IDENTIFICATION OF 19th CENTURY ROMAN CEMENTS BY THE PHASE COMPOSITION OF CLINKER RESIDUES IN HISTORIC MORTARS

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Abstract

The term “cement” in its historic context stands for several groups of highly hydraulic binders which may differ in the temperatures of calcination and hence yield mortars of significantly differing properties. A key to identify the exact type of binder used in a historic cement mortar consists in the textural and mineralogical features of unhydrated residual clinker particles. Employing various techniques of light and scanning electron microscopy allows define fingerprints for given cements, a task hardly addressed in earlier studies on natural cements calcined at low temperature.

The present contribution focuses on the most characteristic residual clinker phases found in historic Roman cement mortars, a group of materials widely used in the 19th century urban architecture and civil engineering. These binders were produced from natural marlstones through shaft kiln calcination at temperatures virtually below sintering. High amounts of non-crystalline reactive compounds form in this low temperature regime. Along with fine-grained impure C₂S, they have developed into a relatively homogeneous hydrated matrix. In parallel, however, non- or low reactive compounds have assembled together in binder-related nodules characteristic for Roman cement mortars. Most of these compounds are of non-crystalline nature, they comprise solid solution silicate phases as well as crystalline CS (wollastonite), coarse C₂S and C₂AS (gehlenite). By means of thin section and reflected light microscopy, combined with scanning electron microscopy and X-ray microanalysis, the phase assemblages can be observed and identified in virtually all of the historic mortars. Various classes of residues were distinguished within the above general frames. According to their texture and mineral content, they are classified into overfired or underfired in respect to the optimum temperature of calcination. Optimum clinker assemblages with high amounts of reactive phases may form nodules as well, characterised by their specifically dense hydrate structure.

Following a general description of the above mentioned classes, the contribution presents a group of samples from historic façades in the city of Budapest as an example of the usefulness of the classification in the practice of mortar analysis. The data suggest that different brands of Roman cements characterised by specific setting times may have existed and used on purpose for specific mortar applications.

The paper aims at providing information useful for the identification and characterisation of historic natural mortars.

Keywords: Roman cement, natural cement, phenograins, clinker microscopy, SEM
1. Introduction

Natural cements manufactured by the low temperature calcination of marlstones – fine-grained carbonate rocks with significant amounts of clay and other silicates – were amongst the most important building materials of the 19th century in Europe. Almost a century after their recession in the first half of the 20th century and following a period of neglect, these binders, frequently referred to as Roman cements (RCs), are now attracting new interest by the restoration community. This development was accompanied by a number of scientific and technical studies on the composition and properties of the cements, pastes and mortars. Amongst other activities, the EU-funded projects ROCEM (2003-06) and ROCARE (2009-12) have provided detailed information which can be viewed e.g. in the project website www.rocare.eu.

A number of handbooks and other texts edited in the 19th and early 20th centuries deal with the technical aspects of the Roman cement technology, e.g. Pasley (1830), Tarnawski (1887), Tetmajer (1893), Schoch (1904), Eckel (1905), Bohnagen (1914), Kühl & Knothe (1915). Analyses of the chemical composition of RCs, descriptions of the process of production, and definitions of their key properties can be found in these sources. Historic standards took account of the typically short setting time of Roman cements, which were less than 15 minutes for many brands. Evolvement of the final strength is generally delayed in comparison to Portland cements (PCs), so that the 28-days strength of the former is of not too much significance for its quality. Concerning the temperature of calcination, this was established by trial calcinations yielding binders which match the historic ones by all means (Hughes et al. 2007, 2009). Thus, the temperature needed to produce optimum Roman cements from an appropriate raw feed averages at or even below about 900 °C. At this temperature, the mineralogical composition of a RC analysed by X-ray diffraction is characterised by a specific phase assemblage.

According to Hughes et al. (2010, quoted verbatim in the following), “optimal cements are characterised by maximum α’-belite content, a high content of an amorphous phase and residual calcite and quartz indicating incomplete calcination; Carbonated belite, spurrite, was observed in some cements at low temperatures. As the calcination temperature is increased, the α’-belite converts to the β-belite form observed in natural hydraulic limes and Portland cement; spurrite was also reduced. Additionally, aluminosilicate as gehlenite is observed. These developments are accompanied by a reduction in the amorphous phase and residual calcite and quartz. Brownmillerite was observed in cements with a high iron content.” (End of quotation).

When dealing with the identification of historic RCs, it must be kept in mind that, being natural cements from different sources, they show a relatively wide spread of their chemical composition, sometimes falling within the much narrower range of PCs. This fact, as well as the well-known problems related in general to the analysis of binders in historical mortar samples, makes it difficult to identify a Roman cement mortar by just the chemical composition of the binder. Also X-ray diffraction can be of just a limited use, since “fingerprint” products like α’-belite have reacted away by hydration to C-S-H; similar holds for the reactive portion of the amorphous phase, which is anyway not definable by this method. It is thus due to a petrographic analysis based on methods of microscopy to assess the characteristic features of a historic Roman cement mortar, at
least in cases where the experienced eye of an expert fails to take an unambiguous decision on the nature of the mortar.

Studying the compounds in the way outlined above means to observe and analyse the residual cement clinker in an otherwise hydrated and frequently carbonated mortar sample, by all their petrographic and mineralogical properties accessible to the light and electron microscope. This approach forms the methodical base of the present study which thus aims to contribute to a better knowledge of characteristic fingerprints for the identification of Roman cement in historic mortars. Beyond this, it will be shown that a more precise classification of the type of RC can be achieved.

2. Methods

Following vacuum-impregnation in epoxy resin, the mortar samples were cut perpendicular to the surface and processed to petrographic thin sections. They were then studied under a polarising microscope (PL) in transmitted light, occasionally also in reflective light in the case of polished thin sections. The scanning electron (SEM) studies were performed on polished thin sections, or on their counterpart sections, respectively, employing a back-scattered electron detector (BSE). Usually, the high-vacuum working mode was selected with prior carbon coating of the surfaces, though a number of analyses were also made on uncoated samples in the low-vacuum mode. Chemical analyses were performed by an energy-dispersive X-ray analyser (EDS) linked to the SEM.

3. Phenomenology of residual clinker in historic Roman cement mortars

The most characteristic common features of all historic RC mortars are the binder-related nodules, “phenograins” according to the nomenclature by Diamond & Bonen (1993), which are formed by various types of incompletely hydrated cement particles or densely hydrated agglomerates, respectively. They can be observed in any microscope even at low resolution, though determination of their specific nature needs more precise methods of analysis such as polarising microscopy on thin sections combined with electron microscopy.

The abundant presence of such nodules is believed to be due to the particularities of the historic process of production, see e.g. Weber, Gadermayr, Bayer et al. (2007): The raw feed, a rock material with all its natural impurities and inhomogeneities, enters the vertical shaft kiln unground in fist-sized fragments. The temperature gradients in such a kiln are paralleled by gradients within every single lump of stone, so that the resulting clinker is likely to cover a wide range of different grades of calcination. The low temperatures below effective sintering even favour uneven conditions of reaction. Notwithstanding the occasionally reported fact that obviously over- or underburned material was removed manually before the clinker was ground (Kühl and Knothe 1915), the final product is a blend of differently reacted cement grains which, as a consequence, vary in respect to their reactivity with water to form hydrates.

Given the generally coarse particle size of a historic RC frequently in the range of several hundreds of micrometers up to one millimetre, those clinker particles with non or incomplete hydration remain well visible to the eye of the observer. They bear significant information on the historic process of production as well as on the nature of the raw feed. In earlier studies performed on Roman cements calcined at defined
temperatures in the laboratory, a classification of these phenograins was attempted in respect to the strength development of the corresponding pastes (Weber Gadermayr Kozłowski et al. 2007). Reflecting their respective grades of calcination, the residual clinker can be classified roughly as either “underfired”(1), “optimally fired”(2) or “overfired”(3), even if the boundaries between the groups are fluid to some extent. Residual cement nodules can be observed even in carbonated Roman cement mortars, - as noted by St.John, Poole and Sims (1998) - and classified by their structure.

3.1 Type 1 nodules – “underfired”

Underfired nodules calcined to a sub-optimal degree, herewith referred to as type 1 nodules, still show some textural features inherited from the marl (Figures 1a+b): Unreacted silicates such as predominantly quartz, mica and feldspar can be observed embedded in a flaky to fibrous matrix of Ca-Al-silicates. Partial diffusion of Ca and/or K into silicate minerals can be traced by very thin marginal zoning visible by SEM-BSE, which is in general better developed in quartz grains than in feldspars, but can be also observed in coarse micas. It is especially the quartz which serves as indicator for underfired conditions, as it appears angular and with a still intact crystal lattice, showing the typical birefringence visible under crossed polars in PL, with no or only very thin diffusion rims of Ca or K to be observed by SEM.

Calcite and the matrix clay minerals appear to be the first components to react at elevated temperatures. Calcite is incompletely decomposed, however, and often forms pseudomorphs after fossil shells. These features related to calcite are another significant criterion for sub-optimal calcination. The texture of the clayey matrix, especially in respect to the orientation and porosity of the constituents, forms a third sensitive indicator of the conditions of calcination. Compared to “optimally fired” state, the matrix of underfired nodules principally differs by its relatively dense structure near the limit of resolution of the SEM.

Figure 1. a,b Typical underfired residual grain (type 1). (a): SEM-BSE image, (b): the same particle in the polarising microscope under crossed polars; a characteristic quartz grain can be seen right from the centre of the micrograph.

3.2 Type 2 nodules-“optimally fired”

The common feature of these optimally calcined residues is their relatively high amount of reactive clinker material. Thus, apart from the composition and texture of the
unreacted portion, a significant amount of hydration products is visible either as a compact rim of varying thickness up to 150 µm around the nodules, or even in the form of nearly completely hydrated nodules which, however, include unreacted phase residues. Such densely hydrated areas may have uncarbonated core areas even in otherwise fully carbonated mortars. According to their characteristic constituents, the optimally fired nodules can be subdivided into two types; they contain either non-crystalline silicates with clear zoning (2-A), or- belite clusters (2-B), respectively.

Residues of the type 2-A (Figures 2a+b, 3a+b, 4a+b) are characterised by non-equilibrium features such as solid solution systems, and by significant zoning due to a partial diffusion of Ca – predominantly from carbonates, and K – probably from micas - into silicates. The most common phases are non-crystalline silica with no birefringence, up to a size of 30 µm. Varying amounts of K and Ca are always present, by their diffusion into the silicate they have supposedly contributed to the breakdown of their crystalline lattice. Since K-ions have diffused more easily, this element appears to be concentrated rather in core areas of zoned silicate grains, where eventually it may have caused partial melting visibly by small spherical cavities. Ca, on the other hand, tends to be concentrated rather in the marginal zones, where it may form calcium silicates of stoichiometric composition. Thus, the front of Ca-diffusion into silicates can be observed by a sequence of Ca-silicate minerals with increasing Ca:Si ratios, such as wollastonite CS, rankinite $C_3S_2$ and belite $C_2S$.

Where no full hydration of the clinker matrix has occurred, it consists of very fine Ca-Al-Si-phases at the limits of resolution. These non-crystalline products of calcination of the clayey portion of the raw feed play a dominant role in the early age hydration of a RC (Tišlová 2008). Depending on the specific grade of calcination, the residual matrix appears either as densely fibrous, or as porous and grainy. New formations within the matrix include gehlenite $C_2AS$ along with the Ca-silicate minerals mentioned above.

Figure 2. a,b Characteristic densely hydrated nodule of the 2-A type. (a): SEM-BSE image, note the shrinkage cracks, (b): the same particle in the polarising microscope under crossed polars.
Figure 3. a, b Type 2-A – typical “optimally fired” phenogram: (a) SEM-BSE of the whole nodule, (b) detail of (a) with wollastonite CS and belite C₃S grown around silicate grains.

Figure 4. a, b SEM-BSE images of a “optimally fired” clinker nodule, (b): detail of the same clinker residue: crystallisation of C₃S at the costs of zoned silicate grains – this grain could be classified as transition between types 2-A and 2-B: Belite C₃S is growing around silicates and in form of smaller particles in a more flaky matrix.

Type 2-B residues (Figure 5a+b) are characterised by distinctive clusters of relatively coarse belite C₃S, associated with minor amounts of phases like C₃S₂, CS, C₂AS, and occasionally Ca-Fe-Ti-phases.

These belite crystals of a size up to 8 μm show lamellar structures and equilibrium features such as triple borders. They may contain small amounts of Mg and were obviously formed by a full solid state reaction with the silicates. The crystals are frequently arranged around open spaces probably formed by local melting. As compared to similar voids found in type 2-A clinker nodules, the voids of 2-B tend to be bigger, i.e. up to 80 μm in diameter, and their margins are defined by euhedral clinker crystals.

The coarse nature of belites prevents them from efficient hydration. Thus, usually just a dense rim of hydrates can be found around such clusters.
Figure 5. a,b SEM-BSE micrographs of a remnant of type 2-B: clusters of belite. (a): note the dense rim of hydration; (b): detail of (a), with euahedral belites (light grey) and rankinite, C₃S₂ (dark grey).

3.3 Type 3 nodules – “overfired”

Overfired super-optimal particles (Figures 6a-d) show no or just weak signs of hydraulic activity. They are easily recognised by their very angular and often shard-like structure. Marginal hydration of type 3 nodules can never be observed, though in the case of small particle size their hydration can be assumed.

Due to different cooling rates in the kiln during the manufacturing process, two forms of “overfired” particles can be observed in RC: Angular shaped and coarse crystalline (type 3-A) or shard-like and glassy relics (type 3-B) with air voids.

Abundant compounds of the coarse crystalline nodules (type 3-A, Figure 6a+b) are gehlenite C₂AS, belite C₃S, wollastonite CS, leucite S₂AK, and various phases of the CaO-SiO₂-Al₂O₃-K₂O-FeO-TiO₂ system. The resulting compounds are not only well-defined stoichiometrically, but also in terms of their euahedral crystal habits. Thus, it can be assumed that they were formed under equilibrium conditions.

Glassy nodules (type 3-B, Figures 6c+d) show various stoichiometries in the Si-Al-K-Ca system, though in general they contain significant amounts of aluminium. In the isotropic glass, the presence of small microliths indicates devitrification.

Overfired nodules – probably formed in local areas of higher temperatures in the traditional kilns – seem to play an important role as inert filler, also controlling the rapid setting of RC to some extent (Hughes et al., 2010). Generally, this mixture of various residues is consistent with results of laboratory calcinations of marls, where optimal, sub- and super-optimal calcined cements show similar microstructures (Hughes et al. 2010).
Figure 6. a-d SEM-BSE micrographs of “overfired” phenograins. (a, b): Type 3-A is characterised by its coarse-crystalline structure. (b): detail of the same nodule: C$_2$S (medium grey), wollastonite CS, a mineral of the composition C$_2$S$_2$(A,M) - probably melilite (medium to dark grey), kalsilite KAS (dark), Ca-Ti-Fe-mineral (bright). (c, d): Type 3-B: Si-Al-K-rich glass with small microlithes and bubbles; details of the nodule in (d) - the darker parts are richer in Si.

4. Roman cement clinker residuals in historic mortars from Budapest

Samples collected from seven 19th century apartment houses in Budapest (Figure 6) were selected to check the above described typology of RC clinkers in the course of full mortar analyses. It was hoped that some kind of correlation between the predominant type of clinker nodules and the way of architectural application could be established. A list of samples is given in Table 1.

Approximately 100 phenograins were analysed and statistically evaluated for each of the samples. They were classified into one of the three major phenograin types 1, 2 or 3 described in Section 3 of this study.

In all of the samples, the optimally fired cement grains revealed to dominate (55 to 66%). The amount of under- and overfired nodules varies from 8 to 28% and from 15 to 32%, respectively (Table 1). The samples can be divided into two groups based on the ratio of under- to overfired particles in a mortar (Figure 7): one group, comprising all render samples, contains higher amounts of overfired nodules; the other one, representing all pre-cast elements, shows higher amounts of underfired phenograins.

Based on the statistical evaluation of the observations, the following assumptions can be made. The high amount of optimally fired cement grains in all samples is likely
to indicate a pre-selection of optimally calcined clinker material before the grinding procedure. Furthermore, as suggested by Weber, Gadermayr, Kozłowski et al. (2007), the overfired portion of a Roman cement clinker would hydrate more slowly and thus contribute to a prolonged setting time of a mortar. Given the generally short times of workability of Roman cements, retardation is a prerequisite for on-site render works. Therefore, the higher amount of overfired cement grains in the three in-situ run samples suggest slower setting times of these Roman cement mortars.

In contrast to the above, in the other four samples the predominance of optimally and underfired clinkers suggests a faster speed of set of the mortars (Weber Gadermayr Kozłowski et al. 2007). Since these mortars were also used for render works where prolonged setting times were required, another method of retardation must have been used. A simple method recorded by historic sources was e.g. the storage of Roman cement clinker in the open air for some days. Under these conditions, a certain portion of highly reactive and amorphous Ca-aluminate phases of the clinker would react with the moisture of the air, thus withdrawn from the early hydration responsible for the mortar set. Consequently, a slower speed of set and better workability could have been achieved.

### Table 1. Mortar samples taken from 19th century building façades in Budapest with quantitative classification of the phenograins.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of sampled façade element</th>
</tr>
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<tbody>
<tr>
<td>ROC-1</td>
<td>In-situ run RC mortar, door framing</td>
</tr>
<tr>
<td>ROC-2</td>
<td>RC mortar from diamond-shaped element</td>
</tr>
<tr>
<td>ROC-3</td>
<td>RC mortar from diamond-shaped projection</td>
</tr>
<tr>
<td>ROC-4</td>
<td>In-situ run RC mortar, window framing</td>
</tr>
<tr>
<td>ROC-5</td>
<td>Mortar, quoin element,</td>
</tr>
<tr>
<td>ROC-6</td>
<td>In-situ run RC mortar profile</td>
</tr>
<tr>
<td>ROC-7</td>
<td>Mortar, RC-based artificial stone column</td>
</tr>
</tbody>
</table>
5. Discussion and Conclusions

The selected approach to study the clinker residues in historic mortars arose from the fact that neither chemical nor X-ray diffraction analyses could yield sufficient information to identify natural cements of the Roman cement type versus e.g. Portland cements or highly hydraulic limes. Another objective was related to the search for optimum conditions of calcination in order to reproduce Roman cements matching the historic binders in their properties and composition. To that end, the residual clinkers in historic mortars needed to be studied in comparison with the new products.

In general, the variety of phases and textures present in Roman cement phenograins within even one sample is striking. The basic phenomenology and classification of the most frequent types of nodules found in Roman cement mortars, as presented in this contribution, is based on observations made for a considerable number of samples from many European sources. One should therefore keep in mind that the described phenomena are just indicative in a way that significant deviations can occur for certain Roman cements from specific regions. To give just two examples, clinkers found in RC brands produced from dolomitic marl, e.g., could not be considered in this contribution, for the simple fact that so far the authors have not come across them frequently enough. Some historic RC brands from England, manufactured from septaria by using coal as a fuel rather than timber, show distinct features related to higher temperatures and – sometimes – higher sulphate contents inherited from the stone. The related clinker assemblages were not included in this study.

The classification into different types of phenograins reflecting various grades of calcination forms a promising approach to gain more insight into mechanisms of hydration on the one hand, on the other hand it will enable improved differentiation between RC brands once a more systematic assessment will be made.

It is hoped that increasing numbers of scientist will use the approach presented to publish comparable observations and data on RC mortars from all over Europe, so that our knowledge on the range of composition within this family of binders could grow.

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