An assessment of some properties of Roman cement.

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ABSTRACT: Roman cement is a rapid natural cement produced by burning, below the melting point, limestone bearing abundant clay. Despite its name it has little to do with the lime-pozzolan binders the Romans used. Patented in 1796, it quickly became popular for several reasons. It perfectly imitates stone at lower cost so it was widely used for architectural decoration and sculptures and its fast setting allowed application to water structures. Furthermore, Roman cement led to the establishment of the prefabrication industry, as it produced water pipes with superior resistance than existing ones based on the first Portland cements (PC). Current uses include restoration, fast masonry, water proofing applications and rendering. Despite its fast setting and significant early strength, Roman cement does not reach (near) maximum strength within 28 days, as it is the case with PC materials, but continues to harden over several years, a time scale closer to that of lime mortars. As Roman cement does not contain free lime, this is due to the slow hydration of di-calcium silicate (belite-Ca$_2$S) which begins soon after the rapid initial set and continues rising strength slow and steady up to 10 years. This paper intends to contribute to the knowledge of Roman cement by comparing the density, porosity, capillary suction, mechanical properties and thermal output of Roman cement mortars with those of eminently hydraulic natural lime (NHL5) and PC mortars (CEMI). The mechanical and hygric performance of the Roman cement mortars studied are similar to those of NHL5 mortars. The water/binder ratio (close to 0.50), produced weaker, more porous and permeable Roman cement materials than equivalent PC mixes. Shrinkage and cracking are difficulties associated with binders in construction. However, the results evidenced that Roman cement undergoes slight, near-linear contraction when curing conditions are constantly at 20 °C and 65% relative humidity. This highlights its potential as a rendering material however, the shrinkage measured is lower than site shrinkage. The results also evidenced that Roman cement generates moderate temperatures when curing, and this can avoid problems associated with temperature gradients and heat dissipation on hydration. Roman cement has a wide and varied potential in the field of construction. Although extremely rapid setting, a low-cost, readily available product (citric acid) can retard hydration predictably.

KEY WORDS: Roman cement; Compressive and Flexural Strength; Shrinkage; Capillary suction; Porosity.

1 INTRODUCTION

In 1796, Parker filed a patent on the burning of marl nodules (septaria) [1]. The cement produced represented a major step forward in building because it was an eminently hydraulic binder with faster setting and hardening than the first Portland cements and the lime and lime/pozzolan mixtures of the past. The cement was produced by burning at low temperature (below the melting point) a clayey limestone or marl with a proportion of clay varying approximately from 22 % to 35%, using the simple technology traditionally used for lime furnaces [2]. The cement is simply ground and it does not need to slake due to the almost total lack of quick lime. The low quenching together with no slaking and easy grinding made production simple. As a result, in the early 19th century, production spread throughout Europe.

This cement was called "Roman cement", an incorrect and confusing name as it has very little to do with the hydraulic, lime-pozzolan binders the Romans used. Other names include rapid natural cement, quick setting and prompt cement.

Roman Cement had many uses up until the early 20th century when Portland cement overtook construction. The material quickly became very popular for a number of reasons. Due to its ultra-fine grain size, Roman cement can produce accurate castings and was used to imitate carved stone. It perfectly imitates stone at a lower cost [1] so it was widely used for prefabricated mouldings, architectural decoration and sculptures (Figure 1). In addition, its fast setting allowed application to structures in contact with water. Furthermore, it led to the establishment of the cement-based prefabrication industry, as it was used to produce water outlet pipes of superior resistance to aggressive water than the existing pipes based on the first Portland cements. In Ireland and the UK, it was often used as a facade material in renders, run mouldings and prefabricated mouldings (Figure 1). Today, Roman cement is produced in several countries in Europe and current uses include restoration of facades and sculptures, fast masonry, water proofing applications and rendering.

As a result of the chemical composition of the raw material and the burning at low temperature (600 to 1200°C, slightly higher than that of hydraulic limes), the minerals produced are different to those in modern Portland cements but identical to those in natural hydraulic limes although in different proportions (Figure 2). Part of the raw stone does not heat enough to transform and it simply dehydrates while other parts are transformed into amorphous or low crystalline phases including aluminates (C$_3$AF, C$_3$A, C$_{12}$A$_7$, C$_4$A$_5$S and C$_2$AS) responsible for quick setting and hardening during the first hours of hydration; and silicates in the form of belite.
(C₃S) which are slow strength raisers and increase resistance over several years [2]. There is only seldom clinkerization (melting) in local areas forming a small quantity of alite (C₃S), as this clinker begins to form at temperatures around 1200°C hardly reached in the Roman cement making process. Due to these mineral components, Roman cement builds strength in two distinct phases over a very long period. Initially, on hydration, the aluminates formed at low temperature produce a quick set (at 2 to 3 minutes) which constitutes the first phase. Later, when belite is hydrated, the second strength building phase begins extending over many months. According to the The Louis Vicat Technical Centre [2], a 1:1 mix (by weight) with a water/cement ratio of 0.38 achieves a compressive strength of 14 N/mm² at 1 day of curing; 30 N/mm² at 1 month; and 45 and 65 N/mm² at 1 and 10 years respectively. The strength of the material varies according to mix proportions and water/cement ratio. Roman cement can be used in a very wide range of mix proportions (from 10 to 50% of the dry mortar weight and even 100% in the case of grouting and slurry). In general, water/cement ratios under 0.50 are required for high strength applications that require fast setting and low permeability such as waterproofing whereas water/cement ratios over 0.50 produce weaker, more porous and permeable materials with mechanical and hygric performance closer to those of natural hydraulic lime mortars [2].

This paper investigates Roman cement mortars, retarded with citric acid, with water/cement ratios of 0.47. These conditions were set to make the material workable and compatible with original Roman cement and hydraulic lime mortars and thus more suited to repair a wide range of substrates. Ideal curing conditions for Roman cements require a constant relative humidity > 90% as this enhances hydration, reducing porosity and permeability due to a greater amount of hydrates filling pores. In this paper, curing conditions were ambient temperature and humidity in order to make the curing process comparable to site curing. On site, a more or less intensive drying takes place initially which works against hydration. A site produced mortar will have greater porosity and capillarity than the same mortar having undergone an ideal cure in the laboratory. This paper compares the density, porosity, capillary suction, compressive and flexural strength and thermal output of Roman cement mortar with those of eminently hydraulic natural lime (NHL5) and cement mortars (CEMI).

2 MATERIALS AND METHODS

2.1 Materials and mixing

The cement was delivered as a dry-hydrate. All mixes were 1/3 binder to sand ratio by weight. The overall ratio of binder/sand/water was calculated as approximately 1:3:1 in accordance with EN 196-1 [3]. As aforementioned, the Roman cement mortars were fabricated with high water/cement ratios (0.47) to achieve mechanical and hygric properties closer to those of historic Roman cement specimens. The PC and NHL materials were mixed in accordance with EN 196-1 [3]. With regard to the Roman cement, citric acid was used as a retardant. As the manufacturer’s dosage was vague, experiments were conducted to measure the initial set with varying amounts of citric acid to select the correct amount of retarder.

![Figure 1. Borris House, County Carlow, a 19th century building with Roman cement mouldings.](image1)

**Figure 2. Composition of Roman (prompt) cement compared with other cements in Europe [2].**

| Table 1. Mortar composition. (*)=8 g. (0.7%) citric acid. |
|-----------------|-----------------|-----------------|-----------------|
| **Binder** | **Roman** | **PC** | **NHL5** |
| **cement** | **Binder (g)** | **Aggregate (g)** | **Water/binder** |
| **(0.7%)** | 1100 | 3300 | 0.47 |
| **700** | 700 | 700 | 0.52 |
| **2100** | 2100 | 4.44 |

2.2 Permeability

The permeability was measured with an Autoclamp apparatus on 100mm cubes. The apparatus is assembled over one of the faces of the cube ensuring the seal is not exposed at the edge. The Autoclamp maintains an even head of water upon the face of the cube while simultaneously measuring the amount of water that permeates the surface. The test lasts 15 minutes and pressure readings and quantity of water penetrated are recorded every minute. The values reported are the arithmetic mean of three tests.

![Figure 2. Composition of Roman (prompt) cement compared with other cements in Europe [2].](image2)
2.3 Capillary absorption

The dry specimens were weighed and placed 2 mm deep into water according the RILEM [4] recommendations. The weight was recorded after 15 and 30 minutes and one, three, eight and twenty-four hours. The weight of water absorbed was plotted against the square root of time. The values reported are the arithmetic mean of three tests.

2.4 Densities and porosity

The bulk (δ) and real (δr) densities and porosity were determined according to RILEM recommendations [4] with the equations below: where md is the dry mass; mh the hydrostatic mass and ms the water saturated mass at atmospheric pressure. The values reported are the arithmetic mean of three tests.

\[ \delta = \frac{m_d}{m_h - m_b} \quad \delta_r = \frac{m_d}{m_h - m_s} \]  

(1,2)

The open porosity was calculated according to the following equation.

\[ p = \frac{m_h - m_d}{m_h - m_s} \times 100 \]  

(3)

2.5 Compressive and flexural strength

The compressive strength Rc (MPa=N/mm²) was measured using equation 4 [5]; where A (mm²) is the sectional area and (F) the load at which failure occurred.

\[ Rc = \frac{F}{A} \]  

(4)

The flexural strength (MPa) was calculated using equation 5 [6]; where Ff is the peak load (N); b the side of the prism (mm) and l the distance between supports (mm).

\[ R_f = \frac{1.5 \times F_f \times l^3}{b^3} \]  

(5)

The values reported are the arithmetic mean of three/six tests.

2.6 Shrinkage

The decrease in length of the specimens (40x40x160mm), measured along the longitudinal axis, when the decrease is caused by any factor other than applied forces was measured with gauges accurate to 0.002 mm, on a daily basis for the first two weeks and then regularly for a month [7].

2.7 Thermal output

The thermal output generated by the Roman cement on hydration was recorded. This is an indirect measurement of strength development as hydration produces the cementing hydrates responsible for strength development. Nine thermocouples (K-type) were arranged along the central vertical and horizontal axes inside a cubic mould (250mm side), with one thermocouple placed outside to represent the ambient temperature. They were connected to a computer with a data recorder. After the mortar was poured into the mould and vibrated to remove air voids, recording of data began. As Roman cement reaches the initial set fast (even with a retardant), it was expected that the maximum thermal output will be reached relatively quickly so readings were taken every second for two and a half hours and every ten seconds for the subsequent 11 hours.

Figure 3. Thermocouple arrangement and orientation (left) and thermal output recording of uninsulated Roman cement.
Table 2. Densities and porosity of the mortars in this paper and comparison with other authors [2,8,9,10].

<table>
<thead>
<tr>
<th>Binder</th>
<th>Porosity %</th>
<th>Bulk density kg/m³</th>
<th>Real density kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC</td>
<td>22.07</td>
<td>1946.00</td>
<td>2508.59</td>
</tr>
<tr>
<td>NHL 5</td>
<td>21.97</td>
<td>1933.00</td>
<td>2474.44</td>
</tr>
<tr>
<td>PC</td>
<td>17.63</td>
<td>2069.00</td>
<td>2511.32</td>
</tr>
<tr>
<td>RC</td>
<td>(90%RH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[8]</td>
<td>18 - 22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RC</td>
<td>(ancient)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7]</td>
<td>23 - 40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NHL 5</td>
<td>[9]</td>
<td>1879-1916</td>
<td>-</td>
</tr>
<tr>
<td>PC</td>
<td>[9,10]</td>
<td>1840-2048</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3 Capillary suction

The results evidenced a higher capillarity for the Roman cement. The Roman cement initially absorbs more water at a faster rate than the NHL5 mixes however, after approximately 8 hrs, they have absorbed a similar amount of water and suction stops. The PC mortars absorbed water at a lower rate and showed lower overall suction. These agree with the porosity results. The Roman cement capillarity is comparable to that reported by previous authors ranging from 4 -10 kg/m²/hr⁰·⁵ [8]. The Louis Vicat Technical Centre [2], for Roman cement bearing a higher water/binder ratio (0.95) however cured in optimum hydration conditions, reports a capillary suction of 1.4 Kg/m².min⁻¹(3 hours) and 12.54 Kg/m².min⁻¹(24 hours). The higher capillarity of the Roman cement in this study can be attributed to the existence of more abundant and coarser pores developed as a result of restricted hydration (due to curing in ambient conditions rather than in constant humidity over 90% which enhances hydrate formation). The lower values of the PC and NHL5 mortars also agree with the range reported by previous authors for PC (2 kg/m²/hr⁰·⁵ [8] and 0.055 kg/m²/s⁰·⁵ [9] and NHL5 (14kg/m²/hr⁰·⁵ [8] and 0.25-0.30kg/m²s⁰·⁵ [9].

3.4 Permeability

Two experiments were carried out both producing approximately linear results. However, the older specimens (10 days older) were more permeable. According to Kozłowski et al. [8], Roman cements initially display a coarser pore structure which is a function of the production of hexagonal hydrates (AFm phases) on aluminate hydration. These coarse pores later refine as a result of their infill with calcium silicate hydrates (CSH) formed on belite hydration which yields a final refined pore structure. The higher permeability of the older mortars can be due to the existence of coarser pores developed as a result of restricted hydration (due to curing in ambient conditions rather than in 90% humidity which refines the pore system by enhancing hydrate formation). In addition, some porosity can be related to microcracking induced by shrinkage at late stages. The Roman cement permeability values are higher than those reported for equivalent PC mixes [11].

![Water absorbed by capillarity over time](image)

**Figure 4.** Water absorbed by capillarity over time (at 15 and 30 minutes and 1, 3, 8 and 24 hours).

**Figure 5.** Permeability of Roman cement mortars: water intake over time during Autoclam experiment.

3.5 Compressive and flexural strength

The Roman Cement strength measured was compared with equivalent NHL and PC mortars (Table 3). Values (at 28 days) are average of 3 and 6 tests for compressive and flexural strength respectively. Most COVs ranged from 4.1 to 22. As expected from the water/binder ratio of 0.47, the mechanical performance of the Roman cement is close to that of the natural hydraulic lime mortars. The Roman cement has strength slightly superior than the NHL5 mortars but lower than the PC mortar. The values are comparable with those of PC/lime mixes typically used in construction (Table 3).

The strength results agree with several authors however, they are lower than other values reported. The compressive strength recorded is comparable with the 5.7 N/mm² at 28 days reported by Kozłowski et al. [8] and the 3.8 N/mm² (for equivalent mixes with higher w/b (0.95) cured in optimum hydration conditions) reported by [2]. However, a 1/3 mix (by weight) with a water /cement ratio of 0.50 can achieve a compressive strength of 16 N/mm² at 1 month; and 35.16 N/mm² at 1 year [2]. The lower values in this study (6-9 N/mm² at 1 month) are probably due to the higher dosage of...
retarder used to achieve a specific workable life (it is well known that citric acid delays clinker hydration therefore retarding strength development), a lower humidity during curing and a slightly higher water/cement ratio.

Table 3. Compressive and flexural strength of Roman cement and comparable NHL and PC/lime mortars.

<table>
<thead>
<tr>
<th>Mix composition</th>
<th>Compressive strength (MPa)</th>
<th>Flexural strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roman Cement</td>
<td>6.3-9.1</td>
<td>1.2-5.6</td>
</tr>
<tr>
<td>NHL5 (2.5:1) [12]</td>
<td>3-4</td>
<td>1</td>
</tr>
<tr>
<td>NHL5 [9]</td>
<td>9</td>
<td>1.9-2.4</td>
</tr>
<tr>
<td>NHL5 [13]</td>
<td>6</td>
<td>1.4</td>
</tr>
<tr>
<td>NHL5 [14,15]</td>
<td>4.4</td>
<td>1.5-1.9</td>
</tr>
<tr>
<td>NHL5 [16]</td>
<td>3.8-4.4</td>
<td>1.3</td>
</tr>
<tr>
<td>NHL5 [17]</td>
<td>5.7-6.1</td>
<td>1.3-1.6</td>
</tr>
<tr>
<td>PC [18]</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>PC [9]</td>
<td>16-24</td>
<td>2.9</td>
</tr>
<tr>
<td>PC/lime/sand</td>
<td>9.8</td>
<td>3.5</td>
</tr>
<tr>
<td>1/0/0.6 [19]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC/lime/sand</td>
<td>12.7</td>
<td>4.4</td>
</tr>
<tr>
<td>1/0.25/6 [19]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC/lime/sand</td>
<td>11-14</td>
<td>3.3-5</td>
</tr>
<tr>
<td>1/0.50/4 [20]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.6 Thermal output

Despite its rapid set, Roman cement does not exhibit a strong exothermic output during curing. This is due to the absence of alite, whose reaction is highly exothermic. In Roman cement, the clinker that initially hydrates (responsible for the setting) is aluminate, whose hydration is not as highly exothermic as that of alite. As aforementioned, the retardant provided approximately 35 minutes workability. The end of the workable life is represented on the graph by the beginning of the accelerated thermal output after 20 minutes.

The maximum temperature reached was 29.51°C after 174 minutes (2.9 hrs). Subsequently, the material cools down and reaches ambient temperature after 900 minutes (15 hrs.) This thermal output is lower than that of Portland cement and the heat dissipation seems faster. For example, the surface of a 100cm cube of CEM I reaches 25°C at 10 hours (600 min) and 38°C at 20 hours [21] while the superficial gauge (gauge 9) of the Roman cement investigated reaches approximately 19°C at 10 hours and, after 15 hours, it has already reached ambient temperature. The maximum temperature recorded by the central gauge of the Roman cement investigated (gauge 3) is nearly 29°C after 107 minutes (1.78 hours) and approximately 23°C at 10 hours; after 15 hours, it has reached ambient temperature. In contrast, typical values reached at the centre of a 100 cm cube of CEM I are 30°C at 10 hours and 54°C at 20 hours [21]. As aforementioned, the lower heat evolution and faster heat dissipation of Roman cement when compared to Portland cement is due to its lack of alite. The temperature evolution at different locations remained consistent- the only gauge slightly incongruent is gauge 9 which was located at the top of the specimen and reflects the cool ambient temperature over the course of the night.

Figure 7. Thermal output of Roman cement over time. Gauges 10 and 11 record ambient temperature.

3.7 Linear shrinkage

The shrinkage readings are consistent, running relatively uniformly over the duration of the experiment. As it can be seen from figure 8, shrinkage ranges from approximately 86 to 100 μm. The maximum shrinkage is 100μm (625μm per meter) 0.062% of the original length of 160mm. The large increase in the rate of shrinkage for specimen [28/02 – 3] between the 24th and 28th day deviates excessively from all the other results and is probably due to a flawed reading.

The shrinkage values obtained agree with those reported by former authors [2] for similar mixes at 28 days (260 μm per meter). The shrinkage is lower than that reported by Wilk et al. [22]: 2310μm per meter at 28 days (520 at14 days) in mixes with higher water content (w/b=0.65).

The shrinkage recorded is low, probably lower than site shrinkage. Drying shrinkage lowers with slower drying and increasing aggregate content and humidity, but it is however enhanced with increasing water/binder ratio. The mortars investigated are 1/3 mixes produced in the laboratory, in controlled ambient humidity. However, on site, curing conditions are uncontrolled and drying is often faster (at least initially). Furthermore, castings often use binder rich mixes which are more susceptible to shrink (as it is the cement binder that shrinks while the aggregate remains insensitive to drying). According to Wilk et al. [22], networks of fine cracks are characteristic of Roman cements both historic and new; and this prevents broader acceptance of Roman cement by the construction sector.

The NHL5 and PC shrinkage are comparable, although greater, than those previously reported (110 and 90 μm per meter for NHL5 and PC respectively at 28 days [9]). Generally, Roman cement materials show higher shrinkage than those based on the Portland cement [22]. A 5-month cured Portland cement paste produced at w/c = 0.5 reaches a total shrinkage of approximately 3000 μm/m at 45% RH (Rougelot et al. in [22]).
4 CONCLUSION

The mechanical and hygric performance of the Roman cement mortars studied are close to those of natural hydraulic lime mortars. This is probably due to the fact that they were fabricated with water/cement ratios close to 0.50, and as a result they are weaker, more porous and permeable than equivalent PC mixes.

Despite their fast setting and significant early strength Roman cement mortars do not reach their (near) maximum strength within 28 days, as it is the case with PC materials, but continue to harden over several years, a time scale closer to that of lime mortars. As Roman cement does not contain free lime, this is due to the slow hydration of di-calcium silicate (belite-C₄Aₛ) which begins soon after the rapid initial set and continues rising strength slow and steady, up to 10 years [2].

Shrinkage problems and cracking are difficulties associated with the use of binders in construction. According to the linear shrinkage experiment, Roman cement undergoes slight, near-linear contraction over a 28 day time period when curing conditions are constantly at approximately 20 degrees centigrade and 65% relative humidity. This highlights its potential as a rendering material.

Finally, Roman cement generates moderate temperatures when curing, and this can avoid problems associated with temperature gradients and heat dissipation during hydration. Roman cement has a wide and varied potential in the field of construction. Although it is extremely rapid setting, a cheap and readily available natural product, citric acid, can retard hydration predictably.

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