



## Roman cements – Belite cements calcined at low temperature

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### ABSTRACT

Roman cement was a major material used in the architecture of the nineteenth and early twentieth century across Europe, until it was displaced by Portland cement, and is absent from the palette of materials from which conservationists may now select. Calcination of cement-stones and marls from six sites in Poland, Austria and the UK has been conducted. The resulting mineralogy is dependant upon the characteristics of the original feedstock and the calcination temperatures. The principal hydraulic components are belites and amorphous aluminates. The stable belites in cements calcined at lower temperatures are largely  $\alpha'$   $C_2S$  while  $\beta$   $C_2S$  is stabilised as the calcination temperature is increased. Other components include uncalcined remnants, lime, brownmillerite and gehlenite. Optimum cements, assessed by compressive strength, were produced at relatively low temperatures, typically in the region of 750 °C. Two strength development profiles have been observed.

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### 1. Introduction

Having been patented in 1796 by James Parker, Roman cement became established as a key material for both engineering and architectural works. Its use flourished in the UK until the middle of the nineteenth century, becoming challenged by the improvements to the properties of Portland cement resulting from developments in kiln technologies. An account of the development of Roman cement in the UK may be found in Francis [1]. The continental market for Roman cement was more extensive and prolonged. Tarnawski [2] reports the production of Roman cement in the Austro-Hungarian Empire of the late nineteenth century as being some five times that of Portland cement; the cement was used for renders and cast decorative elements throughout the periods of European Historicism and Art Nouveau (Fig. 1). Its decline came after World War 1 with a change to modern functional architecture and an almost complete lack of decoration. Weber et al [3] describe the exploitation and properties of Roman cement mortars across Europe.

Unlike Portland cement, Roman cement was produced by calcining a single rock source (septaria or marl – a calcareous rock of some 25% or more clay content) at a low temperature with the only pre-calcination processing being to reduce the feedstock to small fragments [4–6]. In this respect it is similar to the production of natural hydraulic limes; however, the calcined clinker has to be ground to a powder as it does not contain sufficient free lime to slake. The use of un-modified raw material meant that each source yielded a cement

with particular characteristics; hence, the term Roman cement covers the genre rather than a unique material. Roman cements were characterised by a brown colour and a rapid setting, typically 10–15 min although the Dictionary of Architecture [7] cites the best cements having a setting time of only 6 min. The most rapid setting was a particular asset in hydraulic engineering.

Conservation of the architecture of the late nineteenth and early twentieth centuries has not received the same considerations as other periods and it is only recently that interest in the materials of the period has revived [e.g., 3,8–13]. One of the fundamental principles of modern conservation is that historic buildings should be repaired by using materials which closely match those of the original structure. However, there only remains a single natural cement produced in Europe, that being Prompt as supplied by the Vicat Company [14]. In the US, Edison Coatings, Inc., re-launched Rosendale cement in 2004 to that market; Rosendale had previously been a major source of natural cement. The American cements frequently had a higher dolomitic content than European materials and produced slower setting times; descriptions of American Natural cements may be found in [15,16].

Although this research has been primarily motivated by the re-establishment of Roman cements into the conservation arena, it also forms part of the developing literature on belite cements produced by various synthesis techniques such as low temperature calcination, sol-gel and spray drying, and the Pechini Process [e.g., 17–19].

As part of its 5th Framework Programme, the European Commission has supported the ROCEM Project to investigate both the properties of the historic materials and their associated technologies together with the means to re-introduce Roman cement to the market [20]. Contemporary accounts of the calcination process are generally poorly specified. Whilst the original patent describes the use of “a

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Fig. 1. Example of the use of Roman cement as a stucco and cast ornament.

heat stronger than that used for burning lime” “nearly sufficient to vitrify them” [21], other descriptions suggest a lower temperature. A frequent comment was that an inferior cement would be the result of calcination in which all of the limestone is decarbonated [e.g. 5]. Eckel [16] developed a Cementation Index (CI) and suggested that raw material with a higher CI, Eq. (1) should be calcined at a lower temperature; a temperature of 900 °C or a little higher being suitable for an Index of 2.0.

$$CI = (2.8 * SiO_2 + 1.1 * Al_2O_3 + 0.7 * Fe_2O_3) / (CaO + 1.4 * MgO) \quad (1)$$

Although novel at the time and based upon assumptions which would now be challenged, the CI bears similarity to the modern Lime Saturation Factor, LSF, Eq. (2).

$$LSF = (CaO + 0.75 * MgO) / (2.85 * SiO_2 + 1.18 * Al_2O_3 + 0.65 * Fe_2O_3) \quad (2)$$

The CI assumes that all reactions have gone to completion. However, the contemporary view that the best cements were those containing a residual amount of calcite would cast doubt on this assumption and the CI should be viewed as being a potential rather than absolute indicator.

Eckel's CI is the only quantitative indicator available in the historic literature that provides guidelines to the chemical composition of raw materials suitable for the production of natural cements. The two existing standard specifications for natural cements – the Austrian Norme of 1878 [2] and the ASTM C 10 Standard of 1974 – stipulate generally that such cements are produced by calcining naturally occurring argillaceous limestones at a temperature below the sintering point. They contain a range of performance requirements of the calcined cements rather than describe specific composition of the raw materials and the conditions of the production process.

This paper reports an intensive programme of calcination of two marls from Poland and Austria together with more limited calcinations of septaria from various UK locations. A pilot study of calcination of septaria (CI=1.4) from Whitby, North Yorkshire has shown that optimum cements may be produced at temperatures of approximately 900 °C [13] and this was used to guide the programme (note: this was

the temperature set on the kiln control panel and no measurement was made of temperature within the charge). The opportunity is also taken to represent an updated mineralogical analysis of the Whitby cements from the pilot study. A principal aim of the study was to identify general criteria for optimum calcinations which would produce the required hydraulic nature and appearance of the final burnt cements. Such criteria will facilitate the future identification of optimum calcination conditions for each given geological material. They require constant modification when the composition and characteristics of the raw material change, which is an inherent feature of natural geological sources.

## 2. Experimental details

Two European marls have been used; one was sourced from Lilienfeld in Austria (AT-L) which was a site of historic cement production in the nineteenth century and the other originated from separate beds in an active quarry in Folwark, Poland (PL-F). Septaria were collected from UK beach sources at Whitby (WLB), Speeton (SP), Sheppey (SH) and Cobbolds Point (CP) which was part of the Harwich cement supplies.

Table 1 indicates the range of geological periods from which material has been sourced.

The identification of the clay minerals in the marls was carried out according to Brindley and Brown [22] and Moore and Reynolds [23]. The mineral content was evaluated semi-quantitatively according to Schultz [24]. Total porosity of each marl was analyzed by mercury intrusion porosimetry in the range 440–0.0035 μm. The BET surface area was measured by nitrogen adsorption at 77.5 °K.

Each source has been calcined over a range of peak temperatures and residence time at this temperature. The combination of temperature and time is used to classify each cement (e.g. 920/300); the temperature cited is the temperature set on the kiln control unit rather than one measured at a specific location within the kiln. The calcination of the Whitby septaria in the pilot study has been described elsewhere [13]. An improved kiln and refined conditions were used for the remainder of the calcinations. An electric kiln (Carbolyte GPC12/36) was used through which an airflow of 21 l/min was maintained to ensure a minimum oxygen content of at least 12% during the decarbonation phase of calcination. All feedstock was reduced to a fragment size of approximately 7–10 mm thickness to homogenise its bulk composition and minimise any temperature gradients within the pieces during calcination.

AT-L was calcined in 10 kg batches and the thermal history monitored at several locations within the charge (Fig. 2). The temperature was increased at 1 °C/min in a two-step sequence. A soaking period of 600 min at 300 °C was included, to reduce the potential for explosive failure of the fragments within the kiln, before the temperature was increased at 1 °C/min until the desired temperature was attained. The thermal history of AT-L (920/300) is shown in Fig. 3 where a large temperature difference is apparent across the charge at any instance resulting from the ambient laboratory air being injected into the kiln.

In order to reduce this influence, the kiln conditions were changed for all calcinations of the remaining marls. The charge size was

Table 1  
Source of raw feedstock

| Marl or septaria | Geological formation           |
|------------------|--------------------------------|
| WLB              | Upper Lias, Lower Jurassic     |
| AT-L             | Gosau Group, Upper Cretaceous  |
| PL-F             | Upper Cretaceous               |
| SH               | London Clay, Lower Eocene      |
| CP               | London Clay, Lower Eocene      |
| SP               | Speeton Clay, Lower Cretaceous |

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