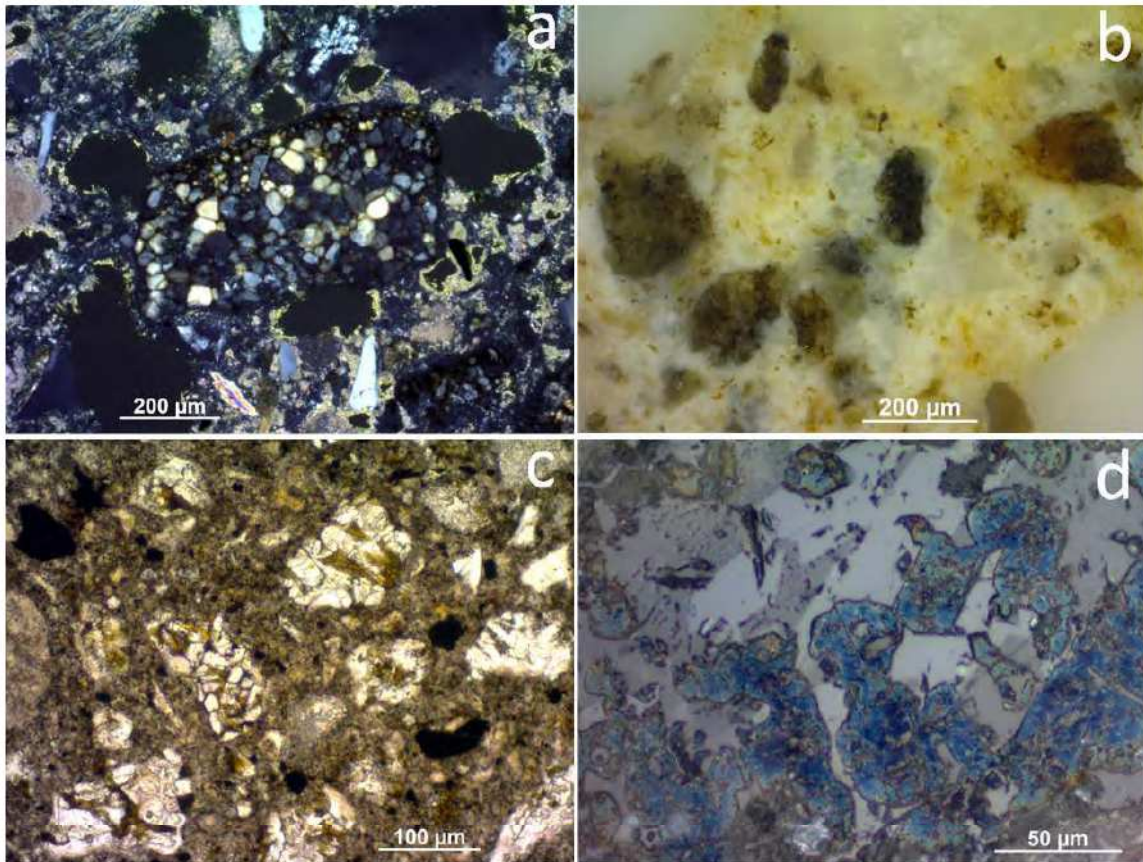

Figure 4 Typical residues in the samples between 1900 and 1908; a: large unhydrous cement grain consisting predominantly of C_2S with few C_3S crystals (A-1903, XPL), b: unhydrated cement grains in sample A-1907 matrix (IL/DF), c: cement residues in a terrazzo sample (H-1908, PPL), d: cement residue with coarse aluminate (grey), prismatic ferrite (white) and partially hydrated C_3S and C_2S (blue; H-1908, RL, Nital etch).

While the older cements clearly bear the properties of a heterogeneous product burned most probably in a shaft kiln, the different appearance of the residual cement grains of the other sample indicates a homogenous firing technique suggesting that the cement was probably calcined in an early rotary kiln (1906: first rotary kiln in Austria). In addition, finer prismatic interstitial aluminate and ferrite phases also indicate faster cooling rates compared to the slowly-cooled PC products of the 19th century and suggest the use of early clinker coolers [20]. Furthermore, residues of solid fuel are also missing in these later samples. However, despite the progress in kiln technology certain parameters also indicate the differences between the PCs of the early 20th and modern OPC. First, based on the crystal grain sizes of the flux phases it is assumed that the cements were cooled by using a simple clinker cooler (e.g. rotary or vertical drum cooler [21]). Although there is only very sporadic information available about the development of clinker coolers, the quenching of clinker, typical for modern OPC, can certainly be excluded. Secondly, cement fineness was comparable to that of the late 19th century products assuming that the grinding technology could not keep up with the calcinations technologies. Consequently, both properties are not

only indicative for the early PCs of the 20th century, but they could also significantly affect the hydration and strength development of mortars and concrete.

Properties and development of hydrate phases

While most historical PC structures contain high amounts of unhydrated residues allowing the extensive analysis of the original cement, the hydrate matrix frequently bears the imprints of secondary processes such as carbonation or infiltration of sulfate. Therefore, and also because of the often restricted sampling possibilities, only a few samples containing uncarbonated binder portions could be analyzed. Based on extensive SEM-EDX measurements on hydrate phases of mortar and concrete samples from five objects (see Table 2) significant differences could be detected between the cements produced around the late 1860s and that of after the 1880s.
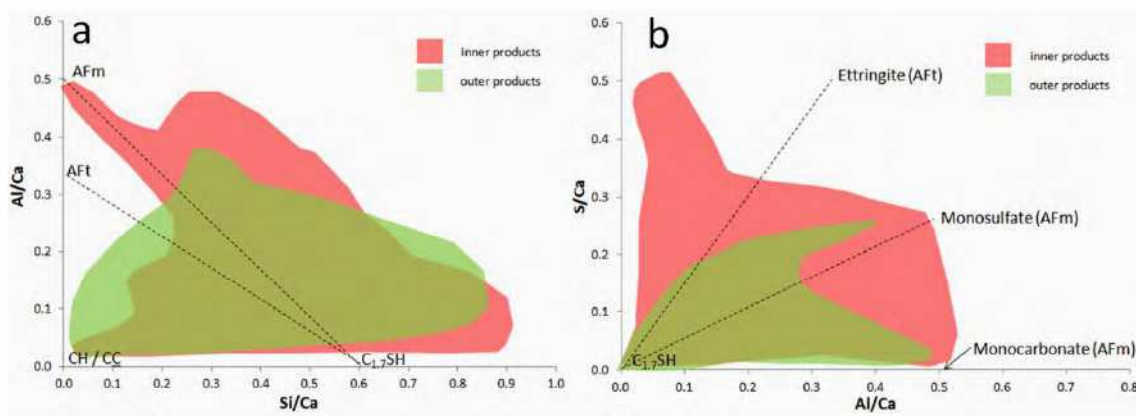

Figure 5 Atomic ratio plots showing the distribution of hydrate phases formed in the inner (red) and outer (green) products (sample A-1869; for explanation see text).

The hydrates phases in the mortars made out of natural PC from Admont, Austria (A-1869) exhibit heterogeneous appearance and a high microporosity. Similarly to OPC, some dense inner products are predominantly related to the hydration of grains rich in C_3S. The outer hydration products form a mixture of compact clusters and platy AFm phases. Figure 5 shows the distribution of the atomic ratios of the inner products (hydrate phases formed at the surface of the larger cement grains) and outer hydration products (hydrate phases formed in the water-filled space) [22]. The composition of the inner products partly overlaps with that of the outer products and the data are very scattered and make the exact intermixing difficult to identify. The inner products are composed of a mixture of C-S-H and AFm (monosulfoaluminate and monocarboaluminate), in which AFt (ettringite) is detected in insubstantial amounts [5]. The outer products contain less sulfo-AFm/AFt than the inner products, contrary to the usual observations made on modern OPC [22].

On the contrary, the distribution pattern of hydration products (Figure 6) of the samples from Germany (1879) and the period of the last decade of the 19th until the early 20th

century show very similar patterns to that of modern OPC. Well-developed inner hydration products are predominantly connected to C_3S in the samples and composed of C-S-H and partly CH. Depending on the existence or lack of secondary processes (i.e. carbonation and/or sulfate ingress) outer products are either composed of a mixture of C-S-H, AFm phases (monosulfoaluminate and/or monocarboaluminate) or AFt (ettringite). If the dominating AFm phase is monocarboaluminate and also ettringite appears, the sulfo-AFm was decomposed and converted into AFt due to subsequent carbonation and/or infiltration of excess sulfate [23].
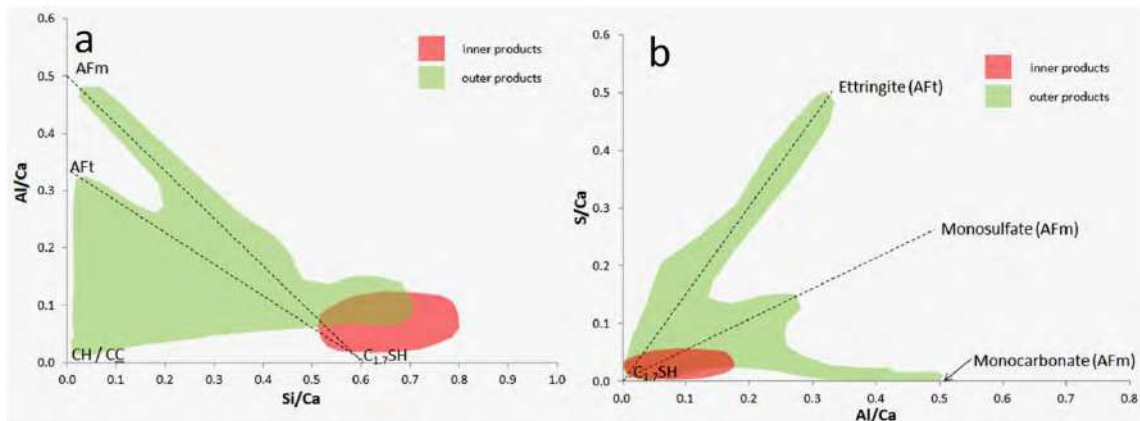

Figure 6 Atomic ratio plots showing the distribution of hydrate phases formed in the inner (red) and outer (green) products (data based on samples G-1879, A-1899 and H-1908; for explanation see text).

On the other hand, the dominance of monosulfoaluminate and the limited amount of ettringite suggest either that the hydrate matrix did not undergo any severe transformation or the amount of sulfate-bearing phases in the cement was low [22].

The main difference between the hydrate phases of the natural PC samples and those from the turn of the century can be found in the distribution of sulfate-bearing components. While sulfo-AFm and AFt concentrate in the outer products in the younger cements and show a similar distribution pattern to that of modern OPC [19], [22] in the older cements monosulfoaluminate and ettringite are predominantly found in the inner hydration products [5]. The later distribution pattern suggests that in the early stage of hydration the amount of sulfate ions was limited in the system which indicates the lack of calcium sulfate as a retarding agent. In practice, the setting time was probably regulated in the "early ages" by a technique described in historical sources [2]; before milling the clinker was stored in a hut for several days, where atmospheric humidity reacted and deactivated to some extent the reactive aluminate phases responsible for prompt setting (i.e. C_3A and probably also amorphous aluminates). The concentration of sulfate-bearing phases in the inner hydration products can be attributed to the dissolution of sulfur-rich cement clinker phases in the later stages of hydration [5]. On the contrary, the enrichment of sulfo-AFm and/or AFt in the outer products detected in German cements from the late 1870s and the samples produced since the 1890s shows a very similar distribution pattern to modern OPC and thus the appearance of calcium sulfate as a retarding agent can be suggested. Around 1880 the

Association of German Cement Plants defined the use of by-mixed calcium sulfate in PC [24], followed by the Association of Austrian Cement Plants in the late 1880s which also allowed the use of a maximum gypsum content of 2% as retarding agent [11]. Nevertheless, it has to be mentioned that many Central European cement producers advertised their products even in the early 1900s as being free of gypsum and thus offering a pure cement binder free of any "contamination" [4]. Furthermore, sulfur content in the fuel (brown coal, coke) could also influence the amount of sulfate in the cements and thus the formation of hydrate phases. Therefore, the use of calcium sulfate as a retarding agent is presumable, but its overall use cannot be verified for that period.

Conclusions

The comprehensive investigation of 20 samples from 9 objects constructed in Central Europe between the 1860s and the early 1900s enabled to get insights into material characteristics, production techniques and hydration mechanisms of historical PCs. Due to the limited amount of examples our study is not intended to completely reconstruct the development of PC in this period, nevertheless results correlate with known technological improvements and in some cases also provided new insights into the characteristics of early PCs. Based on our research following statements can be made:

- large amount of coarse unhydrated cement residues is one of the typical features of early PCs allowing their unambiguous identification, characterization and differentiation from modern PC products;

- there is a slight, but traceable decrease in the average particle size distribution of the cements in the decades following the onset of PC production. However, the maximum grain sizes vary within a wide range and residual cements up to 0.9 mm in diameter were observed even in the youngest binders;

- the comparatively slow increase of cement fineness leads to the assumption that the development of grinding technology could not keep up with the new calcination technologies;

- the oldest cements (1860s) exhibit extremely inhomogeneous compositions which indicates a very heterogeneous heat distribution, long burning and slow cooling rates, typical for (early) shaft kilns. Residues of organic matter are suggestive for the use of solid fuels (e.g. brown coal);

- cements produced between the 1870s and 1890s were still heterogeneous and comparable to those produced some decades earlier, however, they were also slightly finer and the amount of under burned particles decreased as well. Yet all cements of the study originated from this period were produced in shaft kilns;

- cements burned around and shortly after the turn of the century show either similarities with their precursors suggesting that they were calcined in shaft kilns, or they exhibit the features similar to OPC. Later samples suggest the use of early rotary kilns, nevertheless cement residues still indicate relatively slow cooling rates and a less advanced grinding technique;

- the cement hydration products in the samples from the 1860s are characterized by outer products poor in sulfo-AFm and/or AFt suggesting that during the early-age hydration no or only very limited amount of sulfate was available. Therefore, the use of calcium sulfate as a retarding agent can be excluded;

- on the contrary, samples from the turn of the century suggest the application of calcium sulfate as a setting retarder. Therefore, the hydration process was very similar to that of modern OPC even though many of the investigated examples were burned in shaft kilns;

- the results suggest that the introduction of calcium sulfate as a setting retarder took place ten to twenty years before the spread of the rotary kilns indicating that many of the PCs produced in shaft kilns were probably deactivated by gypsum. Nevertheless, its overall use in PCs around the turn of the century cannot be verified;

- many of the objects and cement structures were in good to excellent state of preservation after more than 100 to 140 years of exposure and service life indicating the durability of the cements produced that time. Although not all aspects of this behavior are clearly explainable so far, the grain size distribution of the cements could have a significant impact on the fresh mortar properties (i.e. control of w/c ratio and workability, etc.), the development of macro- and microporosity and thus the durability of the structures.

Acknowledgements

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