Examples of early age Portland cements applied in historical masonries

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Abstract: Early age Portland cements (EAPC) belong to the family of hydraulic binders developed from the middle of the 19th Century until the wide dissemination of rotary kilns and ball mills in the Portland cement production (around the 1910s). The article presents the applications of EAPC mortars used for joint, cast elements and wall-cover, in Switzerland (Aventicum Roman Theatre) and Austria (Collegiate church in Admont), covering a wide period of practice (1866-1900) in restoration and reconstruction projects. The good state of the samples suggest that this type of cement seemed particularly adapted to formulate both durable construction elements (Admont) and restoration mortars (Aventicum)

Introduction

Early Age Portland Cements (EAPC) can name the range of calcareous hydraulic binders developed from the mid-19th C. (W. Aspdin's and I.C. Johnson´s cements, sometimes called meso-Portland cement [1] produced in shaft kilns) until the 1910's when the cement quality was controlled, based on the knowledge of the cement chemistry and the grinding and calcination processes in rotary kilns, to achieve adapted compressive strength [1]. The use of EAPC in civil engineering and historical buildings restoration was concomitant with other binders such as the 19th C. Roman cements [2]. The present paper focusses on the mineralogy and the microstructure of different EAPC mortars used in the 1860's in Styria (reconstruction of the collegiate church in Admont) and later in Switzerland (vestiges conservation of the original Roman masonry at the Aventicum Roman Theatre, 1895-1900). The Roman Theatre of Aventicum (now Avenches) was built at the beginning of the 2th C. as a part of a vast architectural complex constituting the religious section of the Helvetic capital. Subsequently to a large campaign of archaeological and restoration works initiated from 1843, the reconstruction of some original walls was conducted in the period 1897-1900, to preserve the original South West *aditus* (lateral and partially covered main entrance). Although only few technical data were collected by the

architect E. Secretan in 1910 about the technology used for the earlier reconstruction, the current state of knowledge indicates that the vestiges of the original Roman walls were protected by a new layer of masonry using yellow limestone ashlars joined by cement mortars. The origin of the cement used is not clearly reported: *slow cement from St Sulpice or La Reuchenette, or from the plant of Nicolin* (being produced from the 1880's in the Swiss Jura), *or heavy lime [7] from Virieu or Beon* (French production). The present study deals with the mortars used in the period 1897-1900 and analyzed in the frame of a recent restoration campaign (2012-2013) [3].

The medieval collegiate church of the Benedictine monastery in Admont, Styria was reconstructed in neo-Gothic style after a disastrous fire in 1865 which almost destroyed the entire monastery [4]. The selection of the object for the research was largely supported by the historical literature [4,5], the original and unpublished shipping documents and the correspondence between the monastery and the Perlmooser cement plant in Kufstein, Tyrol, regarding the amount and quality of binders (mainly Portland cement) used for the construction. These historical documents clearly proved the former assumption, namely the use of EAPC during the reconstruction of the church between 1866 and 1870.

Sampling and analytical methods

Four different samples were studied using optical and electron microscopy, which are believed to be the only reliable methods to highlight the presence of EAPC in historic masonries and to assess their composition and their state of conservation. At the Aventicum Theatre, the study of the wall n°92 allowed two types of mortars to be analyzed; one sample of pointing mortar (AVE-1) used to join the limestone ashlars of the vertical protection wall and one sample of mortar (AVE-2) from the cover layer (10-12 cm thick) created to protect the surface of the protection wall and the underneath original Roman vestiges. From the abbey church of Admont two samples were analyzed; one from a window ledge (ADM-1) and a cast element at the northern façade (ADM-2). Fig. 1 illustrates the overview (situation and cut sections) of the four samples. Thin and cross sections prepared from the samples were etched with Nital (1.5 ml of HNO_3 in 100 ml of isopropyl alcohol [6] for app. 8 seconds and analyzed with Optical Microscope (Zeiss AXIOScope A1) using reflected and transmitted polarized light.

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[7] "chaux lourde" (In Fench) understood as an intermediate range between hydraulic lime and roman cement, according to the definition of Candlot in Chaux hydrauliques et Ciments 2nd ed., 1898
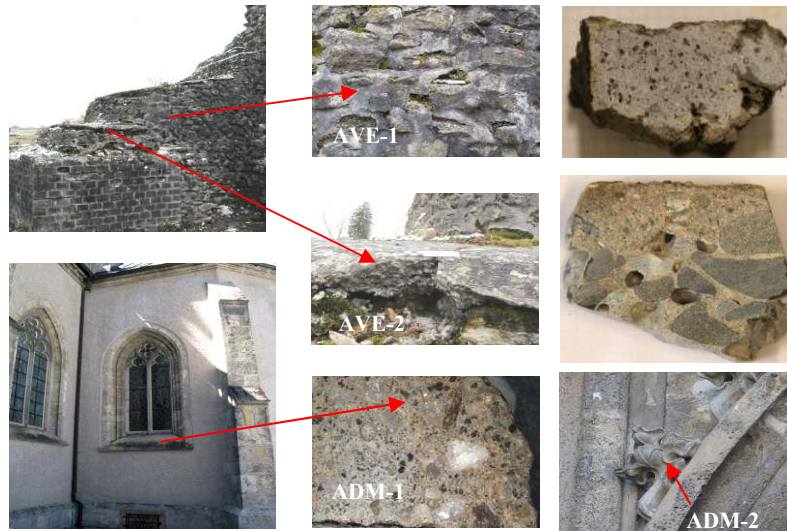
Fig. 1 View (situation and cut section) of the Aventicum (top) and the Admont (below) samples

Non-etched polished sections were coated with carbon and analyzed by Scanning Electron Microscope (Philips Quanta 200), coupled with an Energy Dispersive X-ray Spectrometer (Bruker AXS Quantax). Large number of standardized analysis points and atomic ratio plots were used to identfy the composition of the different phases.

Results and discussion

General macro- and microscopic features of the samples

The AVE-1 sample shows a grey and dense structure with an even distribution of aggregates (round, 5 mm size, mainly siliceous limestone and quartz) within the cement paste. A beige coloration layer (2-3 mm thick), observed at the external sub-surface (Fig. 1), is attributed to the superficial carbonation of the hydrated phases (as confirmed by the limited depth of carbonation from the phenolphtalein test). Numerous micropores resulting from the fresh mortar casting are evenly distributed in the sample. The AVE-2 mortar is likely a micro-concrete structure with coarse aggregates (round, up to 15 mm size, mainly siliceous limestone and quartz) unevenly covered by a grey cement paste. As for the AVE-1 sample, a thin layer of coloration is observed at the external sub-surface. Similarly to the Aventicum samples, the Admont mortars also exhibit a compact structure with beige discoloration of their matrix referring to carbonation of the hydration products. The typical feature of the binders is the large amount of very coarse residual cement particles (250 μm average diameter, max. 1 mm) typical for historical PC mortars and concretes [6,7,8], with a significant fraction remaining unhydrated. The aggregates (0.05 to 2 mm size) are

predominatly of carbonate nature (subrounded dolomite and limestone) with low amounts of silica (quartz, sandstone, etc.).

Mineralogy of the residual cement grains and other binder-related phases

The OM and SEM observations of the AVE-1 and AVE-2 samples reveal a relatively dense microstructure (numerous pores from air but evenly distributed hydration products). The coarsest cement grains (up to 500 μm size) remained unhydrated and allow the usual Portland cement phases to be identified. The Fig. 2a shows a SEM image of the AVE-1 cement grains where calcium silicates (C_2S and C_3S)[8] are included in solid solutions having different composition (ferrite-type or silica containing ferrite with Ca=24_{at}%, Al=13_{at}% and Si =Fe=1.5_{at}%). Except for the grain size (coarser in EAPCs), the general feature of the cement grains is very comparable to that of modern Portland cements. The main difference stands in the higher periclase MgO content found in the Aventicum EAPC. In Fig. 2b, periclase precipitates within the solid solution, partly or massively replacing the calcium silicates grains. At the outer boundary of the cement grain, magnesite $MgCO_3$ is identified as a product of periclase weathering (carbonation subsequently to the intermediate precipitation of brucite $Mg(OH)_2$). Finally, the Fig. 2c shows incompletely burnt quartz grains surrounded by a rim composed of C_2S (as a reaction with calcium during the cement calcination) which remind the morphology of Roman cements produced (in shaft kiln too) in the same period of cement technology [2,9].

The OM and SEM observations of the ADM-1 and ADM-2 samples show a partly dense microstructure with a high degree of cement hydration of the finer cement grains. In terms of composition and grain size, the residual cement grains present very inhomogeneous features (Fig 3a). Unhydrated and partly distorted grains of C_3S often show corroded surfaces and marginal decomposition into belite. The C_2S grains are round to angular and often have atypical or distorted shapes. Ragged belite and segmented fingerlike sections suggest slow cooling (Fig. 3b). Identical features were reported by [6,7] on a historical PC (Aspdin´s cement) from 1850, burned in a shaft kiln. Fig. 2d shows a SEM image of the ADM-1 cement grains where di-calcium silicates is present as two different polymorphisms: C_2S and Mg-rich C_2S (with an average composition $Ca_{24at\%}$, $Si_{14at\%}$ and $Mg_{3at\%}$).

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[8] Expressed using the cement chemistry notation : C=CaO, S= SiO_2, A= Al_2O_3, F= Fe_2O_3, C=CO_3, \$= SO_3, H=H_2O

a) 1 :C_3S, 2 :C_2S, 3 :C_4AF, 4 :(C-A-F-S)ss

d) 1 :C_2S, 2 :C-S-M, 3:(Ca-Al-Si-Fe-Mg-Na)ss

b) 1 : MgO (dark), 2 :mixed (C-A-F)ss and calcium silcates (bright), 3: $MgCO_3$

e) 1 :C-S-\$, 2 : C_2S; 3 : (C-A-F-\$-S-M)ss

c) 1 : quartz core (dark), 2 :C_2S rim (bright)

f) Underburnt grains with remnants of calcite, quartz and formation of calcination rims (arrow)
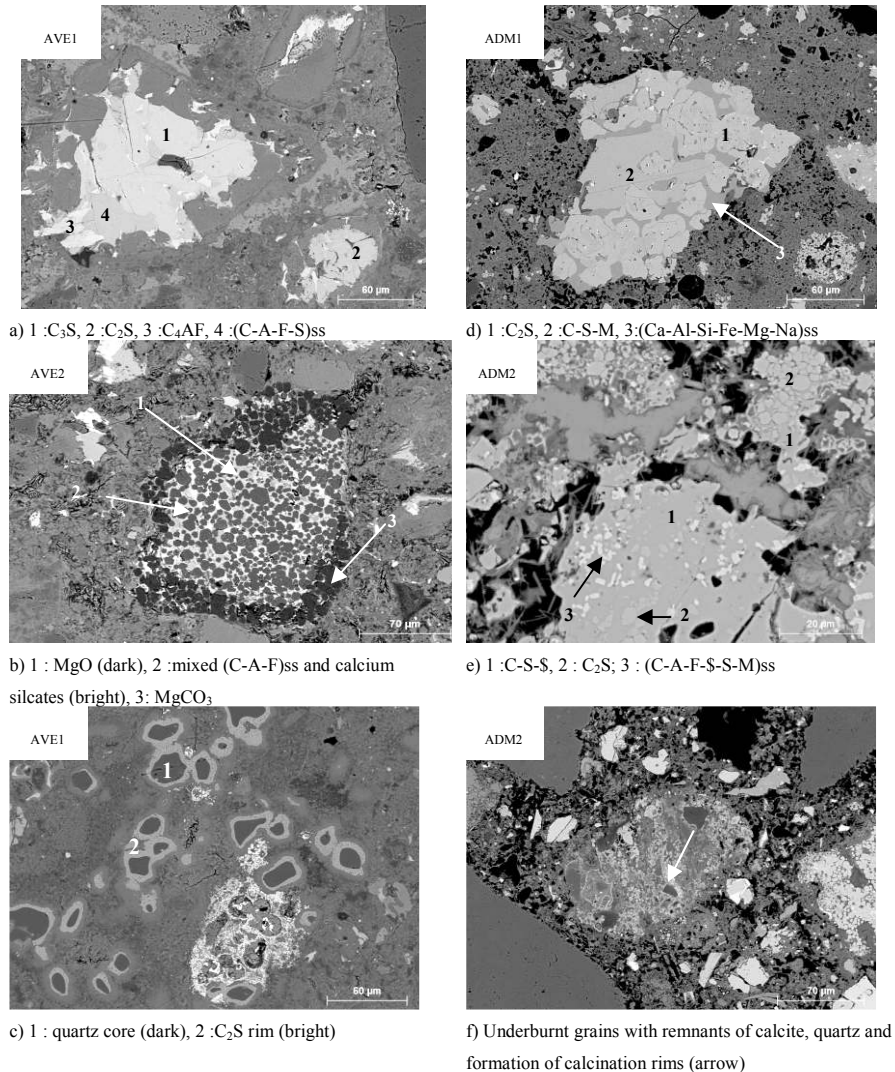
Fig. 2 SEM images of the cement grains remnants in the AVE (a,b,c) and the ADM (d,e,f) samples

The composition of this magnesium-calcium-silicate could match with that of the Bredigite type mineral $Ca_7Mg(SiO_4)_4$ [10,11]. The two C_2S polymorphisms are randomly distributed within a complex solid solution ($Ca_{15at\%}$, $Si_{11at\%}$, $Al_{9at\%}$, $Fe_{3at\%}$, $Mg_{2at\%}$, $Na_{1at\%}$). Sulphur is present in some cement grains, mostly as a solid solution including small grains of C_2S. Fig. 2e shows an example of a grain composed of very fine C_2S grains embedded within a calcium-silico-sulphate solid solution with atomic ratios Ca/(Si+S) of 1.7 and Si/S of 1. Some other grains can include a solid solution with a sulphur content up to 8wt%. The presence of such C-S-\$ solid solution is not reported by the literature on the phases formed during the heating of OPC clinker below 1300°C, e.g. neither silicosulphate $2C_2S.C\$$, so-

called sulphospurrite [12] nor ye'elemite $C_4A_3\$$, a reactive phase present in Vicat Prompt cement [13] and in calcium sulphoaluminate cements CSA [14]. Flux phases such as C_3A and ferrite form very coarse, large and well-developed crystals (Figs. 3a and b) being also a consequence of slow cooling rates.
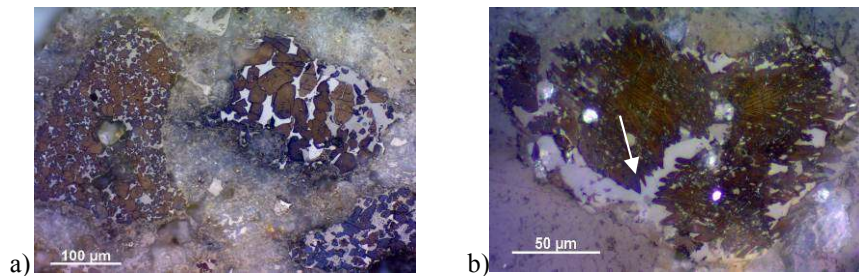

Fig. 3 Coarse, unhydrated residual cements (a) with coarse alite, aluminate and ferrite phases, (b) segmented finger-like sections of C_2S (arrow) in the ADM samples

Finally, numerous grains as shown in Figs 2c and 4a are formed in the lower temperature regimes of the kiln, showing residues of limestone, quartz and mica as parts of the natural raw materials and are comparable to residual low-temperature Roman cement grains [2]. Besides the reactive cement phases described above, the ADM samples contain small amounts of other components indicating also inhomogeneous firing conditions in the kiln. Such grains are frequently composed of platy crystals of the gehlenite-åkermanite series or (pseudo)wollastonite often in a glassy matrix. Angular inclusions rich in organic matter crystals of pyrite can be interpreted as solid fuel remnants (Fig. 4b).
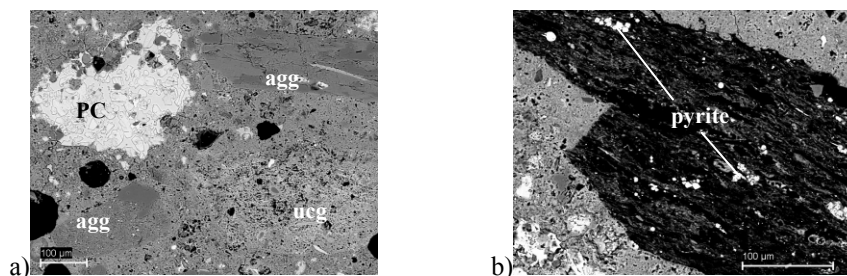

Fig. 4 Binder-related phases and fuel residues in the ADM samples: (a) underburnt (ucg) and "ordinary" Portland cement grain (PC), (agg = aggregates); (b) solid fuel residues with pyrite

Chemical composition of the hydration products

Fig. 5 presents the morphology and the composition the hydration products measured in the different samples. In both mortars, the inner hydration products precipitated at the very close boundary of the cement grains are clearly distinguished from the outer products precipitated further in the matrix. The distribution of the atomic ratio compared to the main

stoichiometric phases (C-S-H, CH, ettringite $C_3A.3C\$.H_{32}$ and calcium monosulphoaluminate $C_3A.C\$.H_{12}$) allows the main phases to be identified.

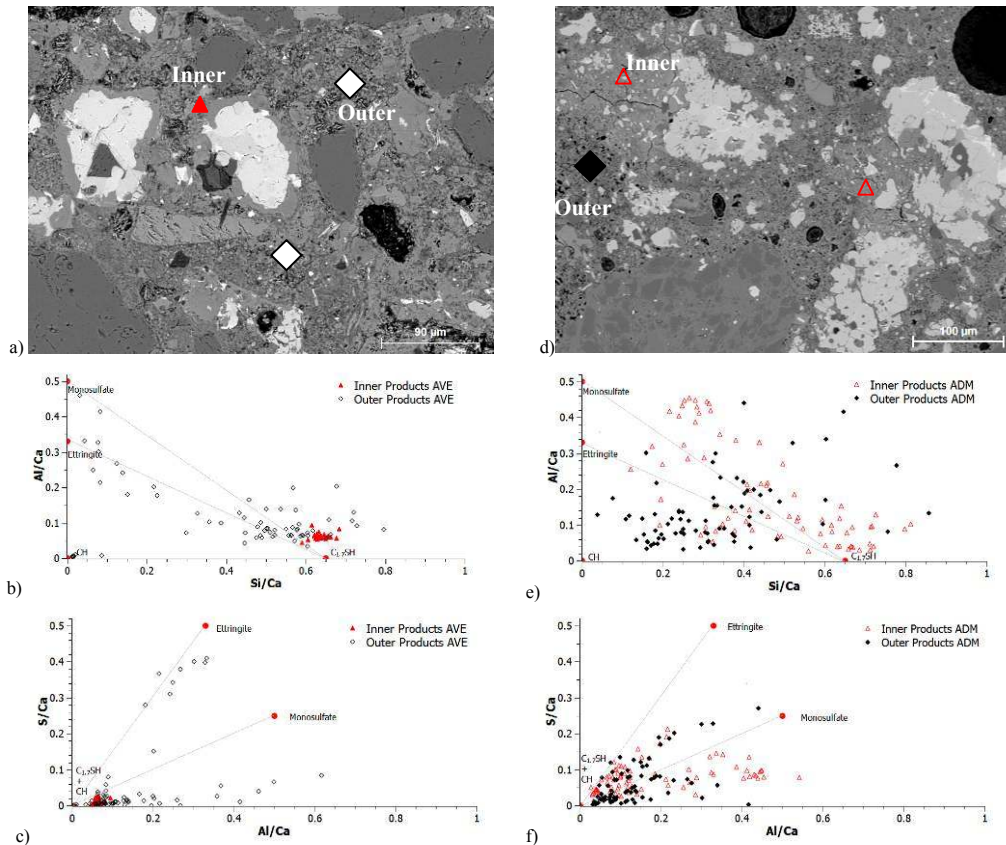**Fig. 5** SEM-EDS data (atomic ratio Al/Ca *vs.* Si/Ca and S/Ca *vs.* Al/Ca) of the inner and outer hydration products measured in the AVE (a,b,c) and the ADM (d,e,f) samples.

Fig. 5a, b and c present the composition of the hydration patterns of the AVE samples. A dense layer of inner products has a constant composition close to that of $C_{1.7}SH$ with a limited substitution of Si by Al (Fig. 5b). Large clusters of calcium hydroxide (CH) can also be observed at the interface between the inner and the outer hydration products (e.g. in Fig. 2a, CH appears in light grey surrounding the inner products). The outer hydration products are composed of C-S-H (with higher Al substitution) intermixed with a little amount of ettringite (Fig. 5b). Fig. 5d, e and f present the hydration patterns of the ADM samples. The outer products have much scattered atomic ratios indicating a composition including C-S-H, CH and a little amounts ettringite. The nature of the inner products seems to be controlled by the dissolution of calcium-silico-sulphate phase (cf. phase 1 in Fig. 2c), leading to the precipitation of C-S-H mixed with significant amounts of monosulphoaluminate.

Conclusions

The article presents the mineralogy and the hydration of two different early age Portland cement mortars, produced in Switzerland and Austria in the second half of the 19th C., and applied in historical objects. The general microstructure and the hydration patterns of the Aventicum cement are comparable to those of contemporary OPCs. Nonetheless the limited amounts of ettringite mixed with outer products would indicate the absence of sulphate in the clinker. By consequence it is assumed that the early age hydration of this specific cement would be likely to that of rapid setting cements (such as Roman cements) in which the setting time could be partly regulated by the coarse particle size distribution. Even though the cement is chemically stable (reduced leaching and carbonation of the hydration products, no damage of the limestone from salts originating from the mortars), the use of EAPC mortar was not an appropriate solution in terms of physical compatibility with stones. The high density of the cover layer (AVE-2) led to the distribution of rain water on the sides and contributed to the degradation of the already reconstructed protection wall. The local failure due to freeze-thaw cycles, and the subsequent leakage through the cracks, constrained the conservators to rebuild this protection wall in 2013.

The collegiate church of Admont shows a successful and durable application of EAPC in ornamental and structural mortars. The reactant phases of the cement are characterized by the presence of sulphur in the solid solution coexisting with the C_2S grains. The origin of sulphur could be explained by the geological situation of the raw marlstone, interlaid with brown coal layers having a high SO_3 content [15], used to produce the cement. Sulfate is identified in the C-S-$ solid solution within the cement grains. This phase dissolves to form mainly monosulphoaluminate at the very boundary of the cement, as it is the case of ye'elemite hydration in sulphate-rich Roman cements (e.g. Vicat Prompt [13]) or modern calcium sulphoaluminate cements [14]. The size, microstructure and inhomogeneity of residual cement phases clearly indicate the use of a simple production technology, namely calcination in a shaft kiln. All four samples contain incompletely burnt nodules similar to those found in Roman cements, produced over the same times than EAPCs. These nodules can be identified by the larger amount of non-crystalline and coarse grains in the AVE samples. In the case of the ADM mortars, underburnt and poorly hydrated remnants of the original raw material suggest the use of a natural clayey limestone instead of an artificial mixture of lime and silica for the cement production. Finally the present data illustrate the need of the microscopic and elemental analysis to better differentiate Roman, early age Portland, and modern Portland cements in the frame of historic mortars characterization.

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