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The origin, composition and early age hydration mechanisms of Austrian natural Portland cement

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ABSTRACT

The chemical and mineralogical properties of cement residues and hydration products have been assessed in historical Portland cement mortars. Results indicate a long time of burning and residence and a slow cooling rate. C_2AS, CS and under burned raw material residues suggest inhomogeneous heat distribution typical for shaft kilns. Additionally, minor amounts of $\$\text{-}C_2S$, $C_5S_2\$$, $C_4A_3\$$ and CaS refer to the burning of a pyrite-bearing marlstone and a brown coal used as a solid fuel. Monosulfoaluminate intermixed with monocarboaluminate predominantly concentrate in the inner hydration products confirming the absence of interground calcium sulfate as a retarding agent. The distribution of AFm phases suggests the dissolution of sulfur from the sulfur-bearing cement residues and subsequent carbonation in the later stage of hydration. The coarse grain size of the cement and the presumable application of a historical deactivation method resulted in the formation of high microporosity.

1. Introduction

The evolution of calcareous hydraulic binders during the course of the 19th century was a consequence of numerous experiments and developments carried out starting in the 1750s [1,2]. These efforts achieved not only the production of watertight binders, but also materials exhibiting higher strength compared to traditional hydraulic mortars based on pozzolanic lime [1]. The first products of these trials were Natural Hydraulic Lime (NHL, 1756) and Roman cement (RC, 1796), which can be considered as the direct precursors of early Portland cements [3,4]. The continuous development of Portland cement (PC) started in the 1840s with William Aspdin's and especially Isaac Johnson's awareness of the importance of sufficiently high temperature during calcination [1,2]. These early, or also called, meso-PCs [1,2] represented heterogeneous materials containing calcium silicate products formed around or slightly above the temperature of sintering, but also phases formed in lower temperature regimes very similar to those found in NHL or RCs [3,5].

Later in the 1870–80s the implementation of continuous shaft kilns, an important factor in the technological development of PC along with the adoption of early standards, led to an increase of quality and quantity of PC production [1–3]. At the turn of the 20th century the increasing requirements of the construction industry [3], along with the introduction of rotary kilns, ball mills and the use of calcium sulfate as a retarding agent, made PC the most widely used hydraulic binder and building material in the world.

While most European cement manufacturers produced their own early PCs by using artificially by-mixed raw materials (i.e. lime and clay), in Austria the first PC was produced by using a local marlstone as the single raw material at the Perlmoos cement plant in Kirchbichl near Kufstein, Tyrol in 1856 [6–8]. This “new cement” was accidentally discovered when residues of over burned clinker of the local RC plant were milled and applied as a mortar binder for a local construction site [7]. The awareness of the astonishingly good quality and much higher compressive strength of this binder compared to those of based on RC, led to further trials, the identification of the exact geological strata of the raw material and finally the beginning of the production of natural PC in Austria [7]. This natural meso-PC was produced similarly to RC: the coarsely crushed raw material containing calcium carbonate, silicate and aluminosilicate minerals in intimate mixture was calcined in vertical shaft kilns using the local brown coal as solid fuel [6,7]. Unlike RCs, however, the calcination temperature was higher and reached or exceed the heat of sintering (i.e. ~1300 °C), where free lime combines with C_2S to form C_3S. The exact mineralogical requirements for the production of good-quality cement meant that only restricted dissemination of natural PCs in Europe in the second half of the 1800s was possible. Based on historical data [6], only three Austrian cement plants and another one near the Black Sea produced natural PC on the

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Continent in the 19th century.

Currently environmental concerns related to cement production has encouraged studies of alternative binders, based on sustainable technology using local raw materials and moderate calcination processes. Beyond these environmental issues, there is a recent and increasing interest in investigating historic PC mortars and concretes due to their significant role in the civil engineering and architecture of the late 19th and the 20th century. Nevertheless, the literature [e.g. 9–17] remains rather sporadic on the mineralogical properties of these binders. Consequently, investigation into the material characteristics of historic objects made out of early PC supports the understanding of their often excellent performance after more than a century, which combined with the analysis of historic mortars and concrete may also contribute to the current development of alternative binders.

The present study deals with 19th century natural PC mortar samples applied at the neo-Gothic collegiate church of the Benedictine monastery of Admont, in Northern Styria, Austria. The original medieval church was reconstructed after a disastrous fire in 1865 [18]. The historical literature [18,19] as well as some unpublished original shipping documents from the former Perlmoos cement plant which produced natural PC in the 1860s and 70s [7], confirm that Perlmoos cement was used during the rebuilding of the church between 1866 and 1870. The study of the mortars was based on optical and electron microscopic techniques, in order to understand their production technology, hydration mechanisms and long-lasting performance.

2. Sampling and methods

Two cement mortars were selected from the building, dating to the reconstruction period in the late 1860s: a window ledge (ADM1) and a floral cast element (ADM2) at the northern façade. After a preliminary drying at 40 °C in a drying chamber, the samples were embedded in epoxy resin (Araldite 2020) to prepare thin sections and two series of polished sections. One series of polished sections was etched with Nital (1.5 ml of HNO_3 in 100 ml of isopropyl alcohol for approx. 7 s, and the residue of the etchant was removed by ethanol [5]). Samples were analyzed with the optical microscope (Zeiss AXIOScope A1) using reflected light (RL) for the etched polished sections and transmitted polarized light (TPL) for the thin sections, respectively. Non-etched polished sections were coated with carbon to be analyzed by scanning electron microscope (Philips Quanta 200, acceleration voltage 12 kV), coupled with an energy dispersive X-ray spectrometer (Bruker AXS Quantax). A large number of standardized analysis points and atomic ratio plots were used to characterize hydration products, residual cement grains and other binder-related phases in order to understand the burning conditions as well as the hydration process. The determination of cement minerals was carried out on the basis of the usual nomenclature used in the cement chemistry without the confirmation of exact crystalline polymorphs (e.g. by micro-diffraction techniques). The cement notation used throughout the document being: $A = Al_2O_3$, $C = CaO$, $\underline{C} = CO_3$, $F = Fe_2O_3$, $H = H_2O$, $M = MgO$, $S = SiO_2$, and $\$ = SO_3$. The binder-to-aggregate ratios and the amount of air voids have been estimated by using the SEM-BSD images.

3. Results

3.1. General macro- and microscopic features

Both samples exhibited a compact structure free of macro cracks and a generally very good state of preservation. A beige-brown discoloration of the surface and the matrix (Fig. 1) is a common feature of early PCs and corresponds to carbonated [17] and/or to oxidised binder areas. The moderately well sorted, angular to rounded aggregates, with a size range of 0.1 to 1.5 mm and 0.1 to 3 for the samples ADM1 and ADM2, respectively, are predominantly of carbonate nature with low amounts of silicate components (Fig. 2). These aggregates suggest the use of alluvial deposits connecting to the local sediments of the nearby Enns River. The estimated b/a ratios are approx. 1 to 2.5-3 in both mortars. Irregular water voids up to 2 mm diameter are common in ADM1 (Fig. 3), while approx. 4% of homogenously distributed

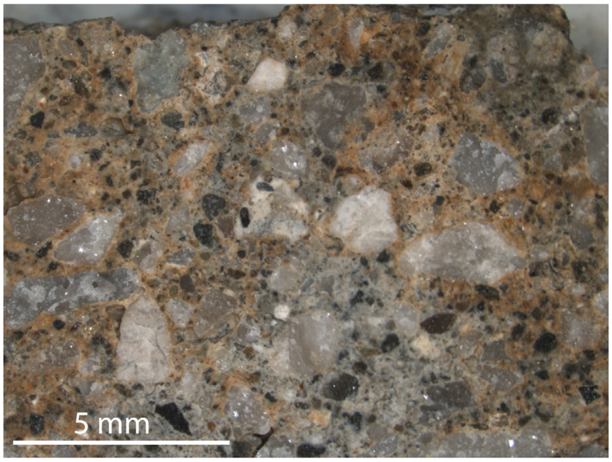

Fig. 1. Beige discoloration of the matrix on the broken surface (ADM2) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

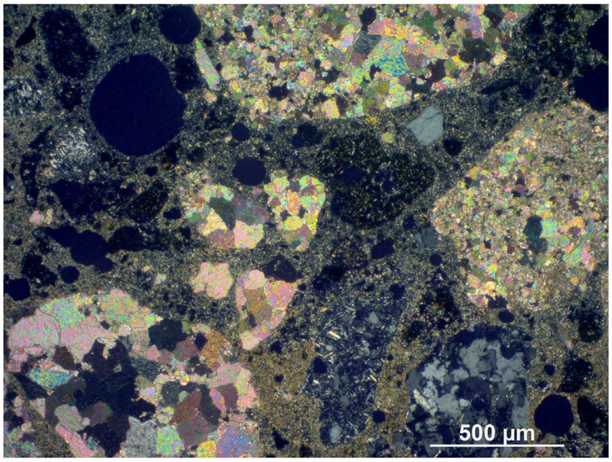

Fig. 2. Dolomite and polycrystalline quartz aggregates in the carbonated cement matrix (ADM1); TPL.

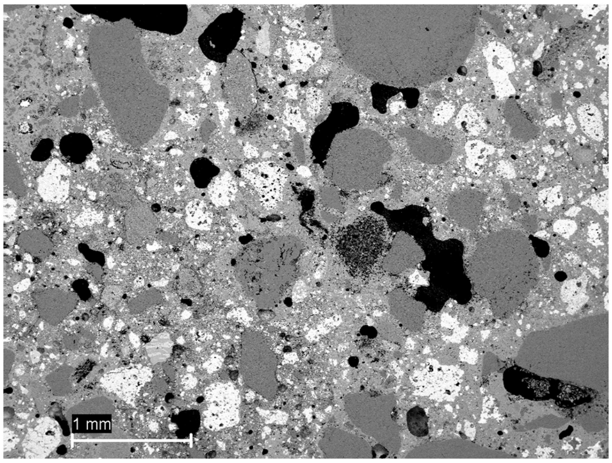

Fig. 3. Coarse residual cement (white) and irregularly shaped water voids (ADM1); SEM-BSD.